

# Atmospheric CO<sub>2</sub>: Causes of Variability

Don Bogard, July 2018

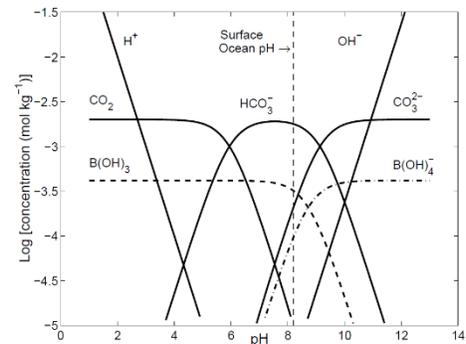
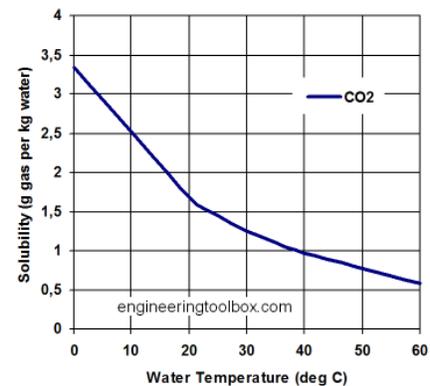
**Short-Term Variations.** Changes to Atmos CO<sub>2</sub> concentrations on short (years) time scales can be driven by temperature and environmental changes those produce. Consider years of a strong El Nino. Deep, cold (few degrees) ocean water comes to the surface in the western tropical Pacific. That cold water likely contains CO<sub>2</sub> in equilibrium concentrations reflecting past (and lower) Atmos CO<sub>2</sub> levels and CO<sub>2</sub> solubility for cold ocean water. That large volume of water is considerably heated when it spreads eastward across the Pacific surface and warms global surface temperature. Warmer water decreases the CO<sub>2</sub> solubility, and considerable CO<sub>2</sub> degassing could be expected. Thus, there results an observed correlation between increased Temp and Atmos CO<sub>2</sub> during El Ninos. Smaller ocean circulation such as the AMO and Pacific oscillation likely produce smaller effects.

Figure 1 right suggests that warming deep ocean water from a few deg-C to 20-25 deg-C at the surface of the tropical Pacific during an El Nino would decrease the CO<sub>2</sub> solubility by possibility half. Warming the entire upper ocean over times of decades (as climate science argues) would change the CO<sub>2</sub> solubility little, because most ocean warming does not exceed 1 deg-C. However, this graph of CO<sub>2</sub> solubility is for pure water, whereas CO<sub>2</sub> in the ocean exists in a complex equilibrium with other carbon phases, primarily bicarbonate and carbonate (Figure 2 below, right). Changes in water pH (as well as some other variables) influence the relative proportion of CO<sub>2</sub> present relative to HCO<sub>3</sub><sup>-1</sup> and CO<sub>3</sub><sup>-2</sup>. Note that at an average ocean pH of 8.1, the equilibrium CO<sub>2</sub> content is quite low, and much lower than carbonate. Ocean chemistry varies among different regions, which can be expected to differ somewhat in CO<sub>2</sub> degassing upon warming.

The seasonal variation in CO<sub>2</sub> anticorrelates with northern hemisphere Temp. But it is higher summer Temp promoting plant growth that causes this effect, and not increased Temp directly. Periods of drought in regions of high plant growth caused by changes in weather patterns could also be expected to influence the seasonal CO<sub>2</sub> curve.

Proxy data strongly indicate that during past glacial cycles, increasing Temp into warm interglacials preceded (sometimes by a few hundred years) growth in atmospheric CO<sub>2</sub>. Paleoclimate scientists do not claim the opposite. Although global warming, especially of northern oceans, probably was a major factor in the CO<sub>2</sub> rise, it seems (to me) unreasonable to explain a 100 ppm CO<sub>2</sub> increase solely on a few degrees of global warming. I suggest that increased Temp during interglacials released captured CO<sub>2</sub> in frozen NH ground, in melting glacial ice, and increased micro-biotic activity in NH ground.

**Exchange & Equilibrium.** There exists a constant, equilibrium exchange of CO<sub>2</sub> between the Atmos and the oceans, plants, & land-soil. Figure 3 gives the approximate **total carbon** inventories in petagrams (units 10<sup>15</sup> g; reservoir values in black boxes) in some major C reservoirs. The deeper ocean has much more C than the atmosphere, but it directly interchanges only with other ocean levels and its C recycle time is much longer. The approximate flux of CO<sub>2</sub> between reservoirs in the recent past (when Atmos. CO<sub>2</sub> was lower and stable) is

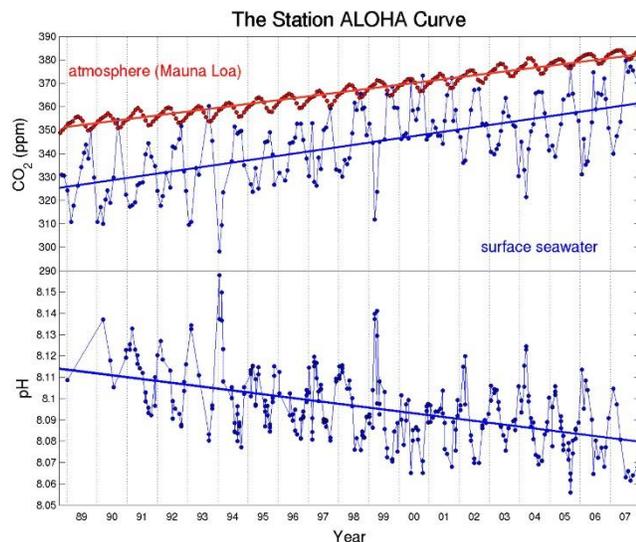
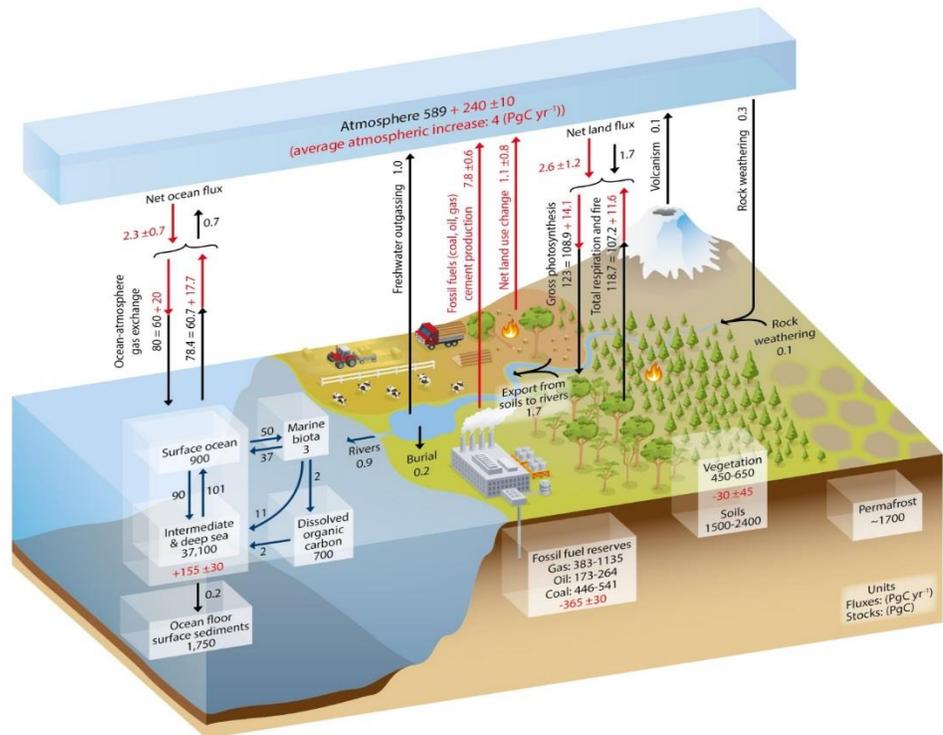


given by values associated with black arrows. The approximate change in the rates of carbon exchange between reservoirs since Amos CO<sub>2</sub> and temperature began rising is given by the red arrows and values.

Unless there is a significant change in one of the conditions controlling these C equilibrium levels (e.g., gas concentration, temperature), the rates of exchange between reservoirs tend to remain constant. Exchange with the surface ocean shows the largest C flux change, with C entering the ocean having increased by 33% and C exiting the ocean having increased by 29%, i.e., a net movement of Atmos. CO<sub>2</sub> into the oceans. The second largest change in C exchange rates occurs for plants, where uptake of Atmos CO<sub>2</sub> due to increased photosynthesis has increased by ~13%, and return of CO<sub>2</sub> to the Atmos (plant respiration, decay, and fires) is ~11%. Human activities in land use provide additional C to the Atmos, whereas some other C sources are much smaller. Major recent increases in Atmos CO<sub>2</sub> was a disturbance that drove significant shifts in C exchange rates between reservoirs. These shifts now amount to ~2.3 Pg-C/yr into the oceans and ~2.6 Pg-C/yr into plants (including subsurface plant activity).

**Temperature Vs. Gas Concentration.** Above I argue that temperature changes may produce modest, short term changes in CO<sub>2</sub> exchange rates involving the surface ocean, but that global ocean warming has been too little to produce the changes in Figure 3. Also, data exist that demonstrate the correlation between increasing Atmos CO<sub>2</sub>, ocean pH, and increasing ocean dissolved CO<sub>2</sub> (Figures 4 & 5, right & below, representing warm and cool ocean surfaces).

Many measurements indicate decreasing ocean pH values produced by increased dissolved CO<sub>2</sub>. The ocean surface is increasing its net dissolved CO<sub>2</sub>, not degassing it.



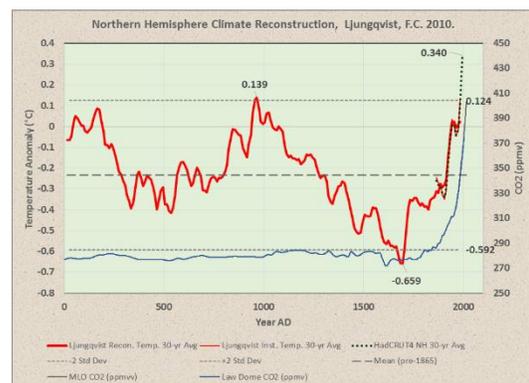
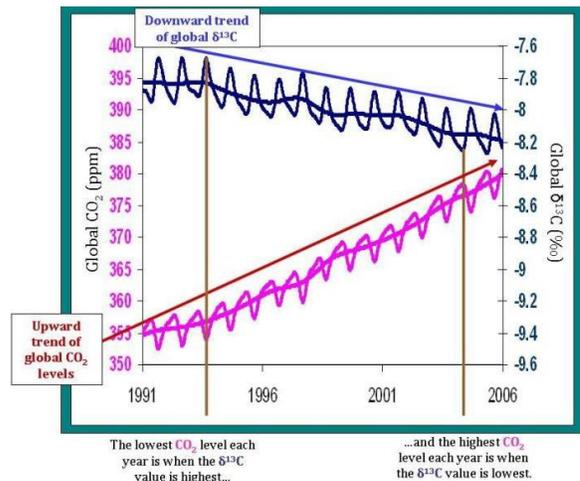
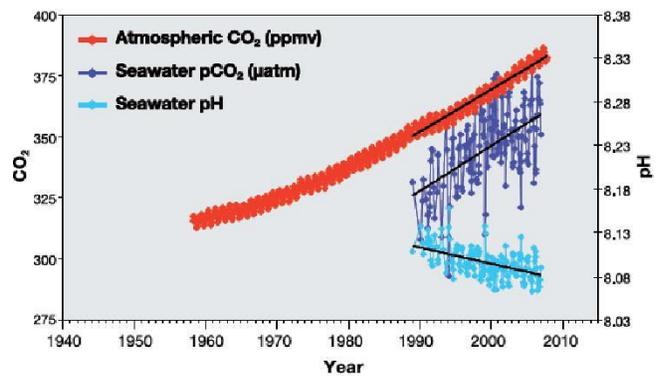
An additional argument against the growth of Atmos CO<sub>2</sub> deriving from increased ocean degassing resides in the isotopic <sup>13</sup>C/<sup>12</sup>C ratio in Atmos CO<sub>2</sub>, as shown by Figure 6 from NOAA. Plants significantly concentrate <sup>12</sup>C over <sup>13</sup>C during photosynthesis. In contrast, dissolved ocean CO<sub>2</sub> is in equilibrium with various solid carbonates, and neither ocean C nor carbonates are so <sup>12</sup>C enriched. Consequently, land plants, marine organisms, soils, and fossil fuels all have similar <sup>13</sup>C/<sup>12</sup>C, which is lower than <sup>13</sup>C/<sup>12</sup>C in the ocean and in limestones. Figure 6 shows that as Atmos CO<sub>2</sub> has increased (red), the <sup>13</sup>C/<sup>12</sup>C ratio (black) has decreased, consistent with an increasing Atmos component from fossil fuels and plants, and not from the ocean. Note in Figure 6 that the <sup>13</sup>C/<sup>12</sup>C ratio follows the seasonal variation in Atmos CO<sub>2</sub>.

**Plants & Soils.** The C inventory of plants and the biotic component of soils that plants promote is considerably larger than either the Atmos or surface ocean C inventories. Recent evidence demonstrates that plant photosynthesis and associated shift in the plant CO<sub>2</sub> exchange rate (Fig. 3) has been caused by increasing Atmos CO<sub>2</sub>. Of the ~123 Pg-C/yr used in photosynthesis, approximately half is quickly returned to the Atmos via plant respiration. The other half is incorporated into the soil as dead biotic material and as living micro-organisms, both of which eventually (over years to centuries) release their C as CO<sub>2</sub> into the Atmos. In addition to effects of increased Atmos CO<sub>2</sub>, temperature likely is a factor in both the rate of incorporation of CO<sub>2</sub> into plants and soils and the rate of return of dead biotic material to the Atmos. This effect is difficult to quantitatively measure because the distribution of C in soils is highly variable.

Although increases in temperature could, in principle, produce more decay of dead soil biotic material and increase Atmos CO<sub>2</sub>, I can offer two arguments against that being a major source of the growth in Atmos CO<sub>2</sub>. First is CO<sub>2</sub> data from multiple Antarctic ice cores, which yield constant Atmos CO<sub>2</sub> values of ~280 ppm between years zero-CE and 1800, with only a very slight decrease through the Little Ice Age around 1650-1730 (Fig. 7, right). Apparently the ~0.7 deg-C temperature decrease between 1000 CE and ~1700 CE produced only a very small decrease in CO<sub>2</sub>. Beginning ~1850, the CO<sub>2</sub> values all show a smooth and constant increase up to recent times.

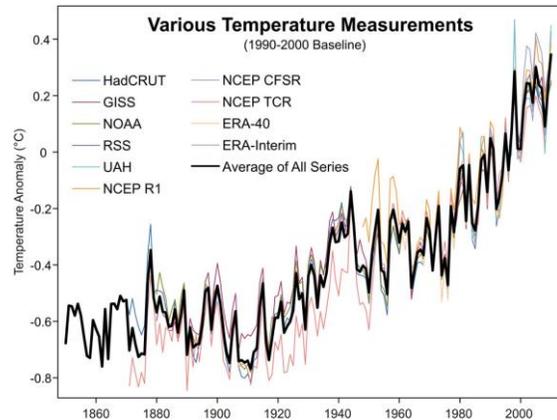
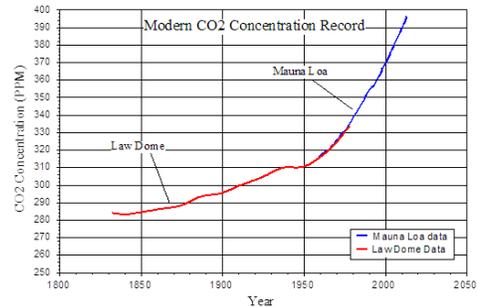
CO<sub>2</sub> data from the Law Dome ice core give a smooth upward trend from 1850 until ~1975, with only a flattening of the growth rate in the late 1940s, but a smooth trend between 1910-1940 (Fig. 8, below). The global temperature increase over ~1910-1940 was about as large as the temperature increase after 1980 (each

CO<sub>2</sub> and pH time series in the North Pacific Ocean



about 0.5 deg-C; Fig. 9, below). Yet the increase in Atmos CO<sub>2</sub> in the earlier years was much smaller than the increase since 1980. This indicates that higher soil decay rates resulting from increasing temperature were not the major source of more recent and larger increases in Atmos CO<sub>2</sub>. However, the rate of Atmos CO<sub>2</sub> increases shown by these ice core CO<sub>2</sub> data does match the increase in CO<sub>2</sub> produced from fossil fuel burning.

**Fossil Fuel CO<sub>2</sub>.** The most logical explanation for the increases in land and ocean C is the significant increase in Atmos CO<sub>2</sub> produced by fossil fuel burning, a source that did not exist over a century ago. Further, for many years records of the amount of CO<sub>2</sub> produced by burning fossil fuels closely correlate with the increase in Atmos CO<sub>2</sub>. This fossil fuel source of CO<sub>2</sub> today is about 7.8 Pg-C/yr (Fig. 3). Because of good records of fossil fuel resources recovered and used, this rate of CO<sub>2</sub> addition to the Atmos is reasonably well know, and is reported by several large, global organizations such as the IEA, BP, etc. Note that increased uptake of Atmos CO<sub>2</sub> by the oceans and plants/soil (~4.9 Pg-C/yr) is about 60% of the current Atmos CO<sub>2</sub> addition from fossil fuel burning. Some evidence indicates that ratio has been increasing over the past few decades as Atmos CO<sub>2</sub> grows.



**Chemical Disequilibrium & Exchange.** Increased fluxes of C out of the Atmos and into other C reservoirs caused by an increase in the Atmos CO<sub>2</sub> level due to human activities is to be expected based on basic chemical principles. Prior to significant addition of fossil fuel CO<sub>2</sub> to the Atmos, reservoir inventories of C and C exchange rates were relatively stable. Relatively constant global temperature for thousands of years during the Holocene did not act to alter these equilibria. However, an increase in the concentration of CO<sub>2</sub> (as with any gas) in one reservoir acts to shift the concentration equilibrium and increase the CO<sub>2</sub> in other exchanging reservoirs. Because the increase in Atmos CO<sub>2</sub> has been so large (from ~280 ppm to ~405 ppm today), this driving force has been strong and sufficient to overpower the tendency for warming oceans to degas CO<sub>2</sub>.

Some have argued that because of some indication that the current atmosphere contains only a few percent of the **actual CO<sub>2</sub> molecules** produced by fossil fuel burning, this constitutes evidence that most of the increase in Atmos CO<sub>2</sub> was not from burning fossil fuels. Different values have been given for the fraction of fossil fuel CO<sub>2</sub> in the atmosphere (ranging over about 4% to 15%), and many are based on isotopic analyses of the <sup>13</sup>C/<sup>12</sup>C or <sup>14</sup>C/<sup>12</sup>C ratios. This view totally ignores the important chemical principle of elemental exchange between reservoirs. As Fig. 3 indicates, individual C atoms and molecules, on a yearly basis, experience relatively large exchanges between reservoirs; e.g. about 8% of the C atoms in the Atmos and ocean surface exchange over a year. Clearly such C exchanges would rapidly diminish the specific Atmos C atoms produced by fossil fuels and replace them with C atoms from these other reservoirs, C atoms that may not carry any diagnostic signature of fossil fuels. The fraction of Atmos C atoms directly produced by fossil fuels are a measure of C reservoir exchange rates and the rate by which new fossil fuel C enters the Atmos, but they say little about the actual source of Atmos CO<sub>2</sub> growth.

**To summarize.** C exchange rates among C reservoirs tend to be at equilibrium unless and until a significant environmental change disturbs that. A significant increase in Atmos CO<sub>2</sub> concentration over the past century has been such a disturbance, and as a consequence a large fraction of that growth in Atmos CO<sub>2</sub>

has manifested as new plant growth and to increased ocean C levels. Increased temperature over the past century (which mostly has only modestly affected the ocean) and any tendency for warmer surface ocean to degas more CO<sub>2</sub>, has been over-powered by higher Atmos CO<sub>2</sub> shifting the chemical equilibrium toward more dissolution of Atmos CO<sub>2</sub> into the oceans. Higher decay rates of soil biotic material caused by the increased temperatures may be a source of part of the Atmos CO<sub>2</sub> increase over the past century. However, it is most unlikely that organic decay has been other than a minor source, especially in the past few decades when Atmos CO<sub>2</sub> was growing most rapidly.

Anyone who would argue that human activities, and especially burning of fossil fuels, are not a major original source of the growth in Atmos CO<sub>2</sub> must answer the following questions.

- 1) Fossil fuel burning and other human activities have undeniably generated significant CO<sub>2</sub>, which has been well documented. What happened to that CO<sub>2</sub> if it did not enter the Atmos?
- 2) Given that it is most unlikely that existing ocean or land reservoirs are losing net C to the Atmos, what other source of CO<sub>2</sub> could possibly cause the large Atmos growth in CO<sub>2</sub> over a relatively short time period?