

Dear editor,

Thanks for your attention and careful review to our work. These comments and suggestions have improved our manuscript very much.

The main concern is about the empirical model to calculate levels of OH radicals (Eq.2). The strong nearly linear correlation between OH and $J(O^1D)$ is proposed by Rohrer and Berresheim (2006), based on the observations in a lightly polluted site, where the reaction of HO_2 with NO produce most of OH radicals. This relationship has been also verified by the OH campaigns in the polluted areas of China, where the most striking feature is the almost equal slope of the OH- $J(O^1D)$ relation for different locations and seasons (Rohrer et al., 2014; Tan et al., 2018). We can make assumptions that the comprehensive impact of reactants (e.g. NO_x and VOCs) on OH cannot compete with that of UV light to OH, and the chemical environments of OH are similar in polluted area of China. What's more, in the case of low concentration of NO and high value of $J(O^1D)$, the error of $P_{unknown}$ from OH radicals will be restrained significantly (Figure S1(d)). In summary, the empirical model to calculate the concentrations of OH radicals can be reasonable to a certain extent and the error of derived OH radicals has been assessed as not subverting the relative conclusions in this study (Fig. S1(a) and Fig. S1(d)).

For details, we divided this response into 3 part.

1. Response to the concern about the empirical model to calculate levels of OH radicals.

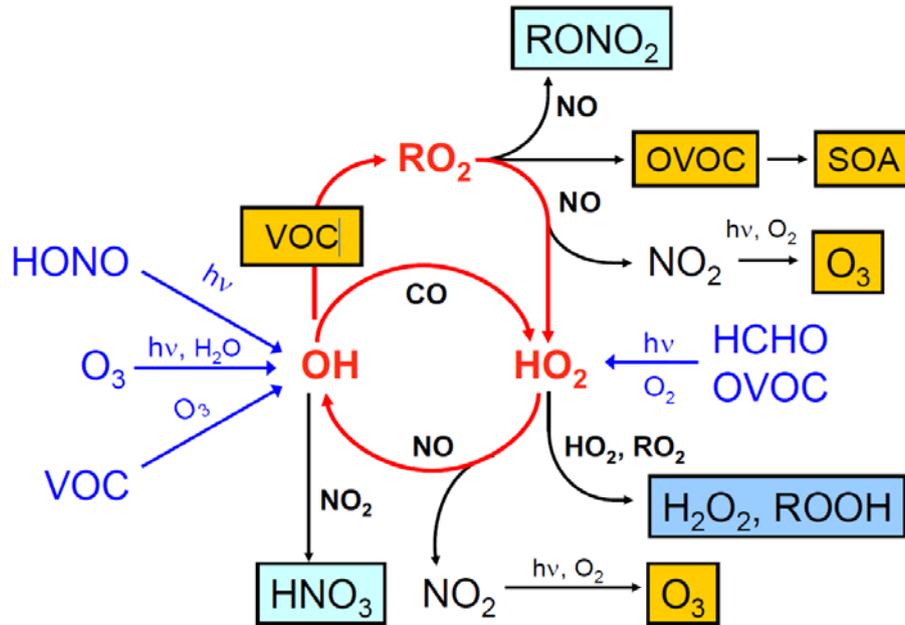
Hydroxyl radicals (OH) in the troposphere mainly come from:

1. primary production

- The reaction of $O(^1D)$ atoms, formed in the photolysis of ozone at wavelengths below 320 nm, with water;
- The photolysis of aldehydes (mainly HCHO) can form HO_2 radicals, which are converted to OH radicals in the presence of NO;
- The photolysis of HONO upon irradiation with UV light;
- The reactions of ozone with alkenes.

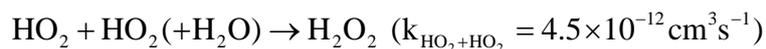
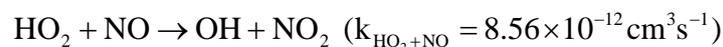
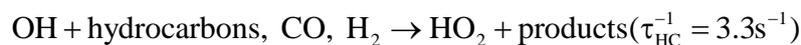
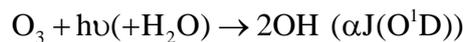
2. secondary production

- Reactions of HO_2 (RO_2), which are produced by the ozonolysis of alkenes, nighttime reactions of NO_3 radicals with alkenes, and OH reactions with CO and VOCs, with NO can reproduce OH.



Schematic drawing of HOx chemistry, illustrating established, major chemical pathways in the troposphere. Radical chemistry is initiated by primary radical production (blue arrows), and radical chain reactions (red arrows) cause cycling between OH, HO₂, and RO₂ (Lu et al., 2012).

The strong correlation of between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation, found in Rohrer and Berresheim (2006), is not only caused by the reaction of O(¹D) atoms with H₂O. Actually, the observation location in that study is lightly polluted, whose mean concentration of NO_x is 2.19 ppb and max concentration of NO_x is 76.3 ppb, and the reaction of HO₂ with NO produce most of OH radicals. A generalized reaction scheme for OH photochemistry has been discussed by Rohrer and Berresheim (2006):



$$\alpha = \frac{k_{\text{O}^1\text{D}+\text{H}_2\text{O}}[\text{H}_2\text{O}]}{k_{\text{O}^1\text{D}+\text{H}_2\text{O}}[\text{H}_2\text{O}] + k_{\text{O}^1\text{D}+\text{N}_2}[\text{N}_2] + k_{\text{O}^1\text{D}+\text{O}_2}[\text{O}_2]}$$

By using the steady-state approach for OH, HO₂, and NO, and neglecting minor terms, finally deriving the final expression for OH:

$$[\text{OH}] = \frac{k_{\text{HO}_2+\text{NO}} \tau_{\text{HC}} [\text{NO}_2] F_J}{k_{\text{NO}+\text{O}_3}} \times \sqrt{\frac{\alpha}{k_{\text{HO}_2+\text{HO}_2} [\text{O}_3]}} \times J(\text{O}^1\text{D})$$

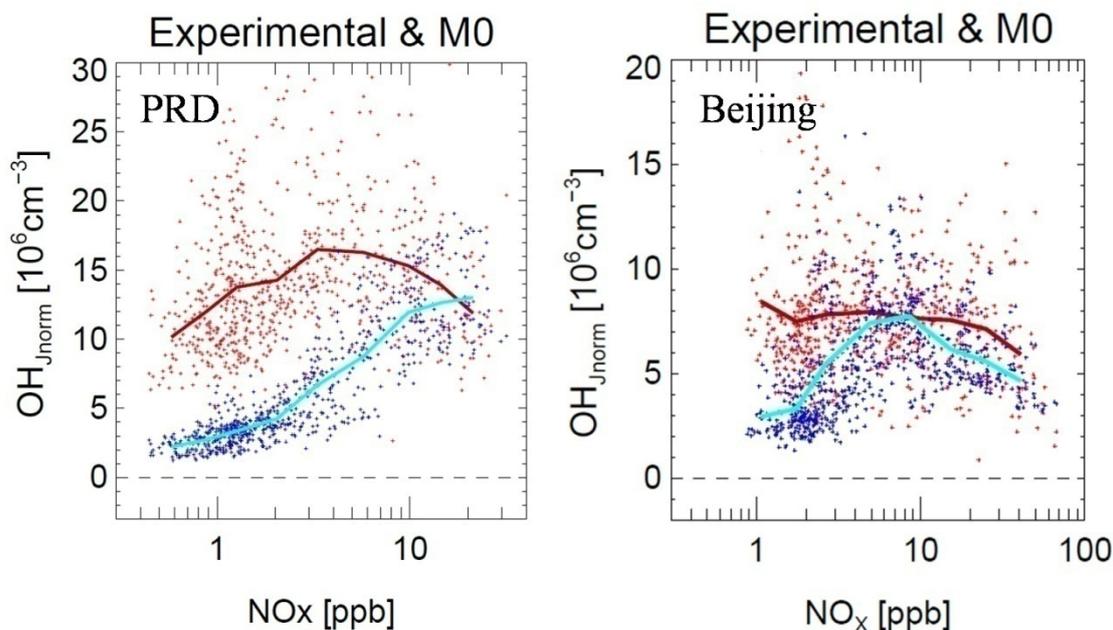
$$J(\text{NO}_2) = F_J \sqrt{J(\text{O}^1\text{D})}$$

Notably, the observed strong linear relation of OH radicals to J(O¹D) is a direct consequence of the efficient recycling of OH by way of the reaction HO₂+NO, implying that the empirical model to calculate OH (Eq. 2) may apply to the polluted area—for example, the SORPES station in our study.

For Eq. (2), The dependence of OH on reactants such as NO_x, hydrocarbons, ozone or H₂O is condensed into the single pre-exponential coefficient, **a**; The exponent **b** reflects the combined effects of all photolytic processes—for example, the photolysis of ozone, NO₂, HONO, H₂O₂ and HCHO. Each of these processes generates OH either directly or via production of and recycling from HO₂, and all are highly correlated but not necessarily in a linear manner; the parameter **c** includes all processes that are light-independent—for example, the reactions of ozone with alkenes.

In addition, other dependencies of OH (for example, on NO_x and VOCs concentrations) can result in the variability of the correlation plot of OH with J(O¹D), i.e. the variability of the coefficients **a**, **b** and **c** of Eq. (2), but the diversity is not as big as we thought based on the measurements. As listed in Table S1, the value of coefficient **b** is indeed mainly distributed around 1; the value of coefficient **a** does not show a great difference in different seasons or regions; It seems that the value of coefficient **c** in polluted areas is higher than that in clean areas, and the value of coefficient **c** in summer is higher than that in winter, probably due to variability of the strength of nighttime ozone or NO₃ radicals reacting with biogenic or anthropogenic VOCs.

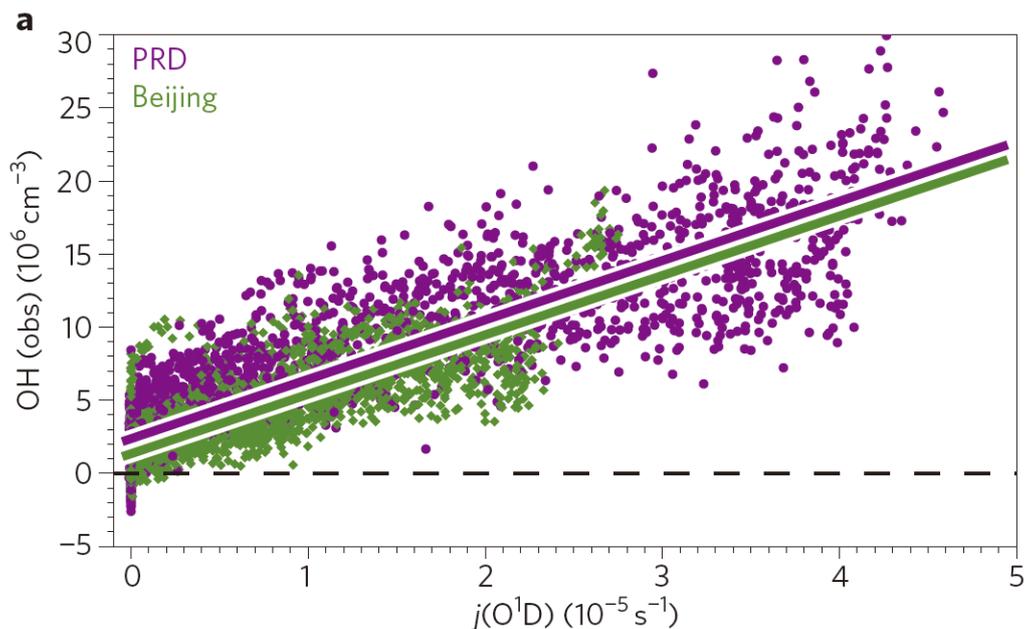
To further show how the OH–J(O¹D) relation results in a linear dependence, a sensitivity analysis is complemented, showed in Supplementary Table 5 in Rohrer and Berresheim (2006). Except for the combined photolysis frequencies, all parameters (levels of NO_x, CO, ozone, VOCs and so on) have very much attenuated influence on OH. Although there are still uncertainty for this conclusion resulting from the simplified reaction scheme for the chemical regime, we can find some evidences from the OH observations in China. As showed in the following figure, the functional dependence of OH_{Jnorm} on NO_x for the observed dataset shows a relatively flat curve, which cannot be predicted by models.



The solid lines give the averaged values of the measured (red) and modeled (blue) OH_{Jnorm} over equally spaced $\ln([NO_x]/ppb)$ intervals at the Pearl River Delta (PRD) (Lu et al., 2012) and in Beijing (Lu et al., 2013). For inspection of the OH dependence on NO_x , removing

the strong influence of $j(O^1D)$ by normalization as shown in: $[OH_{Jnorm}] = \frac{[OH]}{J(O^1D)} \overline{J(O^1D)}$

Focusing on the OH campaigns in China (Table S1), we can find the approximately equal slope of the OH– $J(O^1D)$ relation (i.e. the coefficient **a**), on various spatial (at the PRD and in Beijing) and temporal scales (in summer and winter in Beijing). This may be caused by two reasons: One is that the comprehensive impact of reactants (e.g. NO_x and VOCs) on OH cannot compete with that of UV light to OH. Another is that the chemical environments of OH are similar in polluted areas of China, and have no great difference in different seasons. The not significant diversity of the coefficient **a** has been proved partly from observations and models in Rohrer and Berresheim (2006). The OH radicals seem to be regulated in such a way that its relation to the driving force—solar radiation—is stabilized in a characteristic functional dependence.



Correlation of observed (obs) hydroxyl-radical concentrations with simultaneously observed ozone photolysis frequencies ($J(O^1D)$) for the campaigns at the Pearl River Delta (PRD) and in Beijing. The most striking feature is the equal slope of this relation ($4.0 \times 10^{11} \text{ cm}^{-3} \text{ s}$, uncertainty 20%) for both locations, which are 2,000 km apart (Rohrer et al., 2014).

Moreover, we estimate the uncertainty of OH radicals caused by Eq. (2) (Figure S1(a)) and the influence of the uncertainty of calculated OH on the strength of missing daytime source (P_{unknown}). In the case of low concentration of NO and high value of $J(O^1D)$, the error of P_{unknown} from OH radicals will be restrained significantly (Figure S1(d)).

In summary, the empirical model to calculate the concentrations of OH radicals can be reasonable to a certain extent and the error of derived OH radicals has been assessed as not subverting the relative conclusions in this study (Fig. S1(a) and Fig. S1(d)).

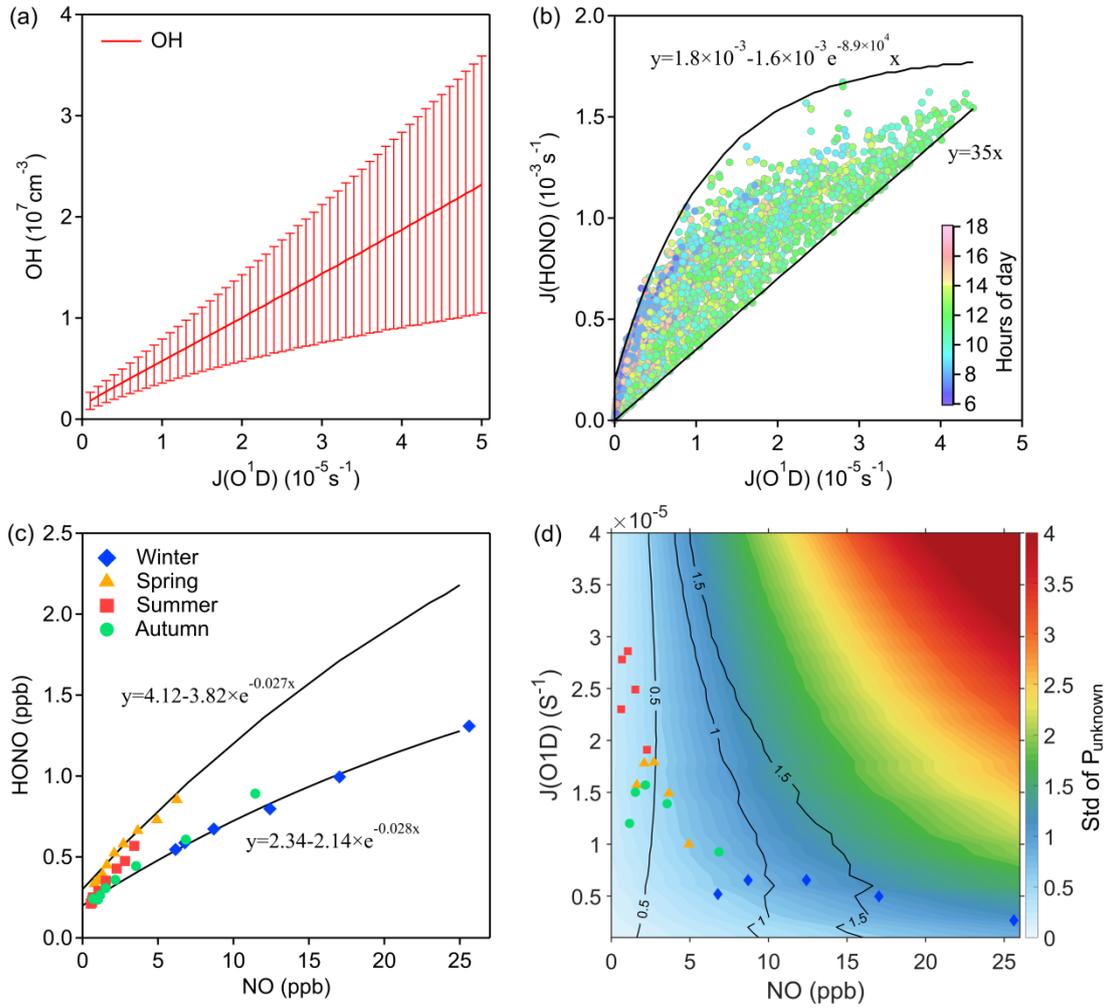


Fig. S1. (a) The average concentration and standard deviation of OH radicals derived from Eq. (2) by changing the values of the coefficients **a**, **b**, **c**; (b) the relationship of the calculated $J(\text{HONO})$ and $J(\text{O}^1\text{D})$; (c) the relationship of observed HONO and NO based on diurnal variations (10:00-14:00 LT); (d) the standard deviation of the strength of missing daytime source (Std of P_{unknown}) under various values of $J(\text{O}^1\text{D})$ and NO, and the solid isolines show the ratio of standard deviation to mean value of P_{unknown} . The colored and shaped markers in (c) and (d) represent the situations in different seasons.

2. Response to why the second term ($-k_{\text{NO}+\text{OH}}[\text{NO}][\text{OH}]$) should be included on the right side of Eq. 3

During the daytime, the photolysis of HONO is a reversible reaction, and HONO can be recycled by the homogeneous gas phase reaction of NO with OH. For a given concentration of HONO, when only considering the forward and backward reaction, not all HONO contributes to OH radicals eventually. So we calculate the net OH production rate of HONO by Eq. 3.



3. Response to the meaning of $P_{unknown}$ in Eq. (10)

Eq. (10) is a deformation of Eq. (9) without minor terms (T_v and T_h):

$$\frac{dHONO}{dt} = (P_{NO+OH} + P_{emis} + P_{unknown}) - (L_{phot} + L_{HONO+OH} + L_{dep}) + T_v + T_h$$

$$P_{NO+OH} = k_{NO+OH} [NO][OH]$$

$$P_{emis} = \frac{0.79\% \times \Delta NO_x}{\Delta t}$$

$$P_{NO+OH} = k_{NO+OH} [NO][OH]$$

$$L_{phot} = J(HONO)[HONO]$$

$$L_{HONO+OH} = k_{HONO+OH} [HONO][OH]$$

$$L_{dep} = \frac{v_{HONO}}{H} [HONO]$$

So we can get the strength of missing source of HONO at daytime:

$$P_{unknown} = J(HONO)[HONO] + k_{HONO+OH} [HONO][OH] + \frac{v_{HONO}}{H} [HONO] + \frac{\Delta HONO}{\Delta t} - k_{NO+OH} [NO][OH] - \frac{0.79\% \times \Delta NO_x}{\Delta t}$$

Sincerely,
Wei Nie

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