

Review of manuscript by Weber et al.

Weber et al. present a flawed carbon cycle model and the manuscript cannot be published.

Model assumptions: The authors build a simplistic model to describe the uptake of anthropogenic carbon by the ocean and land. The authors assume that (i) the net carbon flux into the ocean is proportional to the perturbation in the atmospheric CO₂ inventory relative to preindustrial (their eq. 1) with a constant proportionality constant $1/\tau$ and (ii) the flux into the land biosphere is proportional to the growth rate in atmospheric CO₂ (their eq. 2, proportionality constant is termed b).

Essentially, the model describes the removal of an anthropogenic CO₂ perturbation by assuming that a fraction of emissions, $b/(1+b)$, is removed instantaneously and the rest decays according a single e-folding time scale, $\tau_{\text{eff}} = (1+b)\tau$, as shown by their Eq. (5).

No process-based justification is given for these two bold assumptions.

Determination of parameters: The two model parameters, $1/\tau$ and b , are select to match the atmospheric carbon budget given by the Global Carbon Project. The proportionality constants $1/\tau$ for the atm-to-ocean flux is determined by setting the time-integrated model flux into to ocean to the flux determined by the models used in the global carbon project (GCP) for the period from 1959 to 2013. Similarly the proportionality constant b is determined by setting the model's atm-to-land flux equal to the flux given by the Global Carbon Project.

The consequence of this calibration procedure is that the atmospheric CO₂ increase over the calibration period must also be matched when forcing the model with prescribed fossil and land use emissions from the Global Carbon Project. This is shown in Figure 2 and 3. The agreement of the model with the estimates of the Global Carbon Project is thus by design and not a proof of the quality of the model.

The flawed concept of a single perturbation life time:

As noted above, the model describes the removal of a perturbation in the atmospheric CO₂ inventory, $\Delta N_a = N_a - N_0$, by assuming that a fraction of emissions is removed instantaneously and the rest with an e-folding time scale. The authors show this in their equation (5) which is written here:

$$\frac{d}{dt} \Delta N_a = \frac{1}{(1+b)} \text{Emissions} - \frac{1}{(1+b) \cdot \tau} \Delta N_a$$

According their calibration (Table 1), b is equal to 0.668 and τ is equal 81.7yr (or 80.3 or 84 yr). Then, a fraction of 40% of the Emission does not see the atmosphere, while 60% ($1/(1+b) = 0.60$) of the emissions are injected into the model atmosphere. The effective time scale to remove the remaining emissions is then ~136 yr. In other words, atmospheric CO₂ is relaxing back to preindustrial concentrations with an e-folding time scale of 136 years. The authors neglect basic facts, e.g. that the ocean has a finite volume.

This type of model is critically reviewed in the online discussion of Atmospheric Chemistry and Physics for the paper by (Joos et al., 2013). Specifically, the following text is taken from reply to the review of Schwartz et al. by Joos et al., 2013 with reference to a single life time model by Jacobson:

[begin citation] It is no surprise that this single equation works to represent the atmospheric CO₂ increase over the industrial period. This increase is driven by approximately exponentially increasing emissions. It is basic calculus that many systems with a wide range of intrinsic time scales respond to an exponential forcing exponentially and with a single "apparent" time scale.

The agreement of this model with the 20th century atmospheric CO₂ record is not a sufficient justification for the single time scale model. To illustrate this we construct a model that is as simple as possible and constrained by atmospheric CO₂ and get a "constant airborne fraction model":

$$\Delta\text{CO}_{2,\text{atm}}(t) = c \cdot I_{\text{Emission}}(t)$$

Where $\Delta\text{CO}_{2,\text{atm}}$ is the perturbation in the atmospheric CO₂ inventory, c is a constant (the airborne fraction of the recent decades, about 0.5) and I_{Emission} the time-integrated anthropogenic carbon emissions. Both the constant airborne fraction model and the single time scale model are able to approximately match the observed CO₂ record for the carbon emission history from fossil and land use sources. However, both models are purely diagnostic, applicable to approximately exponential forcing only, and do not represent the functioning of the global carbon cycle.

The single life time model is in conflict with observations.

- a) It is known that CO₂ is chemically stable under current environmental conditions and not oxidized as other chemical species (e.g. CH₄). Thus, CO₂ does not undergo a first order decay.

Anthropogenic carbon is redistributed among the major carbon reservoirs in the Earth System. These are the ocean with an inventory of 38000 GtC, the atmosphere (280 ppm = 590 GtC; 390 ppm = 828 GtC), vegetation on land (~600 GtC) and soils (~3000 GtC). The marine biosphere (3 GtC) is too small and exchange with ocean sediments and the geosphere occur on multi-millennial time scales.

- b) CO₂ is exchanged between the atmosphere and the mixed-layer of the ocean where it reacts with water to form carbonate and bicarbonate ions. The air-sea exchange rate is approximately known from experiments and observations (e.g., Wanninkhof, JGR, 1992) and the typical time scale to equilibrate the surface layer with an atmospheric perturbation is about 1 year. The carbonate chemistry in the ocean is well known (Zeebe and Wolf-Gladrow, 2001) and observational data firmly establish the relationship between pCO₂ (or fCO₂, the fugacity), dissolved CO₂, bicarbonate and carbonate ions. (Revelle and Suess, 1957) showed that the Revelle factor (or buffer factor) which is defined by the relative change in pCO₂ divided by the relative change in dissolved inorganic carbon ($\Delta\text{pCO}_2/\text{pCO}_{2,0}/(\Delta\text{DIC}/\text{DIC}_0)$) is about 10. This means that the relative change in dissolved inorganic carbon is ten times smaller than the relative change in pCO₂ in a water parcel. Accordingly, the relative perturbation in the oceanic concentration is ten times smaller than the perturbation in pCO₂. (We note that the Revelle factor increases with increasing CO₂).

Any observation-informed model considers these text-book relationships (Dickson et al., 2007; Stumm and Morgan, 1996) between pCO₂, dissolved CO₂, bicarbonate and carbonate ions and the equilibration between atmospheric CO₂ and the dissolved species in the ocean.

The assumption of the single life-time model of Jacobson that the atmospheric concentration will

simply relax back to the preindustrial concentration with a multi-decadal time scale is not justified and not in accordance with basic chemistry data and the limited volume of the ocean.

Can transport processes within the ocean be approximated with a single time scale? There is the GLODAP data base on CDIAC which includes CFCs and radiocarbon data sampled over the past decades (Key et al., 2004). These data show that mixing time scales for the upper thermocline are decadal and mixing time scales for the deep ocean are multi-centennial. The lowest radiocarbon ratios of dissolved inorganic carbon are found in the deep Pacific with values that are about 240 permil or so lower than the atmosphere or about 200 permil lower compared to the surface ocean. This corresponds to a water age of roughly 1800 years.

The assumption of the Jacobson model that the CO₂ sink follows a single time scale is in conflict with oceanic tracer data (e.g., CFCs and radiocarbon).

The implicit assumption of the Jacobson model that the deep ocean is ventilated with a time scale of order 50 years is in conflict with radiocarbon observations.

- c) Carbon uptake by the land occurs through photosynthesis and the related conversion of CO₂ to organic carbon. Carbon release occurs through oxidation (autotrophic, heterotrophic, fire) of organic material back to CO₂. Carbon sink processes in the land biosphere include forest regrowth and woody encroachment, fertilization of plant growth by increased availability of fixed nitrogen and higher CO₂ concentrations. Manipulative experiments indicate the potential magnitude of C and N fertilization (e.g., (Norby et al., 2010)). Similarly as for the ocean, radiocarbon data indicate that there are multiple time scales for soil overturning that are in the range from years to centuries (e.g., (Gaudinski et al., 2000)).

In summary, the single life time model is in conflict with radiocarbon data (and other tracer data) and with first order principles of chemistry. [end of citation]

It may be noted that the 15 different carbon cycle-climate models used in (Joos et al., 2013) span the full model hierarchy from reduced form models to state-of-the-art Earth System Models. Two models, GENIE and Bern3D-LPJ ensembles were explicitly constrained by observations.

In brief, the model by Weber et al. is in conflict with observations.

Wrong implementation of the Impulse Response experiment:

As outlined above and evident from eq. 5 in the MS by Weber et. al. 40% of the emissions are removed instantaneously in their model. Figure 5 is flawed and does not show the impulse response of the model by Weber to an emission pulse of 100 GtC. The impulse response should show an immediate decrease from 100% to 60% in year of the pulse input (2010).

(As an aside, Weber et al., do not follow the experimental protocol used to derive the Response for the 15 models in Joos et al., and shown by the grey range in Fig. 5).

No independent observational data used to evaluate the model:

In the introduction, the authors talk about carbon isotopes and the radiocarbon perturbation by bomb test. However, the authors do not hindcast any observations, e.g. the penetration of the bomb-

radiocarbon signal into the ocean, with their model. Anyway, the model is too simple and would not produce any meaningful results.

Further comments/ a few other wrong statements in the manuscript

p. 2045, line 8-10: “However, no systematic comparison of the extensive CDIAC data with any CO₂ global circulation model has been published till now.”

This is not true. See for example (Friedlingstein et al., 2006; Joos et al., 2001; Eby et al., 2013)

P2045, line 14: Change “15 best known complex carbon circulation models” to “15 known carbon cycle models”

It is not clear whether these are the 15 best known models. The term “carbon circulation” model is not wrong, but not common in the literature.

P2045, line 22: “¹⁴C concentration measurements” change to “measurements of the ¹⁴C/¹²C ratio” to be correct

p 2045 line 26: another wrong statement: “the rapid decrease of ¹⁴CO₂, of an initial thousandfold concentration compared to the natural level“

The fractionation corrected ¹⁴C/¹²C ratio approximately doubled in tropospheric air between 1950 and 1963. After 1963, when the bomb-test ban treaty were set in place the ratio decreased again in the troposphere. The authors should check the details of isotopic notation. Delta ¹⁴C increased from -20 permil in the early 1950ies to close to 1000 permil in the Northern Hemisphere 1963. See e.g. (Levin et al., 2010)

P 2046, line 6: another wrong statement: “¹⁴CO₂ flux from atmosphere into the ocean without a counterpart of the opposite way. In contrast to this, the ¹²CO₂ fluxes are always in two directions”

Also ¹⁴CO₂ molecules are transported from the ocean to the atmosphere and vice versa.

P2049: coal reserves: the important quantity are not the “reserves”, but the fossil fuel “resources”. Fossil resources are higher and estimated to be order 5000 GtC for conventional fossil resources (coal, gas, oil) and likely higher when considering unconventional resources such as methane clathrates and tar sands.

P2054, line 21ff: “The difference in the long run may stem from the Revelle effect, included in the elaborate models, a resistance to absorbing atmospheric CO₂ by the ocean due to bicarbonate chemistry. However, as Gloor (2010) underlines, there exists so far no evidence for the Revelle effect. Thus, such effects are presently hypothetical.”

Carbonate chemistry in water is by no means hypothetical, but understood since more than 100 years. It is fundamental acid-base chemistry. CO₂ reacts with water to form H₂CO₃. H₂CO₃ may dissociate to H⁺ and HCO₃⁻ ions (or the reverse) until equilibrium. HCO₃⁻ may further dissociate to H⁺ and CO₃⁻. The citation of Gloor et al., 2010 is inappropriate. Gloor is referring to the fact that carbonate chemistry is non-linear, but that the non-linearity in the carbonate chemistry is not yet large enough to be detectable in the trend of the airborne fraction. This is related to uncertainties in current estimates of emissions as well as to the noise in the airborne fraction due to natural climate variability.

References

Dickson, A. G., Sabine, C. L., and Christian, J. R.: Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water, 2007.

Eby, M., Weaver, A. J., Alexander, A., Zickfeld, K., Abe-Ouchi, A., Cimadoribus, A. A., Crespin, E., Drijfhout, S. S., Edwards, N. R., Eliseev, A. V., Feulner, G., Fichefet, T., Forest, C. E., Goose, H., Holden, P. B., Joos, F., Kawamiya, M., Kicklighter, D., Kienert, H., Matsumoto, K., Mokhov, I. I., Monier, E., Olsen, S. M., Pedersen, J. O. P., Perrette, M., Philippon-Berthier, G., Ridgwell, A., Schlosser, A., Schneider von Deimling, T., Shaffer, G., Smith, R., Spahni, R., Sokolov, A. P., Steinacher, M., Tachiiri, K., Tokos, K., Yoshimori, M., Zeng, N., and Zhao, F.: Historical and idealized climate model experiments: an intercomparison of Earth system models of intermediate complexity, *Climate of the Past*, 9, 1111–1140, doi:10.5194/cp-9-1111-2013, 2013.

Friedlingstein, P., Cox, P., Betts, R., Bopp, L., von Bloh, W., Brovkin, V., Doney, S., Eby, M., Fung, I., Govindasamy, B., John, J., Jones, C., Joos, F., Kato, T., Kawamiya, M., Knorr, W., Lindsay, K., Matthews, H. D., Raddatz, T., Rayner, R., Reick, C., Roeckner, E., Schnitzler, K.-G., Schnur, R., Strassmann, K., Thompson, S., Weaver, A. J., Yoshikawa, C., and Zeng, N.: Climate-carbon cycle feedback analysis, results from the C4MIP model intercomparison., *Journal of Climate*, 19, 3337-3353, 2006.

Gaudinski, J. B., Trumbore, S. E., Davidson, E. A., and Shuhui, Z.: Soil carbon cycling in a temperate forest: radiocarbon-based estimates of residence times, sequestration rates and partitioning of fluxes, *Biogeochemistry*, 51, 33-69, 2000.

Joos, F., Prentice, I. C., Sitch, S., Meyer, R., Hooss, G., Plattner, G. K., Gerber, S., and Hasselmann, K.: Global warming feedbacks on terrestrial carbon uptake under the Intergovernmental Panel on Climate Change (IPCC) emission scenarios, *Global Biogeochemical Cycles*, 15, 891-908, 2001.

Joos, F., Roth, R., Fuglestad, J. S., Peters, G. P., Enting, I. G., von Bloh, W., Brovkin, V., Burke, E. J., Eby, M., Edwards, N. R., Friedrich, T., Frölicher, T. L., Halloran, P. R., Holden, P. B., Jones, C., Kleinen, T., Mackenzie, F. T., Matsumoto, K., Meinshausen, M., Plattner, G.-K., Reisinger, A., Segsneider, J., Shaffer, G., Steinacher, M., Strassmann, K., Tanaka, K., Timmermann, A., and Weaver, A. J.: Carbon dioxide and climate impulse response functions for the computation of greenhouse gas metrics: a multi-model analysis, *Atmos. Chem. Phys.*, 13, 2793-2825, 10.5194/acp-13-2793-2013, 2013.

Key, R. M., Kozyr, A., Sabine, C. L., Lee, K., Wanninkhof, R., Bullister, J. L., Feely, R. A., Millero, F. J., Mordy, C., and Peng, T. H.: A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP), *Global Biogeochem. Cycles*, 18, GB4031, 10.1029/2004GB002247, 2004.

Levin, I., Naegler, T., Kromer, B., Diehl, M., Francey, R. J., Gomez-Pelaez, A. J., Steele, L. P., Wagenbach, D., Weller, R., and Worthy, D. E.: Observations and modelling of the global distribution and long-term trend of atmospheric $^{14}\text{CO}_2$, *Tellus B*, 62, 26-46, 10.1111/j.1600-0889.2009.00446.x, 2010.

Norby, R. J., Warren, J. M., Iversen, C. M., Medlyn, B. E., and McMurtrie, R. E.: CO_2 enhancement of forest productivity constrained by limited nitrogen availability, *Proceedings of the National Academy of Sciences*, 107, 19368-19373, 2010.

Revelle, R., and Suess, H. E.: Carbon dioxide exchange between atmosphere and ocean and the question of an increase of atmospheric CO_2 during the past decades, *Tellus*, 9, 18-27, 1957.

Stumm, W., and Morgan, J. J.: *Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters*, 3rd ed. John Wiley & Sons, Inc., New York, 1022 pp., 1996.

Zeebe, R. E., and Wolf-Gladrow, D.: *CO_2 in seawater: equilibrium, kinetics, isotopes*, Elsevier Oceanography Series, 2001.