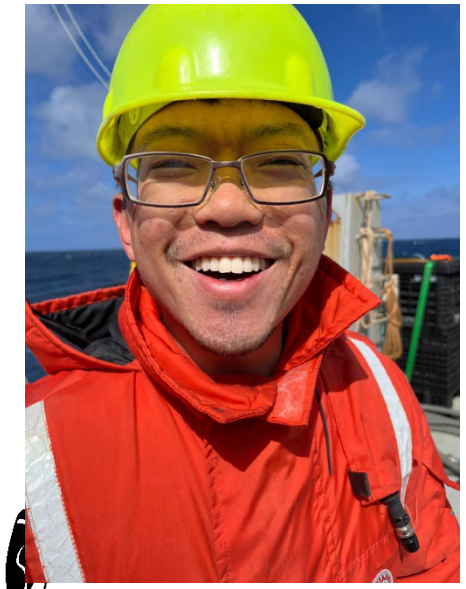
ICMGP 2024
CAPE TOWN • SOUTH AFRICA • 21 - 26 JULY

Air-sea exchange of elemental Hg and dimethylmercury in the South Pacific and Southern Ocean



Yipeng He (Florida International University)
Hannah Inman, Robert Mason (University of Connecticut)
Marissa Despins, Carl Lamborg (University of California, SC)

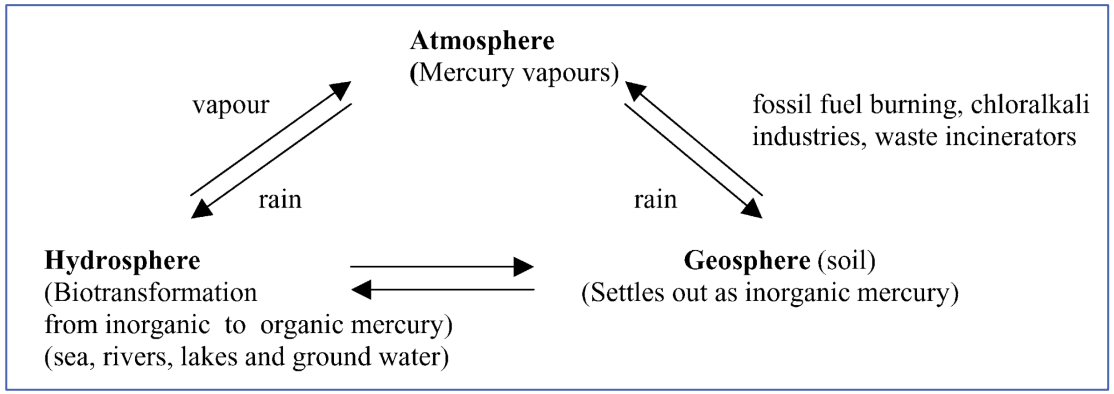
July 23

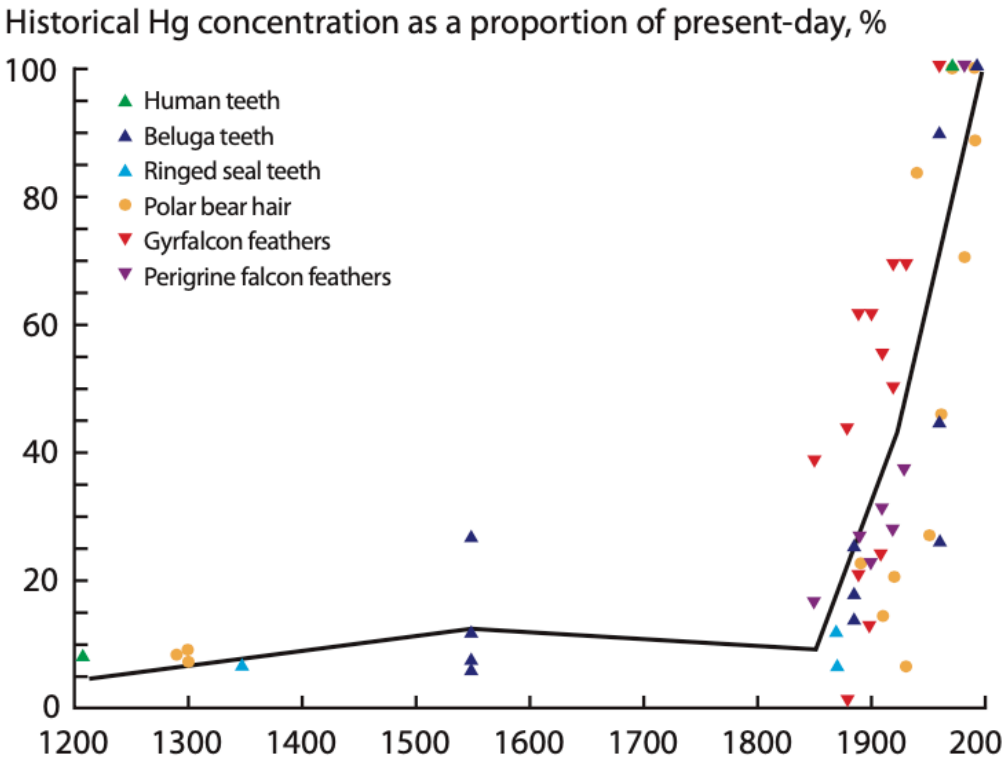
Outline

- Introduction
  - Biogeochemical cycling; Mercury speciation in atmosphere; Air-sea exchange;
- Method
  - Hg species in atmosphere; Dissolved Hg^0 and DMHg in seawater; Air-sea exchange flux;
- Results
  - Air side: gaseous Hg^0;
  - Seawater side: dissolved Hg^0 and DMHg ;
  - Air-sea exchange flux;
- Conclusions

Introduction

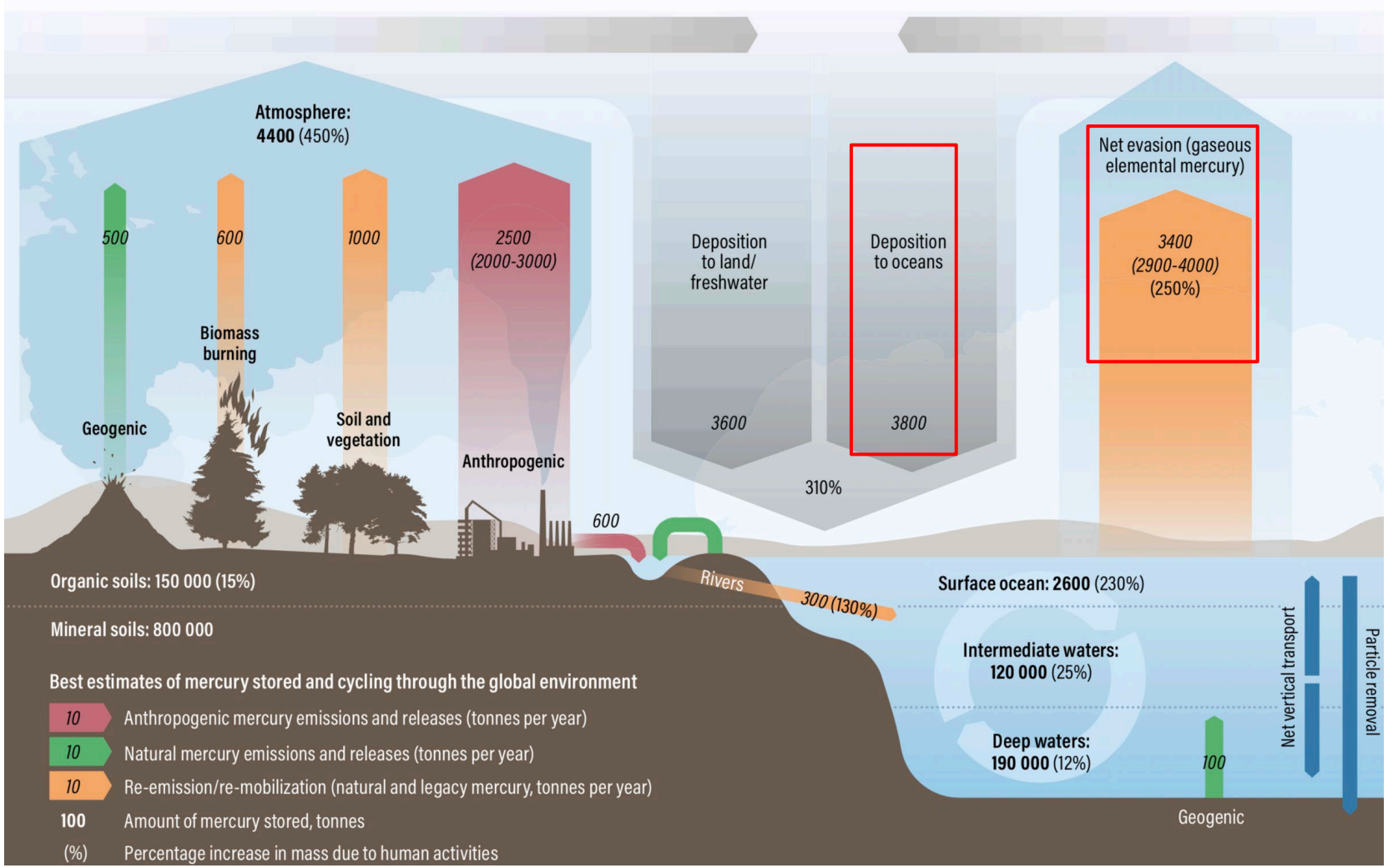
- Anthropogenic activities have enriched mercury in the biosphere by at least a factor of three since industrial period, leading to increases in total mercury (Hg) in the oceans and methylmercury (MeHg) in marine food webs.





(UNEP 2013)-Global mercury assessment 2013 report.

Introduction



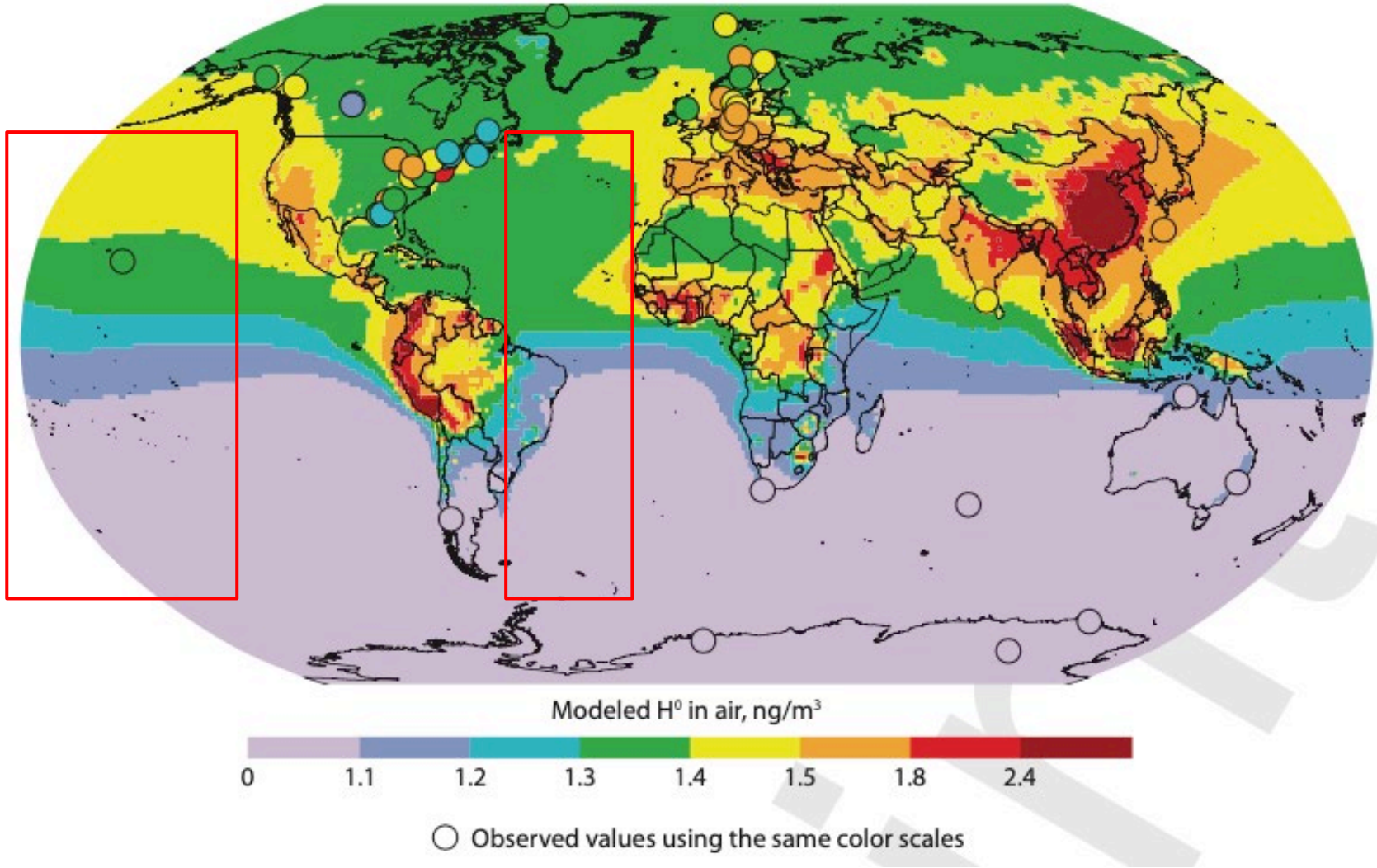
Major processes for the open ocean

- Deposition
- Evasion

(UNEP 2018)-Global mercury assessment 2018 report.

Introduction

- Modeled air Hg^0 decreasing trend from NH to SH



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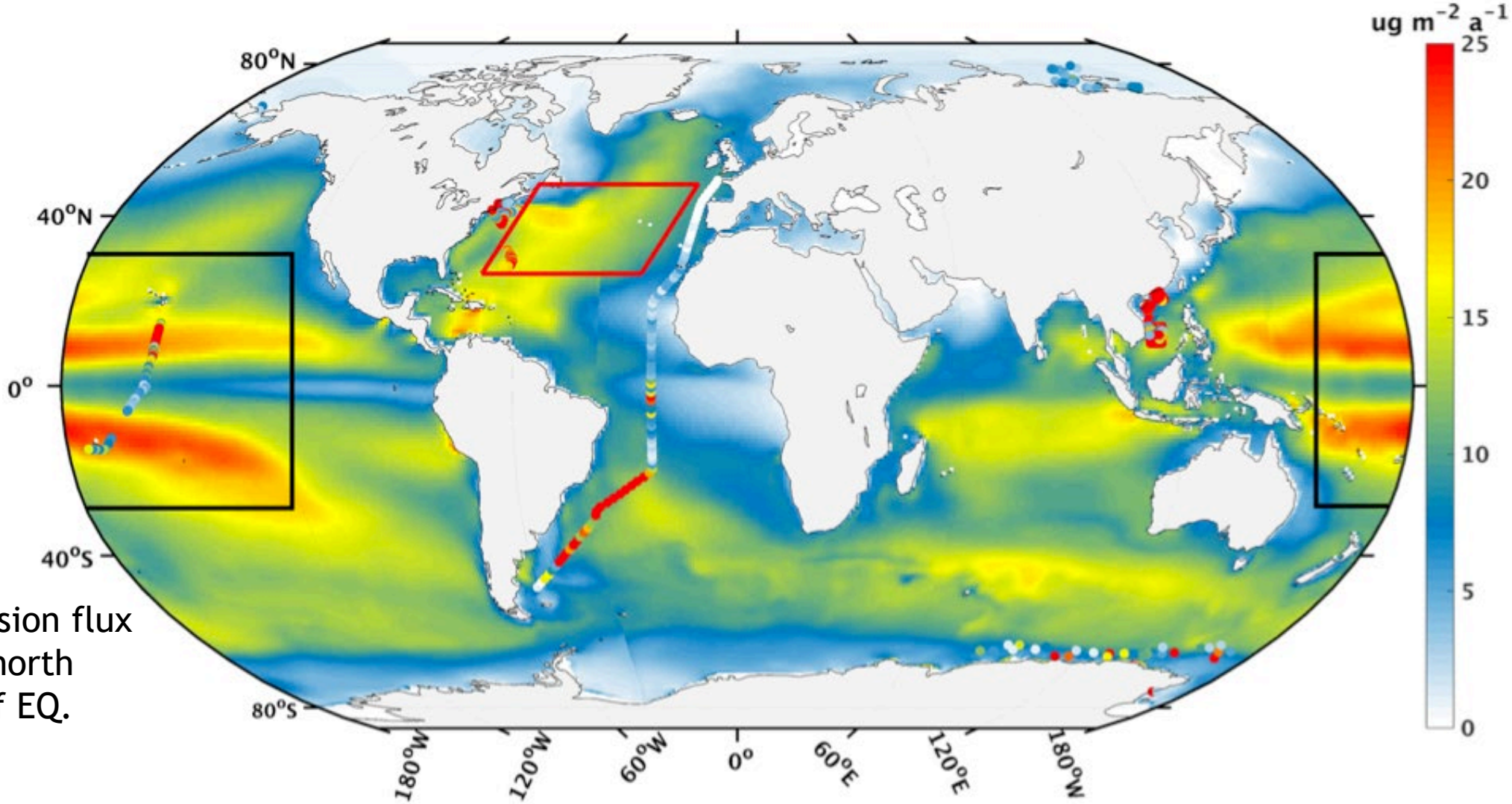
Introduction



Equatorial region:

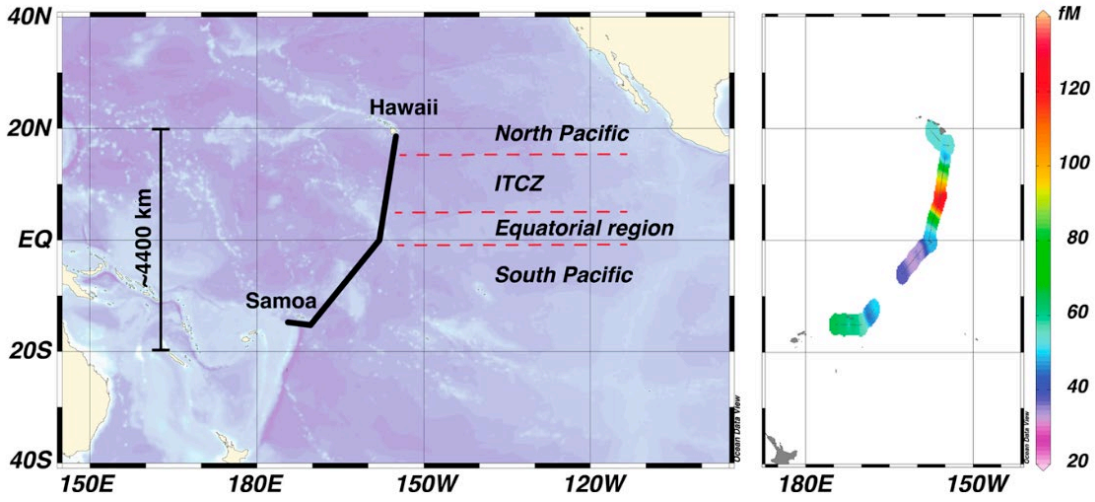
- Modeled Hg^0 evasion flux shows peaks on north and south side of EQ.

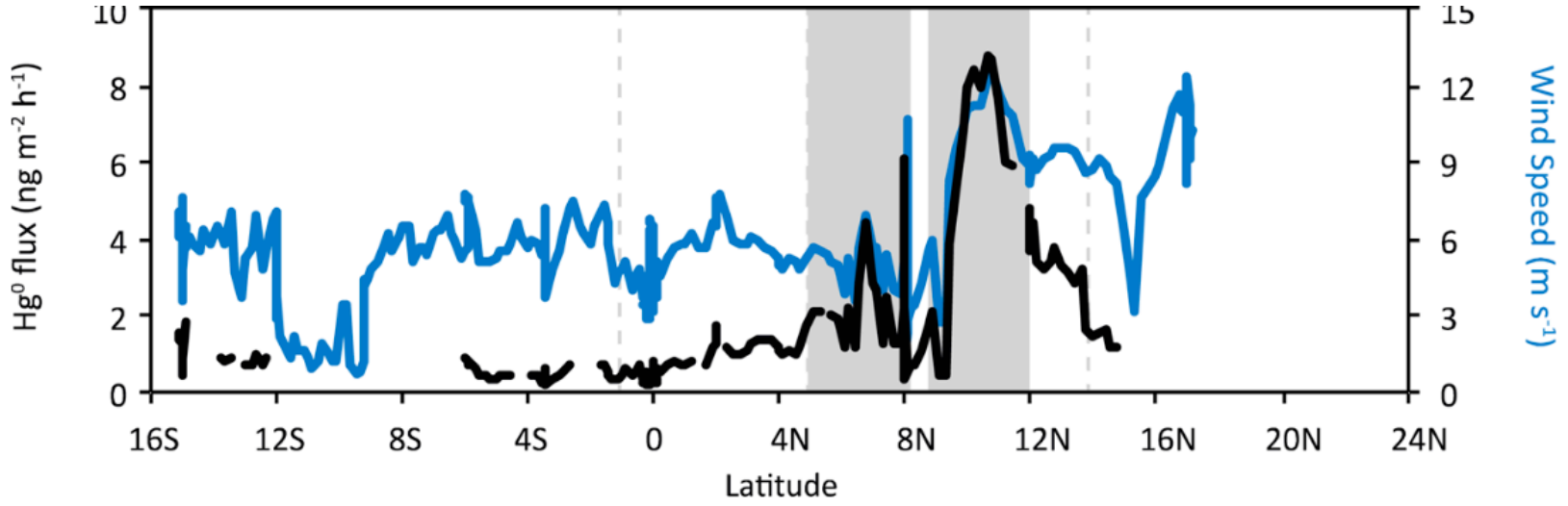
Huang and Zhang, 2020

Introduction

Equatorial region:

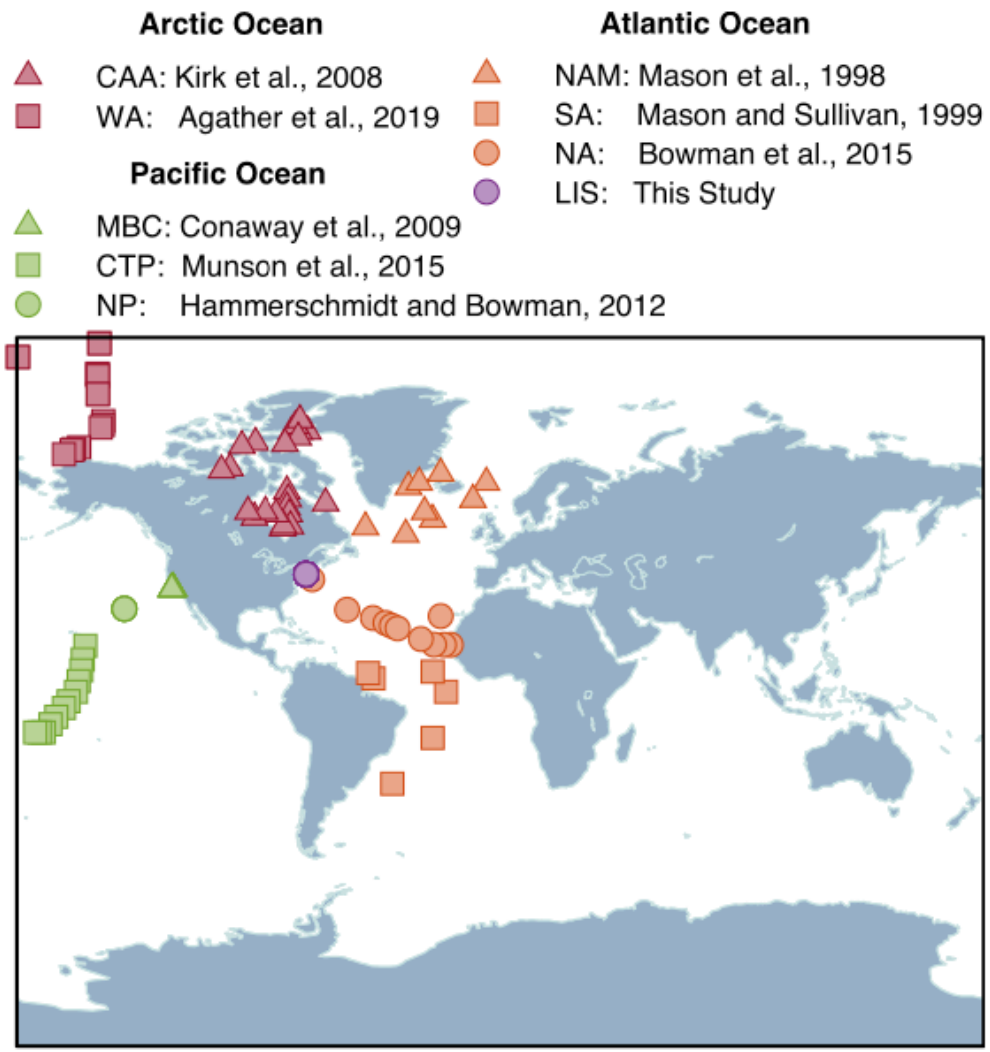
- Measured Hg^0 evasion flux doesn't show two peaks on north and south side of EQ. Only North side.



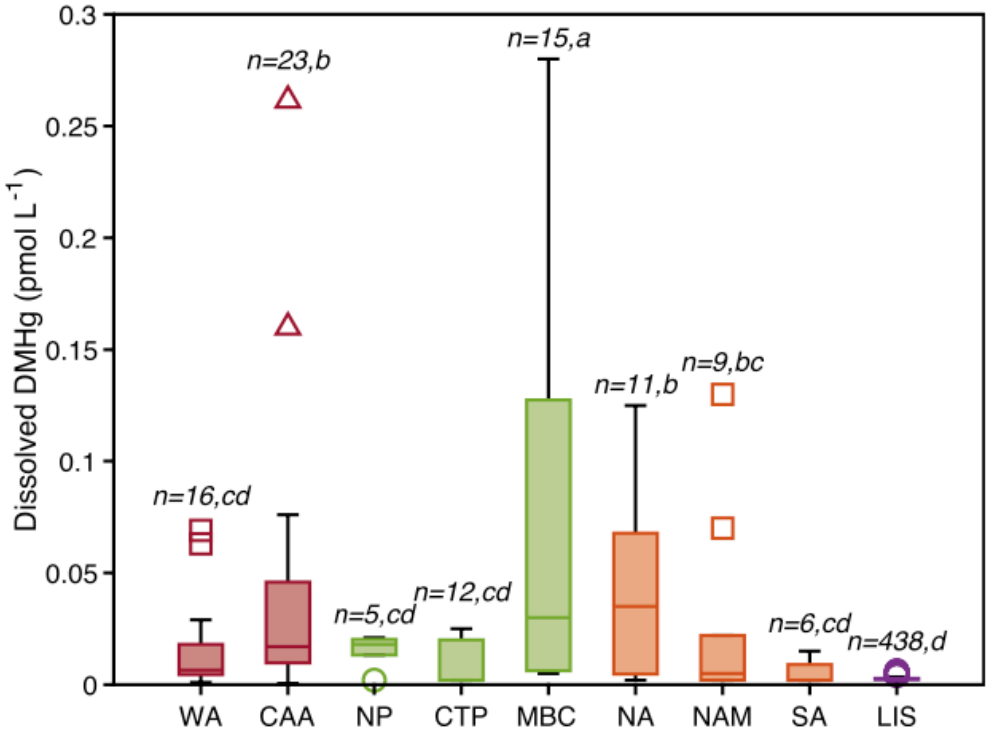


Soerensen et al., 2014

Introduction



- Past 30 years, there are no more than 200 DMHg data points in surface ocean globally
- However, in this study, more than 1000 DMHg data points are made in the surface South Pacific and Southern Ocean by our DMHg Auto-Analyzer



He et al., 2022

Introduction

- DMHg could play an important role as MMHg source in marine boundary layer and influence a large region, eg, coastal California

Figure 5. Conceptual diagram showing the hypothesized sources and mechanisms of transfer of organic Hg species from the ocean to the coastal terrestrial food web in central California, USA. Bar charts indicate the mean concentrations of MMHg observed in this work plus fog and rainwater concentration from[16].

Weiss-Penzias et al., 2019

Objectives


Air-sea exchange
Inorganic Hg
Methylated Hg
Evasion & Deposition

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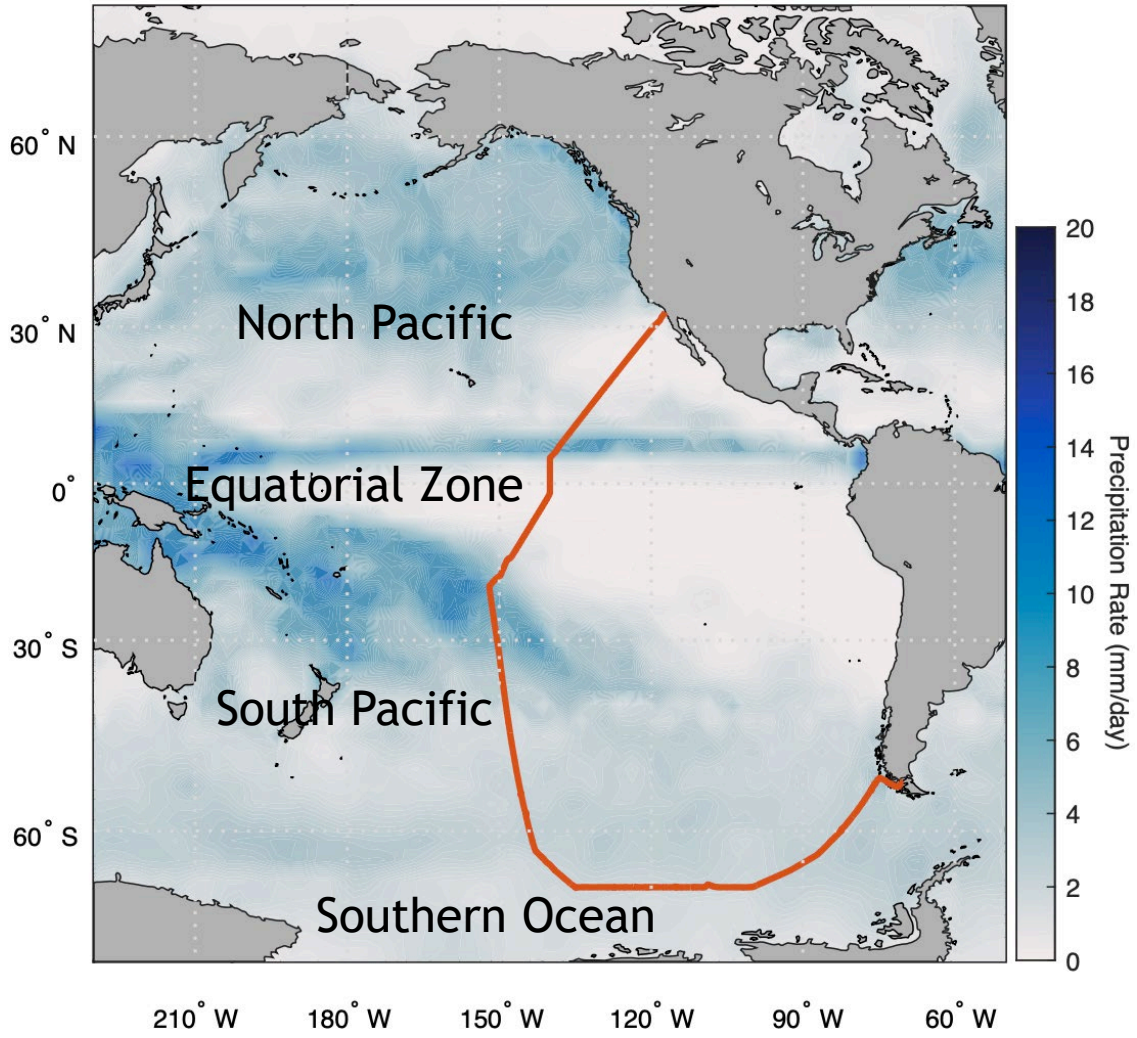
Cruise Info



US GEOTRACES GP17 Cruise

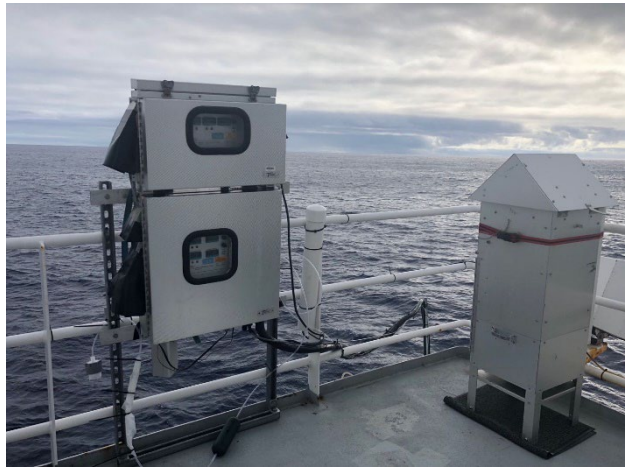
- Depart: San Diego, CA, USA (Nov 13, 2022)
- Arrive: Punta Arena, Chile (Jan 25, 2023)
- Ship: R/V Roger Revelle

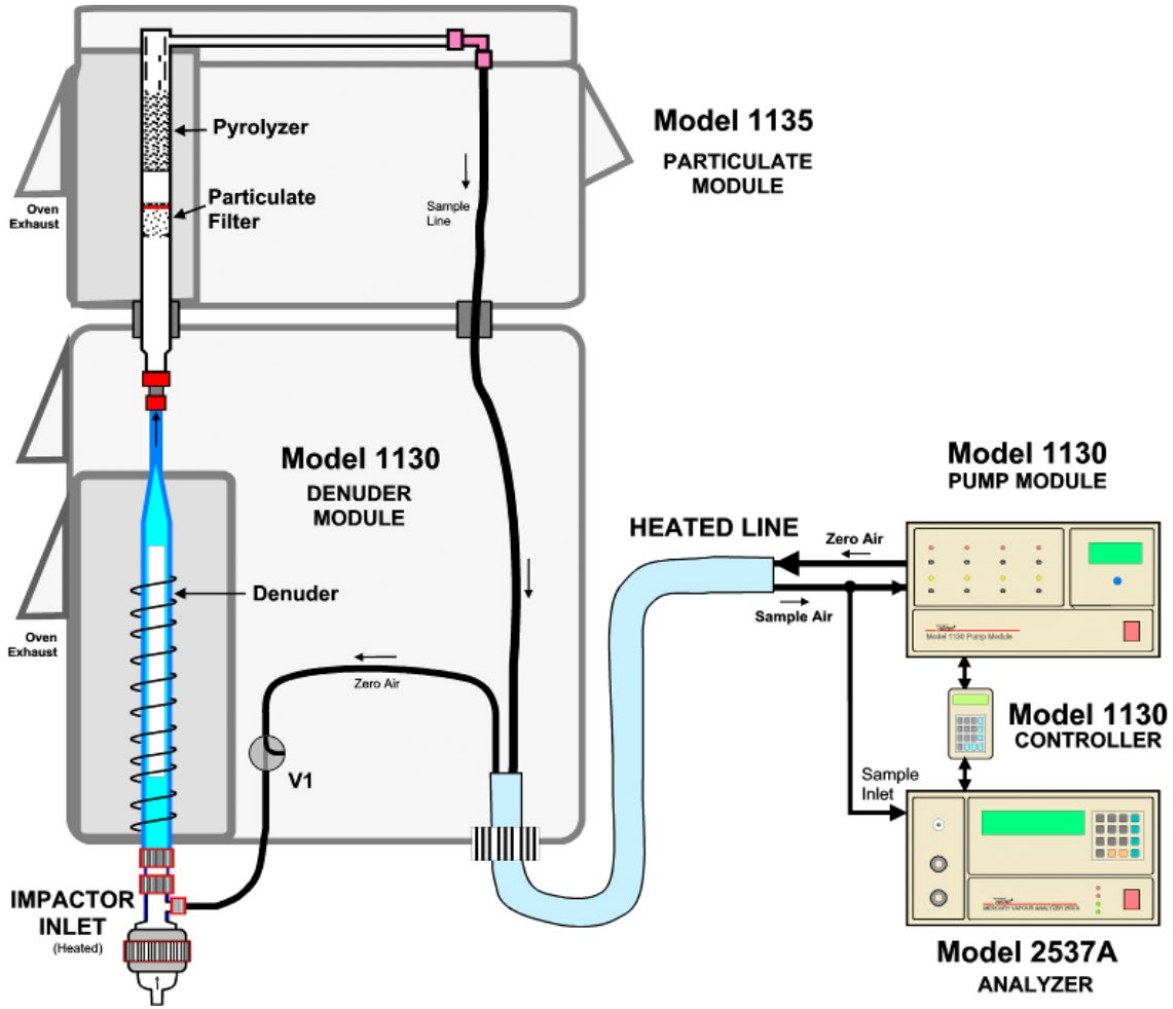
- Air Side:
  - GEM, PBM, RGHg (Tekran Speciation System)
  - Bulk aerosol total Hg (Aerosol Sampler)
  - Total Hg stable isotope (Carbon Trap)
- Seawater Side:
  - Dissolved Hg^0 (Flow Chamber & Tekran 2537)
  - Dissolved DMHg (Flow Chamber & DMHg Auto-Analyzer)
  - Dissolved Hg^0 stable isotope (Carbon Trap)

Method

Measuring mercury species in atmosphere

- Tekran Model 1135 Particulate Mercury Unit is used with Model 1130 Speciation Unit and Model 2537 Mercury Analyzer to simultaneously monitor particulate bound mercury (Hg^P), elemental mercury (Hg^0) and reactive gaseous mercury (RGHg) in ambient air
- Advantage: high resolution
- Disadvantage: efficiency on RGHg collection



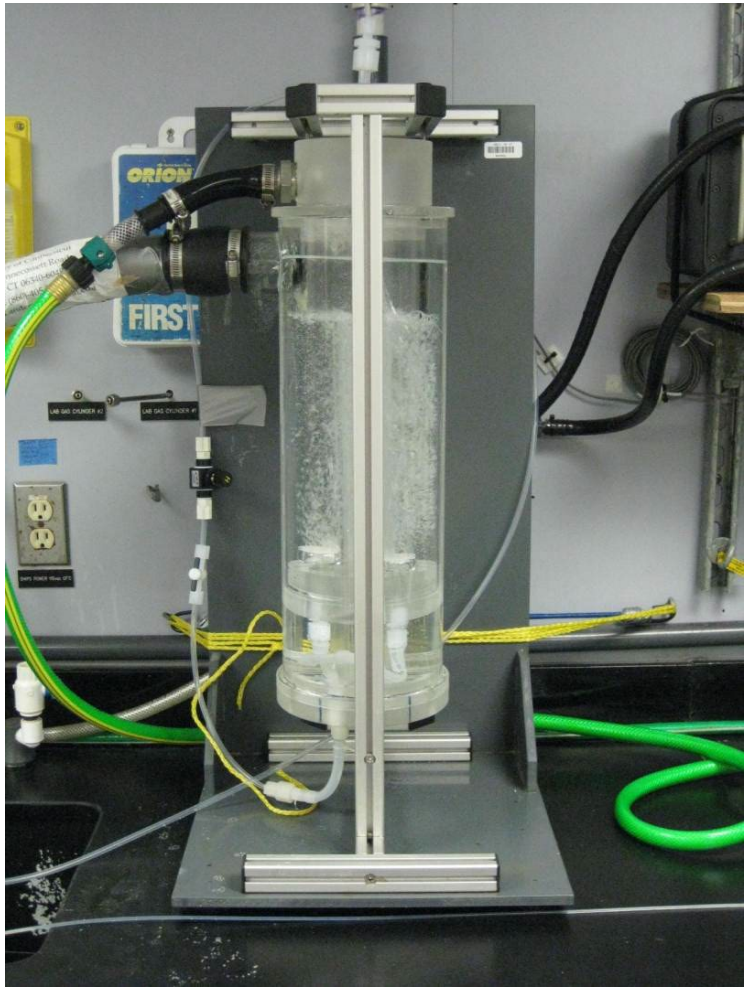


Method

Measuring dissolved Hg^0 and DMHg:

- Ship-pumped surface seawater flow 15 ± 1 L/min
- Ship's clean air 1.2 L/min at pressure below 5 psi on regulator

- Dissolved Hg^0: measured by Tekran 2537
  - High resolution (5 min)
  - Low DL (~1 fM)
- Dissolved DMHg: measured by Auto-DMHg Analyzer
  - High resolution (1 hr)
  - Low DL (~0.1 fM)



Method

Air-sea exchange flux calculation for Hg^0 and DMHg

- The air-sea exchange flux (F) is determined by the following equation:

$$F_{Hg^0} = k_{w,Hg^0}\left(Hg^0_{diss} - \frac{C_{air,Hg^0}}{H_{Hg^0}}\right)$$

$$F_{DMHg} = k_{w,DMHg}\left(DMHg_{diss} - \frac{C_{air,DMHg}}{H_{DMHg}}\right)$$

- The k_w is the water-air transfer velocity which is mainly driven by wind. H is the dimensionless Henry's law coefficient, which is temperature dependent.

Wilke and Chang, 1955; Nightingale et al., 2000; Andersson et al., 2008; Wanninkhof, 1992; Poissant et al., 2000;

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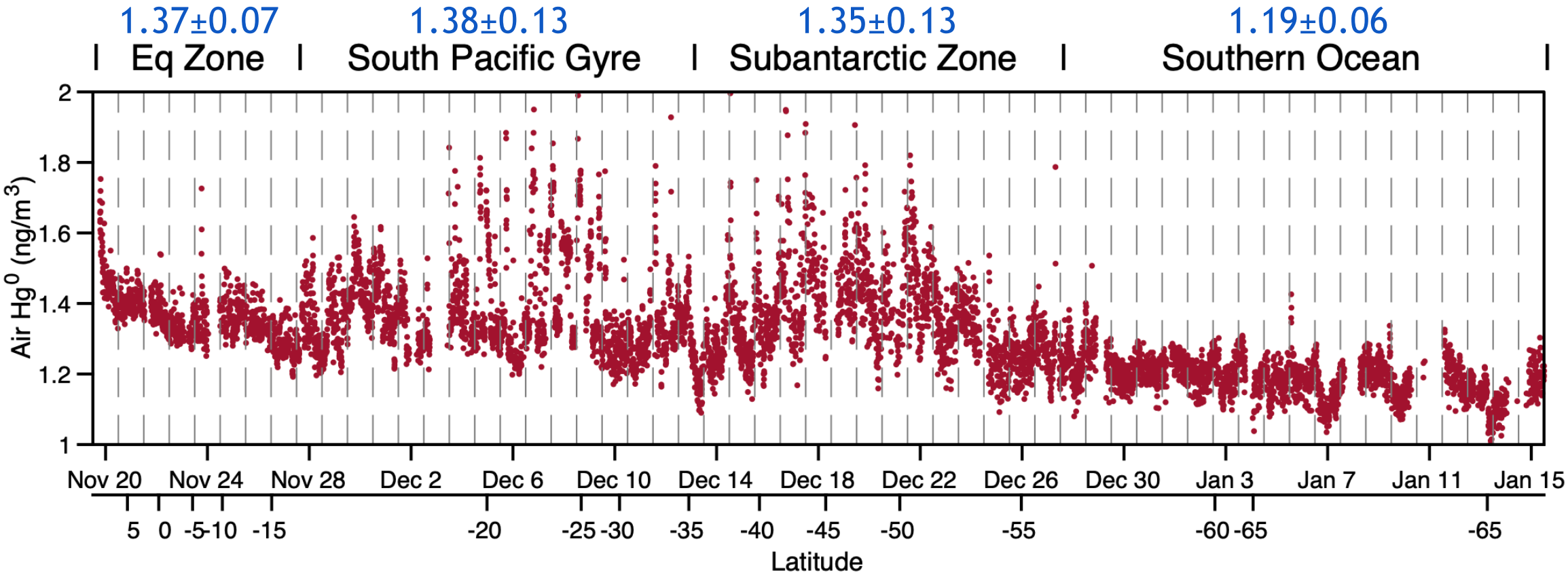
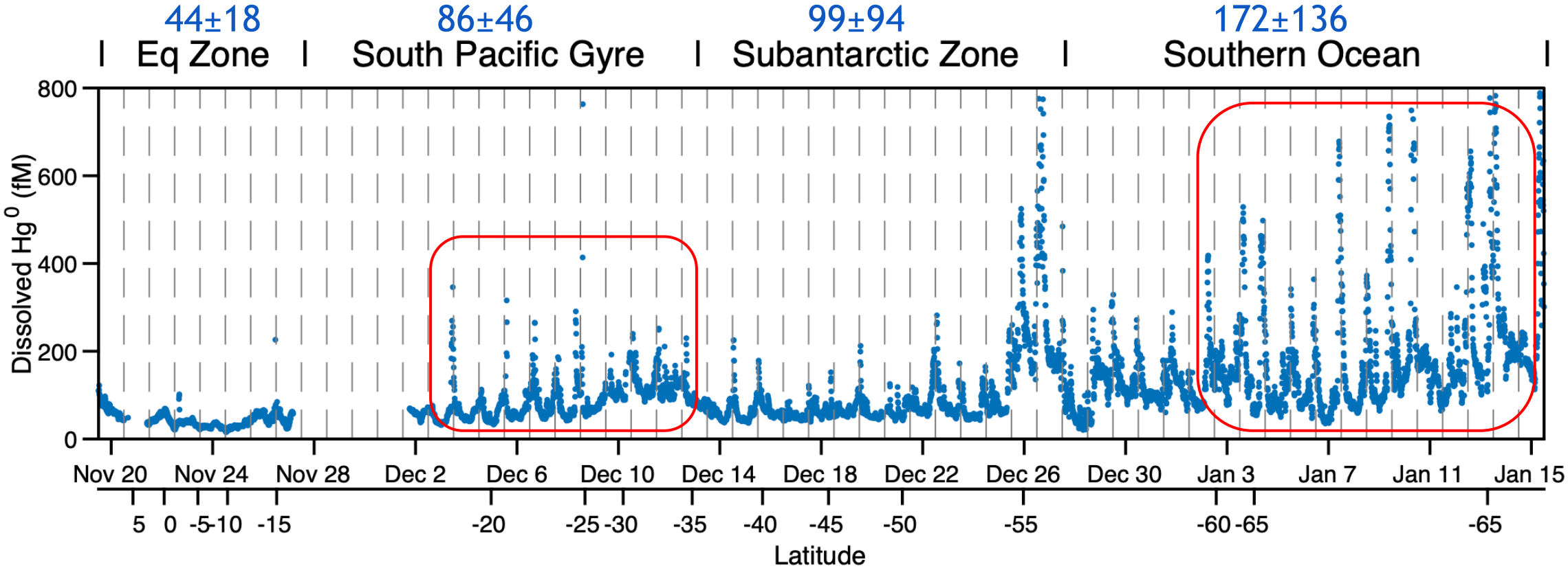
Results - Atmospheric Hg^0



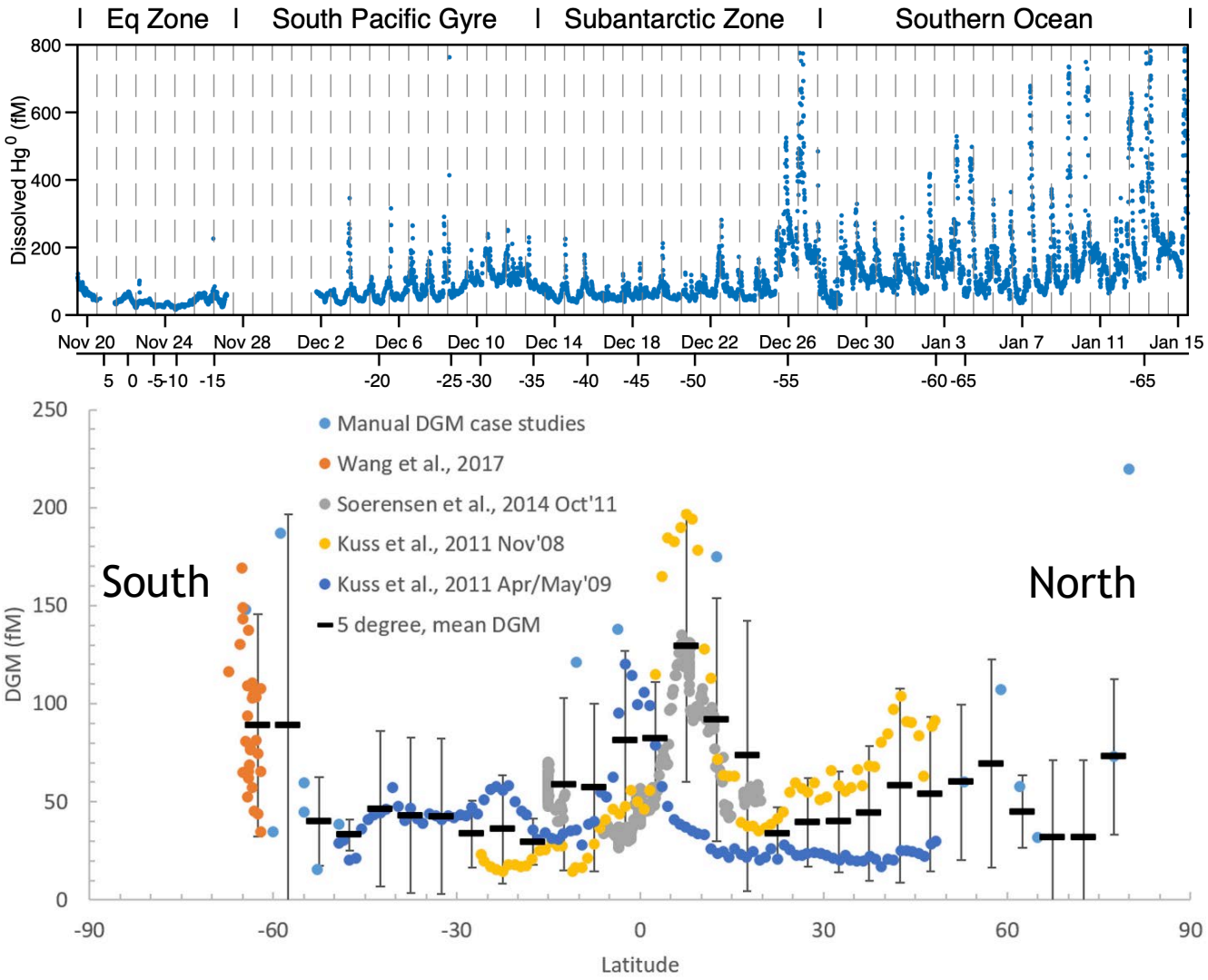
- Observed more dynamic in the South Pacific than the Southern Ocean
- Observed a diurnal pattern, explained by an assumption of ‘photoreaction’

Results – Dissolved Hg^0



- Observed a diurnal pattern, could be explained by an assumption of 'photoreaction in surface ocean'
- Less dynamic in Equatorial Zone, but more daily variability towards south

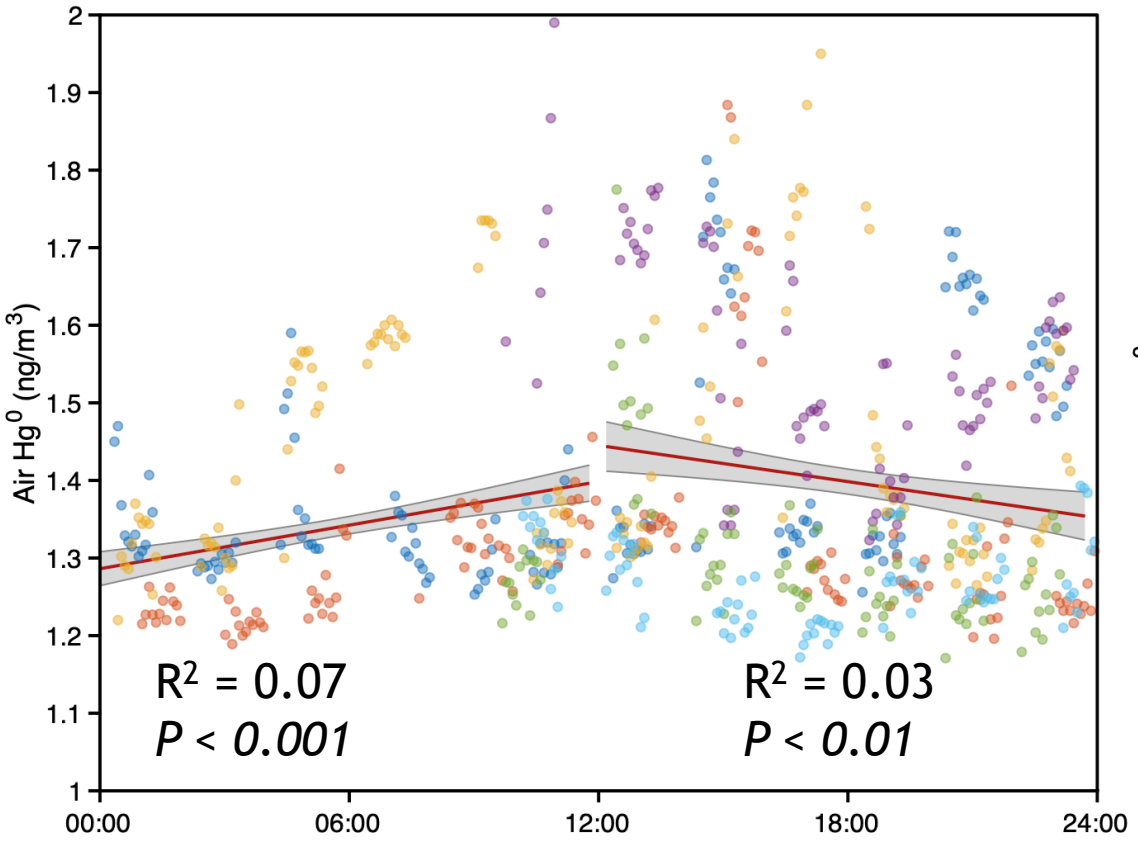
Results – Dissolved Hg^0

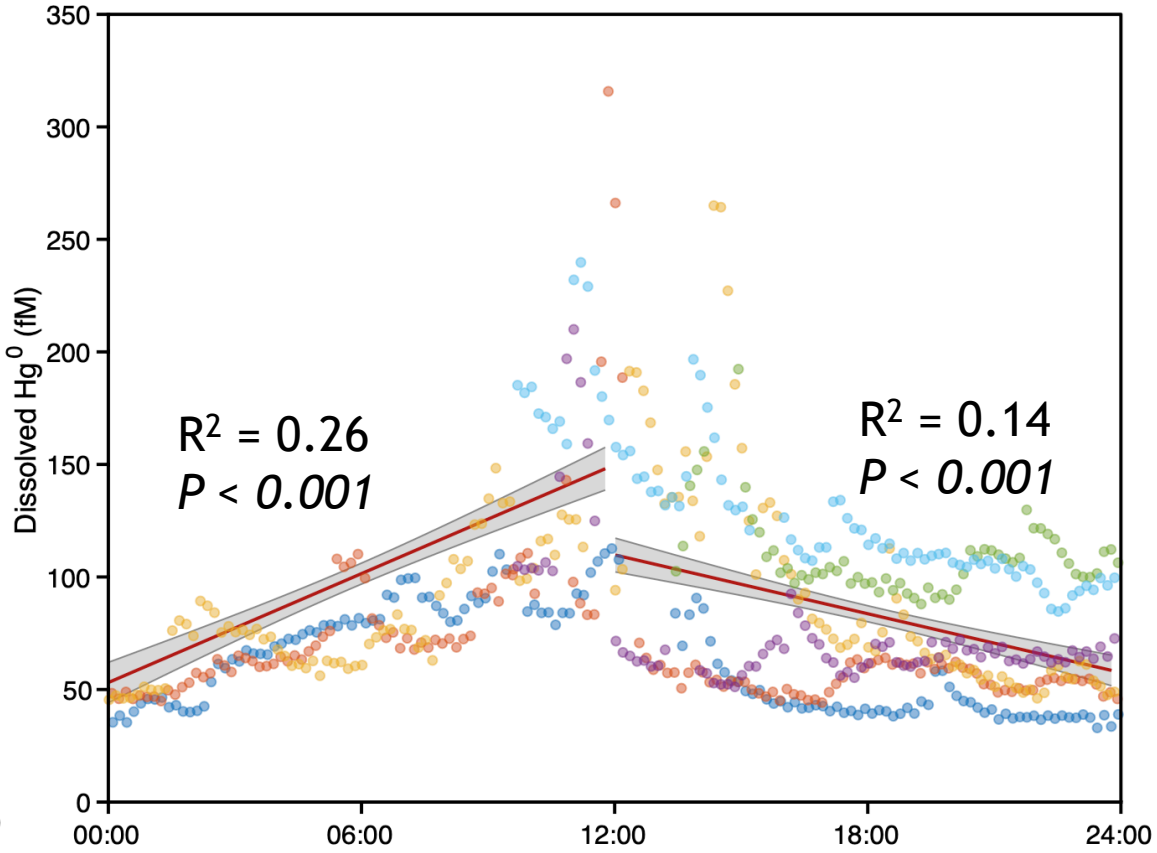


- Our measurements from South Pacific and Subantarctic zone are higher than previous measurements from similar latitude bands of the South Atlantic
- Perhaps DGHg has become more dynamic and variable recently?

Jiskra et al., 2021

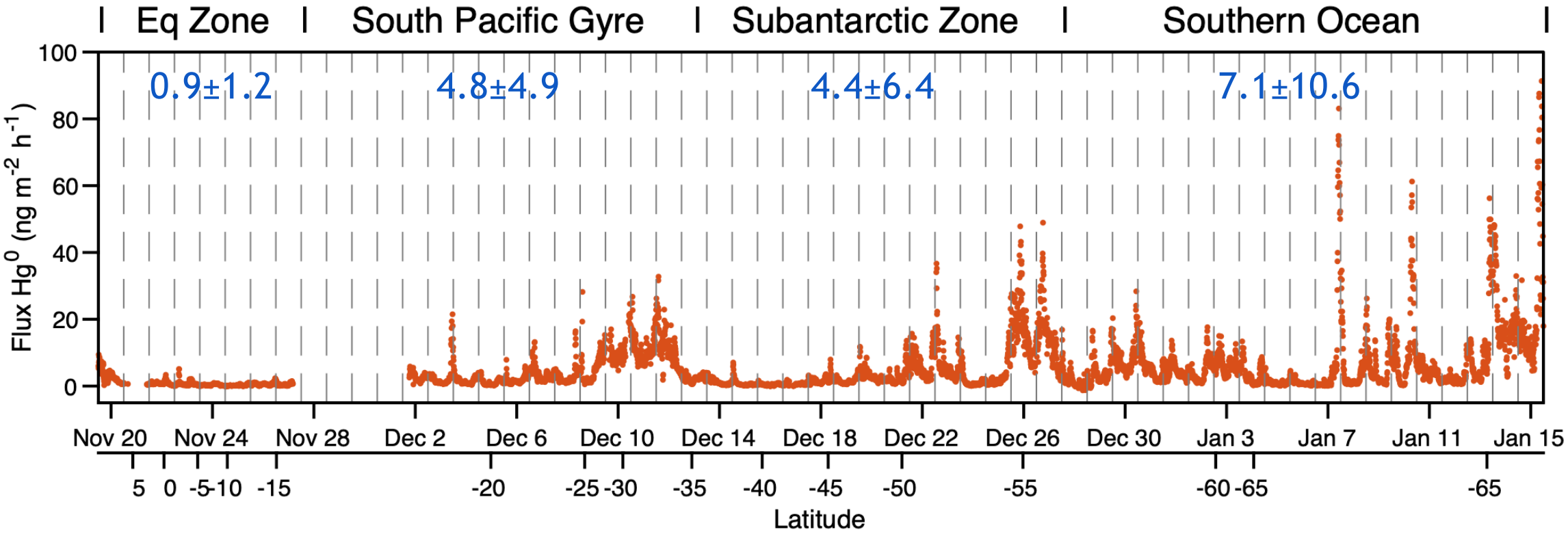
Results – The Diurnal Pattern





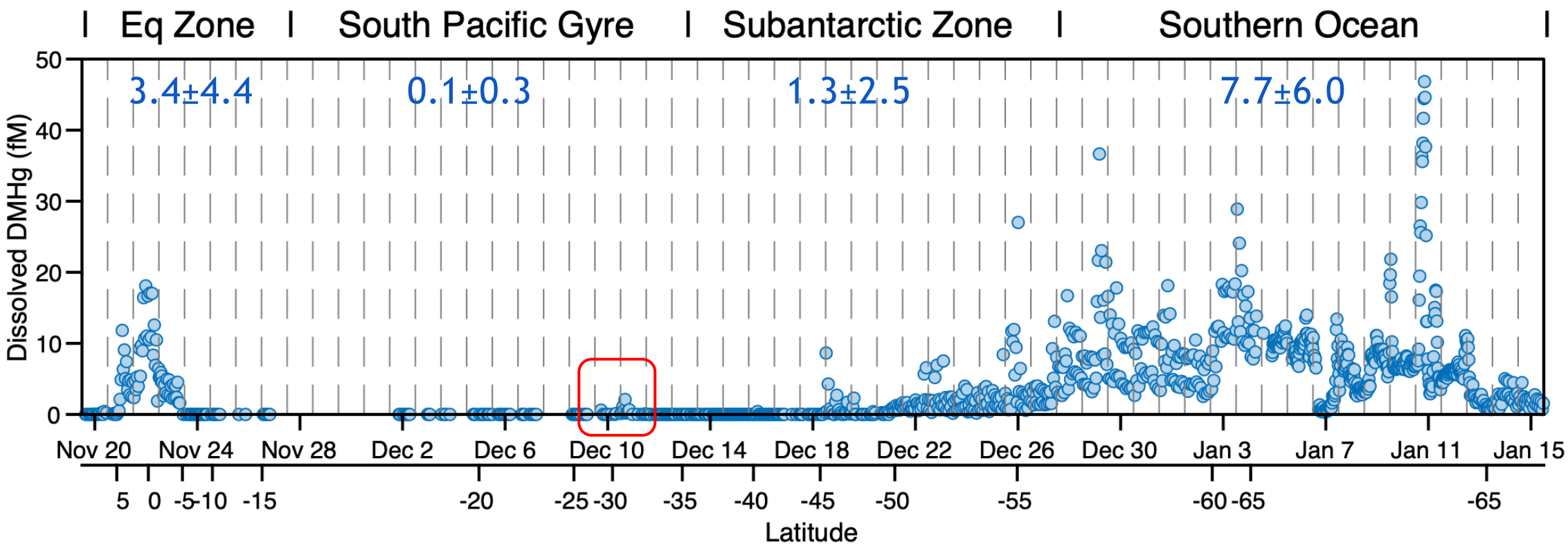
- Higher evasion of Hg^0 from surface ocean can explain the diurnal pattern in atmospheric Hg^0

Results – Air-Sea Flux Hg^0



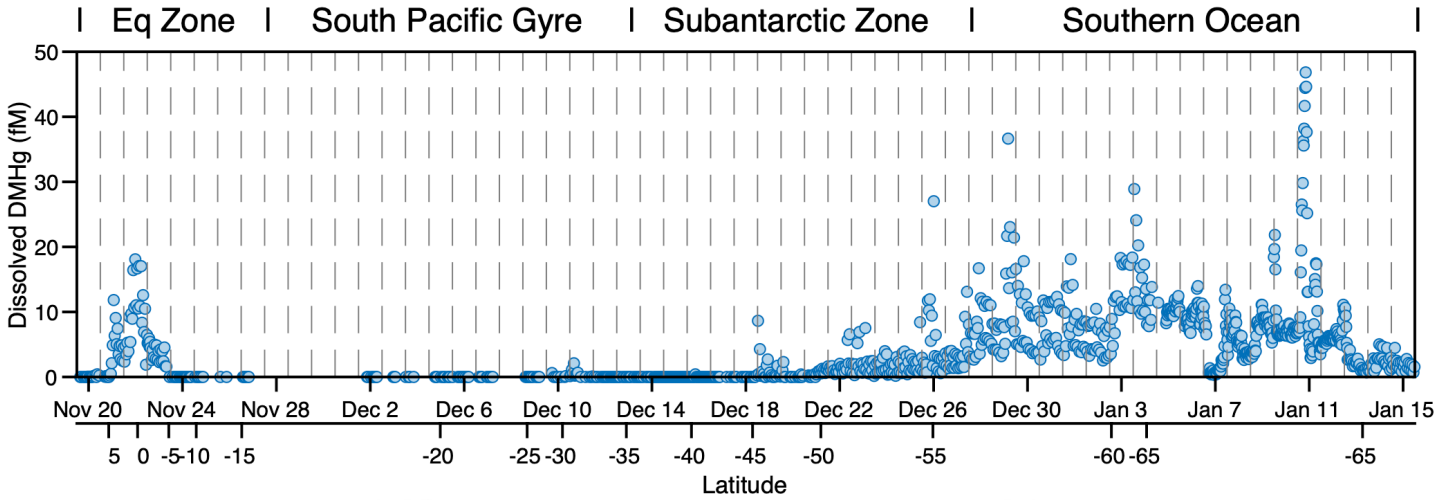
- Positive flux means the supersaturation at the surface ocean
- Less dynamic in Equatorial Zone, but more dynamic towards south
- We propose that the diurnal pattern is due to photoreduction

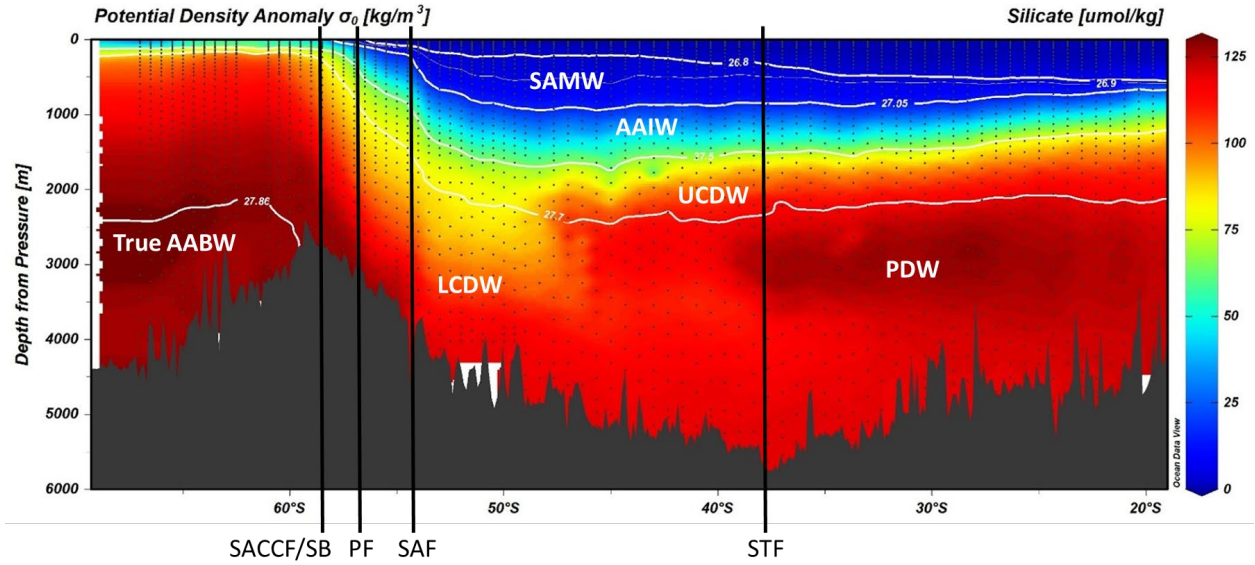
Results – Dissolved DMHg



- Large amount of dissolved DMHg at Equatorial Zone (but air DMHg is below DL)
- No DMHg in the South Pacific Gyre, except a surprise DMHg peak near 30°S
- Gradually increased DMHg after passing through the South Pacific Gyre and into the Southern Ocean

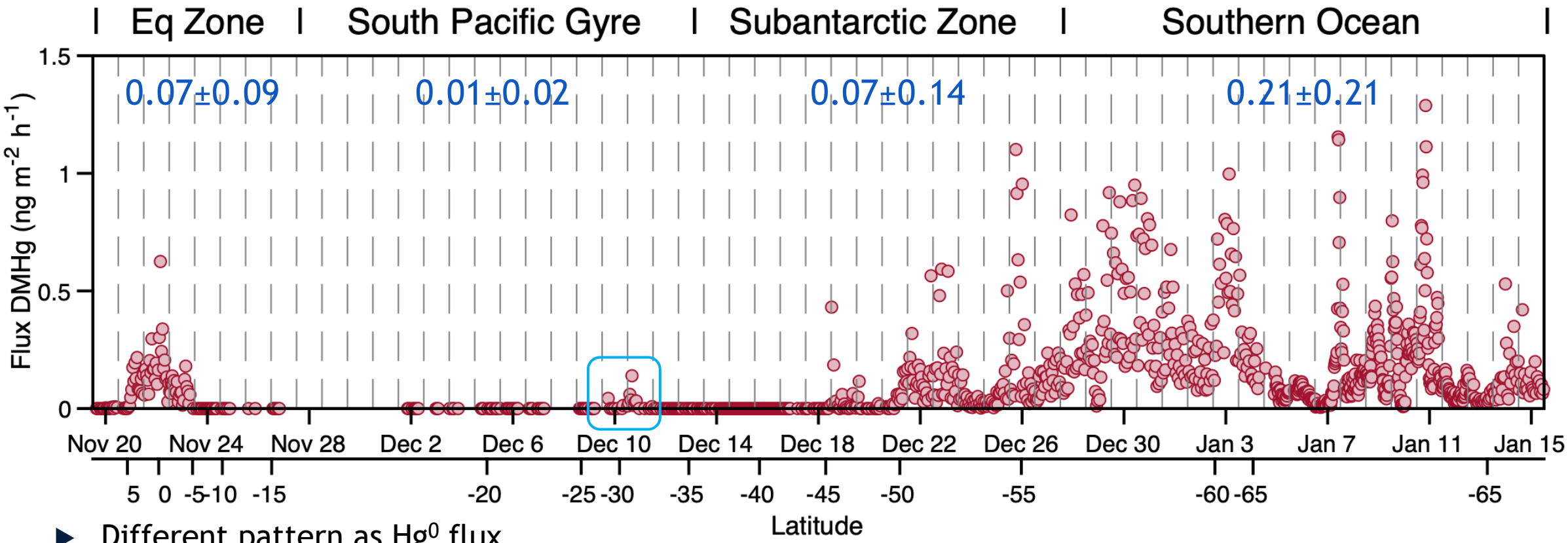
Results – Dissolved DMHg





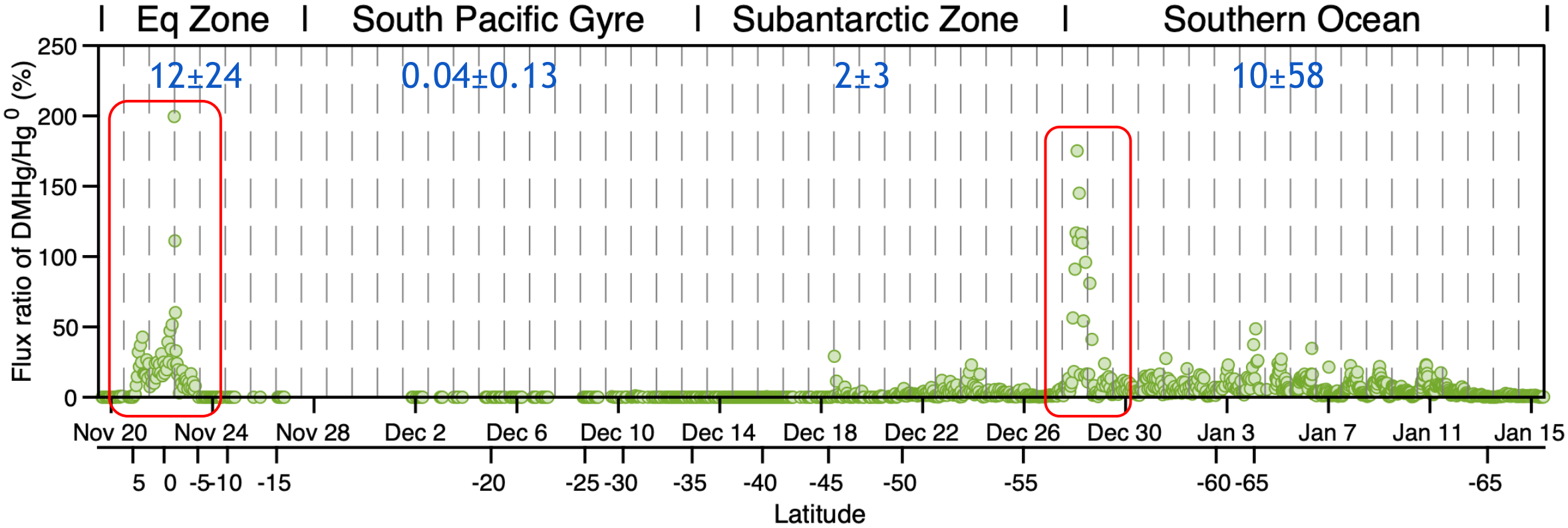
- More DMHg appears where there are more nutrients present (N and Si)
- Biological pathway of DMHg production in the Southern Ocean

Results – Air-Sea Flux DMHg



- Different pattern as Hg^0 flux
- Flux within the South Pacific Gyre suggests that DMHg is more stable than expected in these waters, which may be derived from upwelled Subantarctic Zone and carried to here over long distance.
- Increased DMHg flux southwards into the Southern Ocean but with higher variability (different water bodies)

Results – Flux Ratio of DMHg/Hg^0



- Generally, DGHg flux is usually less than 2% of Hg^0 flux
- However, higher ratio appears at Equatorial Zone and transition region between Subantarctic and Southern Ocean, more than 50%
- The highest ratio is more than 100%, which means DMHg flux is higher than Hg^0 flux. Unbelievable!

Conclusions

Air side:

- Air Hg^0 is generally lower in the South Pacific than the North Pacific
- Observed a diurnal pattern likely caused by the rapid air-sea exchange process in this region
- Observed more dynamic air Hg^0 in the South Pacific than the Southern Ocean

Seawater side:

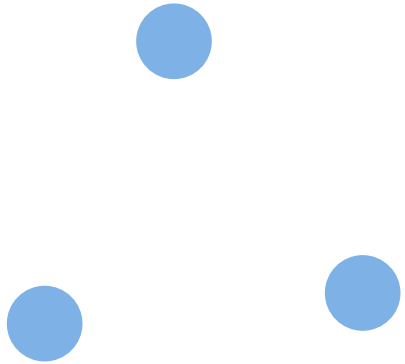
- Dissolved Hg^0 displays a diurnal pattern due to photoreduction in surface seawater
- Observed higher dissolved Hg^0 in the South Pacific and Southern Ocean than previous measurements in the South Atlantic
- Dissolved DMHg is more likely to follow the nutrients level (N and Si), due to its biological production
- DMHg flux can be higher than Hg^0 flux in Equatorial and Southern Ocean regions, suggesting its important role as a MeHg source in marine boundary layer

Acknowledge

We would like to thank the captain and crew of the ship, the R/V Roger Revelle, as well as our colleagues on the U.S. GEOTRACES cruise for collecting seawater, ocean particles, rain and aerosols. This study is funded by National Science Foundation.

I personally thank Dr Mark Stephens for the travel support for this ICMGP conference

Thank you! Questions?

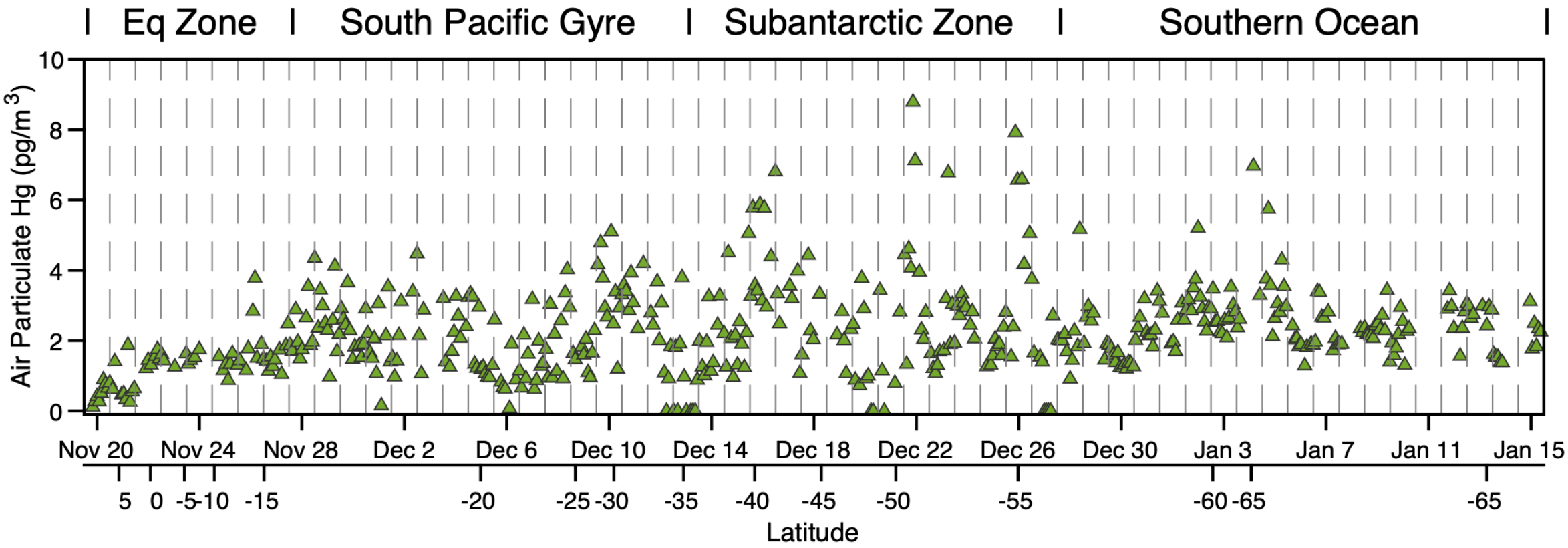


I will arrive at CPT Tuesday night. Happy to talk with you by then!

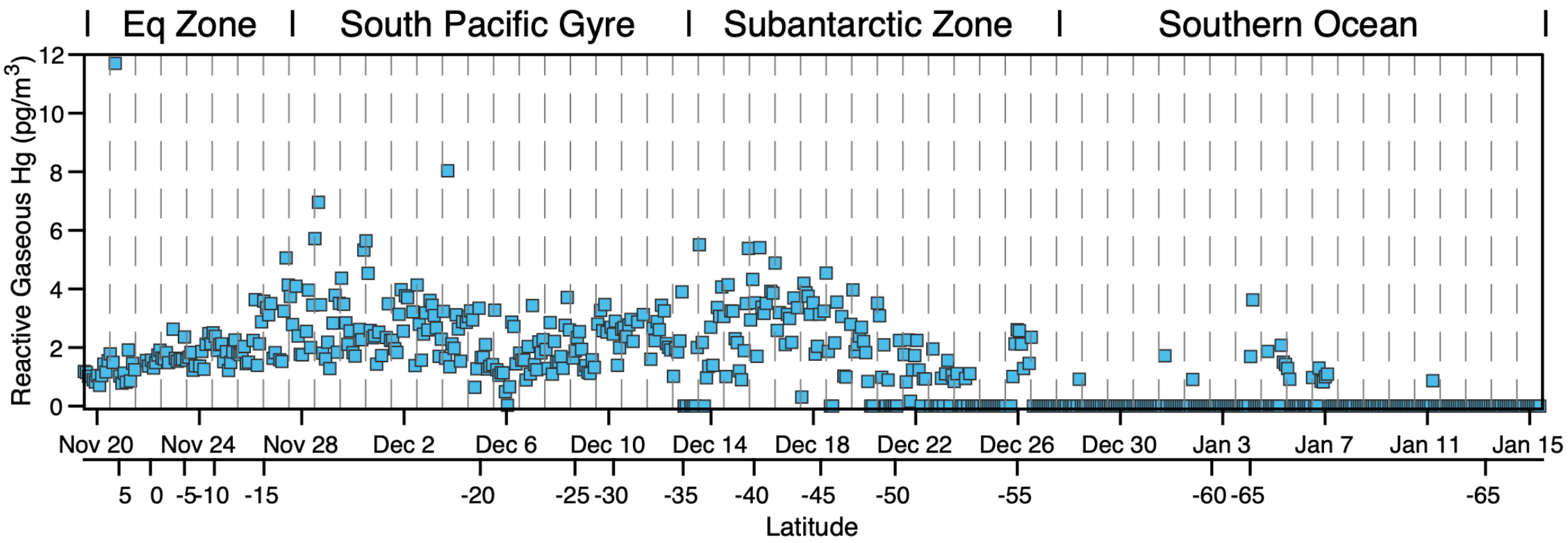
yihe@fiu.edu

Extra Slides!

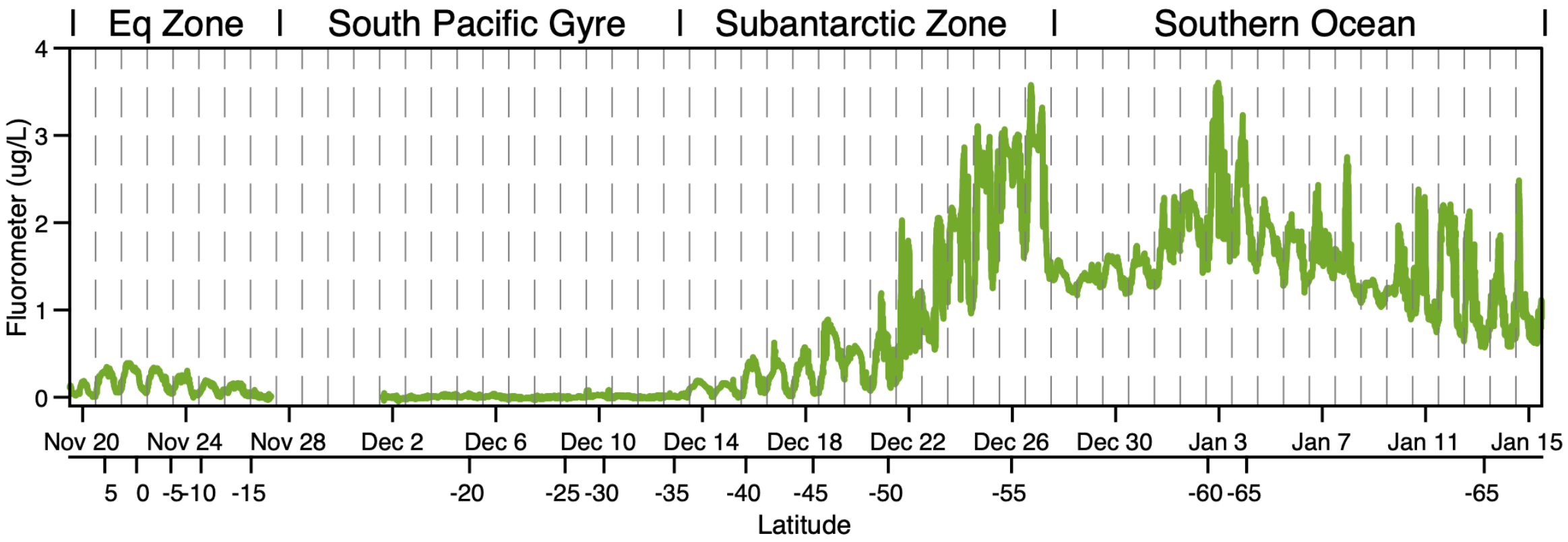
Results – Atmospheric Particulate Hg



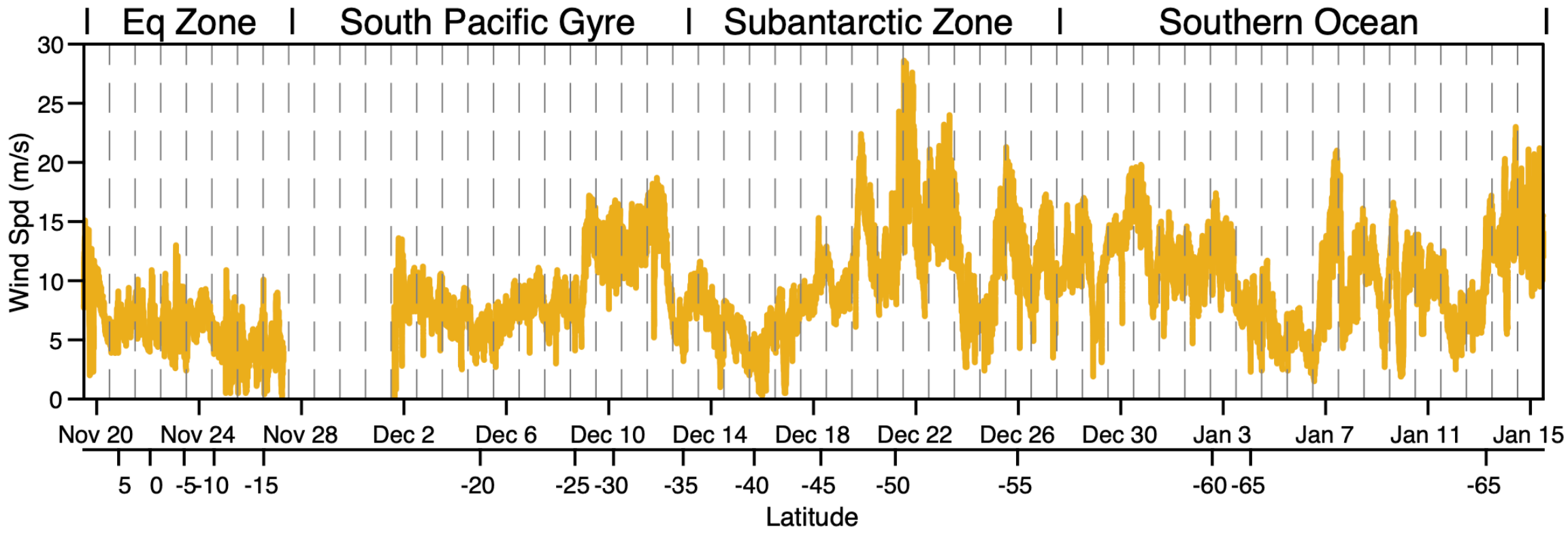
Results – Atmospheric Reactive Gaseous Hg



Results – Fluorescence Chl*a*



Results – Wind Speed



Results – Sea Surface Salinity & Temp