

On Modeling the Atmospheric Carbon Dioxide Change

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Abstract

A simple chemical equilibrium model for the atmospheric and hydrospheric carbon dioxide change is presented. According to this model the observed average increase in the atmospheric carbon dioxide concentration during the last 30 years can be explained by the combination of a minor increase in the acidity of ocean water and the accumulation of carbon in the equilibrium system. The rise in the average atmospheric carbon dioxide concentration has been approximately 35 ppm during the last 30 years (the 1990 value being approximately 352 ppm). This change can be explained by a relatively insignificant decrease in the average pH -value by approximately 0.02 for ocean water, by assuming chemical equilibrium with the atmosphere. Since the model does not consider the local carbon dioxide concentration distribution in the atmosphere or in the oceans it is found most suitable to use the water volume as a parameter explaining also local phenomena. The water volume thus explains both local interactions between the ocean surface and the atmosphere as well as horizontal and vertical diffusion (and circulation) of carbon dioxide in the oceans in terms of an equivalent water volume. By assuming that the increase in acidity is because of the known atmospheric emissions of carbon, sulfur and nitrogen oxides, from burning fossil fuels and other man-made emission sources, the equivalent water volume is estimated to be between 8 and 10 % of the total ocean water volume. This assumption also leads to a very good fit to observed data. The relative importance of the emission of carbon dioxide and the sulfur and nitrogen emission contributing to the change of the carbon dioxide concentration in the atmosphere can also be estimated. It is found that approximately 1 % of the increase in average carbon dioxide concentration in the atmosphere is because of the emission of sulfur and nitrogen oxides while the remaining 99 % is explained by the emission of carbon dioxide.

1. Introduction

The fact that the annual average atmospheric concentration of carbon dioxide has been increasing continuously during this century is well established. Continuous records on the carbon dioxide concentration level at different stations in both the southern and northern hemispheres indicate that the annual increase since the middle of this century has been about 1-1.5 ppm. It is also well established that carbon dioxide is one of the most essential heat-trapping gases in the atmosphere. The local effects on global climate change because of the increase in the atmospheric concentration of the heat-trapping gases seem, however, to be less well understood, and many controversial predictions have been given.

Modeling the underlying mechanisms resulting in the increasing atmospheric carbon dioxide concentration has been the subject of a great number of research papers during recent years. The most complex general circulation models and three-dimensional transport models used today also give quite appropriate predictions and global distribution of CO_2 with respect to specific assumptions about the strength and location of surface fluxes of CO_2 [10, 15, 16]. But even in the most complex models, rough simplifications must be made especially regarding the transport phenomena both in the atmosphere and in the oceans. Dividing the ocean into volume elements with each side equal to 1 km still require more than 10^9 volume elements to cover the whole ocean water volume. It should be observed that in this case we have only approximately 4 volume elements in the vertical direction. Thus, there is a great difficulty in modeling the transport phenomena in the oceans. Simple models usually do not fit data very well, while complex models often do. The difficulty, however, comes from the fact that it is not obvious to find out whether a complex model (but rough simplification) fits the data well because of the general flexibility of the models structure or if the model's structure really correspond to the real phenomena.

Since it can not be shown uniquely what limiting phenomena most significantly contribute to the observed carbon dioxide increase, there still is a need to make both rigorous and simplified models able to explain the carbon dioxide concentration increase by means of realistic assumptions. Candidates for the most significant phenomena are diffusion limited processes, chemically limited processes, biologically limited processes, transport phenomena both in the oceans and the atmosphere, etc. Also, variations in flow rates other than the carbon dioxide emission from burning fossil fuels might be of primary importance.

In this paper a simple chemical equilibrium model is considered. Models with a similar structure have also been proposed earlier [15, 16]; however, in this paper we try to find out which parameter in particular is the most suitable in which to express local phenomena which have not been considered. An equivalent ocean water volume in equilibrium with the atmosphere is therefore introduced. It is shown that a very simple, model based on an equivalent water volume is obtained considering only chemical equilibrium between the atmosphere and the equivalent ocean water volume. In terms of the model the considered, chemical reactions seems to be of major importance when explaining the observed atmospheric carbon dioxide increase. The acidity of water then also becomes an important

related factor. The increase in acidity is modelled by assuming a pseudo-equilibrium state in the oceans (equilibrium between the gas and liquid phase and only partly with the solid phases), and that it is caused mainly by the emission of carbon, sulfur and nitrogen oxides from burning fossil fuels. It should make a large difference in the short-term environmental protection programs for lowering the atmospheric CO₂ concentration, whether a primary reason for the observed concentration changes is in the change in acidity of water. In the long term (thousands of years) the carbon dioxide concentration will supposedly not increase as much as predicted by the actual model since it is also regulated by other solid-liquid equilibrium reactions which stabilize the pH and the carbon dioxide concentration both in the atmosphere and hydrosphere [2].

Table 1 contains pertinent data on the CO₂-concentration in the reservoirs and flows of carbon [1].

	Reservoirs	Flow	Flow
	Gton C	Gton C/year	Gton C/year
World vegetation	560		
World soil	1500		
Atmosphere	735		
Oceans	36000		
Fossil fuel	5000-10000		
Burning fossil fuels		5.3	
Respiration by plants		50	
Deforestation		2	
Soil respiration		50	
Physico-chemical diffusion from ocean		100	
Photosynthesis by plants			100
Physico-chemical diffusion into ocean			104
Annual increment in the atmosphere			3

Table 1. Reservoirs and flows of Carbon.

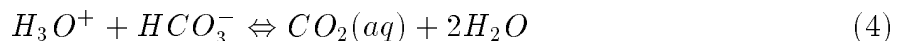
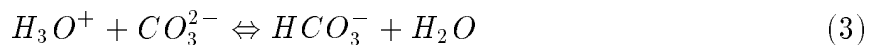
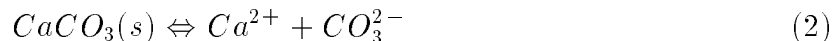
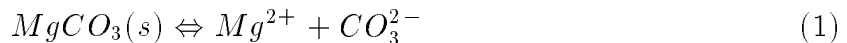
From table 1 it can be seen that the CO₂ emission rate from burning fossil fuels is 1-2 times greater than the annual increment of CO₂ in the atmosphere. On the other hand, the CO₂ emission rate from burning fossil fuels is small relative to the other flows. It therefore seems unlikely that solely this source should be responsible for the accumulation in the atmosphere.

Let us also briefly discuss some other processes that obviously have some bearing on the carbon balance in our biosphere. The short-term accumulation (last 30 years) of solid carbon in man-made products (industrial products, buildings, clothes, etc.) also constitutes a term in the carbon balance, reducing the accumulation rate in the atmosphere or hydrosphere. For example the consumption rate of carbon through the production of paper alone equals about 3 % of the accumulation rate of carbon in the atmosphere. Whether the origin of this carbon is from fossil fuels or a decreasing reservoir of vegetation is difficult to say. Other short-term rates of accumulation as solid carbon are also difficult to estimate. It can, however, be assumed that these short-term accumulation rates of solid carbon are relatively insignificant in comparison with the other values listed in table 1. The production rate of CO_2 through human respiration is about 1/10 of the accumulation rate of CO_2 in the atmosphere. This production rate is also relatively insignificant in comparison with the other production rates in table 1 and will therefore be neglected. The photosynthesis rates depend on the time of the year, the cycles being in different phases on the northern and southern hemisphere, and the atmospheric CO_2 concentration also shows a very regular yearly oscillation. The oscillation amplitude is up to 15 times the yearly atmospheric accumulation rate according to plots of measured concentrations [11, 12, 14]. The amplitude seems also to be increasing with time [13]. In spite of these oscillations the accumulation trend is clearly visible, and this yearly regular cycle is the reason for expressing the rates in table 1 as if they were yearly production (consumption).

2. The CO_2 -model

The model is based on five equilibrium reactions relating the atmospheric CO_2 concentration to the most essential dissolved components containing carbon.

The following equilibrium reactions are considered



$CO_2(aq)$ in reactions (4) and (5) denotes both aqueous CO_2 and H_2CO_3 . The dissociation reaction of water is further considered,

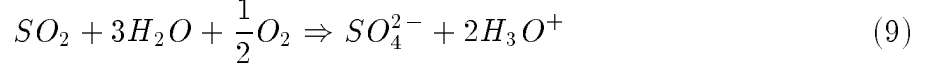


It is also assumed that all carbon and sulfur from burning fossil fuels is oxidized to carbon and sulfur dioxide according to,





The sulfur dioxide is then assumed to be completely dissociated in water according to,



Thus we have modelled the carbon dioxide reaction system by 6 equilibrium reactions and 3 reactions describing "complete" oxidation and dissociation.

From the equilibrium reactions (1-6) the following equilibrium expressions are obtained,

$$k_1 = [Mg^{2+}] \cdot [CO_3^{2-}] \quad (10)$$

$$k_2 = [Ca^{2+}] \cdot [CO_3^{2-}] \quad (11)$$

$$k_3 = \frac{[HCO_3^-]}{[CO_3^{2-}] \cdot a_{H_3O^+}} \quad (12)$$

$$k_4 = \frac{[CO_2(aq)]}{[HCO_3^-] \cdot a_{H_3O^+}} \quad (13)$$

$$k_5 = \frac{x_{CO_2}}{[CO_2(aq)]} \quad (14)$$

where $a_{H_3O^+}$ is the hydronium ion activity and x_{CO_2} the atmospheric carbon dioxide concentration. Mixed equilibrium constants for the reactions are given in table 2. By relating eqs. (10-14) to the mass of carbon in the atmosphere and hydrosphere, the equilibrium Ca^{2+} content can be obtained from a carbon mass balance resulting in the expression,

$$[Ca^{2+}] = \left(1 + k_3 \cdot a_{H_3O^+} \left(1 + k_4 \cdot a_{H_3O^+} \left(1 + k_5 \frac{n_{air}}{V_{water}} \right) \right) \right) \cdot \frac{M_C}{m_C} \cdot V_{water} \cdot k_2 \quad (15)$$

where m_C is the total mass of carbon in the atmosphere and dissolved in the ocean water which is in equilibrium with the atmosphere. m_C is given by,

$$m_C = m_C^* + ([Mg^{2+}] - [Mg^{2+}]^* + [Ca^{2+}] - [Ca^{2+}]^*) \cdot V_{water} \cdot M_C + m_{C,emiss} \quad (16)$$

Where m_C^* defines the mass of carbon in the atmosphere and the water volume V_{water} at a reference state. $[x]^*$ denotes the corresponding concentration of x at the reference state. $m_{C,emiss}$ is the total emission of carbon since the reference state. V_{water} is the volume of ocean water being in equilibrium with the atmosphere and $n_{air} = 0.177 \cdot 10^{21}$ mole is

the total amount of air in the atmosphere. The total volume of water in the oceans is $V_{tot} = 1.37 \cdot 10^{21}$ l. M_C is the molar mass of carbon. The amount of solid phase carbon in contact with ocean water, mostly as CaCO_3 and MgCO_3 , is hard to estimate. However, the concentrations of dissolved Ca and Mg in ocean water are known more accurately. It is therefore convenient to define the reference state. In [2] the values 0.01024 mole Ca/l and 0.05357 mole Mg/l were given. These high concentrations could change by observable amounts only if enormous quantities of solid material would be dissolved.

The atmospheric CO_2 concentration can be obtained by combining the equilibrium expressions (11-14) resulting in,

$$x_{\text{CO}_2} = k_2 \cdot k_3 \cdot k_4 \cdot k_5 \cdot \frac{a_{\text{H}_3\text{O}^+}^2}{[\text{Ca}^{2+}]} \quad (17)$$

Since the Ca^{2+} concentration will be almost constant it can be observed that eq. (17) can be used directly for simplified calculations estimating the relation between the atmospheric carbon dioxide concentration and the acidity of the ocean water. The Mg^{2+} , CO_3^{2-} , HCO_3^- and $\text{CO}_2(aq)$ concentrations are obtained from the equilibrium expressions according to,

$$[\text{Mg}^{2+}] = \frac{k_1}{k_2} \cdot [\text{Ca}^{2+}] \quad (18)$$

$$[\text{CO}_3^{2-}] = k_2 / [\text{Ca}^{2+}] \quad (19)$$

$$[\text{HCO}_3^-] = k_2 \cdot k_3 \cdot a_{\text{H}_3\text{O}^+} / [\text{Ca}^{2+}] \quad (20)$$

$$[\text{CO}_2(aq)] = k_2 \cdot k_3 \cdot k_4 \cdot a_{\text{H}_3\text{O}^+}^2 / [\text{Ca}^{2+}] \quad (21)$$

Assuming $a_{\text{H}_3\text{O}^+}$ being equal to $[\text{H}_3\text{O}^+]$ we obtain from a charge balance,

$$a_{\text{H}_3\text{O}^+} = 2 \cdot [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + 2 \cdot [\text{SO}_4^{2-}] + \frac{k_w}{a_{\text{H}_3\text{O}^+}} - 2 \cdot [\text{Ca}^{2+}] - 2 \cdot [\text{Mg}^{2+}] + \Delta^* \quad (22)$$

where k_w is the ion product of water and Δ^* is the difference between the concentrations of other negative and positive charges than those defined by CO_3^{2-} , HCO_3^- , SO_4^{2-} , OH^- , Ca^{2+} , Mg^{2+} and H_3O^+ at the reference state. Since the other ions are assumed to be invariant Δ^* will not change from the value obtained at the reference state. The SO_4^{2-} concentration is obtained from the expression,

$$[\text{SO}_4^{2-}] = [\text{SO}_4^{2-}]^* + \frac{m_{\text{S,emiss}}}{M_S \cdot V_{\text{water}}} \quad (23)$$

where $[SO_4^{2-}]^*$ is the SO_4^{2-} concentration at the reference state and $m_{S,emiss}$ the total emission of sulfur since the reference state. M_S is the molar mass of sulfur. Inserting equations (18-21) into equation (22) then $a_{H_3O^+}$ and $[Ca^{2+}]$ can be obtained from the nonlinear equations (15) and (22). The atmospheric CO_2 equilibrium concentration as well as the equilibrium Ca^{2+} , Mg^{2+} , CO_3^{2-} , HCO_3^- , $CO_2(aq)$, SO_4^{2-} concentrations and the acidity of the ocean water are then obtained for different values of the emission of carbon and sulfur.

If the solid-liquid reactions (1-2) are neglected the expression (16) will be modified to,

$$m_C = m_C^* + m_{C,emiss} \quad (24)$$

3. Equilibrium Constants

Mixed equilibrium constants for the reactions (2-5) (and combinations of these reactions) can be found in [2,5,6 and 7]. For solutions corresponding to ocean water mixed equilibrium constant has been found only for reaction (2). In Kramer (1958 and 1959) values of the mixed equilibrium constant for the overall reaction, combined from reactions 2-5, obtained from equilibrium measurements for solutions with a ionic strength corresponding to ocean water were given. Kramer obtained $pk(5^\circ C)=-10.93$ and $pk(25^\circ C)=-10.29$. In Sillén [2] equilibrium data for the reaction combined from reactions (2 and 3) at different temperatures and ionic strength corresponding to ocean water has been found. For the other reactions mixed equilibrium constants at a ionic strength near that of ocean water have been obtained. In table 2 mixed equilibrium constants at different temperatures and ionic strength obtained from [2, 5, 6] are given.

θ	Medium	pk_2	pk_3	pk_4	pk_5	pk_2+pk_3	$\sum_{i=2}^5 pk_i$
0	$\mu = 0$	7.91	-10.625	-6.579	-1.114		
5	$\mu = 0$	7.94	-10.557	-6.517	-1.194		
25	$\mu = 0$	8.06	-10.33	-6.352	-1.464		
5	3.5 % salinity	5.55				-3.5 *	-10.93 **
25	3.5 % salinity	6.19				-2.8 *	-10.29 **
25	1 M NaCl		-9.37				
25	0.26 M KNO ₃			-6.06			
25	1 M KNO ₃			-5.99			
25	1 M Na(ClO ₄)		-9.57	-6.04	-1.51		

Table 2. Negative logarithm of the mixed equilibrium constants obtained from [5], * [2] and ** [6].

The most important compounds in ocean water are Cl, Na, Mg, S, Ca, K, C, Br, Sr, F and O. According to [2] ocean water contains on average 0.54830 mole Cl^- /l, 0.47015 mole Na^+ /l, 0.05357 mole Mg^{2+} /l, 0.02824 mole SO_4^{2-} /l, 0.01024 mole Ca^{2+} /l, 0.00996 mole K^+ /l, 0.00234 mole HCO_3^- /l, 0.00083 mole Br^- /l, 0.00015 mole Sr^{2+} /l and 0.00007 mole F^- /l. From this composition it can be calculated that the average ionic strength of ocean water is approximately 0.7.

Since the ratio between the Mg^{2+} and Ca^{2+} concentrations in the ocean water is very close to 5.23, and that these concentrations can change by observable amounts only if enormous quantities of solid material would be dissolved, we estimate the negative logarithm of the mixed equilibrium constant for the reaction (1) from reaction (2) by the approximation,

$$pk_1 = pk_2 - \log(5.23) \quad (25)$$

From table 2, the following equations estimating the negative logarithm of the mixed equilibrium constants at a ionic strength corresponding to ocean water for reactions (2-5) have been obtained. From table 2 we obtain, by combining the data in the first and the second last column, the following models for pk_2 and pk_3 ,

$$pk_2(T) = 15.09 - \frac{2654}{T} \quad (26)$$

$$pk_3(T) = -8.156 - \frac{248.8}{T} \quad (27)$$

where T is the absolute temperature. For pk_4 we have, by considering the data in table 2, approximated the pk_4 value to -6.05 at 25° and a ionic strength corresponding to ocean water. The temperature correction is thereafter obtained from the data at zero ionic strength. The model for pk_4 is thus given by,

$$pk_4(T) = -3.524 - \frac{753.0}{T} \quad (28)$$

Finally the model for pk_5 is obtained such that the overall reaction (2-5) fits the data in table 2. The model for pk_5 is then given by,

$$pk_5(T) = -4.804 + \frac{1003}{T} \quad (29)$$

The model for the negative logarithm of the mixed equilibrium constant for the overall reaction (2-5) can now also be obtained from eqs. (26-29) resulting in,

$$pk(T) = -1.394 - \frac{2653}{T} \quad (30)$$

At temperature 5°C (corresponding to the average temperature of ocean water) the following values of the negative logarithm of the mixed equilibrium constants are obtained

from the above expressions ($pK_1=4.83$, $pK_2=5.55$, $pK_3=-9.05$, $pK_4=-6.231$, $pK_5=-1.198$). The ion product of water also changes with the temperature and the ionic strength. In [5] we obtain $pK_w=13.73$ at $25\text{ }^\circ\text{C}$ and $pK_w=12.97$ at $50\text{ }^\circ\text{C}$ in a $0.5\text{ M Na(ClO}_4\text{)}$ solution. Using these values we have used the following model in order to estimate the temperature change of this constant at an ionic strength near that of ocean water according to,

$$pK_w(T) = 3.906 + \frac{2929}{T} \quad (31)$$

the value at $5\text{ }^\circ\text{C}$ being $pK_w=14.436$. The mixed equilibrium constants may vary within a limit approximately $\pm 5\%$. However, since we are more interested in relative changes rather than absolute values and most of our calculations are made at $5\text{ }^\circ\text{C}$ we believe the expressions given in eqs. (25-31) are sufficiently accurate for the objective of this paper.

4. Calculating a Reference State in the Oceans

Since we have good estimates of the atmospheric carbon dioxide concentration and the Ca^{2+} concentration in the ocean water, it is convenient to calculate a reference state based on these values. Using the pK_i values above the equilibrium pH and the mass of carbon in the equilibrium system at the reference state can uniquely be calculated from the atmospheric carbon dioxide concentration and the Ca^{2+} concentration [8]. The average atmospheric carbon dioxide concentration was 30 years ago approximately 317 ppm and the Ca^{2+} concentration close to 0.01024 mole/l [2]. Inserting these values together with the pK_i values at $5\text{ }^\circ\text{C}$ given by expressions (26-29) into equation (17) we obtain a pH value of 8.210 at this reference state.

To our knowledge no continuous records of the the average pH of ocean water exist. However, the average pH -value of ocean water was in the beginning of 1960 8.1 ± 0.2 according to a paper by Sillén [2]. In this study we have also measured the pH -value from an ocean water sample taken from the Pacific Ocean (at Mission Beach in San Diego, U.S.). The pH of the sample was 8.11 at $5\text{ }^\circ\text{C}$ and it was measured by a Metrohm EA 120-16 combined glass pH electrode. The pH -value was calibrated at $pH = 4.00$ by a potassium hydrogen phthalate, $C_8H_5KO_4$, solution. The results from the calculations thus seems to be in quite good agreement with the results from the sample. It should however be observed that the calculated value is an estimate of the average pH -value of the whole ocean water volume 30 years ago and our measurement is based on a single local sample, 1989. Both values are however within the limits given by Sillén [2]. Thus our model seems to predict the acidity quite well so far.

Now inserting the calculated pH together with the total ocean water volume and the total number of moles of air into equation (15) we obtain an estimate of the total mass of carbon in the atmosphere and hydrosphere equal to 37003 Gton C at the reference state. Since the mass of carbon in the atmosphere is defined by the concentration (317 ppm) and the number of moles of air n_{air} ($0.177 \cdot 10^{21}$ mole) to be 673.3 Gton C, the mass of carbon in the hydrosphere at the reference state will be 36330 Gton C. This value is also very close to the estimate 36000 Gton C given in table 1.

Furthermore, inserting the Ca^{2+} concentration, a reference SO_4^{2-} concentration together with the pH -value at the reference state into equations (18-22) we can calculate the Δ^* value at the reference state from equation (22). By letting the SO_4^{2-} concentration be equal to 28.24 mmol/l as given in [2] we obtain the value $\Delta^* = 0.06867$ mole/l. From the previously given concentrations of Cl^- , Br^- , F^- , Na^+ , K^+ and Sr^{2+} obtained from [2] the value 0.06879 mole/l is obtained. Thus our model seems to fit all essential data very well so far.

5. Estimating the Atmospheric Carbon Dioxide Concentration

To explain the increasing carbon dioxide concentration in the atmosphere during the last 30 years the model is used to calculate the equilibrium atmospheric carbon dioxide concentration by taking into account the emission of carbon dioxide during the last 30 years. It can be estimated that the emission of carbon dioxide (that has caused decreasing reservoirs of solid carbon) has been approximately 150 Gton C during the actual period. Burning of fossil fuels has contributed 80 % of the emission, with the rest resulting primarily from deforestation.

Sulfur and nitrogen oxide emissions also will have an influence on the results. Based on data in [3, 4] the sulfur and nitrogen emission during the last 30 years from burning fossil fuels corresponds to the release of approximately 0.86 Gton S and 0.6 Gton N. An estimate of the total man made emission of sulfur and nitrogen oxides to the oceans is 1.85 Gton S and 0.9 Gton N during the actual period [3]. Since the average pH of ocean water is approximately 8.1 the sulfur and nitrogen oxides will mainly form sulfate SO_4^{2-} and nitrite NO_3^- ions when dissolved in ocean water. Thus the acidifying effect from sulfur is twice as high as for the nitrogen, on a mole basis. On a weight basis, the acidifying effect from nitrogen is approximately 16/14 relative to the effect from sulfur. Therefore we use the value $m_{S,emiss} = 2.85$ Gton S in our calculation to estimate the total man-made acidifying effect from both the sulfur and nitrogen oxides to the oceans during the actual period.

Using these values the model can be used to estimate the increase in the atmospheric carbon dioxide concentration caused by the carbon dioxide, sulfur dioxide and nitrogen oxide emissions. Inserting the emission of carbon dioxide (150 Gton C) and the emission of sulfur dioxide (2.85 Gton S) together with the previously calculated reference state for the whole ocean water volume into eqs. (15-23) we obtain the equilibrium atmospheric carbon dioxide concentration equal to 322.5 ppm while the equilibrium pH value being 8.2062. From the calculation we also find that the acidifying effect of the ocean from the sulfur and nitrogen oxides being approximately 1% while the remaining 99 % is because of the emission of carbon dioxide. Since measurements of the atmospheric carbon dioxide concentration gives a global mean value (1990) approximately 352 ppm [10], our model seems to clearly underestimate the carbon dioxide concentration, at least with the numerical values given in this first calculation.

6. Sensitivity Analysis

However, as other estimates of all parameters and variables included in the model have an influence on the results we will solve the opposite problem of calculating the numerical values of these variables and parameters such that we obtain the desired atmospheric carbon dioxide concentration. Parameters and variables that have been considered are: the emission of carbon dioxide, the emission of sulfur and nitrogen oxides, the volume of ocean water in equilibrium with the atmosphere as well as a possible effect from an increasing ocean water temperature. A sensitivity analysis of this kind is especially of importance in a simplified model where one can not assume that the model will fit the data with real values for all its parameters. In this case we particularly try to find out which variable or parameter is the most suitable to explain all local phenomena which are not included in the model's structure. In table 3 it is shown that the increase in the atmospheric carbon dioxide concentration during the last 30 years can be explained by assuming an emission of carbon dioxide (as well as the sulfur and nitrogen oxides) approximately 6 times higher than the emission calculated from table 1. From table 3 we also find that the actual atmospheric carbon dioxide concentration can be explained by an increased ocean water temperature by 1.054 °C or be explained by assuming that 8.8 % of the ocean water is in equilibrium with the atmosphere.

V_{water}/V_{tot}	Temp °C	$m_{C,emiss} + m_{S,emiss}$ Gton C+ Gton S	x_{CO_2} ppm
1	5	150+2.85	322.5
1	5	943+17.9	352.0
1	6.054	150+2.85	352.0
0.088	5	150+2.85	352.0

Table 3. Equilibrium atmospheric CO_2 concentration for different volumes of ocean water in equilibrium with the atmosphere, different ocean water temperatures and different emissions.

Next we make a more general calculation for the case when we solve for both the temperature and the volume of ocean water for different values of the carbon dioxide emission that correspond to the actual atmospheric carbon dioxide concentration 352 ppm. The results are given in figure 1.

From figure 1 it can be observed, for example, that the increase in the atmospheric carbon dioxide emission during the last 30 years can be explained by assuming a 333 m thick layer of ocean water being in equilibrium with the atmosphere if the emission of carbon dioxide is 150 Gton C and the ocean water temperature does not increase. If the carbon dioxide emission is increased to 200 Gton C the corresponding ocean layer thickness will be 551 m, in this case. On the other hand, if the whole ocean water volume is assumed to be in equilibrium with the atmosphere and the atmospheric carbon dioxide emission is left unchanged at 150 Gton C, the increase in the atmospheric carbon dioxide concentration during the last 30 years can be explained by an increased temperature of the ocean water by 1.054 °C. If the carbon dioxide emission is incre-

ased to 200 Gton C the corresponding ocean water temperature increase is 0.986 °C.

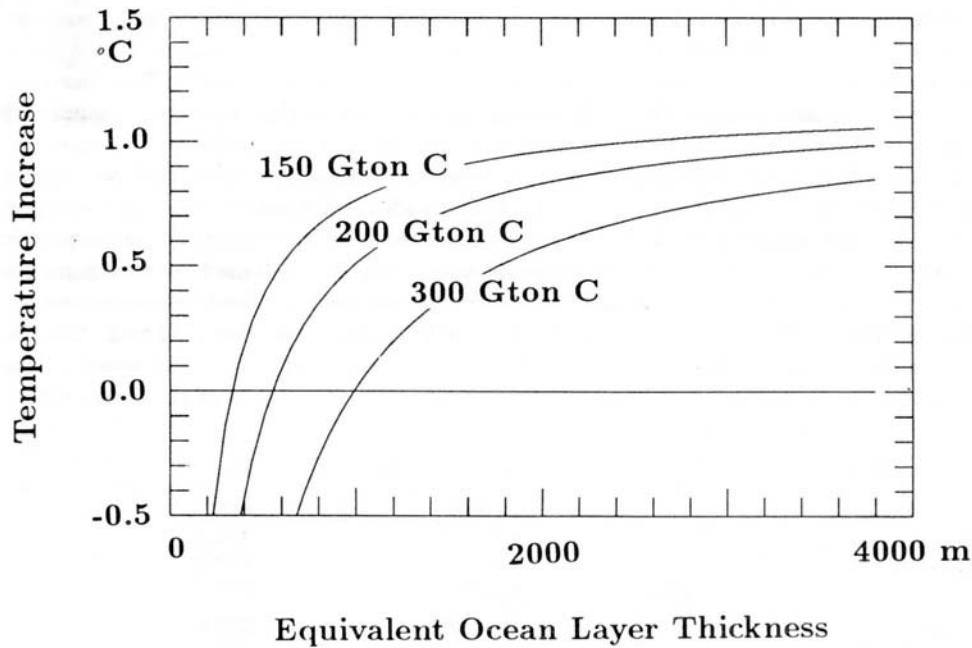


Figure 1. Parameter values explaining the carbon dioxide increase.

Since a most probable estimate of the increase in the ocean water temperature during the last 30 years is less than 0.2 °C and the carbon dioxide emission has most probably been less than 175 Gton C, it can be found from figure 1 that in order to explain the increased carbon dioxide concentration in the atmosphere by an equilibrium model the corresponding ocean layer thickness in equilibrium with the atmosphere must be in the region 300-400 m. The ocean layer thickness should not be regarded as a true ocean layer thickness, but a most suitable parameter to explain all local phenomena that are not considered in the models structure. The layer of well mixed water is on the average 75 m and the thermocline lies on an average depth of less than 300 m [15]. Since the calculated value of the ocean layer thickness is expected to be greater than the layer of well mixed water we find the obtained value very realistic. We will therefore use the obtained value 333 m on the ocean layer thickness and call the ocean layer thickness an equivalent ocean layer thickness or an equivalent ocean water volume in the following analysis.

7. Local Sources and Sinks of Carbon Dioxide

It is well known [10] that the average carbon dioxide concentration changes locally. The average carbon dioxide concentration being higher on the northern hemisphere than on the southern hemisphere. This being partly an effect from the nonuniform global distribution of oceans and land. Although the attempt of this paper has not been to make a rigorous model an interesting observation can be made concerning the changing amount of dissolved carbon in ocean water at different temperatures. At 5°C the total concentration of dissolved carbon is 2.2 - 2.3 mol/m³ and the pH approximately 8.21 according to our calculations. If the ocean water temperature increases the amount of dissolved carbon decreases rapidly. In table 4 the mass ratio of dissolved carbon at different temperatures have been calculated.

Temp °C	ΔpH	$\frac{m_{C,diss}(\theta)}{m_{C,diss}(5^{\circ}C)}$
0	0.087	1.3
5	0	1.0
10	-0.084	0.78
15	-0.165	0.62
20	-0.244	0.49
25	-0.320	0.39

Table 4. pH change and mass ratio of dissolved carbon at different temperatures.

From table 4 it can be observed for example that if ocean water is heated from 5°C to 15°C, 38 % of the dissolved carbon will be removed from the water (to the gas and solid phase). In [10] it has been found by observations that the sink of carbon dioxide in the Atlantic subarctic, Atlantic gyre, North Pacific, Southern gyres and Antarctic regions is over 3 Gton C/year. However the Equatorial region (between 15 °S to 15 °N) is a carbon dioxide emission source of approximately 1.6 Gton C/year.

Assuming that the average temperature difference between the bottom cold water transported from the Northern and Southern regions to the Equatorial region is approximately 10 °C we find from table 4, that in order to explain a carbon dioxide emission source of 1.6 Gton C/year the downward transport of water must be at least $5 \cdot 10^6$ m³/s. As the water temperature increases the water will be supersaturated with respect to Ca^{2+} and Mg^{2+} and solid $CaCO_3$ as well as $MgCO_3$ will be formed. Thus a part of the dissolved carbon will also be transformed to the solid phase. The estimate of the downward transport of water to the equatorial region must thus be of order 10^7 m³/s. This value is also of the same order of magnitude as the real ocean currents.

8. Future Predictions of the Atmospheric Carbon Dioxide Concentration

Finally in table 5 future predictions of the average atmospheric carbon dioxide concentrations are made based on the assumptions that an equivalent ocean water volume equal to 8.8 % of the total ocean water volume is in equilibrium with the atmosphere and a constant ocean water temperature. The future yearly emission of carbon dioxide, becau-

se of deforestation and burning of fossil fuels, has been assumed to increase by 0.05 Gton C/year, the current value (1990) being 7 Gton C/year. The emission of sulfur and nitrogen oxides has been assumed to follow the carbon dioxide emission by using the same emission ratio (between the sulfur+nitrogen oxides to carbon dioxide) as 1990. In the appendix the equilibrium composition of all components in the equilibrium system 1960, 1990 and 2050 are given. From the compositions in the appendix it may be noted that the dissolution of $CaCO_3$ and $MgCO_3$ will contribute to an amount of carbon, approximately equal to 50 % of the emission of carbon from burning fossil fuels, to the equilibrium system.

Year	pH	$m_{C,emiss}+m_{S,emiss}$ Gton C+ Gton S	x_{CO_2} ppm
1800	8.237	-365-6.9	280
1960	8.210	-150-2.9	317
1990	8.187	0+0	352
2000	8.177	72+1.4	369
2025	8.149	276+5.2	418
2050	8.120	510+9.7	477

Table 5. Predicted future average atmospheric carbon dioxide concentrations.

From table 5 it can be found that the future atmospheric carbon dioxide concentration will increase from approximately 1.7 ppm/year at the end of this century to 2.5 ppm/year at the middle of the next century, the absolute value being approximately 477 ppm in the year 2050. The future predictions are highly dependent on the carbon dioxide emission. From 1850 to this date the man made carbon dioxide emission increase has been on the average 8 kg C/person/year with some fluctuations the last 20 years. The man made carbon dioxide emission is approximately 1 ton C/person in 1990. Whether the carbon dioxide emission calculated per person will increase or not, it is obvious that the future carbon dioxide emission will be highly dependent on the population increase. Based on the assumption that the yearly carbon dioxide emission in the future would be 1 ton C/person, the emission values in table 5 correspond to a world population approximately 7, 8 and $10 \cdot 10^9$, at 2000, 2025 and 2050 respectively. The world population can be estimated to be very close to $7 \cdot 10^9$ at 2000 but the values $8 \cdot 10^9$ and $10 \cdot 10^9$ at 2025 and 2050 respectively are most probable heavily underestimated. It should, however, be observed that the population increase is biggest in the nonindustrialized countries, while the carbon dioxide emission mainly is produced in the industrialized countries. How the increasing population will affect the carbon dioxide emission after the year 2000 gives therefore rise to a great uncertainty in the predictions.

In table 5, the average atmospheric carbon dioxide concentrations at 1800 and 1960 have also been calculated by considering the estimated emission of carbon dioxide as well as sulfur and nitrogen emission since that time. Calculation of the hypothetical case of burning all fossil fuels (10000 Gton C) result in an average atmospheric carbon dioxide concentration of 3462 ppm and a pH of 7.682 in the ocean layer in this case. An interesting hypothetical observation can further be made concerning the reservoirs of carbon. If all

vegetation (560 Gton C), instead of fossil fuels, would be burned after 1990 the average atmospheric carbon dioxide concentration would be 490 ppm and the average pH value 8.11. Both cases will, of course, also have an influence on the other flow rates of carbon dioxide.

9. Discussion

A simple chemical equilibrium model for the change in the atmospheric CO_2 -concentration has been presented. The model shall not be taken as an equilibrium model, between approximately 8.8 % of the ocean water and the whole atmosphere. It is obvious that the remaining 91.2 % of the ocean water is also of importance. Since the carbon dioxide exchange between the atmosphere and the surface as well as the diffusion and circulation of different carbon compounds changes both in horizontal and vertical direction, simple models can not fit data with "true" values on its parameters. In our case, the ocean water volume has therefore been considered as an equivalent ocean water volume explaining the increasing atmospheric carbon dioxide concentration by an equilibrium model. The equivalent ocean water volume (or layer thickness) thus has to be understood as an integrated mean value explaining all local phenomena contributing to the average carbon dioxide increase in terms of an equivalent ocean water volume. We find this parameter as a most suitable "averaging" parameter. The model provides a good fit to the data used in the calculations, and takes into account what are believed to be the most essential equilibrium reactions for the carbon dioxide change. Bounds for the atmospheric carbon dioxide concentration, caused by increases in both the amount of carbon in the equilibrium system and the temperature of the ocean water, were predicted. More precise predictions require more accurate estimates of the emissions and of the mixed equilibrium constants for the considered reactions.

The hypothesis assuming chemical equilibrium between a layer of ocean water and the atmosphere seems to be quite satisfactory and gives a very good fit to observed data. The calculations in this paper were performed by assuming the average temperature of the ocean water at the reference state to be equal to 5 °C. This is of course a simplification. However, it should be pointed out that the calculations are not very sensitive to moderate changes in the absolute value of the temperature, while the difference in the temperature from the reference state is of importance. An increasing reference temperature result in a decreasing absolute pH value, however, also for the pH value only the difference from the reference state is of importance in the calculations.

For long-term calculations the solid dissolution reactions and mixing of deep ocean water need be considered more carefully. The solid dissolution reactions probably compensate for other factors trying to change the acidity, resulting in a constant pH -value and correspondingly an almost constant average atmospheric carbon dioxide concentration on a very-long-term basis. Vertical pH measurements in upper and deep ocean layers (at a constant reference state) could give interesting information about the system on a short term basis. Also analysis of deep ocean water samples might provide information which indicate if the dissolution of carbonates have caused some variation in the calcium concentration

[9].

The pH of ocean water has previously been modelled as a pH -stat model [2] allowing no changes in the pH . However the pH -stat model requires the solution to be in equilibrium with at least three other solid phases SiO_2 (quartz), $Al_2Si_2O_5(OH)_4$ (kaolinite) and $KAl_3Si_3O_{10}(OH)_2$ (K-glimmer). It is our belief that these solid dissolution reactions are very slow compared to the ionic reactions, allowing a pseudo equilibrium in the liquid phase. For long term calculations (hundreds and thousand of years) the solid dissolution reactions have, however, to be considered more carefully, most probably resulting in a constant pH allowing almost no change in the atmospheric carbon dioxide concentration, as in the pH -stat model [2].

In order to explain the increasing average atmospheric carbon dioxide change during the last 30 years and to predict the carbon dioxide concentration 10-100 years ahead, the model presented here seems very attractive. It should be pointed out that the carbon dioxide emission from burning fossil fuels will not be accumulated in the atmosphere in any greater proportion than any of the other production rates in table 1. Only the difference between the flow rates of carbon dioxide into and from the atmosphere is of importance. Whether this difference is caused by burning fossil fuels only, or fluctuations in the other flow rates also have a significant contribution, is difficult to say. The increasing mass of carbon in the atmosphere and hydrosphere is of primary importance for estimation of the equilibrium atmospheric carbon dioxide concentration. Thus a proper estimate of the changing mass of carbon in the equilibrium system is of importance in the calculations. In the absence of other reliable data, the increasing mass of carbon in the atmosphere and hydrosphere was calculated in this paper as if approximately 80 % was caused by the emission of carbon dioxide from burning fossil fuels and the remainder from deforestation.

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APPENDIX

	$pH=8.210$	$pH=8.187$	$pH=8.120$
Mg^{2+}	53.570 mmole/l	53.613 mmole/l	53.752 mmole/l
Ca^{2+}	10.240 mmole/l	10.248 mmole/l	10.275 mmole/l
CO_3^{2-}	0.276 "	0.276 "	0.275 "
HCO_3^-	1.913 "	2.015 "	2.343 "
$CO_2(aq)$	0.020 "	0.022 "	0.030 "
SO_4^{2-}	28.240 "	28.241 "	28.243 "
Mass C (Ocean layer)	3188 Gton C	3338 Gton C	3821 Gton C
CO_2	317 ppm	352 ppm	477 ppm
Mass C (atmosphere)	673 Gton C	747 Gton C	1013 Gton C
Emission of S		2.85 Gton S	12.54 Gton S
Emission of C		150 Gton C	660 Gton C
Mass C from $CaCO_3$		12 Gton C	50 Gton C
Mass C from $MgCO_3$		62 Gton C	263 Gton C
Total dissolved mass of C in the ocean layer and the atmosphere	3861 Gton C	4085 Gton C	4834 Gton C

Table A.1. Mg^{2+} , Ca^{2+} , CO_3^{2-} , HCO_3^- , $CO_2(aq)$, SO_4^{2-} and $CO_2(g)$ concentrations 1960, 1990 and 2050 assuming chemical equilibrium between the atmosphere and a ocean water layer with the equivalent thickness of 333 m.