# Missing OH source in a suburban environment near Beijing : observed and modelled OH and $HO_2$ concentrations in summer 2006

Online supplementary materials

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### This file includes:

- 1. HOx and  $k_{\rm OH}$  measurement results in Sep 2006 (Fig. S1)
- 2. Averaged diurnal profiles of  $O_3$ , NO, NO<sub>2</sub>,  $j(NO_2)$ , and VOC speciations for southerly wind days and that of Aug 20 (Fig. S2)
- 3. Intercomparisons of the modelled HOx concentrations between M0 and RACM-MIM-GK, and that between M5 (MCMv3.2) and MCMv3.1 (Fig. S3, Fig. S4)
- 4. Retrieved diurnal profiles of X and Y for M1 and M2 (Fig. S5)
- 5. Model uncertainties from unconstrained OVOCs (HCHO) (Fig. S6, S7).

## 1. HOx and $k_{\text{OH}}$ measurement results in Sep 2006

We performed HOx and  $k_{\rm OH}$  measurements during Sep 2006 as well as Aug 2006 (see Fig. S1). In general, similar levels of OH, HO<sub>2</sub> and  $k_{\rm OH}$  values and diurnal variabilities were observed for both periods. In this study, the model analysis was limited to the time period in which high precision NO measurements were available.



**Figure S1.** Full time series of the measured (red pluses) and M0 modeled (blue lines) OH,  $HO_2^*$  and  $k_{OH}$  at the Yufa site during CAREBeijing2006 campaign. Cyan line in panel (c) give the modeled HO<sub>2</sub>. The model results are limited to the existence of the high precision NO data. The wind pattern is given as support information.

# 2. Averaged diurnal profiles of $O_3$ , NO, NO<sub>2</sub>, $j(NO_2)$ , and VOC speciations for southerly wind days and that of Aug 20

In Fig. S2, we provide basic photochemical characteristics of the two periods, namely southerly wind days and Aug 20, in discussion of the main paper. For these two periods, similar  $j(NO_2)$  and VOC speciation were observed whereas the major photochemical difference was characterized by the afternoon NOx concentrations.



Figure S2. The averaged diurnal profiles of NO, NO<sub>2</sub>, O<sub>3</sub>,  $j(NO_2)$  and the speciation of observed HC reactivities during southerly wind days and that of Aug 20. Butenes=1-Butene, *i*-Butene, *trans*-2-Butene, *cis*-2-Butene; Xylenes=o-,m-,p-Xylene.

### 3. Intercomparisons of the modelled HOx concentrations between M0 and model scenario with RACM-MIM-GK, and that between M5 (MCMv3.2) and model scenario with MCMv3.1

By including the  $R(C=O)R'O_2+HO_2 \rightarrow OH$  chemistry proposed by Dillon and Crowley (2008); Jenkin et al. (2007) and the isoprene epoxide chemistry (Paulot et al., 2009) into RACM-MIM-GK, we defined the new base case model mechanism, namely RACM-MIM-GK2 used by M0. Recently, comprehensive updates were done for MCMv3.1 and a new mechanism – MCMv3.2 was released accord-The major updates are refered ingly. to http://mcm.leeds.ac.uk/MCM/project.htt#New\_3.2 of which the updates of the isoprene chemistry part also including the above two OH regeneration channels. Therefore, we consider MCMv3.2 to be a better benchmark mechanism comparing to our updated base case model mechanism RACM-MIM-GK2.

As shown by Fig. S3 and Fig. S4, the impact on the modelled HOx concentrations by these two additions is small. For RACM-MIM-GK, the change is less than 1% for OH while about 2% for HO<sub>2</sub>. For MCMv3.1, the change is about -2% for OH and 2% for HO<sub>2</sub>. The reduction of modelled OH in MCMv3.2 is due to the reduced reaction rate constant of HO<sub>2</sub> + NO (-4%) which overcome the enhanced mechanistic OH recycling.



Figure S3. Regression analysis of the modelled OH concentrations between M0 and model scenario with RACM-MIM-GK, and those between M5 (MCMv3.2) and model scenario with MCMv3.1.



Figure S4. Regression analysis of the modelled  $HO_2$  concentrations between M0 and model scenario with RACM-MIM-GK, and those between M5 (MCMv3.2) and model scenario with MCMv3.1.

#### 4. Retrieved diurnal profiles of X and Y for M1 and M2

By taking observed OH concentrations as the target parameter, the numerically retrieved diurnal profiles of X and Y for M1 and M2, respectively, were shown as Fig. S5. The merit function in this retrieval is set to be

$$\chi^{2} = \sum_{t=10:00}^{18:00} \left(\frac{\text{OH}_{obs} - \text{OH}_{mod}}{\sigma(\text{OH}_{obs})}\right)^{2}$$
(E1)

of which  $OH_{obs}$  denote the observed values, the  $OH_{mod}$  denote the modelled values,  $\sigma(OH_{obs})$  is taken as the measurement accuracy and the time window (10:00 – 18:00) for optimization is selected to match the daytime period when the model-measurement discrepancy of OH concentrations takes place (cf. Fig 8a in the main paper).



Figure S5. The retrieved diurnal profiles of X and Y for M1 and M2 during 10:00 - 18:00, respectively.

5. Model uncertainties from unconstrained OVOCs (H-CHO). Sensitivity model runs are performed for each scenarios of the mechanistic model tests (M0 – M4) which is constrained with M0 calculated HCHO concentrations and also half of the M0 calculated HCHO concentrations. The resulted images for the two series of sensitivity model runs for OH,  $HO_2^*$ ,  $k_{OH}$  and  $HO_2$  are analyzed as Fig. S6 and S7 with the same style of Fig. 8 in the main paper.



Figure S6. Comparison of measured and calculated OH (a),  $\text{HO}_2^*$  (b),  $k_{\text{OH}}$  (c) for six different mechanistic scenarios (M0–M4) that additionally constrained to M0 calculated HCHO concentrations at southerly wind conditions. In addition, model results are compared for HO<sub>2</sub> (d).



Figure S7. Comparison of measured and calculated OH (a),  $\text{HO}_2^*$  (b),  $k_{\text{OH}}$  (c) for six different mechanistic scenarios (M0–M4) that additionally constrained to half of the M0 calculated HCHO concentrations at southerly wind conditions. In addition, model results are compared for HO<sub>2</sub> (d).

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