Supplement of Comment on “Transport of substantial stratospheric ozone to the surface by a dying typhoon and shallow convection” by Chen et al. (2022)

Xiangdong Zheng¹, Wen Yang², Yuting Sun¹,³, Chunmei Geng², Yingying Liu², Xiaobin Xu¹

¹Key Laboratory for Atmospheric Chemistry of CMA & Institute of the Tibet Plateau, Chinese Academy of Meteorological Sciences, Beijing 100081, China

²State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

³Nanjing University of Information Science & Technology, Nanjing, Jiangsu, 210044, China

Correspondence to: Xiaobin Xu (xiaobin_xu@189.cn)

Figure S1: Map modified from Figure 1 in Chen et al. (2022) showing the NCP and its topography with locations of related cities Hengshui (HS), Jinan (JN), Binzhou (BZ), Weifang (WF), Qingdao (QD), Weihai (WH), and Zibo (ZB, red star, newly added in this study). ZB roughly occupies the area of 36.5°-36.8°N and 117.9°-118.0°E. Other details see Chen et al. (2022).
Text S1. Estimating photochemical ages of air masses arrived at the Zibo supersite

Once emitted into the atmosphere, all hydrocarbons experience decay caused mainly by the oxidation of OH radical and atmospheric mixing (McKeen et a., 1990; Parrish et al., 1992). The relative compositions of hydrocarbons were used to study the histories of air masses over rural areas (Roberts et al., 1984) and remote marine areas (Rudolph et al., 1990). The so-called photochemical ages of air masses can be derived from observed ratios of hydrocarbons and OH mixing ratios either measured or estimated. However, the calculated photochemical ages may be significantly impacted by atmospheric mixing on the ratios during transport (McKeen and Liu, 1993). Nevertheless, the estimation of photochemical age based on hydrocarbon ratios in air masses has been a current practice in atmospheric researches (e.g., Kleinman et al., 2003; Irei et al., 2016). Here, we follow the practice to estimate photochemical ages of air masses arrived at the Zibo (ZB) supersite during the NOE reported in Chen et al. (2022) and a few days before and after.

Hourly measurements of hydrocarbons at the supersite between 25 July and 5 August 2021 were used to calculated hydrocarbon ratios. Good correlations were found among some of the hydrocarbon ratios. Among the alkanes ratios, the best correlation existed between Ln(Butane/Ethane) and Ln(Propane/Ethane), with $R^2=0.63$ (Figure S2). Among the aromatics ratios, the best correlation existed between Ln(o-Xylene/Benzene) and Ln(Ethylbenzene/Benzene), with $R^2=0.89$ (Figure S3). In addition, there were also excellent correlations between Ln[Butane] and Ln[Propane] ($R^2=0.78$, Figure S4) and between Ln[o-Xylene] and Ln[Ethylbenzene] ($R^2=0.85$, Figure S5). These results indicate that ethane, propane and n-butane observed the supersite were very likely from the same sources and so were benzene, ethylbenzene and o-Xylene. Therefore, it is proper to estimate photochemical ages using the ratios between these alkanes and aromatics. We derived photochemical ages from the ratios [Butane]/[Propane] and [o-Xylene]/[Ethylbenzene].

Figure S2: Correlation between Ln(Butane/Ethane) and Ln(Propane/Ethane).
Figure S3: Correlation between \( \text{Ln(o-Xylene/Benzene)} \) and \( \text{Ln(Ethylbenzene/Benzene)} \).

\[
Y = 0.325 + 0.998X \\
R^2 = 0.89
\]

Figure S4: Correlation between \( \text{Ln(Butane)} \) and \( \text{Ln(Propane)} \).

\[
Y = -0.73 + 1.184X \\
R^2 = 0.78
\]

Figure S4: Correlation between butane and propane concentrations.
Figure S5: Correlation between o-xylene and ethylbenzene concentrations.

Since the concentration of hydrocarbon X is enhanced by emissions and lowered by reaction with OH and mixing with background air, the change of the X concentration with time can be generally expressed as:

\[ \frac{d[X]}{dt} = S_x - k_x[OH][X], \]  
\[(S1)\]

where, \([X]\) is the concentration of X; \(S_x\) represents collective impact on \([X]\) of physical processes such as emissions, dilution, etc.; \([OH]\) indicates the OH concentration averaged over the transport way; \(k_x\) is the rate constant for the X+OH reaction.

Similar expression can be given for hydrocarbon Y:

\[ \frac{d[Y]}{dt} = S_y - k_y[OH][Y]. \]  
\[(S2)\]

In Eq. S1 and Eq. S2, \(S_x\) and \(S_y\) are unknown and difficult to obtain. However, their impacts on hydrocarbon concentrations are assumed to be low if the hydrocarbons are relatively reactive. After ignoring \(S_x\) and \(S_y\) in Eq. S1 and Eq. S2, the following equations can be obtained by integration from time 0 to t:

\[ \ln [X] = \ln[X_0] - k_x[OH]t \]  
\[ \text{and} \]
\[ \ln [Y] = \ln[Y_0] - k_y[OH]t, \]  
\[(S3)\]

\[(S4)\]

with \(X_0\) and \(Y_0\) being the respective concentrations of X and Y initial after emissions.

Finally, a formula for calculating photochemical ages can be derived from Eq.S3 and Eq. S4:

\[ t = \frac{1}{(k_y - k_x)[OH]} \cdot (\ln \frac{[Y_0]}{[X_0]} - \ln \frac{[Y]}{[X]}). \]  
\[(S5)\]
Rate constants \((k_x\) and \(k_y\)) are available in literature. Table S1 lists the rate constants at 298K for the reactions of OH with n-butane, propane, ethylbenzene and o-xylene. These rate constants were used in the estimation of photochemical ages without considering the influences of atmospheric conditions.

Table S1: Rate constants of the reactions of the OH radical with some hydrocarbons at 298K

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant, (\text{cm}^3/\text{mol/s})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butane + OH</td>
<td>(1.45\times10^{12})</td>
<td>Talukdar et al. (1994)</td>
</tr>
<tr>
<td>Propane + OH</td>
<td>(6.58\times10^{11})</td>
<td>DeMore et al. (1997)</td>
</tr>
<tr>
<td>ethylbenzene + OH</td>
<td>(4.52\times10^{12})</td>
<td>Atkinson (1986)</td>
</tr>
<tr>
<td>o-xylene + OH</td>
<td>(8.85\times10^{12})</td>
<td>Atkinson (1986)</td>
</tr>
</tbody>
</table>

There was no observation of OH radical over ZB and surroundings. An assumption had to be made for the value of [OH] in Eq. S5. A recent study shows that the diel-average tropospheric column mean OH concentrations over the Yellow Sea and East China Sea areas were in the range of \((1.5-3)\times10^6\) molecules/cm\(^3\) during July-August 2016 (Thompson et al., 2022). In-situ observations of vertical profiles of OH showed that the OH mixing ratio for 29 April 1994 varied roughly in the range of 0.2-0.4 pptv (about \((5-10)\times10^6\) molecules/cm\(^3\)) at the altitudes from 1 km to 12 km over Oklahoma, USA, with no consistent gradients (Brune et al., 1998). Ground measurements in summer of 2014 at Wangdu, a rural site in the North China Plain, showed median values of OH varying from \(5\times10^5\) molecules/cm\(^3\) at night to \(6.8\times10^6\) molecules/cm\(^3\) during 12:00-16:00 LT (Tan et al., 2017). Earlier observations made in August 2006 at Yufa, a suburban site in Beijing, showed the OH level varying from \(6\times10^5\) molecules/cm\(^3\) (detection limit) at night to \((4-17)\times10^6\) molecules/cm\(^3\) around noontime (Lu et al., 2013). Given these data of OH values, we assumed the average value of OH over ZB and surroundings for the period in consideration (i.e., 25 July - 5 August 2021) to be \(5\times10^6\) molecules/cm\(^3\).

To obtain a better estimate of the range of photochemical ages, we calculated photochemical ages using both \([\text{Butane}] / [\text{Propane}]\) and \([\text{o-Xylene}] / [\text{Ethylbenzene}]\). The initial values of \([\text{Butane}] / [\text{Propane}]\) and \([\text{o-Xylene}] / [\text{Ethylbenzene}]\) were not available. Therefore, we substituted the maximum \([\text{Butane}] / [\text{Propane}]\) \((2.25)\) and \([\text{o-Xylene}] / [\text{Ethylbenzene}]\) \((2.31)\) for the initial values of \([\text{Butane}] / [\text{Propane}]\) and \([\text{o-Xylene}] / [\text{Ethylbenzene}]\), respectively. These maximum ratios should be lower than the initial ones because they represented ratios certain time after the hydrocarbons were emitted. This may more or less underestimate photochemical ages but does not change our conclusion.

The photochemical ages of air masses arrived at the ZB supersite during 25 July – 5 August 2021 were calculated using Eq. S5, and based on \([\text{Butane}] / [\text{Propane}]\) and \([\text{o-Xylene}] / [\text{Ethylbenzene}]\), respectively. The two sets of estimated photochemical ages are shown in Figure 3, together with the observed \(O_3\) data.


