

### Anonymous Referee #3

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

#### *Comments*

(1)

*page 1, line 19: "In case of RO<sub>2</sub>, 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<sub>2</sub> measurements." This is a likely but not exclusive explanation. I recommend to rephrase the sentences: "In case of RO<sub>2</sub>, the budget could be closed by attributing the missing OH reactivity to unmeasured VOCs. Thus, unmeasured VOCs are directly linked to the RO<sub>2</sub> measurements."*

We changed the sentence as follows.

In case of RO<sub>2</sub>, 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<sub>2</sub> measurements.

(2)

*page 1, line 25: "These observations suggest the existence of a chemical mechanism that converts RO<sub>2</sub> 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<sub>2</sub> to OH without the involvement of NO, increasing the RO<sub>2</sub> 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-NO<sub>x</sub> conditions". Please define the term "low-NO<sub>x</sub> conditions".*

We changed the sentence to

... tendency to underpredict OH under low-NO<sub>x</sub> conditions (NO < 300 pptv).

(4)

*Page 4, line 4: Please explain in the supplement table caption the term "RO<sub>2</sub>#".*

In the footnotes of Table S1, we included the following explanation.

RO<sub>2</sub># are organic peroxy radicals from large alkanes (> C<sub>4</sub>), 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 N<sub>2</sub>?*

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 HO<sub>2</sub> 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 HO<sub>2</sub> 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  $(2\pm 1)\times 10^7$  cm<sup>-3</sup> and  $(1\pm 1)\times 10^7$  cm<sup>-3</sup> for HO<sub>2</sub> and RO<sub>2</sub>, respectively, and is routinely subtracted from the measurements.

(9)

*Page 5, line 8: It is unclear which instruments have been used for CO and CO<sub>2</sub> in this study.*

We added a sentence on Page 5 Line 9.

The CO and CO<sub>2</sub> 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 NO<sub>3</sub> photolysis Liebmann et al. , 2018, found during daytime a fractional loss of NO<sub>3</sub> of 25% by reaction with BVOC. What is the daytime NO<sub>3</sub> 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<sub>3</sub> is produced by reaction of NO<sub>2</sub> with ozone. It is generally assumed that during the bright hours of the day, NO<sub>3</sub> 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<sub>3</sub> was removed by biogenic VOCs. The possible role of NO<sub>3</sub> 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<sub>3</sub> 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  $\text{NO}_3$  with VOCs are an additional  $\text{RO}_2$  source which is neglected in the budget calculation in Section 2.3.4. The relevance can be estimated from the production rate of  $\text{NO}_3$ , which is calculated from the reaction of  $\text{NO}_2$  with  $\text{O}_3$  ( $k(\text{NO}_2+\text{O}_3)=1.47\times 10^{-13}\times\exp(-2470/T)$ ; MCM3.3.1). In this campaign, the  $\text{NO}_3$  production rate was in the order of 1.4 ppbv/h and 0.7 ppbv/h at day- and nighttime, respectively. Because  $\text{NO}_3$  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  $\text{NO}_3$  reacted with biogenic VOCs. Under the conditions at Heshan 2014, the main loss process at daytime is the reaction with  $\text{NO}$ . If we neglect unmeasured VOCs, the percentage removal of  $\text{NO}_3$  in the morning is 96% by  $\text{NO}$ , 3% by photolysis, and 1% by measured VOCs. In the afternoon, the corresponding values are 72%, 21%, and 7%. Thus, the estimated  $\text{RO}_2$  production rate from  $\text{NO}_3$  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  $\text{RO}_2$ . The tendency is to slightly increase the imbalance between the production and destruction rate of  $\text{RO}_2$  observed in the afternoon (Fig. 3). At sunset and in the night, the  $\text{NO}_3$  production rate of 0.7 ppbv/h can be considered as an upper limit for the  $\text{RO}_2$  production. This value can possibly explain at least partly the imbalance of about 0.5 ppbv/h in the  $\text{RO}_x$  budget after sunset (Fig. 2).

(12)

*Page 9, line 38, What is the upper limit of  $\text{RO}_x$  production by  $\text{NO}_3$  during night time, i.e. what is the  $\text{NO}_3$  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  $P^{(2)}_{\text{RO}_2}$  calculated by Equation E8 (Fig. 3e) matches  $D_{\text{RO}_2}$  relatively well.

(14)

*Page 11, line 6: "The completeness of the radical measurements allows a budget analysis for all radicals (OH, HO<sub>2</sub>, RO<sub>2</sub>) 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  $j_{\text{O}_1\text{D}} > 1\times 10^{-6} \text{ s}^{-1}$  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  $\text{NO}_x$  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 NO<sub>x</sub> 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<sub>2</sub>, and RO<sub>2</sub> 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 negligible 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 1 km and a maximum deposition velocity of 1 cm/s (e.g., Wesely 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<sub>2</sub> term is (14±3) ppbv.

(20)

*Page 14, line 4: Please include the statement that the loss term HO<sub>2</sub>\*NO generating NO<sub>2</sub> can be replaced by the production term of HO<sub>2</sub> under the assumption that other HO<sub>2</sub> losses, like HO<sub>2</sub>+RO<sub>2</sub>, HO<sub>2</sub>+HO<sub>2</sub> are negligible.*

We added the following sentence.

This replacement implicitly assumes that other HO<sub>2</sub> losses such as HO<sub>2</sub>+RO<sub>2</sub> and HO<sub>2</sub>+HO<sub>2</sub> are negligible, which is valid during this study.

## References:

Liebmann, J., Karu, E., Sobanski, N., Schuladen, J., Ehn, M., Schallhart, S., Quéléver, L., Hellen, H., Hakola, H., Hoffmann, T., Williams, J., Fischer, H., Lelieveld, J., and Crowley, J. N.: Direct measurement of NO<sub>3</sub> radical reactivity in a boreal forest, *Atmos. Chem. Phys.*, 18, 3799-3815, 10.5194/acp-18-3799-2018, 2018.

Wesely, M. L., and Hicks, B. B.: A review of the current status of knowledge on dry deposition, *Atmos. Environ.*, 34, 2261-2282, [https://doi.org/10.1016/S1352-2310\(99\)00467-7](https://doi.org/10.1016/S1352-2310(99)00467-7), 2000.

Yang, Y. D., Shao, M., Kessel, S., Li, Y., Lu, K. D., Lu, S. H., Williams, J., Zhang, Y. H., Zeng, L. M., Noelscher, A. C., Wu, Y. S., Wang, X. M., and Zheng, J. Y.: How the OH reactivity affects the ozone production efficiency: case studies in Beijing and Heshan, China, *Atmos. Chem. Phys.*, 17, 7127-7142, <https://doi.org/10.5194/acp-17-7127-2017>, 2017.