Review of *Probing the exchange of CO2 and O2 in the shallow critical zone during weathering of marl and black shale* submitted to Earth Surface Dynamics

I found this paper to be a very interesting, detailed, and innovative exploration of how to quantify CO_2 production from oxidative weathering in situ. To me, the paper is clearly written and well organized. Admittedly, the details of the diffusion calculations were not always very straightforward for me to follow, but that probably lies more in my lack of background than in unclear writing. I only have a few minor comments that I invite the authors to consider before publication.

Calculation and significance of contributing rock-volumes

In L515ff, you calculate the contributing volumes. Do these calculations of the contributing rock volume assume that that all of the 1216 cm^3 (or the 1.9 cm length) contribute equally? Somehow, I would have expected a decay in the contribution with distance from the chamber where the closest rock contributes most and then the rock farther away contributes less. Then, the length or volume would be some characteristic length-scale (or volume-scale) that describes the decay?

What are the significance of these (short) length-scales of CO_2 diffusion for the weathering of an entire outcrop or soil profile? Would you expect, form your results, that only the topmost few centimeters contribute to direct degassing into the atmosphere and the products from deeper weathering pathways go into the groundwater? This question touches on the previous one, wondering about the length scales over which CO2 production is relevant

Line comments

L40: The citations here (Gaillardet et al., 1999; Moon et al., 2014) only justify the global CO2 drawdown flux from silicate weathering, they do not support the first part of the sentence which also warrants a citation, I think.

L123/Figure 1: To make the figure even clearer, I suggest to either add the catchment names on the map, or the colored circles on the sub-catchments in the legend as well

L131: "To measure in situ the production of CO2 […]". Here, you could specify where you (want to) measure the fluxes (in bedrock, regolith, soil etc.).

L135: Which shape?

L136: Perhaps "Install the chambers *at*"?

L138: Here you switch from past tense in the previous sentences to present tense in this and the following section. Suggest to keep consistent

L181: "with respect to"?

L192: “the curvature of the mass change” is unclear to me. Is the curvature of the mass change the second derivative of the mass change with respect to time? That would mean the third derivative of mass with respect to time?

L193: When you say “For this” what does “this” refer to? Do you use equation (3) to calculate the variable m(t) in equation (2)? If yes, is there one of the variables in equation (3) that is a function of time (Probably pCO_2)? That could be marked with *(t)* to clarify.

L238: Could you describe a bit more how you get from Fick’s law (equation 1) to this expression of the diffusive flux? In particular, I do not quite understand the variable ω. First, you write that it describes a diffusion “over depth and area”, but the units (cm^1 cm^{-2}) look like “a depth over an area”. Can the meaning of this spatial scale be explained in a sentence? Also, this variable has units of an inverse length [L^{-1}] whereas dz in equation (1) has units of a length [L] – so, it seems that the units of the resulting flux are different (it is possible that I am making an algebraic mistake somewhere)? Could you comment on the link to equation (1)?

L283: Could you specify how to get SR>1? This would imply that you recover more CO_2 in the lab than you measure in the field. I guess that is only possible because of uncertainties in the measurements, or could you have gained some CO_2 elsewhere?

L288: could you specify “change in x-axis scale” (which is what you refer to, I think?).

L290: switch to past tense? (“consisted”)?

L298: You could refer to a figure or table to substantiate the statement.

L368 - 370: As far as I understand, these two sentences note two contrasting observations (CO_2 production maximized either during dry or during wet conditions). In L371, the sentence starts with “This observation”. Can you clarify which of the two options you refer to?

Also, more importantly, I didn’t walk away from the paragraph with an understanding what could cause these contrasting observations or whether that is even still an open question. The following explores how diffusivities should be lower during wet conditions but that can only explain one of the observations – at least I think?

L417 & 421: In both cases, that should be Fig. 6I, I think?

L461: Should there be a “dt” in the equation?

L498: Maybe “The coincidence also *suggests* […]”?

Fig9: I wonder if the trends in the data would be clearer with a logarithmic x-axis?

L556: Is it possible to convert this number into an estimate of equivalent CO2 production in terms of tons per square kilometer per year, a number that readers may be familiar with?

L593: I think I know what the dark and light colors mean, but I can imagine that some readers might miss the link to what you mean by “extrapolated” or “stabilized”. You could refer here to figure 5 or L339f.

L736-737: Did I miss something, or did you give a reason for why you did not directly contrast your O_2 consumption rates (Figure 12) with the corresponding CO_2 accumulation rates?

L738ff: Why do you not mention silicate weathering with sulfuric acid as the alternative option that you had discussed earlier? If you gave a reason for dismissing it, I missed it.

I hope that the comments are helpful, and I remain with best wishes to the authors and editor.

Aaron Bufe

References

Gaillardet, J., Dupré, B., Louvat, P., and Allègre, C. J., 1999, Global silicate weathering and CO2 consumption rates deduced from the chemistry of large rivers: Chemical Geology, v. 159, no. 1, p. 3-30.

Moon, S., Chamberlain, C. P., and Hilley, G. E., 2014, New estimates of silicate weathering rates and their uncertainties in global rivers: Geochimica et Cosmochimica Acta, v. 134, p. 257-274.