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**Interactive
comment**

Interactive comment on "What effect does VOC sampling time have on derived OH reactivity?" *by* H. Sonderfeld et al.

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We are grateful to the referee for their insightful and constructive comments and we have responded in full to them.

Reply to specific comments:

SC 1) p.3, l.10- p.4, l.6: The authors present a very good compilation of studies about missing OH reactivity based on the comparison of individually measured OH sinks and the directly detected total OH reactivity. As stated later in the introduction (paragraph p.4, l.14-22) the different time resolutions of OH reactivity and individual compound measurements might bias the comparison hence the resulting missing OH reactivity. With this in mind and following the scope of the entire manuscript, it would be interesting for the reader to get some information about typical instrumentation (e.g. GC)

and sampling times (e.g. first 10 min of a 40 min cycle) that have been used for VOC measurements and compared to the directly detected total OH reactivity. Is it possible to include this additional information, either for all or some of the examples that are provided in the text already?

These details can only be extracted from a few of the cited studies. Sampling times are mentioned occasionally, but the analysis process how the different time resolved data are compared to each other is rarely mentioned precisely. This is a real gap in the OH reactivity literature.

Where the information is available it has been added to the paragraph now on p. 4, L15 – 28.

SC 2) p.3, l.28-29: Indeed both of the studies presented here concluded that the missing OH reactivity is possibly due to unmeasured oxidation products. However, they did not exclude the contribution of undetected forest emissions that may add to the missing reactivity, as well.

Sentence added to p3, l29: "Undetected biogenic emissions and transport of reactive compounds are also cited as other reasons for missing OH reactivity."

SC 3) p.5, l.14-15 and p.7, l. 9: For both measurement campaigns that are chosen for presenting data in this manuscript a calibration was performed before (and for PARADE also after) the campaign. Was the calibration done at the measurement site or in the laboratory?

The calibration measurements for the ClearfLo data were done in the laboratory. Clarified on p5, l24 now.

The PTR-ToF-MS used for PARADE was calibrated in the laboratory. Mentioned on l10, p7 now.

SC 4) Table 2: How did you calculate the accuracy as error for the measurements?

ClearfLo: The accuracy was calculated from the error of the calibration measurements.

PARADE: In Table 2 the given accuracy is the mean uncertainty calculated with error propagation based on uncertainties in calibration, background measurements and fragmentation patterns.

Why did you chose 1 sigma for the ClearfLo campaign and 2.6 sigma for the PARADE campaign as LOD?

The two field campaigns were conducted independently of each other. So, the LOD were calculated in a way to reflect each data set and the format they chose to report these for each of the campaigns. As it does not have an effect on the results of this study, they were not recalculated to match each other, but instead stated clearly.

SC 5) p.11, l.2-3: Since the different monoterpenes have very different reactivities towards OH, it is critical to know their atmospheric composition for calculating the OH reactivity due to monoterpenes. Especially the two contrasting sites presented here might have very different typical ambient monoterpene distributions resulting in different characteristic OH reactivities. Unfortunately, the PTR-MS cannot separate the different monoterpenes and detects all of them as one single signal. Therefore, the authors decided to use the reaction rate of a-pinene only. In case that during the campaigns the monoterpene composition was characterized by accompanying instrumentation (e.g. GC-MS) could you use that data to estimate a typical monoterpene OH reaction rate coefficient? Or in case that you did not have such observations during the campaign, are there any studies in the literature that could give you hints about the typical monoterpene distribution at the campaign sites? A typical monoterpene composition will help you to estimate a typical monoterpene reaction rate with OH that is representative for location and timing of the two campaigns.

That is an important point, when calculating OH reactivity from monoterpene measurements.

For ClearfLo the monoterpene signal of the PTR-ToF-MS was not analysed, so this has no effect on the presented results from ClearfLo.

For PARADE the monoterpene signal was analysed and is presented in this study (Tab 4 and Fig.12). Applying a different reaction rate would affect the calculated OH reactivity in Tab. 4 by shifting them to higher values. Nevertheless, the slope of the correlations analysed here for the monoterpenes does not change, as the reaction rate would be changed in x-axes and y-axes in the same way. A test was done by applying the weighted reaction rate presented in Nölscher et al. (2013), based on GC measurements in spring at the same site. The same slope presented in Fig 12 was observed.

SC 6) p.12, l.19: Why do you need to generate a randomized data set? What do we learn from comparing this fictive distribution of OH reactivities to the field data?

The randomly generated data set was generated and compared to the field data to rule out, that the observed effects arise owing to sampling artefacts. Also it provides a clear counterfactual to the measured data.

SC 7) p.14, l.20-28 and p.16 Table 5: Could you please explain why you chose to not include _R in Table 5?

The mean of ΔR can be expected to be very close to zero and the range will reflect the extreme values, so I found, that this would not add any useful information here. These values could still be added to Tables 5 to 7, if this would be beneficial for the reader.

The standard deviation of ΔR is used as a measure of variance and presented in Table 5. However, I wonder if it would be more accurate to look at the standard deviation relative to the hourly average ΔR?

By looking at the residuum ΔR we are investigating the absolute difference/spread between the hourly mean and the shorter sampling time. The relative variance is investigated by the frequency distribution of their ratio and its FWHM.

Also, could you please clarify the physical meaning of the values presented by the Gaussian Fit Centre and the FWHM (full width at half maximum)? You say that the Gaussian function was fitted on the frequency distribution of the ratio of shorter interval averages (R(t<60)) to the hourly average (R(t=60min)). In this case a value of 1 would be calculated for perfect overlap of those two averages and the FWHM would convert to zero, right?

Sentence added now on p15, l 9,10: "Ideally, the centre of the Gaussian fit is 1, while the full width at half maximum (FWHM) describes the spread of the distribution around its centre."

SC 8) p. 16, l. 7-8: These two sentences seem to have contradicting statements: The small standard deviation of _R highlights the narrow range of calculated OH reactivity. And the high variability of the data is reflected by the relatively high FWHM. Could you please explain? Would you get a different result if looking at the relative standard deviation?

This is directly connected to the reply to SC7). The comparably small standard deviation of ΔR results from the much lower range in OH reactivity of the discussed VOC during PARADE. When looking at the relative spread (FWHM of Gaussian fit to ratio), we find a slightly higher variance compared to ClearfLo.

SC 9) p.18, l.12-15: A more general remark in this context: It could be interesting, regarding the discussion about the difference of variabilities at the two different sites, to have a look at the variability-lifetime relationship as for example presented in Williams et al. 2000 (http://dx.doi.org/10.1029/2000JD900203). Similarly for section 3.4 in which the effect of different VOC classes on OH reactivity is discussed.

Interesting point. Lines added:

"These results are in line with observations from Williams et al. (2000), who investigated the variability-lifetime relationship of VOC measured in an unpolluted region of

Surinam based on the standard deviation of the natural logarithm of their concentration. They found a higher variability for toluene compared to acetone and methanol. Compounds with a lifetime below 2 days did not seem to fit into this relationship."

SC 10) p. 26, Figure 13: The effect of VOC variability on the calculated OH reactivity is presented in this figure for the ClearfLo campaign. How does it look like for the PARADE campaign data? Are there significant differences?

The share of OH reactivity based on the different classes of VOC was calculated from the GC measurements, which provides a wide range of VOC, that were done during ClearfLo at the same site like the PTR-ToF-MS measurements. GC data from the PARADE campaign were not analysed in this study.

SC 11) p. 28, l. 4-5: The missing variability in VOC data, that you mention here, is only due to the short interval sampling time. Is this correct?

Yes. Changed to missed.

SC 12) p. 28, l.5-6: The divergence between 5 min and 60 min averaged calculated OH reactivity is given here to be between 1-28% (PARADE) and 0-44% (ClearfLo). These numbers appear in the text for the first time at this point within the conclusions. Could you please include some reference in the text beforehand? And also it would be good to stronger point out the conditions and the statistical test (e.g. first 5 min of hour, consecutive 5 min intervals, regression methods, number of data points, effect of different VOC classes, : : :) that lead to the greatest divergence.

Thanks for pointing this out. Actually for PARADE the wrong range was given, which should have been 2 - 26% and is now corrected

Line added to P20:

"Depending on the selected 5 min interval the bvf resulted in a divergence of - 0.1% to 44 % for ClearfLo, 1% to 13% for PAR1, - 3% to 26% for PAR2 and – 2% to 10% for the randomised data."

Reply to general comments:

GC 1) Within the presented study you solely compare VOC data with the OH reactivity calculation based on the measurement of individual OH sink compounds. Do you have any directly measured total OH reactivity data available to compare to?

Direct OH reactivity measurements as part of ClearfLo were made during the summer IOP (22 July to 18 August 2012) (Whalley et al., 2016) and can thereby not directly be compared to the here presented PTR-TOF-MS data set from the winter IOP.

During PARADE OH reactivity was directly measured from a branch enclosure system. As they focus on the biogenic emissions of a single tree, they are not directly representative to the VOC mixture observed at the top of Kleiner Feldberg and were not added to this study.

GC 2) For the statistical analysis of the two field campaigns (ClearfLo and PARADE) the entire data-set was used. How does your overall conclusion depend on the time of the day? Did you test the small sampling interval averages against the hourly averaging for example for day and nighttime data only? Is it possible that some VOC show decreased variability within the nocturnal boundary layer whereas during daytime the close distance to emission sources and turbulent mixing increase their overall variability?

This is an interesting aspect, which would be worth exploring in more detail. However, the analysed data sets only cover a short amount of time (ClearfLo – 1 week; PARADE – 2 times 1 week), which seems not to be sufficient for good statistics over a diurnal cycle. No day-/nighttime effects were analysed here. The PARADE campaign provides a data set of 4 weeks in total and diurnal cycles were observed for some VOC. The complete analysis described in the manuscript would need to be repeated to analyse day/night effects.

Reply to technical comments:

TC 1) p.2, l.10: "Its actual concentration being determined by the balance between its sources and sinks." It seems to me that the verb in this sentence needs to be "is" rather than "being".

Changed.

TC 2) p.2, l.17: Here, a list of references about in-situ measurements of OH reactivity is provided. However, it should be indicated (e.g. with "e.g.") that this list only presents a fraction of the actual literature.

Changed.

TC 3) p.3, l. 10: ": : : good agreement between measured and calculated OH reactivity have been found." It should be "has" instead of "have".

Fixed.

TC 4) Table 1: Are here averages or median values presented for the mixing ratios and concentrations? What is the given uncertainty? Standard deviation?

The table reports mean and stdev of the mixing ratio and concentration, the OH reactivity is calculated from that mean value. The table caption is has been changed to make that clear.

TC 5) p.7, l.25: I think you do not need the "whether" in this sentence.

Right.

TC 6) p.8, l.8: Here you repeat yourself by having "values" twice in one sentence.

Changed.

TC 7) p.10 Figure 2: It would be great, if you could add a legend to the two graphs explaining the different markers used.

Added.

TC 8) p.10 Table 3: Table 3 basically repeats what is shown in Figure 2. I wonder if it is really necessary to include the same information twice. You might want to decide whether to present the figure or the table. Also, what units did you use to present the range of VOC mixing rations in Table 3?

Units added to the table's caption.

TC 9) p.11 Table 4: Please correct the format of the VOC reactivity unit. Also, to be precise it is the OH reactivity due to the selected VOC.

Corrected.

TC 10) p.12, section heading and terminology: The term "VOC reactivity" can be misleading because atmospheric VOC typically react with various oxidants such as O3, NO3, Cl or OH. Hence, it is more precise to use the terminology OH reactivity. This applies already for most of the presented manuscript (e.g. Title, Figure 3 ect.) but should be checked for consistency, especially in this section 2.2.

The term "VOC reactivity" has been changed to "OH reactivity (of VOC)" throughout the manuscript.

TC 11) p.12, l.13: In the previous section you define the notation for different OH reactivity calculations which depends on the instrumentation, campaign and compounds taken into account. The example shows that OVOC during the ClearfLo campaign only includes acetone. Probably during the Parade campaign it would also include methanol. Then in section 2.2 the OH reactivity was calculated for VOC detected by GC during the ClearfLo campaign. However, what do you mean with TVOC as referred to in line 13?

Explained in line 6 on page 12 now.

TC 12) p.18, l. 20-21: Here, it is referred to Figure 4, which shows the randomly generated data set. In the context of presenting residual slopes as in Figure 9, I found this confusing and it might be a mistake.

It should be Fig. 5. Corrected.

Also, from this point on you look at the residual slopes (as plotted in Figure 9). In the figures and sections before (e.g. Fig. 6, 7, 8) the slope was shown. Is there a reason for not being consistent about that?

The residual of the slopes was introduced to highlight the deviation from the ideal slope of one.

TC 13) p. 24, Table 9: With "Random numbers" do you mean the "Randomly generated data set"?

Yes.

References

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Williams, J., Fischer, H., Harris, G., Crutzen, P., Hoor, P., Hansel, A., Holzinger, R., Warneke, C., Lindinger, W., and Scheeren, B.: VariabilityâĂŘlifetime relationship for organic trace gases: A novel aid to compound identification and estimation of HO concentrations, Journal of Geophysical Research: Atmospheres, 105, 20473-20486, 2000.

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