

Response to the comments of referee #1:

We thank the reviewer for the helpful comments.

Comment: Although a complete description of OH reactivity measurements is performed, the descriptions of ancillary measurements are not sufficiently detailed. Even if these measurements are described elsewhere (Tan et al., ACPD, 2016), the section 2.2 is too short and description of different measurements, especially for NO, HONO and VOCs (both GC-FID/MS and PTR-MS measurements), should be given in more details. For example: What are the model and brand of instruments? What were the frequencies of calibration for the various measurements? How were they performed? How many VOCs were measured by different instruments?

Response: We add more information about instrument models and brands.

We also add information about calibrations for (1) HONO measurements on p5 l93: "This instrument was calibrated by using a liquid standard as described in Li et al. (2014) every ten days." (2) NO_x on p4 l86: "Daily calibrations were performed using a certified gas standard." (3) VOC measurements by GC on p5 l96: "Full calibrations using certified gas standards (Air Environmental, Spectra Gases) were done before and after the campaign. Drifts of the sensitivity during the campaign were accounted for by measuring the instrument sensitivity for bromochloromethane, 1,4-difluorobenzene, chlorobenzene, and 1-bromo-3-fluorobenzene every second day." (4) VOC detection by PTR-MS on p5 l105: "Calibration of the PTR instrument was done every day using a certified gas standard (Air Environmental Inc.)." (5) and HO_x measurements on p4 l81: "The instrument sensitivity was calibrated every 3 to 4 days by a custom-built calibration source described in detail in Fuchs et al. (2011)."

The number of organic compounds measured by GC (59) is provided on p5 l94, species measured by PTR-MS are mentioned on p5 l98-103.

Comment: Authors report only acetaldehyde and sum of MVK and MACR as species measured by PTR-MS only, other species measured by PTR-MS being also measured by GC system (isoprene, benzene, toluene, styrene, C8-aromatics, C9-aromatics) (see P5, line 98-103). If so, PTR-MS measurements seem under-exploited (see de Gouw and Warneke, Mass Spectrom. Rev., 26, 223 – 257, 2007, for a review). Did you really measure so few compounds with PTR-MS during the campaign? If more compounds were measured by PTR-MS, it should be clarified in the section 2 of the manuscript.

Response: Indeed, only these compounds were measured during this campaign due to the lack of calibration for other compounds that can be additionally detected by this kind of instrument.

Comment: Furthermore, no description of NO₂ or photolysis frequency measurements is made in the section 2, while these measurements are used for estimation of calculated OH reactivity and OH production rate, respectively.

Response: We rephrase the text on p4 l85 to explain how NO₂ was measured: "Nitrogen oxides (NO and NO₂) were also detected by several instruments applying chemiluminescence technique (Thermo Electron model 42i NO-NO₂-NO_x analyzer and Eco Physics model TR 780) that were equipped with a photolytic converter." We add information about photolysis frequency measurements on p5 l103 in addition to specifications given in Table 1: "Photolysis frequencies were calculated from the spectral actinic photon flux density measured by a spectrometer that was calibrated against absolute irradiance standards (Bohn et al., 2008)."

Comment: P4, line 85: "Nitrogen monoxide was also detected by several instruments". Please indicate how many instruments measured NO as well as their model and brand.

Response: We add more information about instrument models and brands for NO_x (see above).

Comment: P4, line 86: "Measurements from one of the instruments". Please detail which instrument it is.

Response: We rephrase this statement: “Measurements from of the Thermo Electron instruments appeared to be more precise and are taken here (see Tan et al., 2016 for details).”

Comment: P5, line 89-90: “Nitrous acid (HONO) concentrations were simultaneously measured by several instruments applying different measurement techniques”. Please specify which instruments were used to measure HONO (brand, model, technique).

Response: We add on p5 l90: “Custom-built instruments from FZJ (Li et al., 2014) and from PKU (Liu et al, 2016) utilized long-path absorption photometry (LOPAP). In addition, three custom-built instruments applied cavity enhanced absorption spectroscopy (CEAS) for the detection of HONO. They were operated by the US National Oceanic and Atmospheric Administration (NOAA) (Min et al., 2016), by the Anhui Institute of Optics and Fine Mechanics (AIOFM), and by the University of Shanghai for Science and Technology (USST). A gas and aerosol collector (GAC), which is based on the wet denuder/ion chromatography technique, could also detect HONO (Dong et al., 2012). Only measurements by the two LOPAP instruments and the CEAS by NOAA resulted in good data coverage.”

Comment: P5, line 90-91: “The agreement between instruments was diverse”. Please develop this statement.

Response: We add: “Differences were often less than 30 %, but could be as high as a factor of two for certain periods (several hours). The reason for the disagreement during these times is not clear.”

Comment: While the authors observed an imbalance between total OH production and OH destruction rates, especially in the late afternoon and at night when NO concentrations are low, only few hypotheses, from literature, are given to explain it. It would be interesting to investigate further this observed discrepancy to identify potential unaccounted OH sources in POH calculations in Wangdu.

Response: We agree that further insights would be good to have. However, measurements in this campaign did not give hints about the nature of a possible unknown OH source. Moreover, the difference is hardly significant as discussed on p14 l415.

Comment: P13, line 399-400: “Ozonolysis of alkenes species made only a minor contribution to the OH production at all time”. This is not necessarily expected in anthropogenic dominated environments where these reactions can represent an important fraction of OH production in the late afternoon and at night (e.g. Ren et al., *Atmos. Environ.*, 37, 3639 – 3651, 2003; Kanaya et al., *J. Geophys. Res.*, 112, 2007; Dusanter et al., *ACP*, 9, 6655 – 6675, 2009), precisely the time period when the largest imbalance between POH and DOH is observed. How many and which alkenes were measured? Is it possible that an underestimation of the contribution of ozonolysis of alkenes in OH production rate, due to unmeasured alkenes, is, at least partly, responsible for the discrepancy observed between POH and DOH in the late afternoon and at night?

Response: GC measurements provided C2-C6 alkene concentrations (see Table 1). Ozonolysis reactions from unmeasured alkene cannot be excluded to contribute to missing OH production, specifically monoterpene species were not measured. However, the good agreement between measured and calculated OH reactivity does not hint that a large fraction of alkene species were not measured. We add on p13 l400: “Only C2 to C6 alkene species were measured, so that ozonolysis reactions of undetected alkene species (potentially monoterpenes) could have additionally contributed to the OH production. However, the good agreement between measured and calculated OH reactivity does not hint that a large fraction of alkene species are missed.”

Previous measurements indeed give partly higher contributions from ozonolysis reactions to the OH production. However, NMHC concentrations in Tokyo and Mexico City (Kanaya et al., Dusanter et al.) were much higher compared to concentrations measured in this campaign. The total OH production rate from ozonolysis reactions in New York City was not high. We add on p15 l460: “The

contribution of alkene ozonolysis to the OH production in other campaigns in urban environments were partly significantly higher (Kanaya et al., 2007; Dusanter et al., 2009; Elshorbany et al, 2009) compared to the Wangdu site due to higher alkene concentrations.”

Comment: Figure 2: Large discrepancies are observed between DOH and POH on 10 and 15 June. Maybe these days could be studied in more details to investigate potential missing OH source. At least, the large imbalance between OH production and destruction rates observed these two days could be discussed in the manuscript.

Response: We also hoped that the extended set of measurements during this campaign would allow identifying reasons for discrepancies like observed on these days. However, no hint was found in the measurements.

Comment: P9, line 246: Please indicate how many and which species are considered in the estimation of calculated OH reactivity? What are the reaction rate constants used? All these information could be given, for example, in a table in supplementary material. These information are important to estimate the representativeness of missing OH reactivity.

Response: The conclusion of this campaign is that there is overall only little missing reactivity during the first part of the campaign which could be related to local emissions. All species mentioned in Table 1 were included in the calculation. Reaction rate constants were taken from IUPAC or from reaction rate constants derived from structure-activity relationship (SAR) as stated in the Master Chemical Model. We do not think that an explicit list of all rate constants is necessary, but we give more details on p9 l255: “The calculated reactivities were determined from measured CO, CH₄, C₂ to C₁₁ alkanes, C₂ to C₆ alkenes, C₆ to C₁₀ aromatics, formaldehyde, glyoxal, acetaldehyde, MVK, MACR, NO, NO₂, SO₂ (Table 1). Reaction rate constants were taken from IUPAC recommendations (IUPAC) or structure-activity relationship (SAR) as stated in the Master Chemical Model (<http://mcm.leeds.ac.uk/MCM/>).”

Comment: P9, line 247-249: “Because of the similarity of diurnal profiles of observations during the first and the second part of the campaign, measured k_{OH} and calculated reactivity from major contributors are shown as median diurnal profiles with percentiles in Fig. 5”. I do not understand this statement since median diurnal profiles of the first and the second part of the campaign are presented separately in figure 5. Please clarify.

Response: We rephrase the sentence: “During each of the two parts of the campaign (before and after 19 June), diurnal profiles of observations appear to be similar. Therefore measured k_{OH} and calculated reactivity from major contributors are shown as median diurnal profiles with percentiles for each period in Fig. 5.”

Comment: P11, line 310-313: “Largest differences of 5 to 6 s⁻¹ (approximately 20 %) occurred during nighttime and early morning during the first two weeks of the campaign, when also nitrogen oxide concentrations were highest. This could hint that unmeasured OH reactants were emitted concurrently with nitrogen oxides in combustion processes”. Can you correlate the missing reactivity to several source tracers (e.g. NO_x, Acetonitrile etc...) trying to identify the nature of the OH reactants responsible for missing reactivity, especially during the first part of the campaign?

Response: We did this kind of correlations, when we analyzed our data. Unfortunately, no further measured trace gas could be identified, which correlates with missing reactivity that would give additional information about the nature of missing reactivity. We add on p11 l313: “Therefore, there is no clear further hint about the nature of missing reactivity during this period. Emissions of organic compounds from biomass burning may have not been detected during the first part of the campaign. During nighttime also near-by sources for OH reactants as indicated by the short duration of high reactivity could have contributed to the missing reactivity.”

Comment: P11, line 322: “the photochemical age of air masses was short”. Can you make an estimate of photochemical age of air masses during the campaign to support this statement?

Response: The photochemical age of air masses is not easily determined from measurements (like from concentration ratios) during this campaign. This is most likely due to the heterogeneity of emissions that contributed to the air masses that were encountered at measurement site and led to a mixture of air masses with different photochemical age. Therefore, we see this statement only as a possible explanation.

Comment: Figure 2: High concentrations of isoprene (up to 4 ppbv for example on 26 and 28 June) are sometimes observed after sunset. What are the sources of isoprene at night? Could it be due to interferences? These high concentrations lead, in particular, to large OH reactivity from isoprene in the late afternoon (after 18:00) and at night especially during the second period of the campaign (see Figure 5).

Response: There is no indication that isoprene GC measurements were impacted by interferences. Transport of residual isoprene that was not oxidized during daytime could be the reason for elevated concentrations in the early evening. We add on p10 l302: “Isoprene also contributed to the reactivity in the early evening most likely because isoprene that was emitted during daytime was only partly oxidized by OH before sunset.”

Comment: Figure 8: Dark grey area should also be defined in the legend.

Response: Because this grey area is only the difference between OH production and destruction rate and does not originate from calculations of a OH production rate using measurements, we think that this is qualitatively different from the other colored areas. It is only meant to guide the eye, but does not add in the same way to the other colored areas. The meaning is already explained in the caption, so that we do not think that changes are needed.

Other minor comments are corrected as suggested by the reviewer.

Response to the comments of referee #2:

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.

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 HO₂ that avoids interference from RO₂ 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 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 130s^{-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 PM_{2.5} measurements in Fig. 2 and add text on p9 l234: "Typical daytime maximum PM_{2.5} concentrations ranged between 30 and 90 $\mu\text{g}/\text{m}^3$ but were as high as 300 $\mu\text{g}/\text{m}^3$ 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 PM_{2.5} was observed on 19 June when also OH reactivity dropped, PM_{2.5} 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 cylin-

der?

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.”.

Response to the comments of referee #3:

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) 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 -4.2 s^{-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 accuracies..." 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/averaging 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 $+0.7\text{s}^{-1}$ 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.

Response to the comments of referee #4:

We thank the reviewer for the helpful comments.

Comment: 305 – 310: Most of uncertainty analysis that I have encountered uses at least 2 sigma uncertainty rather than 1 sigma. If you use 2 sigmas probably the calculated OH reactivity would be able to account measured OH reactivity.

Response: We fully agree with this statement. We rephrase the statement on p11 l305: “Even during times when measured reactivity was higher than calculations from OH reactants, the gap is within the combined 2σ uncertainties.”

Comment: Figure 7 and Figure 8: It has been highly controversial about the nighttime OH. As observed, the lifetime of OH is much shorter during the nighttime so it is rather surprising to see observed nighttime OH such a low OH production during the night. There is an obvious attempt to account the observation such as ozonolysis of terpenoids and dissociation of potential contributions from PANs but could not provide a quantitative assessment since there is no observation data. However, as it is so important issue, I think at least the authors should attempt to assess what kind of PANs or terpenoids levels you would need to account the night time OH. Otherwise, as the discrepancy between OH production rates and OH destruction rates are appeared almost identical except in the early morning, some may conclude that the discrepancy may be simply accounted by an instrument artifacts as described in the manuscript.

Response: There is no direct way to estimate PAN concentrations, because the impact on OH is indirect. PAN has to be transported and decomposes then to HO₂/RO₂, if the PAN that is transported disturbs the thermal equilibrium. An estimate would require a 1D model calculation that is beyond the scope of this paper. In the paper by Lu et al. 2014 it was shown that the impact of PAN decomposition alone made only a small HO_x source of less than 0.01ppbv/h, which would not be sufficient to balance the OH loss rate. In order to balance the OH production rate by an ozonolysis reaction, the alkene concentration can be calculated. We add on p14 l431: “In order to balance the calculated OH destruction rate during nighttime, a rather large concentration of an alkene would be required. Assuming an ozone concentration of 30ppbv, a reaction rate constant for the ozonolysis reaction of $1.8 \times 10^{-15} \text{ cm}^3\text{s}^{-1}$ for δ -terpine and an OH yield of one (Atkinson and Arey 2003), the concentration would need to be around 600pptv.”

Comment: (minor comment) Recently, Kim et al (2016) reported observed OH reactivity in the Seoul Metropolitan Area. The addition of this reference to the comparison could be useful.

Response: We include this reference on p12.

Manuscript prepared for Atmos. Chem. Phys.

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Date: 24 November 2016

OH reactivity at a rural site (Wangdu) in the North China Plain: Contributions from OH reactants and experimental OH budget

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Abstract. In 2014, a large, comprehensive field campaign was conducted in the densely populated North China Plain. The measurement site was located in a botanic garden close to the smaller town Wangdu without major industry, but influenced by regional transportation of air pollution. The loss rate coefficient of atmospheric hydroxyl radicals (OH) was quantified by direct measurements of the OH reactivity. Values ranged between 10 and 20 s⁻¹ for most of the daytime. Highest values were reached in the late night with maximum values around 40 s⁻¹. OH reactants mainly originated from anthropogenic activities as indicated (1) 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). Total OH reactivity was measured by a laser flash photolysis - laser induced fluorescence instrument (LP-LIF). Measured values of total OH reactivities can be well explained by measured trace gas concentrations including organic compounds, oxygenated organic compounds, CO and nitrogen oxides. Significant, unex-

plained OH reactivity was only observed during nights, when biomass burning of agricultural waste occurred on surrounding fields. OH reactivity measurements also allow investigating the chemical
15 OH budget. During this campaign, the OH destruction rate calculated from measured OH reactivity and measured OH concentration was balanced by the sum of OH production from ozone and nitrous acid photolysis and OH regeneration from ~~hydroperoxyhydroperoxy~~ radicals within the uncertainty of measurements. However, also a tendency for higher OH destruction compared to OH
20 production at lower concentrations of nitric oxide is observed consistent with previous findings in field campaigns in China.

1 Introduction

Hydroxyl radicals (OH) are the most important oxidizing agent for inorganic and organic pollutants in the atmosphere (Ehhalt, 1999). A large number of field campaigns have been conducted in the past to improve our understanding of radical chemistry in the atmosphere at various locations all over the world (Rohrer et al., 2014). However, only few have taken place in China, where air pollution is still a severe problem (Lu et al., 2010). Measurements during field campaigns in the Pearl-River-Delta (PRD) and at a suburban location south of Beijing (Yufa) revealed a lack of understanding of radical chemistry by state-of-the-art chemical models pointing to unknown OH radical sources (Hofzumahaus et al., 2009; Lu et al., 2012, 2013). Similar results were found at other locations, which were mainly dominated by biogenic emissions (Rohrer et al., 2014).

In summer 2014, 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 in the North China Plain south-west of Beijing (Tan et al., 2016). A large set of instruments was deployed to detect radicals (OH, HO₂, RO₂), reactive trace gases (e.g., CO, NO_x, volatile organic compounds (VOC)) and aerosol properties. 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 HO₂ that avoids interference from RO₂ was applied (Fuchs et al., 2011). Time series of radical measurements and a comparison with results from a chemical box model calculation are discussed in our accompanying paper by Tan et al. (2016). ~~the discussion here focusses on the analysis of measured OH reactivity.~~

OH reactivity (k_{OH}) is the pseudo-first order loss rate coefficient of OH radicals and represents the inverse chemical lifetime of OH.

$$k_{\text{OH}} = \sum_i k_{\text{OH}+\text{X}_i} [\text{X}_i] \quad (1)$$

X_i represents any OH reactant. Because of the large number of OH reactant in the atmosphere, it is of high value for the interpretation of radical chemistry to compare the direct measurement of k_{OH} with reactivities calculated from measured atmospheric OH reactant concentrations. ~~The difference measured and calculated reactivity is often referred to as missing reactivity.~~

Depending on the instrumentation that were available in field campaigns in the past, up to more than 70 % of the measured reactivity was found to remain unexplained in different types of environments (e.g., cities, forests) (Yang et al., 2016). For our previous field campaigns in China, the measured OH reactivity was two times larger than the calculated k_{OH} . The discrepancy could be quantitatively explained by the reactivity from oxygenated VOCs (OVOC), which were not mea-

sured, but estimated by a chemical model (Lou et al., 2010; Lu et al., 2013). In this campaign, the number of measured species was extended and included important atmospheric OVOCs, for example formaldehyde, acetaldehyde, isoprene oxidation products (methyl-vinyl ketone and methacrolein),
60 and glyoxal.

Measurements of OH reactivity and OH concentrations can be combined to calculate the loss rate of OH radicals. This can then be compared to the sum of OH production rates from ozone and nitrous acid photolysis, and reaction of hydroperoxyhydroperoxyl radicals with nitric oxide and ozone as well as ozonolysis reactions of alkenes. All quantities that are required to do this calculation
65 were measured in this campaign. This allows for a model-independent analysis of the chemical OH budget. This approach was successfully applied to quantify unaccounted OH production in our field campaigns in China in 2006 (Hofzumahaus et al., 2009).

In the following, we describe the technique for OH reactivity measurements applied in the campaign in Wangdu, discuss the time series of measurements, compare OH reactivity measurements
70 with calculations from single reactant measurements and analyze the OH budget.

2 Experimental

The instruments, their setup at the field site and the measurement conditions are described in Tan et al. (2016). Therefore, only a brief description is given here.

2.1 Measurement site

75 Measurements took place inside a botanic garden close to the small town Wangdu in China between 7 June and 8 July 2014. Wangdu is located in the densely populated North-China Plain, but does not have major industry itself. Major cities are located mainly in the sector from north-east to south-west from Wangdu, whereas there is a mountainous area with less industry north-west of Wangdu. The closest large city is Baoding 35 km north-east of Wangdu. The measurement site had a distance of
80 2 km from a road with only local traffic. The botanic garden was surrounded by agricultural fields. Trace gases from local biogenic emissions of trees, bushes and from farming can be expected.

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.

85 Instruments were housed in seven shippingsea containers, which were partly stacked up, so that inlets of instruments were at a height of 7 m above the ground.

2.2 Instrumentation

A large number of instruments characterized meteorological conditions, trace gas concentrations and aerosol properties. The measurements used for the OH reactivity analysis are listed in Table 1.

90 OH and HO₂ radical concentrations were measured by a newly built instrument applying laser-
induced fluorescence technique (PKU-LIF) (Tan et al., 2016). This instrument detects OH fluores-
cence by time-delayed single photon counting after excitation by short laser pulses at 308 nm in a
low-pressure cell (Holland et al., 2003; Fuchs et al., 2011). HO₂ radicals are detected as the sum of
OH and HO₂ (=HO_x) after chemical conversion to OH in the reaction with nitric oxide (NO). In
95 order to avoid significant simultaneous conversion of organic peroxy radicals (RO₂) (Fuchs et al.,
2011), the amount of NO was adjusted to yield an HO₂ conversion efficiency of only 6 %. The in-
strument sensitivity was calibrated every 3 to 4 days by a custom-built calibration source described
in detail in Fuchs et al. (2011).

A commercial cavity ring-down instrument (Picarro model G2401) monitored CO, CH₄ and H₂O
100 concentrations. Concentration measurements of ozone by two commercial UV absorption instru-
ments (Environment S.A. model 41M; Thermo Electron model 49i) agreed well within
their accuracies during the campaign. Nitrogen oxides (NO and NO₂) were also detected by several instruments applying chemiluminescence technique (Thermo Electron
model 42i NO-NO₂-NO_x analyzer and Eco Physics model TR 780) that were equipped with a pho-
105 tolytic converter. Daily calibrations were performed using a certified gas standard. The field mea-
surements differed on average by 20 %. Measurements of the Thermo Electron instruments appeared
to be more precise and are used here (see Tan et al. (2016) for details). Because the reason for the dis-
agreement could not be identified, the 20 % difference adds to the uncertainty of NO measurements
here.

110 Nitrous acid (HONO) concentrations were simultaneously measured by several instruments ap-
plying different measurement techniques (Tan et al., 2016). Custom-built instruments from FZJ (Li
et al., 2014) and from PKU (Liu et al., 2016) utilized long-path absorption photometry (LOPAP). In
addition, three custom-built instruments applied cavity enhanced absorption spectroscopy (CEAS)
for the detection of HONO. They were operated by the US National Oceanic and Atmospheric
115 Administration (NOAA) (Min et al., 2016), by the Anhui Institute of Optics and Fine Mechanics
(AIOFM), and by the University of Shanghai for Science and Technology (USST). A gas and aerosol
collector (GAC), which is based on the wet denuder/ion chromatography technique, could also de-
tect HONO (Dong et al., 2012). Only measurements by the two LOPAP instruments and the CEAS
by NOAA resulted in good data coverage. The agreement between these instruments was diverse.
120 Differences were often less than 30 %, but could be as high as a factor of two for certain periods
(several hours). The reason for the disagreement during these times is not clear. For the purpose of
the analysis here, measurements by the LOPAP instrument from Forschungszentrum Jülich are used
(Li et al., 2014) because this instrument showed best data coverage and the lowest detection limit.
This instrument was calibrated by using a liquid standard as described in Li et al. (2014) every ten
125 days. The choice of the HONO data set has a rather small impact on the calculated OH reactivity,

as well as on the calculated total OH production rate which was dominated by OH recycling from HO₂ during daytime (see below).

For the analysis of the OH reactivity, measurements of organic trace gases are essential. 59 organic species (C₂-C₁₁ alkanes, C₂-C₆ alkenes, C₆-C₁₀ aromatics, and isoprene) were detected by a custom-built gas-chromatography system equipped with a flame ionization detector (FID) (Wang et al., 2014). Full calibrations using certified gas standards (Air Environmental Inc., Spectra Gases Inc.) were done before and after the campaign. Drifts of the sensitivity during the campaign were accounted for by measuring the instrument sensitivity for bromochloromethane, 1,4-difluorobenzene, chlorobenzene, and 1-bromo-3-fluorobenzene every second day. Formaldehyde (HCHO) was detected by a commercial Hantzsch monitor (Aerolaser model AL4021) and glyoxal (CHOCHO) by a custom-built cavity enhanced spectrometer (Min et al., 2016). In addition, acetaldehyde and the sum of methyl vinyl ketone (MVK) and methacrolein (MACR) were measured by a commercial proton transfer reaction - mass spectrometry system (PTR-MS, Ionicon). Some of the species or family species were simultaneously detected by the GC system and the PTR-MS. The PTR-MS also measured part of the same species like the GC system (isoprene, benzene, toluene, styrene, C₈-aromatics, C₉-aromatics). Measurements, which during daytime well in general agreed with measurements by GC within 30 to 50 % (Tan et al., 2016). Calibration of the PTR-MS instrument was done every day using a certified gas standard (Air Environmental Inc.).

Photolysis frequencies were calculated from the spectral actinic photon flux density measured by a spectrometer that was calibrated against absolute irradiance standards (Bohn et al., 2008).

2.3 OH reactivity measurements

The OH reactivity instrument measures directly pseudo first-order loss rate coefficients (Eq. 1) of OH in the ambient air. The measurement is based on artificial OH generation by pulsed laser-flash photolysis (LP) of ozone in ambient air combined with the detection of the temporal OH decay by laser induced fluorescence (LIF). The method was initially developed for field application by Sadanaga et al. (2004) and is applied today by several other groups (Lou et al., 2010; Parker et al., 2011; Stone et al., 2016). The instrument deployed in this campaign is similar to the instrument described in Lou et al. (2010), which was used for measurements in our two field campaigns in 2006 in China. Since then, a second instrument was built specifically for the deployment on a Zeppelin NT airship (Li et al., 2014), but can also be operated at ground. This instrument was deployed like in this campaign. Figure 1 gives a schematic representation of the instrument without the pump (Edwards model XDS35i) needed for the operation of the low-pressure LIF cell and without the laser that provides the 308 nm radiation for the excitation of OH. The 308 nm radiation is delivered by the dye laser system that is also used in the instrument for the OH HO₂, and RO₂ concentration measurements described in Tan et al. (2016). This laser has three output fibers to provide laser light, one of which is used for the OH reactivity instrument.

The k_{OH} instrument is mounted in a 19" rack that was placed inside one of the upper shipping containers at the field site. The inlet line (outer diameter 10 mm, length approximately 6 m) was made of stainless steel that had a SilcoNert 2000 coating. 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. Approximately 20 Liter/min of ambient air is sampled through a flow-tube made of anodized aluminium (length: 60 cm, inner diameter: 4 cm). Downstream of the flow tube, the flow rate is measured by a flow-meter and controlled by a blower.

The pressure inside the flow tube is 1 atm and the temperature was the same as in the field container (between 22 and 30 °C). 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 (Lou et al., 2010). 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.

High OH concentrations on the order of 10^9 cm^{-3} are produced by flash photolysis of O_3 at 266 nm with subsequent reaction of O^1D with water vapor. The 266 nm laser pulses (pulse energy 20 to 28 mJ, repetition rate 1 Hz, pulse duration less than 10 ns) are provided by a compact, frequency quadrupled Nd:YAG laser (Quantel model Ultra 100). The laser is mounted on one side of an optical rail, on which the flow tube is mounted on the opposite side. The laser beam is widened by an optical telescope to a diameter of 3 cm and guided to the flow tube by two turning mirrors.

Water vapor, temperature and pressure in the flow tube are continuously monitored. Normally, ozone and water vapor concentrations in the sampled ambient air are sufficiently high in order to produce high OH concentrations. However, ozone can be depleted during night due to its reaction with nitric oxide/nitrogen oxides and by deposition processes. Therefore, a small flow of synthetic air (0.2 Liter/min) that has passed an ozonizer (glass tube of fused silica with a mercury lamp providing 185 nm radiation) can be added, in order to increase ozone mixing ratios in the flow-tube by 40-50 ppbv. The injection is controlled by a solenoid valve which is automatically opened, if the ozone mixing ratio in ambient air drops below 30 ppbv.

At a distance of 48 cm from the inlet of the flow-tube, 1 Liter/min of the total flow is sampled from the center of the flow tube through a conical nozzle into the OH detection cell. The design of the OH fluorescence cell is the same as used for OH concentration measurements (Tan et al., 2016).

In the cell, OH is excited by 308 nm radiation from a tunable frequency-doubled dye laser, which is operated at a pulse repetition rate of 8.5 kHz. The OH fluorescence is detected by gated photon counting and accumulated in time bins of 0.6 ms. This way, the chemical decay of OH in the flow

200 tube is recorded for 1 s after the photolysis laser pulse. For photon detection, a gated multichannel photomultiplier (Photek, PM325) is used in combination with a multichannel counting card (Sigma Space, AMCS).

In order to achieve sufficiently precise ~~reactivity measurementseounts-rates~~, 60 decay curves are taken for one reactivity measurement ~~resulting in an amplitude of 50 to 100 counts of the decay curve~~. Because of the scanning of the laser over the absorption line of OH in order to track slow drifts in the wavelength of laser, the amplitude of the decay curve changes periodically. Therefore, 205 ten OH decay curves are summed up to ~~equalizeequalizes~~ the amplitude. Six of the summed curves are then averaged to determine realistic error estimates needed for the fit procedure. A weighted single-exponential fit (Levenberg-Marquardt minimization) is then applied to derive the OH reactivity (Eq. 1). Approximately the first 30 to 50 ms of the decay curve are not included in the fit, 210 because these points deviate from the single-exponential behavior that is observed at later times. ~~The fit is started, if the count rate has decreased to the 90 % level of the maximum count rate~~. The likely reason ~~for an inhomogeneous initial OH distribution~~ 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~~.

215 Diffusion to the wall of the flow tube, where OH is lost by wall reactions, causes loss of OH even in the absence of OH reactant. This zero loss rate is regularly measured in humidified air (purity 99.999 %). Typical zero loss rates measured in laboratory characterization measurements are around 3 s^{-1} for this instrument. A slightly higher value of 3.8 s^{-1} was derived in measurements sampling synthetic air from a gas cylinder during the campaign. Analysis of the synthetic air in 220 this gas cylinder by gas-chromatography yielded contaminations with an OH reactivity of 0.7 s^{-1} . Therefore, an instrumental zero decay value of 3.1 s^{-1} was subtracted from ambient OH reactivity measurements consistent with previous values for this instrument. The reactivity measured in the synthetic air is considered as a potential systematic error of the OH reactivity measurements in this campaign. The accuracy of our LP-LIF technique has been tested with CO and CH₄ mixtures in 225 synthetic air. Measured k_{OH} agreed better than 10 % with the expected, calculated OH reactivity for values up to 60 s^{-1} in agreement with previous studies by Lou et al. (2010). At higher k_{OH} values, the initial non-exponential part of the OH decay curve starts to influence the quality of the fitted OH decay curve, but such high k_{OH} values were not encountered in the campaign at Wangdu (Fig. 2).

Potential interferences that could be present in the OH concentration detection would not affect 230 the measured OH reactivity, because OH that would be artificially produced inside the measurement cell would only increase the background signal, but not the decay time as long as it does not change on the time scale of the OH decay measurement (1 s). In any case, however, effects are expected to be negligible due to the high OH concentration inside the flow tube that are much higher compared to ambient OH concentrations, for which interferences have been recognized. This holds for the 235 known interference from ozone photolysis by the 308 nm laser radiation, but also for other potential

interferences that have been reported for OH concentration measurements (Mao et al., 2012; Novelli et al., 2014) and which could not be fully excluded for this campaign (Tan et al., 2016).

If ambient NO concentrations are high enough to lead to a significant regeneration of OH from secondarily formed HO₂, the shape of the decay curve changes to a bi-exponential behavior. This can be derived from reaction kinetics. The faster decay time represents approximately the OH reactivity for certain chemical conditions. As shown in Lou et al. (2010) no significant effects are expected for NO mixing ratios of up to 20 ppbv for realistic OH reactant mixtures in our instrument. During the campaign in Wangdu, NO mixing ratios were generally well below 20 ppbv. No and, thus, no bi-exponential behavior was observed that would have been seen in the residuum of the fit. NO mixing ratios exceeded 20 ppbv only for some short periods mainly during nighttime on three days, but measurements still appeared as single exponential decays in these cases.

3 Results and Discussion

3.1 Time series of OH reactivity

Measured OH reactivity values ranged between 10 and 20 s⁻¹ during this campaign for most of the time (Fig. 2). In general, values were lower during daytime (median value 12.4 s⁻¹) than at night (median value 15.4 s⁻¹). During the first two weeks, midday OH reactivity increased from 10 s⁻¹ on 8 June to values higher than 20 s⁻¹ between 15 and 19 June. After 19 June, OH reactivity was generally lower and more uniform till the end of the campaign.

Maximum values were observed during nighttime and early morning hours, when OH reactivities show spikes with values of up to 60 s⁻¹ for short periods of less than one hour. The high reactivity values were probably caused by emissions into the shallow nocturnal boundary layer. The short duration indicates that nearby local sources were responsible for these events. This happened more frequently during the first part of the campaign and only few spikes were observed after 19 June.

The overall changes in OH reactivity values from day to day were likely dominated by anthropogenic activities during this campaign. The measured OH reactivities show an increasing trend with CO, which cannot be explained by the reactivity of CO alone (Fig. 3). The increase of k_{OH} with CO was only partly due to the increase in reactivity from CO alone. Therefore, other reactants that were co-emitted with CO for example in combustion processes most likely contributed to the increase in reactivity. The correlation still holds, if only reactivity from measured OH reactants other than CO, NO_x and isoprene is taken into account. This further supports that also OH reactivity from organic compounds is co-emitted with CO.

Back-trajectories were calculated for this campaign using the NOAA (Nation Oceanic and Atmospheric Administration) HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory Model) model (Stein et al., 2015), in order to test, if measured OH reactivities are correlated with the origin of advected air masses. 24-hour back-trajectories were calculated for air masses at the measurement

site for each hour. During most days, one-day back-trajectories were typically very similar. Therefore, and therefore, trajectories between 10:00 and 19:00 were averaged (Fig. 4). shown in Fig. 4 are averages of trajectories calculated between 10:00 and 19:00. The majority of back-trajectories are pointing to locations south of Wangdu and less often to locations east or north of the measurement site. Mountains that are west and north of the measurements site appear as barriers for air masses. Only on three days (08, 27, 28 June) back-trajectories indicate that air masses originated from locations in the mountains, north of the measurement site. Lowest k_{OH} values ($< 10 \text{ s}^{-1}$) were observed in these cases due to less emissions from industry and from other anthropogenic activities less dense population in this area. In contrast, there is dense population in the sector from east and south of the measurements site. This likely explains why OH reactivity values were highest, if air masses were coming from this area. Also the relation between k_{OH} and with CO as a proxy for the pick-up of emissions from anthropogenic activities is consistent with the assumption that OH reactivity was dominated by anthropogenic activities in this case origin of air masses.

The increase in OH reactivity during the first two weeks could be related to a change of the origin of air masses from the north (08 June) to the east (13 June) and finally to the south (15 June). However, no obvious difference between of back-trajectories is seen before and after 20 June for similar origins of air masses, so that back-trajectories are not sufficient to explain, why measured OH reactivity would be generally higher and more spiky before 20 June.

The more likely reason for differences in OH reactivity is emissions connected with harvesting of crop and combustion of straw and crop residuals on nearby agricultural fields in the first two weeks of June. On 13 June, for example, crop was harvested on the field directly next to the measurement place. Indicators for biomass burning activities were visually observed fires in surrounding areas, reduced visibility, and an increase in measured particle number concentrations. Typical daytime maximum PM_{2.5} concentrations ranged between 30 and 90 $\mu\text{g}/\text{m}^3$ but were as high as 300 $\mu\text{g}/\text{m}^3$ on one day due to the local biomass burning (Fig. 2). No clear connection between OH reactivity and aerosol number concentration was observed. Although a sharp drop in PM_{2.5} was observed on 19 June when also OH reactivity dropped, PM_{2.5} increased again to higher values till the end of the campaign. Elevated concentrations of acetonitrile (a marker for biomass combustion) were measured between 12 and 19 June (Tan et al., 2016).

3.2 Contributions of OH reactants to the OH reactivity and missing reactivity

OH reactivity measurements are of particular value in order to test if all important OH reactants were detected. Volatile organic compounds (VOCs) and inorganic compounds such as nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) and carbon monoxide (CO) are typically major contributors to the total OH reactivity. However, the number of OH reactants, specifically of organic compounds is very large, so that a complete measurement is not necessarily expected. Therefore, comparison of direct k_{OH} measurements with calculations from measured reactants can reveal to which extend unmeasured re-

active compounds contributed to total OH reactivity. This presents a gap in the constraints of model calculations used to test our knowledge of radical chemistry (Tan et al., 2016). In addition, VOCs and NO_x concentrations are key species for understanding ozone and particle formation, so that an incomplete knowledge of OH reactivity would lead to a systematic underprediction of ozone production by chemical models (e.g., Whalley et al. (2016); Griffith et al. (2016)).

The full time series of the calculated k_{OH} is plotted together with the measured total k_{OH} in Fig. 2. The calculated reactivities were determined from measured CO, CH₄, C₂ to C₁₁ alkanes, C₂ to C₆ alkenes, C₆ to C₁₀ aromatics, formaldehyde, glyoxal, acetaldehyde, MVK, MACR, NO, NO₂, SO₂ (Table 1). Reaction rate constants were taken from IUPAC recommendations (Atkinson et al., 2013) or structure-activity relationship (SAR) as stated in the Master Chemical Model (<http://mcm.leeds.ac.uk/MCM/>).

During each of the two parts of the campaign (before and after 19 June), diurnal profiles of observations appear to be similar. Therefore, measured k_{OH} and calculated reactivity from major contributors are shown as median diurnal profiles with percentiles for each period in Fig. 5. Median diurnal profiles of all measured contributions are summed up and compared to measured k_{OH} in Fig. 6. Ambient temperature was used for the calculation of reaction rate constants, but the differences between ambient temperature and the actual temperature in the instrument does not change any of the results shown here.

Overall, measured OH reactants can explain measured OH reactivity. The most important OH reactants were CO (on average 20 to 25 % of the total OH reactivity), nitrogen oxides (on average 12 to 22 % of the total OH reactivity) and OVOCs (on average 25 % of the total OH reactivity). Formaldehyde made the largest contribution to the reactivity from OVOCs (more than 50%) and acetaldehyde the second largest contribution (20 to 25%). The reactivity from isoprene makes a substantial contribution (often 20 %) to the total k_{OH} in the afternoon. In contrast, reactivity from other measured OVOCs such as acetone and glyoxal made only small contributions to the OH reactivity. Reactivity from alkanes and alkenes were dominated by small alkenes, mostly ethene and propene.

The median diurnal profile of the total OH reactivity had a maximum late at night in the late night. It decreased during the day by nearly 50 % and started to increase after sunset. Accumulation of OH reactants during the night could be due to fresh emissions that are released into the shallow nocturnal boundary layer. A similar diurnal profile was also observed for contributions from NO_x, alkane and alkene species. Their concentrations are typically connected to emissions from anthropogenic activities. OH reactivity from NO_x was also the largest contribution to k_{OH} during night and early morning (20 to 30 %). The diurnal profile of NO_x appears as the major driver for the diurnal profile of the entire k_{OH} , whereas nearly all other contributions exhibited a less distinct diurnal profile. A different The opposite diurnal behavior to that for NO_x was observed for isoprene, which is

emitted by plants. The emission strength scales with light and temperature and, therefore, maximum
345 mixing ratios were reached in the afternoon. Isoprene also contributed to the reactivity in the early evening most likely because isoprene that was emitted during daytime was only partly oxidized by OH before sunset. The diurnal profile of isoprene counteracted partly the decrease of OH reactivity due to the decrease of NO_x, alkane and alkene species.

CO mixing ratios ranged between 300 and 1000 ppbv during this campaign. Therefore, reactivity
350 from CO made always a large fraction of the total k_{OH} . The OH reactivity from CO showed only a weak diurnal variation profile with a median value of 3 s^{-1} and could therefore be used as indicator for the overall origin of pollutants apart from diurnal changes. As discussed above, measured k_{OH} scaled with CO indicating that also co-emitted OH reactants such as alkenes were important (Fig. 3).

A number of oxygenated volatile organic compounds (OVOCs) were measured in this campaign
355 (Table 1). These included formaldehyde, acetaldehyde, glyoxal, methyl-vinyl ketone and methacrolein. Their reactivity made a large fraction of the total reactivity with median values between 2 and 4 s^{-1} over the course of one day. The largest contributions to the reactivity from OVOCs (more than 50 %) came from formaldehyde and acetaldehyde (20 to 25 %), while reactivity from other measured OVOCs such as acetone and glyoxal made only small contributions. This was approximately one third of the total reactivity. Most of the reactivity from OVOC compounds were from formaldehyde and acetaldehyde. These species can also originate from primary emissions. The good agreement between measured and calculated OH reactivity indicates nevertheless that these species were the most important organic oxidation products that contributed to the OH reactivity.

The reactivity of measured OVOCs shows a weak diurnal variation, with a decrease by a factor
365 of about two from the morning to the evening. This behavior suggests that during daytime dilution due to a raising boundary layer height or chemical removal had a stronger influence on the observed OVOCs than fresh production by photochemistry. Similar to CO, there was only a weak diurnal profile of reactivity from OVOCs with decreasing values during the afternoon. This might be unexpected, because photochemistry that produces OVOCs is most active in the afternoon, so that OVOC species may accumulate. The higher concentrations could indicate that these OVOC species were regionally transported or were products from nighttime oxidation processes. Also direct emission of these species could explain such a diurnal profile, because concentrations would decrease, if the rise of the boundary layer height during morning hours diluted these species.

Although the general behavior features of OH reactivity and OH reactants were similar during
375 the entire campaign, there were distinct differences in the magnitude of total OH reactivity during the first (7 June to 19 June) and second half (20 June to 8 July) of the campaign (Fig. 5). also some differences. Measured OH reactivity was on average lower after 20 June specifically during the second half of the night and early morning, when median values were higher than 25 s^{-1} before 20 June and 16 to 20 s^{-1} later. Afternoon values were only slightly less after 20 June compared to the first
380 part of the campaign. This is reflected in a decrease in median OH reactant concentrations during

the second part of the campaign. It is most prominently seen in median alkene and alkane concentrations during nighttime (Fig. 5). In contrast, isoprene concentrations increased faster in the morning and high afternoon concentrations persisted in the evening during the second part of the campaign. Air temperatures were generally a few degrees higher than during the first two weeks, so that temperature driven biogenic emissions could have been larger after 20 June. The largest fraction of higher OH reactivity observed in the first part of the campaign remains unexplained by OH reactant measurements. However, even during times when measured reactivity was higher than calculations from OH reactants, the gap is within the combined 2σ uncertainties—only slightly larger than the combined 1σ uncertainties: The k_{OH} calculated from OH reactants has a 1σ uncertainty of $\pm 10\%$ to $\pm 15\%$ depending on the relative distributions of reactants and the measured k_{OH} has a 1σ uncertainty of maximum $\pm 10\%$ plus $+0.7\text{ s}^{-1}$ (Table 1).

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) between both values (Fig. 7). 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 -4.2 s^{-1} . The larger intercept is due to a slightly non-linear relationship between measured and calculated reactivity for this subset of data.

Largest differences of 5 to 6 s^{-1} (approximately 20%) between measured and calculated OH reactivity occurred during nighttime and early morning during the first two weeks of the campaign, when also NO concentrations were highest. This could hint that unmeasured OH reactants were committed with nitrogen oxides in combustion processes. Unknown compounds causing the missing reactivity are the main reason for the higher observed OH reactivity in the first two weeks. Mainly the missing reactivity causes the higher measured OH reactivity in the first two weeks, whereas OH reactant concentrations (e. g. OVOCs) were only slightly higher. Therefore, there is no clear further hint about the nature of missing reactivity during this period. Emissions of organic compounds from biomass burning may have not been detected during the first part of the campaign. During nighttime also nearby sources for OH reactants as indicated by the short duration of high reactivity could have contributed to the missing reactivity. In addition, undetected products from the oxidation by the nitrate radical could have been part of missing reactivity in the night.

Exceptionally good agreement is seen at nearly all times after 20 June in the time series as well as in the median diurnal profile (Fig. 2 and 6). The median value of missing reactivity is only 0.3 s^{-1} . Such good agreement is not necessarily expected due to the large number of possible OH reactants in the atmosphere (Goldstein and Galbally, 2007). Specifically the number of OVOCs that were measured in this campaign is rather small (see above) and additional reactivity from other oxidation products could be expected to contribute to the total OH reactivity.

The good agreement between measured and calculated k_{OH} indicates that other oxidation products than measured were not significantly contributing to the OH reactivity at the measurement site. 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. One explanation could be that the photochemical age of air masses was short and therefore, oxidation products could not accumulate. This could be the case for fresh emissions close to the measurement site. In addition, the uncertainty of OH reactant measurements (up to 20 % for single compounds) would allow that unmeasured oxidation products significantly contribute to the total OH reactivity.

3.3 Comparison with previous field campaigns

In our previous field campaigns in China 2006 in the Pearl-River-Delta, PRD, (Hofzumahaus et al., 2009; Lou et al., 2010; Lu et al., 2012) and Yufa close to Beijing (Lu et al., 2013), OH reactivity was considerably higher, but exhibited a similar diurnal profile. Maximum values were 40 to 50 s^{-1} in the night and early morning during the PRD and Yufa campaigns and reached minimum values around 20 s^{-1} in the afternoon. Absolute contributions from CO and NO_x were comparable with contributions in Wangdu 2014, with slightly higher CO concentrations in Yufa 2006. However, contributions from measured VOC were significantly higher in both previous campaigns compared to the Wangdu campaign in 2014 explaining partly the higher reactivity in these campaign.

In both previous campaigns, measurements of OVOCs were completely missing and the measured OH reactivity was found to be about two times larger than the total reactivity of measured CO, NO_x and hydrocarbons (Lou et al., 2010). The missing reactivity could be quantitatively explained by OVOCs which were simulated by a model from the photo-oxidation of the measured VOCs. The major modelled OVOCs were formaldehyde, acetaldehyde, MVK, MACR and some minor isoprene oxidation products, which together could explain 70 % of the missing reactivity (i.e., about one third of the total reactivity). In the Wangdu campaign, the calculated total OH reactivity was largely in agreement with the measured k_{OH} . This time, formaldehyde, acetaldehyde, MVK, MACR and glyoxal were directly measured and also accounted for one third of the total reactivity. These species were also the most important OVOC species in other campaigns in anthropogenic dominated environments such as in Beijing (Shao et al., 2009), London (Whalley et al., 2016) and Tokyo (Yoshino et al., 2012). This confirms the high relevance of these specific carbonyl compounds as reactants for OH in the polluted boundary layer.

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)). The total reactivities lie within the range of values observed during summertime at other locations that were mainly influenced by anthropogenic emissions like Nashville

(Kovacs et al., 2003), New York (Ren et al., 2003), Houston (Mao et al., 2010) in the US, Tokyo in Japan (Chatani et al., 2009), Beijing (Williams et al., 2016) in China, Seoul in South Korea (Kim et al., 2016) and London (Whalley et al., 2016) in Great Britain. Also the shapes of the diurnal profiles were similar with peak values between 15 s^{-1} and 50 s^{-1} in the early morning and minimum values in the afternoon. Significantly higher morning values of 130 s^{-1} were observed in Mexico City 2003 (Shirley et al., 2006). Here, as well as in Wangdu and other urban sites, the diurnal shape of k_{OH} was strongly determined by the variation of anthropogenically emitted NO_x and co-emitted VOCs. Also diurnal profiles of k_{OH} were similar in these campaigns with peak values between 15 and 50 s^{-1} in the early morning and minimum values in the afternoon. Like in this campaign, the shape of the diurnal profile was often determined by reactivity from nitrogen oxides.

Care has to be taken, if missing reactivity is compared between different campaigns, because the number of measured OH reactants used to calculate the reactivity can significantly differ (Lou et al., 2010; Yang et al., 2016, and ref. therein). For the measurements in Beijing (Williams et al., 2016) approximately 25 % of the measured reactivity remained unexplained, although oxygenated organic species were partly measured. Approximately 30 % of the reactivity measured in Nashville could not be explained, even if modelled organic compounds were taken into account. For the other campaigns in anthropogenic influenced areas, measured OH reactivity could be explained by either measured OH reactants alone (London, New York, this campaign) or if in addition product species from model calculations were included (Yufa, PRD, Tokyo, London).

3.4 Experimental OH budget

OH reactivity measurements can be used not only to quantify the possible contribution of unmeasured OH reactants, but also allows quantification of the total OH production rate. Because OH is short-lived, it reaches a steady state within seconds. Thus, the total OH production rate (P_{OH}) equals the total destruction rate (D_{OH}). D_{OH} can be calculated as the product of k_{OH} and the OH concentration:

$$D_{\text{OH}} = k_{\text{OH}} \times [\text{OH}] \quad (2)$$

This rate can be compared with the sum of production rates (P_{OH}) from known OH sources. In this campaign, OH production from HONO and O_3 photolysis, ozonolysis of alkenes, and radical recycling reactions of HO_2 with NO and ozone can be calculated from measurements:

$$P_{\text{OH}} = P_{\text{OH}}(h\nu + \text{O}_3) + P_{\text{OH}}(h\nu + \text{HONO}) + P_{\text{OH}}(\text{HO}_2 + \text{O}_3) + P_{\text{OH}}(\text{HO}_2 + \text{NO}) + P_{\text{OH}}(\text{O}_3 + \text{alkene}) \quad (3)$$

Potentially unknown OH sources can then be determined as the difference between D_{OH} and P_{OH} . This was successfully applied for data from our previous field campaigns in China (Hofzumahaus

485 et al., 2009) revealing significant unaccounted OH sources and in chamber studies (Fuchs et al.,
2013, 2014; Nehr et al., 2014).

The time series of calculated OH production and destruction rates are plotted in Fig. 2 and median diurnal profiles of quantities that are required for this calculation in Fig. 8. Unfortunately, the data coverage of simultaneous measurements before 20 June (mostly due to missing radical measurements) is not sufficient to allow for an independent analysis of the first part of the campaign as done like for the analysis of OH reactants. However, results do not change significantly, whether the first part is included in the median diurnal profiles that are discussed below or not.

Figure 9 shows the median diurnal profile of the OH destruction and production rates and their difference including an estimate of the accuracy of the calculated difference. The diurnal profile of the OH production rate was mainly driven by solar radiation as expected from the photolytic nature of primary radical production, which also determines the overall abundance of HO₂. During the daytime, the known OH production was dominated by the recycling reaction of HO₂ with NO reaching a maximum of about 10 ppbv/h shortly before noon. The relative contribution of primary OH production by either O₃ or HONO photolysis to the total OH production was increasing during the day to reach median maximum values of 1.2 ppb/h and 1.5 ppb/h, respectively. The ozone photolysis exhibited a strong diurnal profile because both, solar radiation and ozone concentration had maximum values at noon and early afternoon. An OH production rate from HONO photolysis of 1 to 1.5 ppb/h persisted into the afternoon due to relatively high HONO concentrations measured throughout the day. The budget of HONO will be discussed in a separate paper, but it is clear that HONO production from the reaction of OH with NO cannot explain the high HONO concentrations in the afternoon. Ozonolysis of alkene species made only a minor contribution to the OH production at all times. Only C₂ to C₆ alkene species were measured, so that ozonolysis reactions of undetected alkene species (potentially monoterpenes) could have additionally contributed to the OH production. However, the good agreement between measured and calculated OH reactivity does not hint that a large fraction of alkene species were missed.

The time series of the total OH production and destruction rates, determined by Eq. 2 and 3, respectively, were nearly balanced for most of the time (Fig. 2). The OH destruction rate is on average only 20 % higher than the sum of OH production during daytime. The median diurnal profiles of P_{OH} and D_{OH} agree especially well in the morning (Fig. 9), whereas in the afternoon, the loss rate is slightly larger than the production rate. Although the difference is hardly significant with respect to the experimental accuracies (Fig. 9), a systematic trend of the ratio between OH production and destruction rates with NO can be seen (Fig. 10), which points to a missing OH source at low NO concentrations.

For NO mixing ratios of less than 0.3 ppbv, OH destruction was nearly twice as large as the OH production, whereas production and destruction was balanced for NO mixing ratios higher than 1 ppbv. 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 describe HO₂ and k_{OH} correctly under these conditions at the Wangdu site. The good description of HO₂ and k_{OH} 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. A similar behavior was found in our previous field campaigns in China in 2006. However, the ratio of $P_{\text{OH}}/D_{\text{OH}}$ was much smaller, with a value of about 0.25 for NO mixing ratios of 0.1 to 0.2 ppbv NO in PRD (Hofzumahaus et al., 2009). In this case, the missing OH source was highly significant with respect to the experimental uncertainties of the calculated reaction rates, whereas in Wangdu, the much weaker imbalance of the OH budget can be almost explained by the experimental errors.

In addition to the measurement uncertainties stated in Tab. 1, instrumental tests during this campaign cannot exclude that OH concentration measurements are partly affected by an artifact as discussed in detail in Tan et al. (2016). The upper limit for an instrumental interference was estimated to be equivalent to an OH concentration of $1 \times 10^6 \text{ cm}^{-3}$. This positive bias would also give a positive bias in the calculated OH destruction rate.

In the night, OH production from sources taken into account in this calculation is close to zero because there is no radiation. This suppresses both OH production from photolysis reactions and OH regeneration by the reaction of peroxy radicals with NO that is mainly formed from NO₂ photolysis. Because of the relatively high OH reactivity OH concentrations are expected to be very small. However, median measured OH concentrations ranged between 0.5 to $1 \times 10^6 \text{ cm}^{-3}$ (Fig. 8). A median OH production of 1 to 3 ppbv/h would be required to explain measured nighttime OH concentrations (Fig. 9).

Potential reasons for additional OH production at night have been recently discussed by Lu et al. (2014), such as OH production by ozonolysis of terpenoids or dissociation of radical reservoir species like PAN that may be transported downward in the nocturnal boundary layer. Such mechanisms may have played a role at Wangdu, but we have no suitable measured data to test these hypotheses. In order to balance the calculated OH destruction rate during nighttime, a rather large concentration of an alkene would be required. Assuming an ozone concentration of 30 ppbv, a reaction rate constant for the ozonolysis reaction of $1.8 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ for δ -terpine and an OH yield of one (Atkinson and Arey, 2003), the concentration would need to be around 600 pptv.

However, the impact of a potential interference in the OH concentration measurements would also be largest in the night (Fig. 9), because nearly the entire OH signal could be due to interferences. As a consequence, the difference between calculated OH production and destruction during nighttime is within this additional uncertainty. The calculated OH destruction rate is less affected during daytime,

when a potential OH interference of less than $1 \times 10^6 \text{ cm}^{-3}$ would only be a small fraction of the total measured OH (Tan et al., 2016).
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In our previous field campaigns in China 2006, the OH ~~destruction and production rates were~~ ~~turnover rate was~~ significantly higher than in this campaign. In PRD and Yufa, maximum mean turnover rates (OH destruction rates) of 40 ppbv/h and 20 ppbv/h, respectively, were reached around noontime (Lu et al., 2012, 2013). These values are 1.5 to 3 times higher than median OH turnover rates in this
565 campaign. As discussed above, the major difference is that measured OH reactivities were significantly higher in the previous campaigns. The resulting higher loss rate was only partly balanced by a higher OH production from the reaction of HO₂ with NO, which was nearly a factor two larger in PRD and Yufa. Therefore, also the gap between calculated OH destruction and production was clearly above the level of significance ~~with respect to the measurement uncertainties~~ (Hofzumahaus
570 et al., 2009).

Also the distribution of primary OH sources is different in this campaign compared to our previous campaigns in China, when HONO photolysis exhibited a diurnal profile with maximum values in the morning. These values were larger compared to this campaign, but HONO mixing ratios dropped to lower values in the afternoon, so that production by HONO photolysis was less in Yufa and PRD
575 than in Wangdu 2016. Nevertheless, total primary OH production was higher (factor of 2 in PRD and factor of 1.5 in Yufa) in the previous campaigns.

HONO photolysis was also the most important primary source for OH radicals in other campaigns that were conducted in anthropogenic dominated environments for example in New York (Ren et al., 2003), in Paris (Michoud et al., 2012), Mexico City (Dusanter et al., 2009), Santiago (Elshorbany
580 et al., 2009), and Tokyo (Kanaya et al., 2007). 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. Our measurement site in Wangdu was not directly located in an urban area and therefore the NO_x concentrations were only moderately high in the morning and rather small in the afternoon, so that the importance of HONO as largest primary source
585 for OH was not necessarily expected. ~~The contribution of alkene ozonolysis to the OH production in other campaigns in urban environments were partly significantly higher~~ (Kanaya et al., 2007; Dusanter et al., 2009; Elshorbany et al., 2009) compared to the Wangdu site due to higher alkene concentrations.

4 Summary and conclusions

590 OH reactivity was measured during a comprehensive field campaign at Wangdu in summer 2014. Additional measurements of OH reactants, OH concentrations and quantities that are required to calculate OH production (HO₂, NO, O₃, HONO, photolysis frequencies) allowed comparing OH

reactivity measurements with calculations from measured OH reactants and analyzing the chemical OH budget from measurements alone.

595 Overall, measured OH reactivity can mostly be explained by OH reactants measurements, specifically during the second half of the campaign. **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.** The diurnal profile of OH reactivity, the distribution of OH ~~reactant~~**reactants** and the good correlation of the OH reactivity with
600 CO indicates that the chemical composition at the measurement site was mainly impacted by anthropogenic emissions. In our previous field campaigns in China 2006, the number of OH reactants that were measured was less and, thus, only approximately 50 % of the measured OH reactivity was explained by measured OH reactants (Lou et al., 2010; Lu et al., 2012, 2013). However, additional OH reactants determined by model calculations could close the gap in these cases. In this campaign, the
605 good agreement between measured and calculated reactivity indicates that ~~most~~**the** important organic compounds were measured including oxidation products.

OH production and destruction were mainly balanced within the uncertainty of measurements. The accuracy of this calculation was lowered by additional uncertainty in the OH concentration measurements due to a potential bias (Tan et al., 2016). Despite this uncertainty, the OH destruction
610 tends to be higher than OH production in the late afternoon, when NO concentrations were lowest. This result is consistent with the analysis of model calculations (Tan et al., 2016) and findings in previous field campaigns (Hofzumahaus et al., 2009).

However, in 2006 the observed discrepancy between the OH production and destruction rates was significantly larger requiring an additional OH source to close the gap. The major difference to this
615 campaign was that the measured OH reactivity was much higher. Therefore, a significant gap in OH production and destruction rates were found in contrast to results in this campaign. **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
620 measured and calculated OH reactivity that have been observed in other campaigns.**

Acknowledgements. We thank the science teams of Wangdu-2014 campaign. This work was supported by the National Natural Science Foundation of China (Major Program: 21190052 and Innovative Research Group: 41121004), the Strategic Priority Research Program of the Chinese Academy of Sciences (grant no. XDB05010500), the Collaborative Innovation Center for Regional Environmental Quality, and by the EU-project AMIS (Fate
625 and Impact of Atmospheric Pollutants, PIRSES-GA-2011-295132). The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (<http://www.ready.noaa.gov>) used in this publication.

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Table 1. Instruments deployed in the campaign and used for data analysis.

	measurement technique	time resolution	1 σ detection limit	1 σ accuracy
k_{OH}	LP-LIF ^a	180 s	0.3 s ⁻¹	$\pm 10\%$ +0.7 s ⁻¹
OH	LIF ^b	32 s	0.32×10^6 cm ⁻³	$\pm 11\%$
HO ₂	LIF ^b	32 s	0.10×10^8 cm ⁻³	$\pm 16\%$
photolysis frequency	spectroradiometer	20 s	^c	$\pm 10\%$
O ₃	UV photometry	60 s	0.5 ppbv	$\pm 5\%$
NO	chemiluminescence	180 s	60 pptv	$\pm 20\%$
NO ₂	chemiluminescence ^d	600 s	300 pptv	$\pm 20\%$
HONO	LOPAP ^e	300 s	7 pptv	$\pm 20\%$
CO, CH ₄ , CO ₂ , H ₂ O	cavity ring down	60 s	^f	^g
SO ₂	pulsed UV fluorescence	60 s	0.1 ppbv	$\pm 5\%$
HCHO	Hantzsch fluorimetry	60 s	25 pptv	$\pm 5\%$
volatile organic compounds ^h	GC-FID/MS ^l	1 h	20 to 300 pptv	± 15 to 20 %
volatile organic compounds ⁱ	PTR-MS	20 s	0.2 ppbv	$\pm 15\%$
glyoxal	CEAS ^j	1 s	0.02 ppbv	$\pm 5.8\%$

^a laser photolysis - laser induced fluorescence^b laser induced fluorescence^c process specific, 5 order of magnitudes lower than maximum in noon time^d photolytical conversion to NO before detection, home built converter^e long-path absorption photometry^f species specific, for CO: 1 ppbv; CH₄:1 ppbv; CO₂: 25 ppbv; H₂O: 0.1 % (absolute water vapor content);^g species specific, for CO: 1 ppbv; CH₄: ± 1 ppbv; CO₂: ± 25 ppbv; H₂O: $\pm 5\%$ ^h VOCs including C₂-C₁₁ alkanes, C₂-C₆ alkenes, C₆-C₁₀ aromaticsⁱ OVOCs including acetaldehyde, methyl-vinyl ketone and methacrolein^j cavity-enhanced-absorption spectroscopy

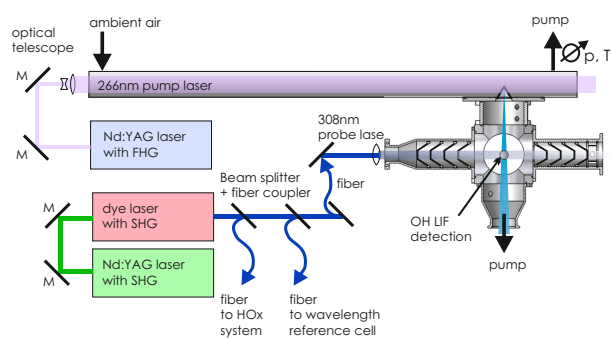


Figure 1. Schematics of the Jülich OH reactivity instrument (M: turning mirror). Ambient air is sampled into a flow tube. A small part of the air is drawn into the OH detection cell that is operated at a pressure of 4 hPa. High OH concentrations are produced by flash photolysis of ozone at 266 nm at a low frequency of 1 to 2 Hz. The OH concentration is probed at a high frequency of 8.5 kHz, so that the loss of OH radicals due to their reaction with OH reactants in the ambient air can be observed.

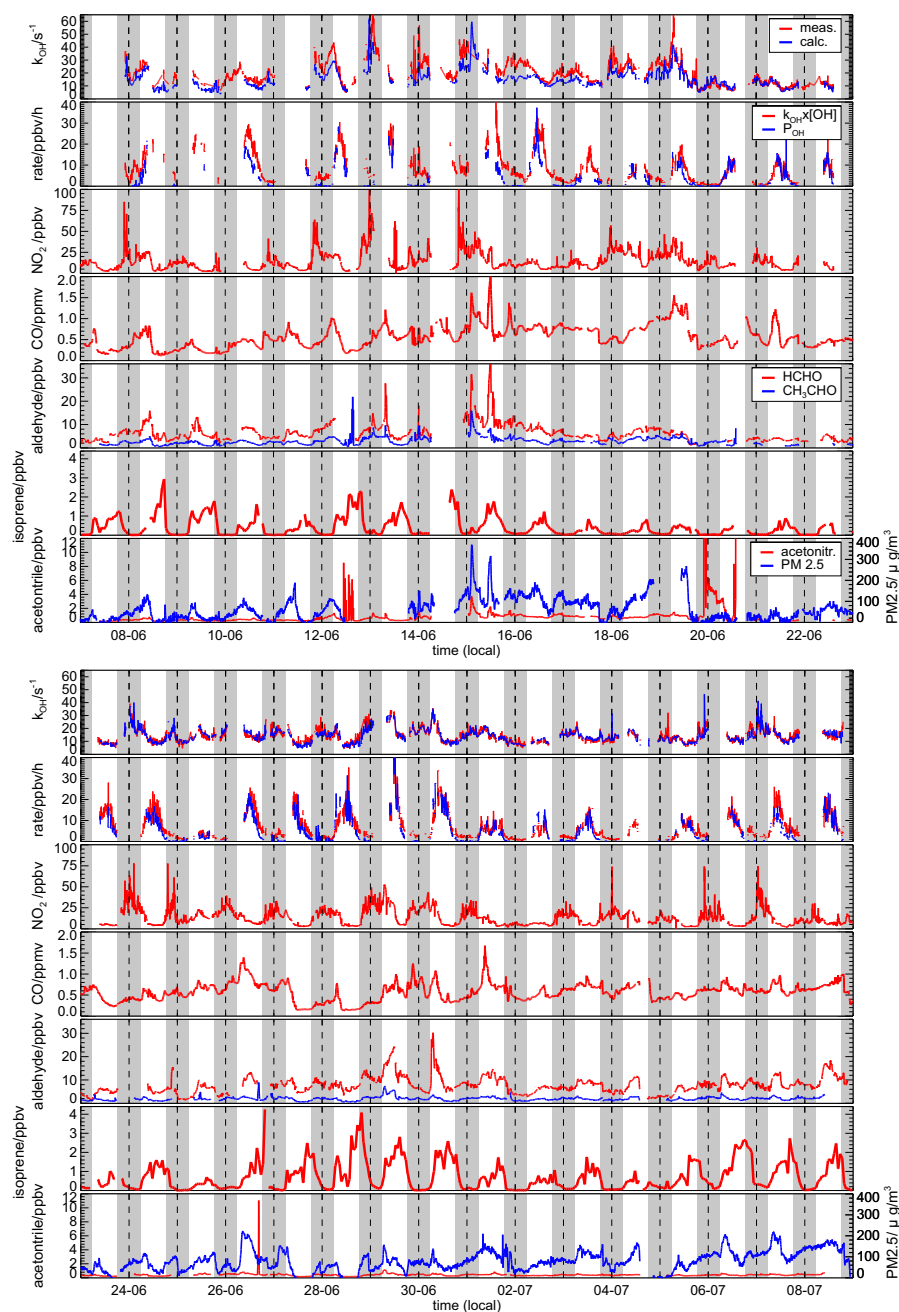


Figure 2. Time series of measured and calculated OH reactivity. In addition, time series of the OH destruction rate (D_{OH}) calculated from measured OH concentrations and OH reactivity is shown together with the sum of measured OH production rates (P_{OH}) from O_3 and HONO photolysis and reactions of HO_2 with NO and O_3 . Lower panels give time series of important trace gas measurements contributing to the OH reactivity. Gray areas indicate nighttime.

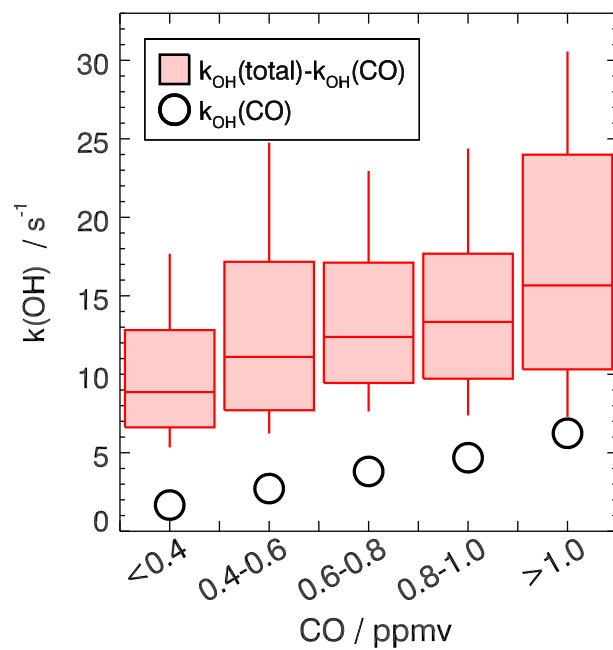


Figure 3. Correlation between OH reactivity excluding CO and CO mixing ratios. Red boxes give 25 and 75 percentiles and whiskers 10 and 90 percentiles of the k_{OH} distribution. Black circles show median values of OH reactivity that is caused by CO.

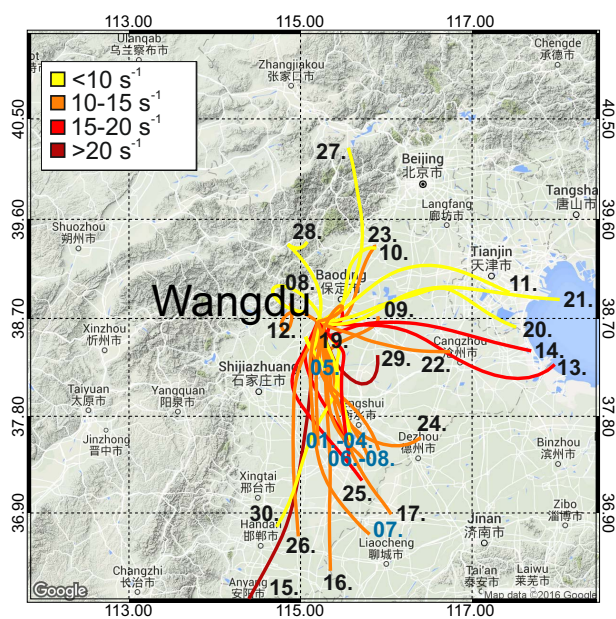


Figure 4. NOAA Hysplit 24-hour back-trajectories during the campaign calculated as averages of hourly back-trajectories between 10:00 and 19:00 local time. Colors of trajectories indicate the OH reactivity level measured at the field site in Wangdu. Black numbers indicate the date in June, dark blue numbers the date in July.

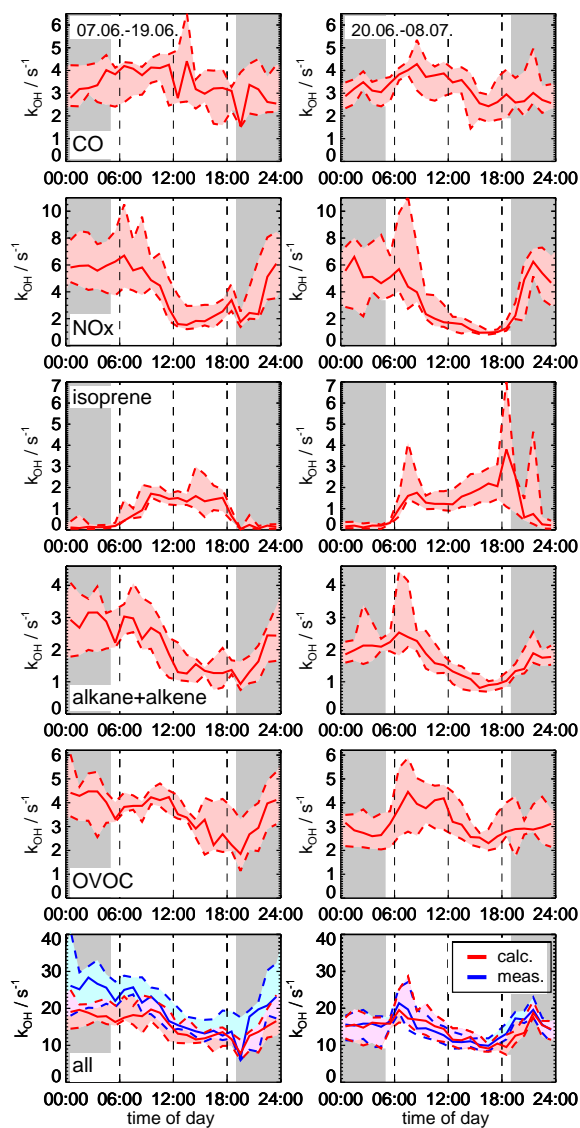


Figure 5. Median diurnal profiles of reactivity from major measured OH reactants and of the total measured and calculated OH reactivity for the first and second part of the campaign. Data is only included, if all major OH reactants and OH reactivity were concurrently measured. Colored areas give 25 and 75 percentiles. Gray areas indicate nighttime.

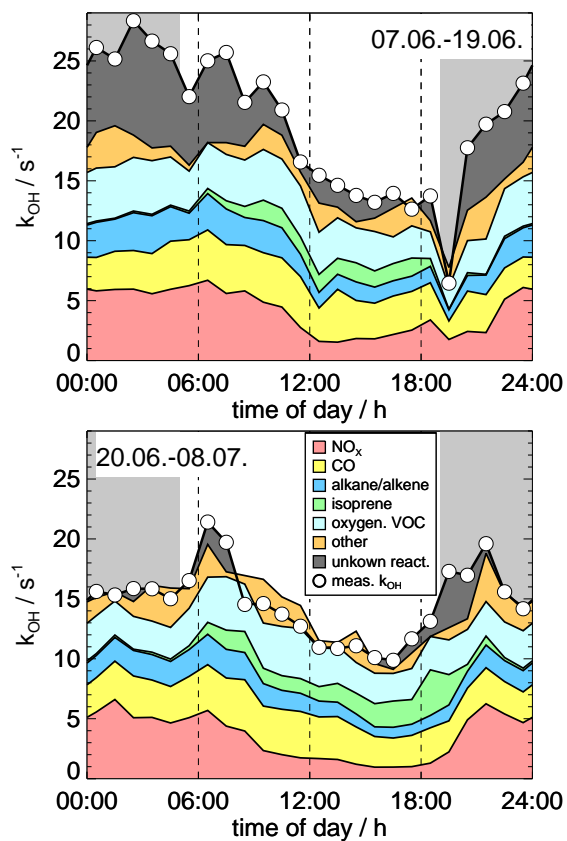


Figure 6. Sum of median diurnal profiles of reactivities from all measured OH reactants compared to the measured OH reactivity for the first and second part of the campaign. Data is only included, if all major OH reactants and OH reactivity were concurrently measured. “Other” include small contributions from measured OH reactants listed in Table 1 (CH_4 , SO_2 , aromatics). The dark grey area indicates missing OH reactivity from unmeasured OH reactants. Light gray areas indicate nighttime.

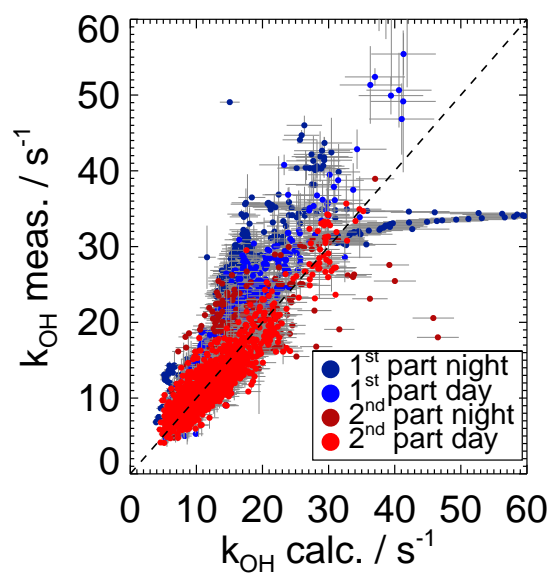


Figure 7. Correlation between calculated and measured OH reactivity with color coded periods. The linear correlation coefficient (R^2) is 0.77 for the entire data set and both data from both periods alone.

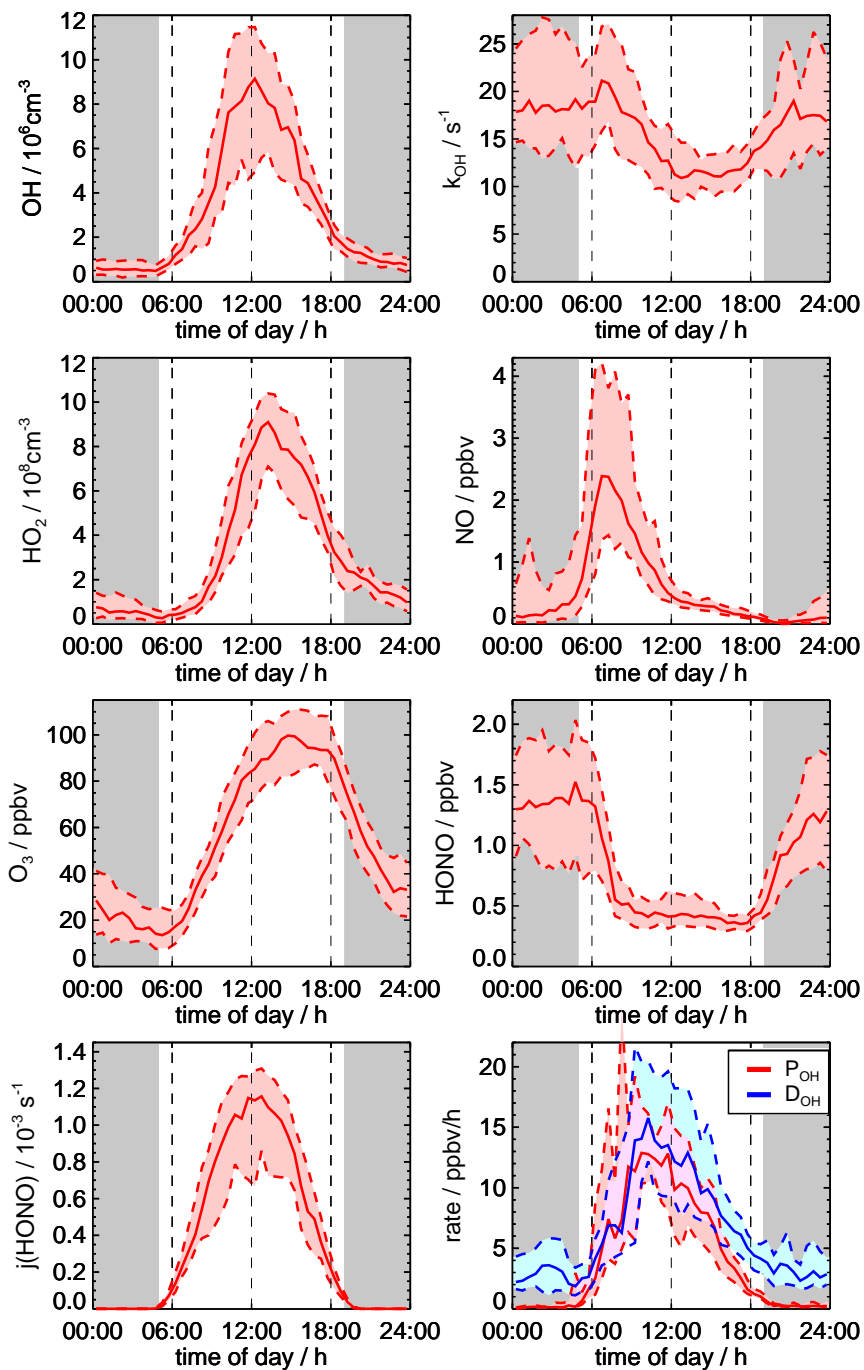


Figure 8. Median diurnal profiles of trace gas concentrations used for the calculation of the total OH production rate (P_{OH}) and destruction rate (D_{OH}). Data is only included, if all required trace gas concentrations and OH reactivity were concurrently measured. Colored areas give 25 and 75 percentiles. Gray areas indicate nighttime. Note that the selection of data is different for median profiles shown in our accompanying paper by Tan et al. (2016).

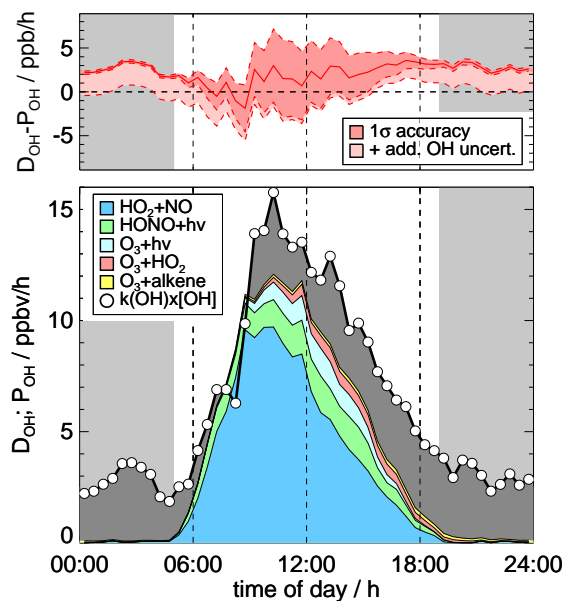


Figure 9. Median diurnal profiles of OH production (P_{OH}) and destruction (D_{OH}) rates. Data is only included, if all required trace gas concentrations and OH reactivity were concurrently measured. Dark grey areas indicate missing OH production. The upper panel gives the 1σ accuracy of the difference ($D_{OH} - P_{OH}$) calculated from the uncertainties of measurements (Gaussian error propagation). The effect on the accuracy from an upper limit of potential interferences in the OH measurements is shown separately.

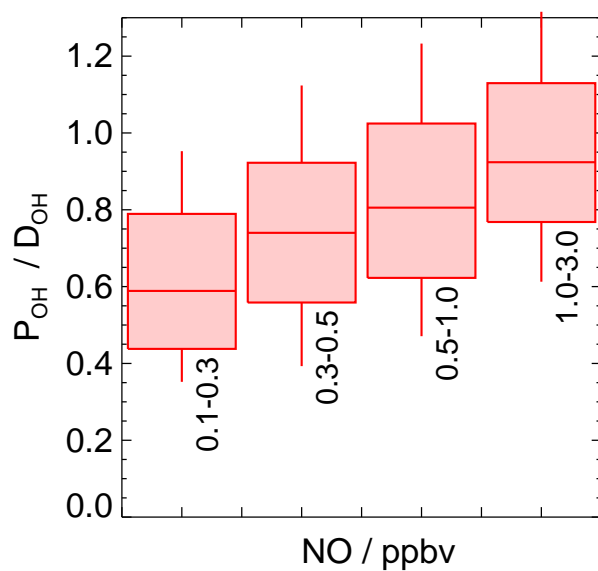


Figure 10. Box and whisker plot of the ratio of the total OH production (P_{OH}) and the OH destruction rate (D_{OH}) as a function of the NO mixing ratio for daytime values. Boxes give 25 and 75 percentiles and whiskers 10 and 90 percentiles. Data is only included, if all required trace gas concentrations and OH reactivity were concurrently measured. Gray areas indicate nighttime.