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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Modelling trends in OH radical concentrations using generalized additive models" *by* L. S. Jackson et al.

L. S. Jackson et al.

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Response to referees' comments on 'Modelling trends in OH radical concentrations using generalized additive models' by Jackson et al., acpd-2008-0339

We would like to thank both of the referees for their helpful comments which have allowed us to clarify a few outstanding issues. We address the points raised by the referees in order and have made amendments to the manuscript as detailed in the responses below.

Referee #1

The major concern of referee #1 is the **lack of discussion of experimental errors.**

We do not agree that it is unfair to compare the predicted OH concentrations with measured values. One advantage of the GAM methodology is that it produces unbiased

predictions. Whilst the discrepancy between MCM results and measurements is not significant, the MCM result is still a *biased* estimate. However, in order to clarify this issue, we have added the following new paragraph to the manuscript.

Page 14626 line18

We have inserted a new paragraph

The proportion of variation in OH data which can be explained by the GAM$_{ME}$ and GAM$_{MO}$ models is limited to less than 100% by the precision of experimental measurements. Imprecision in the measurement of OH concentrations introduces variability that affects the fit of GAM$_{ME}$ to measured OH concentrations but not the fit of GAM$_{MO}$. The deviance explained by GAM$_{ME}$ is, therefore, lower than that explained by GAM$_{MO}$. Adjustment of the deviance explained requires an accurate estimate of the precision of OH measurements which is not available for the TORCH data. The estimate reported by Smith et al. (2006) from the NAMBLEX experiment (20% at an OH concentration of 3x10^{6} molecule cm^{-3}) would limit the maximum deviance explained to 60% for GAM$_{ME}$, clearly too low given the 77.9% achieved. Uncertainties in measurements of predictor variables also introduced noise into the data used for GAM$_{ME}$ and GAM$_{MO}$ models and also data used to constraint the MCM box model. These measurement errors may affect the relative importance of some of the less influential predictor variables in GAM models but not the qualitative interpretation of the shapes of the smooth functions which is the primary focus of this research.

Minor issues:

1. **Insert reference to Rohrer and Berresheim**

   This reference has now been added as follows:

   Page 14624 line 8

   After

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"directly and indirectly."

We have inserted the sentence:

"This is consistent with the strong correlation between measured OH concentrations and observed J(O^1D) photolysis rates recorded at the Meteorological Observatory Hohenpeissenberg in southern Germany, Rohrer and Berresheim (2006)."

Page 14630 line 22

We have inserted

Rohrer, F. and Berresheim H.: Strong correlation between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation, Nature 2006 Jul 13;442(7099):184-7

We deal with the Lelieveld reference under the response to referee #2.

2. **Define deviance explained**

   Page 14613 line 17

   After

   "ranked in order of deviance explained"

   We have inserted the following:

   ", the proportion of the variance in OH data explained by a GAM model."

Referee #2

The main issue for referee #2 relates to **extending our analysis to investigate the GAM models at low and high NO, and also to carry out new GAM analyses for HO2 and for the ratio HO2/OH.**

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As suggested GAM results were produced for high and low NO concentrations and also for HO_2 and for the ratio log(HO_2/OH). GAM models for OH based on high and low NO concentrations retained photolysis as the key variable. Changes in other variables were not found to be very informative as both modelled and measured OH exhibited as weak statistical dependency on NO. The presence of strong dependencies with NO would have been identified by the original GAM approach anyway. To clarify the connection between this work and previous results for HO_2/OH, the following change has been made.

Page 14625

The paragraph from line 8 to line 12 has been replaced with

"It is interesting that the difference in NO dependency for the modelled and measured HO_2/OH ratio, noted by Emmerson et al. (2007), was not prominent for OH in this study. Table 6 shows the deviance explained by GAM models using NO as the sole explanatory variable. Results for the log(HO_2/OH) ratio show a large discrepancy in the deviance explained between modelled and measured data. The shapes of the underlying smooth functions were also different; consistent with Emmerson et al. (2007). By contrast, neither modelled nor measured OH exhibited a strong statistical dependency on NO. Further, the root mean square of the difference between NO smooth functions for modelled and measured OH concentrations was found to be less than the equivalent result for the log(HO_2/OH) ratio. This indicates that the difference between modelled and measured OH dependencies on NO was not as marked as for log(HO_2/OH). For HO_2, there was also only a weak statistical association with NO concentrations for both modelled and measured data."

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Table 6. Deviance explained (%) by NO in single variable GAM models for OH, HO_2 and log(HO_2/OH).

GAM model	Modelled	Measured
OH∼s(NO)	19.2	8.7
Log(HO_2/OH)∼s(NO)	72.5	18.1
HO_2∼ s(NO)	21.1	1.5

The second point raised by this referee referred to whether or not the deviance represented the main factors affecting OH concentration. The text has been modified as follows:

Page 14625 line 1

After “biogenic hydrocarbons”

The following sentence was added:

“Efficient recycling of OH by isoprene, as observed by Lelieveld et al. (2008) over a tropical forest, may also account for the lack of impact of high isoprene concentrations on OH concentrations. The efficient recycling of OH radicals is not discernible using GAMs which model net changes in concentrations.”

Page 14630 line 10

We inserted:

Lelieveld, J., Butler, T. M., Crowley, J. N., Dillon, T. J., Fischer, H., Ganzeveld, L., Harder, H., Lawrence, M. G., Martinez, M., Taraborrelli, D., and Williams, J.: Atmospheric oxidation capacity sustained by a tropical forest, Nature, 452, 737-740, 10.1038/nature06870, 2008.

1) Minor points

Page 14622 line 23

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After

“GAM model”

We inserted

“by re-calculation of the constant parameter and smooth functions.”

2) Page 14615 line 17

We changed

“The value for the intercept was 1.32$\times$10^6 molecule cm^{-3}, the mean value of the measured OH radical concentrations”

to

“The value for the intercept was defined as the mean value of the measured OH radical concentrations, 1.32x10^6 molecule cm^{-3}. Including this intercept improved the fit of the models to the data and simplified interpretation of the smooth functions which represent variations from this mean value.”

3) We believe the section on acetone is relevant given the dependence of the measured OH on this species.

4) The accuracy of GAM predictions was quantified by comparing predicted and measured mean values and comparing root mean square errors for the GAM predictions and MCM modelled OH. Results were disclosed in Table 4.

Other minor edits:

Table 3

We changed “Photolysis rate of HNO_3” to “Photolysis rate of CH_3CHO”

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 14607, 2008.

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Interactive Comment