Temperature effects on the atmospheric carbon dioxide level

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A simple two-box model has been designed to describe the main kinetic characteristics of carbon dioxide exchange between the atmosphere and the hydrosphere. The model is based on reported equilibrium data for the system, includes reported temperature changes and rates of anthropogenic emissions as perturbation factors, and uses the turnover time of airborne carbon dioxide and the activation energy for outgassing of waterborn carbon dioxide as adjustable parameters.

Analysis of the temperature dependent multiannual fluctuations of the Keeling curve provides evidence that they derive from thermal outgassing with an activation energy of 165 kJ/mol/K and a turnover time of 14 years. For these values of the adjustable parameters, the model gives an almost perfect description of the long-term trend of the Keeling curve and attributes the rising concentration of airborne carbon dioxide during the industrial era to approximately equal contributions from anthropogenic emissions and thermal outgassing of carbon dioxide from the hydrosphere.

The results provide clear evidence that the atmospheric carbon dioxide level is strongly affected by temperature changes due to the temperature dependence of the solubility of carbon dioxide in water. Climate models that that do not take thermal outgassing of carbon dioxide from the hydrosphere into account will gravely overestimate anthropogenic effects on future temperatures.

The Keeling curve describes the time-dependence of the atmospheric carbon dioxide concentration, as determined by C. D. Keeling and collaborators at the Mauna Loa observatory since 1958 [1]. The curve exhibits both seasonal and multiannual fluctuations around its long-term trend towards higher values. In a thorough analysis of such fluctuations, Keeling found that the seasonal ones may reflect such a multitude of effects of uncertain strength and partly non-global character that their precise origin cannot yet be unequivocally established [2].

The multiannual fluctuations, however, were found to be strongly and positively correlated to global temperature changes associated with the El Niño–Southern Oscillation cycle. Rapidly rising air levels of carbon dioxide typically occur during El Niño events with their global scale temperature increases, as was first noted by Bacastow [3]. Subsequent analyses have shown that fluctuations of the atmospheric carbon dioxide level lag several months behind the temperature changes [4]. This means that the fluctuations are caused by the temperature changes and hence are of thermal origin.

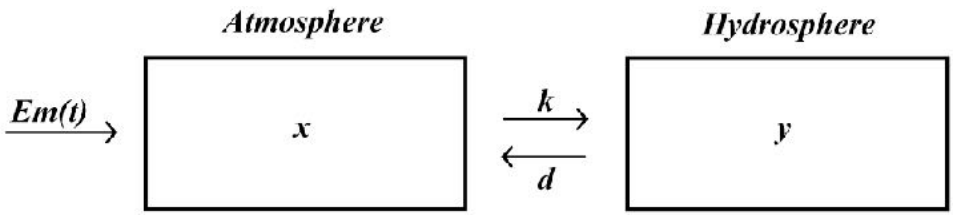
Keeling pointed out that the multiannual fluctuations are unrelated to the rates of anthropogenic emissions of carbon dioxide [2], and volcanic emissions can be anticipated to remain unaffected by global temperatures. Consequently, the multiannual fluctuations are likely to derive from thermal effects on the rate of exchange of airborne carbon dioxide with the hydrosphere or the biosphere. Globally representative effects of increasing temperature on the biosphere are associated with increased growth and carbon dioxide consumption. Thermal effects on the biosphere, therefore, should be negatively correlated to changes of the carbon dioxide level and cannot account for the observed positive correlation.

Gas exchange between air and water, however, has been firmly established to be thermally affected in the direction required to explain the observed positive correlation. Warm water holds less dissol-

ved carbon dioxide than cold water. This means that a temperature increase by necessity will trigger an outflow of carbon dioxide from the hydrosphere to the air and implies that such outgassing must contribute to the multiannual fluctuations of the Keeling curve. The analyses and model studies now reported were undertaken to estimate the magnitude of that thermal effect and hence to obtain information on the extent to which thermal outgassing has contributed to the long-term trend of the Keeling curve.

Theory and procedures

Scheme 1 shows a simple two-box reaction system describing the main processes contributing to the relaxation of airborne carbon dioxide. The rate constant *k* characterizes the transfer of carbon dioxide from the atmosphere to the hydrosphere; its reciprocal value stands for the turnover time of airborne carbon dioxide, as defined by the IPCC [5]. The rate constant *d* characterizes the reverse process of degassing of the hydrosphere and refers to the total amount of aquatic carbon dioxide, *i. e*. to the dissolved gas and its hydrated derivatives carbonic acid, bicarbonate ions and carbonate ions. The latter four species are assumed to equilibrate rapidly over the time-scales considered and, therefore, need not be treated individuall



Scheme 1. *Kinetic two-box model for the exchange of carbon between the atmosphere and the hydrosphere. Em(t) stands for the emission rate of anthropogenic carbon*

If the atmospheric and hydrospheric carbon contents are denoted *x* and *y*, respectively, the law of mass action prescribes that their time-dependence will be governed by the simultaneous diffential equations

$$dx/dt = Em(t) - k\,x + d\,y \qquad (1)$$

$$dy/dt = k\,x - d\,y \qquad (2)$$

where $Em(t)$ represents the rate of emission of anthropogenic carbon dioxide to the atmosphere.

Explicite sixth degree polynomial expressions for *Em(t)* were obtained by regression analysis of data reported by the Carbon Dioxide Information Analysis Center (CDIAC) for anthropogenic emissions of fossil carbon dioxide 1850–2009 [6] and of emissions due to land-use changes 1850–2005. Emissions occurring prior to 1850 were assumed to be of negligible magnitude. Emissions

due to land-use changes over the period 2006–2010 were put equal to 1.48 Giga ton carbon (GtC) per year, the mean value for the period 2001–2005 according to the CDIAC.

The rate constants k and d define the corresponding equilibrium constant Q as

$$Q = d/k \tag{3}$$

According to carbon cycle data presented by the Intergovernmental Panel on Climate Change (IPCC) [8], pre-industrial equilibrium values of x and y are given approximately by 600 GtC and 38 000 GtC respectively. The pre-industrial value of the equilibrium constant, therefore, was assumed to be given by $Q' = 600/38000$.

The temperature dependence of the carbon exchange process was simulated with the assumption that the thermal effect derives from the degassing rate constant d and conforms to the Arrhenius equation

$$d = A\ \mathbf{Exp}[-E^*/RT(t)] \tag{4}$$

where $T(t)$ represents the absolute temperature, R the gas constant, and E^* the activation energy of the degassing process. The temperature $T(t)$ was described as a best-fit sixth degree polynomial in t, obtained by regression analysis of reported global temperature anomalies vs. time (normally the HadSST3-series [9]). These anomalies refer to a reference temperature of 14.0 ˚C [10], for which reason 287.15 K was added to convert them into absolute temperatures.

The time-course of x was evaluated by solving Eqns. (1–2) numerically for selected periods of time, starting with the year 1850. The above preindustrial values of x, y and Q' were taken to refer to that year and to the absolute temperature $T(t)' = 286.76$ K, which corresponds to the temperature anomaly of –0.39 ˚C that was found to apply for 1850 according to the above regression analysis. The proportionality constant A in Eqn. (4) was eliminated using year 1850 as a reference point, *i. e.* by using the relationship

$$\mathrm{A} = k\ Q'/\mathbf{Exp}[-E^*/RT(t)'] \tag{5}$$

which can be readily derived from Eqns. (3–4). This means that Eqns. (1–5) constitute a kinetic model that defines the time-dependence of x using the rate constant k and the activation energy E^* as the only adjustable parameters.

In climatology, the rate constant k usually is referred to in terms of its reciprocal value, the turnover time. The outcome of the model calculations, therefore, will be presented by stating what activation energy and turnover time they are based on.

Results

The El Niño fluctuations of the Keeling curve

Fig. 1 shows the correlation between global temperatures and the rate of change of the atmospheric carbon dioxide level, as reported by Keeling for the period 1985–2000 [2]. The El Niño event occurring around 1998 was strong and caused an exceptionally clearcut response in form of a corresponding single peak in the rate of change curve. The amplitude of that peak, therefore, should be exceptionally well suited for analysis of the strength of the temperature effect.

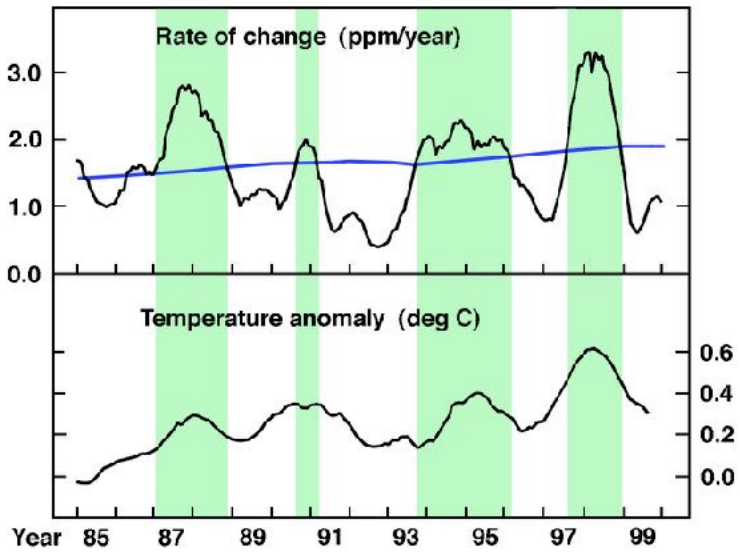


Figure 1. *Data presented by Keeling [2] to illustrate the correlation between El Niño increases of the temperature and rapid increases of the rate of change of the atmospheric carbon dioxide level. The blue curve shows the longterm trend of the rate of change.*

Kinetic analysis of the El Niño fluctuations

The kinetic model presented in the theory section is based on the assumption that the level of airborne carbon dioxide is controlled mainly by the rates of gas exchange between the atmosphere and the hydrosphere, which are determined by the atmospheric turnover time of the gas and the equilibrium constant for the exchange process. The model equations describe how the level of airborne carbon dioxide will be affected by anthropogenic emissions and temperature changes, when the thermal effects are attributed to the step of carbon dioxide outgassing from the hydrosphere and controlled by the activation energy E* for that step.

Fig. 2 illustrates some basic properties of the model predictions by example of results obtained for a fixed turnover time of 14 years and varied values of the activation energy E*. The featureless grey bottom curve in Fig. 2A was calculated for E* = 0. It provides evidence that the observed fluctuations of the rate of change of atmospheric carbon dioxide cannot be attributed to anthropogenic emissions and will not occur in the assumed absence of thermal outgassing.

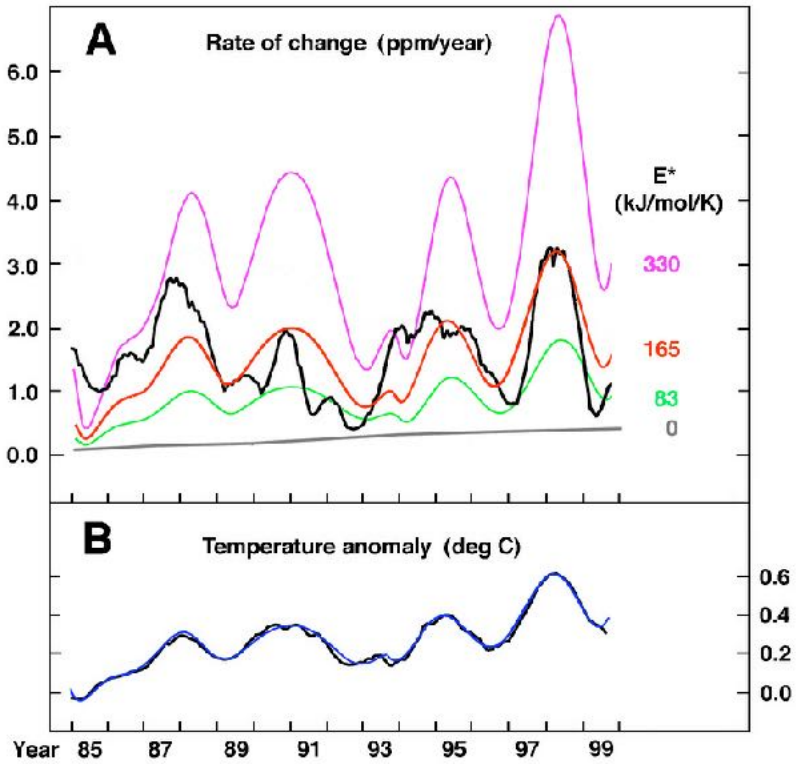


Figure 2. *Black curves iterate the empirical data in Fig. 1. Other curves in panel A indicate the modelled rate of change, as calculated for a turn-over time of 14 years and varied values of the activation energy E*. The blue curve i panel B represents the temperature anomaly, as described by the polynoms used in the model calculations.*

For non-vanishing values of E*, the model curves in Fig. 2A do exhibit temperature dependent fluctuations. These fluctuations invariably mimic the temperature curve (Fig. 2B), showing that the El Niño fluctuations of the Keeling curve indeed may derive from thermal outgassing. The modelled amplitude of the fluctuations is strongly dependent on (almost proportional to) the magnitude of the activation energy. E* = 83 kJ/mol/K (green curve) underestimates the amplitude of the observed fluctuations. E* = 330 kJ/mol/K (violet curve) overestimates the amplitudes. The best description of the amplitudes in general, and that of the 1998 El Niño peak in particular, was obtained for E* = 165 kJ/mol/K (red curve).

The model system was found to behave similarly when the turnover time was set to other values. For any postulated turnover time, a corresponding value of E* can be found that gives a satisfactory reproduction of the observed peak-to-trough amplitude of the 1998 El Niño peak of the rate of carbon dioxide change. This means that there is an infinite number of sets of joint turnover time and E* values that may account for the observed strength of the temperature effect by this criterion. Three representative sets of that kind are listed in Table 1.

Table 1. Typical sets of joint parameter values that account satisfactorily for the observed amplitude of the 1998 El Niño peak of the rate of change of atmospheric carbon dioxide

Turnover time (years)	*Activation energy (kJ/mol/K)*
4	60
14	165
100	750

Model predictions regarding the longterm trend of the Keeling curve

The different sets of joint turnover time and E* values that account for the amplitude of the 1998 El Niño peak result in widely different model predictions as to the carbon dioxide levels that will be reached due to temperature changes and anthropogenic carbon dioxide emissions since 1850. This is illustrated by Fig. 3, which shows that the modelled carbon dioxide level in 1985 (the midpoint of the time range presently covered by the Keeling curve) steadily increases with increasing values of the turnover time moiety of such parameter sets. The experimentally observed level in 1985 is best reproduced by the parameter set in which the turnover time equals 14 years (the middle set in Table 1). As shown in Fig. 4, this parameter set actually provides an almost perfect description of the entire Keeling curve. It also accounts satisfactorily for the carbon dioxide levels indicated by proxy values for the time period 1850–1958 [11].

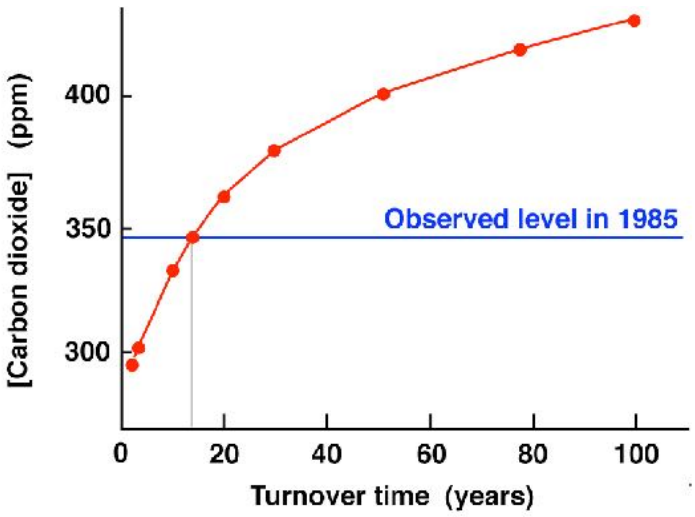


Figure 3. *Variation of the modelled carbon dioxide level in 1985 with the magnitude of the turnover time moiety of parameter sets accounting for the amplitude of the 1998 El Niño peak. The experimentally observed level is reproduced only by the set where the turnover time equals 14 years.*

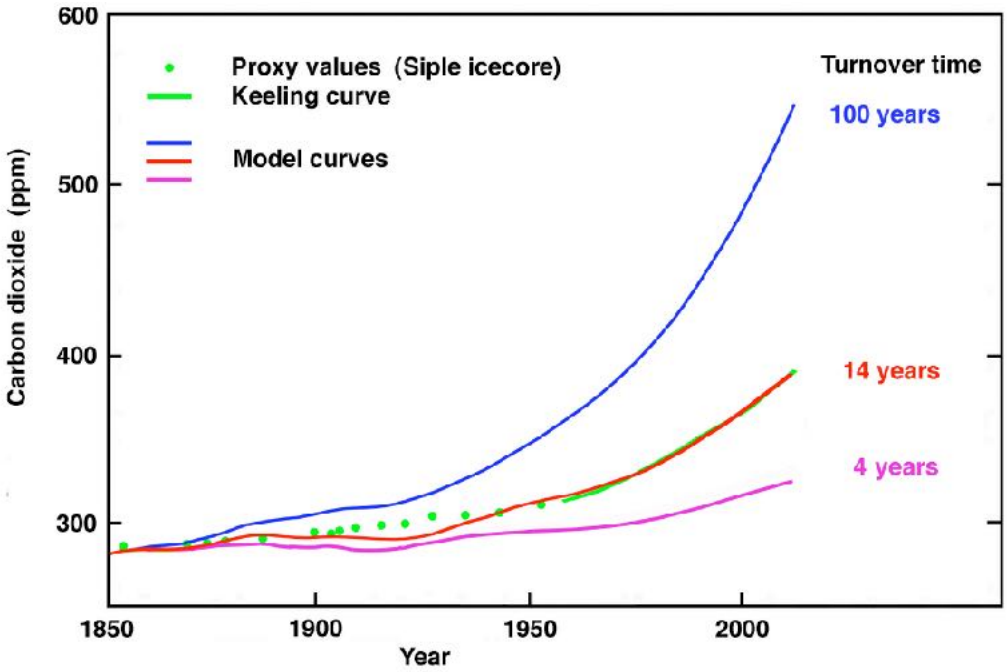


Figure 4. *Variation of the atmospheric carbon dioxide level since 1850, as indicated by empirical data (green) and the model now described. Model curves were calculated for the three parameter sets listed in Table 1.*

Interrelationship between anthropogenic emissions and thermal outgassing

Perturbations caused by temperature changes on one hand and anthropogenic emissions on the other give rise to relaxation fluxes that, according to Scheme 1, must show a kinetic interdependence. To obtain information on the significance of this interdependence, the model calculation resulting in the red curve in Fig. 4 was repeated, first with the hypothetical assumption that the temperature has remained unchanged since 1850 and then with the assumption that there has been no anthropogenic carbon dioxide emissions since 1850. In other words, the effect of each perturbation factor was examined separately in the assumed absence of the other.

The results are given in Fig. 5, where the blue curve shows how the level of atmospheric carbon dioxide level would be expected to vary due to thermal outgassing alone when the turnover time is 14 years and E* = 165 kJ/mol/K. The black curve shows the analogous response of the modelled carbon dioxide level to anthropogenic emissions alone. The separately calculated carbon dioxide increases indicated by the black and blue curves add up to the red curve in Fig. 4. The latter curve agrees within 0.4 ppm with the red curve in Fig. 3, *i. e.* with the curve describing the combined effect of the two perturbation factors.

These observations provide evidence that the kinetic interdependence of anthropogenic emissions and thermal outgassing is practically negligible. The effects of these two perturbation factors seem to be largely additive, such that they can be estimated separately as indicated in Fig. 5.

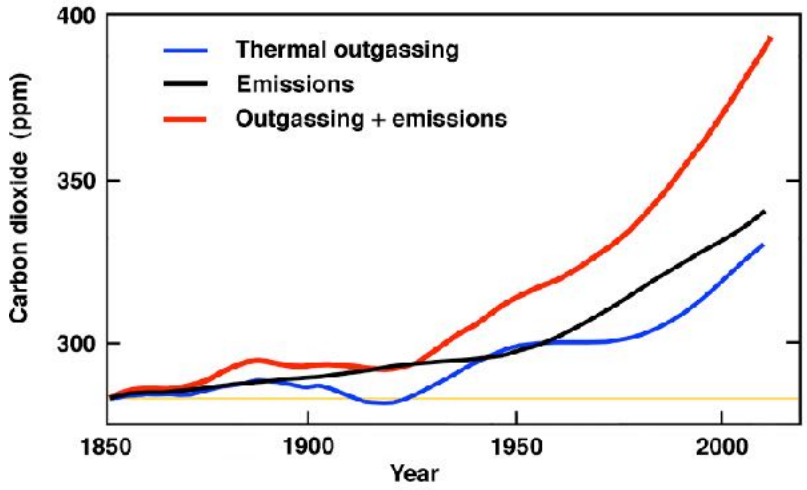


Figure 5. *Separately estimated effects of anthropogenic emissions and thermal outgassing add up to a curve that is practically indistinguishabe from the model curve obtained for the combined effects of the two perturbation factors*

Table 2 expresses the results in Fig. 5 numerically with regard to the relative importance of the two perturbation factors over some representative periods of time. The numerical data provide the main inference that anthropogenic emissions and thermal outgassing have been of approximately equal importance as contributors to the rising atmospheric carbon dioxide levels since 1850. During the last two modelled decades, thermal outgassing has contributed more than anthropogenic emissions to the long-term trend of the Keeling curve (the slope of the blue curve is larger than that of the black curve after 1990).

Table 2. Contributions from anthropogenic emissions and thermal outgassing to the atmospheric carbon dioxide level over different periods of time, as modelled for each perturbation factor alone in the assumed absence of the other (column 3 and 4) and for the simultaneous effect of both perturbation factors (column 2; red curve in Fig. 5).

Time period	*Increased air level of carbon dioxide (ppm)*	*Anthropogenic emissions (ppm)*		*Thermal outgassing (ppm)*
1850–2009	107.0	58.2	(54%)	48.4
1990–1999	18.1	7.1	(39%)	11.0
2000–2009	20.3	9.0	(44%)	11.2

Carbon cycle budget considerations

Summing up the above results, 124 GtC (23%) of the cumulative total amount of anthropogenic carbon dioxide emissions (531 GtC) since 1850 remained airborne in 2010. The rest (407 GtC) had been removed from the atmosphere. Concomitantly, 103 GtC of carbon dioxide had been released to the atmosphere through thermal outgassing driven by global warming.

With the reasonable simplifying assumption that the removed amount of carbon dioxide emissions has been taken up mainly in the hydrosphere, these data indicate that the net flux of carbon dioxide from the atmosphere to the hydrosphere has been 407–103 = 304 GtC during the examined time period (1850–2010). This corresponds to an average net flux of 1.9 GtC/year, consistent with the IPCC assessment that the net flux was 1.8 ± 0.8 GtC/year in the 1980s and 2.2 ± 0.4 GtC/year in the 1990s [8].

Discussion

Effect of temperature on the Keeling curve

The reaction system defined in Scheme 1 includes the carbon dioxide pools and reaction steps that minimally have to be considered for a quantitative evaluation of thermal outgassing under realistic conditions. The model derived by strict kinetic analysis of this system shows that combined effects of temperature changes and anthropogenic emissions on the level of atmospheric carbon dioxide will be a function of two critical parameters (the carbon dioxide turnover time and the activation energy E* that characterizes the strength of the temperature effect in accordance with the Arrhenius equation). Figs. 2–3 illustrate that the model accounts for the observed amplitude of the 1998 El Niño peak of the rate of carbon dioxide change and the observed carbon dioxide level in 1985 when, and only when, the turnover time equals 14 years and E* = 165 kJ/mol/K.

It is not surprising that a fit of the model to two particular characteristics of the Keeling curve will provide best fit estimates of the model's two adjustable parameters. But it is highly remarkable that the model for the parameter estimates thus obtained gives an almost perfect description of the entire Keeling curve (Fig. 4) and accounts satisfactorily for the El Niño fluctuations of the curve over the entire time period they have been recorded [12]. This provides clear evidence that the model equations adequately describe how the examined two disparate and rather irregular perturbation events (temperature changes and anthropogenic emissions) affect the atmospheric carbon dioxide level.

Results now reported establish that the simple two-box system in Scheme 1 is sufficient to explain and quantitatively account for the El Niño fluctuations of the Keeling curve in terms of thermal outgassing. The observed fluctuations are by no means minor, but document the existence of a very strong temperature effect that drastically affects the observed rates of carbon dioxide change (see Fig. 1). Evidence has been previously presented which suggests that this temperature effect, due to global warming, has contributed most significantly also to the long-term trend of the Keeling curve [13,14]. The model data in Figs. 4–5 confirm that such indeed is the case and provide quantitative estimates of the magnitude of the contributions.

The turnover time estimate of 14 years obtained by application of the model falls within the range of turnover time values determined experimentally by various methods [15]. This lends credence to the model and supports the conclusion of Starr [16] that amplitudes of the seasonal fluctuations of the Keeling curve are too large to be consistent with turnover times of the order of 100 years. Table 1 lists representative sets of joint parameter values that account for the amplitude of the 1998 El Niño fluctuation. As illustrated by Fig. 4, such sets fail to reproduce the long-term trend of the Keeling curve when the turnover time moiety differs significantly from 14 years.

The model now described is the only one so far presented that is capable of reproducing both the long-term trend of the Keeling curve and the El Niño fluctuations of it. The excellent agreement between the observed and the modelled Keeling curve corroborates that carbon dioxide exchange between the atmosphere and the hydrosphere represents the largely predominant mechanistic factor controlling the air level of the gas. The combined effects of anthropogenic emissions and thermal outgassing, as now modelled, are sufficient to account for the observed increases of airborne carbon dioxide. This provides the additional inference that factors such as volcanism [17] and feedbacks involving the biosphere [8] are unlikely to have had any appreciable influence on the long-term atmospheric carbon dioxide level during the industrial era.

According to Fig. 5 and Table 2, thermal outgassing has been almost as important as, and during the last two decades more important than, anthropogenic emissions as a source of the increasing levels of atmospheric carbon dioxide. The large thermal contribution calculated for 2000–2009 might seem difficult to reconcile with the fact that global temperatures have not changed significantly over that time period, but is fully consistent with the expected response of the system to previous temperature changes.

To understand that, one has to recognize that temperature changes perturb equilibrium conditions and trigger relaxation processes tending to adjust concentration variables to the new conditions. The effect of temperature on individual rate constants is instantaneous. This explains why the observed and modelled rate of change of carbon oxide (dx/dt) mimics the temperature curves without any time delay (Figs. 1–2). The consequent change of the carbon dioxide level (x), however, will be time-dependent and reflect the turnover time of the gas [16]. A turnover time of 14 years implies that it will take several decades for the system to adjust to a temperature change. The large thermal contribution to the increased carbon dioxide levels over he period 2000–2009 derives mainly from the global warming that occurred during the preceding two decennia.

Thermal outgassing and climate modelling

Carbon dioxide is a greenhouse gas. Climate model calculations of future effects of anthropogenic carbon dioxide emissions require estimates of future concentrations of anthropogenic carbon dioxide as input data. Such estimates invariably have been calculated for postulated emission scenarios using carbon cycle models which presume that the observed increases of airborne carbon dioxide derive exclusively from anthropogenic emissions. Results now presented indicate that such models gravely underestimate the rate of removal of anthropogenic carbon dioxide from the air and render the climate model predictions unacceptably biased already at the level of data input.

According to Table 2, anthropogenic emissions account only for about half of the observed increase of atmospheric carbon dioxide during the twentieth century. The other half derives from thermal outgassing of the hydrosphere. This supports the view that the increased carbon dioxide levels to a large extent have been a consequence, rather than the source, of global waming.

The strong temperature effect on the atmospheric carbon dioxide level implies that calculations of future carbon dioxide levels not only require assumptions about future emission rates, but also about future temperatures. Climate modellers are facing the delicate problem that they have to know what the future temperatures will be before they can predict them by calculation of the greenhouse

effect caused by future carbon dioxide levels. This complication can possibly be circumvented by extensive modification of the calculation procedures, but it certainly cannot be ignored.

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