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Role of atmospheric ammonia in particulate matter formation in Houston during summertime

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HIGHLIGHTS

- Simultaneous measurements of gaseous and aerosol species were conducted.
- Atmospheric NH_3 contributed to increases in measured particle mass and measured/modeled particle number concentrations.
- NH_4^+ existed in the form of $(NH_4)_2SO_4$ and NH_4HSO_4; NH_4NO_3 and NH_4Cl formation was suppressed in summer.

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ABSTRACT

Simultaneous high-time-resolution measurements of atmospheric NH_3, HNO_3, soluble gas-phase chloride, and aerosol species were made in Houston, TX, from August 5, 2010 to August 9, 2010. Gaseous NH_3 was measured using a 10.4-μm external cavity quantum cascade laser-based sensor employing conventional photo-acoustic spectroscopy, while gaseous HNO_3 and HCl were sampled using a mist chamber–ion chromatograph (IC) system. Particle chemical composition was determined using a particle-into-liquid-sampler–IC system. There was a large amount of variability in the gas phase mixing ratios of NH_3 (3.0 ± 2.5 ppb), HNO_3 (287.4 ± 291.6 ppt), and HCl (221.3 ± 260.7 ppt). Elevated NH_3 levels occurred around mid-day when NH_4^+ (0.5 ± 1.0 μg m^{-3}) and SO_4^{2-} (4.5 ± 4.3 μg m^{-3}) also increased considerably, indicating that NH_3 likely influenced aerosol particle mass. By contrast, the formation of NH_4NO_3 and NH_4Cl was not observed during the measurements. Point sources (e.g., power plant and chemical plant) might be potential contributors to the enhancements in NH_3 at the measurement site under favorable meteorological conditions. Increased particle number concentrations were predicted by the SAM-TOMAS model downwind of a large coal-fired power plant when NH_3 emissions (based on these measurements) were included, highlighting the potential importance of NH_3 with respect to particle number concentration. Separate measurements also indicate the role of NH_3 in new particle formation in Houston under low-sulfur conditions.

1. Introduction

Ammonia (NH_3) is widely present in the atmosphere due to many anthropogenic and natural sources (Clarisse et al., 2009), usually at trace concentration levels ranging from parts per trillion (ppt) to parts per billion (ppb). Agricultural (e.g., fertilizer application and animal husbandry) (Mount et al., 2002; Rumburg et al., 2008) and industrial and motor vehicle (e.g., chemical production and traffic emission) (Kean and Harley, 2000; Hsieh and Chen, 2010) activities contribute to significant increases in local and/or regional NH_3 levels. In addition, National Emissions Inventory (NEI)

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air pollutant emissions trends data prepared by the United States Environmental Protection Agency (U.S. EPA) indicate that annual NH_3 emissions from the source category of electric utilities have risen continuously since 2005 (U.S. EPA, 2008).

Gaseous NH_3 can increase particulate matter (PM) mass concentrations through the formation of ammonium salts such as ammonium sulfate ($(NH_4)_2SO_4$), ammonium nitrate (NH_4NO_3), and ammonium chloride (NH_4Cl) via chemical reactions with sulfuric, nitric, and hydrochloric acids, respectively. Experiments also reveal that NH_3 plays a vital role in aerosol nucleation events (Kulmala et al., 2002). For example, McMurry et al. (2005) observed a positive correlation between number concentrations of nucleated particles and NH_3 in the sulfur-rich Atlanta atmosphere.

The resultant PM affects the Earth's radiation budget through direct and/or indirect effects and modifies the properties of clouds by serving as cloud condensation and/or ice nuclei (U.S. Climate Change Science Program, 2009). Epidemiological studies also have demonstrated a strong correlation between human exposure to PM and increased rates of respiratory and cardiovascular illness and other adverse human health effects (Pope et al., 2002; Pope and Dockery, 2006). Despite these implications for its negative impacts on air quality, NH_3 currently is not regulated under the National Ambient Air Quality Standards by the U.S. EPA. As a result, there are substantial uncertainties in spatial and temporal variations of NH_3 due to the scarcity of ground-based observations.

Conventional NH_3 studies primarily have focused on the measurements near source areas (e.g., farms) (Robarge et al., 2002; Ferm et al., 2005) using a bulk denuder technique with off-line analysis (e.g., ion chromatography (IC)) (Baek and Aneja, 2004; Wilson and Serre, 2007). Newly developed NH_3 instruments using laser spectroscopy and chemical ionization mass spectrometry have improved time resolution and detection limits and minimized human-induced errors (Nowak et al., 2007; Pogány et al., 2010). Meanwhile, relatively little previous work has investigated the effect of gas-particle partitioning of NH_3 and the interaction between NH_3 and acidic gaseous and particulate species due to a paucity of simultaneous datasets. In addition, information about NH_3 levels for the industrial and urban area of Greater Houston is still scarce. Nowak et al. (2010) conducted a 14-day aircraft measurement campaign including atmospheric NH_3 along the Houston Ship Channel (HSC) area during the second Texas Air Quality Study (TexAQS II). Gong et al. (2011) characterized the seasonal and diurnal patterns of gaseous NH_3 levels in Houston. According to a photochemical model, the estimated NH_3 mixing ratios for the Houston area are in the range of 1–15 ppb (Pavlovic et al., 2006).

The Toxics Release Inventory (TRI) of the U.S. EPA highlights the importance of NH_3 as an air pollutant in urban communities nationwide (U.S. EPA, 2010). Fig. 1(a) presents the total air toxics releases (20.8 million pounds) by species in the Houston–Sugar Land–Baytown metropolitan area according to the TRI in 2010 (U.S. EPA, 2010). It can be seen that NH_3 has the third largest individual magnitude of emissions after ethylene and propylene. Based on the NEI (U.S. EPA, 2008), agricultural and automobile activities are major contributors to gaseous NH_3 emissions. Fig. 1(b) summarizes the NEI NH_3 emissions (10.2 million pounds) by source categories specifically for Harris County, Texas in 2008 and indicates that on-road gasoline light duty vehicles and fertilizer application account for approximately 56% of the annual NH_3 emissions.

In order to examine the effects of NH_3 on air quality in Houston, measurements of gas-phase NH_3, nitric acid (HNO_3), soluble chloride (assumed to be hydrochloric acid (HCl)), and aerosol species were performed during the summer of 2010 by simultaneous on-line gas- and particle-phase instrumentation. In addition, NH_3 and particle number concentrations were measured synchronously during a one-month period in the summer of 2012. Finally, we performed model simulations aimed to elucidate the role that NH_3 plays in nucleation within power plant plumes in Houston.

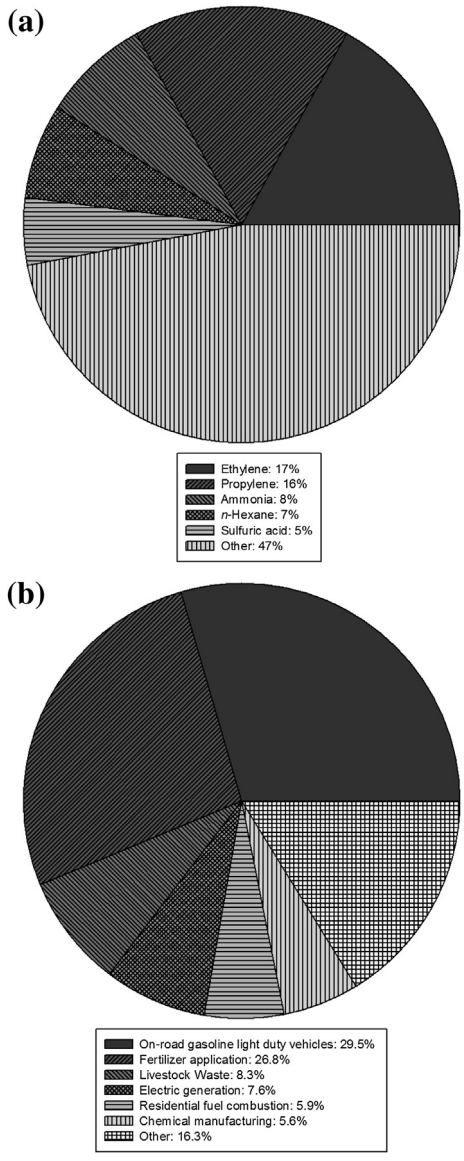

Fig. 1. (a) Annual total air toxics releases (20.8 million pounds) by species in the Houston–Sugar Land–Baytown metropolitan area (U.S. EPA, 2010); (b) Annual NH_3 emissions (10.2 million pounds) by source categories in Harris County, Texas (U.S. EPA, 2008).

2. Materials and methods

2.1. Sampling site

In this study, the simultaneous measurements of trace gases and particle chemical composition were carried out from August 5, 2010 to August 9, 2010. Although a five-day dataset is relatively limited, the total number of data points is large due to the highly time-resolved nature of the measurements and therefore can provide insight into air pollution episodes in an urban area potentially affected by industrial activities. All instruments were deployed in a trailer atop an 18-story (~65 m above ground level) building (North Moody Tower) located on the University of Houston (UH) main campus, which is influenced by many local and regional