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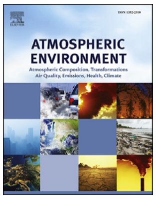

Study on the daytime OH radical and implication for its relationship with fine particles over megacity of Shanghai, China

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HIGHLIGHTS

- Main OH precursors of O3, HCHO, HONO and other trace gases were measured by LP-DOAS.
- OH concentration was estimated approximately by a simple steady-state model.
- HONO photolysis contributes more than half of the daytime OH production.
- Heavy fine particle loads can decrease the OH production and concentration.
- OH levels significantly impact the secondary organic part of the fine particles.

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ABSTRACT

To investigate on the daytime OH and its implication to fine particle, the long-path differential optical absorption spectroscopy (LP-DOAS) system was employed to observe the main OH precursors of O_3, HCHO and HONO, as well as NO_2 and NO_3 radical from April to August 2013 over Shanghai, China. The main OH production paths from HONO, HCHO and O_3 were estimated to be occupied around 57.6%, 30.5% and 11.9% during daytime. The daytime OH radical concentration under steady-state was averaged at 1.02×10^7 molec cm^{-3}, which was significantly impacted by the photolytic processes. The relationship between photolysis frequency $j(O^1D)$ and OH radical suggests that heavy fine particle loads can make the photolytic reactions less efficiently and decrease the OH production and concentration. Utilizing CO as the indicator, the part of $PM_{2.5}$ mass related to primary emitted sources was found less impacted by the OH levels. The contribution of secondary organic aerosol with metrics of O_3 was enhanced with the increases of the OH levels, while secondary inorganic part of $PM_{2.5}$ was favor of the condition that smaller OH concentrations that 5×10^5–5×10^6 molec cm^{-3}. Meantime, a simplified multivariate model was employed to evaluate the influences of OH levels on different parts of fine particles related to different emission and sources. Normalized by solar radiation, this part of OH unrelated to radiation was found to be inversely related to the $PM_{2.5}$, which indicates the self-cleansing capability of the atmosphere.

1. Introduction

The particulate matter (PM) has strong impacts on both the global earth-climate system and the local air quality worldwide (IPCC, 2013; Fuzzi et al., 2015 and therein). It can also result in a variety of adverse health effects on human beings (Gualtieri et al., 2011). Especially, the fine particles, with aerodynamic diameter equal or less than 2.5 μm ($PM_{2.5}$), have higher biological toxicity than PM_{10} (Yorifuji et al., 2015). $PM_{2.5}$ pollution has been observed more frequently and severely in China, and became the most serious environmental problem over megacities (Ma and Jia, 2016). $PM_{2.5}$ can be emitted directly as primary particles like natural dust, anthropogenic emissions and biomass combustion, or formed from a variety of secondary physical and chemical processes, such as heterogeneous reactions and photochemical process, etc. (Huang et al., 2012; Fuzzi et al., 2015; Zheng et al., 2015b; Wen et al., 2016). The secondary formation mechanism

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of $PM_{2.5}$ is so complex that extensive research works have already been conducted (e.g. Gelencsér et al., 2007; Kroll and Seinfeld, 2008; Baker and Foley, 2011; Ram and Sarin, 2011; Guo et al., 2013). Although numerous measurements and methods were applied, there are still uncertainties in source appointment and unknown formation of $PM_{2.5}$.

To investigate the $PM_{2.5}$ evolution affected by directly emission or formation by precursor gases, the $PM_{2.5}$ mass concentrations are discussed here by dividing into three portions. *(i)* Automobile exhaust is considered to be responsible for the ambient CO emissions in urban area. Therefore, CO can be served as the metric for parts of $PM_{2.5}$ related to primary emission (Wang et al., 2008; Both et al., 2013). *(ii)* Precursors of SO_2 and NO_2 are well known to form secondary sulfate and nitrate aerosols, respectively, via atmospheric heterogeneous reaction (Zheng et al., 2015a). Owing to long-term control measures on SO_2 emission, SO_2 is no longer a mainly pollutant in Shanghai (Huang et al., 2013). However, NO_2 is still the major pollutant with the increases of vehicles population in last few years (Wang et al., 2013a). Hence, NO_2 is used as the index of part of $PM_{2.5}$ related to secondary inorganic constituents (Baker and Foley, 2011; Zheng et al., 2015b). *(iii)* Oxidation of non-methane organic compounds by ozone, OH and NO_3 is also the important pathway of secondary organic aerosol (SOA) formation (Sato et al., 2013). Shi et al. (2015) also found $PM_{2.5}$ increased significantly during severe O_3 pollution episodes in Shanghai. O_3 is proposed to be an indicator of part of $PM_{2.5}$ mass related to secondary organic part.

Atmospheric oxidation capacity (OC) determines the lifetime of many trace gases, and the formation and removal of $PM_{2.5}$ as well, which is generally the most important factor influencing significantly the rate of self-cleansing process of atmosphere. In current study, OC is defined as the sum of the respective oxidation rates of the atmospheric constituent Y_i (VOCs, CO, CH_4) by the oxidant X (X = OH, O_3, NO_3) (Geyer et al., 2001; Elshorbany et al., 2009).

$$OC = \sum k_{Y_i}[Y_i][X] \tag{1}$$

As the dominant daytime oxidant, hydroxyl (OH) radical is capable of removing the majority of trace gases in the troposphere and controlling principally the OC of atmosphere (Stone et al., 2012). Nitrate (NO_3) radical is the nocturnal oxidant, while O_3 is the most abundant oxidant all through the day (Wang et al., 2013b; Mogensen et al., 2015).

With respect to the OH radical production, on a global scale, the main mechanism of OH production is likely the formation of excited $O(^1D)$ atoms from the photolysis reaction of O_3 with radiation at wavelengths below 320 nm (Stone et al., 2012). The $O(^1D)$ atoms can react with water (gas) to produce OH radical directly or be quenched by air molecules to the primitive state as the following reactions:

$$O_3 + hv \rightarrow O(^1D) + O_2 (\lambda \le 320\text{nm}) \tag{2}$$

$$O(^1D) + H_2O \rightarrow 2OH \tag{3}$$

$$O(^1D) + M \rightarrow O(^3P) + M \quad M = (N_2 \text{ or } O_2) \tag{4}$$

Another main source of OH is the photolysis of formaldehyde (HCHO) at wavelengths below 370 nm, generating H or HCO radicals, which can react with O_2 in the air and then produce HO_2 radical, followed by rapid reaction of HO_2 with NO to form OH radical (Meller and Moortgat, 2000).

$$HCHO + h\nu \rightarrow H + HCO \ (\lambda \le 370\text{nm}) \rightarrow H_2 + CO \tag{5}$$

$$H + O_2 \rightarrow HO_2 \tag{6}$$

$$HCO + O_2 \rightarrow HO_2 + CO \tag{7}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{8}$$

Other aldehydes also have the similar reactions to produce OH radical. However, HCHO is the most abundant carbonyl compounds, accounting for 70–80%, its contribution to OH radical cannot be ignored (Zheng et al., 2013).

In addition, photolysis of HONO also contributes largely to the daytime OH production in the contaminated atmosphere (Elshorbany et al., 2010; Lu et al., 2013; Chan et al., 2017):

$$HONO + h\nu \rightarrow OH + NO \ (\lambda \le 400\text{nm}) \tag{9}$$

In general, the OH radical is dominating the OC of atmosphere, which was reported to represent nearly 90% of the total OC through the entire day (Elshorbany et al., 2009). Especially during daytime, the OH radical play a critical role in atmospheric photochemistry by reacting with most organics, often initiating their oxidation and subsequent loss and resulting in the formation of ozone, other oxidants, acids, and fine particles in polluted areas (Ren et al., 2004). The daytime OH chemistry and its abundance are determined by the concentration of VOCs and NO_x, and solar radiation (Monks, 2005; Lelieveld et al., 2008). Distinguish from the polluted and weather conditions, the concentration and production pathway of OH changed greatly in different locations. For example, HONO photolysis has been found to comprise around 60% of the total initial production rate of primary OH radical source, after that comes alkene ozonolysis (~24%), photolysis of HCHO (~16%) and O_3 (~5%) during the daytime in Santiago, Chile (Elshorbany et al., 2009). In China, Lu et al. (2012, 2013) have observed that photolysis of dicarbonyls contributed as much as HCHO photolysis in polluted air mass in Beijing surrounding and Pearl River Delta (PRD) areas. However, significant contribution of ozonolysis of alkenes to OH production were highlighted by Elshorbany et al. (2009). Moreover, the nocturnal OH concentrations in both Beijing and PRD areas were observed on the order of $(0.5-3) \times 10^6$ molec cm^{-3}, which suggests a significant nighttime oxidation rate of pollutants on the order of several ppb per hour (Lu et al., 2014). So far, the observation and modelling studies for OH radical are rarely reported in Shanghai.

To aim the interplays between OH and fine particles, a continuous observation for major precursors of OH radical, $PM_{2.5}$ and radiation was performed from April 1 to August 31, 2013 at Shanghai, China. Based on a simplified steady-state model, the daytime OH concentration and the relative contributions of HCHO, HONO and O_3 to OH production were estimated. The impacts of approximated OH radical on different parts of $PM_{2.5}$ mass were investigated, i.e. related to primary emission, secondary organic and inorganic formation. Furthermore, a linear model was employed to describe the $PM_{2.5}$ source appointment under different OH levels. Meanwhile, the effect of $PM_{2.5}$ to photolysis sources of OH was also discussed.

2. Measurements and methods

2.1. Measurement site and experimental setup

The long-path differential optical absorption spectroscopy (LP-DOAS) method was utilized to measure the trace gases on the campus of Fudan University (FDU, 31°18′N, 121°29′E). The measurement site is located in the northeastern subdivision of urban