
Atmospheric Carbon Dioxide Control Mechanisms

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PART TWO : - A POSSIBLE SOLUTION THE OCEAN CONTROL THEORY

Synopsis:- Part Two

Using the very basic principles that the partial pressure exerted by a gas in solution in water is proportional to its concentration (Henry's Law) and that flow of gas is determined simply by pressure differences, a model for the ocean/atmosphere system is constructed by reference to observations of atmospheric CO₂ levels, anthropogenic CO₂ emissions, sea surface temperature and atmospheric O₂ variations. While the result, in common with the IPCC theories, suggests that the increase in atmospheric CO₂ levels is caused mainly by anthropogenic emissions, the mechanisms through which this occurs are vastly different to those described in IPCC TAR and AR4, leading to significant implications for the prediction of future atmospheric CO₂ trends and hence future global temperatures.

The theory also has the unexpected benefit of a logical explanation for the unexplained low temperatures experienced in the deep ocean.

Contents

2.0 THE OCEAN CONTROL THEORY

2.1 The Properties of CO₂

2.2 Ocean Control Theory

2.3 Effects of Temperature

2.4 Quantitative Analysis of the Ocean Control Model

2.4.1 Transfer Functions g_1 and g_2

2.4.2 Sea Surface/Atmosphere Response τ_2

2.4.3 Thermocline Response τ_1

2.4.4 The Effects on Atmospheric Oxygen Levels

2.4.5 Atmospheric O₂ Response Times

2.4.6 Calculated O₂ Levels

2.4.7 Oceanic CO₂ Fluxes

2.5 Calculation of CO₂ and O₂ Variations

2.6 The Deep Ocean as a CO₂ Source

2.7 Conclusions to Part 2

2.8 References

Appendix (i) Derivation of Equations for C_a and C_s

Appendix (ii) Assumptions and Values used to Compute CO₂ and O₂ Levels

List of figures

Figure 2.1: The Ocean Control Model

Figure 2.2: Ocean Structure

Figure 2.3: Water Tank Analogy for the Ocean Control Concept

Figure 2.4: Calculated CO₂ actual CO₂ Increase from 1960 to 2010

Figure 2.5: Calculated atmospheric O₂ decrease from 1960 to 2010 including SST variations.

Figure 2.6: Calculated Atmospheric CO₂ Variations

Figure 2.7: Calculated O₂ Variations

Figure 2.8: Ocean Control model

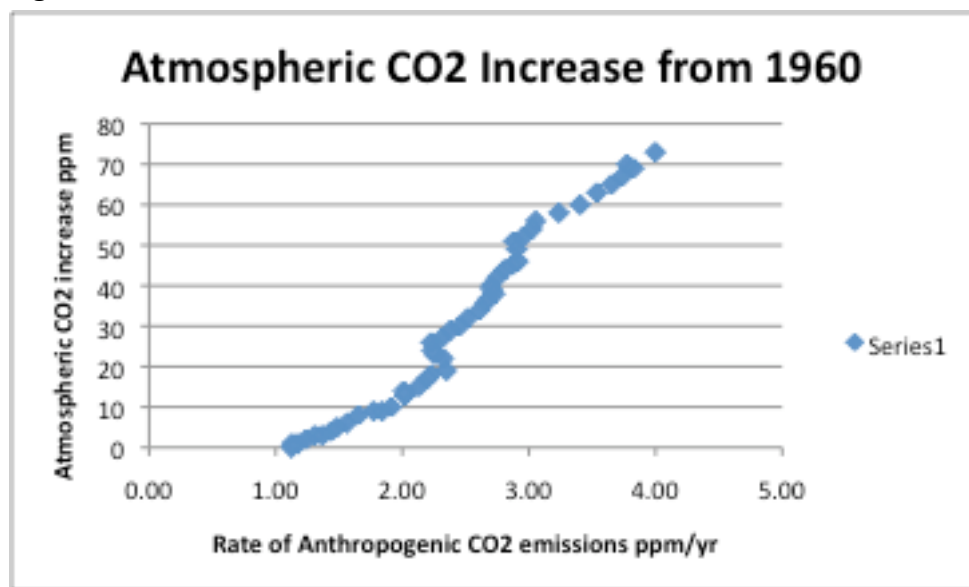
2.0 THE OCEAN CONTROL THEORY

2.1 The Properties of CO₂

The explanation for the increased atmospheric CO₂ levels provided in the IPCC assessment reports, not only fails even to ask the fundamental questions of how and why, but also does not correspond to any of the observations and measurements detailed in the main papers cited in those reports. Indeed the, so-called, anthropogenic fingerprint evidence actually suggests that the explanation is profoundly incorrect. So, how do we answer the questions posed in section 1 of this paper, while establishing agreement with observed data?

The IPCC claim very specifically that 50% of anthropogenic CO₂ emissions are simply accumulating in the atmosphere. This may be what appears to be happening but, as is previously shown, it is not consistent with any physical science. An alternative explanation for what appears to happen is that **atmospheric CO₂ levels are proportional to the rate of anthropogenic emissions** as displayed in figure 2.1, which shows the estimates of annual global emissions in ppm/yr (from Carbon Dioxide Information Analysis Centre) plotted against the actual CO₂ increase observed at Mona Loa from 1960 to 2010. Such a linear relationship is either a total fluke or has some relevance. Let us assume that it is relevant.

Figure 2.1



CO₂ has an armoury of interesting capabilities, one of which is its readiness to dissolve in water. It is widely accepted that there is over 50 times more CO₂ dissolved in the oceans of the world than exists in the atmosphere, much of it held at high pressure in the deep ocean. Moreover, it is well established that equilibrium exists between a dissolved gas and its neighbouring atmosphere, summarised in the form of Henry's Law¹ and Henry's Constant, which determines the equilibrium between partial pressure of the gas in solution and in vapour form.

The usual definition of Henry's law states that the partial pressure of a gas in solution is proportional to its dissolved concentration and the proportionality constant is Henry's constant. We should thus expect there to be an equilibrium between the oceans and the atmosphere with the partial pressure of the CO₂ in the surface layer of the oceans being equal to the partial pressure of CO₂ in the atmosphere. From this simple concept it should be possible to develop a theory to describe how the atmosphere would respond to an influx of anthropogenic CO₂.

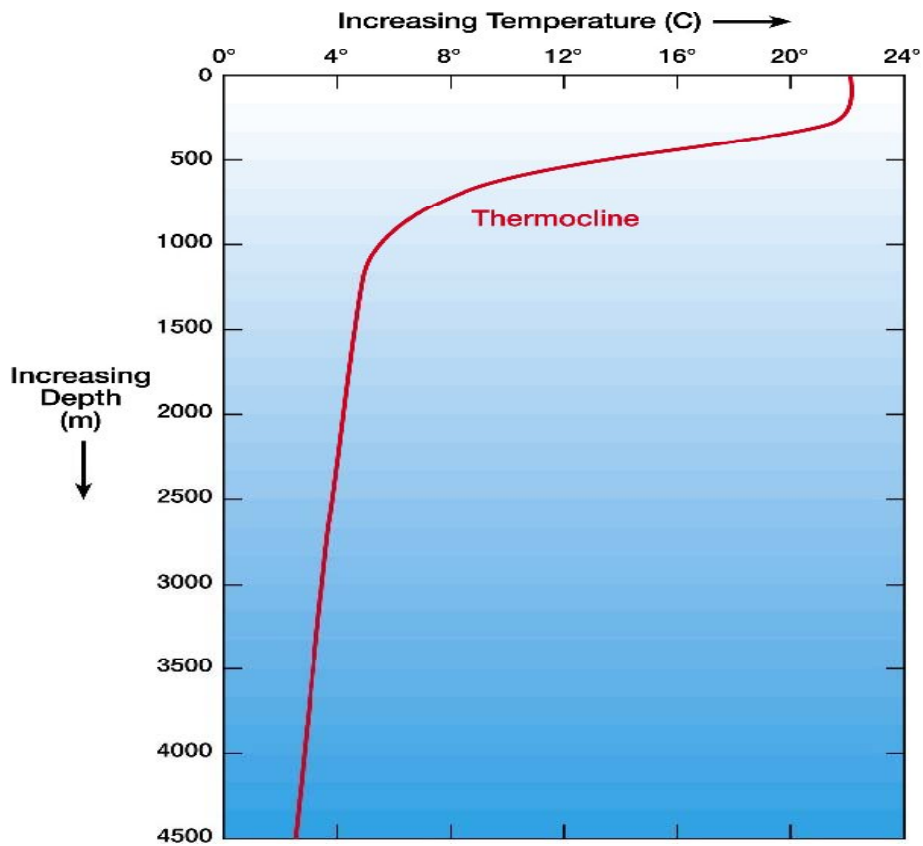
2.2 Ocean Control Theory

The oceans are vast and immensely complex. The simplest commonly used model to describe the oceans is a two box model where the deep oceans, represented by one box, are overlaid by a higher temperature sea surface zone, represented by the second box, the two being separated by the thermocline, a thin layer of water with a high temperature gradient (Figure 2.2). The existence of the thermocline implies restricted mixing between these two ocean layers. The bulk ocean is known to contain over 50 times more CO₂ than the atmosphere and is the engine of CO₂ production from inorganic carbon. Consider it to be an infinite source of CO₂ such that any flow of CO₂ from the deep ocean to the sea surface zone will have no impact on the concentration of CO₂ remaining.

The sea surface zone is of course in intimate contact with the atmosphere. If there were no external CO₂ fluxes, such as photosynthetic fluxes, in either the sea surface zone or atmosphere, we would expect that the partial pressures of CO₂ in each zone, deep ocean, sea surface and atmosphere to be the same after allowing for the effects of hydrostatic pressure.

1 It is often argued that the complex chemistry involved in the dissolution of CO₂ in water invalidates the application of Henry's Law. The paper by Carrol and Mather – The System Carbon Dioxide – Water and the Krichevsky-Kasarnovsky Equation shows that at temperatures below 100degC and pressures up to 1000bar, the Krichevsky method can be used successfully to obtain Henry constants for the CO₂/H₂O system.

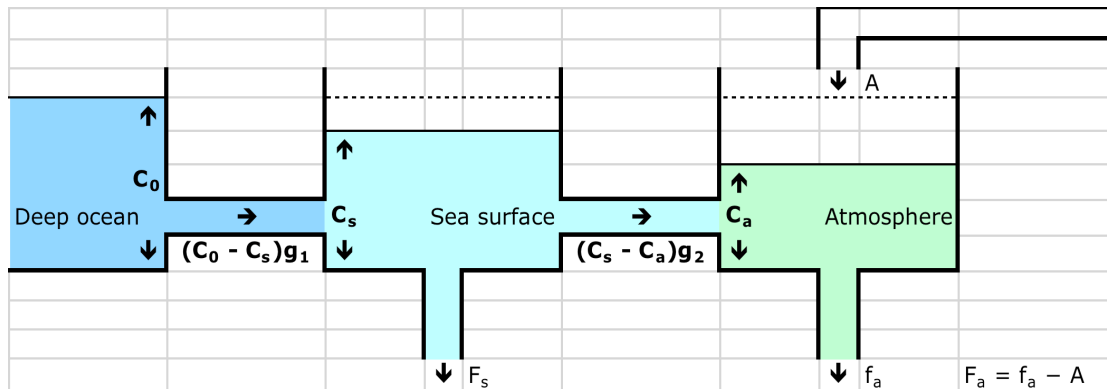
Figure 2.2: Ocean Structure



There are, however, significant external fluxes in both the sea surface zone and the atmosphere. The dominant flux in both is an absorptive flux due to photosynthesis by phytoplankton in the sea surface layer and the biosphere in the atmosphere. These fluxes will act to reduce the partial pressure of CO_2 in both the sea surface and atmosphere.

In order to fully understand the implication of these fluxes let us consider the analogy of three inter-connected water tanks, representing the deep ocean, the sea surface and the atmosphere. The amount of water in each tank represents the CO_2 levels in each ocean/atmosphere zone.

Figure 2.3: Water Tank Analogy for the Ocean Control Concept



Let the deep ocean be presented by an infinitely long tank, whose water level remains constant throughout. A second, but finite, interconnected tank represents the sea surface and a third interconnected tank the atmosphere. The water levels in the tanks represent the oceanic and atmospheric CO₂ partial pressures.²

If there were no net loss of water from any of the tanks the water level would be the same in each of the three tanks.

If, however, water was allowed to drain from the atmosphere tank, representing the loss of CO₂ due to biospheric photosynthesis, the water level in that tank would begin to fall causing water to flow from the sea surface tank into the atmosphere tank. Of course as water flows from the sea surface tank, the water level falls in that tank also, allowing water to flow from the deep ocean tank.

A new stable equilibrium is established when the water levels in the three tanks are such that the flow of water from the deep ocean tank and from the sea surface tank to the atmosphere tank are both equal to the loss of water representing atmospheric photosynthesis.

A similar effect in the sea surface tank would be produced by a water outflow representing photosynthetic activity in the sea surface.

The equilibrium conditions can be described by the following two simple equations for the sea surface and atmospheric CO₂ levels. The flow of water between the tanks is proportional to the difference in water levels between the tanks.

2 Transport of gases is governed by partial pressure differentials. Henry's law enables the partial pressure exerted by a solute to be determined by its concentration in solution. In the atmosphere CO₂ concentration is usually expressed as parts per million (ppm) fraction, which is also equivalent to the partial pressure of CO₂ measured in μ atmos. For the purposes of calculations we shall use partial pressures in μ atmos, although the results will often be compared to measured data of CO₂ concentration in ppm.

For the atmosphere the balance of fluxes is given by

$$(C_a - C_s) \cdot g_2 = F_a$$

so that atmospheric CO₂ levels $C_a = C_s - 1/g_2 \cdot F_a$ (1)

while for the sea surface

$$(C_o - C_s) \cdot g_1 = (C_a - C_s) \cdot g_2 + F_s = (F_a + F_s)$$

and sea surface CO₂ levels $C_s = C_o - 1/g_1 \cdot (F_a + F_s)$ (2)

where F_a and F_s are the outflows from the atmosphere and sea surface tanks, representing atmospheric and sea surface photosynthetic fluxes and g_2 and g_1 are CO₂ transfer factors for flows between the tanks, determined by the diffusive properties of CO₂ and the physical characteristics of the sea surface/atmosphere interface and thermocline. C_o represents the partial pressure of CO₂ in the deep ocean.

These equations represent the controlling effect of the ocean on both the sea surface zone and the atmosphere. In the absence of any external CO₂ fluxes the partial pressure of CO₂ in both the atmosphere and sea surface would be the same as that of the deep ocean, and because of the much higher concentration of CO₂ in the deep ocean we would witness significantly higher atmospheric and sea surface CO₂ concentrations. These sea surface and atmospheric levels are being suppressed by the absorptive fluxes due to photosynthesis. This simple action of flow being determined by partial pressure differentials provides an entirely rational explanation for the relative stability of historic values of CO₂ at a specific value of CO₂ determined by the deep ocean CO₂ level and the net photosynthetic fluxes in the sea surface and atmosphere. **The impact of anthropogenic CO₂ emissions is simply to offset slightly these photosynthetic fluxes allowing the CO₂ levels to rise not only in the atmosphere but also in the sea surface.** The water tank analogy is to turn on an inflow A of water into the atmosphere tank (figure 2.3). This would have the impact of reducing the net water flow from all the tanks, thus causing an increase in the water level in both the atmosphere and sea surface tanks. A more detailed mathematical analysis is given in appendix (i)

According to this simple rational explanation **the atmospheric CO₂ increase is proportional to the rate of anthropogenic emissions**, as is observed in figure 2.1. Once that emission rate stabilises, so will the atmospheric CO₂ level, after a time determined by the thermocline and sea surface transfer factors. There is simply no question of anthropogenic CO₂ emissions being partitioned between the oceans, biosphere and atmosphere.

2.3 Effects of Temperature

Like many physical and chemical constants, Henry's constant is not constant. It varies with temperature, having a coefficient at 15degC of around +4%/degC. This has an impact on the equilibrium between ocean and atmosphere and must be taken account of in equations 1 & 2. It is necessary to modify equation 2 so that

$$Ca = Cs (1 + k\Delta T) - 1/g_2.Fa$$

Where k is the temperature coefficient of Henry's constant and ΔT the temperature variation in the sea surface.

This temperature effect, while detectable, is quite small, a 1degC change in sea surface temperature producing a change in atmospheric CO₂ levels of around 12ppm. It should therefore be absolutely clear that the increases in atmospheric CO₂ levels over the last century cannot be attributed to increases in sea temperature, as has been claimed by some observers.

2.4 Quantitative Analysis of the Ocean Control Model

It should be possible by inputting data for the sea surface and net atmospheric CO₂ fluxes into equations 1 & 2 to determine how closely this theory fits with observational evidence. As a rough first estimate let us assume that net biospheric CO₂ absorptive fluxes are equivalent to a reduction in atmospheric CO₂ levels of 20ppm/yr (20 μ atmos/yr). It is usually assumed that oceanic photosynthesis is of a similar order of magnitude to the biosphere so lets also use a figure of sea surface absorptive flux of 20 μ atmos/yr.

We can obtain reasonably good estimates of anthropogenic emissions from CDIAC (Carbon Dioxide Information Analysis Centre) CDIAC with a 12% lift to compensate for an estimated increase in deforestation. Sea surface temperature changes are taken from the global SST anomaly data set from HadSST2 compiled by the Hadley Centre of the UK Met Office. All that remains is to find values of the thermocline and sea surface/atmosphere transfer values g_1 and g_2 .

2.4.1 Transfer Functions g_1 and g_2

A time variable form of equations 1 & 2 can be shown to be

$$\begin{aligned} \text{and} \quad Ca &= Cs - 1/g_2.Fa.(1 - e^{-t/\tau_2}) \\ Cs &= Co - 1/g_1(Fa + Fs)(1 - e^{-t/\tau_1}) \end{aligned}$$

The transfer functions g_1 and g_2 have the units year⁻¹. They are related to the response times τ_1 and τ_2 of the thermocline and sea surface/atmosphere interface.

2.4.2 Sea Surface/Atmosphere Response τ_2

Table 1 Atmospheric CO₂ Residence Times (Segalstad 1997)

Authors [publication year]	Residence time (years)
<i>Based on natural carbon-14</i>	
Craig [1957]	7 +/- 3
Revelle & Suess [1957]	7
Arnold & Anderson [1957]	10
including living and dead biosphere (Siegenthaler, 1989)	4-9
Craig [1958]	7 +/- 5
Bolin & Eriksson [1959]	5
Broecker [1963], recal. by Broecker & Peng [1974]	8
Craig [1963]	5-15
Keeling [1973b]	7
Broecker [1974]	9.2
Oeschger et al. [1975]	6-9
Keeling [1979]	7.53
Peng et al. [1979]	7.6 (5.5-9.4)
Siegenthaler et al. [1980]	7.5
Lal & Suess [1983]	3-25
Siegenthaler [1983]	7.9-10.6
Kratz et al. [1983]	6.7
<i>Based on Suess Effect</i>	
Ferguson [1958]	2 (1-8)
Bacastow & Keeling [1973]	6.3-7.0
<i>Based on bomb carbon-14</i>	
Bien & Suess [1967]	>10
Münnich & Roether [1967]	5.4
Nydal [1968]	5-10
Young & Fairhall [1968]	4-6
Rafter & O'Brian [1970]	12
Machta (1972)	2
Broecker et al. [1980a]	6.2-8.8
Stuiver [1980]	6.8
Quay & Stuiver [1980]	7.5
Delibrias [1980]	6.0
Druffel & Suess [1983]	12.5
Siegenthaler [1983]	6.99-7.54
<i>Based on radon-222</i>	
Broecker & Peng [1974]	8
Peng et al. [1979]	7.8-13.2
Peng et al. [1983]	8.4
<i>Based on solubility data</i>	
Murray (1992)	5.4
<i>Based on carbon-13/carbon-12 mass balance</i>	
Segalstad (1992)	5.4
² Atmospheric residence time (i.e. lifetime, turnover time) of CO ₂ , mainly based on the compilation by Sundquist (1985; for references in brackets).	

There is much evidence to suggest that the response time of the sea surface/atmosphere interface is of the order of a few years. For example a paper by Roger Revelle and Hans Suess of the Scripps Institution of Oceanography in 1957 stated

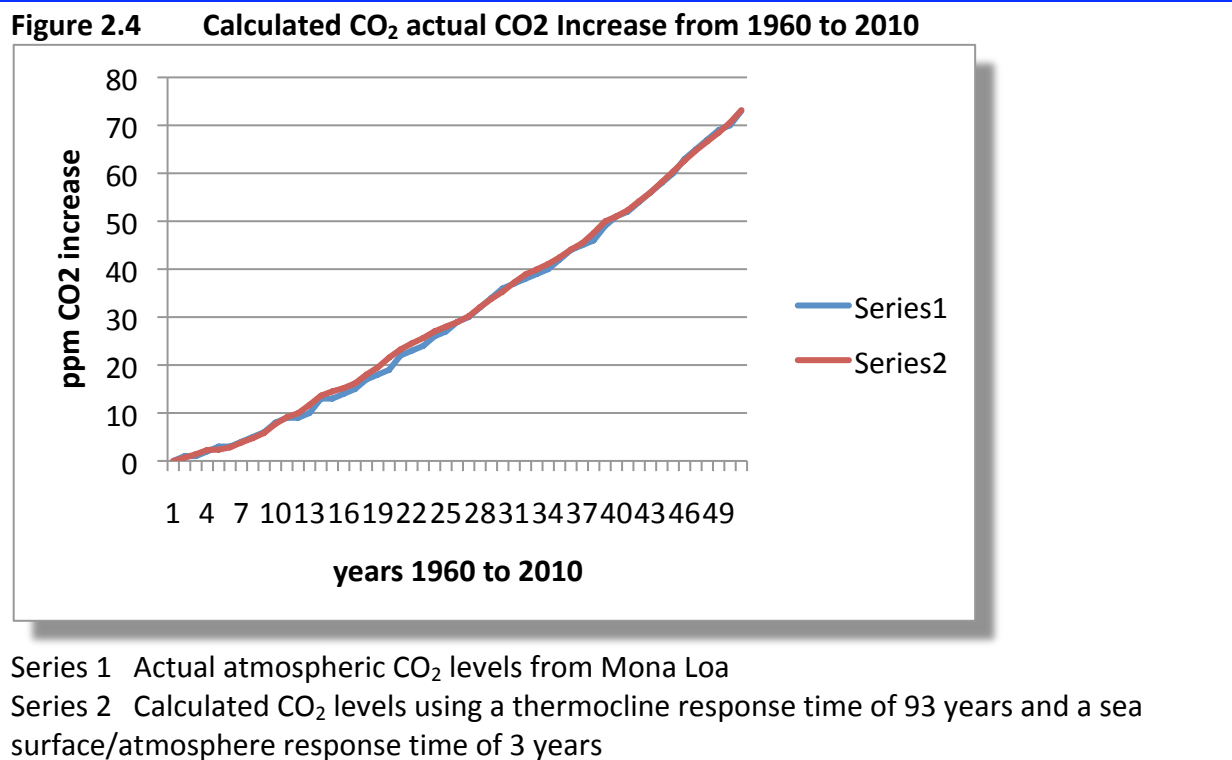
“From a comparison of C^{14}/C^{12} and C^{13}/C^{12} ratios in wood and in marine material and from a slight decrease of the C^{14} concentration in terrestrial plants over the past 50 years it can be concluded that the average lifetime of a CO_2 molecule in the atmosphere before it is dissolved into the sea is of the order of 10 years.

Table 1 summarises the estimates made for atmospheric residence times by various researchers over the past 50 years (data from Segalstad 1997). It is clear that, without exception, estimates of atmospheric residence times are measured in the range 2 to 15 years.

Residence time however is an imprecise parameter. Response time by contrast defines the exponential time constant of the sea surface/atmospheric interface. It will take typically three time constants to reach a 99% completion of the equilibrium control action. Thus for this exercise we will assume a time constant τ_2 of 3 years, approximately equivalent to a residence time of 9 years.

2.4.3 Thermocline Response τ_1

A value for τ_1 of 93 years is necessary to produce the agreement with observation as shown in Figure 2.4. **This however is not a complete picture. It neglects the evidence provided by atmospheric O_2 variations.**



2.4.4 The Effects on Atmospheric Oxygen Levels

As reported in the IPCC TAR atmospheric oxygen levels are also changing, those changes also being attributed to anthropogenic CO₂ emissions. A similar set of equations derived for CO₂ control must also apply to O₂, except that the signs of the fluxes are reversed. Whereas photosynthesis extracts CO₂ from the atmosphere it adds O₂ and the oceans, instead of supplying CO₂ to the atmosphere to maintain control of atmospheric levels, will be absorbing O₂. A typical ratio for O₂/CO₂ photosynthetic fluxes is 1.1.

The relevant equations for atmospheric O₂ levels are thus

$$\begin{aligned} O_s &= O_o + 1/\gamma_1(\Phi_a + \Phi_s)(1 - e^{-t/\tau_1}) \\ \text{and} \quad O_a &= O_s + 1/\gamma_2\Phi_a(1 - e^{-t/\tau_2}) \end{aligned}$$

Where Φ_a and Φ_s are the atmospheric and sea surface photosynthetic oxygen fluxes respectively.

As with CO₂ let us assume that the only time variable fluxes are the anthropogenic component of the atmospheric flux Φ_a , and that this flux will be 1.33 times the CO₂ flux (1.33 being the average stoichiometric O₂/CO₂ ratio for combustion of carbon), and the impact of deforestation estimated to be at a rate of 12% of the anthropogenic emissions. The O₂ flux due to deforestation will be 1.1 times the CO₂ flux since this is a photosynthetic effect. All other fluxes will be deemed to be constant.

We must also allow for the temperature coefficient of the O₂/N₂ ratio. This is a very small number, around 0.00014/degC. That this is a very small temperature coefficient is because it results from the difference between the coefficients for O₂ and N₂, however, the actual ppm shift resulting from this small coefficient is certainly not small because it must be multiplied by the atmospheric partial pressure of O₂ which is of course 210,000µatmos or 21%. This results in an increase in O₂ of around +30ppm/degC of sea surface temperature change. This of course is in the opposite direction to the shift in recorded atmospheric O₂ concentration.

2.4.5 Atmospheric O₂ Response Times

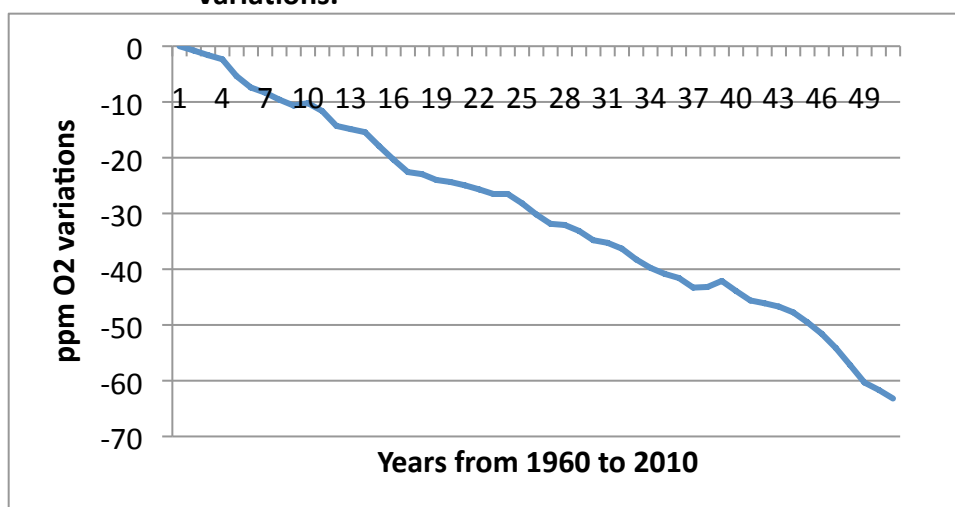
The two transfer factors γ_1 and γ_2 are governed primarily by physical properties of the thermocline and sea surface/atmosphere boundaries and will be related to the similar constants used for the CO₂ calculations. However we should be prepared to acknowledge that the differing molecular weights of CO₂ and O₂ might influence these values. For example transport of molecules across the thermocline and sea surface/atmosphere interface will involve a process not dissimilar to molecular diffusion. Following from the kinetic theory of gases let us assume that the transfer constants γ_1 and γ_2 will be proportional to the molecular weight of the gas

Using this assumption we can readily calculate that the response times τ_1 and τ_2 for O_2 will be reduced by 32/44 of the same values for CO_2 . That is 68 years and 2.2 years for O_2 rather than the 93 and 3 years used for CO_2 .

2.4.6 Calculated O_2 Levels

Figure 2.5 shows the resultant calculated atmospheric O_2 variations from 1960 to 2010. Between the years 1990 and 2000, according to TAR, there has been an observed reduction in atmospheric O_2 levels of 33ppm. Figure 2.5 is showing a calculated O_2 reduction of only 10ppm, a variance of 23ppm.

Figure 2.5 Calculated atmospheric O_2 decrease from 1960 to 2010 including SST variations.



Calculated O_2 levels using a thermocline response time of 68years and a sea surface/atmosphere response time of 2.2 years including the effects of sea surface temperature variations. The resulting O_2 reduction during the period 1990 to 2000 is 10ppm.

The conclusion to be drawn is that there is still a time variable flux of O_2 , and therefore of CO_2 , which has not yet been accounted for, and moreover, that flux must have a stoichiometric O_2/CO_2 ratio much greater than the 1.33 attributed to fossil fuel combustion in order to explain the observed O_2 decrease. According to equations 1 & 2 there are two fluxes, which are relevant, F_a and F_s , the atmospheric and oceanic biospheric CO_2 photosynthetic fluxes and their O_2 counterparts Φ_a and Φ_s . These might not be constant as has been assumed. However we can immediately rule out the atmospheric photosynthetic flux since the stoichiometric ratio is only 1.1.

That leaves the oceanic fluxes F_s and Φ_s as the only candidates. Would such fluxes result in an amplified atmospheric O_2 change necessary to account for the 23ppm difference in observed and calculated O_2 shifts?

2.4.7 Oceanic CO₂ Fluxes

Ocean phytoplankton employs photosynthesis to capture carbon for their production of the complex hydrocarbons necessary for life. In doing so they also release O₂ in the ratio 1.1 moles of O₂ for each mole of CO₂ absorbed, just as for the land based biosphere. The difference however is that the reactions involve dissolved CO₂ and O₂, and while the stoichiometry is the same the effect on partial pressures is very different. For oceanic primary production it is necessary to take into account the relative Henry coefficients of CO₂ and O₂ in water. An addition of 1 mole of O₂ has a much greater impact on the partial pressure of O₂ than does 1 mole of CO₂ on the partial pressure of CO₂ because of the big differences in solubility of the two gases.

For a given change in CO₂ molecular concentration due to photosynthesis, the equivalent change in O₂ molecular concentration δO_2 will be $-1.1 \cdot \delta CO_2$ from photosynthetic stoichiometry.

And the partial pressure change $\delta O_2 \mu\text{atmos} = -1.1 \cdot \delta CO_2 \mu\text{atmos} \cdot H_{O_2}/H_{CO_2}$

The ratio of Henry coefficients H_{O_2}/H_{CO_2} can be ascribed the value 26.1 at 20degC, representing the fact that CO₂ is 26.1 times more soluble in water than O₂.

Henry's law thus applies a large multiplier (26.1) to the partial pressure change in CO₂ due a change in photosynthetic flux, for O₂. The observed reduction in atmospheric O₂ could thus easily be ascribed to a small reduction in sea surface photosynthetic activity.

Remember that we are discussing a possible reduction in sea surface oceanic activity and hence a relative increase in CO₂ concentrations. An increase in sea surface CO₂ concentration sufficient to produce an increase in CO₂ partial pressure of 1 μatmos will result in a decrease in sea surface O₂ concentration 1.1 times that of the CO₂ increase but will result in a reduction in O₂ partial pressure of 28.7 μatmos ($1.1 \cdot 26.1 = 28.7$). Has such a change been observed?

A paper presented by Gregg et al in Geophysical Research Letters in 2003, titled "Ocean primary production and climate: Global decadal changes" summarises that

"Satellite in-situ blended ocean chlorophyll records indicate that global ocean annual primary production has declined more than 6% since the early 1980".

The observations of Gregg suggest a decline in oceanic primary production of 3% per decade. Let us assume that oceanic photosynthetic activity is reducing as suggested by Gregg, but at a rate consistent with the observed changes in atmospheric O₂ levels. This reduction in activity will result in a net reduction in both CO₂ and O₂ fluxes F_s and Φ_s , resulting in an increase in CO₂ levels and decrease in O₂ levels.

2.5 Calculation of CO₂ and O₂ Variations

We thus have two data sets to satisfy, one for the increase in atmospheric CO₂ and one for the decreasing atmospheric O₂. We also have two variables to adjust, the rate of reduction of oceanic primary production F_s and the thermocline response time τ_1 in order to satisfy the data sets. This should result in a unique solution to the equations,

For the sea surface

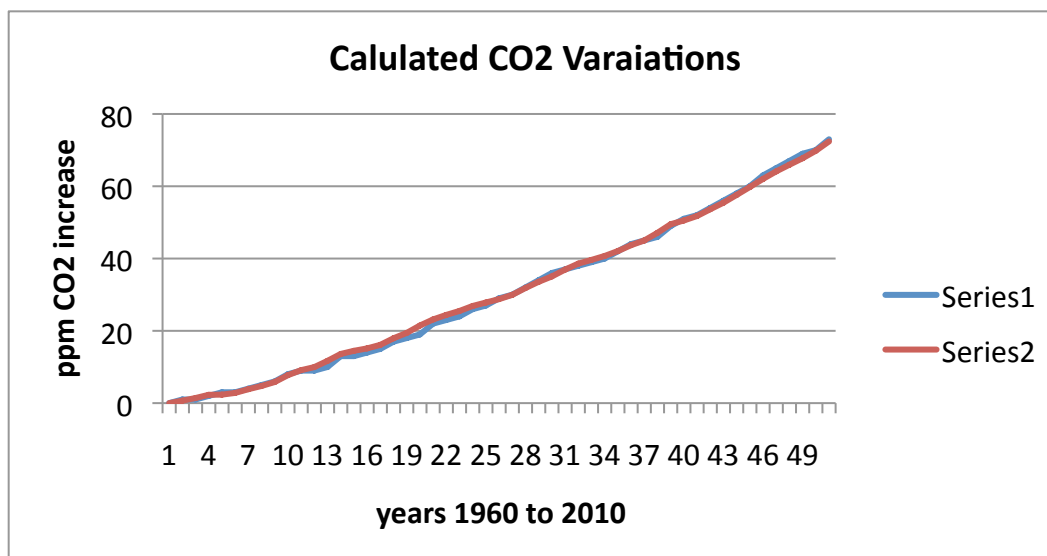
$$\begin{aligned} pC_s &= pC_0 - 1/g_1 \cdot (F_a + F_s)(1 - e^{-t/\tau_1}) \\ pO_s &= pO_0 + 1/\gamma_1 \cdot (\Phi_a + \Phi_s)(1 - e^{-t/\tau_1}) \end{aligned}$$

and for the atmosphere

$$\begin{aligned} pC_a &= pC_s - (1/g_2 \cdot F_a - k \cdot C_s \cdot \Delta T) (1 - e^{-t/\tau_2}) \\ pO_a &= pO_s + (1/\gamma_2 \cdot \Phi_a + k_o \cdot O_s \cdot \Delta T) (1 - e^{-t/\tau_2}) \end{aligned}$$

The result (figures 2.6 and 2.7) indicates that the thermocline response time is now of the order of 70 years and that the sea surface primary production is reducing at a rate equivalent to 0.03ppm/year/year CO₂ or approximately 1.5%/decade. This equates to half the rate reported by Gregg. Since Gregg was reporting a result peculiar to the Pacific region and these calculations refer to a global average, and use very crude estimates for net sea surface primary production, the result is hopefully not unreasonable.

Figure 2.6: Calculated Atmospheric CO₂ Variations

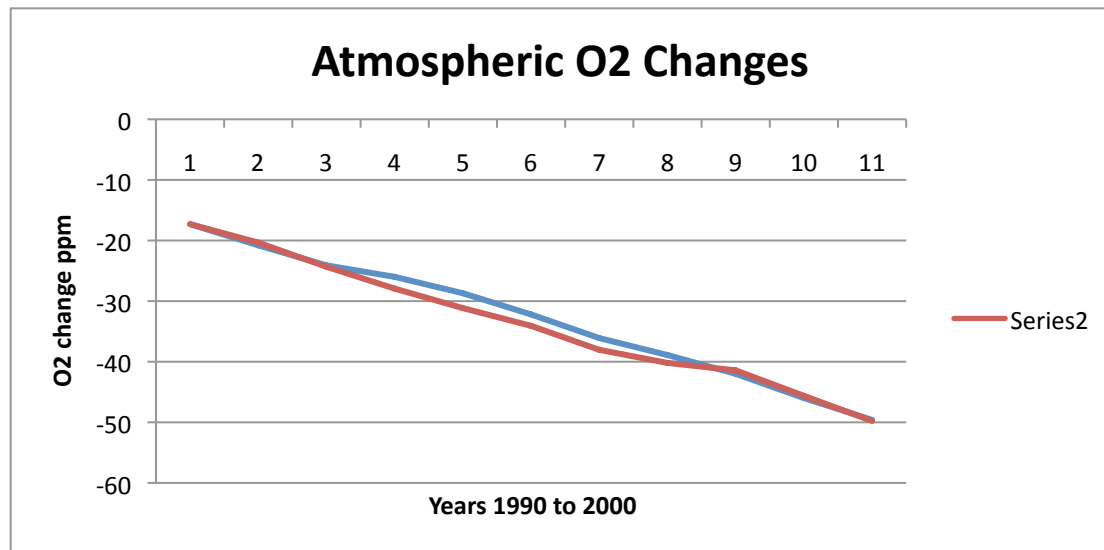


Series 1 Actual CO₂ measurements at Mona Loa

Series 2 CO₂ values calculated from Ocean Control Theory

The comparison of calculated O₂ values with observed values reported by Manning and Keeling (ref 8) for the years 1990 to 2000 is shown in Figure 2.7. Appendix (ii) provides details of the assumptions and values used in these calculation.

Figure 2.7: Calculated O₂ Variations



Series 1 Actual atmospheric O₂ levels from Manning and Keeling (ref 8)

Series 2 Calculated O₂ levels using a thermocline O₂ response time of 51 years and a sea surface/atmosphere response time of 2.1 years (32/44 x equivalent CO₂ response times)

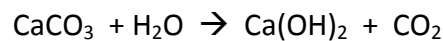
We have thus postulated a mechanism for atmospheric CO₂ control by the oceans acting as an infinite sink of CO₂. The atmospheric CO₂ level is controlled to a set point determined by the deep ocean CO₂ content and sea surface temperature, modified by the product of the external CO₂ fluxes F in both the sea surface and atmosphere through either natural or anthropogenic actions and the ocean/atmosphere time constant τ_2 , estimated to be of the order of 3 years and a deep ocean/sea surface interface time constant τ_1 of 70 years. Importantly the equations and observations both show a linear relationship between increases in atmospheric CO₂ levels and the rate of anthropogenic CO₂ emissions.

It is important to understand that the anthropogenic CO₂ emissions are not being taken up by the oceans or indeed by the biosphere as is assumed in the IPCC assessment reports. One CO₂ molecule is indistinguishable from any other. We can never know what happens to individual molecules. The effect of the anthropogenic emissions is that they reduce the net atmospheric CO₂ flux, which is predominantly photosynthetic, and by reducing the corresponding suppression of sea surface and atmospheric CO₂ levels, allow both levels to increase.

2.6 The Deep Ocean as a CO₂ Source

We have so far considered the deep ocean to be an infinite source of CO₂. However, continuous removal of CO₂ from the atmosphere and sea surface by photosynthetic activity requires a balancing flux of CO₂ from the deep ocean. While there may be far more CO₂ in the deep ocean than in the atmosphere, such a continuous transfer would soon deplete the oceans as a source of CO₂. There must therefore be a mechanism for CO₂ generation in order to prevent such depletion.

There is a large concentration of insoluble carbonates, particularly calcium carbonate, in suspension in the world's oceans. Although principally insoluble these carbonates can dissociate in water to form hydroxides



Like all chemical reactions this is reversible with an equilibrium defined by the constant

$$K = \frac{[\text{Ca(OH)}_2] \cdot [\text{CO}_2]}{[\text{CaCO}_3] \cdot [\text{CO}_2]}$$

As CO₂ is transferred out of the deep ocean to balance the photosynthetic fluxes of the ecosphere, in order to maintain equilibrium the equation will move to the right to rebalance the equilibrium condition. CO₂ levels will be replenished. Calcium hydroxide will also be produced but this will simply be precipitated out as solid suspension as the solution saturation point is reached. There is however a cost for this action. The above chemical process is endothermic. It requires energy to dissociate the calcium carbonate, 92kj/mole of CO₂ to be precise.

There is also an additional energy input requirement in terms of the internal energy of the generated CO₂ at the immense hydrostatic pressures of the deep ocean. This energy can be expressed by

$$U = \int PdV$$

But since for an ideal gas $PV = nR\theta$ $PdV + VdP = 0$

Thus $U = - \int VdP = - \int nR\theta/P dP$

And therefore $U = nR\theta \ln(P1/Po)$

Where Po = atmospheric pressure (1 atmos) and P1 is the pressure at the deep ocean. P1 will vary with depth and range from 100 atmos at 1000m depth to 1000 atmos at 10,000m depth. Let us take an average value of 500 atmos. (Since the function is a log function the error generated from this assumption will be not unduly large.)

For 1 mole of CO₂ generated (n=1) the energy input required to provide the necessary internal energy is calculated as (R = 8.31j/K/mole and θ = 278K)

$$U = R\theta \ln(500) = 14.3 \text{ kj/mole}$$

Thus the total energy required for the generation of the ocean CO₂ flux is 91 +14 = 105kj/yr

I have estimated earlier that the net CO₂ flux due biological processes is equivalent to a reduction in CO₂ concentration of 40ppm/yr, divided equally between the sea surface and atmosphere. This is equivalent to approximately 10% of the mass of CO₂ in the atmosphere, or 3.2 x 10¹⁴kg of CO₂. This amount of CO₂ therefore must be generated annually within the deep ocean. The energy required for this is 105kj/mole x 3.2x10¹⁴ kg/0.044kg/mole = 7.6 x 10¹⁷ kj.

What is the source of this energy? The answer has to be the deep ocean itself.

In Part 1 we noted that the energy input conducted from the earth's core totaled some 6.7 x 10¹⁷ kj/yr and wondered where this energy went since it could not be convected or conducted upwards to the sea surface zone, already at a higher temperature. We now realise that this energy could well be the energy source for CO₂ production in the deep ocean.

Not only that, but there is still an energy deficiency of 0.9 x 10¹⁷ kj/yr which would result in the cooling of the deep ocean over a long period of time. The thermal energy removed can be estimated by

$$E = M. Cp. \Delta\theta$$

Where the deep ocean mass M = 1.4 x 10²¹ kg

Specific heat of water Cp = 4.2 kj/kg/degC

And the temperature loss Δθ = 20 degC

$$E = 1.2 \times 10^{23} \text{ kj}$$

It would thus take of the order of a million years to chill the deep ocean by the action of CO₂ generation, a mere blink of an eye in geological terms. That the deep ocean does not continually decrease in temperature can be explained by the fact that as it cools heat is conducted into the ocean from the hotter sea surface zone, via the temperature gradient that develops across the thermocline. Thus a thermal equilibrium is reached at a deep ocean temperature where the heat in from the sea surface balances the net heat required for CO₂ generation. That temperature appears to be around 5degC.

2.7 Conclusions to Part 2

With zero net absorptive CO₂ fluxes, equilibrium will exist where the partial pressure of CO₂ is the same for the deep ocean, sea surface zone and atmosphere. A positive absorptive flux, or positive net biome production will, however, result in a lowering of partial pressures in both the atmosphere and sea surface as CO₂ is absorbed. This partial pressure reduction will result in a new equilibrium condition where a flux of CO₂ from the deep ocean generated by the developing partial pressure differences exactly balances the net biome production. In this way, sea surface and atmospheric CO₂ levels are suppressed by photosynthetic activity. The recent phenomenon of anthropogenic CO₂ release is simply reducing the effective atmospheric net biome production thereby allowing **CO₂ levels to increase proportionally to the rate of anthropogenic emissions**, in total agreement with observation.

This increase is not an accumulation of emissions destined to grow year on year, as expounded by the IPCC TAR. Stabilise those emissions and you stabilise the both the sea surface and atmospheric CO₂ levels. There is simply no question of anthropogenic CO₂ emissions being taken up by either the biosphere or the oceans.

Of course, a continuous flux of CO₂ from the deep ocean requires the continuous generation of CO₂ in order that the oceans do not become CO₂ depleted. A mechanism for this generation using CaCO₃ as the feedstock is postulated, which provides an unexpected explanation for the uniformly low temperatures within the deep ocean. The energy required for the generation of CO₂ necessary to fuel photosynthetic activity is derived from the deep ocean itself. Effectively the biosphere is operating as a gigantic heat pump, thereby refrigerating the oceans.

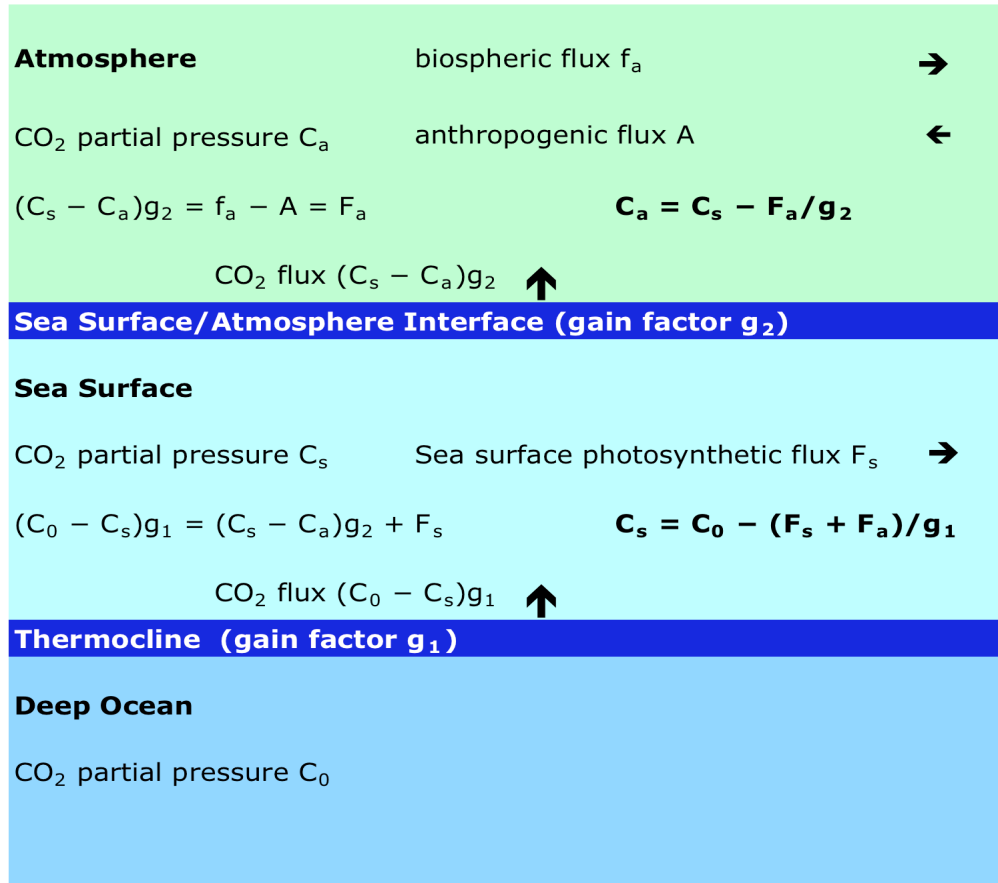
Of course it is necessary to see if this theory stands up to the scrutiny provided by observations. Time to look in Part 3 at the further evidence.

2.8 References

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Appendix (i) Derivation of Equations for C_a and C_s

Figure 2.8 Ocean Control Model



For the atmosphere the rate of increase of CO_2 partial pressure will be equal to the net CO_2 flux into the atmosphere. From figure 2.8

$$dC_a/dt = (C_s - C_a) \cdot g_2 - F_a \quad (1)$$

and for the sea surface the rate of increase of CO_2 is also equal to the net inward CO_2 flux, so that

$$dC_s/dt = (C_0 - C_s)g_1 - (C_s - C_a)g_2 - F_s \quad (2)$$

differentiating equation (1)

$$d^2C_a/dt^2 = g_2 \cdot dC_s/dt - g_2 \cdot dC_a/dt$$

and substituting dC_s/dt from (2)

$$\begin{aligned} d^2C_a/dt^2 &= (C_0 - C_s)g_1g_2 - (C_s - C_a)g_2^2 - F_s g_2 - g_2 \cdot dC_a/dt \\ &= C_0 \cdot g_1g_2 + C_a \cdot g_2^2 - C_s(g_1g_2 + g_2^2) - F_s \cdot g_2 - g_2 \cdot dC_a/dt \end{aligned}$$

but from (1) again

$$C_s = C_a + 1/g_2 \cdot dC_a/dt + 1/g_2 \cdot F_a$$

Thus solving for C_a

$$d^2C_a/dt^2 + g_2 \cdot dC_a/dt = C_0 \cdot g_1g_2 + C_a \cdot g_2^2 - (C_a + 1/g_2 \cdot dC_a/dt + 1/g_2 \cdot F_a)(g_1g_2 + g_2^2) - F_s \cdot g_2$$

and

$$d^2C_a/dt^2 + (g_1 + 2g_2)dC_a/dt + C_a \cdot g_1g_2 = C_0 \cdot g_1g_2 - F_s \cdot g_2 - F_a \cdot (g_1 + g_2) \quad (3)$$

This is a second order differential equation with a particular integral

$$\begin{aligned} C_a &= C_0 - (1/g_1 + 1/g_2)F_a - 1/g_1 \cdot F_s \\ &= C_0 - 1/g_1(F_a + F_s) - 1/g_2 F_a \end{aligned}$$

representing the steady state equilibrium condition for atmospheric CO_2 .

Solving similarly for C_s reveals a further second order equation

$$d^2C_s/dt^2 + (g_1 + 2g_2)dC_s/dt + C_s \cdot g_1g_2 = C_0 \cdot g_1g_2 - g_2(F_s + F_a)$$

with a particular integral providing the equilibrium condition for sea surface CO_2

$$C_s = C_0 - 1/g_1(F_s + F_a)$$

This equilibrium atmospheric CO_2 level can then be written as

$$C_a = C_s - 1/g_2 \cdot F_a \quad (4)$$

and

$$C_s = C_0 - 1/g_1 \cdot (F_a + F_s) \quad (5)$$

To calculate the time dependent function of C_a and C_s we must determine solutions to the complementary function for equation 3, namely

$$d^2C_a/dt^2 + (g_1 + 2g_2)dC_a/dt + C_a \cdot g_1g_2 = 0$$

Assume the solution is of the form

$$C_a = A e^{-t/\tau}$$

Substituting in the equation above results in

$$A/\tau^2 - A(g_1 + 2g_2)/\tau + A.g_1g_2 = 0$$

The two solutions to this quadratic equation are given by

$$\begin{aligned} 1/\tau &= \{(g_1 + 2g_2) \pm \sqrt{(g_1 + 2g_2)^2 - 4g_1g_2}\}/2 \\ &= (g_1/2 + g_2) \pm \sqrt{(g_1^2/4 + g_2^2)} \end{aligned}$$

so that $1/\tau_1 = g_1/2 + g_2 - \sqrt{(g_1^2/4 + g_2^2)}$ (6)

and $1/\tau_2 = g_1/2 + g_2 + \sqrt{(g_1^2/4 + g_2^2)}$ (7)

The solution to equation 3 can thus be written

$$C_a = A.e^{-t/\tau_1} + B.e^{-t/\tau_2} + C_0 - 1/g_1(F_a + F_s) - 1/g_2F_a$$

The constants A and B are derived from the boundary condition.

At time $t = 0$ when $C_a = C_0$

$$C_a = A + B + C_0 - 1/g_1(F_a + F_s) - 1/g_2F_a$$

Thus $A + B = 1/g_1(F_a + F_s) + 1/g_2F_a$

Let $A = 1/g_1(F_a + F_s)$ and $B = 1/g_2F_a$

So that the complete solution to equation 3 can now be written as

$$C_a = C_0 - 1/g_1.(F_a + F_s)(1 - e^{-t/\tau_1}) - 1/g_2.F_a(1 - e^{-t/\tau_2})$$

Appendix (ii) Assumptions and Values used to Compute CO₂ and O₂ Levels

The following assumptions are made in the calculation of atmospheric CO₂ and O₂ levels shown in figures 2.6 and 2.7

- 1 The quantity of CO₂ and O₂ in the deep ocean is sufficiently large for their concentrations to be unaffected by oceanic and biospheric fluxes.
- 2 Biospheric and oceanic photosynthetic net fluxes are equal at the equivalent of 20ppm CO₂ per year absorption.
- 3 Anthropogenic CO₂ emissions are as detailed in CDIAC data.
- 4 The thermocline CO₂ gain factor g_1 is to be determined by best fit to observed data.
- 5 Biospheric O₂ fluxes are calculated at 1.1 times the equivalent CO₂ fluxes. O₂ fluxes due to fossil fuel burning are 1.33 times the corresponding CO₂ fluxes. Oceanic O₂ fluxes measured in terms of partial pressure changes are 28.7 times (1.1 x 26.1) the CO₂ fluxes.

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- 6 The sea surface/atmosphere CO₂ gain factor g₂ is 6.2 years, consistent with evidence previously considered.
 - 7 O₂ gain factors g₁ and g₂ are calculated as 32/44 x CO₂ gain factors
 - 8 The temperature coefficient of the CO₂ Henry coefficient is 3%/degC and that of O₂/N₂ is 0.014%/degC.
 - 9 Sea surface photosynthetic CO₂ flux is reducing at a rate given by

$$\delta F_s = F(\exp(0.02t) - 1)$$

The value of F will be determined by best fit to the observed O₂ reduction of 33ppm between 1990 and 2000.

There are thus only two adjustable variables, the thermocline gain factor g₁ and the sea surface flux factor F, available to obtain a match between calculations and observations of both CO₂ and O₂ atmospheric values.