

## ***Interactive comment on “Wintertime photochemistry in Beijing: Observations of RO<sub>x</sub> radical concentrations in the North China Plain during the BEST-ONE campaign” by Zhaofeng Tan et al.***

**Anonymous Referee #2**

Received and published: 20 May 2018

Review of “Wintertime photochemistry in Beijing...” by Tan et al.

This paper reports in situ ground-based measurements of atmospheric radical species at a suburban site to the north of Beijing. State-of-the-science techniques are used to measure OH, HO<sub>2</sub> and RO<sub>2</sub> radicals, and the OH lifetime, augmented by established methods for other important trace gas components. The potential for interferences in the OH measurements is carefully considered and could be dismissed.

A budget analysis derived from the observed data, and 0-D box model simulations,

C1

is presented, the key result from which is that the model performed reasonably well (agreement within 50%) for “clean” days, but under more polluted conditions with higher NO<sub>x</sub> levels, the observed RO<sub>2</sub> levels exceeded those modelled by up to a factor of 5, pointing to a significant discrepancy in understanding (or observations).

The subject of the paper is directly within the ACP remit, and the issues addressed are topical and at the forefront of our understanding. The paper is broadly well written and clearly presented; the figures are of high quality. I have several minor comments, and three more significant points I would like the authors to consider in the ACPD Discussion :

Main comments

-While the measurements and analysis presented appear robust, the paper concludes that there is a significant discrepancy in quantitative understanding – but without assessing potential causes for this. I find this a little unsatisfactory – I would like the authors to add some suggestions – both related to measurement methods, model limitations and potential new chemical understanding – which could resolve these. These may include suggestions for future work to move the situation forwards.

-Is the site location representative of Beijing ? Huairou is on the northern perimeter of Beijing, adjacent to the higher ground to the north and outside of much of the city development. Is the chemical environment then representative of “downtown” Beijing, in the city centre. The authors should confirm this (eg through comparison of basic AQ metrics), and I would like them to reflect the presentation of their location as different from (e.g.) the CARE campaigns etc in the text, and potentially the manuscript title

-Accumulating evidence is pointing to Cl chemistry being important for radical formation; ClNO<sub>2</sub> observations were not made during this campaign – what is the sensitivity of the conclusions to the assumed ClNO<sub>2</sub> / Cl atom levels – how might this (and the NO<sub>x</sub>-dependence of the availability of Cl vs inorganic reservoir formation) affect the radical budgets ?

C2

#### Other Comments

p. 1Line 34 – “series of control provisions” give dates to increase the relevance of the paper in future years

P2 L1 – national trends needs a reference

P2 L7 “attack” ?

P2 L12 “guarantees” is a bold word to use – what about species with slow OH reaction (eg CH<sub>4</sub>)

P2 L14 O<sub>3</sub> photolysis is not the dominant source of HO<sub>x</sub> in the BL, outside of remote marine environments – as shown by eg fig 9 of this paper

P2 L 18 “general expectation” – what about previous measurements of OH

P2 L25+ Needs reference to Hofzumahaus et al. Science paper

P3 L10 Compare NO<sub>x</sub> PM etc with central Beijing to justify site description as “Beijing”

P5 L10+ The description of the checks of OH-chem vs OH-wave is good and reassuring, but more detail on the RO<sub>2</sub> and HO<sub>2</sub> method and particularly the uncertainties in these would be useful

P6 L5 Does the LOPAP discrepancy correlate with other factors – eg aerosol nitrite levels ?

P6 L30 How did the model constraint work. Was the model simply updated to the observed levels every ?15 mins – does this introduce noise into the output concentrations. What about spin-up time to simulate intermediate species.

P7 L14 Give values for the thresholds used to define the pollution regimes

P9 L12 jO<sub>1</sub>D and jNO<sub>2</sub> should not be correlated given the different adsorption spectra and quantum yield wavelength dependence for O<sub>3</sub>-O<sub>1</sub>D and NO<sub>2</sub> photolysis. See discussion in Rohrer & Berresheim, Nature 2006 and other HO<sub>x</sub> measurement / j cor-

C3

relation analyses eg Smith et al. ACP 2006

P9 L38 – can you expand on the “NO measurement artefact” ?

P11 L18 reword

P13 L33 – Need to be clear that the observations and model only determine the local chemical ozone production rate, while a wider view (Eularian or trajectory) is needed to compare with O<sub>3</sub> levels (ie accounting for advection). Also relevant to Fig 12b. -Modelling – how significant were modelled VOC degradation products in terms of increasing the OH reactivity, compared with the measured (parent) VOCs ?

P15 L35 – see main comment above

---

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-359>, 2018.