Limits to existing quantitative understanding of past, present and future changes to atmospheric carbon dioxide concentration

A presentation by
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Synopsis

It is commonly assumed that the rise in atmospheric carbon dioxide (CO_2) concentration during the twentieth century (approx. 30% rise) is a result of anthropogenic emissions of CO_2 [1,2,3]. However, the annual pulse of anthropogenic CO_2 into the atmosphere should relate to the annual increase of CO_2 in the atmosphere if one is causal of the other, but their variations greatly differ from year to year [4]. This presentation considers mechanisms in the carbon cycle and uses the model studies of Rörsch et al. (2005) [4] to determine if other factors may be significant contributors to the observed rise to the atmospheric CO_2 concentration. These considerations indicate that any one of three natural mechanisms in the carbon cycle alone could be used to account for the observed rise. This indicates that the observed rise may be entirely natural; indeed, it suggests that the observed rise to the atmospheric CO_2 concentration most probably is natural. Hence 'projections' of future changes to the atmospheric CO_2 concentration and resulting climate changes have high uncertainty if they are based on the assumption of an anthropogenic cause.

1.   Introduction

It is commonly assumed that the rise in atmospheric carbon dioxide (CO_2) concentration during the twentieth century (approx. 30% rise) is a result of anthropogenic emissions of CO_2 [1,2,3]. However, the annual pulse of anthropogenic CO_2 into the atmosphere should relate to the annual increase of CO_2 in the atmosphere if one is causal of the other, but their variations greatly differ from year to year [4] (see Figure 1).
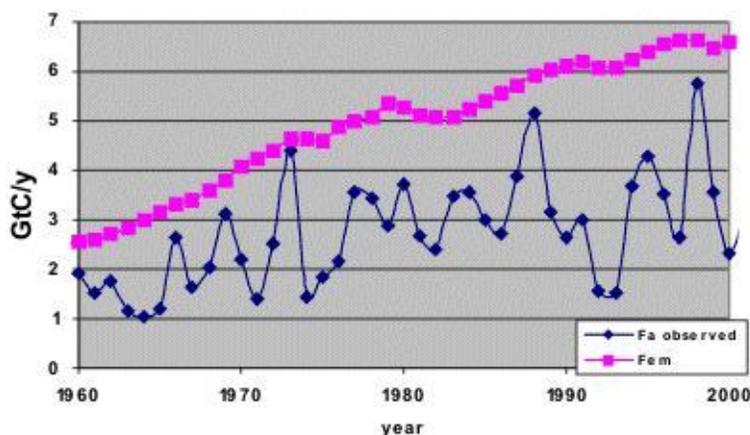

Figure 1.   Annual human emission (F_{em}) and the measured flow of carbon dioxide into the atmosphere (F_a) in GtC/y [4]

Furthermore, the annual increase to CO_2 in the atmosphere is the residual of the seasonal changes to CO_2 in the atmosphere, and the Northern Hemisphere seasonal changes (decrease and increase) each year are approximately an order of magnitude greater than both the total annual increase and the total annual anthropogenic emission [4].
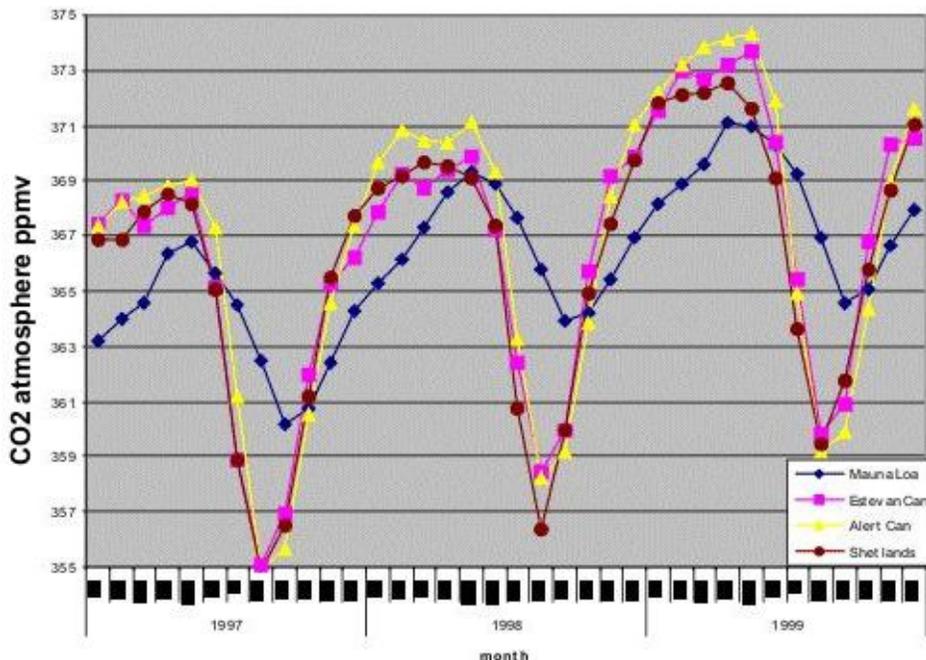
Figure 2.   Rise and fall of carbon dioxide concentration in the atmosphere at four sites, Mauna Loa Hawaii, Estevan Canada, Alert Canada, Shetland Islands. Here three years are selected from the long term graph 1991- 2000, C.D. Keeling and T.P. Whorf. "On line trends", cdiac.ornl [4]

Little of the carbon and CO_2 in the Earth/ocean/atmosphere system is in the air. Figure 2 shows that throughout each year the CO_2 in the air increases and reduces as natural processes emit CO_2 to the air and sequester CO_2 from the air. The system would need to be near saturation in CO_2 for it to fail to adjust for the relatively small anthropogenic additions to the CO_2 in the air.

The rapid changes to atmospheric CO_2 concentration shown in Figure 2 indicate that during each year the system very rapidly adjusts to seasonal changes that are an order of magnitude greater than the anthropogenic emission each year. The anthropogenic emission is to the air, but the rapid changes in atmospheric CO_2 concentration shown in Figure 2 do not suggest that the system is near to saturation that would prevent the system from sequestering the anthropogenic emission from the air.

Any assessment of the causes of the rise of atmospheric CO_2 concentration over a period of years requires assessment of the changes that occur each year (because the annual increase to CO_2 in the atmosphere is the residual of the seasonal changes to CO_2 in the atmosphere).

2.   Mechanisms of the carbon cycle

In our paper, Rörsch et al. (2005) [4], we considered the most important processes in the carbon cycle to be:

Short-term processes

1. Consumption of CO_2 by photosynthesis that takes place in green plants on land. CO_2 from the air and water from the soil are coupled to form carbohydrates. Oxygen is liberated. This process takes place mostly in spring and summer. A rough distinction can be made:
    1a.   The formation of leaves that are short lived (less than a year).
    1b.   The formation of tree branches and trunks, that are long lived (decades).

2. Production of CO_2 by the metabolism of animals, and by the decomposition of vegetable matter by micro-organisms including those in the intestines of animals, whereby oxygen is consumed and water and CO_2 (and some carbon monoxide and methane that will eventually be oxidised to CO_2) are liberated. Again distinctions can be made:
    2a.   The decomposition of leaves, that takes place in autumn and continues well into the next winter, spring and summer.
    2b.   The decomposition of branches, trunks, etc. that typically has a delay of some decades after their formation.
    2c.   The metabolism of animals that goes on throughout the year.

3. Consumption of CO_2 by absorption in cold ocean waters. Part of this is consumed by marine vegetation through photosynthesis.

4. Production of CO_2 by desorption from warm ocean waters. Part of this may be the result of decomposition of organic debris.

5. Circulation of ocean waters from warm to cold zones, and vice versa, thus promoting processes 3 and 4.

Longer-term process

6. Formation of peat from dead leaves and branches (eventually leading to lignite and coal).

7. Erosion of silicate rocks, whereby carbonates are formed and silica is liberated.

8. Precipitation of calcium carbonate in the ocean, that sinks to the bottom, together with formation of corals and shells.

Natural processes that add CO_2 to the system:

9. Production of CO_2 from volcanoes (by eruption and gas leakage).

10. Natural forest fires, coal seam fires and peat fires.

Anthropogenic processes that add CO_2 to the system:

11. Production of CO_2 by burning of vegetation ("biomass").

12. Production of CO_2 by burning of fossil fuels (and by lime kilns).

Several of these processes are rate dependant and several of them interact.

At higher air temperatures, the rates of processes 1, 2, 4 and 5 will increase and the rate of process 3 will decrease. Process 1 is strongly dependent on temperature, so its rate will vary strongly (maybe by a factor of 10) throughout the changing seasons.

The rates of processes 1, 3 and 4 are dependent on the CO_2 concentration in the atmosphere. The rates of processes 1 and 3 will increase with higher CO_2 concentration, but the rate of process 4 will decrease.

The rate of process 1 has a complicated dependence on the atmospheric CO_2 concentration. At higher concentrations at first there will be an increase that will probably be less than linear (with an "order" <1). But after some time, when more vegetation (more biomass) has been formed, the capacity for photosynthesis will have increased, resulting in a progressive increase of the consumption rate.

Processes 1 to 5 are obviously coupled by mass balances. Our paper [4] assessed the steady-state situation to be an oversimplification because there are two factors that will never be "steady":

     I.   The removal of CO_2 from the system, or its addition to the system.
     II.   External factors that are not constant and may influence the process rates, such as varying solar activity.

Modeling this system is a difficult because so little is known concerning the rate equations. However, some things can be stated from the empirical data.

At present the yearly increase of the anthropogenic emissions is approximately 0.1 GtC/year (see Figure 1). The natural fluctuation of the *excess* consumption (i.e. consumption processes 1 and 3 minus production processes 2 and 4) is at least 6 ppmv (which corresponds to 12 GtC) in 4 months (see Figure 2). This is more than 100 times the yearly increase of human production, which strongly suggests that the dynamics of the natural processes here listed 1-5 can cope easily with the human production of CO_2. A serious disruption of the system may be expected when the rate of increase of the anthropogenic emissions becomes larger than the natural variations of CO_2.   But the above data indicates this is not possible.

The accumulation rate of CO_2 in the atmosphere (1.5 ppmv/year which corresponds to 3 GtC/year) is equal to almost half the human emission (6.5 GtC/year). However, this does not mean that half the human emission accumulates in the atmosphere, as is often stated [1,2,3]. There are several other and much larger CO_2 flows in and out of the atmosphere. The total CO_2 flow into the atmosphere is at least 156.5 GtC/year with 150 GtC/year of this being from natural origin and 6.5 GtC/year from human origin. So, on the average, 3/156.5 = 2% of all emissions accumulate.

The above qualitative considerations suggest the carbon cycle cannot be very sensitive to relatively small disturbances such as the present anthropogenic emissions of CO_2. However, the system could be quite sensitive to temperature.   So, our paper [4] considered how the carbon cycle would be disturbed if – for some reason – the temperature of the atmosphere were to rise, as it almost certainly did between 1880 and 1940 (there was an estimated average rise of 0.5 °C in average surface temperature: see Figure 3).
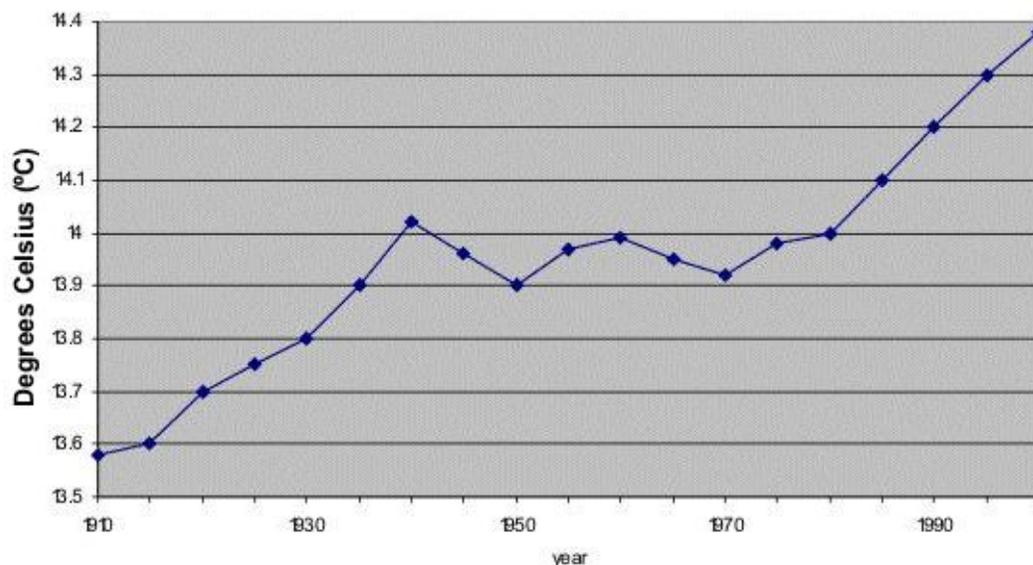
Source: Redesigned from B. Lomborg[5].

Original reference: Jones et al, (2001,2002), In "Trends", cdiac.ornl[6]

Figure 3. Moving nine year average of average temperature at the Earth's surface.

As temperature rises the rate of the main CO_2 production processes 2 (decomposition of organic matter) and 4 (desorption from the oceans) would rise, as would the rate of the consumption process 1 (photosynthesis). However, the rate of absorption in the ocean (process 3) will not be increased. The rates of processes 1a and 2a will rise more quickly than the rates of processes 1b and 2b, but it is not obvious which would rise most. Obviously, the net result would be an increase of CO_2 production by desorption from the oceans. This is a relatively slow process, because the mass transfer coefficient between the sea water and its surface is relatively low (the rates of both absorption and desorption in the oceans have time constants that are probably of the order of decades). This would mean that a disruption by a temperature rise would result in a relatively slow increase of CO_2 production. Gradually, the consumption processes 1 (photosynthesis) and 3 (absorption in cold ocean waters) will increase and slow down the excess CO_2 formation.

As long as the anthropogenic production of CO_2 is less than, say, 10% of the average natural production (2.5 times the present level), the CO_2 level in the atmosphere might become 2.5 times higher than it was originally. However, it will eventually become much lower again, due to the delayed action of process 8 (the "true sink").

The above considerations of available data strongly suggest that the anthropogenic emissions of CO_2 will have no significant long term effect on climate. The main reason is that the *rate of increase* of the anthropogenic production of CO_2 is very much smaller that the observed maximum *rate of increase* of the natural consumption of CO_2.

In the light of all the above considerations it would appear that the relatively large increase of CO_2 concentration in the atmosphere in the twentieth century (some 30%) is likely to have been caused by the increased mean temperature that preceded it. The main cause may be desorption from the oceans. The observed time lag of half a century is not surprising. Assessment of this conclusion requires a quantitative model of the

carbon cycle, but – as previously explained – such a model cannot be constructed because the rate constants are not known for mechanisms operating in the carbon cycle

3.   Attribution Studies

It is often suggested that the anthropogenic emission of CO_2 is the cause of the rise in atmospheric CO_2 concentration that has happened in the recent past (i.e. since 1958 when measurements began), that is happening at present and, therefore, that will happen in the future [1,2,3].   But Section 2 of this presentation explained that this suggestion may not be correct and that a likely cause of the rise in atmospheric CO_2 concentration that has happened in the recent past is the increased mean temperature that preceded it. A quantitative model of the carbon cycle might resolve this issue but Section 2 also explained that the lack of knowledge of the rate constants of mechanisms operating in the carbon cycle prevents construction of such a model. However, this lack of knowledge does not prevent models from providing useful insights into ways the carbon cycle may be behaving. 'Attribution studies' are a possible method to discern mechanisms that are not capable of being the cause of the observed rise of atmospheric CO_2 concentration during the twentieth century.

In an attribution study the system is assumed to be behaving in response to suggested mechanism(s) that is modeled, and the behaviour of the model is compared to the empirical data. If the model cannot emulate the empirical data then there is reason to suppose that the suggested mechanism is not the cause (or at least not the sole cause) of the changes recorded in the empirical data.

It is important to note that attribution studies can only be used to reject hypothesis that a mechanism is a cause for an observed effect. Ability to attribute a suggested cause to an effect is not evidence that the suggested cause is the real cause in part or in whole.

Our paper considered three models of the carbon cycle. Each model assumed that a single mechanism is responsible for the rise in atmospheric CO_2 concentration that has happened in the recent past (i.e. since 1958 when measurements began). The model was then compared to the empirical data to determine if the modeled mechanism could be rejected as a sole cause of the rise in atmospheric CO_2 concentration.

We used a common terminology for each of the models; viz.

F_{in} total flux of CO_2 from Earth into the atmosphere (GtC/y)
F_{out} total aborption flux of CO_2 by Earth (GtC/y)
F_{em} extra flux of CO_2 of human origin into the atmosphere (GtC/y)
F_{na} extra flux of CO_2 of other (natural origin) into the atmosphere (GtC/y)
F_a accumulation rate of CO_2 in atmosphere (GtC/y)
F_o is the assumed yearly passage CO_2 through the cycle if F_{em} and $F_{na} = 0$.
             its average value is estimated as 150 GtC/y. [7]
C_{air} concentration CO_2 in the atmosphere (ppmv)
C_e The concentration CO_2 in the atmosphere in the equilibrium state $F_{out} = F_{in}$.

The models were:

The A Model

This is the much respected model of Ahlbeck [7] that is based on a postulated linear relationship of the sink flow and the concentration of CO_2 in the atmosphere according to an equation

$$F_{out} = a^*C_{air} + b \qquad\qquad [1]$$

In it, a is a rate constant of the dimension GtC y^{-1} ppmv^{-1}, and it is very probably subject to variation due to climate changes (e.g. temperature changes). The assumption that this process is first order with respect to the CO_2 concentration is arbitrary. There are two main simultaneous absorption processes (i.e. uptake by vegetation on land and absorption in the oceans) and, therefore, "a" is a compound rate constant. Both processes are no doubt limited by chemical reactions, since the data show that the physical rate constant for mass transfer is an order of magnitude higher. The compound coefficient "a" can only be determined empirically and is expected to be dependent on a host of physical conditions. The same can be said for the constant k in the second model which we called the P Model.

The P Model

Process (chemical) engineering often uses a power equation

$$F_{out} = k^*C_{air}{}^p \qquad \text{in which } 0<p<1 \qquad\qquad [2]$$

This power equation model we called the P model. It stems from the assumptions, described in Section 2, that several different processes determine the flow into the sinks.

In process engineering equipment the absorption rates are usually determined either by mass transfer alone or by mass transfer and simultaneous chemical reaction. These processes have reaction orders (p) of 1 or 0.5 respectively. However, the rate of absorption in vegetation is determined by complex chemical reactions that are very much slower. Such processes can have orders between 0 and 1, but mostly close to 0.

The M Model

The third model we called the M Model and it is derived from biology, or rather biochemistry, because we were mindful that the absorption of CO_2 takes place at least partly in the biosphere. The theory behind enzyme kinetics says the surface of an enzyme is continuously in equilibrium with its substrate and that a part of the substrate at the enzyme surface (its active site) will be digested to a product.

$$[E] + [S] \xleftrightarrow{k} [ES] \xrightarrow{v} P$$
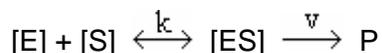
The rate v is dependent on the amount of [ES] present which in turn is dependent on the concentration of the substrate and the amount of enzyme present, or in other words the amount of reactive interface available. This line of thought is certainly not restricted to enzymology. It leads for example in economics to the formulation of the law of diminishing returns. And many systems show the behavior in which an available active interface is the limiting factor for processing (even military theory uses the concept of 'engagement area' in battles).

The Michaelis Menten (MM) description of enzyme action reads:

$$V = Vm \times \frac{S}{Km + S}$$

In which V the actual rate, Vm, the maximum rate determined by the reactive surface available, S, the substrate concentration and Km a constant which is specific for the surface and represents its affinity for the substrate.

When we translate the MM equation to the interaction of sink surface with CO_2 in the atmosphere, it reads

$$F_{out} = (F_o + F_{em} - F_a) = V_{max} * C_{air} / (K_m + C_{air})$$

This can be transformed into a linear relationship by introducing the coefficient

$$r = C_{air} / (F_o + F_{em} - F_a)$$

which represents a resistance for the flow, and then [3] reads as:

$$(K_m + C_{air}) = V_{max} * r$$

or $\quad\quad\quad C_{air} = V_{max} * r - K_m$ $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ [3]

in which $0 < p < 1$

Determination of the constants in the three models

It should first be noted that there are few available empirical data that can be trusted. In fact, these are limited to the observed increase of the concentration of CO_2 in the atmosphere, well recorded at Mauna Loa since 1958 (see Figure 2). The annual flow F_a into the atmosphere can be derived from this (see Figure 1). Second best are the data collected by cdiac.ornl on the human emission (F_{em}), but they may be an underestimate if nations have not provided the correct figures.

It is obvious from Figure 1 that the annual flow into the atmosphere is not correlated with the annual anthropogenic emission. Either the estimates of the anthropogenic emission are very wrong or there must be an interfering influence. If the extra emission of human origin was the only emission, then in some years, almost all of it seems to be absorbed into the sinks, and in other years almost none. So, it might well be that – under the influence of annual changing climate conditions – assumed constants in the equations of the models, are not that constant. For example, there can be little doubt that the constant *a* in the A Model will be subject to temperature variation. Nevertheless, we can try to average over the period 1959 to 2000.

First, we considered the condition that the anthropogenic emission is the sole contributing source to the increased observation of the rise of the CO_2 concentration in the atmosphere. Using that assumption, Figure 4 presents the flow into the sinks in each year ($F_{out} = F_o + F_{em} - F_a$) as a function of the CO_2 level in that year. It shows the same high variability as F_a that can be seen in Figure 1 because there is no direct relationship between F_a, C_{air}, and F_{em} and the latter two increase rather gradually.
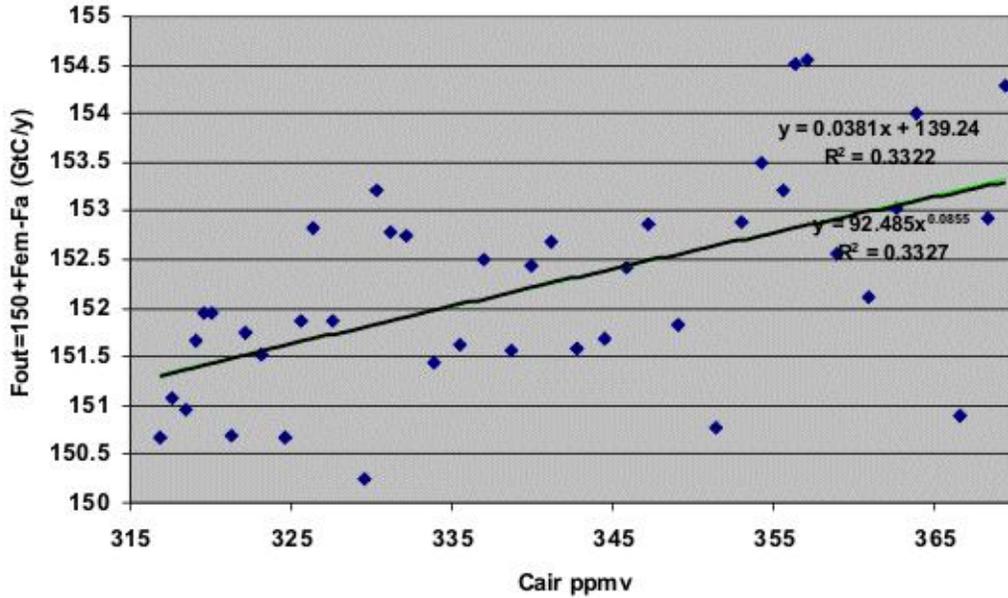
Figure 4. The best fit lines for the two models A and P.
The flow into sinks as function of the concentration of CO_2 for observed values of F_{em}, F_a and C_{air} in each year between 1959 and 2000.

The equations for the A and P model can be derived directly from the plot in Figure 4. But for the M model the constants V_{max} and K_m are derived from equation a plot C_{air} as a function of r. The result is shown as Figure 5. Its regression line shows higher correlation than those in Figure 4, but this is a statistical artifact because the values of r are calculated from the same scattered data of F_a.
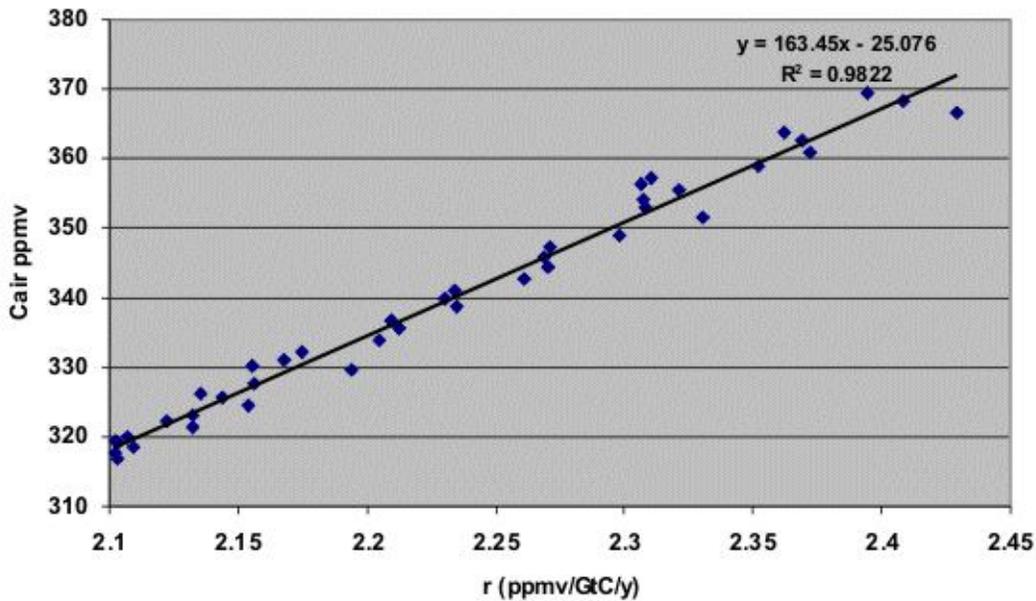
Figure 5. The relationship between the resistance of the flow of CO_2 into the sinks r and its concentration in the atmosphere (C_{air}) according to the M model.

The functions for the sink flows read:

A model $\qquad$ F_{out} = 0.0381 * C_{air} + 139.24 $\qquad$ [4]
P model $\qquad$ F_{out} = 92.485 * $C_{air}^{0.0855}$ $\qquad$ [5]
M model $\qquad$ F_{out} = 163.45 * C_{air} / (25.076+C_{air}) $\qquad$ [6]

In pre human emission time $\qquad$ F_{em} = 0, F_a = 0, and F_{out} = F_o = 150 GtC/y.

On the basis of ice core data, it is expected that with these values a C_{air} will be found near 280 ppmv. The result is

For the A model: $\qquad$ 282.41 ppmv
For the P model: $\qquad$ 286.00 ppmv
For the M model: $\qquad$ 280.04 ppmv

The time course

The annual flux into the atmosphere expressed in GtC/y can be written as dC_{air}/dt, using the conversion factor 2.1
$$F_a = (F_o + F_{em}) - F_{out} = 2.1 * d\, C_{air} / dt$$

A dynamic equilibrium state towards each emission level can be attributed when F_a becomes zero and $(F_o + F_{em}) = F_{out}$

Using formulae [4], [5] and [6] for the emission in each year, the equilibrium level for the concentration of CO_2 in the atmosphere can be calculated:

A model: $\quad C_{eD}$ = (F_o + F_{em} − b) / a $\qquad$ [7]
P model: $\quad C_{eP}$ = [(F_o + F_{em}) / k]$^{(1/p)}$ $\qquad$ [8]
M model: $\quad C_{eM}$ = (F_o + F_{em}) * K_m / (V_{max} − F_o − F_{em}) $\qquad$ [9]

How C changes with time, with a specific flux into the atmosphere follows from integration of the above differential equation that includes the conversion factor of 2.1, and this reads for the three models:

A model: $\quad$ 2.1 * d C_{air} / (a C_{air} + b − F_o − F_{em}) = -dt $\qquad$ [10]
P model: $\quad$ 2.1 * d C_{air} / (k C_{air}^p − F_o − F_{em}) = -dt $\qquad$ [11]
M model: $\quad$ 2.1 * d C_{air} * (K_m + C_{air}) / ([C_{air} (V_{max} − F_o − F_{em}) - K_m * (F_o +F_{em})] = -dt [12]

Unfortunately equation [8] cannot be integrated. The integration of [7] and [9] becomes with the introduction of C_e:

A model: $\quad$ ln ((C_e - C_2) / ((C_e - C_1)) = -(1 / 2.1) * a* $\qquad$ [13]
M model: $\quad$ (K_m+C_e) * ln ((C_e- C_2) / (C_e - C_1)) + C_2 - C_1 = (1/2.1) * -(V_m − F_o − F_{em}) * t [14]

In which C_2 is the C_{air} reached after time t when C_{air} was C_1 under the condition that F_o and F_{em} are constant over that time lapse. The match between these two models and the observed increase of C is shown in Figure 6.
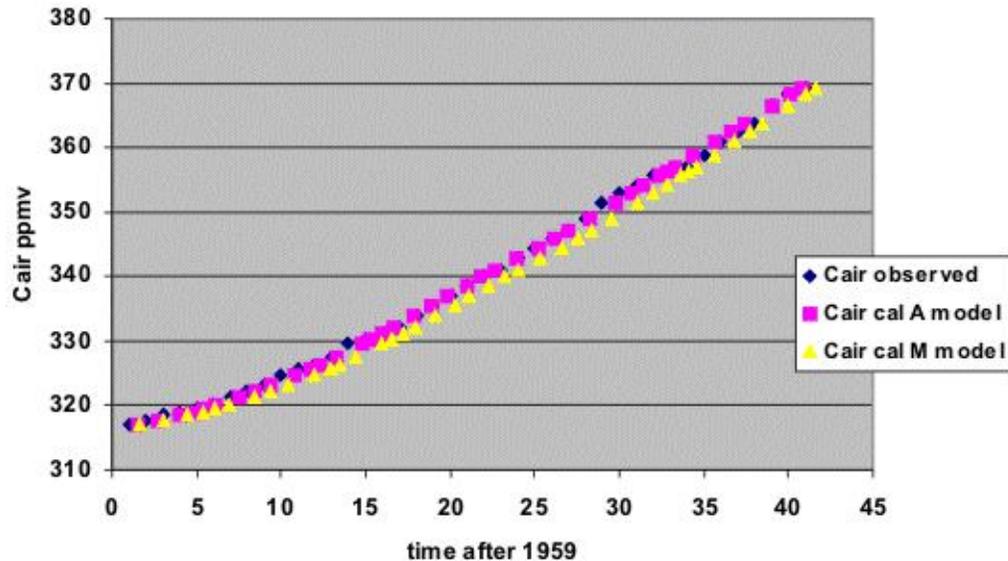
Figure 6. **Comparison of the observed CO_2 in the atmosphere with the predictions of the M and A models.**

It is clear that Figure 6 shows the two models both provide calculated values for C_{air} that fit with the observed values rather well, and they can hardly be distinguished from each other.

Figures 1 and 6 provide an apparent paradox. The annual anthropogenic emission of CO_2 should relate to the annual increase of CO_2 in the atmosphere if one is causal of the other but Figure 1 shows these two parameters do not correlate. However, Figure 6 shows that – using each of these different models – we were able to model the increase of CO_2 in the atmosphere as being a function solely of the annual anthropogenic emission of CO_2. It is important to note that we did not use any 'fiddle factors' such as the 5-year-averageing used by the IPCC (that cannot be justified because there is no known physical mechanism that would have such effect).

The apparent paradox is resolved by consideration of the calculated equilibrium CO_2 concentration values, C_e. These are shown in Figure 7. Each model indicates that the calculated CO_2 concentration for the equilibrium state in each year is considerably above the observed values. This demonstrates that each model indicates there is a considerable time lag required to reach the equilibrium state when there is no accumulation of CO_2 in the atmosphere. In other words, one has to reckon with a considerable time lag to reach the equilibrium state $F_a = 0$ when F_{in} increases to a certain value with increasing F_{em}. As Figure 2 shows, the short term sequestration processes can easily adapt to sequester the anthropogenic emission in a year. But, according to these models, the total emission of that year affects the equilibrium state of the entire system. Some processes of the system are very slow with rate constants of years and decades. Hence, the system takes decades to fully adjust to the new equilibrium. And Figure 6 shows the models predicting the atmospheric CO_2 concentration slowly rising in response to the changing equilibrium condition that is shown in Figure 7.

This slow rise in response to the changing equilibrium condition also provides an explanation of why the accumulation of CO_2 in the atmosphere continued when in two subsequent years the flux into the atmosphere decreased (the years 1973-1974, 1987-1988, and 1998-1999).
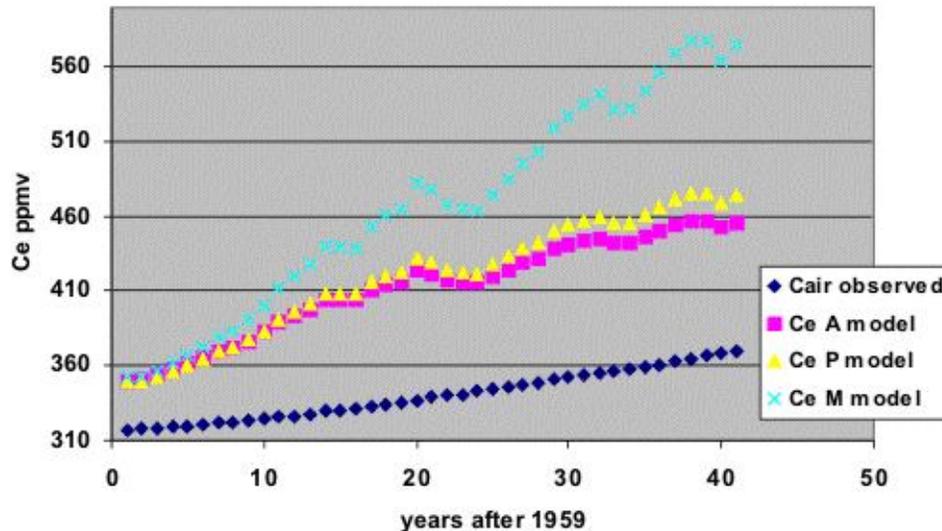

Figure 7. The equilibrium state of CO_2 concentration in the atmosphere, according to models A, P and M

However, Figure 7 also shows an important difference between the models. While it shows the calculated CO_2 concentration for the equilibrium state in each year is considerably above the observed values, it also shows the calculated equilibriums are diverging.

Consideration of a hypothetical additional natural flux F_{na} into the atmosphere.

The above calculations of constants use the assumption that there is no extra source of CO_2 in addition to the anthropogenic emission. And all three models emulate the empirical data. This demonstrates that it is possible to attribute the recent rise in atmospheric CO_2 concentration to be entirely caused by the anthropogenic emission by using any of the models. Nevertheless, we have to recognise that the equations for the models [4], [5] and [6] represent situations far from reality because the anthropogenic emission (6-7 GtC/y) is still only a small addition the natural annual flux of 150 GtC/y.

Also, as was pointed out in Section 2, there are several qualitative indications why changing climate conditions may influence the observed accumulation of CO_2 in the atmosphere. Unfortunately, a quantitative approach is impossible because the effect can be caused by both an increased influx and a decreased outflux. In other words, there are two unknowns when considering effect on atmospheric CO_2 concentration of changed climatic conditions.

If there were another natural source, caused by changing climate conditions, then the Y axis in Figure 4 should not read

$F_{out} = 150 + F_{em} - F_a$ but should be enlarged to

$F_{out} = 150 + F_{em} + \mathbf{F_{na}} - F_a$, with the same values for the observed F_a.

If one did not know the existence of the anthropogenic emission then one could draw any line in the sink flow diagram (Figure 4) to match the observed increase of CO_2 in the atmosphere. However, the line would have to obey the condition that once in the past the equilibrium condition $(C_e, F_o)_{Fa=0} = (280,150)$ existed.

The following exercise provides a number of examples that are presented as Figures 8, 9 and 10. In each example, the constants in the equations [4], [5] and [6] have been adjusted in such a way that they still match the observed flow F_a into the atmosphere and concurrently the observed rise of $C_{air..}$ The curves for the A model are by definition straight lines. Also, Figures 9 and 10 demonstrate that over the C_{air} range studied for the P and M models there was little deviation from a similar linear relationship.
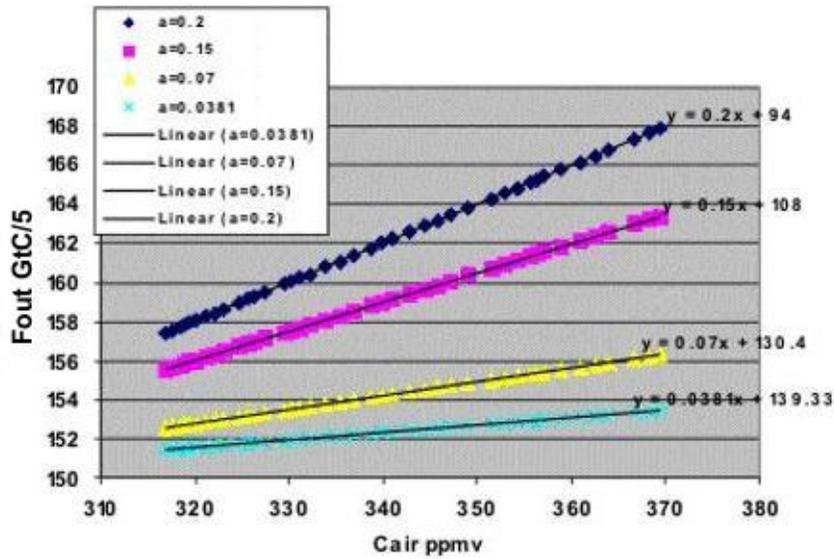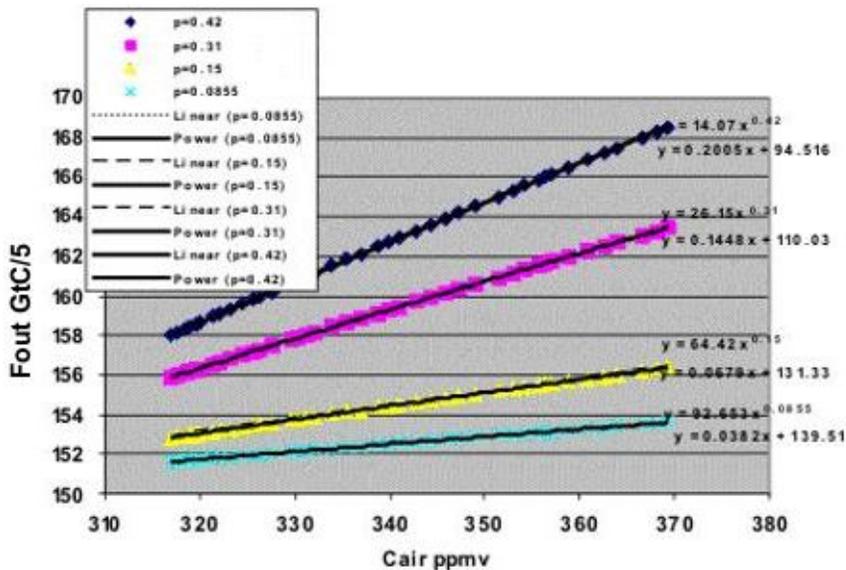

Figure 8.   **Hypothetical curves for flow into the sinks with model A:**

$$F_{out} = aC_{air} + b \text{ with assumed } F_{na} > 0$$

Figure 9.   **Hypothetical curves for flow into the sinks with model P:**

$F_{out} = k*C_{air}^{p}$ with assumed $F_{na} > 0$
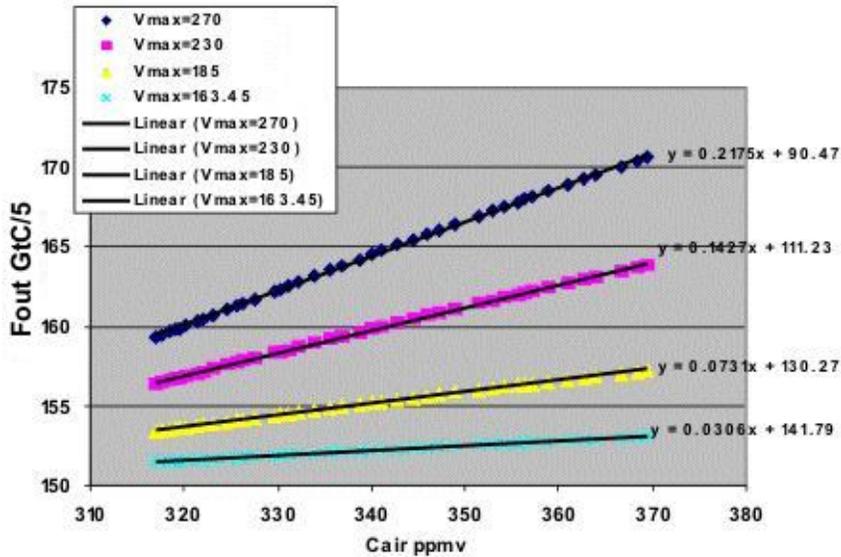**The regression lines indicate the correspondence of the power equation with linear equations.**

Figure 10. **Hypothetical curves for flow into the sinks with model M:**
$F_{out} = V_{max} * C_{air} /(K_m + C_{air})$ with assumed $F_{na} > 0$
The regression lines indicate the correspondence of the Michaelis Menten equation with linear equations.

Figure 11 demonstrates that the assumed higher sink flow in the D and in the M models still match very well with the observed rise of CO_2 in the atmosphere.
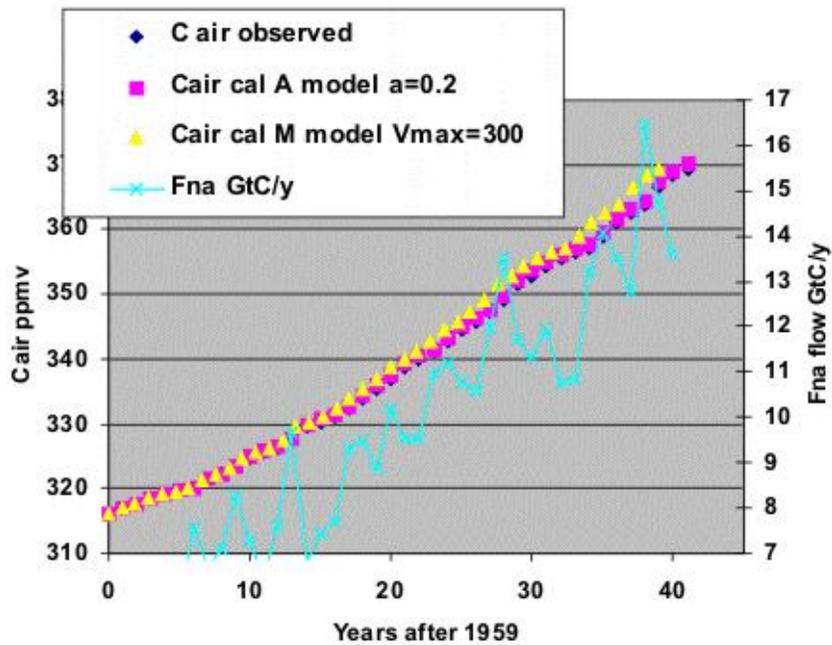

Figure 11. **The match of calculated rise of CO_2 in the atmosphere with model A and model M when a high natural flux (F_{na}) is involved.**
The F_{na} flow (right Y axis) is calculated from the equation:

$$F_{na} = 0.2*C_{air} + 94 - (F_o + F_{em} - F_a)$$

It is not possible to discriminate which of these different physical models is preferable. They all hardly deviate from a linear relationship of flow into the sinks with C_{air} (the observed rise of CO_2 in the atmosphere). Thus to assume such a linear relationship as deduced from the A model, may be jumping to a conclusion. Models P and M may be preferred if a more complicated process than only diffusion is involved. Experiences of process engineering suggest that if such a more complicated process is involved, then a rather larger value for the p factor than 0.0855 is expected (e.g., 0.42). And, in the simulated linear relationship, this corresponds with a value for $a=0.2175$, which is much higher than would follow from the absorber model of Ahlbeck that only considers F_{em} as an extra flow into the atmosphere. If it is accepted that the sink flow process is more complicated than being ruled by diffusion laws, then this is an additional argument that an extra natural flux F_{na} should be involved in an explanation of the observed rise of the concentration of CO_2 in the atmosphere.

The calculated curve for the F_{na} flux (Figure 11) follows the yearly increasing and decreasing flux (F_{na}) into the atmosphere (see Figure 1), but this not a proof of the existence of the F_{na} flux because the fluctuations result from the calculation method.
The equation $F_{na} = 0.2*C_{air} + 94 - (F_o + F_{em} - F_a)$ merely shows the deviations, caused by F_a , from the mean $F_{out} = 0.2*C_{air} + 94$. The revised models with higher rate constants ($a=0.2$ GtC/ppmv and $V_{max} = 300$ GtC/y) suggest only that the flux into the air may be higher and may be increasing more rapidly than expected from considering the anthropogenic emission F_{em} alone.

If we adopt the occurrence of this increasing natural flow, due to changes in climate conditions, then the introduction of F_{na} has interesting consequences for the expected equilibrium states described by equations [7], [8] and [9]:

A model: $C_{eD} = (F_o + F_{em} + \mathbf{F_{na}} - b) / a$ [15]
P model: $C_{eP} = [(F_o + F_{em} + F_{na}] / k]^{(1/p)}$ [16]
M model: $C_{eM} = (F_o + F_{em} + F_{na}) * K_m / (V_{max} - F_o - F_{em} - F_{na})$ [17].

The effects of the changing values of the rate constants on C_e are not immediately obvious because they change concurrently in different directions, but these effects show up when the values for C_e are calculated with equations [15], [16] and [17] with the application of the increased rate constants in the three models. This is shown in Figure 12.
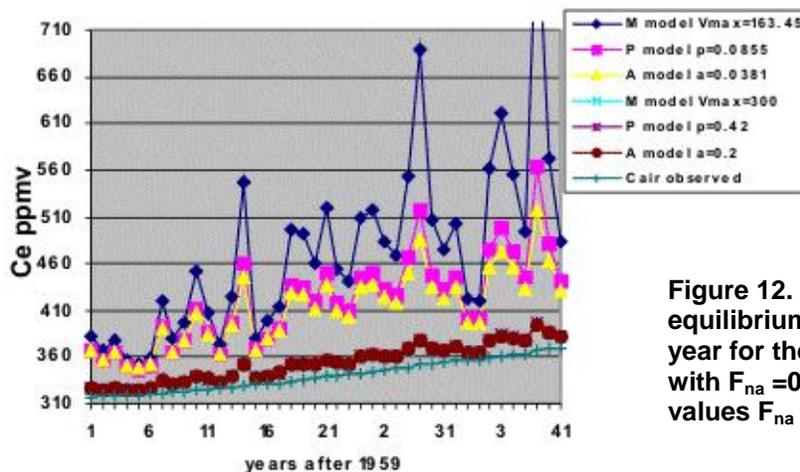

Figure 12. The calculated equilibrium state in each year for the three models with F_{na} =0 and assumed values F_{na} >0.

A strong reduction in the values for C_e are observed when assuming a high natural flux of CO_2 into the atmosphere if the rate constants in the models are increased. This is easily understood. The introduction of the hypothetical natural flux F_{na} into the atmosphere leads to sink flow equations with higher rate constants and these indicate that the whole system may adapt much quicker to changes of the concentration of CO_2 in the atmosphere than when the anthropogenic emission is supposed to be the sole overload of a previously assumed existence of an equilibrium state $(C_e, F_o)_{Fa=0} = (280,150)$.

These numerical exercises are certainly not proof for an extra flux above F_{em} into the atmosphere. But they do demonstrate that the scarce available empirical data may be subject to different interpretations than have been presented until now by those who attribute the rise of CO_2 levels in the atmosphere solely to anthropogenic emissions.

Also, these numerical exercises are a caution to estimates of future changes to the atmospheric CO_2 concentration. The three models used in these exercises each emulate different physical processes and each agrees with the observed recent rise of atmospheric CO_2 concentration. They each demonstrate that the observed recent rise of atmospheric CO_2 concentration may be solely a consequence of the anthropogenic emission or may be solely a result of, for example, desorption from the oceans induced by the temperature rise that preceded it. Furthermore, extrapolation using these models gives very different predictions of future atmospheric CO_2 concentration whatever the cause of the recent rise in atmospheric CO_2 concentration.

4.   Conclusions

It is commonly assumed that the rise in atmospheric carbon dioxide (CO_2) concentration during the twentieth century (approx. 30% rise) is a result of anthropogenic emissions of CO_2 [1,2,3]. However, the annual pulse of anthropogenic CO_2 into the atmosphere should relate to the annual increase of CO_2 in the atmosphere if one is causal of the other, but their variations greatly differ from year to year [4] (see Figure 1).

Qualitative consideration of the carbon cycle suggests the carbon cycle cannot be very sensitive to relatively small disturbances such as the present anthropogenic emissions of CO_2. However, the system could be quite sensitive to temperature. Indeed, the considerations suggest that the relatively large increase of CO_2 concentration in the atmosphere in the twentieth century is likely to have been caused by the increased mean temperature that preceded it. The main cause may be desorption from the oceans. The observed time lag of half a century is not surprising. Assessment of this conclusion requires a quantitative model of the carbon cycle, but such a model cannot be constructed because the rate constants are not known for mechanisms operating in the carbon cycle.

Attribution studies have used three different models to emulate the causes of the rise of CO_2 concentration in the atmosphere in the twentieth century. These numerical exercises are a caution to estimates of future changes to the atmospheric CO_2 concentration. The three models used in these exercises each emulate different physical processes and each agrees with the observed recent rise of atmospheric CO_2 concentration. They each demonstrate that the observed recent rise of atmospheric CO_2 concentration may be solely a consequence of the anthropogenic emission or may be solely a result of, for example, desorption from the oceans induced by the temperature rise that preceded it. Furthermore, extrapolation using these models gives very different

predictions of future atmospheric CO_2 concentration whatever the cause of the recent rise in atmospheric CO_2 concentration.

The above findings cause severe doubt to any 'projections' of future atmospheric CO_2 concentration and to any projections of future climate that consider atmospheric CO_2 concentration to be significant.

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