

# Verifying the consolidated theory of atmosphere-ocean CO<sub>2</sub> fluxes and the importance of the skin: First comparison between bulk and eddy covariance measurements.



Ian Ashton (Exeter PI fluxes), Javier Blanco Sacristan, Sophie Corrigan, Jamie Shutler, Tom Holding, Tom Bell, Mingxi Yang, Gavm Tilstone (overall project PI)

[i.g.c.ashton@exeter.ac.uk](mailto:i.g.c.ashton@exeter.ac.uk); [j.d.shutler@exeter.ac.uk](mailto:j.d.shutler@exeter.ac.uk)



# Importance of the ocean

## Global carbon budgets

The global land sink of carbon cannot be measured.

Ocean carbon sink provides a powerful constraint for identifying the land carbon sink.

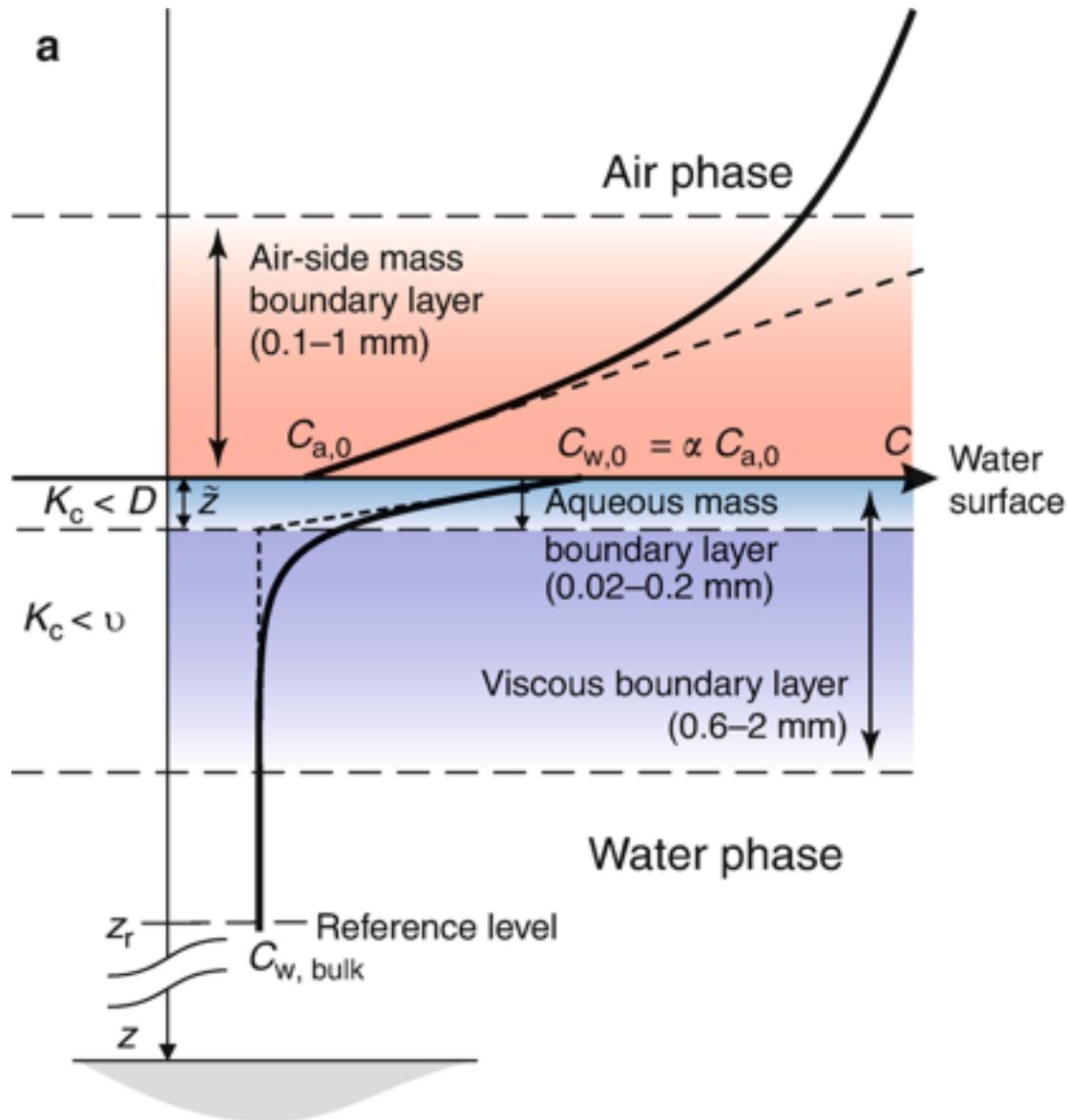
## Food security and conservation

Monitoring the ocean sink also identifies regions and ecosystems at risk.

Accurate estimates of CO<sub>2</sub> absorption provide a powerful constraint on carbon budgets and are needed to inform policies to motivate societal shifts towards reducing carbon emissions.

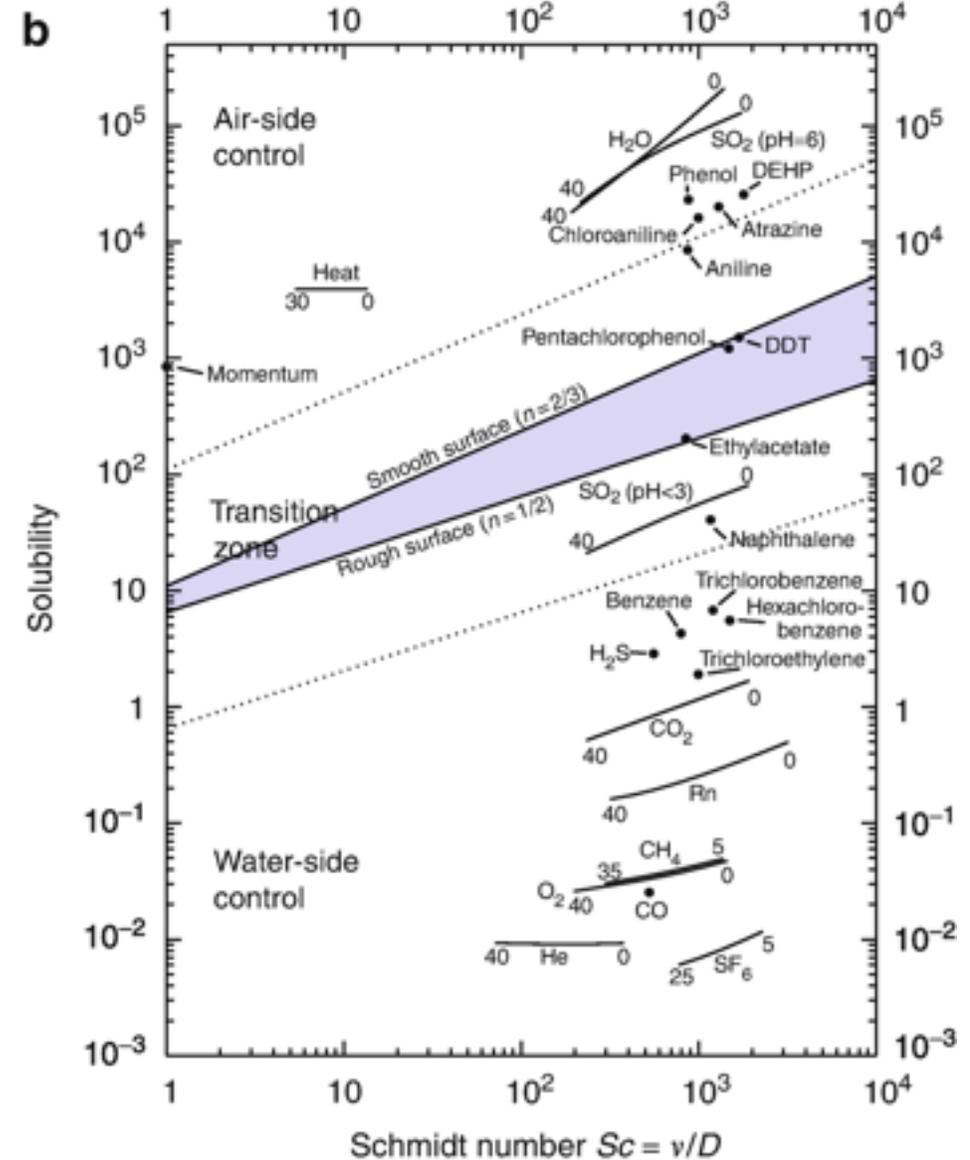
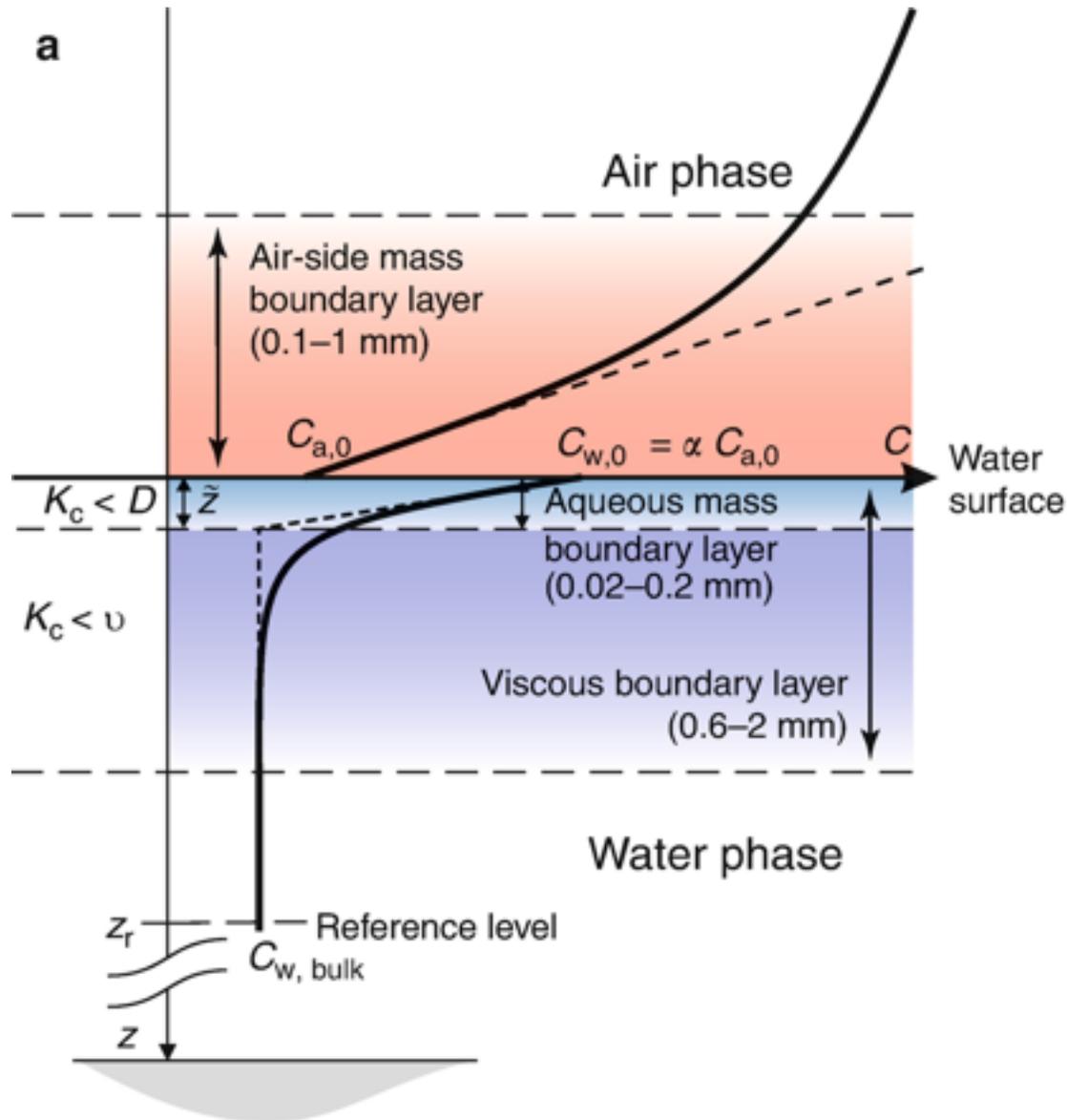


# Exchange across the air-sea interface



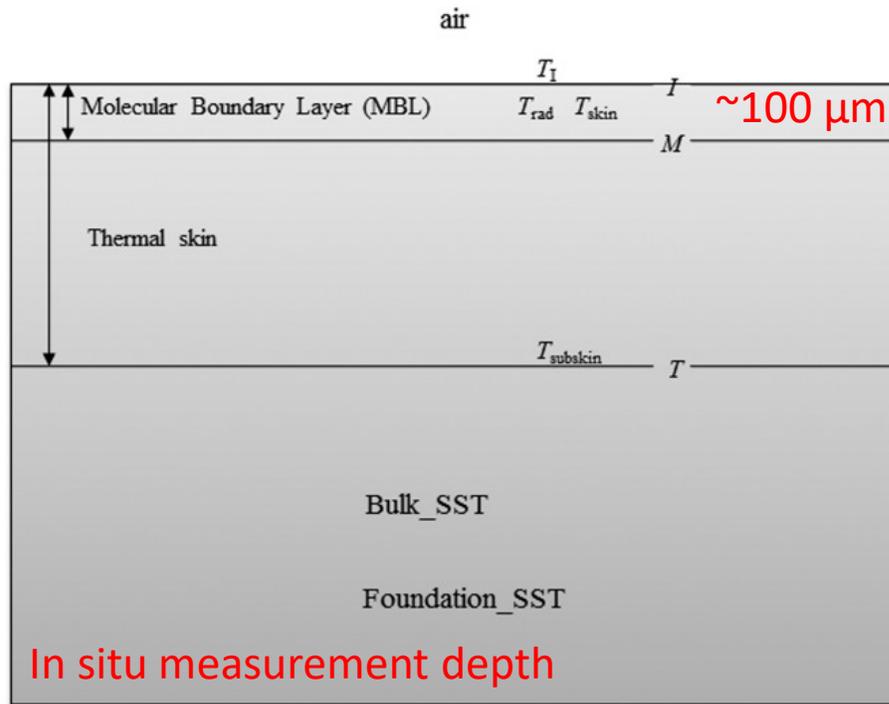
Source: Transfer across the air-sea surface, (2013), Springer.

# Exchange across the air-sea interface

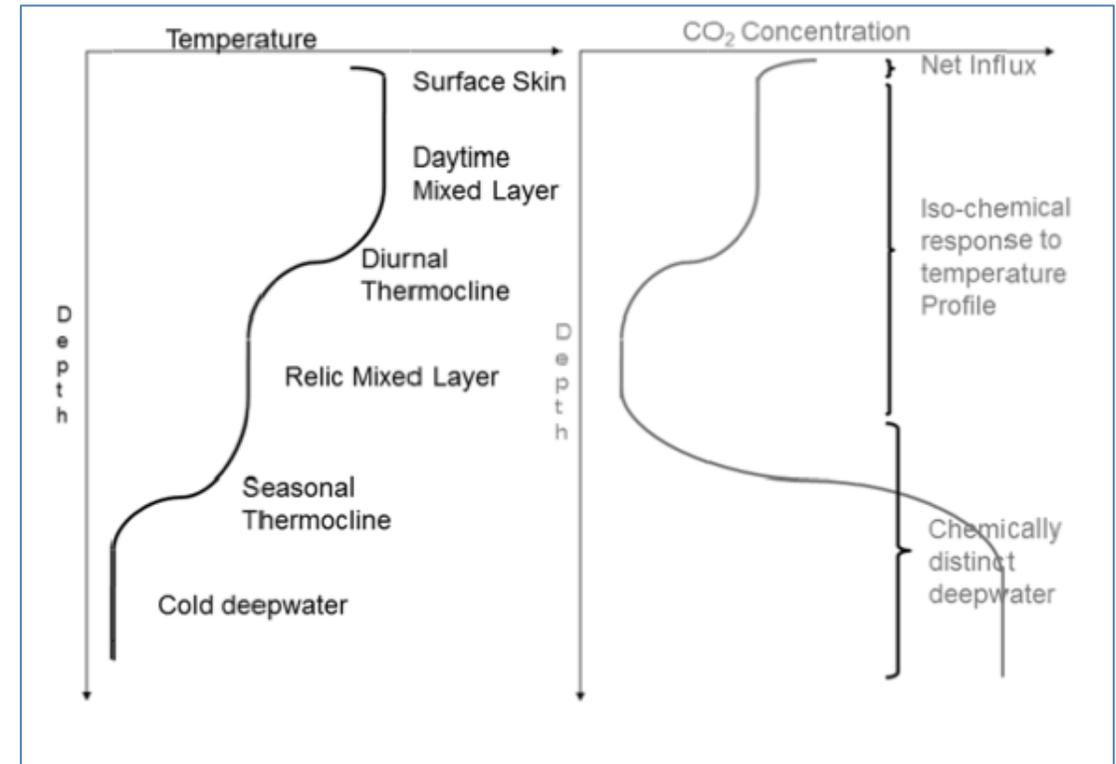


Source: Transfer across the air-sea surface, (2013), Springer.

# Consolidated methods for temperature and salinity handling within gas flux calculations



Source: Woolf *et al.*, (2016)



Woolf, D. K., *et al.*, (2016) On the calculation of air-sea fluxes of CO<sub>2</sub> in the presence of temperature and salinity gradients, *JGR*.

Goddijn-Murphy, L. *et al.*, (2015) The OceanFlux Greenhouse Gases methodology for deriving a sea surface climatology of CO<sub>2</sub> fugacity in support of air-sea gas flux studies. *Ocean Science*.

# Consolidated methods for temperature and salinity handling within gas flux calculations



Quantified the thermal influences on calculation of air-sea gas fluxes:

**Table 1.** Thermal Effects on the Calculation of Air-Sea Gas Fluxes (Carbon Dioxide and Other Poorly Soluble Gases), Notation, and the Significance of Each

Origin of Effect	Subsection and Scaling	Scaling Parameter	Approximate Scaling Factor (CO <sub>2</sub> )	Effect on Unreactive, Ideal Gases
Vapor pressure and nonideality	Section 2.1, $\Phi_1$	$C_1$	-0.2%/K	Similar, but smaller effect related to nonideality vanishes
Solubility	Section 2.2, $\Phi_2$	$C_1$	-2.5%/K	Variable, but typically most important
Carbonate chemistry	Section 2.3, $\Phi_3$	$C_M$	1.5%/K	Not applicable
Schmidt number	Section 2.4, $\Phi_4$	$C_1 - C_M$	2.5%/K	Variable, but typically significant

Clarified a misconception

$$F = k\alpha_w(f\text{CO}_{2W} - f\text{CO}_{2A})$$



Reduced accuracy

$$F = k(\alpha_w f\text{CO}_{2W} - \alpha_s f\text{CO}_{2A}),$$



More accurate calculation

Woolf, D. K., *et al.*, (2016) On the calculation of air-sea fluxes of CO<sub>2</sub> in the presence of temperature and salinity gradients, *JGR*.

Goddijn-Murphy, L. *et al.*, (2015) The OceanFlux Greenhouse Gases methodology for deriving a sea surface climatology of CO<sub>2</sub> fugacity in support of air-sea gas flux studies. *Ocean Science*.

# Open source FluxEngine air-sea gas flux toolbox (Python)

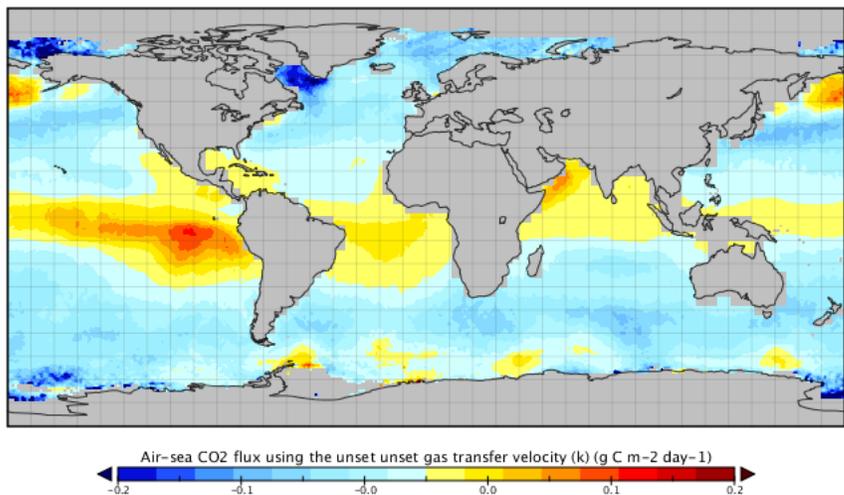
<https://github.com/oceanflux-ghg/FluxEngine>

**RINGO** | Readiness  
of ICOS

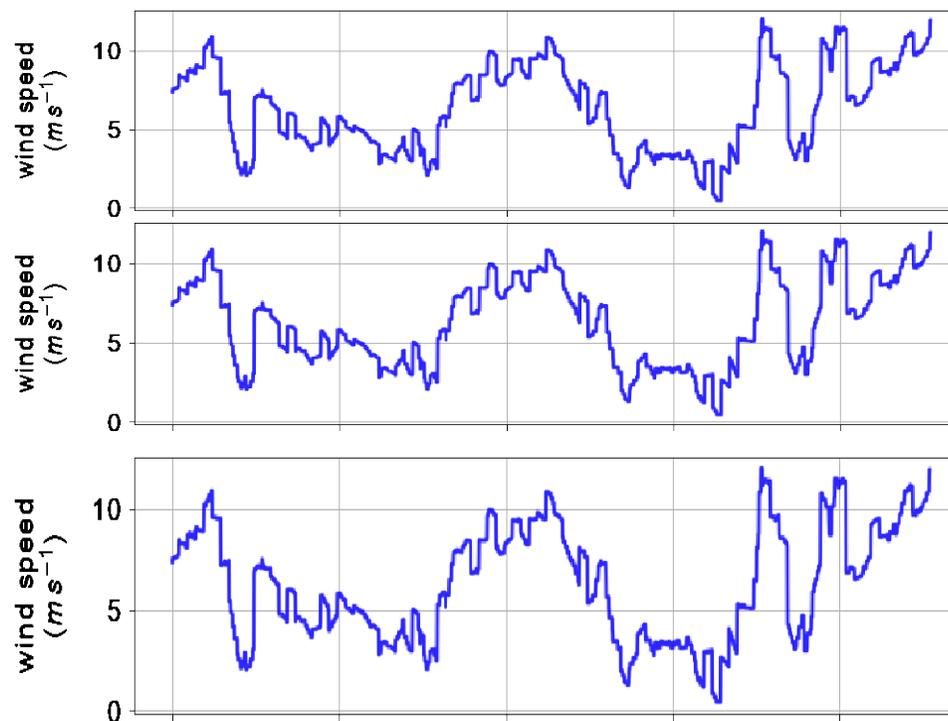


Toolbox developed for community use:

- Open source license and Python library.
- Net flux tool with traceable land/ocean/basin templates.
- User configurable calculation.
- Extensively verified and version controlled.
- **Interactive tutorials**, used in IOCCP training school.
- So far used within 13 journal papers,



Example global mean daily flux output



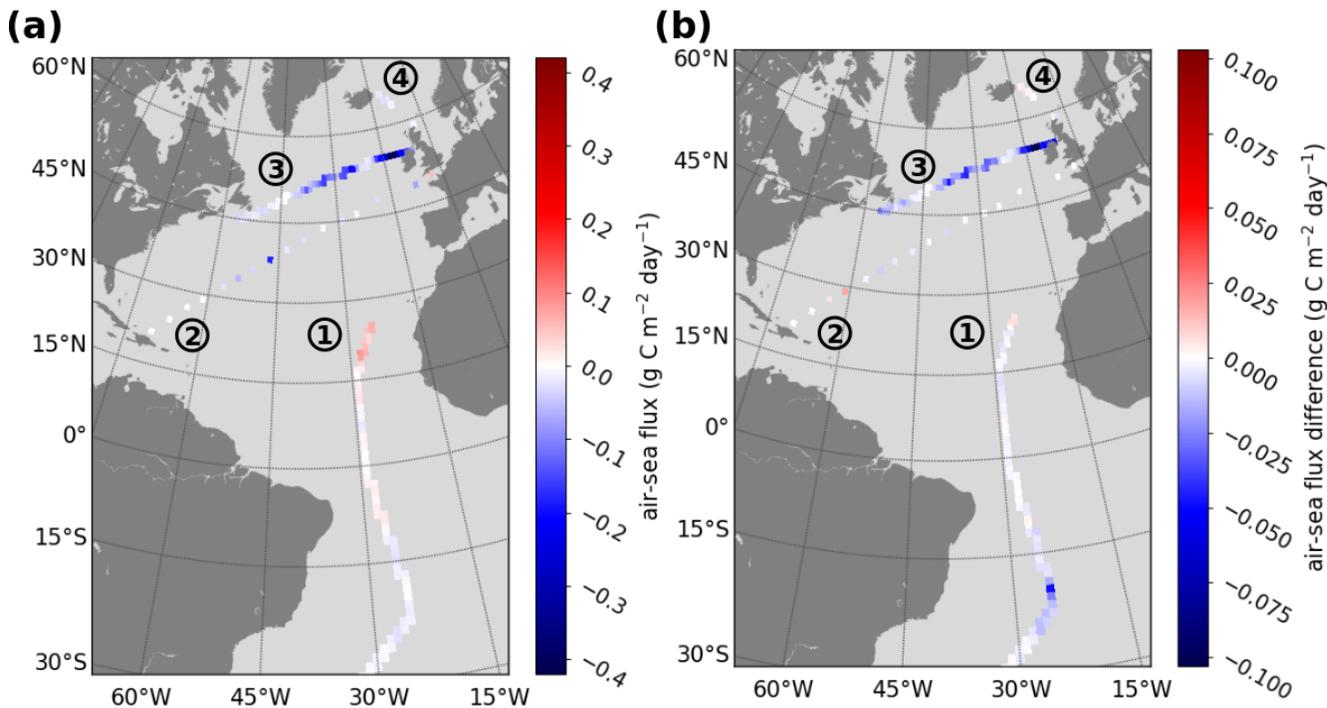
Example analysis of in situ cruise data



Shutler, J. D. *et al.*, (2016) Flux Engine: A flexible processing system for calculating air-sea carbon dioxide gas fluxes and climatologies, *Journal of Atmospheric and Oceanic Technology*.

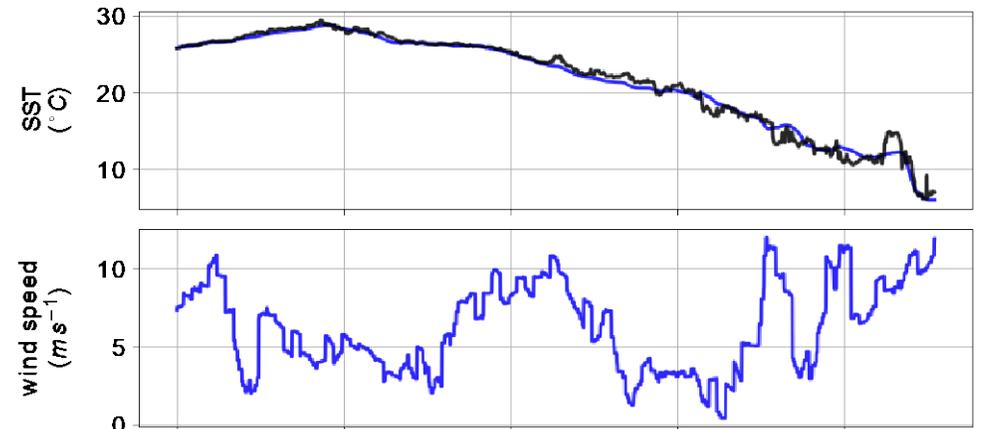
Holding, T., *et al.*, (2019), The FluxEngine air-sea gas flux toolbox: simplified interface and extensions for *in situ* analyses and multiple poorly soluble gases, *Ocean Sciences*.

# Consolidated methods - Impact of mishandling temperature for an *in-situ* research cruise

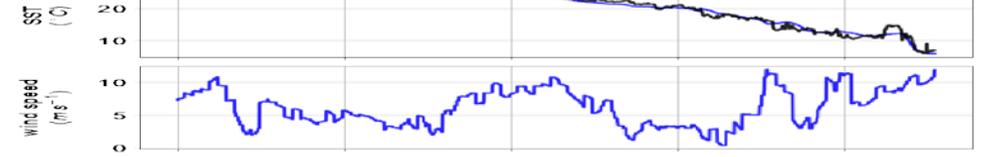


Holding, T., et al., (2019), The FluxEngine air-sea gas flux toolbox: simplified interface and extensions for *in situ* analyses and multiple poorly soluble gases, *Ocean Sciences*.

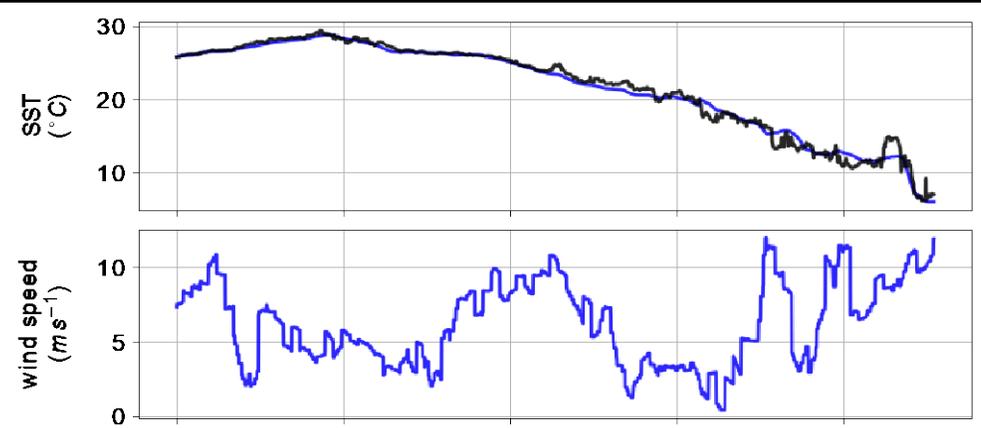
— *in situ* — satellite — reanalysed — difference due to reanalysis



— *in situ* — satellite — reanalysed — difference due to reanalysis



— *in situ* — satellite — reanalysed — difference due to reanalysis

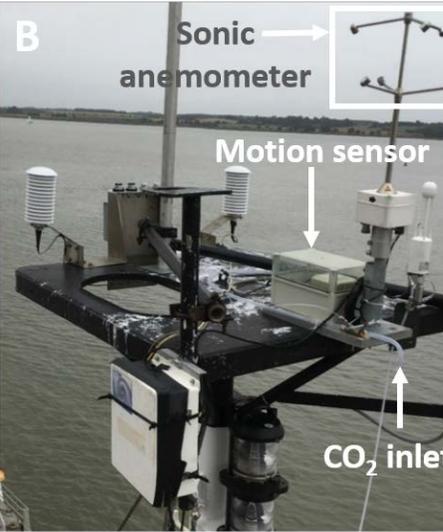
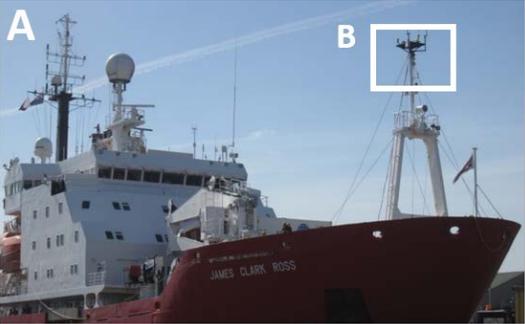
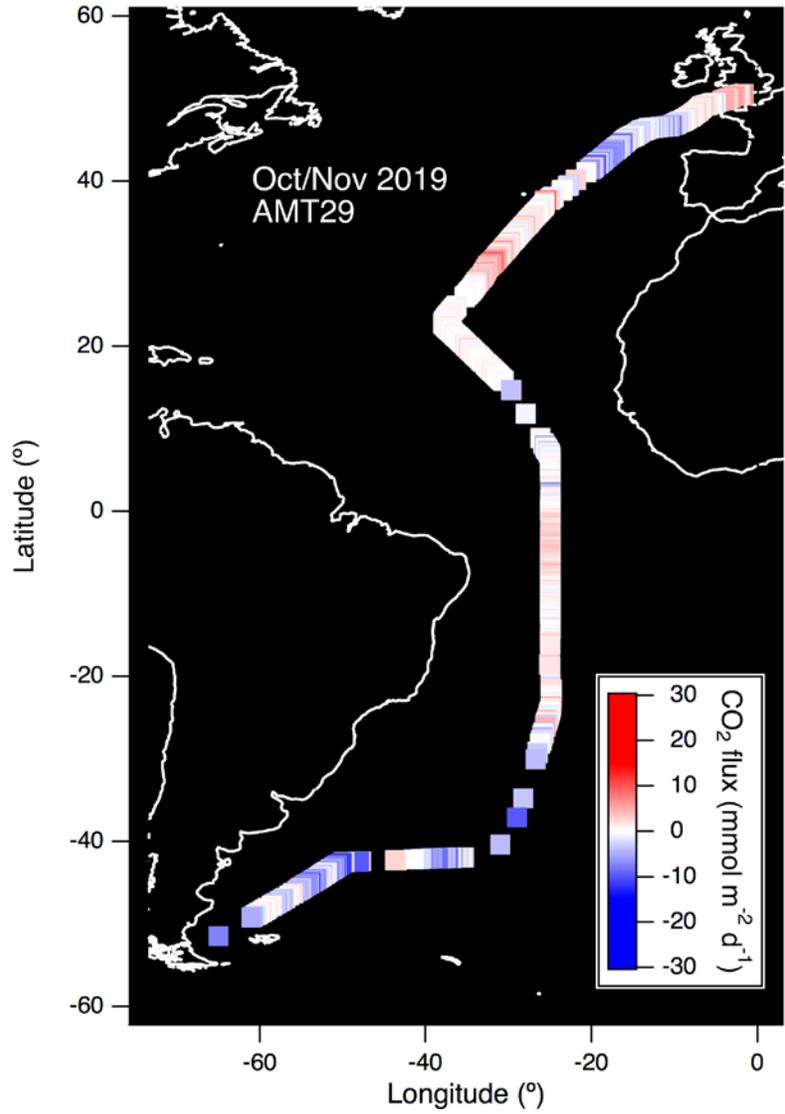


**RINGO**

Readiness of ICOS

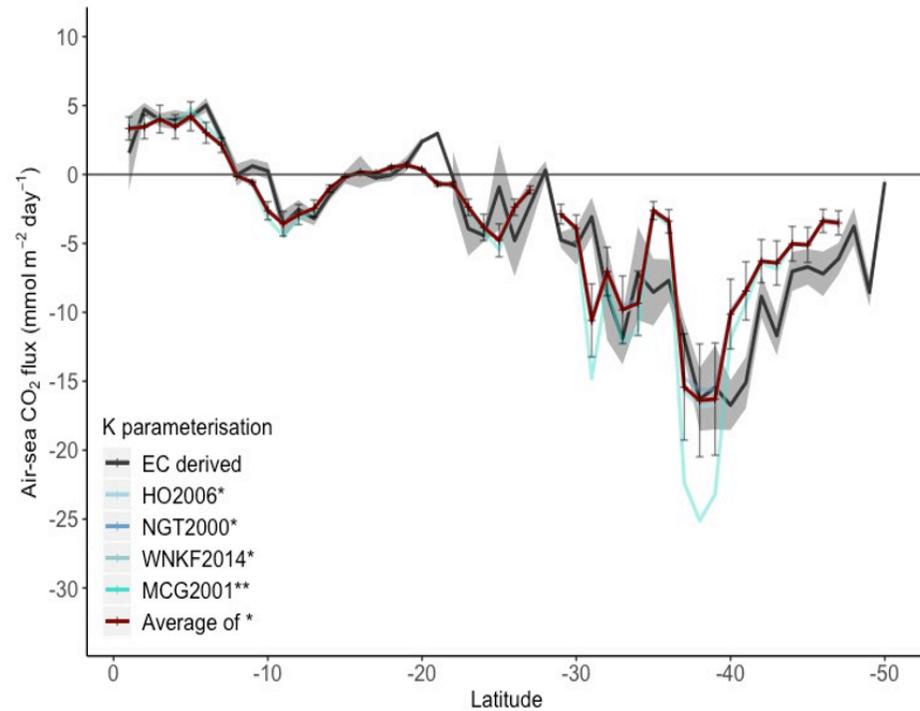


# ESA OceanSatFlux – simultaneous in situ bulk and eddy covariance measurements, including SST skin

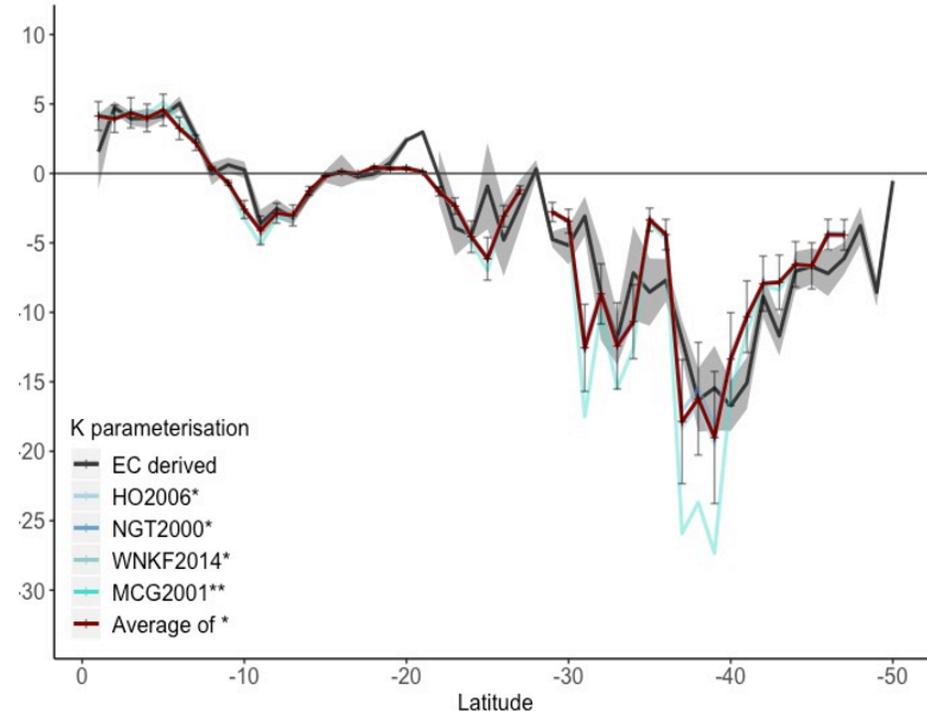


# Direct bulk fluxes versus indirect eddy covariance

Well used low accuracy calculation using SST at depth



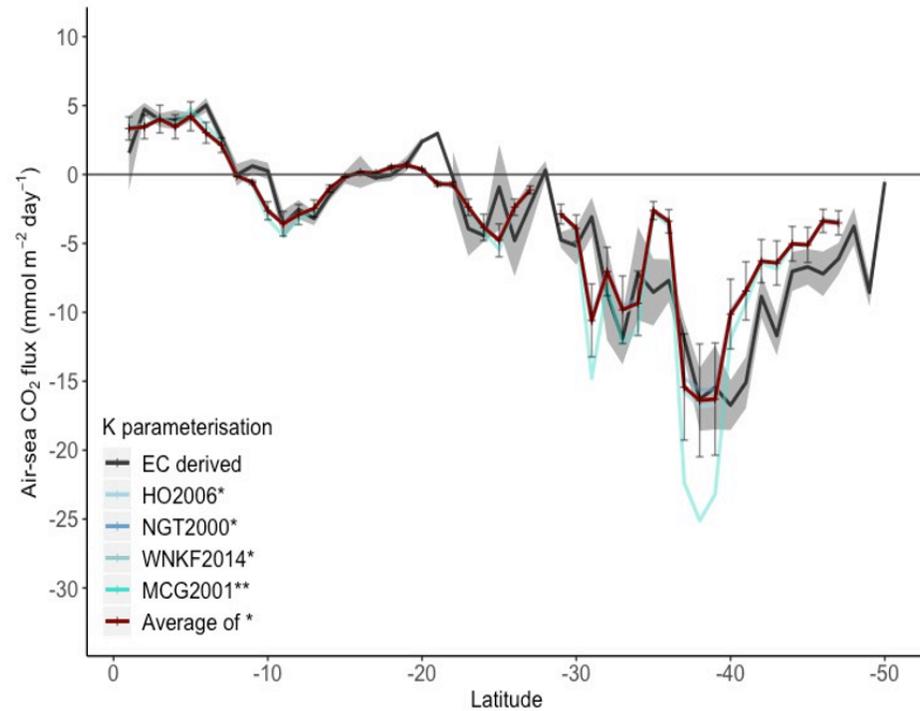
High accuracy calculation using SST<sub>skin</sub> at SST at depth



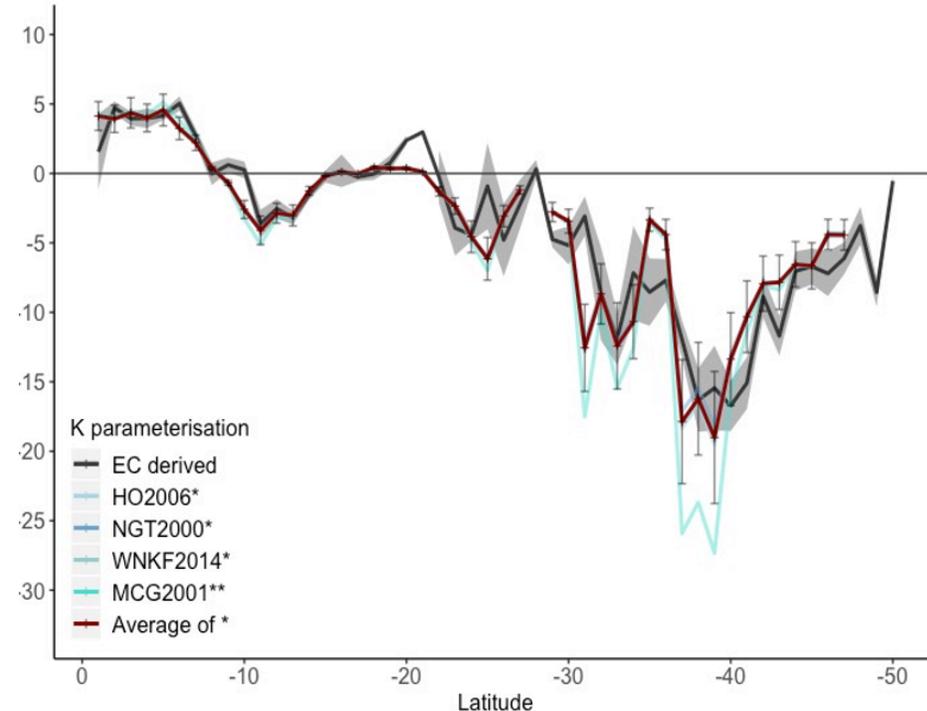
K parameterization used	Net air-sea CO <sub>2</sub> flux (mmol m <sup>2</sup> d <sup>-1</sup> )	Mean K <sub>CO2</sub>	Difference from EC net flux (mmol m <sup>2</sup> d <sup>-1</sup> )		Difference from EC derived K <sub>CO2</sub>		Net air-sea CO <sub>2</sub> flux (mmol m <sup>2</sup> d <sup>-1</sup> )	Mean K <sub>CO2</sub>	Difference from EC net flux (mmol m <sup>2</sup> d <sup>-1</sup> )		Difference from EC derived K <sub>CO2</sub>	
			Net	RMSD	Net	RMSD			Net	RMSD	Net	RMSD
EC	-3.74±0.81	22.96±1.61	-	-	-	-	-3.74±0.81	22.96±1.61	-	-	-	-
HO2006*	-3.30±0.76	20.01±1.37	-0.49	2.78	3.07	9.68	-3.92±0.86	18.79±1.35	0.12	2.72	4.93	11.81
NGT2000*	-3.18±0.72	19.44±1.29	-0.61	2.73	3.71	9.49	-3.79±0.81	18.27±1.23	-0.007	2.55	5.48	11.73
WNKF2014*	-3.27±0.73	19.81±1.35	-0.52	2.79	3.28	9.68	-3.88±0.84	18.59±1.32	0.08	2.70	5.12	11.86
MCG2001**	-4.06±0.96	23.33±1.98	0.26	3.73	-0.49	12.07	-4.76±1.07	21.88±1.89	0.97	4.18	1.73	13.27
Combined mean of *	-3.25±0.72	19.75±1.36	-0.54	2.76	3.35	9.61	-3.86±0.83	18.55±1.34	0.06	2.65	5.18	11.81
Combined mean of * and **	-3.45±0.78	20.65±1.52	-0.33	2.89	2.39	9.96	-4.09±0.89	19.38±1.48	0.29	2.94	4.32	11.98

# Direct bulk fluxes versus indirect eddy covariance

Well used low accuracy calculation using SST at depth



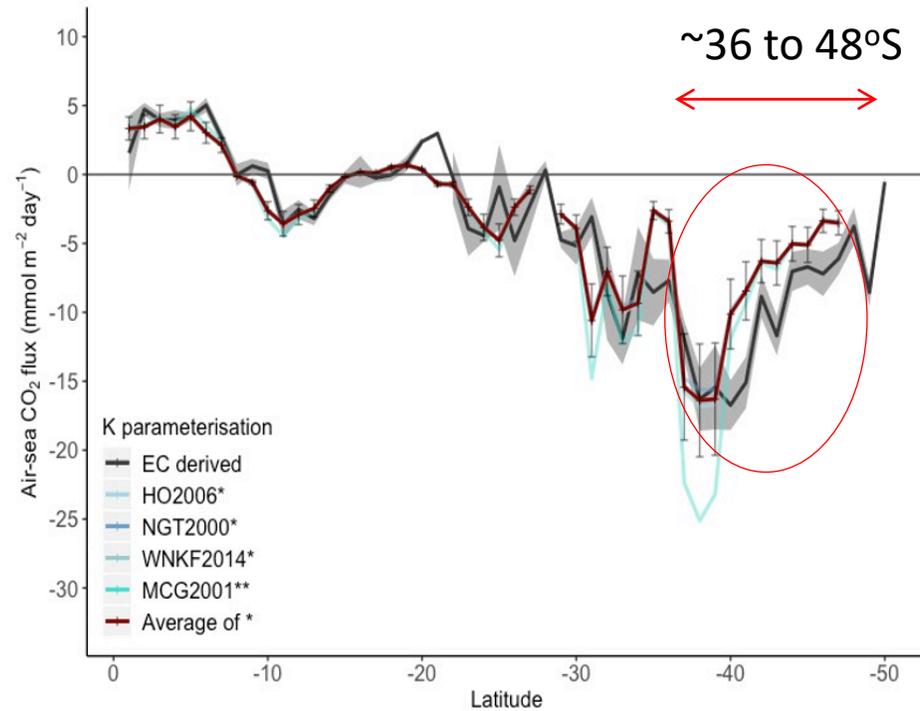
High accuracy calculation using SST<sub>skin</sub> at SST at depth



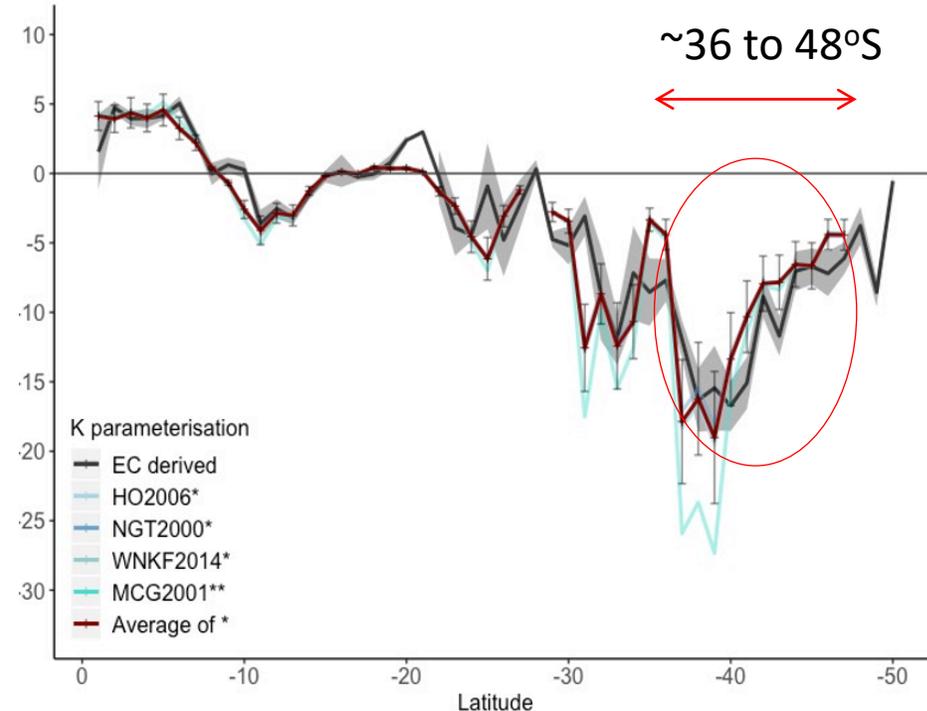
K parameterization used	Net air-sea CO <sub>2</sub> flux (mmol m <sup>2</sup> d <sup>-1</sup> )	Mean K <sub>CO2</sub>	Difference from EC net flux (mmol m <sup>2</sup> d <sup>-1</sup> )		Difference from EC derived K <sub>CO2</sub>		Net air-sea CO <sub>2</sub> flux (mmol m <sup>2</sup> d <sup>-1</sup> )	Mean K <sub>CO2</sub>	Difference from EC net flux (mmol m <sup>2</sup> d <sup>-1</sup> )		Difference from EC derived K <sub>CO2</sub>	
			Net	RMSD	Net	RMSD			Net	RMSD	Net	RMSD
EC	-3.74±0.81	22.96±1.61	-	-	-	-	-3.74±0.81	22.96±1.61	-	-	-	-
HO2006*	-3.30±0.76	20.01±1.37	-0.49	2.78	3.07	9.68	-3.92±0.86	18.79±1.35	0.12	2.72	4.93	11.81
NGT2000*	-3.18±0.72	19.44±1.29	-0.61	2.73	3.71	9.49	-3.79±0.81	18.27±1.23	-0.007	2.55	5.48	11.73
WNKF2014*	-3.27±0.73	19.81±1.35	-0.52	2.79	3.28	9.68	-3.88±0.84	18.59±1.32	0.08	2.70	5.12	11.86
MCG2001**	-4.06±0.96	23.33±1.98	0.26	3.73	-0.49	12.07	-4.76±1.07	21.88±1.89	0.97	4.18	1.73	13.27
Combined mean of *	-3.25±0.72	19.75±1.36	-0.54	2.76	3.35	9.61	-3.86±0.83	18.55±1.34	0.06	2.65	5.18	11.81
Combined mean of * and **	-3.45±0.78	20.65±1.52	-0.33	2.89	2.39	9.96	-4.09±0.89	19.38±1.48	0.29	2.94	4.32	11.98

# Direct bulk fluxes versus indirect eddy covariance

Well used low accuracy calculation using SST at depth



High accuracy calculation using SSTskin at SST at depth

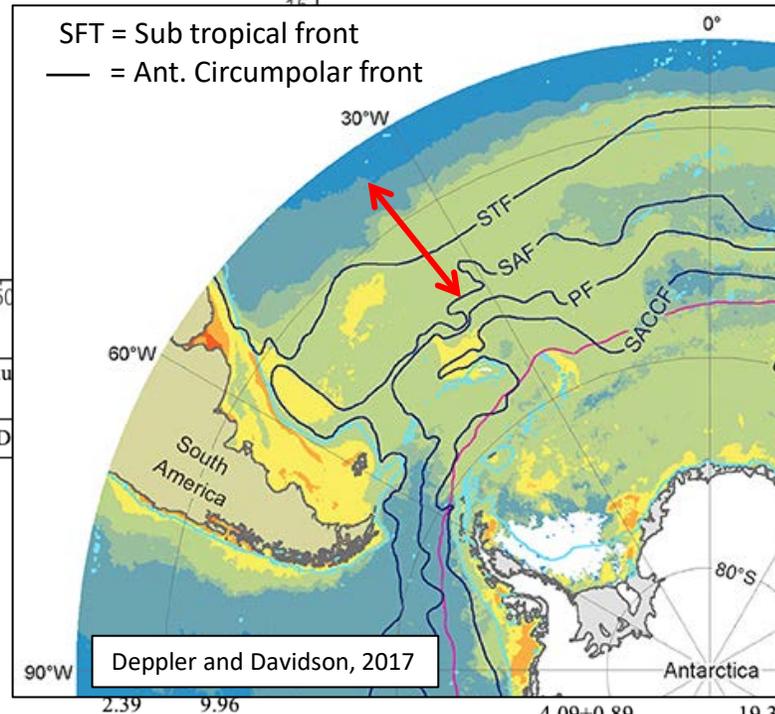
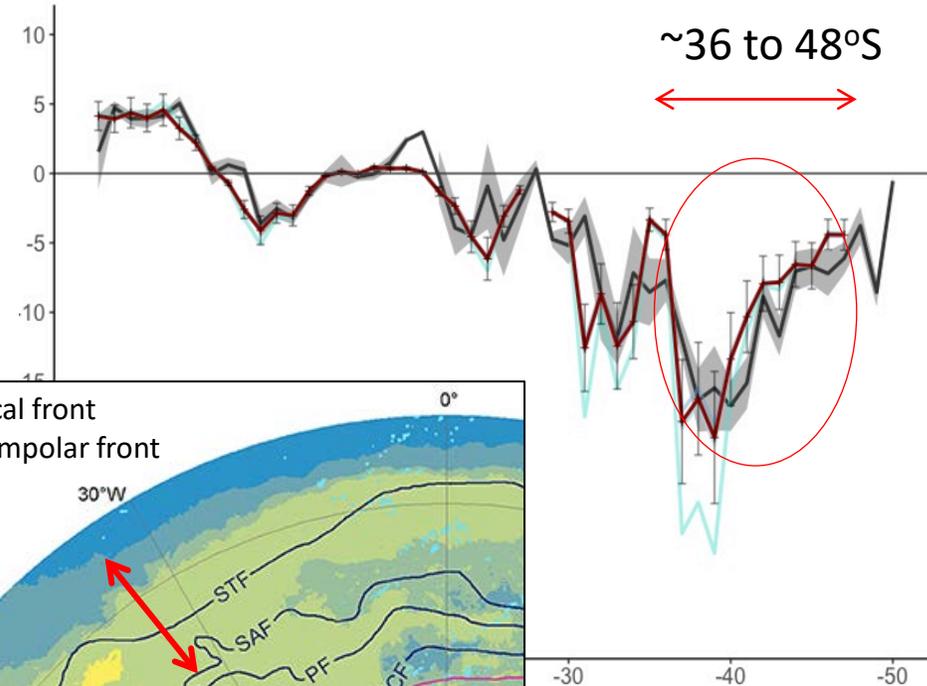
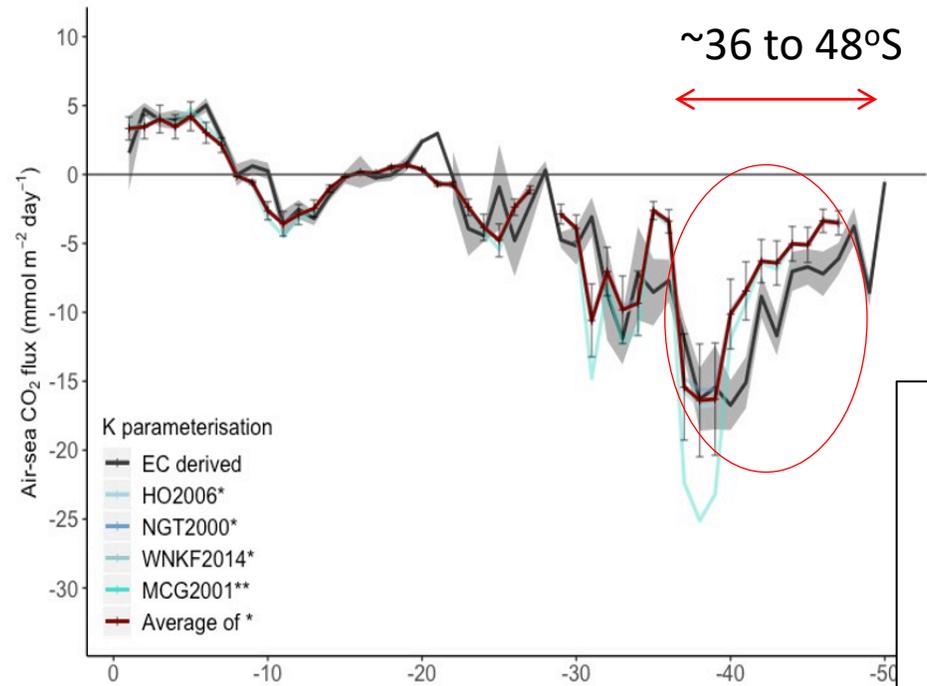


K parameterization used	Net air-sea CO <sub>2</sub> flux (mmol m <sup>2</sup> d <sup>-1</sup> )	Mean K <sub>CO<sub>2</sub></sub>	Difference from EC net flux (mmol m <sup>2</sup> d <sup>-1</sup> )		Difference from EC derived K <sub>CO<sub>2</sub></sub>		Net air-sea CO <sub>2</sub> flux (mmol m <sup>2</sup> d <sup>-1</sup> )	Mean K <sub>CO<sub>2</sub></sub>	Difference from EC net flux (mmol m <sup>2</sup> d <sup>-1</sup> )		Difference from EC derived K <sub>CO<sub>2</sub></sub>	
			Net	RMSD	Net	RMSD			Net	RMSD	Net	RMSD
EC	-3.74±0.81	22.96±1.61	-	-	-	-	-3.74±0.81	22.96±1.61	-	-	-	-
HO2006*	-3.30±0.76	20.01±1.37	-0.49	2.78	3.07	9.68	-3.92±0.86	18.79±1.35	0.12	2.72	4.93	11.81
NGT2000*	-3.18±0.72	19.44±1.29	-0.61	2.73	3.71	9.49	-3.79±0.81	18.27±1.23	-0.007	2.55	5.48	11.73
WNKF2014*	-3.27±0.73	19.81±1.35	-0.52	2.79	3.28	9.68	-3.88±0.84	18.59±1.32	0.08	2.70	5.12	11.86
MCG2001**	-4.06±0.96	23.33±1.98	0.26	3.73	-0.49	12.07	-4.76±1.07	21.88±1.89	0.97	4.18	1.73	13.27
Combined mean of *	-3.25±0.72	19.75±1.36	-0.54	2.76	3.35	9.61	-3.86±0.83	18.55±1.34	0.06	2.65	5.18	11.81
Combined mean of * and **	-3.45±0.78	20.65±1.52	-0.33	2.89	2.39	9.96	-4.09±0.89	19.38±1.48	0.29	2.94	4.32	11.98

# Direct bulk fluxes versus indirect eddy covariance

Well used low accuracy calculation using SST at depth

High accuracy calculation using SST<sub>skin</sub> at SST at depth



K parameterization used	Net air-sea CO <sub>2</sub> flux (mmol m <sup>2</sup> d <sup>-1</sup> )	Mean K <sub>CO2</sub>	Difference from EC net flux (mmol m <sup>2</sup> d <sup>-1</sup> )		K <sub>CO2</sub>	Difference from EC net flux (mmol m <sup>2</sup> d <sup>-1</sup> )		Difference from EC derived K <sub>CO2</sub>	
			Net	RMSD		Net	RMSD	Net	RMSD
EC	-3.74±0.81	22.96±1.61	-	-	-	-	-	-	-
HO2006*	-3.30±0.76	20.01±1.37	-0.49	2.78	±1.35	0.12	2.72	4.93	11.81
NGT2000*	-3.18±0.72	19.44±1.29	-0.61	2.73	±1.23	-0.007	2.55	5.48	11.73
WNKF2014*	-3.27±0.73	19.81±1.35	-0.52	2.79	±1.32	0.08	2.70	5.12	11.86
MCG2001**	-4.06±0.96	23.33±1.98	0.26	3.73	±1.89	0.97	4.18	1.73	13.27
Combined mean of *	-3.25±0.72	19.75±1.36	-0.54	2.76	±1.34	0.06	2.65	5.18	11.81
Combined mean of * and **	-3.45±0.78	20.65±1.52	-0.33	2.89	2.39 9.96	0.29	2.94	4.32	11.98
					-4.09±0.89				
					19.38±1.48				

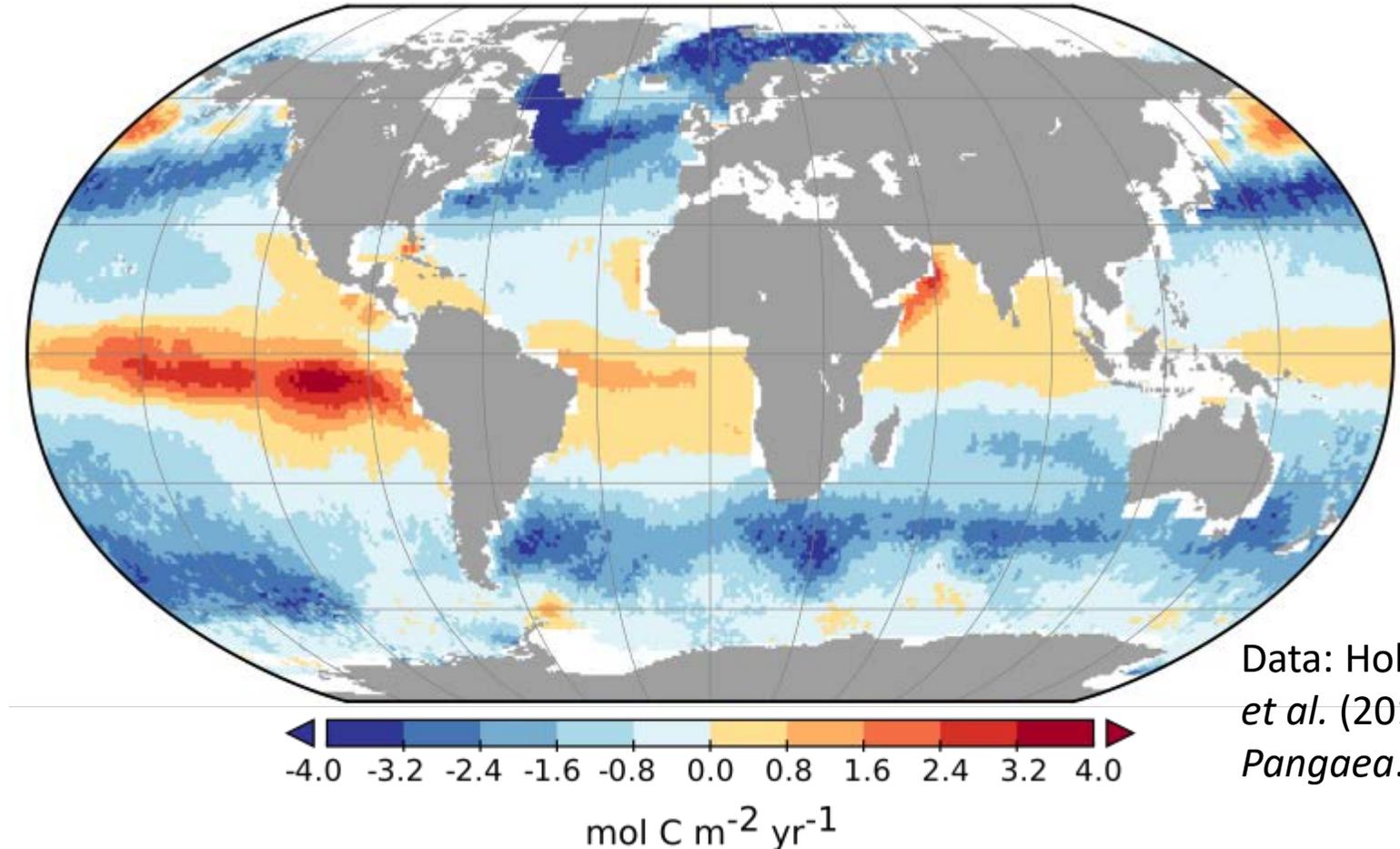
# Global implications of consolidated methods for temperature and salinity handling within gas flux calculations



## Results

Oceanic sink is at least 0.37 to 0.44 PgC larger than previously thought (Shutler *et al.*, 2019).

Global ocean sink value for 2010 is:  
 **$3 \pm 0.6$  PgC** (Woolf *et al.*, 2019).



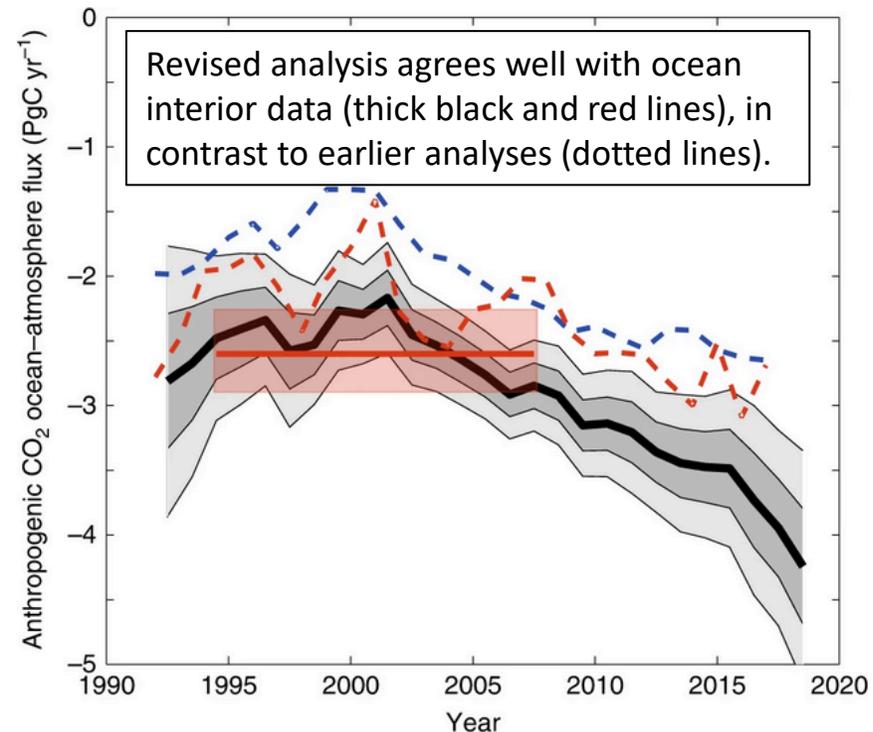
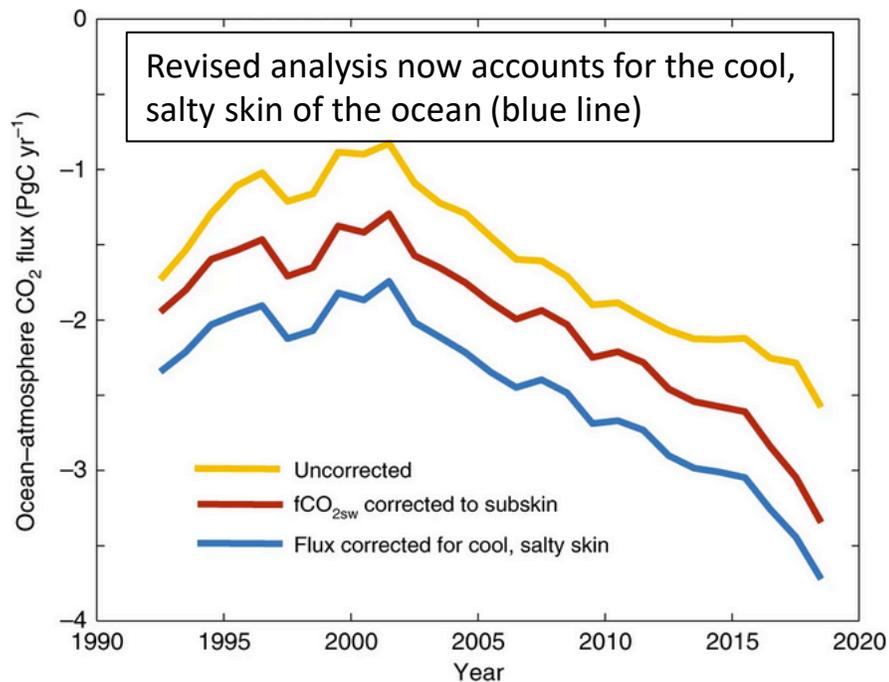
Shutler, J. D., *et al.* (2019) Satellites will address critical science priorities for quantifying ocean carbon, *Frontiers in Ecology and Environment*. doi: 10.1002/fee.2129

Woolf, D. K., *et al.* (2019) Key uncertainties in recent air-sea CO<sub>2</sub> flux, *Global Biogeochemical cycles*, doi: 10.1029/2018GB006041

# Global implications of consolidated methods for temperature and salinity handling within gas flux calculations



- Ocean sink is much larger than most ocean carbon models suggest.
- **The annual difference in ocean uptake can amount to ~10% of annual global fossil fuel emissions.**
- Result agrees well with an independent synthesis of interior ocean hydrography data.
- Analysis supports the revision of land to ocean riverine flux to around 0.5 Pg C yr<sup>-1</sup>.
- Work suggests that some revision of the global carbon budget is now required.



# Conclusions

## OceanSatFlux

Inter-comparison between direct and indirect air-sea CO<sub>2</sub> flux measurement techniques to:

- evaluate the theory of the impact of vertical temperature gradients on air-sea CO<sub>2</sub> exchange.
- advance uncertainty analyses within air-sea exchange studies (bulk and eddy covariance).

Using simultaneous SST skin measurements, underway and eddy covariance measurements.

The study:

- Confirmed that the consolidated theory appears correct.
- Found the largest impact within oceanic boundaries where SST vertical profiles are more variable (eg due to mixing and productivity).

Accurate SST measurements and their depth are essential for accurately measuring air-sea CO<sub>2</sub> fluxes. Ignoring vertical temperature gradients results in a systematic underestimate of the oceanic CO<sub>2</sub> sink.

Global implications for the ocean carbon sink, land to ocean riverine sink, quantifying the land carbon sink, global carbon and thus advice for reducing emissions.





## **Example 3: Revised estimates of ocean-atmosphere CO<sub>2</sub> flux are consistent with ocean carbon inventory**

# **Mail** Online

**World's oceans soak up 900 million tonnes of CO<sub>2</sub> a year MORE than previously thought — the amount emitted by 2.2 billion petrol cars**

- **Previous models did not account for temperature differences at different depths**
- **This alters how much carbon is soaked up by the water in total**
- **Researchers believe the world's oceans actually soak up far more carbon, equivalent to ten per cent of global fossil fuel emissions**

# But satellite observations offer much more!

Simplified view of interactions, exchange and circulation of CO<sub>2</sub> within the ocean, identifying where satellite Earth observation is likely to play a leading role in expanding understanding and capability.

