

An Empirical Estimate of the Southern Ocean air-sea CO₂ flux

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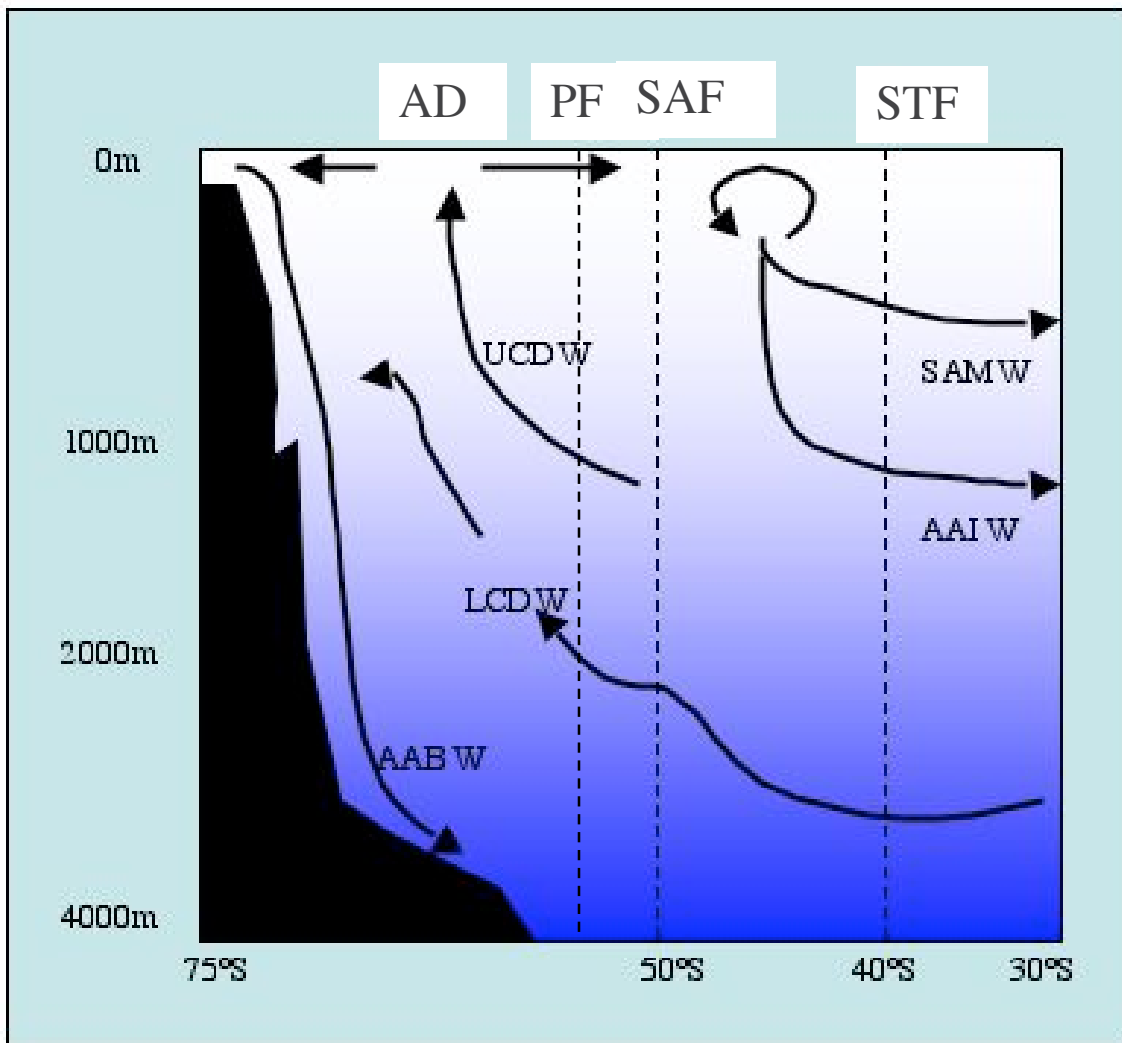
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CSIRO - Marine Research, Hobart

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Southern Ocean - Zonation and Circulation



STF- sub-tropical Front

SAF - sub-Antarctic Front

PF - Polar Front

AD - Antarctic Divergence

UCDW - Upper Circumpolar Deep Water

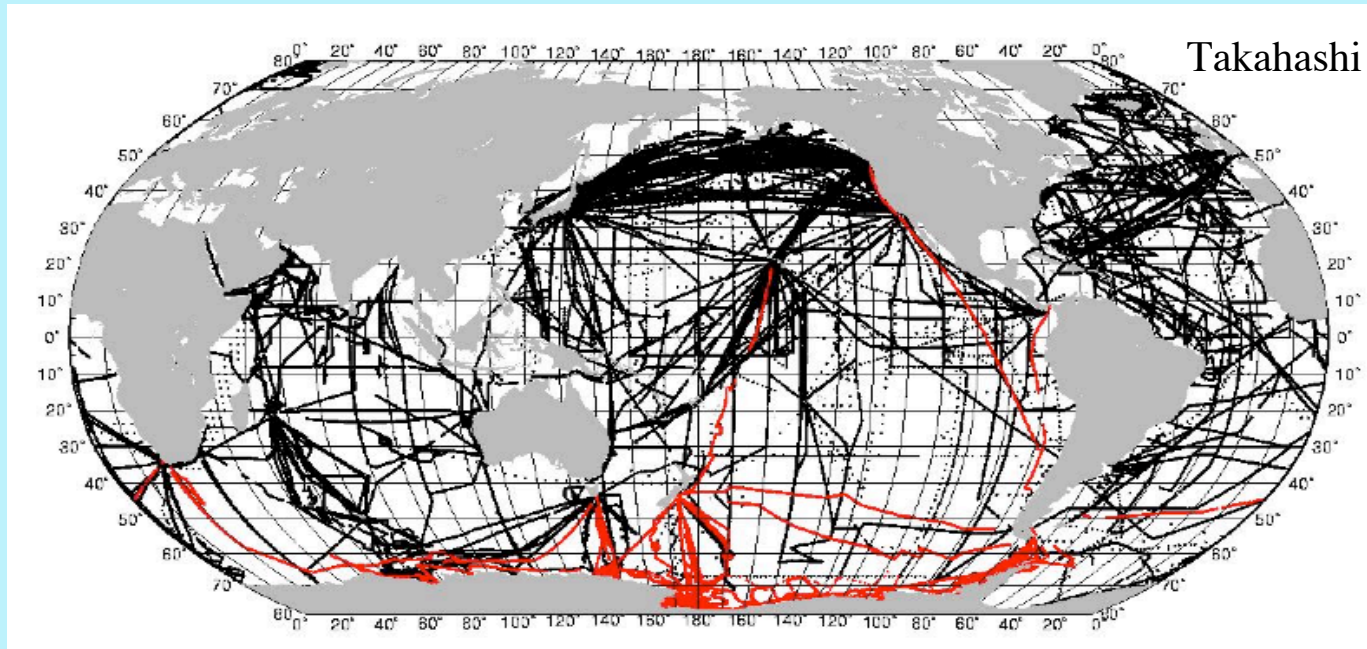
SAMW - sub-Antarctic Mode Water

AAIW - Antarctic Intermediate Water



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Most direct way to measure air-sea CO₂ fluxes



Takahashi et al, 2002

pCO₂



$$\text{Flux} = \Delta p\text{CO}_2 \times k$$

(gas-exchange coeff)

Atmosphere

pCO₂

Surface Ocean

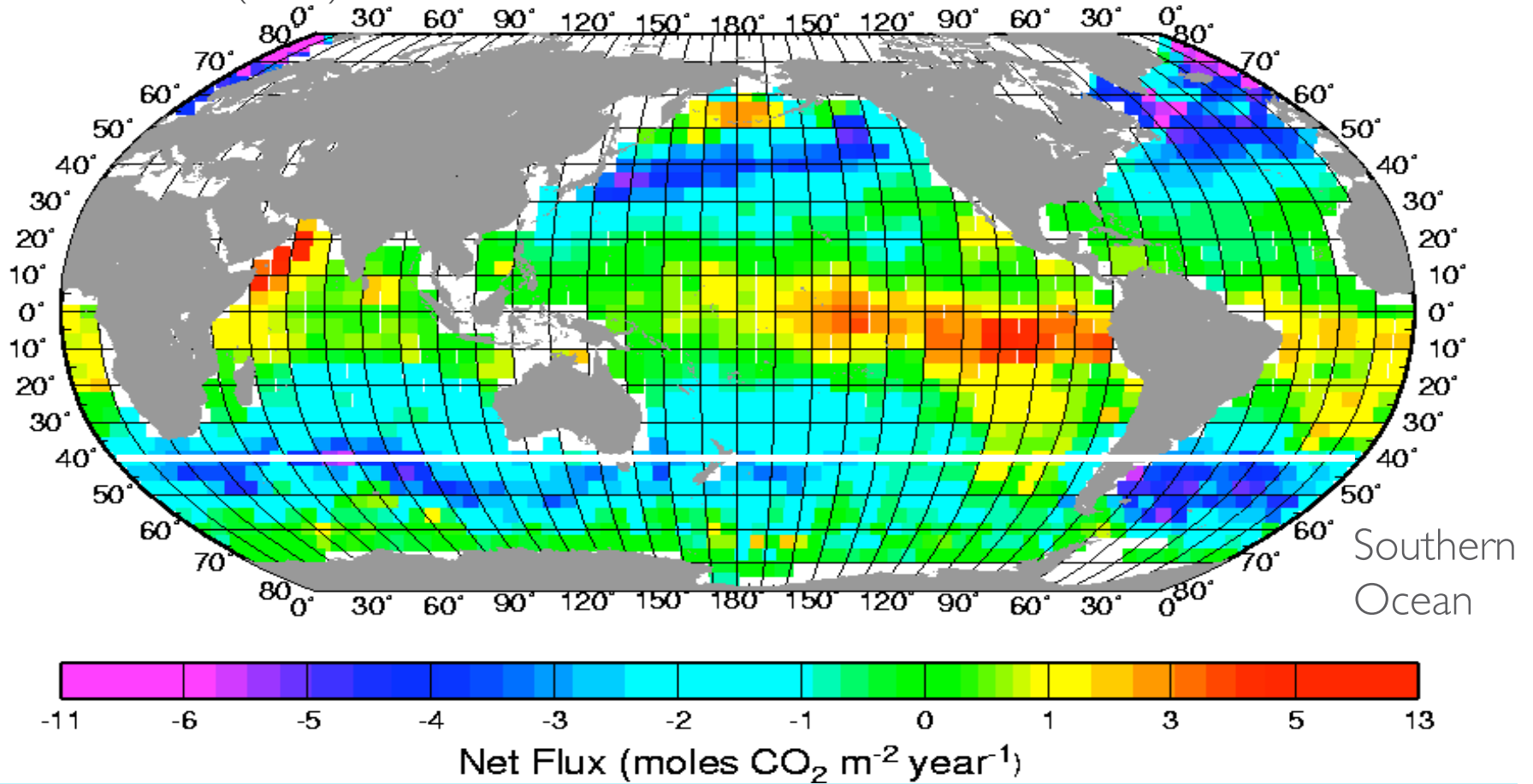


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Mean Annual CO₂ Flux via Takahashi pCO₂ database

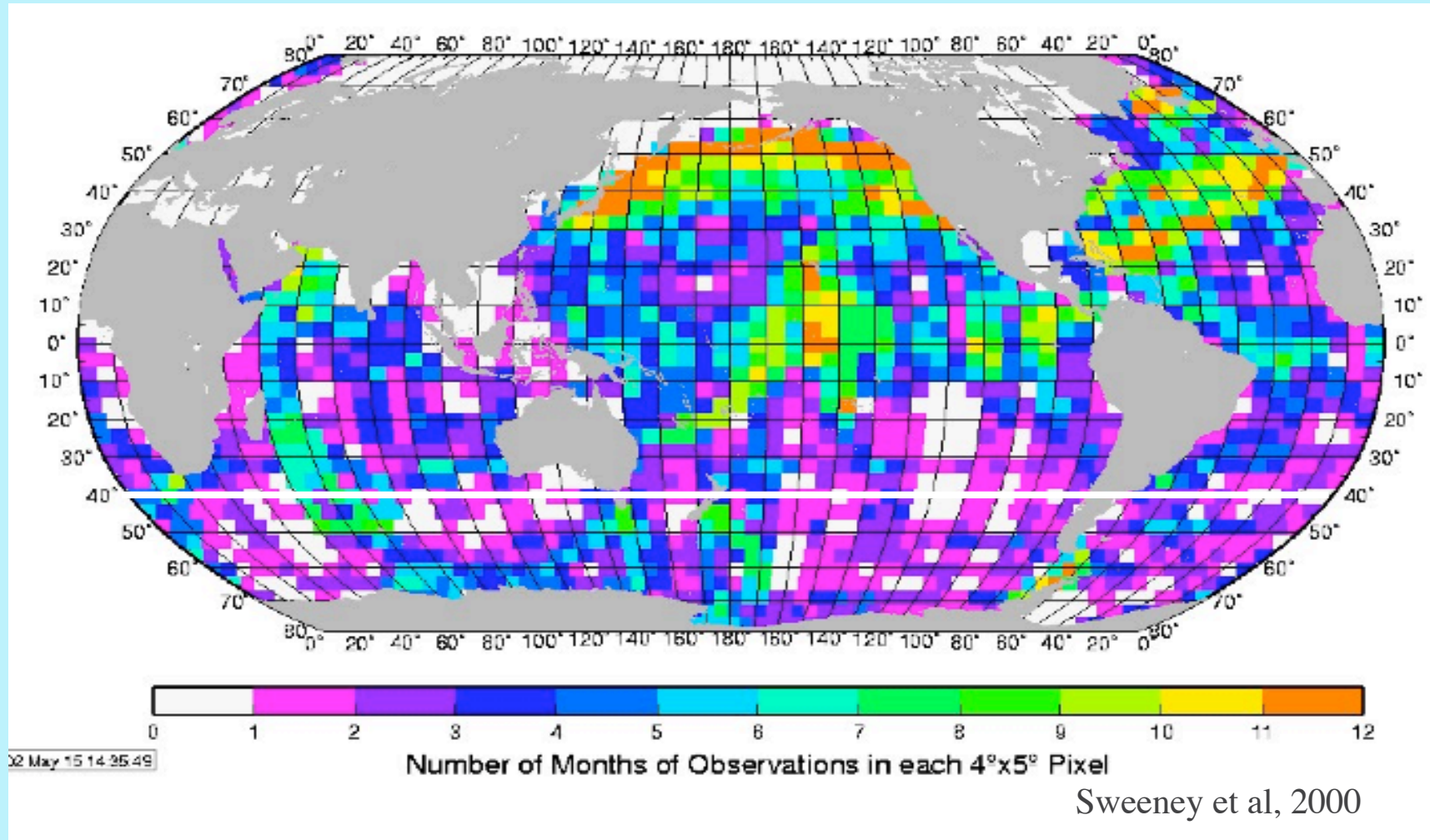


Takahashi et al, (2002)



- From this, Southern Ocean is a considerable net CO₂ sink (~0.6PgC/yr)
- Most uncertainty in the Southern Ocean CO₂ flux

Problems with the pCO₂ database in the Southern Ocean



- Seasonal sampling bias
- Inter-annual sampling bias



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Concept to estimate the air-sea CO₂ flux



- 1) Gather all available DIC/ALK surface measurements and normalise the anthropogenic CO₂ signal to a given year (1995)
- 2) Derive empirical fits for surface DIC/ALK using standard hydrographic measurements (T,S,nuts). Similar to previous studies that derive these empirical fits (Feely et al, 2002; Millero et al, 1998, Lee et al, 2000)
- 3) Extrapolate these fits using the known seasonal cycles of T,S,nuts from the World Ocean Atlas 2001
- 4) Calculate the seasonal pCO₂ distribution from the extrapolated seasonal cycles of DIC/ALK
- 5) Determine the seasonal and annual air-sea CO₂ flux and associated uncertainties.

Advantage: Not subject to seasonal/interannual biases since the extrapolations are based on standard hydro parameters whose seasonal cycles are well known

Disadvantage: Indirect determination of pCO₂ and reliant on uncertain choice of CO₂ dissociation constants

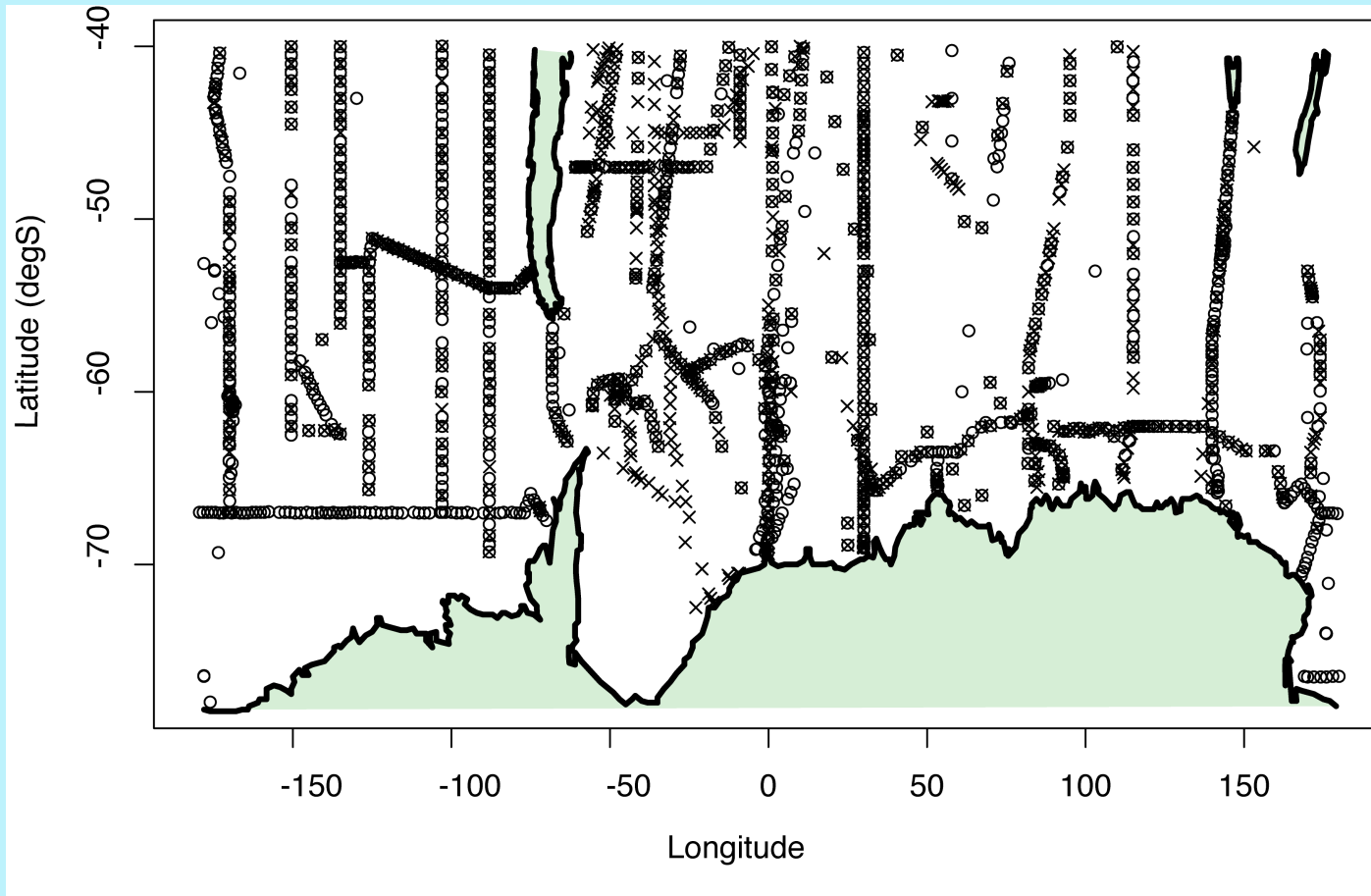


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Concept for estimating CO_2 flux in the Southern Ocean



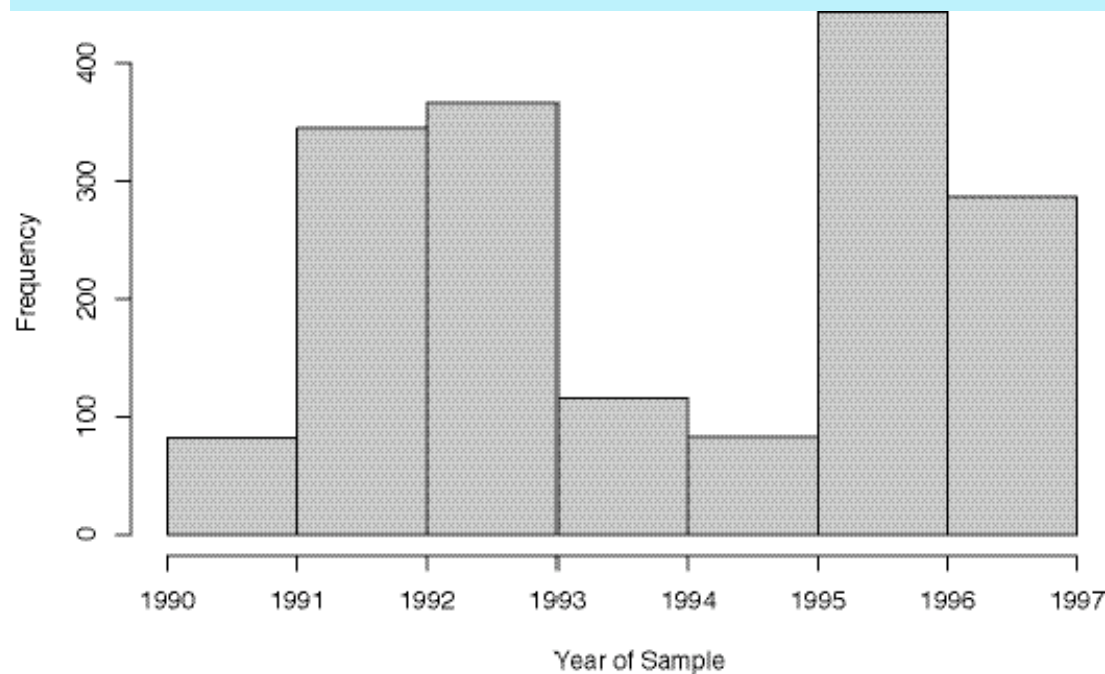
Step 1) Gather all available DIC/ALK surface measurements
Fit surface DIC measurements using more regularly sampled hydrographic measurements (temp, sal, nutrients)



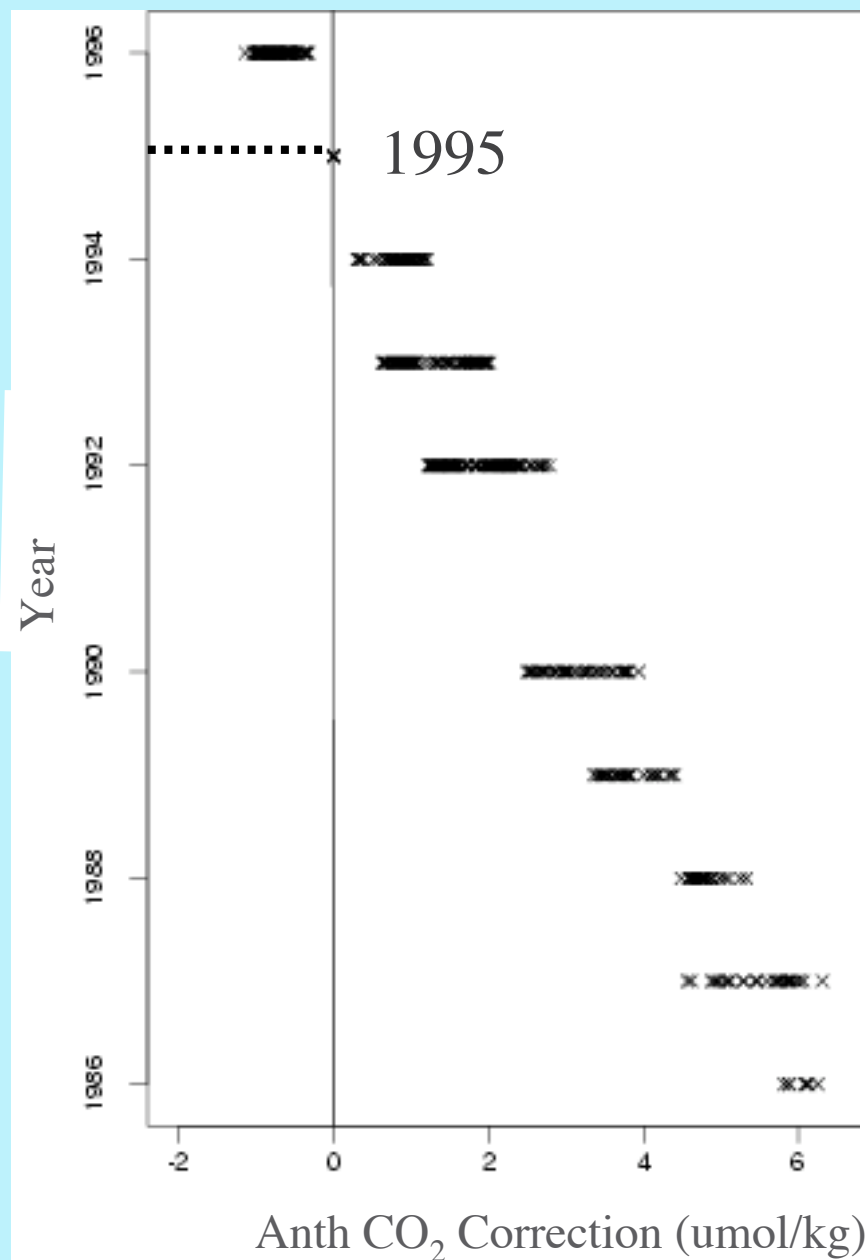


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Correct for the Anthropogenic CO₂ Component



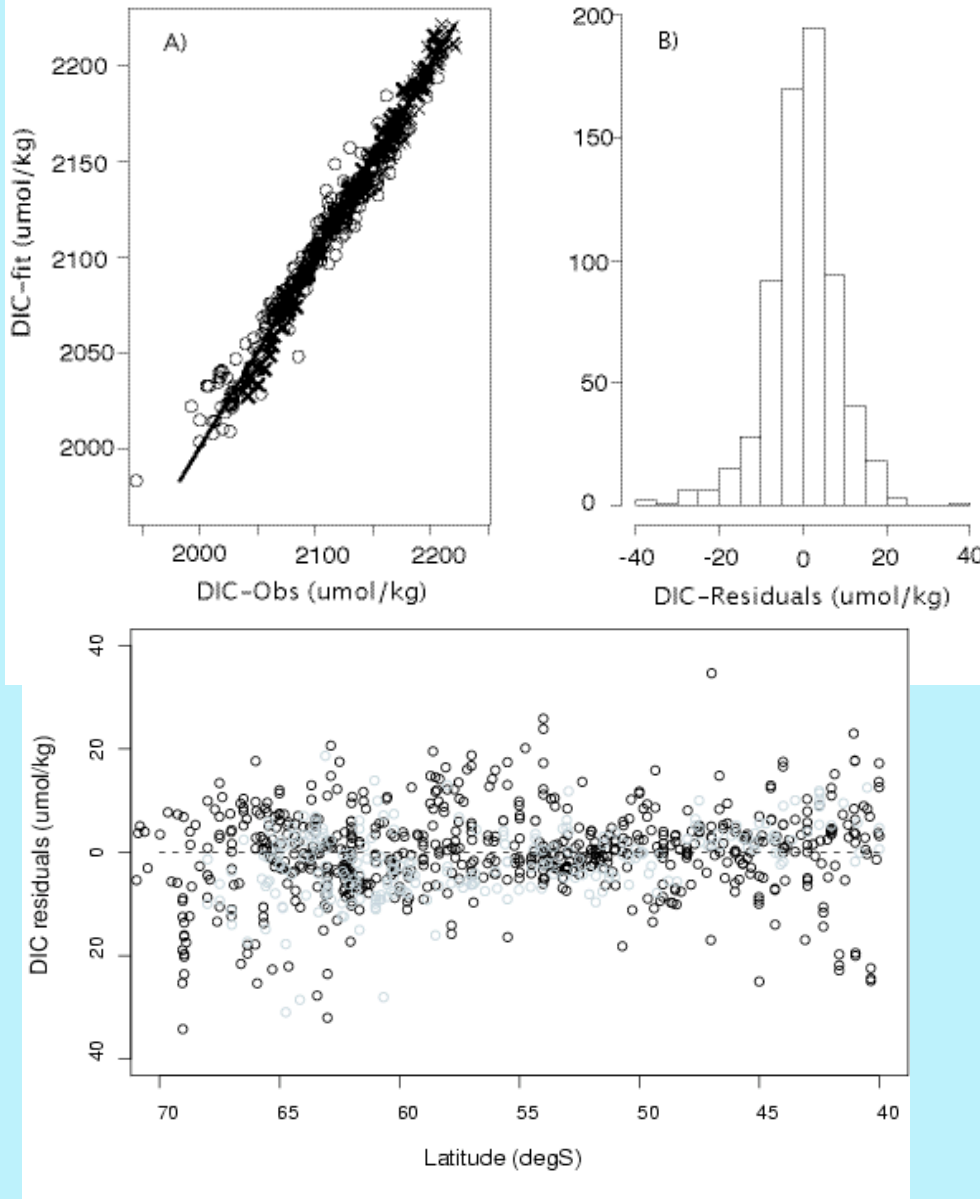
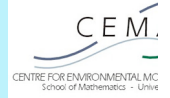
- DIC concentrations were corrected to the year 1995 using the CFC-age methodology





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Derive Empirical fits for surface DIC / ALK



$$DIC_{obs} = \alpha_0 + \sum_{i=1}^n \alpha_i P_i + \epsilon$$

DIC= f(temp, sal, nitrate, silicate, oxygen)

S.E = ± 8 umol/kg

n=668

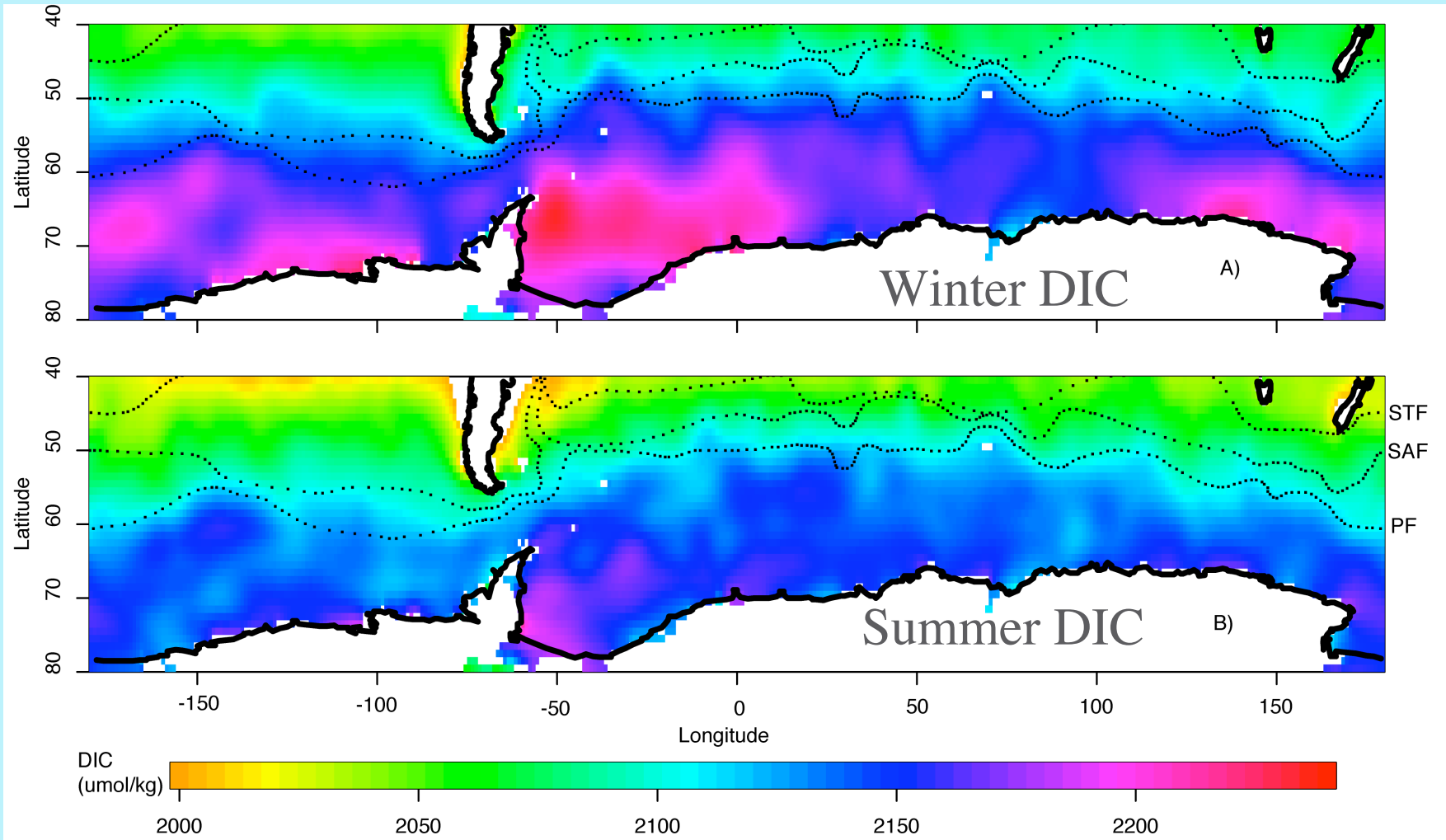
ALK=f(temp,sal)

S.E= ± 9 umol/kg

- Similar to previous regression applications only using more data (eg Feely et al, 2002, Lee et al, 2000, Millero et al, 1998)
- No change to the fit with season
- No strong residual pattern indicating potential biases



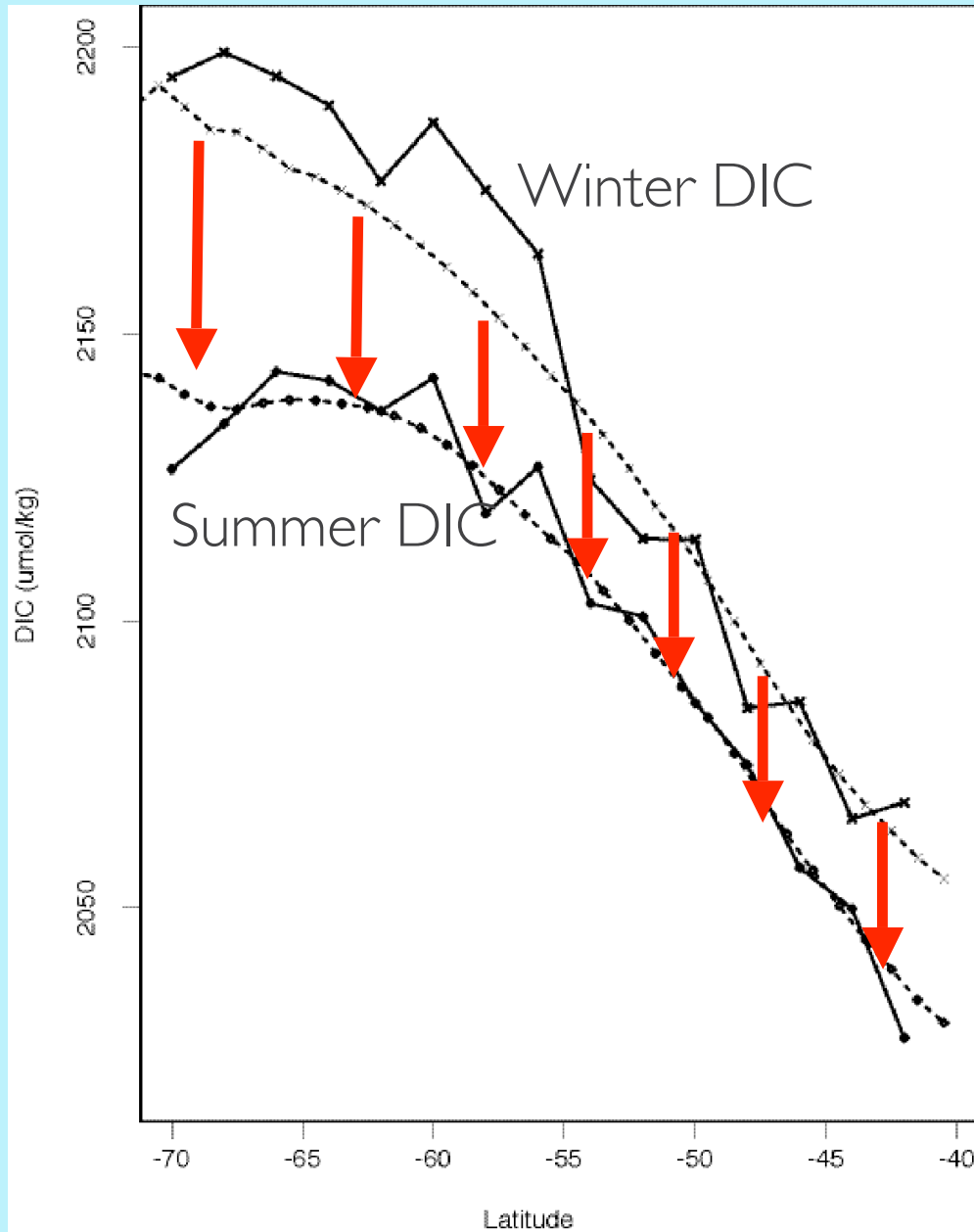
Step 2) Extrapolate using World Ocean Atlas climatology 2001



- Results in a full seasonal cycle for DIC and ALK in the Southern Ocean



Test the results with direct DIC observations



- Reproduces the meridional DIC structure and seasonal drawdown quite well

- Winter to summer drawdown of $\sim 30\mu\text{mol/kg}$

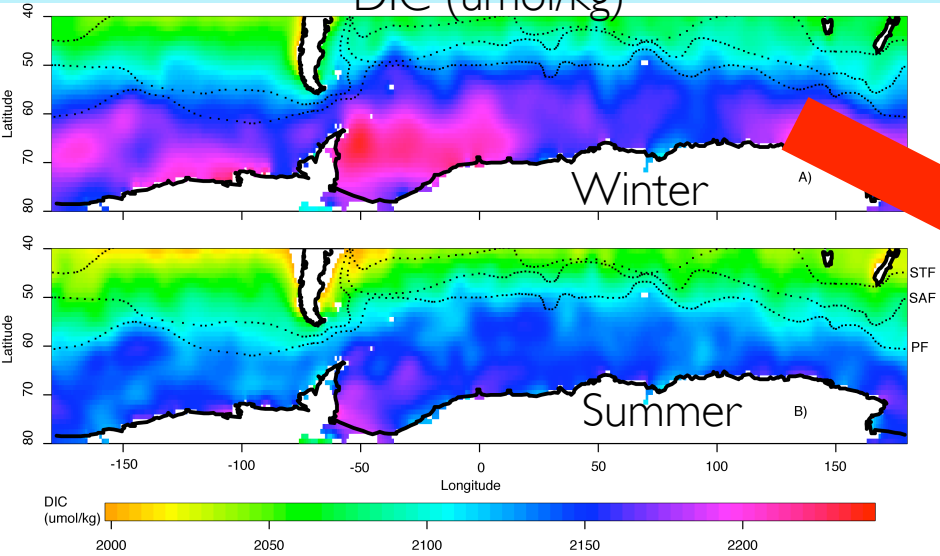


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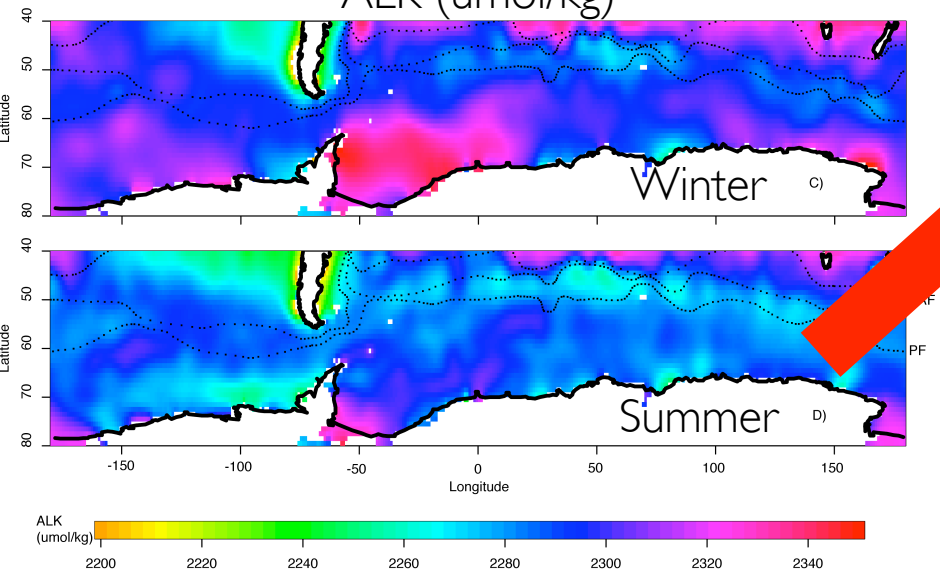
Step 3) Calculate seasonal $p\text{CO}_2$ from DIC/ALK



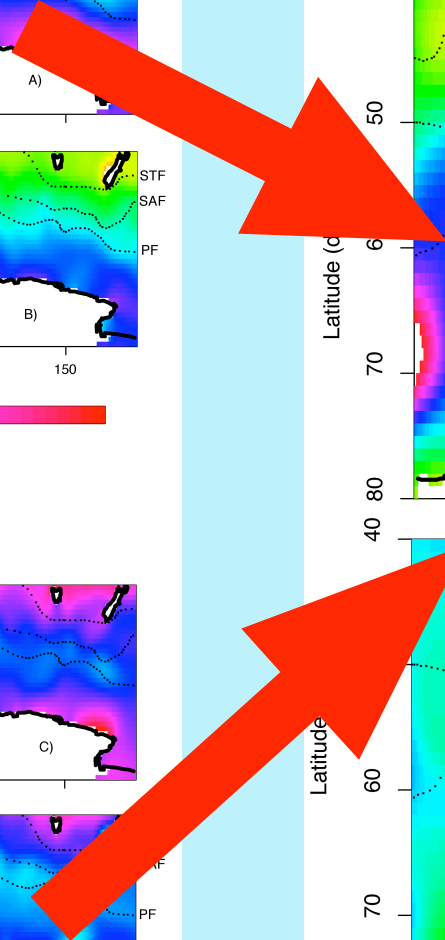
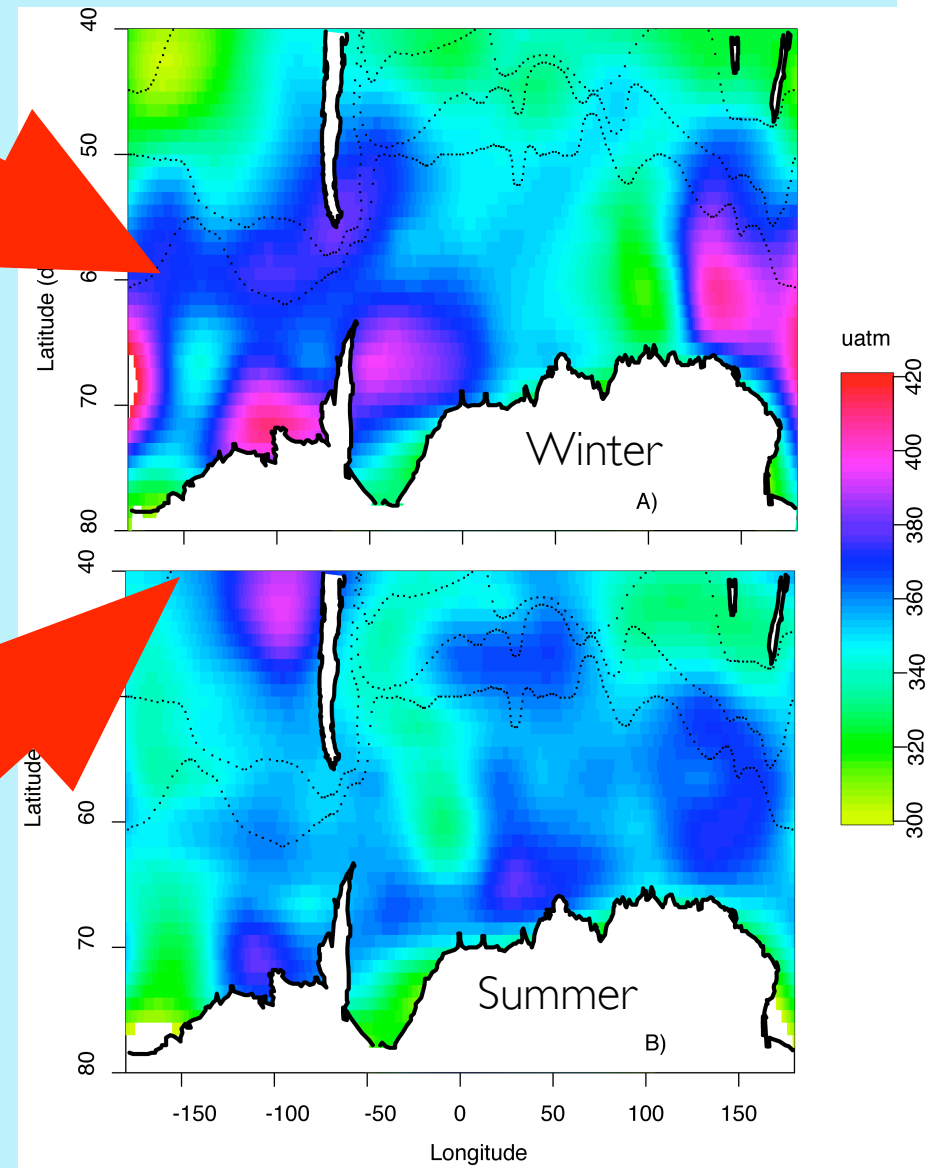
DIC ($\mu\text{mol/kg}$)



ALK ($\mu\text{mol/kg}$)

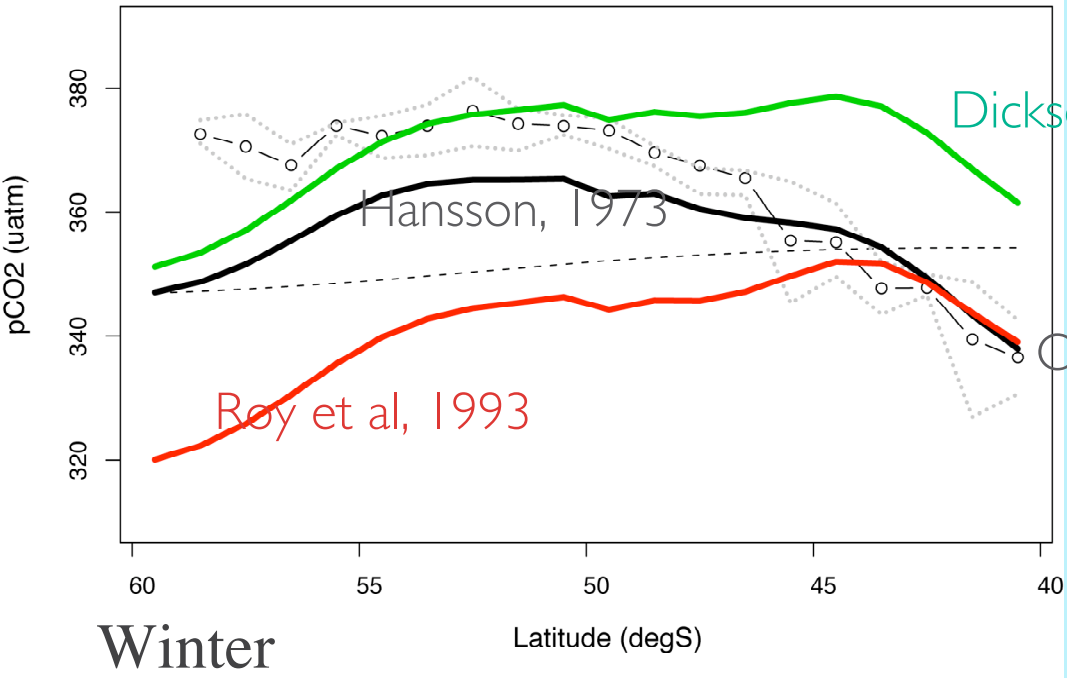


$p\text{CO}_2$ (μatm)





Impact of CO₂ dissociation constants



Dickson and Millero, 1987

Hansson, 1973

Roy et al, 1993

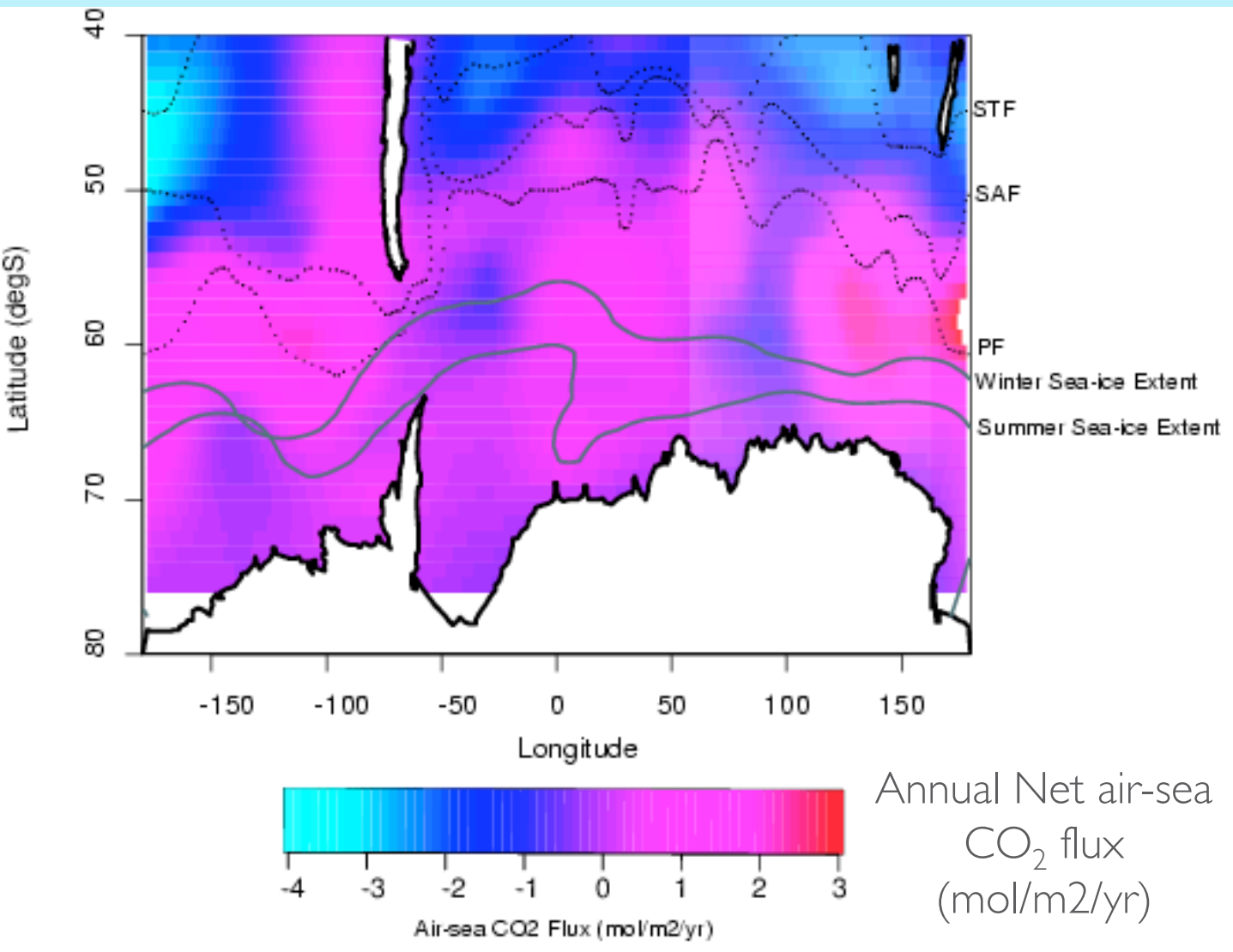
Observations (Metzl et al, 2005)

- Varies by about ± 10 uatm
- Used Hansson(1973) - middle estimate
- Not optimal - need tri-carbon sampling strategy of DIC/ALK/pCO₂ for future measurements



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Step 4) Calculate the CO₂ flux



$$\text{Flux} = \Delta p\text{CO}_2 \times k$$

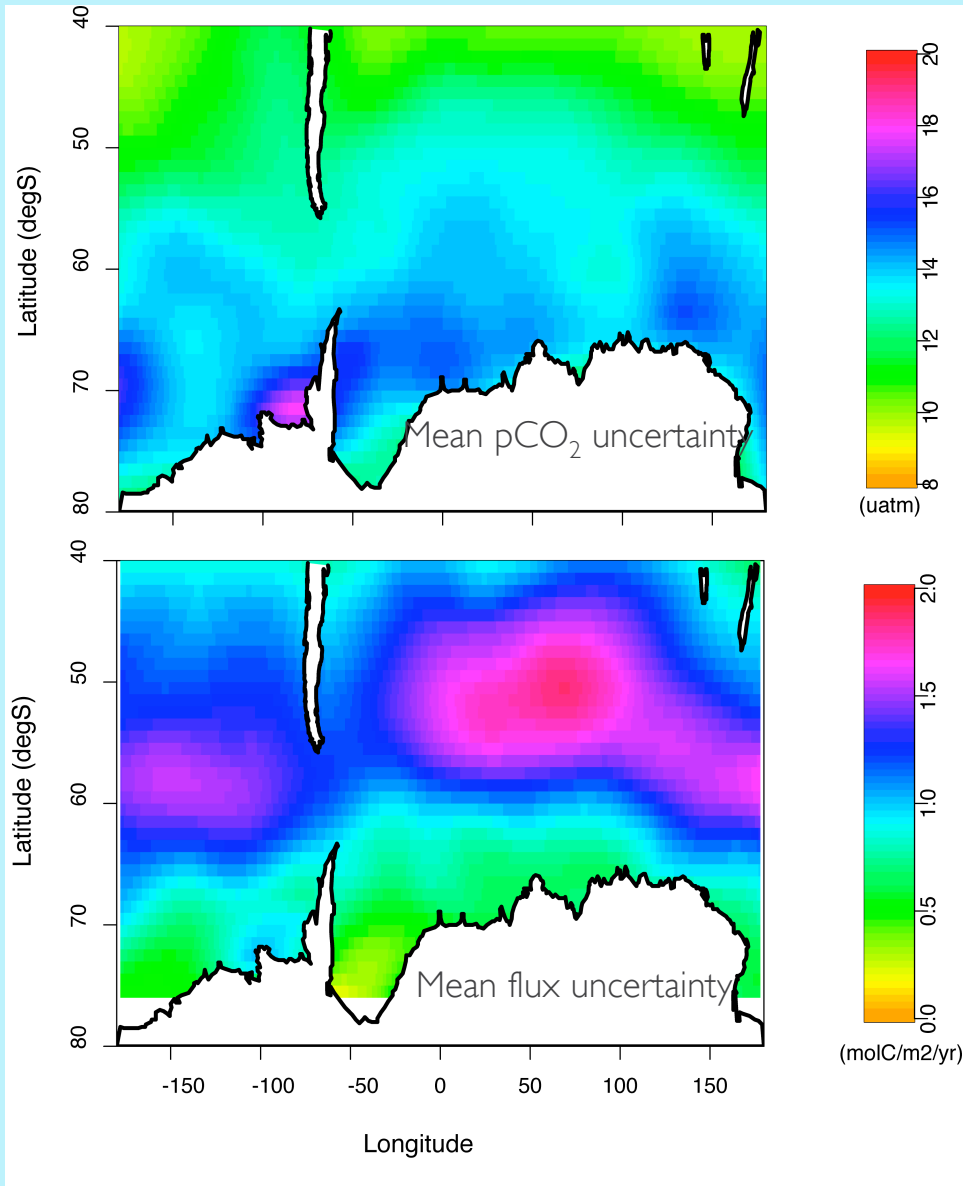
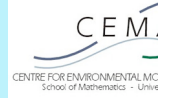
- NCEP 10m winds
- Wanninkhof (1992) gas exchange
- Sea-ice concentration taken into account

• Integrating over entire SO implies a moderate CO₂ sink (~0.2PgC/yr)



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Uncertainty Estimate from Monte-Carlo Analysis



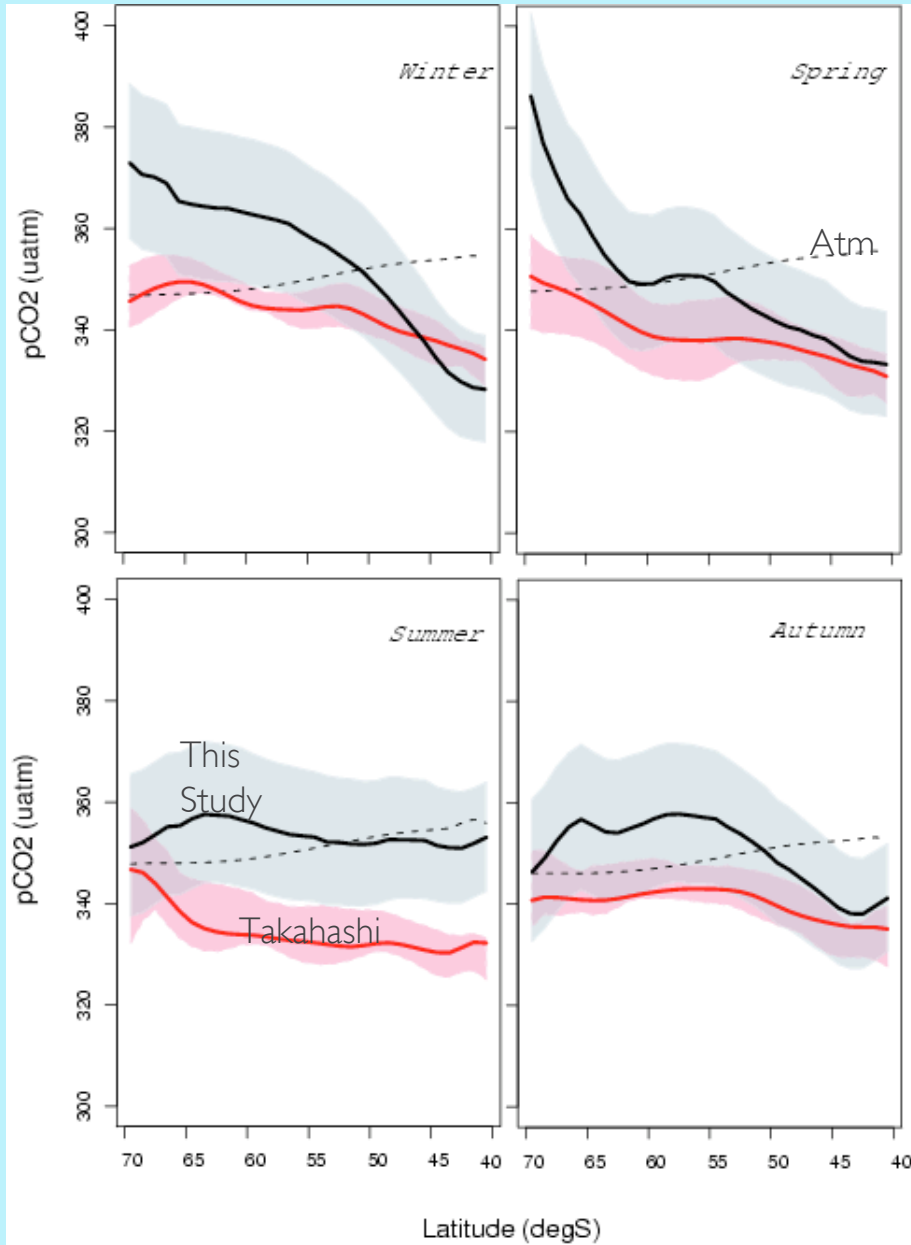
Propagation of uncertainties

- DIC $\sim \pm 8 \mu\text{mol/kg}$, ALK $\sim \pm 9 \mu\text{mol/kg}$
- Wind $\sim \pm 2 \text{m/s}$
- CO₂ dissociation constants $\sim \pm 10 \text{uatm}$

- Final integrated error $\sim \pm 0.26 \text{PgC/yr}$



Zonal Comparison with Takahashi pCO₂ database



Important Points

- In general higher pCO₂ than Takahashi
- Strong winter pCO₂ source south of the PF (~50degS)



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Evidence of strong winter-time source south of PF



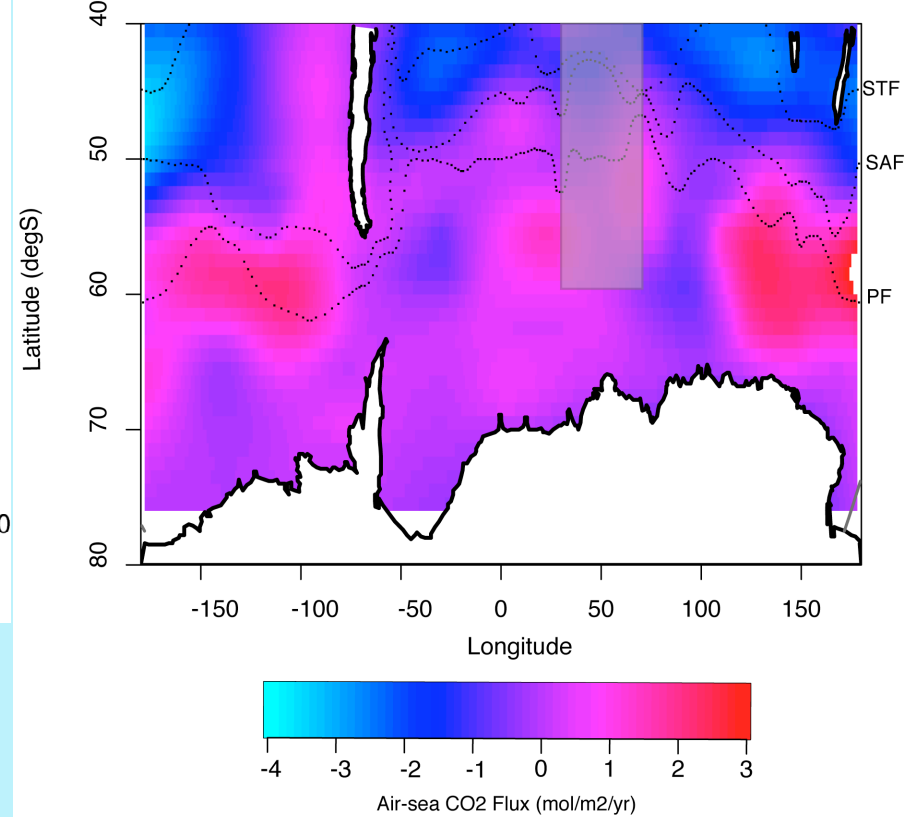
Direct pCO₂ measurements from Metzl et al, (2005)

Empirically derived pCO₂ from this study

Takahashi et al (2002)

Winter

Annual Mean CO₂ Flux



- Direct and indirect pCO₂ suggests a source of CO₂ south of the PF
- Probably associated with ventilation of deep waters and inadequate biological drawdown
- Takahashi seems to be underestimating winter source

Southern Ocean Flux Mechanisms



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Slightly Revised Schematic from
Niki Gruber



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Summary of recent observational estimates for SO CO₂ uptake



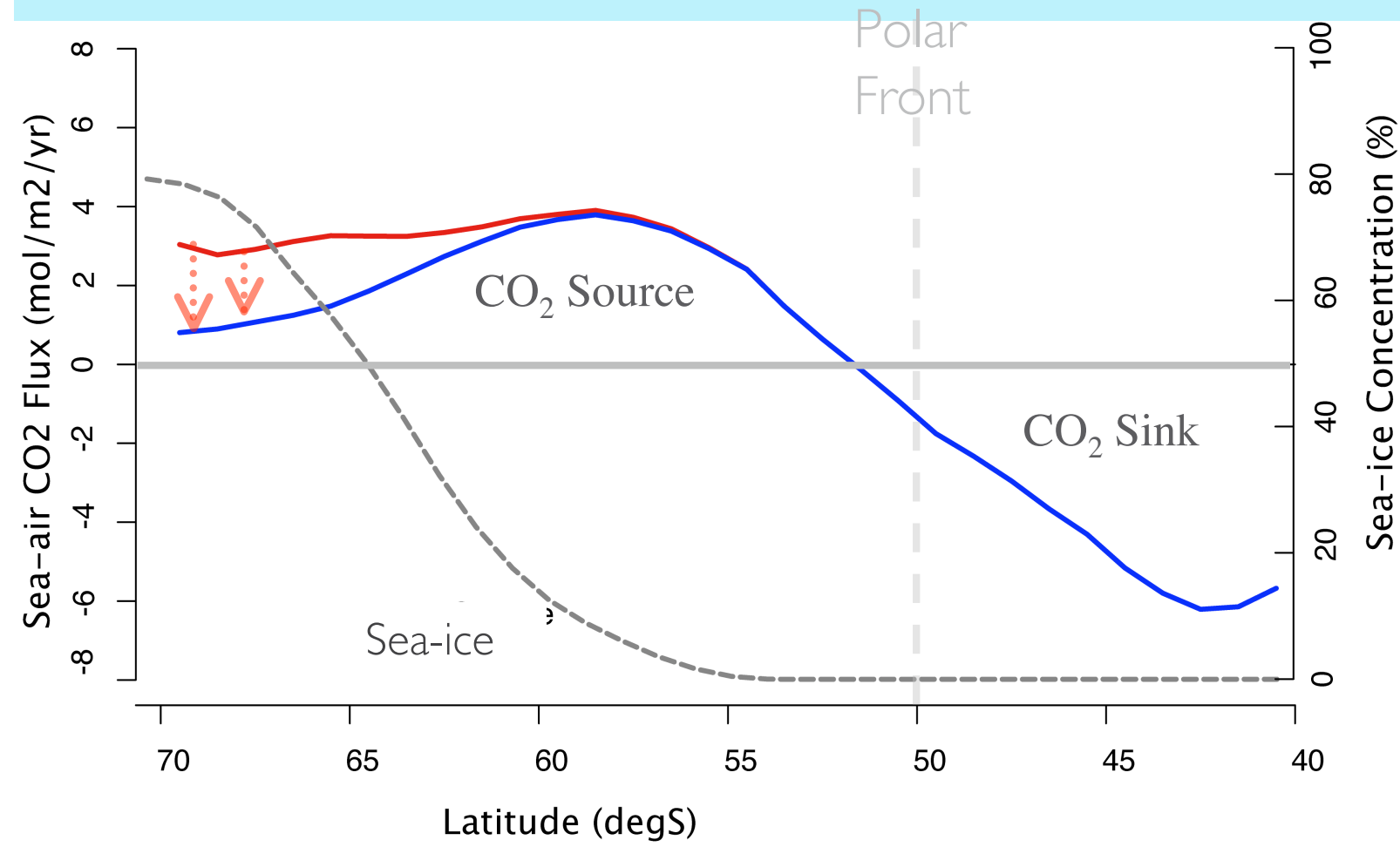
Methodology	Reference	Net CO ₂ flux (Pg C/yr)		
		40-50°S	50-60°S	60-70°S
Oceanic Inversion	[Gloor et al., 2003]	-0.4		-0.1
TRANSCOM-2 Atmospheric Inversions	[Gurney et al., 2002]	-0.3		-0.1
Atmospheric Inversion	[Roy et al., 2003]		-0.2 ± 0.2	
Oceanic pCO ₂ climatology – NCEP 10m winds	[Takahashi et al., 2002] - corrected		-0.45 to -0.35	
Summer/winter pCO ₂ measurements	[Metzl et al., 2005]		-0.1	
Summer/winter pCO ₂ measurements	[Metzl et al., 1999]	-1		
Oceanic/Atmospheric Inversion	[Jacobson et al., 2005]		-0.4±0.3	
Oceanic DIC/ALK climatology – using NCEP 10m winds and sea-ice effects on air-sea gas exchange	This Study	-0.47±0.25	0.16±0.08	0.12±0.08
		-0.19±0.26		

- Methods are converging suggesting a moderate Southern Ocean CO₂ sink (~0.3PgC/yr)

NB: Needs to be a consistent definition of the Southern Ocean within these methods



Including the effects of sea-ice important



- Sea-ice limits the high latitude outgassing by $\sim 0.1 \text{ PgC/yr}$



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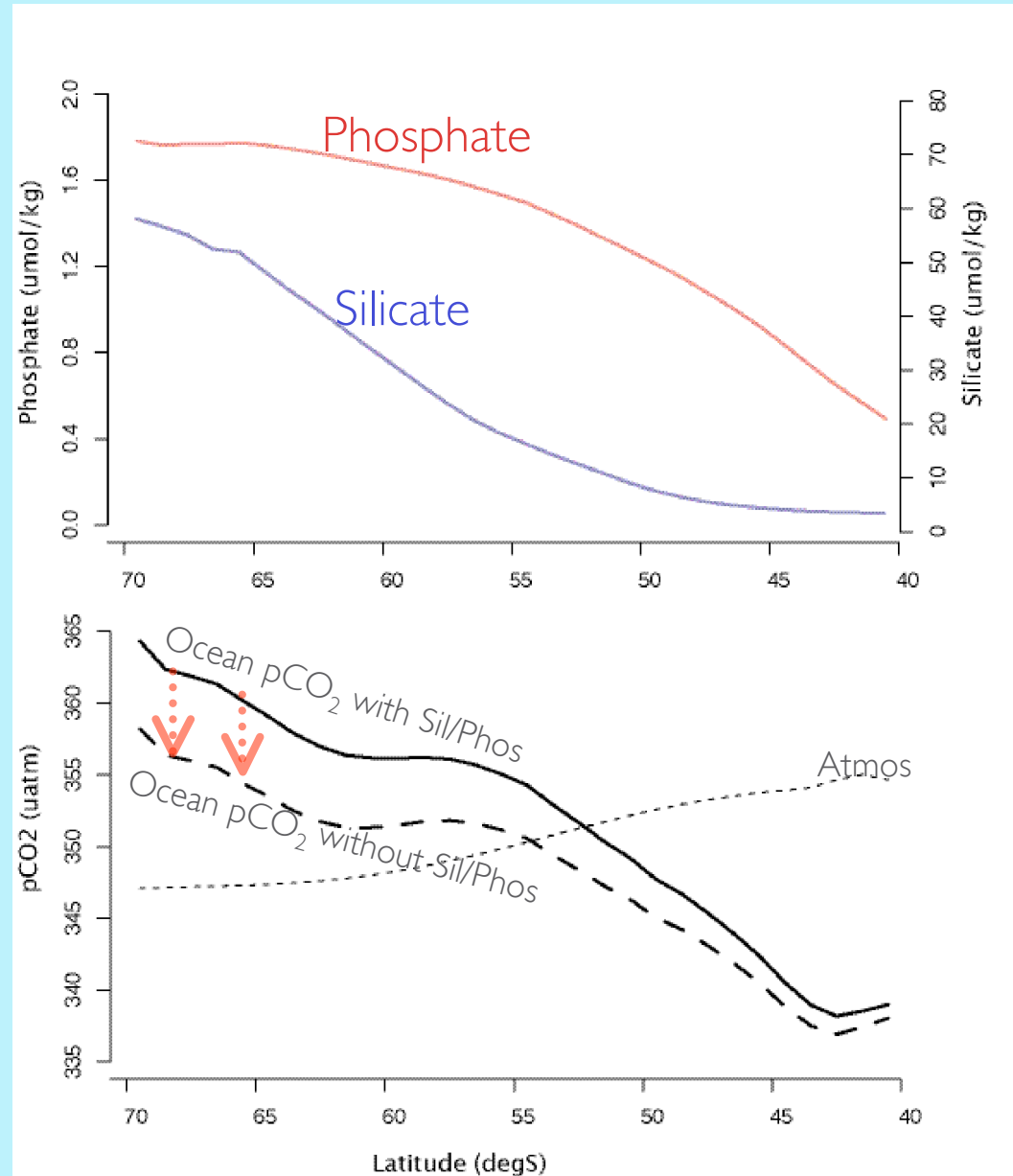
Importance of including silicate and phosphate when calculating pCO₂ in the Southern Ocean



Total Alkalinity

$$\begin{aligned}
 ALK_{TOTAL} = & [HCO_3^-] + 2[CO_3^{2-}] + \\
 & [B(OH)_4^-] + [OH^-] + \\
 & [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] \\
 & + [NH_3] + [HS^-] \dots \\
 & - [H^+] - [HSO_4^-] - \\
 & [HF] - [H_3PO_4]
 \end{aligned}$$

- Without including Sil/Phos results in an underestimation of pCO₂ by ~8uatm!
- Models need to include these terms when calculating pCO₂ in the Southern Ocean





Summary

- Surface DIC can be empirically derived in the Southern Ocean ($\sim 8 \mu\text{mol/kg}$), useful for all types of carbon cycle analysis
- Empirically-derived pCO_2 distribution implies a strong sub-Antarctic CO_2 sink ($\sim 0.5 \text{PgC/yr}$), which is partially offset by a CO_2 source south of the Polar Front ($\sim 0.3 \text{PgC/yr}$)
- Implies the Southern Ocean to be a moderate CO_2 sink ($\sim 0.2 \text{PgC/yr}$) and is in relative agreement with other independent methods
- Method could be improved by implementing a tri-carbon sampling strategy for each sample in order to find out optimal CO_2 dissociation constants for the SO
- Important to include silicate/phosphate in calculating pCO_2 from DIC/Alk in the Southern Ocean for modelling studies
- Finally, there needs to be a consistent agreement in defining the northern latitude extent of the Southern Ocean for all differing methodologies



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Direct way to measure air-sea CO₂ fluxes

