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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.

Anonymous Referee #1

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Fuchs et al. present direct measurements of OH reactivity performed during a comprehensive field campaign conducted in June-July 2014 close to the small town of Wangdu. After a description of OH reactivity measurements and a brief description of radicals and trace gases measurements, the authors discuss the OH reactivity time series and compare the OH reactivity measurements with calculated OH reactivity estimated using measured OH reactant concentrations. This comparison shows, generally, good agreement between calculated and measured OH reactivity. Finally, the authors analyze the OH budget and perform a comparison between total OH production and destruction rates to quantify unaccounted OH production. This highlights an imbalance in the late afternoon and at night when NO concentrations were lowest.

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This manuscript is within the scope of ACP and will be of interest for the atmospheric community. I therefore recommend publication in ACP after the authors address the comments listed below.

Main comments:

1) 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?

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.

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.

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.

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

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).

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

2) 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.

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?

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.

Minor comments:

P3, line 51-52: “from ozone and nitrous acid photolysis and reaction of hydroperoxyl radicals with nitric oxide": Please add reactions of ozonolysis of alkenes and reaction of hydroperoxyl radical with ozone to these OH sources list to be exhaustive.

P4, line 85: "nitrogen monoxide" is used to define NO while the term "nitric oxide" is used elsewhere in the manuscript. Please harmonize.

P6, line 136: "nitrogen oxides" to "nitric oxide". Ozone depletion at night is due to its titration by NO.

P7, line 181: Typo: "(??)"

P7, line 181-182: "could not fully excluded" to "could not be fully excluded".

P7, line 193: "In general, values were lower during daytime than at night". Please indicate daytime and nighttime median values of OH reactivity.

P9, line 240: "is not necessarily expected" to "is not expected".

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.

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.

P10, line 279: "Only relatively few oxygenated volatile organic compounds". Please indicate how many OVOCs were measured.

P10, line 284: "the most important organic oxidation products". This statement should be moderated or removed since formaldehyde and acetaldehyde are also emitted di-

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rectly in the atmosphere by anthropogenic and biogenic sources (e.g. Chen et al., ACP, 14, 3047-3062, 2014).

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?

P11, line 315: “Exceptionally good agreement is seen at nearly all times after 20 June”. Please be more quantitative.

P11, line 317-318: “the number of OVOCs that were measured in this campaign is rather small”. Please indicate how many OVOCs were measured.

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?

P13, line 395: typo: “vales” to “values”.

P14, line 422-423: “NO that is mainly formed from NO2 photolysis”. The main source of NO is its emission from combustion processes. Please rephrase or remove this statement.

P15, line 464: typo: “NO O3” to “NO, O3”

Figure 2: Please replace “ppm” by “ppmv” for CO to be consistent with the other units.

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).

Figure 6: Please define which species exactly are considered in the “other” group.

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

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