Ozone formation under low solar radiation in eastern China

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Abstract

PM$_{2.5}$, a particulate matter with a diameter of 2.5 micrometers or less, is one of the major components of the air pollution in eastern China. In the past few years, China's government made strong efforts to reduce the PM$_{2.5}$ pollutants. However, another important pollutant (ozone) becomes an important problem in eastern China. Ozone ($\text{O}_3$) is produced by photochemistry, which requires solar radiation for the formation of $\text{O}_3$. Under heavy PM$_{2.5}$ pollution, the solar radiation is often depressed, and the photochemical production of $\text{O}_3$ is prohibited. This study shows that during fall in eastern China, under heavy PM$_{2.5}$ pollutions, there were often strong $\text{O}_3$ photochemical productions, causing a co-occurrence of high PM$_{2.5}$ and $\text{O}_3$ concentrations. This co-occurrence of high PM$_{2.5}$ and $\text{O}_3$ is un-usual and is the main focus of this study. Recent measurements show that there were often high HONO surface concentrations in major Chinese mega cities, especially during daytime, with maximum concentrations ranging from 0.5 to 2 ppbv. It is also interesting to note that the high HONO concentrations were occurred during high aerosol concentration periods, suggesting that there were additional HONO surface sources in eastern China. Under the high daytime HONO concentrations, HONO can be photo-dissociated to be OH radicals, which enhance the photochemical production of $\text{O}_3$. In order to study the above scientific issues, a radiative transfer model (TUV; Tropospheric Ultraviolet-Visible) is used in this study, and a chemical steady state model is established to calculate OH radical concentrations. The calculations show that by including the OH production of the photo-dissociated of HONO, the calculated OH concentrations are significantly higher than the values without including this production. For example, by including HONO production, the maximum of OH concentration under the high aerosol condition ($\text{AOD}=2.5$) is similar to the value under low aerosol condition ($\text{AOD}=0.25$) in the no-HONO case. This result suggests that even under the high aerosol condition, the chemical oxidizing process for $\text{O}_3$ production can occurred, which explain the co-occurrence of high PM$_{2.5}$ and high $\text{O}_3$ in fall season in eastern China. However, the $\text{O}_3$ concentrations were not significantly
affected by the appearance of HONO in winter. This study shows that the seasonal variation of solar radiation plays important roles for controlling the OH production in winter. When the solar radiation is in a very low level in winter, it reaches the threshold level to prevent the OH chemical production, even by including the HONO production of OH. This study provides some important scientific highlights to better understand the O3 pollutions in eastern China.

Keywords; High PM$_{2.5}$ and O$_3$, eastern China, HONO photolysis
1. Introduction

Currently, China is undergoing a rapid economic development, resulting in a higher demand for energy and greater use of fossil fuels. As a result, the high emissions of pollutants produce heavy pollutions in mega cities of eastern China, such as Beijing and Shanghai. For example, in the city of Shanghai (a largest mega city in China), the urban and economical developments of the city are very rapid. During 1990 to 2015, the population increased from 13.3 to 24.1 million. The number of automobiles increased from 0.2 million (1993) to 2.0 million (2011). The rapid growing population and energy usage caused a rapid increase in the emissions of pollutants, leading to severe air pollution problems in these mega cities (Zhang et al., 2006; Geng et al., 2007; Deng et al., 2008).

Measurements, such as satellite observations have revealed much higher aerosol pollution in eastern China than in eastern US (Tie et al., 2006). The high aerosol pollution causes a wide range of environmental consequences. According to a study by Tie et al. (2009a), exposure to extremely high particle concentrations leads to a great increase of lung cancer cases. High PM (particular matter) concentrations also significantly reduce the range of visibility in China’s mega cities (Deng et al., 2008). According to a recent study, the high aerosol pollution causes important effects on the crop (rice and wheat) production in eastern China (Tie et al., 2016).

In the troposphere, ozone formation is resulted from a complicated chemical process, and requires ozone precursors, such as VOCs (volatile organic carbons) and NOX = NO + NO2 (nitrogen oxides) (Sillman, 1995). As the increase in industrial activity and number of automobiles, the precursors of ozone (O3) and the global budget of oxidation are also significantly increased (Huang et al., 2017; Huang et al., 2018). As a result, O3 pollutions are becomes a serous pollution problem in Shanghai and other Chinese mega cities (Geng et al., 2010; Tie 2009b; Tie et al., 2015). The effects on O3 production rate can be characterized as either NOX-sensitive or VOC-sensitive conditions (Sillman, 1995; Zhang et al., 2003; Lei et al., 2004; Tie et al., 2013). Thus, better understanding the trends of O3 precursors (VOCs, NOX) is important to...
determine the O$_3$ trends in Shanghai (as well as many large cities in China). In the past few years, China's government made strong efforts to reduce the PM$_{2.5}$ pollutions. However, another important pollutant (O$_3$) becomes an important problem in eastern China. Several studies regarding the O$_3$ formation are previously studied in Shanghai. For example, Geng et al. (2007; 2008) study the relationship between O$_3$ precursors (NOx and VOCs) for the ozone formation in Shanghai. Tie et al. (2009) study the short-term variability of O$_3$ in Shanghai. Their study suggested that in addition to the ozone precursors, meteorological conditions, such as regional transport, have also strong impacts on the ozone concentrations. During September 2009, a major field experiment (the MIRAGE-Shanghai) was conducted in Shanghai, and multiply chemical species were measured during the experiment. The summary of the measurements by Tie et al (2013) suggests that the ozone formation in Shanghai is under VOC-sensitive condition. However, if the emission ration of NOx/VOCs reduces to a lower value (0.1-0.2), the ozone formation in Shanghai will switch from VOC-sensitive condition to NOx-sensitive condition.

Despite of some progresses have been made for the ozone formation in mega cities in China, it is still lack of study of ozone development in large cities of China. For example, this study shows that during fall in eastern China, under heavy PM$_{2.5}$ pollutions, there were often strong O$_3$ chemical productions, causing the co-occurrence of high PM$_{2.5}$ and O$_3$ concentrations. Under heavy aerosol condition, the solar radiation is depressed, significantly reducing the photochemical production of O$_3$. This co-occurrence of high PM$_{2.5}$ and O$_3$ is an unusual and is the focus of this study. Recent measurements show that there were often high HONO concentrations in major Chinese mega cities, especially during daytime, with maximum concentrations ranging from 0.5 to 2 ppbv (Huang et al., 2017). It is also interesting to note that the high HONO surface concentrations were occurred during high aerosol concentration periods, suggesting that there are additional HONO surface sources in eastern China. Under the high daytime HONO concentrations, HONO can be photo-dissociated to be OH radicals, which enhance the photochemical production of O$_3$. 
The paper is organized as follows: in Section 2, we describe the measurement of O$_3$ and PM$_{2.5}$. In Section 3, we describe the calculation of photo-dissociated rate of HONO and a steady state model for the calculation of OH, and the causes of high O$_3$ production under the heavy aerosol condition. Section 4 shows a brief conclusion of the results.

2. Measurements of O$_3$ and PM$_{2.5}$

There are long-term measurements in Eastern China by Chinese Environment Protection Agency (CEPA) for monitoring the air quality in China. In eastern China, especially in the capital city of China (Beijing), there are often heavy air pollutions, especially for fine particular matter (PM$_{2.5}$ – the radium of particle being less than 2.5 um). Figure 1 shows the measurement sites in Beijing, in which the measured concentrations of PM$_{2.5}$ and O$_3$ are used to the analysis. In the region, the air pollutions were very heavy, especially in winter (Long et al., 2016; Tie et al., 2017). The previous studies suggested that the both aerosol and O$_3$ pollutions became the major pollutants in the region (Li et al., 2017).

Figure 2 shows the daily averaged concentrations of PM$_{2.5}$ and O$_3$ in the Beijing region in 2015. The daily averaged concentrations show that there were strong daily and seasonal variations for both the concentrations of PM$_{2.5}$ and O$_3$. Despite the daily variation, the concentrations of PM$_{2.5}$ existed a strong seasonal variation. For example, there were very high concentrations during winter, with maximum of ~300 $\mu$g/m$^3$. While in summer, the maximum concentrations reduced to ~150 $\mu$g/m$^3$. The seasonal variability of O$_3$ concentrations were opposite with the PM$_{2.5}$ concentrations, with lower concentrations in winter (< 50 $\mu$g /m$^3$) and higher concentrations in summer (> 150 $\mu$g/m$^3$). These seasonal variations of PM$_{2.5}$ and O$_3$ have been studied by previous studies (Tie and Cao, 2017; Li et al., 2017). Their results suggest that the winter high
PM$_{2.5}$ concentrations were resulted from the combination of both the high emissions (heating season in the Beijing region), and poor meteorological ventilation conditions, such as lower PBL (Planetary Boundary Layer) height (Quan et al., 2013; Tie et al. 2015). According to the photochemical theory of O$_3$ formation, the summer high and winter low O$_3$ concentrations are mainly due to seasonal variation of the solar radiation (Seinfeld, J. H. and Pandis, 2006).

In addition to the seasonal variation of solar radiation, the heavy aerosol concentrations play important roles to reduce solar radiation, causing the reduction of solar radiation and O$_3$ formation (Bian et al., 2007). As we show in Fig. 3a, during wintertime, the O$_3$ concentrations were strong anti-correlated with the PM$_{2.5}$ concentrations, suggesting that the reduction of solar radiation by aerosol particles have important impact on the reduction of O$_3$ concentrations. Figure 3a also shows that the relationship between O$_3$ and PM$_{2.5}$ was not linearly related. For example, when the concentrations of PM$_{2.5}$ were less than 100 µg/m$^3$, O$_3$ concentrations rapidly decreased with the increase of PM$_{2.5}$ concentrations. In contrast, when the concentrations of PM$_{2.5}$ were greater than 100 µg/m$^3$, O$_3$ concentrations slowly decreased with the increase of PM$_{2.5}$ concentrations. This is consistent with the result of Bian et al (2007).

It is interesting to note that during late spring, summer, and early fall periods, the correlation between PM$_{2.5}$ and O$_3$ concentrations was positive relationship compared to the negative relationship in winter (see Fig. 3b). This result suggests that O$_3$ production was high during the heavy haze period, despite the solar radiation was greatly depressed. In order to clearly display this unusual event, we illustrate diurnal variations of PM$_{2.5}$ and O$_3$ and NO$_2$ during a fall period (from Oct.5 to Oc. 6, 2015). Figure 4 shows that during this period, the PM$_{2.5}$ concentrations were very high, ranging from 150 to 320 µg/m$^3$. Under such high aerosol condition, the solar radiation should be significantly reduced, and O$_3$ photochemical production would be reduced. However, the diurnal variation of O$_3$ was unexpectedly strong, with high noontime
concentration of >220 µg/m³ and very low nighttime concentration of ~25 µg/m³. This strong diurnal variation was due to the photochemical activity, which suggested that during relatively low solar conditions, the photochemical activities of O₃ production was high. According to the theory of the O₃ chemical production, the high O₃ production is related to high oxidant of OH (Seinfeld and Pandis, 2006), which should not be occurred during lower solar radiation. This result brings important issue for air pollution control strategy, because the both air pollutants (high PM₂.₅ and O₃) were important air pollution problems in eastern China.

2. Method

In order to better understand the O₃ chemical production occurred in heavy aerosol condition in eastern China, the possible O₃ production in such condition is discussed. Ozone photochemical production (P[O₃]) is strongly related to the amount of OH radicals (OH) (Chameides et al., 1999). According to the traditional theory, the amount of surface OH radicals is proportional to the surface of solar radiation, which is represented by

\[
[\text{OH}] = \frac{P[\text{HOx}]}{L[\text{HOx}]*} \quad \text{(R-1)}
\]

Where [OH] represents the concentration of hydroxyl radicals (#/cm³); HOx represents the concentration of HO₂ + OH (#/cm³); P[HOx] represents the photochemical production of HOx (#/cm³/s); and L[HOx]* (1/s) represents the photochemical destruction of HOx, which is normalized by the concentrations of OH.

The major process for the photochemical production of P[HOx] is through the O₃ photolysis and follows by the reaction with atmospheric water vapor. It can express by

\[
P[\text{HOx}] = J_1[O_3]/(k_1 \times \text{am}) \times 2.0 \times k_2[H_2O] = P_1[\text{HOx}] \quad \text{(R-2)}
\]
Where $J_1$ represents the photolysis of $O_3 + hv \rightarrow O_1^D$; $k_1$ represents the reaction rate of $O_1^D + am \rightarrow O_3^P$; and $k_2$ represents the reaction rate of $O_1^D + H_2O \rightarrow 2OH$. As we can see, this HOx production is proportional to the magnitude of solar radiation ($J_1$), and $J_1$ is the $O_3$ photolysis with the solar radiation. Figure 5 shows the relationship between the values of $J_1$ and aerosol concentrations in October at middle-latitude calculated by the TUV model Madronich and Flocke (1999). This result suggests that under the high aerosol concentrations (AOD = 2.5), the $J_1$ value is strongly depressed, resulting in significant reduction of OH concentrations and $O_3$ production. For example, the maximum $J_1$ value is about $2.7 \times 10^{-5}$ (1/s) with lower aerosol values (AOD = 0.25). According to the previous study, the surface PM$_{2.5}$ concentrations were generally smaller than 50 µg/m$^3$ with this AOD value (Tie et al., 2017). However, when the AOD value increase to 2.5 (the PM$_{2.5}$ concentrations are generally >100 µg/m$^3$), the maximum $J_1$ value rapidly decreases to about $6 \times 10^{-6}$ (1/s), which is about 450% reduction compared to the value with AOD=0.25. This study suggests that under high PM$_{2.5}$ concentrations (>100 µg/m$^3$), the photochemical production of OH ($P[HOx]$) is rapidly decreased, leading to low OH concentrations, which cannot initiate the high oxidation of $O_3$ production. As a result, the high $O_3$ production shown in Fig. 4 cannot be explained. Other sources for $O_3$ oxidation are needed to explain this result.

Recent studies show that the HONO concentrations are high in eastern China (Huang et al., 2017). Because under high solar radiation, the photolysis rate of HONO is very high, resulting in very low HONO concentrations in daytime (Seinfeld and Pandis, 2006). These measured high HONO concentrations are explained by their studies. One of the explanations is that there are high surface HONO sources during daytime, which produces high HONO concentrations (Huang et al., 2017).

Figure 6 shows the measured HONO concentrations in two large cities in China (Shanghai and Xi’an) during fall time. It shows that the measured HONO concentrations were high, with a maximum concentration of 2.3 ppbv during morning,
and about 0.5-1.0 ppbv in daytime. It is also interesting to note that the high HONO concentrations were occurred during high aerosol concentration periods. Figure 7 illustrates that when the PM$_{2.5}$ concentrations increased to 70-80 µg/m$^3$, and the HONO concentrations enhanced to 1.4-18 ppbv during September in Shanghai. This measured high HONO concentrations were significantly higher than the calculated concentrations (shown in Fig. 6), suggesting that some additional sources of HONO are needed. This result is consistent with the HONO measurements in other Chinese cities (Huang et al. 2017).

Under the high HONO concentrations in daytime, HONO can be photolyzed to be OH, and become another important process to produce OH. As a result, the OH production rate ($P[\text{HOx}]$) can be written to the following reactions.

$$P_2[\text{HOx}] = J_2 \times [\text{HONO}] \quad \text{(R-3)}$$

$$P[\text{HOx}] = P_1[\text{HOx}] + P_2[\text{HOx}]$$

$$= J_1[O_3]/(k_1 \times \text{am}) \times 2.0 \times k_2[H_2O] + J_2 \times [\text{HONO}] \quad \text{(R-4)}$$

Because the chemical lifetime of OH is less than second, OH concentrations can be calculated according to equilibrium of chemical production and chemical loss. With the both OH chemical production processes, the OH concentrations can be calculated by the following equation (Seinfeld and Pandis, 2006).

$$P_1 + P_2 = L_1 + L_2$$

Where $P_1$ and $P_2$ are the major chemical productions, expressed in R-4, and $L_1$ and $L_2$ are the major chemical loss of OH, and represent by

$$L_1: \quad \text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3 \quad \text{(R-5)}$$

$$L_2: \quad \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad \text{(R-6)}$$
Under high NOx condition, such as in the Shanghai region, NOx concentrations were often higher to 50 ppbv (shown in Fig. 3), the L1 term is larger than L2. The OH concentrations can be approximately expressed by

\[
[\text{HO}] = \frac{\{J_1[O_3]/(k_1 \times \text{am})\} \times 2.0 \times k_3[H_2O] + J_2 \times [\text{HONO}]\}}{k_3[\text{NO}_2]} \quad (R-5)
\]

Where \(k_3\) is the reaction coefficient of \(\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3\).

3. Result and analysis

3.1. OH productions in different HONO conditions

In order to quantify the individual effects of these two OH production terms (P1 and P2) on the OH concentrations, the P1 and P2 are calculated under different daytime HONO conditions (calculated low HONO and measured high HONO concentrations). Figure 8 shows that under the low HONO condition, the P1 is significantly higher than P2, and P2 has only minor contribution to the OH values. For example, the maximum of P1 occurred at 13 pm, with a value of \(65 \times 10^6 \text{ #/cm}^3/\text{s}\). In contrast, the maximum of P1 occurred at 10 am, with a value of \(15 \times 10^9 \text{ 15 #/cm}^3/\text{s}\). However, under high HONO condition, the P2 plays very important roles for the OH production. The maximum of P1 occurred at 11 am, with a value of \(350 \times 10^6 \text{ #/cm}^3/\text{s}\), which is about 500% higher than the P1 value. It is important to note that this calculation is based on the high aerosol condition (AOD = 2.5) in September. This result can explain the high O₃ chemical production in Fig. 4.

3.2. OH in different aerosol conditions

In order to understand the effect of aerosol conditions, especially high aerosol conditions, on the OH concentrations. Figure 9 shows the OH concentrations with and without HONO production of OH. With including the HONO production (i.e.,
including P1 and P2), the calculated OH concentrations are significantly higher than without including this production (i.e., only including P1). The both calculated OH concentrations are rapidly changed with different levels of aerosol conditions. For example, without HONO production, the maximum OH concentration is about $7.5 \times 10^5$#/cm$^3$ under low aerosol condition (AOD=0.25). In contrast, the maximum OH concentration rapidly reduced to $1.5 \times 10^5$#/cm$^3$ under high aerosol condition (AOD=2.5), and further decreased to $1.0 \times 10^5$#/cm$^3$ with the AOD value of 3.5. In contrast, with including HONO production, the OH concentrations significantly increased. Under higher aerosol condition (AOD=2.5), the maximum of OH concentration is about $7.5 \times 10^5$#/cm$^3$, which is the same value under low aerosol condition in the no-HONO case. This result suggests that the measured high O$_3$ production occurred in the high aerosol condition is likely due to the high HONO concentrations in Shanghai.

### 3.3. OH in winter

The measurement of O$_3$ also shows that the concentrations in winter were always low (see Fig. 2), suggesting that the O$_3$ concentrations were not significantly affected by the appearance of HONO. Figure 10 shows the OH concentrations in September and December. It shows that under different aerosol conditions, OH concentrations in December were very low compared with the values in September. Both the calculated OH concentrations include the HONO production term. For example, under the condition of AOD=2.5, the maximum OH is about $7.5 \times 10^5$#/cm$^3$ in September, while it rapidly reduces to $1.5 \times 10^5$#/cm$^3$ in December. Under the condition of AOD=3.5, the maximum OH is still maintaining to a relative high level ($4.5 \times 10^5$#/cm$^3$) in September. However, the maximum OH values are extremely low in December, with maximum value of $0.5 \times 10^5$#/cm$^3$ in December. Because both the OH chemical productions (P1 and P2) are strongly dependent upon solar radiation (see equation R-4), the seasonal variation of solar radiation plays important roles for controlling the OH production in winter. When the solar radiation is in a very low level in winter, it
reaches a threshold level to prevent the OH chemical production, even by including the HONO production term.

**Summary**

Currently, China is undergoing a rapid economic development, resulting in a high demand for energy, greater use of fossil fuels. As a result, the high emissions of pollutants produce heavy aerosol pollutions (PM$_{2.5}$) in eastern China, such as in the mega city of Beijing. The long-term measurements show that in addition to the heavy aerosol pollution, the O$_3$ pollution becomes another major pollutants in the Beijing region. The measured results show that there were very strong seasonal variation in the concentrations of both PM$_{2.5}$ and O$_3$ in the region. During winter, the seasonal variability of O$_3$ concentrations were anti-correlated with the PM$_{2.5}$ concentrations. However, during late spring and fall periods, the correlation between PM$_{2.5}$ and O$_3$ concentrations was positive compared to the negative in winter. This result suggests that during heavy aerosol condition (the solar radiation was depressed), the O$_3$ chemical production was still high, appearing a double peak of PM$_{2.5}$ and O$_3$ during fall period. This co-occurrence of high PM$_{2.5}$ and O$_3$ is the focus of this study. The results are highlighted as follows;

1. There are high daytime HONO concentrations in major Chinese mega cities, such as in Beijing and Shanghai. It is also interesting to note that the high HONO concentrations were occurred during high aerosol concentration periods. Under the high daytime HONO concentrations, HONO can be photo-dissociated to be OH radicals, and becomes an important process to produce OH.

2. With including the OH production of measured HONO concentrations, the calculated OH concentrations are significantly higher than without including this production. For example, without HONO production, the maximum OH concentration is about $7.5 \times 10^5$ #/cm$^3$ under low aerosol condition (AOD=0.25),
and rapidly reduced to 1.5×10^5 #/cm^3 under high aerosol condition (AOD=2.5) in September. In contrast, by including HONO production, the OH concentrations significantly increased. For example, under higher aerosol condition (AOD=2.5), the maximum of OH concentration is about 7.5×10^5 #/cm^3, which is similar to the value under low aerosol condition in the no-HONO case. This result suggests that even under the high aerosol conditions, the chemical oxidizing process for O_3 production can be active. This result is likely for explaining the co-occurrence of high PM_{2.5} and high O_3 in fall season in eastern China.

(3) The measurement of O_3 also shows that the concentrations in winter were always low, suggesting that the O_3 concentrations were not significantly affected by the appearance of HONO. The calculated result shows that the seasonal variation of solar radiation plays important roles for controlling the OH production in winter. When the solar radiation is a very low level in winter, it reaches a threshold level to prevent the OH chemical production, even by including the HONO production term.

Because in recent years, the PM_{2.5} pollutions are reduced due to the large control efforts by the Chinese government, the O_3 pollutions become another severe pollution problem in eastern China. This study is important, because it provides some important scientific highlights to better understand the O_3 pollutions in eastern China.

Author contributions. XT came up with the original idea of investigating the scientific issue. XT and JX designed the analysis method. XL, GL and SZ provided the observational data and helped in discussion. XT prepared the manuscript with contributions from all co-authors.

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**Figure Caption**

**Fig. 1.** The geographic locations of the measurement sites in Beijing, in which the measured concentrations of PM$_{2.5}$ and O$_3$ are used to the analysis.

**Fig. 2.** The daily averaged concentrations of PM$_{2.5}$ and O$_3$ in the Beijing region in 2015. The concentrations are averaged over all sites shown in Fig. 1. The blue lines represent the PM$_{2.5}$ concentrations (µg/m$^3$), and the red bars represent the O$_3$ concentrations (µg/m$^3$). The rectangles show some typical events during winter (green), spring and fall (orange), and summer (red).

**Fig. 3.** The correlation between O$_3$ and PM$_{2.5}$ concentrations during winter (upper panel) and during late spring and fall (lower panel). During winter, O$_3$ concentrations were strong anti-correlated with the PM$_{2.5}$ concentrations. During late spring and fall, O$_3$ concentrations were correlated with the PM$_{2.5}$ concentrations.

**Fig. 4.** The diurnal variations of PM$_{2.5}$ (blue line) and O$_3$ (red line), and NO$_2$ (green line) during a fall period (from Oct.5 to Oc. 6, 2015). It shows that with high PM$_{2.5}$ condition, there was a strong O3 diurnal variation.

**Fig. 5.** The effect of aerosol levels with AOD = 0.25 (black line), AOD = 2.5 (red line), AOD = 3.5 (blue line), and AOD = 4.0 (green line) on the O$_3$ photolysis calculated by the TUV model in October at middle-latitude.

**Fig. 6.** The measured HONO concentrations (ppbv) in two large cities in China. The red line was measured in Xi’An from 24 July to August 6, 2015. The blue line was measure in Shanghai from 9 to 18 September, 2009. The green line is calculated by the WRF-Chem model. The measurement in fall of Shanghai is applied to the calculation for the OH production of HONO.

**Fig. 7.** The measured HONO (upper panel) and PM$_{2.5}$ concentrations (lower panel) in fall in Shanghai. It illustrates that the high HONO concentrations were corresponded with high PM$_{2.5}$ concentrations.

**Fig. 8.** The calculated OH production P(HOx) (#/cm$^3$/s) by using the model calculated HONO (low concentrations) (in the upper panel) and by using the measured HONO (high concentrations) (in the lower panel). The red bars represent the calculation of the P1 term, and the red bars represent the calculation of the P2 term (OH production from HONO).

**Fig. 9.** The calculated OH concentrations (#/cm$^3$) with (upper panel) and without (lower panel) HONO production of OH, under different aerosol levels. Dark red (AOD=0.25), red (AOD=2.5), red (AOD=3.5), and red (AOD=4.0).
Fig. 10. The calculated OH concentrations in September (blue bars) and December (dark red bars), under different aerosol levels.
Figures

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Fig. 9. The calculated OH concentrations (#/cm$^3$) with (upper panel) and without (lower panel) HONO production of OH, under different aerosol levels. Dark red (AOD=0.25), red (AOD=0.5), black (AOD=1.0), blue (AOD=2.5), green (AOD=3.5), and brown (AOD=4.0).
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