

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

Anonymous Referee #3

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Comments This is an interesting paper that merits publication after revision. It addresses the interesting problem of the extraordinary disequilibrium of the Earth’s atmosphere, and it shows how this is maintained by an apparently very weak biological input. The topic is well within the scope of the journal. However there are concerns both of context (interpretation of the behavior of the planetary atmosphere) and content (e.g. methane budget). The title is a misnomer also: it should include methane.

Simoncini et al. consider the simultaneous and disequilibrium presence of CH₄ and O₂ in the Earth’s air. They use simple equilibrium calculations to quantify the power required to maintain the methane-oxygen disequilibrium, and then consider the implications of their findings. There has been considerable discussion of the physics of maximum entropy atmospheres, but less of the biochemistry of sustaining a key green-

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house driver, methane. The main greenhouse gas is water, but CO₂ and CH₄ are controlling gases, so the bio-power that sustains CH₄ in the air is of great interest. The paper's conclusion is that the driving energy is small, comparable to that driving abiotic processes affecting the air. This problem is well in the scope of the journal and is extremely interesting (especially in the context of the deep Precambrian): therefore the journal should be favourably inclined to the work.

However there are some significant problems in the interpretation.

First, though perhaps not importantly as the data are roughly right and methane emission varies significantly year on year with meteorological and human vagaries, the authors are somewhat out of date in their methane literature citation. Possibly Dlugokencky et al. (2011) *Phil. Trans, R. Soc. Lond. A.* 369, 2058–2072 would be a better overall review of the methane budget.

The authors take a very simplistic view of methane production and destruction. The atmospheric methane burden is sustained by both methanogenesis and geological methane, while the sinks include both the OH reactions and the soil methanotrophic sink as well as marine Cl. Since biological processes are fundamentally in disequilibrium and use kinetics to cheat equilibria, and also since minor inorganic processes are also at work (e.g in abiotic methane from hydrothermal systems). the equilibrium calculation is surely a minimum value.

The key interest of Simoncini et al is the methane production. But in atmospheric terms, what is important is not the production as such, but the sustained atmospheric methane burden – how much is actually sustained in the air, to sustain greenhouse warming. The burden depends on both production and sink – in other words, on lifetime. If the lifetime is 100 years, then production as low as 50Tg per yr will sustain the present burden. This is important in considering the distant past, especially in the Archean and very earliest Proterozoic, before the Great Oxidation Event.

More generally, Simoncini et al take a narrow methane-led view of the biospheric input

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to the atmospheric management system. It would be helpful if they discussed net primary productivity and CO₂ more (e.g. see Andre, 2011, Biosystems, 103, 239–251), and also albedo change. Possibly reference to the work of the Kasting group would help (numerous papers, especially in the deep past when methane may have been much more important, e.g. Kharecha et al 2005 Geobiology 3, 53–76) and Nisbet et al 2012 (Solid Earth, 3, 1–10)

Thermodynamically the work uses classical chemical thermodynamics to assess an extremely complex biological-atmospheric interaction in extreme disequilibrium. Is the 'power' a valid concept, given that a change in atmospheric OH* (for example caused by CO from fires or biological OCS or N₂O emissions, or some change in water vapour) would radically alter the methane burden even if production stayed constant? Also, perhaps there should be a comment on the climatological view that the physical state of the system tends to maximize entropy increase through convective heat transport upwards from the surface, eventually to space.

Nevertheless, this is an extremely interesting paper, stimulating, and thoughtful. I recommend that it should be returned for revision, but viewed positively.

Specific Section 3 is perhaps a little over-pedagogic.

Interactive comment on Earth Syst. Dynam. Discuss., 3, 1287, 2012.

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