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Atmospheric Chemistry and Physics Discussions

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: The comparisons between measured and calculated OH reactivity are presented only as time series, the manuscript would benefit from a scatterplot showing the calculated OH reactivity against the measurements, enabling a more direct comparison.

Response: We add a scatter plot and add text on p11 l309: "The good agreement between measured and calculated OH reactivity is also demonstrated by the high linear correlation coefficient ($R^2 = 0.77$ for the entire data set and both subsets of data)

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Discussion paper

between both values (Fig. new). For the second part of the campaign a linear regression analysis yields a slope of 0.96 with a negligible intercept of -0.33 s^{-1}. As already discussed missing reactivity was higher during the first part of the campaign, so that a regression analysis yields a higher slope of 1.7 with an intercept of -4.2s^{-1}. The larger intercept is due to a slightly non-linear relationship between measured and calculated reactivity for this subset of data."

Comment: The manuscript reports a limited role for oxidation intermediates. Model results reported for OH concentrations in the manuscript by Tan et al. could be used to quantify the contributions of unmeasured oxidation intermediates to the total OH reactivity, but are only briefly discussed.

Response: Please refer to our answers to reviewer #2.

Comment: Abstract: Mention the technique used to make the OH reactivity measurements.

Response: We add on p1 l8: "Total OH reactivity was measured by a laser flash photolysis - laser induced fluorescence instrument (LP-LIF)."

Comment: Lines 7-8: Quantify "good correlation" and "high contribution".

Response: We rephrase p1 l7-8: "...by a good correlation between measured OH reactivity and carbon monoxide (linear correlation coefficient $R^2 = 0.33$), and (2) by a high contribution of nitrogen oxide species to the OH reactivity (up to 30 % in the morning)."

Comment: Line 63-69: Can you comment on the prevailing wind direction?

Response: A discussion of the origin of air masses is given by back trajectory calculations presented in Fig. 4 and discussed on p8 l209-223.

Comment: Line 84: quantify the agreement (and elsewhere, e.g. line 102).

Response: We will rephrase the statement on p4 l84: "...agreed well within their ac-

curacies..." and on p4 l102: "...which during daytime in general agreed with measurements by GC within 30 to 50%...". See also answers to reviewer #1 for further modifications concerning this comment.

Comment: Line 85: How many instruments? What was the standard deviation of the average? How did one of the instruments "appear to be more precise"? How does the uncertainty in the NO measurements impact the analysis of OH reactivity?

Response: Please refer also to our answer to a similar comment from reviewer #1. "More precise" means that the reproducibility of calibration was better for one of the instruments. The impact of the additional uncertainty of the NO measurements on the analysis is taken into account in the estimate of uncertainties given on p11 l304-309 and shown in Fig. 8.

Comment: Line 93: How small is "rather small"? Quantify the impact.

Response: We rephrase the statement: "The choice of the HONO data set has a rather small impact on calculated OH reactivity, as well as on the calculated total OH production rate which was dominated by OH recycling from HO_2 during daytime (see below)." Please refer also to our answers to comments from reviewer #1.

Comment: Line 101: "part of the same species" – please rephrase to clarify the meaning.

Response: We rephrase this sentence: "Some of the species or family species were simultaneously detected by the GC system and the PTR-MS..."

Comment: Line 113: Please clarify that it is the previously reported Zeppelin instrument that is being used in this campaign.

Response: We will add on p6 l157: " This instrument was deployed in this campaign."

Comment: Line 121: Does the length of the sampling line affect the measurements?

Response: A sampling line of similar length and the same coating has been used

for the measurement of OH reactivity in our simulation chamber SAPHIR for a variety of different chemical conditions. So far, no unexpected difference between measured and calculated has been observed that would hint to an impact of the inlet line on measurements. Therefore, we are confident that there are no significant effects on measurements from the sampling line. We will add on p5 l122: "Such sampling line has been used for OH reactivity measurements in the Jülich atmosphere simulation chamber SAPHIR for many years without notable effects on measurements."

Comment: Line 126: How does the change in temperature affect the measured OH reactivity? What is the difference from the external ambient temperature?

Response: We will add on p6 l126: "Ambient temperature was higher with up to 38 °C for some periods during the campaign. Differences in temperature and pressure potentially effect the measured reactivity due to changes of the reactant concentrations and of reaction rate constants. Measured reactivities were corrected for changes in the reactant concentration calculated from measured ambient and flow-tube temperature and pressure values (corrections were less than 2 %). Sensitivity studies taking either ambient temperature or flow-tube temperature for the calculation of OH reactivity from measured OH reactant concentrations (see below) indicate that the effect of temperature differences on reaction rate constants resulted in changes in the OH reactivity of typical less than 1 % (maximum values 4 %) for conditions of this campaign."

Comment: Line 150: Clarify what you mean by "sufficiently precise". How does the summing of decay curves affect the reported values? Does it make any difference to simply average 60 decays before fitting as opposed to summing ten decays and then averaging six summed decays?

Response: Typical maximum counts for a single decay curve that was evaluated were 60 to 100 counts during this campaign. From counting statistics this gives an error of 10%. In this case, the fit result does not change significantly, if more traces are added. We will add the typical maximum counts on p6 l150. Changes in the decay

time within the time of summing/avering are small enough that results are not affected by this procedure other than that the precision is improved. Summing up and averaging has the advantage that realistic errors can be used for the fit procedure as stated in the text. Realistic errors can give more accurate results, if the noise of the decay curve is different from the assumption of pure shot noise. Both approaches have been regularly used by us in various campaigns. Results agree within their uncertainties in most cases.

Comment: Line 165: What is the uncertainty/precision of the measurements?

Response: Uncertainties and precision of measurements are specified in Table 1. The measurement of contamination in the zero air was done with the same GC instrument that also performed measurements during the campaign.

Comment: Line 187: What was the mean/standard deviation/median NO?

Response: Please refer to Fig. 7, which gives median NO concentrations and 25 and 75 percentiles.

Comment: Line 203: Quantify the correlation.

Response: See our answer to the comment above. We will rephrase the sentence by replacing “correlated with” by “related to”.

Comment: Lines 215-234: Much of this is poorly phrased and difficult to follow (particularly lines 224-228), please consider re-writing.

Response: We rephrase this paragraph.

Comment: Line 308: Re-iterate the source of the uncertainties and why they have been separated into two terms.

Response: The 10% accuracy of the OH reactivity measurements originates from consideration described in Lou et al 2009. It is based on the assumption that the accuracy is limited by the uncertainty in the reaction rate constants of CO, because

the accuracy of OH reactivity measurements were tested by measuring the reactivity from known CO concentrations. The additional uncertainty of $+0.7 s^{-1}$ is campaign-specific due to the uncertainty of the zero decay (see answers above). Because the first uncertainty is a relative value and the second one is an absolute value they are stated separately.

Comment: Line 315: Quantify the "exceptionally good agreement".

Response: Please refer to the answer to the first comment.

Comment: Line 364: The measured OH reactivity in London contained significant contributions from model-generated intermediates.

Response: We correct this error.

Comment: Line 402 and following paragraph: Quantify "nearly balanced", "slightly larger" and "hardly significant".

Response: We quantify "nearly balanced" by adding on p13 l402: "The OH destruction rate is on average only 20 % higher than the sum of OH production during daytime." and cancel the statement containing "slightly larger". "hardly significant" is already quantified as "hardly significant with respect to 405 the experimental accuracies (Fig. 8)".

Comment: Line 411: Quantify "much larger and highly significant".

Response: We add "up to a factor of four" on p14 l411.

Comment: Line 422: What about the possibility of OH regeneration through peroxy radical reactions with the nitrate radical?

Response: Model calculations of OH concentrations discussed in our accompanying paper by Tan et al. 2016 indicates that NO3 chemistry did not significantly contribute to nighttime OH production.

Comment: Line 445: Quantify or define the level of significance in the term “clearly above the level of significance”.

Response: We add on p14 l445 “...with respect to the measurement uncertainties”.

Other minor comments are corrected as suggested by the reviewer.

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