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

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We thank the reviewer for the helpful comments.

Comment: 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) NOx 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 HOx 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 NO_2) were also detected by several instruments applying chemiluminescence technique (Thermo Electron model 42i NO-NO_2-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 NOx (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, CH_4, C_2 to C_{11} alkanes, C_2 to C_6 alkenes, C_6 to C_{10} aromatics, formaldehyde, glyoxal, acetaldehyde, MVK, MACR, NO, NO_2, SO_2 (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 kOH 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. NOx, 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.

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