Biogeosciences Discuss., 3, S330–S338, 2006
www.biogeosciences-discuss.net/3/S330/2006/

Biogeosciences
Discussions

Interactive comment on "On the application and interpretation of Keeling plots in paleo climate research – deciphering δ^{13}C of atmospheric CO_2 measured in ice cores" *by* P. Köhler et al.

G. Munhoven (Referee)

Guy.Munhoven@ulg.ac.be

Received and published: 27 July 2006

General comments

Keeling plots have been used for almost 50 years now, mostly in terrestrial ecosystem studies, to identify perturbation fluxes from combined atmospheric pCO_2-δ^{13}C data. The approach is simple and elegant, and as such, based on rather restrictive underlying assumptions (data must relate to a single reservoir, only submitted to the perturbation flux; constant isotopic signature of the perturbation flux). It is, e.g., commonly accepted that it is only applicable for fast processes. However, there are, to our knowledge, no well established quantitative arguments about *how fast* processes have to be for the approach to yield reliable results (except for recent arguments put forward by Pataki et al. (Global Biogeochem. Cycles 17, 1022, DOI: 10.1029/2001GB001850, 2003) regarding the minimum pCO_2 range that has to be covered).

Köhler et al. propose in this paper to explore the limitations of the Keeling-plot analysis tool and to extend it in order to improve its usefulness for the interpretation of ice-core data. To do so, they first enlarge the framework by including an additional carbon reservoir: the oceans. The new tool is shortly discussed. Its potential is then explored with a number of synthetic time series for atmospheric pCO_2 and δ^{13}C generated with BICYCLE, a model of the ocean-atmosphere-terrestrial biosphere subsystem of the global carbon cycle.

The proposed extension is just as elegant as the original device. It is promising and, despite the simplicity of the basic idea it rests upon, it is, to my best knowledge, original. The extension introduces of course additional hypotheses which may appear rather strong at first (e.g., the hypothesis of equilibrium between the ocean and atmosphere, and the equilibration is not necessarily a fast process). The extended tool is nevertheless formidable from the point of view of the increased predictive power it offers at little extra complexity.

The large number of simulations, and the provided details make this paper extremely long and difficult to read to the end. Readers are drowned by details of the simulation experiments. Whereas the experimental exploration is exhaustive, the theoretical developments would benefit from some additional developments. There is probably pertinent information that can be extracted from the intercept. In the discussion of their results, the authors merely notice that the observed intercept explains a certain fraction of the actual isotopic signature of the perturbation source. The validity of this interpretation is, by the way, questionable. A thorough theoretical exploration of the properties of the intercept will certainly be useful for the purpose of estimating the signature of the perturbation flux.

BGD

3, S330–S338, 2006

I encourage the authors to reconsider their paper, to improve and extend the theoretical part (for suggestions, see below) and to restrict the experimental part to the most important cases only (three of them might be optimal). The other results need not to be dropped. They can be shortly commented in a paragraph or two.

The subject of this paper is important, and the extension to the Keeling plot that Peter Köhler and co-authors propose is ingenious and worth publishing. They should now make it perfect by exploring all of the possibilities that it may offer.

Specific comments

Page 515, lines 20ff: ϵ is not a fractionation *factor*. It is commonly called the *fractionation*, and is related to the *fractionation factor*, α, by $\epsilon = (\alpha - 1) \times 10^3$.

Page 520, lines 20–24: One of the characteristics (or shortcomings) of the original two-reservoir Keeling approach was that it could basically only be applied for the study of fast exchange processes.

The extension proposed here introduces the ocean as a third reservoir, under the assumption that ocean and atmosphere are in equilibrium. The equilibration of the atmosphere with the *whole* ocean will usually take a long time, especially when perturbations such as those related to transfer of carbon between the terrestrial biosphere and the ocean during the deglaciation are considered. Is this not contradictive? Or will the inclusion of this reservoir possibly ease the constraint that Keeling plots should only be used for fast processes?

Furthermore, is it possible to estimate the impact of considering the ocean as one single homogeneous oceanic reservoir?

Page 522, line 8 (Eq. (12)): It might be helpful for your readers to indicate that Eq. (12) is actually equivalent to Eq. (4). It will furthermore be helpful to rewrite it in a second

BGD

3, S330–S338, 2006

Interactive Comment

instance in the same way as Eq. (5), showing that once again, $\delta^{\Delta A}$ represents the y-axis intercept of a linear regression line on a $1/A$-δ^A diagram (if that regression bears any significance).

Page 523, lines 6–14: It is not obvious *a priori* that the denominator in Eq. (12) becomes 0 for $B = 0$. It might be helpful to mention that $O_0 + B - O = B \times (\beta A_0)/(\beta A_0 + O_0)$ (from Eqs. (6) and (9)), which makes the conclusion straightforward.

The conclusion that $\delta^{\Delta A}$ is not defined for $B = 0$ (line 16) is *incorrect*. The authors show that there is a well-defined limiting value for $\delta^{\Delta A}$ when $B \rightarrow 0$. The numerator in Eq. (12) must then also converge to 0 when $B \rightarrow 0$. It is easy to verify that it does indeed. Since the limiting value is non-zero, we may furthermore expect that the numerator is of the order of B in the vicinity of $B = 0$ (i.e., that the denominator can be written as the product of B with a (possibly complicated) function that has a finite non-zero limiting value as $B \rightarrow 0$). It can actually be proven that the numerator is of the order of B everywhere. Hence, the $0/0$ indeterminacy for $B = 0$ in Eq. (12) is only an artefact of the chosen formulation and can be completely lifted. The required developments are cumbersome but nevertheless worth the effort, as they lead to an interesting relationship between $\delta^{\Delta A}$ and the isotopic signature δ^B of the source (or sink) B. This relationship may provide the possibility for a more thorough interpretation of $\delta^{\Delta A}$ in terms of δ^B!

Possible stages to derive that relationship are as follows:

1. Write $\delta^{\Delta A}$ from Eq. (11) as $\delta^{\Delta A} = \delta_0^A + A \times (\delta^A - \delta_0^A)/(A - A_0)$.

2. Use Eqs. (6) and (9) to express $(A - A_0)$ and $(O - O_0)$ as a function of B, β, and A_0/O_0 (these will be linear expressions in B!).

3. In Eq. (7), substitute $\delta^O = \delta^A - \epsilon_{AO}$ and $\delta_0^O = \delta_0^A - \epsilon_{AO}$, then collect the terms in δ^A, ϵ_{AO} and δ_0^A respectively. Use Eq. (6) to substitute $(A - O)$ and the relationship from 2. to substitute $(O - O_0)$. Finally, express $(\delta^A - \delta_0^A)$ as a function of δ_0^A, B, A_0, O_0, β, ϵ_{AO}

BGD

3, S330–S338, 2006

EGU

and δ^B.

4. Use the relationships from 2. and 3. above to transform the ratio $(\delta^A - \delta_0^A)/(A - A_0)$ (and also to get rid of the A that multiplies it) at the righthand side of the expression for $\delta^{\Delta A}$ in 1. The B-factors in the numerator and denominator cancel and the indeterminacy that was inherent to the formulation of $\delta^{\Delta A}$ in Eq. (12) disappears.

The expression obtained can now be used to derive conclusions about how δ^B (the information of interest) relates to $\delta^{\Delta A}$ (the information available). In a first time, it will also help to demonstrate that $\delta^{\Delta A} = \delta^B$ when $\beta = 1$ and $\epsilon_{AO} = 0$.

If we are only interested in the limiting value of $\delta^{\Delta A}$ as $B \to 0$, it may be sufficient to notice that, since $A - A_0 = B/(\beta A_0/O_0 + 1)$ (from 2. above), $A - A_0 \to 0$ as $B \to 0$. $\delta^{\Delta A}_{\delta C \to 0}$ is thus equal to the value of the derivative $d(A\delta^A)/dA$ in $A = A_0$.

The assumption of a constant ϵ_{AO} is critical for the developments carried out above. In case ϵ_{AO} is variable, $\delta^{\Delta A}$ only has a limiting value as $B \to 0$ if $d\epsilon_{AO}/dB$ exists for $B = 0$.

Finally, it would be interesting to learn what the meaning of the limiting value $\delta^{\Delta A}_{\delta C \to 0}$ is. Actually, on pages 531–532, it is discussed that the y-axis intercept for the model with complete re-equilibration after the release of 10 PgC in one year is close to the limiting value $\delta^{\Delta A}_{\delta C \to 0}$, which is somewhat counterintuitive for me.

Page 526, lines 4–15: Is there any reason to put special focus on Point Barrow data?

Page 528: Lines 1–2: I have reservations about the conclusion that "[. . .] only a fraction of $9/25 = 0.36$ is explainable by the Keeling plot approach." The Keeling-plot approach (i.e., determination of the y-axis intercept of the linear regression in a $1/A$-δ^A diagram) only provides $\delta^{\Delta A}$, from which δ^B may possibly be deduced (or at least some bracketed estimate of it). The calculated $\delta^{\Delta A}$ is in the current case equal to $0.36\delta^B$, but does this really mean that only that fraction is *explained* by the Keeling plot approach? Actually,

BGD

3, S330–S338, 2006

it would be interesting to check whether $\delta^{\Delta A}$ might not even exceed δ^{B} under certain conditions. In this case, it would be difficult to argue that the Keeling plot approach explains more than 100% of the signal.

Page 532, lines 1ff: What are the possible reasons for the intercepts for the re-equilibration model to fall close to $\delta^{\Delta A}_{\delta C \to 0}$? I would rather expect that an intercept close to $\delta^{\Delta A}_{\delta C \to 0}$ would require "regression lines" to be successively drawn through the initial point of release and one other point that gets closer and closer to this initial point (such that $B \to 0$).

Page 534, lines 1–5: Is the Keeling plot approach not invalid if ϵ_{TB} is (strongly) changing?

Page 536, lines 8–16: As mentioned above, the existence of $\delta^{\Delta A}_{\delta C \to 0}$ of the system with variable ϵ_{AO} requires the derivative of ϵ_{AO} with respect to B to exist for $B = 0$. The developments outlined above for the derivation of the alternative formulation of $\delta^{\Delta A}$ need to be modified for a variable ϵ_{AO}.

Page 538, lines 1–5: Please check if this could not be an artefact of the procedure. The short time window is perhaps not the true problem. Pataki et al. (2003) indicate that a pCO_2 range of about 75 ppm must be covered to yield reliable results.

Table 1, caption: The interpretation of the ratio $y_0/\delta^{13}C_{ant}$ as the "fraction explained" by the Keeling plot approach may be unjustified (see above, *ad* Page 528).

Technical corrections

Throughout: Except in the caption of Fig. 4., "boundary" should be replaced by "limiting value." (16 instances)

BGD

3, S330–S338, 2006

Interactive Comment

EGU

Througout: Please consider replacing the notation $\delta^{\Delta A}_{\delta C \to 0}$ by $\delta^{\Delta A}_{B \to 0}$, as the δC in index position might lead to confusion: it could be interpreted as a flux times an isotopic signature.

Page 514, line 17: "extension"

Page 515, line 23: "C_3 plants *exhibit* [. . .]"

Page 516, lines 10–12: Please rephrase. I do not see how the "application and interpretation of Keeling plots" can be "used."

Page 516, lines 13–15: Here we are getting to the core of the subject of the paper. It would be important to state here rightaway what limitations there are, why "[. . .] it seems that they [. . .] have not been adequately taken into account [. . .]" and to what extent previous applications might not have been "meaningful".

Page 516, line 23: I recommend to rename section 2 "The original Keeling plot."

Page 517, lines 9–10: $\delta^{13}C_{add}$ is not an isotopic ratio!

Page 517, line 12: I rather see the *content* of the reservoir added, not the reservoir.

Page 517, line 18: "[. . .] to *interpret* [. . .]"

Page 518, lines 17–19: This sentence is very long, and not clear.

Page 519, line 7: "[. . .] *is up to* the expectations [. . .]"

Page 519, line 8: Activity may be human in this context, but not anthropogenic.

Page 519, line 17: Should "the residual" not rather read "the result" ?

Page 520, line 8: Replace "accompanied" with "concomitant"

Page 521, lines 3–11: This paragraph is difficult to read. Please rephrase.

Page 521, lines 18–19: "[. . .] distributed *between* the two reservoirs [. . .]"

BGD

3, S330–S338, 2006

Interactive Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

EGU

Page 522, line 15: “[. . .] $\delta^{\Delta A}$ varies nearly *linearily* with B [. . .]”

Page 522, line 25: “[. . .] $\delta^{\Delta A}$ records correctly [. . .]” does not make much sense here. Replace by “[. . .] $\delta^{\Delta A}$ is equal to [. . .]”.

Page 525, lines 2–6: This can be discarded without any loss.

Page 528, line 1: “[. . .] this *situation* [. . .]”

Page 528, line 9: “[. . .] times and *depths*.”

Page 528, line 22: Replace “un-regular data gaps” with “irregular gaps”

Page 528, line 23: Replace “be therefore” with “therefore be”

Page 528, lines 24–25: “[. . .] will be *sufficient to* resolve [. . .]”

Page 528, line 26: “Human activities”, not “Anthropogenic activities”

Page 529, lines 12–13: Correct to“maximum possible impacts”

Page 530, line 15: Modify to “This *is* the scenario that [. . .]”

Page 534, line 8: “[. . .] values *derived* from

Page 535, line 3: “extended” should read “enhanced”

Page 536, line 15: The meaning of this sentence is not clear. Perhaps “derivation” should read “divergence”? Or do you want to say that the limiting value will not be the same for different perturbations?

Page 537, line 1: Replace “happens” with “take place”

Page 537, line 25: Replace “finds” with “yields”

Page 543, lines 11–12: Modify to “[. . .] which depends on DIC itself and on the pH-dependent speciation of DIC (Ridgwell, 2001).”

Page 545, line 15: “[. . .] and *that* they can explain [. . .]”

BGD

3, S330–S338, 2006

Interactive Comment

Page 545, lines 26–27: Please rephrase. This is not a good sentence.

Page 545, line 25: Replace “converts” with “converges”

Page 546, line 17: Replace “they vary” with “they differ” (or do you possibly mean “they diverge” ?)

Page 546, lines 22–23: Modify “[. . .] in which a Keeling plot analysis leads to [. . .]” to “[. . .] for which the classical Keeling plot analysis yields [. . .]”

Page 546, lines 26ff: Please discard the comment related to the results from Eyer (2004). These results are neither published nor openly accessible.

Table 1, caption line 4: “reported” would be more appropriate here than “displayed”.

Figure 8. Ticks are barely visible, and there appear to be ‘ghost’ ticks on the horizontal axis at the top.

Figure 11: This figure is overloaded. Either reduce the amount information presented, or separate in several parts.

Figure 16: Same comment as Fig. 11.

Interactive comment on Biogeosciences Discuss., 3, 513, 2006.

BGD

3, S330–S338, 2006