Anonymous Referee #2

Received and published: 9 October 2018

We would like to thank the reviewer for comments and questions which helped us to improve the manuscript. Referee comments are given in italics, our responses are in normal font. Changes made to the manuscript are marked in blue.

Comments

(1)

page 4, lines 19-20. "The interference is most effective when the amount of added NO is sufficiently high to convert most of the atmospheric HO_2 to OH in the LIF cell" This sentence is followed by the statement that the concentration of NO was reduced by a factor of 10. Does this mean that the conversion of HO_2 to OH in the HO_2 cell is not complete? Could this lead to underestimation of HO_2?

The reduction of NO does not lead to an underestimation of the measured HO_2 concentration. The sensitivity of the HO_2 measurement channel depends on many instrumental parameters, one of which is the HO_2 conversion efficiency. The overall sensitivity is experimentally determined by the calibration, which determines the fluorescence signal for a given HO_2 concentration provided by the calibration source.

(2)

page 5, lines 32-34. "The main reactants are NO and the peroxy radicals themselves, all of which were measured allowing the total loss rates from the individual reactions to be calculated." I am not sure this statement is correct. The ROxLIF technique certainly provides new information, but it still measures the sum of peroxy radicals, so I don't think the authors can claim that all of the peroxy radicals were measured.

The assumption that all RO_2 have similar rate coefficients (with HO_2, other RO_2 and/or NO) is a very common one, but it is still a rather big assumption. The MCM itself uses two different generic rate coefficients for RO_2+RO_2, RO_2+NO and RO_2+HO_2 reactions, depending on the type of peroxy radical. This issue is also mentioned on pages 6 and 7, and may be relevant for the discussion of the RO_2 budget in Section 3.7. Moreover, if part of the argument is that the RO_2 budget is closed within the instrumental uncertainty, but still slightly negative (page 12) than this could be a factor to consider. The authors correctly discuss on page 13 how the assumptions on the nitrate yields, which are a similar issue, affect the conclusions of the paper. But I don't see a similar discussion for the rate coefficients.

We agree with the referee in both points. The ROxLIF technique is measuring the sum of RO_2 radicals and the technique is not equally sensitive to all RO_2 radical species. In the Supplementary Text, we added an explanation how this measurement bias influences our budget analysis (see below). The second point is also true. RO_2 radicals have different rate constants for their reaction with NO, HO_2, and RO_2. The error that comes from the use of effective rate coefficients for the lumped RO_2 in Table 1 will be addressed in the revised text and explained in the Supplementary Text.

In the main paper, Section 4.2 was renamed to "4.2 Radical budgets, their relationships and uncertainties" and the following text was added on page 13.

Another uncertainty is caused by the measurement and incomplete representation of the RO_2 chemistry. Due to the measurement principle of the ROxLIF instrument, only those RO_2 species are measured which are converted in the instrument to HO_2 by reaction with NO. This measurement is suitable to quantify the HO_2 production rate (Equation E5). Among the RO_2 radicals which are not completely captured by ROxLIF are species which produce a new RO_2 radical when they react with NO. As these reactions are neutral with respect to the total amount of RO_2, the RO_2 budget (*D-P*) is not sensitive to the bias of the RO_2 measurement caused by these species (see Supplementary Text).

Other uncertainties in the RO_2 budget are caused by the rate constants for the reactions of RO_2 with NO (Reaction R8, R14), RO_2 (Reaction R15), and HO_2 (Reaction R16) that are given in Table 1 as effective values for the lumped RO_2 radicals. In this work, the uncertainties of the rate coefficients for Reaction R15 and R16 play only a minor role, because the daytime loss of the peroxy radicals was largely dominated by the reaction with NO (see Supplementary Text). The relevant range for the reaction rate constants of different RO_2 species with NO (Reaction R8, R14) is between 8×10^{-12} cm^3s^{-1} and 1.1×10^{-11} cm^3s^{-1} (see Supplementary Text). As a sensitivity test, Figs. S5 and S6 show the budgets of ROx, RO_2 and HO_2 for a rate constant of 1×10^{-11} cm^3s^{-1}. The results are essentially the same as in Figs. 2 and 3 where a rate constant of 9×10^{-12} cm^3s^{-1} was applied for Reaction R8 + R14. Thus, an increased rate constant cannot explain the missing RO_2 sink in the RO_2 budget.

In the Supplementary Text, the following text was included.

Uncertainties related to the measurement and chemistry of RO_2

Uncertainties in the radical budgets may be caused by the measurement and incomplete representation of the RO_2 chemistry. Due to the measurement principle of the applied ROxLIF technique, only those RO_2 species can be measured which are converted to HO_2 by reaction with NO for conditions of the ROxLIF system. This measurement is exactly what is needed to quantify the HO_2 production rate (Equation E5) in the atmospheric HO_2 budget. However, using the measured RO_2 data for the calculation of the RO_2 loss rate (Equation E9) may cause a systematic bias. RO_2 radical species exist which react with NO and produce a new RO_2 radical rather than HO_2. An example is the reaction $(CH_3)_3C(O_2)+NO$ leading to $CH_3O_2+acetone+NO_2$ as products. The result is a low-biased measurement of atmospheric RO_2 radicals. Its use in Equation E9 leads to an underestimation of D_{RO2} since the RO_2 loss leading to new RO_2 species is not included due to the measurement bias. On the other side, the production P_{RO2} in equation E8 is underestimated by the same amount, because the production term for RO_2 species which are produced by RO_2+NO is missing. As a result, the balance term $D_{RO2}-P_{RO2}$ in Fig. 2 remains correct as the production and destruction terms are smaller by the same unknown amount. Another group of RO_2 radicals which are not well captured by ROxLIF are nitrate peroxy radicals, which are formed by the reaction of NO_3 radicals with alkenes. Some nitrate peroxy radical species (e.g., from propene and butenes) react with NO and produce carbonyl compounds and NO_2 as products. The latter reaction constitutes an ROx sink. In the present work, NO_3 reactions with VOCs play a minor role (Section 4.2).

Other uncertainties in the RO_2 budget are caused by the rate constants that are given in Table 1 as effective values for the lumped RO_2 radicals. It is well known that the rate coefficients for the reactions of RO_2 with NO, HO_2, and RO_2 depend on the chemical structure of the RO_2 species. According to Jenkin et al. (2019), experimentally known rate constants for RO_2+NO can be broadly

categorized into three classes: [1] CH_3O_2 (C1), [2] other hydrocarbon ($\geq$ C2) and oxygenated peroxy radicals, and [3] acyl peroxy radicals. At room temperature, recommended rate constants for these categories are 7.7×10^{-12} cm^{3}s^{-1}, 9.0×10^{-12} cm^{3}s^{-1}, and 2.0×10^{-11} cm^{3}s^{-1}, respectively (Jenkin et al., 2019). The MCM value used in Table 1 for Reaction R8 + R14 (9.0×10^{-12} cm^{3}s^{-1}) fits to the second class. The high rate constants for acyl peroxy radicals have no relevance for the budget analysis, because their reaction with NO produces another RO_2 radical. Thus, their reaction does not contribute to the HO_2 production and is neutral in the RO_2 budget as explained above. Published rate constants of the second category range between 8×10^{-12} cm^{3}s^{-1} and 1.1×10^{-11} cm^3 s^{-1} (Jenkin et al., 2019). Here, the lower limit is almost equal to the rate coefficient of CH_3O_2 (first class). As a sensitivity test, Figs. S5 and S6 show the budgets of ROx, RO_2 and HO_2 for a rate constant of 1×10^{-11} cm^{3}s^{-1} (R8 + R14). The results are essentially the same as in Figs. 2 and 3 where a rate constant of 9×10^{-12} cm^{3}s^{-1} is applied. As the RO_2 budget indicates a missing RO_2 sink, a larger rate constant could help resolve the discrepancy. However, the 10% increase of the rate constant for Reaction R8 + R14 in Figs. S5 and S6 is far too small to explain the observed imbalance.

The reaction of RO_2 radicals with NO can form HO_2 (Reaction R8) resulting in radical chain propagation, or produce organic nitrates (Reaction R14) resulting in chain termination. As the branching ratio can be different for each RO_2 species and as most of the organic reactivity was caused by unmeasured VOCs, the branching ratios of most RO_2 species are not known. Typical yields for organic nitrates lie in the range between 1% and 35% (Atkinson et al., 1982; Lightfoot et al., 1992). For the budget analysis (Figs. 2 - 4), an organic nitrate yield of 5% is assumed. Figs. S7 and S8 show cases where higher yields (10%, 20%) are assumed. Higher organic nitrate yields compensate the slightly negative bias of $D-P$ in the ROx budget (Fig. S7). An average yield of 10% would lead to similar difference between production and destruction rate of ROx during daytime, whereas a yield of 20% would result in a slightly positive bias of up to +1 ppbv/h in $D-P$. For the HO_2 production rate, these changes have little impact. Thus, in all cases (80%, 90%, 95% yield of HO_2), the HO_2 budget is balanced within the experimental uncertainties.

Published rate constants for the reaction $RO_2 + HO_2$ (Reaction R16) lie in the range between 0.5×10^{-11} cm^{3}s^{-1} and 2.2×10^{-11} cm^{3}s^{-1} at 298K (Jenkin et al., 2019). In the MCM, a general value of 2.3×10^{-11} cm^{3}s^{-1} (298K) is assumed and scaled by an RO_2 specific factor which is typically 0.5 - 0.7. In the budget analysis we have used the upper limit with a scaling factor of one. Thus, the possible bias of the calculated $RO_2 + HO_2$ rate is in the order of a factor of 2. Under the polluted conditions of the campaign, the loss of RO_2 and HO_2 is largely dominated by NO. The reaction $RO_2 + HO_2$ contributes only a few percent to the ROx loss during daytime and no more than 10% at sunset, when NO is small. Thus, the bias in the calculated ROx loss rate remains well below 5% at daytime. Similar considerations apply to the loss of RO_2 and HO_2, which is also dominated by NO during the day.

Rate coefficients for self and cross reactions of RO_2 are diverse and difficult to parameterize (Jenkin et al., 2019). The rate constants for the most abundant species are generally an order of magnitude smaller than for the reaction R16 ($RO_2 + HO_2$). Self reactions of oxygenated RO_2 and cross reactions of some RO_2 can be as fast as reaction R16 (Jenkin et al., 2019). Overall, $RO_2 + RO_2$ reactions play a smaller role than $RO_2 + HO_2$ reactions in the Heshan campaign. The uncertainty of the RO_2 radical budget due to the lumped rate coefficient for R15 is therefore negligible.
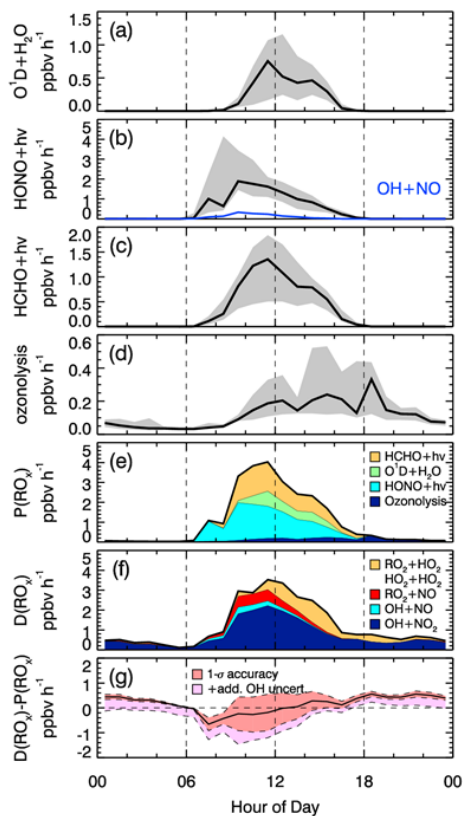
Figure S5 Same as Figure 2, but assuming a rate constant of 1×10^{-11}cm^{-3}s^{-1} for the reaction of RO$_2$ with NO (R8, R14) .
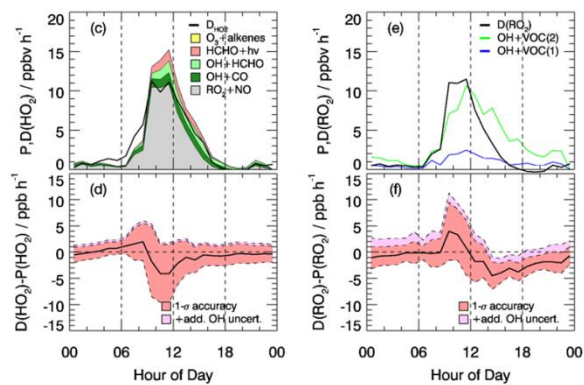

Figure S6 Same as Figure 3, but assuming a rate constant of 1×10^{-11}cm^{-3}s^{-1} for the reaction of RO$_2$ with NO (R8, R14) .

(3)

page 7. The two methods to calculate RO2 production from OH+VOC reactions take into consideration the possible effect of unmeasured VOC, which is correct. However, a similar approach was not taken with regard to unmeasured alkenes that react with ozone. Such missing VOC may be an issue for the calculation of OH sources in E4 and the discussion of the HO2 budget in Section 3.6. The potential problem is acknowledged on page 6, but there is no discussion of how it may affect the conclusions of the paper.

The budget analysis for $RO_2\#$ suggests that there were not many more alkenes present besides the measured ones. We mentioned this point in the original version of the Supplementary Text, but obviously our explanation was not clear. We extended the explanation in the Supplementary Text as follows.

Information about the abundance of alkenes in this campaign can be obtained from the $RO_2\#$ budget analysis. $RO_2\#$ is produced by OH reaction with alkenes, aromatics and large alkanes. The budget analysis (Fig. 3) shows that the calculated production rate $P^{(1)}_{RO2\#}$ from these compounds is balanced by the calculated $RO_2\#$ loss rate. If an essential fraction of the unmeasured VOCs consisted of alkenes, it would increase the $RO_2\#$ production rate correspondingly. Within experimental uncertainty, a doubling of the alkene contribution in the $RO_2\#$ production would be acceptable without disturbing the balance in the $RO_2\#$ budget. Doubling of the alkenes would explain 15% of the missing OH reactivity. In this case, the radical production from ozonolysis, which is less than 0.1 ppbv/h for OH and 0.05 ppbv/h for HO_2 at daytime taking measured species into account, would increase by about a factor of 2. This increase would have a negligible impact on the radical budgets of OH and HO_2.

(4)

page 12, lines 1-2. It is not clear if the authors are discarding the hypothesis of Yang et al (2017) that the missing reactivity is at least partly due to OVOC and, if so, why.

The same question was raised by referee #1. See our response there.

(5)

Figure 3, panels f and g. In one panel the difference between destruction and production is compared to that derived from VOC(1) and in the other is compared to that derived from VOC(2). I see what the authors are trying to do, but it is a bit misleading. Maybe both differences could be shown by adding a third panel for both RO2 and RO2# or maybe different colors could be used.

For clarification, we modified the legends in panels (e) and (g), and we added consistent labels in panels (f) and (g), which make direct reference to Equations E7 and E8.
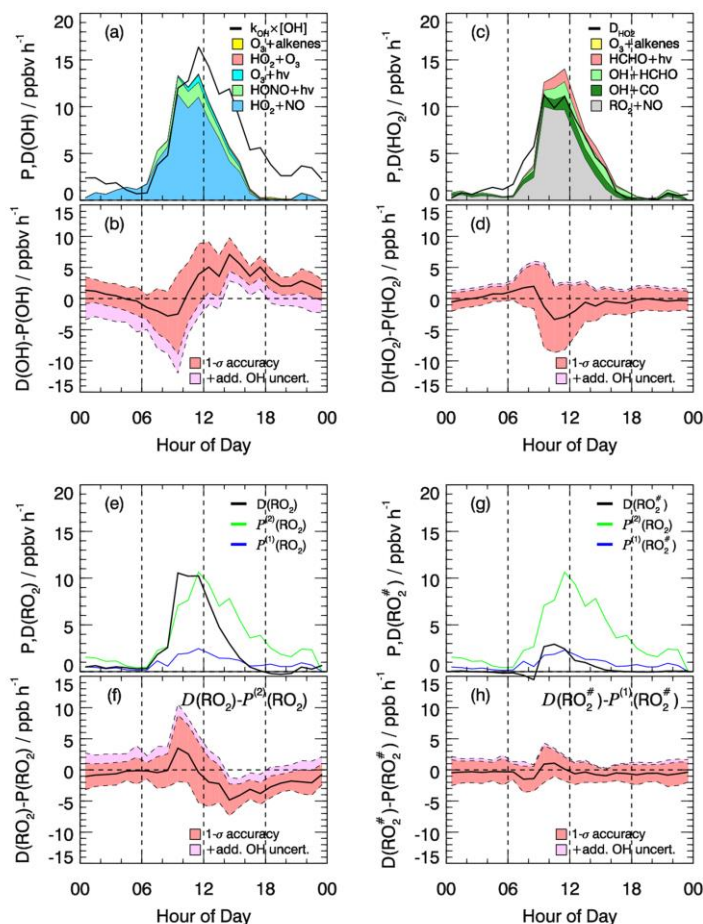
Figure 3 Experimental budgets for OH (a, b), HO$_2$ (c, d), RO$_2$ (e, f) and RO$_2^{\#}$ (g, h). In the respective upper panels (a, c, e, g), solid black lines denote the median total destruction rates. The colored areas in (a) and (c) represent cumulative plots of the production rates from different reactions. The blue solid lines in (e) and (g) denote the production rates $P^{(1)}_{RO2}$ and $P^{(1)}_{RO2\#}$, respectively, calculated from measured VOCs (Equation E7). The green lines represent $P^{(2)}_{RO2}$ calculated from k_{OH}(VOC(2)) (Equation E8). In all four budgets (OH, HO$_2$, RO$_2$, RO$_2^{\#}$) the radical production from ozonolysis is hardly noticeably small. The respective lower panels (b, d, f, h) show the difference between the total destruction and production rates. Red shaded bands indicate the 1σ uncertainty due to experimental errors of the measured quantities (Table S1) and the reaction rate coefficients. The pink shaded areas represent the maximum possible bias from a potential OH interference.

References:

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