Response to reviewers and changes made to the manuscript

We would like to thank all reviewers for their questions and comments, which have helped us to improve the manuscript. Below you find comments to the editor and our detailed answers to the comments of the reviewers. Referee comments are given in italics, our responses are in normal font. Changes made to the manuscript are marked in blue.

Comments to the editor

We corrected a few minor errors which we discovered during the revision of the manuscript and we added clarifications in the text. The corrections and changes do not affect the results and conclusions of the paper.

(1)

On page 14 of the original manuscript (line 18-19), the values of 15% and 30% must read 15 ppbv and 30 ppbv, respectively. The corrected sentence reads:
In the present case, such an RO_2 sink would remove 15 ppbv (22%) of the daily produced RO_2 resulting in an integrated ozone production that is 30 ppbv lower than expected from the rate of VOC oxidation.
Likewise, we corrected the corresponding sentences in the abstract and conclusion section.

(2)

For better understanding of the daily ozone production at Heshan, we added an illustration. The new Figure 5 shows the major reaction pathways and the corresponding reaction rates leading to ozone formation.

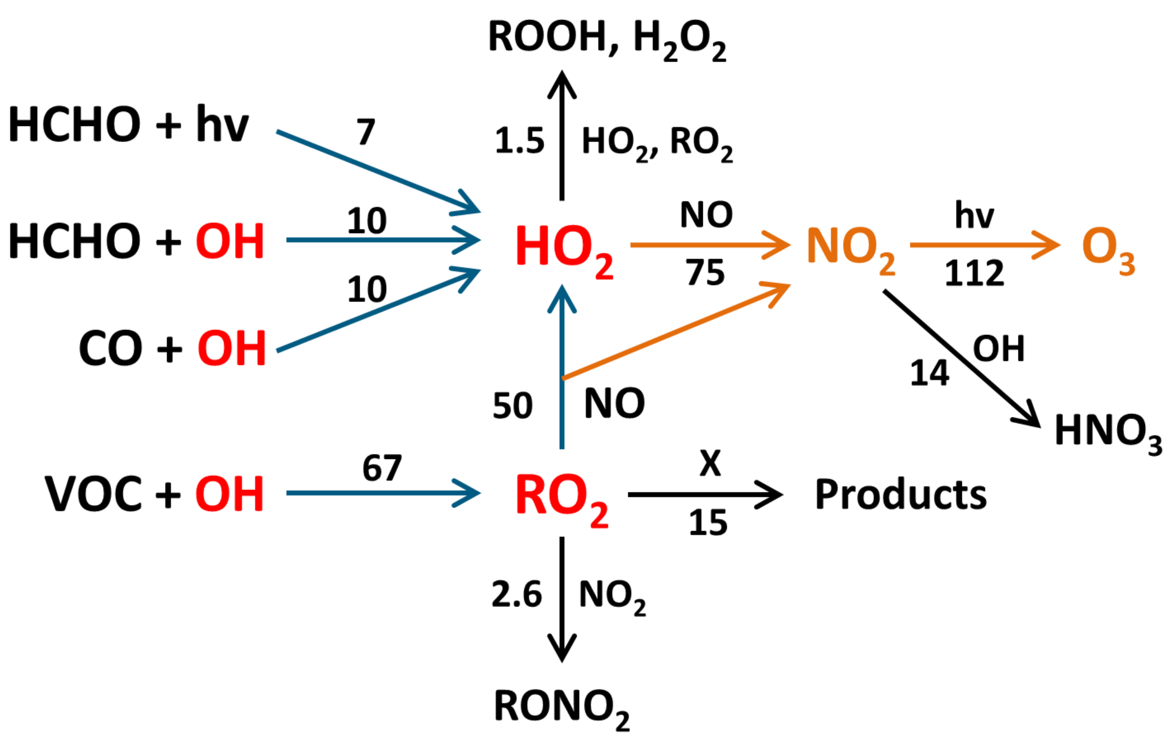
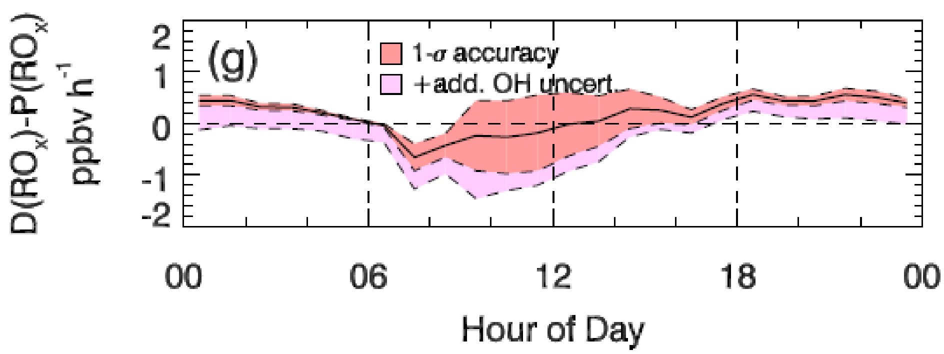


Figure 5 Main reaction pathways leading to photochemical net ozone formation during the Heshan

campaign. Blue arrows show the reaction paths leading to RO_2 and HO_2, yellow arrows indicate the oxidation reactions of NO to NO_2 by peroxy radicals with subsequent NO_2 photolysis yielding ozone. Black arrows represent reactions that remove peroxy radicals or NO_2 and thus reduce ozone production. Numbers represent median daily-integrated reaction rates (ppbv) calculated by equation E12. The value for VOC+OH corresponds to kOH(VOC(2))×[OH] (see equation E8). The reaction with X indicates an unknown process that removes RO_2 without producing NO_2.

(3)

In Figure 2g (original manuscript), *D*(ROx)-*P*(ROx) was incorrectly calculated as the difference of the medians of *D*(ROx) and *P*(ROx). In the revised version, we have recalculated *D*(ROx)-*P*(ROx) as the median of the difference of *D*(ROx) and *P*(ROx), which is more correct. Due to the recalculation, the numerical balance between production and destruction rates improved slightly. However, given the experimental uncertainties, the improvement plays a minor role. The conclusions drawn from the figure remain unchanged.



On page 9 (line 32-34), the description of the figure was revised and a statement about the possible role of NO_3 chemistry for the ROx budget at night was added (see our response to question 12 by Referee #3). During daytime, there is an imbalance between production (P_{ROX}) and destruction (D_{ROX}) rates, which increases from -0.5 ppbv (8:00) to +0.5 ppbv (18:00). The deviations are small (< 15%) compared to the total ROx turnover rate at noontime and can be explained by the experimental errors of the data between 8:30 and 17:30. After sunset until 2 hours after midnight, D_{ROx} remains about 0.5 ppbv/h larger than P_{ROx}. The deviation may be caused, at least partly, by RO_2 formation from reactions of VOCs with NO_3 radicals, for which an upper limit of 0.7 ppbv/h can be estimated (see Section 4.2). The deviation can also largely be explained by experimental errors, when the upper limit of a possible OH interference is included in the total experimental uncertainty (Fig. 2g).

Anonymous Referee #1

Comments

(1)

The authors provide evidence that the missing OH reactivity is due to missing VOCs that react to produce RO_2 radicals. While this provides strong evidence that the missing OH reactivity is not due to radical termination reactions, it is not clear from the discussion on pages 11 and 12 that this rules out that the missing reactivity is due to unmeasured OVOCs as discussed by Yang et al. (2017). This should be clarified.

We do not rule out that unmeasured OVOCs may be responsible for the missing OH reactivity and produce RO_2 by reaction with OH. Many oxygenated VOCs (ketones, C2- and higher aldehydes, C3- and higher alcohols) produce RO_2 when they react with OH. Examples are acetaldehyde, acetone, MACR, MVK, methyl glyoxal etc. Other OVOCs like formaldehyde, glyoxal etc. do not produce RO_2.

For clarification, we have modified the text (bottom of page 11 and top of page12) as follows.

Many oxygenated VOCs produce RO_2 when they react with OH. Examples are acetaldehyde and higher aldehydes, acetone and higher ketones, MACR, MVK, and methyl glyoxal, all of which were not measured in the present study. In the following discussion we assume based on the considerations given above that the missing reactivity in the present study is entirely due to VOCs (including also OVOCs) which can produce RO_2 by reaction with OH.

(2)

One of the main conclusions of the paper is that the budget analysis suggests a missing RO_2 radical sink and an OH radical source in the afternoon. While the authors suggest that RO_2 isomerization reactions from isoprene and methacrolein may not be important given the low concentrations of isoprene measured, there may be other autoxidation processes that could be important in the afternoon when NO concentrations are low (see Praske et al., PNAS, 115, 64-69, 2018). This should be discussed in more detail.

We agree that this topical aspect deserves a deeper discussion. In fact, there is a fast growing body of literature reporting experimental and theoretical results about autoxidation reactions which involve H-migration in RO_2 species at atmospheric conditions that can possibly regenerate OH radicals at low NO conditions. We extended the discussion in Section 4.2. The revised section reads as follows.

An alternative explanation for the non-closure in the OH and RO_2 budgets would be a chemical mechanism that effectively converts RO_2 to OH. Unimolecular isomerisation and decomposition reactions of RO_2 can be such an OH source when the competing reaction with NO is slow. This chemistry is known for a long time as autoxidation, for example, in low-temperature combustion (e.g., Cox and Cole, 1985; Glowacki and Pilling, 2010). Its potential relevance for atmospheric chemistry at ambient temperatures has only recently been recognized (e.g., Peeters et al., 2009; da Silva et al., 2010; Crounse et al., 2013; Praske et al., 2018). Autoxidation involves an intramolecular H-shift in the RO_2 molecule leading to a hydroperoxy alkyl radical, which is often named QOOH. This radical can generally undergo various types of reactions such as reaction with O_2 producing an oxygenated VOC + HO_2, or decomposition to an oxygenated VOC by elimination of OH from the -OOH group (e.g., Peeters et al., 2009; daSilva et al., 2010; Crounse et al., 2013; Praske et al., 2018). Another path is the addition of O_2 forming a hydroperoxy peroxy radical (O_2)QOOH. This new peroxy radical can then react with NO, HO_2, RO_2, or undergo another internal H-shift reaction. Repetitive sequential H-shift reactions followed by O_2 addition lead to highly oxidized RO_2 radicals which produce highly oxidized molecules (HOMs) by radical termination reactions (e.g., Ehn et al., 2014, 2017; Jokinen et al., 2014). Due to their low vapour pressure, HOMs are efficient precursors for organic particles, which are produced from the original VOCs with yields in the low percent range (e.g., Ehn et al., 2014; Jokinen et al., 2015).

RO_2 isomerisation producing HOx radicals is known to occur in the oxidation of isoprene (Peeters et al., 2009, 2010, 2014; Da Silva et al., 2010; Crounse et al., 2011; Fuchs et al., 2013; Teng et al., 2017) and methacrolein (Crounse et al., 2012; Fuchs et al., 2014). In Heshan, the production rate of isoprene peroxy radicals from the reaction of isoprene with OH never exceeded 0.5 ppbv/h. Even if every isoprene derived RO_2 radical regenerated one OH molecule (which is not likely because of the competing reaction with NO), the process could explain only a small fraction of the missing OH production rate. The concentration of methacrolein (MACR) was not measured, but is generally not larger than that of isoprene (Karl et al., 2009; Shao et al., 2009). Since the OH rate constant is smaller than that for isoprene, OH regeneration by unimolecular reactions of MACR derived RO_2 is expected to be even less important.

Besides for isoprene and methacrolein, autoxidation of RO_2 leading to HOx formation has been experimentally studied for only few other VOCs, including 3-pentanone (Crounse et al., 2013), glyoxal (Lockhart et al., 2013), n-hexane and 2-hexanol (Praske et al., 2018), hydroxymethyl hydroperoxides (Allen et al., 2018), and 2-hydroperoxy-2-methylpentane (Praske et al., 2019). While isoprene and methacrolein chemistry is especially important in biogenically controlled environments, the new studies demonstrate that autoxidation can also be expected to play a role in urban atmospheres when NO concentrations are as low as 500 pptv (cf., Praske et al., 2018). Systematic theoretical studies have shown that the rates of H-shifts in RO_2 depend very much on their chemical structure (e.g., Crounse et al., 2013; Otkjær et al., 2018; Møller et al., 2019) and range from 10^{-4} s^{-1} to 10 s^{-1} at ambient temperature. Low rate coefficients can be expected, for example, for 1,5-H or 1,6-H shift reactions in linear alkyl radicals, whereas the presence of (multiple) functional groups like -OH, -OOH, or -CHO may increase the H-shift rate by orders of magnitude. The possible yield of OH, HO_2, or higher-oxidized RO_2 radicals from a hydrogen shift depends on the chemical structure and functionality. Elimination of OH or HO_2 is generally supported by the presence of functional groups (e.g., -OH, -OOH, or -CHO).

In the present campaign, the potential conversion of RO_2 to OH by a unimolecular reaction would require a rate of about 0.08 s^{-1} to close the budgets of OH and RO_2, if all measured RO_2 radicals could produce OH from H-shift reactions (Fig. S4). Although the rate is in the possible range of H-shift reactions, it is questionable if a major fraction of RO_2 was structurally capable to undergo a fast H-shift leading to OH formation. As approximately half of the measured OH reactivity is likely due to unmeasured VOCs with unknown speciation and owing to the general lack of kinetic and mechanistic studies for specific RO_2 radicals, it is not possible to be more quantitative here. If the missing reactivity at Heshan was caused by photochemically aged, functionalized oxygenated VOCs, there is a chance that RO_2 radicals from these compounds could have contributed significantly to the missing RO_2 sink, or missing OH source. If autoxidation played a significant role, additional HO_2 formation from H-shift reactions would also be expected. However, the closed HO_2 budget gives no indication for this.

In Page 15 Line 5, our statement about the X mechanism was revised as follows.

Here, the NO concentration of 0.4 ppbv corresponds to the rate coefficient of 0.08 s^{-1} discussed above. When using the X mechanism, the closure of the HO_2 and RO_x budgets remains unaffected.

The caption of Figure S3 (now S4) was revised as follows.

Figure S4: Same as Fig. 3, but with additional RO_2 conversion to OH assuming a first-order rate coefficient of 0.08 s^{-1}. This scenario can also be seen as an application of the X mechanism which recycles OH by the hypothetical sequence $RO_2 + X \rightarrow HO_2$, $HO_2 + X \rightarrow HO_2$ with X equivalent to 0.4 ppbv NO.

(3)

The authors provide some evidence that their OH measurements are free from interferences through some chemical modulation tests. While the majority of these measurements appear to be below the detection limit for the instrument, it is not clear from Table 3 whether the data presented represent an average of multiple tests during the time period indicated, or a single modulation experiment. It would useful clarify the number and duration of the modulation experiments, perhaps by showing some of the raw data from the experiments in the supplement.

The results presented in Table 3 are an average of multiple tests during the specified time period. We have added the following explanation in the caption of Table 3 and included as an example a new Figure S3 in the Supplement.

Given numbers are average values of multiple tests that were performed in the specified time period (as an example, see Fig. S3).

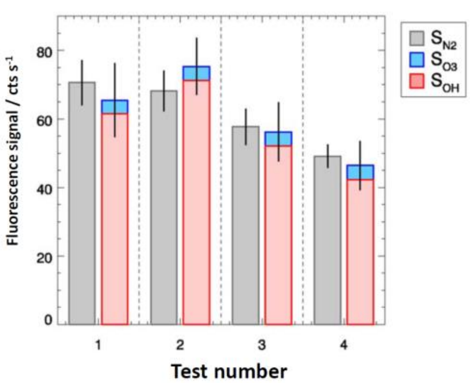


Figure S3 Results from the chemical modulation tests performed on 31 October 2014 between 12:50 and 13:50. The measured OH signal without scavenger (S_{N2}) can be explained within experimental errors by the sum of the signal from ambient OH (S_{OH}) and the known interference from O_3 (S_{O3}). Error bars denote 1σ statistical errors. S_{OH} is calculated by the expression (S_{N2} - $S_{propane}$)/ε, where $S_{propane}$ is the signal with scavenger (propane) and ε is the efficiency of scavenging (for details, see Tan et al., 2017). A fluorescence signal of 60 cts/s is equivalent to an OH concentration of 1×10^{7} cm^{-3}.

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Anonymous Referee #2

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 (≥ 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^3s^{-1}, 9.0×10^{-12} cm^3s^{-1}, and 2.0×10^{-11} cm^3s^{-1}, respectively (Jenkin et al., 2019). The MCM value used in Table 1 for Reaction R8 + R14 (9.0×10^{-12} cm^3s^{-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^3s^{-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^3s^{-1} (R8 + R14). The results are essentially the same as in Figs. 2 and 3 where a rate constant of 9×10^{-12} cm^3s^{-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 RO_x 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^3s^{-1} and 2.2×10^{-11} cm^3s^{-1} at 298K (Jenkin et al., 2019). In the MCM, a general value of 2.3×10^{-11} cm^3s^{-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.

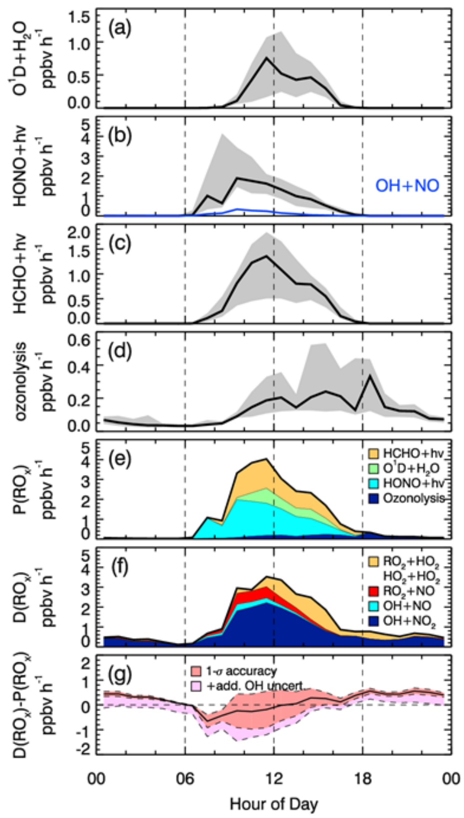

Figure S5 Same as Figure 2, but assuming a rate constant of $1\times10^{-11}cm^{-3}s^{-1}$ for the reaction of RO_2 with NO (R8, R14) .

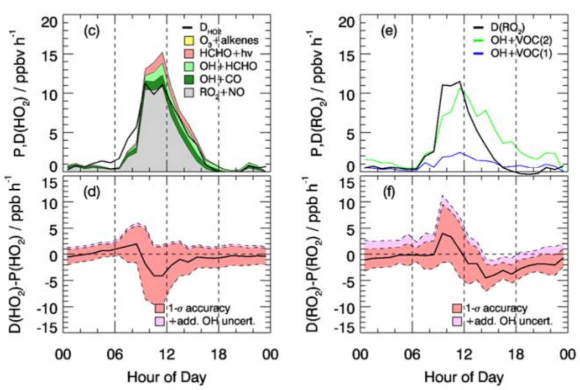

Figure S6 Same as Figure 3, but assuming a rate constant of $1\times10^{-11}cm^{-3}s^{-1}$ for the reaction of RO_2 with NO (R8, R14) .

(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.

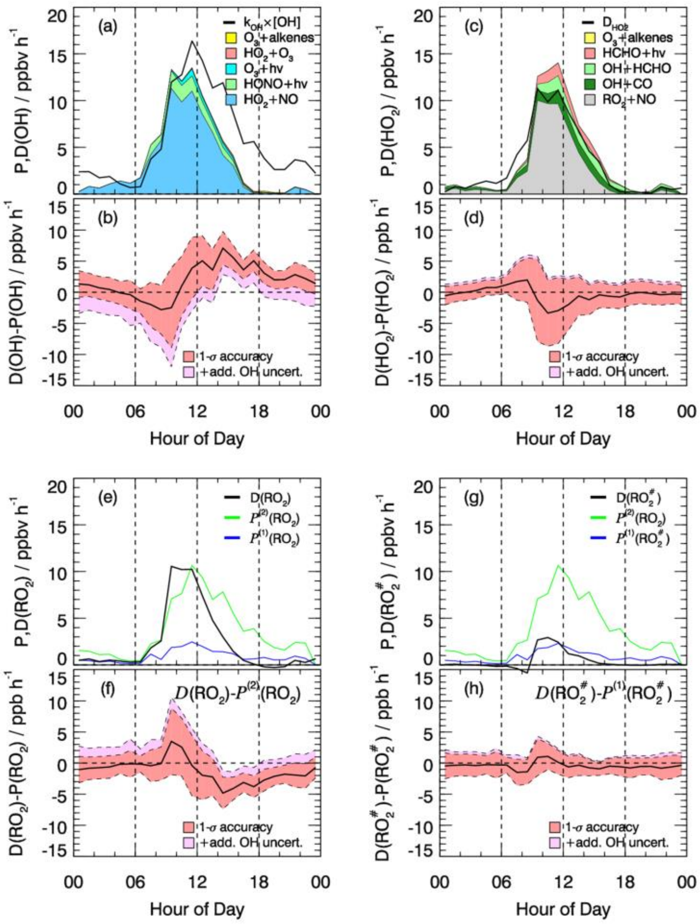

Figure 3 Experimental budgets for OH (a, b), HO_2 (c, d), RO_2 (e, f) and $RO_2^{\#}$ (g, h). In the respective upper panels (a, c, e, g), solid black lines denote the median total destruction rates. The colored areas in (a) and (c) represent cumulative plots of the production rates from different reactions. 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.

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Anonymous Referee #3

Comments

(1)

page 1, line 19: "In case of RO2, the budget can only be closed when the missing OH reactivity is attributed to unmeasured VOCs. Thus, the existence of unmeasured VOCs is directly confirmed by RO2 measurements." This is a likely but not exclusive explanation. I recommend to rephrase the sentences: "In case of RO2, the budget could be closed by attributing the missing OH reactivity to unmeasured VOCs. Thus, unmeasured VOCs are directly linked to the RO2 measurements."

We changed the sentence as follows.
In case of RO_2, the budget could be closed by attributing the missing OH reactivity to unmeasured VOCs. Thus, the presumption of the existence of unmeasured VOCs is supported by RO_2 measurements.

(2)

page 1, line 25: "These observations suggest the existence of a chemical mechanism that converts RO2 to OH without the involvement of NO. Please quantify the average contribution of this channel to the total turnover rate.

We added conversion rates in the sentence, which reads now
These observations suggest the existence of a chemical mechanism that converts RO_2 to OH without the involvement of NO, increasing the RO_2 loss rate at daytime from 5.3 ppbv/h to 7.4 ppbv/h, on average.

(3)

page 2, line 36: " ... tendency to underpredict OH under low-NOx conditions" . Please define the term "low-NOx conditions".

We changed the sentence to
... tendency to underpredict OH under low-NOx conditions (NO < 300 pptv).

(4)

Page 4, line 4: Please explain in the supplement table caption the term "RO2#".

In the footnotes of Table S1, we included the following explanation.
RO_2# are organic peroxy radicals from large alkanes (> C4), alkenes (including isoprene) and aromatics.

(5)

Page 4, line 12: Please quantify how much OH is internally removed.

We added the following the sentence.
In the OH detection cell, scavenging of artificially produced OH by the added propane is calculated to be less than 0.3%.

(6)

Page 4, line 13: How did you account for possible impurities in N2?

We added the following explanation.
For nitrogen, we used research grade purity (>99.9990%). A GC analysis of the nitrogen showed no significant contamination by VOCs, which would scavenge OH in the chemical modulation system.

(7)

Page 4, line 21: Please quantify the upper limit of the HO2 interference.

We added the value (5%) for the upper limit of the interference to the text.

(8)

Page 4, line 33: How did you quantify the HO2 background signal?

We added the following explanation on Page 4 Line 33.
The signal was regularly determined in humidified synthetic air during calibration and found to be stable over the campaign. It is equivalent to $(2\pm1)\times10^{7}$ cm^{-3} and $(1\pm1)\times10^{7}$ cm^{-3} for HO_2 and RO_2, respectively, and is routinely subtracted from the measurements.

(9)

Page 5, line 8: It is unclear which instruments have been used for CO and CO2 in this study.

We added a sentence on Page 5 Line 9.
The CO and CO_2 measurements from the Thermo Electron and Picarro instruments agreed within the instrumental accuracies. The Picarro measurements were used in this work due to the better data coverage.

(10)

Page 6, line 36: Please quantify the impact of the assumption that the nitrate yield is 5%. Please add a reference for the nitrate yield.

In the text (page 6, line 36), we refer to section 2.3.1 where we have provided references and the range of possible nitrate yields. The impact of our assumption of a yield of 5% is explained in the discussion (Section 4.2, Additional uncertainties in the budget analyses) and in the corresponding Supplementary Text).

(11)

Page 7, line 17: Despite the fast NO3 photolysis Liebmann et al. , 2018, found during daytime a fractional loss of NO3 of 25% by reaction with BVOC. What is the daytime NO3 production rate in this study and what would be an upper limit for its contribution?

This is a very good question. We revised the text as follows.

NO_3 is produced by reaction of NO_2 with ozone. It is generally assumed that during the bright hours of the day, NO_3 is predominantly destroyed by photolysis and reaction with NO. Recently, Liebmann et al. (2018) reported measurements in a forested environment in southern Germany demonstrating that more than 25% of daytime NO_3 was removed by biogenic VOCs. The possible role of NO_3 reactions with VOCs at Heshan is discussed in Section 3.4 and 4.2.

In the presentation of the ROx budget (Section 3.4) a comment about NO_3 was included (see Comment 3 to the editor). In the general discussion of uncertainties of the radical budgets (Section 4.2) the following text was added.
Reactions of NO_3 with VOCs are an additional RO_2 source which is neglected in the budget calculation in Section 2.3.4. The relevance can be estimated from the production rate of NO_3, which is calculated from the reaction of NO_2 with O_3 ($k(NO_2+O_3)= 1.47\times10^{-13}\times\exp(-2470/T)$; MCM3.3.1). In this campaign, the NO_3 production rate was in the order of 1.4 ppbv/h and 0.7 ppbv/h at day- and nighttime, respectively. Because NO_3 is efficiently photolysed in the bright hours of the day, it is generally assumed that it plays a negligible role as an oxidant during daytime. Liebmann et al. (2018) have recently shown that this is not always the case. They reported measurements in a forested environment in southern Germany demonstrating that more than 25% of the daytime NO_3 reacted with biogenic VOCs. Under the conditions at Heshan 2014, the main loss process at daytime is the reaction with NO. If we neglect unmeasured VOCs, the percentage removal of NO_3 in the morning is 96% by NO, 3% by photolysis, and 1% by measured VOCs. In the afternoon, the corresponding values are 72%, 21%, and 7%. Thus, the estimated RO_2 production rate from NO_3 reactions with known VOCs was probably not more than 0.1 ppbv/h at daytime. It is conceivable, that unmeasured VOCs, which probably accounted for 50% of the OH reactivity, contributed by a similar magnitude. During daytime, these contributions are relatively small compared to the total production rate of RO_2. The tendency is to slightly increase the imbalance between the production and destruction rate of RO_2 observed in the afternoon (Fig. 3). At sunset and in the night, the NO_3 production rate of 0.7 ppbv/h can be considered as an upper limit for the RO_2 production. This value can possibly explain at least partly the imbalance of about 0.5 ppbv/h in the ROx budget after sunset (Fig. 2).

(12)

Page 9, line 38, What is the upper limit of ROx production by NO3 during night time, i.e. what is the NO3 production rate?

See our reply to comment (11) above.

(13)

Page 10, line 24 Is it the only exclusive explanation or a possible explanation that fits the result ?

It is a possible and plausible explanation. We revised the sentence.
Once the missing OH reactivity is attributed to unmeasured VOCs, the resulting production rate $P^{(2)}_{RO2}$ calculated by Equation E8 (Fig. 3e) matches D_{RO2} relatively well.

(14)

Page 11, line 6: "The completeness of the radical measurements allows a budget analysis for all radicals (OH, HO2, RO2) based on experimental data only, ...". Please add: "under the assumption that for the production and loss rates all relevant species were measured."

We added the sentence as suggested.

(15)

Page 11, line 9: How do you define daytime?

In Section 3.1 we added the following definition.
In this work, conditions with $j_{O1D} > 1\times10^{-6}$ s^{-1} are referred to as daytime conditions lasting from 6:00 to 18:00 local time.
On page 11, line 9, we added the time window (6:00 to 18:00).

(16)

Page 11, line 30: It is not obvious that under NOx regimes, controlling radical propagation and termination schemes, the resulting intermediates or even the emitted VOC found in Yang et al are comparable with the ones in this study.

We agree and changed the sentence.
Although the percentage value is smaller than in the present paper (50%), the absolute values for the OH reactivity from unmeasured reactants are comparable. The speciation of the missing reactivity, however, can be different because the higher NOx loading in the period analyzed by Yang et al. (2017) may lead to different photochemical products and may be correlated with different VOC emissions.

(17)

Page 12, line 4: Please specify uncertainties.

We modified the sentence and added uncertainties.
The imbalances in the OH, HO_2, and RO_2 budgets (*D*-*P*) reach median values of up to (7±2.5) ppbv/h, -(3±5) ppbv/h, and -(5±2.5) ppbv/h, respectively, during the day.

(18)

Page 13, line 35 Please quantify "negligible" including upper limit for dry deposition

We modified the sentence and added loss rates for ozone.
Chemical loss of ozone by photolysis (R2), ozonolysis reactions (R4) and dry deposition is neligible under the given conditions. Calculated losses of ozone by photolysis and ozonolysis are not larger than 0.2 ppbv/h. The dry deposition rate at daytime is estimated to be no more than 1 ppbv/h assuming a mixed boundary layer height of 1km and a maximum deposition velocity of 1 cm/s (e.g., Weseley et al., 2000).

(19)

Page 13, line 36&37; Page 14 line 7 : Specify uncertainties

We added uncertainties. The sentence reads now

… a daily integrated net ozone production of (102±31) ppbv is calculated (06:00 h to 18:00h). For comparison, the daily integrated $OH+NO_2$ term is (14±3) ppbv.

(20)

*Page 14, line 4: Please include the statement that the loss term HO2*NO generating NO2 can be replaced by the production term of HO2 under the assumption that other HO2 losses, like HO2+RO2, HO2+HO2 are negligible.*

We added the following sentence.
This replacement implicitly assumes that other HO_2 losses such as HO_2+RO_2 and HO_2+HO_2 are negligible, which is valid during this study.

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Experimental budgets of OH, HO_2 and RO_2 radicals and implications for ozone formation in the Pearl River Delta in China 2014

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Abstract. Hydroxyl (OH) and peroxy radicals (HO_2, RO_2) were measured in the Pearl River Delta which is one of the most polluted areas in China, in autumn 2014. The radical observations were complemented by measurements of OH reactivity (inverse OH lifetime) and a comprehensive set of trace gases including carbon monoxide (CO), nitrogen oxides (NO_x = NO, NO_2) and volatile organic compounds (VOCs). OH reactivity was in the range between 15 s^{-1} and 80 s^{-1}, of which about 50% was unexplained by the measured OH reactants. In the three weeks of the campaign, maximum median radical concentrations were 4.5×10^6 cm^{-3} for OH at noon, and 3×10^8 cm^{-3} and 2.0×10^8 cm^{-3} for HO_2 and RO_2, respectively, in the early afternoon. The completeness of the daytime radical measurements made it possible to carry out experimental budget analyses for all radicals (OH, HO_2, and RO_2) and their sum (ROx). The maximum loss rates for OH, HO_2, and RO_2 reached values between 10 ppbv/h and 15 ppbv/h during daytime. The largest fraction of this can be attributed to radical ~~interconveresion~~ interconversion reactions while the real loss rate of ROx remained below 3 ppbv/h. Within experimental uncertainties, the destruction rates of HO_2 and the sum of OH, HO_2, and RO_2 are balanced by their respective production rates. In case of RO_2, the budget could be closed by attributing the missing OH reactivity to unmeasured VOCs. Thus, the presumption of the existence of unmeasured VOCs is supported by RO_2 measurements.~~In case of RO_2, the budget can only be closed when the missing OH reactivity is attributed to unmeasured VOCs. Thus, the existence of unmeasured VOCs is directly confirmed by RO_2 measurements.~~ Although the closure of the RO_2 budget is greatly improved by the additional unmeasured VOCs, a significant imbalance in the afternoon remains indicating a missing RO_2 sink. In case of OH, the destruction in the morning is compensated by the quantified OH sources from photolysis (HONO, O_3), ozonolysis of alkenes and OH recycling (HO_2+NO). In the afternoon, however, the OH budget indicates a missing OH source of (4-6) ppbv/h. The diurnal variation of the missing OH source shows a similar pattern as that of the missing RO_2 sink so that both largely compensate each other in the ROx budget. These observations suggest the existence of a chemical mechanism that converts RO_2 to OH without the involvement of NO, increasing the RO_2 loss rate at daytime from 5.3 ppbv/h to 7.4 ppbv/h, on average. The photochemical net ozone production rate calculated from the reaction of HO_2 and RO_2 with NO yields a daily integrated amount of 102 ppbv ozone with daily integrated ROx primary sources being 22 ppbv in this campaign. ~~This value~~The produced ozone can be attributed to the oxidation of measured (18%) and unmeasured (60%) hydrocarbons, formaldehyde (14%) and CO (8%). An even larger integrated net ozone production of 140 ppbv would be calculated from the oxidation rate of VOCs with OH, if HO_2 and all RO_2 radicals would react with NO. However, the unknown RO_2 loss (evident in the RO_2 budget) causes ~~30%~~30 ppbv less ozone production than would be expected from the VOC oxidation rate.

1 Introduction

Hydroxyl radicals (OH) constitute the major atmospheric oxidant which is produced in the global troposphere by UV photolysis of ozone (Levy, 1971). The photolysis produces electronically excited $O(^1D)$ atoms which react with water molecules to form OH. In the polluted lower atmosphere, OH can also be produced efficiently by photolysis of nitrous acid (HONO). The reaction with OH initiates the degradation of most trace gases (e.g., CO, VOCs), which leads in many cases to the formation of peroxy radicals, including hydroperoxy radicals (HO_2) and organic peroxy radicals (RO_2, R = alkyl group). In the presence of nitric oxide (NO), peroxy radicals recycle OH, an important mechanism that increases the oxidizing power of the atmosphere. The above reactions and other fundamental reactions controlling the formation and destruction of ROx radicals are listed in Table 1 (Ehhalt, 1999). The reaction of peroxy radicals with NO has another important implication. NO_2 is formed as a product which can be photolyzed. The photodissociation produces ground-state oxygen atoms $O(^3P)$, which combine with O_2 and form ozone. The combination of these reactions (R8, R9, and R11) establishes the basic mechanism of photochemical ozone formation in the troposphere (Fishman et al., 1979).

China is a country with a large population and a fast-growing economy, which has caused increasing air pollution during the last decade (Chan and Yao, 2008). However, only few field campaigns have been carried out so far studying photochemistry under polluted conditions in China with the support of OH and peroxy radical measurements. The campaigns were performed in the Pearl River Delta in southern China (Lu et al., 2012; Hofzumahaus et al., 2009) and in the North China Plain around Beijing (Tan et al., 2018b; Tan et al., 2017; Fuchs et al., 2017; Lu et al., 2013; Tan et al., 2018a). Both large regions are densely populated and characterized by air pollution from energy production, traffic, industry, and farming. Chemical box model simulations of OH concentrations have shown general good agreement with measured OH in these regions at NO concentrations above 1 ppbv, but a tendency to underpredict the measured OH at less than 1 ppbv NO. The largest underprediction of OH by a factor of 3 - 5 was observed in Backgarden near Guangzhou in Pearl River Delta (PRD) in summer 2006 (Hofzumahaus et al., 2009). The PRIDE-PRD 2006 (Program of Regional Integrated Experiments of Air Quality over the Pearl River Delta, 2006) campaign was characterized by high OH reactivities with mean daytime values of (20 - 50) s^{-1}, where biogenic isoprene and its oxidation products made a contribution of 40% in the afternoon. The results of this campaign showed similarities to those from studies in forested regions, where a model underprediction of OH by up to a factor of ten was reported in isoprene rich air (Tan et al., 2001; Ren et al., 2008; Lelieveld et al., 2008; Pugh et al., 2010; Whalley et al., 2011). The unexplained OH in forests and in the Pearl River Delta was generally assumed to be caused by an unknown OH recycling mechanism that is likely linked to the photochemical degradation of isoprene. In fact, subsequent research discovered previously unknown HOx regeneration reactions, which involve unimolecular isomerisation and decomposition reactions of RO_2 in the oxidation of isoprene (Peeters et al., 2014; Peeters and Muller, 2010; Peeters et al., 2009; da Silva, 2010; Crounse et al., 2011; Fuchs et al., 2013; Teng et al., 2017) and methacrolein (Crounse et al., 2012; Fuchs et al., 2014). These reactions do not require NO and explain an OH enhancement by a factor of about two when the OH loss is dominated by isoprene (Fuchs et al., 2013). The mechanism is, however, not sufficient to resolve the large model-measurement discrepancies previously reported.

Another possible reason for the high OH observations could be an interference in the OH measurements. Artefacts of up to 80% have been reported when OH was measured by laser-induced fluorescence (LIF) in forest environments (Mao et al., 2012; Hens et al., 2014; Novelli et al., 2014; Feiner et al., 2016). The interference was presumably caused by oxidation products of biogenic VOCs in the measuring system and was quantified by chemical modulation of ambient OH before the measured air enters the device. When the measurements were corrected for the artefact, the measured OH could be explained by a photochemical box model (Hens et al., 2014; Feiner et al., 2016). In other field studies, where different LIF instruments were used, chemical modulation resulted in only marginal unexplained OH signals at the instrumental limit of detection. One study was in an isoprene rich forest (Griffith et al., 2016), the other in the polluted North China Plain (Tan et al., 2017). In both studies, the models could explain the OH measurements relatively well, but showed a tendency to underpredict OH under low-NOx conditions (NO < 300 pptv). These discrepancies could not be explained by OH measurement artefacts. Thus, while some of the previously reported high OH observations could have been affected by measurement interferences, there are also indications for an incomplete understanding of radical recycling in VOC rich atmosphere.

In the present paper, we report new radical measurements in PRD during the campaign PRIDE-PRD2014 together with measurements of a large set of atmospheric trace gases. The campaign took place in a suburban area near Guangzhou and was carried out in autumn 2014, the enhanced pollution period for PRD, to elucidate the radical chemistry and secondary pollution formation. Compared to the previous campaign PRIDE-PRD2006, RO_2 was measured in addition to OH and HO_2 radicals. Chemical modulation was applied to test the OH instrument with respect to possible OH interferences. In the present work, an experimental budget analysis approach is used to quantify the main chemical reactions that control the radical abundances. This approach is possible, as the production and destruction rates of all radical species can be constrained by measurements. The concept has been applied before for OH, when its loss rate could be constrained by OH reactivity measurements (e.g., Shirley et al. ,2006; Hofzumahaus et al., 2009; Whalley et al., 2011; Griffith et al., 2013; Hens et al., 2014). However, the budget analysis for HO_2 and RO_2 was generally done by chemical box models due to missing RO_2 measurements. Here, the completeness of the radical measurements at daytime is used for the first time to quantify the production and destruction processes for all radicals (OH, HO_2, RO_2) and their sum (ROx) and to analyze their role in photochemical ozone formation. New evidence is found for missing radical recycling under low NOx conditions ~~that~~ which is a source of OH, but not of ozone.

2 Methodology

2.1 Measurement site

The field campaign took place at a long-term monitoring station, the Guangdong Atmospheric Supersite of China (112.929° E, 22.728° N), which is located about 6 km south-west of the city of Heshan. The site is situated on a 60 m high hill, surrounded by woods, small villages, and factories in the surrounding area. A closest highway is about 2 km away to the North West and showed moderate traffic during the measurement campaign. Two major cities, Guangzhou and Foshan, are located at a distance of 50 km north-east of the site. The measurement site is located about 140 km south west of the measurement site (Backgarden) of the former PRIDE-PRD 2006 campaign. The campaign was carried from October to November to be representative for the photochemical polluted season in PRD (Zhang et al., 2008).

2.2 Instrumentation

An overview of the instrumentation used for the radical budget analysis is given in Table S1. The inlets of all instruments were located close to the radical measurement inlets at a height of 1.7 m above the roof of the building and 20 m above ground.

2.2.1 Radicals

OH and HO_2 radicals were measured by the Peking-University Laser Induced Fluorescence system (PKU-LIF), which was built by Forschungszentrum Jülich (FZJ). OH radicals are detected by laser-induced fluorescence at 308 nm in a gas expansion inside a low-pressure (4 hPa) measurement cell (Hofzumahaus et al., 1996;Holland et al., 2003). In a second cell, HO_2 radicals are chemically converted with NO yielding OH, which is detected by LIF (Fuchs et al., 2011). The PKU-LIF instrument was applied first at Wangdu in the North-China Plain in summer 2014 (Tan et al., 2017). It was then moved to the Heshan site for the present study. At both sites, the PKU-LIF system was complemented by devices from FZJ to measure RO_2 (ROx-LIF) and OH reactivity (k_{OH}). In the ROx-LIF system, the radicals RO_2, HO_2, and OH are quantitatively converted to HO_2 in a pre-reactor by addition of 0.7 ppmv of NO and 0.11% of CO at a total pressure of 25 hPa. In a second stage at lower pressure (4 hPa), the HO_2 is further converted by a large excess of 0.5% NO to OH, which is then detected by LIF (Fuchs et al., 2008). RO_2 concentrations are calculated from the total sum of ROx (from ROxLIF) by subtracting the contributions of OH and HO_2 measured in the other two detection chambers. A detailed description of the whole measurement system is given by Tan et al. (2017). Due to a technical problem, the integration time for the radical measurements in Heshan was increased to 5 min to achieve 1σ detection limits of $3.9\times10^5 cm^{-3}$ for OH, $1.2\times10^7 cm^{-3}$ for HO_2 and $0.6\times10^7 cm^{-3}$ for RO_2 (Table S1). The accuracy of the calibrations depends on the uncertainty of the calibration source (10%, 1σ) and the reproducibility of the calibrations, resulting in total accuracies of ±13%, ±20% and ±26% for OH, HO_2, and RO_2, respectively (Table S1).

As outlined by Tan et al. (2017), attention was paid to possible interferences in the measurement of HOx. Like in the Wangdu campaign, chemical modulation was applied on several occasions to test whether the OH measurements obtained normally by laser wavelength modulation are perturbed by artificial OH formation in the detection cell. Such kind of interference has been detected in some LIF instruments by applying chemical modulation in field campaigns (Mao et al., 2012; Novelli et al., 2014; Feiner et al., 2016). The chemical modulation system used at Wangdu and Heshan consisted of a flow tube in front of the OH measurement cell and allowed to scavenge ambient OH by addition of propane in the sampled air flow. Switching between propane and nitrogen additions allows discriminating ambient OH from instrumental OH. For nitrogen, we used research grade purity (>99.9990%). A GC analysis of the nitrogen showed no significant contamination by VOCs, which would scavenge OH in the chemical modulation system. In the OH detection cell, scavenging of artificially produced OH by the added propane is calculated to be less than 0.3%. A description of the prototype chemical-modulation reactor used with PKU-LIF is given by Tan et al. (2017). Results of the chemical modulation experiments during the PRIDE-PRD2014 campaign are presented in Section 3.3.

The detection of HO_2 by chemical conversion with NO has two known interferences. First, particular RO_2 radicals (called $RO_2^{\#}$) from large alkanes (> C4), alkenes (including isoprene) and aromatics can be converted to OH in the HO_2 detection cell, leading to a systematic positive bias of the HO_2 measurement (Nehr et al., 2011;Fuchs et al., 2011;Whalley et al., 2013;M. Lew et al., 2018). 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. In the campaigns in Wangdu and Heshan, the concentration of the NO reagent was ~~reduced~~ lowered by more than a factor of ten, thereby ~~eliminating~~ reducing the interference in the HO_2 cell to less than 5% (Tan et al., 2017).

On the other hand, the chemical conversion of $RO_2^{\#}$ can be used intentionally for $RO_2^{\#}$ concentration measurements (Whalley et al., 2013). For that purpose, ROxLIF was operated in an additional measurement mode where the NO addition in the pre-reactor was temporarily turned off and replaced by nitrogen (N_2) (Tan et al., 2017). In this mode, the sum of HO_2 and $RO_2^{\#}$ is detected in the connected LIF cell, which is operated with a large amount of NO for chemical conversion. The concentration of $RO_2^{\#}$ is then determined as the difference of HO_2+$RO_2^{\#}$ (ROxLIF) and HO_2 (HO_2 cell). The experimental error of the difference is quite large and exceeds occasionally 100% in the present study, because $RO_2^{\#}$ was much smaller than HO_2 (cf. Fig. 1). Also, the calibration error of $RO_2^{\#}$ is larger than that of HO_2. The detection sensitivity for individual $RO_2^{\#}$ species lies in the range of (0.8 ± 0.2) times the detection sensitivity for HO_2 (Fuchs et al., 2011;Lu et al., 2012). As the speciation of atmospheric $RO_2^{\#}$ is not exactly known, the possible range of sensitivities causes an additional error of 25% that has to be added to the normal calibration error yielding a total accuracy of ±32% (1σ).

The second NO-related artifact, which is relevant for measurements in the HO_2 cell and ROx-LIF system, comes from spurious OH signals generated by the addition of NO in the LIF cells. The signal was regularly determined in humidified synthetic air during calibration and found to be stable over the campaign. It is equivalent to $(2\pm1)\times10^{7}$ cm^{-3} and $(1\pm1)\times10^{7}$ cm^{-3} for HO_2 and RO_2, respectively, and is routinely subtracted from the measurements.~~This background signal is equivalent to $(2\pm1)\times10^{7}$ cm^{-3} and $(1\pm1)\times10^{7}$ cm^{-3} for HO_2 and RO_2, respectively, and is routinely subtracted from the measurements.~~

The total OH reactivity was measured by an instrument based on laser-flash photolysis laser-induced fluorescence (LP-LIF) (Fuchs et al., 2017;Lou et al., 2010). Ambient air is sampled and pulled through a laminar flow tube at ambient conditions. Artificial OH is produced in the sampled air by pulsed laser photolysis (266 nm, FWHM 10 ns) of ozone, which produces OH in nanoseconds according to reaction R2. The OH decay due to the reaction with atmospheric trace gases is then monitored in real-time by LIF. k_{OH} is determined as a pseudo first-order rate coefficient from the decay curves. The precision of the measured k_{OH} data is ± 0.3 s^{-1} (1σ) and the accuracy is 10% (Table S1) at an integration time of 180 s.

2.2.2 Trace gases and photolysis frequencies

As summarized in Table S1, the instrumentation used in the PRIDE-PRD2014 campaign was similar to that used in Wangdu (Tan et al., 2017; Fuchs et al., 2017). Photolysis frequencies were determined from spectral actinic photon-flux densities measurements (Bohn et al., 2008). Meteorological parameters, including relative humidity, ambient pressure, and temperature, as well as wind speed and direction, were also regularly measured at the site.

NO and NO_2 were measured by a commercial chemiluminescence instrument (Thermo Electron model 42i). NO_2 was converted to NO by a custom-built photolytic converter instead of an original molybdenum converter. O_3, SO_2, CO and CO_2 measurements were also measured by commercial instruments from Thermo Electron (model 49i, 43i-TLE, 48i-TLE and 410i). Greenhouse gases, including CO, CO_2, CH_4, and H_2O were measured by a cavity ring-down spectroscopy instrument (Picarro model G2401). The CO and CO_2 measurements from the Thermo Electron and Picarro instruments agreed within the instrumental accuracies. The Picarro measurements were used in this work due to the better data coverage. HONO measurements were performed using a custom-built long-path absorption photometer (LOPAP) from PKU (Liu et al., 2016). Measurements of ~~VOCs~~ non-methane hydrocarbons (NMHCs) were performed by a gas chromatograph (GC) using a flame ionization detector (FID) and mass spectrometer (MS) for detection. The GC-FID/MS system provided measurements of C_2-C_6 alkanes, C_2-C_6 alkenes, and C_6-C_8 aromatics (Wang et al., 2014). ~~A list of the measured VOCs is given in the Supplement (Table S2).~~ Formaldehyde was measured by a commercial Hantzsch fluorimeter instrument (Aerolaser GmbH model AL4021). A list of the measured VOCs is given in the Supplement (Table S2).

2.3 Experimental radical budget calculations

The radical budget analysis in this work is applied to OH, HO_2, RO_2, as well as to the whole ROx family. The analysis is based on the chemical mechanism in Table 1, which describes fundamental reactions controlling the abundance of the radicals in the lower troposphere. The reactions include radical chain propagation reactions, which convert one radical species into another one, initiation reactions that produce radicals from closed-shell molecules, and chain termination reactions that destroy radicals. For the budget calculations, measurements for all relevant reactants and photolysis frequencies together with published reaction rate coefficients (Table 1) are used. Unlike in model studies, the analysis does not include model-calculated species.

In the budget analysis, the total production and loss rates of each radical species are calculated and compared to each other. Since all radicals are short-lived (the OH lifetime is less than a second, the lifetime of peroxy radicals is in the order of a minute), their concentrations are expected to be in steady-state with total production and loss rates being balanced. In chemical box models, the balance is always enforced by the numerical solver of the rate equations, even if the chemical mechanism is incorrect. In the experimental budget analysis, however, imbalances are possible and indicate either unknown errors of the experimental input data (concentrations, photolysis frequencies, rate coefficients) or an incorrect chemical mechanism.

The concept of an experimental radical budget analysis has been applied to atmospheric OH in previous studies, where the determination of the total OH loss rate was facilitated by the measurement of k_{OH}. OH reactivity measurements avoid the problem that some relevant OH reactants may not be captured by direct measurements.

In the present work, the experimental budget analysis is extended to HO_2 and RO_2 radicals. In the case of peroxy radicals, no technique exists for the measurement of their atmospheric total reactivity. However, unlike for OH, the number of known reactant species removing peroxy radicals is relatively small. 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.

2.3.1 ROx budget equations

The ROx budget is entirely controlled by initiation and termination reactions. ROx is primarily produced by photolysis of HONO (R1), O_3 (R2) and HCHO (R3), and ozonolysis of alkenes (R4). The total production rate is calculated as

$$P_{ROx} = j_{HONO}\,[HONO] + \phi_{OH}\, j_{O1D}\,[O_3] + 2\, j_{HCHO\text{-}r}\,[HCHO] + \sum_i\{(\phi^i_{OH} + \phi^i_{HO2} + \phi^i_{RO2})\, k^i_4[alkene]_i[O_3]\} \qquad (E1)$$

In case of ozone photolysis, ϕ_{OH} is the yield of OH from the reaction of $O(^1D)$ with H_2O, which competes with collisional deactivation of $O(^1D)$ with M (N_2, O_2). In the ozonolysis reactions, the yields ϕ^i_{OH}, ϕ^i_{HO2}, and ϕ^i_{RO2} are specific for each alkene species *i*. The summation of the radical production from ozonolysis is performed over all measured alkenes. This sum may be not complete if relevant alkenes were not measured (see discussion in Section 4.2).

The total destruction rate of ROx is given by the reactions of OH with NOx (R12, R13), RO_2 with NO (R14), and self-reactions of peroxy radicals (R15 - R17).

$$D_{ROx} = (k_{12}[NO_2] + k_{13}[NO])[OH] + k_{14}[NO]\,[RO_2] + 2\,(k_{15}[RO_2]^2 + k_{16}[RO_2]\,[HO_2] + k_{17}[HO_2]^2) \qquad (E2)$$

Since RO_2 is measured as a sum of organic peroxy radicals, it is treated as a single species. The generalized rate coefficients are adopted from MCMv3.3.1 (see footnotes in Table 1). Reaction R14, leading to the formation of organic nitrates, competes with reaction R8 which produces HO_2 radicals. The branching ratio between reactions R8 and R14 depends on the carbon chain lengths and structure (Atkinson et al., 1982; Lightfoot et al., 1992). The organic nitrate yield generally increases with carbon number and lies typically between 1% for ethyl RO_2 and 35% for RO_2 of C8 alkanes. Here, a nitrate yield of 5% is assumed. The impact of larger nitrate yields is discussed in Section 4.

The thermal decomposition of HO_2NO_2 into HO_2 and NO_2 (an initiation reaction) and the back reaction to HO_2NO_2 (a termination reaction) are not explicitly considered in the budget equations. The two reactions reach a thermal equilibrium within seconds under the conditions of the campaign and have no net effect on the RO_x balance. Likewise, equilibrium is assumed between thermal decomposition of PAN and its formation by the reaction of acetyl peroxy radicals with NO_2. Also, this equilibrium is not explicitly considered in the budget equations E1 and E2.

2.3.2 OH budget equations

As explained above, the total OH destruction rate can be directly quantified as the product of the OH concentration and the OH reactivity, both of which were measured during the PRIDE-PRD2014 campaign.

$$D_{OH} = [OH]\, k_{OH} \qquad (E3)$$

The total OH production rate is calculated from the primary (R1, R2, R4) and secondary (R9, R10) sources of OH. The primary sources are treated in the same way as in the ROx budget. The secondary sources include OH recycling from the reaction of HO_2 with NO (R9) and O_3 (R10).

$$P_{OH} = j_{HONO}\,[HONO] + \phi_{OH}\,j_{O1D}\,[O_3] + \sum_i \{\phi^i_{OH}\,k^i_4[\text{alkene}]_i\,[O_3]\} + (k_9[NO] + k_{10}[O_3])[HO_2] \quad \text{(E4)}$$

2.3.3 HO_2 budget equations

The total production rate of HO_2 is calculated from primary sources, i.e. photolysis of HCHO (R3) and ozonolysis of alkenes (R4), and secondary sources which involve the conversion of OH and RO_2 to HO_2. The treatment of the primary production by reactions R3 and R4 is explained in Section 2.3.1. Photolysis of other OVOCs (besides HCHO) could contribute to the HO_2 production, but this is not considered here due to the absence of OVOC measurements.

OH to HO_2 conversion can occur by reaction of OH with CO, HCHO, H_2, and O_3. Under the conditions of the campaign, the reaction rates for H_2 and O_3 were at least two orders of magnitude smaller than those for the reactions with HCHO (R6) and CO (R7). Therefore, only R6 and R7 are considered in the budget analysis. Also, the reaction of RO_2 with NO (R8) constitutes an important secondary source of HO_2. Reaction R8 competes with the radical termination reaction R14, for which a nitrate yield of 5% is assumed (see Section 2.3.1). Accordingly, an HO_2 yield of 95% is taken for reaction R8. The total HO_2 production rate is then calculated as

$$P_{HO2} = 2\,j_{HCHO\text{-}r}\,[HCHO] + \sum_i\{\phi^i_{HO2}\,k^i_4[\text{alkene}]_i[O_3]\} + (k_6[HCHO] + k_7[CO])[OH] + k_8[NO][RO_2] \quad \text{(E5)}$$

HO_2 is chemically removed by reaction with NO, O_3, HO_2, and RO_2, all of which were measured in this campaign. It should be noted that the effective rate constant k_{17} for the self-recombination of HO_2 has a water vapor dependence which is taken into account in k_{17} (Table 1). The total HO_2 destruction rate is then given by

$$D_{HO2} = (k_9[NO] + k_{10}[O_3] + k_{16}[RO_2] + 2\,k_{17}[HO_2])\,[HO_2] \quad \text{(E6)}$$

As explained in Section 2.3.1, the thermal equilibrium between HO_2+NO_2 and HO_2NO_2 is not explicitly considered in the budget equations.

2.3.4 RO_2 budget equations

Primary RO_2 production is possible by the ozonolysis of alkenes and the photolysis of OVOCs. Owing to the lack of OVOC measurements (except HCHO) in this study, only ozonolysis is considered as a primary source. It is treated as described in Section 2.3.1.

In a broader sense, also reactions of hydrocarbons with NO_3 radicals and chlorine atoms can be considered as primary production processes, because they do not consume ROx species. However, neither NO_3 nor Cl were measured. ~~The budget analysis here focusses on daytime conditions when NO_3 is depleted by photolysis, such that RO_2 production from NO_3 chemistry can be neglected. Cl atoms, however, may play a role in the morning.~~ NO_3 is produced by reaction of NO_2 with ozone. It is generally assumed that during the bright hours of the day, NO_3 is predominantly destroyed by photolysis and reaction with NO. Recently, Liebmann et al. (2018) reported measurements in a forested environment in southern Germany demonstrating that more than 25% of daytime NO_3 was removed by biogenic VOCs. The possible role of NO_3 reactions with VOCs at Heshan is discussed in Section 3.

Cl atoms may play a role in the morning. Gaseous $ClNO_2$ can be formed at night by heterogeneous reaction of N_2O_5 with Cl^- ions and photolyze quickly after sunrise~~,~~ producing Cl atoms ~~during the morning hours~~ (Osthoff et al., 2008; Tham et al., 2016; Li et al., 2018). This mechanism followed by the reaction of Cl with VOCs made some contribution to the early morning RO_2 production in a previous campaign in summertime in the North China Plain (Tan et al., 2017) and will be ~~further~~ discussed in Section 4.2.

The main secondary source of RO_2 is the reaction of OH with VOCs. As it is generally difficult to measure all reactive organic compounds in the atmosphere, we follow two different approaches to determine the RO_2 production from OH reactions. The first approach calculates the RO_2 production rate as the sum of the reaction rates of OH with all measured hydrocarbon species, denoted VOC(1). The resulting total RO_2 production rate can be considered as a lower limit.

$$P^{(1)}_{RO2} = \Sigma_i\{\phi^i_{RO2}\, k^i_4[\text{alkene}]_i[O_3]\} + \Sigma_j\{\, k^j_5[\text{VOC(1)}]_j\}[\text{OH}] \qquad \text{(E7)}$$

Here, the first sum represents the primary production by ozonolysis, the second term the RO_2 production rate by OH reactions. Another approach estimates the total atmospheric amount of organic reactants, here denoted VOC(2), from the measured OH reactivity (e.g., Shirley et al., 2006; Whalley et al., 2016). For this purpose, the reactivity of measured CO, NO, NO_2, HCHO, SO_2, and O_3 is subtracted from the measured k_{OH} to determine the total reactivity of VOCs that can potentially form RO_2. This reactivity is called k_{OH}(VOC(2)). This approach makes the implicit assumption that the missing OH reactivity found in the present study (see Section 3.2) is caused by unmeasured VOCs. The RO_2 production rate is then given by

$$P^{(2)}_{RO2} = \Sigma_i\{\phi^i_{RO2}\, k^i_4[\text{alkene}]_i[O_3]\} + k_{OH}(\text{VOC(2)})\,[\text{OH}] \qquad \text{(E8)}$$

The RO_2 destruction is determined by the reaction with NO (R8, R14) and with other peroxy radicals (R15, R16). These reactions and the thermal equilibrium of PAN are treated as in the ROx budget analysis (Section 2.3.1). Accordingly, the total destruction rate of RO_2 can be calculated as

$$D_{RO2} = \{(k_8+k_{14})[\text{NO}] + (2k_{15}[RO_2] + k_{16}[HO_2])\}[RO_2] \qquad \text{(E9)}$$

Equations E7 and E9 can be adapted for the budget analysis of $RO_2^{\#}$ radicals. In this case, the second term in equation E7 contains only OH reactions of VOCs that are known to produce $RO_2^{\#}$. In equation E9, only the concentration of RO_2 at the end of the equation has to be replaced by $RO_2^{\#}$ assuming all $RO_2^{\#}$ reacts with RO_2.

3 Results

3.1 Meteorological and chemical conditions

The complete suite of measurements (radicals, trace gases, meteorological parameters) started on 22 October and ended on 14 November. The weather was generally cloudy with temperatures in the 20°C to 30°C range and water vapor volume mixing ratios were around 2 %. Solar UV radiation showed variability due to cloudy weather conditions as can be seen from the photolysis-frequency variations of j_{O1D} and j_{NO2} (Fig. S1). In this work, conditions with $j_{O1D} > 1\times10^{-6}$ s^{-1} are referred to as daytime conditions lasting from 6:00 to 18:00 local time. After 6 November, the weather changed and became rainy with little photochemical activity. Therefore, the current study was restricted to the time period from 22 October to 5 November. During this period, air transportation was dominated by north-easterly and easterly winds. The time dependence of measured trace gas concentrations is shown in Fig. S1 and median values are listed in Table 2. The chemical conditions are characterized by anthropogenic pollution. High concentrations of ozone were observed with daily maxima reaching 100 ppbv on several days. In the morning and afternoon, median O_3 values were 16 ppbv and 69 ppbv, respectively. NO mixing ratios reached maximum values of 10 ppbv, and median values were 3.7 ppbv in the morning and 0.4 ppbv in the afternoon. NO_2 mixing ratios were 17 ppbv and 9 ppbv in the morning and afternoon, respectively.

3.2 OH reactivity

The measured OH reactivity showed variations in the range between 15 s^{-1} and 80 s^{-1} (Fig. S2), with median values of 32 s^{-1} in the morning and 22 s^{-1} in the afternoon (Fig. 1). OH reactivities (k^{calc}_{OH}) that were calculated from measured trace gas concentrations, [i] (Table 2) and their OH reaction rate coefficients (k_{i+OH}) show a similar temporal behavior as the measured k_{OH}, but underestimate its value systematically during the whole campaign (Fig. S2).

$$k^{calc}_{OH} = \sum_i k_{i+OH} [i] \quad \text{(E10)}$$

The comparison of measured and calculated OH reactivities (Fig. 1) indicates that the measured trace gases account for only half of the atmospheric OH reactivity. The contributions of CO, NOx, and measured ~~VOCs~~ NMHCs during daytime were about 10%, 14%, and 20%, respectively. Among the measured ~~VOCs~~NMHCs, the groups of alkanes, alkenes (without isoprene) and aromatics had similar shares of reactivity during the day. In the night and in the morning, alkenes and aromatics were the dominating hydrocarbons, while isoprene made a contribution with up to 6% of the total k_{OH} during daytime. Formaldehyde was the only measured OVOC. It contributed 5% - 8% during the day. The chemical nature of the missing reactivity (about 50%) is not known, but was likely caused by unmeasured VOCs (see Section 3.7).

3.3 OH, HO_2, and RO_2 concentrations

Time series and median diurnal profiles of the measured radical concentrations are shown in Fig. S2 and Fig. 1. As in previous campaigns, the diurnal profile of OH shows a high correlation with j_{O1D}, which is a proxy for the solar UV radiation driving much of the primary radical production during summer time (e.g., Rohrer et al., 2014; Ehhalt and Rohrer, 2000). It is noteworthy that the measured OH persisted even after sunset at levels with median values of 0.7×10^6 cm^{-3} until midnight (Fig. 1). Thereafter, OH concentrations dropped continuously until they reached values below the limit of detection shortly before sunrise.

In order to test, whether the OH measurements at Heshan could have been affected by an unknown interference, chemical modulation experiments were performed between noon and midnight on several days (Table 3). Within instrumental precision, no significant unexplained OH interference was detected. This result applies equally to day and night. Therefore, the OH concentration of 1.8×10^6 cm^{-3} measured on 30 October after sunset during the chemical modulation test (Table 3) must be considered as real ambient OH. On the other hand, all unaccounted OH signals are slightly positively biased except the last one in Table 3. The mean value ($\pm$ 1σ) of the unaccounted OH signals is equivalent to an OH concentration of $(0.3\pm0.3) \times 10^6$ cm^{-3} which is at the limit of instrumental detection. In the further analysis, the mean plus 1σ is assumed to be the upper limit for a possible OH interference.

The peroxy radicals, HO_2 and RO_2, show qualitatively a similar diurnal behavior as has been reported for other urban environments (e.g., (Holland et al., 2003;Shirley et al., 2006;Kanaya et al., 2007;Emmerson et al., 2007)). The photochemical build-up of peroxy radicals after sunrise is delayed due to their reaction with high NO concentrations in the morning. The peroxy radical concentrations reach a late maximum around 14:30h in the afternoon when NO is decreasing (Fig. 1). Median ozone concentrations reach a maximum of 76 ppbv at the same time as the occurrence of the peroxy radical maxima. The concentration of $RO_2^\#$ represents about (15±15)% of the total organic peroxy radicals, RO_2, during daytime. This percentage is surprisingly small as measured $RO_2^\#$ precursors (alkenes, isoprene, aromatics and large alkanes) dominated the reactivity of the measured hydrocarbons (Fig. 1, lowest panel). A possible reason would be unmeasured VOCs which produce RO_2, but not $RO_2^\#$.

3.4 RO_x budget

In the RO_x budget analysis, only radical initiation and termination reactions play a role. Calculated median diurnal profiles for production (E1) and destruction (E2) rates of ROx are shown in Fig. 2. Both rates have maximum values in the order of 3 - 4 ppbv/h at noontime (Fig. 2e and 2f).

The observed daytime production of RO_x (Fig. 2a - 2e) is dominated with 51% by the photolysis of HONO (R1), followed by photolysis of formaldehyde (R3) and ozone (R2) which have contributions of 34% and 15%, respectively. The counteracting reaction forming HONO from OH and NO is comparatively slow (<5%; Fig. 2b, blue line). Therefore, the net OH production from HONO photolysis is still the major primary source of ROx. Ozonolysis of measured alkenes (R4) contributes 7% during daytime and is the only primary source considered here at night.

RO_x radical termination occurs via reactions with NO_x (R12 - R14) and by peroxy radical self-reactions (R15 - R17). In the morning, when the median NOx concentration is about 21 ppbv (Table 2), the reaction of OH with NO_2 (R15) is the dominating loss process (69%), followed by the reaction of RO_2 with NO (R14, 13% on average) and the reaction of OH with NO (R13, 7% on average). Radical self-reactions play a negligible role in the morning. They gain importance (12%) in the afternoon, when the median NO_x concentration decreases to 9.5 ppbv. Overall, ROx loss during the PRIDE-PRD2014 campaign was mainly controlled by reactions with NOx during the whole day.

The difference between the total ROx production and destruction rates is shown in Fig. 2g. ~~During daytime, there is a small imbalance with the production rate P_{ROX} being larger than the destruction rate D_{ROX}. The difference reaches 15% of the total ROx turnover rate at noontime. The observed differences at daytime can be explained by experimental errors of the data used in the budget and are therefore not significant (Fig. 2g). At night, the imbalance is reversed with D_{ROX} being slightly larger than P_{ROX}. The difference is about 0.2 ppbv/h to 0.4 ppbv/h, which can be explained by experimental errors when the upper limit of the possible OH interference is included in the total experimental uncertainty (Fig. 2g). The possible nighttime production of ROx by reactions of NO_3 with VOCs is not considered here due to the lack of NO_3 measurements.~~ During daytime, there is an imbalance between production (P_{ROx}) and destruction (D_{ROx}) rates, which increases from -0.5 ppbv (8:00) to +0.5 ppbv (18:00). The deviations are small (< 15%) compared to the total ROx turnover rate at noon and can be explained by the experimental errors of the data between 8:30 and 17:30. After sunset until 2 hours after midnight, D_{ROx} remains about 0.5 ppbv/h larger than P_{ROx}. The deviation may be caused, at least partly, by RO_2 formation from reactions of VOCs with NO_3 radicals, for which an upper limit of 0.7 ppbv/h can be estimated (see Section 4.2). The deviation can also largely be explained by experimental errors, when the upper limit of a possible OH interference is included in the total experimental uncertainty (Fig. 2g).

3.5 OH budget

The median OH production (E4) and destruction (E3) rates show diurnal profiles with noontime maxima of 13 ppbv/h and 16 ppbv/h, respectively (Fig. 3a). The calculated OH production rate is dominated throughout the whole day by the recycling reaction of HO_2 with NO, which contributes on average 79% during the day. The most important primary daytime source is the photolysis of HONO. It contributes on average 13% to the total OH production, whereas the photolysis of ozone and ozonolysis of alkenes add 4% each. The OH destruction rate is balanced by the calculated production rate between sunrise and noon, but is considerably larger than the production rate in the afternoon (Fig. 3b). The difference of (4-6) ppbv/h cannot be explained by the combined experimental uncertainties Fig. 3b), even if the upper limit of the potential OH interference is taken into account (Fig. 3b). Since the measured k_{OH} provides a constraint for the total OH loss rate, the imbalance with P_{OH} less than D_{OH} indicates a significant missing OH source in the calculation of P_{OH}. Only after sunset, the remaining discrepancy would be explainable by a potential OH artifact.

3.6 HO_2 budget

The calculated HO_2 production (E5) and destruction rates (E6) are in good agreement throughout the whole day. The maxima of the rates are in the order of (12 - 14) ppbv/h shortly before noontime (Fig. 3c). The major sources are the reactions of RO_2 with

NO (63%) and the reactions of OH with CO (14%) and formaldehyde (13%). Primary production processes (photolysis of formaldehyde, ozonolysis of alkenes) contribute 10% to the total HO_2 production. Owing to the relatively high NO concentrations during the campaign, the HO_2 loss is dominated with 96% by the reaction with NO. The HO_2 budget is closed within the experimental uncertainties (Fig. 3d). The magnitude of unexplained OH signals observed in the chemical modulation experiments has no noticeable influence on the closure of the budget (Fig. 3d).

3.7 RO_2 budget

Like for HO_2, the destruction rate of RO_2 (E9) is dominated with 98% by the reaction with NO and reaches a maximum shortly before noontime (Fig. 3e). In this case, the maximum has a value of (10 - 11) ppbv/h. The production rate $P^{(1)}_{RO2}$ calculated by equation E7 from measured hydrocarbons (~~VOC(1),~~ Fig. 3e) is far from being able to compensate the loss of RO_2 radicals. At noontime, the production rate is a factor of 4 - 5 too small. Once the missing OH reactivity is attributed to unmeasured VOCs, the resulting production rate $P^{(2)}_{RO2}$ calculated by equation E8 matches D_{RO2} relatively well.~~Only when the amount of atmospheric VOCs is estimated from the measured total OH reactivity, the production rate $P^{(2)}_{RO2}$ (VOC(2), Fig. 3e) matches D_{RO2} relatively well~~. From sunrise to noon, the budget becomes closed within the experimental uncertainties (Fig. 3f). This result strongly supports the hypothesis that the missing OH reactivity in the morning is caused by unmeasured VOCs.

Assuming that unmeasured VOCs are also responsible for the missing reactivity at other times of the day, an imbalance of (2 - 5) ppbv/h in the RO_2 budget is left in the afternoon, where $P^{(2)}_{RO2}$ is greater than D_{RO2} (Fig. 3f). Considering the experimental uncertainties in the budget equations, the difference is significant from noontime to midnight and indicates a missing RO_2 sink. Even if the maximum potential OH interference is taken into account, the imbalance remains from the afternoon until 21:00h, while it becomes insignificant later in the night (Fig. 3c).

The $RO_2^{\#}$ radical budget can be treated in a similar way as for RO_2 (see Section 2.3.4). The calculated destruction rate of $RO_2^{\#}$ shows a similar diurnal shape as RO_2 and is also entirely determined by the reaction with NO (Fig. 3g). Within experimental uncertainty the destruction rate is balanced by the production rate $P^{(1)}_{RO2\#}$ calculated from the measured VOCs known to produce $RO_2^{\#}$ (Fig. 3h). Note that $P^{(1)}_{RO2\#}$ in panel (g) looks almost the same as $P^{(1)}_{RO2}$ in panel (e) as most of the measured VOCs produce $RO_2^{\#}$.

If the missing OH reactivity was caused entirely by $RO_2^{\#}$ precursor VOCs, the production rate of organic peroxy radicals would be up to factor of 5 higher than the $RO_2^{\#}$ loss rate (Fig. 3). This suggests that the missing OH reactivity is caused by chemical species that do not produce $RO_2^{\#}$.

4 Discussion

The completeness of the radical measurements allows a budget analysis for all radicals (OH, HO_2, RO_2) based on experimental data only, without application of a chemical box model, under the assumption that for the production and loss rates all relevant species were measured. The RO_x budget analysis compares whether the radical initiation reactions of RO_x are balanced by the known radical termination reactions; the analysis of the OH, HO_2 and RO_2 budgets gives insight into the completeness of our understanding of the radical cycling. The interpretation of the budgets below will focus on daytime chemistry (6:00-18:00), as conclusions concerning the nighttime chemistry would be rather limited due to the possible OH interference and the lack of NO_3 measurements.

4.1 Missing OH reactivity

Of the atmospheric OH reactivity measured at Heshan, approximately 25% is explained by measured inorganic compounds (CO, NOx) and another 25% by measured ~~VOCs~~NMHCs and formaldehyde. The missing reactivity of about 50% indicates a considerable fraction by unmeasured reactants. Similar missing reactivities have been observed also in forests and other urban environments (Williams et al., 2016; Whalley et al., 2016; Ramasamy et al., 2016; Kaiser et al., 2016; Lu et al., 2013; Edwards et al., 2013; Dolgorouky et al., 2012; Lou et al., 2010; Sadanaga et al., 2005). Depending on the local conditions, missing k_{OH} is generally attributed to unmeasured ~~emitted VOCs, or their oxidation products~~VOCs which have been emitted or produced by atmospheric oxidation. This hypothesis is plausible, since the atmosphere contains thousands of unknown organic species (Goldstein and Galbally, 2007), but the assumption of unmeasured VOCs is generally difficult to prove. In the present work, the existence of unmeasured atmospheric VOCs deduced from missing OH reactivity is independently confirmed by the analysis of the experimental RO_2 budget presented in Section 3.7. Only if the missing reactivity is due to VOCs, the discrepancy of up to a factor of 5 between observed RO_2 production and destruction rates can be reconciled (Fig. 3e, f). In addition, the budget analysis for $RO_2^{\#}$ provides evidence that the unmeasured VOCs are mostly species that do not produce $RO_2^{\#}$ radicals (Fig. 3g, h). As such, they probably do not belong to the class of alkenes or aromatics.

Missing reactivity at the measurement site has also been reported by Yang et al. (2017), who analyzed k_{OH} data measured from 20 October to 19 November 2014 using the comparative reactivity method developed by Sinha et al. (2008). Although their time window encompasses the present study, there is little overlap of the data due to data gaps. As far as simultaneous data are available, the two instruments agreed within their combined errors (1σ = ±20% for the CRM instrument, ±10% for the LP-LIF instrument). For the time period analyzed by Yang et al. (2017) the fraction of missing reactivity to the total reactivity was reported to be 30%. Although the percentage value is smaller than in the present paper (50%), the absolute values for the OH reactivity from unmeasured reactants are comparable. The speciation of the missing reactivity, however, can be different because the higher NOx loading in the period analyzed by Yang et al. (2017) may lead to different photochemical products and may be correlated with different VOC emissions.~~Although the percentage value is smaller than in the present paper (50%), the absolute values for the missing k_{OH} are comparable due to higher OH reactivities with higher NOx pollution in the period analyzed by Yang et al. (2017).~~ Missing OH reactivity of about 50% was also reported for the Backgarden site about 140 km north-east of Heshan, where daytime OH reactivities between 20 s^{-1} and 50 s^{-1} were measured in summer 2006 (Lou et al., 2010). In that study, the missing reactivity could be explained by unmeasured OVOCs (e.g., formaldehyde, acetaldehyde, MVK, MACR) which were simulated by a chemical box model as products from measured hydrocarbons. With a similar approach, Yang et al. (2017) explain one to two-thirds of the missing reactivity at Heshan by organic oxidation products (e.g. aldehydes, dicarbonyl compounds) and suspect that the remaining missing reactivity was caused by unknown primary VOC emissions.

Many oxygenated VOCs produce RO_2 when they react with OH. Examples are acetaldehyde and higher aldehydes, acetone and higher ketones, MACR, MVK, and methyl glyoxal, all of which were not measured in the present study. In the following discussion we assume based on the considerations given above that the missing reactivity in the present study is entirely due to VOCs (including also OVOCs) which can produce RO_2 by reaction with OH. ~~In the following discussion, we assume based on the considerations given above that the missing reactivity in the present study is entirely due to VOCs.~~

4.2 ~~Relationship between radical budgets~~Radical budgets, their relationships and uncertainties

The imbalances in the OH, HO_2, and RO_2 budgets (*D*-*P*) reach median values of up to (7±2.5) ppbv/h, -(3±5) ppbv/h, and -(5±2.5) ppbv/h, respectively, during the day.~~The imbalances in the OH, HO_2, and RO_2 budgets (D-P) reach median values of up to 7 ppbv/h, -3 ppbv/h, and -5 ppbv/h, respectively, during the day.~~ Interestingly, the imbalance in the ROx budget does not exceed ±-0.5 ppbv/hr (Fig. 2). This means that the largest uncertainties in the speciated radical budgets compensate each other in the ROx budget. The largest differences between destruction and production rates are found for OH (Fig. 3b) and RO_2 (Fig. 3f). The respective diurnal profiles look similar in shape, but with opposite signs. When added up in the ROx budget, their values largely compensate each other. The imbalances in the OH and RO_2 budgets become large in the afternoon and show a growing trend when NO falls below 1 ppbv (Fig. 4). Above 1 ppbv NO (i.e., in the morning), however, both budgets are closed within their experimental uncertainties. In case of HO_2, the destruction and production rates are balanced within experimental error during the whole day independent of the NO mixing ratio (Fig. 3c and Fig. 4).

One possible explanation for the imbalances in the OH and RO_2 radical budgets would be an unknown radical initiation reaction for OH and an unknown termination reaction for RO_2, respectively, which fortuitously balance each other in time and quantity in the ROx budget. This coincidence seems unlikely, also because this would mean a drastic increase in ROx production and destruction rates by a factor of 2.5 to 3 in the early afternoon. A more plausible explanation is a partially insufficient description of the radical chain propagation, which proceeds during the day at much higher rates of 10 - 16 ppbv/h.

OH interference

The non-closure in the OH and RO_2 budgets could be explained, for example, by experimental artifacts as recently reported for OH measurements in some LIF instruments (Mao et al., 2012; Novelli et al., 2014; Feiner et al., 2016). An experimental overestimation of the OH concentration would result in too high reaction rates calculated for the OH destruction ($k_{OH}\times$[OH]) and the RO_2 production from the reactions of VOCs with OH. However, the chemical modulation tests carried out under low NO conditions (< 1ppbv) do not show a significant interference. This result is consistent with other tests that were performed with our LIF technique in field campaigns in China (Tan et al., 2018b; Tan et al., 2017) and in laboratory and chamber experiments (Fuchs et al., 2016; Fuchs et al., 2012). For this reason, we consider OH interference as an unlikely explanation here, although we cannot strictly exclude the possibility that there were OH interferences only at times, when the chemical modulation system was not used.

OH regeneration mechanisms

An alternative explanation for the non-closure in the OH and RO_2 budgets would be a chemical mechanism that effectively converts RO_2 to OH. Unimolecular isomerization and decomposition reactions of RO_2 can be such an OH source when the competing reaction with NO is slow. This chemistry is known for a long time as autoxidation, for example, in low-temperature combustion (e.g., Cox and Cole, 1985; Glowacki and Pilling, 2010). Its potential relevance for atmospheric chemistry at ambient temperatures has only recently been recognized (e.g., Peeters et al., 2009; daSilva et al., 2010; Crounse et al., 2013; Praske et al., 2018). Autoxidation involves an intramolecular H-shift in the RO_2 molecule leading to a hydroperoxy alkyl radical, which is often named QOOH. This radical can generally undergo various types of reactions such as reaction with O_2 producing an oxygenated VOC + HO_2, or decomposition to an oxygenated VOC by elimination of OH from the -OOH group (e.g., Peeters et al., 2009; daSilva et al., 2010; Crounse et al., 2013; Praske et al., 2018). Another path is the addition of O_2 forming a hydroperoxy peroxy radical (O_2)QOOH. This new peroxy radical can then react with NO, HO_2, RO_2, or undergo another internal H-shift reaction. Repetitive sequential H-shift reactions followed by O_2 addition lead to highly oxidized RO_2 radicals which produce highly oxidized molecules (HOMs) by radical termination reactions (e.g., Ehn et al., 2014, 2017; Jokinen et al., 2014). Due to their low vapour pressure, HOMs are efficient precursors for organic particles, which are produced from the original VOCs with yields in the low percent range (e.g., Ehn et al., 2014; Jokinen et al., 2015).

RO_2 isomerisation producing HOx radicals is known to occur in the oxidation of isoprene ((Peeters et al., 2014; Peeters and Muller, 2010; Peeters et al., 2009~~Peeters et al., 2009, 2010, 2014~~; Da Silva et al., 2010; Crounse et al., 2011; Fuchs et al., 2013;

Teng et al., 2017) and methacrolein (Crounse et al., 2012; Fuchs et al., 2014). In Heshan, the production rate of isoprene peroxy radicals from the reaction of isoprene with OH never exceeded 0.5 ppbv/h. Even if every isoprene derived RO_2 radical regenerated one OH molecule (which is not likely because of the competing reaction with NO), the process could explain only a small fraction of the missing OH production rate. The concentration of methacrolein (MACR) was not measured, but is generally not larger than that of isoprene (Karl et al., 2009; Shao et al., 2009). Since the OH rate constant is smaller than that for isoprene, OH regeneration by unimolecular reactions of MACR derived RO_2 is expected to be even less important.

Besides for isoprene and methacrolein, autoxidation of RO_2 leading to HOx formation has been experimentally studied for only few other VOCs, including 3-pentanone (Crounse et al., 2013), glyoxal (Lockhart et al., 2013), n-hexane and 2-hexanol (Praske et al., 2018), hydroxymethyl hydroperoxides (Allen et al., 2018), and 2-hydroperoxy-2-methylpentane (Praske et al., 2019). While isoprene and methacrolein chemistry is especially important in biogenically controlled environments, the new studies demonstrate that autoxidation can also be expected to play a role in urban atmospheres when NO concentrations are as low as 500 pptv (cf., Praske et al., 2018). Systematic theoretical studies have shown that the rates of H-shifts in RO_2 depend very much on their chemical structure (e.g., Crounse et al., 2013; Otkjær et al., 2018; Møller et al., 2019) and range from 10^{-4} s^{-1} to 10 s^{-1} at ambient temperature. Low rate coefficients can be expected, for example, for 1,5-H or 1,6-H shift reactions in linear alkyl radicals, whereas the presence of (multiple) functional groups like -OH, -OOH, or -CHO may increase the H-shift rate by orders of magnitude. The possible yield of OH, HO_2, or higher-oxidized RO_2 radicals from a hydrogen shift depends on the chemical structure and functionality. Elimination of OH or HO_2 is generally supported by the presence of functional groups (e.g., -OH, -OOH, or -CHO).

In the present campaign, the potential conversion of RO_2 to OH by a unimolecular reaction would require a rate of about 0.08 s^{-1} to close the budgets of OH and RO_2, if all measured RO_2 radicals could produce OH from H-shift reactions (Fig. S4). Although the rate is in the possible range of H-shift reactions, it is questionable if a major fraction of RO_2 was structurally capable to undergo a fast H-shift leading to OH formation. As approximately half of the measured OH reactivity is likely due to unmeasured VOCs with unknown speciation and owing to the general lack of kinetic and mechanistic studies for specific RO_2 radicals, it is not possible to be more quantitative here. If the missing reactivity at Heshan was caused by photochemically aged, functionalized oxygenated VOCs, there is a chance that RO_2 radicals from these compounds could have contributed significantly to the missing RO_2 sink, or missing OH source. If autoxidation played a significant role, additional HO_2 formation from H-shift reactions would also be expected. However, the closed HO_2 budget gives no indication for this.

Another possibility to convert RO_2 to OH under low NO conditions is the reaction of RO_2 with HO_2. The reaction is generally considered to be chain terminating, but in the case of acyl peroxy and α-carbonyl peroxy radicals, a parallel reaction channel can produce OH with yields up to 80% (Fuchs et al., 2018; Winiberg et al., 2016; Praske et al., 2015; Groß et al., 2014; Hasson et al., 2012; Dillon and Crowley, 2008; Hasson et al., 2004; Jenkin et al., 2008). With reaction rate constants in the range of $(1 - 2) \times 10^{-11}$ cm^{-3} s^{-1}, the OH production would be less than 0.1 ppbv/h even if all measured RO_2 species produced OH. In conclusion, the already known mechanisms for conversion of RO_2 to HO_2 are not sufficient to explain the missing RO_2 sink and missing OH source.

The observations in Heshan resemble qualitatively that of the previous PRIDE-PRD 2006 campaign in Backgarden (Hofzumahaus et al., 2009), where the experimental OH budget indicated a missing OH source (28 ppbv/h) in the afternoon, when NO was less than 1 ppbv. Box model simulations underestimated the measured OH concentrations by a factor 3-5 at low NO, but agreed well with measured HO_2 concentrations. In that study, the isoprene concentrations were considerably higher reaching several ppbv. Isomerisation reactions of isoprene peroxy radicals could explain only a small part (max. 20%) of the missing OH source (Lu et al., 2012; Fuchs et al., 2013). The observed behavior of OH and HO_2 could be reproduced by assuming a hypothetical mechanism in which RO_2 is converted to HO_2 and HO_2 to OH by an unknown reactant X with a concentration equivalent to 0.8 ppbv NO. Owing to the lack of RO_2 measurements, the mechanism could not be directly tested for RO_2. In Heshan, the same mechanism would be able to close both the RO_2 and OH budgets, if an equivalent of 0.4 ppbv NO is assumed (Fig. ~~S3~~S4). Here, the NO concentration of 0.4 ppbv corresponds to the rate coefficient of 0.08 s^{-1} discussed above. When using the X mechanism, the closure of the HO_2 and RO_x budgets remains unaffected.~~The closure of the HO_2 and RO_x budgets would remain unaffected~~. Therefore, the X mechanism is one possibility to describe all radical budgets at Heshan consistently, although its chemical nature remains unresolved.

Additional uncertainties in the budget analyses

As pointed out in Section 4.1, unmeasured VOCs were most likely responsible for the observed missing OH reactivity. This not only considerably influences the radical chain propagation from OH to RO_2 (Fig. 3e, g), but can also affect the primary production of radicals by ozonolysis and photolysis (see Supplementary Text). Furthermore, Cl reactions with measured and unmeasured VOCs may have initiated ROx chain reactions in the early morning. These reactions could have slightly influenced the ROx budget, but are of minor importance compared to the radical chain propagation reactions (Supplementary Text).

Reactions of NO_3 with VOCs are an additional RO_2 source which is neglected in the budget calculation in Section 2.3.4. The relevance can be estimated from the production rate of NO_3, which is calculated from the reaction of NO_2 with O_3 ($k(NO_2+O_3)= 1.47\times10^{-13}\times\exp(-2470/T)$; MCM3.3.1). In this campaign, the NO_3 production rate was in the order of 1.4 ppbv/h and 0.7 ppbv/h at day- and nighttime, respectively. Because NO_3 is efficiently photolysed in the bright hours of the day, it is generally assumed that it plays a negligible role as an oxidant during daytime. Liebmann et al. (2018) have recently shown that this is not always the case. They reported measurements in a forested environment in southern Germany demonstrating that more than 25% of the daytime NO_3 reacted with biogenic VOCs. Under the conditions at Heshan 2014, the main loss process at daytime is the reaction with NO. If we neglect unmeasured VOCs, the percentage removal of NO_3 in the morning is 96% by NO, 3% by photolysis, and 1% by measured VOCs. In the afternoon, the corresponding values are 72%, 21%, and 7%. Thus, the estimated RO_2 production rate from NO_3 reactions with known VOCs was probably not more than 0.1 ppbv/h at daytime. It is conceivable, that unmeasured VOCs, which probably accounted for 50% of the OH reactivity, contributed by a similar magnitude. During daytime, these contributions are relatively small compared to the total production rate of RO_2. The tendency is to slightly increase the imbalance between the production and destruction rate of RO_2 observed in the afternoon (Fig. 3). At sunset and in the night, the NO_3 production rate of 0.7 ppbv/h can be considered as an upper limit for the RO_2 production. This value can possibly explain at least partly the imbalance of about 0.5 ppbv/h in the ROx budget after sunset (Fig. 2).

~~Another uncertainty is caused by the unknown branching ratio in the reaction of RO_2 with NO, which can produce HO_2 (R8, chain propagating) or organic nitrates (R14, chain terminating) (Section 2.3.1). Changing the yields for organic nitrates from 5% to 20% has a small, but notable influence on the ROx budget, reversing the slightly negative bias (D < P) to a lightly positive one (D > P) (Fig. S4). In both limits, the ROx budget remains closed within experimental errors. The influence of the different HO_2 yields on the production rate of HO_2 is small (Fig. S5). For the range of tested yields, the HO_2 budget remains balanced within experimental uncertainties.~~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 those species which produce a new RO_2 radical when they react with NO. As these reactions are neutral with respect to the total RO_2, the RO_2 budget (*D*-*P*) is not sensitive to the RO_2 measurement bias 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 uncertainty of the rate coefficients for Reaction R15 and R16 plays 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, 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.

Also the unknown branching ratio in the reaction of RO_2 with NO, which can produce HO_2 (R8, chain propagating) or organic nitrates (R14, chain terminating) is uncertain (see Section 2.3.1 and Supplement). Changing the yields for organic nitrates from 5% to 20% has a small, but notable influence on the ROx budget, reversing the slightly negative bias ($D < P$) to a lightly positive one ($D > P$) (Fig. S7). In both limits, the ROx budget remains closed within experimental errors. The influence of the different HO_2 yields on the production rate of HO_2 is small (Fig. S8). For the range of tested yields, the HO_2 budget remains balanced within experimental uncertainties.

4.3 Photochemical ozone production

Photochemical ozone production in the troposphere is due to the oxidation of NO to NO_2 by reaction with peroxy radicals (R8, R9), followed by NO_2 photolysis yielding NO and $O(^3P)$ atoms. The O atoms combine with O_2 and form ozone. The net ozone production can be estimated from the production rate of NO_2 via reactions R8+R9, corrected for chemical loss of NO_2 by reaction with OH (R12) (e.g., Kanaya et al., 2007; Ren et al., 2013; Brune et al., 2016).

$$P^{(1)}_{O3} = k_8[RO_2][NO] + k_9\,[HO_2]\,[NO] - k_{12}[NO_2][OH] \qquad \text{(E11)}$$

Chemical loss of ozone by photolysis (R2), ozonolysis reactions (R4) and dry deposition is neligible under the given conditions. Calculated losses of ozone by photolysis and ozonolysis are not larger than 0.2 ppbv/h. The dry deposition rate at daytime is estimated to be no more than 1 ppbv/h assuming a mixed boundary layer height of 1km and a maximum deposition velocity of 1 cm/s (e.g., Weseley et al., 2000).~~Chemical loss of ozone by photolysis (R2) and ozonolysis reactions (R4) is neligible under the given conditions.~~ Using the rates shown in Fig. 2f ($OH+NO_2$), Fig 3c (D_{HO2}) and Fig 3e (D_{RO2}), a daily integrated net ozone production of (102±31) ~~102~~ ppbv is calculated (06:00 h to 18:00h). For comparison, the daily integrated $OH+NO_2$ term is (14±3)~~14~~ ppbv~~/h~~. About 70% of the ozone is produced in the morning (06:00 - 12:00h) and 30% in the afternoon (12:00 - 18:00h).

The radical budgets for OH, HO_2, and RO_2 allow tracing back which chemical processes are driving the production of peroxy radicals and therefore ozone formation. The first term ($k_8[RO_2][NO]$) in equation E11 can be considered as the contribution of the VOCs that form RO_2 which continue to react with NO to HO_2. As the HO_2 budget is essentially balanced, the HO_2 loss term (k_9 $[HO_2]$ $[NO]$) can be replaced by the rate of HO_2 producing processes (R3, R6, R7, R8) shown in Fig. 3c. This replacement implicitly assumes that other HO_2 losses such as HO_2+RO_2 and HO_2+HO_2 are negligible, which is valid during this study. The ozone production from RO_2 and HO_2 can then be expressed as

$$P^{(2)}_{O3} \cong 2\times k_8[RO_2][NO] + 2\times j_{HCHO\text{-}r}\,[HCHO] + (k_6[HCHO] + k_7[CO])[OH] - k_{12}[NO_2][OH] \qquad \text{(E12)}$$

Using equation E12 yields a daily net-ozone production of 112 ppbv (Fig. 5). This ~~values~~ value is in close agreement with the result of equation E11 which is using different experimental input parameters. According to equation E12, a percentage of 78% of the daily net-ozone production results from the oxidation of VOCs ~~(~~via reactions R5, R8, and R9~~)~~, 14% from reactions of

HCHO (R3+R6, followed by R9) and 8% from CO oxidation (R7, R9). Measured VOCs that produce RO_2 account for only 18% of the total ozone production, while unmeasured VOCs contribute the dominant fraction of 60%.

In principle, the first term ($k_8[RO_2][NO]$) in equations E11 or E12 could be replaced by the production rate calculated from the total VOC reactivity (k_{OH}(VOC(2))×[OH]), if the RO_2 budget was balanced.

$$P^{(3)}_{O3} \cong 2\times k_{OH}(VOC(2))\times[OH] + 2\times j_{HCHO\text{-}r}[HCHO] + (k_6[HCHO] + k_7[CO])[OH] - k_{12}[NO_2][OH] \quad (E13)$$

Using this equation, an integrated net-ozone production of 140 ppbv would be calculated. However, the RO_2 budget is not balanced (Fig. 3e) and indicates a missing RO_2 sink, which does not oxidize NO, and therefore does not produce ozone. This possibility was first suggested when the RO_2 to OH conversion by X was proposed to explain a missing OH source in PRD 2006 (Hofzumahaus et al., 2009). In the present case, such an RO_2 sink would remove ~~15%~~15 ppbv (22%) of the daily produced RO_2 resulting in an integrated ozone production that is ~~30%~~30 ppbv lower than expected from the rate of VOC oxidation.

The possible underprediction of the photochemical ozone production from unknown (unmeasured) atmospheric VOCs has been pointed out in previous studies, where RO_2 concentrations have been modelled (e.g., Griffith et al., 2016) or estimated from OH reactivities (Whalley et al., 2016). In the ClearfLo campaign 2012 in central London, the ozone production calculated from the oxidation of C2-C8 VOC species (measured by a standard GC-FID) was about 60% smaller than calculated from the total organic OH reactivity (≤ C12). The ozone underprediction for the case of using standard VOC measurements (C2-C8) alone is comparable to the present work. However, the calculated ozone production from the oxidation of VOCs may be overestimated, if an unknown RO_2 loss exists as is shown above. In a further study related to observations in the ClearfLo campaign, the comparison of measured and modelled radical concentrations (OH, HO_2, RO_2#, RO_2) points to a significant missing OH source and a missing sink for peroxy radicals at NO concentrations below 1 ppbv (Whalley et al., 2018), which is a similar trend as in the Heshan campaign for OH and RO_2. The results of both campaigns indicate significant gaps in the understanding of the radical chemistry and ozone formation in urban air at low NO conditions, which will require further investigations.

~~4~~ 5 Summary and Conclusions

A field campaign was carried out near the city of Heshan in autumn 2014 studying the radical chemistry under anthropogenically polluted conditions in the Pearl River Delta in southern China. Measurements of radical concentrations (OH, HO_2, RO_2, $RO_2^{\#}$), OH reactivity, and numerous other trace gases were performed. OH reactivity was in the range between 15 s^{-1} and 80 s^{-1}, with median values of 32 s^{-1} in the morning and 22 s^{-1} in the afternoon. Approximately 25% of the reactivity could be explained by measured CO and NOx, another 25% by measured hydrocarbons and formaldehyde, with a remainder of 50% missing reactivity from unmeasured components. OH concentrations reached maximum median values of 4.5×10^6 cm^{-3} at noon. HO_2 and RO_2 reached their maximum concentrations later in the afternoon with values of 3×10^8 cm^{-3} and 2.0×10^8 cm^{-3}, respectively. Measured $RO_2^{\#}$ (peroxy radicals mainly from alkenes and aromatics) made up only a small part (15%) of the total RO_2, although the fraction of $RO_2^{\#}$ producing VOCs made the largest contribution (94%) to the reactivity of measured VOCs. It suggests that at least part of the missing reactivity was due to unmeasured VOCs which produce RO_2, but not $RO_2^{\#}$.

The diurnal profile of OH was highly correlated with solar radiation and a significant median OH concentration of 0.7×10^6 cm^{-3} remained after sunset until midnight. In the remaining night, the concentrations dropped below the limit of detection (0.4×10^6 cm^{-3}, 1σ). Chemical modulation experiments were performed on several days between noon and midnight in order to test, whether the OH measurements could be biased by artificially produced OH in the low-pressure LIF detection cell. The test experiments were performed at OH reactivities of (14 - 26) s^{-1}, NO mixing ratios below 1 ppbv, relative high ozone concentrations (45 - 124 ppbv), and high air temperatures (25 - 30°C). A possible OH interference equivalent to a concentration of $(0.3\pm0.3)\times10^6$ cm^{-3} was found at the limit of detection.

In one of the test experiments, high OH nighttime values (around 1.8×10^6 cm^{-3}) were measured after sunset. These relatively high values are significantly larger than the possible OH interference determined in that test, suggesting that the measured OH was real.

The completeness of the radical measurements at daytime allowed for the first time to perform experimental budget analyses for all radicals (OH, HO_2, RO_2). There are differences between this method and the analysis often performed in model-based studies. In those studies, turnover rates are calculated from radicals and species that are simulated by a box model. Furthermore, balances between radical production and destruction rates are enforced even if the chemical mechanism is incorrect. In contrast, imbalances in a fully constrained experimental budget analysis, as applied here, indicate directly unknown experimental errors in the input data or an inconsistent chemical mechanism underlying the evaluation.

The balance between radical initiation and termination was studied in the ROx budget. ROx was mainly produced by photolysis of HONO (51%), HCHO (34%) and ozone (15%), and ozonolysis of alkenes (7%). The production with a maximum rate of 3-4 ppbv/h was essentially balanced within 0.5 ppbv/h by the destruction of ROx species with NO or NO_2.

In case of RO_2, the production rate calculated from measured VOCs is a factor of 4-5 too small to compensate the destruction rate of up to 11 ppbv/h in the afternoon, which is mainly determined by the loss reaction with NO. Only when the missing OH reactivity is explained by unmeasured VOCs can the RO_2 loss rate be balanced. The general assumption that missing OH reactivity is equivalent to unmeasured VOCs is thus directly confirmed by RO_2 measurements. Although the closure of the RO_2 budget is greatly improved, a significant imbalance of (2-5) ppbv/h remains in the afternoon indicating a missing RO_2 sink under low NO conditions. As far as $RO_2^{\#}$ is concerned, the chemical budget can be quantitatively closed within relatively large experimental error margins, if only measured VOCs are considered for RO_2 production. This result implies that the unmeasured VOCs did not produce $RO_2^{\#}$ and therefore do not belong to the group of alkenes and aromatics.

The OH destruction is compensated in the morning by the known OH sources from photolysis (HONO, O_3), ozonolysis of alkenes and OH recycling (HO_2+NO, R9). In the afternoon, however, the destruction rate is significantly higher than the calculated production rate, which indicates a considerable missing OH source of (4-6) ppbv/h. The daily variation of the missing OH source looks similar to that of the missing RO_2 sink, but with the opposite sign, so that both compensate each other largely in the ROx budget. Contrary to OH and RO_2, the HO_2 budget is essentially balanced over the whole day. The difference between production and destruction rates for OH and RO_2 shows an increasing trend when NO falls below 1 ppbv and becomes insignificant above 1 ppbv NO.

The observations indicate the existence of chemical processes that convert RO_2 to OH without the involvement of NO. Such processes have been discovered in recent years in the photochemical degradation of isoprene and methacrolein, where OH is regenerated by unimolecular RO_2 reactions. However, due to the low abundance of isoprene in the present campaign, these reactions account for only a small fraction (< 10%) of the missing RO_2 sink and missing OH source. A generic mechanism has been postulated previously to explain a missing OH source in the PRD under low NO conditions (Hofzumahaus et al., 2009). It involves the successive conversion of RO_2 to HO_2 and then to OH by an unknown reactant X. A concentration of X equivalent to 0.4 ppbv NO would close the budgets of RO_2 and OH in the present study, and leave the budgets of HO_2 and ROx unchanged. The X mechanism is, therefore, one possibility to describe all radical budgets at Heshan consistently, although its chemical nature remains unresolved.

The photochemical net ozone production rate was calculated from the reaction rates of HO_2 and RO_2 with NO, yielding a daily integrated amount of 102 ppbv O_3. This amount is due to the oxidation of VOCs (78%), formaldehyde (14%) and CO (8%).

About 60% of the ozone production is caused by unmeasured VOCs, which account for half of the measured OH reactivity. An even larger integrated net-ozone production would be calculated from the reaction rate of measured and unmeasured VOCs with OH, if all RO_2 radicals would react with NO. However, the unknown RO_2 loss reaction removes ~~15%~~22% of the daily RO_2 production and thus causes ~~30%~~30 ppbv less ozone production per day than would be expected from the VOC oxidation rate.

In summary, the current work provides new arguments for the existence of a missing OH source, which is most likely due to the conversion of RO_2 radicals without the involvement of NO. Our line of arguments depends critically on the assumption that the OH measurement technique is free of artifacts which would erroneously increase the calculated OH loss and RO_2 production rates. The experimental tests that were performed in the campaign give no evidence for such an interference, but there remains uncertainty because the tests have not covered the whole period of the campaign. Therefore, further field experiments with continuous control of the LIF measurements by chemical modulation are planned.

Data availability.

The data used in this study are available from the corresponding author upon request (a.hofzumahaus@fz-juelich.de).

Author contributions.

YZ, AW, and KL organized the field campaign. AH and ZT analyzed the data and wrote the manuscript. All authors contributed to measurements, discussing results, and commenting on the manuscript.

Acknowledgments

We thank the science teams of PRIDE-PRD2014. The work was supported by the National Natural Science Foundation of China (**21522701**, **91544225**, **21190052**, **41375124**), the National Key R&D Plan of China (**2017YFC0213000**), the National Science and Technology Support Program of China (**2014BAC21B01**), the Strategic Priority Research Program of the Chinese Academy of Sciences (**XDB05010500**), the Collaborative Innovation Center for Regional Environmental Quality, the BMBF project: ID-CLAR (**01DO17036**) and the EU-project AMIS (Fate and Impact of Atmospheric Pollutants, **PIRSES-GA-2011-295132**).

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Table 1 Chemical reactions considered in the radical budget analysis of OH, HO_2 and RO_2. The radical species are cyclically linked by chain reactions.

No.	Reaction	k(298 K) [a]
	Initiation reactions	
R1	$HONO + hv\ (< 400nm) \rightarrow OH + NO$	j_{HONO} [b]
R2	$O_3 + hv\ (< 340nm) \rightarrow O(^1D) + O_2(a^1\Delta_g, X^3\Sigma_g^-)$	j_{O1D} [b]
	$O(^1D) + H_2O \rightarrow OH + OH$	2.1×10^{-10} [c]
	$O(^1D) + M \rightarrow O(^3P) + M$	3.3×10^{-11} [c]
R3	$HCHO + hv\ (< 335nm) + 2\ O_2 \rightarrow 2\ HO_2 + CO$	$j_{HCHO\text{-}r}$ [b]
R4	$Alkenes + O_3 \rightarrow OH, HO_2, RO_2 + products$	[d]
	Chain propagation reactions	
R5	$OH + RH + O_2 \rightarrow RO_2 + H_2O$	[d]
R6	$HCHO + OH + O_2 \rightarrow CO + H_2O + HO_2$	8.4×10^{-12} [c]
R7	$CO + OH + O_2 \rightarrow CO_2 + HO_2$	2.3×10^{-13} [c]
R8	$RO_2 + NO \rightarrow RO + NO_2$	8.7×10^{-12} [e]
	$RO + O_2 \rightarrow R'CHO + HO_2$	
R9	$HO_2 + NO \rightarrow OH + NO_2$	8.5×10^{-12} [c]
R10	$HO_2 + O_3 \rightarrow OH + 2 \cdot O_2$	2.0×10^{-15} [c]
R11	$NO_2 + hv\ (< 420nm) + O_2 \rightarrow NO + O_3$	j_{NO2} [b]
	Termination reactions	
R12	$OH + NO_2 \cancel{+ M} \rightarrow HNO_3 \cancel{+ M}$	1.1×10^{-11} [f]
R13	$OH + NO \cancel{+ M} \rightarrow HONO \cancel{+ M}$	7.5×10^{-12} [f]
R14	$RO_2 + NO \rightarrow RONO_2$	4.6×10^{-13} [g]
R15	$RO_2 + RO_2 \rightarrow Products$	3.5×10^{-13} [h]
R16	$RO_2 + HO_2 \rightarrow ROOH + O_2$	$2.3\times10^{\cancel{-12}\,-11}$ [i]
R17[j]	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	1.7×10^{-12} [c]
	$HO_2 + HO_2 + H_2O \rightarrow H_2O_2 + H_2O + O_2$	3.7×10^{-30} [k]

[a] Reaction rate coefficients ($cm^3\ s^{-1}$) are shown in this table for 298 K and 1 atm. In the radical budget analysis (Fig. 2 - 4), the actual measured ambient temperatures and pressures were used.
[b] Measured (cf., Table 2) .
[c] MCM3.3.1.
[d] Specific kinetics data for each measured organic compound are taken from MCM3.3.1.
[e] $k(RO_2+NO) = 2.7\times10^{-12}\times\exp(360/T)$ (MCM3.3.1). The RO yield is assumed to be 0.95 (see text).
[f] NASA-JPL(Burkholder et al., 2015).
[g] Reaction rate coefficient as for R8. The yield of $RONO_2$ is assumed to be 0.05 (see text).
[h] $k(CH_3O_2+CH_3O_2)=1.03\times10^{-13}\times\exp(365/T)$ (MCM3.3.1).
[i] $k(RO_2+HO_2)= f \times 2.91\times10^{-13}\times\exp(1300/T)$ (MCM3.3.1). f is a scaling factor which is assumed to be one (see text).
[j] The effective reaction rate k_{17} contains both reactions with and without water.
[k] $k(HO_2+HO_2+H_2O)=3.08\times10^{-34}\times\exp(2800/T)+2.59\times10^{-54}\times[M]\times\exp(3180/T)$ (RACM2; (Goliff et al., 2013)). This reaction is a termolecular reaction with a unit of $cm^{-6}\ s^{-1}$.

Table 2 Median values of measured parameters in the morning and afternoon.

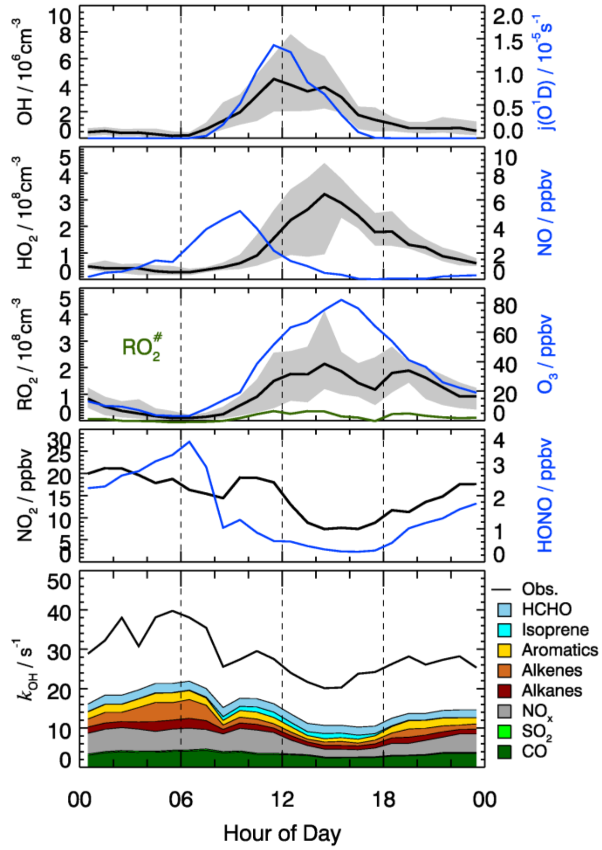
	06:00 -12:00h	12:00 - 18:00h
T [°C]	23.4	27.5
H_2O [a] [%]	2.0	2.0
j_{O1D} [$10^{-5}s^{-1}$]	0.3	0.5
j_{NO2} [$10^{-3}s^{-1}$]	1.6	2.1
j_{HONO} [$10^{-4}s^{-1}$]	2.7	3.6
j_{HCHO-r} [$10^{-6}s^{-1}$]	4.8	6.7
OH [$10^{6}cm^{-3}$]	1.3	2.6
HO_2 [$10^{8}cm^{-3}$]	0.5	2.5
RO_2 [$10^{8}cm^{-3}$]	0.3	1.7
k_{OH} [s^{-1}]	32	22
O_3 [ppbv]	16	69
NO [ppbv]	3.7	0.4
NO_2 [ppbv]	17	9
HONO [ppbv]	1.1	0.4
isoprene [ppbv]	0.3	0.5
HCHO [ppbv]	5.8	6.8
CO [ppmv]	0.7	0.5

[a] volume mixing ratio

Table 3 Unexplained OH signal (mean ± 1σ) and chemical conditions during the OH chemical modulation test experiments. Given numbers are average values of multiple tests that were performed in the specified time period (see as an example, Fig. S3).~~tests.~~

Exp.	Date	Daytime (h)	OH	k_{OH}	O_3	NO	Isoprene	T	Unexplained OH signal
			[10^6 cm^{-3}]	[s^{-1}]	[ppbv]	[ppbv]	[ppbv]	[°C]	[10^6 cm^{-3}][a]
1	19 Oct	16:40-17:40	3.8	18.6	67	0.00±0.11	N.A. [b]	27	0.7±0.4
2	29 Oct	14:30-16:00	3.7	14.1	78	0.18±0.22	0.74	29	0.3±1.0
3	30 Oct	20:20-21:00	1.8	25.7	32	0.21±0.25	0.04	25	0.4±0.5
4	31 Oct	12:50-13:50	9.4	20.1	103	0.32±0.38	0.60	30	0.1±0.8
5	1 Nov	15:10-16:00	6.9	22.2	124	0.10±0.05	1.21	30	0.4±0.7
6	22 Nov	17:00-23:00	0.2	24.4	45	0.14±0.24	0.05	25	-0.3±0.5

[a] Expressed as equivalent OH concentration; [b] Not available.



5 **Figure 1 Median diurnal profiles of measured OH, HO_2, RO_2, $RO_2^{\#}$, k_{OH}, $j(O^1D)$, NO, NO_2, O_3, and HONO. For OH, HO_2 and RO_2, the grey band around the median (black lines) denotes the 25 % and 75 % percentiles of the distributions. In the lowest panel, coloured areas show the speciated reactivity contributions from measured OH reactants.**

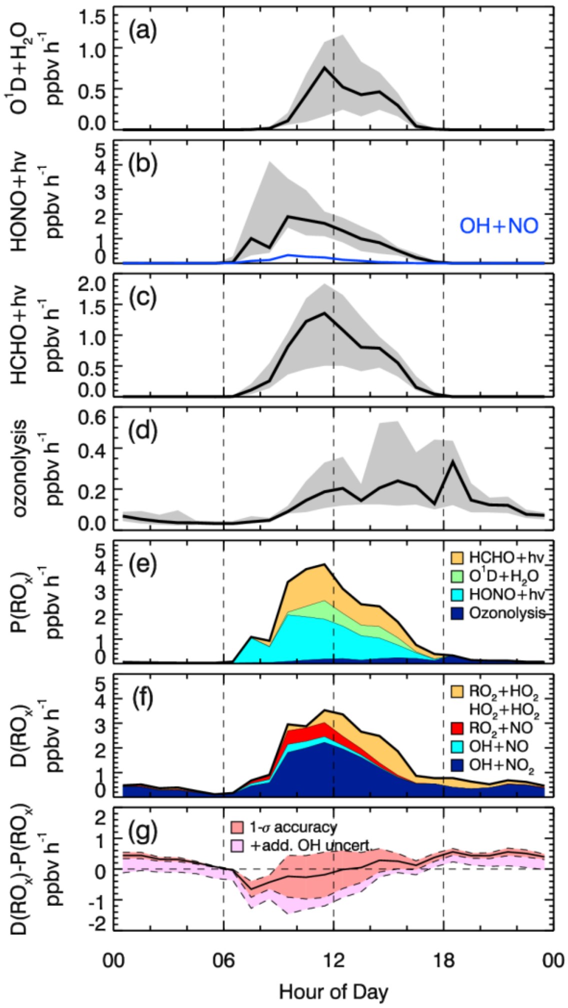


Figure 2 Median production and destruction rates of RO_x. Panels (a - d) show production rates (black lines: median values) from the photolysis of ozone (a), HONO (b), HCHO (c), and ozonolysis of alkenes (d). Grey bands around the median denote 25 % and 75 % percentiles. The blue line in panel (b) represents the back reaction rate of OH+NO yielding HONO. Panels (e) and (f) show cumulative plots of the production and destruction rates, respectively. Panel (g): the solid black line is the difference between the total production and destruction rate. The red shaded band indicates the 1σ uncertainty due to experimental errors of the measured quantities (Table S1) and the reaction rate coefficients. The pink shaded area represents the maximum possible bias from a potential OH interference.

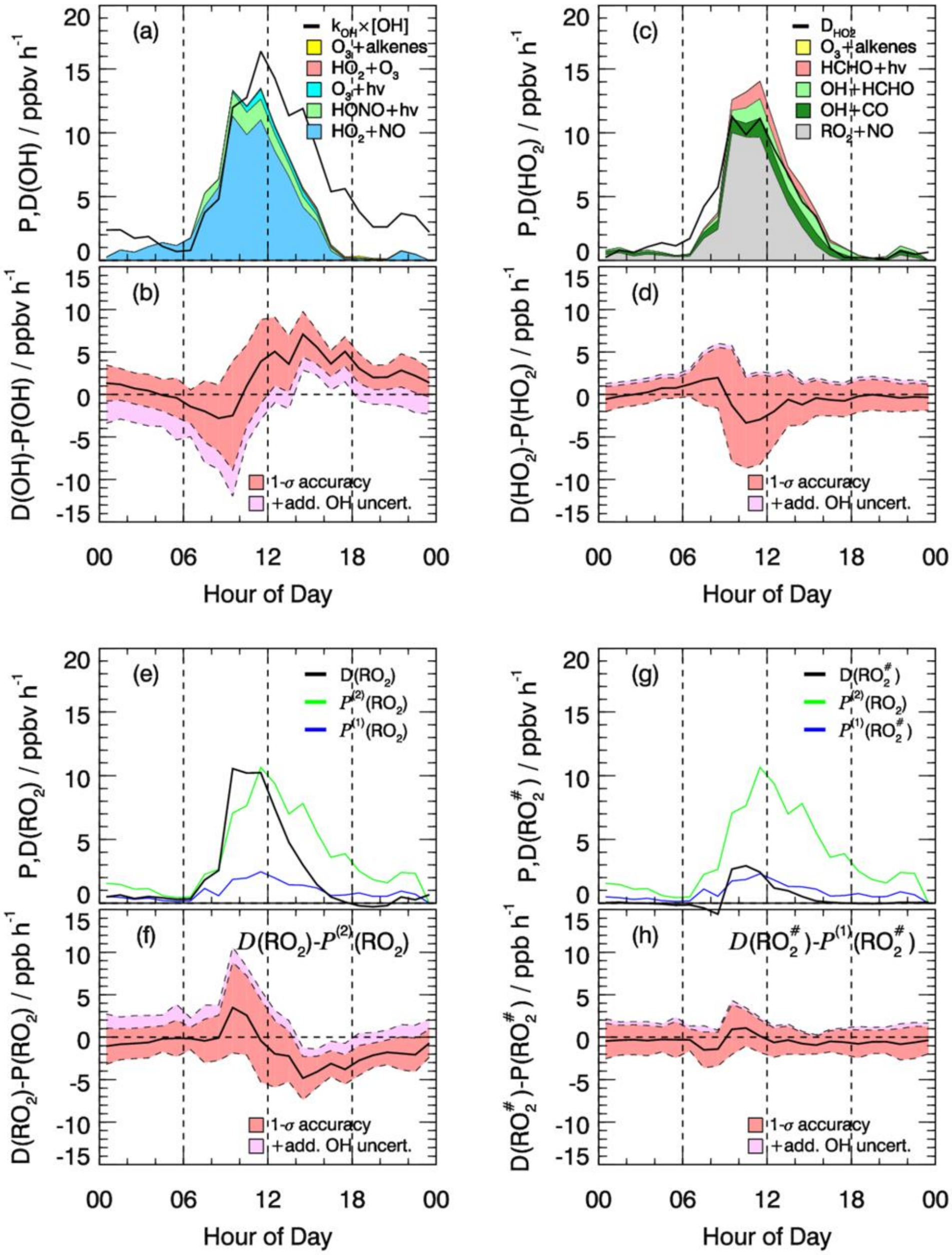


Figure 3 Experimental budgets for OH (a, b), HO_2 (c, d), RO_2 (e, f) and $RO_2^{\#}$ (g, h). In the respective upper panels (a, c, e, g), solid black lines denote the median total destruction rates. The colored areas in (a) and (c) represent cumulative plots of the production rates from different reactions. 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).~~The blue solid lines in (e) and (g) denote the production rate of RO_2 species from measured VOCs (equation E7, VOC(1)), and the green lines represent the RO_2 production rate calculated from k_{OH}(VOC(2)) (equation E8, VOC(2)).~~ 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. ~~Panel (f) shows the difference of D_{RO2} with respect to the case OH+VOC(2). Panel (h) shows the difference with respect to the case OH+VOC(1).~~ 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.

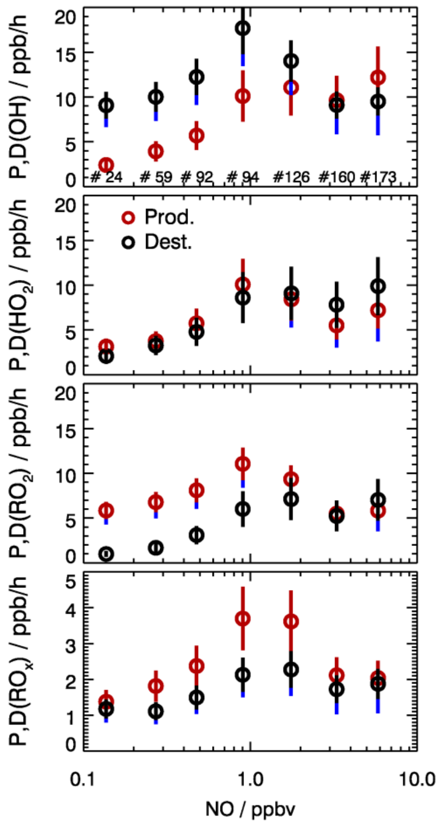


Figure 4 Experimental production and destruction rates for OH, HO_2, and RO_2 as a function of NO. The circles represent median values for NO intervals of $\triangle\ln(NO)/ppbv=0.57$. Data are restricted to daytime conditions ($j(O^1D)>0.1\times10^{-5}$ s^{-1}). The number (#) of data points included in each NO bin is given in the upper panel. Vertical error bars (red and black) denote the 1σ uncertainties due to experimental errors of the measured quantities (Table S1) and the reaction rate coefficients. Vertical blue bars denote the maximum possible bias from a potential OH interference.

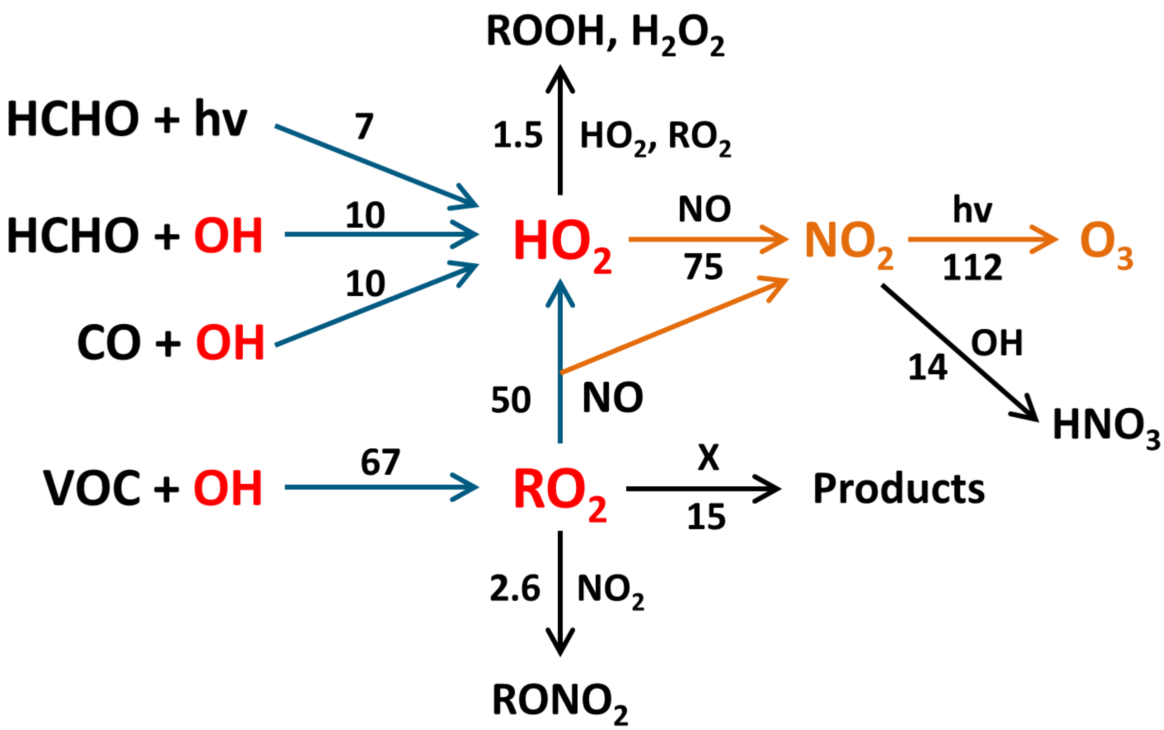


Figure 5 Main reaction pathways leading to photochemical net ozone formation during the Heshan campaign. Blue arrows show the reaction paths leading to RO_2 and HO_2, yellow arrows indicate the oxidation reactions of NO to NO_2 by peroxy radicals with subsequent NO_2 photolysis yielding ozone. Black arrows represent reactions that remove peroxy radicals or NO_2 and thus reduce ozone production. Numbers represent median daily-integrated reaction rates (ppbv) calculated by equation E12. The value for VOC+OH corresponds to kOH(VOC(2))×[OH] (see equation E8). The reaction with X indicates an unknown process that removes RO_2 without producing NO_2.

Supplementary Information

Experimental budgets of OH, HO_2 and RO_2 radicals and implications for ozone formation in the Pearl River Delta in China 2014

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Supplementary text

Addtional uncertainties in the budget analyses

Radical initiation by unmeasured VOCs

As pointed out in Section 4.1, unmeasured VOCs were most likely responsible for the observed missing OH reactivity. This not only considerably influences the radical chain propagation from OH to RO_2 (Fig. 3e, g), but can also affect the primary production of OH, HO_2, and RO_2 radicals. Unmeasured alkenes could form additional radicals through ozonolysis. 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 $P^{(1)}_{RO2}$ of $RO_2^{\#}$ from these compounds is balanced by the calculated $RO_2^{\#}$ loss rate. If an essential fraction of the unmeasured VOCs would consist 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, would increase by about a factor of 2. This increase would have a negligible impact on the radical budgets of OH and HO_2. ~~However, the contribution to radical formation is very likely unimportant as the small amount of $RO_2^{\#}$ compared to RO_2 (Fig. 1), and the analysis of the RO_2 and $RO_2^{\#}$ budgets suggest that most of the missing reactivity is not caused by alkenes (Section 4.1).~~ Unmeasured OVOCs could form additional radicals (HO_2, RO_2)

through photolysis. Such reactions would further increase the gap between the production and destruction rate for RO_2 and disturb the closed RO_x and HO_2 budgets.

Radical initiation by Cl atoms

Gaseous nitryl chloride ($ClNO_2$) can be formed at night by heterogeneous reaction of N_2O_5 with chloride in moist particles (e.g., Osthoff et al., 2008). In the morning, $ClNO_2$ photolyzes and forms Cl atoms which react very fast with VOCs and produce additional RO_2. This mechanism can play a role for 2 - 3 hours after sunrise until the $ClNO_2$ reservoir is depleted. $ClNO_2$ was not measured in Heshan, but was reported for other places in China. Measured concentrations shortly before sunrise are typically below 1 ppbv (e.g., Tham et al., 2016; Wang et al. (2018)), but can occasionally reach a few ppb (e.g., 2.1 ppbv in Wangdu, Tham et al. (2016); 4.7 ppbv in Hong Kong,(Wang et al., 2016)). With photolytical lifetimes of 2 - 3 hours, Cl production rates rarely exceed 0.5 ppbv/h. RO_2 production with a similar rate will make only a minor contribution to the RO_2 budget (Fig. 3e), and make the balance in the ROx budget slightly worse (Fig. 2g).

Uncertainties related to the measurement and chemistry of RO_2 ~~*Chain propagation versus termination in the reaction of RO_2 + NO*~~

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. 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. There exist RO_2 radical species 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 also 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 besides HO_2 in a parallel reaction carbonyl compounds and NO_2 as products. The latter reaction constitutes a 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 (≥ 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^3s^{-1}, 9.0×10^{-12} cm^3s^{-1}, and 2.0×10^{-11} cm^3s^{-1}, respectively (Jenkin et al., 2019). The MCM value used in Table 1 for R8 + R14 (9.0×10^{-12} cm^3s^{-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^3s^{-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^3s^{-1} (R8 + R14). 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. 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 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 (Atkinson et al., 1982)., 1982; Lightfoot et al., 1992). For the budget analysis (Figs. 2 - 4), an organic nitrate yield of 5% is assumed. Figs. ~~S4~~ S7 and ~~S5~~ S8 show cases where higher yields (10%, 20%) are assumed. Higher organic nitrate yields compensate the slightly negative bias of *D-P* in the RO_x budget (Fig. ~~S4~~S7). An average yield of 10% would lead to a perfect balance 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 (R16) lie in the range between 0.5×10^{-11} cm^3s^{-1} and 2.2×10^{-11} cm^3s^{-1} at 298K (Jenkin et al., 2019). In MCM, a general value of 2.3×10^{-11} cm^3s^{-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.

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Table S1 Measured quantities used to evaluate the radical budgets.

Measured quantity	Measurement technique	Time resolution	Detection limit [a]	Accuracy (1σ)
OH	LIF [b]	300 s	3.9×10^{5}cm^{-3}	±13 %
HO_2	LIF [b, c]	300 s	1.2×10^{7}cm^{-3}	±20 %
RO_2	LIF [b, c]	300 s	0.6×10^{7}cm^{-3}	±26 %
$RO_2^{\#}$ [d]	LIF [b, c]	300 s	1.7×10^{7}cm^{-3}	±32 %
k_{OH}	LP-LIF [e]	180 s	0.3 s^{-1}	±10 %, ±0.7 s^{-1}
Photolysis frequencies	Actinic flux spectroradiometry	20 s	f	±10 %
O_3	UV photometry	60 s	0.5 ppbv	±5 %
NO	Chemiluminescence	60 s	60 pptv	±20 %
NO_2	Chemiluminescence [g]	60 s	300 pptv	±20 %
HONO	LOPAP [h]	30 s	7 pptv	±20 %
CO,CH_4,CO_2,H_2O	Cavity ringdown spectroscopy	60 s	i	j
SO_2	Pulsed UV fluorescence	60 s	0.1 ppbv	±5 %
HCHO	Hantzsch fluorimetry	60 s	25 pptv	±5 %
~~Volatile organic compounds~~NMHCs [k]	GC-FID/MS [l]	1 h	20 - 300 pptv	±(15-20) %

[a] Signal to noise ratio = 1; [b] Laser-induced fluorescence; [c] Chemical conversion via NO reaction before detection; [d] $RO_2^{\#}$ ~~is~~ are ~~the~~ organic peroxy radicals ~~particular RO_2 radicals~~ from large alkanes (> C4), alkenes (including isoprene) and aromatics; [e] Laser photolysis – laser-induced fluorescence; [f] Five orders of magnitude lower than maximum at noon; [g] Photolytic conversion to NO before detection, home built converter; [h] Long-path absorption photometry; [i] CO: 1 ppbv; CH_4:1 ppbv; CO_2: 25 ppbv; H_2O: 0.1 % (absolute water vapor content).; [j] CO: ±1 ppbv; CH_4: ±1 ppbv; CO_2: ±25 ppbv; H_2O: ±5 % ; [k] ~~VOCs including~~NMCHs include C_2-C_{11} alkanes, C_2-C_6 alkenes, C_6-C_{10} aromatics; [l] Gas chromatography equipped with mass spectrometer and a flame ionization detector.

Table S2 Measured volatile organic compounds.

Groups	VOC compounds
Alkanes	CYCLOHEXANE, CYCLOPENTANE, ETHANE, I-BUTANE, I-PENTANE, METHYLCYCLOHEXANE, METHYLCYCLOPENTANE, N-BUTANE, N-DECANE, N-DODECANE, N-HEPTANE, N-HEXANE, N-NONANE, N-OCTANE, N-PENTANE, N-UNDECANE, PROPANE, 2,2,4-TRIMETHYLPENTANE, 2,2-DIMETHYLBUTANE, 2,3,4-TRIMETHYLPENTANE, 2,3-DIMETHYLBUTANE, 2,3-DIMETHYLPENTANE, 2,4-DIMETHYLPENTANE, 2-METHYLHEPTANE, 2-METHYLHEXANE, 2-METHYLPENTANE, 3-METHYLHEPTANE, 3-METHYLHEXANE, 3-METHYLPENTANE
Alkenes	CIS-2-PENTENE, CIS-BUTENE, ETHENE, I-BUTENE, PROPENE, TRANS-2-BUTENE, TRANS-2-PENTENE, 1-BUTENE, 1-HEXENE, 1-PENTENE, STYRENE [a]
Aromatics	BENZENE, ETHYLBENZENE, I-PROPYLBENZENE, M-DIETHYLBENZENE, M-ETHYLTOLUENE, M,P-XYLENE, N-PROPYLBENZENE, O-ETHYLTOLUENE, O-XYLENE, P-DIETHYLBENZENE, P-ETHYLTOLUENE, TOLUENE, 1,2,3-TRIMETHYLBENZENE, 1,2,4-TRIMETHYLBENZENE, 1,3,5-TRIMETHYLBENZENE
Alkynes	ETHYNE
Biogenics	ISOPRENE
OVOCs	FORMALDEYHYDE

[a] Styrene is treated as alkene because its major ~~funtional~~ functional group is the C-C double bond with respect to OH reaction.

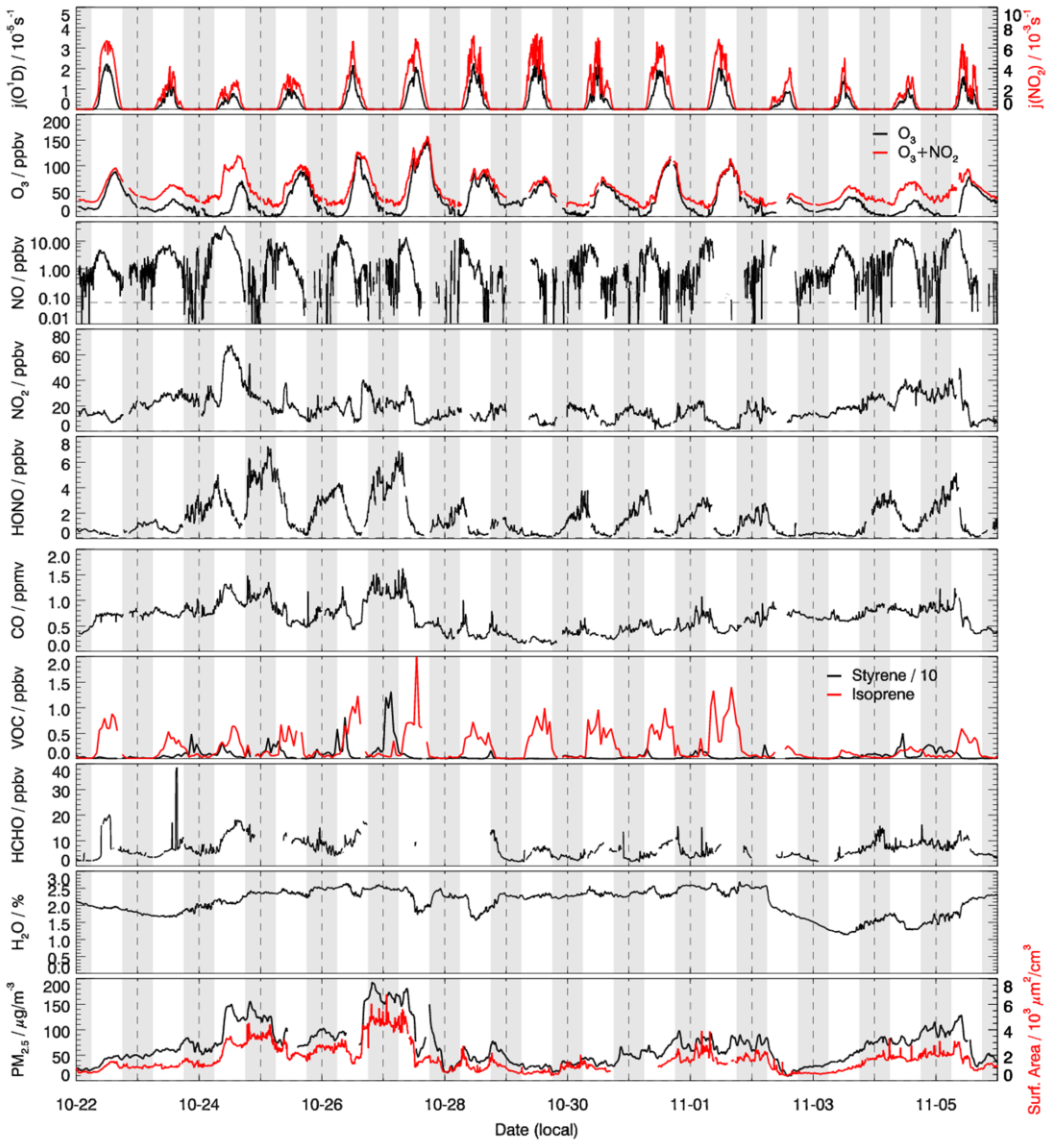

Figure S1 Time series of measured photolysis frequencies, O_3, O_x (O_3+NO_2), NO, NO_2, HONO, CO, isoprene, styrene, HCHO, and H_2O volume mixing ratios, $PM_{2.5}$ mass concentrations and surface area of particulate matter. The vertical dashed lines represent midnight and grey areas represent nighttime.

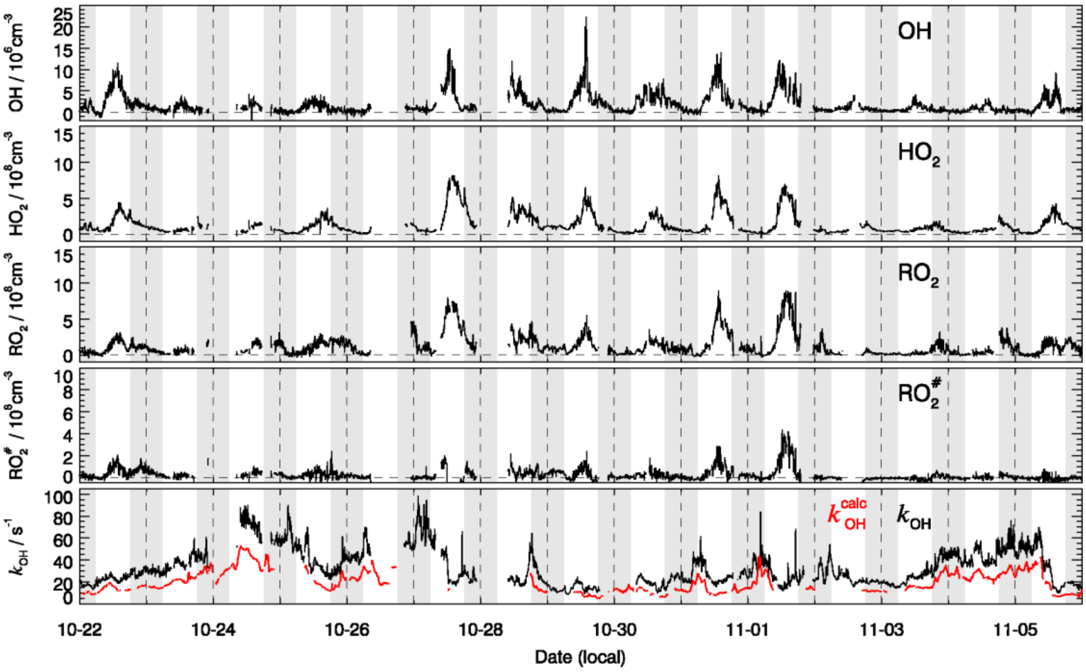

Figure S2 Time series of measured OH, HO_2, RO_2 and $RO_2^{\#}$ concentrations. The lowest panel shows the measured total OH reactivity (k_{OH}) and the calculated OH reactivity (k^{calc}_{OH}) derived from measured concentrations of CO, NO_x, CH_4, NMHCs and HCHO. The vertical dashed lines represent midnight and grey areas represent nighttime.

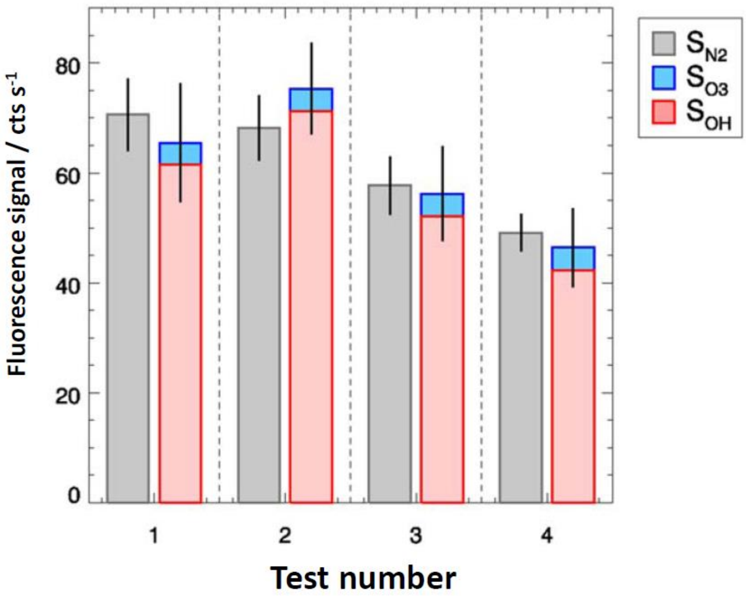

Figure S3 Results from the chemical modulation tests performed on 31 October 2014 between 12:50 and 13:50. The measured OH signal without scavenger (S_{N2}) can be explained within experimental errors by the sum of the signal from ambient OH (S_{OH}) and the known interference from O_3 (S_{O3}). Error bars denote 1σ statistical errors. S_{OH} is calculated by the expression (S_{N2} - $S_{propane}$)/ε, where $S_{propane}$ is the signal with scavenger (propane) and ε is the efficiency of scavenging (for details, see Tan et al., 2017). A fluorescence signal of 60 cts/s is equivalent to an OH concentration of 1×10^7 cm^{-3}.

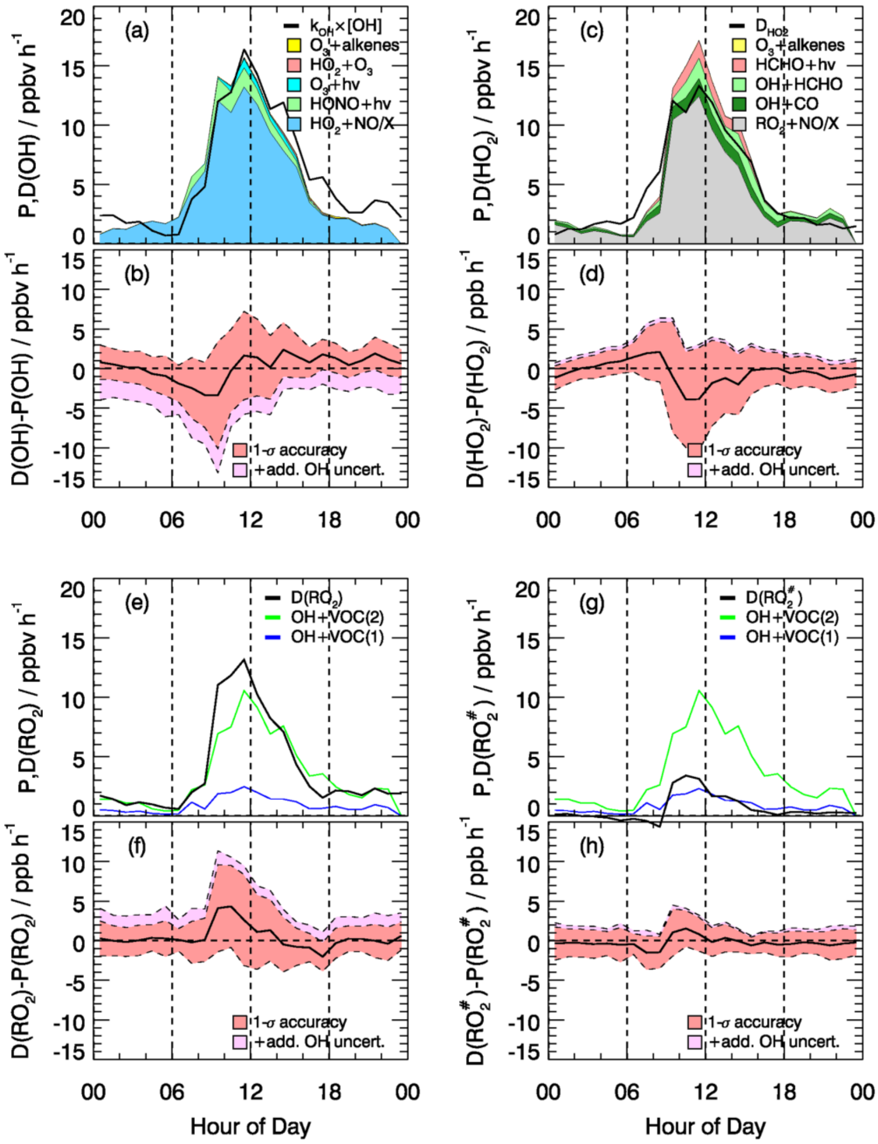

Figure S4 Same as Fig. 3, but with additional RO_2 conversion to OH assuming a first-order rate coefficient of 0.08 s^{-1}. This scenario can also be seen as an application of the X mechanism which recycles OH by the hypothetical sequence $RO_2 + X \rightarrow HO_2$, $HO_2 + X \rightarrow HO_2$ with X equivalent to 0.4 ppbv NO.~~**Figure S3 Same as Figure 3, but with additional OH recyling by X equivalent to 0.4 ppbv NO ($RO_2 + X \rightarrow HO_2$, $HO_2 + X \rightarrow HO_2$).**~~

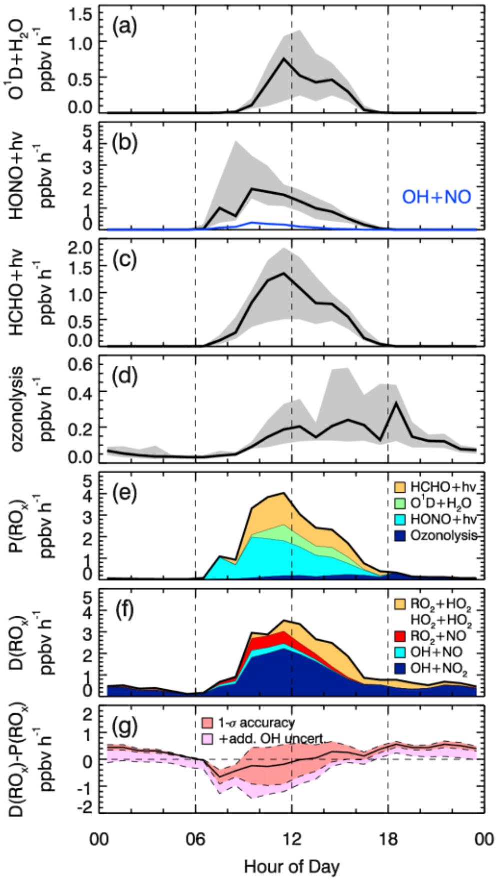

Figure S5 Same as Fig. 2, but assuming a rate constant of $1\times10^{-11}cm^{-3}s^{-1}$ for the reaction of RO_2 with NO (R8, R14) .

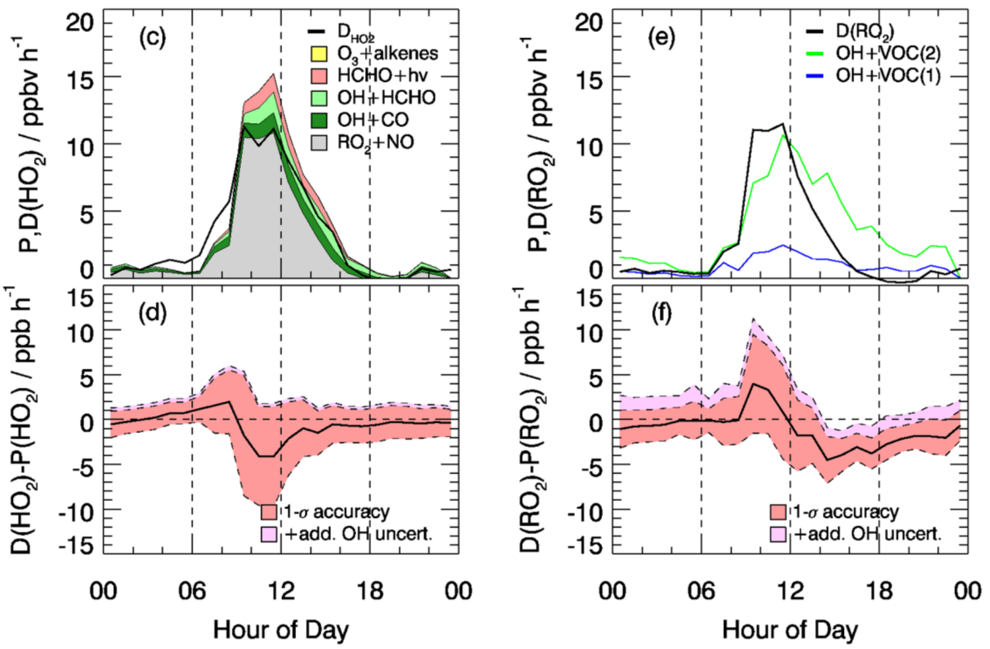

Figure S6 Same as Fig 3. (c, d, e, f) but assuming a rate constant of 1×10^{-11}cm^{-3}s^{-1} for the reaction of RO_2 with NO (R8, R14) .

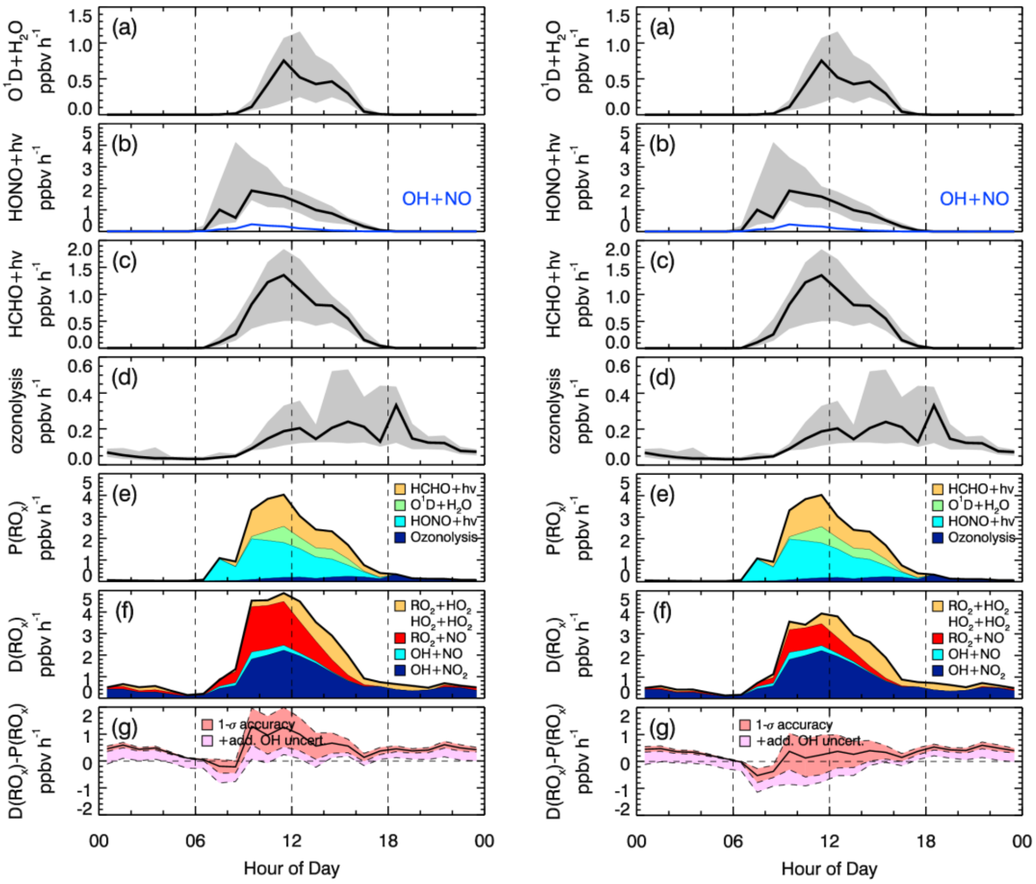

Figure ~~S4~~ S7 Same as Fig. 2, but assuming a different branching ratio between reaction R8 and R14. Left: HO_2 yield is 0.8, organic nitrate yield is 0.2. Right: HO_2 yield is 0.9, organic nitrate yield is 0.1.

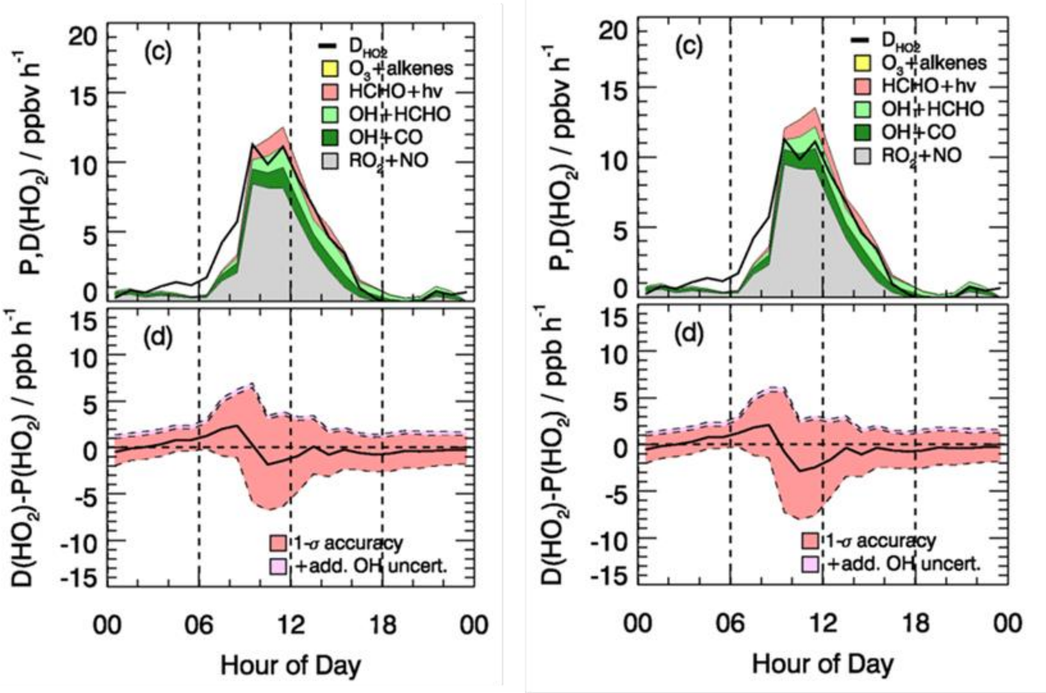

Figure ~~S5~~ S8 Same as Fig. 3(c, d), but assuming a different branching ratio between reaction R8 and R14. Left: HO_2 yield is 0.8, organic nitrate yield is 0.2. Right: HO_2 yield is 0.9, organic nitrate yield is 0.1.