

## ***Interactive comment on “Nighttime observation and chemistry of HO<sub>x</sub> in the Pearl River Delta and Beijing in summer 2006” by K. D. Lu et al.***

### **Anonymous Referee #2**

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#### General comments:

This paper describes nighttime measurements of OH at two locations in China during 2006 that both showed concentrations much larger than predicted by standard models. If correct, these observations suggest shortcomings in current models of HO<sub>x</sub> chemistry, and further suggest that nighttime oxidation rates by OH can be much larger than previously thought. Derived oxidation rates are much larger than those of the conventional nighttime oxidants, O<sub>3</sub> and NO<sub>3</sub>.

The authors discuss three different mechanisms that could explain the observations. These include as yet unknown HO<sub>x</sub> recycling reactions, similar to that used to explain large daytime concentrations of HO<sub>x</sub> from the same campaigns; a source of HO<sub>x</sub>

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from nighttime ozonolysis reactions of highly reactive biogenic VOCs; and transport of radical reservoirs from a layer aloft to the surface. None of the three mechanisms satisfactorily explain the magnitude or time dependences of the observations, but they do suggest useful tests that can be applied in future investigations, especially with regard to the measurements of nighttime vertical gradients.

The major weakness of the analysis, and one that is adequately acknowledged and addressed in the paper, is that the observations could arise from measurement artifacts in the OH instrument. A recent paper from Mao et al. (2012) shows that a different OH zeroing scheme applied to the Penn State OH LIF instrument largely resolved recently observed model to measurement discrepancies, including nighttime observations from the recent literature. The authors of the current paper allow for the possibility that their instrument could be subject to similar interferences during the specific measurements in China in 2006, while arguing that their recent work suggests that such artifacts are unlikely. Because they have directly addressed this issue and argued at least plausibly (if not fully convincingly) for the validity of their nighttime data, I find the paper suitable for publication. The suggestions for additional work to determine the source of the observed nighttime OH, including further work on measurement artifacts, will serve as a useful reference for future investigations.

The authors should address the specific comments below prior to publication.

#### Specific Comments:

Page 319, section 2.2: Why use a RACM scheme for a zero D model rather than a more detailed scheme like the MCM? Is there a use for the lumped model when it is compared to MCM anyway later in the paper?

Page 319, Figures 1 and 2: Headings are missing in these figures. Presumably the right column is PRD and the left is Beijing?

Page 322, lines 1-5: The modeled NO<sub>3</sub> seems too high for periods in which the NO

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is large (e.g., >10 ppbv after midnight in Figure 1 at PRD). Is this a consequence of averaging some nights with lower NO and non-zero NO<sub>3</sub> together with others that have higher NO and zero NO<sub>3</sub>? Or does the model take diurnal average values of the inputs? If the former, could such a model non-linearity have any influence on the OH model to measurement comparison?

Page 322-323, section 3.3: The observations imply large nighttime oxidation rates. Later in the manuscript, however, the authors argue that the high OH may be confined to a shallow layer. The section requires caveats that the nighttime OH oxidation could not represent a quarter of total oxidation if there were strong gradients at night but not during day.

Page 322, lines 25-27 and description of figure 5: How are the NO<sub>3</sub> turnover rates calculated? Is this modeled NO<sub>3</sub> multiplied by an NO<sub>3</sub> reactivity from the VOC measurements, or is it the NO<sub>3</sub> production rate? If the latter, how does this compare to the simpler calculation represented by the former. Also, in Figure 5, suggest showing the NO<sub>3</sub> and O<sub>3</sub> turnover rates on separate scales, or at least multiplied by a factor of 10, so that they are visible. The average values given in the text hide some of the detail of the time dependence, which is not easy for the reader to see in this figure.

Page 323, introduction to section 4: The introduction to this section, and the presentation of the literature in Table 2, gives the impression to the reader that large nighttime OH and model to measurement discrepancies are well accepted. This is not the case, as the later discussion in this section shows. The first four references in Table 2, were they to be corrected by the more recent findings from the same group (see Mao et al, 2012), would not produce large model to measurement discrepancies. Thus, the observations from the studies in China in 2006 are more unusual than implied by this discussion. Strongly suggest rewording this section so that it leads with the results of Mao et al. and does not present high nighttime OH as an accepted finding.

Page 326, lines 12-13: The nighttime isoprene decays at the PROPHET site is contro-

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versial, and likely due to transport, not chemistry. See Sillman et al, JGR, 107, 4043 (2002). The concluding statement of this paragraph is likely more correct than the introductory statement. Suggest omitting chemical arguments regarding isoprene at night.

Page 328, lines 14-16: Would these imbalances be sufficient to sustain turnover rates of 5-10 ppbv hr<sup>-1</sup>, as shown in Figure 5? The argument would imply a PAN + HO<sub>2</sub>NO<sub>2</sub> loss rate of similar magnitude, further implying a very large reservoir of these compounds. Realistic?

Page 334-335, end of section 4.4.2. Although the argument is interesting and certainly consistent with the model of Geyer and Stutz, it produces a large flux of radicals late at night, when they are less needed to resolve the model to measurement discrepancy? The cited flux of 0.25 ppbv hr<sup>-1</sup> at PRD occurs at sunrise, rather than sunset, when it is quite small. The authors should comment on this aspect of the proposed radical source.

#### Technical corrections

Page 314, line 8: comma after radicals Page 314, line 26, comma after "involvement of NO" Page 316, line 11, "electronic" rather than "electronical" Page 329, line 24: "relatively" Page 336, line 6: "well" not needed or awkward. "Easily" would be better if the adverb is needed

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 31311, 2013.

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