Anonymous Referee #1

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

Comments

(1)

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
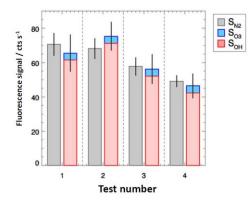
(as an example, see Fig. S3).

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 ($S_{N2} - S_{propane})/\varepsilon$, 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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