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On the summertime air quality and related photochemical processes in the megacity Shanghai, China

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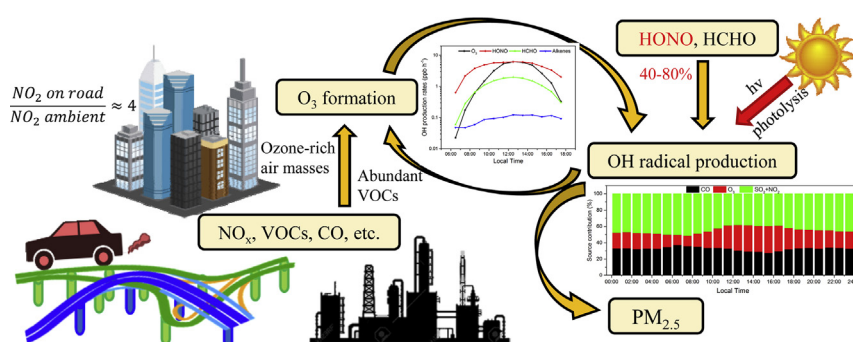
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HIGHLIGHTS

- The air quality in Shanghai during summer was investigated.
- On road NO_2 is on average 4 times as high as the ambient measurement.
- Secondary formation of sulfate and nitrate is the largest source of $\text{PM}_{2.5}$ (~44.8%).
- In summer, HONO is the major OH precursor (40–80%) during daytime.
- The daily O_3 and $\text{PM}_{2.5}$ are related to the HONO levels in the early morning.

GRAPHICAL ABSTRACT



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ABSTRACT

Summertime surface ozone (O_3) and related secondary formation of fine particles are the major air quality concerns in the megacity of Shanghai. We performed mobile Cavity Enhanced Differential Optical Absorption Spectroscopy (CE-DOAS) measurements to investigate the spatial distribution of on-road nitrogen dioxide (NO_2) concentrations along the Inner Ring Elevated Road (IRER) in Shanghai. The observations show a ratio of 4 between CE-DOAS averaged on-road NO_2 and the in-situ ambient measurements, illustrating the strong impact of vehicle emissions over the urban area. The air mass transport analysis suggests that the observed episodic ozone events arise from both the abundance of volatile organic compounds (VOCs) precursors in the sampled plume and the regional transport of ozone-rich air masses. Analysis of the sources of $\text{PM}_{2.5}$ shows that the secondary heterogeneous gas-to-particle conversion of sulfate and nitrate from sulfur dioxide (SO_2) and nitrogen oxides (NO_x) is the largest source of $\text{PM}_{2.5}$ contributing $44.8 \pm 9.2\%$ of the total $\text{PM}_{2.5}$. Ozone-related photochemical formation of fine particles is estimated to contribute about $22.5 \pm 11.9\%$ of the total $\text{PM}_{2.5}$, which is strongly facilitated by solar radiation in summer. According to our results, nitrous acid (HONO) is the major precursor of hydroxyl radicals (OH) accounting for 40% to 80% of the total OH production during daytime. A significant correlation is found between the HONO levels in the early morning and the daily O_3 and $\text{PM}_{2.5}$ levels. The summertime measurements indicate that the photolytic reaction of HONO after sunrise increased the abundance of daytime

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OH and oxidative capacity, resulting in an enhancement of ground level ozone and secondary organic aerosol formation. This study provides quantitative information to better understand photochemical formation of ozone and fine particles in Shanghai during summertime, which is useful for designing collaborative strategies to mitigate emissions of precursor pollutants.

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1. Introduction

Shanghai is one of the most urbanized and modernized cities in China, which has 16 county-level divisions, with its suburbs covering a total area of 6340 km². Located in the Yangtze River Delta (YRD) in east China, Shanghai sits on the south edge of the exit of Yangtze River in the center part of the east coastal area. The city is bounded to the east by the East China Sea, to the north, south and west by the provinces of Jiangsu and Zhejiang, as shown in Fig. 1(a). The total number of inhabitants of the city is >24.25 million by the end of 2014. The vehicle population in Shanghai has been increasing with an average rate of ~10% per year during the last decade, and currently there are >3.04 million vehicles registered in Shanghai (Shanghai Municipal Statistics Bureau, 2015). With the rapid economic growth, Shanghai is facing a series of air pollution problems in recent years. Due to the recent efforts to

reduce industrial emissions, vehicular emissions become the major source of air pollutants and relevant precursors in Shanghai, e.g. vehicular emitted volatile organic compounds (VOCs) in urban Shanghai has been reported to contribute 25–28% of the measured VOCs concentration. It also contributes to the subsequent formation of secondary organic aerosol (SOA) and ozone (Huang et al., 2015). Nitrogen oxides (NO_x) levels are also largely influenced by vehicular emission in the central urban area of Shanghai (Wang et al., 2008; Wang et al., 2012).

In the downtown area of Shanghai, there are several elevated expressways (10–20 m above the ground roads) designed to alleviate the traffic volume on surface streets, e.g. the Inner Ring Elevated Road (IRER), the Middle Ring Elevated Road (MRER), and the Outer Ring Road, together with a crossed Yan'an Viaduct and South-North Viaduct. Nevertheless, traffic in and around Shanghai is often heavy and traffic jams are common during the rush hours. Large number of vehicles

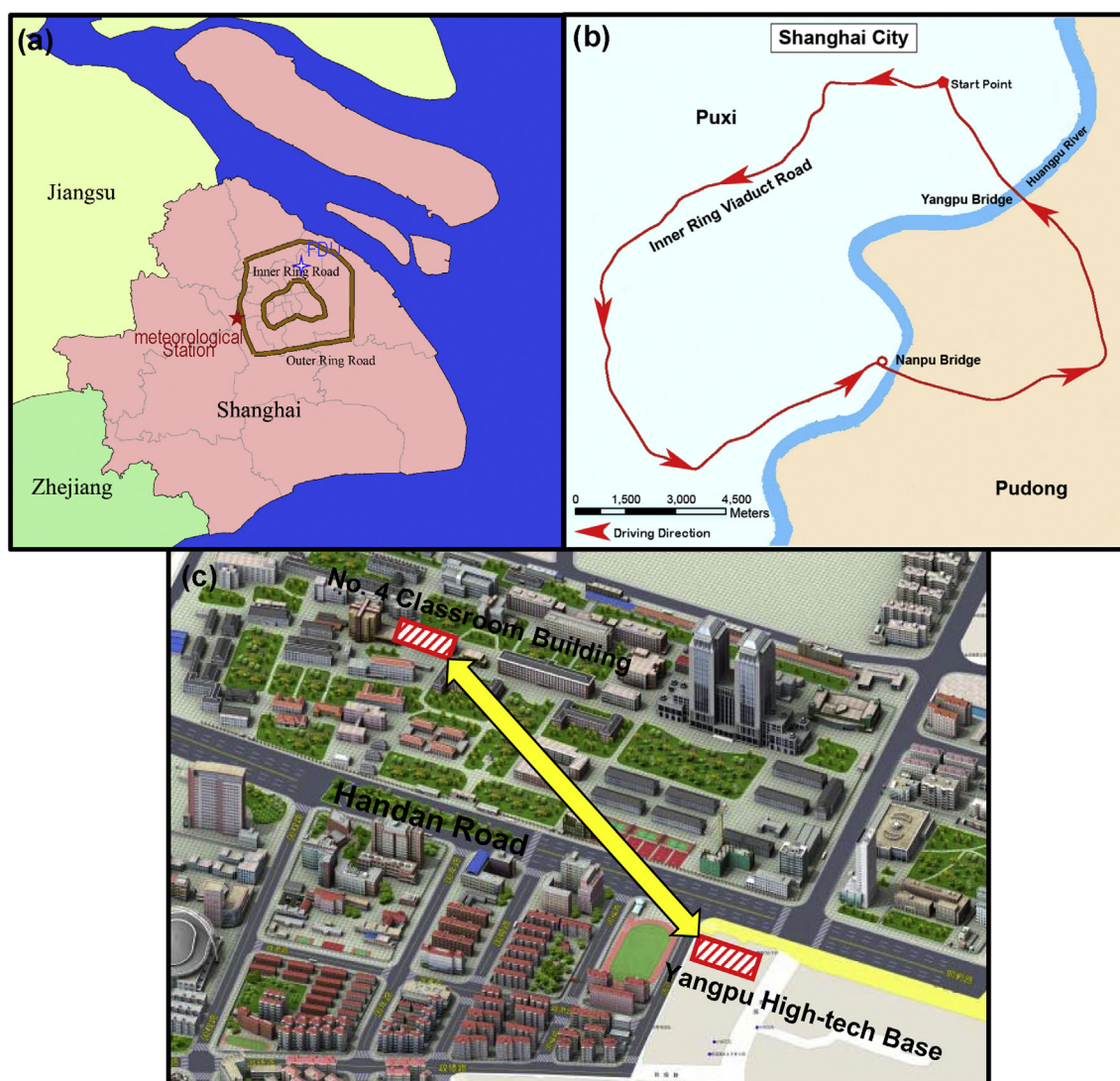


Fig. 1. Overview of the measurement site and the route of the mobile CE-DOAS observation.

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