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Characteristics of atmospheric ammonia and its relationship with vehicle emissions in a megacity in China

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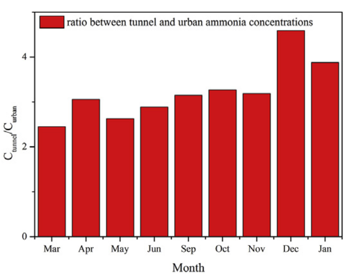
GRAPHICAL ABSTRACT



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ABSTRACT

Atmospheric ammonia plays an important role in haze formation in East China. In this study, long-term measurements of NH_3 concentrations were implemented at urban, suburban, and tunnel sites in Shanghai, the largest city in East China. The average monthly ammonia concentrations at the urban site varied from 3.7 ppb to 14.5 ppb and exhibited the highest levels in summer and lowest levels in winter, indicating that the biological emissions and agriculture in the surrounding areas are important contributors. The suburban NH_3 levels were significantly higher in autumn compared to those at the urban site, indicating the important contribution of agricultural activities. Regardless of the season, the difference of NH_3 concentrations between the tunnel and urban sites remained almost constant. On average, the tunnel NH_3 level was three times higher than that of the nearby urban site, indicating strong vehicle NH_3 emissions in the tunnel. The tunnel NH_3 levels on weekdays were comparable to those on weekends, a result that was in agreement with the daily average traffic volume. It was estimated that the vehicle emissions contributed 12.6–24.6% of the atmospheric NH_3 in the urban area and 3.8–7.5% for the whole area of Shanghai. Our results suggest that vehicle NH_3 emissions should be considered, although agricultural emissions are still more important for mitigating severe haze pollution during wintertime in the megacities of China.

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1. Introduction

Ammonia (NH_3) is the dominant alkaline gas and the third most abundant nitrogen-containing species after nitrogen gas and nitrous oxide in the atmosphere. Classical nucleation theories and laboratory studies demonstrate that the presence of NH_3 at ppt levels significantly enhances the nucleation rates in the H_2SO_4-H_2O system (Zhang et al., 2012), indicating that NH_3 is a critical factor in the nucleation of new particles. The important role of NH_3 in new particle formation events has also been established by field observations. Smith et al. (2005) found that ammonium and sulfate were the only constituents of the 6–15-nm particles during nucleation events in Atlanta. Yue et al. (2010) reported that the neutralization of H_2SO_4 by NH_3 contributed approximately 50% to the initial growth of freshly formed particles. In the atmosphere, ammonia neutralizes readily with acidic species from SO_2 and NO_x precursors and has long been recognized as an important contributor to the formation of secondary sulfate and nitrate aerosols, which are major components of $PM_{2.5}$ around the world (Seinfeld and Pandis, 2006). Moreover, the heterogeneous oxidation of SO_2 is favored in the ammonia-rich atmosphere, promoting persistent sulfate formation (Wang et al., 2016). The increase of secondary inorganic aerosols and $PM_{2.5}$ mass not only degrades atmospheric visibility but also imposes strong impacts on human health (Pui et al., 2014). In addition, both wet and dry deposition of NH_3 and particulate ammonium salts have many effects on the ecosystem, accounting for the soil acidification and water eutrophication (Behera et al., 2013).

Agriculture is undoubtedly the dominant NH_3 source on the global scale, contributing over 80% of global NH_3 emissions (Behera et al., 2013). In contrast, the contribution of on-road transportation to the global NH_3 is negligible (~1% of the total contribution). In China, the total NH_3 emissions was nearly one million tons in 2012, with the largest contribution being from livestock (52% of contribution) and the second largest source being from applied fertilizer (29%). The traffic sector accounted for 4% of the total emissions, followed by biomass burning (3%) and the chemical industry (3%) (Kang et al., 2016). Due to the strong emissions from livestock and applied fertilizer, higher concentrations of atmospheric NH_3 were reported in rural areas (Shen et al., 2011; Xu et al., 2016). However, many studies have found that ambient NH_3 concentrations in many urban areas were comparable to or even higher than those in the nearby rural areas, indicating that non-agricultural emissions may contribute greatly to urban NH_3 sources (Cao et al., 2009; Meng et al., 2011).

The estimation of non-agricultural NH_3 emissions in urban areas is still challenging, since biomass burning, domestic sewage, garbage collection systems, road traffic, industrial emissions, and other factors are contributors of local NH_3 emissions and the relative emission strengths of individual NH_3 sources remain unclear (Behera et al., 2013). For example, Zhang et al. (2017) reported that sewage treatment accounted for ~4% of the ammonia emissions in the urban area of the Pearl River Delta (PRD), whereas the estimated contribution was as high as 34% based on the NH_3 emission inventories compiled by Zheng et al. (2012). Since the introduction of three-way catalytic converters (TWCs), gasoline vehicles generate more NH_3 by over-reducing NOx in vehicular exhaust (Suarez-Bertoa and Astorga, 2016). The adoption of selective catalytic reduction (SCR) by the addition of urea or NH_3 to diesel exhaust to reduce NOx emissions is another potential NH_3 source from road traffic. With the extensive equipment of TWCs or SCR, road traffic is expected to contribute more NH_3 to the urban atmosphere. Fraser and Cass (1998) reported that the contribution of vehicle sources increased from 2% to 15% of the total NH_3 emissions since the installment of TWCs in Los Angeles. Similarly, vehicle emissions have become a significant contributor of atmospheric NH_3 in Houston (Zhang and Ying, 2010). In the United Kingdom, the transport sector was estimated to be the primary source of non-agricultural NH_3 emissions, followed by sewage emissions (Sutton et al., 2000). With the development of urbanization, the emission of NH_3 from traffic sources in Beijing during 2013 was expected to be comparable to agricultural emissions (Pan et al., 2016). Despite these results, the contribution of traffic sources to urban NH_3 concentrations is still an area of debate. For example, Reche et al. (2012) believed that the urban design of the streets should be the determining factor influencing urban NH_3 concentrations. Similarly, Teng et al. (2017) suggested that emissions from local green space inside the urban areas and evaporation of ammonia and ammonium in dew droplets were major sources of atmospheric NH_3 in urban area of Qingdao for that the temporal variation of NH_3 concentrations was synchronized with them.

In past decades, China suffered from severe fine particulate pollution. Existing in the main forms of $(NH_4)_2SO_4$ and NH_4NO_3, the secondary sulfate, nitrate, and ammonium aerosols accounted for a large fraction of $PM_{2.5}$ mass in all haze episodes (Huang et al., 2012a, 2014). It was established that the increase of atmospheric NH_3 concentrations might play a vital role in the enhancement of fine particulate nitrate and $PM_{2.5}$ levels (Chu et al., 2016; Wen et al., 2015; Ye et al., 2011a). In a recent study, Wang et al. (2016) revealed that the ammonia-rich atmosphere was a crucial factor for the periodic occurrence of $PM_{2.5}$ episodes in Beijing. Moreover, Fu et al. (2017) emphasized that the effort of SO_2 and NO_x emissions reduction on mitigating haze pollution in East China was partly offset by the increasing ammonia concentrations. Wu et al. (2016) highlighted that reduction of NH_3 emissions should be more efficient than other particle precursors at mitigating $PM_{2.5}$ pollution in China. With increasing concern over $PM_{2.5}$ pollution, it is crucial to understand the concentrations and sources of urban NH_3. However, ammonia has not been regulated in the national ambient air quality standards of China (GB 3095–2012), and few observations on the urban NH_3 concentrations were reported.

With a population of 24 million and a total land area of 6400 km^2, Shanghai is the biggest megacity and the economic center of the Yangtze River Delta. Chang et al. (2016) estimated that vehicle emissions accounted for 12% of the total NH_3 emissions in the urban area of Shanghai. Wang et al. (2015) found strong positive correlations between the conversion rate of ammonia and particulate sulfate and nitrate mass over the city. In this study, long-term measurements of ambient NH_3 were performed at urban, suburban, and tunnel sites in Shanghai. The objective of this study is thus threefold: (1) to characterize seasonal variability of NH_3 concentration in the city, (2) to identify whether vehicle emissions is an important source of urban NH_3, and (3) to assess the contribution of vehicle emissions on NH_3 budget in urban area and the whole area of Shanghai. These data will help researchers gain a better understanding of ambient NH_3 levels and the importance of vehicle emissions in this area.

2. Experimental

2.1. Sampling sites

Ambient NH_3 samples were collected using Ogawa passive samplers (Ogawa USA, Pompano Beach, Florida) at an urban site, a suburban site, and a tunnel site in Shanghai. The sampling locations are shown in Fig. 1. The urban site was located on the main campus of Fudan University (31.3°N, 121.5°E). The campus can be considered as a representative urban site for Shanghai due to many dwelling quarters and commercial blocks in the surrounding area. The tunnel NH_3 samples were collected over the open section of the Handan Road Tunnel, which is at a distance of approximately 300 m from the urban site. To improve ventilation effects, the 760 m-long tunnel consists of two buried sections at both ends and a 200 m-long open section (fencelike area in the map) at the central tunnel. Thus, the tunnel samples may reflect NH_3 emissions from on-road vehicle sources. The suburban site was located in the town of Zhoupu, which is approximately 30 km to the southeast of the main campus of Fudan University. There are stretches of residential houses and farmlands near this suburban site. The main crops in these farmlands are rice, vegetables, and more.