

Relaxation kinetics of atmospheric carbon dioxide

Gösta Pettersson, University of Lund, Sweden (May 15, 2014)

Evidence is presented to show that the time-course of removal of the excess of airborne C14 created by atmospheric tests of nuclear weapons is monophasic and corresponds to a carbon dioxide turnover time of 14 years. The relaxation curve for the bomb radiocarbon excess can be quantitatively accounted for by a kinetic model which considers only the exchange of carbon dioxide between the atmosphere and the hydrosphere, and which attributes the temperature dependence of the process to the step of carbon dioxide outgassing from the hydrosphere with an Arrhenius activation energy of about 170 kJ/mol/K.

Since the same model and parameter values have been previously shown to account for observed effects of temperature and emissions of anthropogenic carbon dioxide on the atmospheric level of the gas, it may be concluded that the kinetic behaviour now established for C14-carbon dioxide is representative for carbon dioxide in general. The present results provide independent evidence corroborating that emissions of anthropogenic carbon dioxide are removed from the atmosphere at a rate controlled by the air level of the gas and a turnover time of 14 years, without any detectable delay or multiphasicity attributable to slow transfer of carbon from the sea-surface layer to the deep-sea regions.

Atmospheric carbon dioxide contains small amounts of the radioactive isotope C14. This isotope is continuously formed through the interaction of cosmic rays with nitrogen atoms in the air, and decays spontaneously with a halftime of 5 730 years. Due to the steady state balance between these two processes, the air normally contains a fairly constant background amount of naturally produced C14-carbon dioxide that has equilibrated with other natural reservoirs of exchangeable carbon.

During the 1950s and 1960s, several nations performed atmospheric tests of nuclear weapons. The radiation effects of these tests rapidly produced large amounts of anthropogenic C14-carbon dioxide in the air. When the atmospheric bomb tests ceased in 1963, the atmospheric level of C14-carbon dioxide had been raised to about twice its previous natural value.

The subsequent removal of the anthropogenically produced excess of radiocarbon from the air has been monitored at several places around the world. Such data obviously provide information on the relaxation process by which the bomb C14 excess has been transferred from the atmosphere to other natural pools of exchangeable carbon to reestablish equilibrium conditions. The kinetic analyses described in this investigation were undertaken to extract that information and to examine its implications with regard to the time dependence and extent of removal of emissions of anthropogenic carbon dioxide deriving from the combustion of fossil fuels and land use changes.

Theory

The Suess effect

Atmospheric radiocarbon data are usually described in terms of a quantity $\Delta C14$ defined by

$$\Delta C14 = (n14/n12) / (n14r/n12r) - 1 \quad (1)$$

where $n14/n12$ stands for the measured C14/C12 ratio in the experimental carbon dioxide samples and $n14r/n12r$ represents the corresponding isotope ratio in a reference sample that originates from year 1890. Eqn. (1) can be rearranged to give

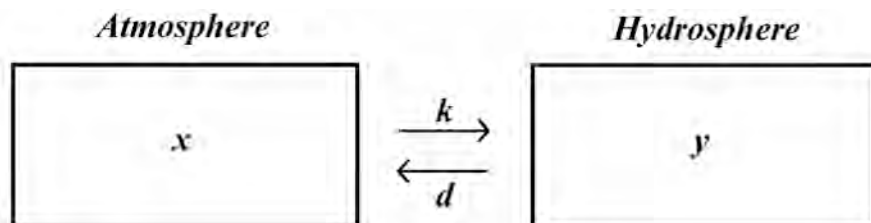
$$n14/n14r = (1 + \Delta C14) n12/n12r \quad (2)$$

which shows that $n14$ will be linearly related to $\Delta C14$ over short periods of time where $n12$ can be assumed to remain constant.

Over the multidecennial periods of time considered in this investigation, the atmospheric level of C12-carbon dioxide has increased significantly. This has caused a dilution of the C14/C12 ratio of airborne carbon dioxide (the Suess effect [1]), which renders $n14$ non-linearly dependent on $\Delta C14$. Eqn. (2), therefore, was applied to convert $\Delta C14$ -values into values that are proportional to $n14$. Such conversions were made with the assumptions that $n12r = 300$ ppm and that $n12$ values after 1963 are those indicated by the Keeling curve (the graph describing how the air level of carbon dioxide has increased after 1958 according to measurements performed by Keeling *et al.* [2] at the Mauna Loa observatory).

Kinetic modelling of the radiocarbon data

In a previous investigation [3], it was shown that the El Niño fluctuations and the long term trend of the Keeling curve can be quantitatively accounted for by a simple two-box model which considers only carbon dioxide exchange between the atmosphere and the hydrosphere. Scheme 1 shows the part of the reaction system that is relevant for application of the same model to radiocarbon data. The rate constant k characterises 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 United Nation's Intergovernmental Panel on Climate Change (IPCC) [5]. The rate constant d characterises the reverse process of outgassing of carbon dioxide from 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 need not be treated individually.



Scheme 1. Kinetic two-box model for the exchange of carbon between the atmosphere and the hydrosphere.

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 differential equations

$$dx/dt = -kx + dy \quad (3)$$

$$dy/dt = kx - dy \quad (4)$$

The outgassing rate constant d is assumed to be temperature dependent in accordance with the Arrhenius relationship, such that its magnitude is determined by the activation energy E^* for the outgassing step as detailed previously [3].

In the absence of temperature changes, Eqns. (3–4) can be readily solved to show that the relaxation of an excess of x will conform to an exponential decay function with a relaxation time (τ) given by

$$\tau = 1/(k + d) \quad (5)$$

As pointed out by Revelle and Suess [5], the available information on the equilibrium partitioning of carbon between the atmosphere and the hydrosphere establishes that $k \gg d$, such that Eqn. (3) reduces approximately to

$$\tau \approx 1/k \quad (6)$$

This means that the relaxation time for atmospheric carbon dioxide under such conditions differs insignificantly from $1/k$, the quantity that represents the turnover time of airborne carbon dioxide in the terminology of the IPCC.

In the presence of irregular temperature changes, Eqns. (3–4) lack analytical solutions and have to be solved by numerical integration. Predictions of the model with regard to radiocarbon data for the time period 1850–2010 were calculated with the assumptions that the value of x ($= n14/n14r$) was 1.006 in 1850 (required to give $x = 1.000$ in the reference year 1890), that the corresponding value of y was 38000/600 times larger [3], and that changes of the temperature after 1850 can be described by polynomial regression analysis of the HadSST3 series as detailed previously [3]. The bomb test perturbation of radiocarbon in the reaction system was simulated with the simplifying assumption that the perturbation was instantaneous, occurred in August 1963, and raised the atmospheric value of $n14/n14r$ by 0.98.

The Bern carbon cycle model

The IPCC in its fourth assessment report favoured the view that anthropogenic carbon dioxide emissions are removed from the atmosphere as prescribed by the carbon cycle model designed by Siegenthaler & Joos [6] at the University of Bern (the Bern model). To illustrate predictions of that model, the IPCC made use of the 'impulse response function' in Eqn. (7) according to which the relaxation of a large pulse of excess atmospheric carbon dioxide exhibits three distinct phases governed by relaxation times of 1.2, 19, and 173 years, respectively [7]:

$$\text{Remaining fraction} = 0.19 \mathbf{Exp}[-t/1.2] + 0.34 \mathbf{Exp}(-t/19) + 0.26 \mathbf{Exp}[-t/173] + 0.22 \quad (7)$$

Results

Observations considered

One of the longest continuously sampled series of bomb C14 data was recorded near Nordkap in Norway by Nydal & Lövsedt [8]. They started their measurements in 1963, and put an end to them in 1993 when the larger part of the original excess of airborne radiocarbon had been removed. Subsequent measurements in Central Europe have established that the excess of atmospheric C14-carbon dioxide has continued to decrease after 1993 [9, 10]. Representative results describing how the anthropogenically produced excess of C14-carbon dioxide has been removed from the air are shown in Fig. 1. Results obtained at Jungfraujoch [9] are shown as yearly means.

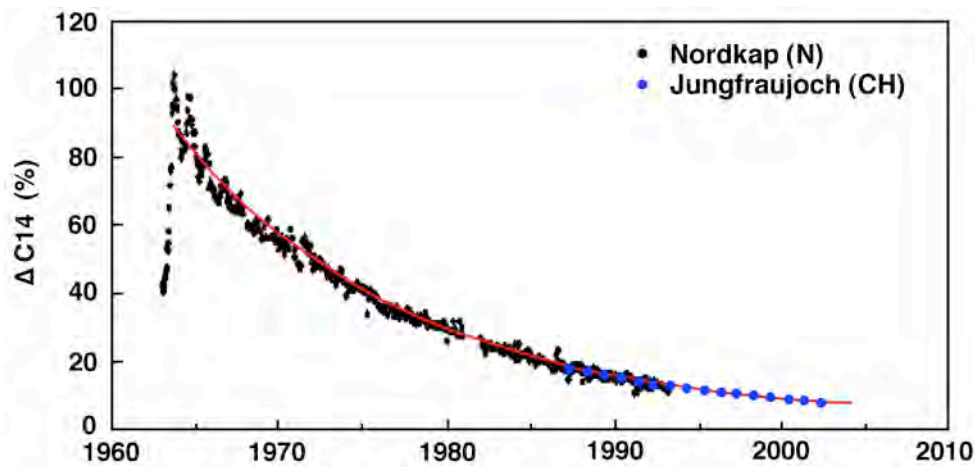


Figure 1. *Observed removal of the excess of airborne C14-carbon dioxide that was produced by atmospheric tests of nuclear weapons*

Inspection of Fig. 1 shows that the $\Delta C14$ -values recorded at Nordkap reached a maximum close to unity in August 1963. The subsequent decrease of $\Delta C14$ can be well described (red curve in Fig. 1) in terms of an exponential decay function tending towards a final value close to zero with a time constant of 14 years. This provides the inference that the same exponential relationship must govern also the initial decrease of the amount of C14-carbon dioxide (Eqn. 2).

Relaxation curve for the bomb C14 excess

The Suess effect was taken into consideration by using Eqn. (2) to convert reported $\Delta C14$ values into a quantity ($n14/n14r$) that is proportional to the atmospheric amount of C14. The results of this conversion are indicated by the black and blue data points in Fig. 2, which confirm that the amount of airborne C14 has decreased after August 1963. This decrease reflects the relaxation of the excess of C14 produced by the bomb tests. The observed C14 levels also include minor contributions from industrial emissions of C14 after the bomb tests. The magnitude and time course of the latter contributions are indicated by the orange curve in Fig. 2, which is based on the extensive bomb C14 inventories described by Naegler & Levin [11].

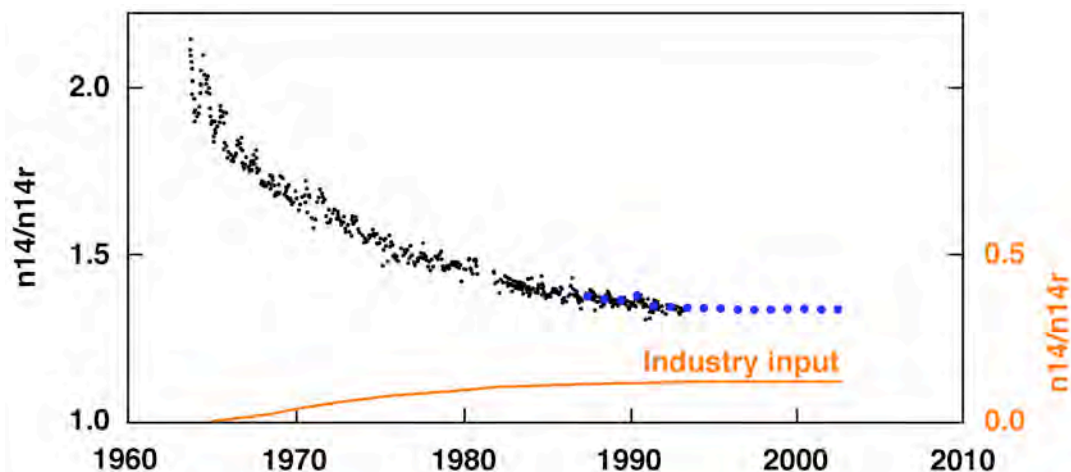


Figure 2. Observed variation with time of the atmospheric amount of C14 (black and blue data points). The orange curve shows how much industrial emissions have contributed to these amounts.

Subtracting the industrial input of C14 from the $n14/n14r$ values plotted in Fig. 2, one obtains the curve in Fig. 3 as a description of the observed relaxation of the bomb C14 excess alone. The latter curve cannot be described as strictly exponential. Furthermore, it tends towards a final equilibrium value of about 1.20, significantly higher than the value (about 1.02) that would be expected [3] from the carbon cycle data presented by the IPCC for the equilibrium state presumed to exist in pre-industrial times (here assumed to end in 1850). Consequently, data in Fig. 3 provide evidence that contemporary equilibrium positions in the system differ from the preindustrial ones in the direction of higher air levels of carbon dioxide.

This is consistent with what one would expect to find, considering that contemporary global temperatures are higher than those in 1850, that warm water hold less dissolved carbon dioxide than cold water, and that the air level of carbon dioxide is likely to reflect mainly the exchange of the airborne gas with the hydrosphere which is the vastly predominant pool of exchangeable carbon dioxide.

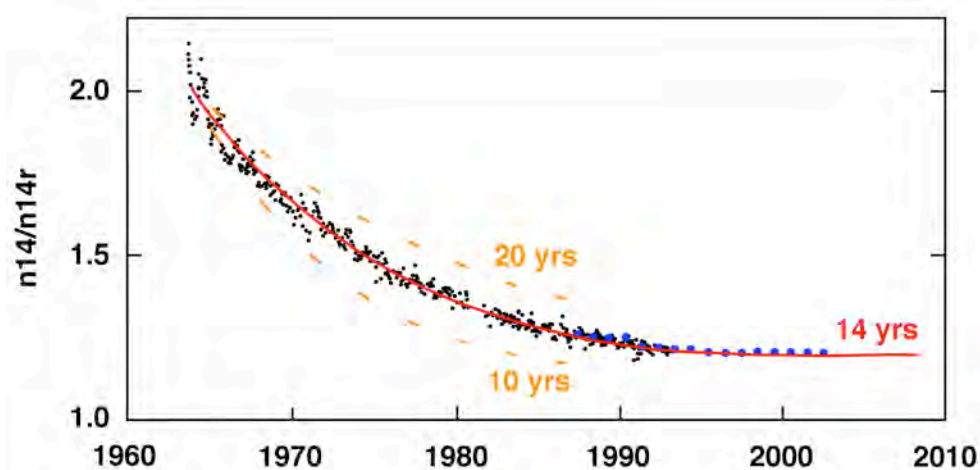


Figure 3. Relaxation curve for the bomb C14 excess. The red curve was calculated from the kinetic model derived for Scheme 1 and corresponds to a turnover time of 14.3 years and an outgassing activation energy of 175 kJ/mol/K. Yellow curves show predictions of the model for turnover times differing from 14 years.

The kinetic behaviour of the atmosphere/ hydrosphere system in Scheme 1 has been examined in a previous study [3], where a model was derived which describes temperature effects on the air level of carbon dioxide in terms of two adjustable parameters (the turnover time $1/k$ of atmospheric carbon dioxide and the activation energy E^* controlling the temperature dependence of the carbon dioxide outgassing step). The main characteristics of the model are outlined in the Theory section, which specifies also the assumptions made to apply the model for calculations of the temperature dependence and consequent time dependence of the quantity n_{14}/n_{14r} .

A least squares fit of the model to experimental points in Fig. 3 with such assumptions gave the best-fit estimates 14.3 years and 175 kJ/mol/K, respectively, for the turnover time and the activation energy. The red curve in Fig. 3 shows that the model for these best-fit parameter values (which do not differ significantly from those reported previously [3]) gives a most satisfactory description of the observed relaxation of the bomb C14 excess. Yellow dashed curves in Fig. 3 illustrate the sensitivity of the model predictions to the assumed magnitude of the turnover time.

Effect of temperature on the equilibrium level of airborne radiocarbon

The grey curve in Fig. 4 shows the variation of the equilibrium value of atmospheric n_{14}/n_{14r} after 1963, as calculated for the reaction system in Scheme 1 with the assumptions used to model the bomb C14 relaxation curve (red). Black and blue data points in Fig. 4 establish that the initially observed n_{14}/n_{14r} excess has relaxed towards the equilibrium level, as expected, and indicate that the equilibrium value actually has now been reached.

This is corroborated by the model simulation of the relaxation process. The red curve in Fig. 4 intersects the grey curve in 2003 which, therefore, may be considered as the year when the initial bomb test perturbation of atmospheric C14 was completely eliminated. After 2003, the modelled n_{14}/n_{14r} values start to increase slightly (from 1.1965 to 1.1998 in 2010) because the equilibrium level continues to increase slightly according to the polynomial used to describe the variation of temperature with time.

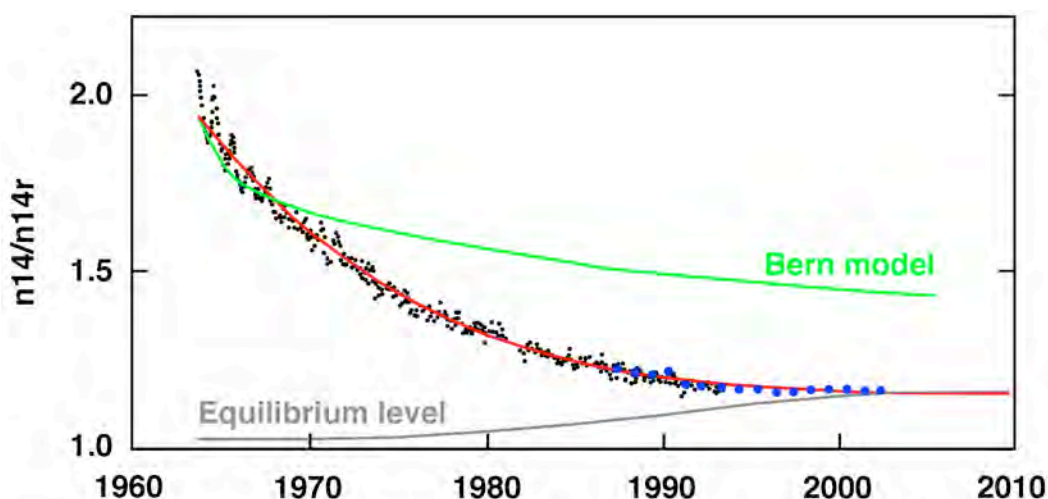


Figure 4. Relaxation curve for the bomb C14 excess according to data in Fig.3, compared with the equilibrium level prescribed by the model (grey curve). The green curve shows the relaxation behaviour predicted by the Bern model according to the impulse response function in Eqn. (7).

If the temperature had remained constant after 1963, the equilibrium level of atmospheric bomb $n14/n14r$ would have remained constant and close to unity (1.05 under the modelled conditions). Eqns. (3–6) prescribe that the relaxation curve for the bomb C14 excess under such conditions should be strictly exponential with a time constant differing insignificantly from the turnover time.

In reality, global temperatures have increased after 1963 and caused a gradual elevation of the equilibrium level. This has introduced mathematically significant deviations from a strictly exponential approach of the bomb C14 excess to the equilibrium level. The observed relaxation curve remains monophasic, however. The bomb test data lend no support to the idea that the relaxation of airborne carbon dioxide excesses exhibits a pronounced multiphasicity reflecting saturation effects or rate-limiting contributions from slow oceanic events. In particular, the green curve in Fig. 4 shows that the triphasic impulse response function calculated with the Bern carbon cycle model (Eqn. 7) is qualitatively and quantitatively inconsistent with the observed relaxation of the bomb C14 excess.

Discussion

The relaxation of C14-carbon dioxide

Radioactive tracers have been extensively used to study the turnover of chemical compounds. If we want to know what happens to anthropogenic emissions of carbon dioxide, a scientifically ideal experiment would be to create an atmospheric emission pulse of C14-labelled carbon dioxide. This would enable us to study at what rate and to what extent the labelled carbon dioxide is removed from the atmosphere.

The nuclear weapon testers inadvertently have set up such an ideal tracer experiment, the outcome of which now has been monitored for more than fifty years. There is no doubt that the decreasing $\Delta C14$ -values in Fig. 1 reflect the removal of carbon dioxide, because the C14-label is attached to one of the carbon dioxide atoms. It is obvious that the decreasing $\Delta C14$ -values reflect a relaxation process (equilibration process), because the bomb tests did create an excess of airborne C14 and the bomb C14 inventories described by Naegler & Levin [11] establish that the disappearance of this excess from the atmosphere is associated with the appearance of quantitatively agreeing amounts of radiocarbon in other parts of the nature. Consequently, experimental points in Fig. 3 can be safely assumed to give an empirically based picture of the relaxation towards equilibrium of the C14-carbon dioxide excess produced by the bomb tests.

The carbon cycle involves a multitude of physicochemical and biochemical processes occurring over widely different time scales. The reaction system in Scheme 1, therefore, might seem to be unrealistic, since it considers only the two reaction steps that account for the exchange of carbon dioxide between the air and the hydrosphere. As documented by the present results, however, this simple two-box system is sufficient to explain the bomb C14 observations made. The kinetic model derived for Scheme 1 provides an almost perfect description (red curve in Fig. 3) of the empirical C14 relaxation data. This can be taken to indicate that the two reaction steps in Scheme 1 have a predominant influence on the relaxation of airborne C14-carbon dioxide, as might be expected considering that the hydrosphere is the vastly predominant sink for atmospheric carbon dioxide excesses from the point of view of final equilibrium levels.

In the absence of temperature effects, Scheme 1 prescribes that the removal of an excess of airborne carbon dioxide will conform to an exponential relaxation function, with a time constant differing insignificantly from the turnover time $1/k$ (Eqns. 5–6) because the uptake of the gas by the oceans is practically irreversible ($k \gg d$). Under such conditions, the rate of the relaxation process will be controlled almost exclusively by the term kx in Eqns. (3–4), i. e. by the air level of carbon dioxide in accordance with the law of mass action.

The model now applied expands upon previous kinetic analyses of Scheme 1 by assuming that the rate constant d for outgassing of carbon dioxide from the hydrosphere shows a temperature dependence conforming to the Arrhenius equation. According to the expanded model, observed changes of the temperature over the period 1963–2005 have raised the magnitude of d by 18% and caused a corresponding increase of the equilibrium level for atmospheric carbon dioxide (the grey curve in Fig. 4). Due to the small magnitude of d in comparison to k , however, the temperature change has had a minor effect, only, on the relaxation time defined by Eqn. (5), decreasing its magnitude from 14.10 years to 14.06 years.

Consequently, the close agreement between model predictions and empirical C14 data in Fig. 3 provides clear evidence that the relaxation of C14 carbon dioxide has occurred at a rate which, even in the presence of the temperature changes, has remained controlled almost exclusively by the air level of the gas (the term kx). The empirically determined relaxation curve for the bomb C14 excess is monophasic and may be regarded as a slightly distorted exponential decay function that corresponds to a turnover time ($1/k$) of approximately 14 years. The relaxation curve shows no detectable multiphasicity attributable to saturation effects or an influence of slow oceanic events.

The distortion of the empirical C14 relaxation curve (as compared to a strictly exponential curve) can be explained as an effect of temperature on the equilibrium level of airborne C14. Since this level has been raised over the examined time period (grey curve in Fig. 4), the unusual situation is encountered that a kinetic relaxation process reaches completion within finite time. Normally, kinetic studies of relaxation processes are performed under conditions where the processes conform to exponential progress curves that approach equilibrium conditions without ever reaching them in a mathematical sense. The bomb C14 relaxation process, however, was completed after a finite time of about 40 years according to the results in Fig. 4. This is consistent with the conclusion drawn by Světlík *et al* from an analysis of $\Delta C14$ -values recorded in Central Europe [12].

The turnover time of atmospheric carbon dioxide

Kinetic carbon isotope effects are small, normally affecting rate constants by less than 4% and hence being of insignificant interest in the carbon cycle contexts considered here. The relaxation behaviour now characterized for C14 carbon dioxide, therefore, would be expected to be representative for the relaxation of carbon dioxide in general.

Results now reported are fully consistent with that expectation. In particular, the turnover time estimated from the bomb C14 relaxation data in Fig. 3 is of the same order of magnitude as the estimates previously obtained by similar methods, as well as with those obtained by the application of methods that refer to natural carbon dioxide and to direct determinations of the turnover time as the quotient between pool sizes and reaction fluxes. The multitude of experimental estimates of the turnover time for atmospheric carbon dioxide invariably have been found to fall within the range 2–15 years [13, 14].

The relaxation of anthropogenic carbon dioxide emissions according to the IPCC

Since its constitution in 1988, the IPCC has based its carbon cycle assessments on the presumption that the long-term trend of the Keeling curve towards steadily increasing carbon dioxide levels is caused almost exclusively by anthropogenic emissions of the gas. That presumption is difficult to reconcile with a carbon dioxide turnover time of the order of 10 years. The IPCC, therefore, has argued that the empirically determined turnover times lack bearing on the rate at which emissions of anthropogenic carbon dioxide are removed from the air.

Instead, the IPCC in its fourth assessment report [7] advocated that the removal of carbon dioxide emissions is adequately described by the carbon cycle model designed by Siegenthaler & Joos [6] (the Bern model), which has been tuned to fit the Keeling curve with the presumption that the long-term trend of the curve derives exclusively from emissions of anthropogenic carbon dioxide. According to the Bern model, the relaxation of a pulse of airborne carbon dioxide is multiphasic and corresponds effectively to an e-fold time of about 100 years (Eqn. 7; green curve in Fig. 4).

The Bern model (and a number of similar carbon cycle models used by climate modellers) is based on the idea that the uptake of anthropogenic carbon dioxide emissions in the sea surface layer gives rise to pH changes that decrease the carbon dioxide uptake capacity of the surface layer (the Revelle effect). This is envisaged to gradually shift the rate-limitation of the uptake of atmospheric carbon dioxide from fast sea-surface events to slow processes transferring carbon from the sea-surface to the deep-sea regions.

Starr in 1993 presented analytical evidence leading him to conclude that e-fold times of the order of 100 years not only are inconsistent with the empirically determined turnover times, but also with the amplitude of the seasonal fluctuations of the Keeling curve and with the bomb $\Delta C14$ data [15]. Evaluating Starr's report [16], the IPCC claimed that $C14$ (as measured by $\Delta C14$ data, which refer to the $C14/C12$ quotient) is a poor tracer analogue for anthropogenic carbon dioxide emissions, because "an atmospheric perturbation in the isotopic ratio disappears much faster than the perturbation in the number of $C14$ atoms". That argument cannot be followed and is contradicted by the present results. Data in Fig. 1 refer to $\Delta C14$ and indicate that the bomb test perturbation of $\Delta C14$ actually disappears somewhat slower than does the perturbation of the number of $C14$ atoms, which is described by the empirical data points in Figs. 3–4.

It would appear that the above claim rather is based on the IPCC assessment of Bern model results showing that a small pulse of excess $C14$ disappears more rapidly than does a large pulse of anthropogenically emitted carbon dioxide [16]. This may certainly be so if the Revelle effect is assumed to be significant, because then the addition of small amounts of carbon dioxide will produce smaller pH changes than those resulting from the addition of large amounts of carbon dioxide. The relaxation of the minute $C14$ amounts produced by the bomb tests, however, has been monitored under conditions where there have been immense emissions of anthropogenic carbon dioxide. If the latter are assumed to result in pH changes that significantly have affected the carbon dioxide relaxation kinetics, then these pH changes must have affected also the relaxation of $C14$ carbon dioxide.

This was pointed out already in 1959 by Bolin & Eriksson [17] and provides some important inferences. Firstly, Segalstad's criticism [14] is justified that the above Bern model results for small pulses of $C14$ carbon dioxide alone cannot be taken to describe the relaxation of the bomb $C14$ excess. The kinetic model now described is the only one that so far has been shown to account for

the observed time dependence of the ΔC_{14} data in Fig. 1. Predictions of the Bern model and related carbon cycle models with regard to the bomb C_{14} observations still remain to be established under relevant conditions of documented continuous emissions of anthropogenic carbon dioxide.

Secondly, if the Revelle effect is assumed to have caused pH changes that appreciably decrease the rate of carbon dioxide uptake by the sea-surface layer, then this should be reflected by a gradually decreasing magnitude of the corresponding reaction fluxes. No such tendency can be found in the multitude of experimentally determined turnover time values [13, 14], which have been estimated from observations that relate to the flux of carbon dioxide from the air to the sea-surface layer.

Finally, the absence of any detectable multi-phasicity in the bomb C_{14} relaxation curve establishes that pH changes and subsequent changes of rate-limiting steps due to the Revelle effect have not had any detectable influence on the relaxation of C_{14} carbon dioxide. The simplest interpretation of this observation is that the same applies for the relaxation of carbon dioxide in general and of anthropogenic emissions in particular.

The relaxation of anthropogenic carbon dioxide emissions according to the two-box model

It has been firmly established that the solubility of carbon dioxide in water decreases with increasing temperature, such that global warming by necessity is associated with thermal outgassing of carbon dioxide from the hydrosphere. Evidence that such outgassing has been of climatological significance comes from the El Niño fluctuations of the rate of change of the atmospheric carbon dioxide level, as deduced from the Keeling curve. A previous analysis [3] of the effects of temperature and anthropogenic emissions on the atmospheric carbon dioxide level showed that both the long-term trend and the El Niño fluctuations of the Keeling curve can be quantitatively accounted for in terms of Scheme 1 and the kinetic model now applied. The kinetic parameter values obtained in that analysis ($E^* = 165 \text{ kJ/mol/K}$; $1/k = 14 \text{ years}$) agree within experimental precision with those determined from the bomb C_{14} relaxation curve in Fig. 3.

The latter observation provides clear evidence that the relaxation kinetics of anthropogenic carbon dioxide emissions do not differ significantly from those now characterized for C_{14} -labelled carbon dioxide. The results in Fig. 3 lead to the inference that C_{14} -carbon dioxide is an excellent tracer analogue for carbon dioxide in general and corroborate the conclusions drawn in the previous analysis of the Keeling curve and its El Niño fluctuations [3].

In particular, data now presented confirm that airborne carbon dioxide relaxes at a rate which is governed mainly by the air level of the gas and which corresponds to a turnover time of 14 years. Data in Fig. 4 confirm that the relaxation process tends towards an equilibrium level that has been significantly affected by the concomitant temperature changes, and show that the estimated strength of this temperature effect on the relaxation of C_{14} -carbon dioxide agrees with that determined from the amplitude of the El Niño fluctuations of the rate of change of the atmospheric carbon dioxide level. The descriptive validity of the two-box model based on Scheme 1 thus has been demonstrated for two independent series of fundamental observations of the relaxation behaviour of atmospheric carbon dioxide.

Concluding remarks

The IPCC supports carbon cycle models that have been derived and tuned to the Keeling curve with the presumption that the rising air levels of carbon dioxide are caused exclusively by anthropogenic emissions of the gas. No empirical evidence has been presented to justify that presumption. On the contrary, the IPCC have been forced to disregard fundamental empirical observations that cannot be readily reconciled with such a view. Reported experimental estimates of the turnover time for atmospheric carbon dioxide are presumed to lack bearing on the relaxation kinetics. The bomb C14 data are presumed to lack relevance for the relaxation of anthropogenic carbon dioxide emissions. Thermal outgassing due to global warming by necessity has contributed to the long-term trend of the Keeling curve, but the IPCC presumes that the contribution is insignificant.

The IPCC's assessment of the relaxation of airborne carbon dioxide along such presumptive lines receives no support by the kinetic analyses presented here and in the previous study of the predictions of Scheme 1 [3]. When the temperature dependence of the water solubility of carbon dioxide is taken into account, the El Niño fluctuations of the Keeling curve and the bomb C14 data consistently indicate that temperature changes have had a most profound effect on the air level of carbon dioxide. The present results reinforce the previous conclusion [3] that the rising levels of carbon dioxide during the industrial era to approximately equal extents derive from anthropogenic emissions and thermal outgassing due to global warming.

The available empirical evidence on the relaxation of atmospheric carbon dioxide, therefore, must lead to a firm rejection of the presumption that the relaxation process is insignificantly affected by temperature changes. As pointed out previously [3], this calls for a drastic re-evaluation of the carbon cycle budget presented by the IPCC, as well as of the approaches taken and results obtained by climate modellers in their attempts to project the effects of future emissions of anthropogenic carbon dioxide. Projections calculated using climate models that disregard thermal outgassing and the available empirical information on carbon dioxide turnover times and relaxation characteristics will be too biased to provide any information of significant prognostic interest.

References

1. P. P. Tans *et al.*, 1979, *Nature* **280**, 826–828.
2. C. D. Keeling *et al.*, Scripps CO2 program (<http://scrippsco2.ucsd.edu>).
3. G. Pettersson, 2014, *Temperature effects on the atmospheric carbon dioxide level*, <http://www.false-alarm.net/paper-4/>
4. IPCC, 1990, *First Assessment Report*, Working Group I, p. 8.
5. R. Revelle & H. E. Suess, 1957, *Tellus* **9**, 18–27.
6. U. Siegenthaler & F. Joos, 1992, *Tellus* **44B**, 186–207.
7. IPCC, 2007, *Fourth Assessment Report*, Working Group I, Chapter 2.10.2.
8. R. Nydal & K. Lövseth, 1996, Carbon Dioxide Information Analysis Center.
9. I. Levin *et al.*, 2008, *Science Total Environment* **391**, 211–216.
10. I. Světlík *et al.*, 2006, *Czechoslovak Journal of Physics* **56**, 291–297.
11. T. Naegler & I. Levin, 2006, *J. Geophys. Res.* **111**, D12311.

12. I. Svetlik *et al.*, 2010, *Radiocarbon* **52**, 815–822.
13. E. T. Sundquist, 1985, American Geophysical Union, *Geophysica Monograph* **32**, 5–59.
14. T. V. Segalstad, 1998, in *Global warming: The continuing debate* (R. Bate, ed.), Cambridge, U.K., pp. 184–219.
15. C. Starr, 1993, *Energy* **18**, 1297-1310.
16. IPCC, 1995, *Second Assessment Report*, Working Group I, pp. 65–86.
17. B. Bolin & E. Eriksson, 1959, in *The Atmosphere and the Sea in Motion* (ed. B. Bolin), Rockefeller Institute Press, New York, pp. 130–142.