Atmospheric Carbon Dioxide Control Mechanisms

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PART THREE: - THE EVIDENCE

ANTHROPOGENIC FINGERPRINTS

Synopsis:- Part Three

An atmospheric control mechanism was proposed in Part 2 of this series of papers in an attempt to overcome the inherent failures of the atmospheric model described in the IPCC assessment reports. These reports fail totally to explain the observations of northern hemisphere CO_2 bias, carbon isotope variations and declining atmospheric O_2 levels. Part 3 of this series is dedicated to determine how each of these observations and others, such as seasonal CO_2 and O_2 variations, interannual CO_2 variations, and sea surface CO_2 concentration variations, is dealt with by the Ocean Control Theory proposed in Part 2 with the result that, in every case examined, values calculated from theory agree well with observed data.

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3.0 THE EVIDENCE

There are numerous observations of phenomena within the atmosphere and sea surface for which the ocean control theory must provide simple and concise explanations. These phenomena include

Seasonal atmospheric CO_2 variations

Interannual atmospheric CO_2 variations

Northern hemisphere CO_2 bias

Carbon isotope signatures

Seasonal atmospheric O_2 variations

Ocean Acidification

In addition to these is the requirement for a rational explanation for the reported reduction in atmospheric O_2 levels. In Part 2 it was explained how CO_2 and O_2 levels are modified in both the sea surface and atmosphere by the net biome production. Because of the large differences in solubility and hence Henry coefficients between CO_2 and O_2, changes in sea surface biome production have a much larger impact on atmospheric O_2 than on atmospheric CO_2. Atmospheric O_2 thus becomes a sensitive indicator of sea surface biospheric activity and is currently indicating a reduction in that activity.

3.1 Seasonal Atmospheric CO_2 Variations

It was observed in Part 1 that there are significant seasonal variations in atmospheric CO_2 levels, attributed to the seasonal activity of photosynthesis. Let us take as an example the seasonal variations monitored at Mona Loa, Hawaii, since this data set is by far the most comprehensive available.

If we make the simplistic assumption that the seasonal variation is sinusoidal, we can express the CO_2 absorptive effects of photosynthesis as a CO_2 flux:

$$Fa = -(M - Ncos(\omega t + \phi)) \qquad (1)$$

Where M is the mean absorptive flux and N the amplitude of the seasonal component.

Variations at Mona Loa can be represented by the expression

$$Fa = -(20 - 8cos(\omega t - 0.2)) \text{ ppm/yr}$$

Substituting this expression into the equations for atmospheric CO_2 developed in Part 2 results in agreement with observation shown in figure 3.1 for the 10 year period 1990 to 2000.

Allowing for the fact that a sine function is not a perfect descriptor for the seasonal flux variations, the agreement with observations is nevertheless good. Seasonal variations are a natural follow on from the general equations developed in part 2 This explanation does not require any assumptions about a balanced biosphere or pondering on the source of the regenerative CO_2 flux. That source is the ocean.

Figure 3.1 – Seasonal CO2 Variations 1990 to 2000
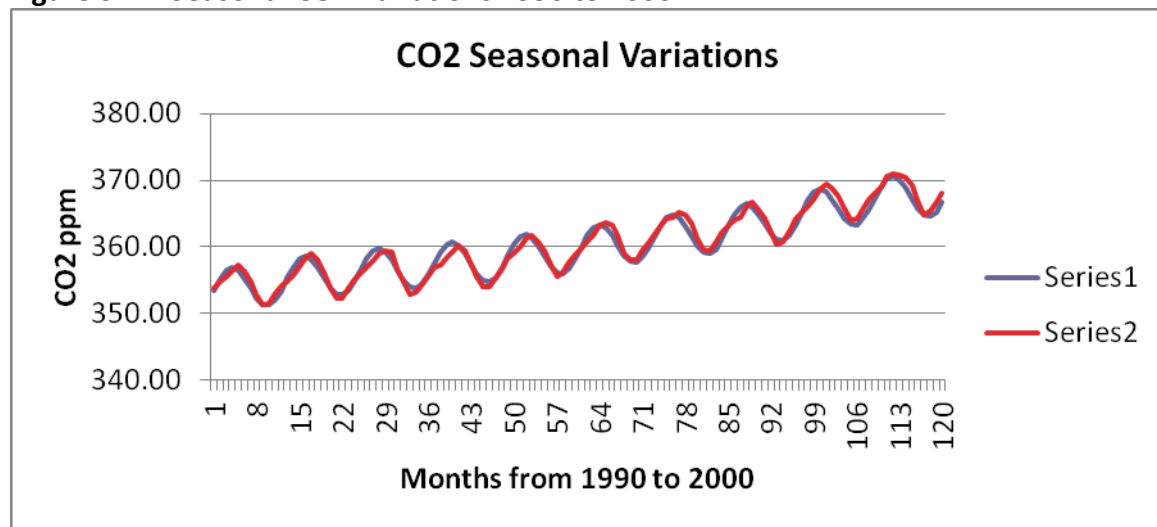
Series 1   Calculated CO_2 levels
Series 2   Observed CO_2 levels at Mona Loa

3.2 Interannual CO$_2$ Variations

In addition to the seasonal CO_2 variations discussed above there is also a pronounced interannual variation, which is illustrated clearly by plotting the annual rates of change of atmospheric CO_2. The variations in atmospheric CO_2 partial pressure calculated using the equation developed in Part 2, which includes the temperature variation of Henry's constant

$$Ca \ = \ Cs - \ (1/g_2.Fa - k.Cs.\Delta T) \ (1 - e^{-t/\tau 2})$$

correlate very closely with actual measurements of atmospheric CO_2 concentrations at Mona Loa (figure 3.2).

As can be seen from the calculations, which take into account the variations in sea surface temperature, compared to those, which do not include temperature effects, the interannual variation of atmospheric CO_2 can be largely attributed to changes in sea surface temperature and the variation of the Henry coefficient with temperature. Such a temperature dependence has previously been noticed, by others including Roy Spencer and Murry Salby.

Figure 3.2 – Interannual CO_2 Variations
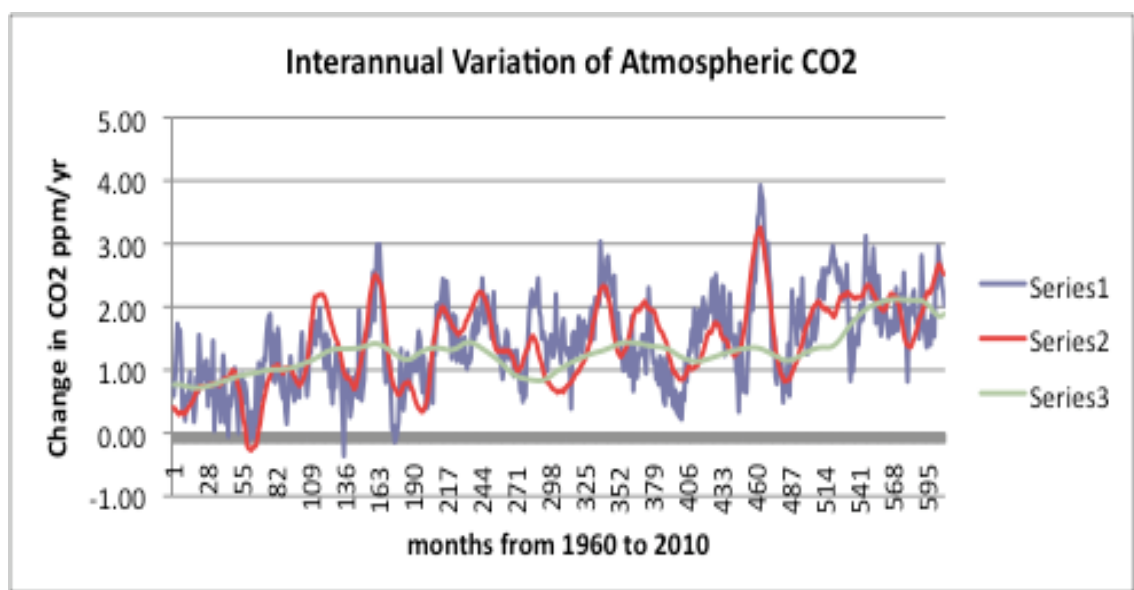
Series 1 Actual Interannual CO_2 variations
Series 2 Calculated CO_2 variations with SST changes
Series 3 Calculated CO_2 variations without SST changes

3.3 Northern Hemisphere CO_2 Bias

There is absolutely no correlation between the stratified CO_2 emission identified in Part 1 of this paper and global CO_2 levels which exhibit both a northern hemisphere bias of around 2ppm and a peak concentration at the equator, even though 50% of all anthropogenic emissions occur between latitudes 30-50 degN equivalent to an emission of CO_2 levels at those latitudes of 14ppm/yr.

This raises several questions. The first is why do we not see such a correlation? We know from a study of the seasonal CO_2 variations that there is significant latitudinal stratification of atmospheric CO_2 levels on time scales less than one year. The second question is why the atmosphere CO_2 concentration is so constant globally, varying by less than 3ppm after taking into account the seasonal photosynthetic variations. Thirdly, why do CO_2 concentrations peak around the equator?

Let us deal with the second question first; why are global CO_2 levels so constant? The answer must be that there is significant atmospheric mixing in order to average out the vast variations in CO_2 fluxes around the world. In order to quantify the effect of atmospheric mixing we need to develop a mathematical model to represent the various atmospheric CO_2 and mixing fluxes. This model is detailed in appendix (i) where the globe is seperated into 18 equiangular lateral bands, each presenting 10^0 of latitude, extending from the North to the South Pole. Each band exchanges CO_2 molecules with its neighbour, governed by the partial pressure gradients between them. The model requires estimates to be made of sea surface temperatures and the extent of net biosperic fluxes for each latitudinal band. Results of such an analysis are shown in Figure 3.3.

Figure 3.3 - Latitudinal CO$_2$ Variations
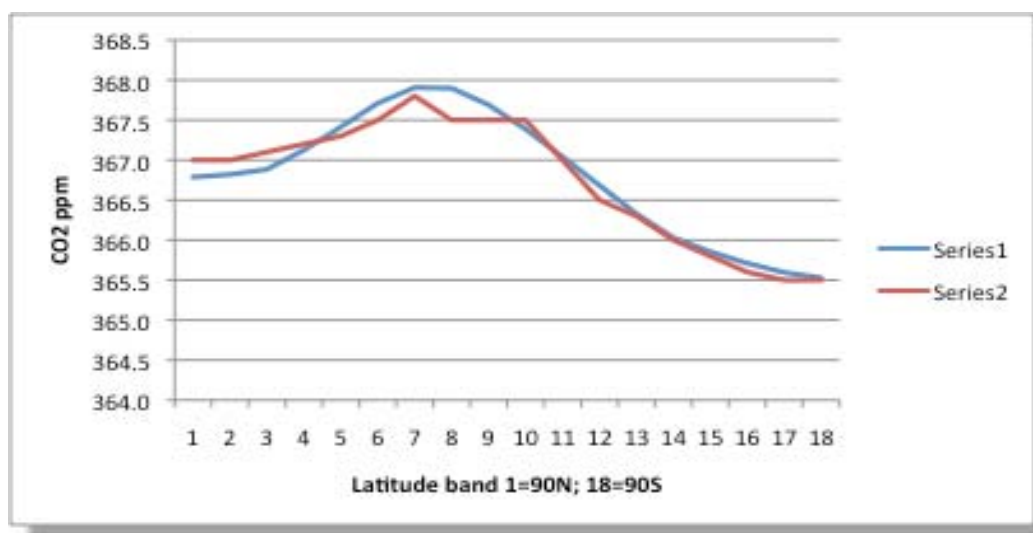
Series 1   Calculated CO_2 levels
Series 2   Observed CO_2 levels

The resulting agreement with observed atmospheric CO_2 levels (Figure 3.3) is good considering the crudeness of the mathematical model and the simplicity of the assumptions. It suggests that the time constant for atmospheric mixing between latitude bands is of the order of 1/100years, or approximately 3 to 4 days.

The answers to the other two questions raised at the beginning of this section now become apparent. The equatorial peak is explained by the high sea surface CO_2 partial pressure in

the tropical regions due to the high prevailing sea temperatures, while the lack of correlation with stratified anthropogenic emissions is because the effects of those emissions are largely overwhelmed by the sea surface partial pressure variations. It is true however that the anthropogenic   emissions lead to the slight bias of CO_2 in the northern hemisphere. Figure 3.4 shows the calculated latitudinal stratification without the anthropogenic content, displaying, this time, almost no bias between the northern and southern hemispheres.

Figure 3.4 - Latitudinal CO_2 Variations without Anthropogenic Contributions
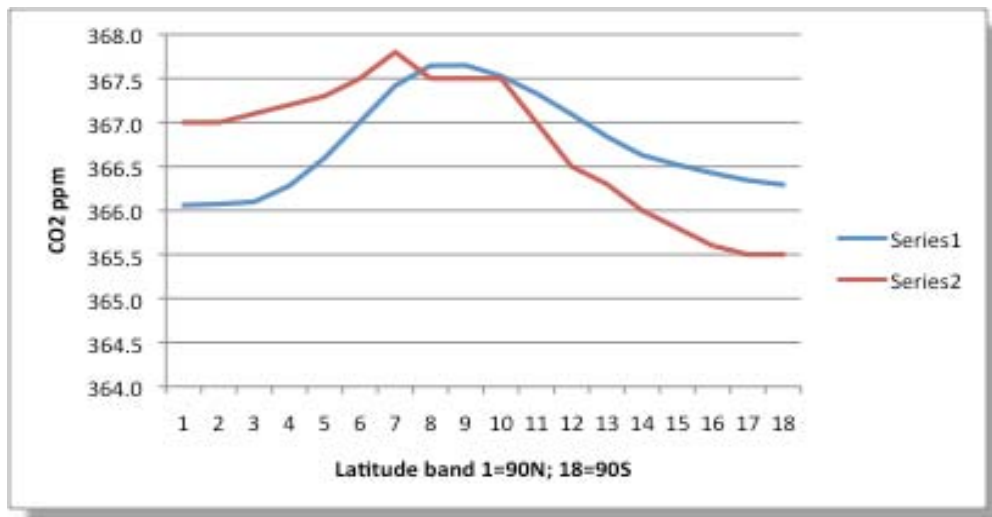
Series 1   Calculated CO_2 levels without anthropogenic contributions
Series 2   Observed CO_2 levels with anthropogenic contributions

3.4 Carbon Isotope Signatures

The claim that the variation of carbon isotope ratio is a unique signature of anthropogenic CO_2 emission comes unstuck when the actual change in $\delta^{13}C$ is, according to Battle, 0.013‰/yr, a figure some six times lower than would be expected from the assumption that the source of increased atmospheric CO_2 is retained anthropogenic CO_2 emissions (See Part 1)!

A surprising omission from the IPCC TAR is a discussion or even mention of a similar reduction in sea surface isotopic ratio or the fact that while the atmosphere has a mean ratio of approximately – 8‰ the sea surface has a ratio of +1.5‰. This data was reported by Keeling et al in 2000 (Figure 3.5) and was well known before the publication of TAR. AR4 similarly has no comment. How do we account for these numbers? Clearly neither the TAR nor AR4 have anything to offer in this respect.

Figure 3.5 – Isotope Ratios

Sea Surface and Atmospheric CO_2 Isotope Ratios

Series 1   Sea surface CO_2 isotopic ratio
Series 2 Atmospheric CO_2 isotopic ratio
Data from Keeling et al
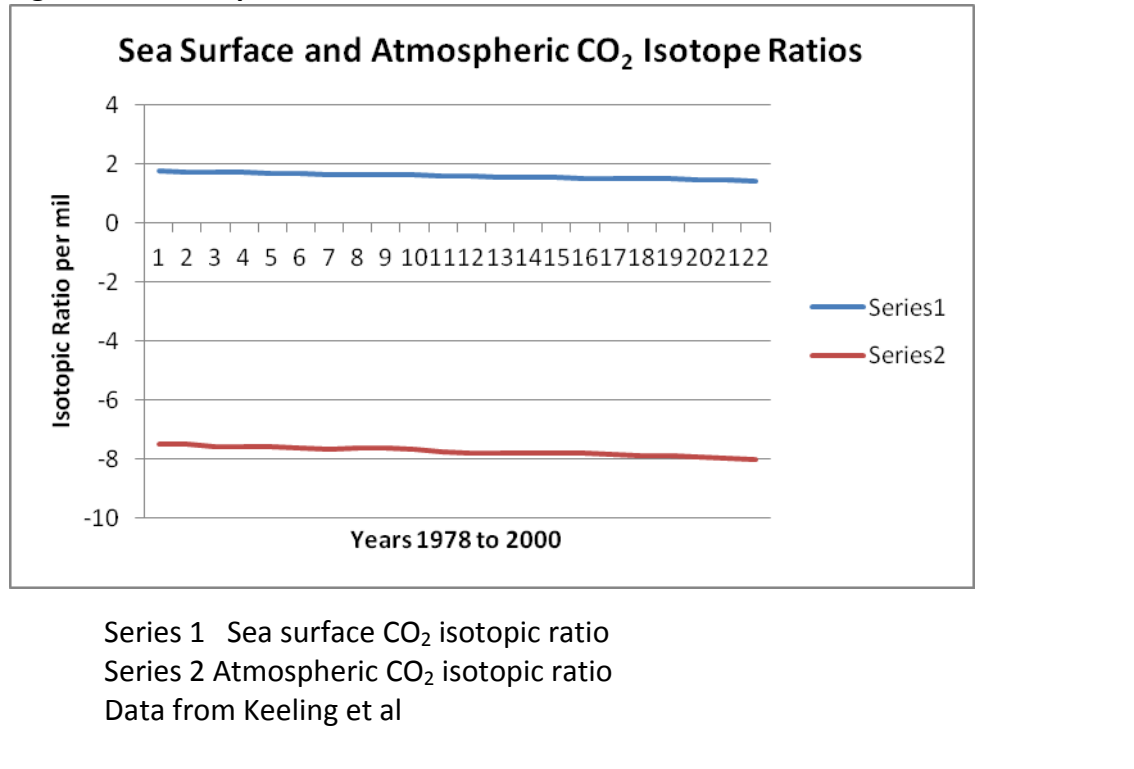
So let us see how the ocean control model predicts these $\delta^{13}C$ observations. From a physics viewpoint, each CO_2 molecule is indistinguishable from another, except for those having different carbon isotopes. While chemically ^{12}C and ^{13}C are identical, physically they are different in respect of their mass. This results in CO_2 composed of ^{13}C atoms having slightly different physical properties to those composed of ^{12}C atoms. Their Henry constants and diffusion coefficients, for example, will be slightly different because of their differing molecular weights. There will be separate control mechanisms in place for atmospheric CO_2 containing ^{12}C and ^{13}C. Each will have its own control equation, of the form derived in section 2

For ^{12}C based CO_2

$$^{12}Ca \ = \ ^{12}Co - (^{12}Fa + {}^{12}Fs)/g_1.(1 - e^{-t/\tau 1}) - {}^{12}Fa \, /g_2.(1 - e^{-t/\tau 2}) \qquad (1)$$

Where ^{12}Fa and ^{12}Fs are the resultant biospheric atmospheric and sea surface $^{12}CO_2$ fluxes, and ^{12}Co is the partial pressure due to $^{12}CO_2$ in solution in the deep ocean.
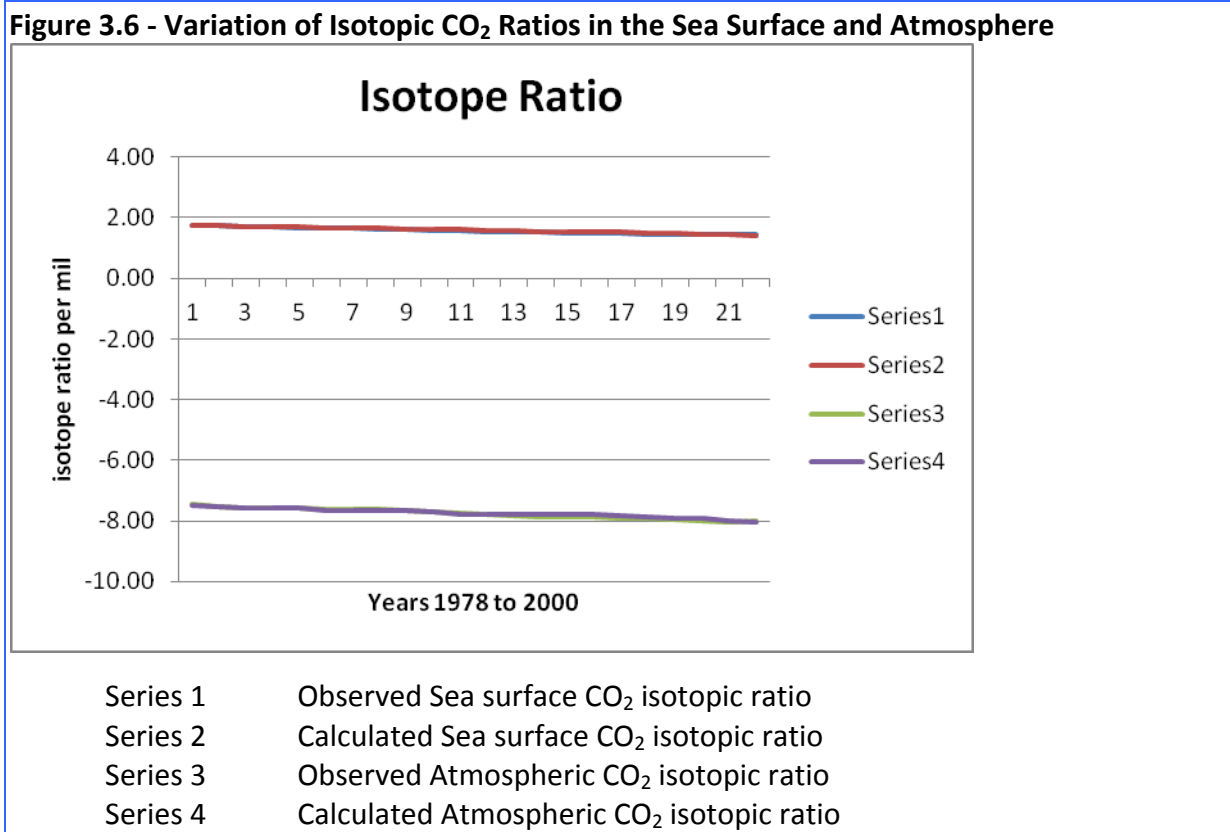
For ^{13}C based CO_2 a similar equation exists

$$^{13}Ca = {}^{13}Co - ({}^{13}Fa + {}^{13}Fs)/{}^{13}g_{1.}(1 - e^{-t/\tau 1}) - {}^{13}Fa/{}^{13}g_{2.}(1 - e^{-t/\tau 2}) \qquad (2)$$

$^{13}g_1$ and $^{13}g_2$ are the transfer factors for the thermocline and sea surface interfaces related to $^{13}CO_2$ transport.

From these equations is possible to calculate the partial pressures of both ^{13}C and ^{12}C based CO_2 for both the sea surface and atmosphere in terms of the following (appendix (ii))

δ_0 the isotopic ratio of the deep ocean CO_2
δ_b the isotopic ratio of the biospheric CO_2 fluxes F_a = 27.0‰
δ_s the isotopic ratio of the sea surface biospheric CO_2 fluxes F_s = 27.0‰
δ_f the isotopic ratio of the anthropogenic CO_2 emissions = 29‰

This then allows the isotopic ratios to be calculated for both the sea surface and atmosphere based upon the time variable CO_2 fluxes used to establish agreement with atmospheric CO_2 and O_2 levels in section 2. The results are shown in figure 3.6

Figure 3.6 - Variation of Isotopic CO₂ Ratios in the Sea Surface and Atmosphere

Series 1	Observed Sea surface CO_2 isotopic ratio
Series 2	Calculated Sea surface CO_2 isotopic ratio
Series 3	Observed Atmospheric CO_2 isotopic ratio
Series 4	Calculated Atmospheric CO_2 isotopic ratio

In order to achieve such close agreement (yes the lines do overlay each other) it has been necessary to assume certain physical values for $^{13}CO_2$ as shown in the table below.

		12C	13C
Thermocline gain 1/g1 =		33.4	35.52
Sea surface/atmos gain 1/g2		6.2	6.37
Henry Constants13H/12H		1	0.9851
δ13Cfuel			-29
δ13Cbio			-27
δ13Csea			1.5
δ13Cocean			5.805

Arbitrary selection of sufficient variables will of course allow any data to be fitted to any curve as was lucidly commented by von Neumann in his quip about reproducing an elephant with four variables and wagging its tail with the fifth.

So what is the justification for selecting the values, which provide this agreement between calculations and observations?

First, the variation in the physical parameters, Henry coefficient and diffusion coefficient (hence thermocline gain factor g_1), are similar to the variations prescribed to O_2 in part 2. We postulated that the diffusion coefficient and hence gain factor g_1 would be inversely proportional to the molecular mass of the molecule in question. In the case of $^{13}CO_2$ this would require an increase in $1/g_1$ of 45/44 = 1.023, whereas the actual increase required is 1.063. Should we really expect a simple linear relationship? Evidently not. It is not unreasonable however for the heavier, slower moving $^{13}CO_2$ molecule to have a lower diffusion rate and hence higher response time than $^{12}CO_2$.

Similarly the change in Henry coefficient at the sea surface/atmospheric interface for $^{13}CO_2$ isotope ratio required is 0.985 (-1.5%). Again we would naturally expect the larger slower moving molecule to exert a lower partial pressure when in solution and hence a lower Henry coefficient.

One necessary prediction of this theory is that the isotope ratio of CO_2 in the deep ocean has a value of +5.8‰. I am unaware of any measurement of this particular value being reported. In so far as the crucial test of a theory is, not only to maintain agreement with known observational data, but to predict otherwise unobserved effects, this measurement of deep ocean CO_2 isotope would be an important corroboration (or otherwise) of this theory. Since it is also postulated that the CO_2 generated within the deep ocean is derived from metallic carbonates, principally $CaCO_3$ we would expect this isotope ratio of the deep ocean to reflect the ratio found in limestone rock formations.

The deep ocean isotopic ratio is important in order to explain the positive ratio in the sea surface ocean layers, while the Henry coefficient variation is necessary for the negative atmospheric values. Without these differences in physical values it becomes impossible to reconcile the observed vales with any credible physical explanation!

The carbon isotope signature is no more than a further example of CO_2 transport responding to the predictable variations of partial pressures and Henry's Law. It is not, as is claimed in

TAR, an indicator of land biospheric uptake of CO_2, and is most certainly not proof of the TAR description of atmospheric CO_2 distribution.

3.5 Seasonal Atmospheric O_2 Variations

Figure 3.7 reproduced from a paper by M Battle et al in Science 2000, illustrates the seasonal variations of atmospheric O_2/N_2 ratios and CO_2 over the period 1991 to 1998.

The interesting feature is that in the northern hemisphere measurements, at Alert and Point Barrow in the Arctic Circle, both CO_2 and the O_2/N_2 ratio exhibit a significant seasonal dependency. The CO_2 seasonal dependency has been discussed earlier in this paper and is accepted to be due to seasonal variations in photosynthetic activity. Of course photosynthesis not only absorbs CO_2 but also produces O_2, so that we should expect an antiphase relationship between CO_2 and O_2. As CO_2 is absorbed, O_2 is released. As seen in Figure 3.7, this is indeed the case. We would expect that, for every mol of CO_2 absorbed, 1.1 mol of O_2 would be liberated by the photosynthetic effect. The observed peak to peak amplitude of the CO_2 variation is around 20ppm, while the peak to peak O_2 variation is of the order of 120 per meg, equivalent to 25ppm (conversion factor ppm to per meg is 4.8). This gives an O_2 variation only 3ppm higher than expected.

Figure 3.7 - Seasonal Variation of O_2/N_2 Ratio
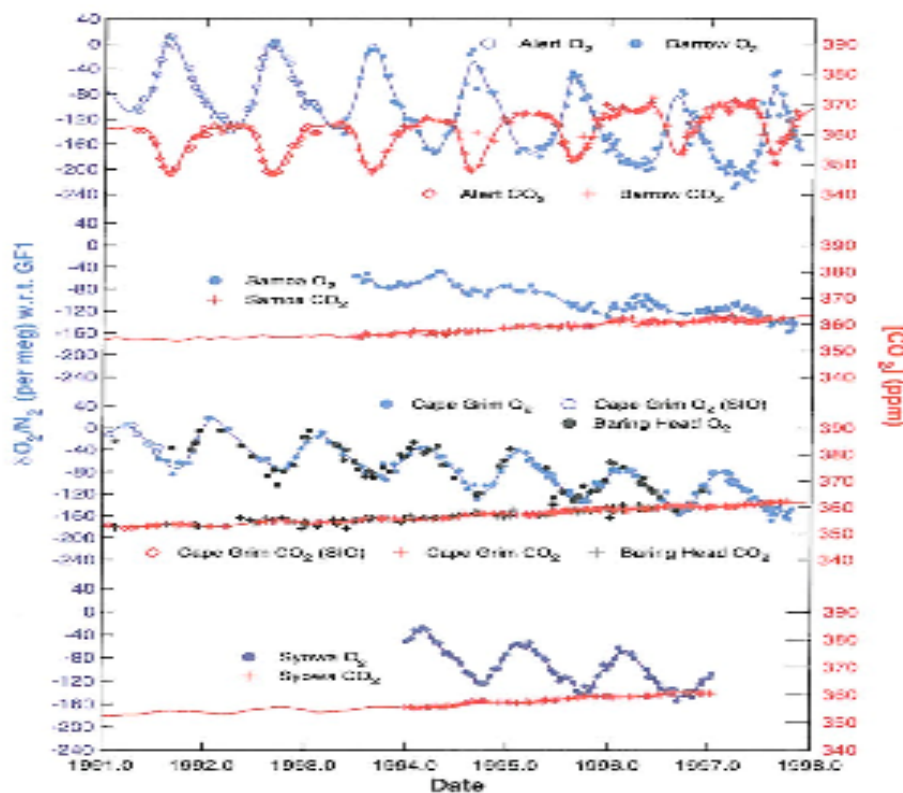
Reproduced from Battle et al – Science 2000

Close to the equator little variation is observed in either CO_2 or O_2 levels, suggesting as would be expected, little seasonal variation in photosynthetic activity.

In the southern hemisphere, however, a totally different picture emerges. Data from Cape Grim and Baring Head both at latitude 40^0S again show a pronounced variation in O_2/N_2 ratio but very little seasonal variation in CO_2. Because of the low land/ocean area ratio at this latitude of the earth, biospheric photosynthetic activity is low and the low CO_2 variation is to be expected. So we are faced with a paradox. Northern latitudes exhibit a seasonal O_2/N_2 variation that can be chiefly attributed to land based photosynthetic activity, while a similar southern hemisphere variation cannot be so attributed.

An explanation is attempted by Battle: -

Every spring, atmospheric O_2/N_2 rises by about 60 per meg [or 0.06 per mil(%)](12ppm) because of ocean biology. Net production of organic matter releases O_2, which supersaturates the mixed layer and escapes to the atmosphere. Every winter, O_2/N_2 falls by 60 per meg as the oceans take up oxygen to re-saturate suboxic waters of the interior.

Quite!

3.5.1 Seasonal Variation of Sea Surface Primary Production

Photosynthesis, whether on land or in the ocean is dependent upon sunlight for its energy. We would naturally expect it also to be seasonally dependent and in the same way that land based primary production is weighted towards the northern hemisphere, oceanic primary production will be weighted towards the southern half of the globe. Furthermore, as explained in Part 2, because of the ratio of solubilities of O_2 and CO_2 we would expect the variation in atmospheric O_2 partial pressure due to oceanic seasonal variations to be some 28.7 times greater than the equivalent variation in CO_2 partial pressure.

Assume a seasonal biospheric photosynthetic CO_2 variation of the form

$$Biospheric\ flux\ Fa\ =\ A - Bcos\omega t\ \ ppm/year$$

It is readily shown (appendix (iii)) that the resultant atmospheric CO_2 seasonal variation is

$$\Delta Ca = B/\omega(sin\omega t + \psi)\ ppm$$

Where ψ represents a phase shift imposed by the control equation.

A similar oceanic photosynthetic CO_2 oceanic variation of the form

Oceanic flux $F_s = D - E\cos\omega t$ ppm/year

however, results in an atmospheric CO_2 variation of (appendix (iii))

$$\Delta C_a = Eg_2/\omega^2(\sin\omega t - \phi) \text{ ppm}$$

The seasonal atmospheric CO_2 variation due to oceanic flux variations is thus attenuated by a factor g_2/ω more than a similar biospheric flux variation. Since, from Part 1, $1/g_2 = 6.2$ and $\omega = 2\pi = 6.3$ this attenuation amounts to a factor of 39. In other words the impact on the atmosphere of a seasonal oceanic CO_2 flux measured in terms of peak to peak ppm CO_2 concentration will be attenuated by a factor of 39.

The corresponding seasonal oceanic O_2 variation will also be subject to this same attenuation of 39, but will also be amplified by the factor 28.7 resulting from the difference in Henry coefficients of CO_2 and O_2

Allocation of a seasonal oceanic CO_2 flux amplitude of 3µatmos/year results in the comparison of calculated and observed seasonal O_2 data shown in figure 3.8.

Agreement with observations is good both for the variation in O_2 and indeed the lack of atmospheric response for CO_2.

Figure 3.8 – Seasonal O_2 Variations
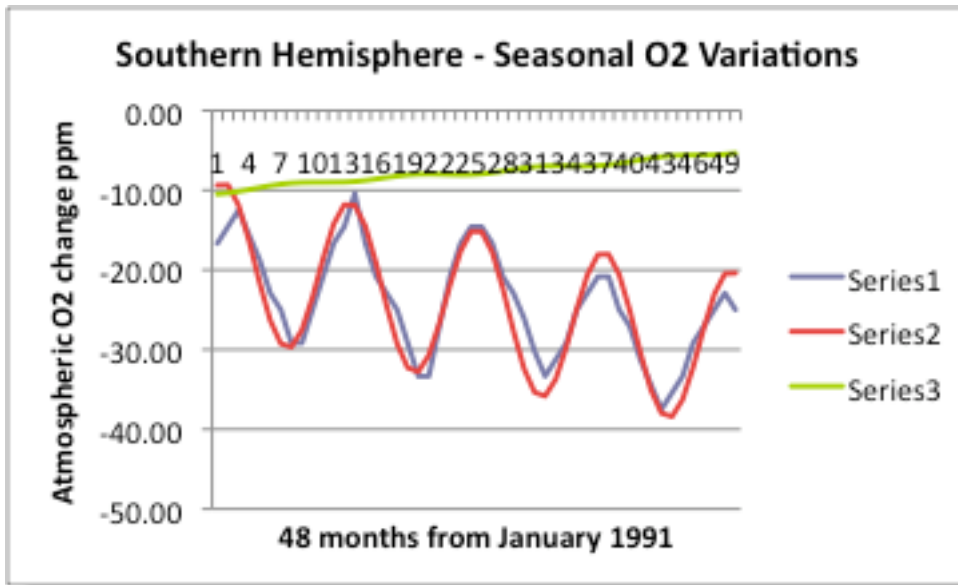
Series 1 Actual O_2 variation derived from Keeling, Piper and Helman, Nature 1996
Series 2 Calculated O_2 variation
Series 3 Calculated atmospheric CO_2 variation in ppm.

This explanation uses the same 2.2 year O_2 sea surface/atmosphere time constant determined previously in Part 2 and the same Henry's Law dependency. It does not require any concept of oxygen supersaturation effects. It predicts that there is prevalent a southern hemisphere seasonal oceanic CO_2 peak to peak variation equivalent to 6µatmos sea surface CO_2 partial pressure.

3.6 Ocean Acidification

It has been noted by many observers that the acidity of the oceans is increasing. This increase has been generally attributed to absorption of anthropogenic emissions of CO_2 within the oceans. For example, It has been reported by Takahashi et al (ref 7) when studying surface water CO_2 levels in the North Pacific that

"*The mean rate of increase for the open ocean area is indistinguishable from the mean atmospheric CO_2 increase rate of 15µatm decade[-1] (or 1.5 ppm yr^{-1}) suggesting that the North Pacific surface waters as a whole have been following the atmospheric CO_2 increase.*"

That approximately 25% of CO_2 emissions is taken up by the oceans is fundamental to the current models used by climate scientists worldwide. Vast studies are made to determine the degree of this take up by the various oceans of the world. That all the observed evidence suggests strongly that this model is incorrect becomes an extremely inconvenient problem.

It should be noted that the increasing sea surface CO_2 concentration is a direct consequence of the observed atmospheric increases when using the Ocean Control model. The sea surface CO_2 partial pressure is described by the equation

$$Cs = Co - 1/g_1(Fa + Fs)(1 - e^{-t/\tau1})$$

It is dependent upon the sea surface and atmospheric fluxes Fs and Fa. If the overall atmospheric absorptive flux Fa is reducing because of emissions of CO_2 in the atmosphere then not only will atmospheric CO_2 increase, but so will the sea surface levels of CO_2

This is illustrated in Figure 3.9, which shows both the atmospheric and sea surface CO_2 partial pressures calculated using the Ocean Control equations and the value for anthropogenic emissions from the CDIAC data used previously. The atmospheric CO_2 levels are increasing slightly faster than the sea surface because of the additional element in the equation for atmospheric CO_2

$$Ca = Cs - (1/g_2.Fa) (1 - e^{-t/\tau2})$$

Figure 3.9 Ocean Acidification

Atmospheric and Sea Surface CO2 Levels
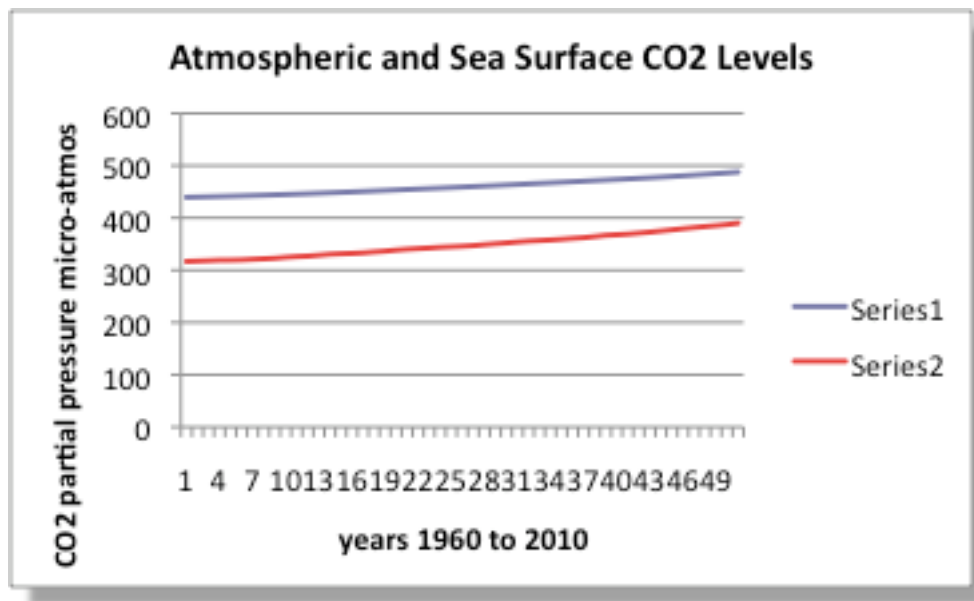
Series 1 Calculated sea surface CO_2 partial pressure
Series 2 Calculated atmospheric CO_2 partial pressure

This model requires no contortionist thinking about how much of the anthropogenic emissions are taken up by the oceans and how much by the biosphere, the increasing sea surface CO_2 is a direct consequence of the reduction in net atmospheric absorptive flux resulting from anthropogenic CO_2 emissions.

3.7 Atmospheric O_2 Level Reduction

According to TAR: -

"The amount of CO_2 that remains in the atmosphere each year has been consistently less than the amount emitted by fossil fuel burning. This is because some CO_2 dissolves and mixes in the ocean, and some is taken up by the land. These two modes of uptake have different effects on the concentration of O_2 in the atmosphere. Fossil fuel burning consumes O_2 and causes a decline in atmospheric O_2 concentration. Dissolution of CO_2 in the ocean has no effect on atmospheric O_2. Terrestrial uptake of CO_2, by contrast, implies that photosynthesis (which releases O_2) is exceeding respiration and other oxidation processes, including fire (which consumes O_2). Thus, net terrestrial uptake of CO_2 implies a net release of O_2, in a known stoichiometric ratio. This difference can be used to partition the total CO_2 uptake into land and ocean components."

It was discussed in Part 1 how this explanation of the use of variation of atmospheric O_2 levels to partition of CO_2 uptake between land and ocean potentially is impossible to reconcile with the laws of physics. Part 2 shows how the apparent discrepancy between the observed O_2 level reduction and that to be expected from fossil fuel combustion can be explained by the variation in oceanic photosynthesis activity reported by Gregg et al in 2003. Apart from the paper by Gregg this phenomenon has been largely ignored and yet could be one of the most interesting, yet serious, aspects of climate study. A persistent reduction in oceanic phytoplankton could have far reaching consequences. What are the reasons for this reduction and will it continue? Further monitoring of atmospheric O_2 levels should be extremely instructive.

AR4 , meanwhile, continues with the partitioning mantra first displayed in TAR.

Recent work by Manning and Keeling (2006) indicates that atmospheric O2 is decreasing at a faster rate than CO2 is increasing, which demonstrates the importance of the oceanic carbon sink.

In fact the paper referred to, by Manning and Keeling, calculates, using the O_2 variations, the respective oceanic and land biotic sinks for the periods 1990 to 2000 and 1993 to 2003.

Period	Oceanic sink	Land sink	
1990 to 2000	1.9 +/− 0.6	1.2 +/− 0.8	Pg C yr^{-1}
1993 to 2003	2.2 +/− 0.6	0.5 +/− 0.7	Pg C yr^{-1}

The so-called land biotic sink, effectively the global land photosynthetic activity, therefore exhibits a huge reduction from 1.2 to 0.5 Pg C yr^{-1} for the years in question, a surprising result considering that the two 10 year data sets overlap by 7 years! No explanation is given for the variation in the calculated land biotic uptake of CO_2. Of course the error bands of the calculated values are so large as to make sensible interpretation of data almost impossible. This however is held aloft as one of the three important "fingerprints" of increased atmospheric CO_2 being due to anthropogenic processes, and is used still as a serious tool to estimate the imaginary CO_2 partition between the biosphere, the oceans and the atmosphere.

3.8 Summary of Part 3

The explanation offered by the IPCC for the inexorable increase in atmospheric CO_2 levels is supposedly derived from the three strands of evidence known collectively as the anthropogenic fingerprints, northern hemisphere CO_2 bias, decreasing atmospheric carbon isotope ratios, and reducing atmospheric O_2 levels. As Part 1 of this paper shows, these "fingerprints" do not support in any way the assertion that anthropogenic CO_2 emissions are partitioned between, the oceans, the biosphere and the atmosphere.

In stark contrast this fingerprint evidence, along with seasonal variations of atmospheric CO_2 and O_2 and interannual variations of CO_2 is explained in a rational and consistent manner by a theory based solely on the precept that transport of gases is governed simply by variations in partial pressure between the deep ocean, the sea surface and the atmosphere.

References

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Appendix (i) Global Atmospheric CO_2 Stratification

Let us consider a model whereby the globe is divided into a number N of latitudinal bands of equal angular size, each band being connected to its neighbour to enable mixing to occur between bands. Each atmospheric band n experiences a photosynthetic flux F_n and is subject to a sea surface control flux $(C_s - C_n)g$. We will assume that the sea surface concentration is unchanging compared to the relatively rapid atmospheric mixing effects. The intermixing between neighbouring bands is assumed to be proportional to the partial pressure and hence concentration differentials between neighbouring bands (assuming constant atmospheric pressure) and can be represented by the expression $(C_n - C_{n+1}).k$ where "k" is the mixing gain factor. We can expect the time constant for the mixing to be therefore $1/k$.
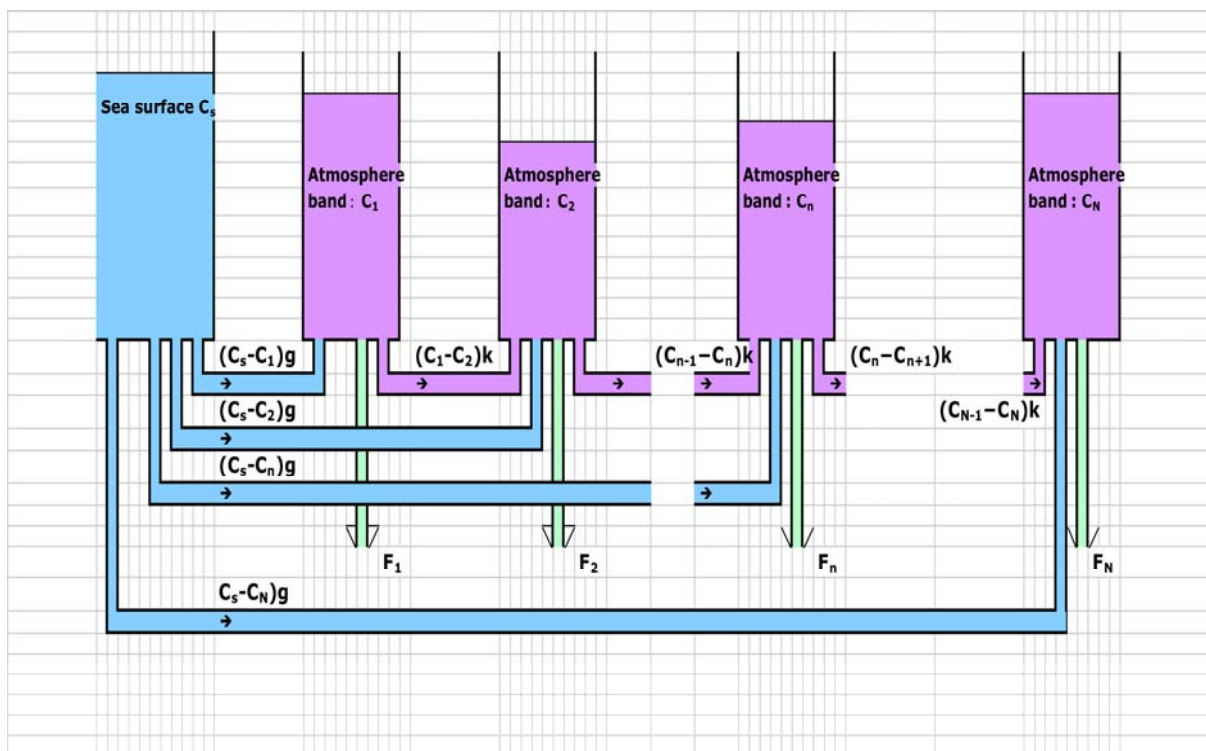
We can now set up an equation of state for each of the N latitudinal bands. For band 1 which we will define as located at the North Pole (latitude 90^0N)

At equilibrium $\qquad\qquad (C_s - C_1).g = (C_1 - C_2).k + F_1$

And for band n $\qquad (C_s - C_n).g + (C_{n-1} - C_n).k = (C_n - C_{n+1}).k + F_n$

While for band N located at the South Pole (latitude 90^0S)

$$(C_s - C_N).g + (C_{N-1} - C_N).k \ = \ F_N$$

We have thus a set of N simultaneous equations with N unknowns, the CO_2 concentrations C_n of the N latitudinal bands.

Rearranging the equations into form

$$a_1 C_1 + a_2 C_2 + \ldots + a_n C_n + \ldots + a_N C_N \ = \ A_1$$

results in
$$(g + k).C_1 - k.C_2 \ = \ g.C_s - F_1$$

$$-k.C_1 + (g + 2k).C_2 - k.C_3 \ = \ g.C_s - F_2$$

$$-k.C_{n-1} + (g + 2k).C_n - k.C_{n+1} \ = \ g.C_s - F_n$$

$$-k.C_{N-1} + (g + k).C_N \ = \ g.C_s - F_N$$

allowing a solution to be obtained from the following matrix after setting the value N = 18

C1	C2	C3		Cn-1	Cn	Cn+1		C17	C18					
(g+k)	–k										C1			g.Cs – F1
–k	(g+2k)	–k									C2			g.Cs – F2
	–k	(g+2k)									C3			g.Cs – F3
				(g+2k)	–k						Cn-1		=	g.Cs – Fn-1
				–k	(g+2k)	–k					Cn-1			g.Cs – Fn
					–k	(g+2k)					Cn+1			g.Cs – Fn+1
								(g+2k)	–k		C17			g.Cs – F17
								–k	(g+k)		C18			g.Cs – F18

The selection of 18 latitudinal bands enables us to define each band as 10^0 of latitude with band 1 representing the North Pole (80-90^{0}N) and band 18 the South Pole at (80-90^{0}S).

It is necessary to allocate values to the various matrix coefficients. This however requires some thought and discussion. There are effectively four basic parameters to be evaluated, namely g, k, Cs and Fn. The gain constant g should of course be identical to the constant g2 used in Part 2 of this paper, representing the sea surface/atmosphere interface. We will

allocate the value equivalent to 1/g = 6.2 years as in Part 2. The gain value k is for us a new value representing the strength of atmospheric mixing. This value must be selected to fit the It is necessary to allocate values to the various matrix coefficients. This however requires some thought and discussion. There are effectively four basic parameters to be evaluated, namely g, k, Cs and Fn. The gain constant g should of course be identical to the constant g2 used in Part 2 of this paper, representing the sea surface/atmosphere interface. We will allocate the value equivalent to 1/g = 6.2 years as in Part 2. The gain value k is for us a new value representing the strength of atmospheric mixing. This value must be selected to fit themeasured data. We will assume for simplicity that the values of g and k will be constant throughout all the latitudinal bands.

The values C_s and F_n, representing the sea surface CO_2 partial pressure and atmospheric CO_2 input/output flux, are not likely to be constant over all latitudes. We would expect that C_s will be strongly influenced by sea surface temperature because of the high temperature dependency of Henry's coefficient (3%/degC). From knowledge of global sea surface temperature distribution we can calculate C_s for each latitude band. Similarly the value of 20.8ppm/year value for net atmospheric CO_2 flux (Net Biome Production NBP) assumed in part 2 is unlikely to be constant over the entire globe. This function is the sum of a variety of fluxes, photosynthetic, respiratory, anthropogenic emissions, impact of deforestation etc. The two contributing elements of most interest are the NBP, which is the net of all fluxes other than anthropogenic emissions and those same anthropogenic emissions, which we will denote A_n.

The latitudinal variation in anthropogenic CO_2 emissions was identified in Part 1 and the same data will be replicated here. Estimation of the variation in NBP will, however, require some assumptions. By far the strongest of the components comprising NBP is photosynthetic absorption of CO_2 and one would expect to see a correlation between this function and arable land surface area and temperature. We would not, for example, expect to see significant NBP fluxes at the Poles, where temperatures are consistently sub zero, and at latitudes where the land mass is insignificant. We can thus estimate the spread of functions F_n and A_n over the 18 latitudinal bands.

The following table identifies the 18 sets of parameters, which we will use. It must be stressed that the F_n values in particular represent a very crude estimation. A full inventory of biospheric fluxes should provide a more accurate assessment providing of course that the concept of a zero NBP prescribed by the IPCC can be abandoned. In addition the gain constants g and k might also be seen to vary over the globe.

latitude	Sea Temp ^{0}C	Cs ppm	F ppm/year	A ppm/year	1/g years	k years^{-1}
90	-2	347	0.00	0.00	6.20	-100
80	-2	347	0.00	0.00	6.20	-100
70	1	380	20.00	0.32	6.20	-100
60	5	424	25.00	10.94	6.20	-100
50	10	480	30.00	11.07	6.20	-100
40	15	535	30.00	13.22	6.20	-100
30	25	646	30.00	5.53	6.20	-100
20	30	701	35.00	1.40	6.20	-100
10	30	701	45.00	0.62	6.20	-100
-10	30	701	50.00	0.52	6.20	-100
-20	20	590	35.00	0.10	6.20	-100
-30	16	546	30.00	1.01	6.20	-100
-40	10	480	25.00	1.02	6.20	-100
-50	4	413	20.00	0.07	6.20	-100
-60	-2	347	0.00	0.00	6.20	-100
-70	-2	347	0.00	0.00	6.20	-100
-80	-3	336	0.00	0.00	6.20	-100
-90	-4	325	0.00	0.00	6.20	-100

Appendix (ii) Calculation of Isotopic Ratios

There will be separate control mechanisms in place for atmospheric CO_2 containing ^{12}C and ^{13}C. Each will have its own control equation, which from Part 2 can be written: -

For ^{12}C based CO_2

$$^{12}Ca \ = \ ^{12}Co - (^{12}Fa - {}^{12}A + {}^{12}Fs)/g_{1.}(1 - e^{-t/\tau 1}) - (^{12}Fa - {}^{12}A)/g_{2.}(1 - e^{-t/\tau 2}) \qquad (1)$$

Where ^{12}Fa and ^{12}Fs are the resultant biospheric atmospheric and sea surface $^{12}CO_2$ fluxes, ^{12}A is the anthropogenic flux and $^{12}C_0$ is the partial pressure due to $^{12}CO_2$ in solution in the deep ocean.

For ^{13}C based CO_2 a similar equation exists

$$^{13}Ca \ = \ ^{13}Co - (^{13}Fa - {}^{13}A + {}^{13}Fs)/^{13}g_{1.}(1 - e^{-t/\tau 1}) - (^{13}Fa - {}^{13}A)/^{13}g_{2.}(1 - e^{-t/\tau 2}) \qquad (2)$$

$^{13}g_1$ and $^{13}g_2$ are the gain factors for the thermocline and sea surface interfaces related to $^{13}CO_2$ transport.

Now the isotopic ratio $\delta^{13}C$ is defined by the relation

$$\delta^{13}C \ = \ (^{13}C/^{12}C - r_s)/r_s$$

so that $\qquad \qquad ^{13}C/r_s \ = \ ^{12}C(\ 1 + \delta^{13}C \ ) \qquad \qquad (3)$

and it follows that from (2) and (3)

$$^{13}Ca/r_s = {}^{12}Co(1 + \delta_0) - ({}^{12}Fa(1 + \delta_b) - {}^{12}A(1 + \delta_f) + {}^{12}Fs(1 + \delta_s))/{}^{13}g_{1.}(1 - e^{-t/\tau 1})$$
$$- ({}^{12}Fa(1+\delta_b) \updownarrow {}^{12}A(1+\delta_f))/{}^{13}g_{2.}(1 - e^{-t/\tau 2})$$

where δ_0 is the isotopic ratio of the deep ocean CO_2

δ_b is the isotopic ratio of the biospheric CO_2 fluxes $= 27.0\%_0$

δ_s is the isotopic ratio of the sea surface biospheric CO_2 fluxes $= 27.0\%_0$

δ_f is the isotopic ratio of the anthropogenic CO_2 emissions $= 29\%_0$

This equation can, as previously, be written in two parts, one for the sea surface CO_2 concentration, and one for the atmosphere.

For the sea surface

$$^{13}Cs/r_s = {}^{12}Co(1+\delta_0) - ({}^{12}Fa(1+\delta_b) \updownarrow {}^{12}A(1+\delta_f) + {}^{12}Fs(1+\delta_s))/{}^{13}g_{1.}(1 - e^{-t/\tau 1}) \quad (4)$$

And for the atmosphere

$$^{13}Ca/r_s = {}^{13}Cs/r_s - ({}^{12}Fa(1+\delta_b) - {}^{12}A(1+\delta_f))/{}^{13}g_{2.}(1 - e^{-t/\tau 2}) \quad (5)$$

The isotope ratio for the sea surface $\delta^{13}Cs$ is then calculated from

$$\delta^{13}Cs = ({}^{13}Cs/r_s - {}^{12}Cs)/{}^{12}Cs$$

while for the atmosphere

$$\delta^{13}Ca = ({}^{13}Ca/r_s - {}^{12}Ca)/{}^{12}Ca$$

Appendix (iii) - Seasonal Variation of Biospheric and Oceanic CO_2 Fluxes

Standard Derivation (no seasonal variation)

Rate of change of atmospheric CO_2

$$dC_a/dt = (C_s - C_a).g_2 - F_a \qquad [1]$$

Rate of change of sea surface CO_2

$$dC_s/dt = (C_0 - C_s).g_1 - (C_s - C_a).g_2 - F_s \qquad [2]$$

From 1

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

$$= (C_0 - C_s).g_1.g_2 - (C_s - C_a).g_2^2 - g_2.Fs - g_2.dC_a/dt$$

$$= C_0g_1g_2 + C_ag_2^2 - C_s(g_1g_2 + g_2^2) - g_2.Fs - g_2.dC_a/dt \qquad [3]$$

Also from 1

$$(C_s - C_a) = (dC_a/dt + F_a)/g_2$$

and

$$C_s = C_a + (dC_a/dt + F_a)/g_2$$

Substituting in 3

$$d^2C_a/dt^2 = C_0g_1g_2 + C_ag_2^2 - (C_a + (dC_a/dt + F_a)/g_2).(g_1g_2 + g_2^2) - g_2.Fs - g_2.dC_a/dt$$

$$d^2C_a/dt^2 + (g_1 + 2g_2)dC_a/dt + C_ag_1g_2 = C_0g_1g_2 - (g_1 + g_2).F_a - g_2.F_s$$

Solution is

$$C_a = C_s - 1/g_2.F_a.(1 - e^{-t/\tau 2})$$

And
$$C_s = C_0 - 1/g_1.(F_a + F_s)(1 - e^{-t/\tau 1})$$

Seasonal Biospheric Variation

Let biospheric flux $F_a = A - B\cos\omega t$

Rate of change of atmospheric CO_2

$$dC_a/dt = (C_s - C_a).g_2 - A + B\cos\omega t \qquad [4]$$

Rate of change of sea surface CO_2

$$dC_s/dt = (C_0 - C_s).g_1 - (C_s - C_a).g_2 - F_s \qquad [5]$$

From 4

$$d^2C_a/dt^2 = g_2.dC_s/dt - g_2.dC_a/dt - B\omega.\sin\omega t$$

$$= (C_0 - C_s).g_1.g_2 - (C_s - C_a).g_2^2 - g_2.Fs - g_2.dC_a/dt - B\omega\sin\omega t$$

$$= C_0g_1g_2 + C_ag_2^2 - C_s(g_1g_2 + g_2^2) - g_2.Fs - g_2.dC_a/dt - B\omega\sin\omega t \qquad [6]$$

Also from 1
$$C_s = C_a + (dC_a/dt + A - B\cos\omega t)/g_2$$

Substituting in 6

$$d^2C_a/dt^2 = C_0g_1g_2 + C_ag_2^2 - (C_a + (dC_a/dt + A - B\cos\omega t)/g_2)(g_1g_2 + g_2^2) - g_2.Fs - g_2.dC_a/dt - B\omega\sin\omega t$$

$$d^2C_a/dt^2 + (g_1 + 2g_2)dC_a/dt + C_ag_1g_2 = C_0g_1g_2 - (g_1 + g_2).(A - B\cos\omega t) - g_2.F_s - B\omega\sin\omega t \qquad [7]$$

Solution

Let the solution be of the form

$$C_a = C_0 - 1/g_1.(A + F_s)(1 - e^{-t/\tau 1}) - 1/g_2.A.(1 - e^{-t/\tau 2}) + M\sin\omega t + N\cos\omega t$$

Differentiating and sustituting in [7]

$$dC_a/dt = -1/\tau_1[C_0 - 1/g_1.(A + F_s)]e^{-t/\tau 1} - 1/\tau_2.Ae^{-t/\tau 2} + M\omega\cos\omega t - N\omega\sin\omega t$$

$$d^2C_a/dt^2 = 1/\tau_1^2[C_0 - 1/g_1.(A + F_s)]e^{-t/\tau 1} + 1/\tau_2^2.Ae^{-t/\tau 2} - M\omega^2\sin\omega t - N\omega^2\cos\omega t$$

Thus

$$1/\tau_1^2[C_0 - 1/g_1.(A + F_s)]e^{-t/\tau 1} + 1/\tau_2^2.Ae^{-t/\tau 2} - M\omega^2\sin\omega t - N\omega^2\cos\omega t +$$
$$(g_1 + 2g_2)\{ -1/\tau_1[C_0 - 1/g_1.(A + F_s)]e^{-t/\tau 1} - 1/\tau_2.Ae^{-t/\tau 2} + M\omega\cos\omega t - N\omega\sin\omega t\} +$$

$g_1 g_2 \{ C_0 - 1/g_1 \cdot (A + F_s)(1 - e^{-t/\tau 1}) - 1/g_2 \cdot A(1 - e^{-t/\tau 2}) + M\sin\omega t + N\cos\omega t \} =$
$C_0 g_1 g_2 - (g_1 + g_2) \cdot (A - B\cos\omega t) - g_2 \cdot F_s - B\omega \sin\omega t$

Equating terms in $\sin\omega t$

$$- M\omega^2 \sin\omega t - (g_1 + 2g_2)N\omega \sin\omega t + g_1 g_2 M\sin\omega t = - B\omega \sin\omega t$$

$$- M\omega^2 - (g_1 + 2g_2)N\omega + g_1 g_2 M = - B\omega$$

or $\qquad M(g_1 g_2 - \omega^2) - (g_1 + 2g_2)N\omega = - B\omega$ $\qquad\qquad$ [8]

Equating terms in $\cos\omega t$

$$- N\omega^2 \cos\omega t + (g_1 + 2g_2)M\omega \cos\omega t + g_1 g_2 N\cos\omega t = (g_1 + g_2)B\cos\omega t$$

$$- N\omega^2 + (g_1 + 2g_2)M\omega + g_1 g_2 N = (g_1 + g_2)B$$

and $\qquad M(g_1 + 2g_2)\omega + (g_1 g_2 - \omega^2)N = (g_1 + g_2)B$ $\qquad\qquad$ [9]

solving equations 8 & 9 for N

$$M(g_1 g_2 - \omega^2)(g_1 + 2g_2)\omega - (g_1 + 2g_2)^2 \omega^2 N = - B\omega^2(g_1 + 2g_2)$$

And $\qquad M(g_1 g_2 - \omega^2)(g_1 + 2g_2)\omega + (g_1 g_2 - \omega^2)^2 N = B(g_1 + g_2)(g_1 g_2 - \omega^2)$

Subtracting
$$[(g_1 g_2 - \omega^2)^2 + (g_1 + 2g_2)^2 \omega^2] N = B[(g_1 + g_2)(g_1 g_2 - \omega^2) + \omega^2(g_1 + 2g_2)]$$

$$= B[(g_1 + g_2)g_1 g_2 + \omega^2 g_2]$$

Thus $N = B[(g_1 + g_2)g_1 g_2 + \omega^2 g_2] / [(g_1 g_2 - \omega^2)^2 + (g_1 + 2g_2)^2 \omega^2]$

Substituting values
$\qquad 1/g_1 = 33.4$ years $\qquad 1/g_2 = 6.2$ years $\qquad \omega = 2\pi$ years^{-1}

or $\qquad g_1 = 0.03$ years^{-1} $\qquad g_2 = 0.16$ years^{-1} $\qquad \omega = 6.3$ years^{-1}

$\qquad N = B[g_2(\omega^2 + g_1(g_1 + g_2))]/\omega^4$ $\qquad$ since $\omega \gg g_1$ and g_2

thus $\qquad\qquad N = g_2 B/\omega^2$

solving for M

substitute $N = g_2 B/\omega^2$ in equation [8]

$$M(g_1g_2 - \omega^2) - (g_1 + 2g_2)\omega g_2 B/\omega^2 = -B\omega$$

Thus
$$-M\omega^2 = -B[\omega + (g_1 + 2g_2)/\omega]$$

since $\omega \gg g_1$ and g_2

$$M\omega^2 = B\omega$$

And
$$M = B/\omega$$

Thus the seasonal variation in $C_a = \Delta C_a$ is

$$\Delta C_a = B/\omega.\sin\omega t + g_2 B/\omega^2.\cos\omega t$$

$$= P.\sin(\omega t + \phi)$$

where
$$P^2 = (B/\omega)^2 + (g_2 B/\omega^2)^2$$

$$= B^2/\omega^2(1 + g_2^2/\omega^2)$$

which approximates closely to
$$P = B/\omega \qquad\qquad And \quad \tan\phi = g_2/\omega$$

Thus
$$\Delta C_a = B/\omega(\sin\omega t + \phi)$$

Since $g_2 = 1/6.2$ and $\omega = 2\pi = 6.3$

$\tan\phi = 0.025$ and therefore the phase shift $\phi = 1.45^0$ or 1.5days.

Seasonal Oceanic Variation

Let oceanic flux $F_s = D - E\cos\omega t$

Rate of change of atmospheric CO_2

$$dC_a/dt = (C_s - C_a).g_2 - F_a \qquad\qquad [10]$$

Rate of change of sea surface CO_2

$$dC_s/dt = (C_0 - C_s).g_1 - (C_s - C_a).g_2 - (D - E\cos\omega t) \qquad\qquad [11]$$

From 4
$$d^2C_a/dt^2 = g_2.dC_s/dt - g_2.dC_a/dt$$

$$= (C_0 - C_s).g_1.g_2 - (C_s - C_a).g_2^2 - g_2(D - E\cos\omega t) - g_2.dC_a/dt$$

$$= C_0 g_1 g_2 + C_a g_2{}^2 - C_s(g_1 g_2 + g_2{}^2) - g_2(D - E\cos\omega t) - g_2 . dC_a/dt \qquad [12]$$

Also from 1

$$C_s = C_a + (dC_a/dt + F_a)/g_2$$

Substituting in [12]

$$d^2 C_a/dt^2 = C_0 g_1 g_2 + C_a g_2{}^2 - (C_a + (dC_a/dt + F_a)/g_2)(g_1 g_2 + g_2{}^2) - g_2(D - E\cos\omega t) - g_2 . dC_a/dt$$

$$d^2 C_a/dt^2 + (g_1 + 2g_2)dC_a/dt + C_a g_1 g_2 = C_0 g_1 g_2 - g_2(D - E\cos\omega t) - (g_1 + g_2)F_a \qquad [13]$$

Solution

Let the solution be of the form

$$C_a = C_0 - 1/g_1 . (F_a + D)(1 - e^{-t/\tau_1}) - 1/g_2 . F_a(1 - e^{-t/\tau_2}) + M\sin\omega t + N\cos\omega t$$

Differentiating and sustituting in [13]

$$dC_a/dt = -1/\tau_1[C_0 - 1/g_1 . (F_a + D)]e^{-t/\tau_1} - 1/\tau_2 . F_a e^{-t/\tau_2} + M\omega\cos\omega t - N\omega\sin\omega t$$

$$d^2 C_a/dt^2 = 1/\tau_1{}^2[C_0 - 1/g_1 . (F_a + D)]e^{-t/\tau_1} + 1/\tau_2{}^2 . F_a e^{-t/\tau_2} - M\omega^2\sin\omega t - N\omega^2\cos\omega t$$

$$1/\tau_1{}^2[C_0 - 1/g_1 . (F_a + D)]e^{-t/\tau_1} + 1/\tau_2{}^2 F_a e^{-t/\tau_2} - M\omega^2\sin\omega t - N\omega^2\cos\omega t +$$

$$(g_1 + 2g_2)\{ -1/\tau_1[C_0 - 1/g_1 . (F_a + D)]e^{-t/\tau_1} - 1/\tau_2 . F_a e^{-t/\tau_2} + M\omega\cos\omega t - N\omega\sin\omega t\} +$$

$$g_1 g_2\{ C_0 - 1/g_1 . (F_a + D)(1 - e^{-t/\tau_1}) - 1/g_2 . F_a(1 - e^{-t/\tau_2}) + M\sin\omega t + N\cos\omega t\} =$$

$$C_0 g_1 g_2 - (g_1 + g_2)F_a - g_2(D - E\cos\omega t)$$

Equating terms in $\sin\omega t$

$$- M\omega^2\sin\omega t - (g_1 + 2g_2)N\omega\sin\omega t + g_1 g_2 M\sin\omega t = 0$$

$$- M\omega^2 - (g_1 + 2g_2)N\omega + g_1 g_2 M = 0$$

or
$$M(g_1 g_2 - \omega^2) - (g_1 + 2g_2)N\omega = 0 \qquad [14]$$

Equating terms in $\cos\omega t$

$$- N\omega^2\cos\omega t + (g_1 + 2g_2)M\omega\cos\omega t + g_1 g_2 N\cos\omega t = g_2 E\cos\omega t$$

$$- N\omega^2 + (g_1 + 2g_2)M\omega + g_1 g_2 N = g_2 E$$

and
$$M(g_1 + 2g_2)\omega + (g_1 g_2 - \omega^2)N = g_2 E \qquad [15]$$

solving equations [14] & [15] for N

$$M(g_1g_2 - \omega^2)(g_1 + 2g_2)\omega - (g_1 + 2g_2)^2\,\omega N = 0$$

And $$M(g_1g_2 - \omega^2)(g_1 + 2g_2)\omega + (g_1g_2 - \omega^2)^2\omega N = g_2E(g_1g_2 - \omega^2)$$

Subtracting
$$[(g_1g_2 - \omega^2)^2 + (g_1 + 2g_2)^2]\omega N = g_2E(g_1g_2 - \omega^2)$$

Thus $$N = Eg_2(g_1g_2 - \omega^2]/\omega[(g_1g_2 - \omega^2)^2 + (g_1 + 2g_2)^2\,\omega^2]$$

Substituting values

$$1/g_1 = 33.4 \text{ years} \qquad 1/g_2 = 6.2 \text{ years} \qquad \omega = 2\pi \text{ years}^{-1}$$
or $$g_1 = 0.03 \text{ years}^{-1} \qquad g_2 = 0.16 \text{ years}^{-1} \qquad \omega = 6.3 \text{ years}^{-1}$$

$$N = - Eg_2\omega^2/\omega^4 \qquad \text{since } \omega \gg g_1 \text{ and } g_2$$

thus $$N = - g_2E/\omega^2$$

solving for M

substitute $$N = - g_2E/\omega^2 \text{ in equation [14]}$$

$$M(g_1g_2 - \omega^2) + (g_1 + 2g_2)\omega g_2E/\omega^2 = 0$$

since $\omega \gg g_1$ and g_2

$$M\omega^2 = Eg_2(g_1 + 2g_2)/\omega$$

And $$M = Eg_2(g_1 + 2g_2)/\omega^3$$

Thus the seasonal variation in $C_a = \Delta C_a$ is

$$\Delta C_a = Eg_2(g_1 + 2g_2)/\omega^3.\sin\omega t - Eg_2/\omega^2.\cos\omega t$$

$$= P.\sin(\omega t + \phi)$$

where $$P^2 = (Eg_2/\omega^2)^2 + (E(g_1 + 2g_2)/\omega^3)^2$$
and since $\omega \gg g_1$ and g_2

$$= (Eg_2/\omega^2)^2$$

or $$P = Eg_2/\omega^2$$

And $$\tan\phi = - Eg_2/\omega^2/(Eg_2(g_1 + 2g_2)/\omega^3)$$

$$= - (g_1 + 2g_2)/\omega$$

Thus
$$\Delta C_a = Eg_2/\omega^2 (\sin\omega t - \phi)$$

Since $g_1 = 0.03$, $g_1 = 0.16$ and $\omega = 2\pi = 6.3$

$\tan\phi = 0.05$ and therefore the phase shift $\phi = 3.2^0$ or 3.3days.