



Ocean carbon and biogeochemistry

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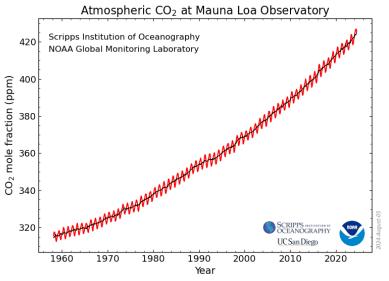


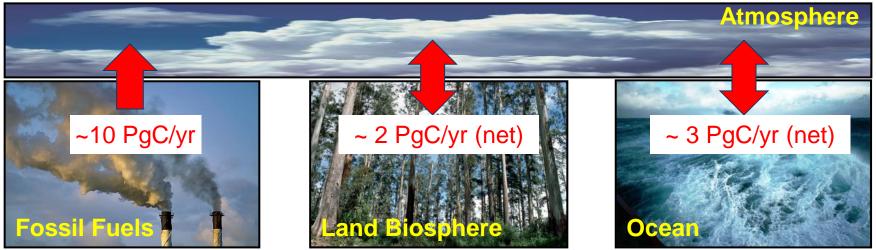




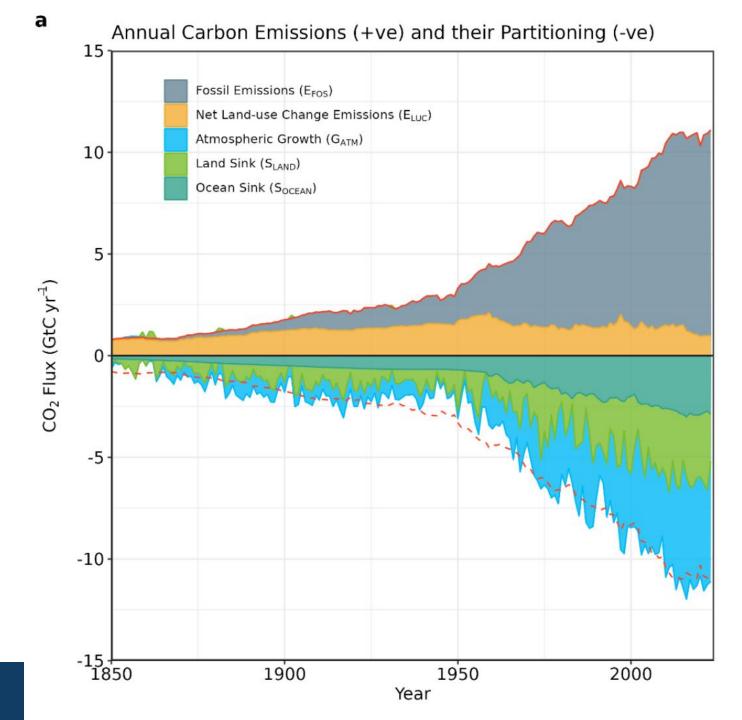
27 May 2025

Atmospheric CO₂ is rising due to human emissions Ocean and terrestrial biosphere absorb ~50% of emissions



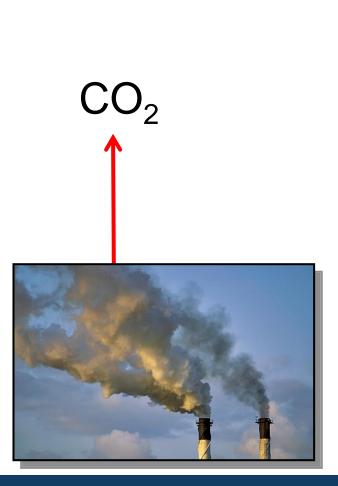


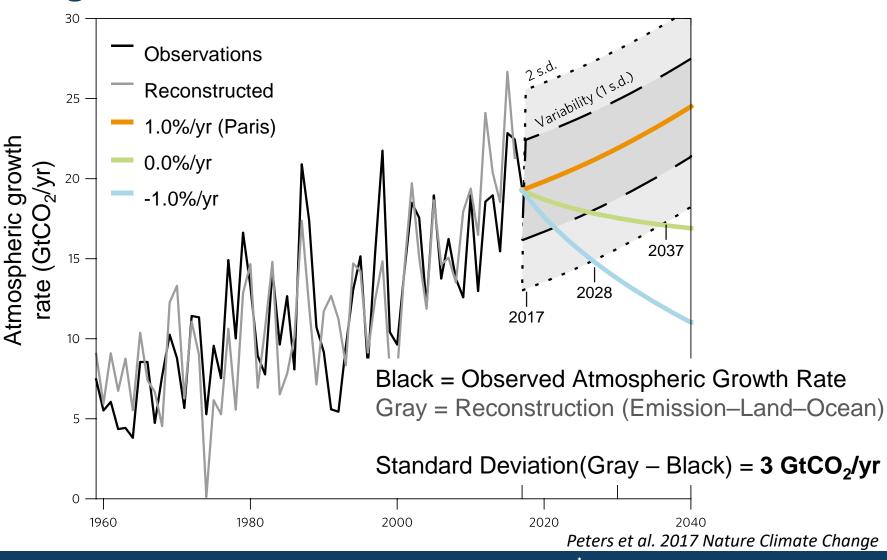
Global Carbon Budget



Friedlingstein et al. 2025, ESSD

Reduced uncertainty in ocean and land sinks required to usefully detect emissions mitigation





Outline

- Key processes of the ocean carbon cycle
- Improving quantification of the ocean carbon sink
 - Models: evaluate ML-based data product skill, given sampling
 - pCO₂ data products: apply to identify model mean-state biases
 - Models and data: combine using ML
 - marine Carbon Dioxide Removal (mCDR) quantifying "additionality"?

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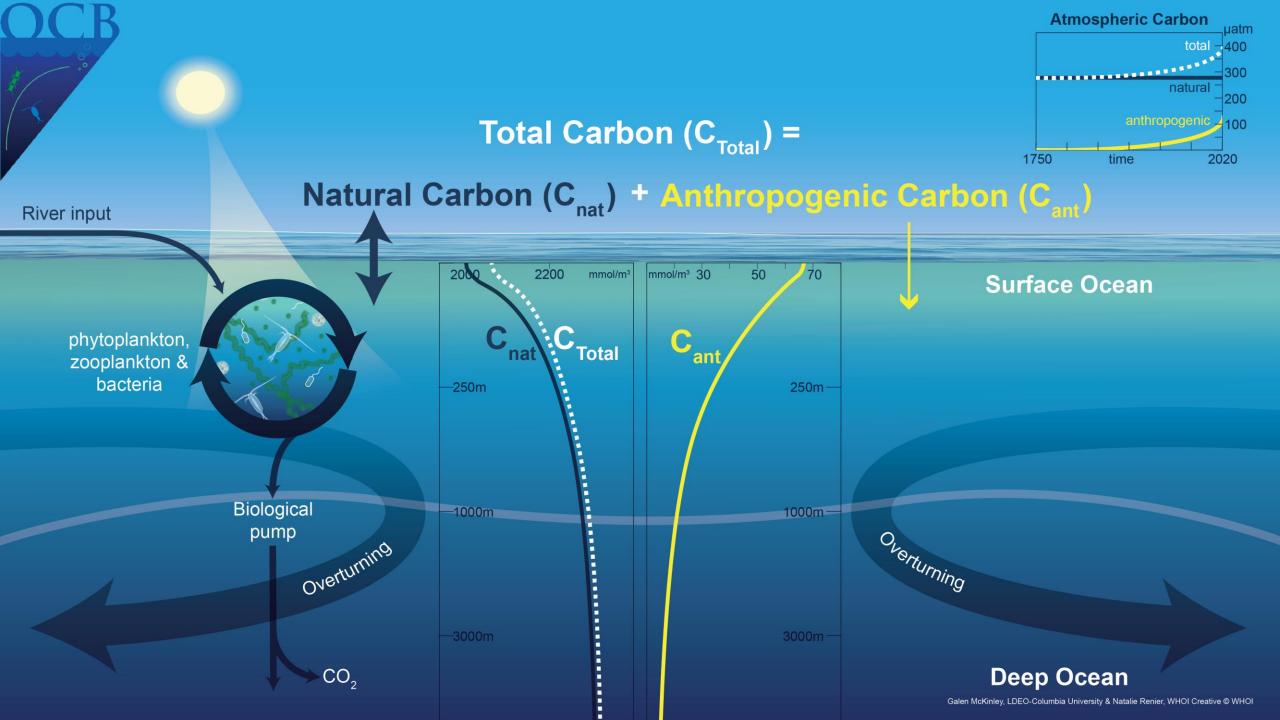
Air-sea CO₂
fluxes vary
across space
and time

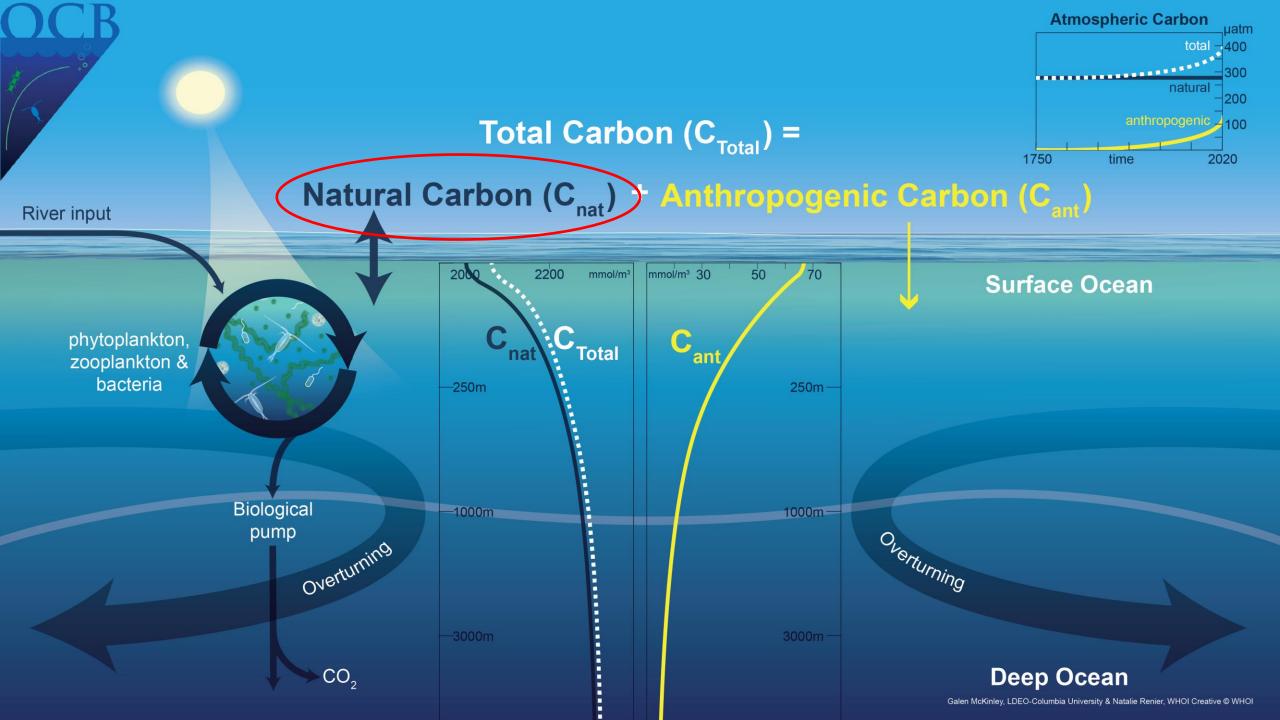
Air-sea CO₂ Flux **ECCO-Darwin Model** 06:00 mol C / m2 / year uptake

outgassing

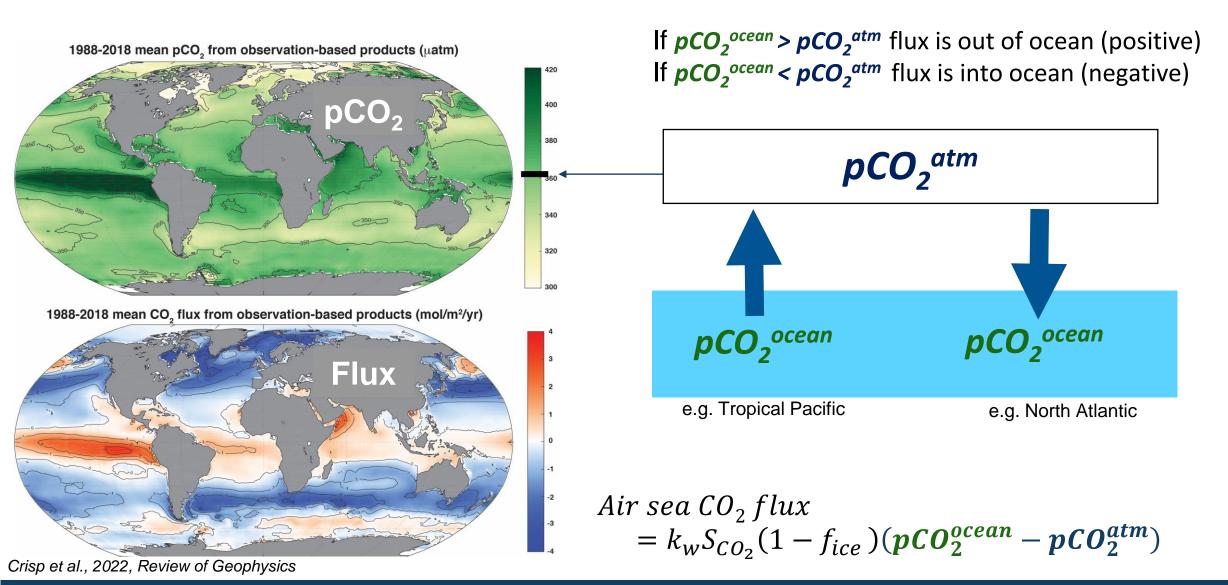
Carroll et al. 2020, 2022

03 Jan 2012

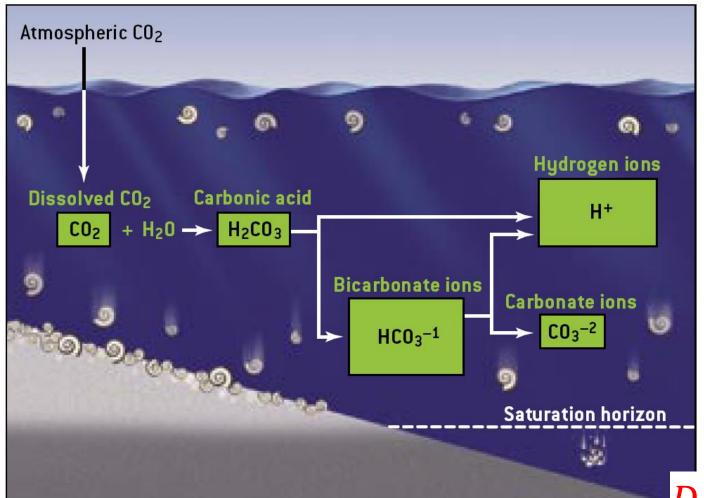




Surface ocean pCO₂ is primary control on air-sea CO₂ flux



Ocean Inorganic Carbon Cycle



$$CO_2^* = H_2CO_3 + CO_2(aq)$$

$$CO_2^* + H_2O \iff HCO_3^- + H^+$$

$$K_1' = \frac{[HCO_3^-][H^+]}{[CO_2^*]}$$

$$HCO_3^- \iff CO_3^{2-} + H^+$$

$$K_2' = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]}$$

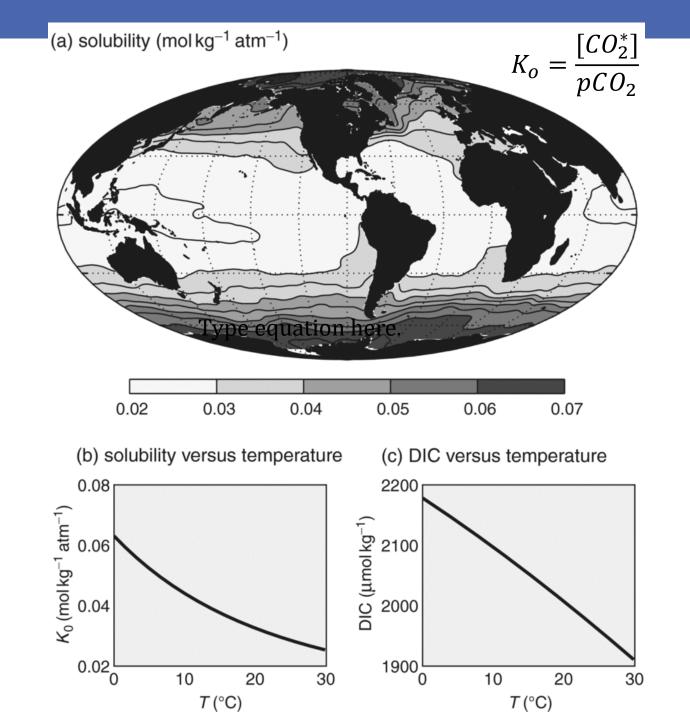
$$DIC = CO_2^* + HCO_3^- + CO_3^{2-}$$

SOLUBILITY

$$pCO_2 = \frac{[CO_2^*]}{K_o}$$

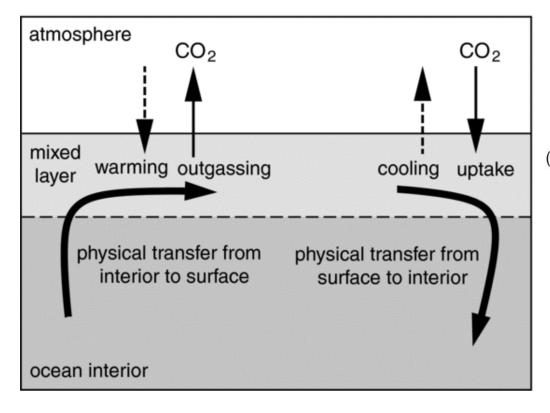
K_o is an inverse function of temperature

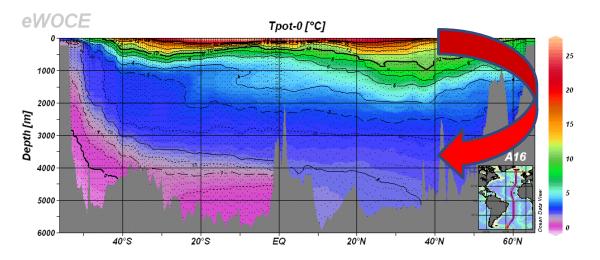
For same [CO₂*], pCO₂ is higher at high temperature, thus warm waters outgas and cold waters absorb CO₂

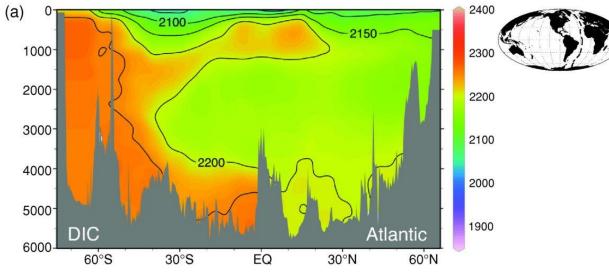


Solubility and physical transport

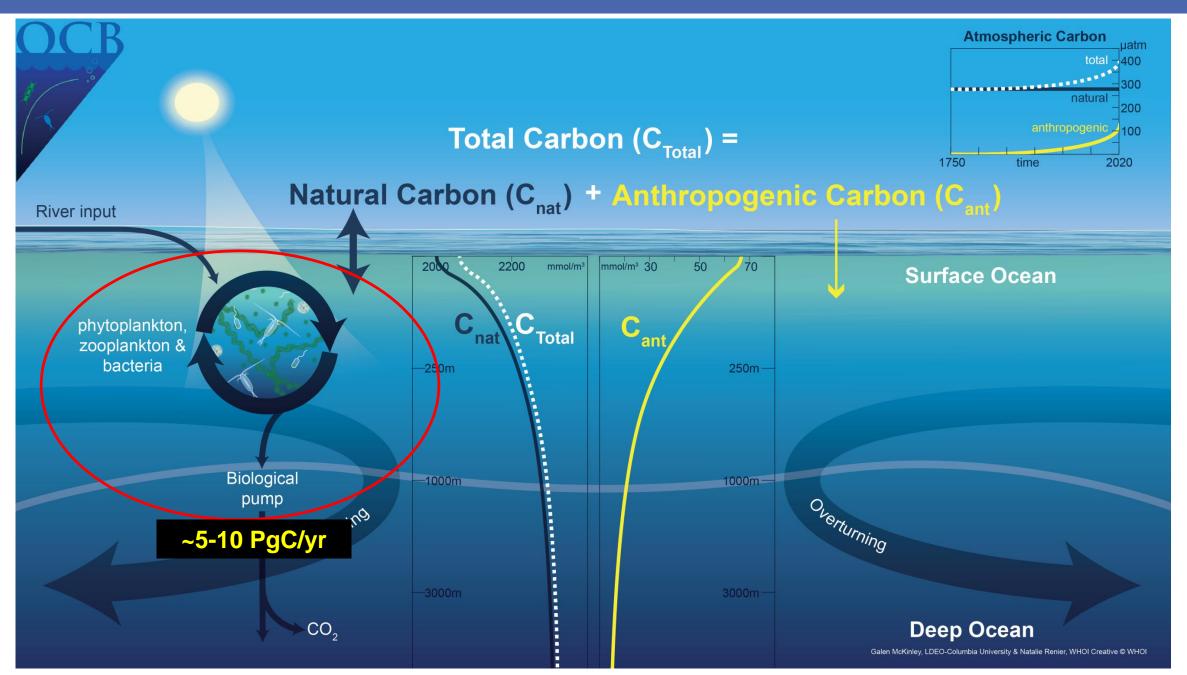
(a) physical transport and solubility



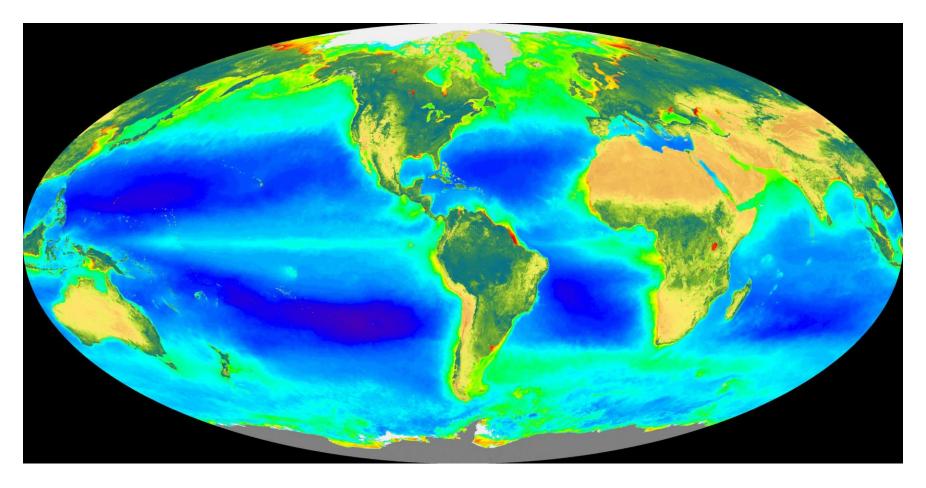




Williams_Fig. 2.24

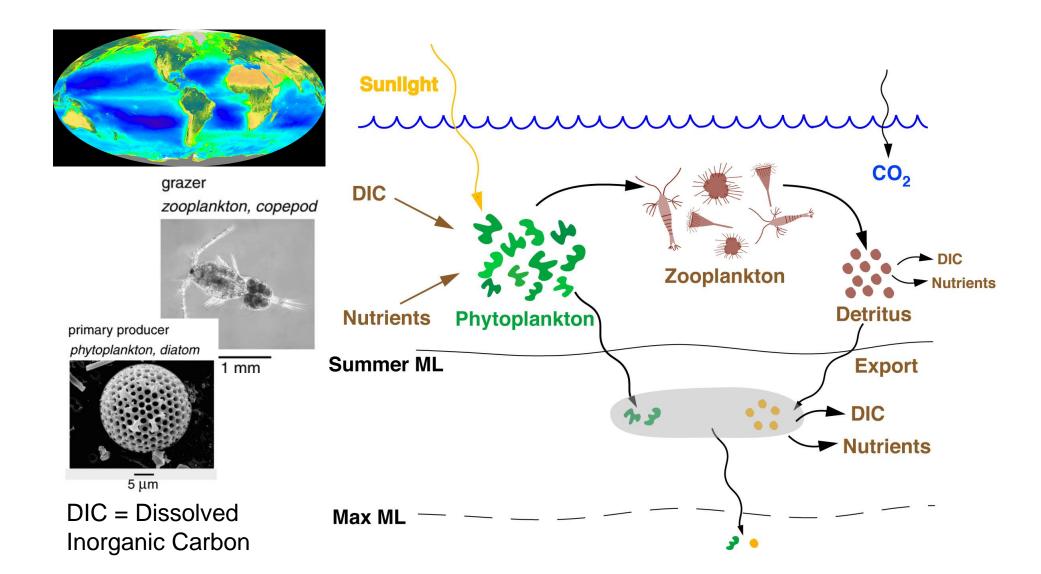


Ocean primary productivity from NASA SeaWiFS satellite

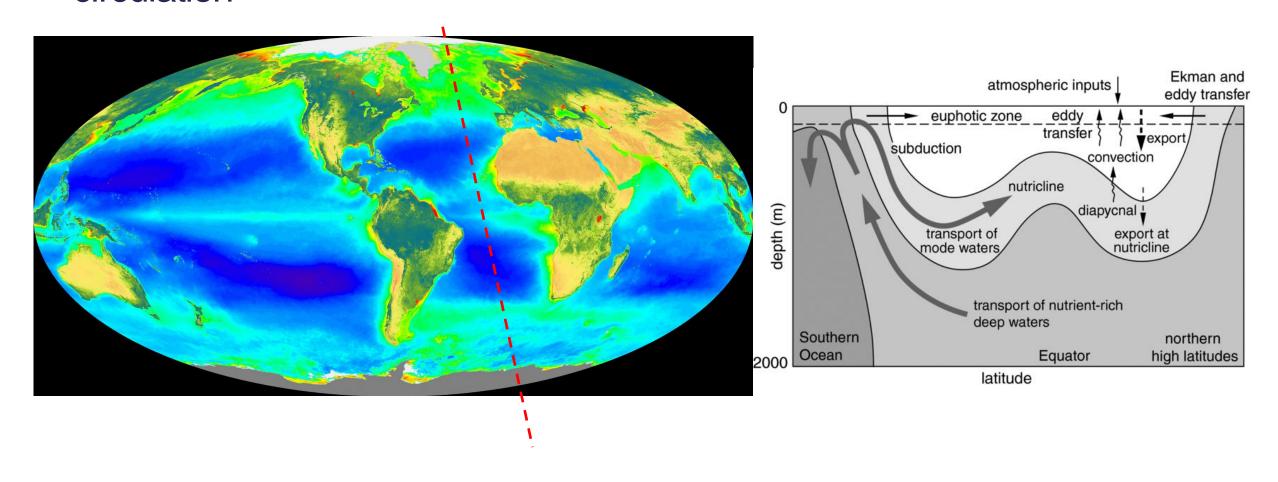


Dark blue = very low chlorophyll; green = moderate chlorophyll; red = very high

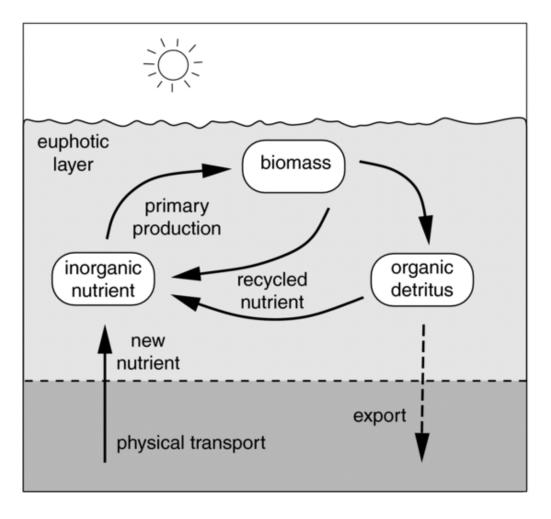
Biological carbon cycling in the ocean



Productivity is structured by nutrients distributions, in turn set by the circulation



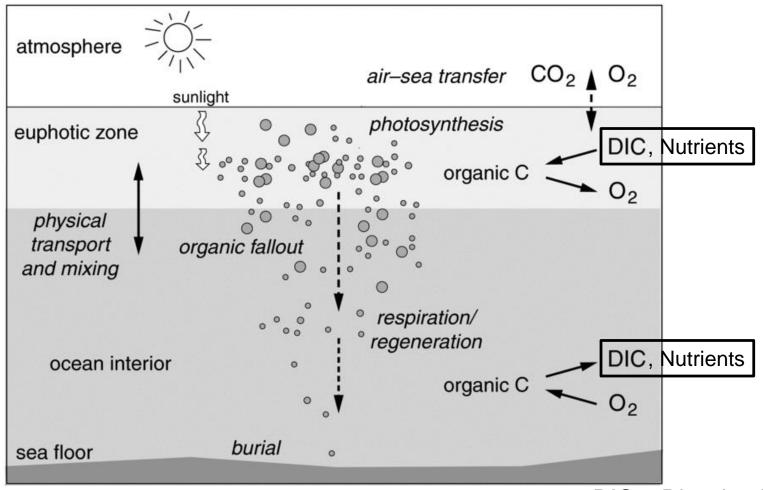
Nutrient cycling between biomass and inorganic nutrients



Williams_Fig. 5.15

Biogeochemical Cycling = Coupled carbon and nutrient cycles

(b) carbon pathways in the ecosystem



DIC = Dissolved Inorganic Carbon

Simplified photosynthesis

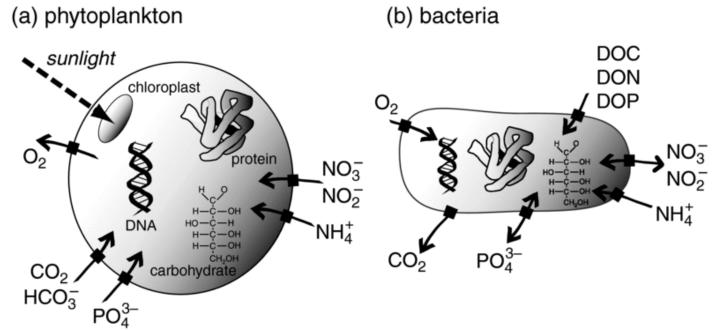
$$CO_2 + H_2O + energy$$
 $CH_2O + O_2$

More realistic

$$\frac{106CO_2 + 16NO_3^- + H_2PO_4^- + 122H_2O + energy}{C_{106}H_{246}O_{110}N_{16}P + 138O_2}$$

Quantitative links between Carbon, Nutrients (N,P), Oxygen

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Williams_Fig. 5.2

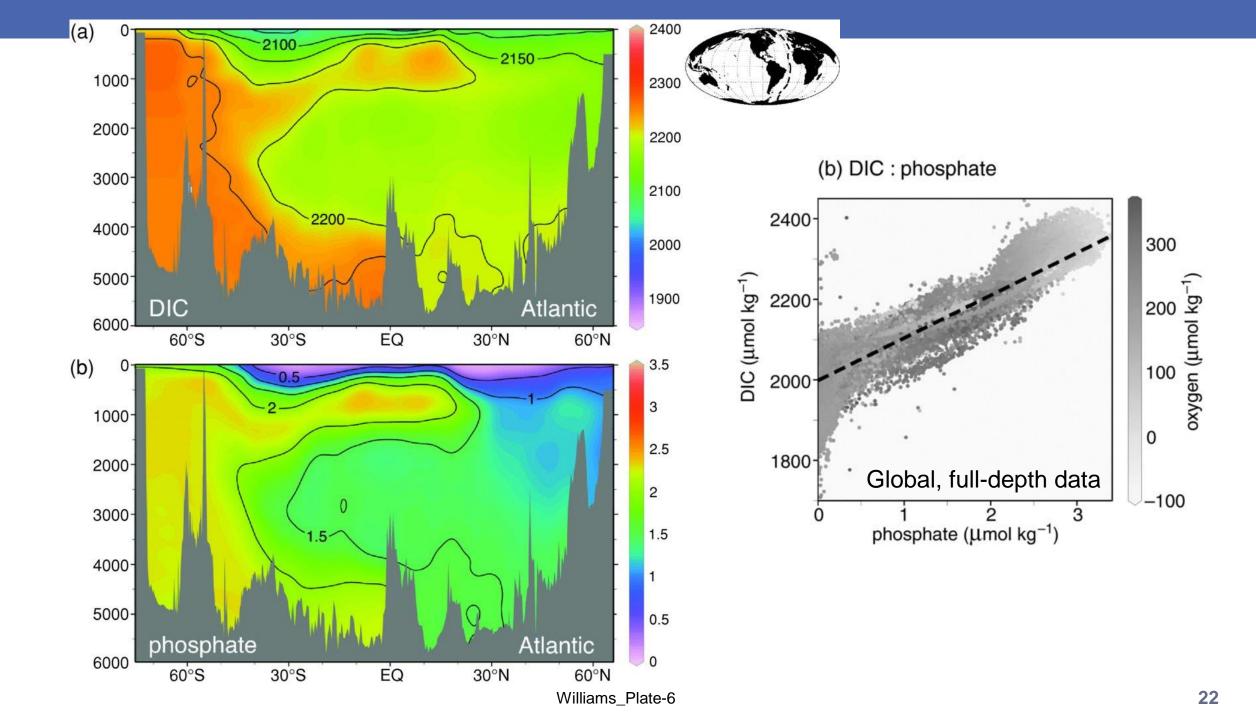
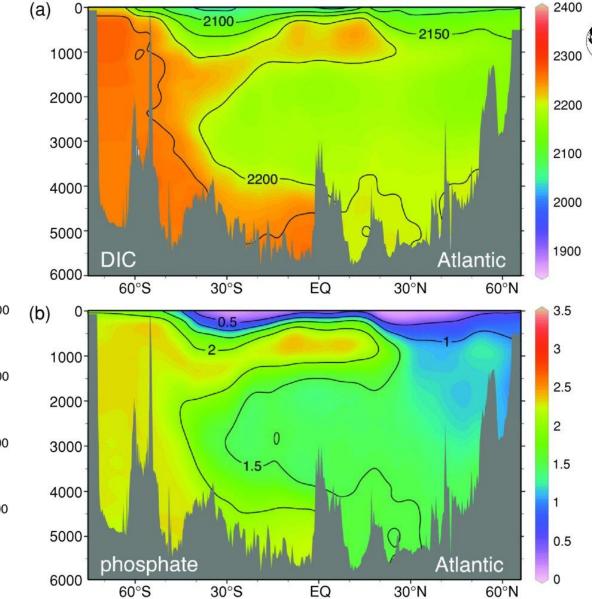


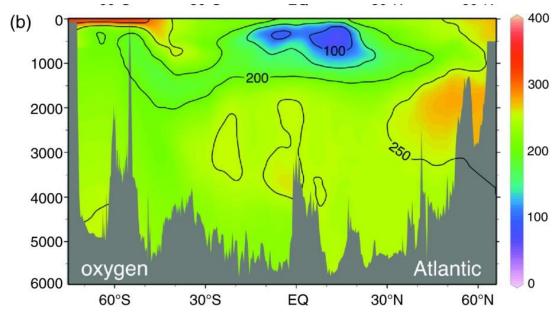
Table 5.2 The ratios of key elements in dissolved inorganic form in the water column and in marine phytoplankton and zooplankton (^aRedfield *et al.*, 1963). The cultured phytoplankton data are the average of 15 species of estuarine, coastal and open ocean phytoplankton grown under controlled laboratory conditions (^bHo *et al.*, 2003). *Prochlorococcus* MED4 is a strain of tiny phytoplankton (about a micron in scale). Elemental ratios were measured in *Prochlorococcus* cultures grown under phosphorus replete and phosphorus limited conditions (^cBertilsson *et al.*, 2003). Ranges of values are also shown for isolated marine bacteria grown under various conditions of nutrient limitation (^dVrede *et al.*, 2002).

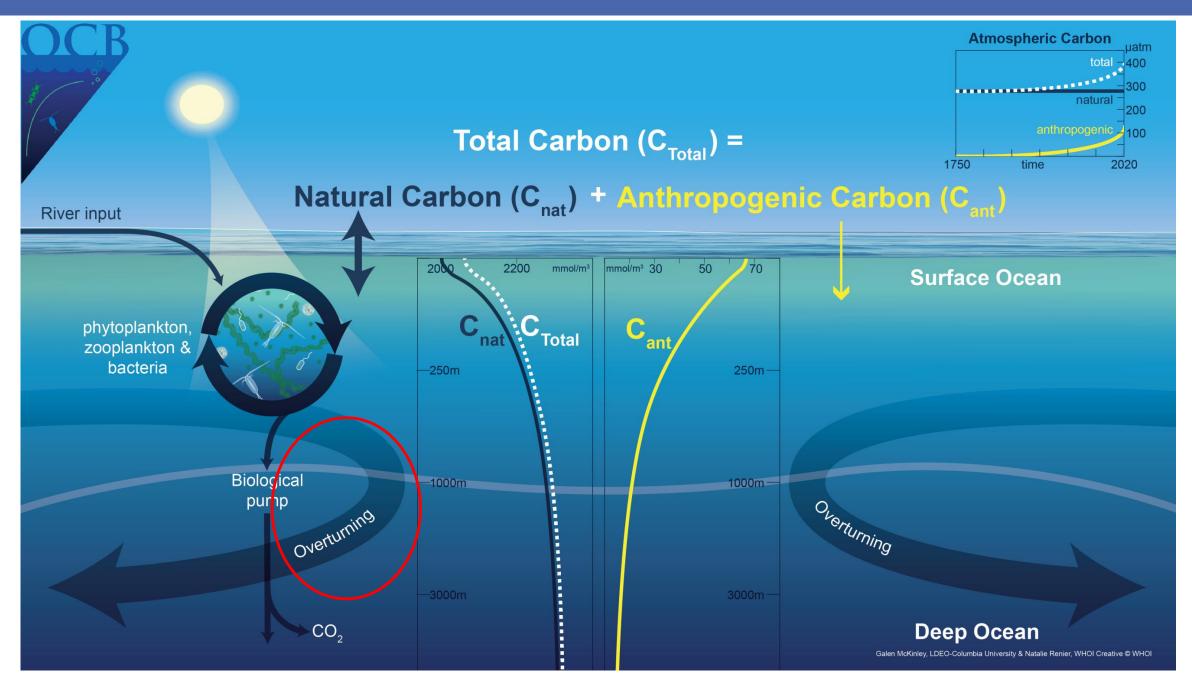
Reservoir	С	Ν	Р
^a Marine inorganic nutrients ^a Bulk marine organic matter ^b Cultured phytoplankton ^c Prochlorococcus MED4 (P-replete) ^c Prochlorococcus MED4 (P-limited)	106 147 ± 19 121 ± 17 464 ± 28	15 16 16 ± 2 21.2 ± 4.5 62.3 ± 14.1	 ± 0.2
^d Marine bacteria	35-178	7–18	I

Updated Redfield C:N:P:-O₂ = $117(\pm 14):16(\pm 1):1:-170(\pm 10)$ Anderson and Sarmiento, 2004

Oxygen distribution is inverse of nutrients and DIC

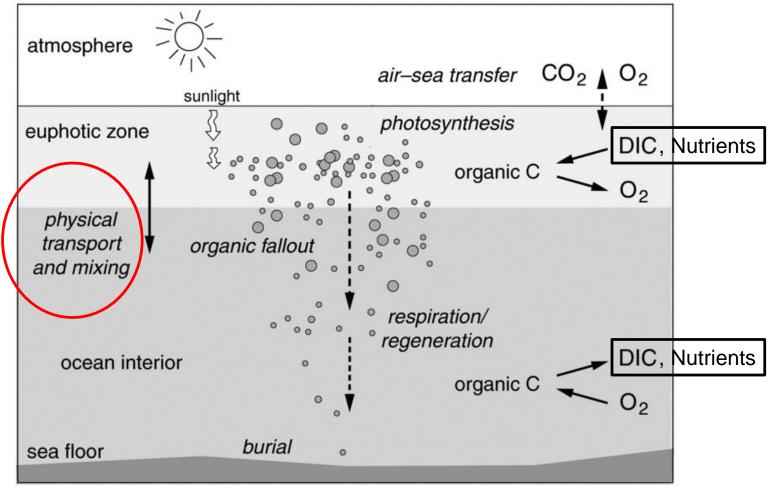






Biogeochemical Cycling = Coupled carbon and nutrient cycles

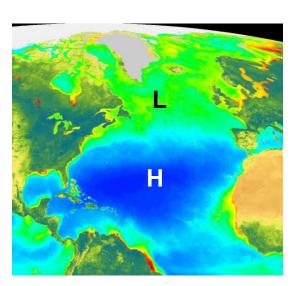
(b) carbon pathways in the ecosystem

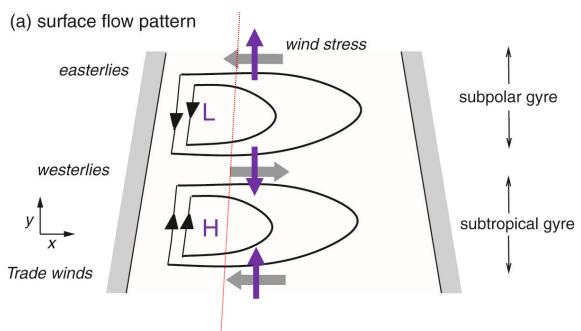


DIC = Dissolved Inorganic Carbon

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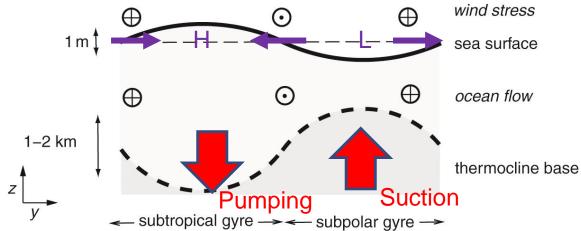
Circulation redistributes carbon and nutrients





Winds + Coriolis force leads to mass convergence, divergence at surface; causing Highs and Lows in surface height

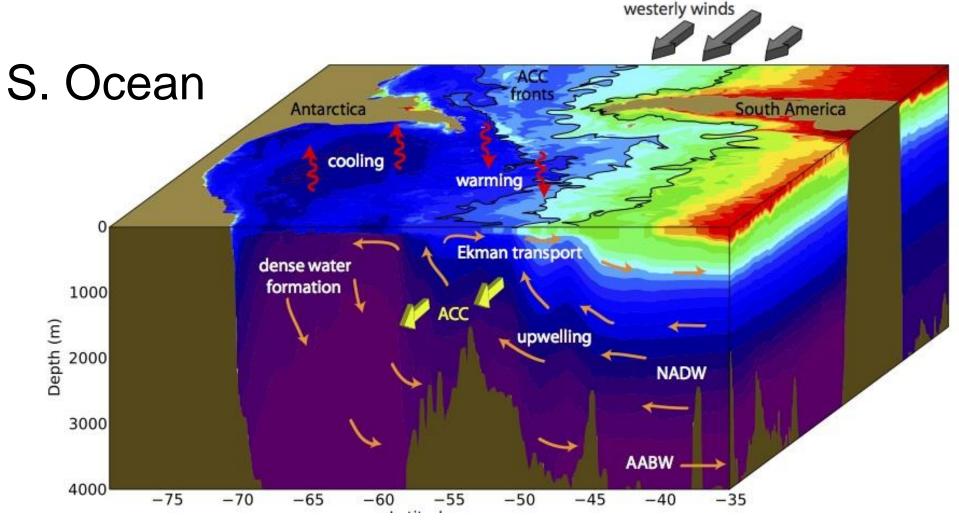
(b) meridional section (along dotted red line above)



Horizontal flows lead to vertical motions; advecting carbon and nutrients

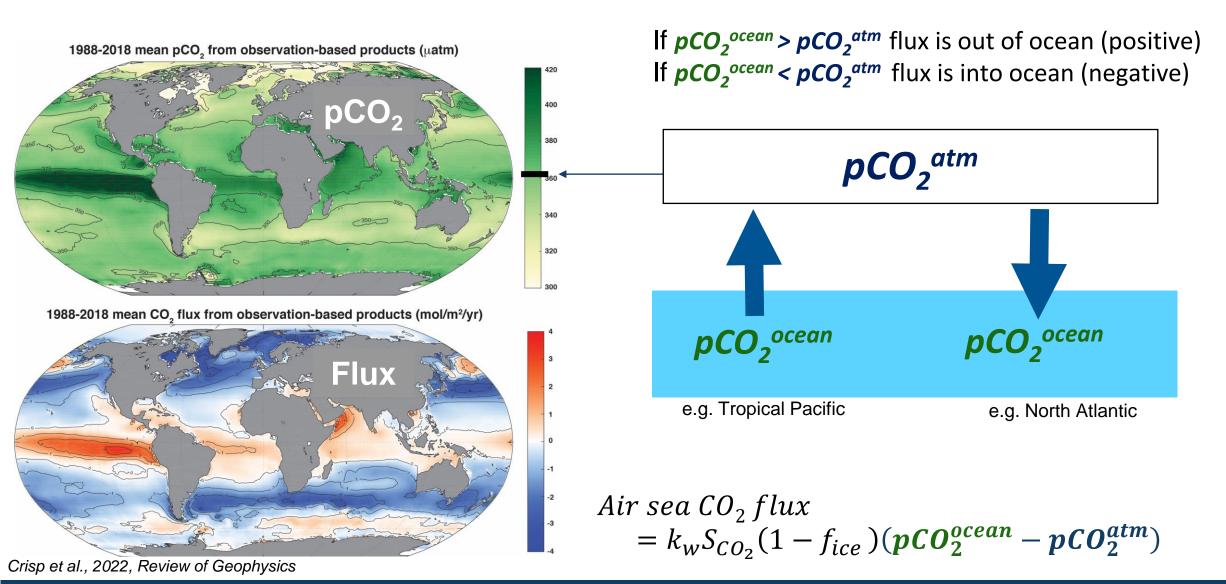
Williams and Follows Fig 8.1

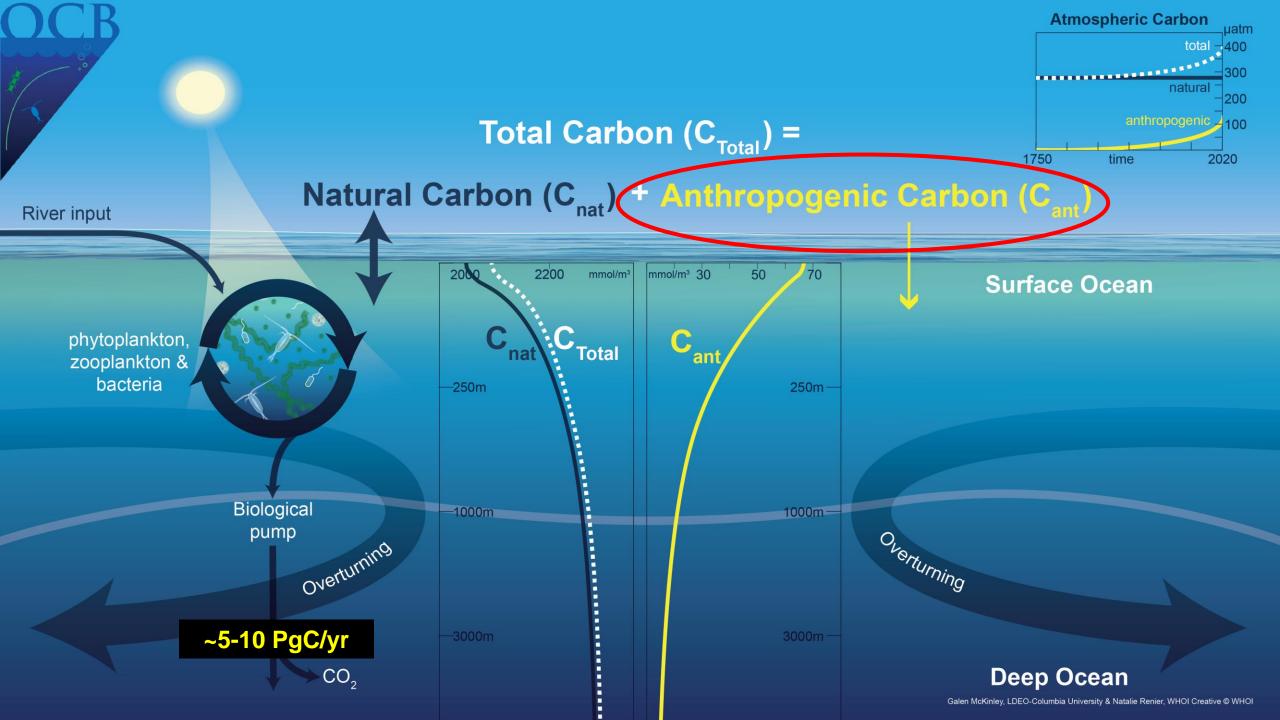
Circulation redistributes carbon and nutrients

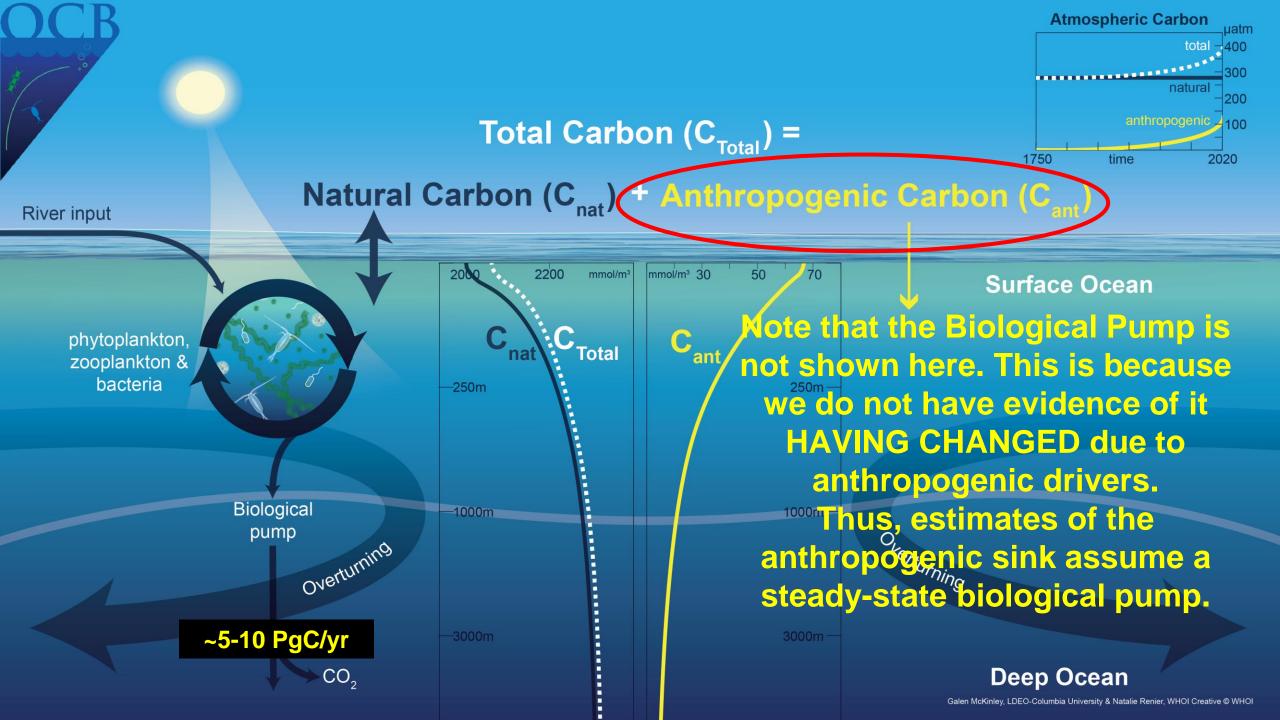


http://rses.anu.edu.au/research/projects/southern-ocean-circulation

Surface ocean pCO₂ is primary control on air-sea CO₂ flux

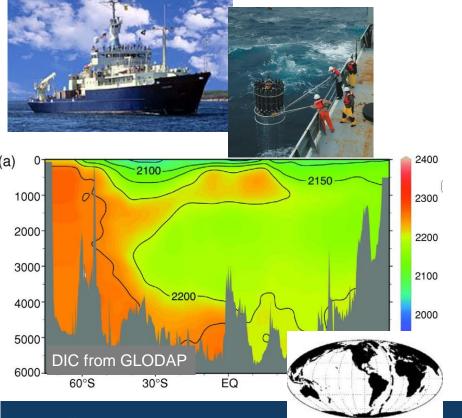




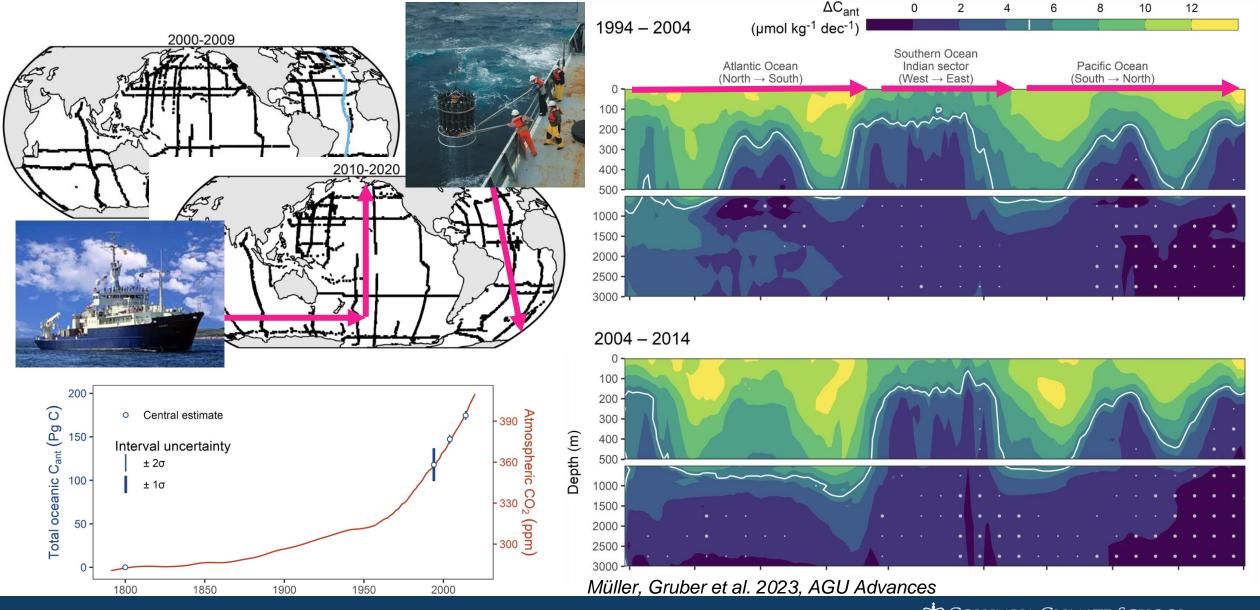


Three independent approaches constrain the ocean carbon sink

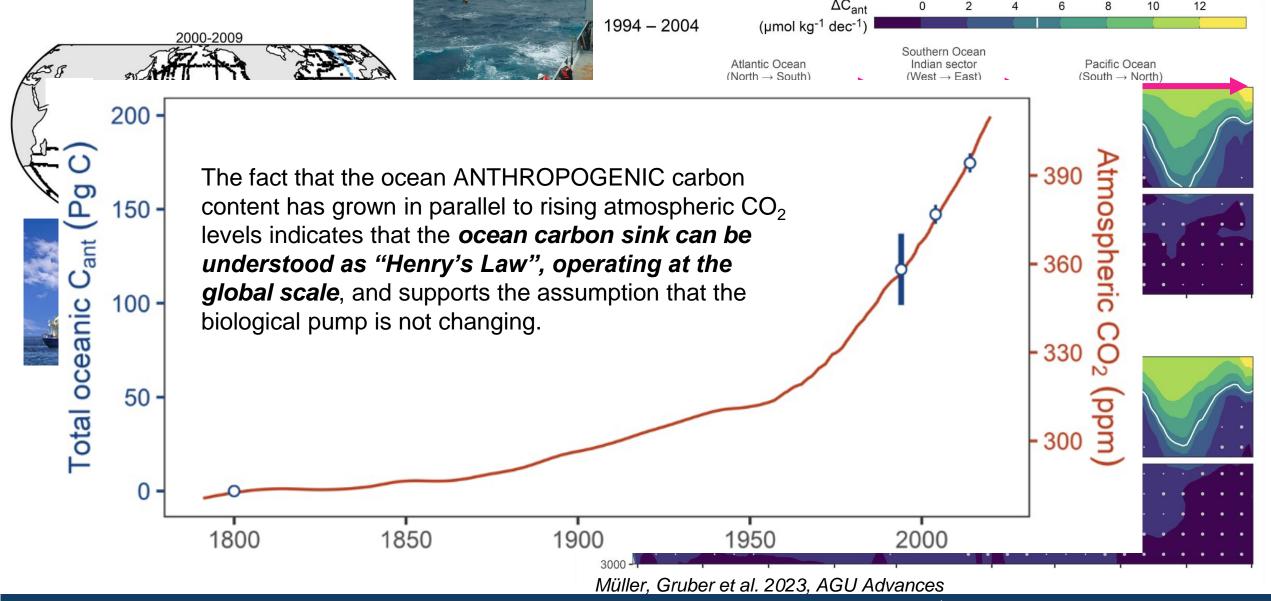
1. Interior observations / products
Interior carbon storage
Decadal closure of global budget
Model validation



Decadal Interior Data: Shows ocean following atmospheric pCO₂

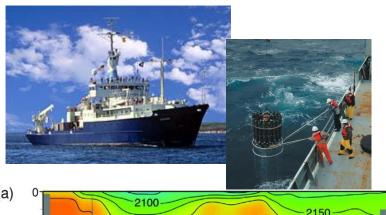


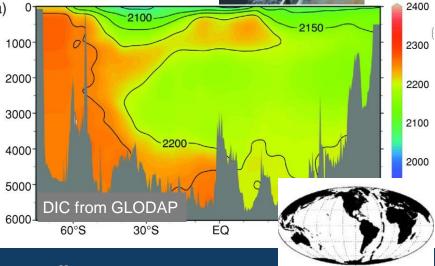
Decadal Interior Data: Shows ocean following atmospheric pCO₂



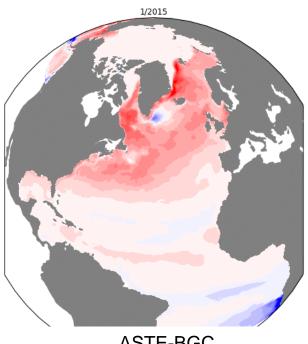
Three independent approaches constrain the ocean carbon sink

1. Interior observations / products
Interior carbon storage
Decadal closure of global budget
Model validation





2. Modeling
Air-sea fluxes
Mechanisms
Projections



ASTE-BGC air-sea CO₂ flux

Moseley et al, in review

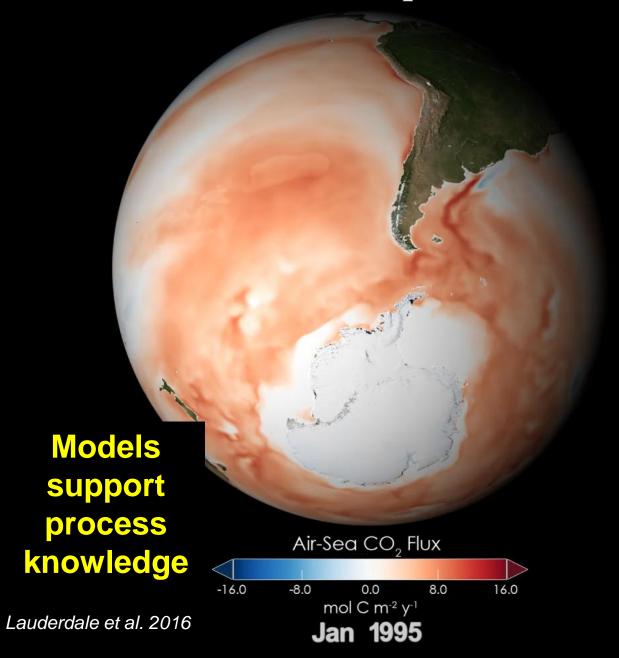
Ocean biogeochemical models

Circulation + Carbon = Air-sea CO₂ fluxes Air-sea interactions **Processes** Momentum (winds) Water vapor Heat Total Carbon (C_{Total}) = Ocean Natural Carbon (C_{nat}) + Anthropogenic Carbon (C_n grid River input Surface Ocean Deep-sea floor **ASTE-BGC** air-sea CO₂ flux

On a 3D grid, calculate circulation and carbon fluxes by integrating over time the equations of motion, conservation, biology and carbon chemistry

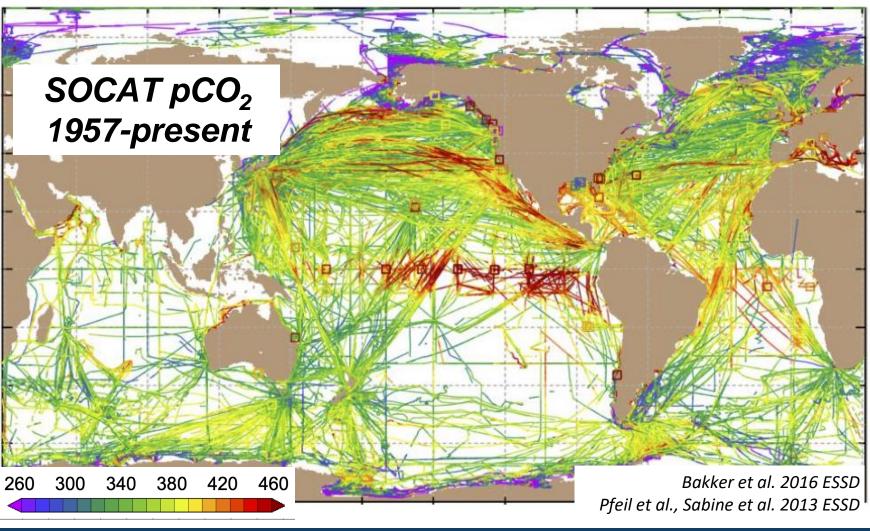
Moseley et al, in review

Heat CO₂ Flux

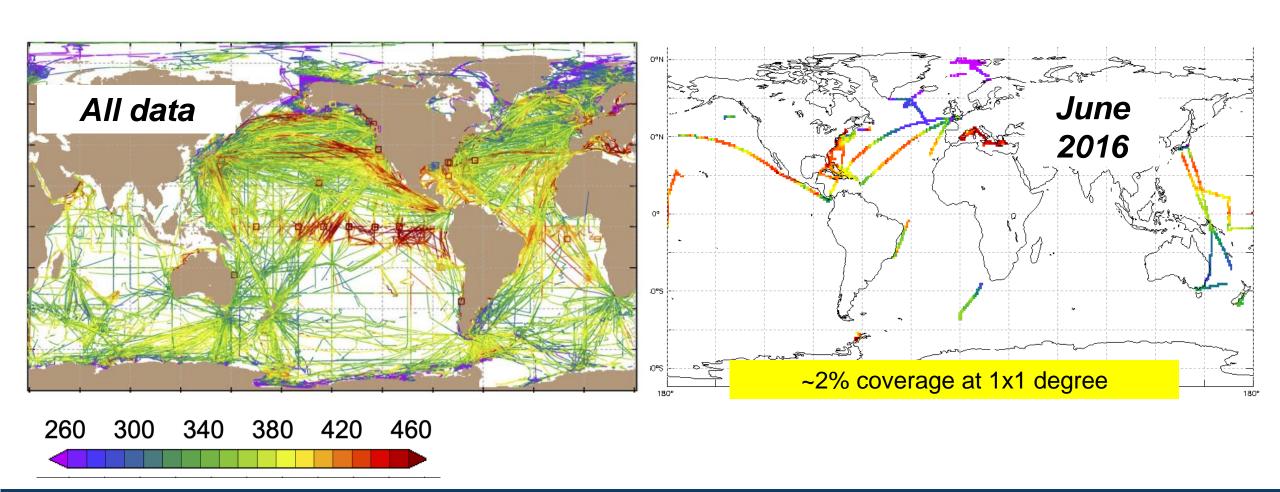


3. Surface ocean pCO₂ data used in reconstructions

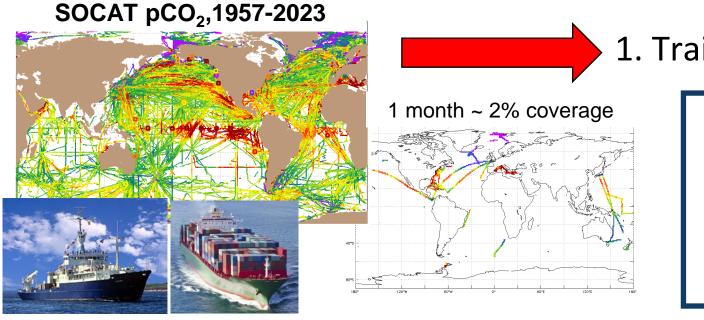




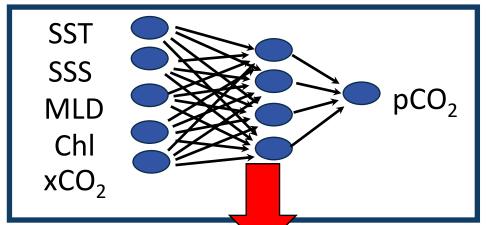
3. Monthly pCO₂ data are very sparse ...

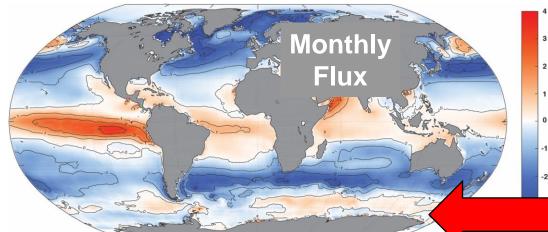


3. Data-based "Products" built with v. sparse pCO₂ data and ML

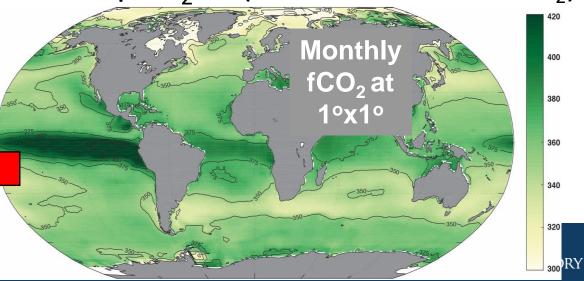


1. Train Machine Learning on sparse data



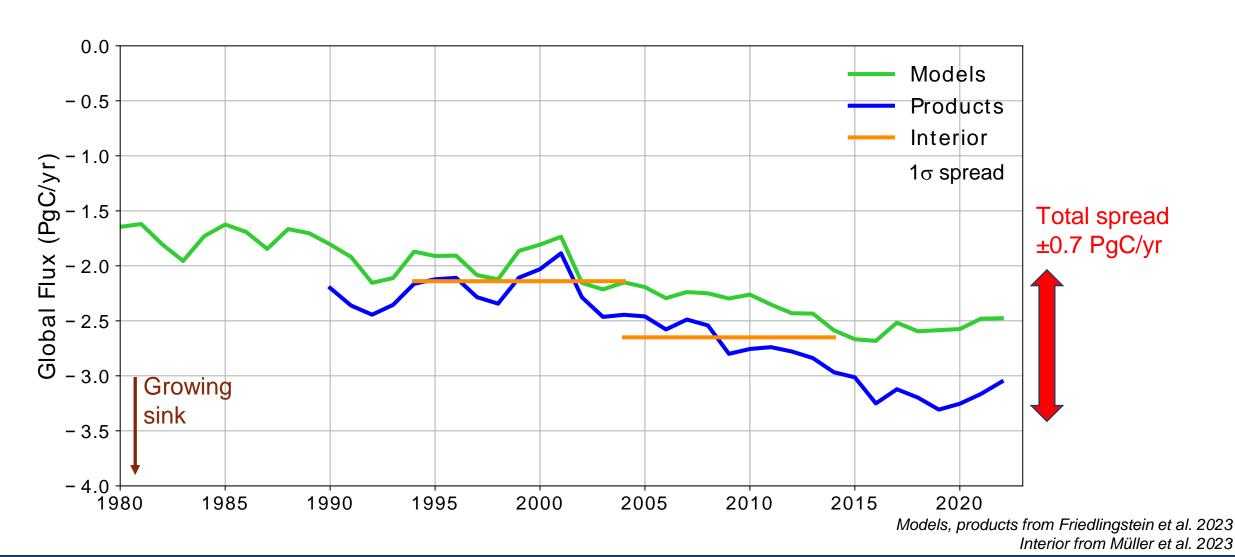


2. Predict pCO₂ = $f(\tilde{S}ST, SSS, MLD, Chl, xCO_2)$



3. Calculate Flux from pCO₂

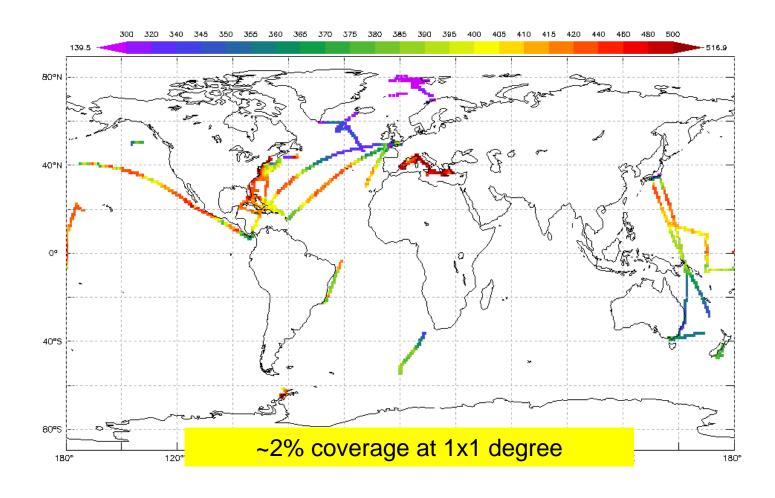
Globally integrated estimates agree, with ~30% uncertainty



Outline

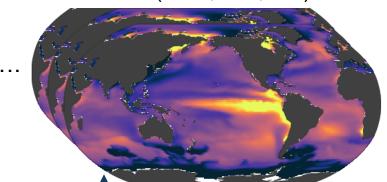
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pCO₂ data are very sparse: Are reconstructions robust?



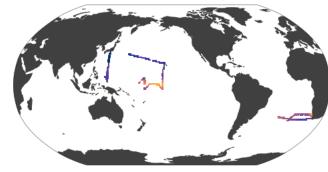
ESM Large Ensembles as testbed for reconstruction skill

Earth System Models provide pCO₂ and drivers (SST, Chl, etc)



50 to 100 ensembles from 4 or 9 ESMs

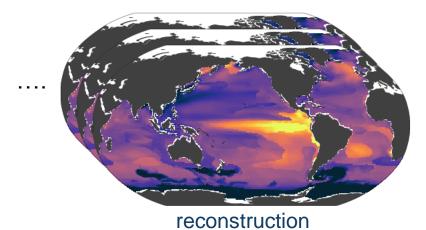
1. Sample model member as SOCAT monthly pCO₂ product





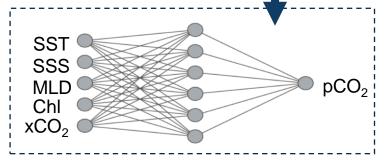


4. Statistically compare reconstructed CO₂ flux to model truth. Each spatial point is temporally decomposed



3. Estimate monthly varying pCO₂ on global scale using trained model, calculate flux

X ensemble members

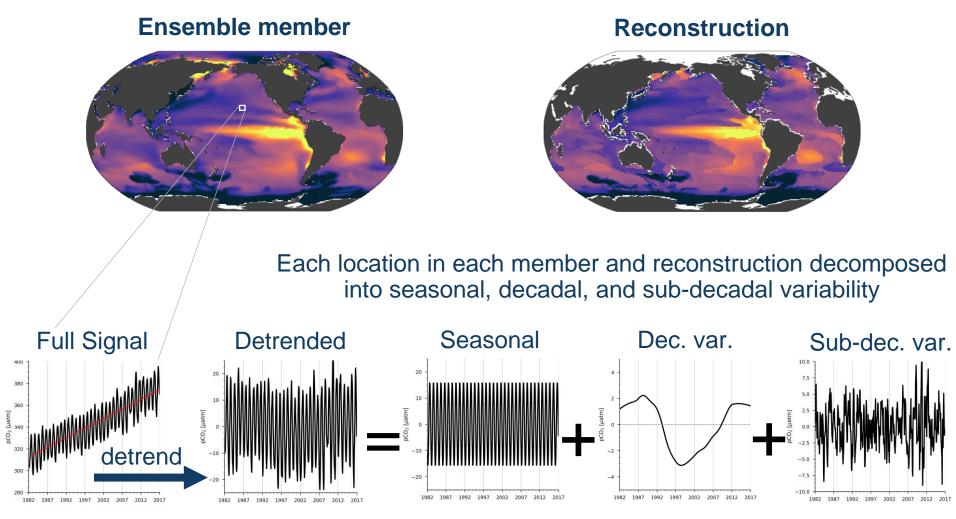


With various ML reconstructions

2. Train, evaluate, test

- MPI-SOMFFN (Gloege et al. 2021)
- NN, RF, XGB (Stamell et al. 2020)
- pCO₂-Residual (Bennington et al. 2022, Heimdal et al, 2024a,b; Heimdal et al. in press)

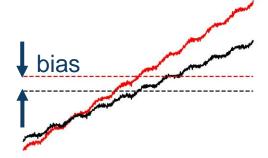
Skill evaluation: temporal decomposition



Gloege et al. 2021, GBC

Model Reconstruction

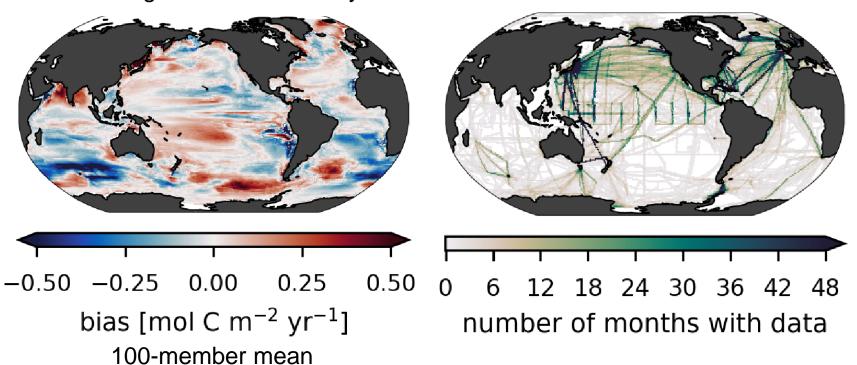
Bias is small globally; larger where data sparse



Global avg = -0.01 molC m⁻² yr⁻¹

1985-2016

MPI-SOMFFN

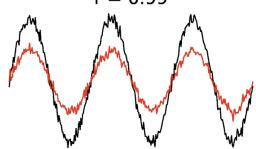


Gloege et al. 2021, GBC

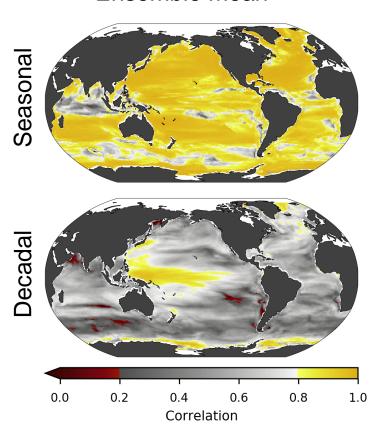
Gloege et al. 2021, GBC

Correlation Is the reconstruction in phase with the original data?





Ensemble mean



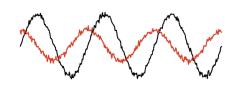
Captures seasonal cycle well everywhere

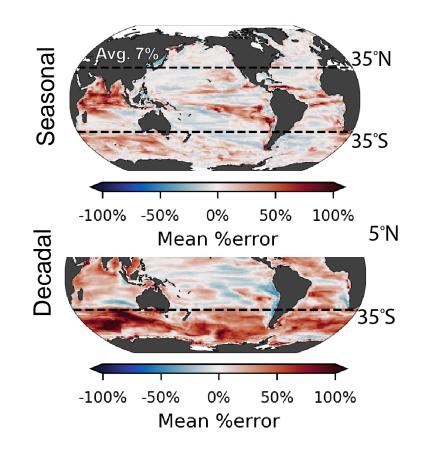
Decadal phase is more challenging to reconstruct

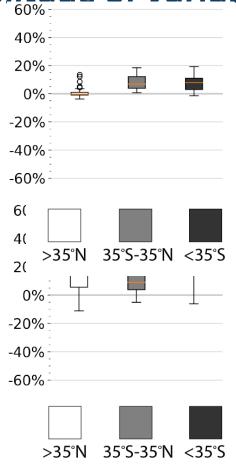
100-member mean 1985-2016 MPI-SOMFFN

Gloege et al. 2021, GBC

Standard deviation of % error Does the reconstruction capture the amplitude of variability?





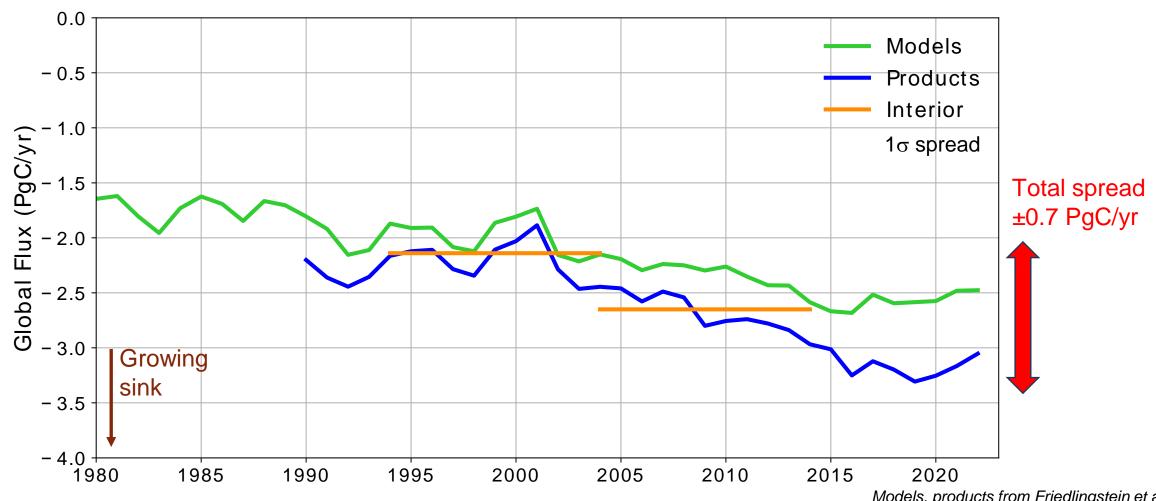


100-member mean 1985-2016 MPI-SOMFFN

- Globally the seasonal cycle is overestimated by ~7%
- Overestimates decadal variability in Southern Ocean by ~39%

Gloege et al. GBC 2021

Reduced decadal amplitude in products should increase agreement between products and models



Models, products from Friedlingstein et al. 2023 Interior from Müller et al. 2023

Take home messages

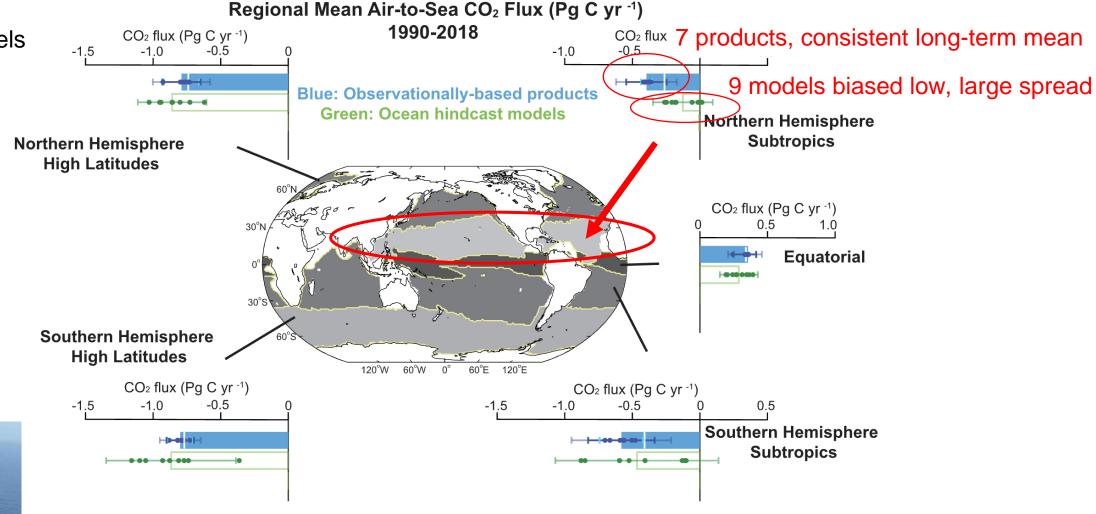
 Air-sea CO₂ flux mean and seasonality can be reconstructed from sparse pCO₂ data, but longer-timescale variability remains uncertain

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Ocean models have significant mean-state errors

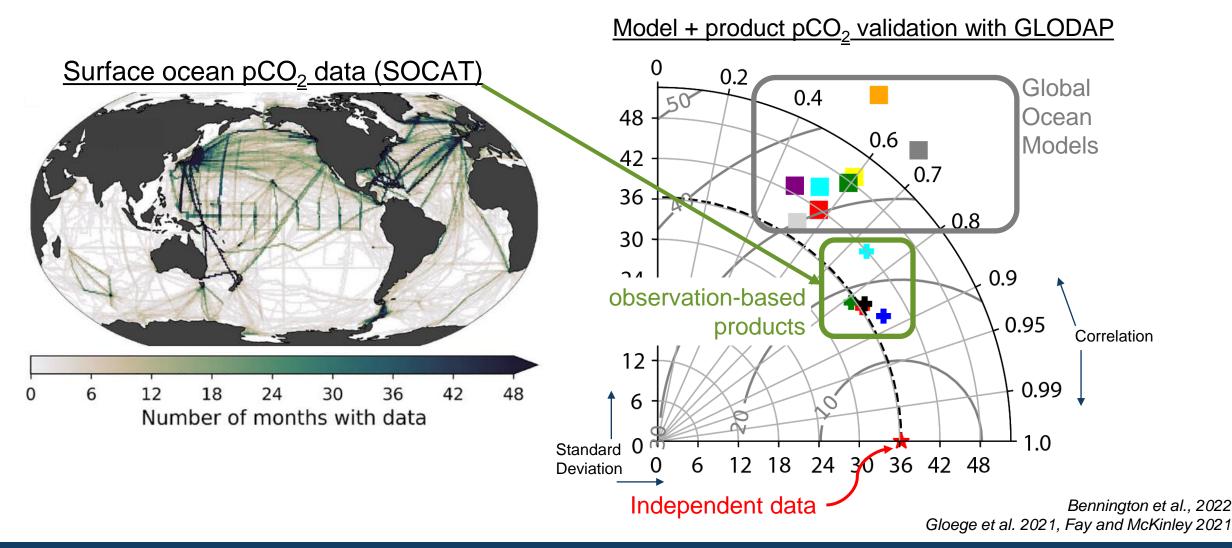
Products and hindcast models for real fluxes 1990-2018





Fay and McKinley 2021

Ocean models have significant mean-state errors



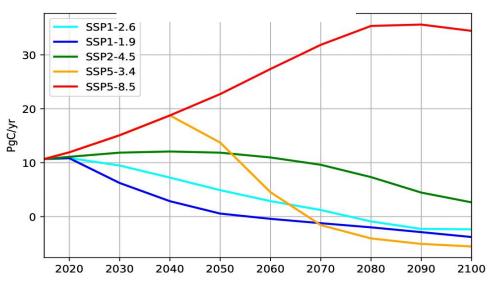
CMIP6

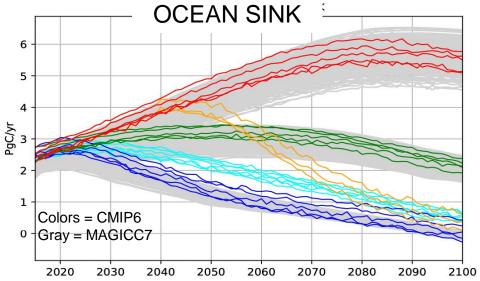
3-6 ensemble means for each scenario

McKinley et al. 2023, ERL

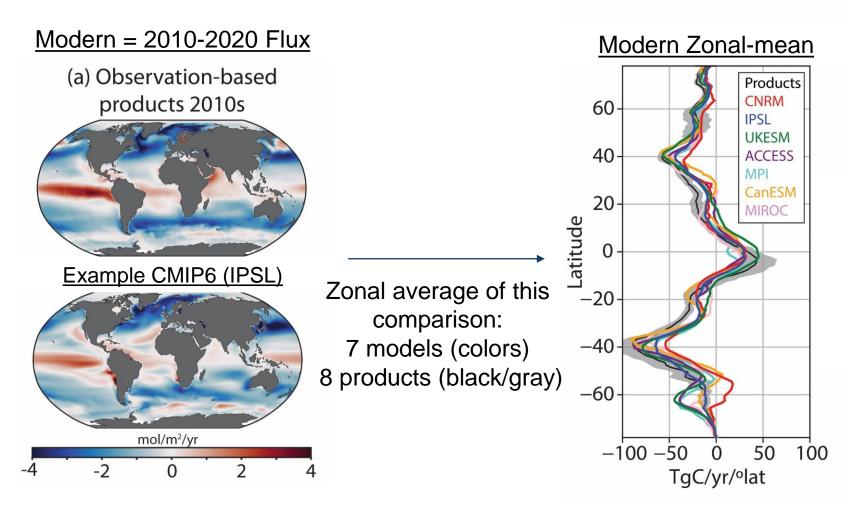
Future Emissions and Ocean Sink

EMISSIONS

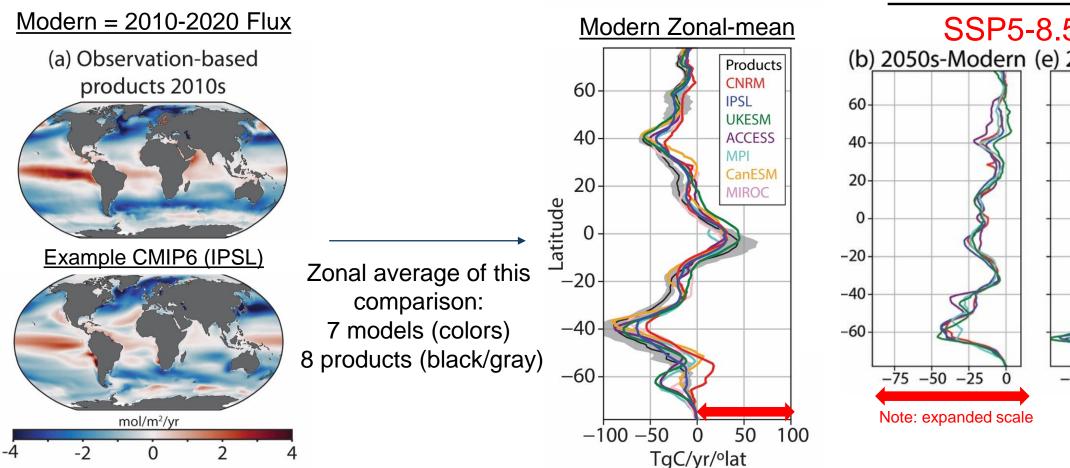




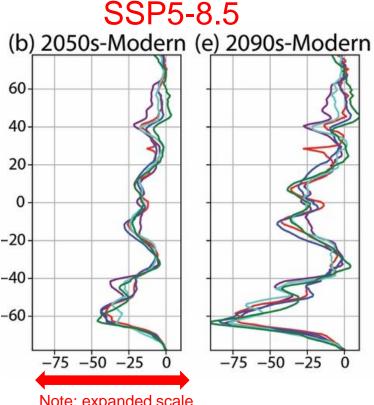
OOL



McKinley et al. 2023, ERL



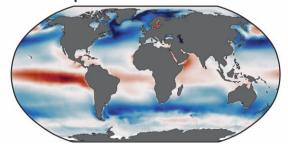
Future Flux change



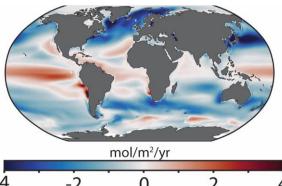
McKinley et al. 2023, ERL

$\underline{Modern = 2010-2020 \ Flux}$

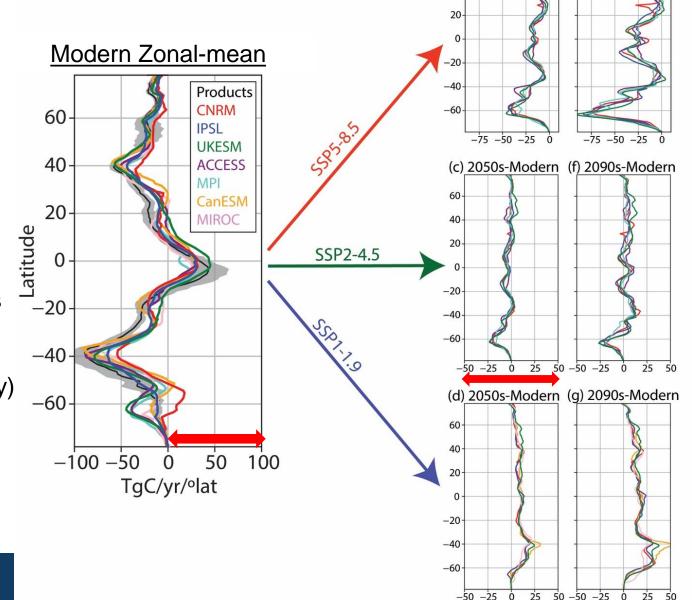
(a) Observation-based products 2010s



Example CMIP6 (IPSL)



Zonal average of this comparison:
7 models (colors)
8 products (black/gray)



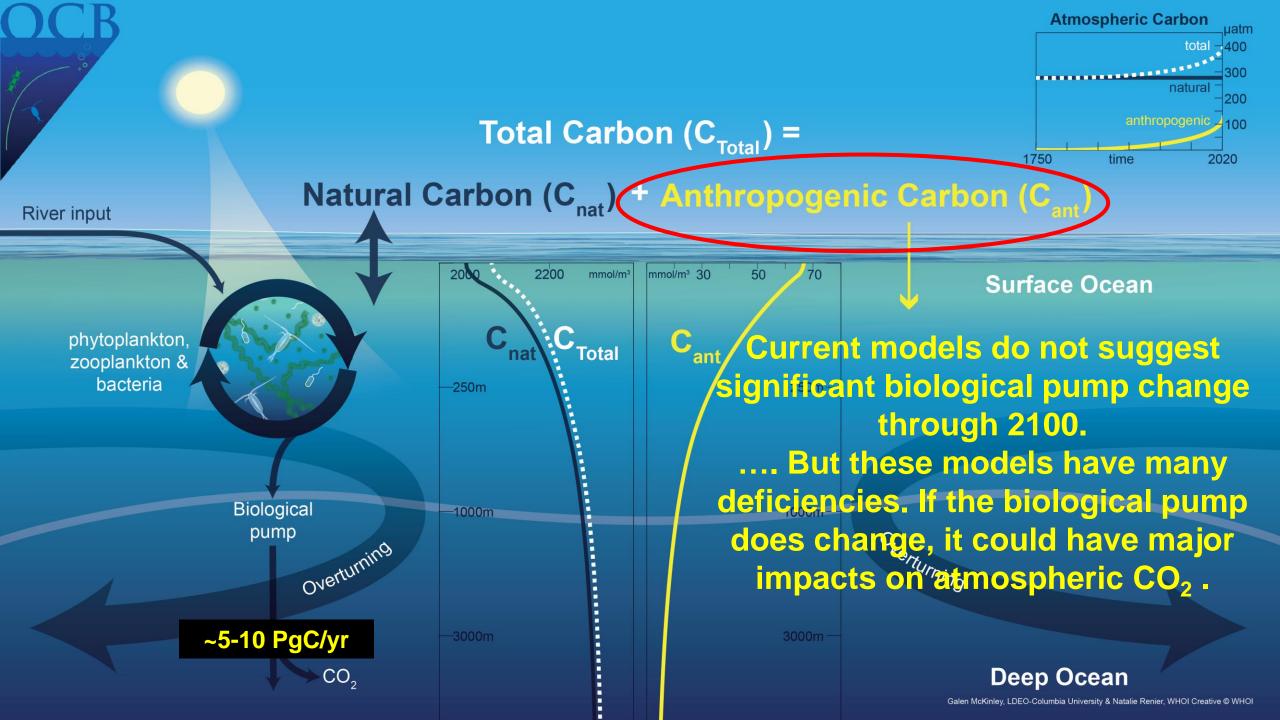
Future Flux change

(b) 2050s-Modern (e) 2090s-Modern

McKinley et al. 2023, ERL

Take home messages

- Air-sea CO₂ flux mean and seasonality can be reconstructed from sparse pCO₂ data, but longer-timescale variability remains uncertain
- Hindcast and Earth System Models have significant mean-state biases

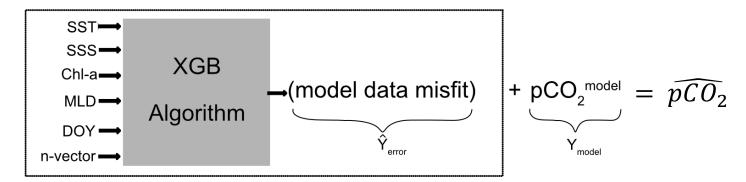


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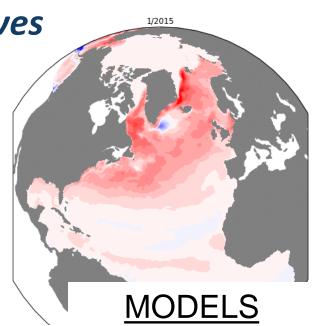
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Using ML to combine models and data improves surface flux estimates (LDEO-HPD)

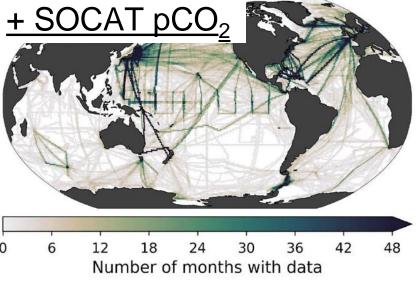
- pCO₂^{model} as priors
- Reconstruct $pCO_2^{misfit} = (pCO_2^{model} pCO_2^{SOCAT})$ (driver data: SST, SSS, Chl-a, MLD, time, location)
- eXtreme Gradient Boost (XGB) algorithm
- Misfits to correct N models; average for final pCO₂



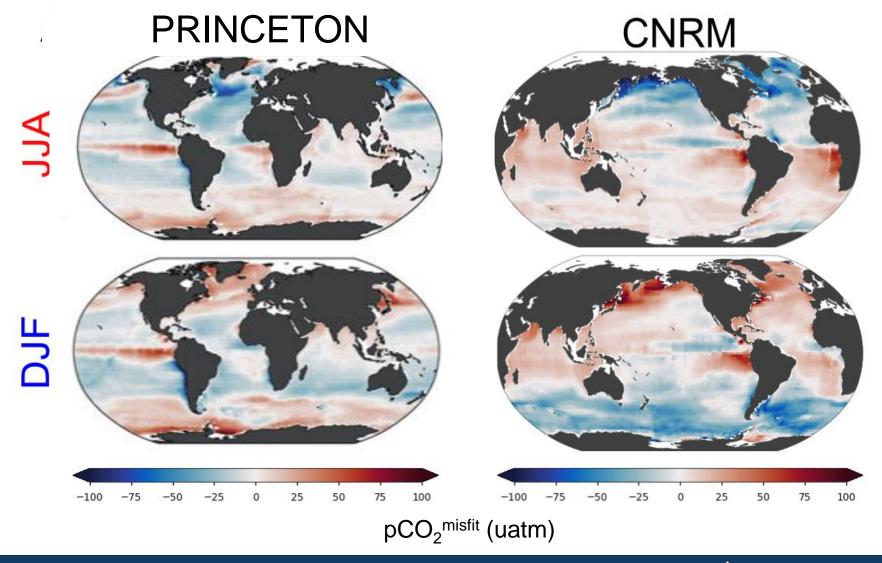
Gloege et al. 2022 JAMES (N=9), Bennington et al. 2022 GRL (N=8)







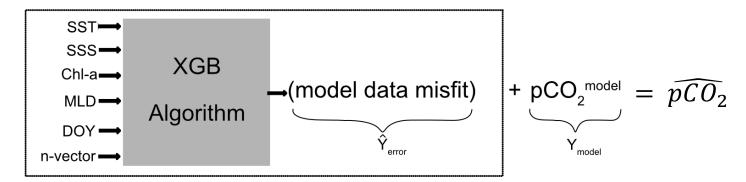
Full-coverage, monthly misfits illustrate substantial model biases



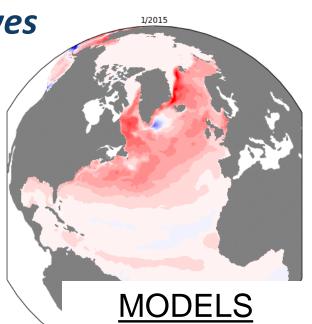
Gloege et al. 2022, JAMES

Using ML to combine models and data improves surface flux estimates (LDEO-HPD)

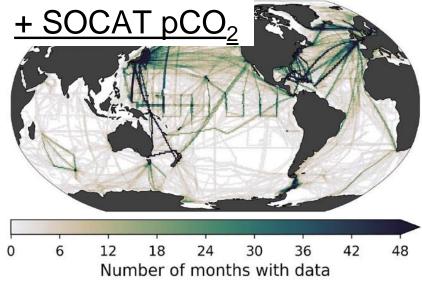
- pCO₂^{model} as priors
- Reconstruct $pCO_2^{misfit} = (pCO_2^{model} pCO_2^{SOCAT})$ (driver data: SST, SSS, Chl-a, MLD, time, location)
- eXtreme Gradient Boost (XGB) algorithm
- Misfits to correct N models; average for final pCO₂



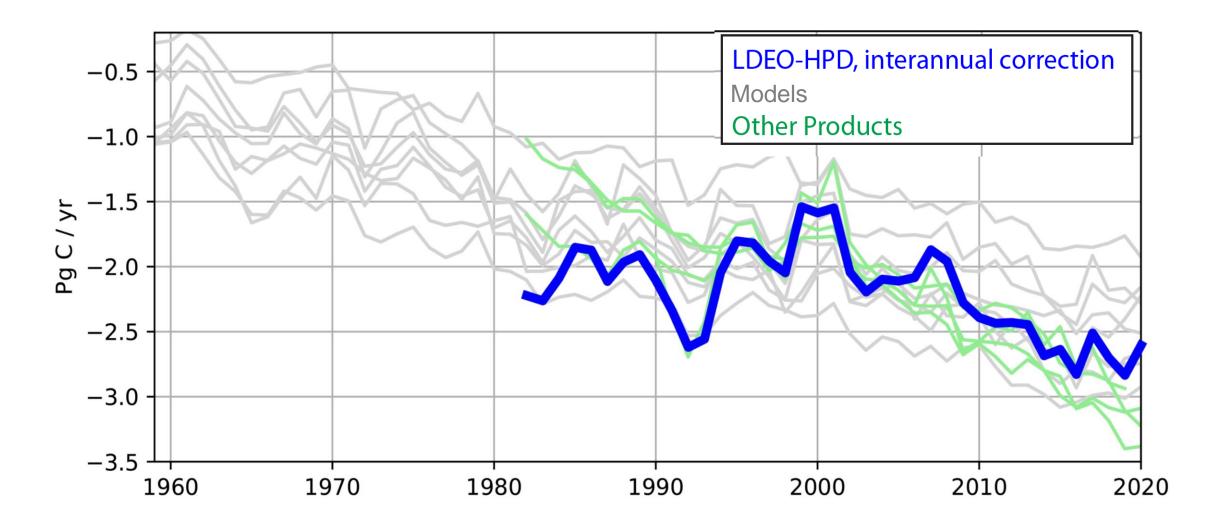
Gloege et al. 2022 JAMES (N=9), Bennington et al. 2022 GRL (N=8)



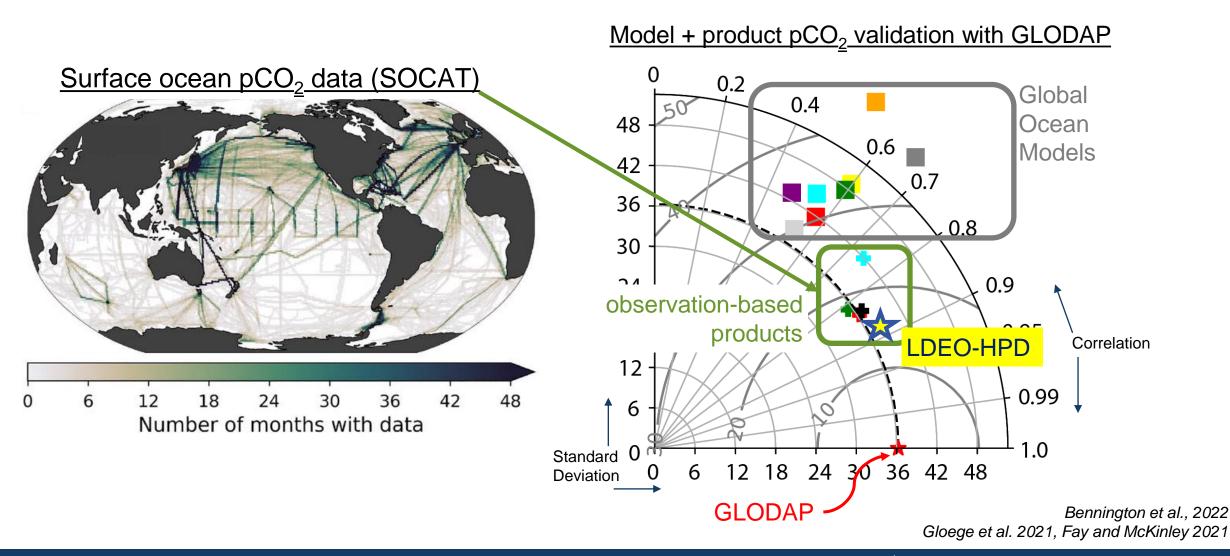




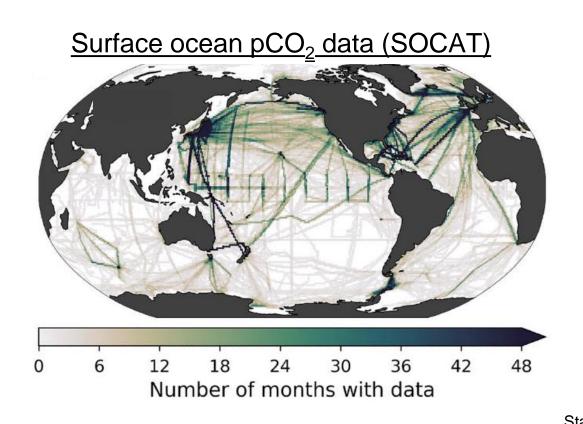
Global air-sea CO2 flux



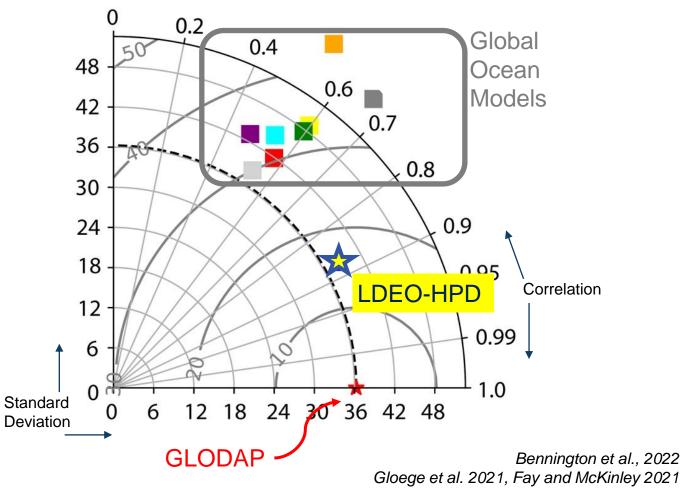
LDEO-HPD hybrid model-data approach offers improved skill



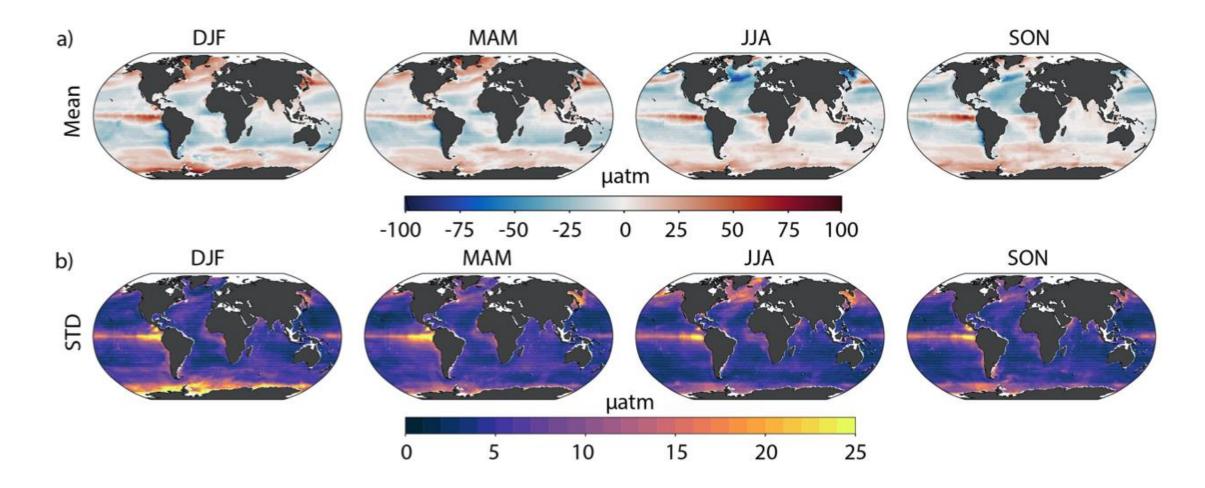
From where does this enhanced skill arise?



Model + product pCO₂ validation with GLODAP



Climatological model-data misfits much larger than interannual

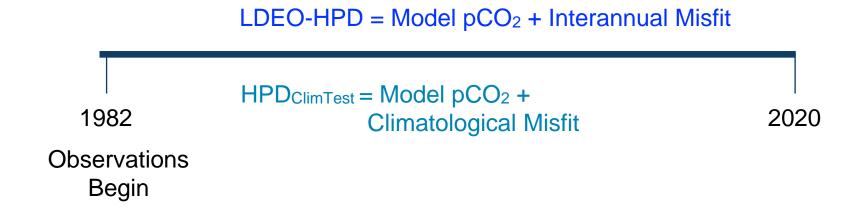


Princeton Model, others similar

Bennington et al. 2022 GRL

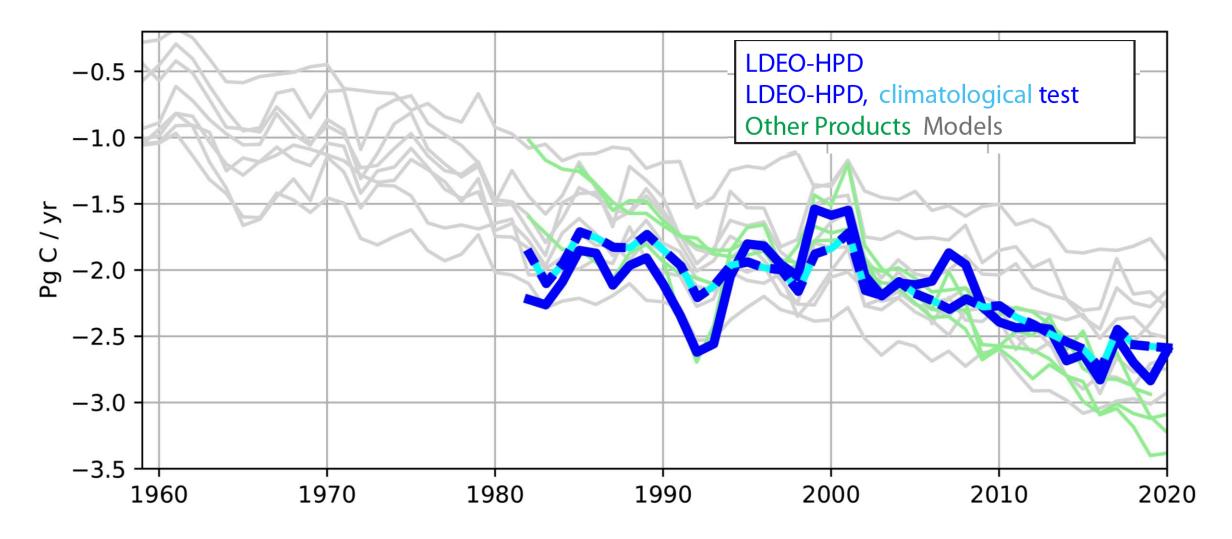
Since climatological misfit dominates, how much skill is gained by applying only this as correction, as opposed to interannual correction?

HPD_{ClimTest} applies the 2000-2020 climatology of the model-observation misfit

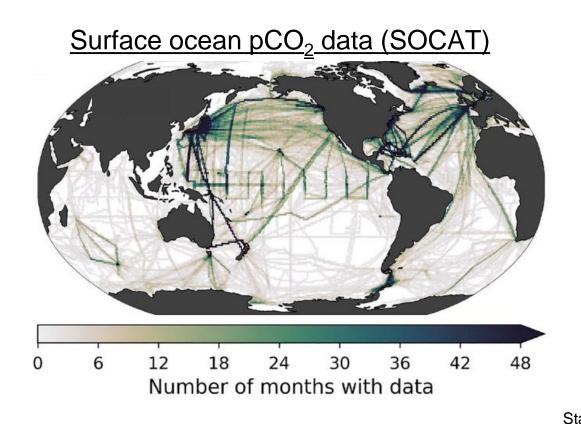


Bennington et al. 2022 GRL

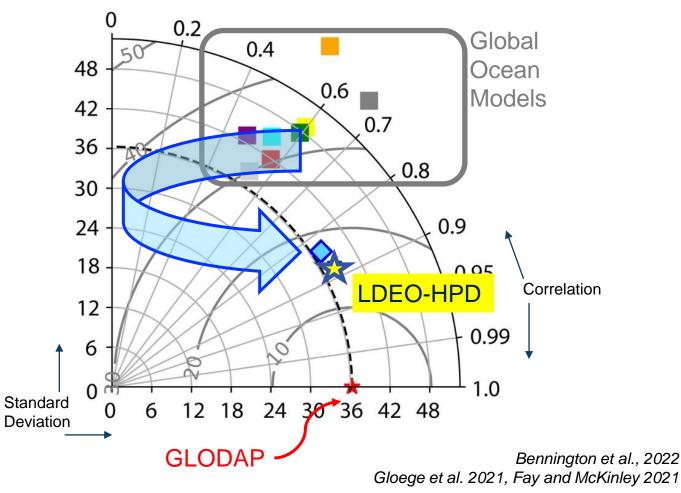
Global air-sea CO2 flux



Most of the improvement comes from the climatological correction

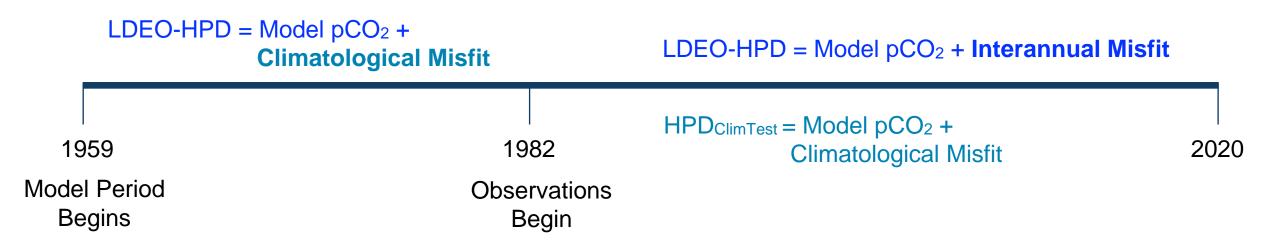


Model + product pCO₂ validation with GLODAP



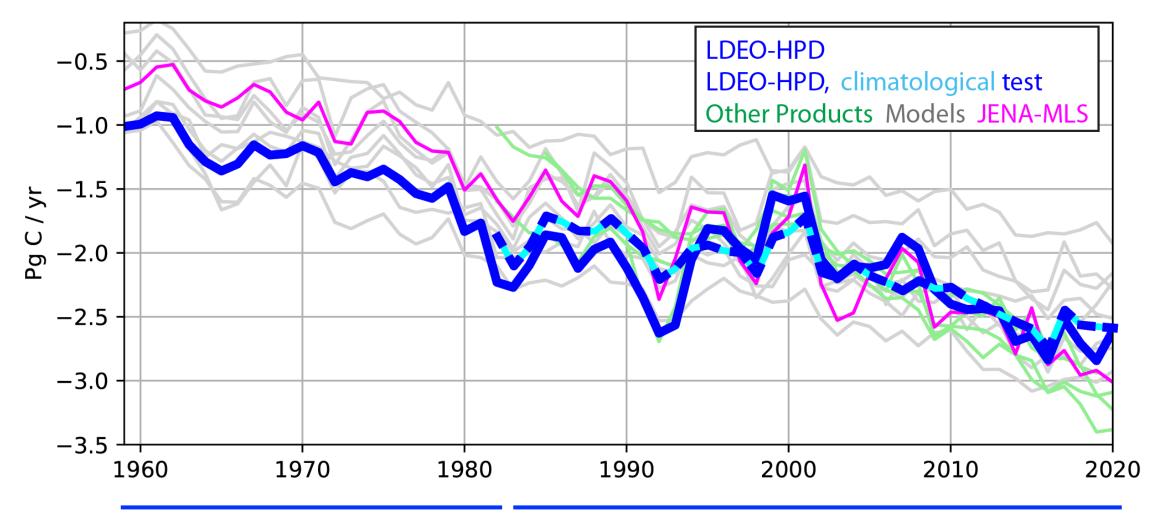
Taking advantage of the climatological misfit being the biggest source of model error, we extend back to 1959

- HPD_{ClimTest} applies the 2000-2020 climatology of the model-observation misfit
- Since the climatological correction provides most of the additional skill, we use it to correct models in the pre-observed period



Bennington et al. 2022 GRL

Global air-sea CO2 flux

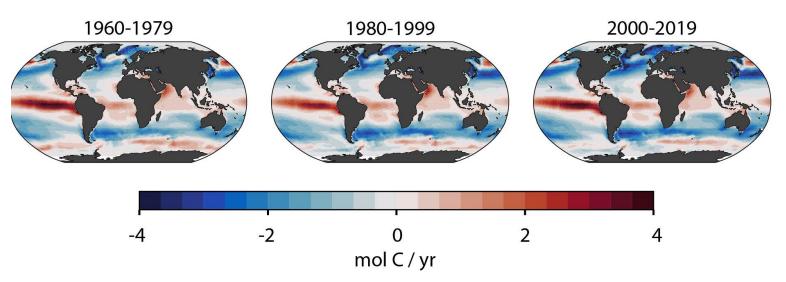


Climatological correction 1959-1982

Interannually varying correction 1982-2020

Bennington et al. 2022 GRL

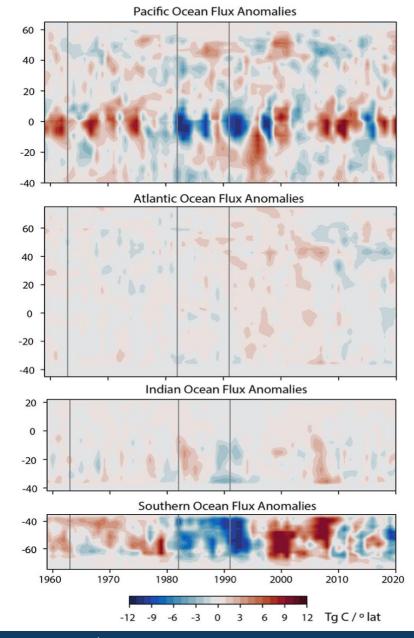
LDEO-HPD: 60+ years of air-sea CO2 fluxes



- 60+ years of monthly 1x1 air-sea CO₂ fluxes
- Significant decadal variations; coherent between equatorial Pacific and Southern Ocean

Bennington et al. 2022 GRL

Detrended Basin Flux Anomalies



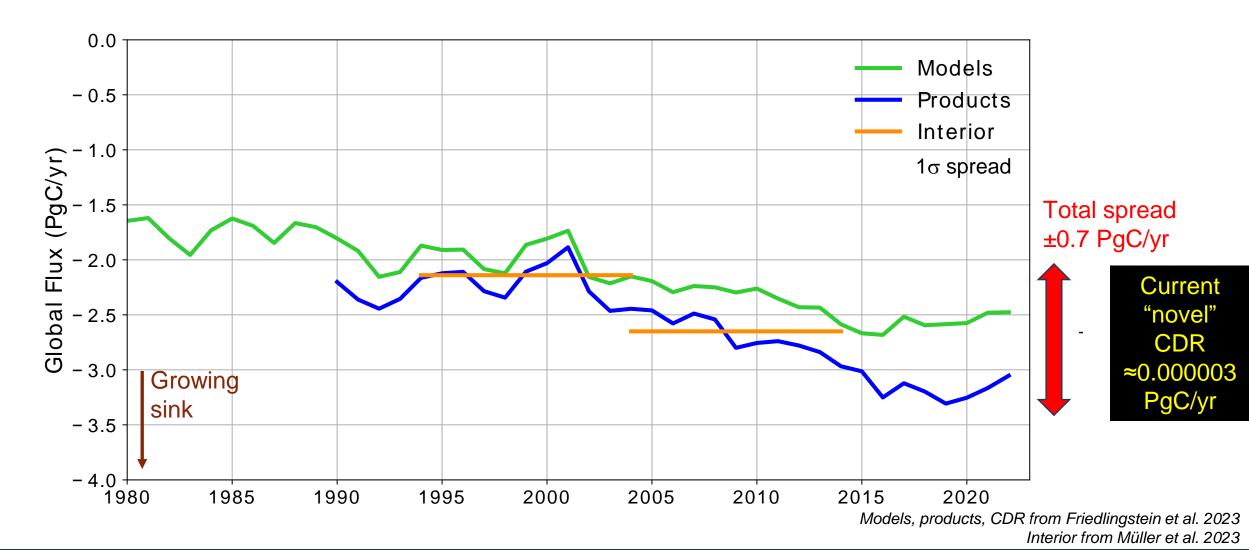
Take home messages

- Air-sea CO₂ flux mean and seasonality can be reconstructed from sparse pCO₂ data, but longer-timescale variability remains uncertain
- Hindcast and Earth System Models have significant mean-state biases
- Correcting models with data offers improved skill and 60+ years of reconstructed monthly surface ocean pCO₂

Outline

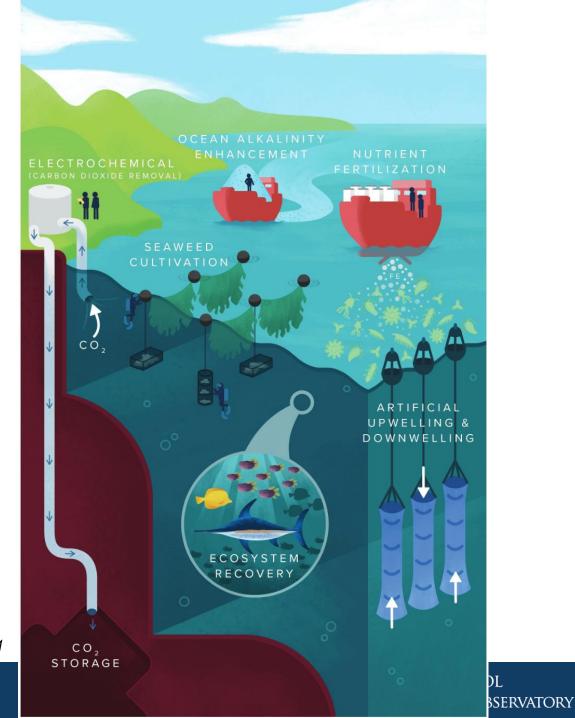
- Key processes of the ocean carbon cycle
- Improving quantification of the ocean carbon sink
 - Models: evaluate ML-based data product skill, given sampling
 - pCO₂ data products: apply to identify model mean-state biases
 - Models and data: combine using ML
 - marine Carbon Dioxide Removal (mCDR) quantifying "additionality"?

"novel" CDR is imperceptible with respect to the ocean sink

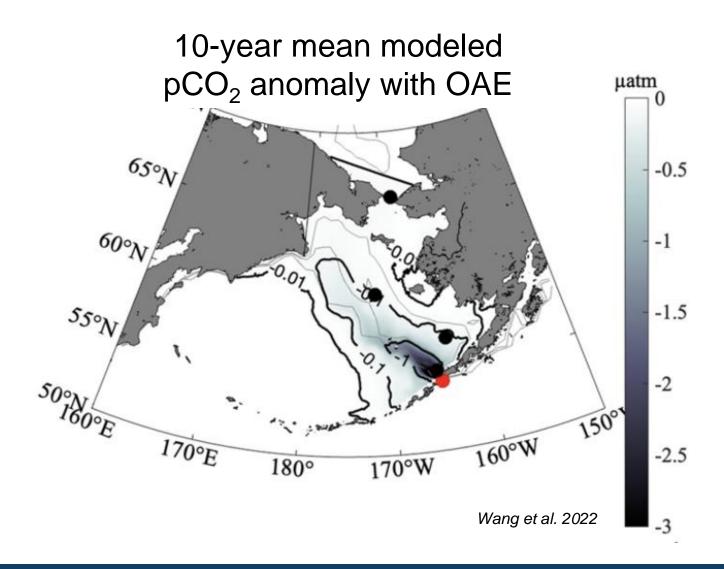


Marine Carbon Dioxide Removal mCDR

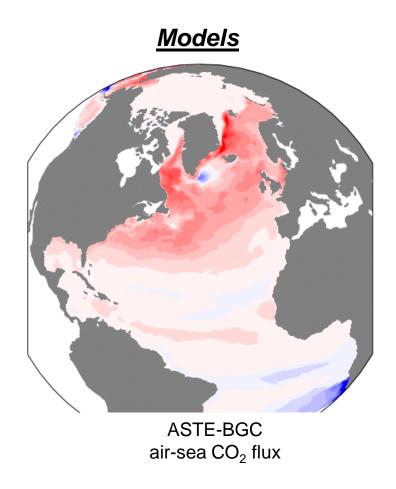
- Efficacy?
- Safety?
- Durability?
- Additionality?



mCDR pCO₂ impacts



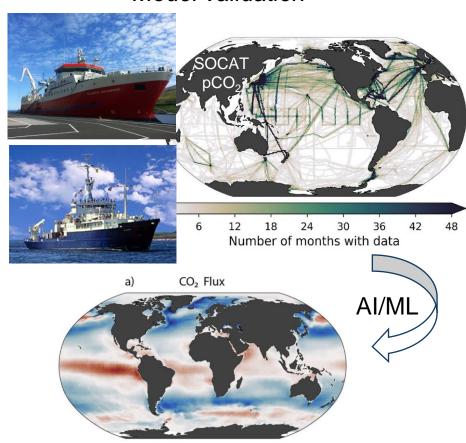
Global approaches potential for time-space resolved baseline



Surface pCO₂ data products

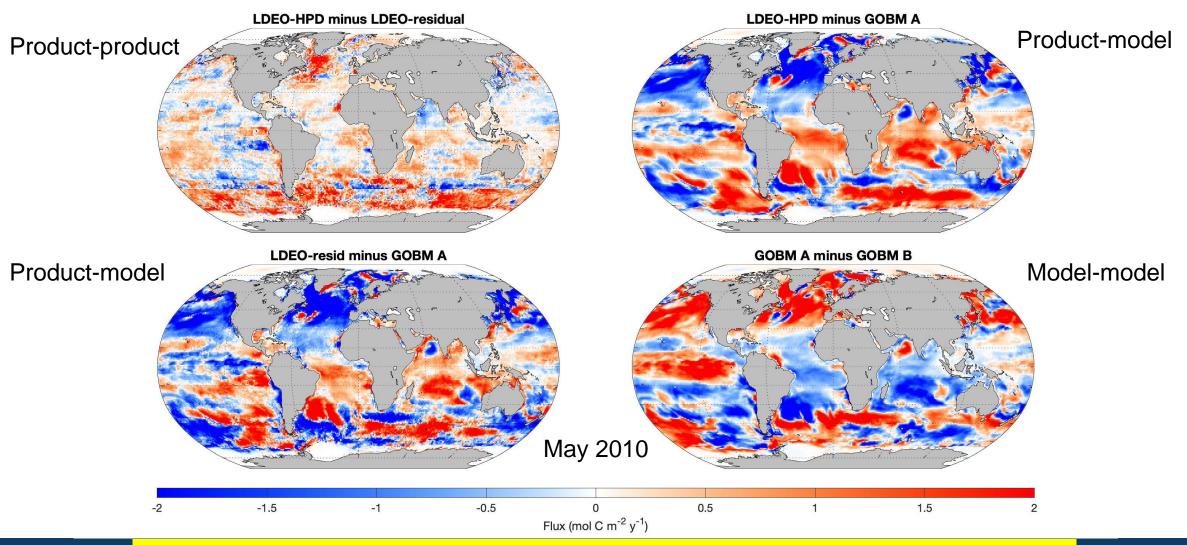
Air-sea fluxes (~monthly)

Model validation



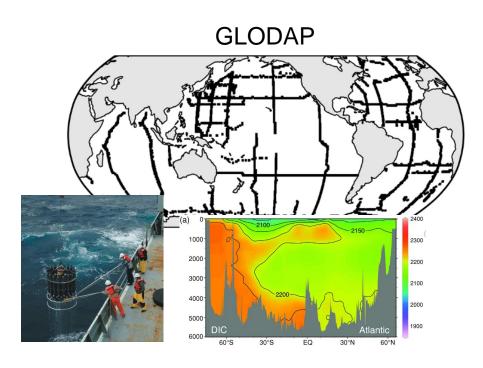
Air-sea flux uncertainties at smaller space-time scales are huge

Uncertainties are estimated here as difference between individual estimates



Independent pCO₂ to assess product and model skill, 2000-2023

Hydrography

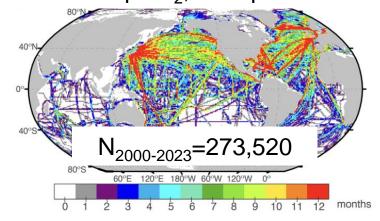


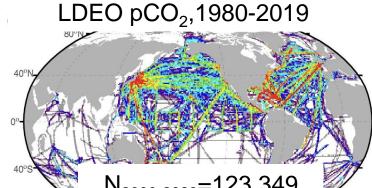
 $N_{2000-2023} = 1,043$

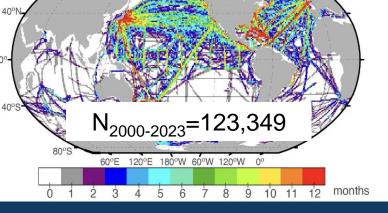
McKinley et al. in prep

Surface pCO₂

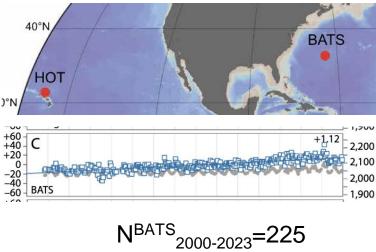
SOCAT pCO₂,1980-present







Timeseries

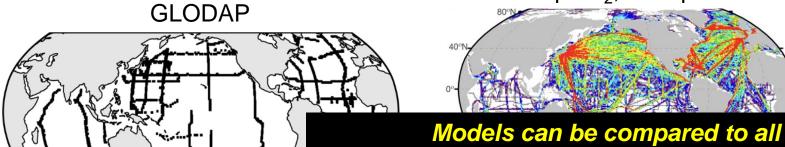


Independent pCO2 to assess product and model skill

Hydrography

SOCAT pCO₂,1980-present

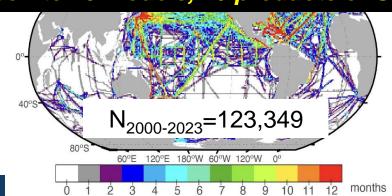
Timeseries



Products are trained with SOCAT, so remove this and any SOCAT points in LDEO from analysis

Surface pCO₂

Comparison to 10 models, 10 products of GCB2024





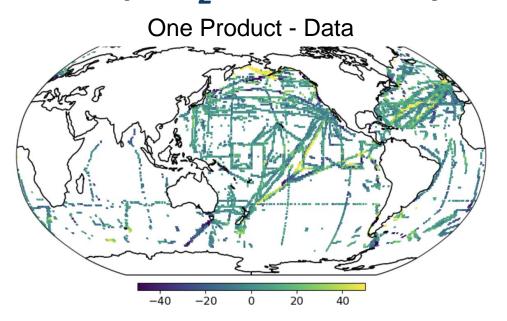
BATS

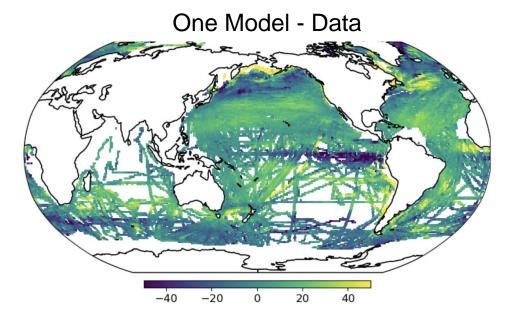
1,900

 $N^{\text{BATS}}_{2000-2023}$ =225

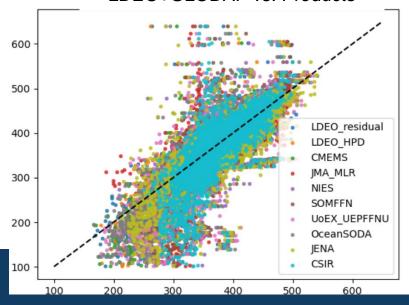
 $N_{2000-2023} = 1,043$

Global pCO₂: Models vs. products, and vs. independent data



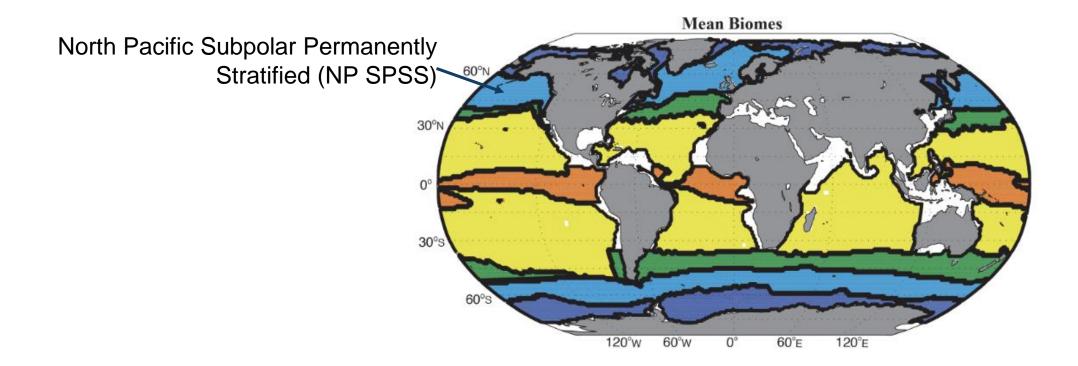


LDEO+GLODAP vs. Products



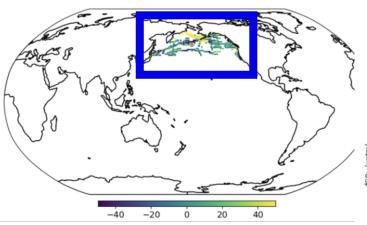
RMSE and correlation -		
2000-2023	10 Product mean	10 Model mean
LDEO + GLODAP (n=12,590)	28.0 μatm r=0.80	
SOCAT + GLODAP (n=285,256)		<mark>32.9 μatm</mark> r=0.63

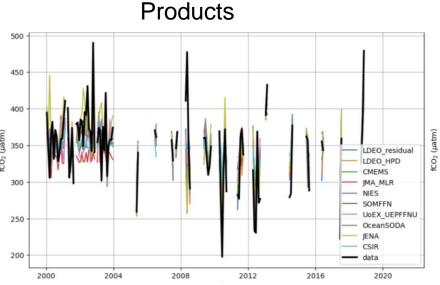
Biomes are mechanistically similar; use these for temporal decomposition

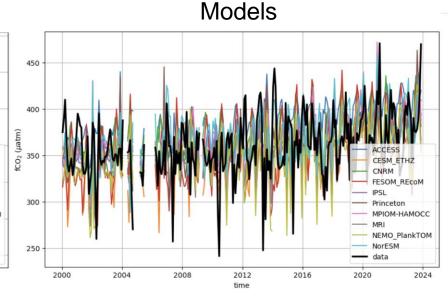


McKinley et al. in prep Fay and McKinley, 2013

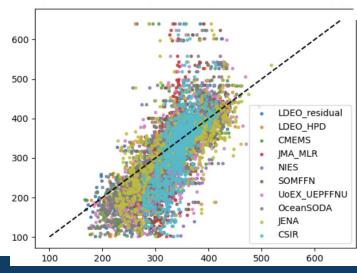
N. Pacific SPSS: Models and products vs. independent data





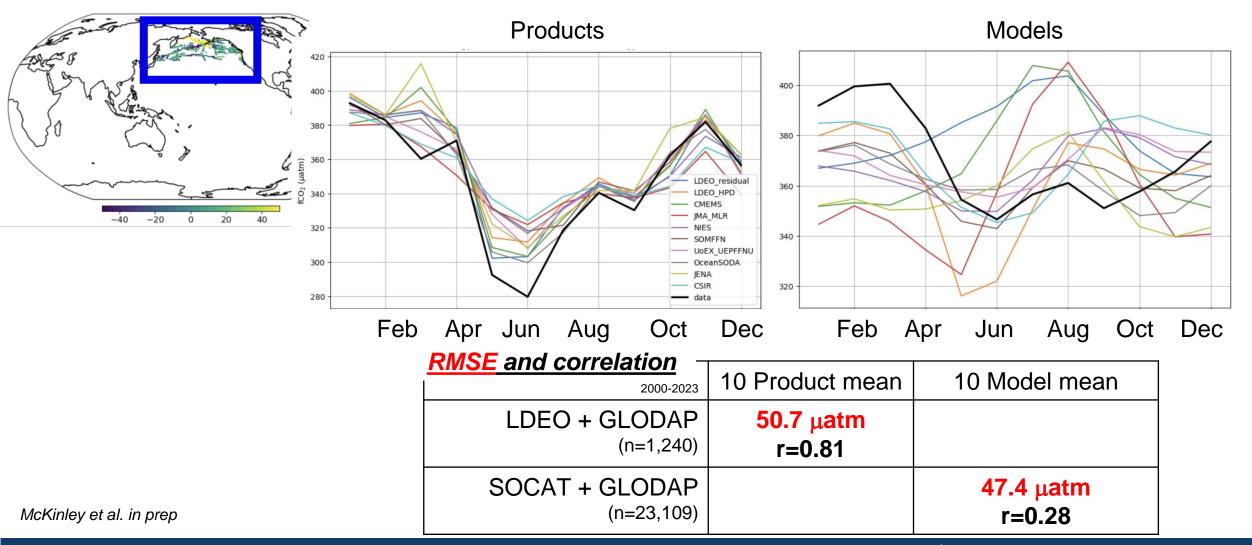




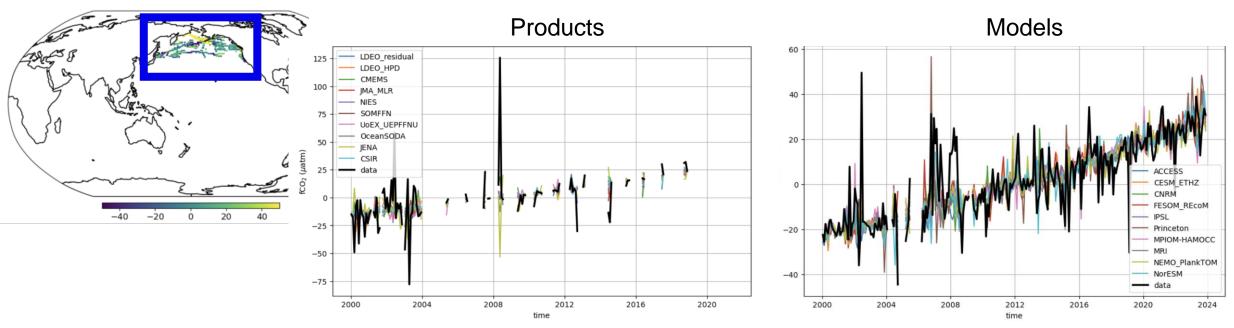


RMSE and correlation -		
2000-2023	10 Product mean	10 Model mean
LDEO + GLODAP (n=1,240)	54.3 _{μatm} r=0.77	
SOCAT + GLODAP (n=23,109)		54.4 _{μatm} r=0.30

N. Pacific SPSS: Climatological



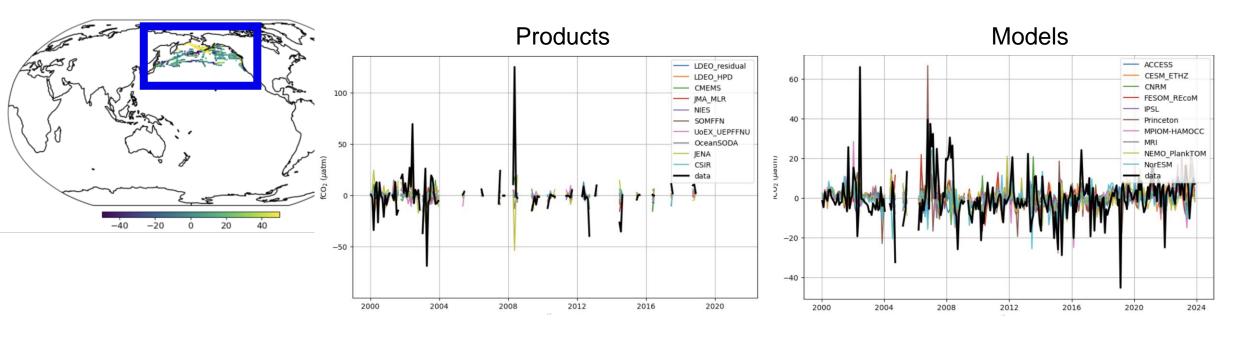
N. Pacific SPSS: Remove climatology



Product, Model, Datasets Trends = 1.9-2.1 uatm/yr

RMSE and correlation -		
2000-2023	10 Product mean	10 Model mean
LDEO + GLODAP (n=1,240)	18.9 _{μatm} r=0.50	
SOCAT + GLODAP (n=23,109)		23.2 _{μatm} r=0.54

N. Pacific SPSS: Remove trend



RMSE and correlation -		
2000-2023	10 Product mean	10 Model mean
LDEO + GLODAP (n=1,240)	18.9 _{μatm} r=0.23	
SOCAT + GLODAP (n=23,109)		<mark>23.2_{μatm}</mark> r=0.14

Take home messages

- Air-sea CO₂ flux mean and seasonality can be reconstructed from sparse pCO₂ data, but longer-timescale variability remains uncertain
- Hindcast and Earth System Models have significant mean-state biases
- Correcting models with data offers improved skill and 60+ years of reconstructed monthly surface ocean pCO₂
- Current models and data products have local uncertainties orders of magnitude larger than expected mCDR impacts

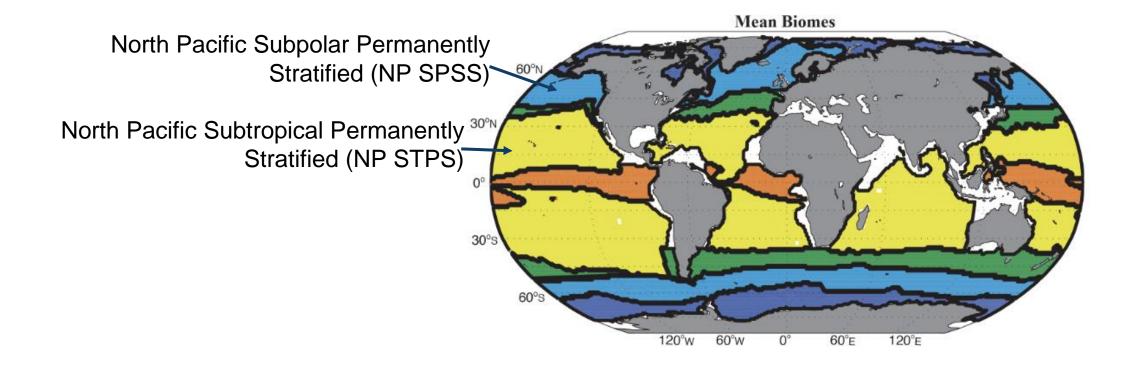
Thank you!





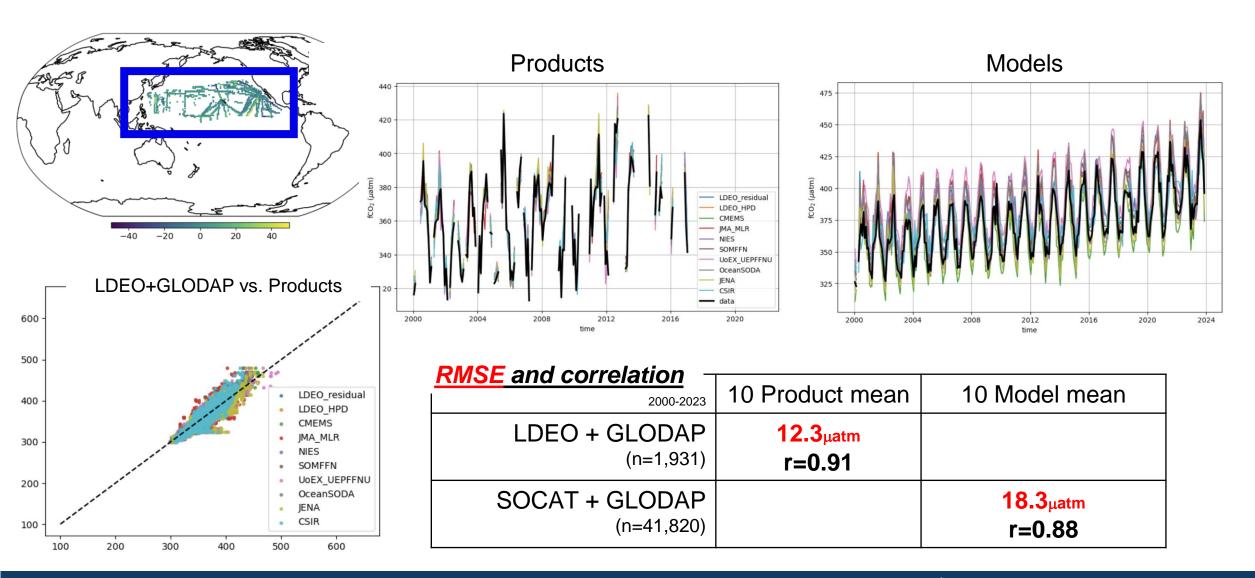
Viviana Acquaviva (professor, CUNY), Ce Bian (postdoc), Galen McKinley Thea Heimdal (scientist), Abby Shaum (PhD student), Amanda Fay (senior scientist)

Biomes are mechanistically similar; use these for temporal decomposition

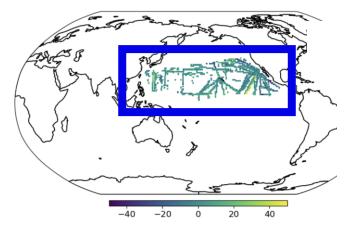


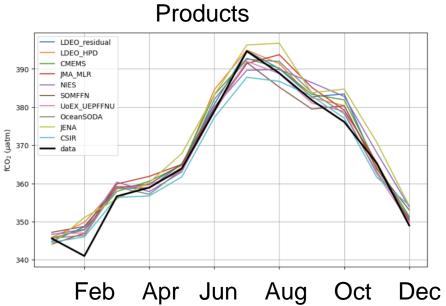
McKinley et al. in prep Fay and McKinley, 2013

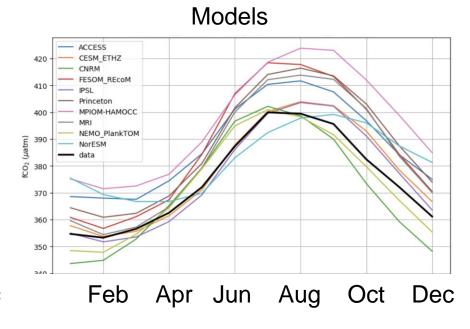
N. Pacific STPS: Models and products vs. independent data



N. Pacific STPS: Climatological

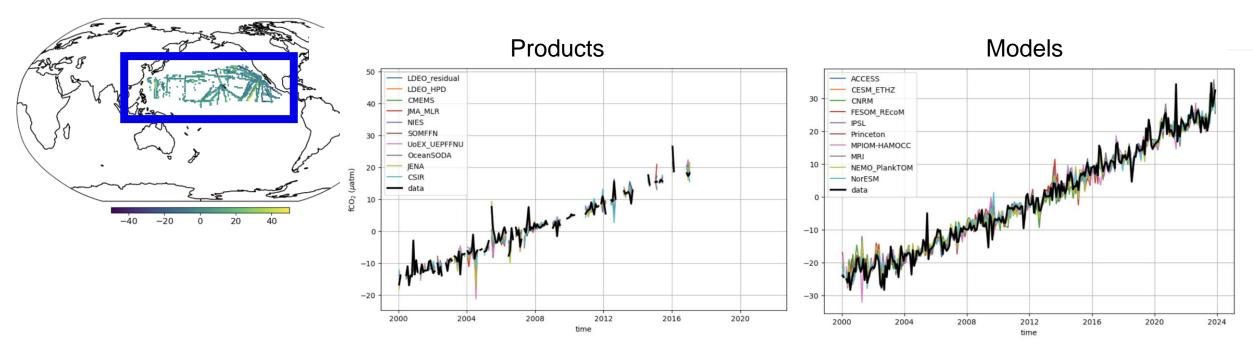






RMSE and correlation 2000-2023	10 Product mean	10 Model mean
LDEO + GLODAP (n=1,931)	12.2 _{μatm} r=0.89	
SOCAT + GLODAP (n=41,820)		17.7 _{μatm} r=0.85

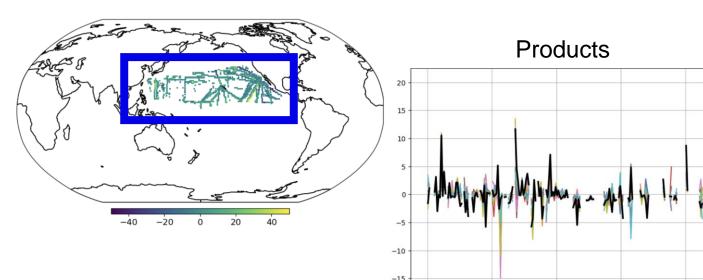
N. Pacific STPS: Remove climatology



Product, Model, Datasets Trend = 2.1-2.2 uatm/yr

RMSE and correlation -		
2000-2023	10 Product mean	10 Model mean
LDEO + GLODAP (n=1,931)	3.7 _{μatm} r=0.92	
SOCAT + GLODAP (n=41,820)		7.2 _{μatm} r=0.89

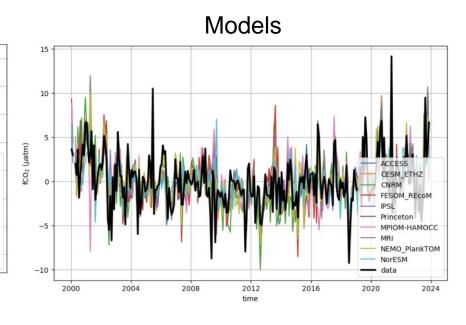
N. Pacific STPS: Remove trend



2004

2012

2016



RMSE and correlation -		
2000-2023	10 Product mean	10 Model mean
LDEO + GLODAP (n=1,931)	3.7 _{μatm} r=0.40	
SOCAT + GLODAP (n=41,820)		7.2 _{μatm} r=0.47

OceanSODA

2020