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# Uncertainty and ambiguity in gas transfer coefficients

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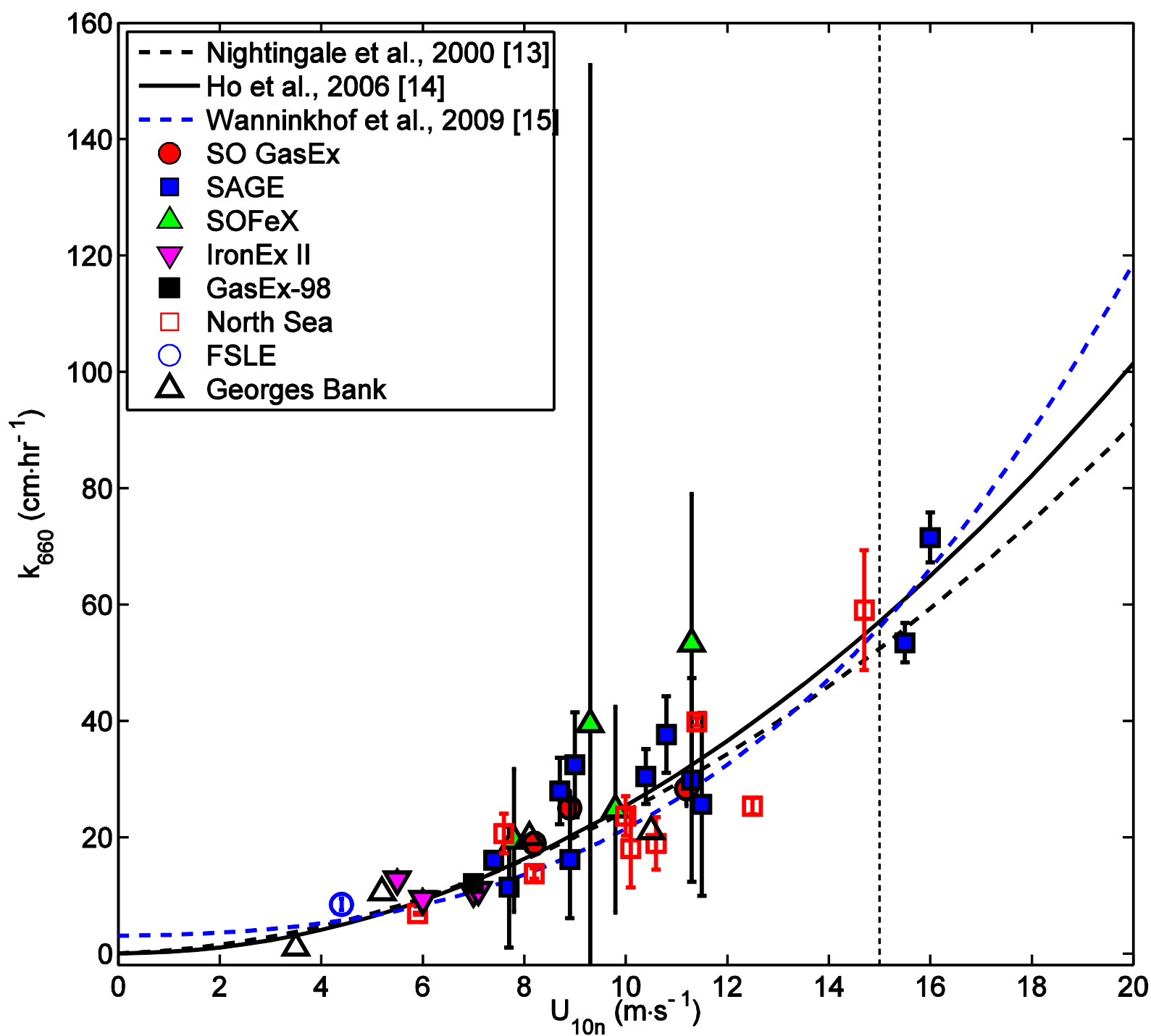


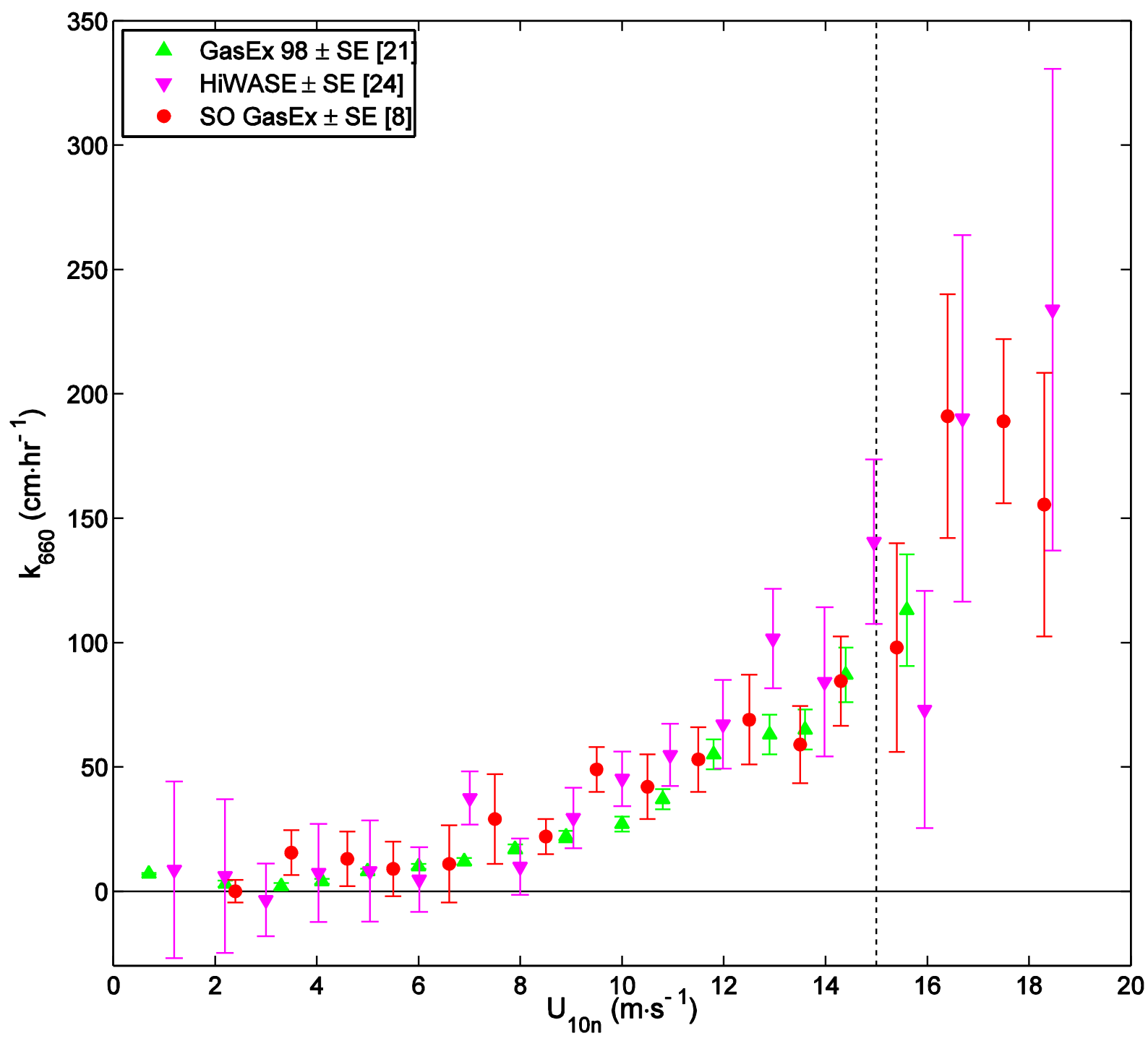
# Overview

- Review of field measurements of  $k$ 
  - Breadth of techniques
  - Classification by gas etc.
  - What do isotopic analyses tell us?
- What can make sense of all/most of the results?
  - Differences between gases
  - Other mechanisms
  - Is temperature a key?
  - Hybrid models revisited

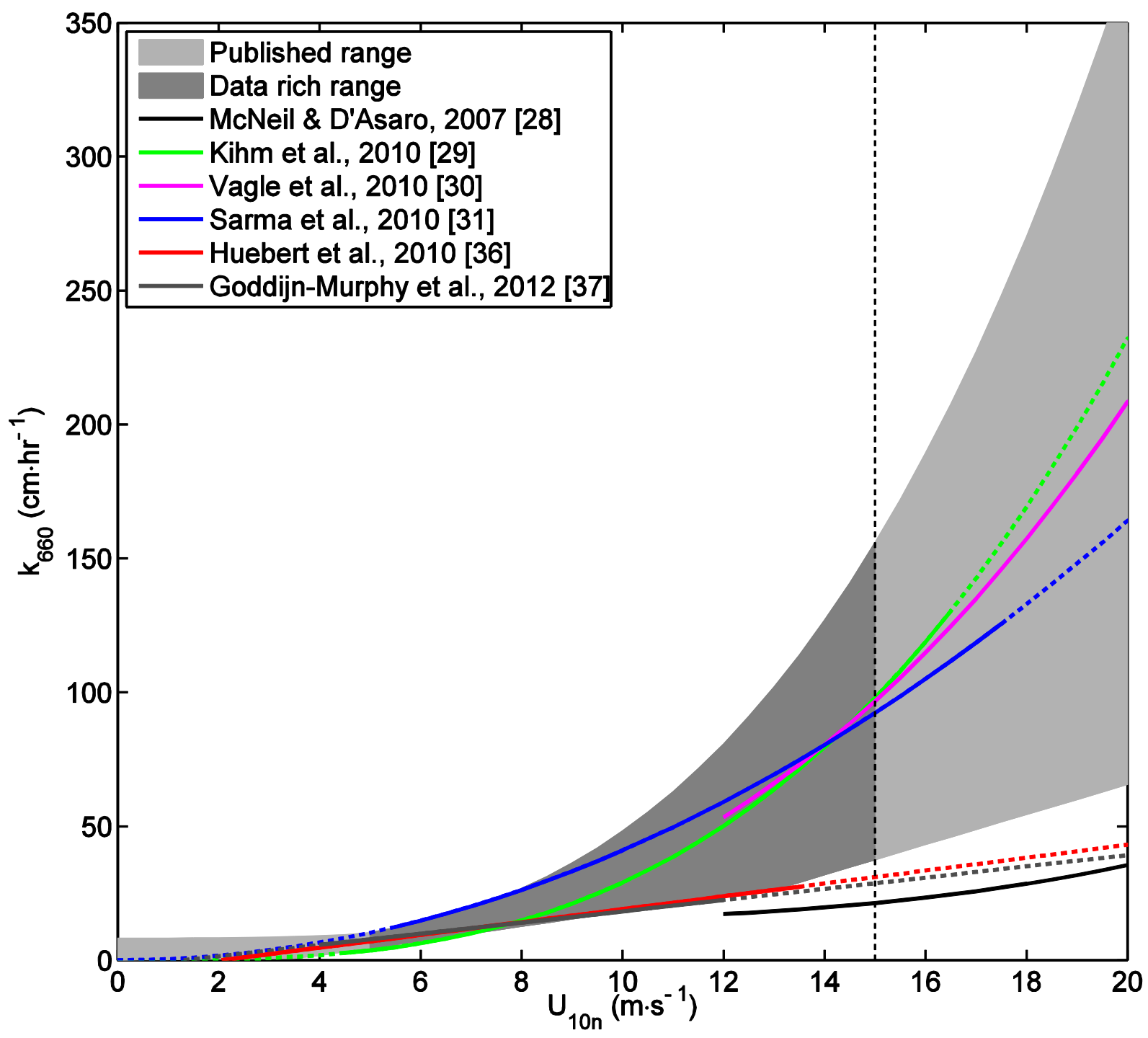
# Methods

- a) Chamber or dome measurements of CO<sub>2</sub> flux
- b) Micrometeorological measurements of CO<sub>2</sub> flux
- c) Budgets of dissolved inorganic carbon (DIC)
- d) Modelling of oceanic DIC
- e) Carbon isotope methods
- f) Oxygen and nitrogen in the atmosphere
- g) Oxygen covariance in the ocean and oxygen deficit method
- h) Oxygen and nitrogen oceanic time series
- i) Triple isotopes of oxygen
- j) Noble gas time series
- k) Radon deficit method
- l) Purposeful tracers (including dual tracer method)
- m) Micrometeorological measurements of dimethyl sulphide









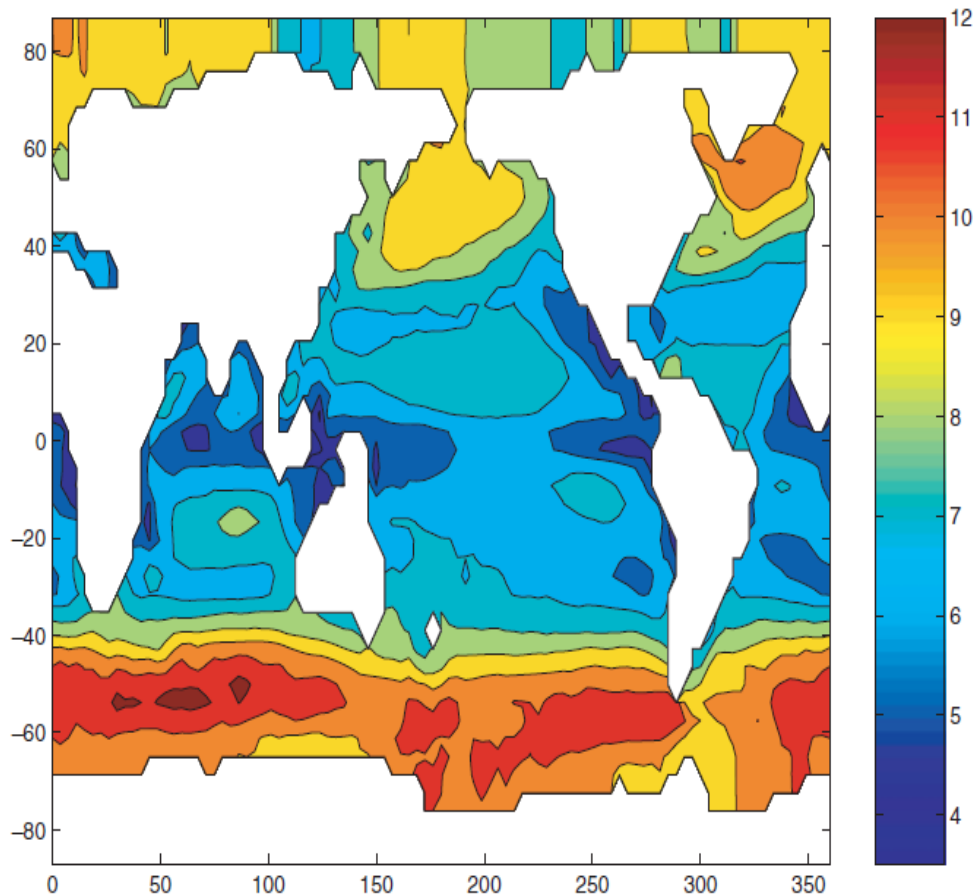
# Isotopic Studies

- Naegler et al., 2006
- Sweeney et al., 2007
- Krakauer et al. 2006

$$k_w = \langle k \rangle \left( \frac{u^n}{\langle u^n \rangle} \right) (Sc/660)^{-0.5}$$

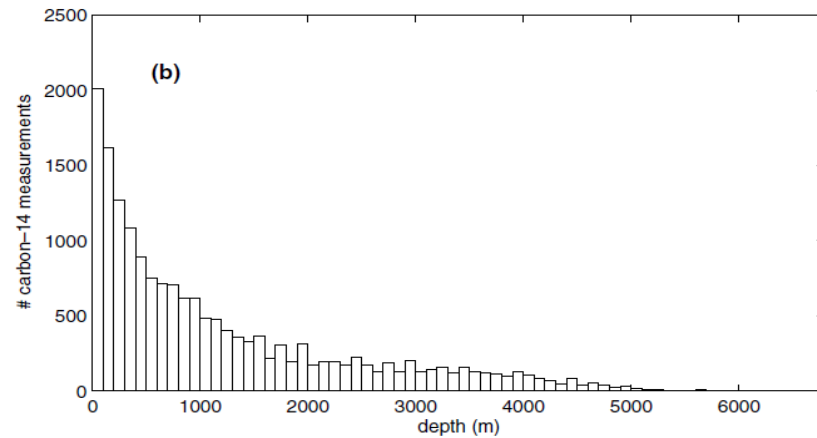
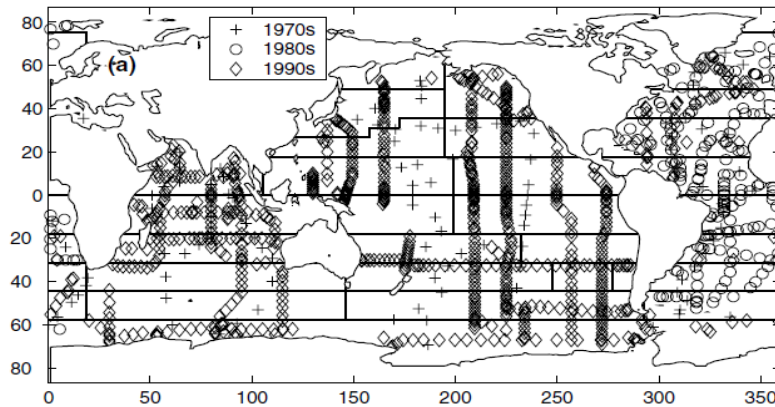


# Latitudinal variation in $k$ and $U$



*Fig. 1.* Annual mean root-mean-square wind speed ( $\text{m s}^{-1}$ ) over the ocean, at 10 m height, from the monthly climatology of Boutin and Etcheto (1997) and Orr et al. (2001), derived from satellite (SSM/I) data. We used the monthly climatology to explore the consequences of different dependences of the air-sea gas transfer velocity on wind speed on ocean  $^{14}\text{C}$  uptake. The root-mean-square wind speed varies from 5 to 6  $\text{m s}^{-1}$  near the equator to around 11  $\text{m s}^{-1}$  over the Southern Ocean.

# Data Density



*Fig. 3.* Distribution of the ocean  $^{14}\text{C}$  measurements used in this analysis (Key et al., 2004). (a) Location of measurements, grouped by decade. The 1970s measurements were made as part of GEOSECS, the 1990s measurements mostly as part of WOCE. The thick lines are the boundaries between the 30 ocean regions we use as basis regions for transport pulse functions. (b) Depth distribution of measurements (100 m bins).

# Problems in the Southern Ocean

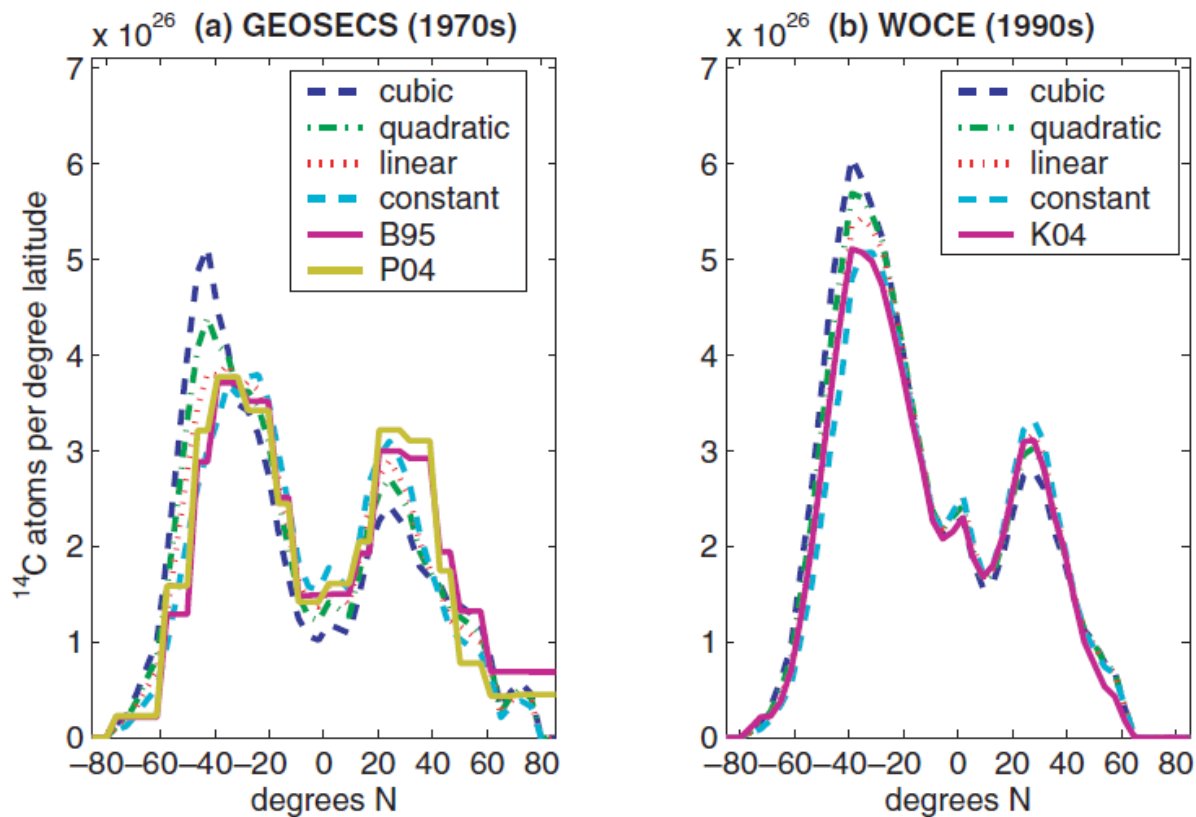
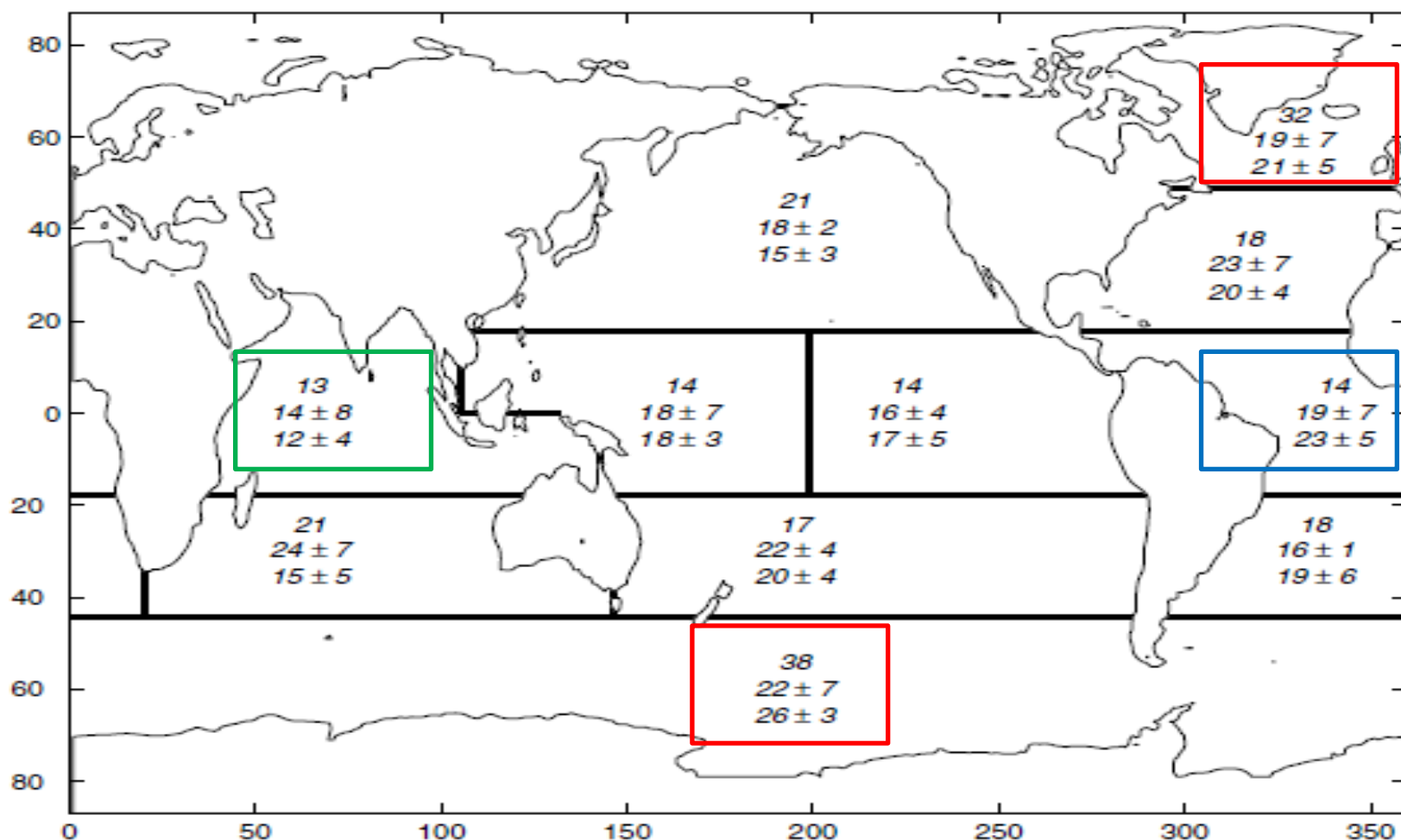
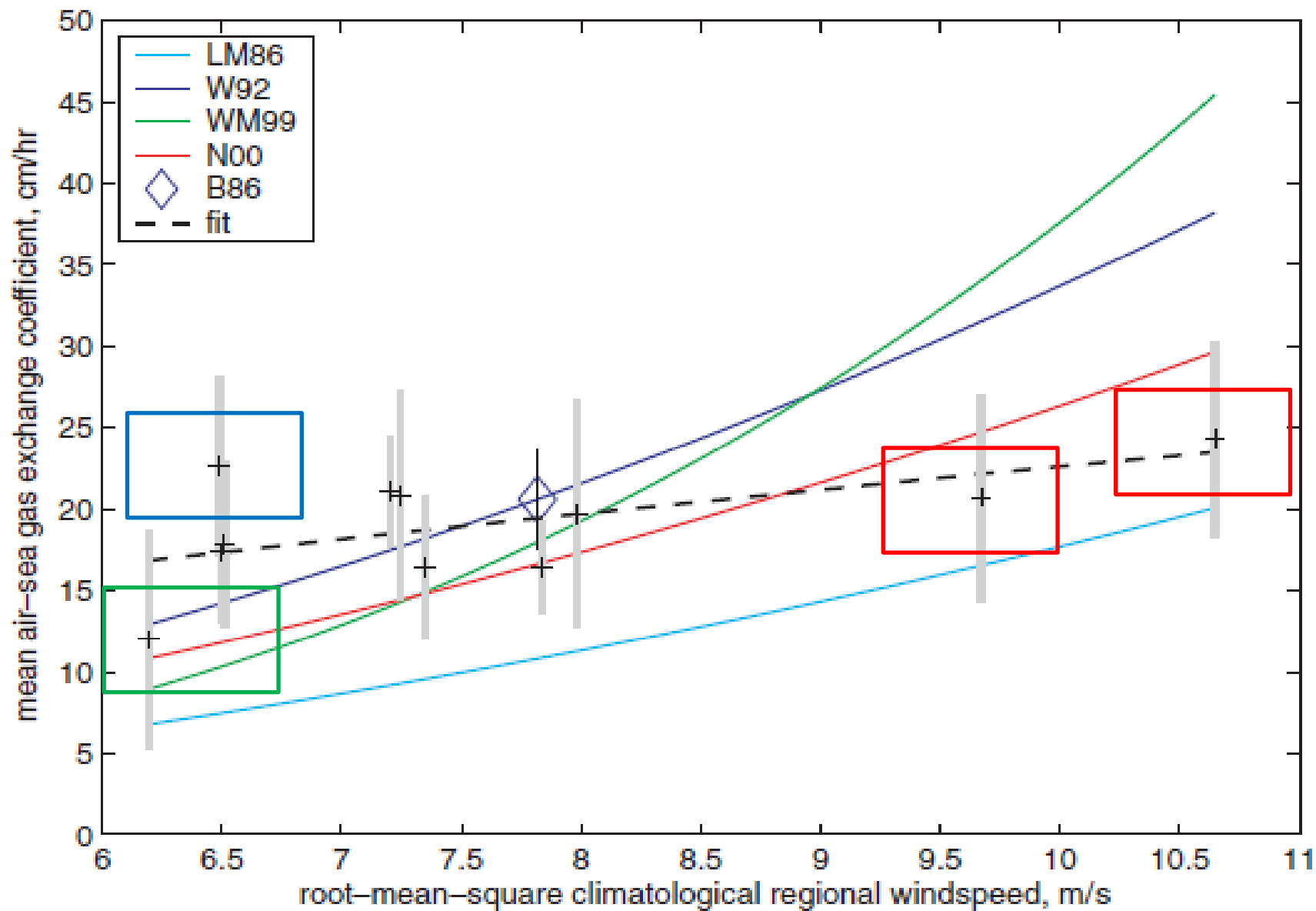


Fig. 6. Modelled latitudinal distribution of bomb  $^{14}\text{C}$  in the ocean, for a global mean gas transfer velocity ( $k$ ) of 20.6 cm/hr and a dependence on wind speed ranging from cubic to none ( $n = 3, 2, 1$  or  $0$ ). A lower dependence on wind speed leads to relatively less uptake at the mid-latitudes and more near the equator. In panel (a), the 1975.0 modelled distribution is compared with extrapolations from GEOSECS observations in  $10^\circ$  bands by Broecker et al. (1995) and by Peacock (2004) (mean of her CFC- and anthropogenic  $\text{CO}_2$ -based extrapolation approaches). In panel (b), the 1994.5 modelled distribution is compared to the GLODAP gridded distribution based on WOCE observations (Key et al., 2004); the modelled distribution is summed only over the grid cells for which the gridded distribution is available, excluding, for example, the Arctic Ocean.



*Fig. 8.* Mean air–sea gas transfer velocities over 11 regions (cm/hr), derived using the quadratic relationship with wind speed of Wanninkhof (1992) and Dutay et al. (2002) (top row in each region) and estimated by optimizing the fit to the 1970s (second row) or the 1980s–1990s (third row) ocean bomb  $^{14}\text{C}$  observations. In the second and third rows, we show the mean and the standard deviation of

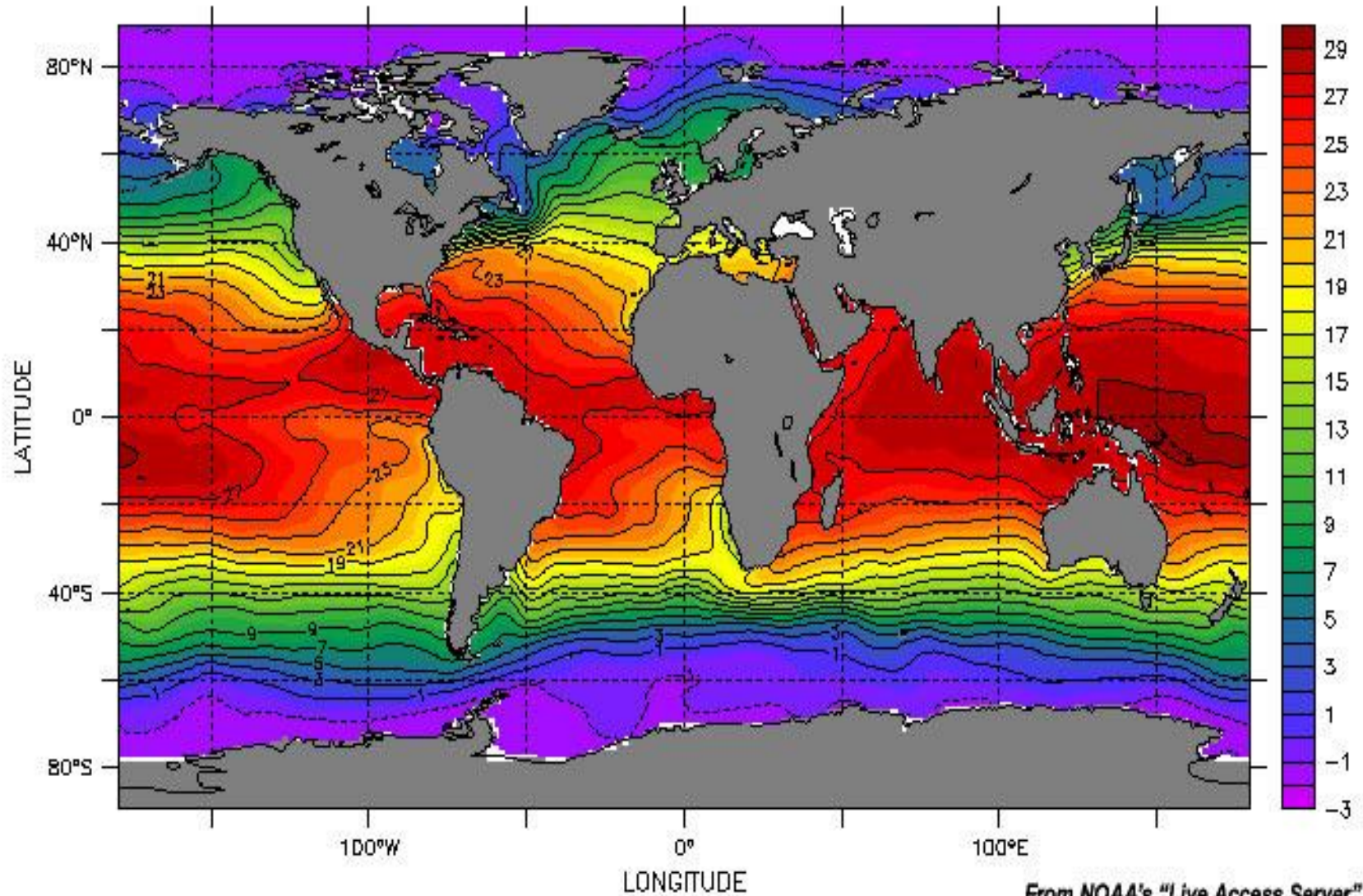


Constraint	Implied $\langle k \rangle$ (cm/hr)	Implied $n$
Ocean bomb $^{14}\text{C}$ measurements		
Ocean total amount (WOCE)	14–27	
Globally optimum fit of $\langle k \rangle$ , $n$ to measurements	$20 \pm 3$	$0.5 \pm 0.4$
Fit of regional gas transfer velocities	$19 \pm 1$	$0.6 \pm 0.7$
Other $^{14}\text{C}$ and $^{13}\text{C}$ measurements <sup>a</sup>		
Atmospheric $\Delta^{14}\text{C}$ : 1990s decline rate	$20 \pm 4$	0.6 (0–2.0)
Atmospheric $\Delta^{14}\text{C}$ : 1990s latitudinal gradient	$28 \pm 13$	1.5 (0–2.9)
Pre-industrial ocean $^{14}\text{C}$ uptake	$22 \pm 4$	
Pre-industrial atmospheric $\Delta^{14}\text{C}$ latitudinal gradient	$26 \pm 10$	1.3 (0–2.7)
Air–sea $^{13}\text{C}$ isotope flux, 1990s	$23 \pm 5$	0 (0–1.1)
Air–sea $^{13}\text{C}$ isotope flux, pre-industrial		1.2 (0.3–1.9)

# An Imposed Temperature Dependence

$$k_w = (k) \left( \frac{u^n}{(u^n)} \right) (Sc/660)^{-0.5}$$

# Average Sea Surface Temperature (°C)



From NOAA's "Live Access Server"  
Levitus 1982 Annual Climatology



# Why the variation in Sc-normalised transfer velocity?

1) Different gases,  $Sc^{-1/2}$  doesn't work

Some evidence of  $k$  less for more soluble gas, but unconvincing

2) Water Temperature

Solubility

Viscosity

Convection

Hydration/Dehydration

3) Water Temperature and Sea State (Reynolds number argument)

$$k_w = \max [k_{\text{minimum}} , Sc^{-1/2} a U_* + b(Sc, \text{solubility, viscosity}) Re_w ]$$

Pessimists  
are rarely  
disappointed