Atmos. Chem. Phys. Discuss., 11, C3636–C3643, 2011
www.atmos-chem-phys-discuss.net/11/C3636/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Quantifying the magnitude of a missing hydroxyl radical source in a tropical rainforest" *by* L. K. Whalley et al.

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Received and published: 20 May 2011

We would like to thank Professor Peeters for his comments on the manuscript. Although we conclude that the new isoprene mechanism proposed by Peeters et al., (2009) alone is unable to reproduce OH and HO2 radical concentrations from the campaign, we remain open to the possibility that this mechanism plus an additional (albeit large) HO2 sink could reconcile the model measurement discrepancy if an OH yield from isoprene oxidation of the order of 2.7 is included (pg 5797).

In the comment Peeters highlights key differences in modelled radical concentrations when using the IMAGEv2 global CTM and the more chemically explicit MCM box model. It is important to reiterate that we have relied on experimental evidence by constraining to the measured OH reactivity. Using this approach we are able to determine the full magnitude of the missing OH source. Any modelling approach that underestimates the OH sinks will also underestimate the magnitude of the unknown OH sources. For HO2, the smaller HO2 sink required by the IMAGEv2 global CTM relative to the MCM suggests that the HO2 production rate in the IMAGEv2 global CTM is slower relative to the MCM. This makes sense as the MCM provides the most explicit treatment of VOC oxidation. In the MCM model CO+OH –> HO2 is not the dominant HO2 source, rather the photolysis of HCHO and RO2 chemistry leading to HO2 (with HCHO and RO2 deriving from OH initiated VOC oxidation) acts as the most important source pathways during the daytime.

As pointed out by Peeters, the HO2+X reaction rate is extremely fast and as such acts as the dominant HO2 sink. Constraining the MCM model to the experimental data (i.e OH reactivity) allows the total HO2 production rate and loss rates to be determined and not under-estimated; this is the turnover rate required to reconcile the OH, HO2 and OH reactivity observations.

Peeters highlights that in previous field campaigns, giving the GABRIEL campaign as an example, the missing OH source has been linked to isoprene. During OP3, we found no direct evidence for this link (as discussed in the manuscript, the missing OH source does not entirely follow the isoprene concentration profile) and instead hypothesize that unmeasured biogenics (potentially an unmeasured primarily emitted BVOC or a BVOC oxidation product) may be responsible for the missing OH reactivity and the missing OH source.

In conclusion, the slower additional HO2 loss rate required in the LIM0 model is likely a lower estimate due to the model underestimating the OH reactivity.

We thanks referee 1 for the helpful comments. In response:

1 As suggested by the referee, in the revised manuscript we will emphasise other ar-

eas of work being pursued in the atmospheric chemistry community that also rely on a satisfactory resolution of this modelled-measured OH discrepancy. As highlighted by the referee, any global atmospheric model (ACM) that is currently able to reproduce isoprene observations should be considered suspect. Low isoprene emission rates are often adopted in global ACMs to ensure agreement between modelled and measured ambient isoprene concentrations (Guenther, 2008) – these emission rates tend to be lower than estimates based on direct emission measurements. The use of higher emission rates serves to dramatically deplete the OH radical concentration and in turn leads to unrealistically high concentrations of certain key atmospheric constituents. The inclusion of a novel OH source mechanism, as discussed in this manuscript, coupled with more realistic emission rates, may improve global ACM predictions and allow the impact of these emissions and oxidation pathways (e.g. SOA formation) to be accurately determined. The possibility of previously unidentified isoprene oxidation pathways, such as those discussed in this manuscript, will also undoubtedly impact any top-down estimates of isoprene emissions derived from satellite observations of isoprene oxidation products such as HCHO. This extremely useful approach to determining global map of isoprene emissions relies heavily on an accurate understanding of isoprene oxidation.

2 The photostationary steady state analyses used to calculate OH concentrations in section 3 (R7-R9) was constrained to the peroxide concentrations measured during GABRIEL, whilst peroxide concentrations in the box model used to calculate [HO2] were left unconstrained and built up to levels controlled by the deposition rate employed and the constrained parent VOC concentrations. Approximately 16% of [OH]calc (when all measured OH sources are included in the PSS calculation alongside p(OH), (R7)) may be attributed to the photolysis of peroxides. Doubling the peroxide concentration increases the peak [OH]calc in (R7) from 3.0 x 105 molecule cm-3 to 3.5 x 105 molecule cm-3; halving the concentration reduces [OH]calc in (R7) to 2.75 x 105 molecule cm-3. Any uncertainties associated with the treatment of the photolysis of the peroxides, therefore, will only have a small impact on the PSS [OH]calc and will not change any of the major conclusions drawn from this work.

3 We have performed a TUV calculation to determine j-values under GABRIEL and OP3 conditions as recommended by the referee. The TUV predicts peak j(O1D) for clear sky conditions of∼ 5.4 x 10-5 s-1 and ∼ 6.2 x 10-5 s-1 for OP3 and GABRIEL respectively. The TUV photolysis rate compares well with reported j(O1D) from the GABRIEL campaign (Martinez et al., 2010) but over-predicts the measured j(O1D) photolysis rate during OP3, being, on average, a factor of ∼1.5 larger than the mean diurnal observations. During OP3iii, a spectroradiometer was run alongside the filter radiometer at the Bukit Atur site and was in good agreement, suggesting that the filter radiometer was working well. If we assume that the observed j-values should be higher and scale to theoretical photolysis rates predicted by the TUV model, this increases [OH]calc in (R7) by ∼23%. The [OH]calc in (R7) still significantly underestimates the OH measured accounting for only ∼15% of the observed [OH] and, as such, still demonstrates a large, unknown OH source. The cause of the discrepancy in the theoretically calculated j(O1D) and measurements is unknown. Cloud-cover will play a role, but even under cloud-free conditions the measured photolysis rates were still ∼15% lower than predictions. During OP3 the radiometry measurements were performed on the ground, below the height of the canopy. The instrument was in full sunlight (from above) from 6 am to 6 pm approximately, but it may be speculated that in this in-canopy location the solar radiation from longer angles would have been slightly reduced due to the trees.

4 The conclusions will be expanded and will include a discussion on potential ways forward that will help to uncover the problem. Clearly one of the next steps should involve laboratory studies focussing on the regeneration of OH and HO2 during isoprene oxidation to test the recently proposed theory. The ability to speciate individual RO2 species in future field experiments would greatly improve understanding of the chemical mechanisms in VOC rich environments and would provide a further parameter to test models against. Flux measurements in future studies to help better constrain the

deposition lifetime would be beneficial as the model has been shown to be particularly sensitive to this parameter. In the revised manuscript we will emphasize other areas of work (as mentioned in the first comment) that are also affected by this discrepancy in the conclusions.

We thanks referee 2 for the helpful comments and corrections. In response to the specific comments:

Much of the early work on the missing OH source in VOC rich, NOx poor environments has focussed on the role of isoprene oxidation as the potential source of OH recycling. Whilst we open the discussion by considering the recent theoretical work by Peeters et al. (2009) that, by far, provides the greatest potential to generate high OH yields, we highlight that the missing OH source does not entirely follow the isoprene profile as the OH observations are still under-predicted during the morning hours even with an OH yield of 2.7 from isoprene oxidation, suggesting that other species may contribute to OH concentrations at this time. With respect to OH reactivity, discussed in much greater detail in Edwards et al., (2011), model simulations are able to reproduce the general trend in the observations (peaking in the early afternoon, and lowest during the night), with the correlation between observed and calculated OH reactivity giving a linear correlation coefficient of R = 0.9; the model, however, under-predicts the magnitude of the observations by $\sim$ 53%. The high correlation between modelled reactivity and measurements is almost entirely due to the dependence of the variability in OH reactivity on the observed concentration of isoprene. Although the reaction of OH with isoprene directly only accounts for $\sim$ 25% of the measured total OH reactivity, the oxygenated VOCs generated from isoprene oxidation, account for a further 12% of the reactivity; this fraction was found to increase further (to $\sim$ 27%) if the model was constrained to the OH observations, and further still if the deposition lifetime of the oxygenated VOCs was increased from 1 to 3 days (to $\sim$55%). Under the third scenario the model was able to reproduce the magnitude of the reactivity observations to within 4%. These findings demonstrate the importance of the unconstrained oxidation products of the

observed BVOCs and highlights that isoprene and its oxidation products can dominate the OH chemistry in this region. Although unmeasured, primary emitted, BVOCs may contribute to OH reactivity and the postulated OH recycling, the unmeasured species would need to be present in concentrations almost an order of magnitude greater than isoprene, and have a reactivity towards OH similar to that of Limonene. Although it is likely that a fraction of the ‘missing’ OH sink identified during OP3 is due to the presence of unmeasured primary emitted BVOCs, the requirement of a species present in concentrations 10 times greater than isoprene is difficult to reconcile with previous work (Edwards et al., 2011).

Under the operating conditions employed during the 2008 OP3 campaign we have found that the instrument was relatively insensitive to detection of the RO2 species. During the campaign only one fluorescence cell was used to make alternate measurements of OH and HO2 and conditions were optimised to maximise its sensitivity to OH. Under this configuration incomplete mixing of NO into the ambient air-stream for the HO2 titration was evident and resulted in low conversion of HO2 to OH. Coupled with the high pumping capacity and therefore fast gas throughput of the fluorescence cell, this configuration effectively minimised the potential interference. Recent laboratory tests have revealed a 12% yield of HO2 due to the decomposition of ethene-derived RO2 in the presence of NO in the FAGE detection cell under OP3 conditions. This provides an upper limit to HO2 yield from RO2 species during OP3 as, under conditions optimised to maximise the interference signal, ethene-derived RO2 species provided the largest HO2 yield compared with other RO2 species tested such as those derived from isoprene (yield of 10%), and higher alkanes (Whalley., 2011). Model simulations suggest that up to 2.1 x 108 molecule cm-3 of alkene-derived RO2 species were present at solar noon during OP3 and thus up to 2.5 x 107 molecule cm-3 of the HO2 concentration may be attributed to these species ($\sim$ 10% of the total HO2 signal). This small reduction in HO2 concentration needed to allow for generation from RO2 only serves to further increase the modelled to measured HO2 discrepancy and suggests that the recycling of HO2 to OH by an unknown species may be slightly faster than originally postulated.

Minor comments Page 5787, line 21-23 will be updated as: In contrast to model predictions, field studies in mid-latitude forests (Carslaw et al., 2001; Tan et al., 2001), and more recently in tropical rainforests (Lelieveld et al., 2008; Butler et al., 2008; Kubistin et al., 2010; Martinez et al., 2010) and other tropical locations (Hofzumahaus et al., 2009) have found that appreciable concentrations of OH are maintained even in the presence of high biogenic emissions.

Page 5788, lines 13-18 will be updated as: "The mechanism of Peeters et al. (2009) postulates an OH radical yield of ∼1 with recent publications (Peeters & Muller, 2010; Stavrakou et al., 2010) assuming this yield may be even greater (up to 3 OH radicals recycled per isoprene molecule oxidised). Calculations suggest that if an OH yield of 3 were to be included. . ."

Page 5788, line 19-20: 'however' and 'any such' deleted.

Page 5788, line 19: PRIDE-PDR changed to PRIDE-PRD

Page 5789, line 22: HCHO was not measured using the GC-FID but other oxygenated VOCs such as acetaldehyde, acetone and methanol were.

Page 5792, line 6: Observations of the physical loss rate of OH within the OH reactivity instrument, , were measured in the laboratory once the instrument returned to Leeds, which gave a value of = 6.1 ± 0.65 s-1. This physical loss rate of OH within the instrument was found to remain the same both before and after cleaning the flow tube at the end of the campaign suggesting that any deposits to the surfaces did not affect the physical loss rate of OH.

Page 5795, line 1-3: a comparison of OH reactivity measured during OP3 and GABRIEL will be included. Only 2 hours of OH reactivity data were taken during the GABRIEL project due to an instrument failure making it difficult to compare the mean diurnal levels. Peak OH reactivities were 72 ± 18 s-1 and 83.6 ± 26.0 s-1 (single

points) during GABRIEL and OP3 respectively.

Page 5797, line 23: this will be changed in the revised manuscript.

References:

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