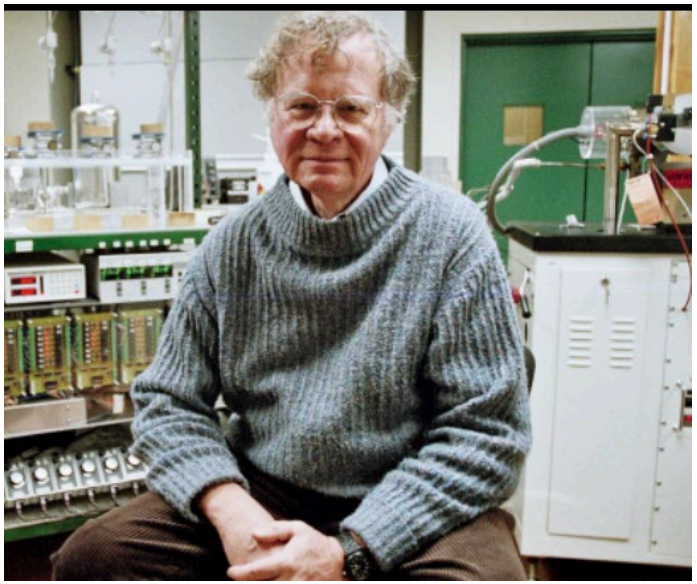
Global Estimates of Air-Sea CO_2 Fluxes

Contributions of Wallace Broecker and Taro Takahashi



1931-2019
"Intuitive thermodynamics"
"Solving puzzles"
"Don't sweat the details"

By:
Rik Wanninkhof
NOAA /AOML.
Miami

1930-2019
"Rigorous thermodynamics applied to natural systems"
"Solving equations"
"The devil is in the detail"

The 8th International Symposium on Gas Transfer at Water Surfaces

Location: Plymouth Marine Laboratory (and online)

Wednesday May 18, 16:40-17:10

Global Estimates of Air-Sea CO_2 Fluxes

The presentation is largely based on application of the bulk flux equation

$$F = k \Delta C = k K_o \Delta pCO_2$$

Outline of ideas that Wally Broecker and Taro Takahashi had a defining role:

- Determination of k (the piston velocity) from natural and man-made perturbations by using radio-isotopes
  a. Natural radio-activity ^{222}Rn, ^{14}C
  b. Results from nuclear bomb tests in the atmosphere "bomb ^{14}C"
- Estimation of ΔpCO_2
  Measurement
  Mapping
- Confounding issues and controversies (boundary layers, chemical enhancement, direct flux measurements)
- Putting it together (flux climatologies)

The piston velocity and film thickness

The gas transfer velocity is a proportionality factor or kinetic driving force relating air-water concentration differences of a gas to air-water fluxes:

$$F = k \Delta C = k \, Ko \, \Delta pCO_2$$

k = [length time^{-1}]

ΔC= concentration gradient between top and bottom of a liquid boundary layer for slightly soluble gases

Also referred to as:

Gas transfer velocity

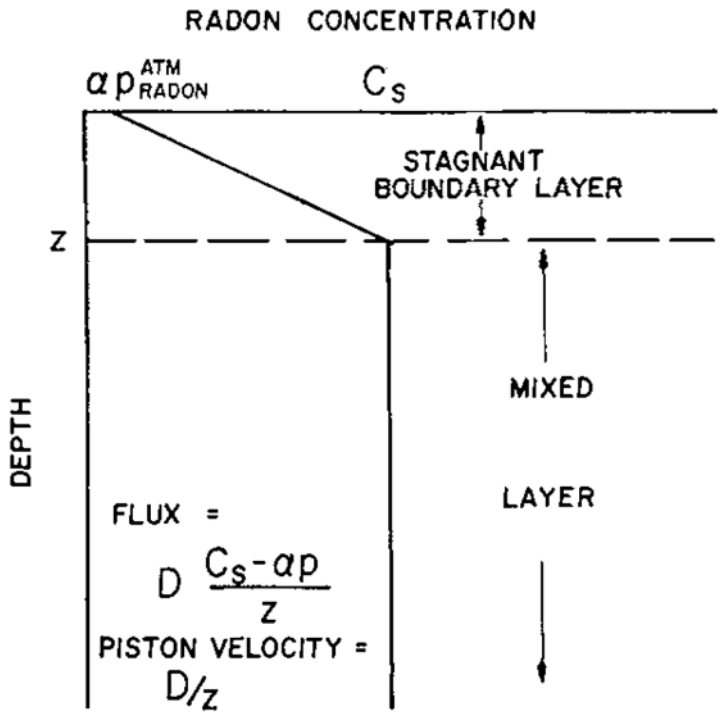
Gas exchange coefficient

Gas transfer coefficient

Reaeration coefficient

Impaction coefficient

Film thickness = molecular diffusion coefficient/ piston velocity (independent of gas)



Broecker and Peng 1974

Gas exchange estimates based on natural radioactivity

Natural ^{14}C: A global constraint

- For steady state: production of ^{14}C in atmosphere and invasion into ocean: invasion of ^{14}C = decay of ^{14}C
- ^{14}C Decay constant =8200 y: Provides a long term constraint
- Need to know average ^{14}C in ocean and atm
- Method "does not work anymore" because of contamination by ^{14}C by nuclear tests
- Gas exchange related to atmospheric residence time

Comparison With Exchange Rate Derived From Radiocarbon

The global mean gas exchange rate can be estimated from the distribution of natural or bomb-produced radiocarbon in the ocean. In the case of natural ^{14}C, the amount of radiocarbon entering the ocean should be balanced by the amount decaying in the ocean (under the steady state condition). The following equation expresses this balance:

$$E(A_{ATM} - A_{SO}) = H[\Sigma CO_2]_{MO} A_{MO} \lambda \quad (6)$$

$$E = D\frac{[CO_2]_{SO}}{z} \quad (7)$$

where E is the exchange rate of CO_2 across the sea surface (moles/m²/yr); A is the ratio of ^{14}C to ^{12}C in surface water at equilibrium with the atmosphere (ATM), surface ocean (SO), and mean ocean (MO); H the mean depth of the ocean; λ the decay constant of ^{14}C; and D the molecular diffusivity of CO_2. Comparing (6) and (7), we get

$$z = \frac{D[CO_2]_{SO}}{\lambda H[\Sigma CO_2]_{MO}} \frac{1 - A_{SO}/A_{ATM}}{A_{MO}/A_{ATM}} \quad (8)$$

Broecker and Peng 1974

Table 4. *Ocean atmosphere exchange rates based on the distribution of natural radiocarbon*

Reference	CO_2 Atm. res. time (yrs)	Equiv. film[a] thickness (microns)	k cm/hr
Arnold & Anderson (1957)	14	46	12.5
Craig (1957)	7 ± 3	23 ± 10	25
Revelle & Suess (1957)	~ 7	~ 23	25
Bolin & Erikson (1959)	5	17	33
Broecker (1963)	8[b]	25	23
Craig (1963)	15 ± 5	50 ± 17	11

[a] Assume D_{CO_2} at 20°C = 1.6×10^{-5} cm²/sec, $[CO_2]_{\text{mixed layer}} = 1 \times 10^{-5}$ M/l, Atmospheric CO_2 = 2.41×10^{18} g, Ocean area = 3.6×10^{18} cm².

[b] Equivalent atmospheric residence time calculated from original exchange rates.

Gas Exchange estimates based on natural radioactivity

^{222}Radon: local constraints

Deficit of (gaseous) ^{222}Rn (relative to (soluble) ^{226}Ra) in surface mixed layer directly related to the rate of gas loss from the surface mixed layer

- For steady state: Efflux = deficit of ^{222}Rn relative to ^{226}Ra (measured by alpha-decay counting)
- Provides a shorter term constraint ^{222}Rn Decay constant =5.5 days
- Need to know Rn deficit in surface mixed layer
- Average film thicknesses are ≈20 % greater than global averages natural and bomb ^{14}C (k lower)
- Works best with well defined mixed layers, intermediate and steady winds

$$F = h\,(A^{226}_{Ra} - A^{222}_{Rn}) \qquad 3\text{-}10$$

Using the stagnant film model, the flux of radon atoms can also be written as:

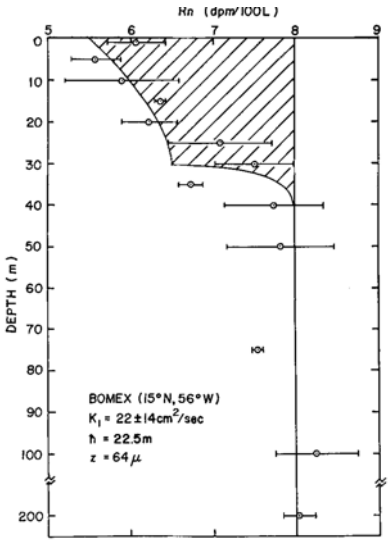
$$F = \frac{D^{222}_{Rn}\,[^{222}Rn]}{z} \qquad 3\text{-}11$$

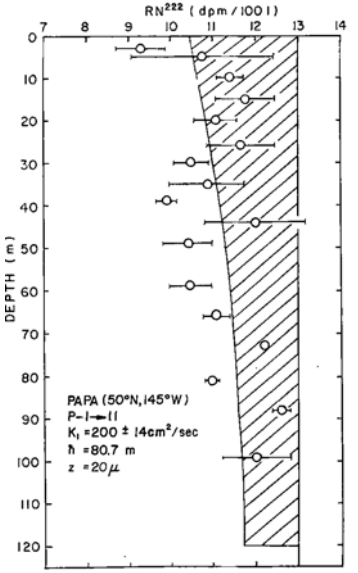
or

$$F = \frac{D^{222}_{Rn}\,A^{222}_{Rn}}{z\lambda^{222}_{Rn}} \qquad 3\text{-}12$$

Setting these two expressions for radon flux equal to one another (i.e., assuming that steady state exists for the radon concentration in surface water) and solving for z, we get:

$$z = \frac{D^{222}_{Rn}}{\lambda^{222}_{Rn}h}\;\frac{1}{\frac{A^{226}_{Ra}}{A^{222}_{Rn}} - 1} \qquad 3\text{-}13$$



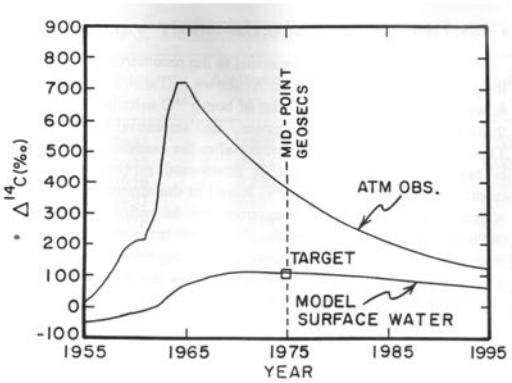


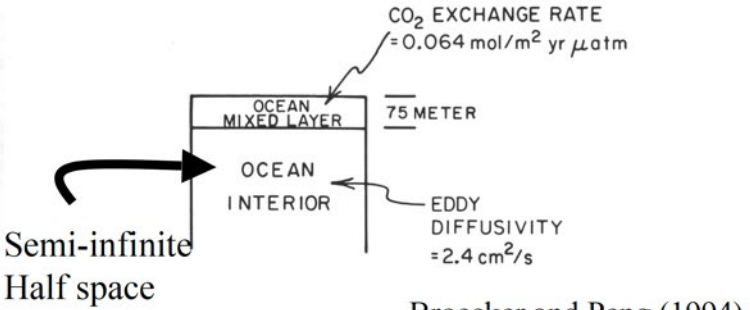
Broecker and Peng (1980)

Gas exchange estimates based on ^{14}C released into environment

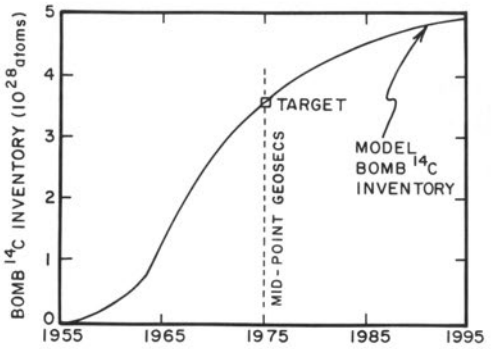
Estimates based on Bomb-^{14}C

- Flux = change in inventory of bomb ^{14}C in the ocean
- Global based estimate using simple model: k ^{14}C atm = ΔI
- Challenge: Need to separate the bomb ^{14}C inventory from the natural ^{14}C
- Improved estimates using numerical models and refined inventory estimates
- Updated estimates ≈ 20 % lower than original estimates





Broecker and Peng (1994)



Transfer velocity
k_{av} = 22 cm/hr
U_{10} = 7.4 m/s
If either ^{14}C inventory or global windspeed is incorrect, k changes

Using constraints and field studies

The effect of wind on film thickness/piston velocity

VOL. 79, NO. 12 JOURNAL OF GEOPHYSICAL RESEARCH APRIL 20, 1974

Surface Radon Measurements in the North Pacific Ocean Station Papa

T.-H. PENG, T. TAKAHASHI, AND W. S. BROECKER

Lamont-Doherty Geological Observatory, Columbia University, Palisades, New York 10964

Eleven surface radon profiles were measured at windy winter station Papa in the North Pacific Ocean during January–February 1972. A steady state two-layer vertical mixing model is proposed to explain the vertical distribution of radon. The vertical eddy diffusivity within the mixed layer at the Papa site was thus estimated to be about 200 cm²/s. The mean radon transfer velocity is estimated to be 3.6 m/d. The corresponding magnitude of the thickness of stagnant boundary film is 20 μ. Comparison of this exchange with that obtained previously in the trade wind dominated Bomex area appears to support the results of Kanwisher's (1963) laboratory experiments that show the rate of gas exchange across the air-water interface to be proportional to the square of wind speed.

1974: [^{222}Rn] results appear to support k proportional to the square of the wind speed
1979: "At this point we suggest caution in adopting a strong wind speed dependence"

Relationship Between Gas Exchange Rate and Wind Speed

Laboratory experiments by *Kanwisher* [1963] suggested that the gas exchange rate varies with the square of the wind velocity. Results by *Liss* [1973] and *Downing and Truesdale* [1955] confirm this relationship. Recently, *Broecker et al.* [1979] have challenged this result by showing through careful wind tunnel experiments a linear relationship between wind velocity and exchange rate.

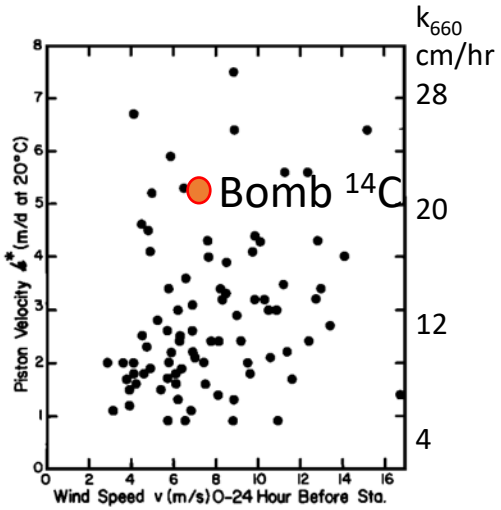


Fig. 12*a*. Plot of observed Geosecs piston velocity (normalized to 20°C) versus observed wind speed 0–24 hours before station.

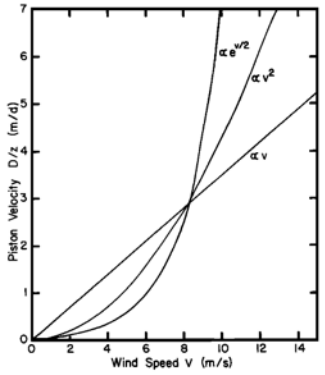


Fig. 11. Piston velocity as a function of wind velocity corresponding to various proposed relationships.

pected for windy leg 3. Thus at this point we suggest caution in adopting a strong wind velocity dependence for gas exchange. The failure to observe the relationship between the wind speed and radon exchange rate, which were determined by the automatic radon measurement, was also reported [*Roether and Kromer*, 1978].

Peng, Broecker, et al. 1979

Determining CO_2 fluxes from ΔpCO_2 and ^{222}Radon

Combining ΔpCO_2 and gas transfer to obtain fluxes

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 90, NO. C4, PAGES 7005–7022, JULY 20, 1985

Gas Exchange and CO_2 Flux in the Tropical Atlantic Ocean Determined from ^{222}Rn and pCO_2 Measurements

WILLIAM M. SMETHIE, JR., TARO TAKAHASHI, AND DAVID W. CHIPMAN

Lamont-Doherty Geological Observatory of Columbia University, Palisades, New York

JAMES R. LEDWELL

NASA Goddard Space Flight Center, Institute for Space Studies, New York, New York

Measurements of ^{222}Rn vertical profiles and pCO_2 in the surface water and the atmosphere were made simultaneously in the tropical Atlantic ocean as part of the TTO/TAS program. The gas exchange rate or piston velocity was determined from the ^{222}Rn profiles, and the ΔpCO_2 between the surface ocean and the atmosphere was determiend from the pCO_2 measurements. The net flux of CO_2 across the sea-air interface was calculated from these two data sets. The piston velocity ranged from 1.4 to 6.9 m/d and was correlated with wind speed. The slope of piston velocity versus wind speed was estimated to be between 0.3 and 1.1 (m/d)/(m/s). The ΔpCO_2 ranged from −35 μatm at 15°N, 55°W to +64 μatm at 5°S, 28°W, with the zero ΔpCO_2 isopleth located at about 10°N. The high ΔpCO_2 values can be explained by lateral advection of surface water from the east with heating and biological consumption of CO_2 and alkalinity during transit. The net flux of CO_2 was into the ocean north of 10°N latitude with values reaching a maximum of 1.4 mol m^{-2} yr^{-1} at 15°N, 50°W. South of 10°N, the net flux was out of the ocean, reaching a maximum value of 2.7 mol m^{-2} yr^{-1} at 8°S, 28°W. The average net flux from 10°N to 10°S was 1.3 mol m^{-2} yr^{-1} out of the ocean, which is equivalent to 0.15 gigatons of carbon per year if the flux determined applied throughout the year.

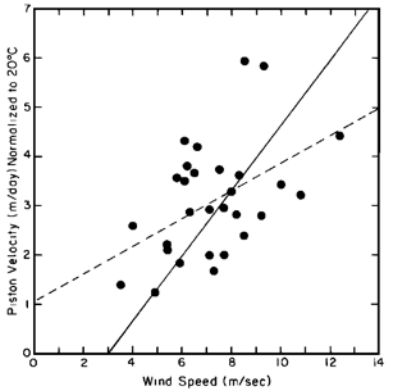


Fig. 9. Radon piston velocity (m/d) normalized to 20°C versus 24-hour mean shipboard wind speed (m/s). Dashed line is the linear regression line with U_0 free. Solid line is the linear regression line with U_0 fixed at 3 m/s.

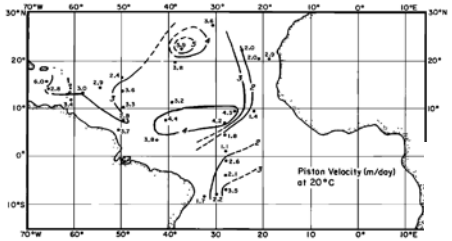


Fig. 4. Map of radon piston velocity (m/d) normalized to 20°C in the tropical Atlantic Ocean from expedition.

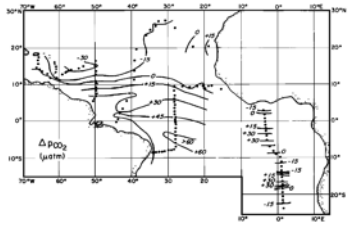


Fig. 5. Map of ΔpCO_2 (μatm) in the tropical Atlantic Ocean from the TTO/TAS (November 1982 to February 1983) and Long Lines (October 1983) expeditions.

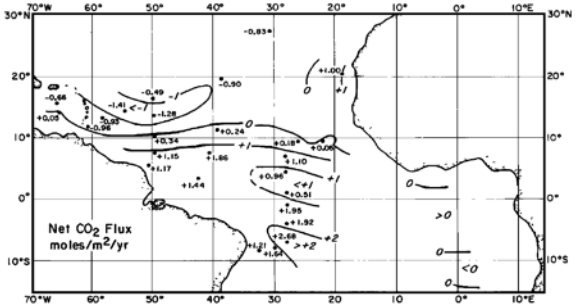


Fig. 6. Map of net CO_2 flux (mol m^{-2} yr^{-1}) in the tropical Atlantic Ocean. Negative values represent flux into the ocean, and positive values represent flux out of the ocean. This was calculated from the TTO/TAS data presented in Figures 4 and 5. For the Long Lines data the zero flux contour, which is defined by $\Delta pCO_2 = 0$, is shown.

From 10˚N to 10˚S the flux was 0.15 Gt C y^{-1} if flux was applied for full year

Sidebar: the skin effect

mine η. The values for ΔT thus computed range from 0.16 to 0.25°C, averaging 0.21°C. This temperature depression corresponds to a reduction of surface water pCO_2 by about 1% (or 3 to 4 μatm). Since Q_0 was not measured at our stations, the ΔpCO_2 values reported in Table 2 were not corrected for ΔT.

Estimates of ΔpCO_2

Measurement of air equilibrated with water (air phase measurement) and marine air

JOURNAL OF GEOPHYSICAL RESEARCH VOLUME 66, NO. 2 FEBRUARY 1961

Carbon Dioxide in the Atmosphere and in Atlantic Ocean Water[1]

TARO TAKAHASHI[2]

Lamont Geological Observatory, Columbia University
Palisades, New York

Abstract. An investigation of carbon dioxide partial pressures in the atmosphere and surface ocean conducted as part of a cooperative study under the general sponsorship of the International Geophysical Year is summarized. Results are given for about 470 hours of air analyses and 200 individual surface ocean water measurements made from 1957 to 1959 between 60°N and 58°S. Over the Atlantic Ocean, the atmospheric carbon dioxide concentration is found to average 316 ppm by volume and to be quite uniform except for a minor increase toward the equator. The total carbon dioxide in the earth's atmosphere is estimated to be 2.41 × 10^{18}g. In the equatorial region, the partial pressure of carbon dioxide appears to be higher in the surface water than in the atmosphere; in the higher latitudes it appears to be lower.

Measure XCO_2 requires T and P at equilibration for pCO_2

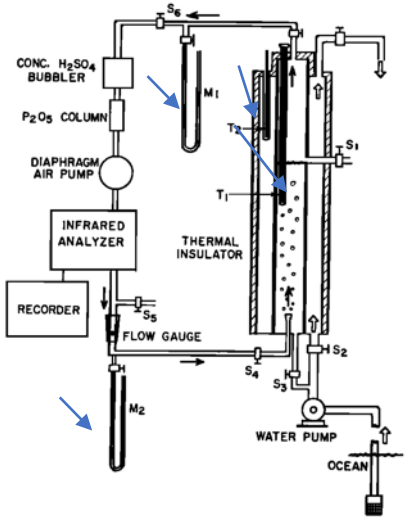


Fig. 3. The equilibrator for the measurement of the partial pressure of carbon dioxide i

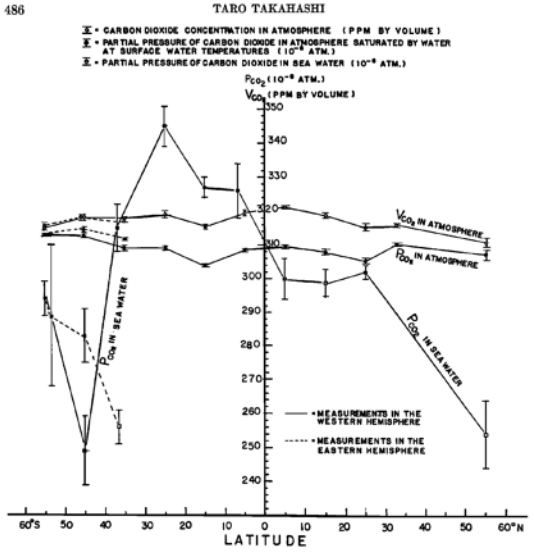


Fig. 6. Partial pressures of carbon dioxide in surface water and carbon dioxide concentrations in air over the North and South Atlantic Oceans.

Implications

The carbon dioxide partial pressure in sea water appears to control the carbon dioxide concentration in the oceanic atmosphere. As

Progression of pCO_{2w} estimates

Global constraints

- Between ≈1961- 1990 few underway surface water CO_2 measurements were performed by Takahashi's group, focusing instead on discrete pCO_2 measurements (better constrained)
- Skepticism (by WSB) if global fluxes could be determined through surface water measurements (due to small disequilibrium and uncertainty in k)

"The observed differences between the partial pressure of CO_2 in the surface waters of the Northern Hemisphere and the atmosphere are too small for the oceans to be the major sink of fossil fuel CO_2. Therefore, a large amount of the CO_2 is apparently absorbed on the continents by terrestrial ecosystems."

"E(moles of CO_2 m^{-2} $year^{-1}$ μatm^{-1})= 0.016 [W($m\ s^{-1}$) – 3] is 0.067 mol of $C0_2$ m^{-2} $year^{-1}$ μatm^{-1} which is consistent with the global mean $C0_2$ gas exchange rate of 20 mol of $C0_2$ m^2 $year^{-1}$, based on the distribution of $^{14}C0_2$ in the atmosphere a oceans

Observational Constraints on the Global Atmospheric CO_2 Budget
Pieter P. Tans; Inez Y. Fung; Taro Takahashi, 1990"

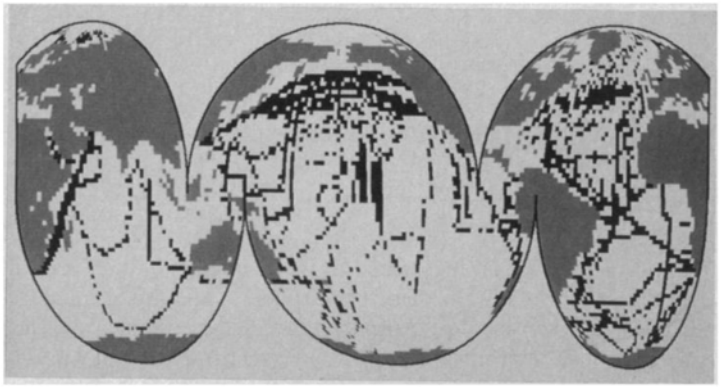
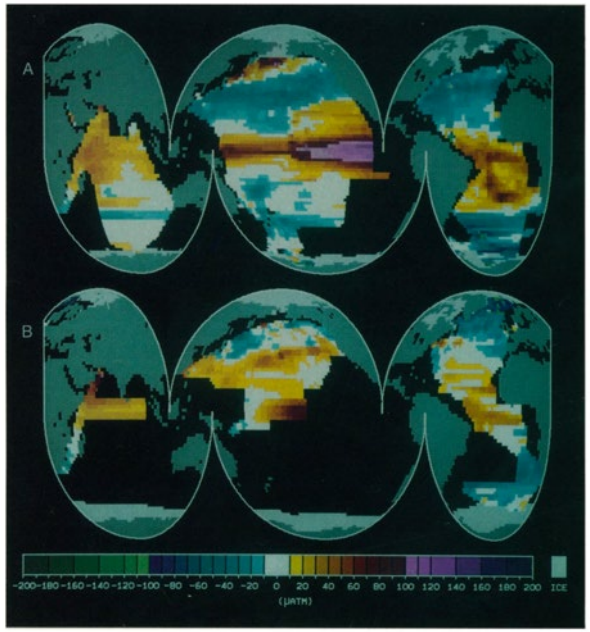


Fig. 2. The distribution of measurements of ΔpCO_2 since 1972. Where observations were made quasi-continuously, the values have been averaged over 2° intervals in longitude and latitude, and each of these intervals is represented by a single dot on the map.

Global air-sea CO_2 fluxes- The Takahashi pCO_2 climatology

The ocean fluxes were calculated from the seasonal ΔpCO_2 maps and monthly climatological winds. This analysis gave a net CO_2 uptake of 1.6 Gt of C per year (1 Gt equals 10^{15} g), which corresponds to about 30% of the current rate of fossil fuel emissions.

Tans, Fung and Takahashi, 1990



To extrapolate ΔpCO_2 values into areas where measurements were not available (black areas in Figure). The seawater pCO_2 was assumed to be a function of temperature alone. The following temperature coefficients were determined on the basis of the measurements made during various seasons and are assumed to be independent of seasons:

1.6% $^{\circ}C^{-1}$ in the western North Atlantic (10˚to 40˚N) and the south Indian Oceans (10˚S to 34˚S);
2.3% $^{\circ}C^{-1}$ in the South Atlantic (10˚S to 34˚S) and South Pacific (10˚S to 34˚S);
4.3% C^{-1} in the eastern North Pacific (10˚N to 34˚N, 84˚W to 154˚W);
1.2% $^{\circ}C^{-1}$ In the Southern Ocean (34˚S to 62˚S).
The climatological sea surface temperature data compiled by S. Levitus (1982)

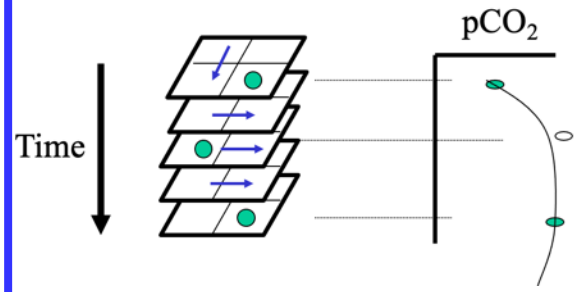
Global air-sea CO_2 fluxes- The Takahashi pCO_2 climatology

Interpolation and gap filling based on pCO_{2w} alone. No inferred dependencies

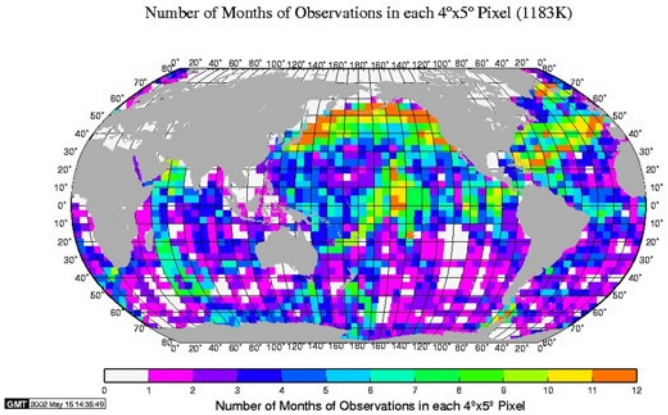
The climatology

1. Exclude all El-Nino years.
   - dramatic change in annual fluxes have been observed El-Nino periods based on SIO<-1.5 and SST changes.
2. Normalize pCO_2 single reference year (1995)
   - In warm waters (lat. <45) ΔpCO_2 remains constant
3. Interpolate data on to 4ºx 5ºx 365 day grid

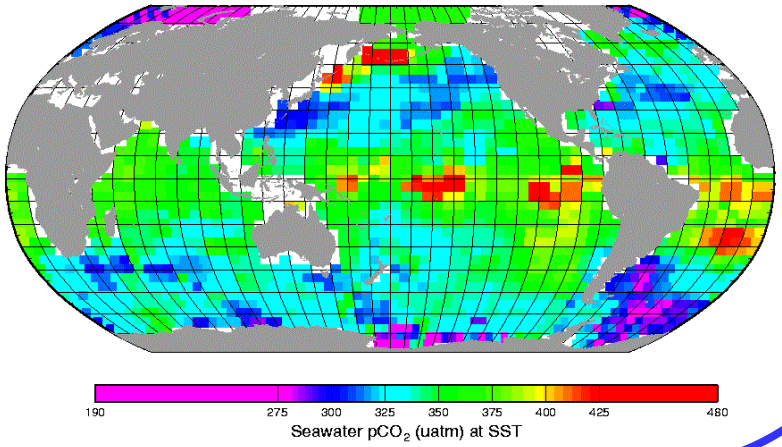
-finite differencing algorithm is used with a 2-D transport model from Toggwieler et al. (1989) to propagate the influence of observed data at one day time steps. Distribution is solved iteratively



Monthly distribution of pCO_2



(B) Climatological pCO_2 in Surface Water for February 1995



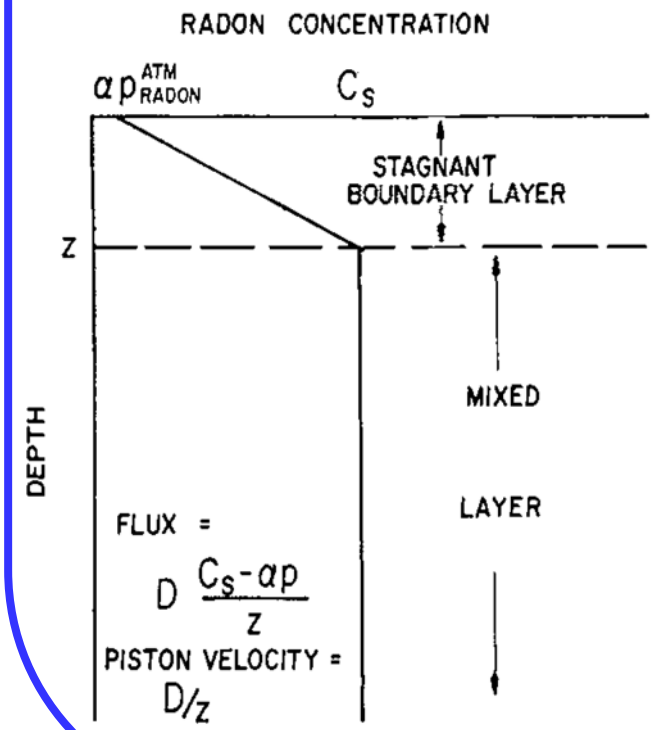
Controversies and unresolved issues with Broecker and Takahashi original works set the stage for improvements

- The stagnant film model was replaced by replacement model, eddy impingement model
- The chemical enhancement of CO_2 exchange remains a "dark horse" in air-sea CO_2 fluxes
- Direct CO_2 flux measurements can be done in nature

Gas transfer models

- Different models indicate a different dependence of gas transfer on the molecular diffusion coefficient ($D^{2/3}$ or $D^{1/2}$ instead of D)
- Practical aspect: Conversion of k between different gases and gases at different temperatures
- Impact: Conversion from k_{Radon} to k_{CO2} yields a 21 % increase in k instead of a 46 % increase and thus a greater discrepancy Rn and ^{14}C exchange

Stagnant film model: k D;



Film replacement model k= $D^{1/2}$

- **Film theory**:
  - $k_L \propto D$, δ - film thickness ⇒ $k_L = \frac{R_A'}{C^* - C} = \frac{D}{\delta}$
- **Penetration theory**:
  - $k_L \propto D^{1/2}$

Higbie model ⇒ $k_L = \frac{R_A'}{C^* - C} = 2\sqrt{\frac{D}{\pi t^*}}$

t^* - life of surface liquid element

Danckwerts model ⇒ $k_L = \frac{R_A'}{C^* - C} = \sqrt{Ds}$

s - average rate of surface renewal

Chemical enhancement

- Reaction between CO_2 and OH^-, H_20 will enhance exchange
- Theoretical and lab studies suggest little enhancement under average oceanic conditions

$$H_2O + CO_2 = H_2CO_3$$
$$OH^- + CO_2 = HCO_3^-$$

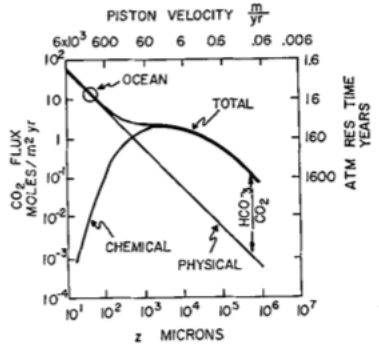


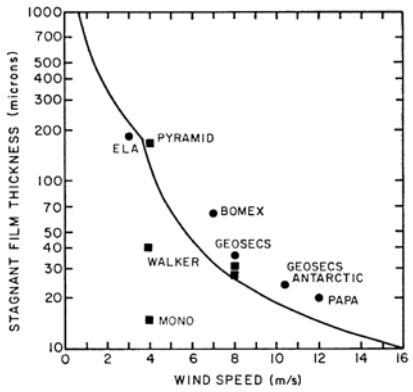
Fig. 2. Chemical enhancement of oceanic CO_2 gas exchange rate resulting from the chemical reaction

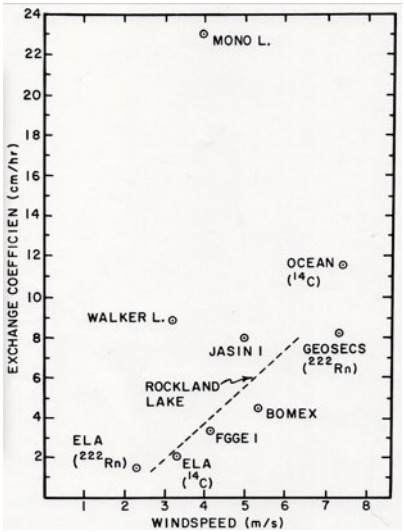
$$CO_2 + H_2O + CO_3^= \rightleftarrows 2HCO_3^-$$

For the range of film thicknesses observed in the ocean the effect is small. The calculations are based on the formulation by BOLIN (1960).

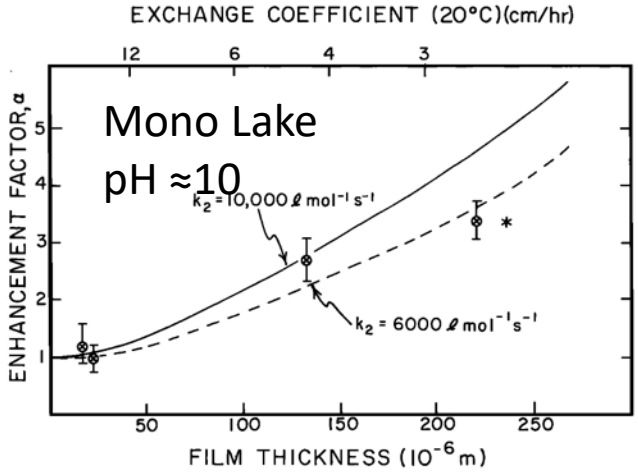
Broecker and Peng, 1974

Gas exchange rate measurements in natural systems





Peng and Broecker, 1980



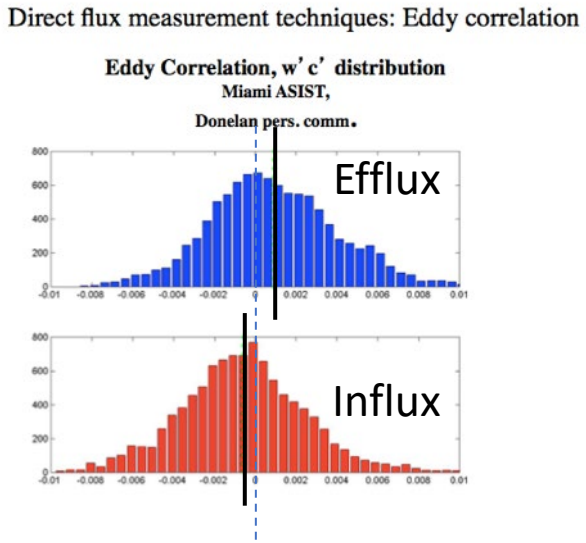
"Dark horse" explanation
Different exchange mechanisms or catalyst (carbonic anhydrase) could make chemical enhancement a contributor to air-sea exchange

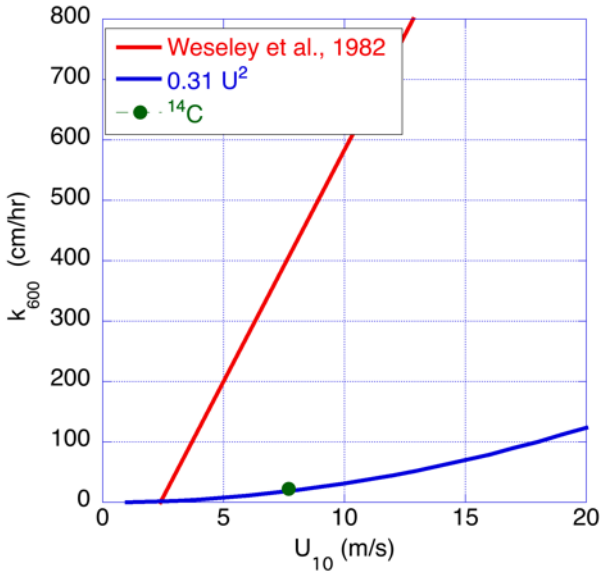
Direct Flux Measurements

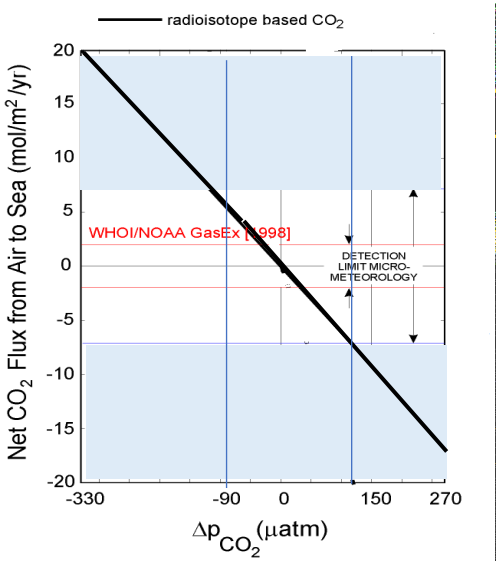
- Investigation of processes on shorter time scale
- Along with ΔpCO_2 we can use the direct Flux (at hourly scales) to determine k
- "It's the real thing"

Eddy correlation/co-variance technique: F = w' c' *Businger & Delaney, 1990*

Global air-sea CO_2 flux density≈ 0.5 mol m^{-2} yr^{-1}





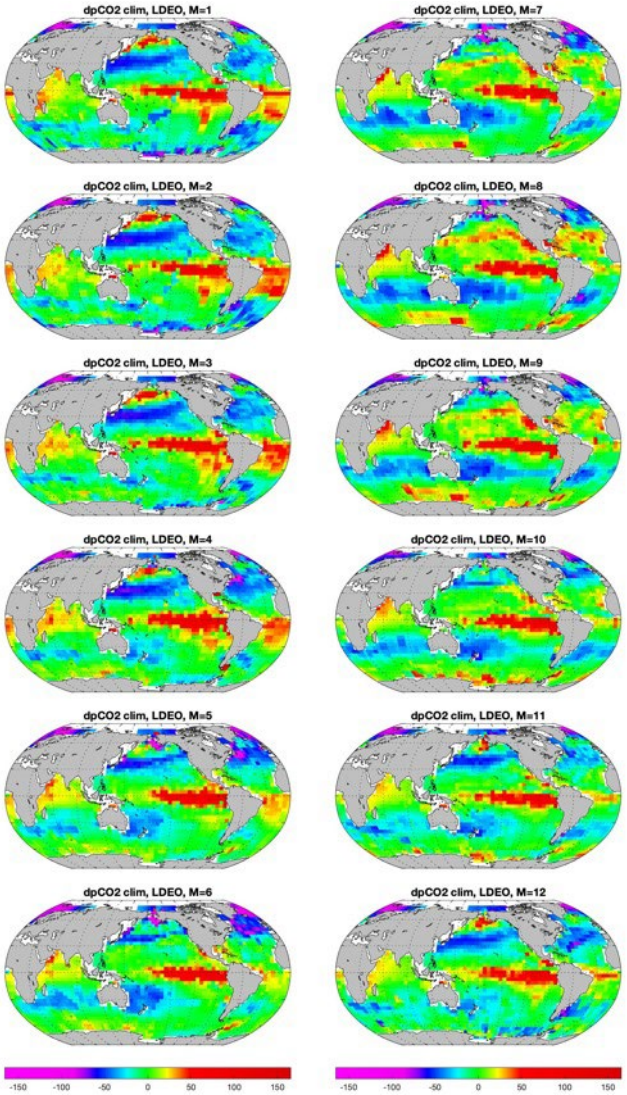


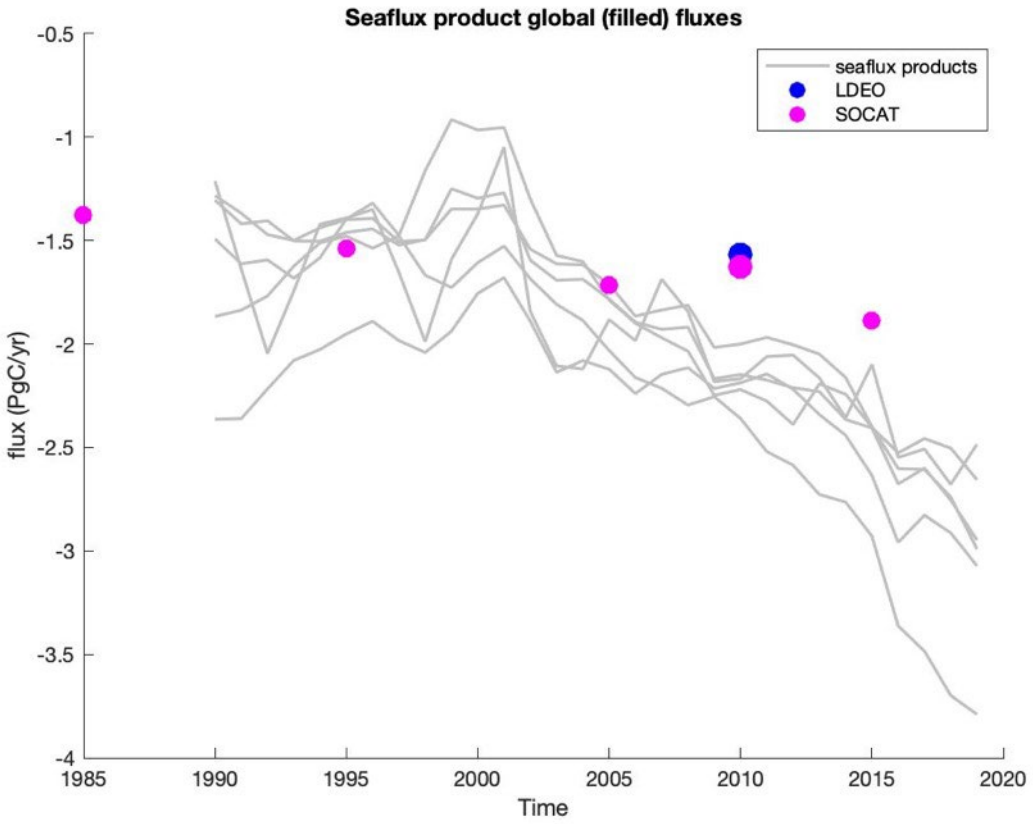
Net flux is small difference between
Large efflux + large influx

Broecker, W. S., Ledwell, J. R., Takahashi, T., Weiss, R., Merlivat, L., Memery, L., et al. (1986). Isotopic versus micrometeorologic ocean CO2 fluxes: A serious conflict. J. Geophys. Res., 91, 10517-10527.

The final chapter of the Takahashi pCO_2 climatology

The climatology centered on 2010 (Munro, Fay and others)





pCO_2 based flux climatologies provide uptakes lower than AI based methods.

Why???

Closing thought and take home messages

Wally Broecker and Taro Takahashi taught us to :

- Use geochemical horse sense
- Adherence to global constraints
- Study processes with opportunistic tracers and natural disequilibria

- [Re]-read the “classic” papers and books
- Recognize the assumptions that went into the conclusions
- Continue to build and improve upon their seminal works

References cited:

Broecker, W. S., & Walton, A. (1959). Radiocarbon from nuclear tests. *Science, 130*(3371), 309-314.

Broecker, W. S., & Peng, T.-H. (1974). Gas exchange rates between air and sea. *Tellus, 24*, 21-35.

Broecker, W. S., & Peng, T.-H. (1982). Tracers in the Sea. Palisades: Eldigio Press.

Broecker, W. S., Ledwell, J. R., Takahashi, T., Weiss, R., Merlivat, L., Memery, L., et al. (1986). Isotopic versus micrometeorologic ocean CO2 fluxes: A serious conflict. J. Geophys. Res., 91, 10517-10527.

Businger, J. A., & Delaney, A. C. (1990). Chemical sensor resolution required for measuring surface fluxes by three common micrometeorological techniques. J. of Atm. Chemistry, 19, 399-410.

Peng, T.-H., Takahashi, T., & Broecker, W. S. (1974). Surface radon measurements in the North Pacific Ocean station PAPA. *J. Geophys. Res., 79*, 1772-1780.

Peng, T.-H., Broecker, W. S., Mathieu, G. G., Li, Y. H., & Bainbridge, A. E. (1979). Radon evasion rates in the Atlantic and Pacific Oceans as determined during the GEOSECS program. J. Geophys. Res., 84, 2471-2486.

Smethie, W. M., Takahashi, T. T., Chipman, D. W., & Ledwell, J. R. (1985). Gas exchange and CO_2 flux in the tropical Atlantic Ocean determined from ^{222}Rn and pCO_2 measurements. *J. Geophys. Res., 90*, 7005-7022.

Takahashi, T. (1961). Carbon dioxide in the atmosphere and in Atlantic Ocean water. *J. of Geophys. Res., 66*, 477-494.

Takahashi, T., Kaiteris, P., & Broecker, W. S. (1976). A method for shipboard measurement of CO2 partial pressure in seawater*. *Earth and Planetary Science Letters, 32*, 451-457.

Takahashi, T., Broecker, W. S., & Werner, S. R. (1980). Carbonate chemistry of the surface waters of the world ocean. In *Isotope marine chemistry* (pp. 291-326). Tokyo: Uchida Rokakuho.

Takahashi, T., Feely, R. A., Weiss, R., Wanninkhof, R., Chipman, D. W., Sutherland, S. C., & Takahashi, T. T. (1997). Global air-sea flux of CO2: An estimate based on measurements of sea-air pCO2 difference. *Proc. Natl. Acad. Sci. USA, 94*, 8292-8299.

Takahashi, T., Sutherland, S. G., Sweeney, C., Poisson, A. P., Metzl, N., Tilbrook, B., et al. (2002). Global sea-air CO2 flux based on climatological surface ocean pCO2, and seasonal biological and temperature effects. *Deep-Sea Res. II, 49*, 1601-1622.

Takahashi, T., Sutherland, S. C., Wanninkhof, R., Sweeney, C., Feely, R. A., Chipman, D. W., et al. (2009). Climatological mean and decadal change in surface ocean pCO_2, and net sea-air CO_2 flux over the global oceans. *Deep -Sea Res II, 2009*, 554-577.

Tans, P. P., Fung, I. Y., & Takahashi, T. (1990). Observational constraints on the global atmospheric CO_2 budget. *Science 247*, 1431-1438.