

Foreword

Both reviewers have not fully perceived the message of my work. Therefore, first I give a short overview of the basics of my paper. I wanted to provide a better understanding of the basic operation of the physical pump. This pump works in two steps. First, the carbonate buffer system of the upmost mixed layer reacts with the CO₂ of the atmosphere to attain chemical equilibrium. The question is: what is the increase of DIC in the mixed layer when the partial pressure of CO₂ in ppm increases by ΔCO_2 . To this end I have calculated DIC (mmol/kg) as a function of CO₂ (ppm) using the program PHREEQC. Differentiating with respect to CO₂ gives $d\text{DIC}/d\text{CO}_2$ (mmol/kg ppm) termed as sensitivity S as a function of CO₂. S is the increase of DIC by increase of CO₂. It tells how much CO₂ is absorbed by the buffer system. S decreases with increasing CO₂. Usually, this buffering is described by the Revelle factor R . Therefore, I had to give the relation between S and R . Although, this is a side result it requires some text. Both reviewers have focussed to this part of the paper. The essential second part of the pump is transport of water of the mixed layer with high DIC by thermo-haline circulation into deep ocean and replacement by water in equilibrium with preindustrial CO₂ level. This part of the pump increases steadily with increasing CO₂. I admit that this is a simple model that needs only the well-known constants of equilibrium chemistry provided by PHREEQC, the depth of the mixed layer, h and the amount of waterflow into deep ocean in S_v . The result gives at least the correct order of magnitude of the observed CO₂ uptake from the atmosphere into the ocean by the physical pump. In summary, my model reveals the basics that may be hidden in many complex models that are not intelligible by non-specialists. This opens understanding to a larger part of the scientific community and to my knowledge has not been published before.

Reply to RC3:

In the following the arguments of the reviewer are in *italic*, my response is in normal, and parts copied from my paper are underlined.

Reviewer 3 declines publication as follows:

*Prof Wolfgang Dreybrodt's presents a couple of different thoughts and back-of-the-envelope calculations on the ocean carbon sink. The main point of the manuscript is about simply rearranging the equation of the Revelle factor: $R = (\Delta\text{DIC}/\text{DIC})/(\Delta p\text{CO}_2/p\text{CO}_2) \Leftrightarrow \Delta\text{DIC}/\Delta p\text{CO}_2 = R * \text{DIC}/p\text{CO}_2 = S$. As such, I do not believe that the scientific novelty or significance of this manuscript is worthy for publication.*

The definition of $R = (\Delta\text{DIC}/\text{DIC})/(\Delta p\text{CO}_2/p\text{CO}_2)$ is wrong. It must read $(\Delta\text{DIC}/\text{DIC})/(\Delta p\text{CO}_2/p\text{CO}_2) = 1/R$ and correspondingly $\Delta\text{DIC}/\Delta p\text{CO}_2 = S = (\text{DIC}/p\text{CO}_2)/R$.

$\Delta\text{DIC} / \Delta\text{CO}_2 = S$ is only used in the paper to give a better understanding to the non-specialised community, how acidification weakens the buffer system because R is not easy to interpret. It is by no means the result of the paper.

The reviewer has not perceived the main message of my paper as explained above and to decline publication is unfounded.

My remarks to some of the reviewer's concerns to the ms.

"In addition to the scientific novelty and significance, I have several major concerns regarding the manuscript."

"While it is recognised that the sink decreases with increasing Revelle factor (Revelle and Suess, 1957), even the high-emission scenario RCP8.5 is not estimated to lead to a collapse of the solubility pump (Rodgers et al., 2020)."

This is exactly the result of my paper. See Fig. 11. The equilibrium pump becomes weak. The transport pump, however, increases. See lines 249-258 in the ms.

The total solubility sink consists of two mechanisms: The equilibrium pump as described and the transport pump that is caused by the global meridional overturning circulation of 36 Sv. This transfers into deep-ocean the difference (DIC ppm - DIC 280) = ΔDIC ocean that has been accumulated in the mixed layer from onset of industrialisation to the actual CO₂ level. This sink increases continuously replacing the failure of the equilibrium pump. At 400 ppm the total sink is 1.9, at 600 ppm it is 3.8 and at 800 ppm it amounts to 5 Gtons/year depending solely on the CO₂ level in the atmosphere for ppm > 600. To conclude, the total solubility pump is not endangered by ocean acidification. In contrast, it increases with increasing CO₂ level of the atmosphere to yield significant contribution to remove anthropogenic CO₂ from the atmosphere into deep-ocean provided the thermo-haline circulation remains constant and is not weakened by climatic change.

Furthermore, the paper of Revelle, R., & Suess, H. E. (1957). Carbon dioxide exchange between atmosphere and ocean and the question of an increase of atmospheric CO₂ during the past decades. *Tellus*, 9, 1– 10 does not contain a definition of the Revelle factor although cited many times by copy and paste.

The Revelle factor has been defined by W. S. Broecker, T. Takahashi, H. J. Simpson, T.-H. Peng. Fate of Fossil Fuel Carbon Dioxide and the Global Carbon Budget. *Science*, 1979, Volume 206, Number 4417

"The steps in pCO₂ and T are far too large to calculate meaningful derivatives. It remains unclear to me why the author does not just use incremental steps or even better, directly the above-shown equation. This leads to several major errors throughout the

manuscript: In Fig. 2, for example, the sensitivity for 'path' and '15°C' at 300 ppm is different although it should be identical as T is still at 15°C for path."

I have fitted the DIC data to a fifth order polynomial with high precision. From this the derivative with respect to CO₂ is calculated to high precision. This does not lead to "several major errors throughout the manuscript." The reviewer should explain the major errors in some detail.

Sensitivity is given by the slope of DIC(CO₂), see Fig. 1 and Fig. 2 and therefore S is different for the path and 15°C at 300 ppm.

In contrast, serious errors arise by following the reasoning of the reviewer.

"In Fig. 3, the Revelle factor should be identical for 'path' and '15°C'. Why is there such a large difference?"

The Revelle factor is related to S by $R = \text{DIC}/(\text{CO}_2 \cdot S) = 2.27/(\text{CO}_2 \cdot S)$ See lines 160-163 in the ms. As path and 15°C have different S, R must be different as well.

Lines 155-163 explain in detail the relation between R and S. This is copied from the ms in the lines that follow (underlined):

Finally, to relate sensitivity S to Revelle factor R, Fig. 9 illustrates R as a function of S. It is obvious why using S should be preferred. If S changes from $1.5 \cdot 10^{-4}$ to $4.5 \cdot 10^{-4}$ by 200 % the corresponding change in R is only about 40 % for 25°C and 20% for 5°C.

Therefore, S gives a more realistic view. Fig. 10 shows R and S as function of pH at 15°C. R changes from 12 to 20 with pH decreasing from 8.3 to 7.85. But, in contrast to the sensitivity from its value no direct meaning can be derived. From its definition a simple relation is: $R = 2.27/(\text{CO}_2 \cdot S)$ because $\text{DIC} \approx 2.27 \text{ mmol/L}$ remains constant within a few percent (see Fig. 1 and Fig. 5). From this one may understand why R is used only qualitatively to judge ocean's physical pump buffer capacity.

Units are not used in a careful manner. As an example: It is often not clear if it is Gt C or Gt CO₂.

As can be seen from lines 168 – 171 in the ms :"Consequently, the amount M t absorbed by a mixed layer with depth t(m) and a change of n ppm CO₂ is $M t = M 1 \cdot t \cdot s \cdot n \text{ mol CO}_2$ when sensitivity $S = s \cdot S 1$. **Converting to g CO₂ one has to multiply by the molecular weight 44 g/mol of CO₂ to obtain $M t = M 1 \cdot t \cdot s \cdot n \text{ mol} \cdot 44 \text{g/mol} = M 1 \cdot t \cdot s \cdot n \cdot 44 \text{ (g)}$.**"

Therefore, where not stated otherwise the units are GtCO₂ throughout the ms.

There are many publications on the importance of the biological and solubility pump but there is no doubt that the solubility pump is the major contribution to the anthropogenic carbon sink (Friedlingstein et al., 2022). This example demonstrates why these 'back-of-

the-envelope' equations cannot be used when treating such a complex system as the global ocean.

It would have been helpful if the reviewer had given a copy of this statement in a paper with 90 pages, that the *“solubility pump is the major contribution to the anthropogenic carbon sink (Friedlingstein et al., 2022).”* I could not find it. (Friedlingstein et al., 2022) deal with the ocean sink and do not give the single contributions of the solubility and the biological sink but only the ocean sink that is the sum of both.

Some assumptions are unreasonable. The author speaks about a time when pH decreases below 4. Even under the high-emission scenarios, such a low pH is not possible on average at the ocean surface.

I do not speak *“about a time when pH decreases below 4.”* Of course, pH = 4 is not reached in any scenario. The intent of this passage was to show the lower limit of the equilibrium sink. The reviewer evidently did not understand the meaning of this part of my paper, lines 184-189:

It must be stressed that the flux calculated so far by equilibrium chemistry represents the capacity to absorb CO₂ from the atmosphere by a stagnant isolated mixed layer that does not sink into depth. Therefore, this sink is caused by equilibrium chemistry and could be termed as equilibrium sink (pump). This pump declines with increasing acidification of the ocean. At pH < 4 the only existing carbonate species are aqueous CO₂ and H₂CO₃. Therefore, the absorption of CO₂ is governed by Henry's law. Therefore, dDIC/dCO₂ = K_H and stays constant with further decreasing pH.

In conclusion the reviewer states:

“Overall, I believe that this manuscript presents no new findings or results and the simplification of complex mechanisms, which are already presented in detail by Sarmiento and Gruber (2006), by simple equations with strong assumptions, leads to erroneous conclusions. Relatively simple 3-D biogeochemical models in the 1990s were already able to estimate the different parts of the ocean carbon sink in a much better and accurate way (Joos et al., 1999).”

The reviewer does not tell what are the erroneous conclusions and how did they arise. My model uses equilibrium chemistry of the seawater carbonate system and the amount of water transported to deep ocean. It is possible to use it to predict the evolution of the physical pump upon impact of weakening of the thermo-haline circulation. The reviewer misses to show where his statement *“Relatively simple 3-D biogeochemical models in the 1990s were already able to estimate the different parts of the ocean carbon sink in a much better and accurate way (Joos et al., 1999)”* is given in this cited paper. Its abstract states: “A low-order physical-biogeochemical climate model

was used to project atmospheric carbon dioxide and global warming for scenarios developed by the 3 Intergovernmental Panel on Climate Change.” There is no discussion about *the different parts of the ocean carbon sink* in that paper.

In conclusion the review is highly biased to decline the paper and most of the objections are unfounded or even wrong. It does not give any hints how to improve the paper. Therefore, I cannot suggest any changes to the paper at present. I leave it to the editor how to proceed.