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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The variability of methane, nitrous oxide and sulfur hexafluoride in Northeast India" *by* A. L. Ganesan et al.

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We thank the reviewer for his/her thorough comments and provide responses below. Reviewer comments are provided with the author's response following each comment.

Author's comment: We have changed the citation for the pre-industrial SF6 concentration from Deeds et al., 2008 to Vollmer et al., 2002 (P3L51).

-Vollmer M.K., et al., Marine Chemistry, 78, 137-148, 2002]

General comments:

1. The authors rely much too heavily IPCC rather than original work for their citations.

Response: Citations have been modified to include original work. The following references have been updated:

-The major sink for CH4 is reaction with the hydroxyl radical (OH), resulting in an atmospheric budget lifetime of 7.8 years [Prather et al., 2010]. (P2L23)

-N2O has the third largest anthropogenic radiative forcing [Hoffman et al., 2006; Montzka et al., 2011]. (P3L33)

-The main sink for N2O occurs in the stratosphere where photolysis and reaction with O(1D) result in an atmospheric budget lifetime of 118 years [Prather et al., 2010]. (P3L34)

-SF6 is the most potent greenhouse gas regulated under the Kyoto Protocol with a 100 year global warming potential of 22,800 [Forster et al., 2007; Rinsland et al., 1990]. (P3L46)

-Its lifetime of 3200 years owes to the fact that destruction of SF6 only occurs in the mesosphere, making it essentially inert on human timescales [Ravishankara et al., 1993]. (P3L48)

2. Perturbation lifetimes for CH4 and N2O are given instead of budget lifetimes, which I believe are much more appropriate for this study.

Response: Budget lifetimes have been provided. Please see the changes made under 'Specific comments' below.

3. The experimental methods section is missing a description of sampling and drying.

Response: A full and detailed experimental methods section including sampling and drying has been provided in the Supplement. This information was provided under the Supplement because the experimental methods have been adapted from previous studies and was not the focus of the study. For brevity, the majority of experimental information is thus given as supplementary information. The text in the main body

states, “Full details of the instrument design and experimental procedure are provided in the supplementary material.”

Under Instrumental Method in the supplementary material, the following text is provided:

The air sample is pumped into the instrument using a custom-built pump module. An oscillating aquarium-style pump (Gast Manufacturing, Inc., Benton Harbor, MI, model DDL8BS) continually flushes the line at 12 L/min to prevent buildup of condensation and to reduce the residence time between the sampling point and the instrument. This flushing pump contains components that could contaminate the air sample so the line is split upstream through a 7 micron filter and to a diaphragm pump (KNF Neuberger, Trenton, NJ, model UN86) that is switched on only during sampling. Air and any water that may have entered or condensed in the line pass through this pump and into a ‘dip-tube’ water trap. The water trap consists of an inner and outer tube, where water droplets fall to the bottom of the outer tube and air is pumped into the instrument from the top. Water and the bulk of air pass through a back-pressure regulator (Go Regulator, Spartanburg, SC) where the majority of the flow is vented at 2 L/min. Only a small amount of sample is introduced into the GC system at 100 mL/min.

A 6-port stream selection valve (SSV, VICI Valco, Houston, TX, model EMT2CSD6MWEPH) with 12-port actuator selects between air sample and standard, alternating between the two to produce a calibrated measurement, and directs the stream to a Nafion dryer (Permapure, LLC, Toms River, NJ, model MD-050-72S-1), which uses a countercurrent gas of zero air supplied by the pure air generator.

4. State more explicitly what quality control measures are applied to the observations. (E.g., target cylinders, comparison with independent measurements, etc.)

Response: Standard drift has been monitored using two cylinders (in addition to the standard) of calibrated air from SIO (calibrated by SIO in October 2012). The concentrations of these tanks (measured against the standard at Darjeeling) match the

calibrated values at SIO within instrumental precision. While it cannot be definitively ascertained that the standard is not drifting and that SIO and Darjeeling are measuring the same values in the tanks, it is unlikely that any cylinder drift and any instrumental artifacts cancel exactly. It is more likely that SIO and Darjeeling are measuring the same values in the cylinders (and the standard has not drifted).

The text has been modified to, “No drift within the repeatability of the instrument has been observed for the three gases and measured values match the SIO-calibrated values in the cylinders, likely indicating that the two measurement systems are also measuring the same values.”

Instrument linearity has been checked and results of the non-linearity analysis are shown in the supplementary material.

Unfortunately, due to the remote nature of the site and the scarcity of other groups conducting measurements in South Asia, no independent measurements of CH4, N2O and SF6 have been made at Darjeeling. The authors note that independent checks are valuable, but at present the resources to exchange samples with other groups/stations is limited.

5. Axis labels on figures are unnecessarily small and detailed, in some cases. For example, in Fig. 4 delete “Mole Fraction”, since the unit is clear from nmol/mol.

Response: Axis labels in Figs. 2, 4, 6-8 have been made larger and ‘mole fraction’ has been removed from labels.

6. State where the data are available for others to use in studies of Asian GHG emissions.

Response: At present, data can be acquired by emailing the lead author of this study. We will be shortly be uploading the data on publically accessible servers (e.g., CDIAC). The text now states at the end of the first paragraph of the ‘Summary and Conclusions’ that, “Data from this study can be acquired for research purposes by contacting the

lead author of this study."

Specific comments:

P2L23: You want the budget lifetime, not the perturbation lifetime. There is a recent paper by Prather et al. with CH4 and N2O budget lifetimes.

Response: The text has been changed to reflect budget lifetimes instead of perturbation lifetimes. CH4 lifetime has been changed to 7.8 years (P2L24) and N2O lifetime (P3L35) to 118 years following Prather et al., 2010.

-Prather M.J., et al., Science, 330, 952-954, 2010

P2L26: CH4 emissions related to fossil fuel are as large as any listed and are likely increasing, so they should be included.

Response: The text has been modified to, "Globally, a large fraction of CH4 emissions are naturally occurring and primarily originate from wetlands, but anthropogenic sources, which include ride paddies, ruminants, biomass burning and fossil fuel emissions dominate with $\sim$60% of the CH4 budget."

P3L7: In AR4, N2O came after CO2, CH4, and CFC-12. There are other sources like NOAA's AGGI that show N2O has replaced CFC-12 as 3rd largest RF.

Response: The citation has been changed to the following:

-Hoffman D.J., et al., The role of carbon dioxide in climate forcing from 1979-2004: Introduction of the Annual Greeenhouse Gas Index, Tellus B, 58B, 614-619.

-Montzka, S.A., et al., Non-CO2 greenhouse gases and climate change, Nature, 476, 43-50.

P3L9: This is the perturbation, not the budget, lifetime. Note that the 2010 WMO O3 assessment had this wrong.

Response: The text has been changed to reflect budget lifetimes. CH4 lifetime is now

changed to 7.8 years (P2L24) and N2O lifetime (P3L35) to 118 years following Prather et al., 2010.

-Prather M.J., et al., Science, 330, 952-954, 2010

P6L18: "...improve SF6 response." is vague. Do you mean increase peak area/ppt? Or, the peak is sharper and easier to integrate than when it comes out after N2O?

Response: The improved response is an increase in SF6 peak height without affecting the N2O response, and results in improved SF6 precisions.

The text has been modified to, "On the post-column, the order of elution of N2O and SF6 is reversed so that SF6 is detected before the much larger N2O peak. This results in an increase in SF6 peak height and improved precision."

P6L28: Measurements began before the standard gas cylinder was filled at SIO; what was used for a standard prior to that?

Response: Many thanks for this comment. The year is a typo in the text. The standard was calibrated in July 2011 and the text has been modified to, " Measurements were calibrated using a dry compressed air standard filled in an aluminum cylinder (Scott Marrin, Riverside, CA) at the Scripps Institution of Oceanography (SIO) in July 2011.

P7L21: add space so 10 Hz.

Response: Space has been inserted.

P9L3: How good is this assumption for CH4 during summer when loss can be more than 1 ppb/day?

Response: For this study we mainly use the air histories to qualitatively show the effect of meteorology at the site and any loss processes would not significantly impact the general trajectories. For the purposes of emissions estimation, which is beyond the scope of this study, it has previously been shown that the errors induced by not including CH4 loss is on the order of 0.7-7% over the timescales of the air histories (Manning

A.J., et al., Journal of Geophysical Research, 116, D02305, 2011). Uncertainties derived on emissions are typically an order of magnitude greater than the errors in the air histories induced by OH loss over 20-30 days.

P9L19: Specify which is latitude and which is longitude.

Response: The text has been modified to ". . .the UM's global meteorology at 0.352 x 0.234 (lon x lat) was used."

P10L23: ...differences...show...

Response: Text has been corrected to "The seasonal differences in the air histories show. . ."

P10L25: spelling: assess; Given the mismatch between the position of the site in the model and reality, can you make an argument as to why the comparison is useful?

Response: Spelling of assess has been corrected.

The comparison between modeled and observed meteorology is useful because it provides a mechanism to understand the model's ability to reproduce flows in a complex environment. The comparison also shows that the diurnal cycle in the observations results from a flow that is being captured by the model (a large scale plains–to –mountains flow) rather than a local Darjeeling ridge flow, which has been an interesting and unexpected result.

We have made this comparison for several model heights and 500 m.a.g.l was chosen because it is the midpoint between the model and true heights. Within several hundred meters (400-600 m.a.g.l), differences in the model meteorology are small. However, meteorology at the model surface results in a better match with observed wind speed but worse fit to observed wind direction. The tradeoff between direction and speed results from the Ekman spiral that is induced by surface friction.

In the text, we state that, "To assess the ability of the UM to reproduce flows at the site

as well as to understand the origin of air masses sampled at the site, observed and modeled wind speeds and wind directions are compared using wind roses (Figure 3). UM modeled winds are shown at 500 m.a.g.l., which is the mid-point particle release height used in the model. . .. Wind speeds are almost always larger in the 500 m.a.g.l model winds than in the 15 m.a.g.l observed winds because surface friction is less significant at this height in the model."

The text now additionally includes:

"This comparison has been performed for a variety of model heights. Only small differences exist in the meteorology at heights between 400-600 m.a.g.l., but surface meteorology shows a better fit to wind speed and a worse fit for wind direction. This tradeoff between wind speed and wind direction at the release height could contribute to errors in the derived air histories."

P11L19-28: I'm not sure of the point you are trying to make with this discussion of sensible heat flux.

Response: The text has been modified to, "Sensible heat flux is a measure of the heat transferred between the surface and atmosphere and is a major driver in the formation of slope winds."

P13, top: Because most emissions are in the NH, there is a strong N/S gradient in SF6, on order of 0.2 ppt. You should be able to see movement of the ITCZ across the site based on SF6 alone. Can you?

Response: The text now states, "A linear fit was applied to the SF6 data (excluding monsoon months of June to September) and interpolated to mid-July. This represents the value, to first-order, that would be expected given only NH air. The observed July data was averaged into weekly values and compared to the interpolated NH-air value. A difference of 0.13 pmol/mol was found at the peak of the monsoon. Previous studies have shown a seasonal SF6 amplitude of 0.17 pmol/mol at the Seychelles [Gloor et al.,

2007]. It is expected that the difference at Darjeeling, which is a continental site, would be smaller than that observed at the Seychelles because SH air entering India first passes over eastern Africa and the Indian subcontinent before reaching Darjeeling."

P16L11: consistent WITH changes in sunrise

Response: Text has been corrected to, "This timing of the morning peak also shifts throughout the year, which is consistent with changes in sunrise time throughout the year."

P17L8: You will not "verify" national scale emissions for S Asia with measurements from this one site. Perhaps "constrain" would be a better choice.

Response: Text has been modified to, "..these data will be used to constrain national-scale emissions from South Asia." P17L16: Delete "throughout the summer period"; "summer monsoon" is pretty explicit about the season.

Response: Text has been modified to, "In contrast with the winter, the summer monsoon flow is predominantly southwesterly, resulting in high surface sensitivity to India and Bangladesh but also the transport of southern hemispheric background air."

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 17053, 2013.