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Interactive comment on "OH reactivity at a rural site (Wangdu) in the North China Plain: Contributions from OH reactants and experimental OH budget" *by* Hendrik Fuchs et al.

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We thank the reviewer for the helpful comments.

Comment: I would suggest to add : - more connections with the conclusions from the accompanying paper (Tan, 2016) in the present paper, particularly because the modeled OH reactivity is presented in (Tan, 2016) as well as sensitivity run constrained on the basis of OH reactivity measurements, - a more detailed discussion on the missing reactivity, - gathering the discussion on the comparison with previous campaigns to avoid repetition and to help the reader to better see the new understanding brought by this campaign and in particular the reactivity measurements.

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Response: We agree that there should be a close connection to the paper by Tan et al.. We try to improve this point as can also be seen in the revision based on comments from all reviewers.

The modelled OH reactivity presented in Tan et al. does not differ significantly from calculations presented in this paper, because only modelled PAN and aldehyde species added to the OH reactivity. Therefore, there is no additional conclusion from that analysis for the kOH. We make a statement on p12 l320: "Therefore, concentrations of oxygenated organic compounds that are produced by model calculations but that were not detected were constrained to zero in calculations presented in our accompanying paper by Tan et al. (2016), in order to ensure that modelled OH reactivity is consistent with measurements."

We also make better use of results from model calculations derived by Tan et al by adding on p13 l408: "The result of the budget analysis is consistent with the finding by Tan et al. (2016) that model calculations underpredict OH by up to a factor of two at NO mixing ratios of less than 0.3 ppbv, but simulate HO2 and kOH correctly under these conditions at the Wangdu site. The good description of HO2 and kOH means that the major known OH source (the reaction of HO2 and NO) and the total OH loss rate are well represented by the model. Further model tests suggest a missing process that recycles OH from RO2 and HO2 by an unknown agent that behaves like 0.1 ppbv NO (Tan et al., 2016). Other trace gases measured at Wangdu give no hint to the nature of the missing source in the OH budget analysis or in the model results."

More discussion on missing reactivity are added. Please refer to details to the answers of the comments by reviewer #1.

We have the feeling that the discussion on the comparison with previous field campaigns is appropriate and would like to keep it as it is.

Comment: L29 : It is mentioned in the introduction that "the effort to improve our knowledge of radical chemistry in Chinese megacity areas was continued by a comprehensive field campaign at a location close to the city Wangdu" please resume the conclusion of the accompanying paper (Tan, 2016) and put in the conclusion of the article the key results from this campaign which contribute to this improvement. What type of environment should be studied in future campaigns to bring complementary information as in the present study the low reactivity and potential OH interferences seem to prevent to draw clear conclusion concerning the OH budget?

Response: We extend the introduction on p3 l33: "Compared to our previous field campaigns in China 2006 (Hofzumahaus et al., 2009), the quality and number of measurements have been improved. A large number of instruments measured a variety of different trace gases, part of which were simultaneously detected by several instruments. Specifically, measurements of organic oxygenated compounds such as formaldehyde and acetaldehyde were achieved, which was not the case in previous campaigns. Radical measurements were improved by performing additional tests of potential interferences in the detection of OH and a modified the detection scheme for HO_2 that avoids interference from RO_2 was applied (Fuchs et al., 2011)."

As stated in the paper of Tan et al. further improvement of the tests for potential interferences in the OH detection will be done in future campaigns to avoid additional uncertainty. Environments with a larger fraction of biogenic reactants could be of interest to complement results of this campaign. We add at the end of the conclusion: "For future field work, comprehensive studies like this campaign in photochemically active environments where larger contributions from biogenic reactants can be expected in addition to anthropogenic emissions may help to solve the still open questions of imbalances in the OH production and destruction and measured and calculated OH reactivity that have been observed in other campaigns."

Comment: It is confusing to see in the introduction that the site is described as "close to the city Wangdu", described at rural in the title and that the campaign location is in a botanic garden close to the "small" town Wangdu. Please clarify how and why this site has been chosen and how it is classified. Linked comment: how the comparison with

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other campaigns has been chosen? L350- 365, related to anthropogenic emissions but without the comparisons with reactivity measurements done in Paris or Mexico, whereas these campaigns are discussed later (l453-460) concerning HONO. I would propose to gather the comparison paragraphs.

Response: We state on p4 l69: “The site was chosen, because it was not directly influenced by strong close-by anthropogenic emissions or the direct outflow of a big city. However, it was expected to observe regionally transported pollution in the North China Plain.”

As shown in the discussion of results, the measurement site was mainly influenced by emission of anthropogenic sources. Therefore, the comparison to results from other campaigns is done for campaigns in urban environments during summertime, which provided information about kOH and the OH budget from measurements (see also the review by Yang et al. Atmos Environ 134, 147-161, 2016). We add a statement regarding the measurements done in Mexico on p12 l355: “Significantly higher morning values of 130 s^{-1} were observed in Mexico City 2003 (Shirley et al. 2006).” The section p15 l453-460 specifically discusses the impact of HONO photolysis for the OH budget, so that we also included measurements in Paris, although they were performed during wintertime. We rephrase the statement on p15 l457: “These campaigns took place in or very close to very large cities the one in Paris during wintertime) and NO concentrations were often exceptionally high, so that HONO formation was favored.” For the same reason we do not think that it should be moved to another position in the manuscript.

Comment: L73: Particle measurements are also available. Could it be commented?

Response: Particle measurements were done, but a detailed discussion is out of the scope of the paper. We add PM2.5 measurements in Fig. 2 and add text on p9 l234: “Typical daytime maximum PM2.5 concentrations ranged between 30 and 90 μ g/m^3 but were as high as 300 μ g/m^3 on one day due to the local biomass burning. No clear connection between OH reactivity and aerosol number concentration was observed.

Although a sharp drop in PM2.5 was observed on 19 June when also OH reactivity dropped, PM2.5 increased again to higher values till the end of the campaign."

Comment: L156: how the delay to start the fit is defined (which level of deviation is considered to discard the points?)

Response: We add on p6 l157: "The fit is started, if the count rate has decreased to the 90 % level of the maximum count rate."

Comment: L157: The reason for the deviation is attributed to the non homogeneity of the OH distribution: could this be clarified? Is it due to the heterogeneous distribution of the laser energy?

Response: We add on p6 l157: "The likely reason is that the spatial OH distribution is not perfectly homogeneous near the inlet nozzle of the OH detection cell right after the laser pulse due to inhomogeneities in the laser power across the laser beam."

Comment: L165: which species considered as contaminations have been identified in the gas cylinder?

Response: The major contamination that was measured by the GC system was toluene (50%) and smaller contributions from mainly butene and acetaldehyde, but also a larger number of other reactants. Concentrations were rather small and therefore the measurement of this contamination has some uncertainty. As stated in the text we therefore consider the correction of data for this contamination as additional uncertainty in our measurements.

Comment: L184: why the assumption of a bi-exponential fit would better describe the conditions with recycling?

Response: A bi-exponential behavior of the OH is expected from reaction kinetics. However, the attribution of the faster decay time to the OH reactivity is only approximately valid within certain limits of chemical conditions (see also Lou et al, ACP 2009). A detailed description is beyond the scope of this paper and also not relevant, because no bi-exponential fitting was applied for measurements in this campaign. We add on p7 l184: “This can be derived from reaction kinetics. The faster decay time represents approximately the OH reactivity for certain chemical conditions.”

Comment: L189: which criterion is used to decide that the measurements appear as single exponential decays?

Response: Deviation from a single exponential decay would be clearly seen in the residuum of the fit which is calculated for each individual fit. We add on p7 l188: “... no bi-exponential behavior was observed that would have been seen in the residuum of the fit.”

Comment: L206 : would be useful to show other correlations with individual species (provide also more details in the repartition of the reactivity for specific periods (L310)

Response: We tried correlation with other species, but no other OH reactant could be identified that would give additional insights to differences between the two parts of the campaign (see also responses to comments from reviewer #1).

Comment: L214/Figure 4: difficult to identify the different trajectories

Response: We tried to visualize trajectories best. For the interpretation of the result, it is not necessary to identify every single trajectory. An alternative presentation would result a larger set of figures, which would not give additional information.

Comment: L232: other species correlate with acetonitrile (could provide the profile in Figure 2)? New peaks (GC, PTR-MS) have been observed during the biomass activities?

Response: We add acetonitrile measurements in Fig. 2. Unfortunately, no clear correlation of acetonitrile measurements with other trace gases could be identified most likely because concentrations of other species were influenced by other sources or chemical transformation.

Comment: L264 and 302: influence of products due to oxidation by nitrate radical could be discussed, parallel with particle profiles could be discussed.

Response: We think that a statement of nighttime oxidation products is best placed on p11 l314: "In addition, undetected products from the oxidation by the nitrate radical could have been part of missing reactivity in the night."

See our response above regarding particle measurements.

Comment: L280-291: some repetitions with 3.1

Response: We move text from p9 l256-261 and merge this with text on p10 l280-291.

Comment: L297: "It is most prominently seen in median alkene and alkane concentrations". Where?

Response: We rephrase this statement: "It is most prominently seen in median alkene and alkane concentrations during nighttime (Fig. 5)."

Comment: L322: possible to use ratio of species with different rate constants with OH to estimate this photochemical age?

Response: Please refer to our answer to the same comment by reviewer #1.

Comment: L350-365: see comment above. What can be concluded from these comparisons?

Response: The conclusion from this comparison is that the reactivity at the measurement site is typical for an environment that is influenced by anthropogenic activities. We add on p350 l350: "The OH reactivities measured at the Wangdu site in the North China Plain show diurnal profiles that are comparable to those reported for other polluted environments all over the world (see review by Yang et al. 2016).".

Comment: L382: What is missing. How it has been concluded that "results do not change significantly, whether the first part is included or not"? Please detail.

Response: We add the requested information on p13 l382: “Unfortunately, the data coverage of simultaneous measurements before 20 June (mostly due to missing radical measurements) is not sufficient...”.

Results are mainly based on the analysis of median diurnal profiles, which were also calculated for only the second part of the campaign. None of the points we discuss in the paper changes, if all data are included or only the second part is taken into account. We rephrase this sentence: “However, results do not change significantly, whether the first part is included in the median diurnal profiles that are discussed below or not.”

Comment: L419: possible to show the results with the bias subtracted?

Response: We would like to emphasize that there is no clear evidence for a bias in the OH measurements as discussed in detail in the paper by Tan et al. 2016. A possible bias is within the uncertainty of tests for potential interferences in the OH measurements that we performed during the campaign. Therefore, there is no reason to subtract a bias.

Comment: L432: Please detail.

Response: A detailed discussion of a potential interferences in OH measurements and the method how tests were performed during the campaign is given in our accompanying paper by Tan et al. 2016. Consequences for the accuracy of the analysis of the OH budget are clearly stated in this manuscript.

Comment: L439: why introducing the term turnover rates there? Useful? Check the consistency of the terms used in the Figure 8.

Response: We change the term to “production and destruction rates” at this position and also change the label in Fig. 8 accordingly.

Comment: L475: but there are periods with significant missing reactivity. It could be mentioned in the conclusion.

Response: We add on p15 l468: “Highest missing reactivity of the median diurnal profile (approximately 25%) was observed during nighttime of the first part of the campaign, which could have been related to nearby emissions or undetected oxidation products.”.

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