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A comparison of Gösta Pettersson's carbon cycle model with observations

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Abstract

A carbon cycle model of a simple two-box type, but improved with a temperature dependent rate constant according to Arrhenius equation, has been developed by Gösta Pettersson. He reported a good agreement between model and observational data. His model results suggest that anthropogenic emissions have a less role compared to other models giving more weight to thermal degassing of the ocean as an explanation for the increasing carbon dioxide mixing ratio. In this work the Pettersson model was studied and tested against observational data. Also in this work a good agreement between model and observations was found.

Introduction

Gösta Pettersson has discussed the global carbon cycle, especially how it is related to the changing carbon dioxide ratio of the atmosphere and the role of human carbon dioxide emissions, in a series of three scientific papers (Pettersson, 2013a, 2013b, 2013c).

His discussion of the carbon cycle is a challenge to some of the foundations of the simple models of the carbon cycle presented by Revelle and Suess (1957) and Bolin and Eriksson (1959) by introducing a new method of accounting for a changing global temperature on the carbon dioxide mixing ratio. Revelle and Suess represented the ocean with a one-box model while Bolin and Eriksson introduced a two-box model with one box for the mixed layer and one box for the deep ocean. They had little reason including the effect of temperature changes in their models because there were very little observations available and no global temperature rise had been observed at that time.

We now know that the carbon dioxide mixing ratio has increased monotonically since the beginning of Keeling's measurements. This has been accompanied by a global temperature rise. During recent years there is an increasing interest in how the carbon dioxide mixing ratio varies on a short time scale correlated to short term variations in the global temperature. Bacastow (1976) noted a connection to ENSO oscillations. Salby and Titova (2013) have presented results in a conference contribution giving an equation describing such short term variations in the carbon dioxide mixing ratio with temperature. Applied on the long term global temperature rise this equation suggests that the increase of the carbon dioxide mixing ratio may almost fully be explained by the global temperature change (Salby, 2013). Humlum et al. (2013) found that the short term changes of the carbon dioxide mixing ratio with a lag of about one year correlated well with short term changes in global temperature but found no correlation with short term changes in anthropogenic carbon emissions.

Those short term variations probably cannot be explained by the change in carbon dioxide solubility in seawater with changing temperature. Thus they presumably have to do with changing kinetics of physicochemical and biogeochemical processes.

The carbon cycle models that have emerged on the basis of the founding works by Revelle and Suess (1957) and Bolin and Eriksson (1959) seem not to discuss a similar superficial dependence of physicochemical or biochemical kinetics on temperature as proposed by Pettersson. Temperature dependence of chemical kinetics is usually described by using activation energies according to Arrhenius' equation (Moore, 1983). This has been adopted by Pettersson for his model.

In the often cited box-diffusion model by Oeschger et al. (1975) temperature dependence on kinetic parameters was not considered. A representative member of modern ocean biogeochemistry models is HAMMOC (Ilyina et al., 2013; Maier-Reimer et al., 2005). According to those publications temperature dependence in HAMMOC is introduced via the temperature effects on individual process steps and concerns solubilities, chemical reaction equilibrium constants, some kinetic parameters as in the case of a Michaelis-Menten kinetic equation. Such models follow another approach than the simple, superficial founding models used by Revelle and Suess (1957) and Bolin and Eriksson (1959).

This background gives a good justification for the box model developed by Gösta Pettersson in Pettersson (2013c). He starts from a box setup similar to the one used by Revelle and Suess (1957) but now with the aim of studying the effect of introducing temperature dependence on a superficial level by activated chemical kinetics according to Arrhenius' equation. This is a very simple approach to begin with but it should be justified by the aim of developing a new line of fundamental understanding.

Pettersson (2013c) determined model parameters from observational data. He found by simulations with his model that only about half of the increase of the carbon dioxide mixing ratio in the atmosphere consists of anthropogenic emissions that have not been absorbed by the ocean. The rest of the increase is due to the global temperature rise. Hence it should be of interest with a second opinion on how well Pettersson's model may describe observational data.

The main purpose of this work is to make an independent study of the power of Pettersson's model to describe observational data for the carbon dioxide ratio and its rate of change.

Gösta Pettersson's model

Gösta Pettersson (2013c) has used a two-box model, one box for the atmosphere and one box for the ocean. This is the same configuration as used by Revelle and Suess (1957). The two reservoirs are assumed to be equilibrated in the past with respect to carbon, more specifically Pettersson assumed that this was the case before 1850 and the same assumption is used in this work. Following Revelle and Suess the rate of carbon transfer from one reservoir to the other is assumed to be proportional to the carbon reservoir amount. In the equilibrated state the two rates to and from the atmosphere from and to the ocean are assumed to be equal. No buffer effect due to carbon chemistry when perturbing the system, as introduced by Revelle and Suess in a second part of their paper, is considered in Pettersson's model.

This results in the following equation for the change in the carbon amount in the atmosphere when the system is perturbed by anthropogenic carbon dioxide emissions (Pettersson, 2013c).

$$\frac{dx}{dt} = Em(t) - kx + d(c - x) \quad (1)$$

where

x = amount of carbon in the atmosphere

$Em(t)$ = amount of anthropogenic carbon dioxide emissions per year

$k = \frac{1}{\tau}$ = rate constant for transfer of carbon from the atmosphere to the ocean

τ = average life time for a carbon dioxide molecule in the atmosphere

d = rate constant for transfer of carbon from the ocean to the atmosphere

c = amount of carbon in the ocean.

In order to use this equation for studying the effect of anthropogenic carbon dioxide emissions over the last centuries one should consider the effect of temperature on the rate constants. While the global average rate of dissolution of carbon dioxide in the ocean may not change much with the fairly small global mean temperature changes the same assumption is not necessarily valid for the degassing of carbon dioxide from the ocean into the atmosphere. There is a complex network of chemical and biochemical processes influencing the degassing process (Ilyina et al., 2013). Hence it is logical to assume that the rate constant d follows Arrhenius' equation (Moore, 1983):

$$d = A e^{-E/RT(t)} \quad (2)$$

where

A = a constant

E = is an activation energy for the degassing process

$R =$ the gas constant

$T(t) =$ the absolute global mean temperature.

Note that the global mean temperature is used, not the global mean ocean temperature or the global mean ocean surface temperature. What is the best choice in this respect is not self evident and will not be discussed further here. However, the variations in global mean temperature and global mean ocean surface temperature are obviously strongly correlated. In this work Pettersson's original choice of using the global mean temperature is followed.

This model may be further developed by using the equilibrated state considering that the amounts of carbon in the reservoirs are not changing in this state:

$$\frac{dx}{dt} = Em(t_0) - kx_0 + d_0(c_0 - x_0) = -kx_0 + d_0(c_0 - x_0) = 0 \quad (3)$$

where index 0 denotes the equilibrated state at $t_0 = 1850$ and assuming that $Em(t_0) \approx 0$. This gives:

$$d_0 = \frac{k x_0}{c_0 - x_0} \quad (4)$$

We may now write

$$d_0 = A e^{-E/RT_0}; \quad d = d_0 e^{E/RT_0} e^{-E/RT(t)} = \frac{k x_0}{c_0 - x_0} e^{E/RT_0} e^{-E/RT(t)} \quad (5)$$

$$\frac{dx}{dt} = Em(t) - kx + d(c - x) = Em(t) - kx + \frac{k x_0}{c_0 - x_0} e^{E/RT_0} e^{-E/RT(t)} (c - x) \quad (6)$$

In this work I have made the approximation that $\frac{c-x}{c_0-x_0} \approx 1$ since the changes in c and x due to both the anthropogenic perturbations and the natural perturbations caused by temperature changes are small. This gives the following equation:

$$\frac{dx}{dt} = Em(t) - kx + k x_0 e^{E/RT_0} e^{-E/RT(t)} \quad (7)$$

It is more useful to express this equation in terms of carbon dioxide mixing ratio y using that:

$$x = x_0 \frac{y}{y_0}; \quad \frac{dy}{dt} = \frac{y_0}{x_0} \frac{dx}{dt} \quad (8)$$

This gives:

$$\frac{dy}{dt} = \frac{y_0}{x_0} Em(t) - ky + k y_0 e^{E/RT_0} e^{-E/RT(t)} \quad (9)$$

Data and methods

For using the model equation (9) we need observational data for carbon dioxide mixing ratio, for anthropogenic emissions and global temperature. Yearly data for carbon dioxide mixing ratio and its

rate of change were taken from the Mauna Loa observations. For the time period from 1850, before the Keeling curve, carbon dioxide mixing ratios from the Law Dome ice core, smoothed over 20 years, were used (CDIAC, 2013a).

For the anthropogenic emissions data from CDIAC was used (CDIAC, 2013b; CDIAC, 2013c). Data for fossil carbon dioxide emissions were available to 2010 while data for emissions for land use changes ended 2005. For the purpose of making calculations up to 2010, emissions from land use changes for 2006-2010 were assumed to be equal to 2005.

For the global temperature, yearly global mean temperature anomalies from HadCRUT4 were used (Morice et al. 2012). Yearly absolute global mean temperatures were calculated from HadCRUT4 yearly anomalies by adding the mean global temperature for the time period 1961-1990, which was adopted to 287.15 K according to Jones et al. (1999).

Calculations were carried out by means of the free software Scilab (Scilab, 2013). The model equation (9) was fitted in various ways to Mauna Loa data for the rate of change of the carbon mixing ratio by minimizing the sum of least squares. Since this may give non-linear least-squares minimization problems in this case, the Levenberg- Marquardt method (Marquardt, 1963). was used applied in the form of the Scilab function *lsqrsolve*. The values of the carbon dioxide mixing ratio were calculated from the calculated values of its rate of change by integration, applying the trapezoidal numerical method in the form of the Scilab function *inttrap*.

Results

Here I will present two calculations. In both cases the values used by Pettersson (2013) for the preindustrial atmospheric carbon reservoir $x_0=600$ Pg and the global temperature of year 1850 $T_0=286.76$ K were used.

In the first case the values of three parameters y_0 , k and E were determined by fitting the model equation (9) to the observed rate of change of the carbon mixing ratio, $\frac{dy}{dt}$, for 1959-2010 according to Mauna Loa observations using least-squares minimization. The parameter values were determined to $y_0=275.1$ ppm, $\tau=\frac{1}{k}=22.5$ years (note that the reciprocal of k is the average life time of a carbon dioxide molecule in the atmosphere) and $E=135.9$ kJ/mol. Figure 1 shows calculated values with those parameter values (blue curve) compared to the observations (green curve). Although there is a good fit in parts of the time period the amplitude of the short term variations in the calculated values is too low.

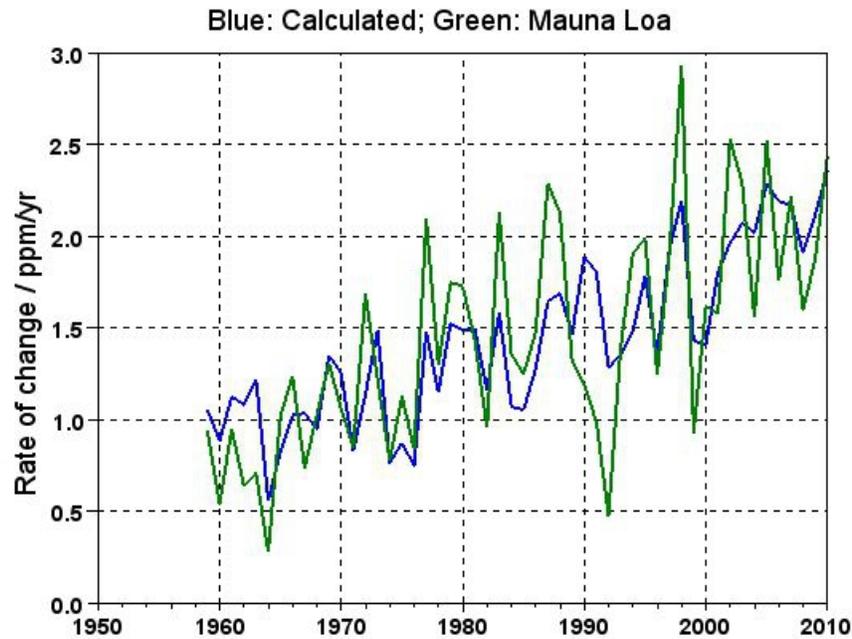


Figure 1. The model was calculated with a life time $\tau = 22.5$ years and an activation energy $E = 135.9$ kJ/mol.

The carbon dioxide mixing ratios were calculated by integrating the yearly rates according to the model equation (9) calculated using the determined parameter values:

$$y(t) = y(t_1) + \int_{t_1}^t \frac{dy}{dt} dt \quad (10)$$

Fig. 2 shows calculated (blue) and observed values (green) with $t_1 = 1959$ in equation (1).

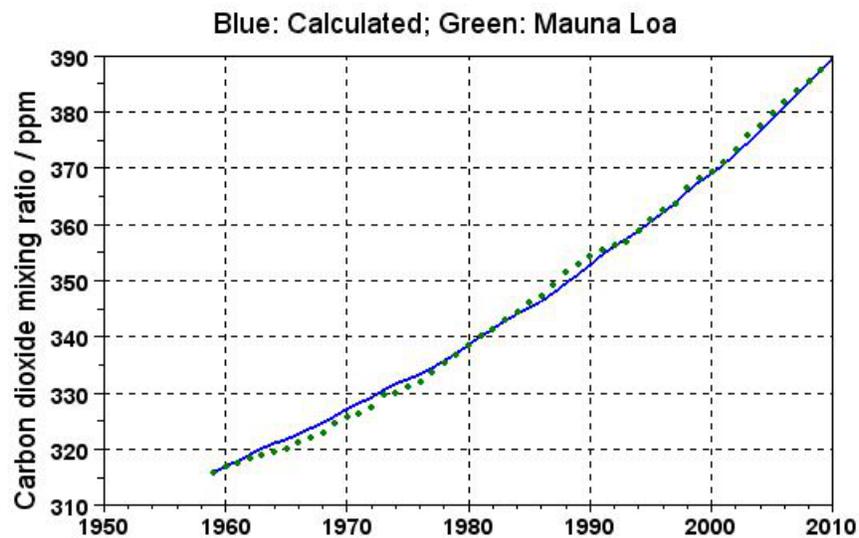


Figure 2. The same model parameters were used as in Fig. 1.

The Keeling curve is well represented by the model using the fitted parameter values. In Fig. 3 the calculated carbon mixing ratios (blue curve) for the whole period 1850-2010 are compared with the Keeling curve amended with Law Dome data (green points).

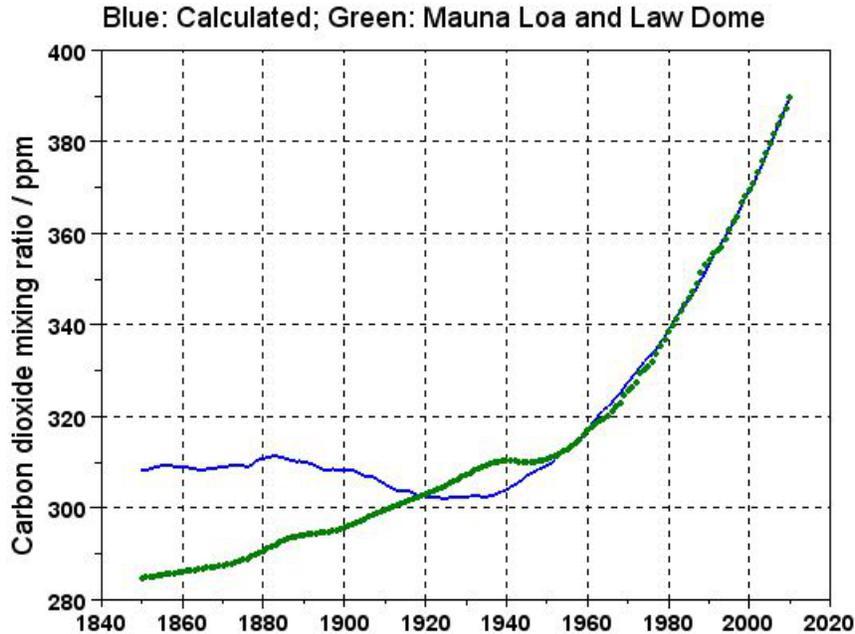


Figure 3. The same model parameters were used as in Fig. 1.

The value of $t_1=2010$ was used in this case, a choice justified by the more uncertain ice core values during the first time period. Obviously the model does not work well for the first period of 50 years.

In the second calculation another line of determining the parameter values of k and E was adopted according to Pettersson (2013c). The values determined by Pettersson were used. He determined the value of $\tau = \frac{1}{k} = 14$ years by using the bomb test curve (Pettersson, 2013a). He determined the activation energy E in such a way that the model equation gave the best amplitude description of the peak in Fig. 1 associated with the El Niño event in 1998 (Pettersson, 2013c). This gave $E=165$ kJ/mol.

As a consequence only one parameter y_0 was determined by fitting. In Fig. 4 the calculated and observed values are compared like in Fig. 1. The fitted parameter value was determined to $y_0=280.6$ ppm.

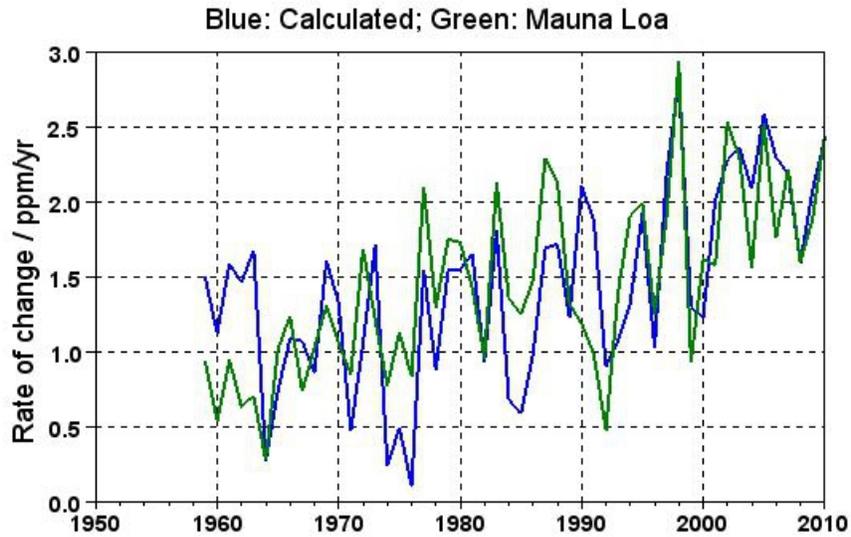


Figure 4. The model was calculated with a life time $\tau = 14$ years and an activation energy $E = 165$ kJ/mol.

Now a calculated curve is obtained that not only shows peaks and valleys like in the observations but give the heights and depths of those more correctly than in Fig. 1. Measured formally by using the sum of least squares Fig. 1 shows the better fit with a value of this sum of 6.9 compared to 11.0 for the calculation in Fig. 4. However, the difference between calculated and observed values in Fig. 4 are not exceptional considering measurement errors in the observations used while the low amplitudes shown in Fig. 1 appears more like a systematic error. Perhaps the lowest sum of least squares does not give the best answer in this case.

Further support for such an assessment is found from the other curves. The same curves for the carbon dioxide mixing ratio as in Fig. 2 and 3 were calculated and are shown in Fig. 5 and 6.

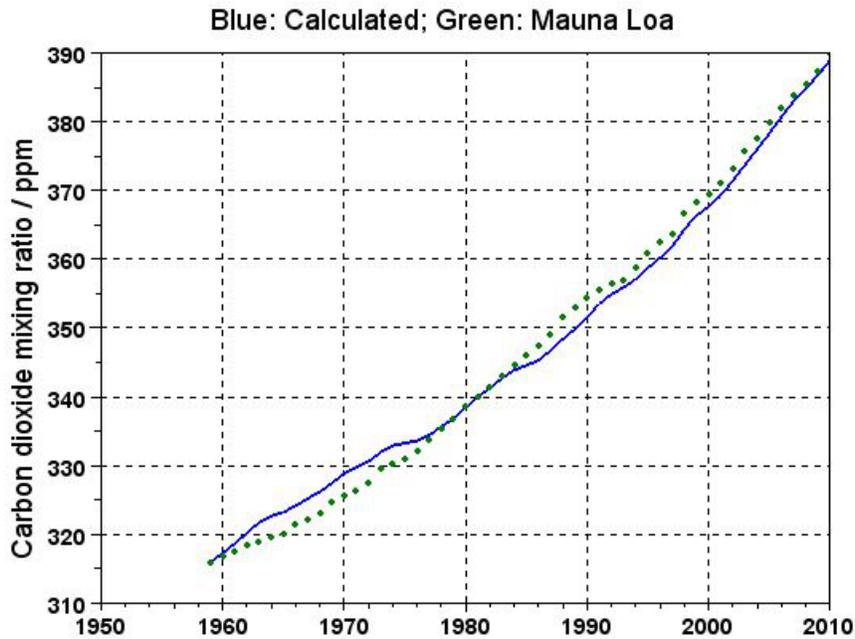


Figure 5. The same model parameters were used as in Fig. 4.

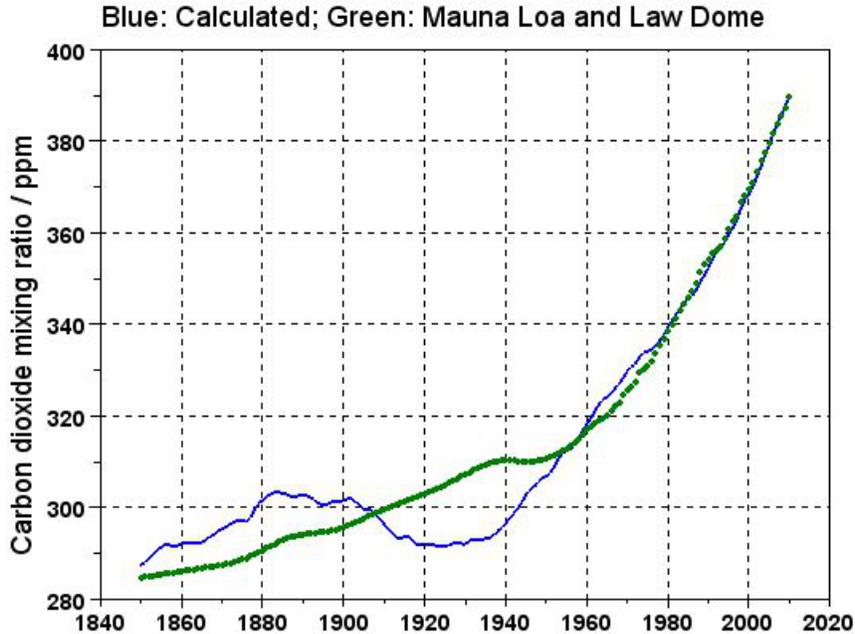


Figure 6. The same model parameters were used as in Fig. 4.

While Fig. 2 and Fig. 5 are equivalent Fig. 6 shows a better fit than Fig. 3. In fact considering that the errors both in carbon mixing ratio data (from Law Dome) and in temperatures are much higher for the first 100 years in Fig. 6 a better fit than obtained is not to be expected.

The Scilab files for computing those results are available in:

[A comparison of Gösta Pettersson's carbon cycle model with observations – computer code](#)

Relation to Murry Salby's equation

The equation that Salby and Titova have shown is describing the changes of the carbon dioxide mixing ratio as a function of temperature changes expresses the rate of change of that ratio as proportional to a temperature difference:

$$\frac{dy}{dt} = k_{MS}(T - T_0) \quad (11)$$

where

k_{MS} = a constant

T = the global mean temperature

T_0 = the global temperature in the equilibrated state.

According to this equation anthropogenic emissions have no impact on the rate of change of the carbon dioxide mixing ratio. This equation is related to Pettersson's model according to the following derivation.

Taylor expansion of the last term in equation (9) around T_0 gives, keeping only the two first terms:

$$k y_0 e^{E/RT_0} e^{-E/RT(t)} = k y_0 + k y_0 \frac{E}{RT_0^2} (T - T_0) \quad (12)$$

Inserting this in equation (9) gives:

$$\frac{dy}{dt} = \frac{y_0}{x_0} Em(t) - k(y - y_0) + k y_0 \frac{E}{RT_0^2} (T - T_0) \quad (13)$$

According to this, Murry Salby's equation may be seen as an incomplete variant of equation (13) neglecting the two first terms. It is not unlikely that the two first terms in equation (13) temporarily describe a curve of a similar form as the third term. That would explain why Murry Salby's equation gives a good fit to observational data. However, the complete equations (9) and (13), unlike Murry Salby's equation (11), show that anthropogenic emissions have an impact on the carbon dioxide mixing ratio. Although the results of Salby and Titova (2013) may not give an accurate picture of the the impact of anthropogenic emissions they support the results from the Pettersson model.

Discussion

In the model used by Pettersson (2013c) no buffer factor is included. How may this be justified?

The buffer factor in the mixed layer is a constant independent of time in the founding model by Bolin and Eriksson (1957) and this was also applied by their followers, for example in the box-diffusion model by Oeschger et al. (1975). However this is the result of assuming a constant carbonate alkalinity in the mixed layer while modern carbon cycle models like HAMMOC include transport equations with sources and sinks for the total alkalinity, see equations (1) and (17) in Ilyina et al. (2013). While Bolin and Eriksson treated the mixed layer as a closed system with respect to alkalinity this is not the case in

modern carbon cycle models. Hence, it is not self evident that the mixed layer has such a restricting effect on the carbon dioxide absorption as follows from the model by Bolin and Eriksson.

Bolin and Eriksson also included ^{14}C in their model, see equations (35) and (36) in their paper. It is easily seen from those equations, and may be confirmed by numerical solution of their model, that the considerable emissions of anthropogenic carbon dioxide as time has gone by should have pushed considerable amounts of $^{14}\text{CO}_2$ out of the mixed layer into the atmosphere. This is contradicted by the finding of Pettersson (2013b) that the mixing ratio of $^{14}\text{CO}_2$ after the cessation of the nuclear bomb tests has followed an e-folding relaxation process with no sign of $^{14}\text{CO}_2$ being pushed out of the ocean.

Those two objections against an effectively working buffer factor is further support that such a two box model as used by Pettersson (2013c) is justified for the purpose of his study.

The usage of Arrhenius' equation for the temperature dependence of the degassing process is well justified. This equation has been found to account for temperature dependence of kinetic parameters in a much more general context than chemical reactions. Solid state diffusion is a prime example (Borg and Dienes, 1988). Even the effect of temperature on the ice flow in glaciers may be described by Arrhenius' equation (Alley, 1992). Pettersson's (2013c) finding that this equation describes the temperature dependence of the rate of the degassing process for carbon dioxide from the ocean should not be surprising.

In summary this discussion suggests that a reasonable explanation for the good fit between the Pettersson model and observational data may be that the buffer factor has not an important effect of restricting the transport of carbon dioxide through the mixed layer. After all the mixed layer is an open system and various feedbacks from lower layers of the ocean may not be excluded.

Pettersson's model is a first step in a possible new line of fundamental understanding. Much further work is needed to develop new models based on this new line of thinking, like how more complex models gradually were developed from the founding work of Revelle and Suess (1957) and Bolin and Eriksson (1959).

Conclusions

The model equation for the rate of change of the carbon dioxide mixing ratio in the atmosphere according to Pettersson (2013a) was studied and tested against observational data. The Pettersson model may be viewed as an improvement of a box model used by Revelle and Suess (1957) by introducing temperature dependence of a rate constant according to Arrhenius equation.

Fitting three model parameters to Mauna Loa data for the rate of change of carbon dioxide mixing ratio gave a fairly good fit for the rates of change and agreed well with the Mauna Loa mixing ratios but failed to agree sufficiently well with ice core mixing ratios from Law Dome.

When values of two parameters, the average life time of carbon dioxide molecules in the atmosphere and the activation energy, independently determined with other methods according to Pettersson (2013a, 2013c), were used and only one model parameters fitted, agreement was also found for the Law Dome data.

Murry Salby's equation (Salby, 2013) was shown to be an approximation of the Pettersson model albeit underestimating the role of anthropogenic emissions compared to the full model. This may explain that this equation can be fairly well fitted to observational data.

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