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From small-scale variability to mesoscale stability in surface ocean pH: implications for air–sea CO_2 equilibration

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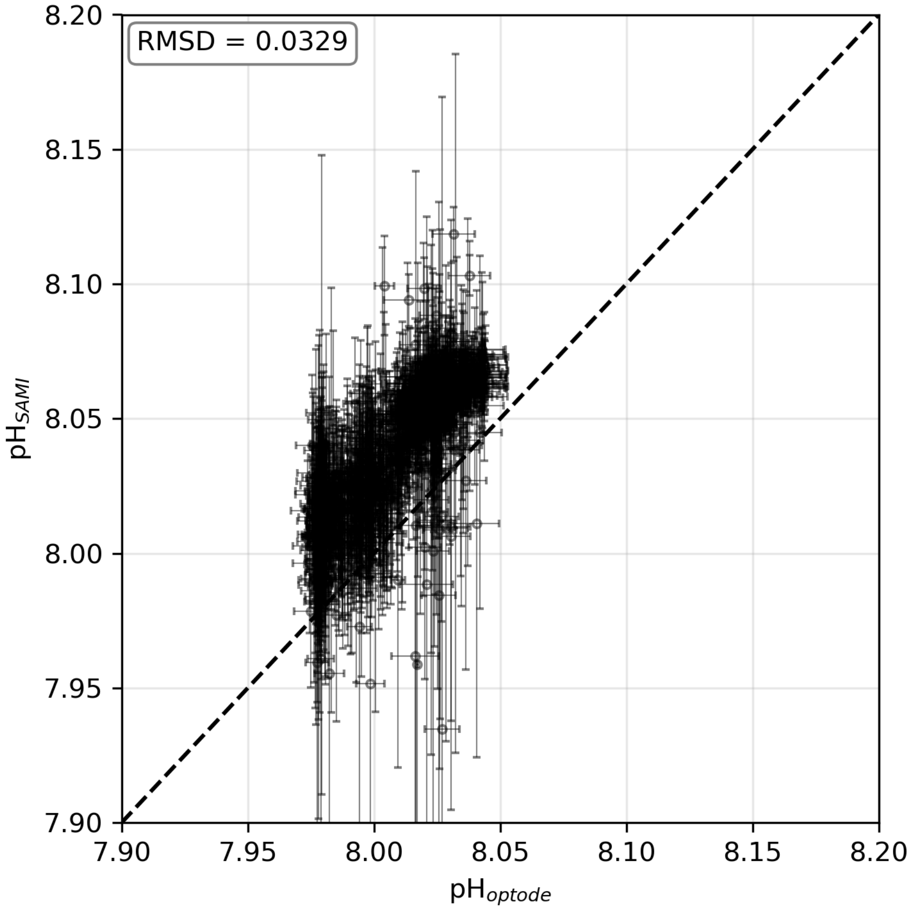

Figure S1. Comparison between corrected pH from the optode and measured pH using the SAMI sensor. The dashed line indicates the 1:1 agreement. Root Mean Square Deviation (RMSD) is provided to quantify the agreement between datasets.

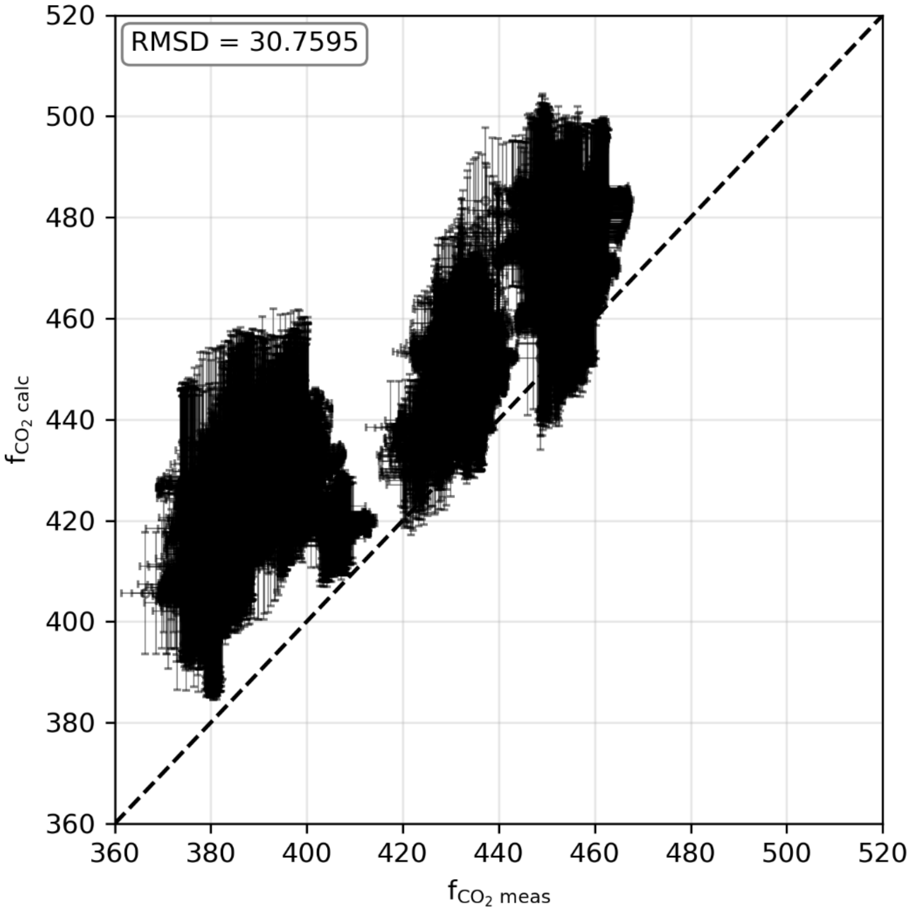

Figure S2. Comparison between calculated fCO_2 from the optode pH and estimated alkalinity, and the independently measured pCO_2 converted to fCO_2 using PyCO2SYS (Version 1.8.2; Humphreys et al. 2022). The dashed line indicates the 1:1 agreement. Root Mean Square Deviation (RMSD) is provided to quantify the agreement between datasets.

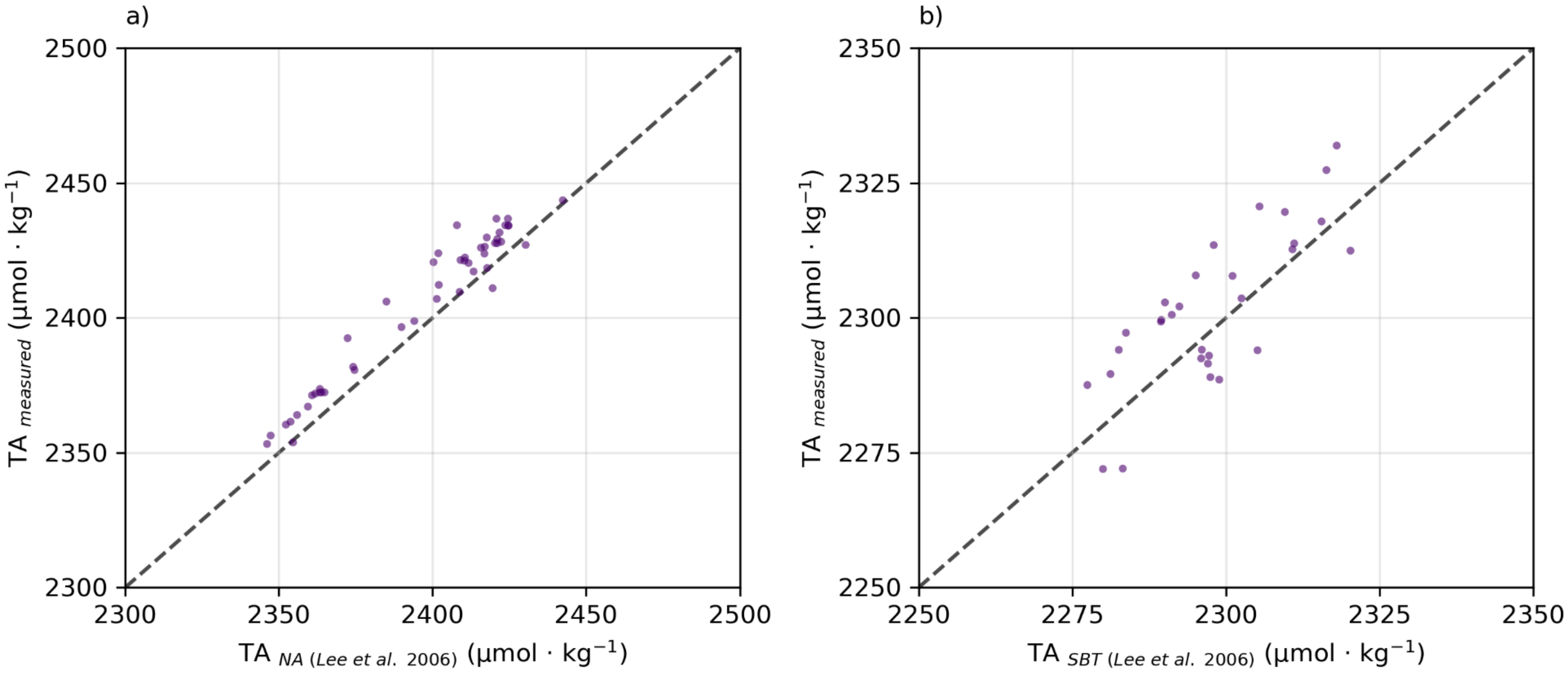

Figure S3. Measured and estimated total alkalinity (TA) using the relationships from Lee et al. (2006) for UWS subsamples for research expeditions a) SO279 (North Atlantic) and b) SO289 (South Pacific).

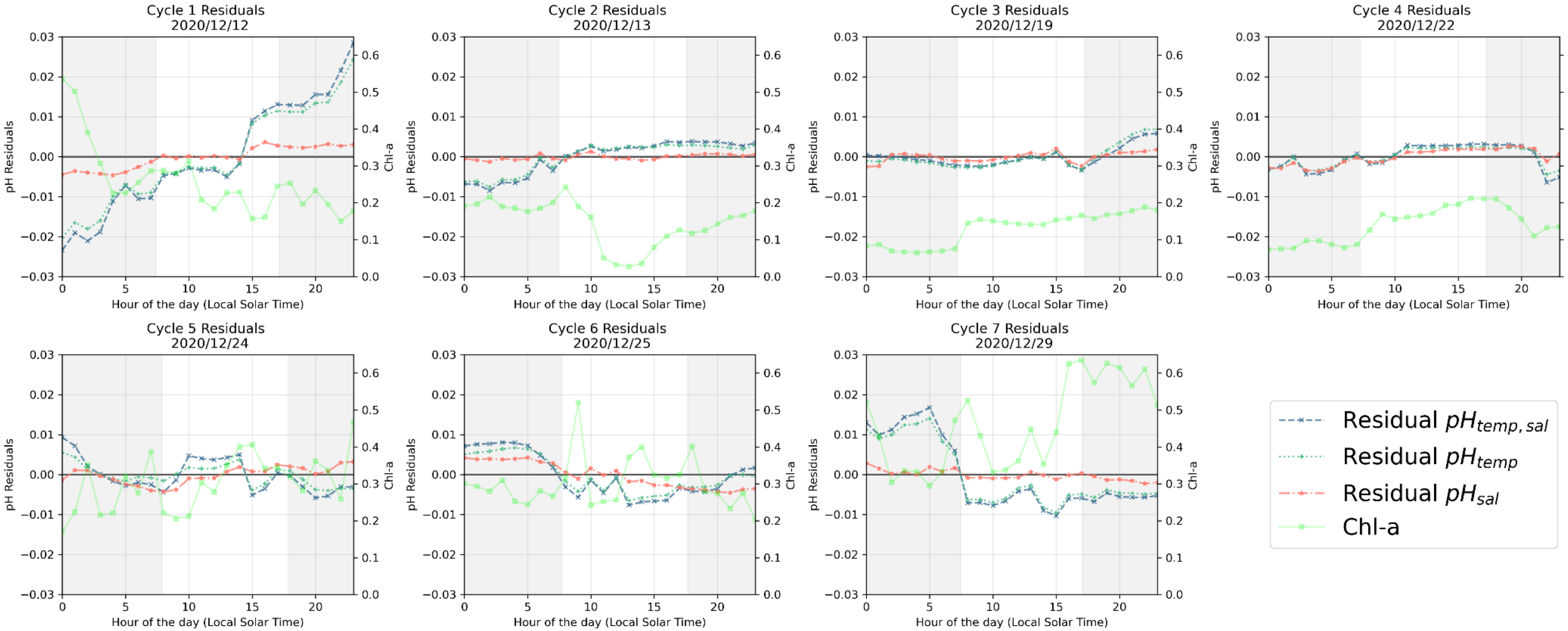

Figure S4. Residual plots for diurnal cycles in the North Atlantic, illustrating the discrepancies between observed pH via optode (pH_{obs}) and pH calculated from temperature and salinity combined ($pH_{temp,sal}$), temperature only (pH_{temp}), and salinity only (pH_{sal}). Horizontal dashed lines at y=0 indicate no deviation between observed and calculated pH values, serving as reference points for assessing overestimations or underestimations. Chl-a has its own y-axis.

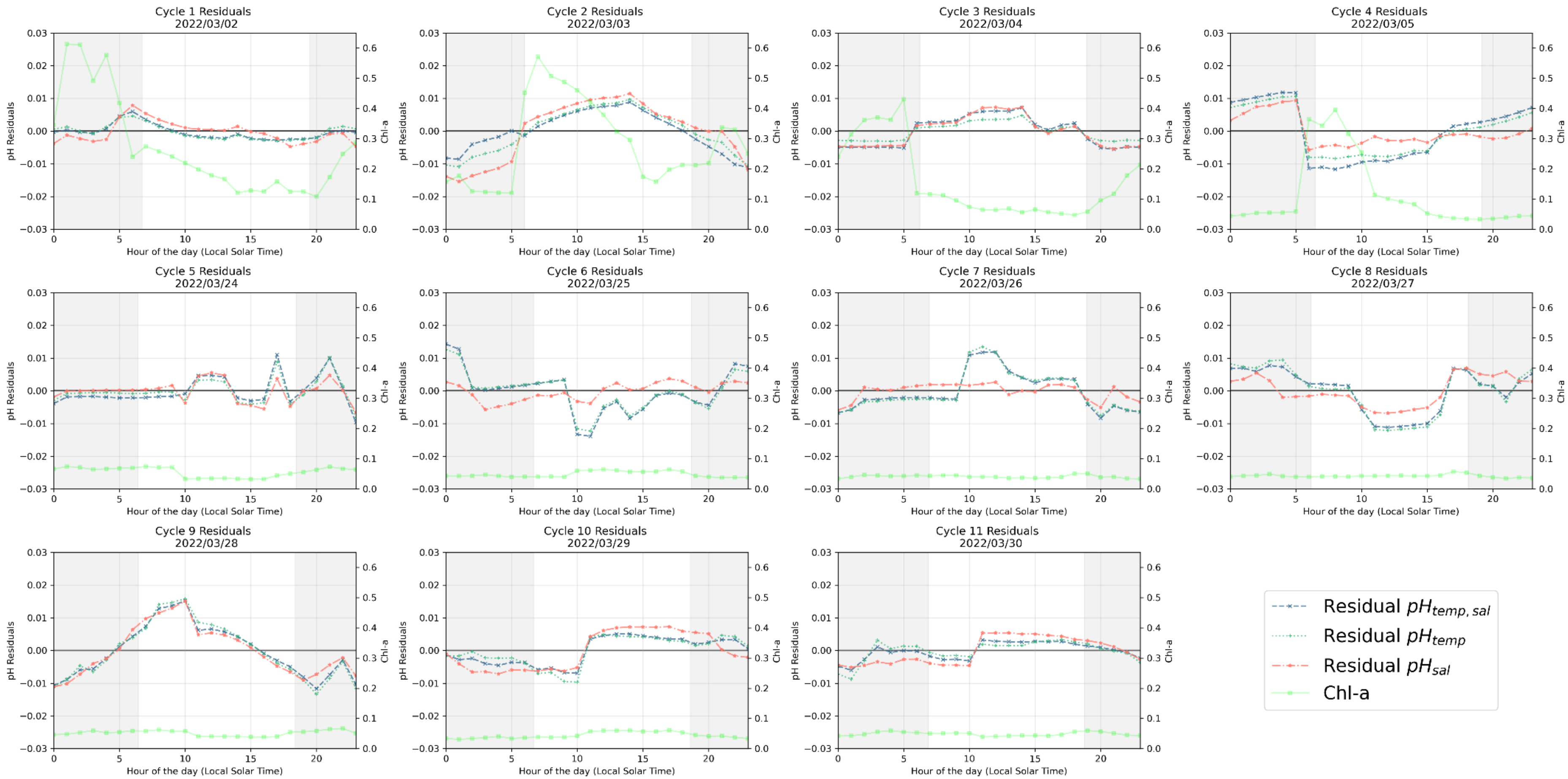

Figure S5. Residual plots for diurnal cycles in the North Atlantic, illustrating the discrepancies between observed pH via optode (pH_{obs}) and pH calculated from temperature and salinity combined ($pH_{temp,sal}$), temperature only (pH_{temp}), and salinity only (pH_{sal}). Horizontal dashed lines at y=0 indicate no deviation between observed and calculated pH values, serving as reference points for assessing overestimations or underestimations. Chl-a has its own y-axis

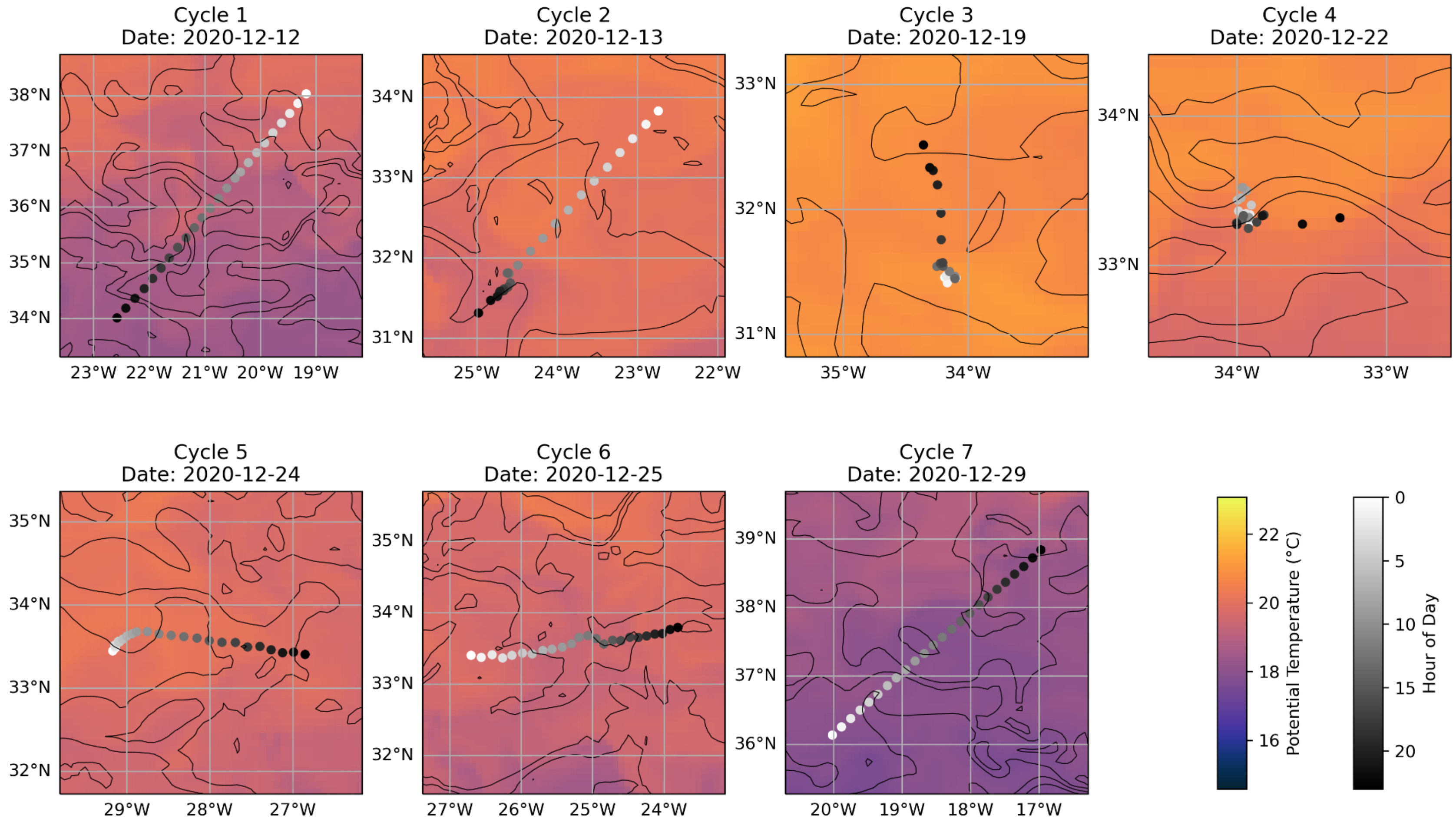

Figure S6. Trajectory for each identified individual diurnal cycles for cruise SO279 in the North Atlantic Ocean. Dot color represents hour of the day. Contour lines are drawn every 0.5°C. Background map shows potential temperature from E.U. Copernicus Marine Service Information; https://doi.org/10.48670/moi-00016.

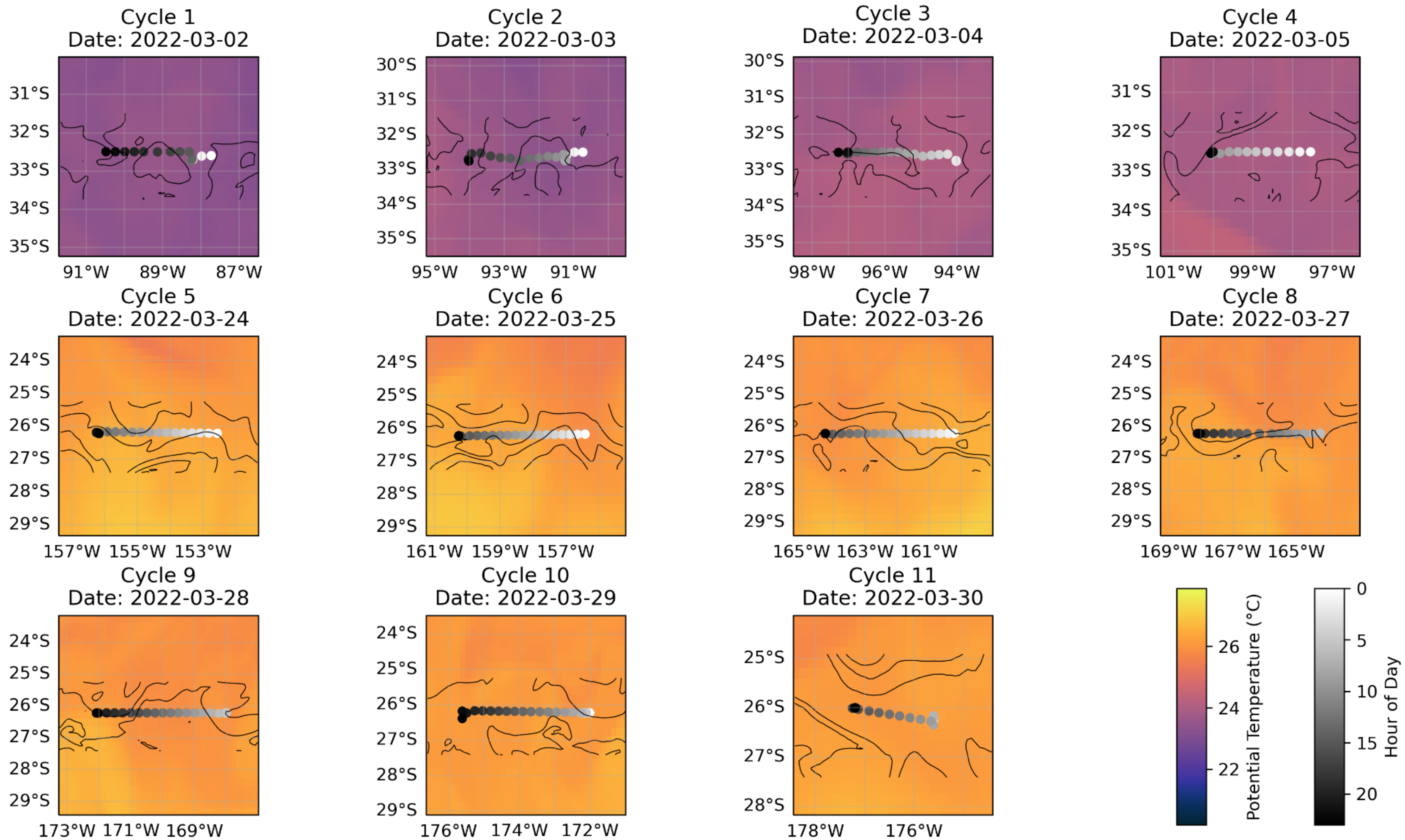

Figure S7. Trajectory for each Figure individual diurnal cycles for cruise SO289 in the South Pacific Ocean. Dot color represents hour of the day. Contour lines are drawn every 0.5°C. Background map shows potential temperature from E.U. Copernicus Marine Service Information; https://doi.org/10.48670/moi-00016.

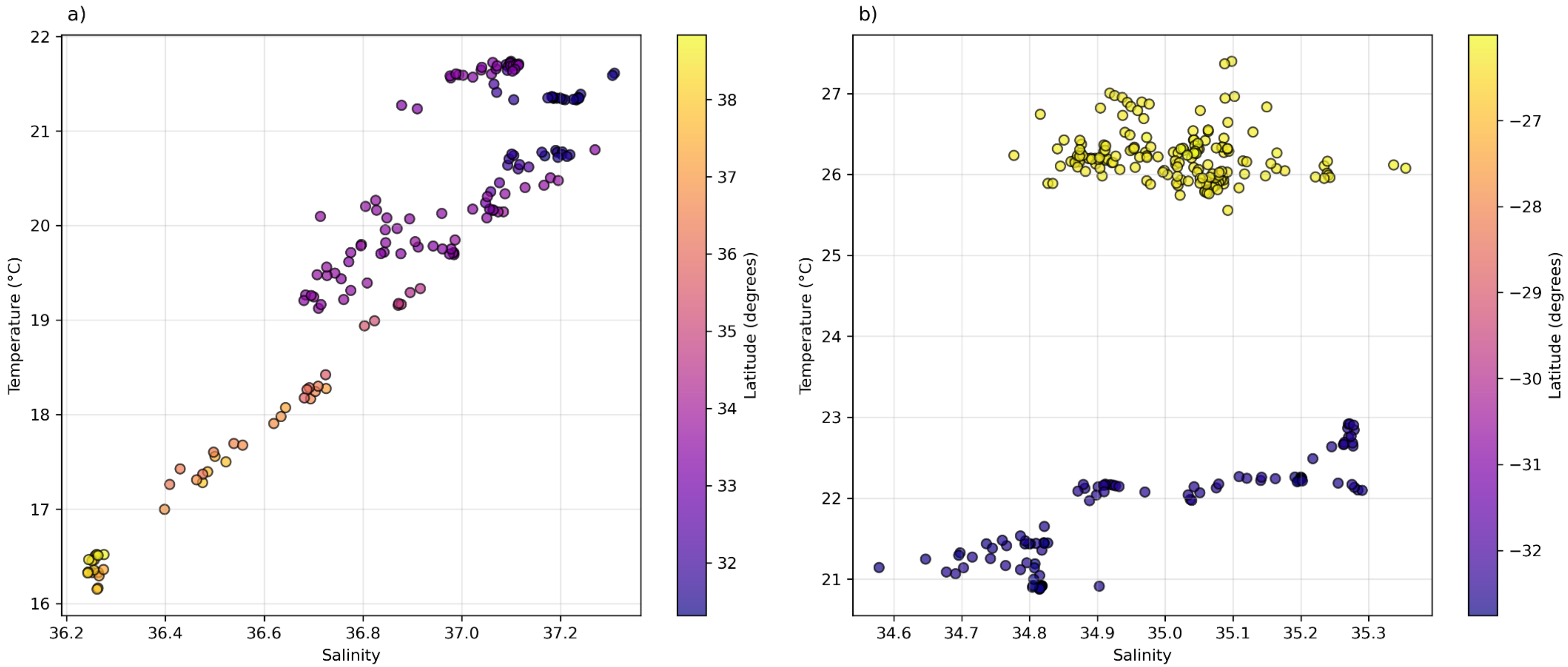

Figure S8. T/S diagram for the a) North Atlantic and b) South Pacific regions, color-coded by observed latitude.

Expected pH	SNR
$pH_{temp,sal}$	1.393560
pH_{temp}	1.202952
pH_{sal}	0.194478
$pH_{TA,fCO2}$	0.143814

Table S1. Signal-to-noise ratio (SNR) for hourly mean pH variations relative to different expected pH estimates for the North Atlantic cruise. An SNR greater than 1 indicates that observed variations exceed measurement noise, suggesting a real signal, while an SNR less than 1 suggests that variability is within the uncertainty range.

Expected pH	SNR
$pH_{temp,sal}$	0.375375
pH_{temp}	0.438769
pH_{sal}	0.587472
$pH_{TA,fCO2}$	0.574092

Table S2. Signal-to-noise ratio (SNR) for hourly mean pH variations relative to different expected pH estimates for the South Pacific cruise. An SNR greater than 1 indicates that observed variations exceed measurement noise, suggesting a real signal, while an SNR less than 1 suggests that variability is within the uncertainty range.

S1. Signal-to-noise ratio

To assess the robustness of observed pH variations, we calculated the Signal-to-Noise Ratio (SNR) for hourly mean pH across the dataset. The signal (σ_{signal}) was defined as the standard deviation of the difference between observed pH and expected pH values, while the noise (σ_{noise}) was estimated from the mean measurement uncertainty of the pH optode. SNR was computed for four expected pH estimates:

1. Temperature and salinity-driven pH ($pH_{temp,sal}$)
2. Temperature-driven pH (pH_{temp})
3. Salinity-driven pH (pH_{sal})
4. pH expected from mean TA and fCO_2 ($pH_{TA,fCO2}$)

SNR was calculated as:

$$SNR = \frac{\sigma_{signal}}{\sigma_{noise}}$$

where

$$\sigma_{signal} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(pH_{obs,i} - pH_{expected,i})^2}$$

is the standard deviation of the difference between observed and expected pH, and

$$\sigma_{noise} = \frac{1}{N}\sum_{i=1}^{N} pH_{uncertainty_i}$$

is the mean measurement uncertainty of the optode.

An SNR > 1 indicates that observed variations exceed measurement noise, suggesting a real signal, while SNR < 1 implies that variability is within uncertainty.

S2. Quantifying changes in DIC required for targeted pH

In this study, we explored the alterations in dissolved inorganic carbon (DIC) required to induce a specific pH change in seawater. The initial conditions of the experiment were set with a Total Alkalinity (TA) of 2300 µmol/kg, an initial DIC concentration of 2000 µmol/kg, salinity at 35 practical salinity units, and temperature maintained at 25°C under atmospheric pressure (0 dbar). These conditions mimic typical oceanic conditions in temperate regions.

We employed the PyCO2Sys package to calculate the carbonate system parameters (parameters describe in Section 2.6; (Humphreys et al., 2022). Initially, we determined the system's pH under the given conditions (TA and initial DIC), with no contributions from phosphate or silicate. The initial pH was calculated on the total scale.

To achieve a decrease in pH by 0.1 units from the initial value, we applied a numerical solver (fsolve from SciPy) to find the DIC level necessary to reach the target pH under the same conditions of salinity, temperature, and pressure. This iterative approach refined the DIC estimate until the desired pH was achieved.

Following the determination of the required DIC to reach the target pH, we calculated the change in DIC needed and converted this value from µmol/kg to mg C/L using the molecular weight of carbon (12.01 g/mol) and the density of seawater (1.025 kg/L). Subsequently, this concentration was converted to mg C/m^3 for practical applications and monitoring purposes.

The daily change in pH of 0.1 corresponds to 687 mg C/m^3/day.

References

Humphreys, M. P., Lewis, E. R., Sharp, J. D., & Pierrot, D. (2022). PyCO2SYS v1.8: marine carbonate system calculations in Python. *Geosci. Model Dev.*, *15*(1), 15-43. https://doi.org/10.5194/gmd-15-15-2022

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