Where is air-sea gas exchange happening? Carbon isotope evidence

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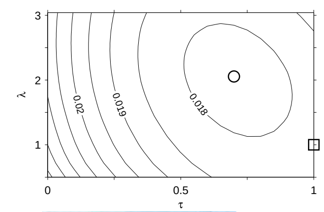
Thesis outline

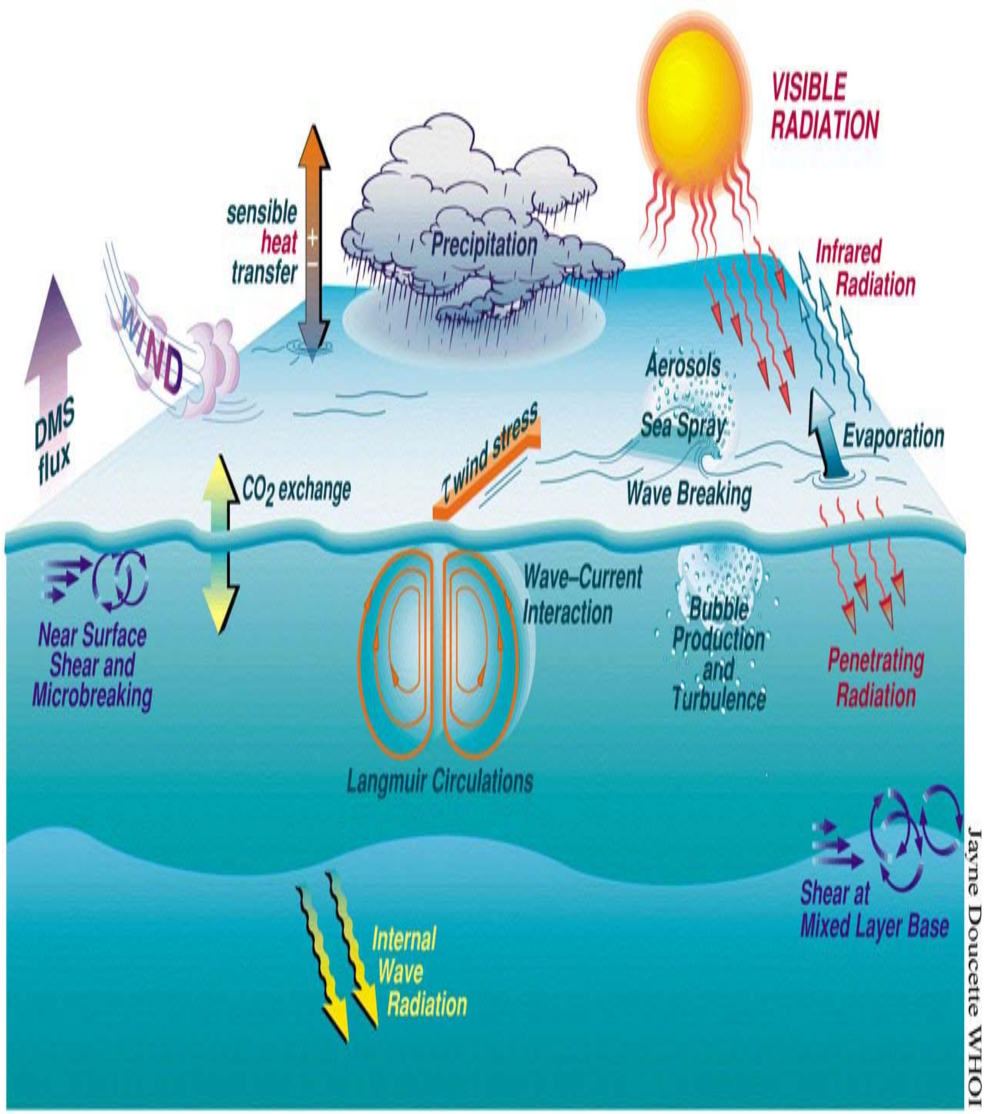
Tracing Recent Carbon Uptake by Oceans and Land Plants

- The impact of volcanic eruptions on global tree productivity
- Inferring flux patterns from atmosphere CO_2 concentrations: An application of generalized cross validation
- The regional distribution of air-sea gas exchange
- Seasonality in fossil fuel emissions, respiration, and cross-tropopause transport in $\Delta^{14}C$ of atmospheric CO_2



Pictures: USGS; LTRR; Ruth Brownlee; Photofusion (via the UK Science Museum)

Gas exchange in perspective

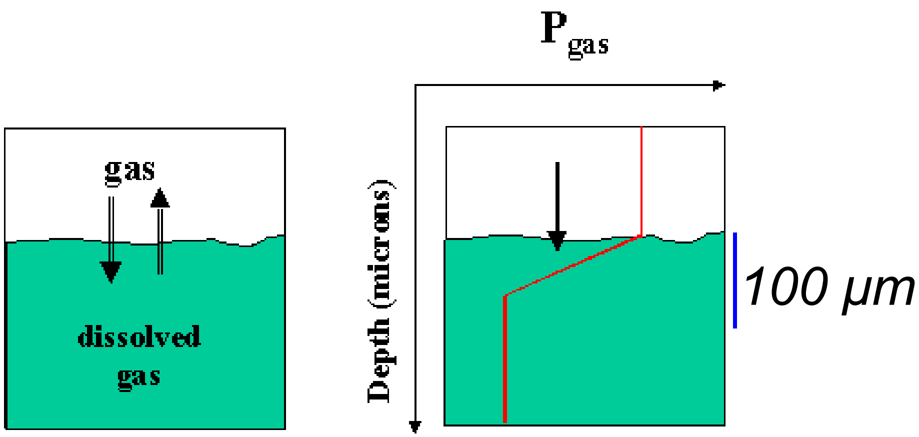


GasEx

Applications of gas exchange rates

- To infer the space and time distribution of ocean CO_2 uptake from extensive sea-surface pCO_2 data
- To infer rates of other sea-surface (e.g. photosynthesis from O_2 and $\Delta^{17}O$ measurements) and atmospheric (e.g. CH_3Cl_3 oxidation) processes
- To infer the ocean source of other gases that affect climate, such as $(CH_3)_2S$ and N_2O.

A conceptual model of air-sea exchange: the stagnant film



Thin Layer/Stagnant Film Model of Gas Exchange

- Gas concentrations are roughly constant in the ocean surface mixed layer, and in the air boundary layer
- Most of the air-sea concentration difference is across a thin (<0.1 mm) water-side surface layer
- Convenient to express the gas flux in terms of the bulk air and sea concentrations

J. Boucher, Maine Maritime Academy

A bulk parameterization of air-sea gas fluxes

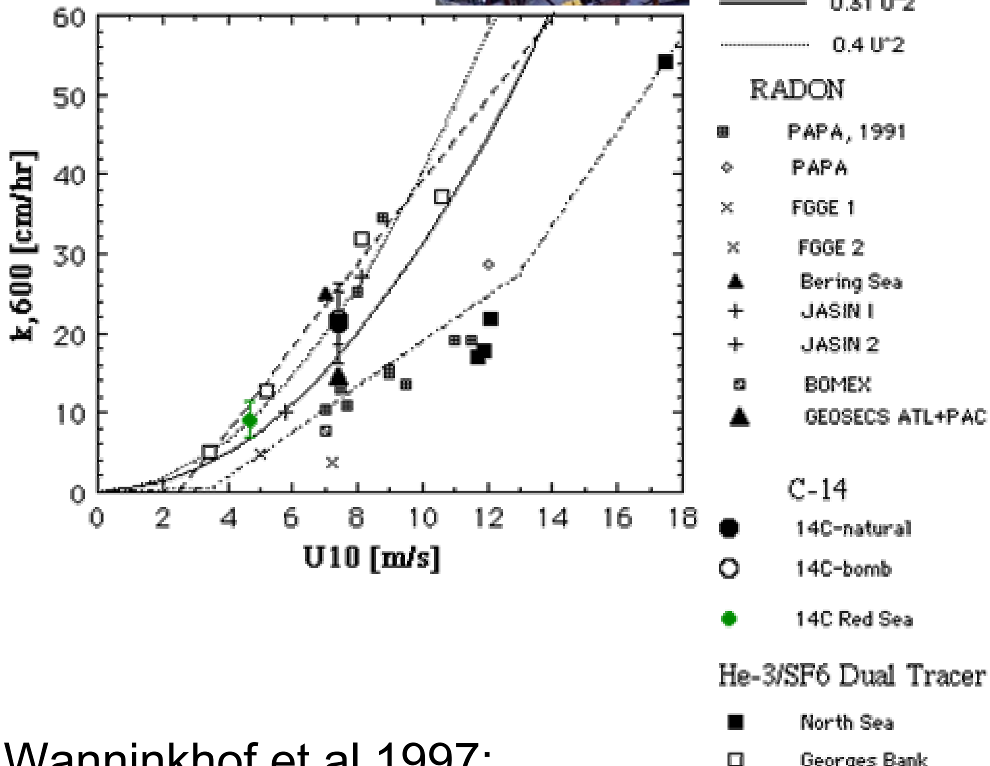
- $F = k_w (C_s – C_a)$
  - F: gas flux (mass per surface area per time)
  - C_s: gas concentration in bulk water (mass per volume)
  - C_a: gas concentration in bulk air (gas partial pressure x gas solubility)
  - k_w: gas transfer coefficient (length per time – a “piston velocity” or “gas transfer velocity”)

How would we measure k_w?

Techniques for measuring the gas transfer velocity

- Lab experiments in stirred tanks or in wind tunnels
- Tracer-release experiments in lakes or in the ocean: measure how fast the tracer gas disappears from the water
- ^{222}Rn (3.8 day half-life) deficiency in the surface ocean
- Eddy correlation measurements to directly estimate fluxes

Measured gas transfer velocities range widely…



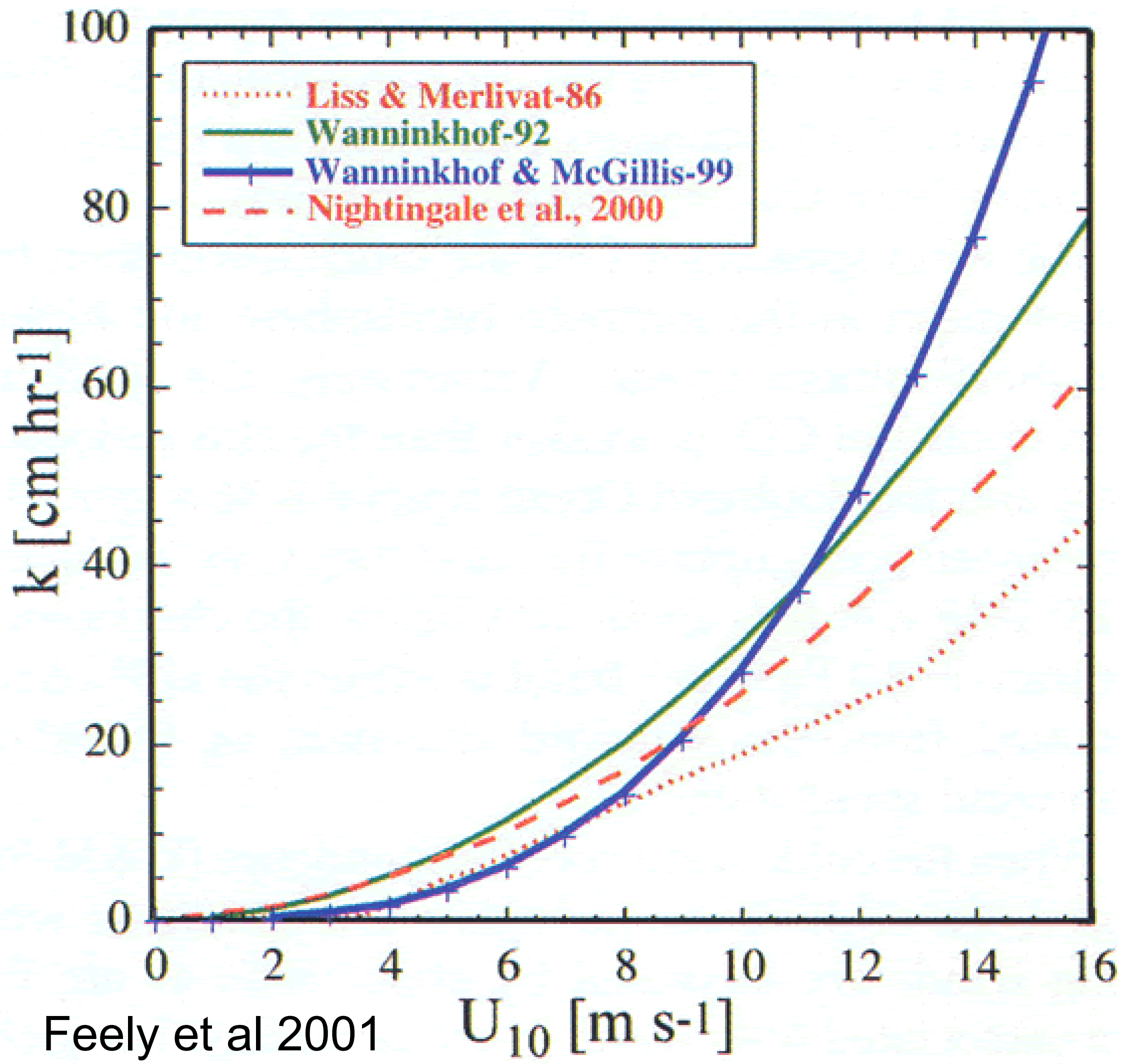
k_w is usually plotted against windspeed

- Idea: greater turbulence at higher winds
  - makes the stagnant boundary layer thinner
  - increases the effective surface area

  enhances gas exchange
- In fact, at the same windspeed, measured values differ by over a factor of 2
- What's a good average to use?

Wanninkhof et al 1997;
Pictures: WHOI

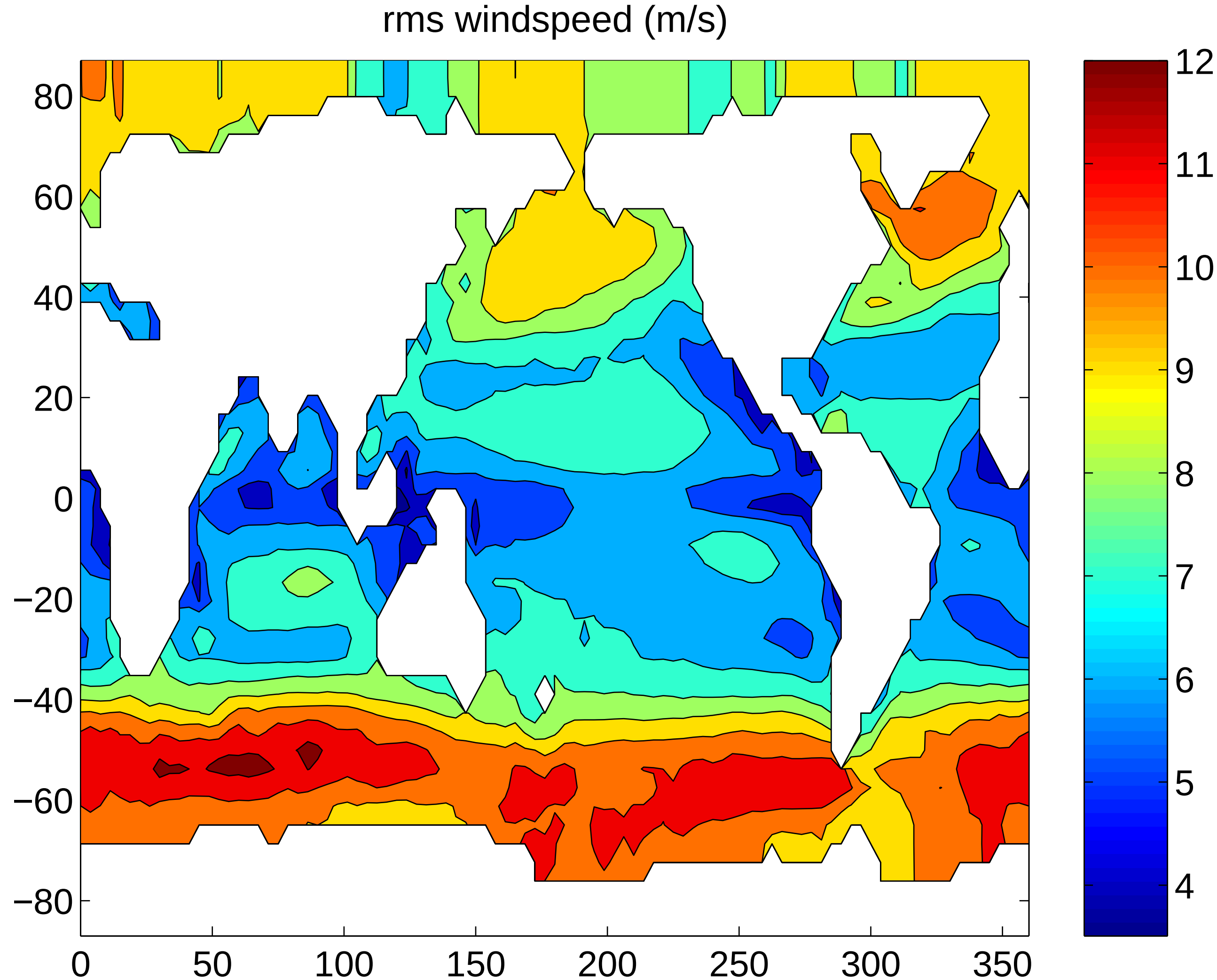
..as do parameterizations of k_w versus windspeed



Feely et al 2001

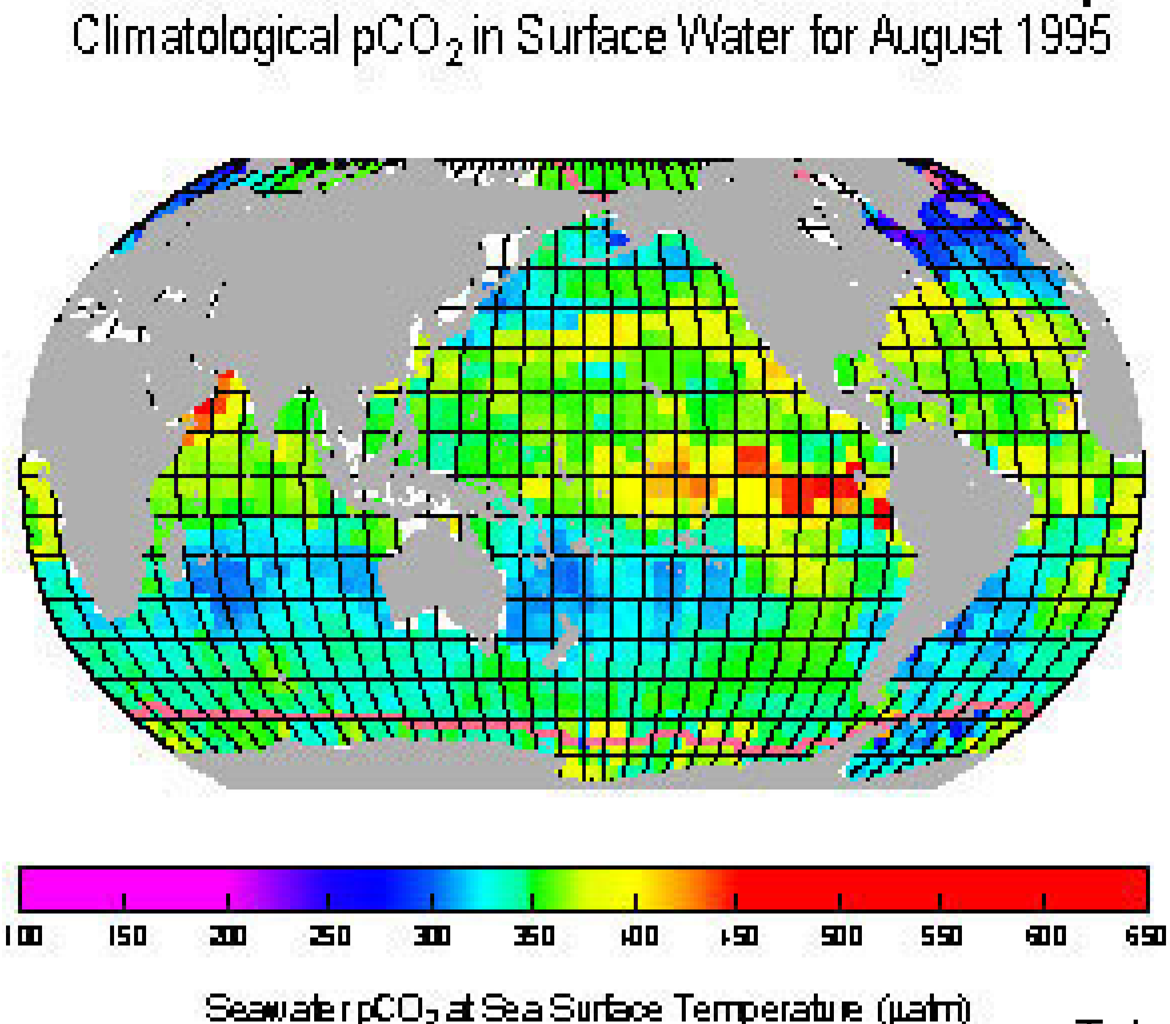
- Commonly used parameterizations assume k_w to increase with windspeed linearly with phase transitions (Liss & Merlivat 1986), quadratically (Wanninkhof 1992) or cubically (Wanninkhof & McGillis 1999)
- Large differences in implied k_w, particularly at high windspeeds (where there are few measurements)
  - *Are these formulations consistent with ocean tracer distributions?*

Because typical windspeed varies by latitude…



SSM/I climatological wind (Boutin and Etcheto 1996)

… the CO_2 flux inferred from sea-surface pCO_2 measurements depends on how k_w varies with windspeed



- Sea-surface pCO_2 is high in the tropics (→ flux out of ocean) and low in the midlatitudes (→ flux into ocean)

Takahashi et al 2002

My approach

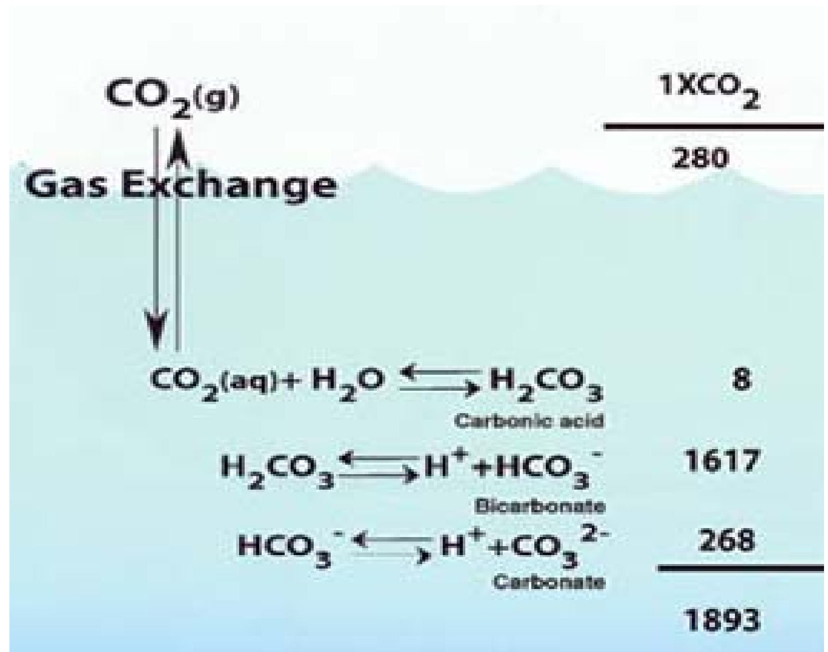
- Use recent perturbations in atmosphere carbon isotope (^{14}C and ^{13}C) levels to infer from the ocean uptake of the isotopic signal
  - The best-fit dependence of k_w on climatological windspeed globally, and
  - what the mean transfer velocity k_w must be by ocean region

- Directly applicable to ocean CO_2 uptake (no inter-gas solubility differences to worry about)

CO_2 isotope gradients are excellent tracers of air-sea gas exchange

O_2	14 d
N_2O	17 d
CFC-11	21 d
CO_2	295 d
C isotopes	2926 d

Sample equilibration times with the atmosphere of a perturbation in tracer concentration for a 50-m mixed layer



Ocean carbonate speciation (Feely et al 2001)

- Because the uncharged CO_2 that exchanges with the atmosphere is only ~1% of ocean carbon at any given time, air-sea gas exchange restores isotopic equilibrium very slowly
- Thus, the size of isotope disequilibria is uniquely sensitive to the gas transfer velocity k_w

Optimization scheme

- *Assume a power law dependence of k_w on windspeed*

$$k_w = \mathbf{<k>} \, (u^{\mathbf{n}}/<u^{\mathbf{n}}>) \, (Sc/660)^{-1/2},$$

(where u is windspeed, <> denotes a global average, and the Schmidt number Sc is included to normalize for differences in gas diffusivity)

and find the values of

<k>, *the global mean gas transfer velocity*

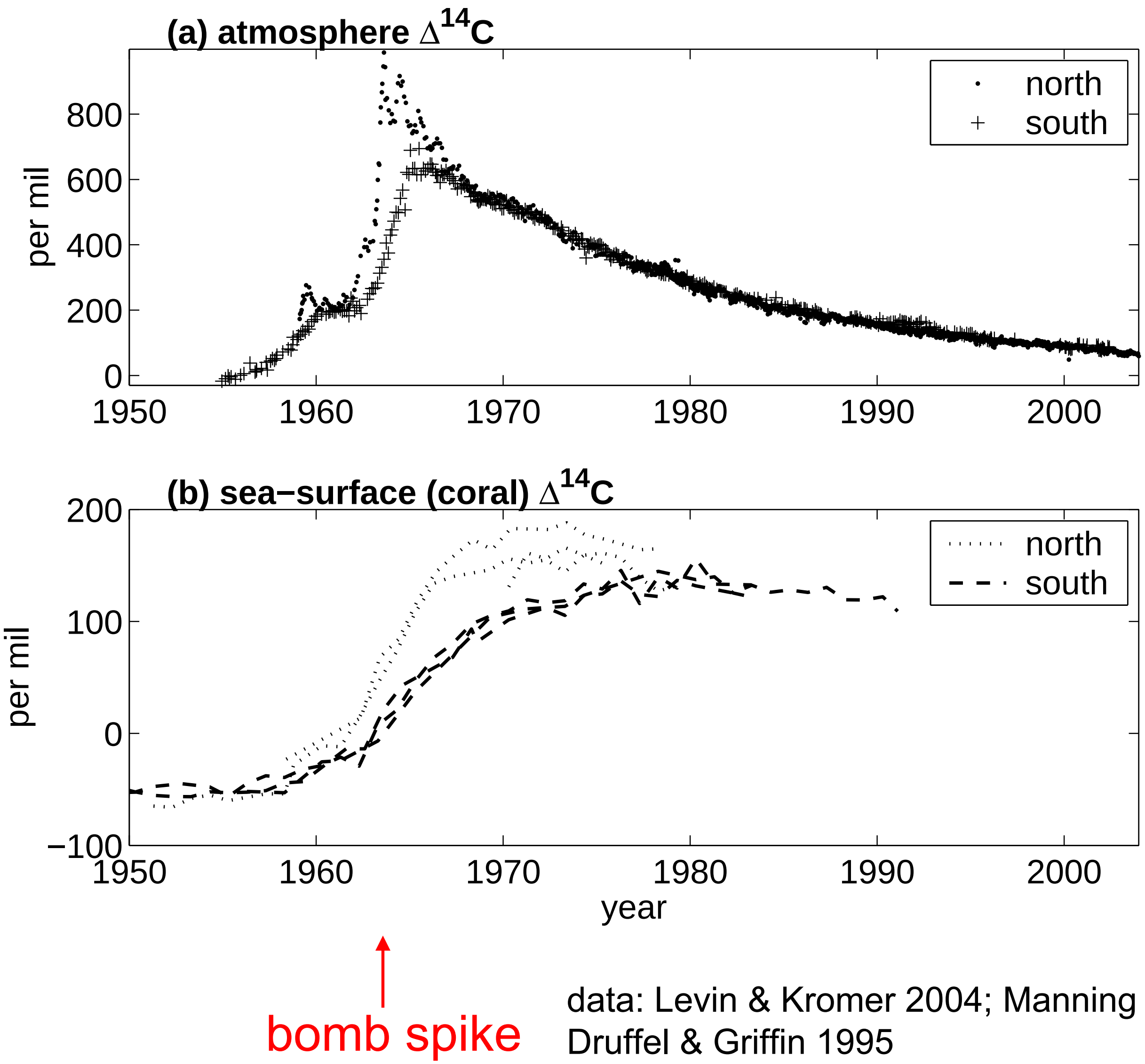
and

n, *the windspeed dependence exponent*

that best fit carbon isotope measurements

using an ocean transport model to relate measured interior concentrations to corresponding surface fluxes

Atmosphere and surface ocean ^{14}C since 1950



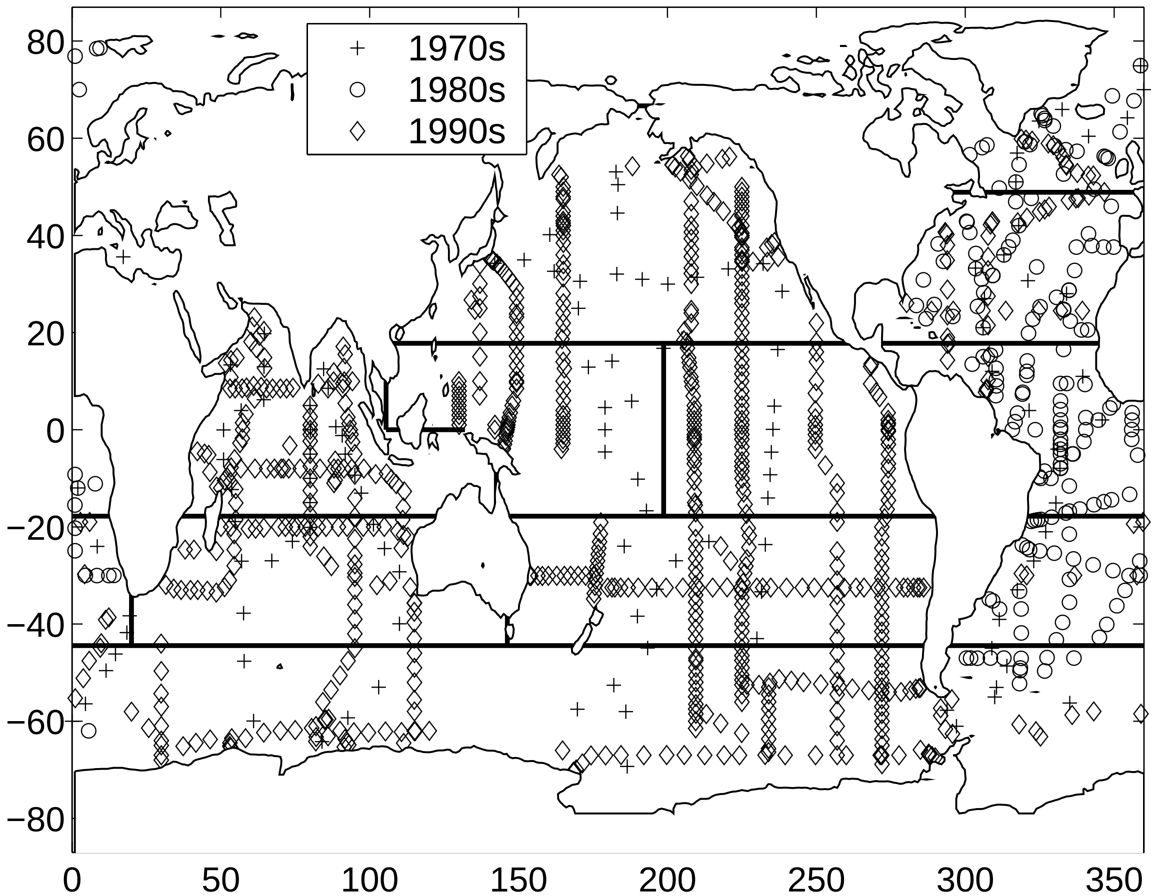
- Cosmogenic production balanced by decay (half-life: 5700 y)
- Massive production in nuclear tests ca. 1960 ("bomb ^{14}C")
- Through air-sea gas exchange, the ocean took up ~half of the bomb ^{14}C by the 1980s
- Notation – $\Delta^{14}C$: $^{14}C/^{12}C$ ratio relative to the preindustrial atmosphere

data: Levin & Kromer 2004; Manning et al 1990; Druffel 1987; Druffel 1989; Druffel & Griffin 1995

Ocean bomb ^{14}C uptake: previous work

- In the early 1980s, Broecker and Peng used 1970s measurements of ^{14}C in the ocean to estimate the global mean transfer velocity, <k>, at 21±3 cm/hr.
- This value of <k> has been used in most subsequent parameterizations of k_w (e.g. Wanninkhof 1992)
- Recent suggestions (Hesshaimer et al 1994; Peacock 2004) are that Broecker and Peng overestimated the ocean bomb ^{14}C inventory, so that the actual value of <k> might be lower by ~25%

My ^{14}C goals

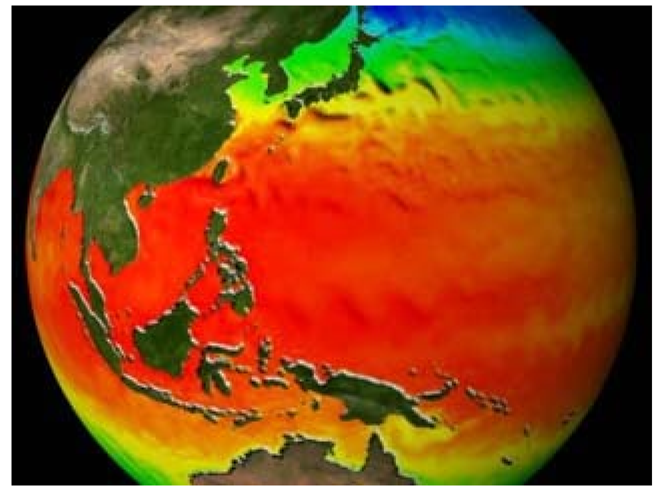


data: Key et al 2004

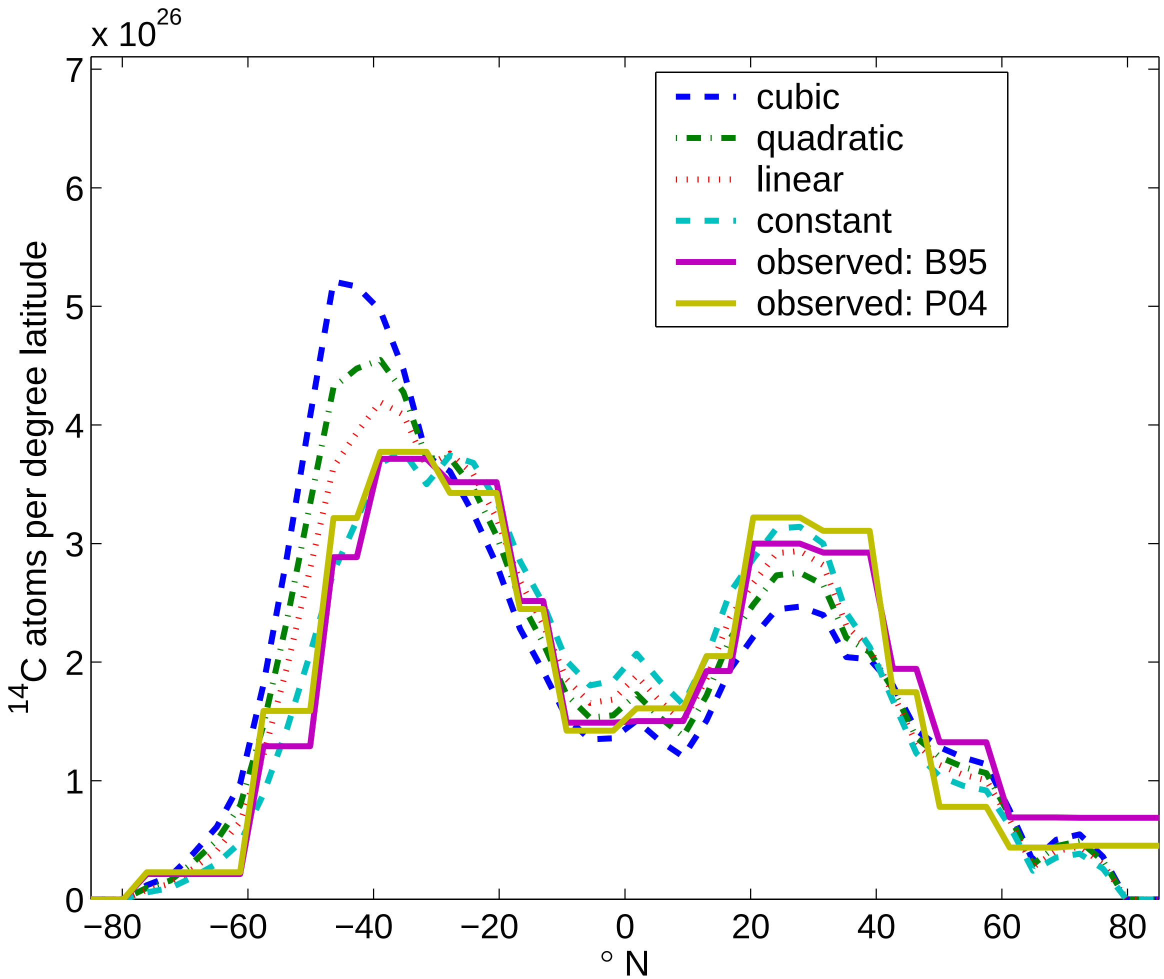
- From available bomb ^{14}C observations, re-estimate <k> and also estimate n
- The 1970s (GEOSECS) observations plus measurements from more recent cruises (WOCE)

Methods

- Use ~17,000 archived (GLODAP) 1970s-1990s oceanographic ^{14}C observations
- Simulate ocean uptake of bomb ^{14}C (transport fields from ECCO-1°), given the known atmospheric history, for different values of <k> and n
- Compare simulated with observed ^{14}C levels to find values of <k> and n that give the best fit



Results: simulated vs. observed bomb ^{14}C by latitude – 1970s

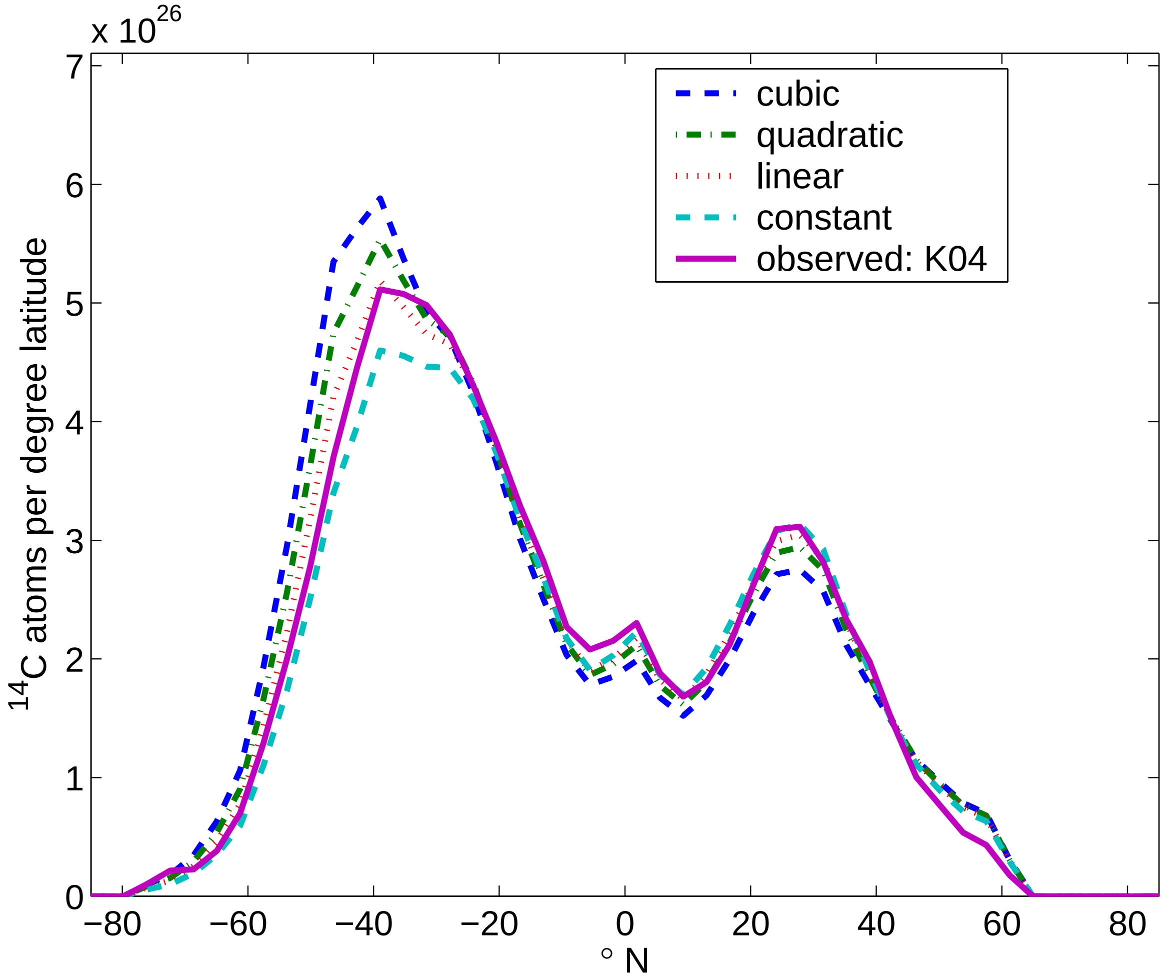


- For a given <k>, high n leads to more simulated uptake in the Southern Ocean, and less uptake near the Equator
- Observation-based inventories seem to favor low n (i.e. k_w increases slowly with windspeed)

Simulations for <k> = 21 cm/h and n = 3, 2, 1 or 0

Observation-based mapping (solid lines) from Broecker et al 1995; Peacock 2004

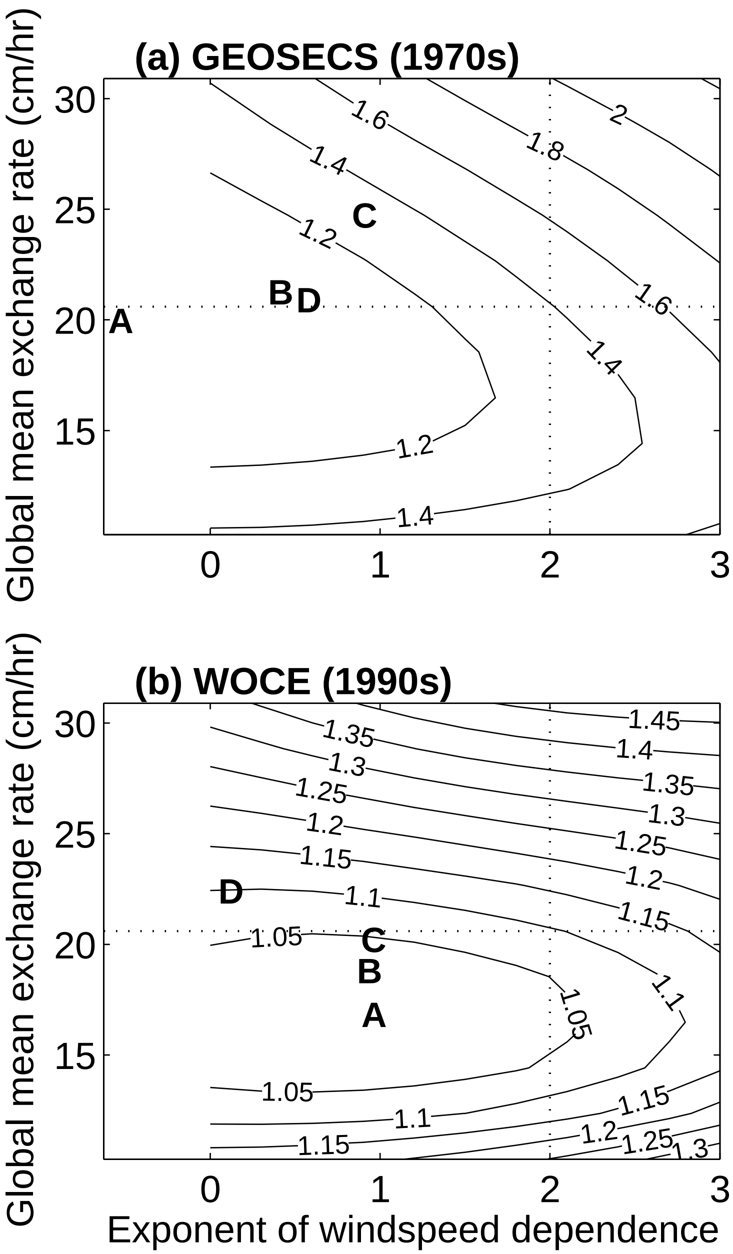
Results: simulated vs. observed bomb ^{14}C by latitude – 1990s



- Similar (weaker) dependence of the simulated latitudinal distribution on n
- The relatively low inventory observed in the Southern Ocean again seems to favor low n

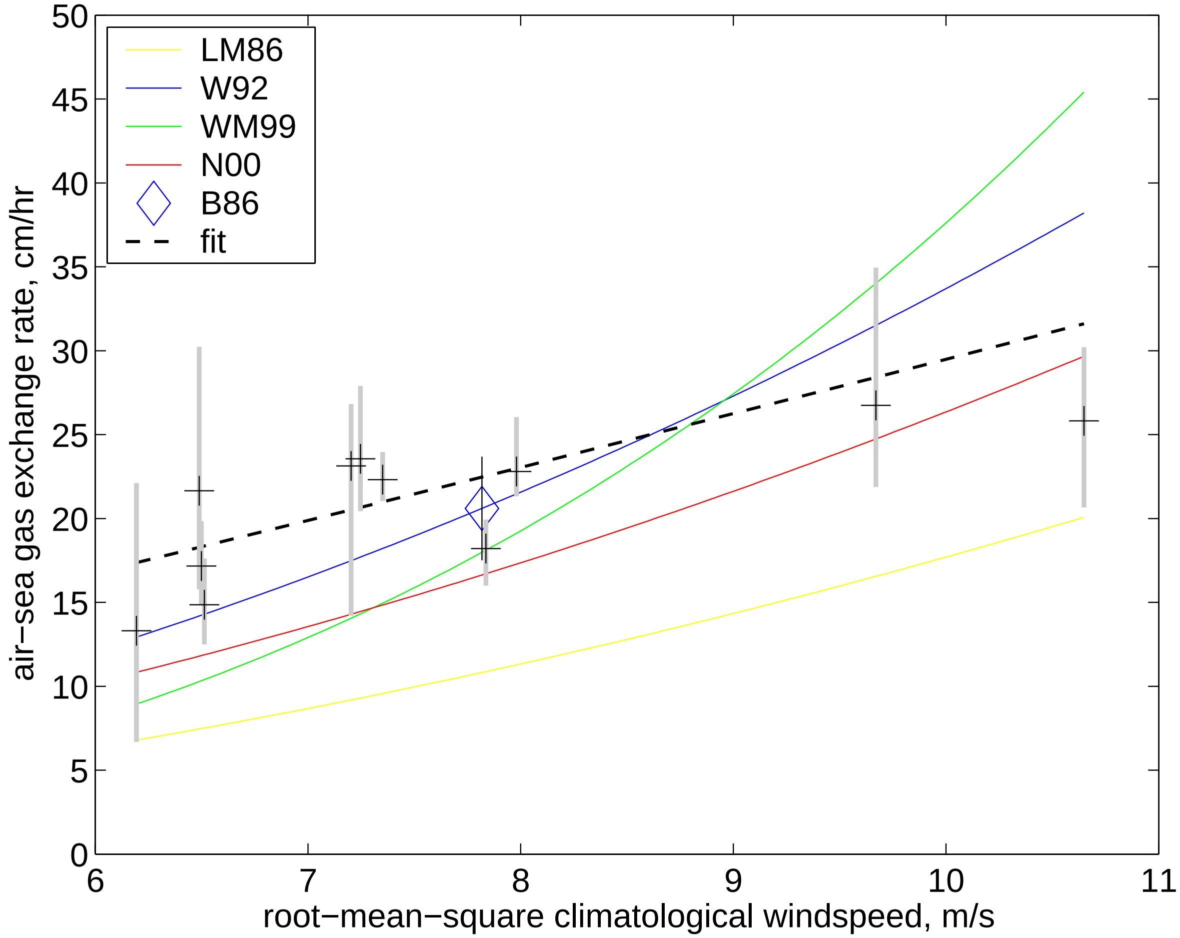
Simulations for <k> = 21 cm/h and n = 3, 2, 1 or 0
Observation-based mapping (solid lines) from Key et al 2004

Simulated-observed misfit as a function of <k> and n



- The minimum misfit between simulations and (1970s or 1990s) observations is obtained when <k> is close to 21 cm/hr and n is low (1 or below)
- The exact optimum <k> and n change depending on the misfit function formulation used (letters) , but a weak dependence on windspeed (low n) is consistently found

Optimum gas transfer velocities by region

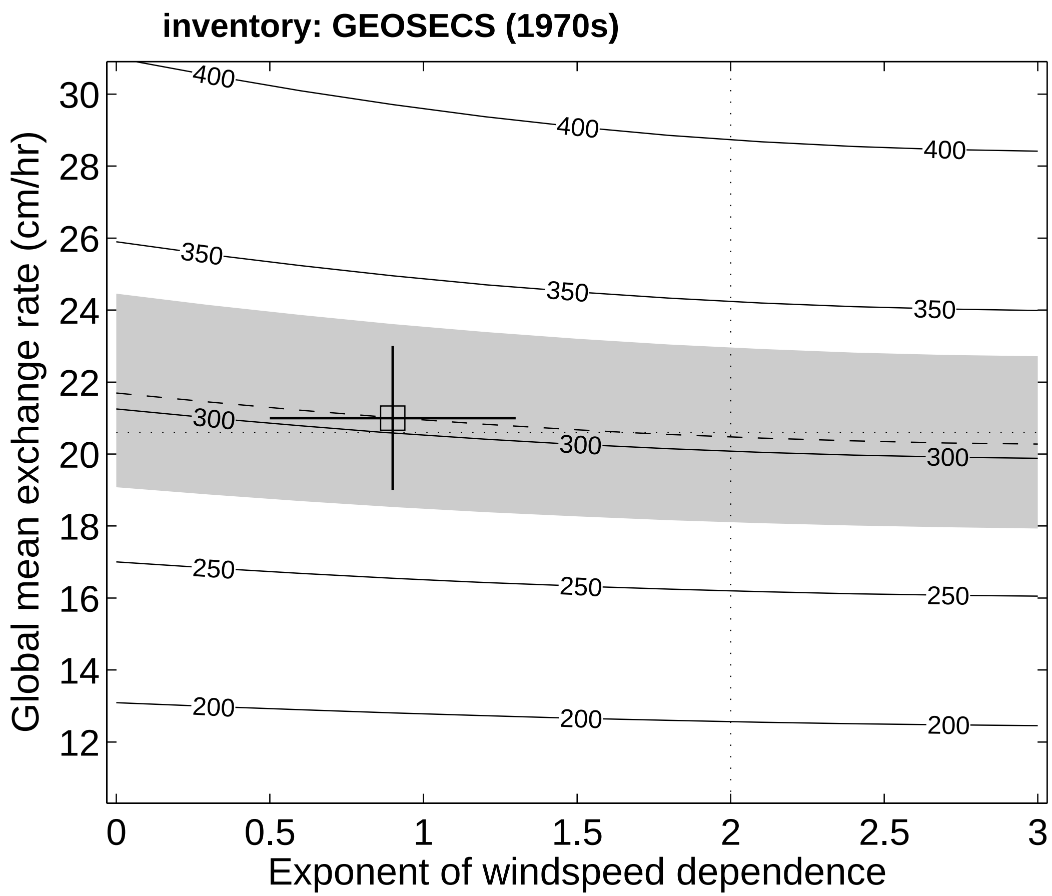


- As an alternative to fitting <k> and n globally, we estimated the air-sea gas exchange rate separately for each region, and fit <k> and n based on regional differences in windspeed
- Compared with most parameterizations (solid lines), we found that k_w is relatively higher in low-windspeed tropical ocean regions and lower in the high-windspeed Southern Ocean (crosses and gray bars)
- Overall, a roughly linear dependence on windspeed (n ≈ 1; dashed line)

^{14}C conclusions

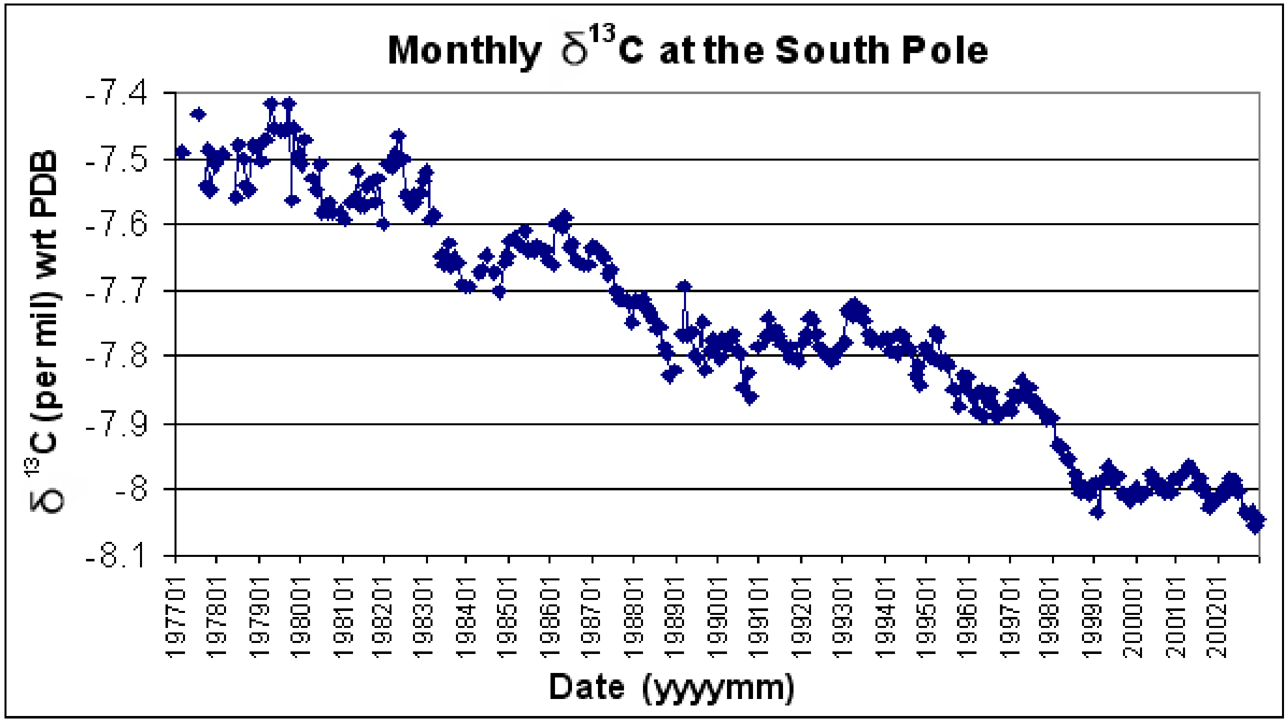
- The power law relationship with the air-sea gas transfer velocity k_w that best matches observations of ocean bomb ^{14}C uptake has
  - A global mean $<k>=21\pm2$ cm/hr, very similar to that found by Broecker and Peng
  - A windspeed dependence $n= 0.9\pm0.4$ (about linear), compared with 2-3 for quadratic or cubic dependences

Simulated mid-1970s ocean bomb ^{14}C inventory vs. <k> and n



- The total amount taken up depends only weakly on n, so is a good way to estimate <k>
- The simulated amount at the optimal <k> (square and error bars) supports the inventory estimated by Broecker and Peng (dashed line and gray shading)

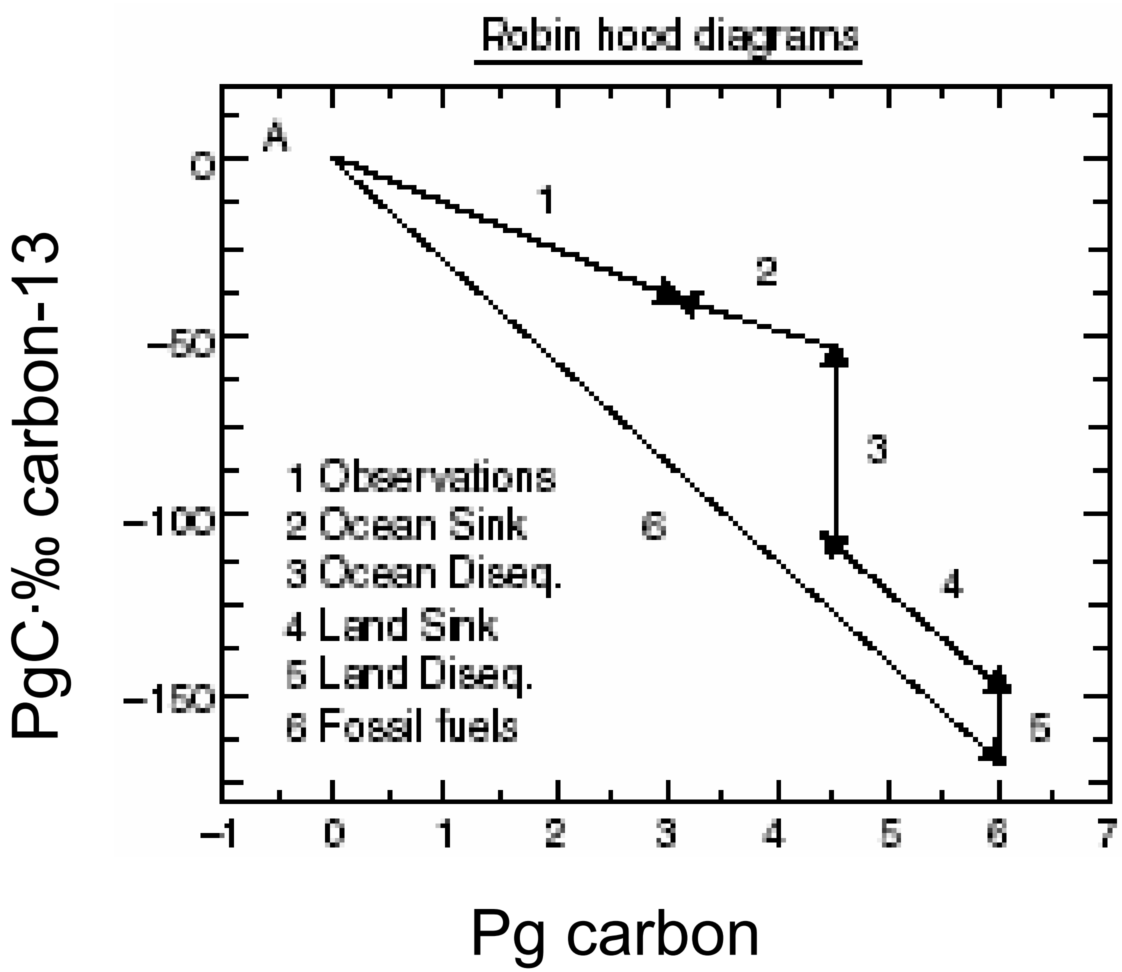
The ocean is now releasing ^{13}C to the atmosphere…



Scripps (CDIAC)

- Notation – $\delta^{13}C$: $^{13}C/^{12}C$ ratio relative to a carbonate standard
- The atmospheric $^{13}C/^{12}C$ is steadily declining because of the addition of fossil-fuel CO_2 with low $\delta^{13}C$; this fossil-fuel CO_2 is gradually entering the ocean

…and the amount can be estimated…



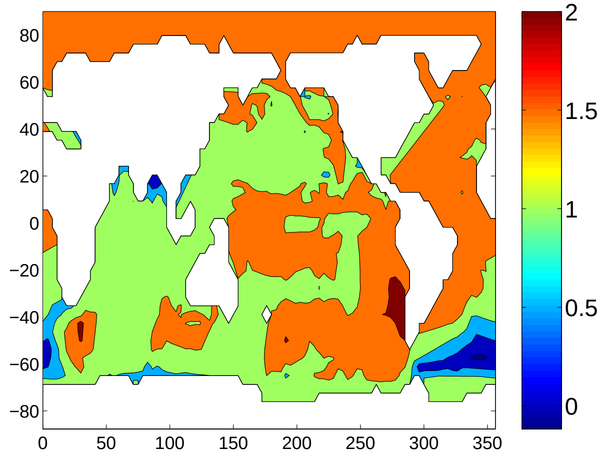
Randerson 2004

- Budget elements
  - the observed $\delta^{13}C$ atmospheric decline rate
  - biosphere disequilibrium flux (related to the carbon residence time)
  - fossil fuel emissions,
  - biosphere and ocean net carbon uptake
- We calculated that air-sea exchange must have brought 70±17 PgC·‰ of ^{13}C to the atmosphere in the mid-1990s, ~half the depletion attributable to fossil fuels

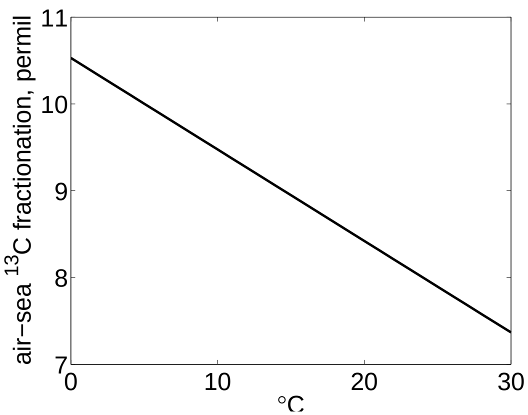
…but the air-sea δ^{13}C disequilibrium is of opposite sign at low vs. high latitudes

data: GLODAP (Key 2004)

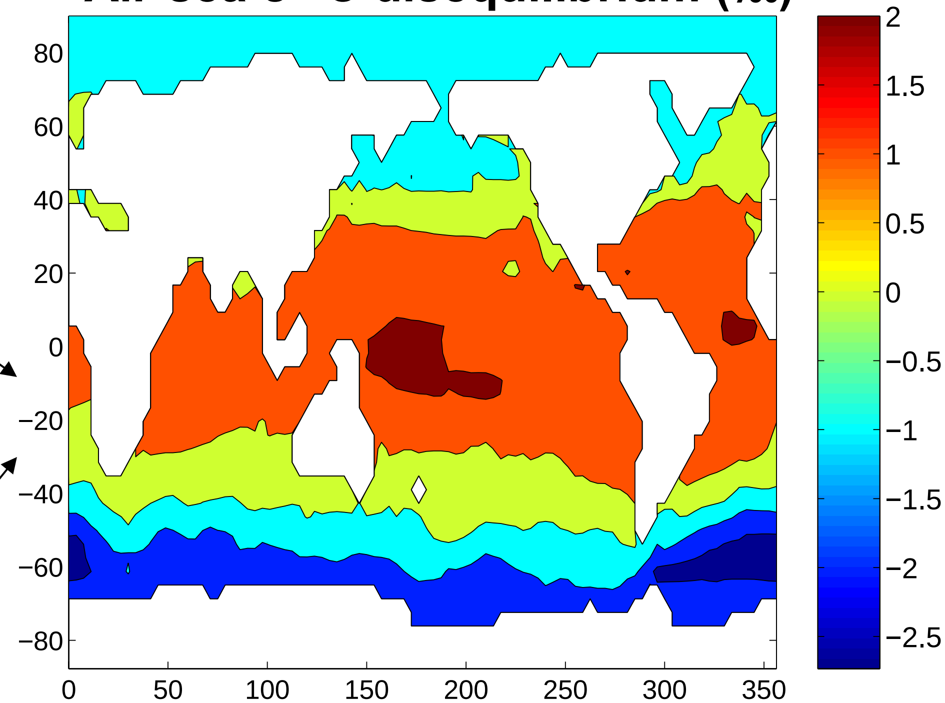
Sea-surface δ^{13}C (‰)



Temperature-dependent air-sea fractionation (‰)

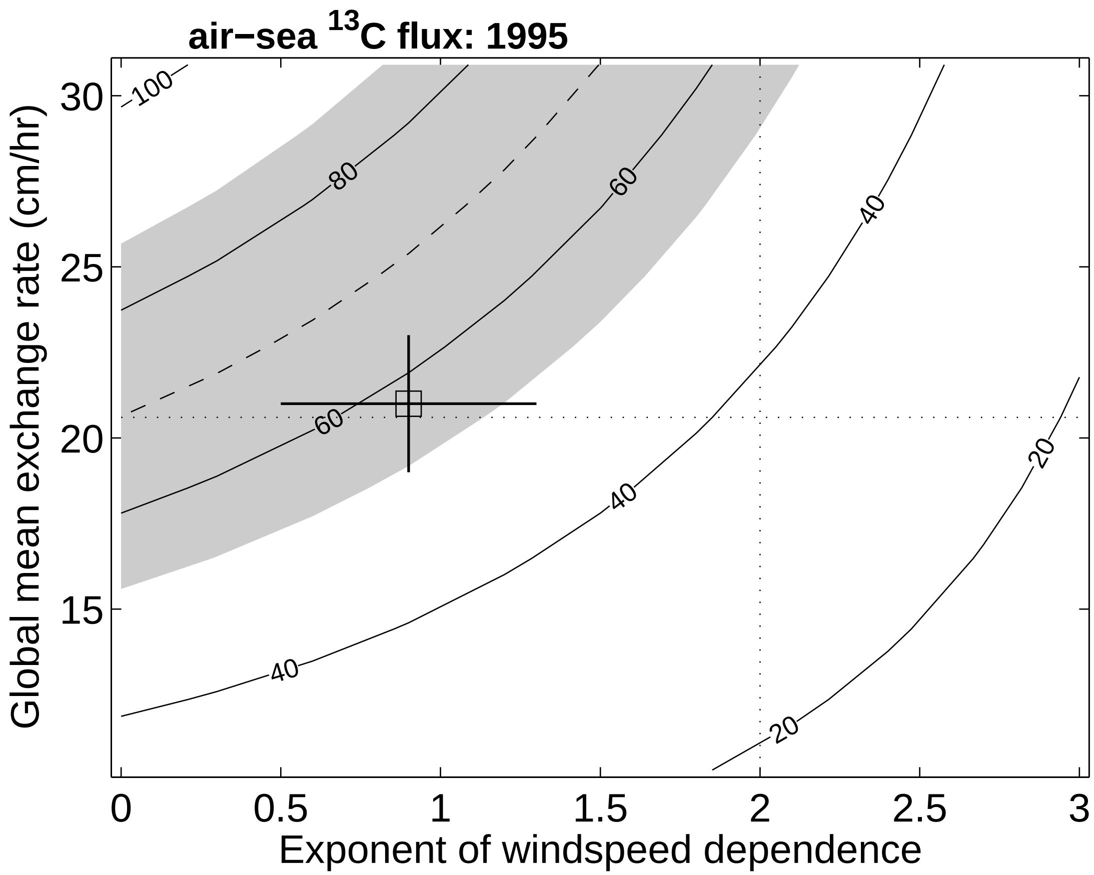


Air-sea δ^{13}C disequilibrium (‰)



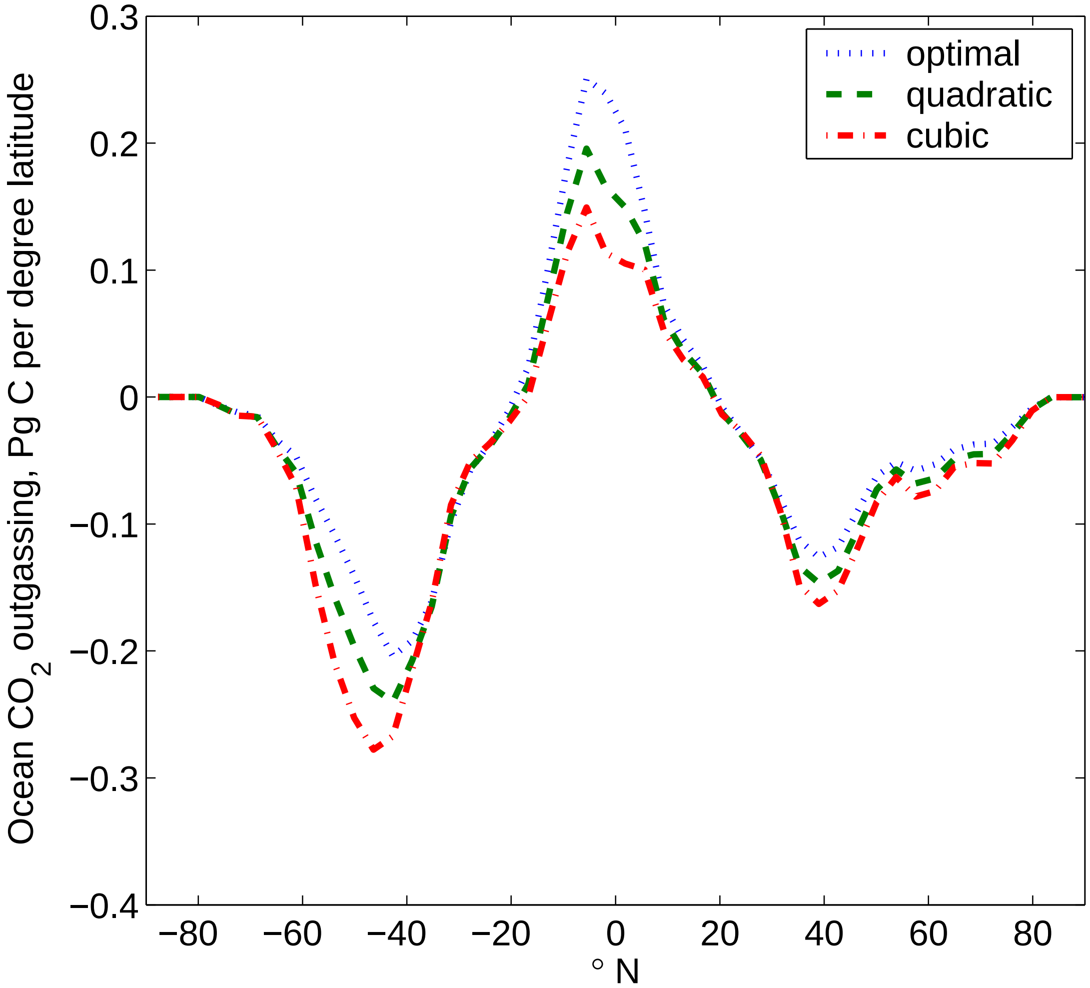
- Fractionation during photosynthesis + temperature-dependent fractionation within the carbonate system
- The dependence of k_w on windspeed must yield the inferred global total flux

Simulated 1990s air-sea $\delta^{13}C$ flux vs. <k> and n



- At high n, the ^{13}C flux into the Southern Ocean almost completely offsets the ^{13}C flux out of the tropics
- The observed rate of decline of atmospheric $\delta^{13}C$, combined with the known fossil fuel emissions, suggests a large ^{13}C flux out of the ocean (dashed line and gray shading), which requires n < 2

Implications for ocean CO_2 uptake



- We can apply the new parameterization of gas exchange to pCO_2 maps:
  - uptake by the Southern Ocean is lower than previously calculated (fitting inversion results better)
  - outgassing near the Equator is higher (reducing the required tropical land source)

Conclusions

- Combining ^{14}C and ^{13}C measurements constrains the mean air-sea gas transfer velocity and its windspeed dependence, averaged over large regions and several years
- The new parameterization promises to allow more confident utilization of ocean pCO_2 measurements to answer where carbon uptake is occurring and how it changes with time (e.g. tropical land vs. ocean)

Gas exchange questions to pursue

- Might a polynomial match the relationship of the gas transfer velocity with windspeed better than a power law (e.g. k_w is not expected to be zero in calm seas)?
- Can we identify regions that have anomalously high or low gas transfer velocities relative to their windspeed?
- Are there other easily measured quantities, such as mean square surface slope or fractional whitecap coverage, that predict gas transfer velocities better than windspeed?

- What are the implications for trace gas budgets?

Other agenda items

- Combine process studies and information on large-scale carbon fluxes into a framework for the effect of interannual climate variability and global warming on agricultural and forest productivity

- Understand the role of ocean circulation in $\Delta^{14}C$ variability (e.g. correlation with ENSO)

- Assimilate CO_2 satellite measurements to work out seasonal biosphere dynamics

Acknowledgements

- Betty and Gordon Moore Foundation and NASA for graduate fellowships
- UC Irvine's Earth System Modeling Facility (funded by NSF) for computing support


Is this a happy ending or what?
Zhonghua Yang
Tina Turner