Carbon cycle modelling and the residence time of natural and anthropogenic atmospheric CO₂: on the construction of the "Greenhouse Effect Global Warming" dogma.

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When you have eliminated the impossible, whatever remains, however improbable, must be the truth.

Sir Arthur Conan Doyle (1859-1930).

Abstract

The three evidences of the United Nations Intergovernmental Panel on Climate Change (IPCC), that the apparent contemporary atmospheric CO_2 increase is anthropogenic, is discussed and rejected: CO_2 measurements from ice cores; CO_2 measurements in air; and carbon isotope data in conjunction with carbon cycle modelling.

It is shown why the ice core method and its results must be rejected; and that current air CO_2 measurements are not validated and their results subjectively "edited". Further it is shown that carbon cycle modelling based on non-equilibrium models, remote from observed reality and chemical laws, made to fit non-representative data through the use of non-linear ocean evasion "buffer" correction factors constructed from a pre-conceived idea, constitute a circular argument and with no scientific validity.

Both radioactive and stable carbon isotopes show that the real atmospheric CO_2 residence time (lifetime) is only about 5 years, and that the amount of fossil-fuel CO_2 in the atmosphere is maximum 4%. Any CO_2 level rise beyond this can only come from a much larger, but natural, carbon reservoir with much higher 13-C/12-C isotope ratio than that of the fossil fuel pool, namely from the ocean, and/or the lithosphere, and/or the Earth's interior.

The apparent annual atmospheric CO_2 level increase, postulated to be anthropogenic, would constitute only some 0.2% of the total annual amount of CO_2 exchanged naturally between the atmosphere and the ocean plus other natural sources and sinks. It is more probable that such a small ripple in the annual natural flow of CO_2 would be caused by natural fluctuations of geophysical processes.

13-C/12-C isotope mass balance calculations show that IPCC's atmospheric residence time of 50-200 years make the atmosphere too light (50% of its current CO_2 mass) to fit its measured 13-C/12-C isotope ratio. This proves why IPCC's wrong model creates its artificial 50% "missing sink". IPCC's 50% inexplicable "missing sink" of about 3 giga-tonnes carbon annually should have led all governments to reject IPCC's model.

When such rejection has not yet occurred, it beautifully shows the result of the "scarethem-to-death" influence principle.

IPCC's "Greenhouse Effect Global Warming" dogma rests on invalid presumptions and a rejectable non-realistic carbon cycle modelling which simply refutes reality, like the existence of carbonated beer or soda "pop" as we know it.

1. Introduction

The atmospheric CO_2 is as important as oxygen for life on Earth. Without CO_2 the plant photosynthetic metabolism would not be possible, and the present life-forms on Earth would vanish. Over the last years it has been constructed a dogma that an apparent increase in atmospheric CO_2 concentration is caused by anthropogenic burning of fossil carbon in the forms of petroleum, coal, and natural gas. This extra atmospheric CO_2 has been claimed to cause global climatic change with a significant atmospheric temperature rise of 1.5 to 4.5°C in the next decennium (Houghton et al., 1990).

There is then indeed a paradox that CO_2 , "The Gas of Life", is now being condemned as the evil "polluting" gas, a gas which will be a threat to people's living on Earth, through a postulated "Global Warming". Even more so when earlier warmer periods in the Earth's history have been characterized as "Climatic Optimum". The construction of the "CO₂ Greenhouse Effect Doom" dogma, based on atmospheric CO_2 level measurements in air and ice cores, carbon cycle modelling, CO_2 residence time (lifetime is here used synonymously), and carbon isotopes, is here examined, and the dogma is rejected on geochemical grounds.

2. The construction of dogmas

In natural sciences the scientific method is based on the testing of hypotheses with the help of (1) empiric observations, (2) laboratory experiments, and (3) theory based on these. If these three parts give identical results, and the theory also is so robust that it will predict future results which will be identical to new observations and experiments, we have found a hypothesis with high significance. With further testing this hypothesis can be exalted to a law of nature, which in turn can be used to reject other hypotheses not supported by observations and experiments. It is of course fundamental that all three major parts of the scientific method is based on sound statistical procedures regarding sampling theory, data representation, significance, error propagation, causality, etc., and should be unbiased and free of advocacy. If any parts of the evidence does not support the hypothesis, the hypothesis should be rejected (Churchman, 1948).

Over the last years, mainly after the fall of the communism, environmentalism seems to have taken the vacant place on the political scene. This new "ism" alleges that Man is destructive, unnatural, evil, and guilty of destructing the environment on this planet. The "proofs" used in this respect are based on selected portions of science, in many cases not based on the objectivity of the scientific method of natural sciences (Sanford, 1992).

Rather the "proofs" concert rejection of reason, and are based on the scientific method of philosophy, where the fundamental 3 parts of the scientific method of natural

sciences do not apply. In natural sciences knowledge is obtained by validating the content of one's mind according to the facts of reality. Truth then corresponds to reality. In philosophy the world is artificial, and truth is redefined to mean coherence among ideas, along the views of the philosopher Immanuel Kant. Hence a dogma can be constructed by ignoring reality, and rather appealing to authority or consensus as invalid substitutes for reason. In philosophy hypotheses can be proposed, validated, and accepted without reference to facts (Sanford, 1992). We see that most often the treatment of what is normal or natural is lacking from the environmental "dooms", and that we only are told what is "abnormal" or "unnatural" without an indisputable baseline reference.

To construct a dogma the methodology is to start with an idea one feels correct and then finding evidence to support it. Reason will then have to be substituted by intuition, belief, faith, emotions, or feelings as the ultimate source of knowledge. Sanford (1992) further points out that the "ecosopher" Arne Næss (1990) begins a book with the section "Beginning with intuitions" and a feeling of "our world in crisis". The dogma will be accepted as truth by the people at large if it will be supported by "authorities", "experts", and well-known important people, not necessarily with their expertise in the relevant field; and especially so if the dogma is being supported by international bodies or assemblies, and given a wide and one-sided coverage by the media. The dogma will be even more appealing if it appears as a self-fulfilling prophecy.

The marketing and influence, i.e. the psychology of persuasion of a dogma, will therefore be important for it to be accepted as truth. The greater the number of people who find any idea correct, the more the idea will appear to be correct among people. People are usually not able to use all relevant information available. They use instead only a single, highly representative piece of the relevant information. When something is presented as a scary scenario, it creates an emotional reaction that makes it difficult to think straight (i.e. consider all facts), especially if there has been created a belief that decisions regarding a common crisis will have to be made fast (Cialdini, 1993). This is what has been called the "scare-them-to-death" approach (Böttcher, 1996), and makes the foundation for creating a doomsday dogma. Stephen Schneider, a climatologist and leading proponent of the global warming theory, says: "To capture the public imagination ... we have to offer up some scary scenarios, make simplified dramatic statements and little mention of any doubts one might have", thereby acting as an advocate for his subjective belief in the "Greenhouse Effect Global Warming" dogma rather than as an objective scientist (Sanford, 1992).

A doomsday dogma made under these conditions will very likely cause a political turmoil. The old saying "Everybody talks about the weather, and nobody does anything about it" is claimed to be invalid when Man's burning of fossil fuel allegedly will change the world's climates. The creation of a " CO_2 Greenhouse Effect Doom" dogma will easily give more power and money to politicians and people at power, letting them introduce legislation and taxation on energy consumption and people's way of living by implementing policies infringing on people's technology, industry, and freedom.

3. The foundation of the CO₂ dogma - early atmospheric CO₂ measurements

In order to construct a "CO₂ Greenhouse Effect Doom" dogma, it will be necessary to justify that (1) pre-industrial atmospheric CO₂ was lower than today, (2) atmospheric CO₂ has steadily risen from its pre-industrial level to today's level, (3) Man's burning

of fossil fuel is causing an increase in atmospheric CO_2 level, (4) hence atmospheric CO_2 must have a long residence time (lifetime), and (5) atmospheric temperatures are increasing due to Man's burning of fossil fuel.

Callendar (1938) revived the hypothesis of "Greenhouse Warming" due to Man's activity, proposed by Arrhenius (1896). Callendar may truly be regarded as the father of the current dogma on man-induced global warming (Jaworowski et al., 1992 b). In order to support his hypothesis, Callendar (1940, 1958) selected atmospheric CO_2 data from the 19th and 20th centuries. Fonselius et al. (1956) showed that the raw data ranged randomly between about 250 and 550 ppmv (parts per million by volume) during this time period, but by selecting the data carefully Callendar was able to present a steadily rising trend from about 290 ppmv for the period 1866 - 1900, to 325 ppmv in 1956.

Callendar was strongly criticized by Slocum (1955), who pointed out a strong bias in Callendar's data selection method. Slocum pointed out that it was statistically impossible to find a trend in the raw data set, and that the total data set showed a constant average of about 335 ppmv over this period from the 19th to the 20th century. Bray (1959) also criticized the selection method of Callendar, who rejected values 10% or more different from the *"general average"*, and even more so when Callendar's *"general average"* was neither defined nor given.

Note that Callendar (1940) wrote: "There is, of course, no danger that the amount of CO_2 in the air will become uncomfortably large because as soon as the excess pressure in the air becomes appreciable, say about 0.0003 atmos., the sea will be able to absorb this gas as fast as it is likely to be produced."

Callendar (1949) repeated this fact, but went on to say: "As the deep waters of the sea move slowly and only shallow contact surface is involved in the carbon-dioxide equilibrium, this reservoir does not immediately control a sudden eruption of the gas such as has occurred this century. It will be hundreds or perhaps thousands of years before the sea absorbs its fair share." Callendar believed that nearly all the CO₂ produced by fossil fuel combustion has remained in the atmosphere. He suggested that the increase in atmospheric CO₂ may account for the observed slight rise in average temperature in northern latitudes during the recent decades.

The "CO₂ Greenhouse Effect Doom" was being substantiated by Revelle & Suess (1957) who wrote: "Thus human beings are now carrying out a large scale geophysical experiment of a kind which could not have happened in the past nor be reproduced in the future. Within a few centuries we are returning to the air and oceans the concentrated organic carbon stored over hundreds of millions of years." But by considering the chemical facts on the exchange of CO₂ between the atmosphere and the ocean, they concluded that only a total increase of 20 to 40% in atmospheric CO₂ can be anticipated by burning all fossil fuel. This is comparable to the 20% increase calculated by Segalstad from the air/sea CO₂ partition coefficient given by chemical equilibrium constants (Segalstad, 1996).

At the same time Craig (1957) pointed out from the natural (by cosmic rays) radiocarbon (14-C) production rate that atmospheric CO_2 is in active exchange with very large CO_2 reservoirs in the ocean and biosphere. However, Callendar (1958) had apparently more faith in his carefully selected CO_2 data, because he commented Craig's conclusion by writing: "Thus, if the increase shown by the measurements

discussed here is even approximately representative of the whole atmosphere, it means that the oceans have not been accepting additional CO_2 on anything like the expected scale."

4. The building of the dogma - recent atmospheric CO₂ measurements

The stir around the atmospheric CO_2 data selected by Callendar made it necessary to start compiling analytical data of contemporary atmospheric CO_2 . 19 North-European stations measured atmospheric CO_2 over a 5 year period from 1955 to 1959. Measuring with a wet-chemical technique the atmospheric CO_2 level was found to vary between approximately 270 and 380 ppmv, with annual means of 315 - 331 ppmv, and there was no tendency of rising or falling atmospheric CO_2 level at any of the 19 stations during this 5 year period (Bischof, 1960). The data are particularly important because they are unselected and therefore free of potential biases from selection procedures, unlike the CO_2 measurements based on the procedures at Mauna Loa (see below). Note that these measurements were taken in an industrial region, and would indeed have shown an increase in CO_2 levels if increasing amounts of anthropogenic CO_2 were accumulating in the atmosphere during this period.

During the same period atmospheric CO_2 measurements were started near the top of the strongly CO_2 -emitting (e.g., Ryan, 1995) Hawaiian Mauna Loa volcano. The reason for the choice of location was that it should be far away from CO_2 -emitting industrial areas. At the Mauna Loa Observatory the measurements were taken with a new infra-red (IR) absorbing instrumental method, never validated versus the accurate wet chemical techniques. Critique has also been directed to the analytical methodology and sampling error problems (Jaworowski et al., 1992 a; and Segalstad, 1996, for further references), and the fact that the results of the measurements were *"edited"* (Bacastow et al., 1985); large portions of raw data were rejected, leaving just a small fraction of the raw data subjected to averaging techniques (Pales & Keeling, 1965).

The acknowledgement in the paper by Pales & Keeling (1965) describes how the Mauna Loa CO_2 monitoring program started: "The Scripps program to monitor CO_2 in the atmosphere and oceans was conceived and initiated by Dr. Roger Revelle who was director of the Scripps Institution of Oceanography while the present work was in progress. Revelle foresaw the geochemical implications of the rise in atmospheric CO_2 resulting from fossil fuel combustion, and he sought means to ensure that this 'large scale geophysical experiment', as he termed it, would be adequately documented as it occurred. During all stages of the present work Revelle was mentor, consultant, antagonist. He shared with us his broad knowledge of earth science and appreciation for the oceans and atmosphere as they really exist, and he inspired us to keep in sight the objectives which he had originally persuaded us to accept." Is this the description of true, unbiased research?

The annual mean CO_2 level as reported from Mauna Loa for 1959 was 315.83 ppmv (15 ppmv lower than the contemporaneous North-European average level), reportedly rising steadily to 351.45 in January 1989 (Keeling et al., 1989), by averaging large daily and seasonal variations (the significance of all their digits not justified), but still within the range of the North European measurements 30-35 years earlier. Hence a rise in global atmospheric CO_2 level has not yet been significantly justified by validated methods and sound statistics.

5. Setting the dogma baseline - CO₂ measurements in ice cores

In order to show that recent atmospheric CO_2 levels have risen due to Man's burning of fossil fuel, it was necessary to show a significant level increase above pre-industrial CO_2 levels. We saw how Callendar was able to set a baseline of about 290 ppmv by rejecting values deviating more than 10% from his desired value.

It was believed that snow accumulating on ice sheets would preserve the contemporaneous atmosphere trapped between snowflakes during snowfalls, so that the CO_2 content of air inclusions in cores from ice sheets should reveal paleoatmospheric CO_2 levels. Jaworowski et al. (1992 b) compiled all such CO_2 data available, finding that CO_2 levels ranged from 140 to 7,400 ppmv. However, such paleoatmospheric CO_2 levels published after 1985 were never reported to be higher than 330 ppmv. Analyses reported in 1982 (Neftel at al., 1982) from the more than 2,000 m deep Byrd ice core (Antarctica), showing unsystematic values from about 190 to 420 ppmv, were falsely "filtered" when the alleged same data showed a rising trend from about 190 ppmv at 35,000 years ago to about 290 ppmv (Callendar's pre-industrial baseline) at 4,000 years ago when re-reported in 1988 (Neftel et al., 1988); shown by Jaworowski et al. (1992 b) in their Fig. 5.

Siegenthaler & Oeschger (1987) were going to make "model calculations that are based on the assumption that the atmospheric $[CO_2]$ increase is due to fossil CO_2 input" and other human activities. For this modelling they constructed a composite diagram of CO_2 level data from Mauna Loa and the Siple (Antarctica) core (see Jaworowski et al., 1992 b, Fig. 10). The data from the Siple core (Neftel et al., 1985) showed the "best" data in terms of a rising CO_2 trend. Part of the reason for this was that the core partially melted across the Equator during transportation before it was analysed (Etheridge et al., 1988), but this was neither mentioned by the analysts nor the researchers later using the data (see Jaworowski et al., 1992 b). Rather it was characterized as "the excellent quality of the ice core" and its CO_2 concentration data "are assumed to represent the global mean concentration history and used as input data to the model" (Siegenthaler & Oeschger, 1987). The two CO_2 level curves were constructed to overlap each other, but they would not match at corresponding age.

In order to make a matching construction between the two age-different nonoverlapping curves, it was necessary to make the assumption that the age of the gas inclusion air would have to be 95 years younger than the age of the enclosing ice. But this was not mentioned by the originators Siegenthaler & Oeschger (1987). This artificial construction has been used as a basis for numerous speculative models of changes in the global carbon cycle.

Oeschger et al. (1985) postulated this "air younger than enclosing ice" thesis from an explanation that the upper 70 m of the ice sheets should be open to air circulation until the gas cavities were sealed. Jaworowski et al. (1992 b) rejected this postulate on the basis that air is constantly driven out of the snow, firn, and ice strata during the snow to ice compression and metamorphism, so that ice deeper than about 1,000 m will have lost all original air inclusions. Deep ice cores will fracture when they are taken to the surface, and ambient air will be trapped in new, secondary inclusions. Both argon-39 and krypton-85 isotopes show that large amounts of ambient air are indeed included in the air inclusions in deep ice cores, and air from the inclusions will not be representative of paleoatmospheres (Jaworowski et al., 1992 b). Contamination from drilling fluids and more than twenty physical-chemical processes occurring in the ice before, during, and after drilling, make ice cores unsuitable for paleoatmospheric work (Jaworowski et al., 1992 b).

The most famous ice core, the Vostok (Antarctica) core, with air inclusions allegedly representing the global paleoatmospheres over the last 160,000 years, show CO_2 levels below 200 ppmv for many tens of thousands of years spanning 30,000 to 110,000 years BP (Barnola et al., 1987). "Most geochemists were convinced that changes such as these could not occur", says Sarmiento (1991) about these low alleged paleoatmospheric CO_2 levels. Such low atmospheric CO_2 levels below approximately 250 ppmv (McKay et al., 1991) would have led to extinction of certain plant species. This has not been recorded by paleobtanists, showing clearly that the ice core CO_2 results are not representative of paleoatmospheres (Jaworowski et al., 1992 b), hence the CO_2 -ice-core-method and its results must be rejected.

6. Justifying the dogma - carbon cycle modelling vs. reality

The Intergovernmental Panel on Climate Change (IPCC) uses "carbon cycle modelling" as part of one of their 3 evidences that the observed atmospheric CO_2 increase is indeed anthropogenic (Houghton et al., 1990; page 14, Section 1.2.5 called "Evidence that the contemporary carbon dioxide increase in anthropogenic", last sentence: "qualitatively consistent with results from carbon cycle modelling").

The present chairman of IPCC, Bert Bolin, entered the "Greenhouse Effect Global Warming" scene with his Bolin & Eriksson (1959) paper. Here they expand on the belief of Callendar (1958) that his apparent atmospheric CO_2 increase must be anthropogenic, and that the reason for this is that the ocean is not dissolving the atmospheric CO_2 which the chemical laws (cf. Henry's Law) say it should.

Bolin & Eriksson (1959) correctly state: "First we see that if the partial pressure of CO_2 varies and the hydrogen ion concentration were kept constant, the relative changes would be the same in the sea as in the atmosphere. As the total amount of CO_2 in the sea is about 50 times that in the air, practically all excess CO_2 delivered to the atmosphere would be taken up by the sea when equilibrium has been established." They further cite Revelle & Suess (1957) that: "most of the CO_2 due to combustion has been transferred into the ocean and that a net increase of CO_2 in the atmosphere of only a few percent has actually occurred. Callendar's deduction has therefore been rejected". They also accept an atmospheric lifetime of about 5 years. This is all in accordance with the laws of chemistry and the carbon isotope ratios of the atmospheric CO_2 (Segalstad, 1996).

Such a situation would not fit the heavily criticized atmospheric CO_2 level rise constructed by Callendar (1958) as characterized by Bolin & Eriksson (1959) as: "deduced from a careful survey of all available measurements". Bolin & Eriksson (1959) goes on to model an ocean without its primary chemical buffer agent calcium carbonate and without organic matter (like all later carbon cycle modellers also have done). They further cite from the discussion of Revelle & Suess (1957) that the sea could have a "buffer" factor: "a buffer mechanism acting in such a way that a 10% increase of the CO_2 -content of the atmosphere need merely be balanced by an increase of about 1% of the total CO_2 content in sea water to reach a new equilibrium".... "The low buffering capacity of the sea mentioned by Revelle and Suess is due to a change in the

dissociation equilibrium between CO_2 and H_2CO_3 on one hand and $HCO_3^{[-]}$ and $CO_3^{[2-]}$ ions on the other."

They neglect, however, the conclusion from the discussion by Revelle & Suess (1957, page 25): "It seems therefore quite improbable that an increase in the atmospheric CO_2 concentration of as much as 10% could have been caused by industrial fuel combustion during the past century, as Callendar's statistical analyses indicate."

It is appropriate as this point to add that if Bolin & Eriksson's conditions in the last paragraph were true, carbonated beer (Bohren, 1987) and soda "pop" as we know it would be an impossibility with their "buffer" factor (see below); rain and fresh water would not show the observed equilibrium pH of 5.7 (Krauskopf, 1979); and experiments would not had shown complete isotopic equilibrium between CO_2 and water in just hours, which in turn is the prerequisite for routine stable isotope analysis involving CO_2 (Gonfiantini, 1981).

Experimentally it has been found that CO_2 and pure water at 25 degrees C reaches 99% isotopic equilibrium after 30 hours and 52 minutes; after shaking (like wave agitation) 99% equilibrium is reached after 4 hours and 37 minutes (Gonfiantini, 1981). At 350 ppmv CO_2 in the air, the equilibrium concentration of carbonic acid in pure water will be about 0.00001 molal at 25 degrees C. This chemical equilibrium is reached within 20 seconds (Stumm & Morgan, 1970). At the same temperature, at pH-values between 7 and 9, CO_2 reaches 99% chemical equilibrium with water and calcium carbonate in about 100 seconds (Dreybrodt et al., 1996).

Carbonated beer, soda "pop", and champagne are good analogues to the CO_2 distribution between atmosphere and ocean. In both cases they manifest the equilibrium governed by Henry's Law: the partial pressure of CO_2 in the air will be proportional to the concentration of CO_2 dissolved in water. The proportional constant is the Henry's Law Constant, giving us a partition coefficient for CO_2 between air and water of approximately 1:50 (Revelle & Suess, 1957; Skirrow, 1975; Jaworowski et al., 1992 a; Segalstad, 1996). We have all experienced that carbonated drinks contain much more (about 50 times higher concentration) CO_2 than the air under the bottle cap above the carbonated water. This fact is in harsh contradiction to the Bolin & Eriksson's "buffer" factor claim that the air will contain much more CO_2 than the carbonated water, when trying to increase the partial pressure of CO_2 from the assumed pre-industrial level of 290 ppmv (pressure less than 0.0003 atmospheres) to a pressure of about 3 atmospheres in the CO_2 above the carbonated water in the brewed drink bottle.

Bolin & Eriksson's "buffer" factor would give about 10 times higher CO_2 concentration in air vs. sea water at about 0.0003 atmospheres CO_2 partial pressure, increasing dramatically to an air/water CO_2 partition coefficient of about 50:1 at a CO_2 partial pressure of about 0.003 atmospheres (10 times the assumed pre-industrial level; Bacastow & Keeling, 1973; see Section 7 below for more on the "buffer" factor).

From their untenable conditions Bolin & Eriksson state: "It is obvious that an addition of CO_2 to the atmosphere will only slightly change the CO_2 content of the sea but appreciably effect the CO_2 content of the atmosphere."... "The decisive factor is instead the rate of overturning of the deep sea." From: "the fact that the top layer of the ocean only need to absorb a small amount of CO_2 from the atmosphere", and a CO_2 lifetime of 500 years for the deep ocean, Bolin & Eriksson (1959) reach the conclusion

that: "an increase of the atmosphere's content of CO_2 of about 10 percent would have occurred in 1954. This value compares very favourably with the value of 10% given by Callendar (1958) as the total increase until 1955 deduced from a careful survey of all available measurements." By over-simplifying the properties of the ocean the authors were able to construct a non-equilibrium model remote from observed reality and chemical laws, fitting the non-representative data of Callendar (1958).

At this point one should note that the ocean is composed of more than its 75 m thick top layer and its deep, and that it indeed contains organics. The residence time of suspended POC (particular organic carbon; carbon pool of about 1000 giga-tonnes; some 130% of the atmospheric carbon pool) in the deep sea is only 5-10 years. This alone would consume all possible man-made CO_2 from the total fossil fuel reservoir (some 7200 giga-tonnes) if burned during the next 300 years, because this covers 6 to 15 turnovers of the upper-ocean pool of POC, based on radiocarbon (carbon-14) studies (Toggweiler, 1990; Druffel & Williams, 1990; see also Jaworowski et al., 1992 a). The alleged long lifetime of 500 years for carbon diffusing to the deep ocean is of no relevance to the debate on the fate of anthropogenic CO_2 and the "Greenhouse Effect", because POC can sink to the bottom of the ocean in less than a year (Toggweiler, 1990).

7. Boost for the dogma - the evasion "buffer" factor

Bacastow & Keeling (1973) elaborate further on Bolin & Eriksson's ocean "buffer" factor, calling it an *"evasion factor"* (also called the *"Revelle factor"*; Keeling & Bacastow, 1977), because the "buffer" factor is not related to a buffer in the chemical sense. A real buffer can namely be defined as a reaction system which modifies or controls the value of an intensive (i.e. mass independent) thermodynamic variable (pressure, temperature, concentration, pH, etc.). The carbonate system in the sea will act as a pH buffer, by the presence of a weak acid (H₂CO₃) and a salt of the acid (CaCO₃). The concentration of CO₂ (g) in the atmosphere and of Ca²⁺ (aq) in the ocean will in the equilibrium Earth system also be buffered by the presence of CaCO₃ at a given temperature (Segalstad, 1996).

Bacastow & Keeling (1973) show their calculated evasion factors for average ocean surface water as a function of "the partial pressure of CO_2 exerted by the ocean surface water, P_m , and the total inorganic carbon in the water", here designated C_{total} , relative to the respective values they assumed for preindustrial times. The evasion factor is constructed such that: "if industrial CO_2 production continues to increase, however, the evasion factor will rise with P_m according to the relation shown in Fig. 3. At the same time the short-term capacity of the oceans to absorb CO_2 from the atmosphere will diminish" (Bacastow & Keeling, 1973). The evasion "buffer" factor is defined as

$$\left[\left(P_{m} - P_{m,o} \right) / P_{m,o} \right] / \left[\left(C_{total} - C_{total,o} \right) / C_{total,o} \right]$$

at constant sea water alkalinity. $P_{m,o}$ and $C_{total,o}$ are "preindustrial values" of P_m and C_{total} , respectively (Bacastow & Keeling, 1973). Slightly different definitions are used in various contexts (Kohlmaier, 1979). We clearly see that this evasion "buffer" factor is ideologically defined from an assumed model (atmospheric anthropogenic CO_2 increase) and an assumed pre-industrial value for the CO_2 level. These assumed pre-industrial values are calculated by an iteration technique (Bacastow, 1981) from so-called "apparent dissociation constants", established from empiric measurements at

sea, but showing considerable variation between different authors (Takahashi et al., 1976). "There continues to be considerable uncertainty as to the magnitude of the gas exchange coefficient in the ocean", says Sarmiento (1991). The ideologically constructed non-linear evasion "buffer" factor or "Revelle factor" is later referred to as if it was established as a law of nature: "known from thermodynamic data" (Keeling & Bacastow, 1977); a gross exaggeration, giving a false scientific credibility to the method and the results from carbon cycle modelling using this "buffer" factor.

This is a beautiful example of circular logic in action, when such a construction as the evasion factor is used in all carbon cycle models which the IPCC base their anthropogenic CO_2 -level-rise evidence on. Using the evasion "buffer" factor instead of the chemical Henry's Law will always explain any CO_2 level rise as being anthropogenic, because that very idea was the basis for the construction of the evasion "buffer" correction factor.

The results of carbon cycle modelling using the evasion "buffer" factor is shown in Table 1. Some go even further: according to Revelle & Munk (1977) "the atmospheric carbon dioxide content could rise to about 5 times the preindustrial value in the early part of the twenty-second century", i.e. in slightly more than 100 years from now.

		After 1000 GT		After 6000 GT	
	Pre-in- dustrial content	Content (GT)	% in- crease	Content (GT)	% in- crease
Atmosphere	700	840	20	1880	170
Terrestrial system	3000	3110	4	3655	22
Ocean surface layer	1000	1020	2	1115	12
Deep ocean	35000	35730	2	39050	12

Table 1. Carbon contents in giga-tonnes (GT) for a four-reservoir non-linear nonequilibrium model during the assumed initial pre-industrial situation, after the introduction of 1,000 GT carbon, and after the introduction of 6,000 GT carbon in the form of CO_2 to the atmosphere, using an ideological evasion "buffer" correction factor of about 9. The first introduction corresponds to the total input from fossil fuel up to about the year 2000; the second is roughly equal to the known accessible reserves of fossil carbon. After Rodhe (1992).

In linear systems the fluxes between the reservoirs are linearly related to the reservoir contents, like in chemical equilibrium systems. In non-linear modelling, non-equilibrium complex relations are assumed, like for "logistical growth" models. The results after introduction of carbon to the atmosphere in Table 1 is from a simplified non-linear (non-chemical-equilibrium) non-steady state carbon cycle model with no calcium carbonate and no sea organics. The ideological evasion "buffer" correction factor is set at about 9. As a consequence of this factor a substantial increase in atmospheric CO_2 from introduction of a certain amount of fossil carbon is mathematically balanced by a small increase in carbon cycle models give rise to substantial calculated variations between the reservoirs. The atmospheric reservoir is

in such simplified non-realistic models much more perturbed than any of the other reservoirs (Rodhe, 1992). If this mechanism were true, it would be impossible for breweries to put their CO_2 in beer or soda "pop".

The non-linear modelling results in Table 1 have been made to explain the apparent rise in atmospheric CO₂ today of 20% (vs. an assumed pre-industrial level) from fossil fuel burning by default, and predict a 170% increase in CO₂ when we have burned all our fossil fuel. The sea would in these models only see a maximum rise in CO₂ of 12%.

Holmén (1992) emphasizes that such "box models and box diffusion models have very few degrees of freedom and they must describe physical, chemical, and biological processes very crudely. They are based on empirical relations rather than on first principles."

8. Trouble for the dogma - the CO₂ "missing sink"

The next problem is that the Mauna Loa atmospheric CO_2 level increase only accounts for approximately 50% of the expected increase from looking at the amount of CO_2 formed from production data for the burning of fossil fuels (e.g., Kerr, 1992). This annual discrepancy of some 3 giga-tonnes of carbon is in the literature called *"the missing sink"* (analogous to "the missing link"; Holmén, 1992). When trying to find this "missing sink" in the biosphere, carbon cycle modelling has shown that deforestation must have contributed a large amount of CO_2 to the atmosphere. So instead of finding "the missing sink" in the terrestrial biosphere, they find another CO_2 source! This makes "the missing sink" problem yet more severe.

Trabalka (1985) summarizes the status of carbon cycle modelling and its missing sinks (Trabalka et al., 1985) by: "As a first approximation in the validation of models, it should be possible to compute a balanced global carbon budget for the contemporary period; to date this has not been achievable and the reasons are still uncertain." . . . "These models produce estimates of past atmospheric CO_2 levels that are inconsistent with the historical atmospheric CO_2 increase. This inconsistency implies that significant errors in projections are possible using current carbon cycle models."

Bolin's (1986) conclusion regarding carbon cycle models is on the contrary: "We understand the basic features of the global carbon cycle quite well. It has been possible to construct quantitative models which can be used as a general guide for the projection of future CO_2 concentrations in the atmosphere as a result of given emission scenarios". This is in high contrast to Holmén (1992), who concludes his book chapter on "The Global Carbon Cycle" with: "obviously our knowledge of the global cycle of carbon is inadequate to get ends to meet".

A 50% error, i.e. the enormous amount of about 3 giga-tonnes of carbon annually not explained by a model, would normally lead to complete rejection of the model and its hypothesis using the scientific method of natural sciences. Still the 50% inexplicable error in the IPCC argumentation has strangely enough not yet caused all governments to reject the IPCC model. This fact beautifully shows the result of the "scare-them-to-death" principle (Section 2 above).

9. Problems for the dogma - CO₂ residence time

A number of lifetimes and timescales are being used in both scientific and policy context to describe the behavior of heat-absorbing gases in the atmosphere. These concepts are very important for the discussion on whether anthropogenic CO_2 will be accumulated in the atmosphere and exert an additional global "Greenhouse Effect" warming. If each CO_2 molecule in the atmosphere has a short lifetime, it means that the CO_2 molecules will be removed fast from the atmosphere to be absorbed in another reservoir.

A number of definitions for lifetimes of atmospheric CO_2 has been introduced, like "residence time", "transit time", "response time", "e-folding time", "turnover time", "adjustment time", and more varieties of these (e.g., Rodhe, 1992; O'Neill et al., 1994; Rodhe & Björkström, 1979), to try to explain why atmospheric CO_2 allegedly cannot have the short lifetime of approximately 5 years which numerous measurements of different kinds show. It is being said that because we observe the atmospheric CO_2 level increase, which apparently has not been dissolved by the sea, the turnover time of atmospheric CO_2 "of the combined system" must be several hundred years (Rodhe, 1992).

IPCC defines lifetime for CO_2 as the time required for the atmosphere to adjust to a future equilibrium state if emissions change abruptly, and gives a lifetime of 50-200 years in parentheses (Houghton et al., 1990). Their footnote No. 4 to their Table 1.1 explains: "For each gas in the table, except CO_2 , the "lifetime" is defined here as the ratio of the atmospheric content to the total rate of removal. This time scale also characterizes the rate of adjustment of the atmospheric concentrations if the emission rates are changed abruptly. CO_2 is a special case since it has no real sinks, but is merely circulated between various reservoirs (atmosphere, ocean, biota). The "lifetime" of CO_2 given in the table is a rough indication of the time it would take for the CO_2 concentration to adjust to changes in the emissions . . .".

O'Neill et al. (1994) criticize the IPCC report (Houghton et al., 1990) because it "offers no rigorous definition of lifetime; for the purpose of defining Global Warming Potentials, it instead presents integrations of impulse-response functions over several finite time intervals. Each of these estimates has its own strengths and weaknesses. Taken together, however, they create confusion over what "lifetime" means, how to calculate it, and how it relates to other timescales." IPCC's assertion that CO₂ has no real sinks, have been rejected elsewhere (Jaworowski et al., 1992 a; Segalstad, 1996).

The atmospheric residence time (i.e. lifetime; turnover time) of CO_2 has been quantified based on measurements of natural radiocarbon (carbon-14) levels in the atmosphere and the ocean surface; the changes in those levels caused by anthropogenic effects, like "bomb carbon-14" added to the atmosphere by nuclear explosions; and the "Suess Effect" caused by the addition of old carbon-14-free CO_2 from combustion of fossil fuels; and the application of gas exchange theory to rates determined for the inert radioactive gas radon-222. The results from these measurements are shown in Table 2, mainly based on the compilation by Sundquist (1985), in addition to the solubility data of Murray (1992), and the carbon-13/carbon-12 mass-balance calculation of Segalstad (1992). Both of the last two recent methods happened to give a lifetime of 5.4 years based on completely different methods.

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

Table 2. Atmospheric residence time (i.e. lifetime, turnover time) of CO_2 , mainly based on the compilation by Sundquist (1985; for references in brackets).

Judged from the data of Table 2 there is apparently very little disagreement from early works to later works regardless of measurement method, that the atmospheric CO_2 lifetime is quite short, near 5 years. This fact was also acknowledged early by IPCC's chairman Bolin (Bolin & Eriksson, 1959).

We should also note that a large number of the atmospheric CO_2 lifetime measurements are based on anthropogenic additions of CO_2 to the atmosphere by "bomb carbon-14". It is important for the understanding of the robustness of the ocean to deal with the anthropogenic extra CO_2 that the measured lifetimes are within the same range as for natural carbon-14 before and after the nuclear bomb tests in the early nineteen-sixties. They are also coincident with lifetimes found when considering anthropogenic CO_2 from Man's burning of fossil fuel, both from carbon-14 as well as for carbon-13/carbon-12 isotopes. The measured lifetimes in Table 2 therefore represent the real lifetime of atmospheric CO_2 in dynamic contact with all its sources and sinks with "perturbations" included. Hence other "lifetimes" found by non-linear carbon cycle modelling are irrelevant.

The short atmospheric CO_2 lifetime of 5 years means that CO_2 quickly is being taken out of the atmospheric reservoir, and that approximately 135 giga-tonnes (about 18%) of the atmospheric CO_2 pool is exchanged each year. This large and fast natural CO_2 cycling flux is far more than the approximately 6 giga-tonnes of carbon in the anthropogenic fossil fuel CO_2 now contributed annually to the atmosphere, creating so much political turmoil (Segalstad, 1992; 1996).

Supporters of the "Greenhouse Effect Global Warming" dogma have apparently not been satisfied with these facts based on numerous measurements and methods. They go on by saying that because we observe the atmospheric CO_2 level increase, it must be caused by Man's burning of fossil fuel, and the "lifetime" of atmospheric CO_2 must be 50-200 years (Houghton et al., 1990). Hence, they say, when we construct nonlinear (non-proportional and non-chemical-equilibrium) non-steady-state systems for the fluxes between the ocean surface layer, the atmosphere, and the terrestrial system, the decay time of man-made carbon into the atmosphere must be much longer than the turn-over time (Rodhe & Björkström, 1979). Because if we now use a constructed evasion "buffer" factor (Section 5 and 6 above) of 10, the atmospheric CO_2 "lifetime" will be 10 times the measured (real) lifetime of 5 years, namely 50 years or more (Rodhe & Björkström, 1979; Rodhe, 1992).

To rephrase; an apparent atmospheric CO_2 level rise, assumed to be due to Man's burning of fossil fuel, is being treated with non-linear (non-proportional and non-chemical-equilibrium) non-steady-state modelling, giving theoretical far longer "lifetimes" than actually measured. When this is not explained to the readers, they are led astray to get the impression that the "artificial" un-real model "lifetimes" are real lifetimes.

Or as O'Neill et al. (1994) phrase it: "A growing array of timescales are being extracted from carbon cycle models and data and their relationships have not been clear." . . . "This discrepancy has not been adequately explained and is causing confusion in the literature concerned with the atmospheric "lifetime" of anthropogenic CO_2 "... "Considering the policy implications of such numbers, it is important that their meanings and relationships be fully clarified."

Rodhe & Björkström (1979) conclude their treatment of carbon cycle and CO₂

lifetime modelling by: "Naturally, we do not claim that such very simplified models of the carbon cycle, which we have studied, contain the final answer to the very complex question of how nature will distribute the man-made CO_2 emissions between the major reservoirs. That question should be studied with the aid of much more sophisticated models which take into account more of our knowledge about the physical and chemical processes involved."

10. The breakdown of the dogma - carbon isotopes

Suess (1955) estimated for 1953, based on the carbon-14 "Suess Effect" (dilution of the atmospheric CO_2 with CO_2 from burning of fossil fuel, void of carbon-14), "that the worldwide contamination of the Earth's atmosphere with artificial CO_2 probably amounts to less than 1 percent". Revelle & Suess (1957) calculated on the basis of new carbon-14 data that the amount of atmospheric " CO_2 derived from industrial fuel combustion" would be 1.73% for an atmospheric CO_2 lifetime of 7 years, and 1.2% for a CO_2 lifetime of 5 years.

This is in conflict with IPCC researchers, who assume that 21% of our present-day (as of December 1988) atmospheric CO_2 , the assumed rise in CO_2 level since the industrial revolution, has been contributed from Man's burning of fossil fuel (Houghton et al., 1990).

This large contradiction between the carbon-14 measurements and the dogma, has worried many researchers. In order to make Suess' measurements fit the dogma, it would be necessary to mix the atmospheric fossil-fuel CO_2 with CO_2 from a different carbon reservoir five times larger than the atmosphere alone (Broecker et al., 1979). It was alternatively proposed that the carbon-14-labelled CO_2 would act completely differently than the "ordinary" CO_2 : "However, the system's responses are not the same for the CO_2 concentration and for isotopic ratios" (Oeschger & Siegenthaler, 1978). The explanation is given that the CO_2 levels will be governed by the constructed evasion "buffer" correction factor, while on the other hand (strangely enough) the isotope ratios of the atoms in the very same CO_2 molecules would be unaffected by the evasion "buffer" factor, and further: "would be equal in both reservoirs [the atmospheric CO_2 increase is larger than the Suess effect" (Oeschger & Siegenthaler, 1978). This cannot be accepted, when all chemical and isotopic experiments indicate that equilibrium between CO_2 and water is obtained within a few hours (see Section 5 above).

Ratios between the carbon-13 and carbon-12 stable isotopes are commonly expressed in permil by a so-called delta-13-C notation being the standard-normalized difference from the standard, multiplied by 1000. The international standard for stable carbon isotopes is the Pee Dee Belemnite (PDB) calcium carbonate.

 CO_2 from combustion of fossil fuel and from biospheric materials have delta-13-C values near -26 permil. "Natural" CO_2 has delta-13-C values of -7 permil in equilibrium with CO_2 dissolved in the hydrosphere and in marine calcium carbonate. Mixing these two atmospheric CO_2 components: IPCC's 21% CO_2 from fossil fuel burning + 79% "natural" CO_2 should give a delta-13-C of the present atmospheric CO_2 of approximately -11 permil, calculated by isotopic mass balance (Segalstad, 1992; 1996).

This atmospheric CO₂ delta-13-C mixing value of -11 permil to be expected from

IPCC's model is not found in actual measurements. Keeling et al. (1989) reported a measured atmospheric delta-13-C value of -7.489 permil in December 1978, decreasing to -7.807 permil in December 1988 (the significance of all their digits not justified). These values are close to the value of the natural atmospheric CO_2 reservoir, far from the delta-13-C value of -11 permil expected from the IPCC model.

From the measured delta-13-C values in atmospheric CO_2 we can by isotopic mass balance also calculate that the amount of fossil-fuel CO_2 in the atmosphere is equal to or less than 4%, supporting the carbon-14 "Suess Effect" evidence. Hence the IPCC model is neither supported by radioactive nor stable carbon isotope evidence (Segalstad, 1992; 1993; 1996).

To explain this apparent contradiction versus the IPCC model, the observed delta-13-C value of atmospheric CO_2 "must be affected by other heavier [i.e. with high delta-13-C values] carbon sources, such as is derived from the air-sea exchange process" (Inoue & Sugimura, 1985). One way to make this happen, would be if the isotopic exchange from air to sea were different from the isotopic exchange from sea to air; i.e. a gross non-equilibrium situation would be required. Siegenthaler & Münnich (1981) were able to construct such a simple theoretical kinetic, non-equilibrium model: "Diffusion of CO_2 into the water, which is rate limiting for mean oceanic conditions, fractionates the carbon isotopes only little. 13-C/12-C fractionations are found to be -1.8 to -2.3 permil for atmosphere-to-ocean transfer, and -9.7 to -10.2 permil for ocean-to-atmosphere transfer."

Inoue & Sugimura (1985) attempted to verify these kinetic isotope fractionations experimentally at three temperatures: 288.2; 296.2; and 303.2 Kelvin, versus their equilibrium values of -8.78; -7.86; and -7.10 permil, respectively, all with uncertainty given as +/- 0.05 permil. Their reported air to sea fractionations at these temperatures were -2 +/- 3; -4 +/- 5; and -5 +/- 7 permil, respectively. Their sea to air fractionations were found to be -10 +/- 4; -13 +/- 6; and -12 +/- 7 permil, respectively. (Reported alpha fractionation factors and uncertainties have here been recalculated to alpha minus one, multiplied by 1000, to get comparable fractionation values). They conclude that the agreement is fairly good with the theoretically deduced values of Siegenthaler & Münnich (1981). Looking at the reported uncertainties, however, the experimental data cannot be grouped in three populations: their air-to-sea and sea-to-air data are not significantly different from their reported air/sea/air equilibrium value at the three different temperatures. Hence the experimental data cannot be used as evidence for the proposed theoretical difference in isotopic fractionation for air/sea versus sea/air CO_2 transfer due to differences in kinetic isotope fractionation.

Siegenthaler & Oeschger (1987) touch in their carbon cycle modelling, with carbon isotopes included, on the possibility that the apparent atmospheric CO_2 level increase is due to marine degassing instead of accumulation of anthropogenic CO_2 : "We will also discuss the sensitivity of the model results to uncertainties in the ice core data, to different model assumptions and to the (unlikely) possibility that the non-fossil CO_2 was not of biospheric, but rather of marine origin." The word "unlikely" in parentheses is indeed their wording. Their modelling shows ambiguously that: "as expected, the results are similar to those for the fossil-only input". But their modelling shows a discrepancy with the ice core CO_2 data, in addition to: "it is somewhat surprising that observations and model agree for 13-C but not for 14-C; this can, however, not be discussed here any further". In their abstract, however, they conclude on the contrary: "Calculated 13-C and 14-C time histories agree well with the observed changes."

The carbon cycle modelling of Siegenthaler & Oeschger (1987) run into several problems making their models fit all the data, leading them to write: "One possibility is that the assumptions underlying our results are not fully correct, i.e., that either the Siple ice core data deviate from the true atmospheric concentration history or that the carbon cycle models used do not yield the correct fluxes. If we dismiss these possibilities, then other carbon sinks than the ocean seem to exist." For the lack of validity of the Siple ice core, see Section 4 above.

Based on this kind of modelling, IPCC states as part of their "evidence that the contemporary carbon dioxide increase is anthropogenic" (their Section 1.2.5; Houghton, 1990): "Third, the observed isotopic trends of 13-C and 14-C agree qualitatively with those expected due to the CO_2 emissions from fossil fuels and the biosphere, and they are quantitatively consistent with the results from carbon cycle modelling." Such a correspondence is, however, not evident to the present author.

Segalstad (1992; 1993; 1996) concluded from 13-C/12-C isotope mass balance calculations, in accordance with the 14-C data, that at least 96% of the current atmospheric CO_2 is isotopically indistinguishable from non-fossil-fuel sources, i.e. natural marine and juvenile sources from the Earth's interior. Hence, for the atmospheric CO_2 budget, marine equilibration and degassing, and juvenile degassing from e.g. volcanic sources, must be much more important; and the sum of burning of fossil-fuel and biogenic releases (4%) much less important, than assumed (21% of atmospheric CO_2) by the authors of the IPCC model (Houghton et al., 1990).

The apparent annual atmospheric CO_2 level increase, postulated to be anthropogenic, would constitute only some 0.2% of the total annual amount of CO_2 exchanged naturally between the atmosphere and the ocean plus other natural sources and sinks (Section 9 above). It is more probable that such a small ripple in the annual natural flow of CO_2 is caused by natural fluctuations of geophysical processes. We have no database for disproving this judgment (Trabalka, 1985). Like Brewer (1983) says it: "Nature has vast resources with which to fool us . . .".

Segalstad's mass balance calculations show that IPCC's atmospheric CO_2 lifetime of 50-200 years will make the atmosphere too light (50% of its current CO_2 mass) to fit its measured 13-C/12-C ratio. This proves why IPCC's wrong model creates its artificial 50% "missing sink" (Segalstad, 1996).

11. Conclusion

The atmospheric CO_2 level is ultimately determined by geologic processes. The carbon on the Earth's surface has come from CO_2 degassing of the Earth's interior, which has released about half of its estimated CO_2 contents throughout Earth's history during the 4,500 million years up to now (Holland, 1984). Important geologic processes are volcanism and erosion, releasing carbon from the lithosphere and the Earth's interior to the atmosphere - ocean - biosphere system. These processes are counteracted by sedimentation of carbonate and organic carbon in the hydrosphere (mainly the ocean). The balance between these two main processes determines the CO_2 level in the atmosphere (e.g., Kramer, 1965; McDuff & Morel, 1980; Walker & Drever, 1988; Holmén, 1992). "Thus, while seawater alkalinity is directly controlled by the formation of calcium carbonate as its major sedimentary sink, it is also controlled indirectly by carbonate metamorphism which buffers the CO_2 content of the atmosphere" (McDuff In addition there is a short-term carbon cycle dominated by an exchange of CO_2 between the atmosphere and biosphere through photosynthesis, respiration, and putrefaction (decay), and similarly between aqueous CO_2 (including its products of hydrolysis and protolysis) and marine organic matter (Walker & Drever, 1988).

Analogously to the transfer of anthropogenic CO_2 to the atmosphere, it seems appropriate to cite Walker (1994): "Consider, now some perturbation of the system for example, the doomsday perturbation that suddenly stops photosynthesis. In 20 years or so, all the carbon in the biota reservoir will be released to the atmosphere, leading initially to a large increase in the amount of carbon dioxide in the atmosphere. But in no time at all, in terms of human generations, that extra carbon dioxide will work its way down into the very deep sea reservoir where the addition of 2×10^{17} moles to the 30×10^{17} moles already there will have little effect. The system will not end up with a lot of extra carbon dioxide in the atmosphere, even if photosynthesis stops completely. The figure shows also the fossil fuel rate, which is smaller than the rate of photosynthesis."

It is nature's coupling between the temporary, short-lived atmospheric reservoir, with 0.5×10^{17} moles CO₂, and the relatively enormous oceanic reservoir, with 30×10^{17} moles of dissolved (and hydrolyzed and protolyzed) CO₂ in contact with calcium carbonate, that determines the amount of CO₂ in the atmosphere. This coupling is in turn coupled to the much larger lithospheric reservoir. The rates and fluxes of the latter coupling control the amount of carbon in the surface reservoir of the Earth. All kinds of measurements show that the real residence time of atmospheric CO₂ is about 5 years.

Chemical and isotope equilibrium considerations and the short CO_2 residence time (lifetime) can fully explain the carbon cycle of the Earth. The conclusion of such reasoning is that any atmospheric CO_2 level rise beyond 4% cannot be explained by accumulation of CO_2 from Man's burning of fossil fuel. An apparent CO_2 rise can only come from a much larger, but natural, carbon reservoir with much higher delta-13-C than the fossil fuel pool, namely from the ocean, and/or the lithosphere, and/or the Earth's interior. CO_2 degassing from the oceans instead of IPCC's anthropogenic accumulation is indeed made probable by the measurements of a larger CO_2 increase in Atlantic surface waters than in the contemporaneous atmosphere (Takahashi, 1961; 1979). Kondratyev (1988) argues that: "The fact is that the atmospheric CO_2 content may be controlled by the climate" and not the opposite.

Trabalka (1985) concluded: "The available data on past fluctuations in atmospheric CO_2 and climate suggest that our current carbon cycle models, which emphasize human perturbations, may be missing natural feedback components involving both terrestrial and marine systems, perhaps even climate-induced "mode switches" in ocean circulation patterns, which could be very important in understanding changes in both climate and the carbon cycle over the next century."

Such conclusions will not make the large "doomsday" headings in the news media, will not make the politicians implement extra taxes or legislations, will not make expensive conferences organized by the United Nations or other international bodies, will not make environmental organizations preach about the wickedness of Man, and will not bring any research support money from governments or research foundations.

IPCC (Houghton et al., 1990) claims in their Section 1.2.5 three evidences that the contemporary atmospheric CO_2 increase is anthropogenic: (1) CO_2 measurements from ice cores show a 21% rise from 280 to 353 ppmv (parts per million by volume) since pre-industrial times; (2) the atmospheric CO_2 increase closely parallels the accumulated emission trends from fossil fuel combustion and from land use changes, although the annual increase has been smaller each year than the fossil CO_2 input [some 50% deviation, e.g. Kerr, 1992]; (3) the observed isotopic trends of 13-C and 14-C agree qualitatively with those expected due to the CO_2 emissions from fossil fuels and the biosphere, and they are quantitatively consistent with results from carbon cycle modelling.

Jaworowski et al. (1992 a, 1992 b) reviewed published CO_2 measurements from ice cores, and rejected this method because it cannot give reliable data for neither the CO_2 level history of paleoatmospheres nor the pre-industrial atmospheric CO_2 level. The paper by Jaworowski et al. (1992 a) and this paper have addressed recent atmospheric CO_2 measurements by a non-validated instrumental method with results visually selected and "edited", deviating from unselected measurements of constant CO_2 levels by the highly accurate wet-chemical technique at 19 stations in Northern Europe (Bischof, 1960). Hence a rise in global atmospheric CO_2 level has not yet been significantly justified by validated methods and sound statistics. Stable carbon isotope mass balance calculations based on 13-C/12-C measurements prove why IPCC's wrong model creates their inexplicable 50% "missing sink" (Segalstad, 1996).

Carbon isotopic trends agree *qualitatively* with fossil fuel CO_2 emissions like stated by IPCC, but show *quantitatively* a fossil fuel CO_2 component of maximum 4 % versus the 21% claimed by IPCC. This paper has further examined and rejected the carbon cycle modelling forming the basis for IPCC evidence. It is shown that carbon cycle modelling based on non-equilibrium models, remote from observed reality and chemical laws, made to fit non-representative data through the use of non-linear correction "buffer" factors constructed from a pre-conceived hypothesis, constitute a circular argument and with no scientific validity. IPCC's non-realistic carbon cycle modelling will simply refute reality, like the existence of carbonated beer or soda "pop" as we know it.

The "Greenhouse Effect Global Warming" dogma is based on the hypothesis that Man's release of CO_2 from fossil fuel burning will cause this extra atmospheric CO_2 to increase the temperature of the lower atmosphere. It is important to note that due to the atmosphere's extremely low heat capacity, the heat energy accumulated in the atmosphere from this process will be minute and unable to change the Earth's climate. This compared to the enormous heat energy stored in the oceans, and the enormous heat energy required to melt the cryosphere (ice sheets, sea ice, permafrost, and glaciers). Hence it will be impossible to melt the Earth's ice caps and thereby increase the sea level just by increasing the heat energy of the atmosphere through a few percent of added heat absorbing anthropogenic CO_2 in the lower atmosphere (Segalstad, 1996). Further, there exists no proof of a constantly rising trend for the temperature of the world's lower atmosphere since the industrial revolution (e.g., Jaworowski et al., 1992 a; Michaels & Knappenberger, 1996).

A dogma is, according to dictionaries, considered an arrogant and authoritative declaration of opinion based on a priori principles, not on induction, and often as a sacrament or commandment for religious belief. Review of the basis for the "Greenhouse Effect Global Warming" doom makes its components appear neither supported by reality nor the scientific method of natural sciences, making it rather a preconceived idea or tenet sharing most features of a dogma.

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References

Arrhenius, S. (1896): On the influence of carbonic acid in the air upon the temperature of the ground. *London, Edinburgh, Dublin Philos. Mag. J. Sci., Ser. 5, 41,* 237-276.

Bacastow, R. (1981): Numerical evaluation of the evasion factor. *In:* Bolin, B. (Ed.): *Carbon cycle modelling (SCOPE 16).* John Wiley & Sons, 95-101.

Bacastow, R. & Keeling, C.D. (1973): Atmospheric carbon dioxide and radiocarbon in the natural carbon cycle: II. Changes from A.D. 1700 to 2070 as deduced from a geochemical model. *In:* Woodwell, G.M. & Pecan, E.V. (Eds.): *Carbon and the biosphere.* CONF-72051. Technical Information Center, Office of Information Services, United States Atomic Energy Commission, 86-135.

Bacastow, R., Keeling, C.D. & Whorp, T.P. (1985): Seasonal amplitude increase in atmospheric CO_2 concentration at Mauna Loa, Hawaii, 1959-1982. *Journal of Geophysical Research 90,* 10529-10540.

Barnola, J.M., Raynaud, D., Korotkevich, Y.S. & Lorius, C. (1987): Vostok ice core provides 160,000-year record of atmospheric CO₂. *Nature 329,* 408-414.

Bischof, W. (1960): Periodical variations of the atmospheric CO_2 -content in Scandinavia. *Tellus 12*, 216-226.

Bohren, C.F. (1987): *Clouds in a glass of beer: simple experiments in atmospheric physics.* Wiley Science Editions, John Wiley & Sons, Inc., 195 pp.

Bolin, B. (1986): How much CO₂ will remain in the atmosphere? *In:* Bolin, B., Döös, B.R., Jäger, J. & Warrick, R.A. (Eds.): *The Greenhouse Effect, climatic change, and ecosystems (SCOPE 29).* John Wiley & Sons, 93-155.

Bolin, B. & Eriksson, E. (1959): Changes in the carbon dioxide content of the atmosphere and sea due to fossil fuel combustion. *In:* Bolin, B. (Ed.): *The atmosphere and the sea in motion. Scientific contributions to the Rossby Memorial Volume.* The

Rockefeller Institute Press, New York, 130-142.

Böttcher, F. (1996): Climate change: forcing a treaty. *In:* Emsley, J. (Ed.): *The Global Warming Debate. The report of the European Science and Environment Forum.* Bourne Press, Ltd., Bournemouth, Dorset, UK, 267-285.

Bray, J.R. (1959): An analysis of the possible recent change in atmospheric carbon dioxide concentration. *Tellus 11*, 220-230.

Brewer, P.G. (1983): Past and future atmospheric concentrations of carbon dioxide; carbon dioxide and the oceans. *In: Changing climate*. National Academy Press, 188-215.

Broecker, W.S., Takahashi, T., Simpson, H.J. & Peng, T.-H. (1979): Fate of fossil fuel carbon dioxide and the global carbon budget. *Science 206,* 409-418.

Callendar, G.S. (1938): The artificial production of carbon dioxide and its influence on temperature. *Quarterly Journal of the Royal Meteorological Society 64,* 223-240.

Callendar, G.S. (1940): Variations of the amount of carbon dioxide in different air currents. *Quarterly Journal of the Royal Meteorological Society 66*, 395-400.

Callendar, G.S. (1949): Can carbon dioxide influence climate? Weather 4, 310-314.

Callendar, G.S. (1958): On the amount of carbon dioxide in the atmosphere. *Tellus 10,* 243-248.

Churchman, C.W. (1948): *Theory of experimental inference*. Macmillan, New York, 292 pp.

Cialdini, R.B. (1993): *Influence: the psychology of persuasion, 2nd. rev. ed.* William Morrow & Co., Inc., New York, 320 pp.

Craig, H. (1957): The natural distribution of radio carbon and the exchange time of carbon dioxide between the atmosphere and sea. *Tellus 9,* 1-16.

Dreybrodt, W., Lauckner, J., Zaihua, L., Svensson, U. & Buhmann, D. (1996): The kinetics of the reaction $CO_2 + H_2O \rightarrow H^+ + HCO_3^-$ as one of the rate limiting steps for the dissolution of calcite in the system $H_2O - CO_2 - CaCO_3$. *Geochimica et Cosmochimica Acta 60,* 3375-3381.

Druffel, E.R.M. & Williams, P.M. (1990): Identification of a deep marine source of particulate organic carbon using bomb carbon-14. *Nature 347*, 172-174.

Etheridge, D.M., Pearman, G.I. & de Silva, F. (1988): Atmospheric trace-gas variations as revealed by air trapped in an ice core from Law Dome, Antarctica. *Annals of Glaciology 10,* 28-33.

Fonselius, S., Koroleff, F. & Warme, K.-E. (1956): Carbon dioxide in the atmosphere. *Tellus 8,* 176-183.

Gonfiantini, R. (1981): The delta-notation and the mass-spectrometric measurement

techniques. International Atomic Agency, Technical Report Series 210, 35-84.

Holland, H. (1984): *The chemical evolution of the atmosphere and oceans.* Princeton University Press, 582 pp.

Holmén, K. (1992): The global carbon cycle. *In:* Butcher, S.S., Charlson, R.J., Orians, G.H. & Wolfe, G.V. (Eds.): *Global biogeochemical cycles.* Academic Press, 239-262.

Houghton, J.T., Jenkins, G.J. & Ephraums, J.J. (Eds.) (1990): *Climate Change. The IPCC Scientific Assessment. Intergovernmental Panel on Climate Change.* Cambridge University Press, Cambridge, 365 pp.

Inoue, H. & Sugimura, Y. (1985): Carbon isotopic fractionation during the CO_2 exchange process between air and sea water under equilibrium and kinetic conditions. *Geochimica et Cosmochimica Acta 49,* 2453-2460.

Jaworowski, Z., Segalstad, T.V. & Hisdal, V. (1992 a): Atmospheric CO₂ and global warming: a critical review; 2nd revised edition. *Norsk Polarinstitutt, Meddelelser [Norwegian Polar Institute, Memoirs] 119,* 76 pp.

Jaworowski, Z., Segalstad, T.V. & Ono, N. (1992 b): Do glaciers tell a true atmospheric CO₂ story? *Science of the Total Environment 114,* 227-284.

Keeling, C.D. & Bacastow, R.B. (1977): Impact of industrial gases on climate. *In: Energy & Climate.* Studies in Geophysics, National Academy of Sciences, Washington, D.C., 72-95.

Keeling, C.D., Bacastow, R.B., Carter, A.F., Piper, S.C., Whorf, T.P., Heimann, M., Mook, W.G. & Roeloffzen, H. (1989): A three-dimensional model of atmospheric CO₂ transport based on observed winds: 1. Analysis of observational data. *In:* Peterson, D.H. (Ed.): Aspects of climate variability in the Pacific and the Western Americas. *American Geophysical Union, Geophysical Monograph 55,* 165-236.

Kerr, R.A. (1992): Fugitive carbon dioxide: it's not hiding in the ocean. Science 256, 35.

Kohlmaier, G.H. (1979): Dynamics of the surface ocean - deep sea carbon exchange in its relation to the atmosphere - surface ocean exchange. *In:* Bolin, B. (Ed.): *Carbon cycle modelling (SCOPE 16).* John Wiley & Sons, 307-314.

Kondratyev, K.Y. (1988): *Climate shocks: natural and anthropogenic.* John Wiley & Sons, 296 pp.

Kramer, J.R. (1965): History of sea water. Constant temperature-pressure equilibrium models compared to liquid inclusion analyses. *Geochimica et Cosmochimica Acta 29,* 92-945.

Krauskopf, K.B. (1979): Introduction to geochemistry, 2nd. ed. McGraw-Hill, 617 pp.

Machta, L. (1972): The role of the oceans and biosphere in the carbon dioxide cycle. *In:* Dyrssen, D. & Jagner, D. (Eds.): *The changing chemistry of the oceans. Nobel Symposium 20.* Almquist & Wiksell / Wiley Interscience, 121-145.

McDuff, R.E. & Morel, F.M.M. (1980): The geochemical control of seawater (Sillen

revisited). Environmental Science & Technology 14, 1182-1186.

McKay, CP., Toon, O.B. & Kasting, J.F. (1991): Making Mars habitable. *Nature 352,* 489-496.

Michaels, P.J. & Knappenberger, P.C. (1996): The United Nations Intergovernmental Panel on Climate Change and the scientific "consensus" on global warming. *In:* Emsley, J. (Ed.): *The Global Warming Debate. The report of the European Science and Environment Forum.* Bourne Press, Ltd., Bournemouth, Dorset, UK, 158-178.

Murray, J.W. (1992): The oceans. *In:* Butcher, S.S., Charlson, R.J., Orians, G.H. & Wolfe, G.V. (Eds.): *Global biogeochemical cycles.* Academic Press, 175-211.

Næss, A. (1990): *Ecology, community and lifestyle.* Cambridge University Press, Cambridge, 223 pp.

Neftel, A., Moor, E., Oeschger, H. & Stauffer, B. (1985): Evidence from polar ice cores for the increase in atmospheric CO_2 in the past two centuries. *Nature 315*, 45-47.

Neftel, A., Oeschger, H., Schwander, J., Stauffer, B. & Zumbrunn, R. (1982): Ice core sample measurements give atmospheric CO_2 content during the past 40,000 years. *Nature 295, 220-223.*

Neftel, A., Oeschger, H., Staffelbach, T. & Stauffer, B. (1988): CO_2 record in the Byrd ice core 50,000 - 5,000 years BP. *Nature 331,* 609 - 611.

Oeschger, H. & Siegenthaler, U. (1978): The dynamics of the carbon cycle as revealed by isotope studies. *In:* Williams, J. (Ed.): *Carbon dioxide, climate and society.* Pergamon Press, 45-61.

Oeschger, H., Stauffer, B., Finkel, R. & Langway, C.C., Jr. (1985): Variations of the CO_2 concentration of occluded air and of anions and dust in polar ice cores. *In:* Sundquist, E.T. & Broecker, W.S. (Eds.): The carbon cycle and atmospheric CO_2 : natural variations Archean to present. *American Geophysical Union, Geophysical Monograph 32*, 132-142.

O'Neill, B.C., Gaffin, S.R., Tubiello, F.N. & Oppenheimer, M. (1994): Reservoir timescales for anthropogenic CO_2 in the atmosphere. *Tellus 46 B*, 378-389.

Pales, J.C. & Keeling, C.D. (1965): The concentration of atmospheric carbon dioxide in Hawaii. *Journal of Geophysical Research 70,* 6053-6076.

Revelle, R. & Munk, W. (1977): The carbon dioxide cycle and the biosphere. *In: Energy & Climate.* Studies in Geophysics, National Academy of Sciences, Washington, D.C., 140-158.

Revelle, R. & Suess, H. (1957): Carbon dioxide exchange between atmosphere and ocean and the question of an increase of atmospheric CO_2 during past decades. *Tellus 9*, 18-27.

Rodhe, H. (1992): Modeling biogeochemical cycles. *In:* Butcher, S.S., Charlson, R.J., Orians, G.H. & Wolfe, G.V. (Eds.): *Global biogeochemical cycles.* Academic Press, 55-72.

Rodhe, H. & Björkström, A. (1979): Some consequences of non-proportionality between fluxes and reservoir contents in natural systems. *Tellus 31,* 269-278.

Ryan, S. (1995): Quiescent outgassing of Mauna Loa Volcano 1958 - 1994. *In:* Rhodes, J.M. & Lockwood, J.P. (Eds.): Mauna Loa revealed: structure, composition, history, and hazards. *American Geophysical Union, Geophysical Monograph 92,* 95-115.

Sanford, R.F. (1992): Environmentalism and the assault on reason. *In:* Lehr, J. (Ed.): *Rational readings on environmental concerns.* Van Nostrand Reinhold, New York, 16-31.

Sarmiento, J.L. (1991): Oceanic uptake of anthropogenic CO₂: the major uncertainties. *Global Biogeochemical Cycles 5,* 309-313.

Segalstad, T.V. (1992): The amount of non-fossil-fuel CO_2 in the atmosphere. American Geophysical Union, Chapman Conference on Climate, Volcanism, and Global Change, March 23-27, 1992, Hilo, Hawaii. Abstracts, 25.

Segalstad, T.V. (1993): Stable isotope geochemistry applied to paleoclimatological and greenhouse gas problems. *1st International Symposium on Applied Isotope Geochemistry (AIG-1), Aug. 29 - Sept. 3, 1993, Geiranger, Norway. Program and Abstracts, Institute for Energy Research IFE/KR/E-93/007, 95-96.*

Segalstad, T.V. (1996): The distribution of CO_2 between atmosphere, hydrosphere, and lithosphere; minimal influence from anthropogenic CO_2 on the global "Greenhouse Effect". *In:* Emsley, J. (Ed.): *The Global Warming Debate. The report of the European Science and Environment Forum.* Bourne Press, Ltd., Bournemouth, Dorset, UK, 41-50.

Siegenthaler, U. (1989): Carbon-14 in the oceans. *In:* Fritz, P. & Fontes, J.C. (Eds.): *Handbook of environmental isotope geochemistry, 3 A.* Elsevier, 75-136.

Siegenthaler, U. & Münnich, K.O. (1981): 13-C/12-C fractionation during CO₂ transfer from air to sea. *In:* Bolin, B. (Ed.): *Carbon cycle modelling (SCOPE 16).* John Wiley & Sons, 249-257.

Siegenthaler, U. & Oeschger, H. (1987): Biospheric CO_2 emissions during the past 200 years reconstructed by deconvolution of ice core data. *Tellus 39 B,* 140 - 154.

Skirrow, G. (1975): The dissolved gases - carbon dioxide. *In* Riley, J.P. & Skirrow, G. (Eds.): *Chemical oceanography, Vol. 2; 2nd edition.* Academic Press, 1-192.

Slocum, G. (1955): Has the amount of carbon dioxide in the atmosphere changed significantly since the beginning of the twentieth century? *Monthly Weather Review, October,* 225-231.

Stumm, W. & Morgan, J.J. (1970): Aquatic chemistry: an introduction emphasizing chemical equilibria in natural waters. Wiley-Interscience, 583 pp.

Suess, H. E. (1955): Radiocarbon concentration in modern wood. *Science 122,* 415-417.

Sundquist, E.T. (1985): Geological perspectives on carbon dioxide and the carbon cycle. *In:* Sundquist, E.T. & Broecker, W.S. (Eds.): The carbon cycle and atmospheric

CO₂: natural variations Archean to present. *American Geophysical Union, Geophysical Monograph 32,* 5-59.

Takahashi, T. (1961): Carbon dioxide in the atmosphere and in Atlantic ocean water. *Journal of Geophysical Research 66,* 477-494.

Takahashi, T. (1979): Carbon dioxide chemistry in ocean water. *In:* Elliott, W.P. & Machta, L. (Eds.): *Carbon dioxide effects research and assessment program: workshop on the global effects of carbon dioxide from fossil fuels.* NTIS, U.S. Department of Commerce, 63-71.

Takahashi, T., Kaiteris, P., Broecker, W.S. & Bainbridge, A.E. (1976): An evaluation of the apparent dissociation constants of carbonic acid in seawater. *Earth and Planetary Science Letters* 32, 458-467.

Toggweiler, J.R. (1990): Bombs and ocean carbon cycles. *Nature* 347, 122-123.

Trabalka, J.R. (Ed.) (1985): Executive summary. *Atmospheric carbon dioxide and the global carbon cycle*. United States Department of Energy, DOE/ER-0239, xv-xxiii.

Trabalka, J.R., Edmonds, J.A., Reilly, J., Gardner, R.H. & Voorhees, L.D. (1985): Human alterations of the global carbon cycle and the projected future. *In:* Trabalka, J.R. (Ed.): *Atmospheric carbon dioxide and the global carbon cycle.* United States Department of Energy, DOE/ER-0239, 247-287.

Walker, J.C.G. (1994): Global geochemical cycles of carbon. *In:* Tolbert, N.E. & Preiss, J. (Eds.): *Regulation of atmospheric CO*₂ and O₂ by photosynthetic carbon metabolism. Oxford University Press, 75-89.

Walker, J.C.G. & Drever, J.I. (1988): Geochemical cycles of atmospheric gases. *In:* Gregor, C.B., Garrels, R.M., Mackenzie, F.T. & Maynard, J.B. (Eds.): *Chemical cycles in the evolution of the Earth.* John Wiley & Sons, Ltd., 55-76.

Biography of Tom Victor Segalstad

Born in Norway in 1949. University degrees (natural sciences with geology) from the University of Oslo. Has conducted university research, publishing, and teaching in geochemistry, mineralogy, petrology, volcanology, structural geology, ore geology, and geophysics at the University of Oslo, Norway, and the Pennsylvania State University, USA. At present keeping a professional position as Associate Professor of Geochemistry at the University of Oslo, with responsibility for stable isotope geochemistry. He is past head of the Mineralogical-Geological Museum at the University of Oslo; and past Director of the Natural History Museums and Botanical Garden of the University of Oslo. He is a member of different international and national professional working groups and committees.

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Page 45, line 4 should read: controls the value of an intensive (= mass independent) thermodynamic variable (pressure,

Page 45, 7th last line should read: and a calcium silicate + $CO_2 = calcium carbonate$ + SiO₂ buffer

Page 45, 5th and 4th last lines should read: "security net" underlying the most important buffer: $CO_2(g) = HCO_3^-(aq) = CaCO_3(s)$. All together these buffers, in principle, add

Page 46: all Greek sigmas should read Greek deltas.

Page 46, footnote should read:

1

delta¹³C = $(^{13}C/^{12}C)_{sample} - (^{13}C/^{12}C)_{standard}$ 1000 permil $(^{13}C/^{12}C)_{\text{standard}}$

where the reference standard used here is PDB (Pee Dee Belemnite) CaCO₃.

Page 47, 5th line: d¹³C should read delta¹³C.

