

Interactive comment on “An analysis of atmospheric CH₄ concentrations from 1984 to 2008 with a single box atmospheric chemistry model” by Z. Tan and Q. Zhuang

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General authors' comments: We sincerely thank the anonymous referee for the insightful comments to help us improve the technical note. Our specific responses to each comment are below.

Anonymous Referee 1 (comments):

General comments: I think the study is below the state of the art. It is nowadays quite possible to study methane concentrations and emissions at the global scale with a spatial resolution of the TRANSCOM regions (see http://transcom.project.asu.edu/T4_methane.php) or even finer, either for forward sim-

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ulations or for inversions, even for time periods of two decades. Single-box (or two-box) models are used when a large number of processes are taken into account (for example, more reactions in the methane oxidation chain, e.g. with formaldehyde), which is not the case here. Finally, I do not think this study brings anything new to our knowledge of methane trends and its relation with OH and CO variations.

Response: One-box and two-box models have been widely used in the study of atmospheric methane, carbon monoxide and hydroxyl radical (Tans, 1997; Lassey et al., 2000; Manning et al., 2005; Khalil et al., 2007). For atmospheric methane, compared to 3D chemistry transport model, the one-box or two-box models will not be able to handle the high-resolution variations in space and time but is capable for addressing long-term and global problems. Compared to the one-box and two-box models used before, the models in this study have explicitly formulated the methane emissions from wetlands, one of the largest sources that are sensitive to climate change. In addition, by using two box models, we could test different hypotheses with relatively less model changes.

Specific comments:

1. Observation data: what about the PIs of the measurements used? They are neither co-authors of the paper nor cited in the acknowledgements. Have they been contacted and have they agreed on the use of their data?

Response: The data we used to verify simulations is derived from the GLOBALVIEW product, which is based on NOAA/ESRL network, and AGAGE. We have followed the announcement of data usage by citing and acknowledging them properly.

2. References: a lot of references seem to be out-dated e.g. Etheridge et al. 1992 (see IPCC 2007), Thompson et al. 1986. Some recent studies seem not to have been used e.g. Bousquet et al. 2011 regarding methane source attribution.

3. Section 3.1: the text is not always clear on the hypothesis that is currently com-

mented (e.g. constant or variable OH concentrations).

Response: For point 2, we have updated our citations with several newer references, e.g. Bergamaschi et al. (2007) for source distributions, Spahni et al. (2005) for methane changes from pre-industrial times. For point 3, we have added more details about these two scenarios in the simulation protocol section. The OH in "Changing OH scenario" is simulated from continuity equations we describe in model Section and the OH in "Constant OH scenario" is held constant as 10^6 molecule cm^{-3} (Lawrence, 2001).

Comments for Section 1:

- p. 30261, l. 5: "surprisingly". This has been published, so why be surprised?

- p. 30261, l. 15: "as the largest natural source of methane, emissions from wetlands are very sensitive to environmental factors". Other sources are also sensitive to environmental factors, even anthropogenic sources (e.g. rice paddies).

Responses: We have removed the misuse of "surprisingly" and changed "as the largest natural source of methane, emissions from wetlands are very sensitive to environmental factors" to "as the largest natural source of methane, emissions from wetlands are very sensitive to environmental factors".

Comments for Section 2:

- p. 30262, l. 9: "earlier studies". Which ones?

Response: We added several references here: Thompson (1992); Dlugokencky et al. (1998); and Manning et al. (2005).

- p. 30263, l. 12-14: "as isoprene oxidation has been suggested to serve as both a sink and source for hydroxyl radicals (Taraborrelli et al., 2012), it is necessary to also include OH production from this pathway into OH sources" Isoprene is one of the VOCs that is oxidated by OH. In the rest of the text, isoprene is not mentioned anymore, only

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"VOCs". Could the partition between isoprene and other VOCs be made clearer?

Response: The isoprene oxidation to serve as both a sink and a source for OH (Taraborrelli et al., 2012) is one of claims that OH can be sustained by VOCs released from forests (Lelieveld et al., 2008).

- p. 30263, l. 19: "only wetland methane fluxes show clear evidence of sensitivity to climate change". What of other processes taken into account here, such as the emissions of CO (and CH₄) due to biomass burning or the emissions of CO due to fossil fuel consumption? Could you quantify the sensitivity to climate change of the various processes to justify holding SCH₄ and SCO constant?

Response: We have revised the expression to "wetland emissions are by far the largest CH₄ source that has a temperature sensitivity" to better indicate our idea and we understand that there are other emissions, e.g. biomass burning, linked with climate change. But those factors are much less than wetland emissions (Bergamaschi et al., 2007) and also are difficult to formulate with simple equations. Although assuming SCH₄ and SCO constant in the model, we can still analyze if these two species account for some discrepancies between model and data. For example, since the modeled CH₄ is about 20 ppb higher than measurement by the end of 2008, we infer that there might be about 55 Tg reduction in non-wetland emissions after 1997. By checking with EDGARv4.2 and GFED3 database, we further infer that the fall in biomass burning emissions might be a major source for this reduction.

- p. 30263, l. 26: "by adding a constant southward transportation item to Eq. (1)". I think there is no other information on the choice and magnitude of this item, could you give more details?

Response: This item is derived from a Bayesian-based model calibration process, in which the constraints include the observed methane concentrations from 1984 to 1989 and a prior one-year inter-hemispheric exchange time. We have added the detailed information in a new Section "Parameters of atmospheric chemistry box models" to

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explain it.

- p. 30277, Table 1: Why not indicate the distributions of wetlands, methane oxidation, CO emissions and oxidation, production of OH by ozone photolysis (the Table is "Distribution of sources and sinks")? All the figures given in the caption lack references (and some necessary to the model are missing, e.g. CO emissions,...). Given the difference in land masses, why are the distributions for CO and OH 50/50? Shouldn't the difference in land areas imply for example a difference in the distribution of VOCs and therefore, in OH? Regarding CO surface deposition, what is the reference for the 290 Tg/y? Shouldn't also the deposition be different in the two hemispheres due to the difference in land surfaces?

Response: We have refined tables and texts to give a detailed description of the magnitude and distributions of CH₄, CO and OH sources and sinks. For CH₄ sources and sinks, we define them from the review of two literature sources: one is Fung et al. (1991) and Kai et al. (2011) and another is Bergamaschi et al. (2007). For CO and OH sources, they are calibrated by assuming an equilibrium state at the beginning of simulations, since the lifetimes of CO and OH are relatively short. The deposition of CO is from Bergamaschi et al. (2000). Following the suggestion, we have adjusted to use the difference in land surface to distribute CO surface deposition in the new runs. The magnitude and distribution of CO production due to VOCs oxidation are also from Bergamaschi et al. (2000). We have described these issues in detail in a new Section "Parameters of atmospheric chemistry box models".

- p. 30264, l. 6-7: "the initial concentrations of CH₄, CO and OH". Where do these initial concentrations come from? A spin-up of the model? Observation data?

Response: We have added a new Section "Parameters of atmospheric chemistry box models" to address this comment. The initial concentration of CH₄ is derived from GLOBALVIEW-CH₄ data. The initial concentration of CO is derived by averaging CO mixing ratios from 1991 to 1993 of GLOBALVIEW-CO data. The initial concentration of

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OH is 10^6 molecule cm⁻³ from the review of Lawrence (2001).

- p. 30264, l. 15-16: "we calculate methane fluxes from the Northern and Southern Hemisphere separately and then sum them up together." compared to p. 30270, l. 6: "We also ran our model under the constant OH assumption in the Northern and Southern Hemispheres, respectively." It is not clear for me whether, for each forward or inverse result, there are two runs, one for NH and one for SH and the global results are the sum of there or there are three runs, one for the global and one for each hemisphere. Could you state this more clearly?

Response: In the revised version, we just use one run of a two-box model to simulate CH₄, CO and OH of NH and SH together. In this two-box model, the inter-hemispheric transport item is calibrated by GLOBALVIEW-CH₄ data and a prior one-year exchange time. And the global concentrations of three gases are simulated using the one-box model. We have given a new section to describe the two-box model in detail.

- p. 30266, l. 6-8: "state variables" and "fluxes". Could you state more clearly what is in your state vector? I think there are monthly CH₄ fluxes due to wetlands but maybe there also are the initial concentrations?

- p. 30267, l. 14-15: "Then, for the correlations between this flux and fluxes from J-1 to J-5, they are calculated by analyzing the time series of the Q10 function in Eq. (1)." How are the time series analyzed? What correlations are retrieved?

- Section 2.3: I understand that only CH₄ concentrations are constrained in the inversion. Why not constrain also CO concentrations and even, OH concentrations (with a proxy such as methyl-chloroform as is often done)?

Responses: We have removed the inversion estimation part according to another reviewer's suggestion and the above issues will not appear in the revised manuscript.

Comments for Section 3:

- p. 30268, l. 7-10: "Because the concentrations of hydroxyl radical decline from 10

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to 9.76×10^5 molecule cm^{-3} in the experiment, this slowdown is more likely a result of the stabilization of methane emissions, which was caused either by weakened global warming or by constrained anthropogenic emissions." The variations in OH concentrations are not necessary solely due to its reaction with methane: there may be numerous other causes. There may be also a number of other causes to the stabilization of methane emissions, such as a balance between two different causes, and they do not necessary have a (direct) link to global warming. Why focus on these causes?

Response: This comment helps us to refine our discussion. This should be "Since the modeled oxidizing power ([OH]) declines from 10 to 9.66×10^5 molecule cm^{-3} in the experiment, this growth stalling should be due to the stabilization of methane sources (Dlugokencky et al., 2003), a decline in overall anthropogenic emissions (Bousquet et al., 2006), a fall in fossil-fuel emissions (Aydin et al., 2011), or a reduction in microbial sources due to farming practices in Asia (Kai et al., 2011)".

- p. 30268, l. 10-12: "Our simulation also implies that climate change is responsible for at least one methane concentration anomaly in recent decades: the abrupt global methane increase during the El Nino events of 1997 and 1998 (Dlugokencky et al., 2001)." Why does the simulation imply a direct link between climate change and the El Nino event of 97-98?

Response: We revised the sentence to "Limited by the simple formulations of methane non-wetland sources and OH dynamics, it is difficult for us to sort out those possible correlations. However there are still some anomalies in the experiment that can be linked with wetland emissions, for instance, high emissions from wetlands driven by the unusual high temperature and precipitation during the largest El Niño on record in 1998 (Dlugokencky et al., 2001; Bousquet et al., 2006)".

- p. 30268, l. 17: "this bias". Is it actually a systematic bias computed over 2000-2008?

Response: In our opinion, this is not a systematic bias, but means the modeled methane offsets from observation by either 1) OH drops more than the reality, which

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is addressed by "Constant OH scenario", or 2) there would be the fall of non-wetland methane sources, we provided more detailed description in the revised version.

- p. 30268, l. 17-19: "We think one possible reason for this bias is that the methane emissions from non-wetland sources, such as the natural gas industry, decreased beginning in 2000. However, we lack emission data to validate this hypothesis." Is there really no emission data to check this hypothesis? At least over some industrialized regions, it would probably be possible to use anthropogenic inventories (e.g. EDGAR4 over Europe) or even optimized emissions from independent studies.

Response: Based on this comment, we checked the anthropogenic emissions from EDGARv4.2 and biomass burning emissions from GFED3 and found there is no reduction in anthropogenic emissions but an about 30 Tg decrease in biomass burning emissions. So the latter is a possible factor to contribute this bias but there might be other factors, i.e. rice agriculture (Kai et al., 2011), that can reduce atmospheric methane.

- p. 30268, l. 24-26: "Furthermore, if atmospheric OH declines with time, CO abundance should increase accordingly for the attenuation of oxidation power, as in our model, where the simulated CO rose from 93 to 96.9 ppb." This is only valid if CO emissions do not also decrease with time.

Response: We meant that the model predicts CO increases when atmospheric OH declines with time. We revised the statement with "Besides OH dynamics, there is another weakness in the model that can distort simulation results: our model produces a slightly upward trend in CO mixing ratio ([CO]) from 1984 to 2008 with a rate of about +0.18 ppb yr⁻¹, but the actual [CO] declines a little from 1991 to 2008 with a rate of about -0.44 ppb yr⁻¹. According to EDGARv4.2 and GFED3 data, it could be a result of discrepancies between model assumption and data in CO emissions from biomass burning. A possible consequence of increased [CO] in the atmosphere is to consume hydroxyl radicals and then enrich methane abundance".

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- p. 30269, l. 14-17: "In the model, simulated [CO] increases from 120 to 125.2 ppb in the north and from 66 to 68.6 ppb in the south, and meanwhile simulated [OH] decreases from 10 to 9.73×10^{-5} molecule cm^{-3} in the north and from 10 to 9.8×10^{-5} molecule cm^{-3} in the south." How does this compare to the observations (at least for CO)? What can be deduced from that?

- p. 30270, l. 5: "In this simulation, atmospheric CO increases from 93 to 95.6 ppb." How is this linked to methane variations?

Response: See our response to p. 30268, l. 24-26.

- p. 30270, l. 13-14: "wetland and rice agriculture emissions (both sensitive to climate change)" See specific comment to p. 30263, l. 19: this is not compatible.

Response: The reviewer misunderstood our idea in p. 30263, l. 19. See our response there.

- p. 30270, l. 19-21: "In the simulations, modeled [CO] increases from 120 to 122.9 ppb in the north and from 66 to 68 ppb in the south. " Same as specific comment to p. 30270, l. 5.

Response: See our response to p. 30268, l. 24-26.

- p. 30270, l. 26: "considerably". Quantify.

Response: We quantified this using a linear regression analysis. For methane growth rate before 2004, the slope of regression line is 1.0064.

- p. 30270, l. 28: "the buffer effect of VOC oxidation". What is meant here? VOC oxidation covers a large range of life-times.

Response: The buffering effect of VOC oxidation to OH, also called OH recycling mechanism, was proposed by Lelieveld et al. (2008) and Taraborrelli et al. (2012). It means there is a pathway for VOC oxidation that does not consume OH but produce OH in low-NO_x air, which can compensate the OH loss to sustain OH concentrations.

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- p. 30271, l. 2-4: "So we guess that a mechanism to stabilize OH concentrations should exist, and the lack of formulation of this mechanism in our model has caused the discrepancy in Fig. 4a." OH is lost in many reactions so that there are many other explanations possible for the discrepancy.

Response: This claim has been deleted in the revised version. We found in the old simulation, there was a bug in the calibration algorithm that causes the discrepancy. In our new simulations, the simulated CH₄ is close to the observation.

- p. 30271, l. 17-20: "Because other methane sources besides wetland emissions are set as constant, changes in methane fluxes in other ways would be also attributed to wetland incorrectly, for example, the peak in 1991 should be attributed to the eruption of Mt. Pinatubo." This is a strong limitation to the results of the inversion where only wetland emissions are optimized. Why not optimize other terms of Eq. (1)?

Response: We removed this Section in this revision.

Comments for Section 4:

- p. 30271, l. 22-25: "Using a simple one-box atmospheric chemistry model involving CH₄, CO and OH, we can more efficiently re-construct atmospheric methane concentration trajectory in recent decades in comparison with using 3-D transport and chemistry models (Patra et al., 2011)" This is far-fetched. In modelling, one can always get the "right" results for the wrong reasons. The real point is the knowledge of the modelled mechanisms, on which the TRANSCOM-CH₄ community has been working for several years. I therefore think they would have noticed if a simple one-box model would do the trick to explain such a complex issue.

Response: We revised the sentence to "Using a simple one-box atmospheric chemistry model involving CH₄, CO and OH, we strive to re-construct atmospheric methane concentration trajectory in recent decades".

- p. 30272, l. 1-2: "there should be other sources or sinks that can influence methane

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concentrations significantly, but if OH is constant during our simulation period, atmospheric CH₄ can be predominantly determined by these two factors. " This is only true in this model.

- p. 30272, l. 11-12: "we estimate the global wetland methane emissions to be approximately 128 Tg/yr." Why give a mean when the aim of the inversion is to retrieve fluxes with a monthly (or yearly?) time-resolution, including the trend and inter-annual variability? A figure displaying the retrieved variability of wetlands would be more informative.

Response: This has been removed in this revision.

Comments for Technical corrections:

Response: We have revised our manuscript according to these comments.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 30259, 2012.