

# Summer-time carbonate chemistry in NW European shelf seas



UK Ocean Acidification  
Research Programme

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# Carbonate chemistry

6 June to 9 July 2011, D366

## Surface water:

- $f\text{CO}_2$  (fugacity of  $\text{CO}_2$ ) (UEA, PML),
- DIC (dissolved inorganic carbon) (UEA),
- TA (total alkalinity) (UEA),
- pH (U Soton)

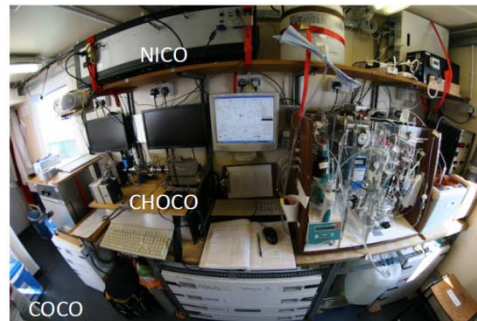
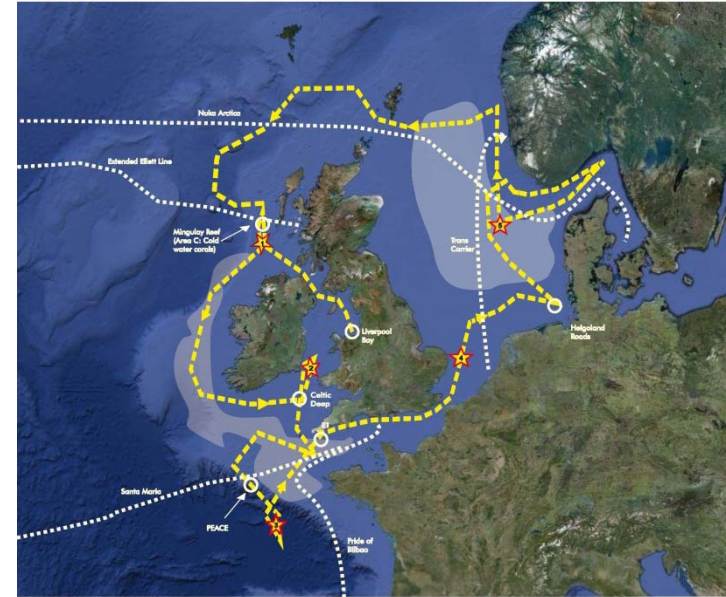
## Vertical profiles:

- DIC & TA (UEA)

Also  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and CO in surface water (UEA).

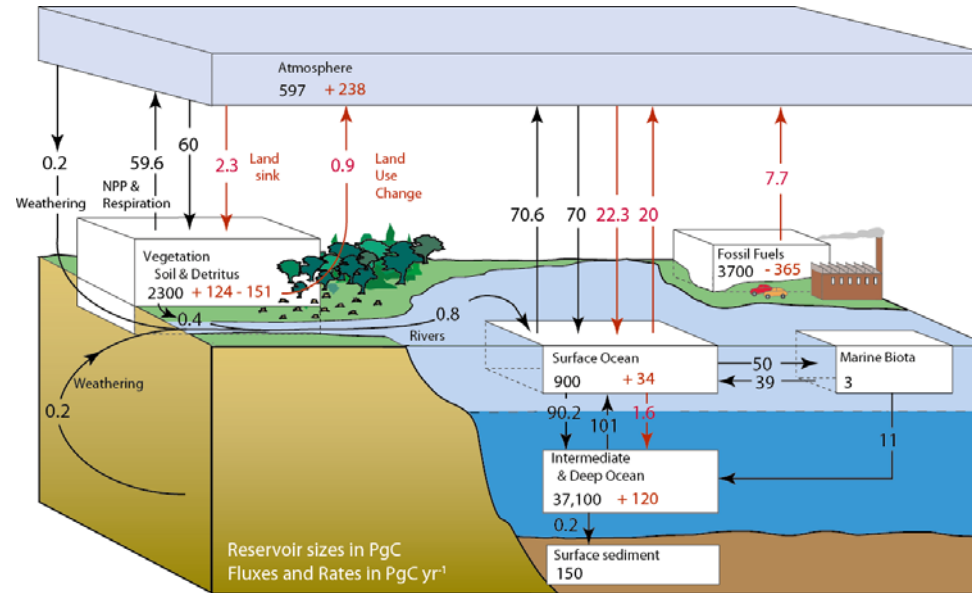
Consistency carbonate parameters – poster 16A by Mariana Ribas-Ribas

Comparison Cefas and D366 data – talk & poster 8A by Naomi Greenwood



*Image credits: Athena Drakou, Sebastian Hennige*

# Shelf sea carbon sink



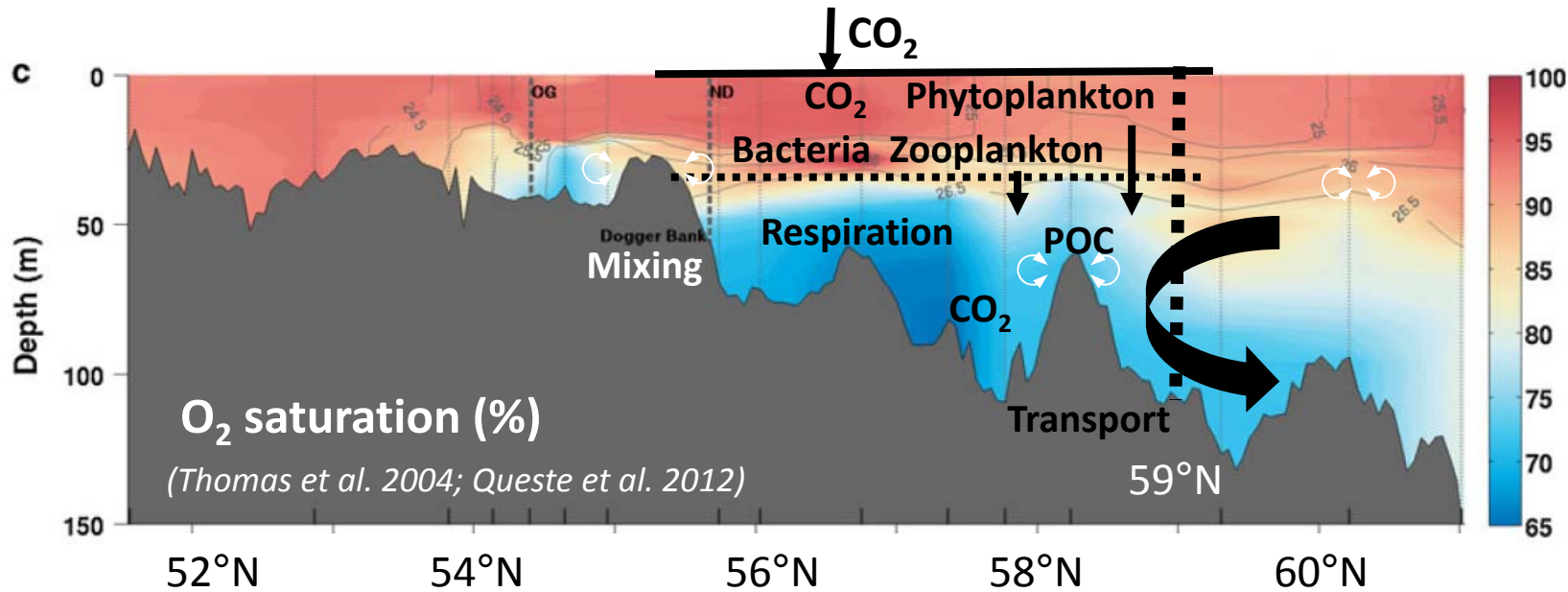
(Bakker et al., in press; after Sarmiento and Gruber 2002)

Ocean carbon sink	-1.6 to -1.7 Pg C/yr	(Takahashi et al., 2009; Gruber et al., 2009)
Shelf sea carbon sink	-0.3 Pg C/yr	(Chen and Borges, 2009; Laruelle et al., 2010)
Near-shore carbon source	+0.3 Pg C/yr	(Laruelle et al., 2010; Cai, 2011)

# Shelf sea carbon pump

Mixed: weak CO<sub>2</sub> source/sink

Seasonally stratified: carbon sink



Northern North Sea:

A shelf sea carbon pump (-1.0 to -2.5 mol C m<sup>-2</sup> yr<sup>-1</sup>):

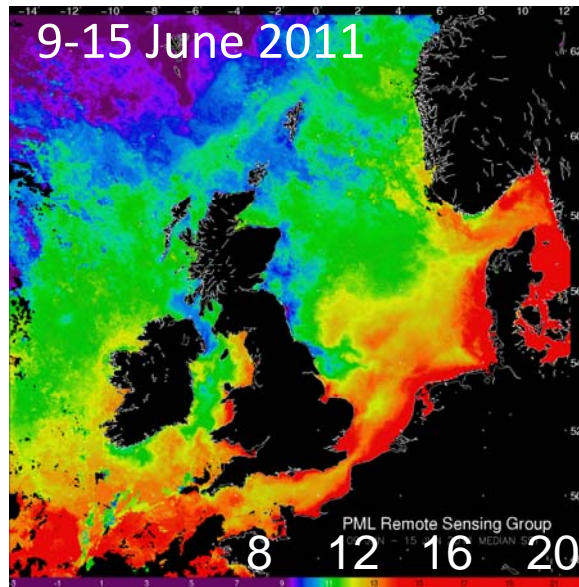
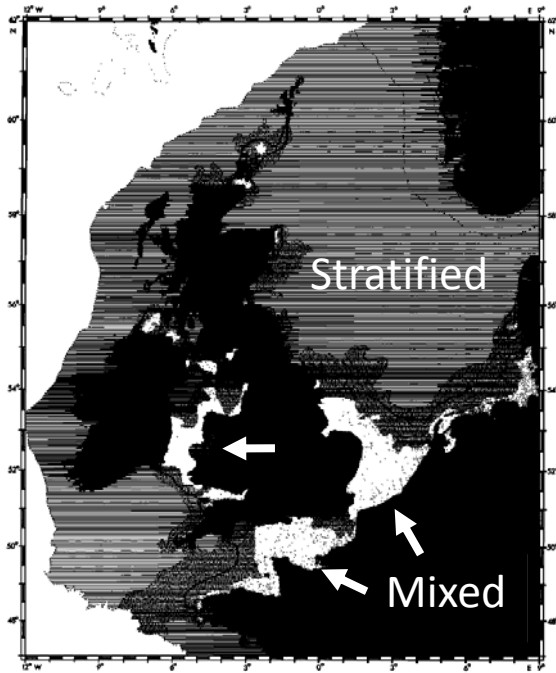
- Seasonal stratification & Biological processes;
- Off-shelf transport of C-rich subsurface water (Thomas et al. 2004).

Other NW European shelf seas:

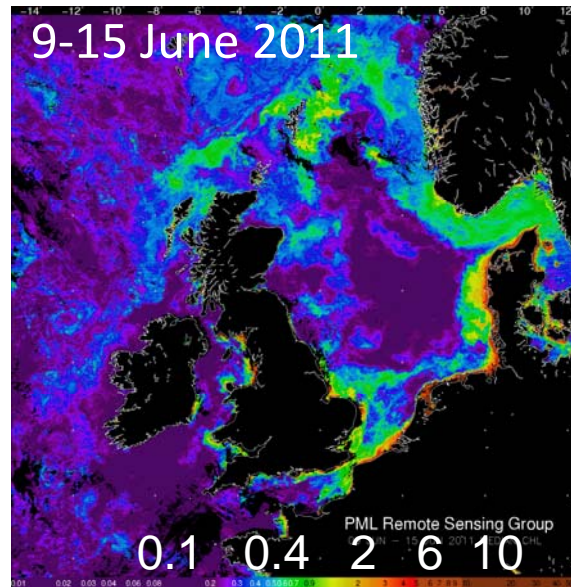
Less off-shelf carbon transport (Wakelin et al. 2012).

# Seasonally stratified and mixed waters

(Pingree and Griffiths, JGR, 1978)

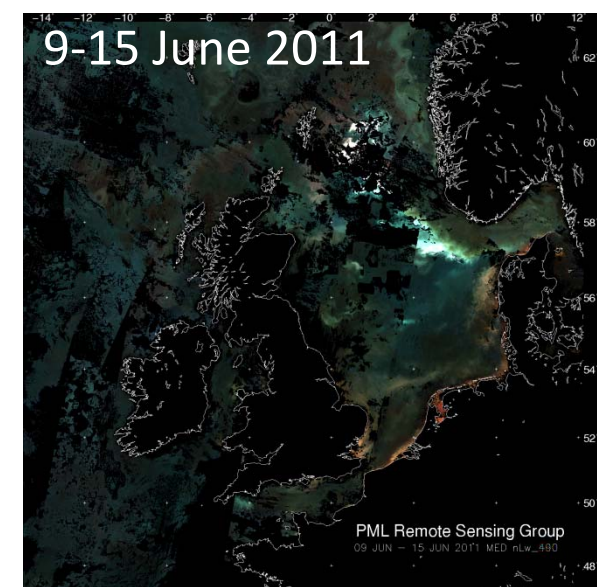


Sea surface temperature  
AVHRR (°C)



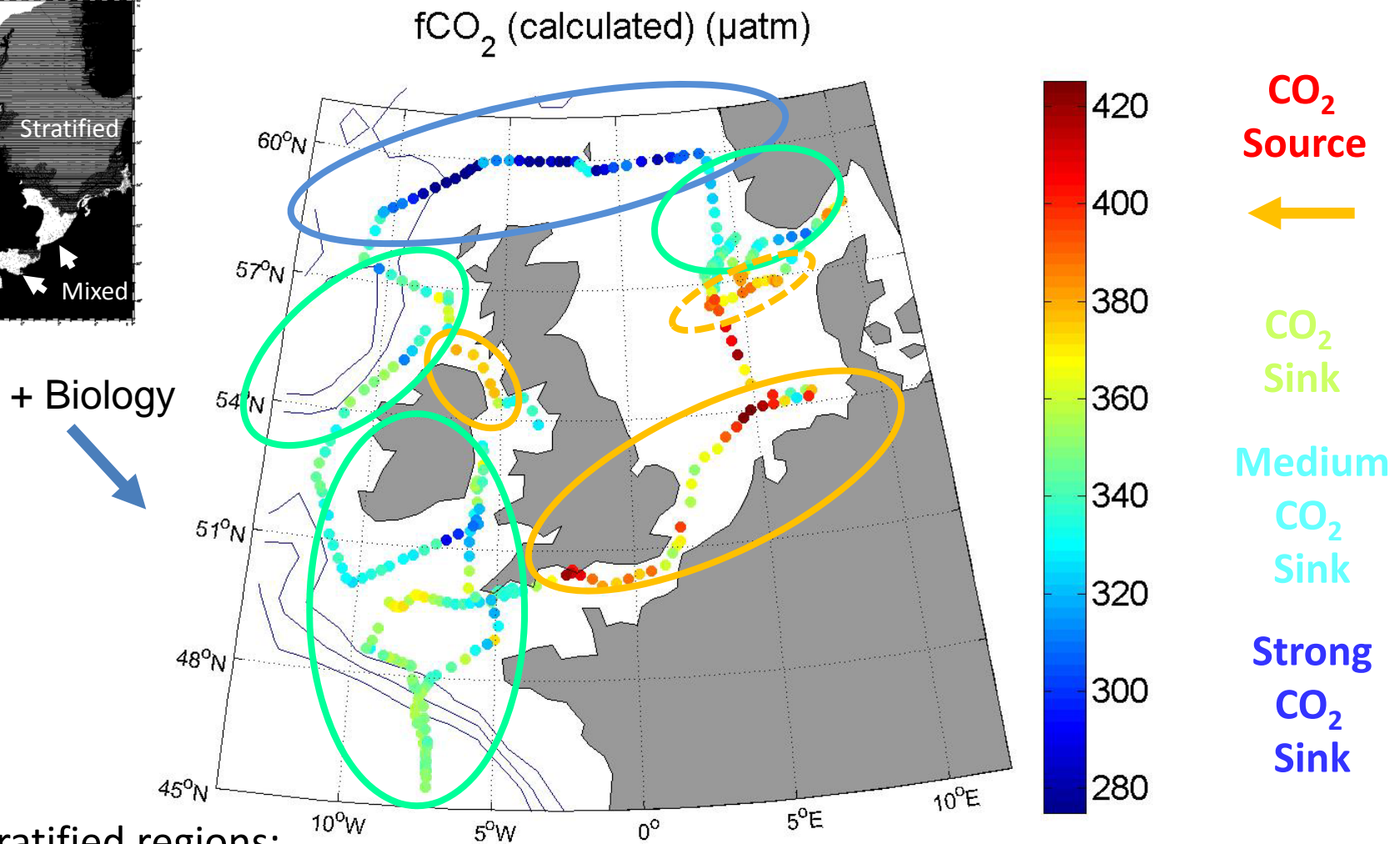
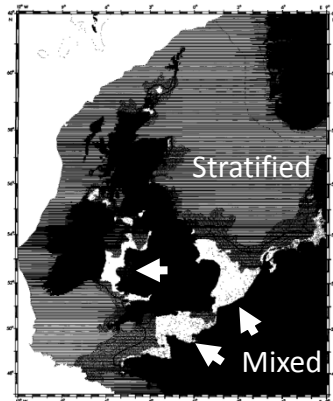
MODIS Chlorophyll

(Plymouth Remote Sensing Group)



RGB MODIS

# Stratified versus mixed waters



+ Biology

Stratified regions:

Northern shelves (60°N):

Western shelves & Skagerrak:

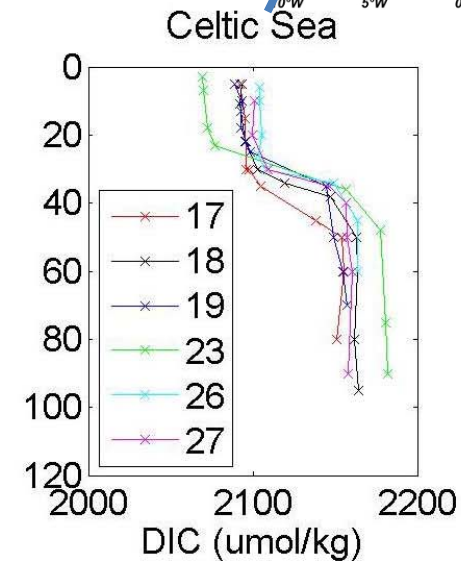
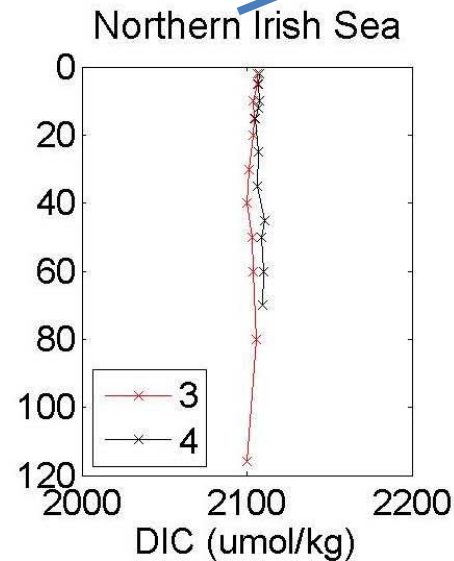
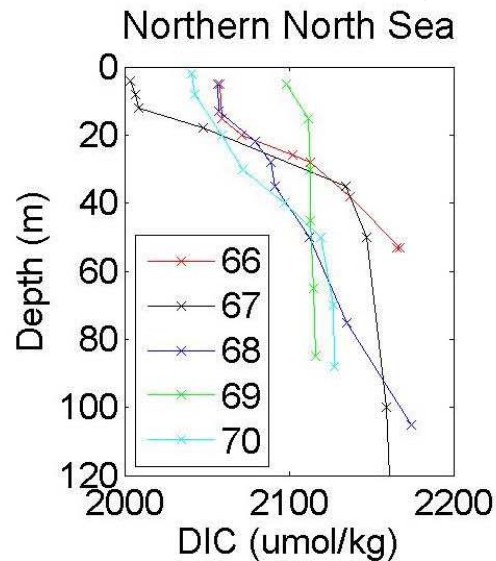
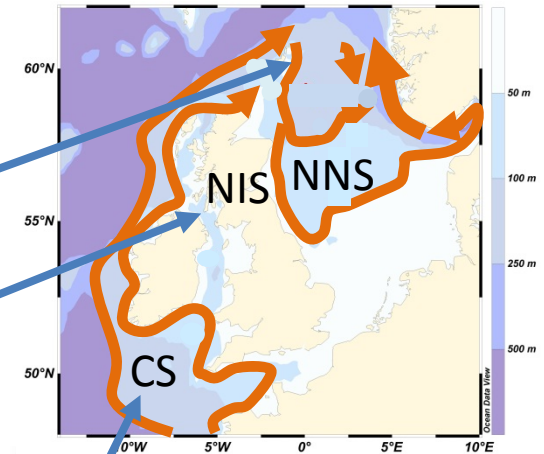
Mixed regions:

Strong CO<sub>2</sub> sink;

Medium CO<sub>2</sub> sink;

Weak CO<sub>2</sub> source to CO<sub>2</sub> sink.

# Shelf sea carbon pumps in June 2011



## Northern North Sea

Annual CO<sub>2</sub> sink;  
Seasonally stratified;  
Transport off the shelf;  
Strong shelf sea carbon pump  
(Thomas et al., 2004).

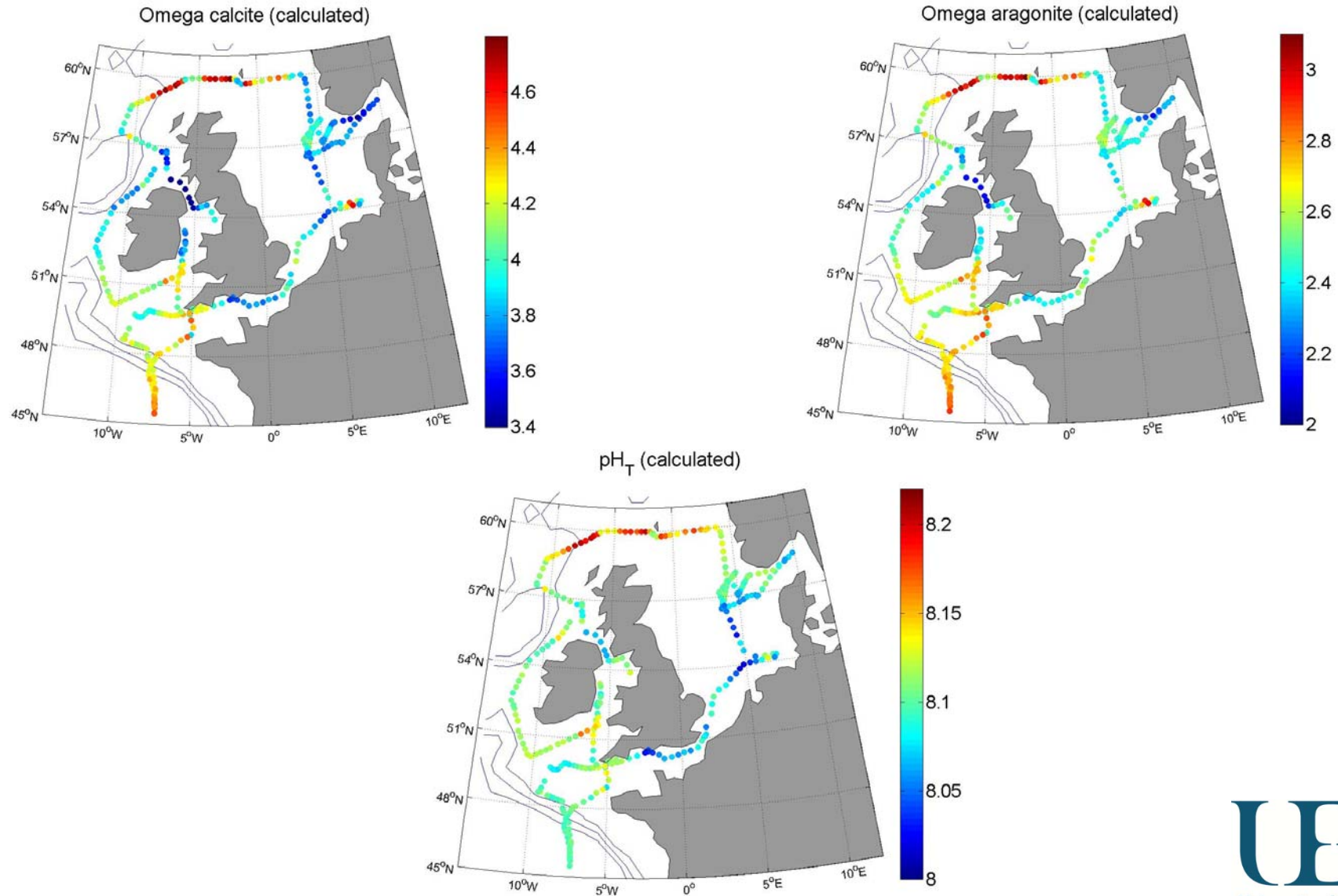
## Northern Irish Sea

Low air-sea CO<sub>2</sub> flux, June'11;  
Mixed;  
Transport off the shelf (?);  
No shelf sea carbon pump (?)

## Celtic Sea

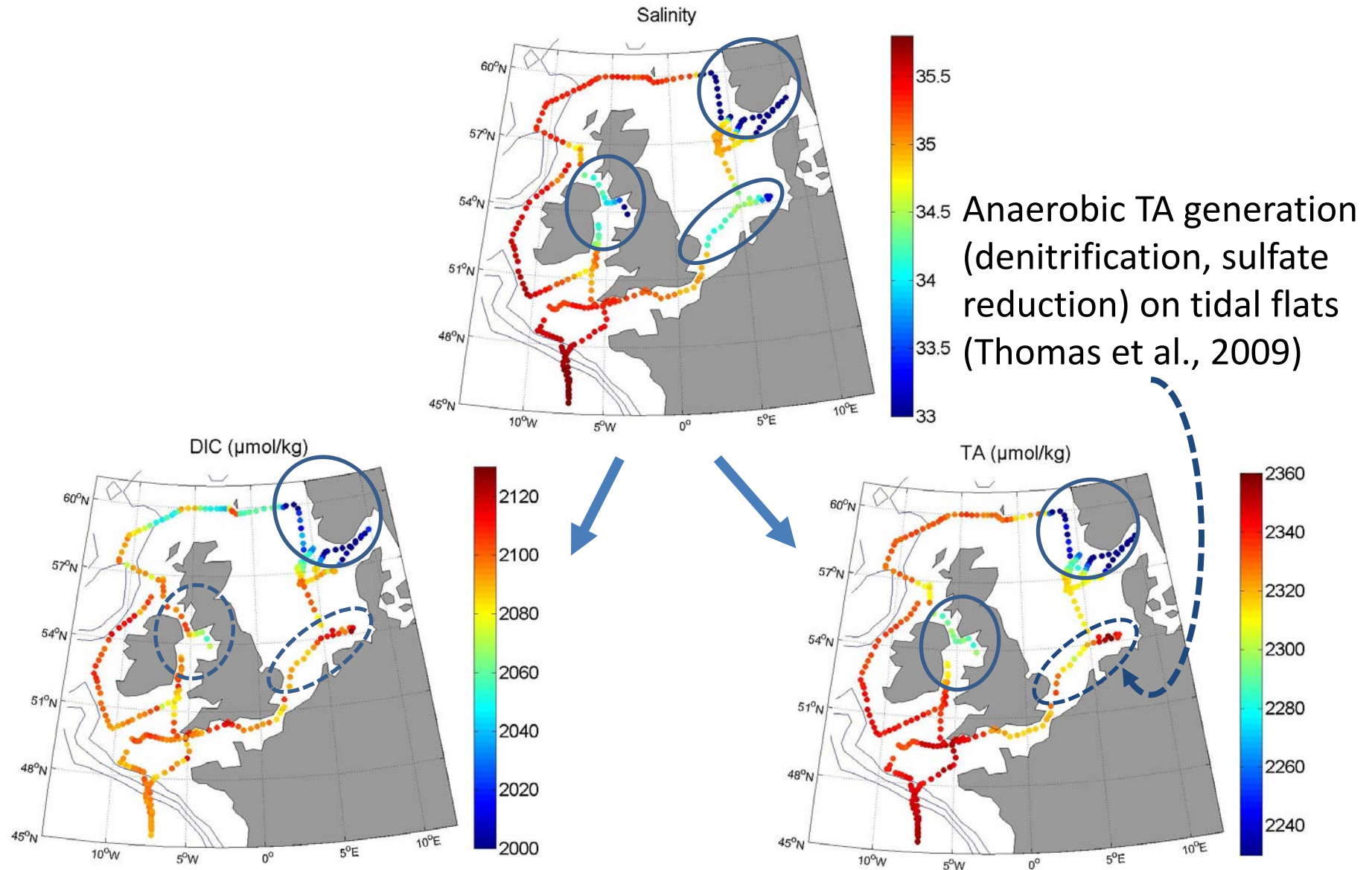
Moderate CO<sub>2</sub> sink in June'11;  
Seasonally stratified;  
Some transport off the shelf;  
Weak shelf sea carbon pump  
(?)

# Supersaturation for calcite and aragonite in surface water





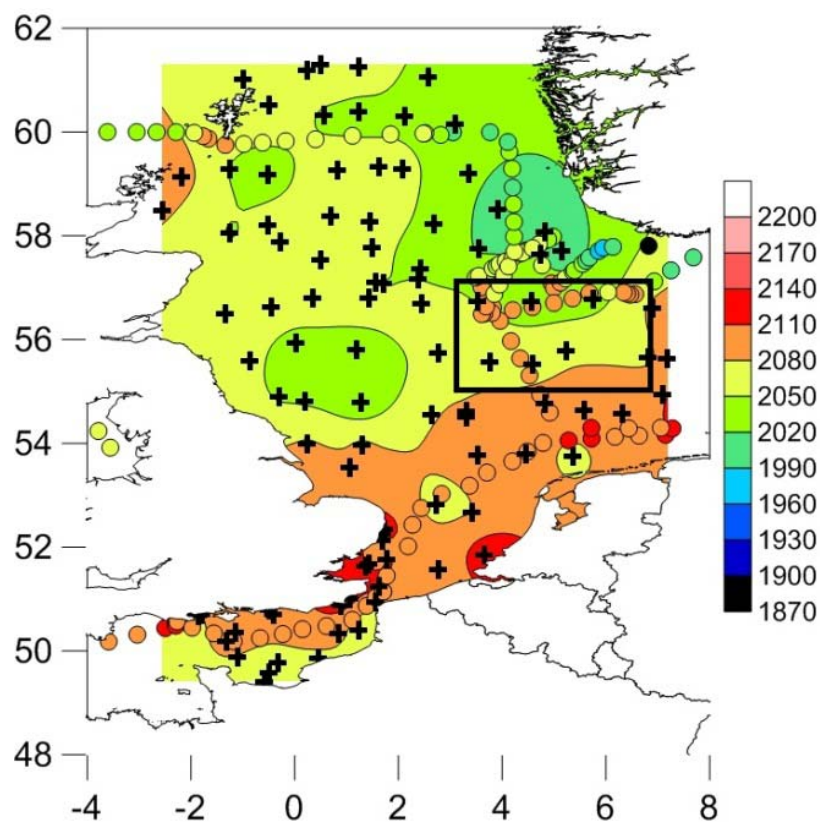
# Effects of river inflow on surface water DIC and TA



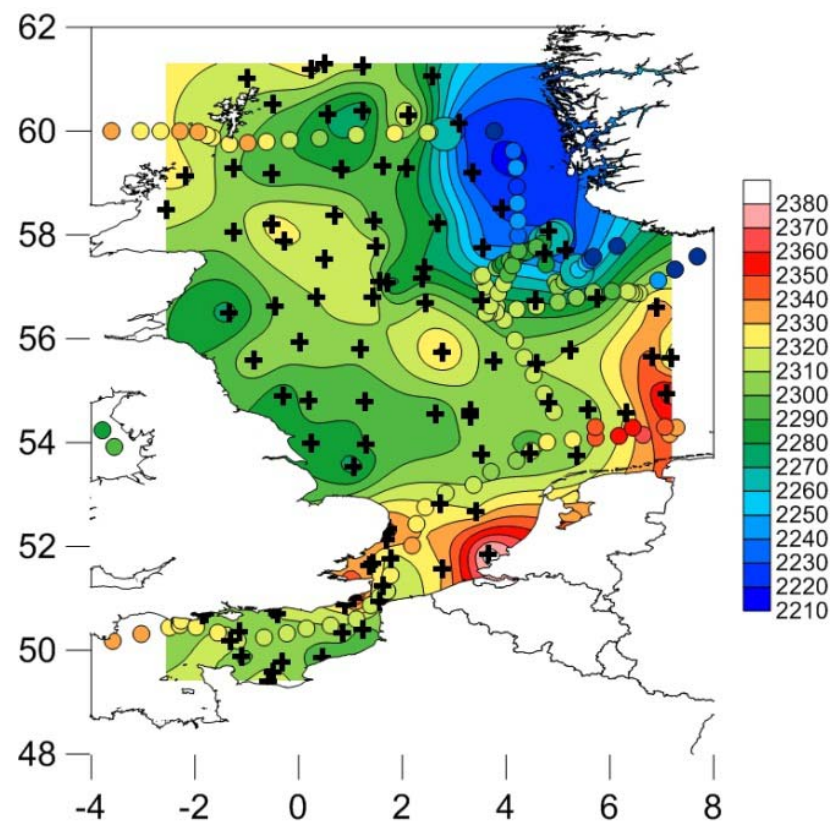
# Spatial pattern, Cefas and D366 data



Talk and poster 8A by Naomi Greenwood



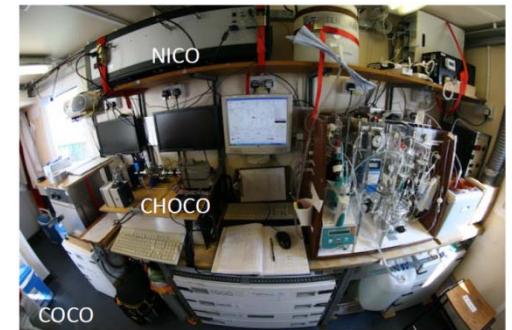
Dissolved inorganic carbon ( $\mu\text{mol/kg}$ )



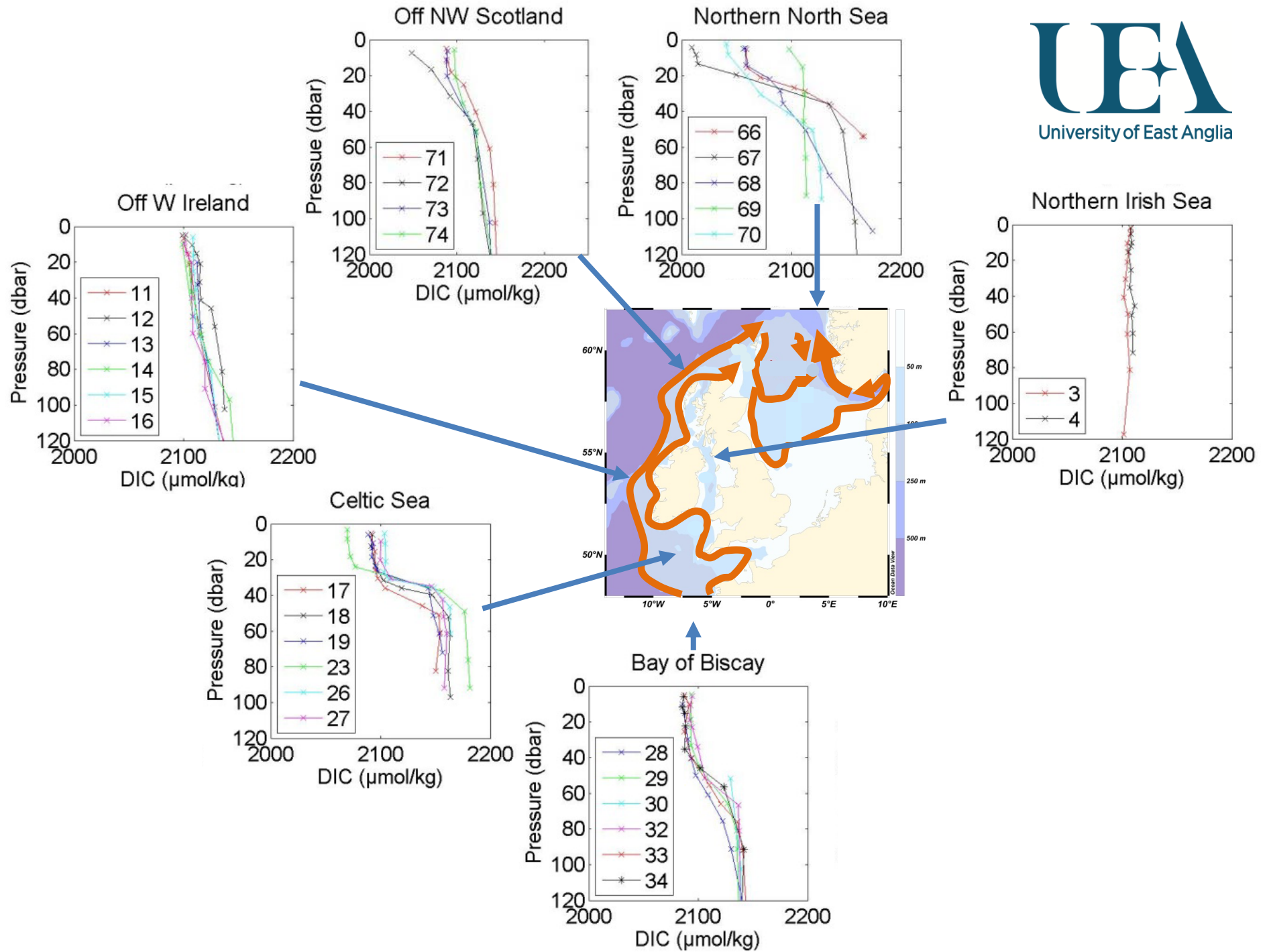
Total alkalinity ( $\mu\text{mol/kg}$ )

# Summertime carbonate chemistry on NW European shelf

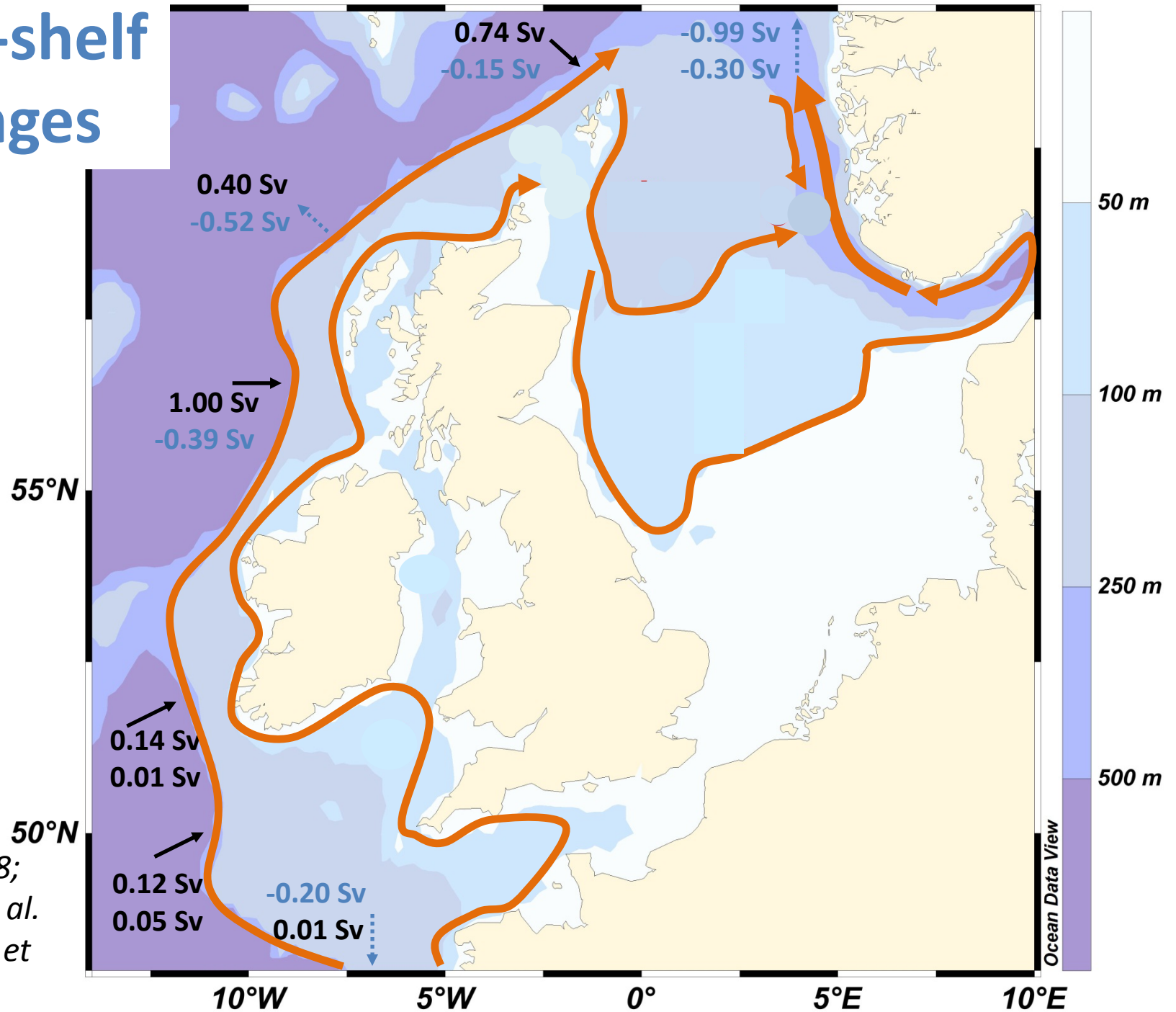
- Imprint on carbonate chemistry of:
  - ❖ Seasonal stratification and mixing;
  - ❖ River inputs and Skagerrak inflow;
  - ❖ Anaerobic TA generation on tidal flats;
  - ❖ Biological processes.
- Stratified waters: Medium to strong CO<sub>2</sub> sinks
- Mixed regions: Weak CO<sub>2</sub> source to sink.
- Varying off-shelf transports around NW European shelves likely to affect carbon sink in regional seas.
- Supersaturation for calcite and aragonite.
- Internal consistency of carbonate parameters (poster 16A);
- Comparison to Cefas data (poster 8A, talk);
- Interpretation of CH<sub>4</sub>, CO, N<sub>2</sub>O in progress.





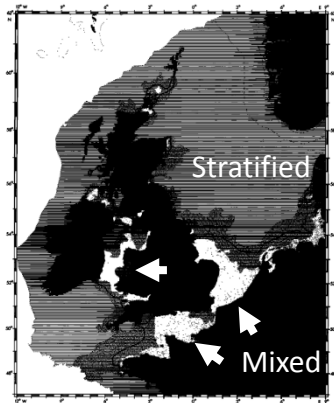


# Ocean-shelf exchanges

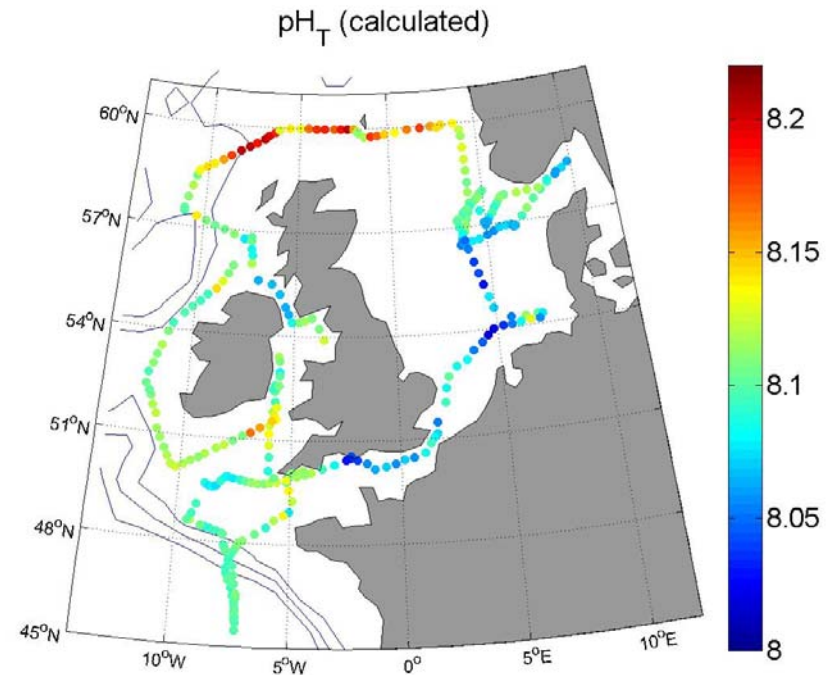
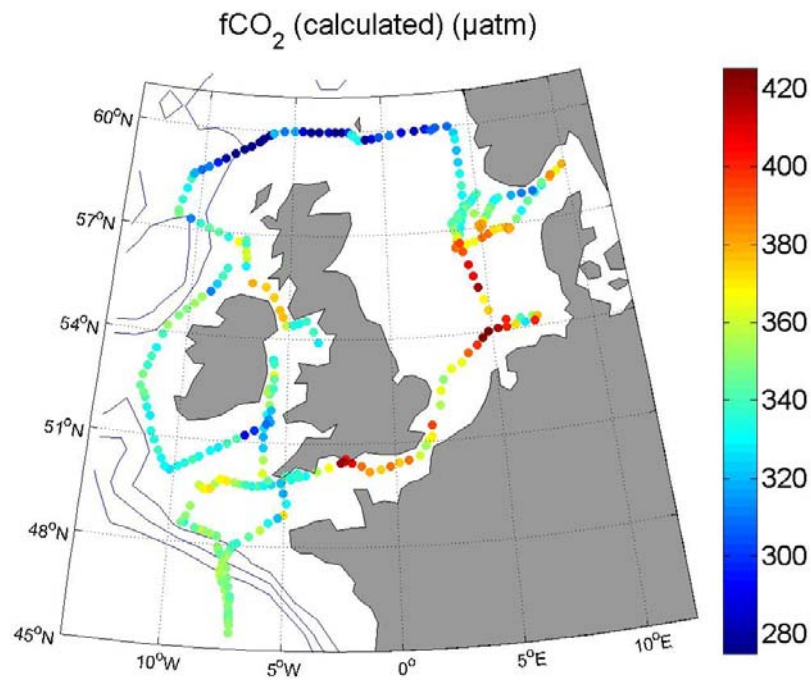


(After Hill et al. 2008; Huthnance et al. 2009; Queste et al. 2012)

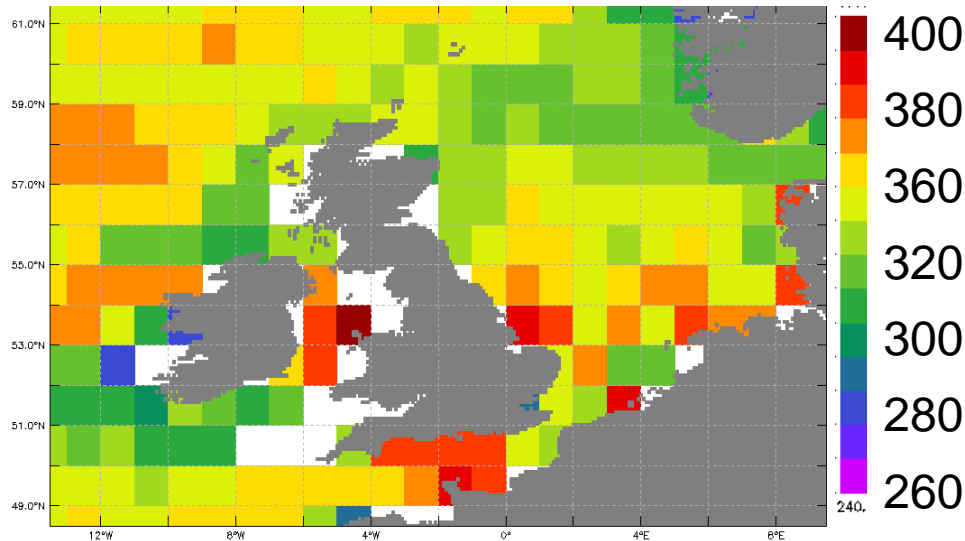
# Opposing patterns of surface water pH and $f\text{CO}_2$



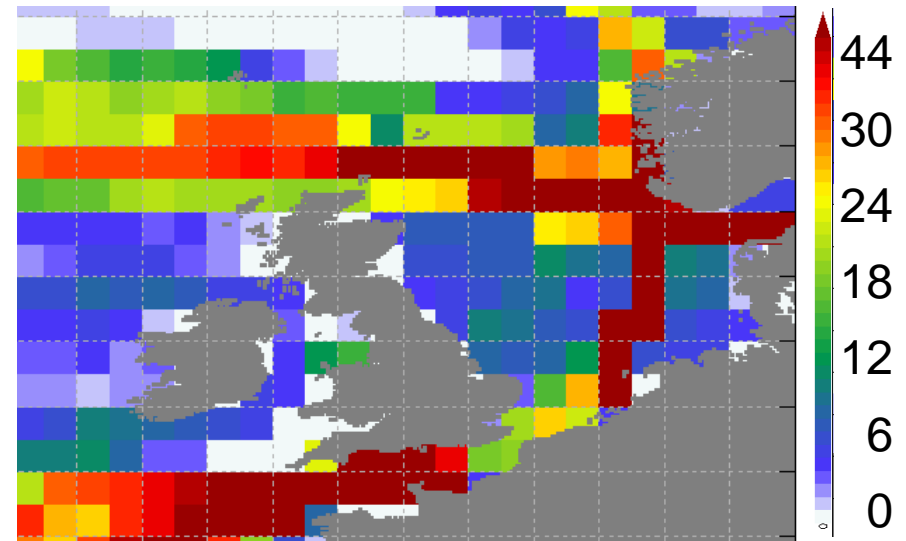
+ Biology



# SOCAT for quantifying the shelf sea carbon sink



Mean  $f\text{CO}_2$  ( $\mu\text{atm}$ ), 2000-2009



Number of cruises, 2000-2009

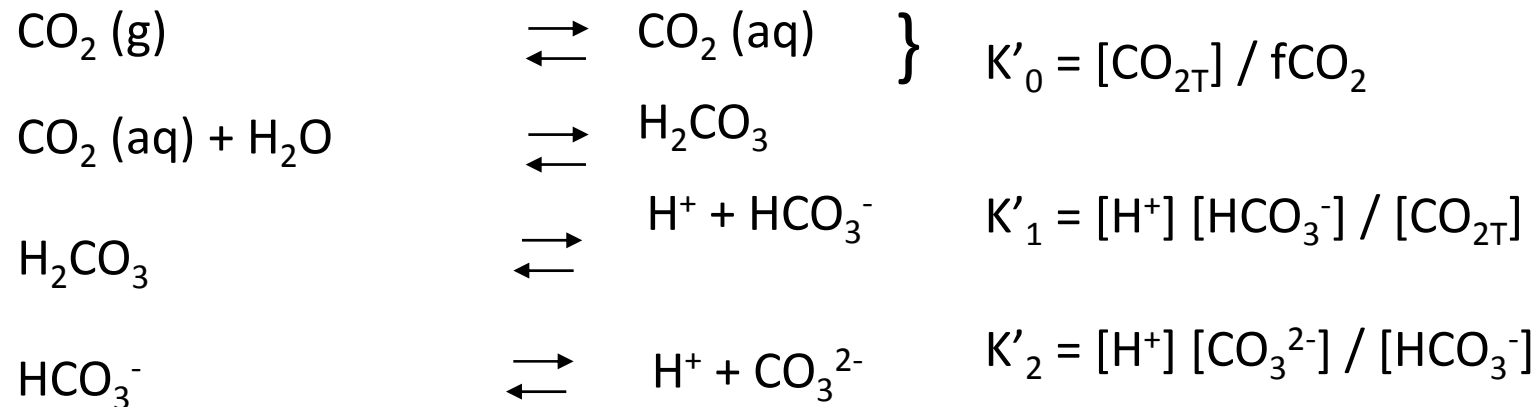
- Good  $f\text{CO}_2$  data coverage from Voluntary Observing Ships.
- Less than 10 cruises and seasonal bias elsewhere.

Surface Ocean  $\text{CO}_2$  Atlas, version 2,  
[www.socat.info](http://www.socat.info) (Bakker et al., submitted to ESSD)





# The marine carbonate system



Air-sea  $\text{CO}_2$  flux =  $k K_0 \Delta f\text{CO}_2(\text{w-a})$

$f\text{CO}_2$  =  $\gamma p\text{CO}_2 = [\text{CO}_{2\text{T}}] / K'_0$  (fugacity of  $\text{CO}_2$ )

DIC =  $[\text{CO}_2] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$  (dissolved inorganic carbon)

TA =  $[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{Bases}] + [\text{OH}^-] - [\text{H}^+] - [\text{HSO}_4^-] - [\text{HF}]$

$\Omega$  =  $[\text{Ca}^{2+}] \cdot [\text{CO}_3^{2-}] / [\text{Ca}^{2+}]_{\text{sat}} \cdot [\text{CO}_3^{2-}]_{\text{sat}}$  (omega)

$\text{pH}_\text{T}$  =  $-\log([\text{H}^+]_\text{T})$