Relaxation kinetics of atmospheric carbon dioxide

Gösta Pettersson, Chemical Center, University of Lund, Sweden

Evidence and arguments are presented to show that reported empirical estimates of the atmospheric relaxation time of carbon dioxide are trustworthy and provide a far better description of the rate of removal of anthropogenic carbon dioxide emissions from the air than do mathematical carbon cycle models such as the Bern model. The latter model, which has been extensively used for projections of the future climate, gravely underestimates both the rate and the extent of removal of anthropogenic carbon dioxide emissions.

According to measurements made at Mauna Loa by C. D. Keeling and collaborators [1], the atmospheric concentration of carbon dioxide has shown a steady long-term increase since 1958; the graph describing this is usually referred to as 'the Keeling curve'. Proponents of the antropogenic global warming (AGW) hypothesis have attributed the increasing carbon dioxide levels to human activities such as land-use changes and combustion of fossil fuels. Opponents of the AGW hypothesis have argued that this would require a turnover time of about 100 years for atmospheric carbon dioxide, which is inconsistent with a multitude of experimental studies indicating that the actual turnover time is of the order of 5–10 years [2, 3].

Since its constitution in 1988, the United Nation's Intergovernmental Panel on Climate Change (IPCC) has argued that the empirically determined turnover times lack bearing on the rate at which anthropogenic carbon dioxide emissions are removed from the atmosphere. Instead, the IPCC in its fourth assessment report [4] presumes that the removal of carbon dioxide emissions is adequately described by the carbon cycle model designed by Joos *et al*. [5] at the University of Bern (the Bern model), according to which airborn carbon dioxide shows an effective turnover time of the order of 50–200 years. This paper examines and invalidates the arguments put forward to support that presumption.

Theory

Turnover time

Turnover time is a concept used by climatologists and others to describe how fast emissions of a compound are removed from the reservoir to which it has been emitted. The turnover time (β) is normally defined as the amount of compound being present in the reservoir divided by the flux rate at which the compound is removed:

$$\beta = \text{Amount/Flux} \qquad (1)$$

Eqn (1) is a reformulation of the thermodynamic law of mass action, which states that reaction flux is proportional to the amount of reactant. In chemical reaction kinetics, the proportionality constant is called 'rate constant'. To a kineticist, therefore, the turnover time represents the reciprocal value of the rate constant for removal of the compound from the reservoir to which it has been emitted.

Since reaction flux is the time derivative of the amount of the compound, Eqn (1) is a differential equation describing the time-dependence of the amount remaining in the reservoir. If there are no other reactions leading to production or removal of the compound, this differential equation can be analytically solved to give

$$\textit{Remaining fraction} = \mathbf{Exp}[-t/\beta] \qquad (2)$$

where t stands for the reaction time. Eqn (2) is of the same functional form as the one governing the decay of radioactive compounds. When Eqn (2) applies, one may talk about the halftime of the emitted compound in the reservoir. The halftime is given by the turnover time multiplied by 0.7 (the natural logarithm of 2).

Relaxation time

Theoretically, all reactions are reversible and tend towards an equilibrium that is characterised by an equilibrium constant (*Keq*). Emission of a compound to a reservoir perturbs the equilibrium and triggers a relaxation process tending to reestablish equilibrium conditions by removing the excess of the compound from the reservoir to which it has been emitted. When the removal of the emitted compound is acknowledged to be reversible, the law of mass action prescribes that Eqn (2) should be replaced by

$$\textit{Remaining fraction} = (\mathbf{Exp}[-t/\tau] + Keq)/(1+Keq) \qquad (3)$$

The relaxation of the emitted compound will still be governed by an exponential function, characterised by a time constant which kineticists call relaxation time (τ). When the relaxation process is completed, a finite part of the emission (corresponding to its equilibrium value) will remain in the reservoir. Furthermore, the relaxation time in a reversible process will no longer be identical to the turnover time but be given by

$$\tau = \beta/(1+Keq) \qquad (4)$$

If the equilibrium constant is less than 0.05, more than 95% of the emission will be removed from the reservoir and the process may be considered as practically irreversible. Under such conditions, the relaxation time will differ less than 5% from the turnover time and be practically equal to it.

Multiple relaxation times

If the amount of the emitted compound is assumed to be affected by reactions additional to a single outflow process, the relaxation function may exhibit a spectrum of relaxation times that cannot be simply related to the turnover time for a single outflow process. The Bern model in its pragmatic approximate form represents such a case. It describes the removal of carbon dioxide emission pulses in terms of a relaxation function (called impulse response function) involving three distinct phases governed by relaxation times of 1.2, 19, and 173 years, respectively [6]:

$$\textit{Remaining fraction} = 0.19\ \mathbf{Exp}[-t/1.2] + 0.34\ \mathbf{Exp}(-t/19] + 0.26\ \mathbf{Exp}[-t/173] + 0.22 \qquad (5)$$

Observations and data evaluation

The bombtest curve

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 level of airborn C14-carbon dioxide had been raised to about twice its previous natural background value.

The subsequent removal of the anthropogenically produced excess of radiocarbon in the atmosphere has been monitored at several places around the world. The longest continuously sampled series of data was recorded near Nordkap in Norway by Nydal & Lövsedt [7]. They started their measurements in 1963, and put an end to them in 1993 when almost 90% of the original excess of airborn radiocarbon had been removed. Subsequent measurements in Central Europe have established that the atmospheric excess of C14-carbon dioxide has continued to decrease after 1993 and now is less than 5% of the original value [8]. Representative results describing how the anthropogenically produced excess of C14-carbon dioxide has been removed from the atmosphere are shown in Fig. 1. Results obtained in Central Europe are shown as yearly means.

Data in Fig. 1 refer to the excess of radiocarbon, as estimated from the isotopic C14/C12 ratio. The Keeling curve establishes that the concentration of C12-carbon dioxide has increased during the bomb C14 measurements. This has caused a dilution of airborn radiocarbon and hence has provided a minor contribution to the decrease of the observed C14/C12 ratio.

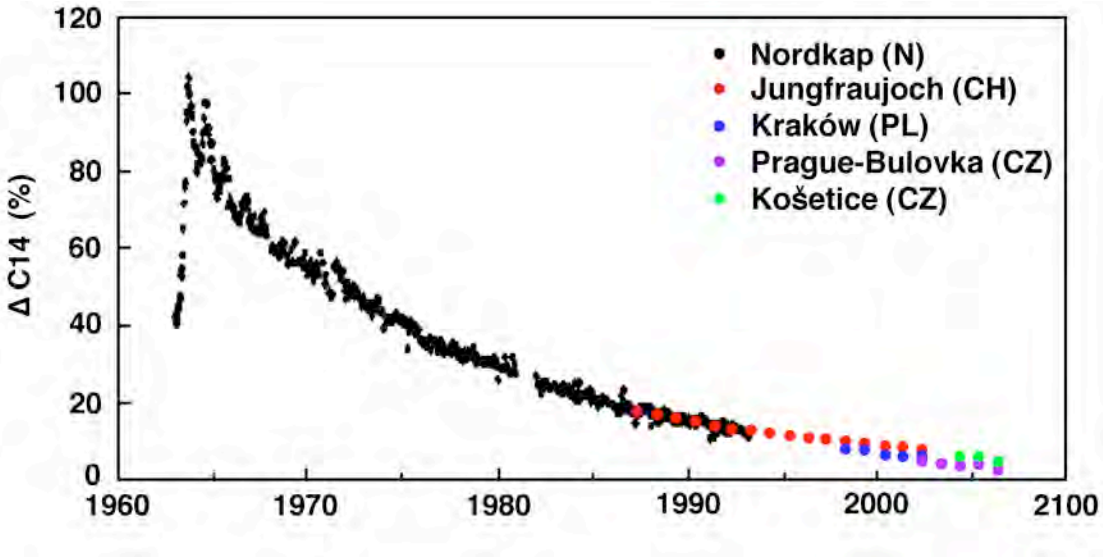

Figure 1. *Observed natural removal of the excess of airborn C14-carbon dioxide that was produced by atmospheric tests of nuclear weapons*

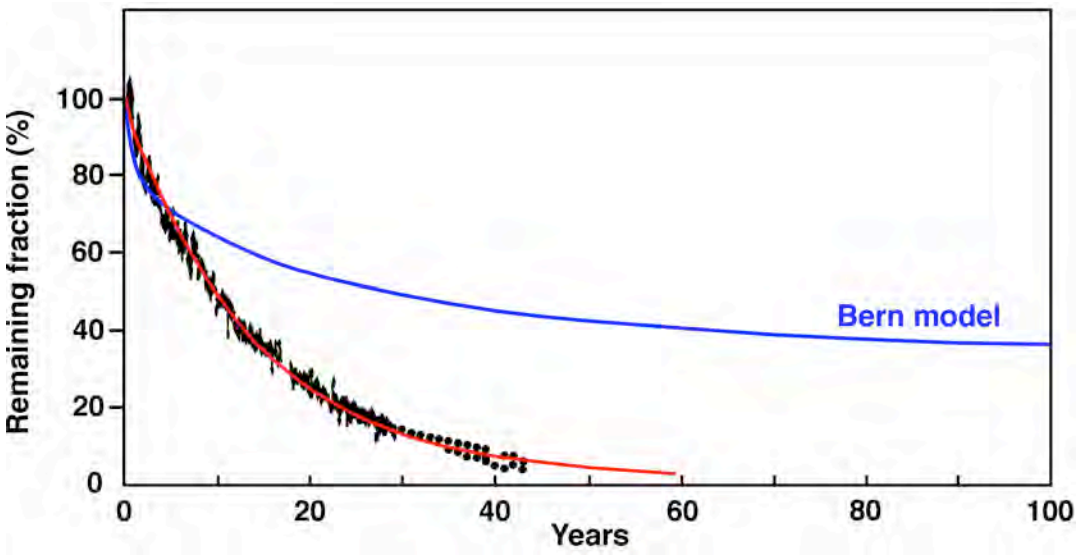

Figure 2. *The bombtest curve, compared with response functions proposed to account for the relaxation of an excess of atmospheric carbon dioxide*

To facilitate comparison with relaxation functions proposed to describe the removal of emission pulses of anthropogenic carbon dioxide, data points in Fig. 1 were corrected for the dilution effect using the Keeling curve as a record of the time-dependence of the concentration of C12-carbon dioxide. The corrected data points were then rescaled so that they correspond to the remaining fraction of the anthropogenically produced excess of airborn radiocarbon. August 1963 (the sampling period 630729–630805 [7]) was set to zero reaction time. The excess of C14-carbon dioxide at that time ($\Delta C14 = 951$ ‰) was assumed to define 100% of the anthropogenic emission pulse. The corrected and rescaled data series thus obtained is shown in Fig. 2 and will be referred to as the 'bombtest curve'.

Kinetic characterisation of the bombtest curve

When the atmospheric bomb tests stopped, they had produced an emission pulse leaving an excess of anthropogenic C14-carbon dioxide in the atmosphere. This has triggered a relaxation process tending to reestablish equilibrium conditions by transferring radiocarbon from the atmosphere to the other two main reservoirs of renewable carbon (the hydrosphere and the biosphere). The bombtest curve gives a direct picture of the larger part of this relaxation process. It shows that less than 5% of the original excess of C14-carbon dioxide now remains airborn, which justifies characterisation of the removal of the excess as a practically irreversible process.

This is consistent with the carbon cycle data presented by the IPCC [9], according to which the preindustrial equilibrium proportions of renewable carbon in the atmosphere:biosphere:hydrosphere are 597 GtC : 2 300 GtC : 38 000 GC. The latter data correspond to $Keq \approx 0.015$ for the relaxation of an excess of airborn carbon dioxide and indicate that the bombtest curve ultimately should tend towards a final value corresponding to 1.5% of the original excess of C14-carbon dioxide.

Regression analysis of the bombtest curve established that it can be satisfactorily described in terms of a single-exponential regression function such as Eqn. (2). Adding a second tunable exponential term to the regression function did not result in any statistically significant improvement of fit. A fit of Eqn. (3) failed to provide any statistically significant estimate of *Keq*, but indicated that its value

is closer to zero than to 0.05. The red curve in Fig. 2 represents the best-fit of Eqn. (3), as calculated with the presumption that $Keq = 0.015$. It corresponds to a relaxation time of 14 (± 1) years.

The Bern model description of the relaxation of airborn carbon dioxide

The blue curve in Fig. 2 represents the graph of Eqn. (5) and shows how the Bern model describes the atmospheric relaxation of an emission pulse of carbon dioxide. The model gives a satisfactory description of the first few years of the empirically observed relaxation curve, but fails completely to account for the long-term observations made.

The Bern model's relaxation (impuls response) function is inconsistent with reported empirical data in three fundamental respects. Firstly, no experimental record of the relaxation of airborn carbon dioxide has shown the pronounced and long-term multiphasicity prescribed by Eqn. (5). The bomb-test curve establishes that the hitherto observed part (≈ 95%) of the relaxation process is satisfactorily described by a single-exponential decay function. If the removal of carbon dioxide emissions is governed by relaxation times on a multidecadal or centennial time scale, such slow processes cannot be assumed to significantly affect more than the final 5% of the relaxation, *i. e.* the part that we have not yet been able to observe.

Secondly, the Bern model's relaxation function gravely underestimates the rate at which an excess of carbon dioxide is removed from the atmosphere. The effective turnover time of 50–200 years reported by the IPCC [4] (the time it takes to reduce an emission to 36.8% of its original value) is 96 years according to Eqn. (5), *i. e.* about 7 times longer than the relaxation time of 14 years governing the bombtest curve and 24 times longer than the turnover time of 4 years supported by the IPCC in its first two assessment reports [10, 11].

Finally, the Bern model's relaxation function also underestimates the extent to which an excess of airborn carbon dioxide is removed. The constant term in Eqn. (3) and (5) represents the carbon dioxide fraction remaining airborn at infinite reaction time, i. e. the equilibrium proportion of airborn carbon dioxide. This fraction is 0.22 according to the Bern model, which corresponds to $Keq \approx 0.28$. The bombtest curve establishes that the equilibrium constant characterising the observed major part of the relaxation process cannot be that high, but certainly must be lower than 0.05. The available carbon cycle data indicate that $Keq \approx 0.015$ [9], which provides the inference that the Bern model makes the removal of airborn carbon dioxide about twenty times more reversible than it has been empirically found to be.

Alternatively expressed, the Bern model's relaxation function prescribes that the removal of an excess of atmospheric carbon dioxide reaches an equilibrium when 22% of the excess remains airborn. According to the empirically supported estimate $Keq = 0.015$, the equilibrium fraction of airborn carabon dioxide should be $Keq/(1+Keq) \approx 1.5\%$. This means that the Bern model overestimates the final equilibrium amount of airborn carbon dioxide by a factor of about 15. Since the hydrosphere is the predominant sink for an excess of atmospheric carbon dioxide, one could say that the Bern model makes carbon dioxide about 15 times less water soluble than it has been empirically established to be according to the carbon cycle data reported by the IPCC [9].

Discussion

The Bern carbon cycle model

Oceanographic studies performed by Oeschger and Siegenthaler at the Bern university have indicated that it may take hundreds of years for carbon dioxide to be transferred from the oceanic surface to the deap-sea regions [12]. The multibox model they designed to account for the oceanic turnover of carbon dioxide was extended by Siegenthaler and Joos to include also a multi-compartment biosphere [13]. The resulting carbon cycle model is usually referred to as the Bern model and has been subjected to subsequent revisions [5].

Due to its multibox character, the Bern model involves a variety of tunable parameters. Values of many of these parameters have been tuned so as to preserve the original ocean model's ability of providing a satisfactory description of the oceanic transport of tracers. Parameter values of particular interest to the atmospheric turnover of carbon dioxide have been chosen so that the model satisfactorily accounts for the time dependence of the carbon dioxide levels observed at Mauna Loa (the Keeling curve), when fed with historical data regarding anthropogenic emissions of carbon dioxide.

Among proponents of the AGW hypothesis, the ability of the Bern model to simulate the Keeling curve has lent credence to the model and its ability to predict future levels of airborn carbon dioxide for presumed emission scenarios. The Bern model (or closely related carbon cycle models tuned to the Keeling curve) is routinely used by climate modellers to obtain the carbon dioxide input data they require to arrive at predictions of anthropogenic effects on the future climate.

Opponents of the AGW hypothesis have pointed out that predictions of the Bern model are inconsistent with reported empirical data for the turnover and relaxation of airborn carbon dioxide [3]. The IPCC has taken the stand that such criticism of the Bern model is unjustified. This particular controversy between AGW proponents and opponents can be readily settled by strict kinetic evaluation of the experimental observations made.

Functional characteristics of the relaxation of atmospheric 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 radioactively 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 fifty years. There is no doubt that the bombtest curve shows the removal of an excess of airborn carbon dioxide, because the radioactive label is attached to one of the carbon dioxide atoms. There is no doubt that the curve reflects a relaxation process, because the disappearance of radiocarbon from the atmosphere has been shown to be associated with the appearance of quantitatively agreeing amounts of radiocarbon in the hydrosphere and biosphere [14]. The bombtest curve in Fig. 2, therefore, provides a direct picture of the removal from the air of more than 95% of an anthropogenic emission pulse of carbon dioxide. We lack empirical information only on the final part of the relaxation process, the part that has not yet occurred and which cannot account for the removal of more than the final few percents of the emission pulse.

This renders the bombtest curve extremely informative and exceptionally well suited for analysis of the main functional characteristics of the relaxation of anthropogenic carbon dioxide emissions. The curve reflects the net outcome of all biospheric and hydrospheric processes contributing to the removal of 95% of an excess of airborn carbon dioxide. The time-course of the curve characterises the kinetics of this relaxation process and contains all the information required to decide how the process can best be described in mathematical terms.

The kinetic analysis reported in this paper establishes that the relaxation of airborn carbon dioxide is a practically irreversible process that can be most satisfactorily described by a single-exponential function and hence by a single relaxation time. These characteristics of the relaxation process are consistent with known equilibrium data for the carbon cycle [9], as well as with the expected kinetic behaviour of a system where there is a practically irreversible uptake of airborn carbon dioxide by one vastly predominant sink (the hydrosphere).

Experimental estimates of the turnover time and the relaxation time

Since the removal of airborn carbon dioxide is practically irreversible, turnover times calculated by application of Eqn. (1) would be expected to agree well with the relaxation times determined using Eqn. (2) or (3). Reported experimental estimates of the two time constants are largely consistent with that expectation and provide clear evidence that the removal of carbon dioxide emissions is governed by a relaxation time of the order of 10 years rather than 100 years [2, 3].

Experimental estimates of the turnover time invariably have fallen within the range 2–14 years, with a predominance of values in the region 5–8 years [2, 3]. Evaluating such data, the IPCC found that the turnover time for natural carbon dioxide is 4 years [10, 11]. The latest two turnover time determinations made use of methods that had not been previously applied and both arrived at the value 5.4 years [3]. The estimated turnover times for natural carbon dioxide, therefore, seem to be generally shorter than the relaxation time of 14 years characterising the bombtest curve.

To explain this discrepancy, Essenhigh has presented model results leading him to propose that the relaxation time is 16 years for C14-carbon dioxide and 5 years for C12-carbon dioxide [15]. This would imply that the relaxation of carbon dioxide exhibits a kinetic C12/C14 isotope effect of 3.2, which is sufficient reason for plain rejection of the proposal. Carbon isotope effects encountered in organic chemistry may occasionally be as high as 1.15 [16], but are normally much lower [17]. The kinetic isotope effects for events associated with the uptake of atmospheric carbon dioxide by the hydrosphere or the biosphere have been extensively studied and are normally lower than 1.02 for C13 and 1.04 for C14 [18, 19].

As pointed out by the IPCC [20], the removal of anthropogenic carbon dioxide (and hence also of bomb C14-carbon dioxide) from the air is governed by the same mechanisms and follows the same pathways as the removal of natural carbon dioxide. Furthermore, the kinetic C12/C14 isotope effect on the relaxation process is likely to be too low to be detected at the precision level of hitherto performed studies of the process. This means that the relaxation of C14-carbon dioxide described by the bombtest curve can be taken to be representative also for the relaxation of carbon dioxide with a natural isotope composition.

The discrepancy between reported turnover times for natural carbon dioxide and relaxation times for C14-carbon dioxide, therefore, cannot be attributed to the isotope effect but must be otherwise explained. Attention then may be drawn to the large variation of reported values for the turnover

time, which indicates that the values are difficult to estimate and rather imprecise. Many turnover times have been calculated from local flux measurements, which raises the question whether they are globally representative. The reported values usually have been presented without any indication of what temperature they refer to, which points to another source of uncertainty.

The bombtest curve is less ambiguous. It has been determined with the standard high precision of radiocarbon measurements and refers to consistent observations made at several different locations. Due to the relatively rapid mixing of airborn carbon dioxide, the bombtest curve is likely to be globally representative and hence can be related to estimated global temperatures. The weight of evidence, therefore, suggests that the relaxation time of 14 years calculated from the bombtest curve presently can be taken to provide the best available estimate of the relaxation time for atmospheric carbon dioxide. In any case, it provides a reliable upper limit for the magnitude of the relaxation time.

The descriptive invalidity of the Bern model

The Bern model and other carbon cycle models tuned to the Keeling curve prescribe that airborn carbon dioxide exhibits an effective relaxation time of the order of 100 years. Starr in 1993 presented evidence leading him to conclude that such long relaxation times are inconsistent with the amplitude of the seasonal fluctuations of the Keeling curve, as well as with the bombtest data [21]. The analysis now performed provides similar inferences. The impulse response function of the Bern model (Eqn. 5) fails gravely and in several fundamental respects (phasicity, rate, extent) to account for the relaxation kinetics of the observed anthropogenic emission pulse of radioactively labelled carbon dioxide (Fig. 2).

Evaluating Starr's report [22], the IPCC claimed that C14 (when measured as the C14/C12 ratio) is a poor analogue tracer 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 the isotopic C14/C12 ratio. Data in Fig. 2 have been corrected so that they refer to one and the same C12 level and thus are proportional to the number of C14 atoms. The difference between the two data sets is so minute that it scarcely can be detected by the eye. Segelstad has attributed IPCC's misinterpretation of the bombtest curve to inadequate modelling of isotopic tracer experiments [3]. However that may be, it seems obvious that the IPCC evaluation concerns properties of the Bern model rather than the kinetics of the experimentally observed relaxation curve.

Oceanic effects on the atmospheric relaxation of carbon dioxide

Proponents of the Bern model have argued that the removal of anthropogenic C12-carbon dioxide emissions exhibits pronounced relaxations on a multidecennial and centennial time scale due to slow oceanic transport of carbon dioxide from the sea surface to the deep-sea. This would imply that slow oceanic events should have a corresponding pronounced effect also on the removal of anthropogenic C14-carbon dioxide excesses. The present regression analysis of the bombtest curve establishes that such effects are of no statistical significance in the 95% of the relaxation process that we now have direct records of.

The absence of pronounced oceanic effects on the relaxation of airborn carbon dioxide is likely to reflect the equilibrium properties of the reaction system. The law of mass action prescribes that the rate of outflow of carbon dioxide from the atmosphere is dependent exclusively on the atmospheric

concentration of carbon dioxide. If the relaxation process is strictly irreversible, the removal of airborn carbon dioxide will be completely unaffected by oceanic events. If the relaxation process is practically irreversible, oceanic effects on it will be correspondingly small. Slow relaxations due to oceanic events are likely to exist, but can be anticipated to affect mainly the removal of the final few percents of anthropogenic carbon dioxide emissions.

The latter conclusion is corroborated by the observation that the bombtest curve can be described in terms of an *exponential decrease* of the concentration of airborn carbon dioxide. According to elementary mathematics, this implies that the *rate of decrease* of the carbon dioxide concentration has been proportional to the atmospheric carbon dioxide concentration, as prescribed for the outflow step by the law of mass action. Consequently, the observed 95% of the relaxation process have been kinetically governed by the concentration of carbon dioxide in the air, without any detectable contributions from other variables or events.

The Bern model allows for a pronounced effect of slow oceanic events on the relaxation of airborn carbon dioxide. This can be attributed to the model's drastic exaggeration of the reversibility of the process. It is beyond the scope of this paper to clarify why the Bern model makes the relaxation process unrealistically reversible. It suffices to note that it does. The model prediction (Eqn. 5) that 22% of a carbon dioxide emission will remain airborn forever is in obvious disagreement with the experimental observation that 95% of the atmospheric C14-carbon dioxide excess created by the bombtests in the early 1960s has already been removed from the atmosphere and transferred to the hydrosphere and biosphere.

Concluding remarks

The relaxation function (impulse response function) for atmospheric emission pulses of carbon dioxide describes the time-course of removal of the emission pulse. A standard kinetic approach for determination of this function would be to tune a model directly to observed data for the relaxation process. This would ensure that the model describes what it is intended to describe. The corresponding relaxation function may then be used to calculate how much anthropogenic emissions have contributed to the increasing air levels of carbon dioxide indicated by the Keeling curve.

Designers of the Bern model have chosen the converse approach of presuming that the increasing carbon dioxide levels derive exclusively from anthropogenic emissions. Tuning their model to the Keeling curve, they arrive at a relaxation function which gives a clear picture (Fig. 2) of how slowly and incompletely emissions would have to be removed to be consistent with their basic presumption. The bombtest curve shows how far this model picture is from reality, i. e. from the empirically observed relaxation process.

The IPCC states [23] that it takes a few centuries to remove the first 80% of a carbon dioxide emission from the atmosphere, which is a description of the predictions of the Bern model. The bombtest curve establishes that 80% of an emission of carbon dioxide actually is removed within less than 25 years. The IPCC lets a mathematical model falsify the empirical observations made, which is scientifically unsound. The results in Fig. 2 must lead to the converse conclusion that the Bern model is falsified by empirical observations and therefore cannot be used to obtain reliable information on the relaxation of anthropogenic carbon dioxide emissions.

The next paper will examine what inferences can be drawn about the relaxation of carbon dioxide emissions from calculations based on the empirically established kinetic behaviour of the system.

References

1. C. D. Keeling *et al.*, Scripps CO2 program (http://scrippsco2.ucsd.edu).
2. E. T. Sundquist, 1985, American Geophysical Union, *Geophysica Monograph* **32**, 5–59.
3. T. V. Segalstad, 1998, in *Global warming: The continuing debate* (R. Bate, ed.), Cambridge, U.K., pp. 184–219.
4. IPCC, 2007, *Fourth Assessment Report*, Working Group I, Chapters 2 and 10.
5. F. Joos *et al.*, 2001, *Global Biogeochem. Cycles* **15**, 891–908.
6. IPCC, 2007, *Fourth Assessment Report*, Working Group I, Chapter 2, p. 213.
7. R. Nydal & K. Lövseth, 1996, Carbon Dioxide Information Analysis Center
8. I. Svetlik *et al.*, 2007, *Czechoslovak Journal of Physics* **56**, Suppl. D1
9. IPCC, 2007, *Fourth Assessment Report*, Working Group I, Chapter 7, Figure 7.3.
10. IPCC, 1990, *First Assessment Report*, Working Group I, p. 8.
11. IPCC, 1995, *Second Assessment Report*, Working Group I, p. 76.
12. H. Oeschger *et al.*, 1975, *Tellus* **27**, 168–192.
13. U. Siegenthaler & F. Joos, 1992, *Tellus* **44B**, 186-207.
14. A. K. Jain *et al.*, 1997, *Journal of Geophysical Research* **102**, 1327–1333.
15. R. H. Essenhigh, 2009, *Energy & Fuels* **23**, 2773–2784.
16. M. L. Bender & D. F. Hoeg, 1957, *J. Am. Chem. Soc.* **79**, 5649–5654.
17. W. A. Van Hook, 2011, *Nukleonica* **56**, 21–240.
18. M. H. O'Leary, 1981, *Phytochemistry* **20**, 553–567.
19. J. F. Marlier & M. H. O'Leary, 1984, *J. Am. Chem. Soc.* **106**, 5054–5057.
20. IPCC, 1995, *Second Assessment Report*, Working Group I, pp. 85–86.
21. C. Starr, 1993, *Energy* **18**, 1297-1310.
22. IPCC, 1995, *Second Assessment Report*, Working Group I, pp. 65–86.
23. IPCC, 2007, *Fourth Assessment Report*, Working Group I, p. 514.