

Interactive comment on “Quantifying drivers of chemical disequilibrium in the Earth’s atmosphere” by E. Simoncini et al.

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Reply to Referee # 3

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The authors thank Referee # 3 for his or her review. The comments made are very stimulating and treat many topics pertinent to the paper. We will take into consideration all the literature suggested, and we will include methane in the title. Nevertheless we will take care to maintain the original focus of the manuscript. In the following we give an answer for each topic raised by the reviewer. In the final version of the manuscript we will include a complete discussion of the updated data of methane emissions and for the analysis of the O_2/CH_4 disequilibrium at different geological periods.

1. **Methane emissions data.** We updated the emissions of methane using the new database of US EPA and IPCC. As we wrote in the reply to Referee # 1, there is a higher accuracy on the human-related methane emissions (which can be measured directly), but a very low accuracy on the natural ones. For the latter the error is about 29 %, giving a total accuracy of 10 % on the whole methane emissions. Updated values will be discussed in the revised version of the paper.
2. The power we calculate is indeed a minimum value: it is a lower bound on the power required to maintain the methane-oxygen disequilibrium, and the total

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power used by the biosphere is much greater. We will place greater emphasis on this in the updated manuscript.

3. **Lifetime and early Earth analysis.** The authors agree that the extent of methane's lifetime in the Earth's atmosphere is a very important topic. In fact, our analysis aims to use a unique thermodynamic tool which considers both input fluxes and chemical depletion rates. This allows us to understand the effect of the actual lifetime of a molecule on the thermodynamic state of the atmosphere. However, we stress that although residence times are of great importance, they are not the main focus of our paper, which is aimed at demonstrating the calculation of the power involved in disequilibrium. The updated manuscript will include a clarification of the relationships between these two different concepts.

Of particular interest is the quantification of the power needed to support the O_2/CH_4 disequilibrium during the early Earth. Using the suggested literature and other references, we made similar calculations for the atmospheric conditions before the presence of any life (Hadean, mostly CO_2 atmosphere), during the methanogens-dominated period (early Archaean, high CH_4 and low O_2) and after the Great Oxidation Event. When free oxygen is not present or in very low concentration in the atmosphere, the O_2/CH_4 disequilibrium is much lower, as well as the power needed to sustain it. A decrease of the methane emissions from early Archaean values to the present one (or lower) further decreases the power needed to maintain the considered disequilibrium, due to a shorter lifetime of methane in the atmosphere. A first analysis of the early Archaean, methanogens dominated Earth gives a value of $4.9 \cdot 10^{-2}$ TW. A more detailed discussion will be provided in the revised version of the manuscript.

4. We did not include any deeper analysis of CO_2 in our work because CO_2 itself does not represent a strong chemical disequilibrium. The reasons for this will be made clearer in the updated manuscript. Similarly, topics such as albedo change fall outside the scope of our analysis. Quantifying the power allows us to compare

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the thermodynamic significance of different Earth system processes, but by itself it says very little about their effect on the system's dynamics. Again we will aim to make this point clearer in the next version of the manuscript.

5. As we have explained in our reply to reviewer # 2, our use of the language of classical thermodynamics does not imply that we have made any unnecessary near-equilibrium assumptions; the argument can be given just as well in the language of non-equilibrium thermodynamics, and we plan to detail this in an appendix in the new version. To answer the reviewer's specific question, the power depends upon *both* the rate of production *and* the concentration. Consequently, if the concentration were changed by an external process while production remained constant, the power as calculated by our method would indeed change. We will add some comments about the relationship between our work and the theory of maximum entropy production in the discussion section.
6. We will consider the potential feedbacks between chemistry and radiative forcing in the discussion.

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