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 airborn 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 if the turnover time is 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 airborn carbon dioxide during the industrial era to approximately equal contributions from anthropogenic emissions and thermal outgassing of carbon dioxide from the hydrosphere. During the last two decades, thermal outgassing has contributed more than anthropogenic emissions to the increased levels of airborn carbon dioxide.

The results indicate that the extensively discussed missing sink problem regarding carbon dioxide emissions derives from an underestimation of the sink capacity of the hydrosphere due to neglect of thermal outgassing. Projections of climate models that do not take thermal outgassing into account will be too biased to provide any information of significant prognostic interest.

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 established [2].

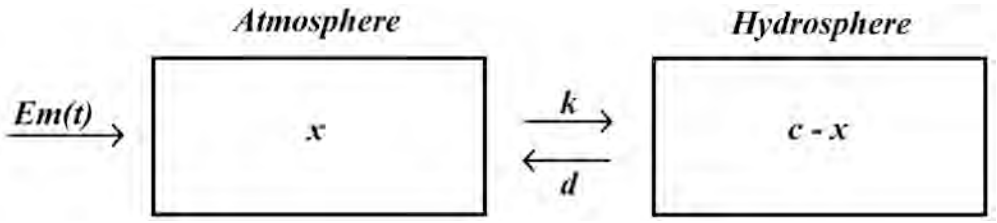
The multiannual fluctuations, however, were found to be strongly and positively correlated to global temperature changes associated with the El Niño–Southern Oscillation cycle. Rapidly rising air levels of carbon dioxide typically occur during El Niño events with their global scale temperature increases, as was first noted by Bacastow [3]. Subsequent analyses have shown that the observed 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 airborn 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 dissolved 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

Scheme 1 shows a simple two-box reaction system describing the main processes contributing to the relaxation of airborn carbon dioxide. The rate constant *k* characterises the transfer of carbon dioxide from the atmosphere to the hydrosphere; its reciprocal value defines the turnover time of airborn carbon dioxide. The rate constant *d* characterises 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 individually.



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*

Denoting the total content of exchangeable carbon by *c*, the distribution of carbon between the two boxes can be expressed as in Scheme 1, where *x* represents the content of carbon in the atmosphere. The law of mass action then prescribes that the time-dependence of *x* will be governed by the diffential equation

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

where $Em(t)$ represents the rate of emission of anthropogenic carbon dioxide to the atmosphere; $Em(t)$ was mathematically characterized as described in the preceding paper and includes emissions due to combustion of fossil fuels, cement production, and land-use changes.

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

$$Keq = d/k \qquad (2)$$

According to the carbon cycle data presented by the Intergovernmental Panel on Climate Change (IPCC) [5], pre-industrial equilibrium values of the hydrospheric and atmospheric contents of carbon are given approximately by 38 000 GtC and 600 GtC, respectively. Pre-industrial values of the parameters *Keq* and *c*, therefore, were assumed to be known and to be given by $Keq' = 600/38000$ and $c' = 38\ 600$ GtC.

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

$$d = A\mathbf{Exp}[-E^*/RT(t)] \qquad (3)$$

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 eigth degree polynomial in *t*, obtained by regression analysis of reported global temperature anomalies vs. time (normally the HadCRUT3-series [6]). These anomalies refer to a reference temperature of 14.0 ˚C [7], for which reason 287.15 K were added to convert them into absolute temperatures.

The time-course of *x* was evaluated by solving Eqn. (1) numerically for selected periods of time starting with the year 1850. The above preindustrial values of *x*, Keq' and c' 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 appliy for 1850 according to the above regression analysis. The proportionality constant A in Eqn. (3) was eliminated using year 1850 as a reference point, *i. e.* by using the relationship

$$\mathrm{A} = kKeq'/\mathbf{Exp}[-E^*/RT(t)'] \qquad (4)$$

which can be readily derived from Eqns. (2–3). This means that Eqns. (1–4) 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. Unless otherwise stated, the turnover time was assumed to equal 14 years, the atmospheric relaxation time determined for C14-labelled carbon dioxide.

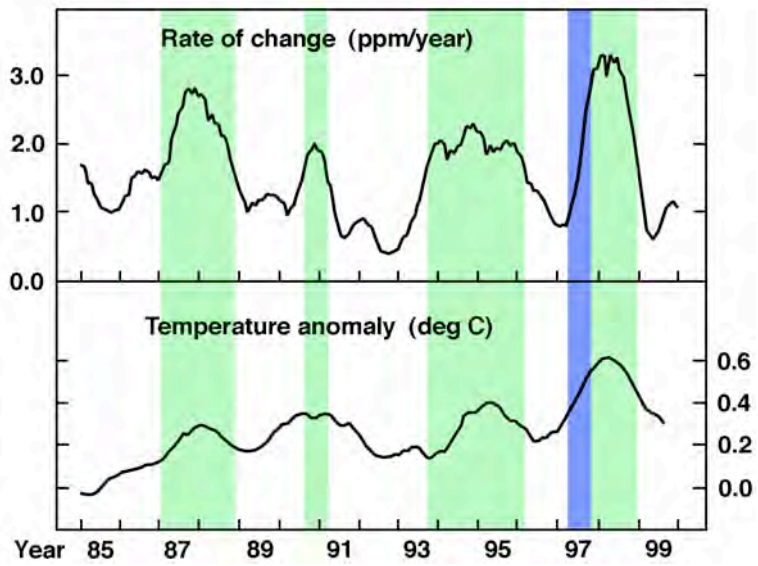


Figure 1. *Data presented by Keeling [2] to illustrate the correlation between El Niño increases of the temperature and rapid increases of the rate of change of the atmospheric carbon dioxide level. The blue area has been added for illustrative purposes*

Results

Semi-empirical analysis of the multiannual fluctuations of the Keeling curve

Fig. 1 describes the correlation between global temperatures and the atmospheric carbon dioxide level, as reported by Keeling for the period 1985–2000 [2]. The El Niño event occurring around 1998 was exceptionally strong and, therefore, should be exceptionally well suited for analysis of the strength of the temperature effect. During the period (6 months in 1997) indicated by the blue area in Fig. 1, the temperature increased 0.18 ˚C. Concomitantly, the rate of change of the atmospheric level of carbon dioxide increased by about 1.8 ppm/year.

Approximating both effects by a straight line, these data provide evidence that a mean temperature increase of 0.09 ˚C during half a year resulted in a in increased mean rate of change (1.8/2 = 0.9 ppm/year) that raised the carbon dioxide level by 0.9/2 = 0.45 ppm above the background average. This corresponds to a sensitivity measure of 5 ppm/˚C, if the carbon dioxide level is assumed to respond instantaneously to temperature changes. The implication of this measure will be considered in the discussion.

Model analysis of the multiannual fluctuations of the Keeling curve

The kinetic model presented in the theory section is based on the assumption that the level of airborn carbon dioxide is controlled mainly by the rates of gas exchange between the atmosphere and the hydrosphere, which are basically characterised by the atmospheric turnover time of the gas and the equilibrium constant for the exchange process. The model equations describe how the level of airborn 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 assumed to be controlled by the activation energy E* for that step.

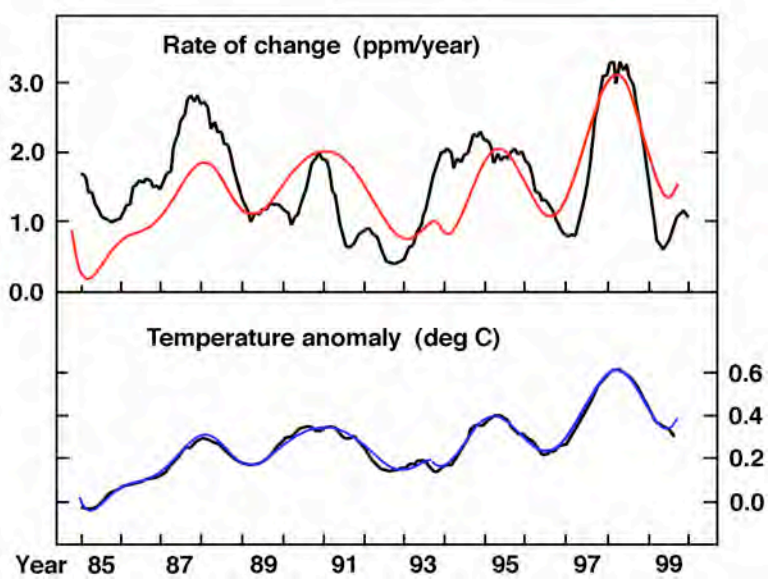


Figure 2. *Black curves iterate the empirical data in Fig. 1. The blue curve represents the temperature anomaly, as described by the polynoms used in the model calculations. The red curve indicates the modelled rate of change, as calculated for a turnover time of 14 years and an activation energy E* of 165 kJ/mol/K.*

In a first series of model calculations, the multi-annual fluctuations of the Keeling curve were analyzed with the assumptions that the emission function *Em(t)* is identical to the one described in the preceding paper, and that temperature anomalies over the period 1985–2000 are those reported by Keeling (Fig. 1). The turnover time was fixed to 14 years, while the parameter E* was varied. Such calculations showed that the modelled rate of change of the carbon dioxide level mimics the temperature curve, which means that the empirically detected correlation between rate of change and temperature certainly may derive from thermal outgassing.

Amplitudes of the modelled rate of change peaks were found to be strongly dependent on the value of E*. The red curve in Fig. 2 was calculated using E* = 165 kJ/mol/K. This E* value gave the best amplitude description of the pronounced rate of change peak associated with the El Niño event in 1998 and, therefore, was taken to provide an empirically estimated measure of the strength of the temperature effect.

Modelling of the long-term trend of the Keeling curve

Using E* = 165 kJ/mol/K and a turnover time of 14 years, the model was applied for calculation of the combined effect of anthropogenic emissons and temperature on the atmospheric level of carbon dioxide over the time period 1850–2010. The emission function *Em(t)* remained identical to the one described in the preceding paper. The temperature function *T(t)* was derived from reported estimates of the global temperature (HadCRUT3) over the examined time period.

Model results thus obtained are indicated by the red curve in Fig. 3. Green data refer to previously reported empirical estimates of the carbon dioxide level [1, 8] and are satisfactorily described by the model. In particular, the model accounts almost perfectly for the carbon dioxide levels that have been directly recorded at Mauna Loa (the Keeling curve). This outcome of the model calculation is remarkable, considering the simplicity of the model and the fact that chosen magnitudes of the two

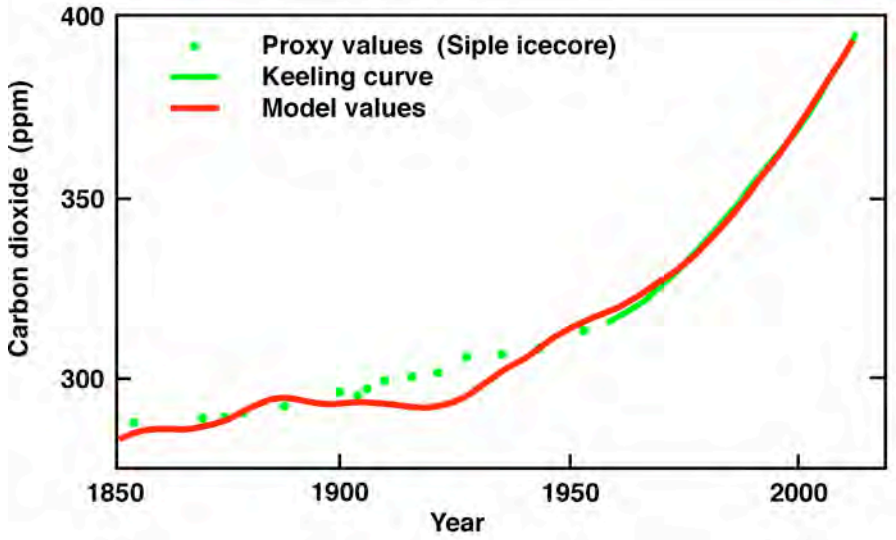


Figure 3. *Variation of the atmospheric carbon dioxide level since 1850, as indicated by empirical data (green) and the model now described (red). The directly measured Keeling curve is almost completely overlapped by the model curve.*

adjustable model parameters have been determined separately by empirical methods that have not involved any tuning to the long-term trend of the Keeling curve.

Kinetic 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 such effects, the model calculation described in the preceding section 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. 4. The black curve shows how much the atmospheric carbon dioxide level would be expected to increase due to anthropogenic emissions alone. It agrees within 0.2 ppm with the curve calculated by the impulse response method applied in the preceding paper, confirming the previous conclusion that anthropogenic emissions account only for about one half of the rising long-term trend of the Keeling curve.

The blue curve in Fig. 4 shows how the atmospheric carbon dioxide level would be expected to change due to thermal outgassing alone. It provides the immediate inference that the temperature effect documented by the multi-annual fluctuations of the Keeling curve is of such strength that it must be assumed to most significantly affect also the long-term trend of the Keeling curve.

The separately calculated carbon dioxide level contributions provided by anthropogenic emissions (black curve) and thermal outgassing (blue curve) 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.

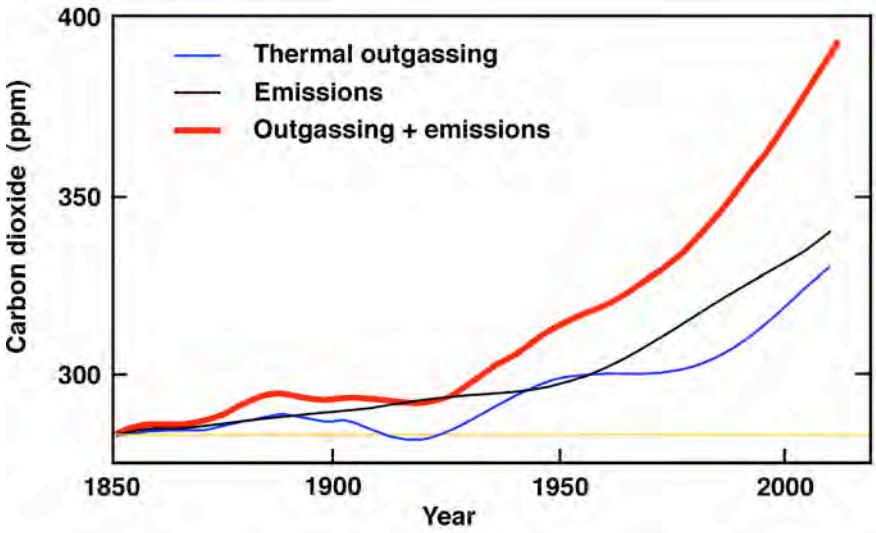


Figure 4. *Separately estimated effects of anthropogenic emissions and thermal outgassing add up to curve that is practically indistinguishabe from the model curve obtained for the combined effects of the two perturbation factors*

These model results provide evidence that the kinetic interdependence of anthropogenic emissions and thermal outgassing is practically negligible, which appears to reflect that the uptake of airborn carbon dioxide by the hydrosphere is a practically irreversible process. The absence of a significant interdependence between the two perturbation factors implies that their effects are practically additive and can be estimated separately as indicated in Fig. 4.

Table 1 expresses the results in Fig. 4 numerically with regard to the relative importance of the two perturbation factors over 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.

Table 1. 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. 3).

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 airborn 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 annual net flux rate of 1.9 GtC/year, consistent with the IPCC assessment that the flux rate was 1.8 ± 0.8 GtC/year in the 1980s and 2.2 ± 0.4 GtC/year in the 1990s [6].

Discussion

Effects of temperature on the Keeling curve

Temperature changes result in perturbations of the prevailing equilibrium conditions. Thermal changes of the atmospheric carbon dioxide level, therefore, represent relaxation processes tending to adjust the system to the modified conditions. As pointed out by Starr in his discussion of seasonal fluctuations of the Keeling curve [9], such adjustments will be kinetically governed by the relaxation time for atmospheric carbon dioxide which certainly is longer than a few months or years.

The implication of this can be illustrated by example of the semi-empirical analysis now performed on basis of the data in Fig. 1. Thermal outgassing of carbon dioxide during the examined six months of the El Niño event in 1997 would be characterised by the estimated sensitivity measure 5 ppm/˚C, if the air level of carbon dioxide adjusts instantaneously to the temperature perturbation. But the adjustment cannot possibly be instantaneous. Elementary reaction kinetic theory prescribes that the outgassing of carbon dioxide from the hydrosphere must be time-dependent and governed by the same relaxation time as the uptake of carbon dioxide by the hydrosphere.

This means that the amount of carbon dioxide released by a temperature perturbation lasting for six months only will be a small fraction of the amount that would be released if the perturbation had been permanent. If the relaxation time is assumed to be 14 years, the fraction outgassed during the first 6 months after a temperature perturbation will be given by 1–**Exp**[-0.5/14] ≈ 0.035. The long-term sensitivy indicated by the semi-empirical analysis, therefore, becomes 5/0.035 ≈ 140 ppm/˚C. The possibility that the relaxation time is of the order of 100 years can be ruled out, because it would imply that the multiannual fluctuations of the Keeling curve correspond to an unrealistically high temperature sensitivity of the order of 5/0.005 = 1000 ppm/˚C. Starr [9] arrived at a similar conclusion based on his analysis of the seasonal fluctuations of the Keeling curve

The above sensitivity measures should be interpreted with great caution, because thermal kinetic effects are related to the absolute temperature and non-linearly dependent on it. Nevertheless, the semi-empirical analysis provides an important main inference: The seemingly minor multiannual fluctuations of the Keeling curve actually provide clear evidence for the existence of a very strong temperature effect attributable to thermal outgassing.

This temperature effect cannot be neglected but, due to global warming, must have contributed most significantly to the long-term trend of the curve. The model results in Figs. 3–4 confirm that such is the case. They show that parameter values accounting for the temperature dependence of the multiannual fluctuations of the Keeling curve in terms of thermal outgassing also give a most satisfactory model description of the long-term trend of the curve.

The excellent agreement between the observed and the modelled Keeling curve provides some additional inferences of interest. Firstly, it would appear that atmosphere-hydrosphere carbon dioxide exchange has been correctly identified as the main mechanistic factor controlling the air level of the gas. Secondly, thermal outgassing has been almost as imporant as, and during the last two decades more important than, anthropogenic emission as a source of the increasing carbon dioxide levels. Finally, the results in Fig. 3 establish that the Keeling curve can be fully accounted for in terms of the combined effects of anthropogenic emissions and thermal outgasssing, as characterised by the model and parameter estimates now presented. This indicates that factors such as volcanism [10] and feedbacks involving the biosphere [6] have not had any appreciable influence on the long-term level of airborn carbon dioxide level during the industrial era.

The missing sink problem

The IPCC has presented the carbon budget data in Table 2 to account for the fate of anthropogenic carbon dioxide emissions in the 1990s [6]. According to these data, the biosphere acts as a source of atmospheric carbon dioxide due land use changes. This leaves the hydrosphere as the only truly identified carbon dioxide sink. The estimated emissions, however, exceed the sum of carbon dioxide taken up by the hydrosphere and carbon dioxide remaining airborn. About one third of the emissions appears to have been taken up by an unidentified 'missing sink'.

The missing sink problem was discussed by the IPCC in its first assessment report [11], where it was presented as a budget imbalance issue. In the fourth IPCC report, the name of the missing sink was changed to 'residual terrestrial sink'. The missing sink still remained unidentified, however, and its contribution was still calculated from the imbalance between identified carbon dioxide sources and sinks. As stated by the IPCC in its first report [11], "the question therefore arises whether an important mechanism has been overlooked".

The present investigation identifies the temperature dependence of the water solubility of carbon dioxide as the important mechanistic factor that has been overlooked. The IPCC budget in Table 2 is based on the unjustified presumption that long-term atmospheric carbon dioxide levels reflect

Table 2. Global carbon budget (GtC/year) for the 1990s, as assessed by the IPCC (2007)

Emissions:	Fossil + cement	6.4		
	Land use change	1.6		
			Sum:	**8.0**
Net uptake by the hydrosphere:		2.2		
Remaining airborn:		3.2		
			Sum:	**5.4**
Net imbalance (missing sink; 'residual terrestrial sink'):				**2.6**

mainly anthropogenic emissions. Neglection of thermal outgassing has led to a misinterpretation of the Keeling curve, as well as of the observed net rate of carbon dioxide uptake by the hydrosphere.

According to the model calculations now reported (Table 1), anthropogenic emissions and thermal outgassing have contributed, respectively, 1.5 and 2.3 GtC/year to the atmospheric increase of carbon dioxide during the 1990s. This adds up to 3.8 GtC/year, agreeing with the increase indicated by the Keeling curve [1]. The IPCC budget in Table 2 presumes that this atmospheric increase represents the amount of anthropogenic emissions remaining airborn. Such attribution of the increase to the less important one of the two contributing perturbation factors leads to an underestimation of the rate at which the emissions are actually removed from the atmosphere.

The model results now reported show that the part of the emissions that does not remain airborn (6.5 GtC/year in the 1990s) has been taken up by the hydrosphere, the only sink considered in the model because of its predominance. This indicates that the IPCC budget in Table 2 underestimates the rate of uptake of emissions by the hydrosphere. The budget estimate is based on the unjustified presumption that empirically determined net fluxes of carbon dioxide from the atmosphere to the hydrosphere provide direct measures of the rate of uptake of anthropogenic emissions. In reality, the observed fluxes must be assumed to represent the net outcome of emission uptake and thermal outgassing, which affect the atmospheric carbon dioxide level in opposite directions. A large part of the uptake of anthropogenic emissions will be hidden by thermal outgassing during periods characterised by long-term global warming.

This would appear to solve the missing sink problem. The major part of the 'residual terrestrial sink' can be identified as the hydrosphere, the sink capacity of which has been underestimated due to neglect of thermal outgassing. The results in Fig. 3 and Table 1 establish that no carbon budget imbalances are encountered when the combined effects of emissions and temperature are evaluated using a model that takes thermal outgassing into account and that is based on empirically estimated kinetic parameter values for the relaxation processes
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Implications of the thermal effect

Carbon dioxide is a greenhouse gas. Climate model calculations of future effects of anthropogenic carbon dioxide emissions require estimates of future concentrations of airborn carbon dioxide as input data. Such estimates invariably have been calculated for postulated emission scenarios using carbon cycle models tuned to the Keeling curve, *i. e.* models presuming that the observed increases of airborn carbon dioxide derive exclusively from anthropogenic emissions. As was shown in the preceding two papers, such models gravely underestimate both the rate and the extent of removal of carbon dioxide from the air and render the climate model predictions unacceptably biased already at the level of data input.

This is born out by the results in Table 1, which confirm that anthropogenic emissions only account for about half of the observed increase of atmospheric carbon dioxide. Furthermore, and possibly more important from a climate modelling point of view, results now reported provide clear evidence that effects of temperature on the atmospheric carbon dioxide level are of such strength that they cannot be neglected. According to Table 1, more than half of the carbon dioxide increase observed during the last two decades derives from thermal outgassing of the hydrosphere.

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.

As long as climate models continue to neglect thermal outgassing, and to use input data based on carbon cycle models that are inconsistent with the experimentally established relaxation properties of airborn carbon dioxide, their predictions will remain of insignificant interest from a prognostic point of view.

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