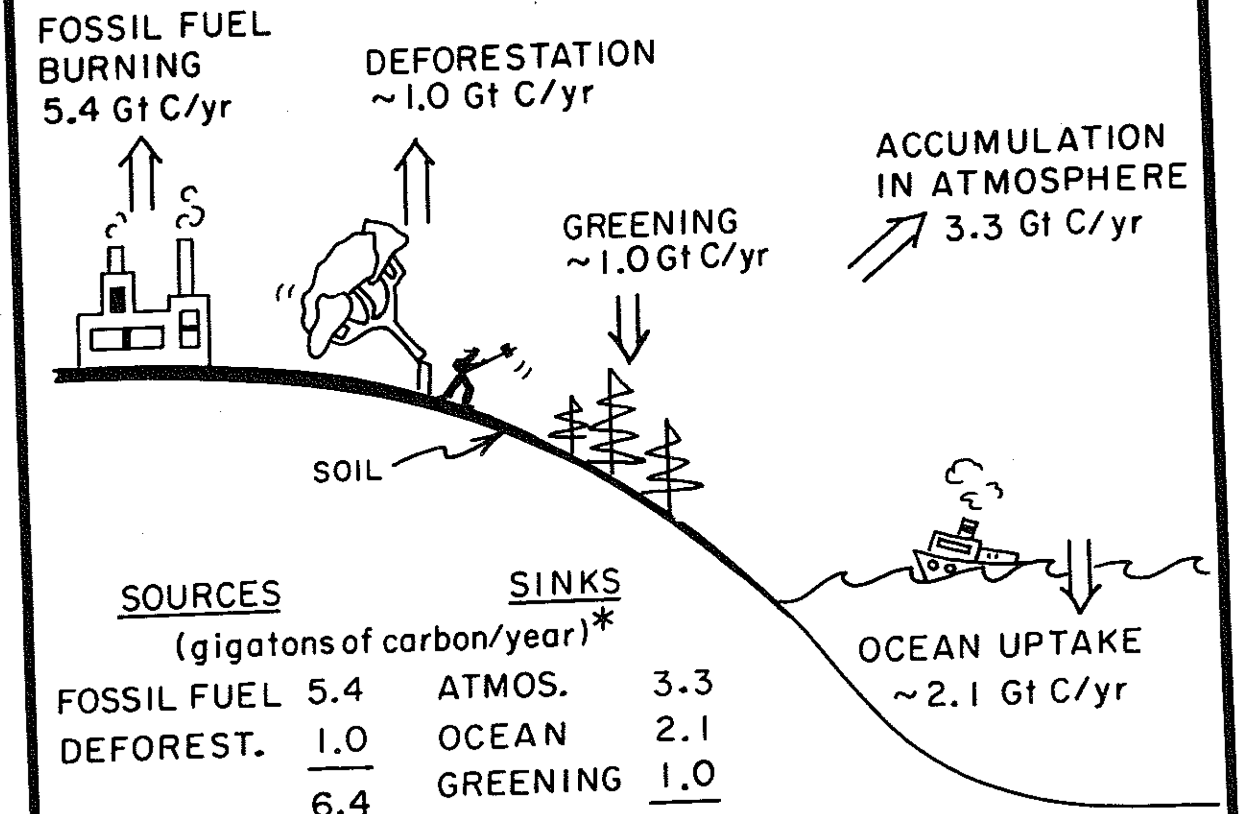
KEELING'S WORLD:

IS CO_2 GREENING THE EARTH?

This section's hero is Charles David Keeling. In the late 1950's, he had the wisdom to establish two stations for the continuous precise measurement of atmospheric carbon dioxide, one high on Hawaii's extinct volcano Mauna Loa and the other at the South Pole. The records from these stations provide the foundation upon which all studies of man's perturbation of the Earth's carbon cycle rest. Not only did Keeling have the foresight to establish these stations but also the tenacity to make sure that year in and year out they produced accurate results. Keeling took on this task as part of a career-long effort to understand the flux of CO_2 *gas through the atmosphere, into the ocean and into and out of the terrestrial biosphere. He was the first to realize the wealth of information contained in the spatial and seasonal texture of the atmosphere's* CO_2 *content. In addition to his direct scientific contribution, he fostered a secondary one. Son, Ralph, is doing for atmospheric* O_2 *all the kinds of things papa did for atmospheric* CO_2*.*

We know from the CO_2 content of air trapped in glacial ice that during the centuries prior to the Industrial Revolution, the CO_2 content of the Earth's atmosphere remained nearly constant. In other words, the world's carbon cycle remained close to steady state; removal of CO_2 through photosynthesis balanced its addition through respiration. But starting in the last century, activities of the expanding human population tipped the balance in favor of respiration. In response to the ever increasing demand for agricultural products, forests were cut and lands were tilled. These activities accelerated the oxidation of carbon stored in trees and in soil. In response to the expanding need for energy, engines fueled by coal, oil and natural gas proliferated. Organic matter which had survived for many tens of millions of years was recovered and burned. As a result of these activities, the CO_2 content of the atmosphere began a rise which steepened with each passing year. When this book was last revised, the CO_2 concentration was 30% higher than that for pre-industrial times

APROXIMATE EARTH CARBON BUDGET FOR THE 1980s; THE ANTHROPOGENIC PERTURBATION



(gigatons of carbon/year)*

SOURCES		SINKS	
FOSSIL FUEL	5.4	ATMOS.	3.3
DEFOREST.	1.0	OCEAN	2.1
		GREENING	1.0
	6.4		6.4

FRAC. TO ATMOS. $\frac{3.3}{6.4} = .52$

FRAC. TO SEA $\frac{2.1}{6.4} = .33$

FRAC. TO CONT. $\frac{1.0}{6.4} = .15$

$\overline{1.00}$

*1 Gt = 1×10^{15} grams
= 1×10^{9} tons

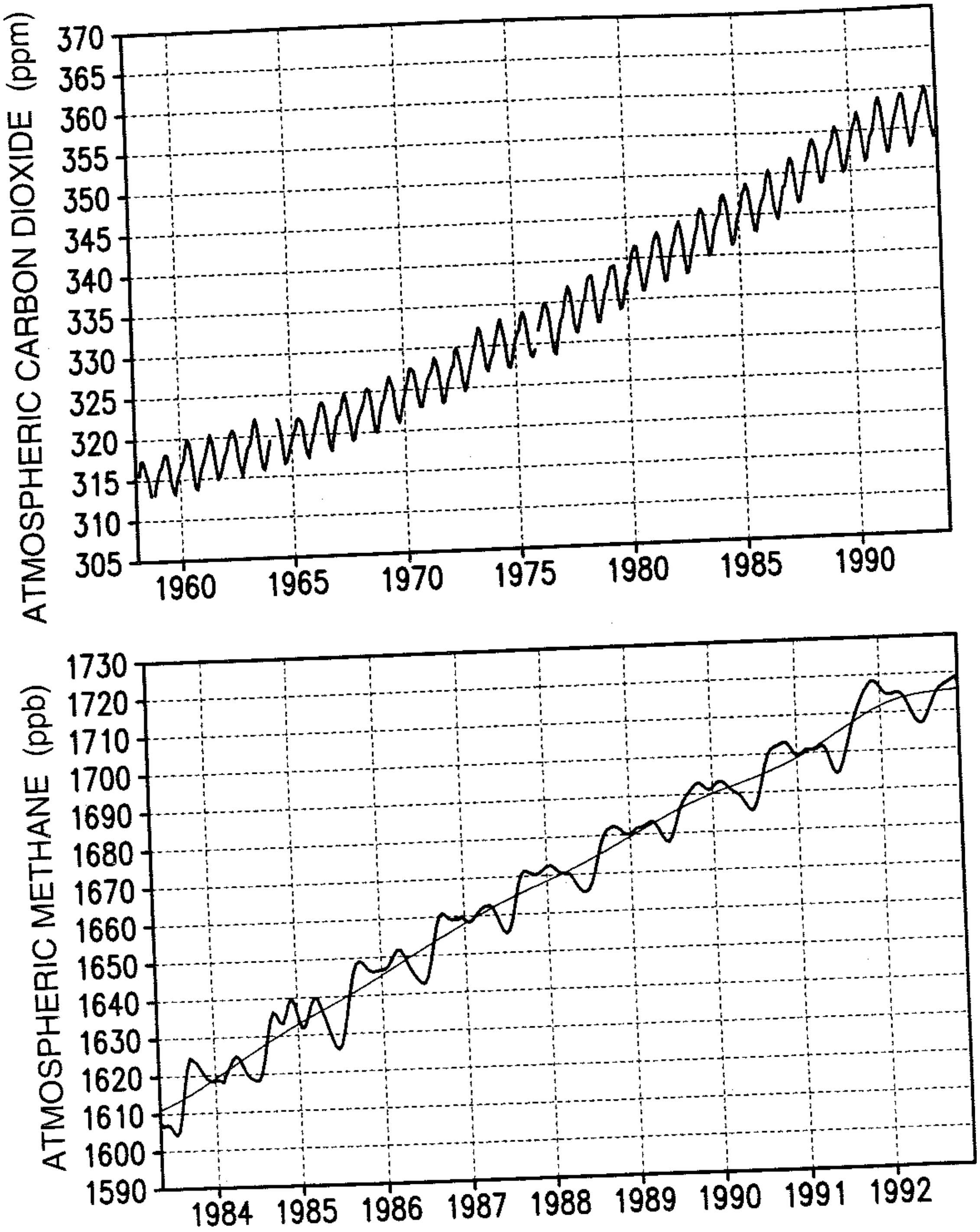
(in the year 1800, the CO_2 content was 280 parts per million ppm; as of 1997, it was 360 ppm).

This section's mystery is not that the atmosphere's CO_2 burden is rising, but rather that it is rising much more slowly than expected. The amount of excess CO_2 appearing in the atmosphere each year is just over one half that produced by fossil fuel burning. Nearly fifty percent has disappeared! The mismatch between CO_2 production and CO_2 buildup becomes even larger when the amount of CO_2 released as the result of forestry is taken into account. Although the magnitude of this activity remains poorly documented, during the last decade or so, an amount of CO_2 averaging about 25% that from coal, oil, and natural gas was released as the result of forest cutting. When this biosphere-derived CO_2 is included as a source term, the fraction of the CO_2 which remains airborne drops to only about 40% of the input. Where has the rest gone?

The most obvious hiding place is the ocean. Excess CO_2 in the atmosphere passes across the air-water interface and reacts with $CO_3^=$ ions dissolved in the sea to produce HCO_3^- ions. Were the atmosphere to be at chemical equilibrium with the entire ocean, about five sixths of the excess CO_2 would take up residence in the sea. Only one sixth would remain airborne. But it's not so simple; the sea mixes so slowly that only a small fraction of its capacity for CO_2 uptake is being utilized. Vast parts of the deep sea are accessible only on the time scale of hundreds of years. When this dynamic limitation is taken into account, it turns out that while the sea is an important hiding place, its uptake can account for only about one half the missing CO_2. Our mystery has to do with the fate of the remainder. Where has it gone?

The search for the so called "missing carbon sink" has been pursued for more than two decades. The conclusion is always the same. Only one reservoir, the organic matter which makes up the terrestrial biosphere, is big enough for the task. Somehow human activity must have increased the rate of photosynthesis. As a consequence, more carbon is being stored in tree trunks and soil humus. One might say, while the terrestrial biosphere

ANTHROPOGENIC INCREASES IN ATMOSPHERIC CO_2 AND CH_4

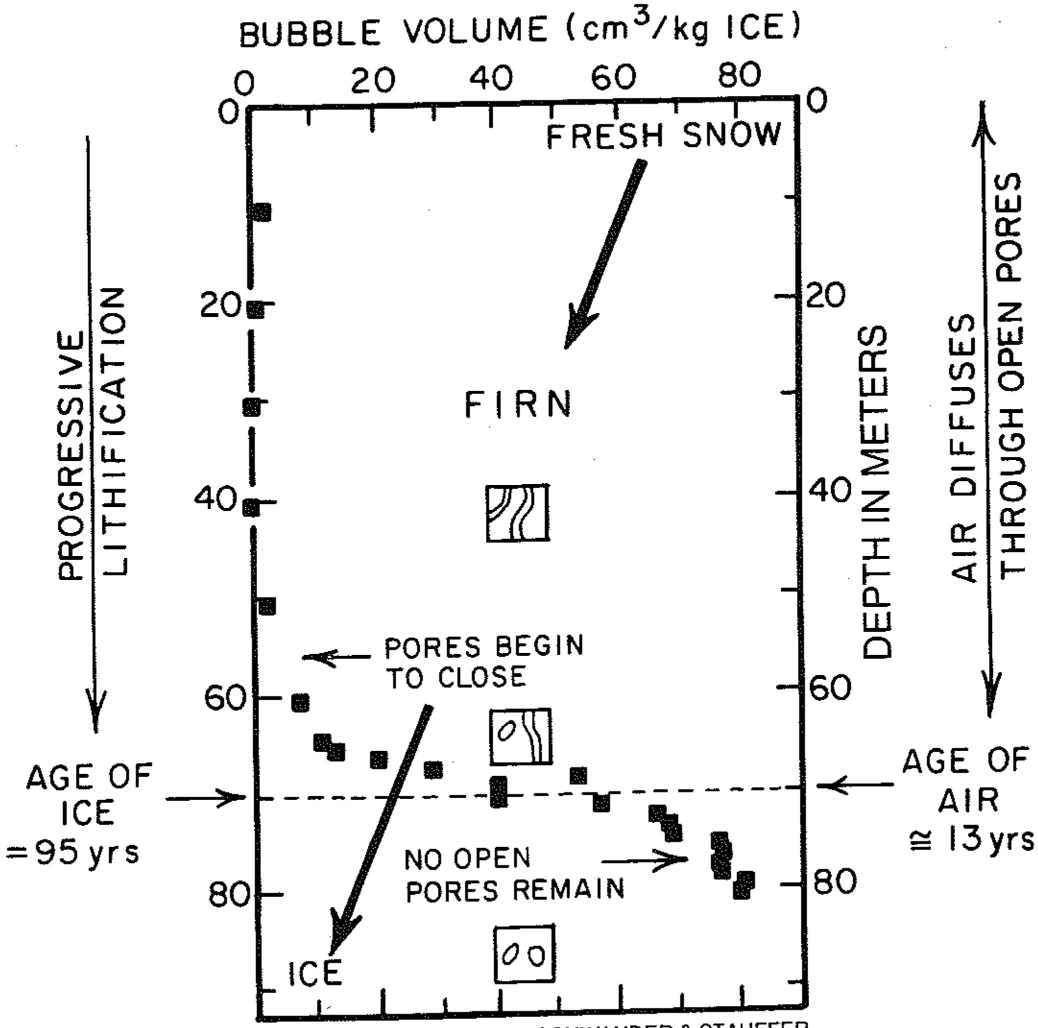


reservoirs is being trimmed around the edges, it is becoming more lush in the interior. Through our activities, we have been "greening", not just agricultural land but the entire planet. Actually, agricultural land is part of the problem, and not of the solution. First, as plants grown on agricultural land are harvested each year, no above ground storage of carbon occurs. More important, agricultural practice has been shown to drive down the humus content of soil. So, if the missing carbon is being packed away in wood and humus, this storage is occurring on lands we classify as uncultivated.

Two mechanisms have been identified which might propel a global greening. The first involves CO_2 itself. As carbon is the primary building block for plant matter, the increased abundance of CO_2 in the atmosphere might be expected to accelerate photosynthesis. More CO_2 flows into the factory allowing more organic matter to be manufactured. Indeed, experiments carried out in growth chambers suggest that, at least on the short term, a 30% increase in the CO_2 content of the air leads to growth enhancements averaging 10%. If CO_2 is driving an enhancement of this magnitude in the wild, then, each year more wood is being generated (leading to fatter forests) and more organics are being pumped into soils (leading to richer humus). The second mechanism involves nitrogen. Growth in most plant communities is often limited by the availability of this important nutrient. Farmers counter this deficiency by fertilizing their fields with ammonia or by allowing them to remain fallow so that plants with nitrogen-fixing root symbionts can generate natural fertilizer. The internal combustion engine extends nitrogen fertilization to the wilds. Atmospheric N_2 molecules are split at the high temperatures achieved in automobile engines producing nitrogen oxide gases. These gases become widely dispersed through the atmosphere before they are transformed to nitric acid molecules which dissolve in raindrops. This automobile-generated fertilizer allows more wood and soil humus to be generated. While a strong case can be made that extra carbon dioxide and fixed nitrogen are greening the planet, as we shall see, this greening process must be operating at maximum efficiency if it is to account for the storage of the missing

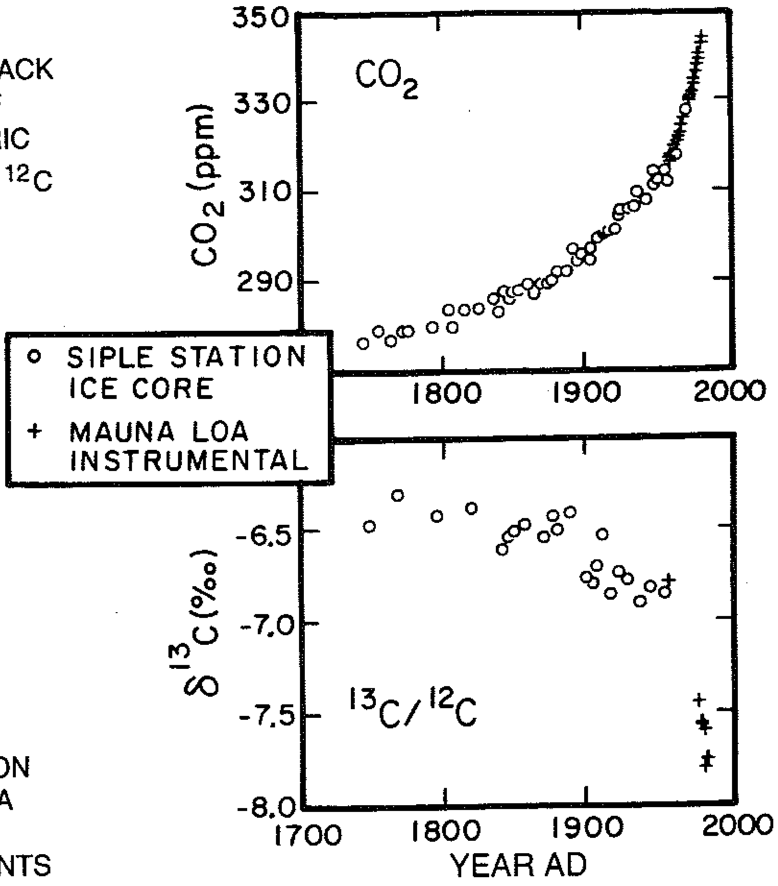
RELATIONSHIP BETWEEN AGE OF ICE AND AGE OF AIR TRAPPED IN BUBBLES IN ICE FOR SIPLE STATION ANTARCTICA

$T_{AIR} = T_{ICE} - 82$ YEARS



SCHWANDER & STAUFFER
BERN, SWITZERLAND

EXTENSION BACK
IN TIME OF
ATMOSPHERIC
CO_2 AND $^{13}C/^{12}C$
RECORDS

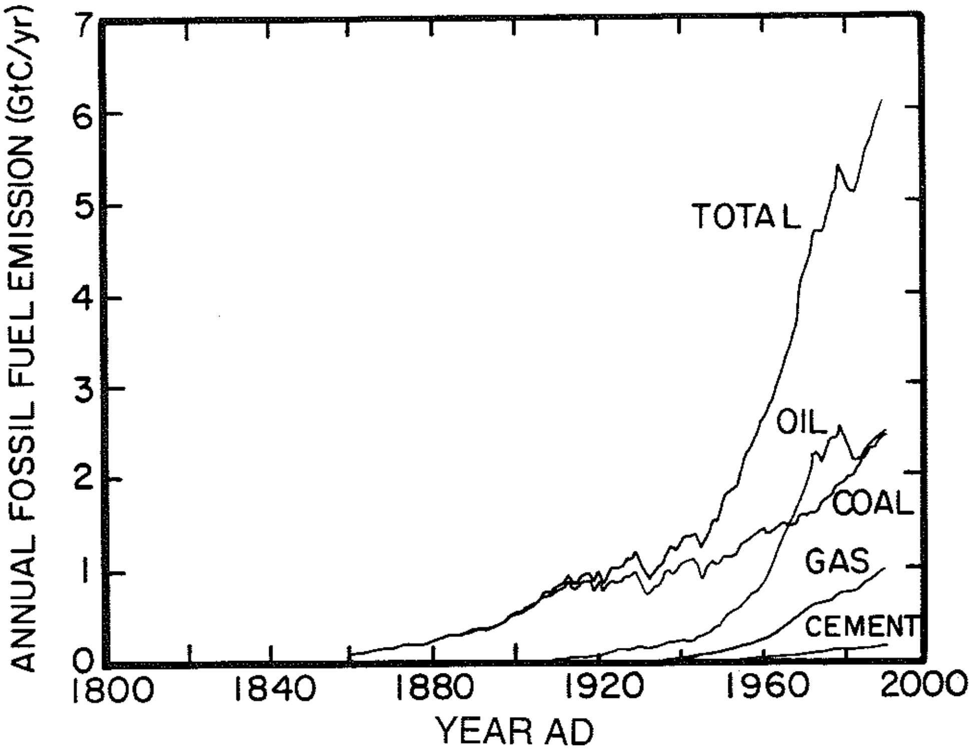


SIPLE STATION
ANTARCTICA
ICE CORE
MEASUREMENTS

Depth (m)	Ice Age (yr. AD)	Gas Age (yr. AD)	CO_2 (ppm)	$\delta^{13}C$ (‰)	
81.22	1871	1953	312.7	- 6.85	← ANNUAL LAYER 113
86.80	1861	1943	307.9	- 6.82	
90.77	1853	1935	306.6	- 6.91	
95.17	1845	1927	305.5	- 6.78	
98.80	1839	1921	301.6	- 6.74	
101.80	1833	1915	300.5	- 6.86	
105.25	1827	1909	299.2	- 6.54	
107.20	1823	1905	296.9	- 6.71	
108.80	1821	1903	294.8	- 6.80	
110.20	1817	1899	295.8	- 6.77	
116.82	1805	1887	292.3	- 6.42	
121.80	1796	1878	290.3	- 6.51	
123.80	1792	1874	289.5	- 6.43	
126.80	1787	1869	289.3	- 6.55	
134.47	1772	1854	288.2	- 6.48	
138.20	1765	1847	286.8	- 6.51	
140.75	1761	1843	287.4	- 6.54	
142.75	1757	1839	283.1	- 6.62	
154.89	1734	1816	283.8	- 6.39	
168.30	1709	1791	279.7	- 6.43	
177.50	1682	1764	276.7	- 6.31	
187.70	1662	1744	276.8	- 6.48	← ANNUAL LAYER 322

FRIEDLI AND COWORKERS, BERN, SWITZERLAND

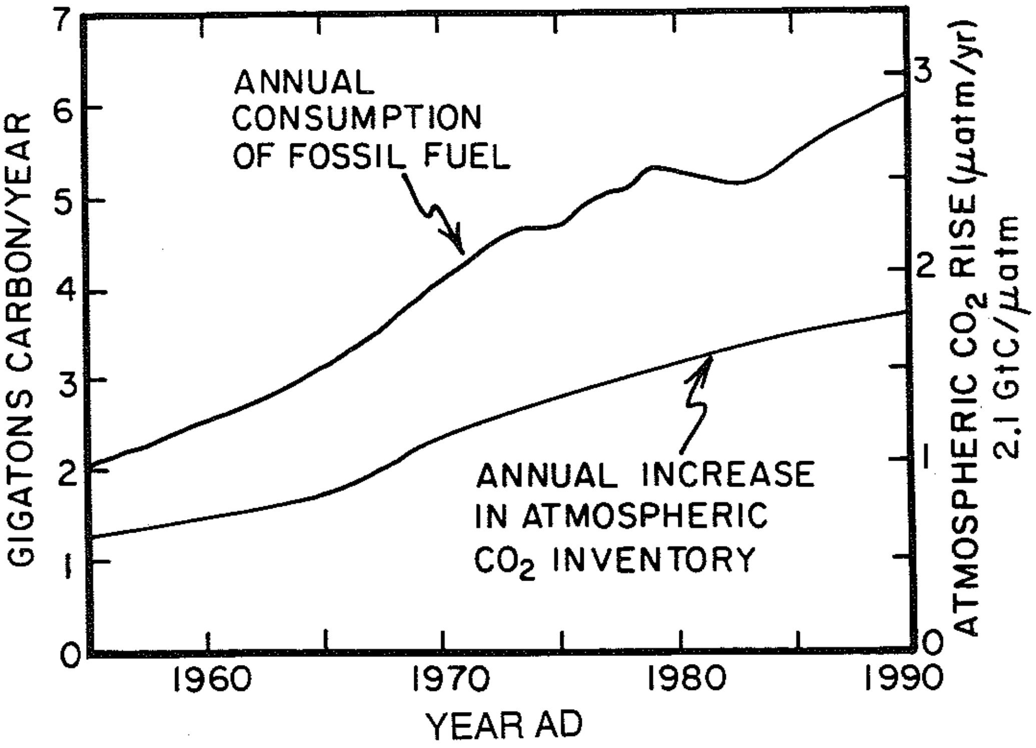
TIME HISTORY OF FOSSIL FUEL CONSUMPTION



FOSSIL FUEL EMISSIONS (GtC/yr)

	1950	1960	1970	1980	1990
COAL	1.1	1.4	1.6	2.5	2.5
OIL	0.4	0.9	1.8	1.9	2.4
GAS	0.1	0.2	0.5	0.7	1.0
$CaCO_3$	0.0	0.0	0.1	0.1	0.2
TOTAL	1.6	2.5	4.0	5.2	6.1

COMPARISON WITH THE RATE OF ACCUMULATION OF CO_2 IN THE ATMOSPHERE



OVER THE TIME PERIOD DURING WHICH THE ATMOSPHERE HAS BEEN ACCURATELY MONITORED, ITS CO_2 CONTENT HAS BEEN RISING AT A RATE ONLY ABOUT 60% THE RATE EXPECTED IF ALL THE FOSSIL FUEL CO_2 RELEASED REMAINED AIRBORNE.

carbon. Before exploring this question, let us review the evidence upon which carbon budgets are based.

The Knowns

Only two of the terms in the carbon budget are directly measured to a reasonably high degree of accuracy. One is the amount of CO_2 generated during each of the last 100 or so years through the burning of fossil fuels and the manufacture of cement. The number of tons of coal mined, the number of barrels of oil pumped, the number of cubic meters of natural gas recovered, and the number of tons of limestone thermally decomposed have been laboriously compiled from records kept by individual nations. The other is the CO_2 content of the atmosphere. In 1957, Charles David Keeling commenced continuous highly accurate measurement of the CO_2 content of air atop the extinct volcano Mauna Loa on the island of Hawaii. Keeling's measurement series has continued unbroken and is now supplemented by measurements at many other locations on our planet. Scientists at Bern, Switzerland and Grenoble, France discovered a means of extending this record back in time. Their trick was to extract gas stored in the bubbles contained in ice recovered from borings atop the Greenland and Antarctic ice caps. They demonstrated that this mode of cold storage nicely preserves the CO_2 content of the trapped air.

These two sets of data constitute our givens. Taken together, they tell us with clarity that, over the time spanned by the instrumental record, CO_2 has built up in the atmosphere at a bit more than one half the rate it was being generated by fossil fuel burning. The remaining three budgetary terms (described in the sections which follow: ocean uptake, deforestation, and greening) must be estimated by less direct means.

The Mirror Image Approach

The CO_2 produced by the burning of fossil fuels must be matched by an equivalent consumption of atmospheric oxygen. For coal, about thirteen molecules of O_2 disappears for each ten atoms of carbon combusted.

$$C_{10}H_6 + 13O_2 \rightarrow 10CO_2 + 3H_2O$$

For petroleum, the ratio is close to 3 O_2 molecules for each 2 carbon atoms.

$$2CH_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

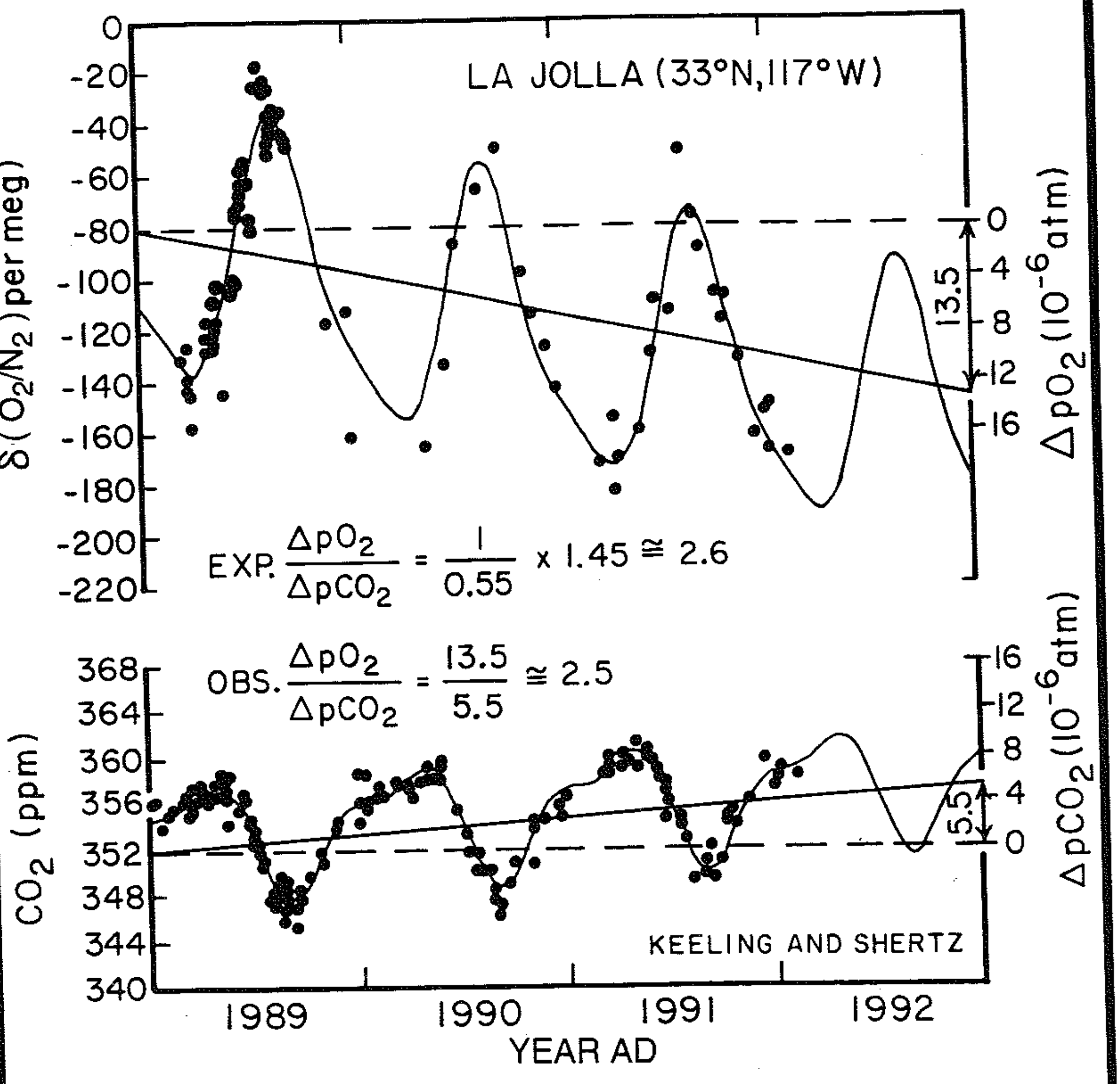
For natural gas, the ratio is 2 to 1.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

The current global mix of these three fuels requires the consumption of 15 molecules of O_2 for each 10 molecules of CO_2 produced. The mirror image strategy is a simple one. The measured rate of O_2 decline is compared with that expected from the amount of fossil fuels consumed. One might ask what advantage this information would have over that obtained from comparing the observed rate of rise in atmospheric CO_2 content with the expected rate. There is a very important difference. While the ocean is capable of absorbing five sixths of all the CO_2 we have produced (and thereby constitutes a very important term in the carbon budget), no comparable term exists in the O_2 budget. The reason is that 95 percent of the earth's O_2 resides in the atmosphere and only 5 percent in the ocean. The tiny amount of O_2 which will flow from the ocean back to the atmosphere to compensate for the loss through fossil fuel burning is unimportant in the O_2 budget. Thus O_2 budgeting is far simpler than CO_2 budgeting. Dead simple in fact. The difference between the observed rate of O_2 disappearance and that expected from fossil fuel burning provides a measure of the rate of change in the overall global biomass. For each molecule of CO_2 released to the atmosphere through deforestation, about one molecule of O_2 disappears. For each unit atom of carbon stored in wood or humus as the result of global greening, about one molecule of O_2 will be released to the atmosphere. Thus if more O_2 is disappearing than required for fossil fuel combustion, then the biosphere as a whole must be shrinking. Or if less O_2 is disappearing than required for fossil fuel burning, then the biosphere must be expanding.

But two difficulties remain. As already discussed, the biospheric carbon inventory is being influenced in opposing ways by man. Farmers and foresters are reducing its size. Greening by excess CO_2 and fixed nitrogen is increasing its size. So, for example, were

COMPARISON BETWEEN ATMOSPHERIC CO_2 AND O_2 RECORDS

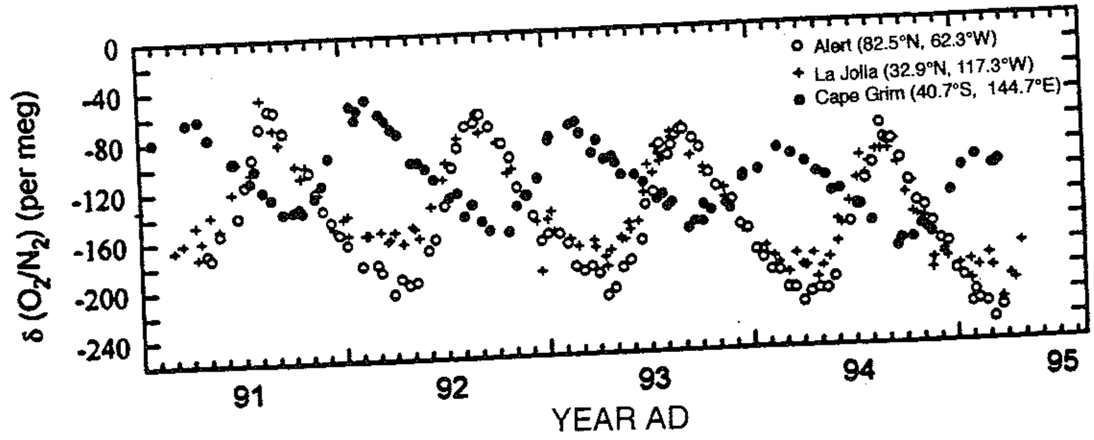


measurements to reveal that O_2 is declining exactly in accord with expectation from fossil fuel burning, it would mean that losses driven by forestry and agriculture were, by chance, just balanced by gains driven by greening. In order to reach our goal of establishing how much greening is occurring, it is necessary to quantify reduction in wood and humus stocks.

The second obstacle is one of measurement. In 1997, the atmosphere contained 364 ppm CO_2. Two years from now, it will contain 367 ppm. This increase can be documented precisely with modern instrumentation. By contrast, the atmosphere contains about 209,000 ppm of O_2. The expected drop during the same two-year period from fossil fuel burning alone is about 5 ppm. This represents a change of only 0.0025%; a daunting challenge to even the most clever experimentalist.

The second challenge was not met until 1989 when Ralph Keeling succeeded in developing a method capable of determining changes in the O_2 content in air to an accuracy of 0.8 ppm. Then, working together with his colleague Shertz, he succeeded in demonstrating that over the three-year period from 1989 to 1992, the O_2 content of air in La Jolla, California dropped at a rate consistent with that expected from global fossil fuel burning. However, at that point the uncertainty in this result was big enough to permit the possibility that the biosphere was either shrinking or expanding at a rate up to 2 gigatons a year. As this range covers virtually all possible scenarios, this early measurement series didn't help much. But as the years clicked by, Keeling's O_2 measurements began to pay off. In fact, he has been able to document an amazing occurrence. Between 1989 when his measurement series began and 1995, the O_2 content of the atmosphere dropped considerably less than would be expected. Taken together with the rise in CO_2 over this period, this shortfall in the magnitude of the O_2 decline indicates that during this period the split of fossil fuel CO_2 flow was 35% to atmosphere, 35% to the ocean, and 30% to the biosphere. This came as a big surprise indicating that the biosphere was taking up an average of about two gigatons of carbon per year during this time interval. If, for example,

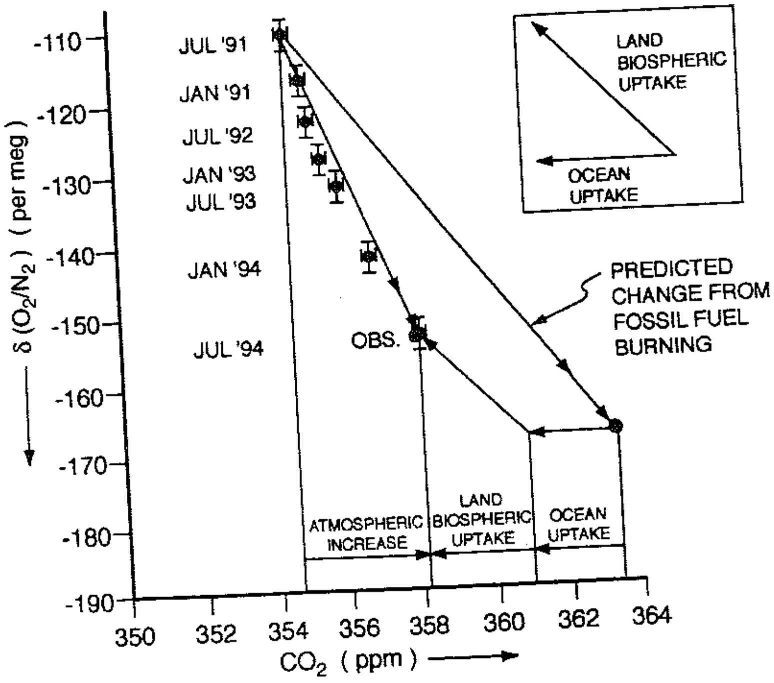
O_2 - CO_2 SYSTEMATICS



$$\delta \frac{O_2}{N_2} = \left(\frac{O_2/N_{2\,\text{SAMP}}}{O_2/N_{2\,\text{STD}}} - 1 \right) \times 10^6$$

4.8 per meg = 1 μatm O_2

PO_2 = 209,500 μatm



forest cutting was releasing one gigaton of carbon per year, this would require a greening of roughly three gigatons a year! We will return to this finding later in this section, but before going on, it must be stated that this rate of greening need not be entirely or even largely anthropogenic. Rather, it might reflect unusually favorable growth conditions across the globe. Even though averaged over many years, respiration must match growth; a pulse in global photosynthesis over a several year period could temporarily outstrip respiration. It is likely that such a pulse occurred in the early 1990s. If so, then respiration will soon gain the upper hand and eliminate this short term excess storage. This finding emphasizes the need for a record of sufficient duration so that the influence of changes in global photosynthesis induced by short term climate changes can be averaged out.

Shortly after Keeling developed his index of refraction technique for precise O_2/N_2 ratio measurement, Sowers and Bender came up with a nearly as precise a means to accomplish this task using conventional mass spectrometry. Impatient with the prospect of the long wait for a definitive result, they developed a hindcasting method. It involves getting air samples from deep in the 70 or so meter thick layer of firn which caps the Antarctic and Greenland ice caps. Firn is partially lithified snow which has open pores which provide access to the overlying atmosphere. But diffusion of gases through this matrix is so slow that the gas deep in the firn is replaced only once per decade or so. The first measurements by Sowers and Bender showed that indeed air from deep in the firn had a higher O_2/N_2 ratio than that in the atmosphere. It also had lower methane and carbon dioxide contents. As the evolution of the methane and carbon dioxide contents of the atmosphere over the last decade or so are well documented, these measurements served to fix the average age for any given sample of firn air. Based on this age and the O_2/N_2 ratio, Sowers and Bender hoped to obtain a rate of O_2 decline for decades past. But again the uncertainty in these preliminary measurements is too great to provide a definitive answer. The reason is that despite the 5 times greater length of the Sowers-Bender record, the measurement uncertainty is considerably larger. While firn provides a superb storage environment in that it is very cold, very dry, free of bacteria, and immune to contamination from underlying earth gas, it is not perfect. The long residence time of gas in the firn allows preferential settling of heavy molecules relative to light ones. As O_2 (mass 32) is heavier than N_2 (mass 28), this settling alters the ratio of interest. Sowers and Bender were, however, armed with a means to correct for this gravitational settling effect. They measured the ratio of $^{15}N^{14}N$ (mass 29) to $^{14}N^{14}N$ (mass 28) in the same samples and used the enrichment of the heavy nitrogen molecule as a basis to correct for the gravitational enrichment of O_2 relative to N_2.

As the record in firn extends back only 10 to 20 years, in order to be successful the Sowers and Bender approach will have to be extended beyond the base of the firn into the underlying ice. In attempting this extension, they have encountered a serious problem. As the bubbles of trapped gas closed off, air diffuses in and out of the tiny residual orifices creating a small separation between O_2 and N_2. In an attempt to develop a means to correct for this separation, Jeff Severinghaus and Michael Bender are currently measuring the Ar to N_2 ratios as well as the O_2 to N_2 ratios in firn and ice. So the question is whether the hares (Bender and coworkers) springing rapidly back time can put aside potential biases created by ice storage and beat out the tortoises (Keeling and coworkers) who are forced to plod along one year at a time. Clearly, however, both results are of extreme importance. One will give information about the state of the biosphere during the coming decades, and the other about its state during past decades.

Ocean Uptake

Another way to approach carbon budgeting is to estimate without the use of O_2 data the uptake of CO_2 by the ocean. Once this term has been defined, then change in the Earth's biomass can be calculated by subtracting the CO_2 increases in the ocean and atmosphere reservoirs from the total amount of CO_2 produced by man's activities. The first point to be made in this regard is that ocean uptake cannot, at present, be estimated from the results of repeated ΣCO_2 inventories. Unlike the atmosphere for which a combination of measurements on air bubbles stored in ice (prior to 1958) and direct sampling (after 1958) provide a complete record of the inventory's evolution, we have no equivalent for the ocean. The first detailed and accurate global survey of the dissolved inorganic carbon content of ocean water (ΣCO_2) was made during the 1970s as part of the GEOSECS (Geochemical Ocean Sections Study) expeditions. But even these measurements were not of sufficient accuracy to provide an adequate base for future surveys. The problem is that even for waters which have taken up their full component of excess CO_2, the increase in ΣCO_2 since the 1970s has only been about one percent. The accuracy of the GEOSECS measurements is no better than 0.5%. Of course, the situation is even less favorable for sub-surface waters which have achieved only a fraction of their uptake capacity. Because of this, the direct inventory approach is at present hopeless.

During the 1990's, a far more detailed and accurate (to ±0.1%) survey was made under the banner of the global WOCE (World Ocean Circulation Experiment) program. If a similar survey is conducted 15 to 25 years hence, it will then be possible for the first time to directly measure the integrated CO_2 uptake by the ocean. But of course this result will apply only to the time between the two surveys.

In the interim, the amount of excess CO_2 which has entered the ocean must be obtained by less direct means. One approach involves ocean models designed to take into account not only the thermodynamic capacity of sea water for the uptake of excess CO_2 but also the two kinetic barriers to its uptake, namely, the resistance posed by transport across the air-sea interface and the resistance posed by vertical mixing within the sea. These models are initialized so as to be at steady state with the pre-industrial atmosphere (pCO_2 $=280$ μatm). Then the model's atmospheric CO_2 content is time stepped to follow the observations. After each step, CO_2 is exchanged between the atmosphere and surface ocean and mixing occurs within the ocean. The output of the model is the evolution of the storage of excess CO_2 in the ocean.

THERMODYNAMIC CAPACITY FOR CO_2 UPTAKE

IDEALIZED SEA WATER (NO BORATE)

CHARGE BALANCE

$$[Na^+]+[K^+]+2[Mg^{++}]+2[Ca^{++}]=[Cl^-]+2[SO_4^=]+[HCO_3^-]+2[CO_3^=]$$

OR

$$[Na^+]+[K^+]+2[Mg^{++}]+2[Ca^{++}]-[Cl^-]-2[SO_4^=]=[HCO_3^-]+2[CO_3^=]$$

OR

$$[ALKALINITY]=[HCO_3^-]+2[CO_3^=]$$

MASS BALANCE FOR DISSOLVED INORGANIC CARBON

$$[\Sigma CO_2]=[CO_2]+[HCO_3^-]+[CO_3^=]$$

CHEMICAL EQUILIBRIUM

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

$$K_c' = \frac{[HCO_3^-]^2}{[CO_2][CO_3^=]} \quad , \quad \alpha = \frac{[CO_2]}{pCO_2} = 0.342 \frac{\mu mol/kg}{\mu atm}$$

EXAMPLE $T = 18°C$ $S = 35‰$ $K_c' = 1445$ $ALK = 2100$

$pCO_2 = 280 \mu atm$	$pCO_2 = 360 \mu atm$	Δ
$[CO_2] = 9.6$	$[CO_2] = 12.3$	$+2.6 \mu mol/kg$
$[HCO_3^-] = 1700$	$[HCO_3^-] = 1769$	$+69 \mu mol/kg$
$[CO_3^=] = 200$	$[CO_3^=] = 166$	$-34 \mu mol/kg$
$[ALK] = 2100$	$[ALK] = 2100$	$0 \mu mol/kg$
$[\Sigma CO_2] = 1910$	$[\Sigma CO_2] = 1948$	$+38 \mu mol/kg$

$$\text{REVELLE FACTOR} = \frac{\Delta pCO_2/pCO_2}{\Delta\Sigma CO_2/\Sigma CO_2} = \frac{80/280}{38/1910} = 14.4$$

ACTUAL SEA WATER (INCLUDING BORATE)

CHARGE BALANCE

$$[\mathrm{ALKALINITY}] = [\mathrm{HCO_2^-}] + 2[\mathrm{CO_3^=}] + [\mathrm{H_4BO_4^-}]$$

MASS BALANCE BORON

$$[\Sigma \mathrm{B}] = [\mathrm{H_3BO_3^0}] + [\mathrm{H_4BO_4^-}] = 410.6 \frac{S}{35}\ \mu\mathrm{mol/kg}$$

CHEMICAL EQUILIBRIUM

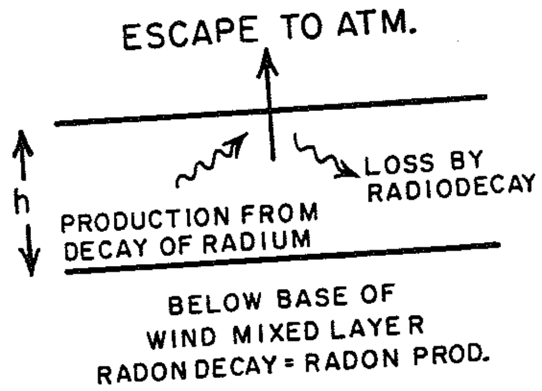
$$K_B' = \frac{[\mathrm{H_4BO_4^-}][\mathrm{HCO_3^-}]}{[\mathrm{H_3BO_3^0}][\mathrm{CO_3^=}]}$$

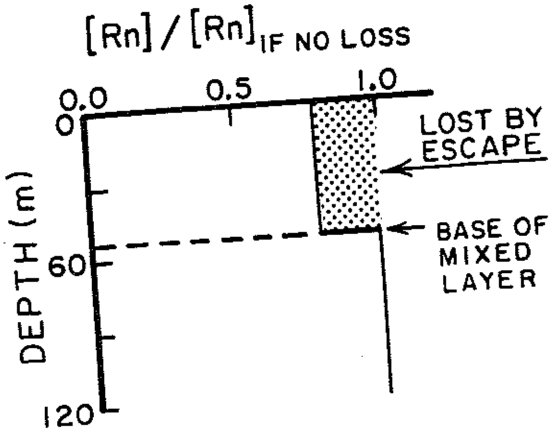
EXAMPLE $T = 18°C$ $S = 35‰$ $K_c' = 1482$ $K_B' = 2.75$
$ALK = 2216$ $SiO_2 = 0$ $NO_3 = 0$ $PO_4 = 0$

$pCO_2 = 280\ \mu atm$	$pCO_2 = 360\ \mu atm$	Δ
$[CO_2]$ = 9.6	$[CO_2]$ = 12.3	+2.6 μmol/kg
$[HCO_3^-]$ = 1702.5	$[HCO_3^-]$ = 1779.5	+77.0 μmol/kg
$[CO_3^=]$ = 203.7	$[CO_3^=]$ = 173.1	−30.6 μmol/kg
$[\Sigma CO_2]$ = 1915.8	$[\Sigma CO_2]$ = 1964.9	+49.1 μmol/kg
$[H_3BO_3^0]$ = 308.9	$[H_3BO_3^0]$ = 323.9	+15.0 μmol/kg
$[H_4BO_4^-]$ = 101.7	$[H_4BO_4^-]$ = 86.7	−15.0 μmol/kg
$[\Sigma B]$ = 410.6	$[\Sigma B]$ = 410.6	0.0 μmol/kg
$[OH^-]$ = 4.4	$[OH^-]$ = 3.6	−0.8 μmol/kg
$[ALK]$ = 2216.0	$[ALK]$ = 2216.0	0.0 μmol/kg

$$\text{REVELLE FACTOR} = \frac{\Delta pCO_2 / pCO_2}{\Delta \Sigma CO_2 / \Sigma CO_2} = \frac{80/280}{49.1/1915.8} = 11.1$$

AIR -SEA CO_2 EXCHANGE BASED ON RADON





$$\frac{[Rn]_{\text{MIXED LAYER}}}{[Rn]_{\text{NO LOSS}}} = \frac{\text{PROBABILITY OF RADIODECAY}}{\text{PROB. OF RADIODECAY} + \text{PROB. OF ESCAPE}}$$

PROBABILITY OF DECAY ($t_{1/2}^{\text{RADON}} = 3.85$ days $= 92.4$ hours)

$$\lambda_{Rn} = \frac{1}{\tau_{Rn}} = \frac{.693}{t_{1/2}} = 7.5 \times 10^{-3}\ \text{hr}^{-1} \text{ or } \tau_{Rn} = 133 \text{ hours}$$

PROBABILITY OF ESCAPE

$$\lambda_{\text{ESCAPE}} = \frac{\text{PISTON VELOCITY}^{*}}{\text{MIXED LAYER THICKNESS}} = \frac{v}{h} \text{ or } \tau_{\text{ESCAPE}} = \frac{h}{v}$$

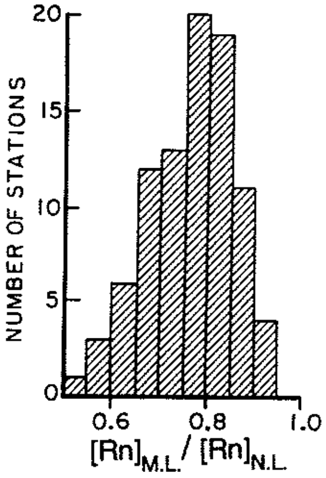
ASSUMES

1) STEADY STATE (*i.e.* [Rn] IN MIXED LAYER REMAINS CONSTANT WITH TIME)
2) NO EXCHANGE OF WATER ACROSS BASE OF MIXED LAYER (*i.e.* NO REPLACEMENT OF ESCAPING RADON FROM BELOW)

$$\frac{[Rn]_{\text{MIXED LAYER}}}{[Rn]_{\text{NO LOSS}}} = \frac{\lambda_{Rn}}{\lambda_{Rn} + v/h}$$

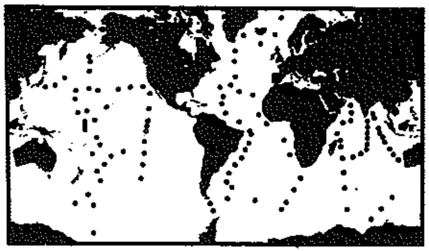
$$v = \lambda_{Rn} h \left(\frac{1 - [Rn]_{\text{M.L.}}/[Rn]_{\text{N.L.}}}{[Rn]_{\text{M.L.}}/[Rn]_{\text{N.L.}}} \right)$$

THE AVERAGE OF MEASUREMENTS AT 90 STATIONS SHOW



$$h_{MEAN} = 54 \text{ meters}$$

$$\frac{[Rn]_{MIXED\ LAYER}}{[Rn]_{NO\ LOSS}} = 0.77$$



GEOSECS STATIONS

YIELDS A PISTON VELOCITY* OF

$$v = 7.5 \times 10^{-3} \times 54 \times \frac{1-0.77}{0.77}$$

$$= 0.12 \frac{\text{meters}}{\text{hr}} = 2.9 \frac{\text{meters}}{\text{day}}$$

APPLYING THIS RESULT TO CO_2 WE GET

$$I_{CO_2} = \frac{[CO_2]}{p_{CO_2}} \; v \left(\frac{D_{CO_2}}{D_{Rn}}\right)^{1/2} \leftarrow \text{RATIO OF MOLECULAR DIFFUSIVITIES} \swarrow (1.36)^{1/2}$$

$$\left.\frac{[CO_2]}{p_{CO_2}}\right)_{\text{AT MEAN SURFACE WATER TEMPERATURE}} \cong 5.0 \times 10^{-5} \frac{\text{mol}/\text{m}^3}{\mu\text{atm}}$$

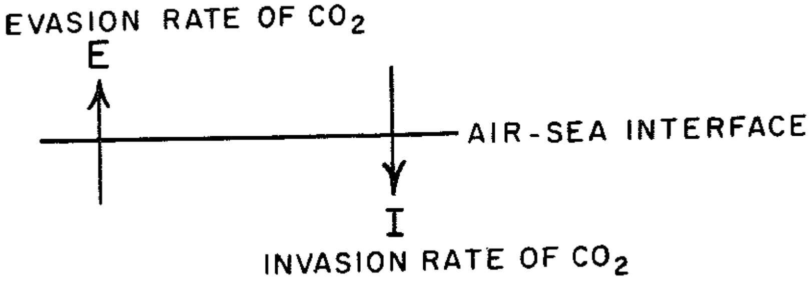
$$v = 2.9 \frac{\text{meters}}{\text{day}} = 2.9 \times 365 \frac{\text{meters}}{\text{year}}$$

$$I_{CO_2} = 5.0 \times 10^{-5} \times 2.9 \times 365 \times (1.36)^{1/2}$$

$$= 0.062 \text{ mol}/\text{m}^2 \text{ yr } \mu\text{atm}$$

* THE VELOCITY OF IMAGINARY PISTONS, ONE MOVING UPWARD PUSHING BEFORE IT GAS AT THE MIXED LAYER CONCENTRATION AND ONE MOVING DOWNWARD PUSHING BEFORE IT GAS AT THE ATMOSPHERIC EQUILIBRIUM CONCENTRATION.

AIR-SEA CO_2 EXCHANGE BASED ON NATURAL RADIOCARBON



ASSUMES:

1) PRIOR TO 1850, E $\cong$ I (*i.e.* THE SEA WAS NEITHER A SOURCE NOR A SINK FOR CO_2)
2) PRIOR TO 1850 THE ^{14}C DISTRIBUTION WAS IN STEADY STATE (*i.e.* RADIOACTIVE DECAY OF ^{14}C WITHIN THE SEA ABOUT BALANCED THE INPUT OF ^{14}C ATOMS ACROSS THE AIR-SEA INTERFACE)

THEN:

INVASION OF ^{14}C INTO SEA $\cong$ EVASION OF ^{14}C FROM SEA + DECAY OF ^{14}C WITHIN SEA

$$\left.\frac{^{14}C}{C}\right)_{ATM}^{1850} I A_{SEA} \cong \left.\frac{^{14}C}{C}\right)_{\substack{SURF\\SEA}}^{MEAN} I A_{SEA} + \left.\frac{^{14}C}{C}\right)_{SEA}^{MEAN} [\Sigma CO_2]_{SEA}^{MEAN} V_{SEA} \lambda_{^{14}C}$$

OR

$$I \cong \frac{\left.\frac{^{14}C}{C}\right)_{SEA}^{MEAN} \Big/ \left.\frac{^{14}C}{C}\right)_{ATM}^{1850}}{1-\left[\left.\frac{^{14}C}{C}\right)_{\substack{SURF\\SEA}}^{MEAN} \Big/ \left.\frac{^{14}C}{C}\right)_{ATM}^{1850}\right]} [\Sigma CO_2]_{SEA}^{MEAN} \frac{V_{SEA}}{A_{SEA}} \frac{1}{\tau_{^{14}C}}$$

$$\left.\frac{^{14}C}{C}\right)_{SEA}^{MEAN} \Big/ \left.\frac{^{14}C}{C}\right)_{ATM}^{1850} \cong 0.85$$

$$\left.\frac{^{14}C}{C}\right)_{\substack{SURF\\SEA}}^{MEAN} \Big/ \left.\frac{^{14}C}{C}\right)_{ATM}^{1850} \cong 0.95$$

$$\frac{V_{SEA}}{A_{SEA}} = \frac{13.7 \times 10^{17}\,m^3}{3.6 \times 10^{14}\,m^2} = 3800\ \text{meters}$$

$$\tau_{^{14}C} = \frac{1}{\lambda^{14}C} = \frac{t_{1/2}}{.693} = 8270\ \text{years}$$

$$\left[\Sigma CO_2\right]_{SEA}^{MEAN} = 2.2\ \text{mol/m}^3$$

$$I = \frac{0.85}{1-0.95} \times 2.2 \times \frac{3800}{8270}$$

$$= 17.2\ \text{mol/m}^2\ \text{yr}$$

$$pCO_2^{1850} = 280\ \mu\text{atm}$$

$$I = 0.061\ \text{mol/m}^2\ \text{yr}\ \mu\text{atm}$$

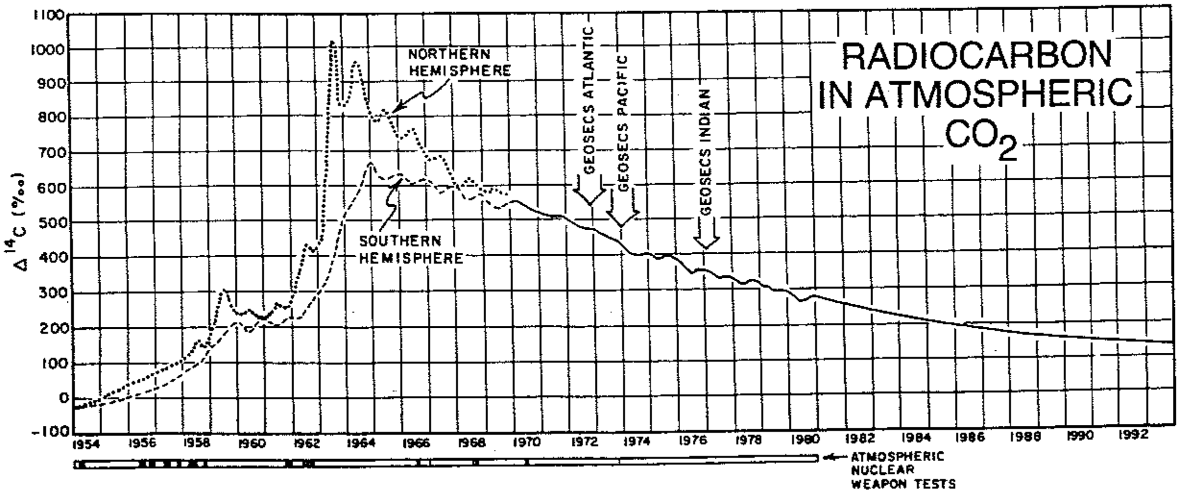
PROBABLE UNCERTAINTY ± 25% ENTIRELY DUE TO UNCERTAINTY IN $\left.^{14}C/C\right)_{SURF\ SEA}^{MEAN}$

The models used for this purpose are of two types, tracer-calibrated reservoir models and atmosphere-driven dynamic models. As the reservoir models are far simpler in design, it makes best sense to discuss them first. In these models, no attempt is made to duplicate the physics associated with either air-sea gas exchange or mixing within the sea. Rather, these transports are represented by transfer coefficients. The magnitudes of these coefficients are chosen to provide the best possible match to the distribution of transient tracers whose distributions within the sea have been measured. The secret of success in this endeavor is to keep the architecture of the model as simple as possible. In this way, the number of variable parameters can be kept to a minimum. In the absence of any dynamics, such models are merely vehicles to permit the measured distributions of transients (i.e., those of bomb produced ^{14}C and ^{3}H and of industrially produced CFCs) to be used as analogues for transients whose distributions we can't document (i.e., those of anthropogenic CO_2 and greenhouse heat). In our estimation, the most successful of these models is that proposed by the Swiss scientists, Hans Oeschger and the late Uli Siegenthaler. Their model is one dimensional consisting of a well-mixed atmosphere and a two box ocean. The upper ocean box represents the wind-stirred upper ocean layer. The lower box represents the remainder of the ocean as a semi-infinite half space (it does not have to have a base because neither the calibration tracers nor the anthropogenic CO_2 reach the 3800 meter-mean depth of the real ocean). Transport through the semi-infinite half space is accomplished by a mixing process mathematically analogous to molecular diffusion. Oceanographers refer to it as "eddy diffusion". In such a model, only three parameters need to be defined: the thickness of the upper-ocean wind-mixed layer, the exchange rate of CO_2 gas between the ocean and atmosphere, and the coefficient of eddy diffusion within the main body of the ocean. The first of these is usually set at value, consistent with observation of the measured mean thickness of wind-stirred layer which everywhere caps the ocean. As discussed below, the assignment of the air-sea CO_2 exchange rate is obtained in three independent ways: i.e., radon deficiencies measured in the oceanic-mixed layer and on the distributions of natural and bomb-produced radiocarbon. These three estimates are broadly consistent. The eddy diffusivity is based on measurements of the measured penetration depth of bomb testing tritium and radiocarbon. Again, the two estimates are consistent with one another. This diffusional representation of penetration of water entering into the body of the ocean carries with it the assumption that the extent of vertical mixing varies as the square root of time. This means, for example, that mixing to 700 meters beneath the base of the mixed layer takes four times as long as mixing to 350 meters below this base. As we shall see, this assumption is consistent with the two available calibration targets. The distribution of natural radiocarbon in the ocean tells us that the entire body of the ocean (mean depth 3800 meters) is mixed on a time scale of about one millennium. The distribution of bomb radiocarbon and tritium at the time of the GEOSECS survey tells us that on the time scale of one decade, the mean penetration depth is about 380 meters (about one tenth of the ocean volume). The ratio of these two mixing depths (i.e., ~10) matches the square root of the ratio of the mixing times i.e.,

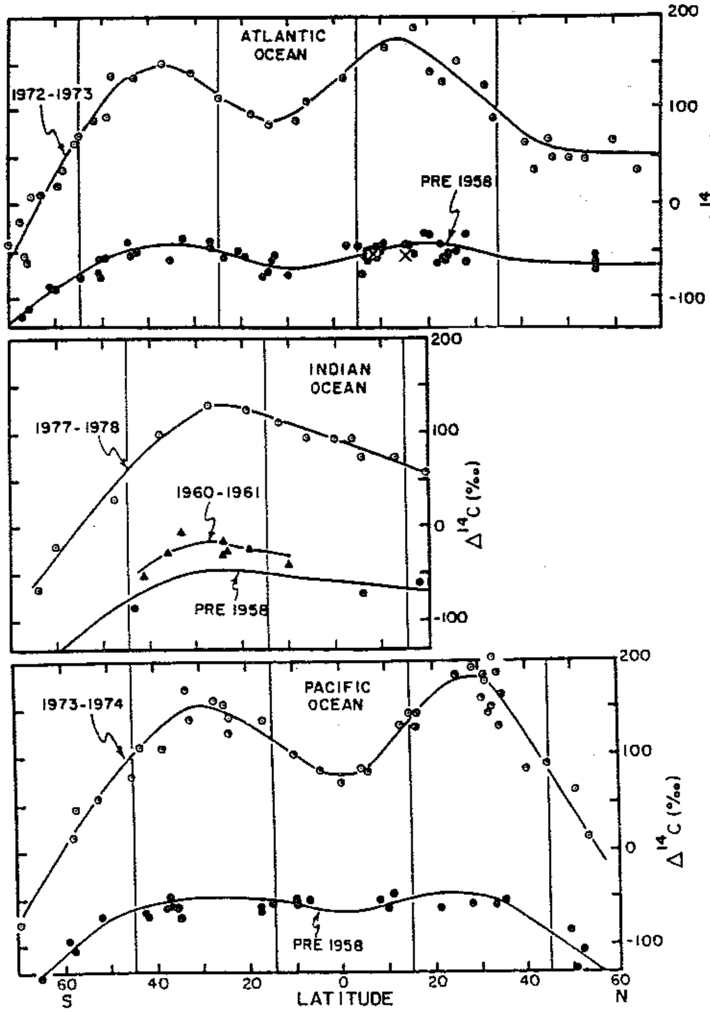
$$\frac{3800m}{380m} \equiv \sqrt{\frac{1000 years}{10 years}}$$

Bomb radiocarbon provides the best tracer for setting both the model's gas exchange rate and its coefficient of vertical eddy diffusion. This tracer was generated as the result of atmospheric H-bomb tests conducted during the 1950s and early 1960s. Neutrons released during these thermonuclear explosions eventually find their way, as do cosmic ray neutrons, into the nuclei of atmospheric nitrogen atoms transforming them to radiocarbon. Most of the products of these blasts were carried into the stratosphere by explosion-generated updrafts. Here the radiocarbon atoms chemically combined with oxygen atoms to form $^{14}CO_2$. On the time scale of a few years these tracer molecules mixed downward into the troposphere. Measurements of the ^{14}C to C ratio in CO_2 extracted from ground level air, at a number of places on the planet, thoroughly document the evolution of the

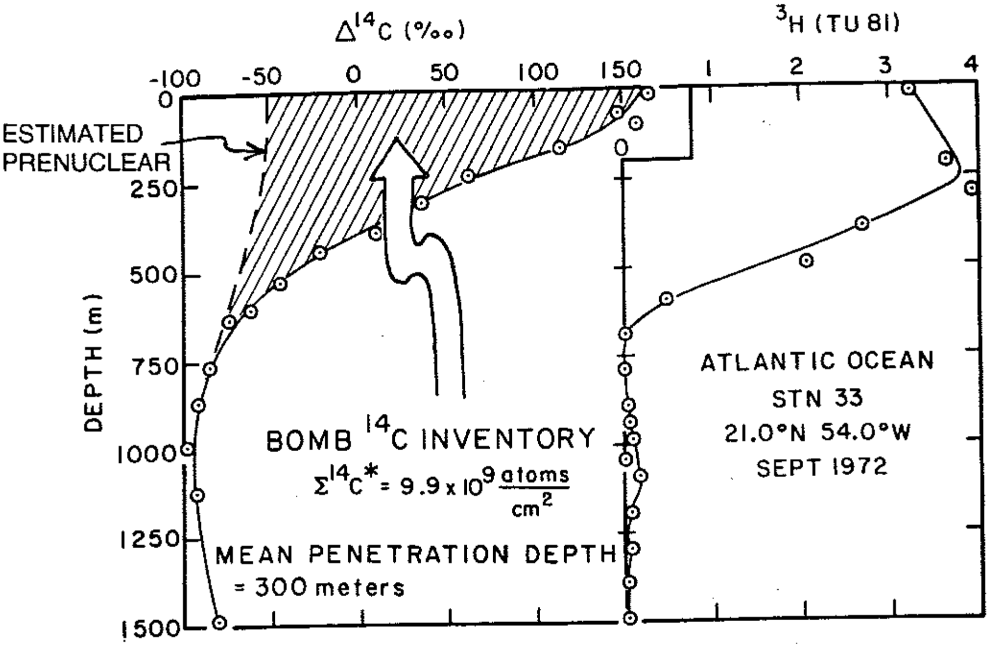
DISTRIBUTION OF BOMB TEST RADIOCARBON AT THE TIME OF GEOSECS SURVEYS



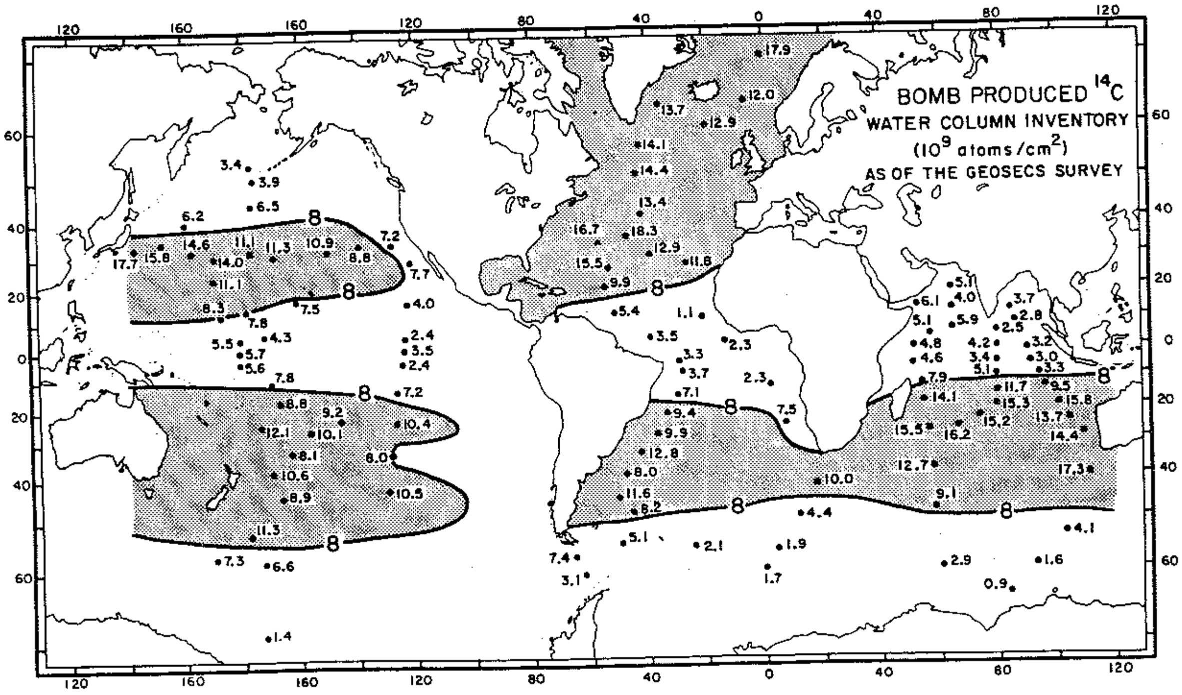
RADIOCARBON IN ATMOSPHERIC CO_2



RADIOCARBON IN SURFACE OCEAN WATER
ΣCO_2



MEAN PENETRATION DEPTH		
GEOSECS EXPEDITION	BOMB ^3H (meters)	BOMB ^{14}C (meters)
Atlantic (1972-3)	591	414
Pacific (1973-4)	336	311
Indian (1977-8)	283	309
World (1972-8)	382	344



resulting tropospheric transient. The $^{14}C/C$ ratio began to climb in 1954. It reached a sharp maximum in mid 1963 shortly after the treaty banning nuclear tests in the atmosphere was implemented. With the cessation of bomb testing, the $^{14}C/C$ ratio in atmospheric CO_2 began a decline which is still in progress. In the northern hemisphere where the tests were conducted, at its maximum, the $^{14}C/C$ ratio in tropospheric CO_2 reached almost twice its pre-nuclear value. In the southern hemisphere, the maximum was somewhat smaller and occurred a bit later, reflecting the roughly one-year time constant for interhemispheric mixing. After four or five years, when the distribution had become nearly uniform, all parts of the atmosphere followed the same decline. Now 35 years after the peak, the $^{14}C/C$ ratio has fallen to 11% above the pre-industrial value. The important point is that the bomb ^{14}C atoms which have left the atmosphere now reside in the ocean and in the biosphere and serve as valuable tracers.

A survey of radiocarbon, encompassing the entire ocean, was conducted during the period 1972-1978 as part of the GEOSECS program. When analyzed together with results of a companion tritium survey, and with radiocarbon measurements on pre-nuclear surface water, it is possible to separate the bomb radiocarbon and the natural radiocarbon components at each station. The distribution of the bomb component is then used to fix the two parameters in the Oeschger and Siegenthaler model. This is accomplished by averaging two important properties of this distribution measured at each station: the bomb ^{14}C to C ratio in surface water and the mean penetration depth of bomb-produced radiocarbon. These two quantities are calculated for each GEOSECS station. They are then globally averaged. The result of this exercise yields an average $^{14}C/C$ ratio for surface water 16% higher at the time of the GEOSECS survey than just prior to nuclear testing and an average penetration depth of 382 meters. These two values become the targets for the calibration of the simple reservoir model. To do this, the model's atmosphere is time stepped to follow both the rise in the atmosphere's CO_2 content and the time history of its ^{14}C to C ratio. The model is run from 1954 (when the bomb ^{14}C rise commenced) to

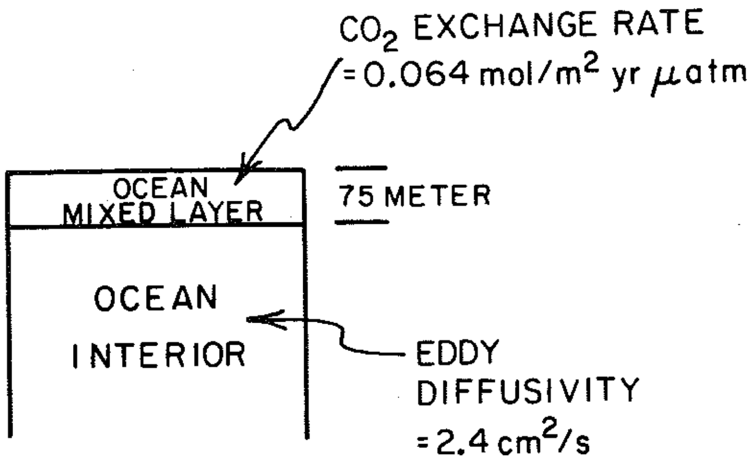
1975, the mid time for the GEOSECS surveys. Runs are made for a range of choices of both the CO_2 invasion rate and the eddy diffusivity. One set of values best fits both targets. The results obtained in this way are 0.064 moles $CO_2/m^2.yr.\mu atm$ for the CO_2 invasion rate and 2.4 cm^2/sec for the coefficient for eddy diffusion.

Having calibrated the model's free parameters, the next step is to calculate the ocean uptake of fossil fuel CO_2. As for bomb ^{14}C, this is done by time stepping the model's atmosphere to follow the time history of atmospheric CO_2 contents obtained from measurements on ice cores and air samples. Of course, the CO_2 invasion and evasion rates and the eddy diffusivity employed are those obtained from the bomb ^{14}C calibration runs.

The model yields an ocean uptake of close to 2 gigatons of C per year for the 1980s. When this is combined with the observed atmospheric inventory increase, the fossil fuel input is pretty much accounted for suggesting that the inventory of terrestrial carbon remained more or less constant. In other words, gains resulting from greening more or less matched losses resulting from deforestation and agriculture.

One might ask whether this approach to ocean uptake accounts for CO_2 carried into the deep sea as part of the ocean's thermohaline circulation. The answer is that it does so only to the extent that the bomb radiocarbon carried to the deep sea has been properly accounted for. This accounting is likely quite poor because the bomb ^{14}C component in deep waters is for the most part so small that it cannot be properly identified. But a small signal distributed over a very large volume of deep-sea water could be quite important. Thus the simple box model may underestimate the amount of CO_2 taken up by the sea. To get some idea how large the deep-sea component might be, we can make a separate estimate. The flux of water into the deep sea is thought to be about 30 Sverdrups (i.e., $30x10^6$ $m^3/second$). As an upper limit, we will assume this water carries with it a full component of excess ΣCO_2 (i.e., it is formed from old deep water free of anthropogenic CO_2 and it fully equilibrates with the atmosphere before descending). If so, then during the mid 1980s when the atmosphere's CO_2 content was about 345 ppm, newly formed

CALIBRATION OF SIMPLE OCEAN MODEL



CO_2 EXCHANGE RATE
= 0.064 mol/m^2 yr μatm

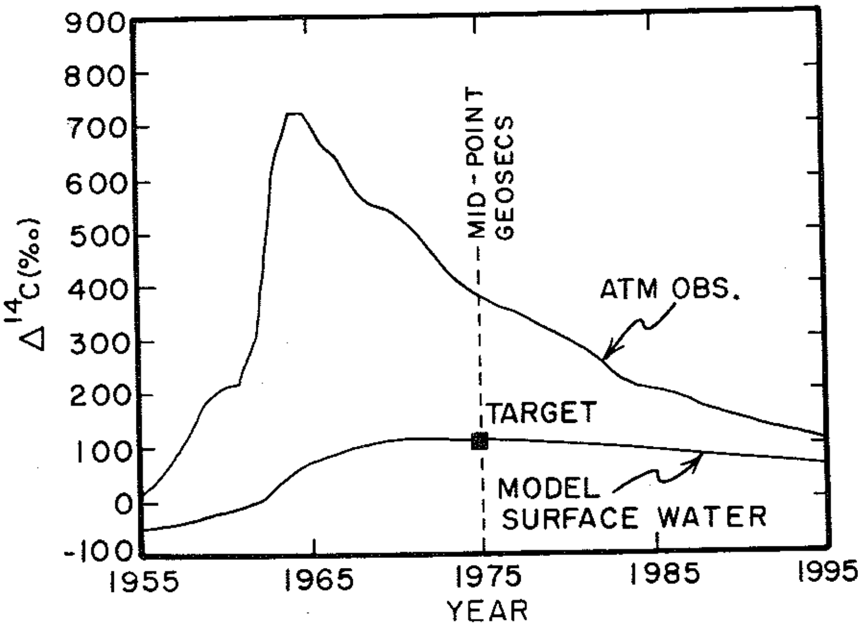
OCEAN MIXED LAYER

75 METER

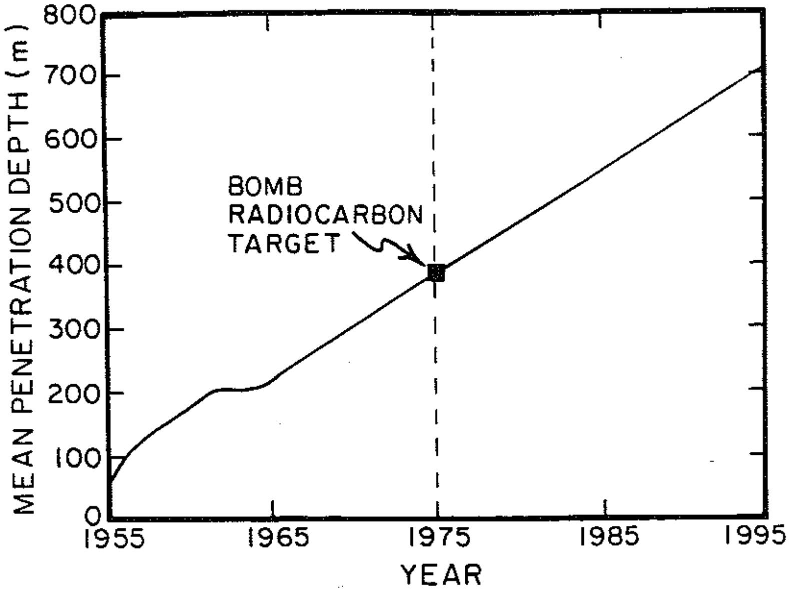
OCEAN INTERIOR

EDDY DIFFUSIVITY
= 2.4 cm^2/s

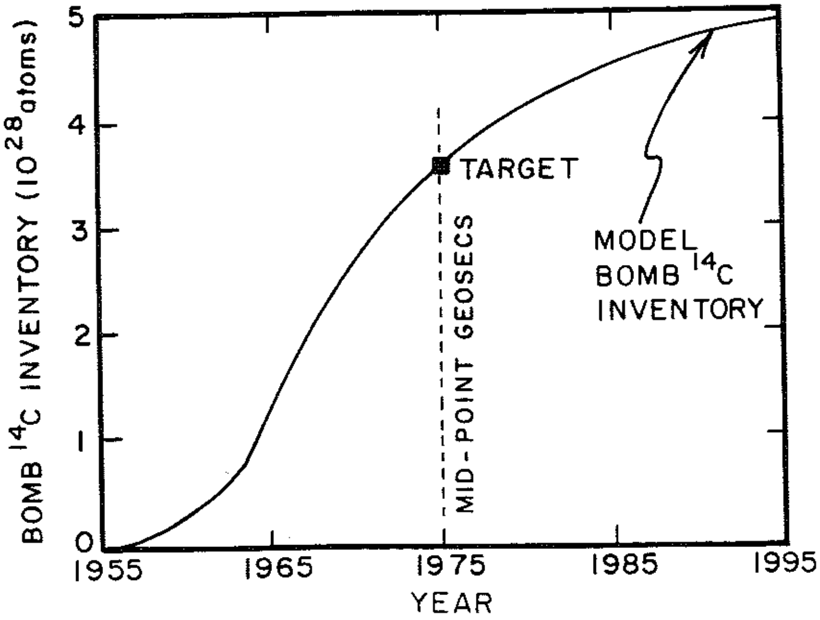
TREND IN SURFACE WATER
Δ ^{14}C CALCULATED USING SIMPLE MODEL



TREND IN MEAN PENETRATION DEPTH CALCULATED USING SIMPLE MODEL



TREND IN BOMB ^{14}C WATER COLUMN INVENTORY CALCULATED USING SIMPLE MODEL



deep water carried with it about 40 µmoles/liter of excess ΣCO_2. This yields an upper limit on the input of anthropogenic CO_2 into the deep sea of 0.5 gigatons of carbon per year. But this must be an upper limit because newly formed deep water cannot become fully charged with excess CO_2 during the brief period of winter-time deep convection.

An adequate assessment of the uncertainty in the ocean uptake estimates made using tracer-calibrated one-dimensional (1-D) models is not possible. The main uncertainty comes from the basic assumption that the depth of mixing increases as the square root of time. For fossil fuel CO_2 molecules, the time available for ocean penetration is about 30 years, while for bomb radiocarbon-tagged CO_2, it is about 10 years. Hence the model drives fossil fuel CO_2 about $\sqrt{3}$ or 1.73 times deeper into the sea than bomb ^{14}C-tagged CO_2. As we have no means to directly determine the extent of ventilation of the real ocean on the time scale of 30 years, the appropriate multiplier could perhaps be as low as 1.4 or as high as 2.0. Were these limits to be adopted as a measure of the uncertainty in the ocean uptake, the answer comes out to be ±20% (0.4 gigatons of C per year during the 1980s).

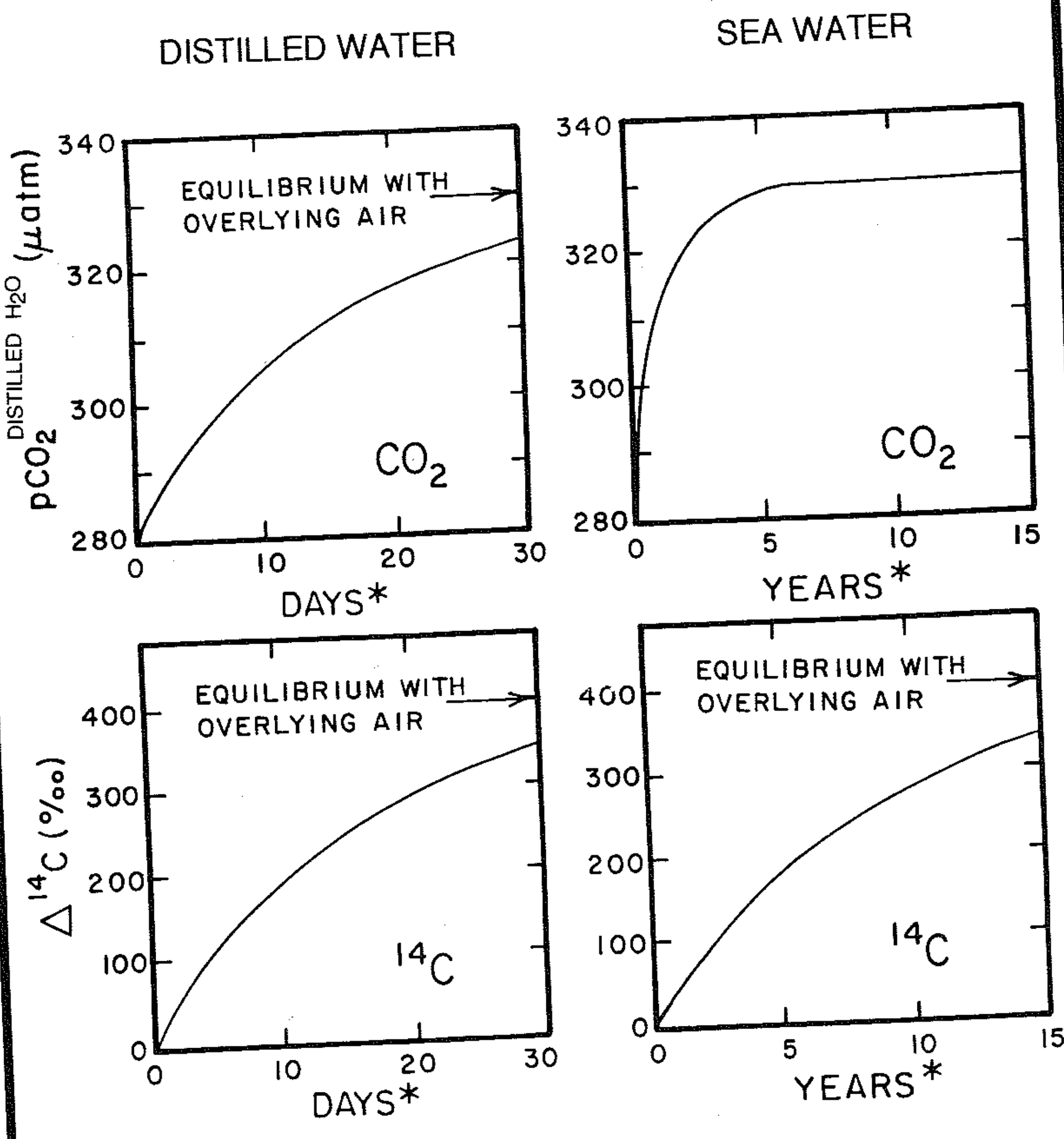
There is a tracer which might be used to overcome the penetration time mismatch between bomb ^{14}C and fossil fuel CO_2. It is the reduction in atmospheric $^{13}C/^{12}C$ ratio due to the introduction of CO_2 produced by fossil fuel burning. This CO_2 has a 2% lower ^{13}C to ^{12}C ratio than that in the atmosphere. Repeated surveys of $^{13}C/^{12}C$ profiles for ocean ΣCO_2 could provide an estimate of the depth of penetration of this signal. As the anthropogenic ^{13}C anomaly is coupled directly to the production of CO_2, no time difference exists. Quay and his colleagues attempted to quantify the redistribution of the anomaly created by the release of ^{13}C deficient fossil fuel CO_2 to the atmosphere by documenting the magnitude of the decline in the $^{13}C/^{12}C$ ratio both for atmospheric CO_2 and for upper ocean ΣCO_2 for the period 1970 to 1990. While the uptake they obtained is consistent with that based on the tracer-calibrated 1-D ocean model, due to the large uncertainties in the measured trends, this approach did not narrow the range of uncertainty in the amount of fossil fuel CO_2 taken up by the ocean during this period.

Chemical Versus Isotope Adjustment Time

One aspect of the 1-D model results is, at least at first glance, puzzling. While, as of 1975, the increase in the CO_2 partial pressure in the model's surface mixed layer had reached 85 to 90 percent of the atmospheric increase, the $^{14}C/C$ ratio in surface water had reached only about 50% of the atmospheric increase. Why such a big difference? The obvious answer is that fossil fuel CO_2 molecules had at that time a greater mean age than bomb ^{14}C-tagged CO_2 molecules (30 years versus 12 years). Hence they had a longer time to get into the ocean. However, this is not the major reason. Rather, the slowness of the ^{14}C response has to do with a fundamental difference between the time required for equilibration of carbon isotope anomalies and the time required for the equilibration of chemical anomalies. This difference is most easily understood by considering two hypothetical 75-meter high towers. One is filled with normal sea water and the other with distilled water. The waters in both towers have the same temperature and CO_2 partial pressure (280 μatm). Also the dissolved carbon in both initially has the pre-nuclear $^{14}C/C$ ratio. The major difference is that the distilled water contains no HCO_3^- or $CO_3^=$. The lids are removed from the tower tops and fans are activated so as to generate CO_2 exchange rates of 0.064 moles/m^2.yr.μatm. The question is, "how rapidly will the CO_2 partial pressures and the $^{14}C/C$ ratios in the tower waters approach those for the overlying 1975 air ($pCO_2 = 330$ μatm and $\Delta^{14}C = 400‰$)?" For the distilled water tower, both the partial pressure and isotope ratio will approach the atmospheric value with an e-folding time of 15 days. For the sea water tower, the isotope equilibration will take 200 times longer, a staggering 8.2 year e-folding time! The reason for this huge difference is that for the sea water tower, not only the isotopic composition of the 10 μmole/liter of dissolved CO_2 gas has to be exchanged but also that of the 2000 μmole/liter of HCO_3^- and $CO_3^=$ ions.

More tricky to understand is the time constant for the CO_2 partial pressure adjustment in the sea water tower. The e-folding time turns out to be close to one year, lying roughly geometrically between that for the distilled water (.04 yrs.) and that for the

TWIN TOWERS EXPERIMENT



* NOTE HUGE DIFFERENCE IN TIME SCALES!

isotopes in the sea water ΣCO_2 (8.2 yrs.). The reason is that rise in the CO_2 partial pressure in the sea water involves mainly the adjustment of its $CO_3^=$ concentration. For surface sea water, the $CO_3^=$ concentration is about 10 times lower than the ΣCO_2 concentration and 20 times larger than the CO_2 concentration. With this tower analogy in mind, it is easy to answer our question regarding the difference between the extent of isotope (^{14}C) and chemical (CO_2) equilibration yielded by the 1-D model for the time of the GEOSECS survey. Isotopic equilibration takes ten times longer than chemical equilibration, thus the $^{14}C/C$ ratio rises toward the atmospheric value far more slowly than the CO_2 partial pressure. This factor of ten reflects the ratio of the ΣCO_2 (isotopic reservoir) to $CO_3^=$ (chemical reservoir) in surface sea water.

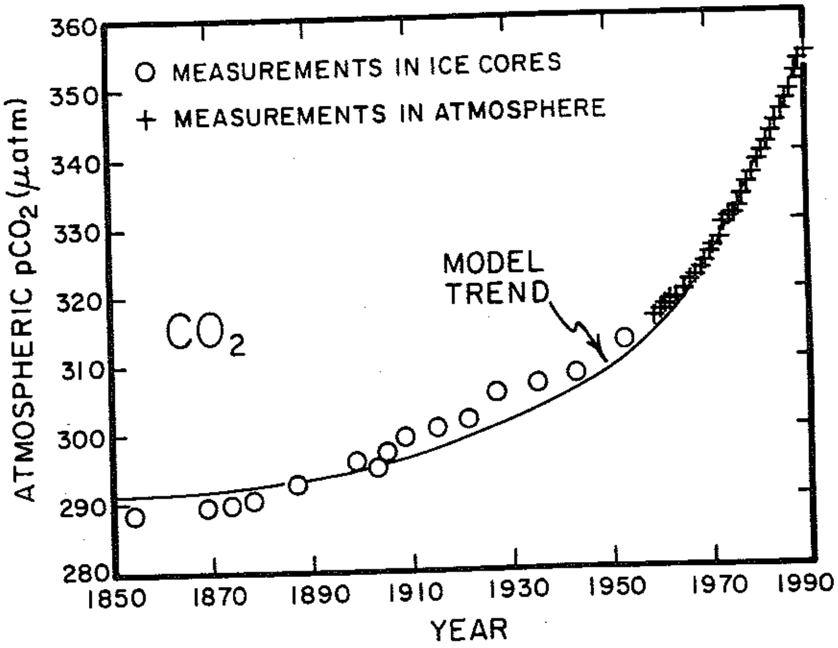
Isotopic Cross Checks

Three cross checks based on carbon isotope measurements can be used to evaluate the performance of the simple model adopted here. The first has to do with the magnitude of the change in the $^{14}C/C$ ratio for atmospheric CO_2 during the hundred-year period from 1850 to 1950 as recorded in tree rings. Because of the advent of bomb testing in the early 1950s, the $^{14}C/C$ lowering approach is viable only for the period before 1950. As the CO_2 generated by fossil fuel burning is free of radiocarbon, the $^{14}C/C$ ratio in atmospheric CO_2 should have decreased during this period. Indeed it did. The magnitude of the decrease depends not only on the amount of fossil fuel CO_2 released, but also on the extent to which this carbon was diluted by exchange of atmospheric carbon with carbon in the sea and in the terrestrial biosphere. As the amount of fossil fuel CO_2 generated is known, the magnitude of the ^{14}C to C ratio decrease tells us the extent of this dilution. Were no exchange with oceanic and biospheric carbon to have occurred, the decrease in atmospheric $^{14}C/C$ between 1850 and 1950 would have been about 12%. The observed decrease was only about 2%. The second cross check is based on the decrease in the $^{13}C/^{12}C$ ratio for atmospheric CO_2 from 1850 to present. Fossil fuel carbon has a $^{13}C/^{12}C$ ratio averaging 2% lower than that for atmospheric CO_2. Thus the release of CO_2 from fuel burning is

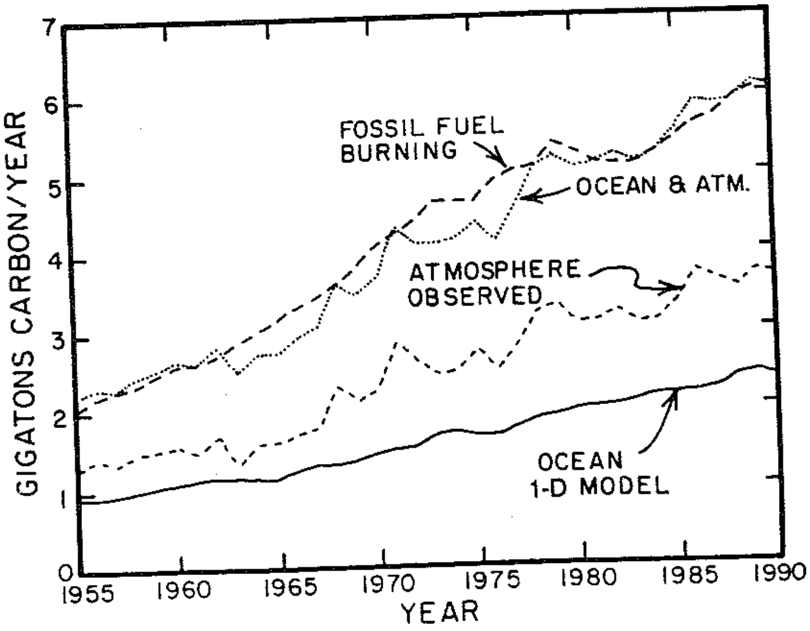
CROSSCHECKS ON THE SIMPLE 1-D MODEL

TREND IN ATMOSPHERIC CO_2 CONTENT

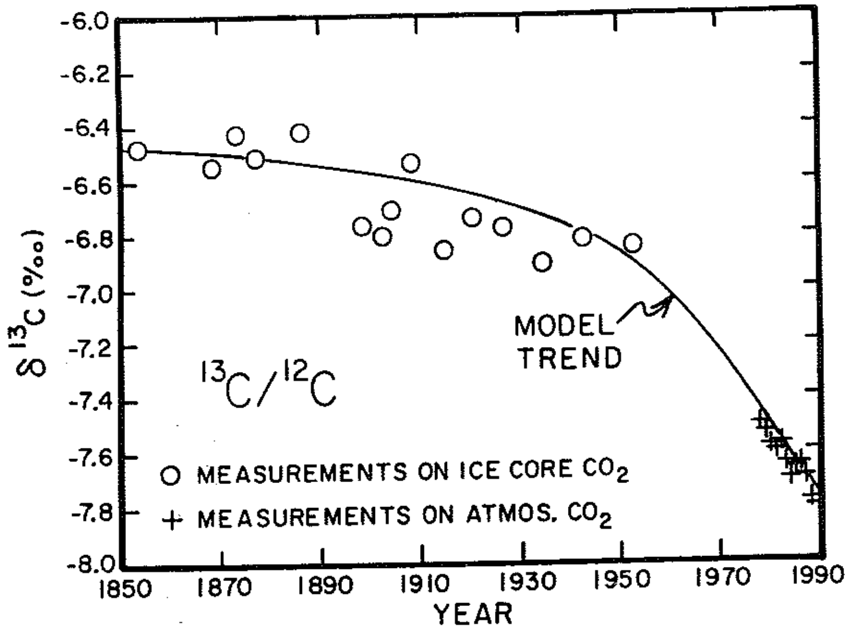
GENERATED WHEN KNOWN CO_2 EMISSIONS ARE ADDED TO THE COMBINED 1-D OCEAN AND BIOSPHERE MODELS



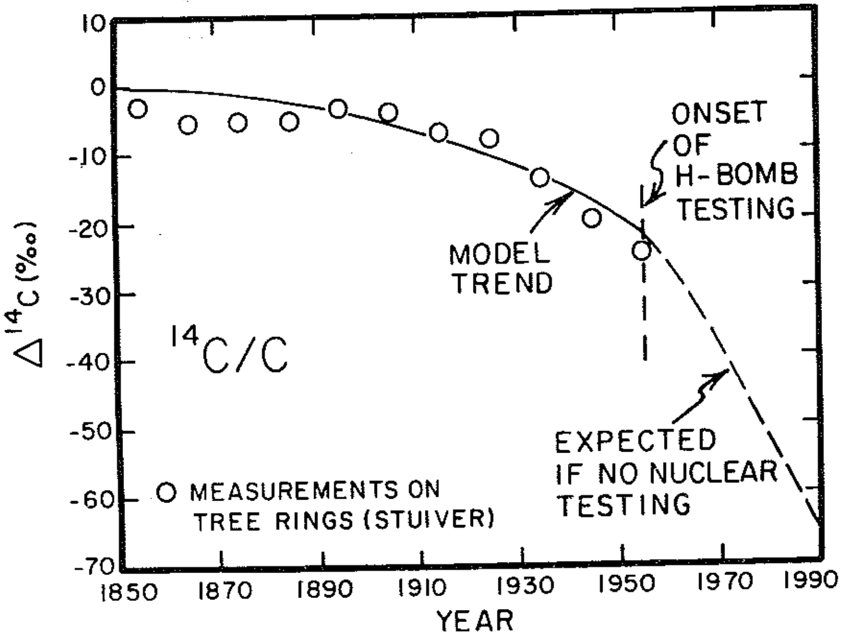
TREND IN OCEAN UPTAKE



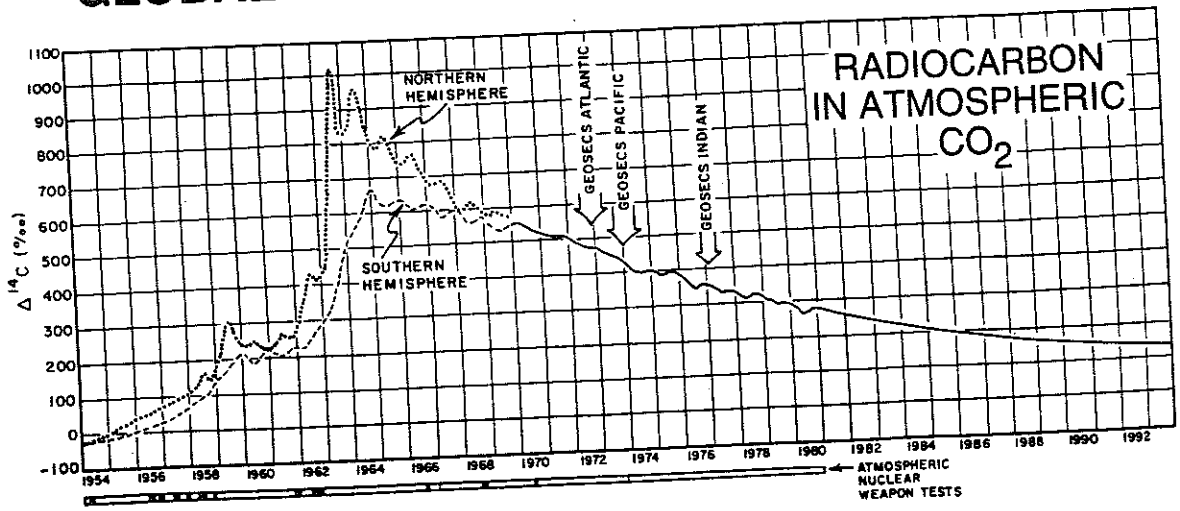
TREND IN ATMOSPHERIC $^{13}C/^{12}C$ RATIO



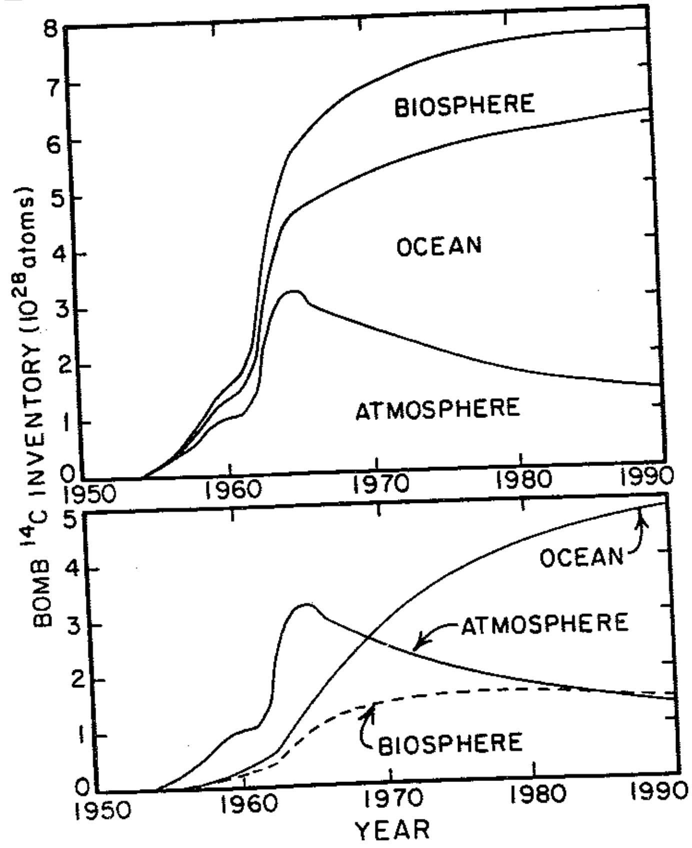
TREND IN ATMOSPHERIC $^{14}C/C$ RATIO



GLOBAL BOMB-RADIOCARBON INVENTORY*



MODEL CALCULATED BOMB ^{14}C INVENTORIES



*EXCLUDING STRATOSPHERIC EXCESS

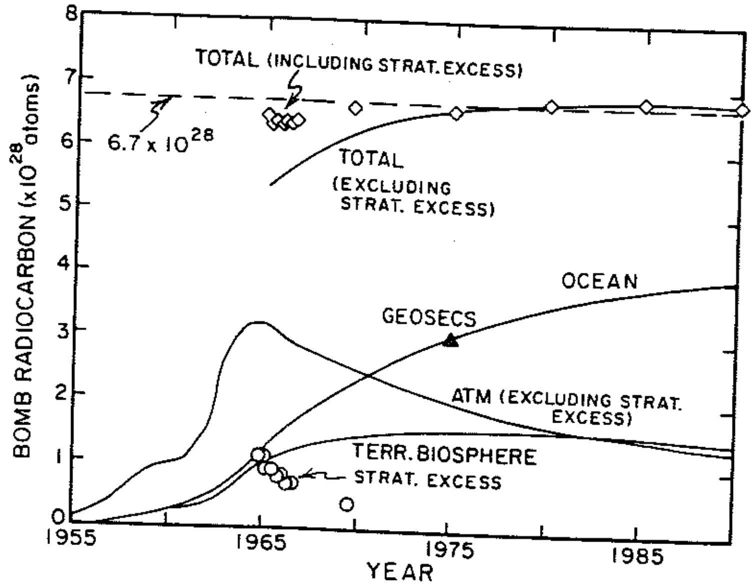
OCEAN BOMB ^{14}C INVENTORY

ESTIMATE OF OCEAN BOMB RADIOCARBON INVENTORY AS OF JANUARY 1, 1975

	OBSERVED 10^{26} ATOMS	NORMALIZED TO JAN. 1, 1975 10^{26} ATOMS
GEOSECS ATLANTIC JULY 1972 TO MARCH 1973	104 *	113
GEOSECS PACIFIC AUG. 1973 TO JUNE 1974	145	151
GEOSECS INDIAN DEC. 1977 TO APRIL 1978	73	67
TOTAL OCEAN AS OF JAN.1975		331
CORRECTION FOR DEFICIENCY IN SHALLOW PORTIONS OF OCEAN		-26
CORRECTED TOTAL		305

*Corrected for a possible overestimate of Arctic contribution

TOTAL BOMB ^{14}C INVENTORY



lowering the $^{13}C/^{12}C$ ratio for atmospheric CO_2. Again the magnitude of this lowering depends not only on the amount of CO_2 released by fossil fuel burning, but also by the extent of dilution resulting from the trading of atmospheric carbon atoms with terrestrial biosphere and ocean. This approach is complicated by the fact that CO_2 released as the result of deforestation and taken up as the result of greening also has a 2% lower $^{13}C/^{12}C$ ratio than atmospheric CO_2. The third cross check involves the decrease in the atmospheric $^{14}C/C$ ratio for the time period from 1970 to present. This decline is primarily the result of mixing of the bomb ^{14}C into the oceanic and biospheric carbon reservoirs.

The strategies for harnessing each of these pieces of isotopic information are similar. The simple one-dimensional model described above is used to estimate the extent of dilution through exchange with ocean carbon. In addition, an even simpler reservoir model is used for exchange with carbon in the terrestrial biosphere. This model divides the terrestrial biosphere into three compartments and treats each as a well-mixed reservoir

	Reservoir size gigatons C	Turnover time years
Short-lived vegetation and litter	150	2
Active soil humus	500	25
Long-lived vegetation	500	60

As the biospheric contribution to the dilution is several times smaller than the oceanic contribution, the larger uncertainties associated with the terrestrial model do not seriously hamper the approach.

The cross checks are conducted as follows. The model is initiated at steady state with the atmospheric CO_2 content at 292 ppm and the $^{13}C/^{12}C$ and $^{14}C/C$ ratios at their observed pre-industrial values. Fossil fuel CO_2 is then added to the model's atmosphere in accord with the known production history. This CO_2 has a $^{13}C/^{12}C$ ratio of -25‰ and carries no radiocarbon. Uptake of excess CO_2 by the model ocean occurs during each time step as does isotopic exchange with the biosphere and ocean. Then the decline in ^{14}C and in ^{13}C obtained from the model can be compared with the observed atmospheric trends.

The bomb radiocarbon calculation is done in a different way. The ^{14}C to C ratio for atmospheric CO_2 is constrained to follow the observed values. After each time step the inventory of bomb ^{14}C atoms in the atmosphere, ocean and biosphere reservoirs is computed (for each it is equal to the total number of radiocarbon atoms minus the steady state number of natural radiocarbon atoms). The post 1964 increase in the global inventory of bomb radiocarbon is the result of the downward mixing of the excess bomb ^{14}C stored in the stratosphere (based on surveys of the $^{14}C/C$ in stratospheric CO_2).

The simple tracer-calibrated model satisfactorily passes all three of these tests. It correctly reproduces the evolution of the atmosphere's ^{13}C to ^{12}C ratio and of its pre-nuclear ^{14}C to C ratio. It also is consistent with the requirement that after the test ban the total inventory of ^{14}C remained constant.

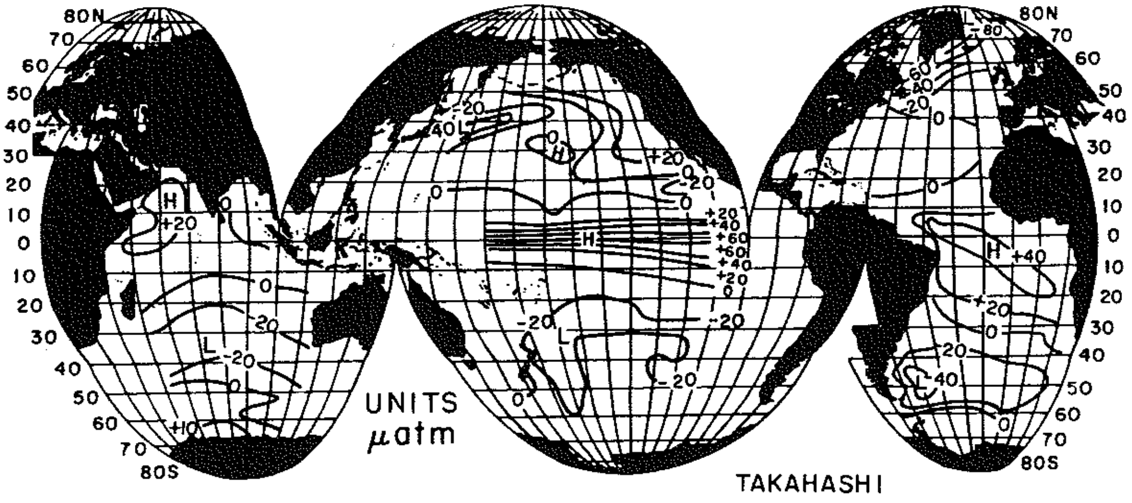
Air to Sea CO_2 Flux

Before returning to the discussion of ocean uptake models, one other means of determining the uptake of excess CO_2 by the ocean needs to be mentioned. The strategy is to measure the pCO_2 in surface ocean water at enough places and at enough times of year to establish the average global air-sea pCO_2 difference. Then, using the CO_2 exchange rate determined from radon, natural radiocarbon, and bomb radiocarbon distributions, the rate of transfer of CO_2 from air to sea can be calculated. To see what the magnitude of this difference might be, we can use the results for the simple 1-D ocean model. During the 1980s, about 2.2 gigatons of carbon per year entered the sea. Adopting the CO_2 invasion rate of 0.064 moles/m^2.yr.μatm, the expected air-sea CO_2 partial pressure difference would be:

$$\Delta pCO_2 = \frac{2.2x10^{15}\,\frac{gC}{yr}}{12\,\frac{gC}{moleCO_2}\,3.6x10^{14}\,m^2}\;\frac{1}{0.064\,\frac{moles}{m^2.yr.\mu atm}} \cong 8\mu atm$$

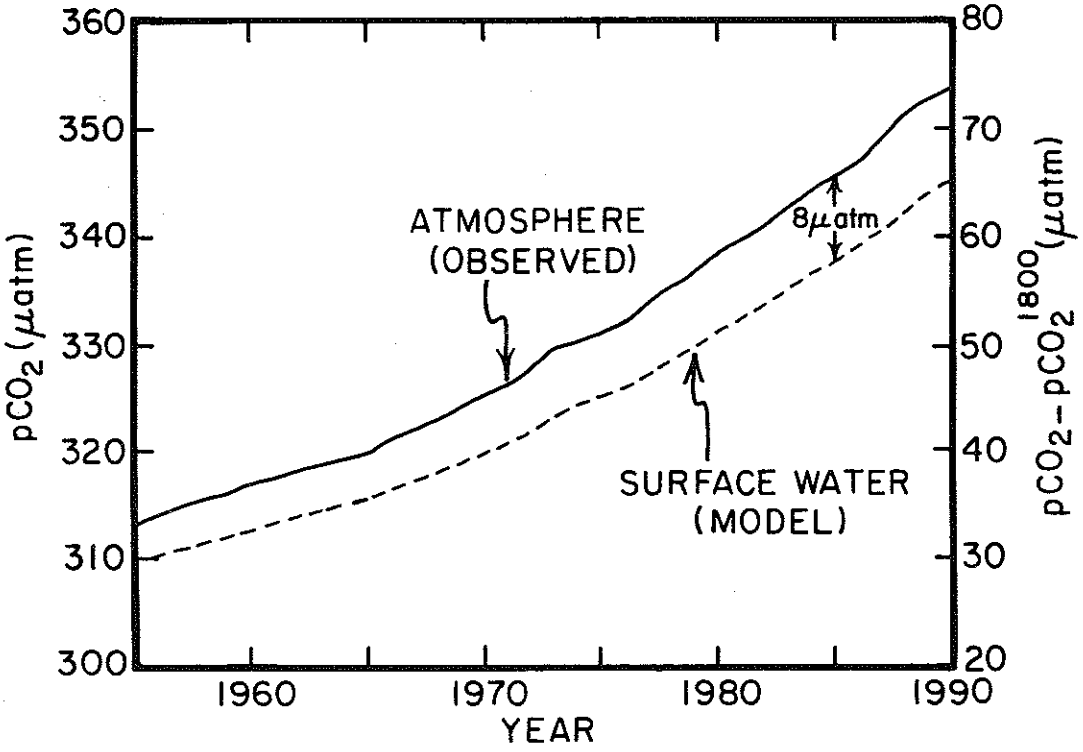
AIR - SEA CO_2 DIFFERENCE

OBSERVATION: pCO_2 SURFACE SEA - pCO_2 ATMOSPHERE



TAKAHASHI

PREDICTION: ONE DIMENSIONAL MODEL



As of 1993, the CO_2 partial pressure in the atmosphere had risen by 65 µatm above its pre-industrial value. Hence the model suggests that the surface ocean had risen 65-8 or 57 µatm achieving about 88% the atmospheric increase. This situation results from the fact that the resistance to CO_2 uptake posed by the air-sea interface is small relative to that posed by mixing within the sea. This is an unfortunate circumstance for those who wish to adopt the CO_2 flux strategy, for it makes the air-sea pCO_2 difference quite small compared to the geographic and seasonal texture of sea surface CO_2 pressures. Thus it is very difficult to establish the air-sea difference with sufficient accuracy. A difference of just 3.6 µatm (i.e., 1% of the atmosphere's pCO_2) drives an ocean uptake of 1 gigaton of carbon per year! To make the situation even worse, two fairly large and as yet uncertain corrections must be introduced. The first has to do with the natural cycling of carbon from sea, to continent, to rivers, and back to sea. About 0.6 gigatons of carbon are carried by rivers to the sea as dissolved organic matter and dissolved bicarbonate. The dissolved organic matter comes from matter generated by terrestrial plants. Upon reaching the sea, it is consumed by marine bacteria returning it to CO_2 form. The bicarbonate dissolved in rivers is also generated from soil CO_2 to balance the positive charge on cations released from soils as the result of weathering. As does the dissolved organic carbon, this bicarbonate eventually reaches rivers and is carried back to the sea. Both the carbon in the dissolved organic matter and bicarbonate ions carried to the sea by rivers originated from CO_2 in the atmosphere. In order to cycle 0.6 gigatons of carbon cycled in this way requires that prior to the Industrial Revolution, the partial pressure of CO_2 in the surface sea averaged about 2 uatm higher than that in the atmosphere.

The second correction involves a temperature difference between the few tens of a micron-thick sea water 'skin' and the ambient temperature for the bulk of mixed layer water. This skin cooling is caused by heat loss during evaporation. The temperature difference created in this way is thought to average about 0.2°C. As for each 0.1°C the skin is cooled, its CO_2 partial pressure drops by a bit over one µatm. In order to balance a

0.2°C skin cooling requires that the pCO_2 of bulk mixed layer water be about 2 μatm higher than that in the overlying atmosphere.

Taken together, these two corrections suggest that, during pre-industrial time, the pCO_2 in the oceanic mixed layer water was about 4 μatm higher than that in the atmosphere. If so, then an uptake of 2 gigatons of anthropogenic carbon by the sea would require that the atmosphere average only 4 rather than 8 μatm higher in partial pressure than the ocean mixed layer. Extensive measurements are now available from most regions of the ocean. Taro Takahashi has summarized these results and concludes that on the average the surface ocean mixed layer water has a CO_2 partial pressure 4±4 μatm lower than that for the atmosphere. While consistent with expectation from the simple tracer-calibrated reservoir model, the error in this estimate remains far too large to be of use in constraining the carbon budget. For this approach to be definitive, CO_2 partial pressure measurement co- verage (both geographically and seasonally) will have to be greatly expanded, river recycling and skin temperature biases will have to be accurately established, and the wind velo- city dependence of in CO_2 invasion rates will have to be taken into account. Our assessment is that this approach will never become competitive with the others available to us.

Interhemispheric CO_2 Gradient

One piece of evidence appears to be at odds with the conclusion that the amount of carbon stored in the terrestrial biosphere has remained nearly constant over the last several decades. It is based on the interhemispheric difference in the CO_2 content of the atmosphere. As expected, measurements show that northern hemisphere air has a higher mean annual CO_2 content than southern hemisphere air. We say "as expected", because 95 percent of the fossil fuel CO_2 emissions occur in the north temperate latitude belt. The problem is that atmospheric models designed to simulate meridional mixing predict a gradient nearly twice as great as is observed. Fossil fuel CO_2 is introduced into these models in accord with the actual geographic pattern of emissions. The models are

EXPECTED AIR - SEA Δp_{CO_2} FOR 1980s

2 gigatons

$$\begin{array}{c}\text{EXCESS}\\ \text{CO}_2\text{ FLUX}\\ \text{INTO SEA}\\ \text{(total)}\end{array} = \frac{2 \times 10^{15}\ \text{gC/yr}}{12\ \text{gC/mol}} = 1.66 \times 10^{14}\ \text{mol/yr}$$

$$\begin{array}{c}\text{EXCESS}\\ \text{CO}_2\text{ FLUX}\\ \text{INTO SEA}\\ \text{(per unit area)}\end{array} = \frac{1.66 \times 10^{14}\ \text{mol/yr}}{3.5 \times 10^{14}\ \text{m}^2} = 0.48\ \text{mol/m}^2\text{yr}$$

$$\text{EXPECTED } \Delta\, \text{pCO}_2^{\text{AIR-SEA}} = \frac{0.48\ \text{mol/m}^2\text{yr}}{0.06\ \text{mol/ m}^2\text{ppm yr}} = 8\ \text{ppm}$$

BASED ON ^{222}Rn, NAT. ^{14}C AND BOMB ^{14}C

$$\begin{array}{rcccc} & \underline{\text{1800 AD}} & & \underline{\text{1985 AD}} & \\ \text{SURF. H}_2\text{O pCO}_2 & 280 & \longrightarrow & 342 & = 62 \\ \text{ATM pCO}_2 & 280 & \longrightarrow & 350 & = 70 \end{array} \quad \frac{62}{70} = 0.89$$

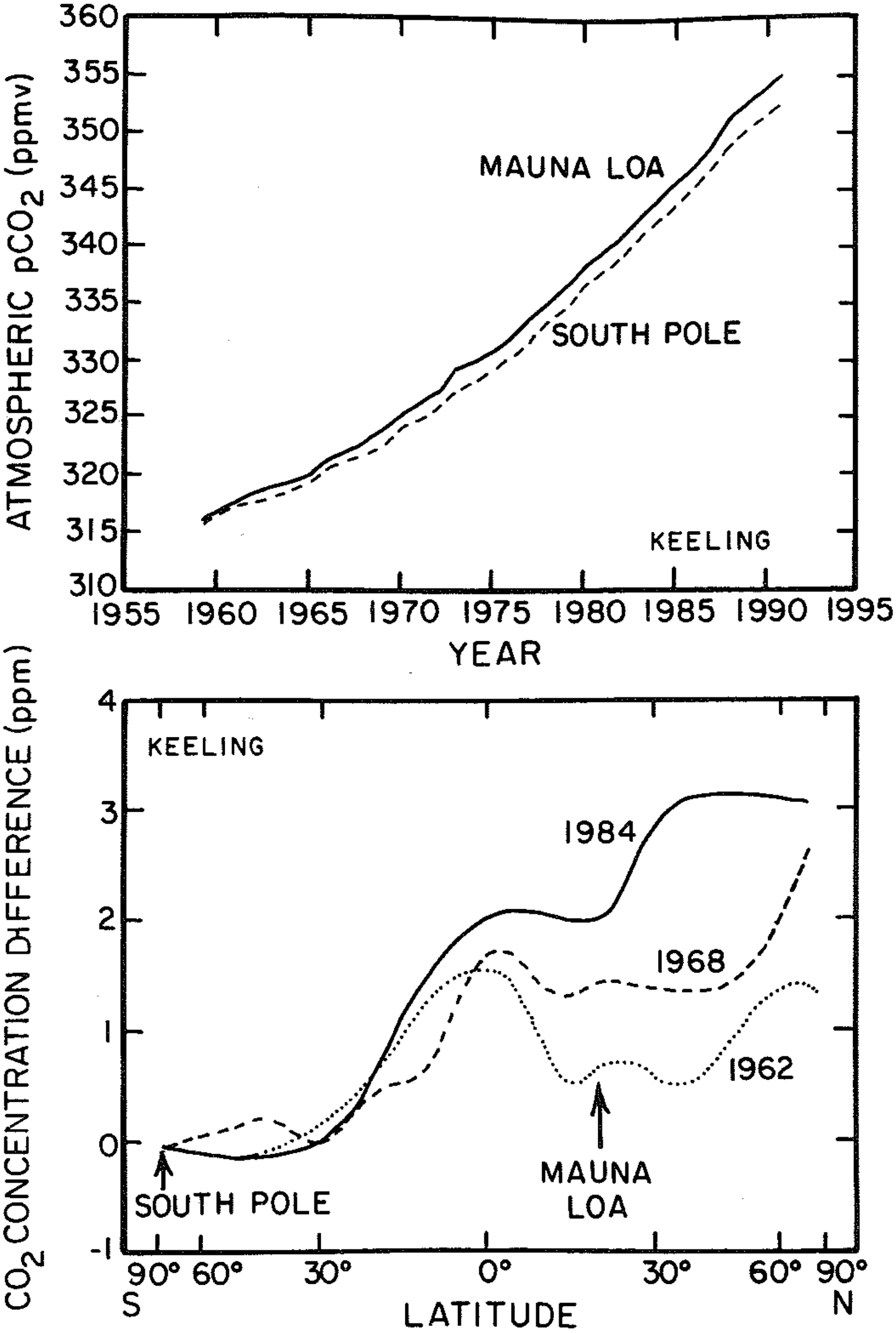
AFTER CORRECTIONS FOR SKIN TEMP. AND RIVER CYCLE

$$\begin{array}{rcccc} & \underline{\text{1800 AD}} & & \underline{\text{1985 AD}} & \\ \text{SURF. H}_2\text{O pCO}_2 & 284 & \longrightarrow & 346 & = 62 \\ \text{ATM pCO}_2 & 280 & \longrightarrow & 350 & = 70 \end{array} \quad \frac{62}{70} = 0.89$$

IN 1985 EXPECTED $\Delta\, \text{pCO}_2^{\text{AIR-SEA}} = 350 - 346 = 4$ ppm programmed to dispense 2 gigatons of C per year to the oceans (uniformly across its surface). The imbalance between fossil fuel production and atmosphere-ocean inventory increase is assumed to enter the terrestrial biosphere (uniformly across the continents). As continents lie mainly in the tropical and northern temperate zones, this uptake, like fossil fuel CO_2 production, is skewed strongly to the northern hemisphere. Models programmed in this way generate an annually averaged 5 μatm difference in CO_2 partial pressure between north temperate and south temperate latitudes for the 1980s. The observed difference is only about 3 μatm. With a 5 ppm interhemispheric gradient, enough CO_2 flows to the southern hemisphere to match both the 1.6 GtC/yr rise in its atmospheric inventory and the 1.2 GtC/yr entering that 60% of the ocean surface lying in the southern hemisphere. With an interhemispheric gradient of only 3 ppm, the models would move only 3/5ths of this amount or 1.7 gigatons of carbon from the northern to the southern hemisphere. As this amount is only slightly greater than that accumulating in the southern hemisphere atmosphere, almost none is left over for uptake by the southern hemisphere ocean. Based on this information in 1989, Tans, Fung and Takahashi stunned the world's carbon budgeters by bluntly stating that the yearly ocean uptake of CO_2 had been greatly overestimated. Rather than being on the order of 2 gigatons carbon per year, it was more likely no more than one quarter this amount. If so, then greening must be even larger than we had thought, outpacing forest cutting at a 2 to 1 clip! Further, if the Tans et al. scenario is correct, the ocean is relegated to a minor role in fossil fuel CO_2 budgeting. The terrestrial biosphere becomes dominant.

In addition to the arguments presented above, two rebuttals have been put forth to counter the Tans et al. argument. One has to do with the reliability of the atmospheric transport estimates. The other has to do with the implicit assumption underlying the Tans et al. argument, namely, prior to the Industrial Revolution, no interhemispheric atmospheric CO_2 gradient existed. Let us first examine the transport rebuttal. Perhaps the atmospheric models are not capable of estimating the interhemispheric transport to better

EVOLUTION OF INTERHEMISPHERIC CO_2 CONCENTRATION DIFFERENCE



than a factor of two. If so, the Tans et al. argument crumbles. But atmospheric modelers have an ace up their sleeves in this regard. Like oceanographers, they have tracer distributions to lean on for verification. Two such tracers, ^{85}Kr and CFCs, are available. Like fossil fuel CO_2, both tracers are generated primarily in the northern hemisphere; ^{85}Kr by nuclear reactors and CFCs by industry, and hence should be found at higher concentrations in the northern hemisphere air. ^{85}Kr is radioactive with a half life of 11 years. Thus even though its concentration in the atmosphere was not rapidly changing during the 1980s, the decay of ^{85}Kr in the southern hemisphere had to be balanced by transport across the equator. For CFCs, the atmospheric burden is steadily rising. The rise in the southern hemisphere atmosphere must be supplied by cross-equatorial transport. Models are checked to see whether they reproduce the observed meridional gradients of ^{85}Kr and/or CFCs. If the match is not satisfactory, the formulation of the mixing dynamics is tweaked until the mismatch has been eliminated. It turns out that models adjusted to meet the ^{85}Kr constraint meet the CFC constraint as well (or vice versa). Because the models which have been used to calculate the transport of CO_2 from one hemisphere to the other have passed the ^{85}Kr-CFC test, modelers are confident that the CO_2 transports they generate is sufficiently accurate that the Tans et al. argument must be taken seriously.

Even so, an escape hatch is still available. The latitudinal gradients for ^{85}Kr and for CFCs undergo only minor changes with season. By contrast, that for CO_2 undergoes large changes. During the October through April period, when respiration greatly exceeds photosynthesis in the northern hemisphere, the CO_2 content of the north temperate atmosphere rises, creating a much enhanced north to south gradient. During the May through September period when photosynthesis dominates, the CO_2 content of the air at these northern latitudes is drawn down well below that for the southern hemisphere. So the difference between the CO_2 content of air of north and south temperate zones actually changes sign during the course of a year! While the ^{85}Kr-CFC test proves that over the course of an entire year the magnitude of cross equatorial air exchange obtained in the models is correct, it does not verify that the seasonality of this exchange is correct. If, for example, the model exchanges too little air during the Fall period, when the CO_2 gradient is lower than its mean annual value, and too much air during the Spring period, when the CO_2 gradient is higher than average, the result would be an underestimation of the amount of CO_2 transported from the northern to the southern hemisphere. However, those who do this modeling are adamant that the seasonality of transport is not flawed. But as we are not conversant with their arguments, we cannot defend them. Sorry!

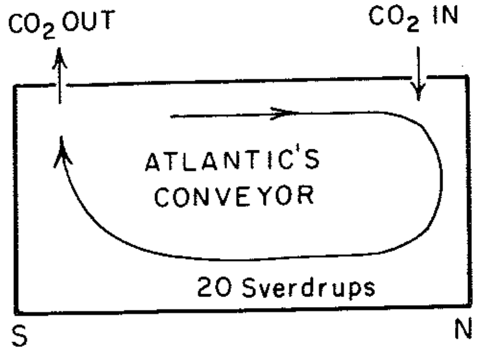
The other rebuttal shows more promise. It is based on an observation made by C. D. Keeling and M. Heimann. They examined the evolution of the difference between the annually averaged CO_2 content measured at Mauna Loa, Hawaii and that measured at the South Pole. As expected, this difference has increased with increasing fossil fuel CO_2 production. At the beginning of the records (1958), the difference was very small. As time progressed, it became larger and larger. What occurred to Keeling and Heimann was that if the trends for these two stations were extrapolated back in time, they would have intersected about 1950. Prior to 1950, the air over Antarctica would have had a higher CO_2 content than that over Hawaii! If so, then prior to the Industrial Revolution, southern hemisphere air must have had a higher CO_2 content than northern hemisphere air. In other words, at that time CO_2 must have been moving through the atmosphere from south to north. Then, as fossil fuel CO_2 generation in the northern hemisphere grew, this natural northward flow of CO_2 was compensated to an ever increasing extent by a southward flow of fossil fuel CO_2 until, about 1950, the two flows became equal, eliminating the gradient.

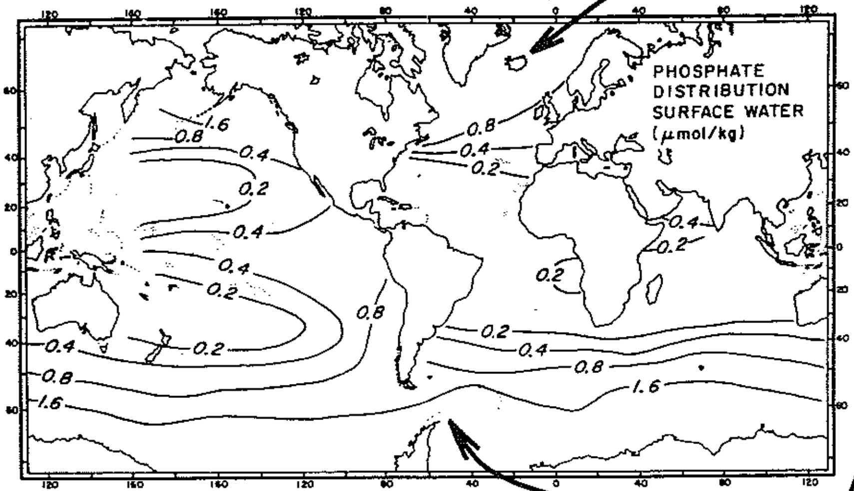
Of course, Keeling and Heimann realized that if, during pre-industrial time, CO_2 was moving from south to north through the atmosphere, then an equal amount must have somehow moved in the opposite direction. Otherwise, the CO_2 content of the northern hemisphere atmosphere would have been going up and that in the southern hemisphere going down. In fact, the ice core record tells us that neither was changing. The only possible routes for such a return flow lie in the ocean.

The most likely ocean route is via the lower limb of what is referred to as the Great Ocean Conveyor. This current system transports 20 million cubic meters per second of water northward in the upper Atlantic. In the vicinity of southern Greenland and Iceland, this water is cooled and sinks to the abyss forming a southward flowing deep water mass, referred to by oceanographers as North Atlantic Deep Water (NADW). Could it be that before sinking, this water picks up CO_2 from the northern Atlantic atmosphere? This CO_2 would then be carried the length of the Atlantic to the Antarctic, returned to the surface and dumped back into the atmosphere. In order to carry 1 gigaton of carbon per year from the northern to the southern hemisphere, NADW would have to contain 130 μmoles/liter (6%) excess ΣCO_2.

A means exists to assess the magnitude of this excess. It involves a comparison of the amount of ΣCO_2 actually present in various waters in the ocean with the amount they would contain were no transport of CO_2 through the atmosphere from one region of the ocean surface to another to occur. These hypothetical ΣCO_2 amounts are based on three measured properties of the water: salinity, phosphate content, and alkalinity (corrected for the nitrate contribution). Salinity is important because the removal of fresh water by evaporation enriches all the ions in sea water (and hence also ΣCO_2) and, of course, the addition of fresh water by precipitation dilutes them. The phosphate content is important because it provides a measure of the changes in ΣCO_2 related to biological cycles. Each mole of phosphorus removed from sea water by photosynthesis is accompanied by about 125 moles of ΣCO_2. Or putting it the other way around, waters rich in dissolved phosphate will have a correspondingly high respiration CO_2 content. The alkalinity is important because it provides a measure of the amount of ΣCO_2 lost to the formation of $CaCO_3$ shells or gained from their dissolution. On the time scale of ocean mixing, only two chemical mechanisms exist to change the alkalinity of sea water, namely, gains or losses of Ca^{++} to $CaCO_3$ and of NO_3^- to organic tissue. The change in the sum of the alkalinity and nitrate contents of the water provides a measure of the change due to calcium

INTERHEMISPHERIC CO_2 TRANSPORT BY THE GREAT OCEAN CONVEYOR





PO$_4$ DIFFERENCE

$\boxed{1.6} - \boxed{0.8} = 0.8 \frac{\mu\text{mol PO}_4}{\text{liter}}$

RESPIRATION CO_2 DIFFERENCE

$\frac{C}{P}$ IN MARINE ORG.

$0.8 \frac{\mu\text{mol PO}_4}{\text{liter}} \times 125$

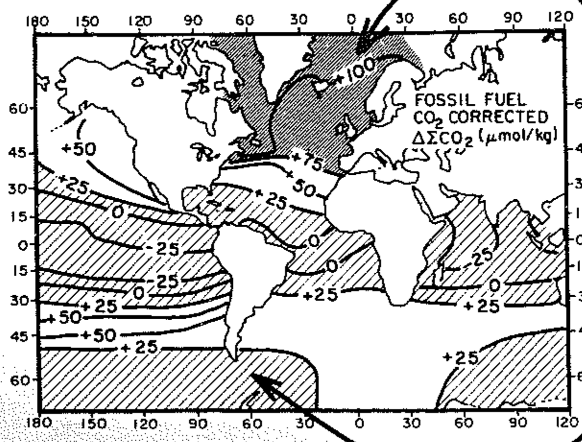
$= 100 \frac{\mu\text{mol } \Sigma CO_2}{\text{liter}}$

$\Delta\Sigma CO_2$

$= \Sigma CO_{2\,OBS.}$

$- \Sigma CO_{2\,EXP.}$

IF NO CO_2 TRANSPORT THROUGH ATMOSPHERE



$\Delta\Sigma CO_2$ DIFFERENCE

$\boxed{100} - \boxed{20} = 80 \frac{\mu\text{mol}}{\text{liter}}$

N TO S CO_2 TRANSPORT

$20 \text{ Sverdrups} \times 80 \frac{\mu\text{mol}}{\text{liter}}$

$= 0.6 \frac{\text{Gt C}}{\text{yr}}$

alone. Were no transport of CO_2 from one oceanic region to another through the atmosphere to have occurred, then ΣCO_2 contents calculated from the measured salt, phosphate, alkalinity, and nitrate contents of the water would be identical to the observed values (of course, a necessary part of the calculation is to reference all the calculated salinities, ΣCO_2s, and alkalinities to one of the measured values).

What is found when this is done is that the differences ($\Sigma CO_{2\text{ measured}} - \Sigma CO_{2\text{ calculated}}$) for surface waters are not all zero. Rather, they cover range of about 130 µmole/liter. The highest values are found in the northern Atlantic and the lowest in the tropical ocean. The fact that they are not all equal to zero requires that CO_2 be given up to the atmosphere from some parts of the surface ocean and extracted from the atmosphere in others. Of importance here, is that values for the northern Atlantic surface waters are considerably higher than those for the Antarctic surface waters. This is consistent with the hypothesis that the conveyor's lower limb is charged with excess ΣCO_2 drawn in from the atmosphere over the northern Atlantic. Part of this excess is dumped back into the atmosphere over the Antarctic Ocean. The difference in excess CO_2 content for surface waters in the northern Atlantic and those in the Antarctic is about 80 µmole/liter or enough to transport about 0.6 gigatons via the lower limb of the Atlantic's conveyor belt from the northern to the southern hemisphere. This is about 60% of the amount needed to void the Tans et al. argument. Of course this assumes that all 20 Sverdrups of NADW make it to the Southern Hemisphere and that all this water upwells in the Southern Hemisphere.

But what is responsible for the great excess of ΣCO_2 in surface waters in northern Atlantic waters relative to those in the Antarctic? The answer has to do with the fact that the northern water has a much lower phosphorus content than the southern water. Winter surface waters in the northern Atlantic have about 0.8 µmoles/liter PO_4 while those in the Antarctic average about 1.6 µmoles/liter. The difference of 0.8 µmoles/liter corresponds to about 100 µmoles/liter of respiration CO_2. This difference endows Antarctic surface waters with a higher CO_2 partial pressure than those in northern Atlantic, creating a tendency for CO_2 to escape from Antarctic waters and invade northern Atlantic waters. If buckets containing these waters were placed side by side in a sealed air space, then the excess respiration CO_2 would escape from the Antarctic bucket and invade the northern Atlantic bucket. This transfer would continue until the difference in CO_2 partial pressure was eliminated. At this point the water in the Antarctic bucket would have lost 50 µmoles/liter of CO_2 and that in the northern Atlantic bucket would have gained 50 µmoles/liter of CO_2. This would create a 100 µmole/liter difference in the $\Delta\Sigma CO_2$ values for these waters. Of course, in the real world, the transfer does not go to completion. Surface waters do not remain in contact with the atmosphere long enough to either give up or absorb their full component of CO_2. It is for this reason that an 80 µmole/liter difference in $\Delta\Sigma CO_2$ is observed rather than the full 100 µmole/liter difference. The residual excess of respiration CO_2 in Antarctic surface waters provides the driving force for the expulsion of CO_2 to the atmosphere and the residual deficiency in respiration CO_2 in the northern Atlantic the driving force for the uptake of CO_2.

Thus the answer to the apparent mismatch between the magnitude of the net cross-equatorial transport of CO_2 and the accumulation of anthropogenic in the southern hemisphere atmosphere and ocean lies in some combination of inadequacies in the atmospheric models and ocean transport of CO_2 via the conveyor. The reason is that we see no way that fossil fuel CO_2 uptake by the ocean can have been any less than about 1.5 GtC/yr. during the 1980s. Our confidence stems from the depth to which bomb testing ^{14}C and ^{3}H had been mixed into the sea as of the time of the GEOSECS program (i.e., circa 1975). These results show that on a decade time scale nearly 10% of the ocean is exposed to the atmosphere. As fossil fuel CO_2 molecules have had three decades to penetrate the sea, regardless of the mixing model adopted, they must have equilibrated with substantially more than 10% of the ocean volume. The distribution coefficient of CO_2 between the atmosphere and one tenth the ocean reservoir would be about 2 to 1. During the 1980s the amount of CO_2 accumulating in the atmosphere averaged about 3 gigatons.

A LOWER LIMIT ON OCEAN UPTAKE OF FOSSIL FUEL CO_2

ATMOSPHERIC CAPACITY

$$\underset{\underset{\dfrac{1000\,\frac{\text{g AIR}}{\text{cm}^2}}{29.5\,\frac{\text{g AIR}}{\text{mol AIR}}}\times 10^4\,\frac{\text{cm}^2}{\text{m}^2}}{\uparrow}}{3.4\times 10^5}\,\frac{\text{mol AIR}}{\text{m}^2}\times \underset{\underset{\text{atm CO}_2\text{ DURING 1980 s}}{\nwarrow}}{3.5\times 10^{-4}}\,\frac{\text{mol CO}_2}{\text{mol AIR}}\times \underset{\underset{\text{AREA OF EARTH}}{\uparrow}}{5.1\times 10^{14}}\,\text{m}^2$$

$$= 60.7\times 10^{15}\,\text{mol}$$

OCEAN CAPACITY

$$\frac{\overset{[\Sigma\text{CO}_2]\text{ SURF. H}_2\text{O}}{\overset{\swarrow}{2\,\frac{\text{mol}}{\text{m}^3}}}}{\underset{\underset{\text{BUFFER FACTOR}}{\nearrow}}{9}}\times \underset{\underset{\text{MEAN DEPTH OCEAN}}{\uparrow}}{3.8\times 10^3}\,\text{m}\times \underset{\underset{\text{AREA OCEAN}}{\uparrow}}{3.6\times 10^{14}}\,\text{m}^2$$

$$= 304\times 10^{15}\,\text{mol}$$

$$\frac{\text{OCEAN CAPACITY}}{\text{ATMOS. CAPACITY}} > \frac{\overset{\text{MINIMUM FRACTION OF OCEAN AVAILABLE FOR UPTAKE}}{\overset{\swarrow}{0.1}}\times 304\times 10^{15}}{60.7\times 10^{15}} \cong \frac{1}{2}$$

I.E. FOR AN ATMOSPHERIC INCREASE OF 3.0 GtC/yr, THE OCEAN UPTAKE MUST BE AT LEAST 1.5 GtC/yr.

Hence at least 1.5 gigatons per year must have entered the sea. This is the absolute minimum!

Ocean Uptake Revisited

Despite its tracer underpinnings and the cross checks provided by the atmospheric O_2 decline and reductions in the atmospheric $^{13}C/^{12}C$ and $^{14}C/C$ ratios, the simple reservoir model approach can yield answers no better than ±15% (i.e., ±0.3 gigatons of uptake for the 1980s). The very simplicity of these models denies the possibility of greater accuracy. To do better will require the development of models which simulate the physics of the ocean's mixing. Models for this purpose are now in use in several laboratories around the world. Particularly advanced are those at the NOAA Geophysical Fluid Dynamics Laboratory in Princeton and at the Max Planck Institute for Meteorology in Hamburg. While it is beyond the scope of this book to describe, in detail, the architecture of these models, a brief accounting is necessary in order to provide an appreciation for their strengths and limitations. The model ocean is divided into egg crate-like boxes with edges several degrees on a side. Ten to twenty such boxes are stacked above each grid square. The thicknesses of these boxes increases logarithmically with depth in the model ocean. The model crudely replicates both the geography and bathymetry of the real ocean. Water flow between adjacent boxes is driven by wind stresses applied to the sea surface and by density differences prescribed across the model's surface. In models designed to estimate the uptake of CO_2 by the ocean over the last century, the winds, temperatures and salinities are held at the observed climatic means. In their more advanced form, these models include seasonality in these forcing factors. Natural radiocarbon is carried as a passive tracer in these runs. The model ocean is then run for several thousand model years to insure that its circulation has reached steady state. The temperatures, salinities, circulation patterns and radiocarbon distributions for the model ocean's interior are then compared with those for the real ocean. Attempts are then made to remove anomalies between model output and observation by modifying the model's wind field, its surface density field, its passage geographies, and its horizontal and vertical eddy diffusivities. As the impacts of such adjustments are globally complex, they are not equivalent to the tuning carried out for the simple reservoir models where the adjustment of each variable parameter has a predictable impact. Rather, changes are made and the new steady state fields are observed. Often improvements in one aspect are accompanied by deteriorations in others.

While the achievement of a match with the observed density and radiocarbon fields provides evidence that the model's large scale thermohaline circulation is more or less correct, this agreement does not guarantee that the ventilation rate of its thermocline and polar water column is correct. As these are the regions where anthropogenic CO_2 is currently being stored, it is important to verify the correctness of this smaller scale ventilation. Clearly, the distribution of the transient tracers produced by bomb testing (^3H and ^{14}C), by reactors (^{85}Kr) and by industry (CFCs) are ideal for this purpose. Unlike the distribution of natural radiocarbon which is sensitive mainly to mixing processes on the century time scale, the distributions of transient tracers are dictated by mixing processes which occur on the time scale of decades. The challenge faced by modelers during the next decade will be to adjust the architecture of their models so as to achieve a satisfactory match to the observed distributions of these tracers.

For the near term, the most powerful constraints are offered by the joint use of bomb ^{14}C and ^3H data. We say joint use because taken alone each tracer has a major drawback. For radiocarbon, the drawback is that a separation must be made between the natural component and the bomb component. This drawback does not apply to tritium, for the bomb component overwhelms the natural component. The drawback for tritium stems from the rather large uncertainties related to the geographic pattern and timing of its input to the sea. Unlike radiocarbon which was spread fairly uniformly through the troposphere and entered the sea as the result of CO_2 exchange, tritium was quickly carried to the planetary surface in precipitation and water vapor. Consequently, its input was subject to large and not well understood geographic gradients. Fortunately, by combining information from the limited number of pre-nuclear radiocarbon data points for surface ocean water and the limit of penetration as established from tritium, it has been possible to make a reasonably reliable separation between the contributions of natural and bomb-testing radiocarbon for most parts of the ocean of interest. This endeavor has been greatly improved by the realization that in the ocean's thermocline a very strong correlation exists between the distributions of dissolved silica and natural radiocarbon.

Down the road a few years, powerful constraints will come from man-made CFCs. No natural background exists They are quite well mixed through the atmosphere. Their solubilities are well known and their concentration in surface water should be very close to equilibrium with the overlying atmosphere. We say "down the road" because CFCs are late comers on the tracer scene. The GEOSECS program was conducted prior to the advent of the technology used for CFC measurements in sea water. Measurements were begun in about 1980. As a result of this late start until the recent WOCE surveys, we lack a global survey. So the full power of the freon constraint awaits the assimilation of the data gathered by this program.

It is interesting to note that ocean circulation models (OCMs) yield CO_2 uptake estimates very similar to those obtained employing the simple tracer-calibrated reservoir models. While both approaches adopt the same thermodynamic capacities and CO_2 exchange rates, the all important rates of physical mixing are handled in totally different ways. The parameters in the simple reservoir models are constrained by transient tracer data. To date, the OCMs have been tuned only to fit the large scale distribution of natural radiocarbon. Hence the match between estimates of ocean uptake of anthropogenic CO_2 obtained by these two quite different classes of models adds confidence to claims that we have a firm handle on this aspect of the carbon budget. It also demonstrates that the reservoir modelers lucked out in their assumption that penetration to greater depths proceeds in accord with the square root of time. By chance, the real ocean came close to following this simple relationship.

Global Greening

Every approach to establishing a carbon budget leads to the conclusion that as the result of human activity the Earth is being greened. On the average over the past 40 years greening must have more or less matched biomass losses attributable to forest cutting. An exception is that during the early 1990s, R. Keeling's O_2 measurements make it clear that greening has exceeded these losses; the terrestrial biosphere appears to have been packing away carbon.

If during the 1980s greening balanced forest cutting, then presumably we could estimate its magnitude from forest statistics. The oft-quoted satellite-based figure of about 1.6 gigatons of carbon per year for the current losses resulting from forest cutting is subject to a large uncertainty. For example, two components of the forest cutting estimates have recently been revised downward. An analysis of satellite observations suggests a reduction in estimates of the acreage cut in the tropics by as much as 30%. New surveys of the mean standing biomass in the tropical forest being cut are also significantly lower than those previously adopted value. Another correction which must be made is that in many northern area forests previously cut are now regrowing. Together, these corrections may bring the net annual decrease in forest stocks resulting from the combination of deforestation and reforestation down to a gigaton or less. Assuming that during the 1980s the humus content of agricultural lands had stabilized, the required rate of greening would then be 0.9 ± 0.3 gigatons of carbon per year.

Is it feasible that carbon is being packed away in the terrestrial biosphere at this pace as the result of increases in the availability of CO_2 and fixed nitrogen? Let us first examine the amount of growth enhancement to be expected from the availability to all plants of excess atmospheric CO_2. As of 1997, the CO_2 content of the atmosphere (365 ppm) was 1.3 times higher than prior to the Industrial Revolution (280 ppm). This extra CO_2 must foster more rapid photosynthesis and hence more rapid production of wood and humus. In turn, an increase carbon storage should result. But by how much?

As is the case for the ocean, estimates based on repeated inventories are not feasible. It is difficult enough to get adequate data to quantify the highly visible impacts of forest cutting across the globe, let alone the data required to document forest fattening and soil humus enrichment. Rather, as for the ocean, we must attempt to model these changes. These models require on three pieces of information. The first is the acceleration of growth rates observed in chamber experiments in which plants are grown under conditions differing only in CO_2 partial pressure. In particular comparisons are made between growth at normal CO_2 and growth at doubled CO_2. The second concerns the size of the reservoirs being greened. Other things being equal, the bigger the reservoir, the more carbon it will pack away. The third is the response time for carbon storage in these reservoirs. By response time, we mean the ratio of the amount of carbon stored in the particular reservoir to that added to the reservoir each year as the result of new growth. These times range from a year or two for leaves and twigs, litter on the ground, and fine rootlets in soils to millennia for the most resistant components of soil humus.

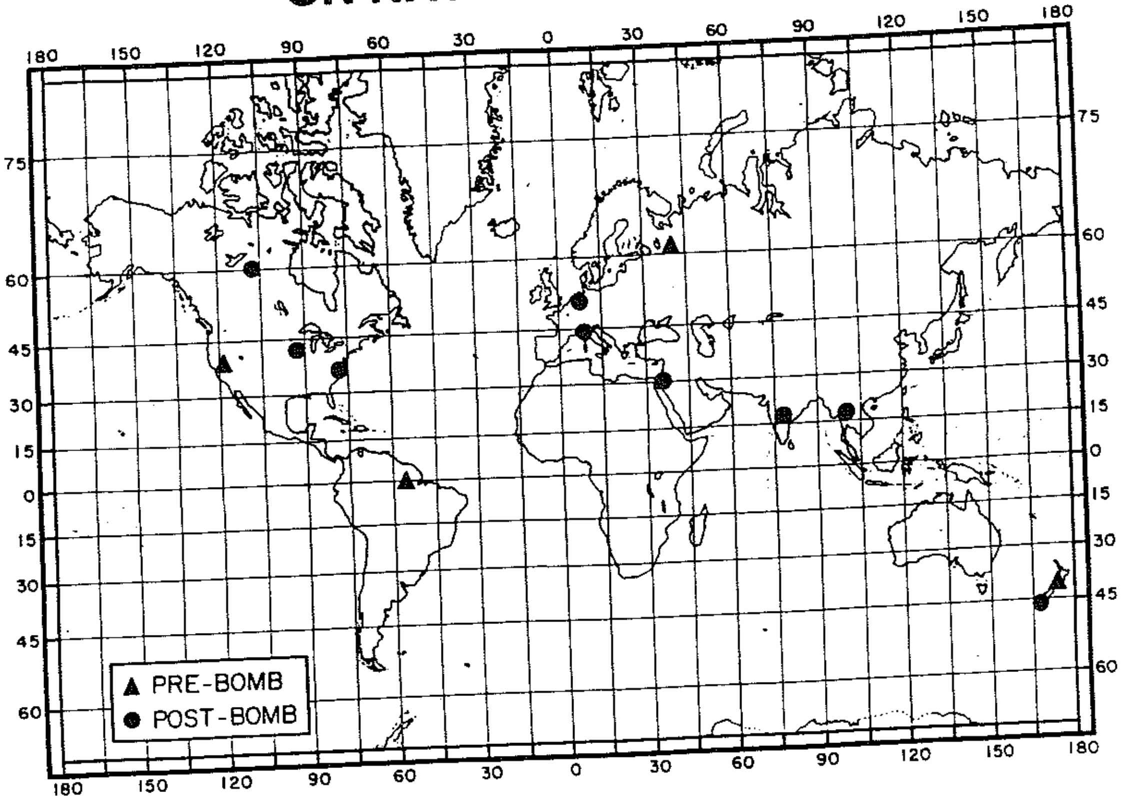
Let us go back over these one at a time. Nearly 1000 growth chamber experiments have been conducted. Most often, the growth rate at ambient CO_2 is compared with that at twice ambient CO_2. While a great variety of species have been used, these tests are by necessity confined to plants or parts of plants small enough to be conveniently housed in chambers. Also the plants are generally well lighted, generously fertilized and adequately watered. Further, for trees the duration of the experiments is only a small fraction of their lifetime. Because of this, a general criticism is leveled at the results of these experiments. As growth conditions are optimal, the response in chambers is likely to exceed that expected for wild environments where not only CO_2 is in limited supply. But as the chamber results are all we have to go by, they are, by necessity, the basis for the greening calculations. One can only add the caveat that the response of plants in the wild may well be smaller than that in the chambers. Hence estimates made in this way are generally considered upper limits. The median growth enhancement observed for plants grown in chambers with CO_2 contents 100% above ambient is 33%. The assumption is then made that this ratio also applies to the smaller CO_2 enhancements experienced by plants in the wild. For example, plants grown in a chamber whose CO_2 content is 365 ppm would be expected to grow at a rate about 10% faster than plants in an identical chamber with a CO_2 content of 280 ppm (i.e., the CO_2 content is 30% higher, so growth rate is 10% higher).

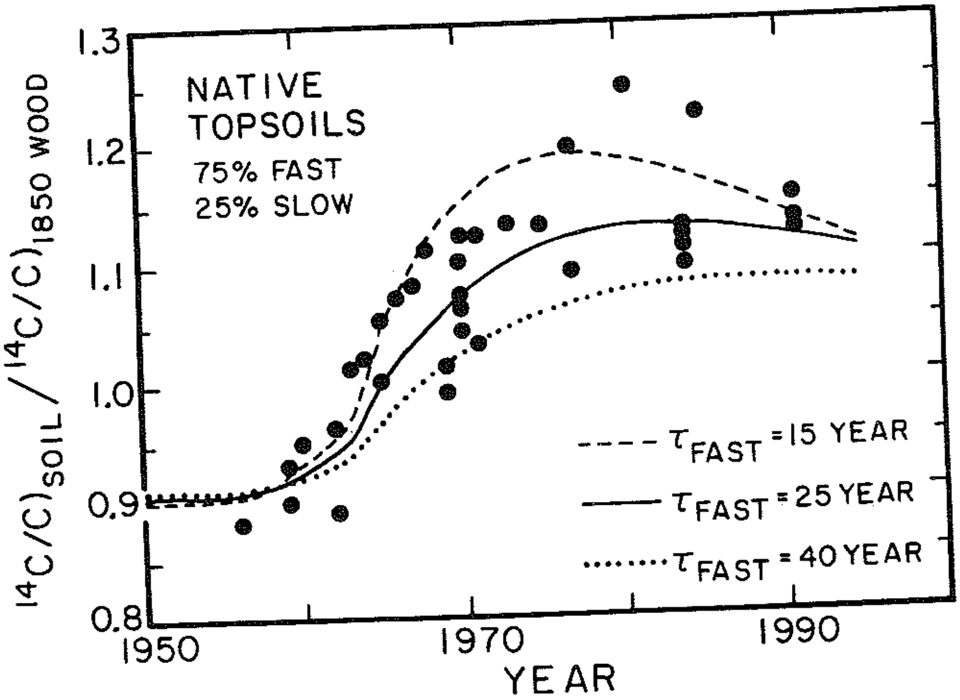
Now the extent of biomass increase in a given reservoir as of 1997 will depend not only on the degree to which the rate of photosynthesis has increased, but also on the turnover time for carbon in the reservoir of interest. The carbon inventory of soil litter reservoir would be expected to pretty much keep pace with the increasing rate of photosynthesis. For today's CO_2 content of 365 ppm, the litter production should be 10% higher than that in the year 1800. Hence the amount of litter should also be about 10% larger. By contrast, no increase in the amount of the millennial time-scale component of soil humics would be expected. For reservoirs with turnover times in the range of a decade to several centuries, the inventory increase will lag the photosynthesis increase. Hence the increase will be smaller than 10%.

To understand this, let us consider a simple model. Think of a hypothetical reservoir of organic matter analogous to a soil. Each year new material is added to the reservoir, tending to increase its size. Each year organic matter within the reservoir is consumed by bacteria, tending to decrease its size. We will assume that prior to the 19th century, the reservoir was at steady state (i.e., input was matched by loss). We also assume that the mean time of survival for each unit of organic matter added to the reservoir is 25 years. If so, then the inventory of organic carbon in the reservoir at that time would have been 25 times the annual input rate. The importance of this turnover time to the inventory response is easily understood if one considers what would happen if the production rate of organics in a reservoir previously at steady state were suddenly to increase by 10% and thereafter remain at this level. Initially, the input rate of new litter would be 10% higher than the rate of bacterial consumption of the material in the reservoir, so the organic content of our hypothetical soil would begin to rise. The rise would continue until the amount of organic matter in the reservoir had become 10% greater than that initially present. Since the bacterial population would grow in proportion to the food supply, at this point, bacterial destruction would once again balance the input of new litter. The buildup of the inventory toward this new steady state value would proceed as follows. After 25 ln2 or 17.3 years, it would be 5% greater; after 2x25 ln2 or 34.6 years, it would be 7.5% greater, after 3x25 ln2 or 51.9 years, it would be 8.75% greater, and so forth.

Assigning residence times to components of the soil humus reservoir proves particularly difficult, for its complex of chemical compounds must have a very wide range of survival times. Unlike trees which build annual rings, soils have no equivalent built in clock. Our best source of information comes from radiocarbon measurements made on bulk humus (i.e., on soil samples from which rootlets and litter have been removed). Measurements based on soils sampled prior to the onset of nuclear testing (i.e., prior to the rise in atmospheric radiocarbon) yield an average radiocarbon age of roughly a millennium. By contrast, soils collected subsequent to the bomb-testing-induced peak in atmospheric radiocarbon yield ^{14}C to C ratios 10 to 20 percent higher than those for the pre-nuclear atmosphere. These results confirm the expectation that a wide spectrum of turnover times exists for the organic compounds in soils. While not permitting this spectrum to be defined, the radiocarbon measurements allow the organics in soils to be divided into two categories, those with lifetimes so long that little change in amount (or in ^{14}C/C) would be expected during the period of CO_2 greening, and those with lifetimes short enough to respond to greening (and to the bomb ^{14}C transient). An estimate of the turnover time for the long residence time component is obtained from radiocarbon measurements on humus from the subsoil. It is assumed that these organics are dominated by the long-lived component. The age obtained on such samples averages 3500 years. Knowing this age and also the bulk age for top soil, it is possible to divide the soil organics into two types and to say what fraction of the carbon falls in each. The result is that with regard to

RADIOCARBON MEASUREMENTS ON NATIVE TOPSOILS



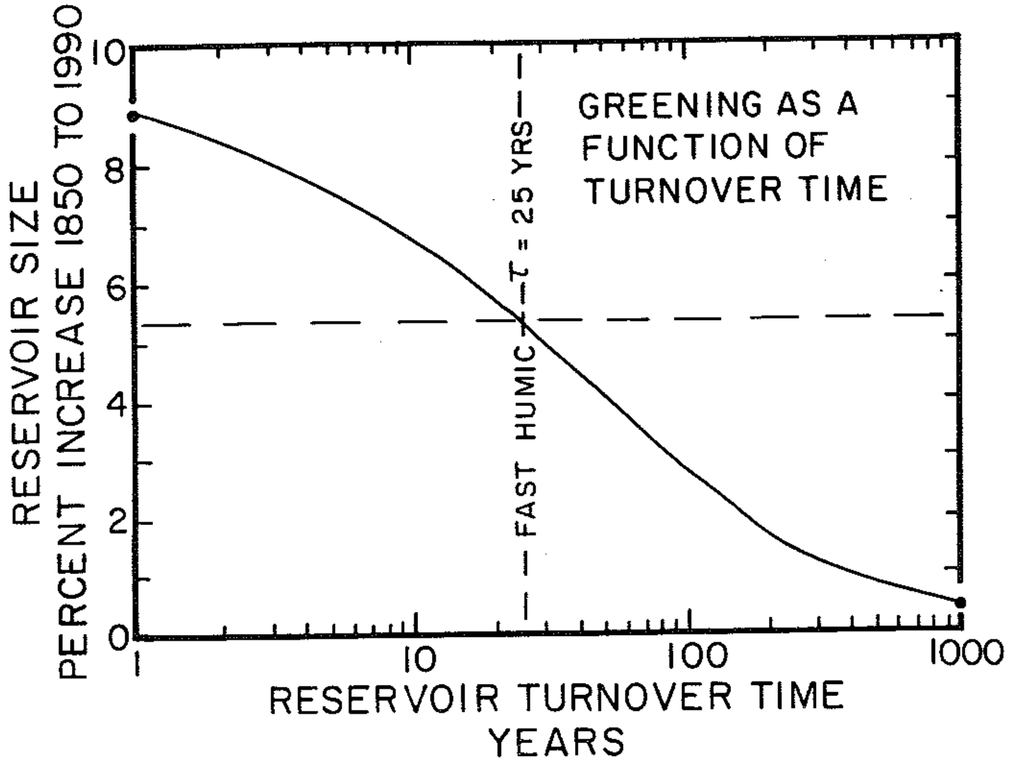


FAST TURNOVER INVENTORY IN 1850

~ 500 GIGATONS CARBON

INCREASE IN INVENTORY FROM 1850 TO 1990

.054 × 500 = 27 GIGATONS CARBON



greening about 25% of the carbon is inert and about 75% 'active'. The turnover time of the active reservoir carbon is obtained through modeling of its response to the bomb radiocarbon transient. What is found is that the best fit to the data for native soils is obtained using a turnover time of 25 years for the 'active' reservoir.

This exercise is much akin to that for the one dimensional ocean model. A globally averaged top soil is divided into a part which is greened and a part which responds too slowly to be greened. This corresponds to a division of the ocean into a part which is accessible to fossil fuel CO_2 and one which is isolated from contact with the atmosphere. Measurements of bomb radiocarbon permit the transient response of the active reservoir to be constrained. It must be emphasized, however, that the reliability of soil model does not match that of the ocean model. It is based on far shakier assumptions and is documented by a far, far smaller data set.

Nevertheless, the soil model provides at least a rough estimate of the extent to which natural soils are being greened. Assuming that 500 gigatons of carbon reside in the active reservoir of soils, 3.3% faster growth for each 10% higher atmospheric CO_2 content, and a 25-year turnover time for carbon in this pool, the rate of accumulation of extra carbon in the Earth's soils would be about 0.6 gigaton of carbon per year. Because of the major uncertainties involved in this calculation, this result can be taken only as an indication that the CO_2 induced greening of the soil reservoir could make a significant contribution to explaining the whereabouts of the missing carbon.

Greening of the wood reservoir can be treated in a similar fashion. This carbon reservoir has a similar size as the active soil reservoir (i.e., 500 gigatons of C), but because of its longer turnover time, the rate at which forests are packing away excess carbon should be somewhat smaller, more like 0.3 gigatons of carbon per year for the 1980s.

The response time of the short lived leaf, litter, rootlet reservoir is so short that its size should closely follow the atmospheric CO_2 rise. During the 1980s, the CO_2 content of the atmosphere was rising at the rate of 1.5 ppm per year. Using the 0.33 greening factor, this means that the rate of production of such material was rising at the rate of 0.14%/year. As the size of this reservoir is about 150 gigatons of carbon, the rate of increase is estimated to be 0.2 gigatons per year.

Taken together, the greening of these three reservoirs adds up to about one gigaton per year. This is about the amount required to balance the carbon budget. One might conclude from this that the results obtained in chamber experiments are providing reasonable estimates of what goes on in the real world.

But the situation is very likely much more complicated for there is another potential greening agent. Most ecosystems, whether they be terrestrial or aquatic, respond to additions of fixed nitrogen. Repeated forest surveys in six European countries show that a substantial increase (~25%) in standing stock of wood occurred between 1970 and 1990. Prior to industrialization, growth in all European forests was nitrogen limited. Currently, because of the fallout of anthropogenic NO_3 and NH_3, the fixed nitrogen is super abundant. Hence the most likely explanation for the fattening of these forests is driven by fixed nitrogen fertilization rather than by excess atmospheric CO_2. While not well established, the amount of fixed nitrogen fallout attributable to anthropogenic sources is about 0.05 gigatons of nitrogen/yr. As the C/N ratio in soils is about 12 and that in aquatic plants about 7, it is tempting to assume that for every mole of fixed nitrogen reaching the planet's surface, about 10 moles of carbon are sequestered. If so, then about 0.5 gigatons of carbon are being stored each year as the result of the fallout of ammonia and nitric acid.

There may however be a flaw in the assumption that fixed nitrogen is used only once and then stored until respiration or decay makes it available for recycling. Rather, it may become part of the photosynthetic factory instead of the product. If so, the number of carbon atoms stored per fixed nitrogen released to the environment may exceed the 10 to 1 ratio assumed above.

Support for the conclusion that nitrogen is an important player in greening comes from the measurements of the interhemispheric gradient in ^{13}C to ^{12}C ratios in atmospheric

CO_2. In order to make a self consistent picture for ^{13}C, CO_2 and O_2, it is necessary to call on the temperate forests of the northern hemisphere as a major site for greening. As most agricultural-, industrial- and automotive-derived fixed N is released in the north temperate zone and since its lifetime in the atmosphere is too short to permit long distance transport, nitrogen fertilization occurs mainly in this zone

Projections to the Future

If international agreements in limiting CO_2 emissions such as that concluded in 1997 in Kyoto are to be implemented, then it will be necessary to have models which permit us to predict the evolution of the CO_2 content of the atmosphere for any given fuel use scenario. Essential to this enterprise are dynamic ocean models. Not only must these models be able to correctly reproduce the temperature and salinity distributions in the sea and the evolution of the transient tracer distributions, but these models will have to undertake the more difficult task of predicting the response of the ocean's operation to the expected warming and freshening of high latitude surface ocean waters. The consequent slowdown in ventilation of the thermocline and deep sea will tend to reduce the rate of uptake by the ocean of fossil fuel CO_2. But countering this to some extent will be the more efficient utilization of the NO_3 and PO_4 in high latitude surface waters.

Putting aside the possible slowdown in ocean circulation, two factors will alter the split of excess CO_2 between the ocean and the atmosphere. First, the $CO_3^=$ and HBO_3^- ion contents of surface waters will gradually become depleted. Already the $CO_3^=$ content is about 25 percent lower than during pre-industrial times. This diminishment will be reflected by a reduction in the proportion of the CO_2 taken up by the sea. Second, as the growth rate of atmospheric CO_2 content slows the mean age of fossil fuel CO_2 molecules will increase. This lengthening will be reflected by an increase in the proportion of the CO_2 taken up by the sea. Will these factors more or less cancel one another? On the short term the answer is likely 'yes'. The reduction in capacity will be just about balanced by the increase in 'swimming' time. To see why this is the case, let's say that by the year 2025 the CO_2 content has risen to 415 ppm (i.e., by 100 x [415-360]/360 or 15 percent). If during the same time period, the mean lifetime of fossil fuel CO_2 molecules rises from let's say 30 to 40 years. Then, the fraction of the ocean available for CO_2 uptake will rise by a factor of $\sqrt{40/30}$ or 1.15. Hence, in this case, the two changes would indeed cancel one another.

Another possibility would be to increase the uptake of CO_2 by the ocean through the addition of fertilizer. The sinking to the ocean interior of the excess organic debris created in this way would lower the CO_2 content of surface water. This deficiency would be compensated by the invasion of CO_2 from the atmosphere. As plant productivity in the temperate regions of the ocean is limited by the availability of fixed nitrogen, one possibility would be to purposefully add ammonia or nitrate. But such an approach would in a sense be self defeating for more CO_2 could be emitted to the atmosphere by the facilities in which the nitrogen was fixed than would be removed from the atmosphere as a result of its application to temperate ocean surface waters.

More promising is the addition of iron to those areas of the surface ocean in which sizable quantities of unused NO_3 and PO_4 are present (mainly the Southern Ocean). The late John Martin pioneered this concept by clearly demonstrating that the sparsity of iron limited plant productivity in these regions. His critics were silenced when an open ocean experiment conducted in the eastern equatorial Pacific produced a dramatic drawdown of nitrate and of CO_2 partial pressure. Further, the required amounts of iron are relatively small - only one mole of iron for each 1000 moles of PO_4 and 16,000 moles of NO_3 utilized by plants. Hence for each mole of iron, the CO_2 removed could range as high as 125,000 moles. Expressed in terms of Redfield ratios:

$$\begin{gathered}\mathrm{Fe:P:N:C} \\ 1:1000:16{,}000:125{,}000\end{gathered}$$

But iron fertilization is not the panacea for the rise of atmospheric CO_2 content. Model calculations reveal that even if all those regions of the ocean containing unutilized

NO_3 and PO_4 were continually dosed with iron for the next 150 years and if this fertilization allowed full utilization of the upwelled NO_3 and PO_4, the rise in the CO_2 content of the atmosphere would only be reduced by 10 percent. If, for example, in the absence of fertilization the CO_2 content of the atmosphere were to reach 750 ppm in the year 2150, then fully successful iron fertilization between now and then would hold this rise to 680 ppm. But keep in mind that if at that time the iron fertilization program were to be abandoned, then the CO_2 removed in this way would be returned to the atmosphere.

CO_2 Management

As the CO_2 content of the atmosphere rises and the planet warms, more and more attention is likely to be focused on stemming this rise. The option of purposeful removal of CO_2 from the air can be ruled out. To do so by scrubbing air would require far, far more energy per CO_2 molecule removed than was gained by producing the CO_2 molecule in the first place! While plants could surely do the job, the cost of harvesting and conversion to a form which could be permanently stored (i.e., carbon block) would be prohibitive.

A more reasonable approach would be to capture the CO_2 created by fossil fuel burning at the source. This CO_2 could be liquefied under pressure and buried either on the ocean floor or in deep wells on the continental interiors. Of course, the capture, liquefaction and storage of CO_2 would require energy. Estimates are that were this to be done, energy derived from fossil fuels would double in cost.

Summary

This section's puzzle regarding the fate of fossil fuel CO_2 boils down to an assessment of the carbon storage in the terrestrial biosphere. What is the balance between the positive terms in its budget (greening by CO_2 and fixed nitrogen and regrowth of previously cut forests) and the negative terms (forest cutting and agriculturally-induced losses of soil humus)? As we have seen averaged over the last several decades, the estimates obtained using tracer-calibrated box models and using ocean general circulation models yield answers which suggest that the sum of excess CO_2 stored in the atmosphere and in the ocean comes close to matching the amount of CO_2 generated by the burning of fossil fuels. This result suggests that during the 1980s global greening was responsible for an increase in the standing biomass of forest and soil carbon of about one gigaton per year. This requires that the excess CO_2 in the atmosphere and excess fixed nitrogen in soils has caused plants to grow about 10% faster. Thus, by chance, cutting around the "edges" of the terrestrial biosphere was matched by a fattening in its "middle". But there is no guarantee that this balance will hold in the future. It is easy to imagine scenarios where greening will wane to the extent that the terrestrial biosphere becomes a net source, thereby aggravating the buildup of CO_2 in the atmosphere.

Commentary on Keeling's World Plates

pg. 2

The concensus view of the annual perturbations experienced by various Earth surface carbon reservoirs during the 1980s. The fossil-fuel source is estimated from records of coal, oil and natural gas production kept by each nation. The deforestation contribution is estimated using satellite photography and ground-based standing biomass measurements. The magnitude of ocean uptake is based on modeling. Greening (i.e., the increase in terrestrial biomass resulting from CO_2 and fixed N-induced growth enhancement) is determined by difference.

pg. 4

In the upper panel is shown the atmospheric CO_2 record for Marina Loa Hawaii from 1958 to 1993. In addition to the temporal trend driven by fossil fuel burning, there are internal changes resulting from small mismatches between respiration and photosynthesis (see for example, the dramatic flattening in the early 1990s). The seasonal cycle is driven by the strong late spring and early summer drawdown of CO_2 by plant growth in the extensive northern hemisphere temperate regions. In the lower panel is shown the atmospheric methane record.

pgs. 6-7

Sufficiently accurate direct measurements of the CO_2 content of the atmosphere are available only for the period 1958 to present. Fortunately, this record can be extended back in time using air trapped in polar ice. One problem in this regard is establishing the exact age of the trapped air. Measurements on material from a shallow core from Antarctica show that the close off of pores in the firn begins at a depth of 60 meters and is complete by about 80 meters. The age of the siple ice at the depth of the midpoint of this close off interval is 95 years (as determined by counting annual layers). Based on CFC measurements, the replacement of the air at the base of the firn via diffusion down through the web of pores is estimated to be about 13 years. Hence the air in bubbles is 82 years less than that of the ice in which the bubbles are encased. Of course, as the bubble close off is not instantaneous but is spread over a period of time and as the diffusive ventilation of the firn mixes air of different ages, the air trapped at any given depth is a mixture spanning a decade or so.

As can be seen on page 7, the ice-core-derived reconstruction of atmospheric CO_2 content and of an $^{13}C^{12}C$ tie in nicely with atmospheric measurements.

pgs. 8-9

Breakdown of the magnitude of individual CO_2 sources as a function of time. While the dramatic use of petroleum use leveled off in the early 1970's, coal and natural gas took up the slack. Since 1957 when CO_2 monitoring began, the rate of increase of the atmosphere's CO_2 content has averaged about 60 percent the rate of CO_2 emissions from fossil fuel burning.

p. 12

Comparison of the La Jolla, California record for O_2 decline with that for the CO_2 rise. When the seasonal cycle is removed, O_2 shows a 13.5 μatm decline over this period and CO_2 a 5.5 μatm rise. Two reasons exist for this difference. First, 145 moles of O_2 are required to produce 100 moles of CO_2 (the extra oxygens are required to convert the H in the fuel to H_2O). Second, part of the CO_2 goes into the ocean.

pg. 14

In the upper panel is shown the relationship between atmospheric O_2 trend for a four-year period. In the lower panel is a comparison between the predicted and observed cumulative trends for O_2 and CO_2. The predicted trend is that expected if the atmosphere were a closed system. In order to account for the difference between the observed and predicted trends, it is necessary to invoke not only CO_2 uptake by the ocean but also a significant increase in the amount of carbon stored in the terrestrial biosphere.

pgs. 18-19

Sea water takes up significant amounts of fossil fuel CO_2 mainly because it is a basic solution. CO_2 from the atmosphere mates with carbonate ion in the sea to form two bicarbonate ions. As shown on the left, were sea water free of borate, the reaction carbonate ion would enhance the uptake by more than a factor of 13 (i.e., 34/2.6) over that resulting from the solution of CO_2 gas alone. When the reaction with borate is included, the enhancement of uptake reaches almost a factor of 19 (i.e., 49.1/2.6). Also note that by adding fossil fuel CO_2 to the sea, we are gradually eroding its capacity for further uptake. Both the $CO_3^=$ and $H_4BO_4^-$ are being consumed. The Revelle factor is the percentage increase in the partial pressure of CO_2 in the atmosphere required to raise the ΣCO_2 content of surface sea water by one percent.

pgs. 20-21

Radon measurements in the ocean-mixed layer provide an estimate of the rate at which gases pass back and forth across the air-sea interface. By measuring the ratio of radon concentration in the water to that which would be present were no radon to escape to the atmosphere (i.e., that amount of ^{222}Rn were its decay rate to just match its production by the decay of its parent ^{226}Ra). Measurements at a large number of stations from throughout the world ocean reveal that on the average about three quarters of the equilibrium amount of radon atoms are present in surface water. The remaining one quarter escape to the atmosphere. This means that the probability of escape is about one third the probability of radio decay. As the mean life of a radon atom with regard to radio-decay is about 5.6 days, the mean lifetime with regard to escape must be about 17 days. The mean thickness of the wind stirred upper ocean at these stations averaged 54 meters. The gases in one seventeenth of this (a layer three meters thick) are replaced each day. However, one correction must be made when this radon-based result is to be applied to other gases such as CO_2. The rate escape of a gas is related to its molecular diffusivity in water: the higher its diffusity, the greater its escape probability.

pgs. 22-23

The distribution of natural radiocarbon permits an estimate of the rate at which CO_2 moves back and forth across the air-sea interface to be made. Assuming that prior to nuclear testing the distribution of ^{14}C was close to steady state, the net number of ^{14}C atoms passing from the atmosphere into the sea must have balanced the number of ^{14}C atoms undergoing radio-decay within the sea. The net number of ^{14}C atoms entering the sea is proportional to the gas exchange rate and to the difference between the $^{14}C/C$ ratio in atmospheric CO_2 and that in surface mixed ΣCO_2. The number of ^{14}C atoms undergoing radio-decay within the sea is proportional to the amount of ΣCO_2 in the sea and its mean $^{14}C/C$ ratio. The CO_2 exchange rate obtained in this way is consistent with that based on radon measurements.

pgs. 26-27

Measurements on CO_2 extracted from the atmosphere at different times and places document the evolution of the nuclear-testing induced transient in the atmospheric $^{14}C/C$ ratio. Because the ^{14}C produced during tests was injected largely into the stratosphere of the northern hemisphere during and just after the period of large scale nuclear testing, CO_2 in the atmosphere of the northern hemisphere had a higher $^{14}C/C$ ratio than that in the southern hemisphere. However, soon after the ban on atmospheric testing had been implemented, the $^{14}C/C$ ratio in the two hemispheres even out.

Through gas exchange, this excess ^{14}C entered the surface ocean. At the time of the global ocean survey carried out during the 1970s, the $^{14}C/C$ ratio in surface water ΣCO_2 had risen by about 160‰ over its pre-nuclear value. The vertical distribution of this excess ^{14}C (and also of tritium released as the result of bomb tests) provides a measure of the depth to which pollutants added to the ocean surface are mixed into its interior on a timescale of about one decade. The so called mean penetration depth is calculated by creating a rectangle on the concentration depth plot whose horizontal side equals the surface excess of ^{14}C (or ^{3}H) and whose vertical side is such that the area in the rectangle is equal in area to that of the observed excess (crosshatched in diagram).

At the mid-point of the GEOSECS survey (1975), these isotopes had penetrated to a mean depth of 360 ± 30 meters (i.e., into nearly 10% of the ocean's volume). Based on these measurements, the number of radiocarbon atoms beneath each square centimeter of sea surface can be computed (using ΣCO_2 measurements as well as $^{14}C/C$ measurements). The geographic pattern of these inventories is strongly influenced by the sea's major circulation systems. The inventories are lower than average in zones of upwelling (i.e., the tropical ocean, the circum Antarctic Ocean and the northern-most Pacific Ocean). In these regions, it is as if the ^{14}C were being added to a fountain in which the waters rise to the surface and then move laterally. The northern Atlantic breaks the global symmetry of this pattern for it is the birthplace of much of the world's deep water (in other words, a zone of downwelling instead of a zone of upwelling).

pgs. 30-31

A simple one-dimensional model yields a remarkably good simulation of the uptake of fossil fuel CO_2 by the sea. It consists of a well-mixed surface layer taken to be 75 meters thick in accord with temperature profiles measured throughout the world ocean. This wind-stirred layer is underlain by the density-stratified main body of the ocean. Vertical mixing in the sea's interior is assumed to proceed in accord with the square root of time (i.e., by eddy diffusion). The CO_2 exchange rate between air and sea and the vertical mixing rate in the stratified part of the ocean are selected so as to give the best possible fit to the horizontally-averaged distribution of excess nuclear-testing ^{14}C as surveyed during the GEOSECS program. Vertical mixing is modeled in this way because the time required to mix the entire ocean (i.e., 1000 years as determined from the distribution of natural radiocarbon) is 100 times longer than the time required for tracers to spread through the upper 10% of the sea. The CO_2 exchange rate and vertical mixing rate are constrained to match the GEOSECS observations (i.e., the increase in $^{14}C/C$ ratio in average surface water and the mean penetration depth of bomb-testing ^{14}C and ^{3}H). Of course, if the model yields a match to the surface excess and to the mean penetration depth, it will also yield the observed total ocean inventory of bomb-testing radiocarbon.

pg. 34

While the time required to exchange the gases in the oceanic mixed layer with overlying air is measured in weeks, the time required for the oceanic mixed layer to reach equilibrium with either a change in the CO_2 content or $^{14}C/C$ ratio in the overlying atmosphere is far longer. This difference can be best understood by comparing the response of two 75 meter high columns of water to a stepwise change in the CO_2 content and $^{14}C/C$ ratio in the overlying air. One column contains distilled water (which is free of HCO_3^- and $CO_3^=$). The other is sea water. As the distilled water contains only CO_2 gas, its response to the stepwise change is rapid with no difference in timing between the CO_2 content and the isotopic ratio. By contrast, because of dissolved HCO_3^- and $CO_3^=$, the sea water responds much more slowly. As its ΣCO_2 content exceeds its CO_2 content by a factor of 200 ($\Sigma CO_2 \cong 2000$ µmol/kg and $CO_2 \cong 10$ µmol/kg) its response time for isotopic change is 200 times longer than that for the distilled water. The response time for the ΣCO_2 content of the sea water lies roughly geometrically between the response time for the distilled water column and the isotopic response time for the sea water. In simplest terms, the reason is that uptake of CO_2 is dictated by the $CO_3^=$ content of the surface sea water (~200 µmol/kg) which lies roughly geometrically between that for ΣCO_2 (~2000 µmol/kg) and that for CO_2 (~10 µmol/kg).

pgs. 36-37

The simple 1-D ocean model can be put to three additional tests. First, if CO_2 is fed into the atmosphere in accord with the fossil fuel emissions, does the model generate a rise in atmospheric CO_2 in accord with observation (assuming that the terrestrial biosphere has remained nearly null). In order to pass this test, the model must be initiated with an atmospheric CO_2 content of 292 µatm rather than the value of 280 µatm obtained from ice core measurements. The second test is to match the decline in $^{13}C/^{12}C$ ratio resulting from the addition to the model's atmospheres of ^{13}C deficient fossil fuel CO_2. As can be seen, the model passes this test handily. The third test is to match the decline of $^{14}C/C$ ratios resulting from the addition to the model's atmosphere of ^{14}C-free CO_2 from fossil fuel burning. Again, the match between model and observation is quite good. It must be noted however, that the observed trend in atmospheric $^{14}C/C$ ratio contains a small natural component (due to fluctuations in the strength of the solar wind and its associated magnetic field). As this contribution cannot be accurately assessed, it is possible that by chance this natural contribution masks a deficiency in the model. It should also be noted that were there no mixing between the carbon atoms in the atmosphere and those dissolved in the sea, both the ^{13}C and ^{14}C changes would be five or so times larger than the observed changes. Hence, these are quite stringent tests of the ocean model.

pgs. 38-39

The model can be put to a fourth test. Does it produce a match to the observed post-test-ban decline in the $^{14}C/C$ ratio of the atmosphere. This crosscheck is performed in a less direct manner. The atmosphere's $^{14}C/C$ and CO_2 contents are programmed to follow their observed time trends. The model's ocean and terrestrial biosphere exchange carbon isotopes with this atmosphere. The excess radiocarbon inventories are calculated for each reservoir and then totaled. What is found is that after 1967 (i.e., the time when the entire atmosphere (including the stratosphere) had become well mixed with respect to bomb ^{14}C, the total inventory of radiocarbon remained nearly constant. This constancy is not found for the period prior to 1967 because up until this point the stratosphere retained a significant excess $^{14}C/C$ over that for the troposphere.

pg. 42

A map for the 1980s showing the difference between the CO_2 partial pressure in atmosphere and that in surface ocean constructed using measurements from along dozens of ship tracks. Although this distribution has a fair amount of texture (for example, a pronounced excess in the eastern equatorial Pacific and a pronounced deficiency in the northern Atlantic), when averaged over the entire ocean, the difference is very small (~4 μatm). But the uncertainty on this measured average (±4 μatm) and in the corrections required to compensate for the skin temperature bias (~2μatm) and for the preanthropogenic excess balancing the river flux of carbon to the sea by rivers (~2μatm), render untenable the use of this approach to make a meaningful independent estimate of the flux of fossil fuel CO_2 into the sea. All that can be said is that once corrected the observed difference is consistent with that of 8 μatm predicted by models for the same time period.

pg. 45

If, as we believe, an average 2 gigatons of fossil fuel carbon was entering the ocean during the 1980s, then based on the global mean gas exchange rate obtained from the distributions of mature ^{14}C and radon (and confirmed by the GEOSECS survey of the distribution of bomb-produced ^{14}C), an average air-sea CO_2 partial pressure difference of 8 micro-atmospheres would be required. However, as prior to the Industrial Revolution the sea surface must have had a p_{CO_2} of about 2 micro-atmospheres higher than the atmosphere to balance the net transport to the sea by rivers of bicarbonate and dissolved organic matter, the actual difference is reduced to 6 micro-atmospheres. Further, as evaporation lowers the skin temperature of the ocean, a further correction is required lowering the expected difference to only 4 micro-atmospheres.

pg. 47

Comparison of the annually averaged atmospheric CO_2 record from atop the extinct volcano, Mauna Loa, on the island of Hawaii with that from atop the Antarctic ice cap. As can be seen, when in 1958 these records began, the two stations recorded nearly the same mean annual CO_2 content and since then, the difference has steadily grown. In one sense, this is consistent with the rising production of CO_2 from fossil fuel burning

(~2.3 GtC in 1958 to ~5.5 GtC in 1985). But one would expect the difference in 1958 to have been 2.3/5.5 that in 1985. The records suggest that in 1958 the difference was close to zero. This led to the speculation that prior to 1955, the difference might have been reversed (in other words, the southern hemisphere had a higher partial pressure of CO_2 than did the northern hemisphere). If so, then one would have to postulate that a natural interhemispheric cycle exists which carries CO_2 from the northern to the southern hemisphere through the ocean and then back through the atmosphere.

pg. 51

The most obvious route for the interhemispheric ocean transport of CO_2 is the Atlantic's conveyor-like thermohaline circulation. Cold water manufactured in the northern Atlantic sinks and flows southward around the tip of Africa into the circum Antarctic deep water current. Much of this water upwells in the southern hemisphere. This water carries excess CO_2. This excess is related to the low nutrient (i.e., NO_3 + PO_4) constituent content and hence respiration CO_2 content of water sinking in the northern Atlantic. In the Antarctic, the excess respiration CO_2 associated with the much higher nutrient constituent content of surface waters (compared to that for the low latitude) more or less balances the reduction of CO_2 partial pressure caused by the lower temperature. Hence little tendency exists for CO_2 to be transported to the Antarctic through the atmosphere from other parts of the surface ocean. However, in the northern Atlantic, the compensation by respiration CO_2 is not adequate and hence the cooling creates a surface water deficit in ΣCO_2 of about 100 μmol CO_2/kg. About 80 μmol/kg of this deficit is compensated by the uptake of atmospheric CO_2. Because of this, the conveyor exports about 0.6 Gt of carbon to other parts of the ocean. While not enough to create a south to north preanthropogenic atmospheric CO_2 gradient big enough needed to explain the seemingly too low current interhemispheric difference in atmospheric CO_2 content, transport by the conveyor might explain up to half of it. A more complete explanation of this phenomenon is provided by the authors in a paper published in *Nature* (1992, v. 356, p. 587-589).

pg. 54

An estimate of the minimum amount of fossil fuel CO_2 taken up by the sea during the 1980s can be obtained by assuming that the mean penetration depth of fossil fuel CO_2 into the sea was no greater than that of bomb produced ^{14}C (or ^{3}H) at the time of the GEOSECS survey. This estimate is a lower limit because during their mean lifetime of 30 years, fossil fuel CO_2 molecules must have penetrated deeper into the sea than the bomb isotopes which, at the time of the GEOSECS survey, had had only a bit more than a decade to "swim". As the mean penetration depth of the bomb-produced tracers was as of 1975 about 360 meters (i.e., approximately, one tenth the mean depth of the sea), this means that at least one tenth of the ocean's capacity for CO_2 uptake was accomplished. This capacity is set by the ΣCO_2 content of the ocean water divided by the Revelle factor (or so called buffer factor) described on pg. 15. For the surface ocean, the average value of this factor is 9 (i.e., for each 9% increase in atmospheric CO_2 pressure the equilibrium increase in ocean ΣCO_2 will be 1%). This yields an ocean capacity one half that of the atmospheric capacity which means that for each three moles of fossil fuel CO_2 added to the atmosphere, one will enter the sea and two will remain airborne. For the 1980s, the measured increase in atmospheric CO_2 was on the order of 3.0 GtC/year. Thus at least 1.5 GtC/year must have entered the ocean during this time period.

pgs. 62-63

Radiocarbon measurements are available for only a few dozen topsoil samples collected at various places during the course of the rapid bomb radiocarbon transient. These measurements suggest that prior to nuclear testing, the $^{14}C/C$ ratio in humus from top soils averaged about 0.9 times the $^{14}C/C$ ratio for preanthropogenic terrestrial vegetation (i.e., an apparent radiocarbon age of about 900 years) and that this ratio rose (as the result of introduction bomb-testing ^{14}C) to a broad maximum in the 1970s and

1980s, about 1.1 times the preanthropogenic ratio. In order to account for both of these observations, it is necessary to call on at least two classes of soil humus, one with a turnover time measured in millennia and one with a turnover time measured in decades. The former pool is necessary to account for the low $^{14}C/C$ ratio prior to bomb testing and the latter for the uptake of appreciable amounts of bomb ^{14}C. A fit to the data can be achieved by assuming that the top-soil humus consists of 75% material with a 25-year turnover time (hence a pre-nuclear $^{14}C/C$ ratio close to 1.0) and 25% material with a 4000-year turnover time (hence a pre-nuclear $^{14}C/C$ ratio of about 0.6). While in reality the situation must be much more complicated (i.e., a wide spectrum of turnover times must exist) based on available constraints, no way exists to improve upon the very simple two reservoir model shown here.

The two reservoir model allows an estimate of the extent of CO_2-induced "greening" of soils to be made. In this calculation, the chamber-experiment-based factor of 3.5% growth enhancement per 10% increase in air CO_2 content is applied to the entire terrestrial biosphere (i.e., during the 1980s when the atmosphere's CO_2 content was about 27% higher than prior to the Industrial Revolution, the growth rate of plants and hence the production rate of new humus was, presumably, about 9% higher than prior to the Industrial Revolution.) The extent to which any reservoir increased its size as a result of this greening would depend on its turnover time. Only reservoirs such as leaves, grass, rootlets... with very short turnover times would show the full 9% increase. By contrast, the millennium response-time fraction of soil humus would show almost no greening. The fast response-time soil reservoir would be expected to show a bit more than half the maximum response. Assuming that the global reservoir of fast responding humus contain 500 Gt of carbon, its inventory should have risen by about 27 GtC since the beginning of the Industrial Revolution (an amount equal to about 9 years accumulation of CO_2 in the atmosphere at the 1980s rate).