The distribution of CO$_2$ between atmosphere, hydrosphere, and lithosphere; minimal influence from anthropogenic CO$_2$ on the global "Greenhouse Effect".

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1. Introduction

It has recently been created a belief among people that an apparent increase in atmospheric CO$_2$ concentration is caused by anthropogenic burning of fossil carbon in petroleum, coal, and natural gas. The 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). This postulate is here discussed and rejected on energetic and geochemical grounds.

2. Heat energy and temperatures

Our relatively high global atmospheric temperature near the surface of the Earth, with an average of 14 to 15°C, is caused by heat-absorbing gases in the atmosphere, mainly H$_2$O vapor. Without the Earth's atmosphere the surface temperature would be approximately -18°C.

The Earth receives about 1368 W/m$^2$ of radiative heat from the Sun. The total amount of this heat withheld, approximately 11%, in the Earth's lower atmosphere, has traditionally been named the Earth's "Greenhouse Effect". For a cloudless atmosphere this effect is on the average about 146 W/m$^2$ for the Earth, with an uncertainty of ± 5 to 10 W/m$^2$ due to analytic uncertainties and natural climatic variations. All human activities have been claimed to contribute about 1.3% of this (approx. 2 W/m$^2$), while a hypothetic doubling of the atmospheric CO$_2$ concentration would contribute about 2.6% (approx. 4 W/m$^2$) to the present "Greenhouse Effect" (Raval & Ramanathan, 1989; Ramanathan et al., 1989).

150 year long time series of temperature measurements are covering too short time spans to be useful for climate prediction, in order to be used as "evidence" for anthropogenic heating (or cooling). The global mean temperature has risen and fallen several times over the last 400 years, with no evidence of anthropogenic causes, although strong explosive volcanic eruptions have caused periodically colder climates (Jaworowski et al., 1992 a).

It should also be noted that clouds can reflect up to approx. 50 W/m$^2$ and can absorb up to approx. 30 W/m$^2$ of the solar radiation (Ramanathan et al., 1989), making the Earth's average "Greenhouse Effect" vary naturally within approx. 96 and 176
W/m². Hence the anticipated anthropogenic atmospheric CO₂ heat absorption is much smaller than the natural variation of the Earth's "Greenhouse Effect" (Segalstad & Jaworowski, 1991).

The oceans act as a huge heat energy buffer; the global climate is primarily governed by the enormous amount of heat stored in the oceans (total mass approx. 1.4 x 10²⁴ g), rather than the minute amount of heat withheld in the heat-absorbing part of the atmosphere (total mass approx. 1.4 x 10¹⁸ g), a mass difference of one million times (Peixoto & Oort, 1992). Most of the atmospheric heat absorption occurs in water vapor (total mass approx. 1.3 x 10¹⁹ g), which is equivalent to a uniform layer of only 2.5 cm of liquid water covering the globe, with a residence time of about 9 days (Peixoto & Oort, 1992).

The total internal energy of the whole ocean is more than 1.6 x 10²⁷ Joule, about 2000 times larger than the total internal energy 9.4 x 10²³ Joule of the whole atmosphere. Note that this energy is defined with respect to 0 Kelvin (Peixoto & Oort, 1992).

Furthermore the cryosphere (ice sheets, sea ice, permafrost, and glaciers; total mass of the continental ice is approx. 3.3 x 10²² g) plays a central role in the Earth's climate as an effective heat sink for the atmosphere and oceans, with a large latent heat of melting on the order of 9.3 x 10²⁴ Joule, a hypothetic energy equivalent to cooling the entire oceans by about 2°C (5.8 x 10²⁴ J/°C). For comparison, the energy needed to warm the entire atmosphere by 1°C is only 5.1 x 10²¹ Joule (Oerlemans & van der Veen, 1984).

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 by added heat absorption of anthropogenic CO₂ in the lower atmosphere.

3. CO₂ measurements in atmosphere and ice cores

Houghton et al. (1990) claim in their section 1.2.5 three evidences that the contemporary atmospheric CO₂ increase is anthropogenic: First, CO₂ measurements from ice cores show a 21% rise from 280 to 353 ppmv (parts per million by volume) since pre-industrial times; second, the atmospheric CO₂ increase closely parallels (sic!) 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 CO₂ input [some 50% deviation, e.g. Kerr, 1992]; third, the isotopic trends of ¹³C and ¹⁴C agree qualitatively (sic!) with those expected due to the CO₂ emissions from fossil fuels and the biosphere.

Jaworowski et al. (1992 a, 1992 b) reviewed published CO₂ measurements from ice cores, and emphasized that the pre-industrial atmospheric CO₂ concentration, according to early accurate analyses, was many times larger (measurements up to 2450 ppmv) than the present atmospheric value. They also pointed out that CO₂ variations in ice is mainly an artificial effect of a large number of natural physical-chemical processes in ice and the recovered ice cores. These effects dominate over the eventual traces of anthropogenic CO₂. Criticism of the methodology has also independently been presented by Heyke (1992 a, 1992 b, 1992 c).
Jaworowski et al. (1992a) have presented a number of criticisms regarding the methodology of atmospheric CO$_2$ measurements, including spectroscopic instrumental peak overlap errors (from N$_2$O, CH$_4$, and CFCs in the air). They also pointed out that the CO$_2$ measurements at current CO$_2$ observatories use a procedure involving a subjective editing (Keeling et al., 1976) of measured data, only representative of a few tens of percent of the total data. There are also fundamental problems connected with the use of stable carbon isotopes ($^{13}$C/$^{12}$C) in tree rings for model calculations of earlier atmospheres' CO$_2$ concentration, a method which now seems to have been abandoned (Jaworowski et al., 1992a).

The third evidence, based on carbon isotopes, will be discussed below in Section 5.

4. Chemical laws for distribution of CO$_2$ in nature

Statistically it has been found that the atmospheric CO$_2$ concentration rises after temperature rises (Kuo et al., 1990), and it has been suggested that the reason is that cold water dissolves more CO$_2$ (e.g. Segalstad, 1990). Hence, if the water temperature increases, the water cannot keep as much CO$_2$ in solution, resulting in CO$_2$ degassing from the water to the atmosphere. According to Takahashi (1961) heating of sea water by 1°C will increase the partial pressure of atmospheric CO$_2$ by 12.5 ppmv during upwelling of deep water. For example 12°C warming of the Benguela Current should increase the atmospheric CO$_2$ concentration by 150 ppmv.

Volk & Liu (1988) modelled the CO$_2$ flux between atmosphere and oceans, and concluded that approximately 70% of the flux was governed by this “thermal solubility pump”, while approximately 30% was governed by the organic nutrient “biological pump”. Faure (1990) estimated that ca. 4000 GT (Gigatonnes = billion metric tonnes) of CO$_2$ is transferred by degassing of the ocean via the atmosphere to the continental biosphere from the end of a glaciation to an interglacial stage.

From a geochemical consideration of sedimentary rocks deposited throughout the Earth’s history, and the chemical composition of the ocean and atmosphere, Holland (1984) showed that degassing from the Earth’s interior has given us chloride in the ocean; and nitrogen, CO$_2$, and noble gases in the atmosphere. Mineral equilibria have established concentrations of major cations and H$^+$ in the ocean, and the CO$_2$ concentration in the atmosphere, through different chemical buffer reactions. Biological reactions have given us sulphate in the ocean and oxygen in the atmosphere.

Carbon dioxide is an equally important requisite for life on Earth as oxygen. Plants need CO$_2$ for their living (the photo synthesis), and humans and animals breath out CO$_2$ from their respiration. In addition to this biogeochemical balance, there is also an important geochemical balance. CO$_2$ in the atmosphere is in equilibrium with carbonic acid dissolved in the ocean, which in term is close to CaCO$_3$ saturation and in equilibrium with carbonate shells of organisms and lime (calcium carbonate; limestone) in the ocean through the following reactions (where s indicates the solid state, $aq$ is the aqueous state, and $g$ is the gaseous state):

$$
\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3
$$

$$
\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}_2\text{O} + \text{CO}_2(g)
$$

$$
\text{CaCO}_3\text{(aq)} + \text{H}_2\text{CO}_3\text{(aq)} = \text{Ca}^{2+}\text{(aq)} + 2\text{HCO}_3^-\text{(aq)} + \text{H}_2\text{O}
$$

$$
\text{CaCO}_3\text{(s)} + \text{H}_2\text{O} + \text{CO}_2(g) = \text{Ca}^{2+}\text{(aq)} + 2\text{HCO}_3^-\text{(aq)}
$$
Partial reactions:

\[
\begin{align*}
&\text{CO}_2 (g) \leftrightarrow \text{CO}_2 (aq) \\
&\text{CO}_2 (aq) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 (aq) \\
&\text{H}_2\text{CO}_3 (aq) \leftrightarrow \text{H}^+ (aq) + \text{HCO}_3^- (aq) \\
&\text{HCO}_3^- (aq) \leftrightarrow \text{H}^+ (aq) + \text{CO}_3^{2-} (aq) \\
&\text{CO}_3^{2-} (aq) + \text{Ca}^{2+} (aq) \leftrightarrow \text{CaCO}_3 (s)
\end{align*}
\]

Net reaction:

\[
\text{CO}_2 (g) + \text{H}_2\text{O} + \text{Ca}^{2+} (aq) \leftrightarrow \text{CaCO}_3 (s) + 2\text{H}^+ (aq)
\]

In addition there are a number of different aqueous metal complexes of lesser concentrations.

A buffer can 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.). Our carbonate system above will act as a pH buffer, by the presence of a weak acid (H$_2$CO$_3$) and a salt of the acid (CaCO$_3$). The concentration of CO$_2$ (g) and of Ca$_{2+}$ (aq) will in the equilibrium Earth system also be buffered by the presence of CaCO$_3$, at a given temperature. If the partial pressure of CO$_2$ (g) is increased, the net reaction will go towards the right because of the Law of Mass Action. If the temperature changes, the chemical equilibrium constant will change, and move the equilibrium to the left or right. The result is that the partial pressure of CO$_2$ (g) will increase or decrease. The equilibrium will mainly be governed by Henry's Law: the partial pressure of CO$_2$ (g) in the air will be proportional to the concentration of CO$_2$ (aq) dissolved in water. The proportional constant is the Henry's Law Constant, which is strongly temperature dependent, and lesser dependent on total pressure and salinity (Drummond, 1981).

Questions have been raised about how strong this buffer is. It has been postulated (Bolin & Keeling, 1963) that an increase in atmospheric CO$_2$ will be balanced when only approximately one tenth of this is dissolved in the ocean. This postulate fails for a number of reasons. An increase in atmospheric CO$_2$ will namely increase the buffer capacity of ocean water, and thereby strengthen the ocean's capacity to moderate an increase of atmospheric CO$_2$; maximum buffer capacity for the system CO$_2$ - H$_2$O is reached at 2.5 to 6 times the present atmospheric partial pressure of CO$_2$, depending on temperature and alkalinity (Butler, 1982). According to Maier-Reimer & Hasselmann (1987) the borate system also increases the ocean storage capacity for CO$_2$ by more than 20% over an ocean with the carbonate-system alone.

Furthermore, this carbonate buffer is not the only buffer active in the atmosphere / hydrosphere / lithosphere system. The Earth has a set of other buffering mineral reactions. The geochemical equilibrium system anorthite CaAl$_2$Si$_2$O$_8$ - kaolinite Al$_2$SiO$_4$(OH)$_4$ has by the pH of ocean water a buffer capacity which is thousand times larger than a 0.001 M carbonate solution (Stumm & Morgan, 1970). In addition we have clay mineral buffers, and a calcium silicate + CO$_2$ ↔ calcium carbonate + SiO$_2$ buffer (MacIntyre, 1970; Krauskopf, 1979). These buffers all act as a "security net" under the most important buffer: CO$_2$ (g) ↔ HCO$_3^-$ (aq) ↔ CaCO$_3$ (s). All together these buffers give in principle an infinite buffer capacity (Stumm & Morgan, 1970).
Stable carbon isotopes ($^{13}$C/$^{12}$C) show that CO$_2$ in the atmosphere is in chemical equilibrium with ocean bicarbonate and lithospheric carbonate (Ohmoto, 1986). The chemical equilibrium constants for the chemical reactions above provide us with a partition coefficient for CO$_2$ between the atmosphere and the ocean of approximately 1:50 (approx. 0.02) at the global mean temperature (Revelle & Suess, 1957; Skirrow, 1975). This means that for an atmospheric doubling of CO$_2$, there will have to be supplied 50 times more CO$_2$ to the ocean to obtain chemical equilibrium. This total of 51 times the present amount of atmospheric CO$_2$ carbon is more than the known reserves of fossil carbon. It is possible to exploit approximately 7000 GT of fossil carbon, which means, if all this carbon is supposed to be burned, that the atmospheric CO$_2$ can be increased by 20% at the most under geochemical equilibrium at constant present surface temperature.

$^{14}$C isotopes show that the circulation time for carbon in the upper part of the ocean is some few decades (Druffel & Williams, 1990). This is sufficient time for the ocean to absorb an increase in atmospheric CO$_2$ from burning of fossil fuel at the present projected rate (Jaworowski et al., 1992a).

5. Carbon isotopes in atmospheric CO$_2$

Houghton et al. (1990) assumed for the IPCC model 21% of our present-day atmospheric CO$_2$ has been contributed from burning of fossil fuel. This has been made possible by CO$_2$ having a "rough indication" (sic!) lifetime of 50 - 200 years. It is possible to test this assumption by inspecting the stable $^{13}$C/$^{12}$C isotope ratio (expressed as $\delta^{13}$C$_{PDB}$) of atmospheric CO$_2$. It is important to note that this value is the net value of mixing all different CO$_2$ components, and would show the results of all natural and non-natural (i.e. anthropogenic) processes involving CO$_2$.

The natural atmospheric CO$_2$ reservoir has $\delta^{13}$C $\approx$ -7‰ when in isotopic equilibrium with marine HCO$_3^-$ and CaCO$_3$ (Ohmoto, 1986). CO$_2$ from burning of fossil-fuel and biogenic materials has $\delta^{13}$C $\approx$ -26‰ (Hoefs, 1980). Mixing these two CO$_2$ components with the ratio 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‰.

* Footnote; see last page of the manuscript.
Keeling et al. (1989) have reported δ¹³C of atmospheric CO₂ over the last decades. δ¹³C reported for atmospheric CO₂ was -7.489‰ in December 1978, decreasing to -7.807‰ in December 1988, values close to that of the natural atmospheric CO₂ reservoir, far from the δ¹³C value of -11‰ expected from the IPCC model. Hence the IPCC model is not supported by ¹³C/¹²C evidence.

Segalstad (1992, 1993) has by isotope mass balance considerations calculated the atmospheric CO₂ lifetime and the amount of fossil fuel CO₂ in the atmosphere. The December 1988 atmospheric CO₂ composition was computed for its 748 GT C total mass and δ¹³C = -7.807‰ for 3 components: (1) natural fraction remaining from the pre-industrial atmosphere; (2) cumulative fraction remaining from all annual fossil-fuel CO₂ emissions (from production data); (3) carbon isotope mass-balanced natural fraction. The masses of the components were computed for different atmospheric lifetimes of CO₂.

The calculations show how the IPCC's (Houghton et al., 1990) atmospheric CO₂ lifetime of 50-200 years only accounts for half the mass of atmospheric CO₂. However, the unique result fits an atmospheric CO₂ lifetime of -5 (5.4) years, in agreement with numerous ¹⁴C studies compiled by Sundquist (1985) and chemical kinetics (Stumm & Morgan, 1970). The mass of all past fossil-fuel and biogenic emissions remaining in the current atmosphere was in December 1988 calculated to be ~30 GT C or less, i.e. maximum ~4%, corresponding to an atmospheric CO₂ concentration of ~14 ppmv.

This small amount of anthropogenic atmospheric CO₂ probably contributes less than half a Watt/m² of the 146 W/m² "Greenhouse Effect" of a cloudless atmosphere, contributing to less than half a degree C of radiative heating of the lower atmosphere.

The implication of the -5 year lifetime is that ~135 GT C (~18%) of the atmospheric CO₂ pool is exchanged each year. This is far more than the ~6 GT C in fossil fuel CO₂ now contributed annually to the atmosphere.

The isotopic mass balance calculations show that at least 96% of the current atmospheric CO₂ is isotopically indistinguishable from non-fossil-fuel sources, i.e. natural marine and juvenile sources from the Earth's interior. Hence, for the atmospheric CO₂ budget, marine equilibration and degassing, and juvenile degassing from e.g. volcanic sources, must be much more important, and burning of fossil-fuel and biogenic materials much less important, than assumed by the authors of the IPCC model (Houghton et al., 1990).

6. Conclusions

Water vapor is the most important "greenhouse gas". Man's contribution to atmospheric CO₂ from the burning of fossil fuels is small, maximum 4% found by carbon isotope mass balance calculations. The "Greenhouse Effect" of this contribution is small and well within natural climatic variability. The amount of fossil fuel carbon is minute compared to the total amount of carbon in the atmosphere, hydrosphere, and lithosphere. The atmospheric CO₂ lifetime is about 5 years. The ocean will be able to absorb the larger part of the CO₂ that Man can produce through burning of fossil fuels. The IPCC CO₂ global warming model is not supported by the scientific data. Based on geochemical knowledge there should be no reason to fear a climatic catastrophe
because of Man's release of the life-governing CO$_2$ gas. The global climate is primarily
governed by the enormous heat energy stored in the oceans and the latent heat of
melting of the ice caps, not by the small amount of heat that can be absorbed in
atmospheric CO$_2$; hence legislation of "CO$_2$ taxes" to be paid by the public cannot
influence on the sea level and the global climate.

Acknowledgements: Technological Oriented Studies, University of Oslo, for financial
support; Dr. Zbigniew Jaworowski for scientific discussions and contributions.

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Footnote to the manuscript:

\[ \delta^{13}C = \frac{\left( ^{13}C/^{12}C \right)_{\text{sample}} - \left( ^{13}C/^{12}C \right)_{\text{standard}}}{\left( ^{13}C/^{12}C \right)_{\text{standard}}} \times 1000 \% \]

where the reference standard used here is PDB (Pee Dee Belemnite) CaCO₃.
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 holding professional positions as Associate Professor of Geochemistry at The University of Oslo; Head of The Mineralogical-Geological Museum at The University of Oslo; and Director of The Natural History Museums and Botanical Garden of The University of Oslo. Member of different international and national professional working groups and committees.

Oslo, December 1995.

Manuscript for the chapter printed on pages 41-50 in the book: