

# THE GLOBAL CARBON CYCLE AND AN ANALYSIS OF THE EFFECTS OF COASTAL EUTROPHICATION

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## Assigned Reading

### REQUIRED

None

### SUPPLEMENTAL

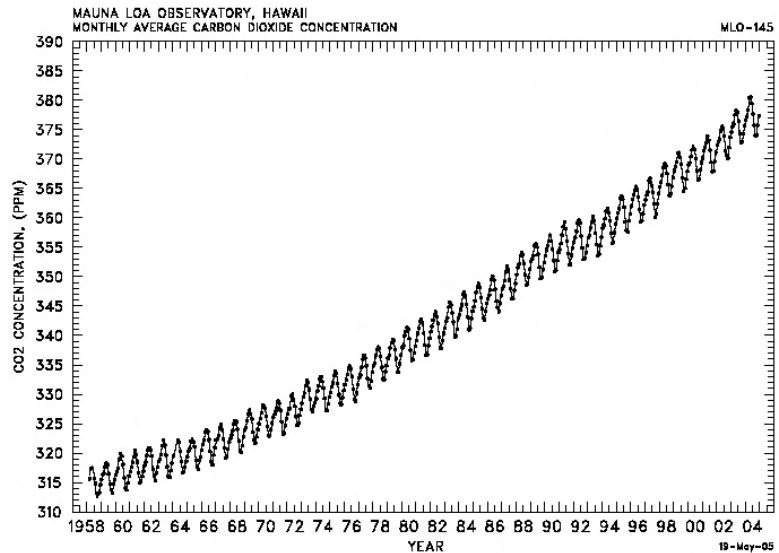
- Christensen, J. P. 1989. Sulfate reduction and carbon oxidation rates in continental shelf sediments, an examination of offshore carbon transport. *Cont. Shelf Res.*9: 223-246. [*Sulfate reduction the major respiratory pathway below 2 cm in Gulf of Me sediments. Burial of 5 gCm<sup>-2</sup>y<sup>-1</sup>. 22% to 50% of Washington shelf carbon may be exported*]{6}
- Miller, C. B. 2004. *Biological Oceanography*. Blackwell Science, Malden MA. 402 pp. Chapter 16 pp. 341-366.
- Quay, P. D., B. Tilbrook, and C. S. Wong. 1992. Oceanic uptake of fossil fuel CO<sub>2</sub>: carbon-13 evidence. *Science* 256: 74-79. [*The net oceanic uptake of fossil-fuel CO<sub>2</sub> is 2.1 Gt C y<sup>-1</sup>, short of the missing 3-3.6 Gt C y<sup>-1</sup>*]
- Williamson, P. and P. M. Holligan. 1990. Ocean productivity and climate change. *Trends in Ecology and Evolution* 5: 299-303 [*Justification for the International Global Ocean Flux Study (GIFS)*]

## Comments on the Readings

### GLOBAL WARMING: SHOULD WE PLANT TREES OR DUMP OR SEWAGE ON CONTINENTAL SLOPES?

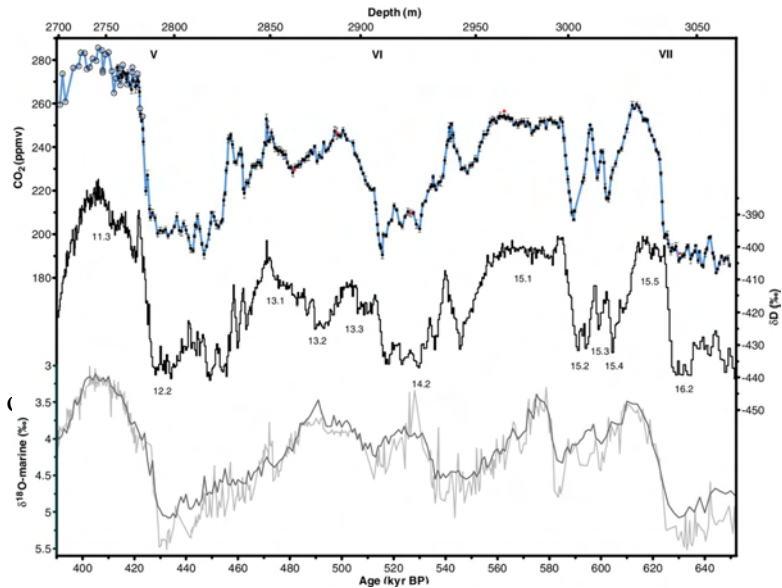
#### Introduction

Keeling developed the sensitive methods for measuring atmospheric CO<sub>2</sub> and found that the levels have been rising steadily since 1958. Figure 1 shows the latest version of the Keeling curve. The 2004 average CO<sub>2</sub> was 377.4 parts per million, whereas the 1959 average was 316.0 ppm.



**Figure 1.** The Keeling curve: atmospheric CO<sub>2</sub> concentrations measured on Mauna Loa (HI) through December 2004 from <http://cdiac.esd.ornl.gov/trends/co2/sio-keel.htm>

Ice-core and  $\delta^{13}\text{C}$  data from tree rings indicate increases in atmospheric CO<sub>2</sub> since the mid 19th century due to deforestation and more recently fossil-fuel burning. **Siegenthaler et al. (2005)** analyzed gasses trapped in ice-core bubbles and concluded that present greenhouse gas levels had not been exceeded in the past 650,000 years. Figure 2 shows the preserved record of atmospheric CO<sub>2</sub>. The present CO<sub>2</sub> concentration of 377 ppm is higher than any value for the last 650,000 years. However, CO<sub>2</sub> concentrations were higher than present values during the Cretaceous period (> 65 million years ago).



**Figure 2.** Figure 4 from **Siegenthaler et al. (2005)**. The upper curve shows the concentration of CO<sub>2</sub> preserved in ice cores. Prior to 430,000 years ago, CO<sub>2</sub> ranged only from 180 to 260 ppm.

In the last 50 years, fossil-fuel emissions have surpassed deforestation as the major input of CO<sub>2</sub> to the atmosphere (**Sundquist 1985**). There has been an increase in global temperature in the last century, but whether the greenhouse effect is the cause remains in doubt (**Solow & Broadus 1989**). Only about half the CO<sub>2</sub> emitted to the atmosphere in the last century from fossil-fuel burning, cement production, and tropical deforestation has remained in the atmosphere (**Sundquist & Broecker 1984**). **Sabine et al. (2004)** report that over the last 2 centuries, the atmospheric increase in CO<sub>2</sub> is equivalent to about 68% of emissions from fossil fuel and cement production (165 Pg C / 244 Pg C). **Sabine et al. (2004)** have provided the most recent global carbon budget, concluding that the oceans are the only net carbon sink for the last two centuries, with land having a net CO<sub>2</sub> emission of about 2 Pg C annually).

The analysis in **Sabine et al. (2004)** largely solves the long-running controversy over the missing carbon sink. Terrestrial ecologists argued that the sink was to be found on land, and most – but not all – marine scientists argued that the sink was in the sea. Three papers in the late 1980s and early 1990s – **Brewer et al. (1989)**, **Tans et al. (1990)**, and **Quay et al. (1992)** – had raised doubts about whether the oceans were a sink for atmospheric CO<sub>2</sub>. **Brewer et al. (1989)** estimated the carbon flux into and out of the North Atlantic and found only a relatively minor net carbon input, however the uncertainties in the fluxes were large in this study. **Tans et al. (1990)** coupled an atmospheric model with a surface ocean model and found that the  $\Delta p\text{CO}_2$  gradients were too small and too short-lived to support a large air-to-ocean CO<sub>2</sub> flux in the North Atlantic. They estimated that the oceans were taking up only 1 Gt C y<sup>-1</sup> [*n.b.*, Gt is short for Gigatons; recent carbon budgets use petagrams C (=10<sup>15</sup> g C; 1 Pg C = 1 Gt C)]. This represents only a minor part of the difference between the roughly 7 Pg C y<sup>-1</sup> now being added to the atmosphere (from land-use change, fossil-fuel burning & cement production) and the 3.25 Pg C y<sup>-1</sup> increase in atmospheric CO<sub>2</sub>. The missing carbon sink problem involved the regions taking up the 3.75 Pg C difference. **Tans et al. (1990)** concluded that terrestrial ecosystems must be the major sink

for the  $\approx 3\text{--}4$  Pg C/yr carbon flux not accounted for in current global carbon budgets, but recent estimates by **Sabine et al. (2004)** indicate that the oceans are indeed the major net carbon sinks for CO<sub>2</sub>. The global modeling and measurements synthesized in **Sabine et al. (2004)** indicates that over the last 20 years, the oceans are the major sites of net carbon uptake:  $1.85 \pm 0.4$  and  $0.75 \pm 0.45$  Pg C per year, respectively. Over the last two centuries, the oceans are the only net carbon sink for anthropogenic CO<sub>2</sub> emissions from fossil fuel and cement production (see Figure 3).

**Quay et al. (1992)** analyzed oceanic  $\delta^{13}\text{C}$  and  $^{14}\text{C}$  profiles in the Pacific and Atlantic and estimated that the oceans were the major sink of anthropogenically produced CO<sub>2</sub>. They estimated the net oceanic uptake of fossil-fuel CO<sub>2</sub> was  $2.1 \text{ Pg C y}^{-1}$ , which is close to the  $1.85 \pm 0.04$  Pg C estimate for the last 20 years in **Sabine et al. (2004)** [See Figure 3 below]. This is more than double **Tans et al.'s (1990)** estimate of oceanic carbon uptake. **Sarmiento (1991)** reanalyzed **Tans et al.'s (1990)** budget and concluded that this budget had underestimated oceanic carbon uptake. Sarmiento's estimate of net oceanic CO<sub>2</sub> uptake is  $1.9 \text{ Gt y}^{-1}$ , very similar to the most recent estimate ( $1.85 \pm 0.04$  Pg C) from **Sabine et al. (2004)**.

The latest global carbon budget from **Sabine et al. (2004)** is shown in Figure 3, indicating a net oceanic uptake of  $1.85 \pm 0.04$  Pg C per year over the last 20 years and  $0.6 \pm 0.1$  Pg C per year over the last 195 years.

### Is the sink located on continental slopes and shelves?

Walsh and coworkers (**1981, 1984, 1985, 1987, 1988**) predicted that sedimentation of organic carbon on continental slopes is a major global sink of organic carbon. They predicted that this accumulation was accelerated by coastal eutrophication in the last century. **Walsh (1984)** calculated that up to 15% of the carbon emitted by fossil-fuel burning could be accumulating on surface-slope sediments. **Walsh et al. (1987)** reassessed slope accumulation and estimated it to be  $0.3$  to  $0.5 \text{ Gt y}^{-1}$ .

Criticism of Walsh's eutrophication hypothesis was devastating and convincing. **Carpenter (1987)** argued that Walsh's slope sediment accumulation rates are high by a factor of 10. **Carpenter (1987)** further argued that no significant increases in organic carbon accumulation occurred in recent decades (or centuries) in the main basin of Puget Sound, nor on the Washington State continental shelf or slope. **Emerson (1985)**, using a sediment diagenetic model, similarly discounted Walsh and co-workers' rates of sediment organic matter accumulation on slopes and estimated that Walsh's rates of organic matter accumulation at slope depths were high by factors of at least 5. **Peng & Broecker (1984)** argued that the rates of nutrient input to the coastal zone and rates of primary production were inadequate to support

Table 1. Anthropogenic CO<sub>2</sub> budget for the anthropocene (1800 to 1994) and for the decades of the 1980s and 1990s.

CO <sub>2</sub> sources and sinks	1800 to 1994 (Pg C)*	1980 to 1999 (Pg C)†
<i>Constrained sources and sinks</i>		
(1) Emissions from fossil fuel and cement production	244‡ ± 20	117 ± 5
(2) Storage in the atmosphere	-165§ ± 4	-65 ± 1
(3) Uptake and storage in the ocean	-118§ ± 19	-37 ± 8
<i>Inferred net terrestrial balance</i>		
(4) Net terrestrial balance = [-(1) - (2) - (3)]	39 ± 28	-15 ± 9
<i>Terrestrial balance</i>		
(5) Emissions from land-use change	100 to 180	24 ± 12
(6) Terrestrial biosphere sink = [-(1) - (2) - (3)] - (5)	-61 to -141	-39 ± 18

\*Errors as estimated by respective sources; errors of sums and differences are calculated by quadratic error propagation. †From (19), with an error estimate of  $\pm 8\%$ . ‡Calculated from the change in atmospheric PCO<sub>2</sub> (1800:  $281 \pm 2$  ppm; 1994:  $359 \pm 0.4$  ppm). §This study includes anthropogenic CO<sub>2</sub> storage in marginal seas and the Arctic Ocean. ||Based on (2); see text for details. ¶From (23), integrated for the period 1980 to 1999.

**Figure 3.** Table 1 from **Sabine et al. (2004)** PgC represents petagrams ( $10^9$  g) of carbon (1 Pg C = 1 gigaton (Gt) C).

Walsh's increased production. Moreover, the open-ocean flux of nutrients, as defined by Broecker's "NO" and "PO" indices [calculated from all all forms of Nitrogen and Phosphorus to produce near-conservative tracers], did not change over a decade time scale. This finding is inconsistent with the Walsh's coastal fertilization model.

**Nixon (1988)** found no evidence for increased accumulation of carbon or nitrogen in North American estuaries and bays resulting from eutrophication. While rates of production and organic matter accumulation may have been underestimated, it is unlikely that shelf or slope burial is increasing at a rate necessary to balance the global carbon budget. Thus, neither the shelf nor coastal embayments appear to be accumulating large amounts of organic matter.

**Christensen (1989)** reviewed Walsh's most recent estimates of carbon accumulation on slopes and concluded that Walsh had underestimated the rate of oxidation of organic material on the east coast shelf and had overestimated rates of export off the shelf. **Christensen (1989)** concluded that no more than 10% of production on the east coast is transported off the shelf and that Walsh overestimated organic matter accumulation on the New England slope.

There are very few estimates of the rates of organic matter accumulation and oxidation in New England coastal waters. **Heinrichs & Farrington (1987)** estimated the rate of organic matter oxidation at one site in Buzzards Bay, MA at 14 gC/m<sup>2</sup>/y with burial rates of 36 gC/m<sup>2</sup>/y.

**McNicholl et al. (1988)** estimated sediment carbon oxidation rates of 69 gC/m<sup>2</sup>/y with burial rates of 5.5 to 33.1 gC/m<sup>2</sup>/y. **Christensen (1989)** found burial rates of up to 5 gCm<sup>-2</sup>y<sup>-1</sup> at 12 deeper stations (32-296 m) in the Gulf of Maine.

A back-of-the-envelope calculation indicates the difficulty of balancing the global carbon budget using only organic matter accumulation in shallow seas. If we assume that 36 gCm<sup>-2</sup>y<sup>-1</sup> of organic carbon is permanently buried in shallow seas (the very high rate from Heinrichs & Farrington 1987) and multiply this accumulation rate by the area of all shallow seas having a depth less than 200 m, which Sverdrup *et al.* (1942, p. 15) estimate as 4.2 x 10<sup>12</sup> m<sup>2</sup>. (This calculation does not include the non-enclosed areas of the continental shelves). The total carbon accumulation in marginal seas at 36 gCm<sup>-2</sup>y<sup>-1</sup> would only be 1.5 x 10<sup>14</sup> or about 8% of annual carbon uptake by the oceans (1.85 ± 0.4 Pg C per year) from **Sabine et al. (2004)**.

### ***The role of diffusion through the air-sea interface***

The missing 2.8 Gt y<sup>-1</sup> is a lot of carbon to hide, even over the vast expanse of the ocean. The entire area of the world's ocean is about 3.6 x 10<sup>14</sup> m<sup>2</sup> (Sverdrup *et al.* 1942, p. 15). The missing 2.8 Gt C m<sup>-2</sup>y<sup>-1</sup> would require an average air-sea flux of 7.7 gCm<sup>-2</sup>y<sup>-1</sup> over the world's ocean. Since tropical waters are not sites of uptake, and the tropical Pacific is a major site of CO<sub>2</sub> outgassing, one should consider only higher latitude waters in calculation of oceanic carbon sinks. If one considers the area of the oceans at latitudes higher than 25° (7.6 x 10<sup>13</sup> m<sup>2</sup> in the Northern hemisphere, 1.2 x 10<sup>14</sup> m<sup>2</sup> in the Southern; total >25°=1.96 x 10<sup>14</sup> m<sup>2</sup>), the air-to-sea carbon flux required to balance the missing 2.8 GtCm<sup>-2</sup>y<sup>-1</sup> is 14 gCm<sup>-2</sup>y<sup>-1</sup>.

Two factors controlling the rate at which CO<sub>2</sub> can diffuse into the ocean: the concentration gradient for CO<sub>2</sub> and the thickness of the molecular diffusive layer at the air-sea interface.

Frankignoulle (1988) provided an estimate of the air-sea exchange of carbon dioxide, given the  $\Delta p\text{CO}_2$  gradient, and a measured piston velocity (a measure of the thickness of the molecular diffusive layer). With a gradient of about  $100 \mu\text{atm } p\text{CO}_2$ , he estimates a diffusive flux from air to sea of about  $150 \text{ mgCm}^{-2}\text{d}^{-1}$ . Thus a gradient of  $100 \mu\text{atm}$  (a **large** gradient) would have to be maintained throughout all oceanic waters at latitudes greater than  $25^\circ$  latitude for a period of 93 days (on average) to produce the needed  $14 \text{ gCm}^{-2}\text{y}^{-1}$  flux. This is **highly** unlikely. The  $\Delta p\text{CO}_2$  gradient in the ocean is never that large except during the relatively short bloom periods, which persist for weeks not months. Tans *et al.* (1990, Table 2) compiled seasonal data on  $\Delta p\text{CO}_2$  gradients, averaged over 3-month periods, and their largest  $p\text{CO}_2$  gradient was  $53 \mu\text{atm}$ . The 1989 spring bloom in the North Atlantic, documented by Chipman *et al.* (1990) in the JGOFS N. Atlantic bloom cruises, found a  $p\text{CO}_2$  gradient of  $119 \mu\text{atm}$  at the peak of the bloom. However, this large  $119 \mu\text{atm}$  gradient was maintained for only a short time ( $<2 \text{ wk}$ ). Tans *et al.* (1990, p. 1431) concluded:

*“The observed differences between the partial pressure of CO<sub>2</sub> in the surface waters of the Northern hemisphere and the atmosphere are too small for the oceans to be the major sink of fossil fuel CO<sub>2</sub>. Therefore, a large amount of the CO<sub>2</sub> is apparently absorbed on the continents by terrestrial ecosystems.”*

Because of the lack of a significant  $p\text{CO}_2$  gradient between air and the oceanic sea surface, the open ocean is not a good locale for locating the missing carbon sink.

### **Coastal Eutrophication and the carbon cycle**

Coastal eutrophication, despite its many ecological problems, has one virtue: it would probably result in reduced atmospheric  $p\text{CO}_2$ . In the Environmental Sciences, it often happens that solving one environmental problem produces another. Weiner's (1990) superb book on the  $\text{CO}_2$  debate clearly illustrates this. The increased fossil-fuel input from  $\text{CO}_2$  was believed by be a Godsend by Arrhenius (1891), who argued that the resultant increase in Global temperature would be beneficial to man. As Weiner describes, one Dupont chemist is responsible for two of the major inventions of the early 20<sup>th</sup> century. This chemist solved a problem that led to the explosion of gas engines by developing leaded gas, and he solved a problem with toxic refrigerants by developing chlorofluorocarbons. These two 'solutions' have led to tremendous environmental problems. As Environmental Scientists, you should be able to analyze the competing environmental costs of "solutions." Did you know that cleaning up Boston Harbor will lead to enhanced  $\text{CO}_2$  input to the atmosphere? In the following sections, I'll describe why this is so. I'll also do some back-of-the-envelope calculations to show that upgrading sewage treatment from primary to secondary treatment isn't going to make any major difference in global carbon budgets. Sewage treatment is a minor, minor term and can be ignored.

At present the relative impacts of various forms of sewage treatment on the global carbon cycle have not been calculated. A gravity-fed raw sewage outfall to deep-water, while having strong adverse ecological impacts, would probably result in enhanced burial rates of organic carbon. The burial rates would be enhanced further if the material were sufficiently toxic to reduce the rates of heterotrophic processes or the activities of conveyor-belt species (Rhoads 1974). More

importantly, this organic carbon would produce CO<sub>2</sub> which would become part of the seawater carbonate system. At least one hundred moles of CO<sub>2</sub> would have to be respired into seawater to produce a 1 mole increase in the ocean to atmospheric flux (Peng and Broecker [1984, p. 8177] put this factor at 1000 by including the Revelle factor of 10, but I am not convinced that the inclusion of the Revelle factor is appropriate). Primary treatment with a long outfall to colder water (e.g., MA Bay) would reduce impacts on atmospheric CO<sub>2</sub> relative to sewage disposal in well-mixed estuaries. Similarly, sludge-disposal to deep-water dumpsites (e.g., 106-mile dumpsite) would result in reduced atmospheric input of CO<sub>2</sub>. At deep-water dumpsites, degradation rates would be low and the carbon would be added to a well-buffered deep-water carbonate pool which has an atmospheric coupling time scale measured in decades or even centuries. Sundquist (1985, p. 13) showed that the exchange rate between the atmosphere and oceanic surface-mixed layer is characterized by a time scale of a few years. The residence time of carbon in the deep sea is of the order 1100 years (Keeling 1979 quoted in Sundquist (1985, p. 13)), with estimates as short at 100-250 years for the deep Atlantic. More important than the time scale of the process, is the efficiency with which CO<sub>2</sub> from sludge will be rapidly returned to the atmosphere. Because the carbon dioxide produced from deep-sea respiration is added to DIC-rich seawater, over 100 moles of carbon would have to be added to deep water at 2000 m depth to result in an increased ocean to atmospheric flux of 1 mole. If this sludge is spread on golf courses and other terrestrial areas as fertilizer and soil conditioner, virtually 100% of the CO<sub>2</sub> will be returned to the atmosphere on very short time scales.

The relative effects of secondary vs. primary treatment on CO<sub>2</sub> flux would be difficult to predict. The secondary plant would result in increased fossil-fuel use and the enhanced primary pretreatment would produce methane (some of which is utilized for energy). A major fraction (approximately 80%, Stumm and Morgan 1981, p. 707) of the organic matter in raw sewage will be removed from the effluent during secondary treatment. About 50% of this material will be respired aerobically, returning the CO<sub>2</sub> immediately to the atmosphere. About 40% of the initial carbon in sewage will end up in sewage sludge. Aerobic degradation of sludge would release this CO<sub>2</sub> to the atmosphere. Methane production from anaerobic degradation of sewage sludge would be especially harmful, because methane is a much more potent green-house gas than CO<sub>2</sub> (approximately 20-fold [Woodwell 1989]).

The nitrogen-rich secondary effluent will also have effects on CO<sub>2</sub> flux. If these nutrients enhance the magnitude and persistence of vernal blooms of fast-sinking diatoms, then secondary effluent will result in increased atmospheric input of CO<sub>2</sub> to coastal marine waters. The enhanced nutrient input resulting from secondary treatment (i.e., phytoplankton biochemical oxygen demand) might produce enhanced CO<sub>2</sub> flux from the atmosphere to coastal waters. However in a 35-m water column, it is highly unlikely that the atmospheric flux of CO<sub>2</sub> could be greatly increased. As noted above, Peng and Broecker (1984) have noted that an additional 1000 moles of carbon would have to be fixed by marine primary producers to result in an enhanced atmospheric exchange of 1 mole C. Peng and Broecker's (1984) calculation does not take into account that spring diatom blooms increase the pH of seawater, greatly changing carbonate speciation and reducing the percentage of DIC which is in the form of CO<sub>2</sub>. The increased alkalinity resulting from the incorporation of NO<sub>3</sub><sup>-</sup>, and release of OH<sup>-</sup> should be considered in modeling the effects of enhanced spring blooms on CO<sub>2</sub> flux. Current rates of nutrient addition appear inadequate to support coastal "fertilization" of seawater as a major carbon sink.



“Back-of-the-envelope” calculations indicate that secondary treatment will release significant additional amounts of CO<sub>2</sub> to the atmosphere, but the amounts are trivial compared to fossil-fuel inputs of CO<sub>2</sub>. The organic carbon content of raw sewage is about 100 mgC/l (Officer and Ryther [1977] provided data only on WBOD, but organic carbon can be calculated from the Redfield ratio. Wallace *et al.* [1990] found only about 7 mg organic carbon/l in CSO effluent. The MWRA produces about 360 million gallons/d of sewage, or about  $5 \times 10^{11}$  l/year. The mass flux of carbon in untreated MWRA sewage, using Officer and Ryther’s (1977) organic carbon values is about  $5 \times 10^{10}$  g C/year. The MWRA eliminated sludge dumping in Christmas 1991, so the current flux is slightly lower now. With secondary treatment, and complete aerobic degradation of the sludge, about 80% of this carbon could be respired heterotrophically directly into the atmosphere. This would result in an increased atmospheric flux of about  $4 \times 10^{10}$  gC per year to the atmosphere from the MWRA district alone. If the MWRA sewage treatment plant represents roughly 2% of the U.S. coastal marine effluent, then one can estimate the U.S. increased CO<sub>2</sub> flux, due to secondary treatment, at about  $2 \times 10^{12}$  g C/year ( $2 \times 10^{-3}$  Gt/year). This is approximately 1/2500th of the annual global fossil-fuel input. Thus, secondary treatment in the U.S. should not lead to significant increases in atmospheric CO<sub>2</sub> concentrations.

### **CO<sub>2</sub> increase and global warming**

Mark Handel, in a 1991 UMASS/Boston Thursday, seminar reviewed the history of atmospheric warming and atmospheric CO<sub>2</sub>. The problem has been studied off and on since the 1820's. Fourier constructed a global heat budget and concluded that water vapor was more important than CO<sub>2</sub> in the global heat budget. The role of water vapor vs. CO<sub>2</sub> is still an active area of research. Pouillet in 1838 constructed a more elaborate heat budget; Tyndall in 1861 again stressed the role of water vapor in controlling global heat. Svante Arrhenius in 1891 stressed the role of CO<sub>2</sub> in global warming and in 1903 discussed how man’s fossil-fuel use may help alleviate the next ice age.

In recent years, climate modelers, led by Hanson, have proposed dramatic increases in global warming due to greenhouse gasses. Others disagree or are skeptical about the evidence (e.g, **Solow & Broadus 1989**). The main unresolved issues appear to be the role of water vapor as opposed to greenhouse gasses in global heat budgets, and more importantly changes in solar heating. Some argue that the increases in global temperature are correlated but not caused by increases in atmospheric CO<sub>2</sub>. Increases in global temperature may be due largely to changes in solar heating, which causes changes in both global temperature and atmospheric CO<sub>2</sub>.

## Tree planting

Reforestation has been touted as the solution to the global warming problem. In his 1990 State of the Union message, George Bush proposed planting 1 billion trees per year to help solve the global warming problem.

Unfortunately, the soils beneath mature forests are not usually sites of organic matter accumulation. The major organic carbon storage is in the trees themselves. Trees are not long-term biological pumps for removing CO<sub>2</sub> from the atmosphere. Successional forests are sites of organic matter accumulation, but in temperate forests this accumulation is not permanent. The 1988 Yellowstone Park forest fire provides a clear example of the recycling of carbon stored as forest biomass to the atmosphere. Interestingly, forest fires are beneficial in the long term in reducing atmospheric CO<sub>2</sub> fluxes. Forest fires are **not** as efficient in returning CO<sub>2</sub> to the atmosphere as is heterotrophic respiration of annual plant production; 10% of the forest carbon after a fire is lost to the soils as refractory charcoal. Forests accumulate organic carbon, largely in the form of tree and root biomass, on time-scales of centuries. However, over this century-long time span, the forest floor is not a site of organic matter accumulation. The decomposer community is active, and at most times food-limited (Hairston *et al.* 1960<sup>1</sup>, Hairston 1989<sup>2</sup>). The tropical forest floor has been found to be remarkably low in accumulated organic matter and nutrients. Hairston (1989, p. 68) is explicit on this point:

*“In most terrestrial habitats, litter does not accumulate, despite the fact that more than 90 percent of the production falls to the ground uneaten. In tropical rain forests, the litter disappears very rapidly; in temperate forests, the decay requires two or more years. The eventual complete decomposition means that decomposers as a whole -the fungi and bacteria- are limited by the supply of litter and that competition must be taking place among them.”*

Tropical rain forest deforestation has led to increases in atmospheric CO<sub>2</sub> concentrations from the burning of plant biomass. This pulsed input of CO<sub>2</sub> will not lead to further persistent increases in atmospheric CO<sub>2</sub> unless significant sediment or soil accumulation of organic matter has also been curtailed. In this respect, the long-term rates of organic matter accumulation at the mouth of the Amazon and other deltaic systems coupled to rain forests are particularly important to the global carbon debate. What percentage of organic matter production in the tropical rain forest is advected to the continental shelf and buried?

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<sup>1</sup>Hairston, N.G., F. E. Smith, and L. B. Slobodkin. 1960. Community structure, population control, and competition. *Amer. Natur.* 94: 421-425.

<sup>2</sup>Hairston, N. G. 1989. Ecological experiments. Purpose, design and execution. Cambridge University Press, Cambridge. 370 pp.

Planting trees in the Boston Common will not solve the CO<sub>2</sub> problem over the long term unless the trees are harvested and buried where they can not be decomposed by heterotrophs. Alternatively, the trees could be disposed of at sea, greatly reducing the flux of carbon to the atmosphere.

### **Geritol solution**

Martin *et al.* (1990) proposed the so-called geritol solution to global warming. They argue that during times of glacial maxima, the atmospheric dust input to the oceans was high. They argue, “...greatly enhanced Fe input from atmospheric dust may have stimulated phytoplankton growth and increased the power and efficiency of the biological pump, thus contributing to the drawing down of atmospheric CO<sub>2</sub> during glacial maxima.” The Southern Ocean, particularly the Drake Passage waters have high macronutrient concentrations but low iron and production. The atmospheric dust contribution to the southern ocean is the lowest in the world. Only 10% of upwelled nitrogen is used for primary production. They argue that addition of iron may stimulate production and reduce atmospheric CO<sub>2</sub>.

Peng and Broecker (1991) have argued that even if Fe stimulated production, it would not result in significantly reduced atmospheric CO<sub>2</sub> levels. Sarmiento and Orr (1991) and Peng and Broecker (1991) concluded that even if primary production was iron limited, Fe fertilization would not reduce to any large extent the anticipated atmospheric increases in CO<sub>2</sub> in the next century. Moreover, Fuhrman & Capone (1991) and Peng and Broecker (1991) argue that iron fertilization, if successful, could lead to anoxia of Southern Ocean deep water. The American Society of Limnology and Oceanography opposes the Geritol solution as an alternative to reducing fossil-fuel CO<sub>2</sub> emissions.

The second field test of Martin’s Geritol solution has now been completed and the results are described in the August 11, 1995 (p. 759) issue of Science in a Random Samples note “Oceanographer’s Green Thumb”:

*“the ocean actually turned green,” says chief scientist Kenneth Coale of Moss Landing Marine Laboratory... Productivity quadrupled...dramatically supporting the iron-deficiency hypothesis.*

*But green does not mean a go for the iron fix for greenhouse warming. Oceanographers warn that large-scale messing with ecology is a risky business. Besides, they say, modeling suggests that even massive fertilization would have a modest effect on rising carbon dioxide...*

## TERMS AND CONCEPTS

Air-sea CO<sub>2</sub> exchange: Frankignoulle (1988) provides direct measurements of air-sea CO<sub>2</sub> exchange based on Fickian diffusion:

$$F = K\alpha \Delta P,$$

where F is the flux (moles m<sup>-2</sup> s<sup>-1</sup>), K is the gas-exchange coefficient or “piston velocity” (ms<sup>-1</sup>) (defined below), α is the CO<sub>2</sub> solubility coefficient (39 moles m<sup>-3</sup> atm<sup>-1</sup>), and ΔP is the difference in CO<sub>2</sub> partial pressure between water and air.

Alkalinity: The concentration of cations needed to balance the negative charge of anions in seawater. In ordinary seawater the only anions of weak acids present at significant concentrations are the bicarbonate, carbonate and borate ions, and it is to the presence of these that seawater owes its alkalinity. The alkalinity of seawater can be determined by potentiometric titration of the sample with standard acid (Stumm and Morgan, pp 171-229). The equivalence point is best determined from the potentiometric data using the graphical Gran plot method (see Appendix in Stumm and Morgan). The part of alkalinity associated with the carbonate system is called the carbonate alkalinity. Alkalinity is unaffected by carbon fixation or respiration but is affected by nitrate and ammonium assimilation. Nitrate assimilation increases alkalinity but ammonium assimilation decreases alkalinity. Tables for calculating total alkalinity and carbonate alkalinity as a function of salinity are provided in Parsons *et al.* 1984<sup>3</sup>.

carbonate alkalinity: calculated from specific alkalinity after correction of the contribution from borate.

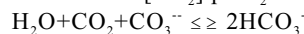
$$\begin{aligned} [\text{Total Alkalinity}] &\approx [\text{H}_2\text{BO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] - [\text{H}^+] \\ [\text{Carbonate Alk}] &= [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \end{aligned}$$

Biological pump: The fixation of carbon in surface waters and sedimentation to deep waters. Highly correlated with new production (see Moore and Bolin 1986) and identical to new production under steady-state conditions.

carbonate system: speciation of the carbon dioxide system is completely described by the relevant equilibrium constants and the values of **any two** of the variables: pH, pCO<sub>2</sub>, ΣCO<sub>2</sub>, and carbonate alkalinity.

$$\text{CO}_2[\text{air}] \leq \geq \text{CO}_2[\text{aqu}]$$

$$\alpha = [\text{CO}_2] / p\text{CO}_2$$



The ratio of CO<sub>2</sub>[aqu] to ΣCO<sub>2</sub> is about 1:180 in warm water to 1:150 in cold water (Broecker & Peng, 1982, p. 307)

Henry's law: The solubility of a gas is directly proportional to its solubility in the gas phase. CO<sub>2</sub>[aqu] = pCO<sub>2</sub> \* α<sub>o</sub>, where α<sub>o</sub> is the solubility constant in mole/l/atm at the given temperature.

Keeling curve: increased atmospheric CO<sub>2</sub> measured at Mauna Loa HI since 1958 and in Antarctica, see Figure 4

Kinetic isotope effects: (=enzyme kinetic fractionation) With no diffusion limitation, carbon in sugars fixed by RuBPCO will be depleted by about -27 to -28 ppt (Prins and Elzenga, 1989). Fractionation of 21 to 22 ppt has also been reported. Fry (1990) finds field fractionation of δ<sup>13</sup>C of up to 28 ppt. Since the δ<sup>13</sup>C value of CO<sub>2</sub>[aqu] is about -8 ppt, and assuming the lower 28 ppt fractionation, then the expected δ<sup>13</sup>C ratio for phytoplankton should be -36 ppt. Only Antarctic phytoplankton have a low δ<sup>13</sup>C composition (= -29ppt). The δ<sup>13</sup>C of ΣCO<sub>2</sub> in ocean surface waters is now about 1.9 ppt (Rau *et al.*, 1982). HCO<sub>3</sub><sup>-</sup> is 9.54 ppt isotopically heavier relative to CO<sub>2</sub> (Prins and Elzenga 1989)

piston velocity: (or transfer velocity) molecular diffusion coefficient divided by thickness of the air-sea diffusive layer (usually 40μm Broecker and Peng 1982, but sometimes larger (≈200 μm, Frankignoulle 1988). A typical piston velocity for CO<sub>2</sub> in the open ocean is 3 m/day, ranging from 10 cm<sup>3</sup>h<sup>-1</sup> in summer to 20 cm<sup>3</sup>h<sup>-1</sup> in winter (Erikson 1989).

<sup>3</sup>Parsons, T. R., Y. Maita, and C. M. Lalli. 1984. A manual of chemical and biological methods for seawater analysis. Pergamon Press, New York, 173 pp.

Revelle factor: [Broecker and Peng 1982] The ratio of time required for CO<sub>2</sub> pressure in surface water to equilibrate with the overlying air to the time required in sea water containing no bicarbonate or carbonate ion. The Revelle factor shows an inverse correlation to the carbonate ion concentration. Also defined as the number by which the ratio of the mixed layer thickness to the piston velocity for CO<sub>2</sub> gas must be multiplied in order to get the actual ΣCO<sub>2</sub> equilibration time. This number ranges from 14 for the coldest waters to 8 for the warmest surface waters. Its ocean-wide average is about 10 (Broecker and Peng 1982).

$$R = (\Delta p\text{CO}_2 / p\text{CO}_2) / (\Delta \Sigma\text{CO}_2 / \Sigma\text{CO}_2) \quad \text{Broecker \& Peng (1982), p. 522}$$

Sherwood number:  $Sh = l * v / D$ , where  $l$  is the length scale,  $v$  is stirring, and  $D$  is the molecular diffusivity. (called stirring number by Purcell, 1977), the ratio of the effectiveness of stirring to diffusion for a given length scale. The Einstein-Smoluchowski relation provides the time required for a molecule to move through a boundary layer by molecular diffusion ( $\approx z^2 / D$ , where  $D$  is molecular diffusivity [ $\text{cm}^2 \text{sec}^{-1}$ ]). The time for transport by stirring is the length divided by the stirring speed. Purcell (1977, p. 9) concludes that small animals can do little to enhance the flux of particles or molecules by local stirring ( $l * v / D \ll 1$ ).

Suess effect: depletion of bomb <sup>14</sup>C in the atmosphere by <sup>14</sup>C-free fossil fuels

viscous sublayer: (Nowell and Jumars, 1984) Occurs in low Re number flows. A layer in which velocity is proportional to distance from the bed and stress is constant. In the lowermost portion of the viscous sublayer, there is a diffusive sublayer, and the only vertical motion in it occurs via molecular diffusion.

## Web Links

Table 1. Web links on CO <sub>2</sub>		
Source	Description	Link
Carbon Dioxide Information Analysis Center	On the 40 <sup>th</sup> Anniversary of Keeling & Keeling Curves	<a href="http://cdiac.ornl.gov/new/keel_page.html">http://cdiac.ornl.gov/new/keel_page.html</a>
Carbon Dioxide Information Analysis Center	Mauna Loa CO <sub>2</sub> data, updated frequently	<a href="http://cdiac.ornl.gov/trends/co2/sio-mlo.htm">http://cdiac.ornl.gov/trends/co2/sio-mlo.htm</a>

# OUTLINE OF PAPERS AND TALKS

## REQUIRED

Miller, C. B. 2004. *Biological Oceanography*. Blackwell Science, Malden MA. Chapter 16.

## RECOMMENDED

Post, W. M., T. H. Peng, W. R. Emanuel, A. W. King, V. H. Dale and D. L. DeAngelis. 1990. The global carbon cycle. *American Scientist* 78: 310-326. [An excellent introduction to oceanic and terrestrial processes. Sugimura and Suzuki's finding of high DOM in oceanic waters may lead to a reevaluation of many oceanic box models.]

1. Introduction
    - a. Important issue
    - b. Fluxes since 1880 not in balance
  2. Carbon reservoirs and fluxes
    - a. 3 reservoirs: atmosphere, ocean, and terrestrial
      - i. atmospheric reservoir
        - (1) known since 1958  
1958: 315 microliters/liter of air
        - (2) 671 gigatons
        - (3) 1988: 351 microliters/l 748 gT of carbon
        - (4) Vostok ice core: 160,000 years
          - (a) 200 at height of glaciation
          - (b) 260-300 microliters during interglacial periods
          - (c) 1750-1800: 279 microliters/l
      - ii. ocean is largest reservoir
        - (1) 37,000 gigatons in the ocean
        - (2) 1000 gigatons of DOC and 30 gigatons of POC
      - iii. land:?
        - (1) plants 420-830 gigatons
        - (2) soil 1200-1600 gigatons
    - b. emissions increasing at 4.3% per year from 1860-1973
      - i. 5.9 gigatons released in 1988
  3. Ocean mixing and circulation
    - a. air-sea exchange
    - b. 26-34% of fossil-fuel carbon from 1958-1980 went into ocean
    - c. deep-water formation
  4. Biological pumping
    - a. transfer of carbon from surface to deep water=new production
    - b. new production estimated at 15-20% of net primary production
    - c. because of problems with <sup>14</sup>C technique, new production may be 8.3 gigatons, old estimate (Koblentz-Mishke *et al.* 1970) was 3.4 gigatons
    - d. reduced ice sheets may increase polar production
- Fig. 8. Outcrop of cold dense water in N. Atlantic
- e. Sugimura and Suzuki's 1988 DOM values
    - i. mean production of 4.3 gigatons per year, comparable to rates of new production
5. **The terrestrial carbon cycle**
    - a. Olson (1983) estimates
    - b. total net primary production of 62 gigatons per year
- Fig. 10. Heterotrophic processes return much of the carbon to the atmosphere
- c. peats and wetland soils may accumulate 0.1 to 0.3 gigatons per year
6. **Impact of human land use**
    - a. reconstruction and deconvolution
    - b. 0.4 to 2.6 gigatons for 1980, largely from the tropics
    - c. reconstruction produced 90-120 gT emission between 1800 to 1980
    - d. budgets don't balance: 162-270 gT increase predicted, 150 gT increase observed

- e. deconvolution: subtract fossil-fuel emissions from the measured changes in atmospheric carbon, making allowances for oceanic uptake, producing contributions from terrestrial systems
  - i.  $\delta^{13}\text{C}$  tree record
  - ii. 90-150 gT release from 1800 to 1980

Fig. 13. reconstruction vs. deconvolution

- f. non-linear effects in the uptake of CO<sub>2</sub> by the oceans Enting and Mansbridge (1987)
- 7. Global system modeling
  - a. Broecker's 1985 model
    - i. takes up 35% of fossil-fuel CO<sub>2</sub>
- 8. Spatial and seasonal patterns
  - a. Tans *et al.* 1990: 1.6 gT uptake by oceans: very low
- 9. Understanding carbon dynamics
- 10. DOC Pools crucial (p. 316)
- 11. 100-yr residence time.

## References

### THE CARBONATE SYSTEM & GLOBAL CARBON BUDGETS

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Weiner, J. 1990. The next one hundred years. Bantam, New York [The personalities inv Eugene Gallagher © 2010



*CO<sub>2</sub> debate]*

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**MISCELLANEOUS**

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**Web resources**

Table 1. Web resources on the global carbon cycle and Iron limitation		
URL	Site	Description
<a href="http://www.acia.uaf.edu/">http://www.acia.uaf.edu/</a>	ACIA	Arctic Climate Impact Assessment
<a href="http://www.agu.org/revgeophys/ducklo01/ducklo01.html">http://www.agu.org/revgeophys/ducklo01/ducklo01.html</a>	AGU: A 1995 report by Hugh Ducklow on Ocean biogeochemical fluxes: New production and export of organic matter from the upper ocean	Excellent html article
<a href="http://www.agu.org/revgeophys/chisho00/chisho00.html">http://www.agu.org/revgeophys/chisho00/chisho00.html</a>	AGU: Penny Chisholm's 1995 report on the geritol solution.	Excellent html article
<a href="http://geosci.uchicago.edu/~archer/ARCHER/archer.html">http://geosci.uchicago.edu/~archer/ARCHER/archer.html</a>	Archer's U. Chicago Web page	Reprints of Archer's outstanding papers
<a href="http://www.aslo.org/meetings/carbon2001/index.html">http://www.aslo.org/meetings/carbon2001/index.html</a>	ASLO	Ocean Fertilization symposium
<a href="http://www.aslo.org/meetings/carbon2001/coal/transcript2.html">http://www.aslo.org/meetings/carbon2001/coal/transcript2.html</a>	ASLO	Slides from an Ocean Fertilization Symposium
<a href="http://cdiac.esd.ornl.gov/trends/co2/sio-keel.htm">http://cdiac.esd.ornl.gov/trends/co2/sio-keel.htm</a>	Atmospheric carbon dioxide record from Mauna Loa	The latest graphics of the Keeling curve are posted here



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URL	Site	Description
<a href="http://cdiac.esd.ornl.gov/">http://cdiac.esd.ornl.gov/</a>	Carbon dioxide information analysis Center	The primary global-change data and information analysis center of the U.S. Department of Energy (DOE).
<a href="http://wind.mit.edu/~emanuel/anthro2.htm">http://wind.mit.edu/~emanuel/anthro2.htm</a>	Emmanuel's MIT web site	Anthropogenic Effects on Tropical Cyclone Activity
<a href="http://yosemite.epa.gov/oar/globalwarming.nsf/content/index.html">http://yosemite.epa.gov/oar/globalwarming.nsf/content/index.html</a>	EPA's global warming site	Not much there but K-12 summaries
<a href="http://www.grida.no/climate/ipcc_tar/wg1/index.htm">http://www.grida.no/climate/ipcc_tar/wg1/index.htm</a>	Intergovernmental Panel on Climate Change	Climate Change 2001: The Scientific Basis
<a href="http://usjgofs.who.edu/mzweb/iron/iron_rpt.html">http://usjgofs.who.edu/mzweb/iron/iron_rpt.html</a> also available as <a href="http://usjgofs.who.edu/mzweb/iron/iron_rpt.pdf">http://usjgofs.who.edu/mzweb/iron/iron_rpt.pdf</a> or <a href="http://usjgofs.who.edu/mzweb/iron/iron_rpt.doc">http://usjgofs.who.edu/mzweb/iron/iron_rpt.doc</a>	JGOFS: Johnson, Moore & Smith (2002): A Report on the US JGOFS Workshop on Iron Dynamics in the Carbon Cycle June 17-19, 2002 Moss Landing, California	A superb summary of the iron experiments to 2000
<a href="http://resourcescommittee.house.gov/archives/109/testimony/2005/terrencejoyce.pdf">http://resourcescommittee.house.gov/archives/109/testimony/2005/terrencejoyce.pdf</a>	Joyce report	Terry Joyce (WHOI) testimony to Congress on ocean currents and climate
<a href="http://svs.gsfc.nasa.gov/vis/a000000/a000200/a000205/">http://svs.gsfc.nasa.gov/vis/a000000/a000200/a000205/</a>	NASA	Movies on the Iron bloom downwind from the Galapagos
<a href="http://earthobservatory.nasa.gov/Library/Giants/Martin/martin_5.html">http://earthobservatory.nasa.gov/Library/Giants/Martin/martin_5.html</a>	NASA	Biography of John Martin, who proposed the geritol solution
<a href="http://earthobservatory.nasa.gov/Library/Giants/Martin/">http://earthobservatory.nasa.gov/Library/Giants/Martin/</a>	NASA	Biography of John Martin, who proposed the geritol solution
<a href="http://news.nationalgeographic.com/news/2002/01/0108_020108oceaniron.html">http://news.nationalgeographic.com/news/2002/01/0108_020108oceaniron.html</a>	National Geographic News	News: Critique of the Geritol Solution. During Ice ages the iron was upwelled,"
<a href="http://www.cgd.ucar.edu/cas/jhurrell/indices.html">http://www.cgd.ucar.edu/cas/jhurrell/indices.html</a>	NCAR Climate Analysis Section. Jim Hurrell's indices, especially NAO	Climate indices, especially NAO
<a href="http://www.newscientist.com/channel/earth/climate-change/">http://www.newscientist.com/channel/earth/climate-change/</a>	New Scientist Climate Change news and articles	News: Dumping CO <sub>2</sub> in the ocean could be a disaster, but legal (10/20/2001). Is global warming making hurricanes stronger (12/5/2005)
<a href="http://www.newscientist.com/news/news.jsp?id=ns99994545">http://www.newscientist.com/news/news.jsp?id=ns99994545</a>	New Scientist	News: Warming threatens millions of species
<a href="http://enews.lbl.gov/Science-Articles/Archive/sea-carb-bish.html">http://enews.lbl.gov/Science-Articles/Archive/sea-carb-bish.html</a>	News article about Lawrence Livermore lab's Jim Bishop's work on carbon sequestration	Interesting graphics of carbon sequestration strategies

Table 1. Web resources on the global carbon cycle and Iron limitation		
URL	Site	Description
<a href="http://www.palomar.edu/oceanography/iron.htm">http://www.palomar.edu/oceanography/iron.htm</a>	Oceanography at Palomar College	The Iron hypothesis, a nice web article
<a href="http://www.physicstoday.org/pt/vol-55/iss-8/p30.html#fig6">http://www.physicstoday.org/pt/vol-55/iss-8/p30.html#fig6</a>	Physics Today	Sinks for Anthropogenic Carbon by Sarmiento & Gruber
<a href="http://www.realclimate.org">http://www.realclimate.org</a>	Real Climate	RealClimate is a commentary site on climate science by working climate scientists for the interested public and journalists. We aim to provide a quick response to developing stories and provide the context sometimes missing in mainstream commentary. The discussion here is restricted to scientific topics and will not get involved in any political or economic implications of the science.
<a href="http://www.agu.org/revgeophys/chisho00/nod e2.html">http://www.agu.org/revgeophys/chisho00/nod e2.html</a>	Rev. Geophys. Vol. 33 Suppl., © 1995 American Geophysical Union	Phytoplankton and the biological pump
<a href="http://www.agu.org/revgeophys/chisho00/nod e3.html">http://www.agu.org/revgeophys/chisho00/nod e3.html</a>	Rev. Geophys. Vol. 33 Suppl., © 1995 American Geophysical Union	The Iron Hypothesis
<a href="http://cdiac.esd.ornl.gov/trends/landuse/houghton/houghton.html">http://cdiac.esd.ornl.gov/trends/landuse/houghton/houghton.html</a>	US Dept of Energy	Carbon Flux to the Atmosphere from Land-Use Changes by Houghton & Hackler (Woods Hole Research Center)
<a href="http://cdiac.esd.ornl.gov/trends/co2/sio-keel.htm">http://cdiac.esd.ornl.gov/trends/co2/sio-keel.htm</a>	US Dept of Energy	Atmospheric CO <sub>2</sub> records from sites in the SIO air sampling network, includes links to Keeling curves from Mauna Loa
<a href="http://www1.who.edu/jgofs.html">http://www1.who.edu/jgofs.html</a>	US JGOFS homepage	
<a href="http://cdiac2.esd.ornl.gov/ocean.html">http://cdiac2.esd.ornl.gov/ocean.html</a>	US Dept of Energy	Ocean Carbon Sequestration Abstracts



Table 1. Web resources on the global carbon cycle and Iron limitation		
URL	Site	Description
<a href="http://cdiac.ornl.gov/new/keel_page.html">http://cdiac.ornl.gov/new/keel_page.html</a>	US Dept of Energy	Profile of Charles Keeling
<a href="http://www.usatoday.com/weather/news/2004-03-21-co2-buildup_x.htm">http://www.usatoday.com/weather/news/2004-03-21-co2-buildup_x.htm</a>	USA Today	News: CO <sub>2</sub> buildup accelerating in atmosphere (3/21/04)

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