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A discussion on the paper “Fossil Fuel Combustion-Related Emissions Dominate Atmospheric Ammonia Sources during Severe Haze Episodes: Evidence from ^{15}N-Stable Isotope in Size-Resolved Aerosol Ammonium”

Pan et al., 2016, EST

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Article

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Fossil Fuel Combustion-Related Emissions Dominate Atmospheric Ammonia Sources during Severe Haze Episodes: Evidence from ^{15}N-Stable Isotope in Size-Resolved Aerosol Ammonium

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9/8/2017

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Background

- In many urban areas, a higher proportion of SIAs relative to SOAs has been observed during haze episodes, suggesting a greater importance of SIAs in haze pollution chemistry (Sun et al., 2014).
- SIAs are mainly formed when the dominant alkaline gas in the lower atmosphere, ammonia (NH_3), reacts with acidic compounds such as sulfuric acid (H_2SO_4) and nitric acid (HNO_3) to form particulate ammonium (NH_4^+) (Griffith et al., 2015).
- Therefore, quantitative estimates based on the $\delta^{15}N$ technique and other top-down constraints are needed to further quantify the NH_3 sources in large cities.

Material & Method

Sampling

Location: on the roof of a building (15 m height) at the State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry (LAPC), Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences (CAS) in urban Beijing (39°58′ N, 116°22′ E)

Period: January 24 to February 1, 2013

Sampler : 9-stage impactor sampler (Anderson Series 20-800)

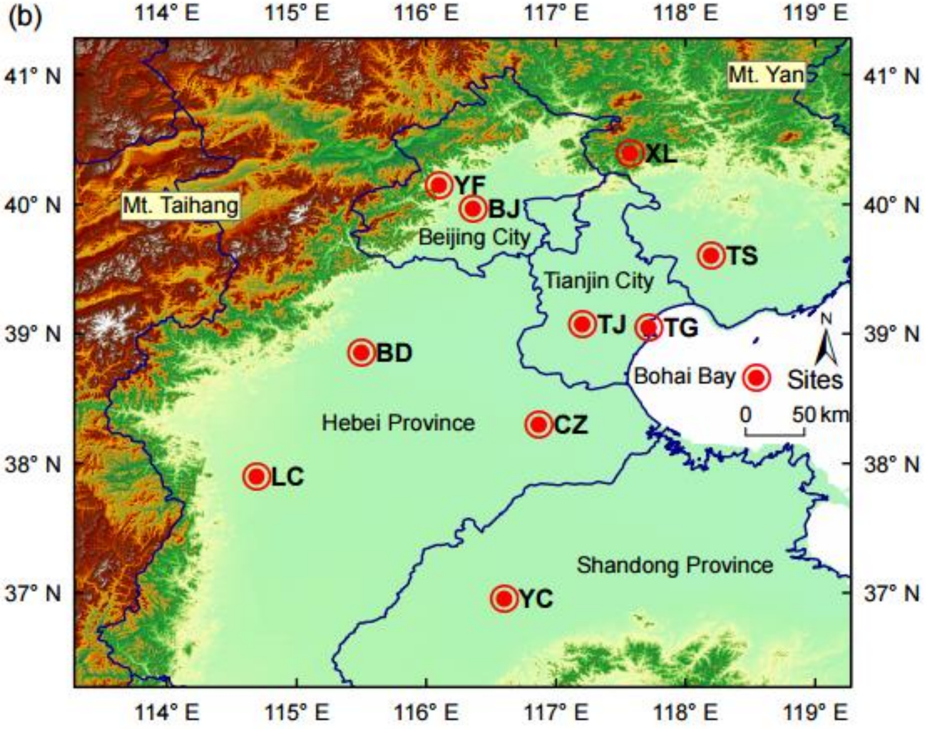


Fig. 1. Locations of the study area and the sampling sites

Material & Method

Chemical Analysis

$$NH_4^+ \xrightarrow{BrO^-} NO_2^- \xrightarrow{NH_2OH} N_2O$$

Experimental principle

Material & Method

Chemical Analysis

- Meteorological conditions: temperature-T, relative humidity-RH, wind speed-WS and wind direction-WD (recorded by an automatic meteorological observation instrument)

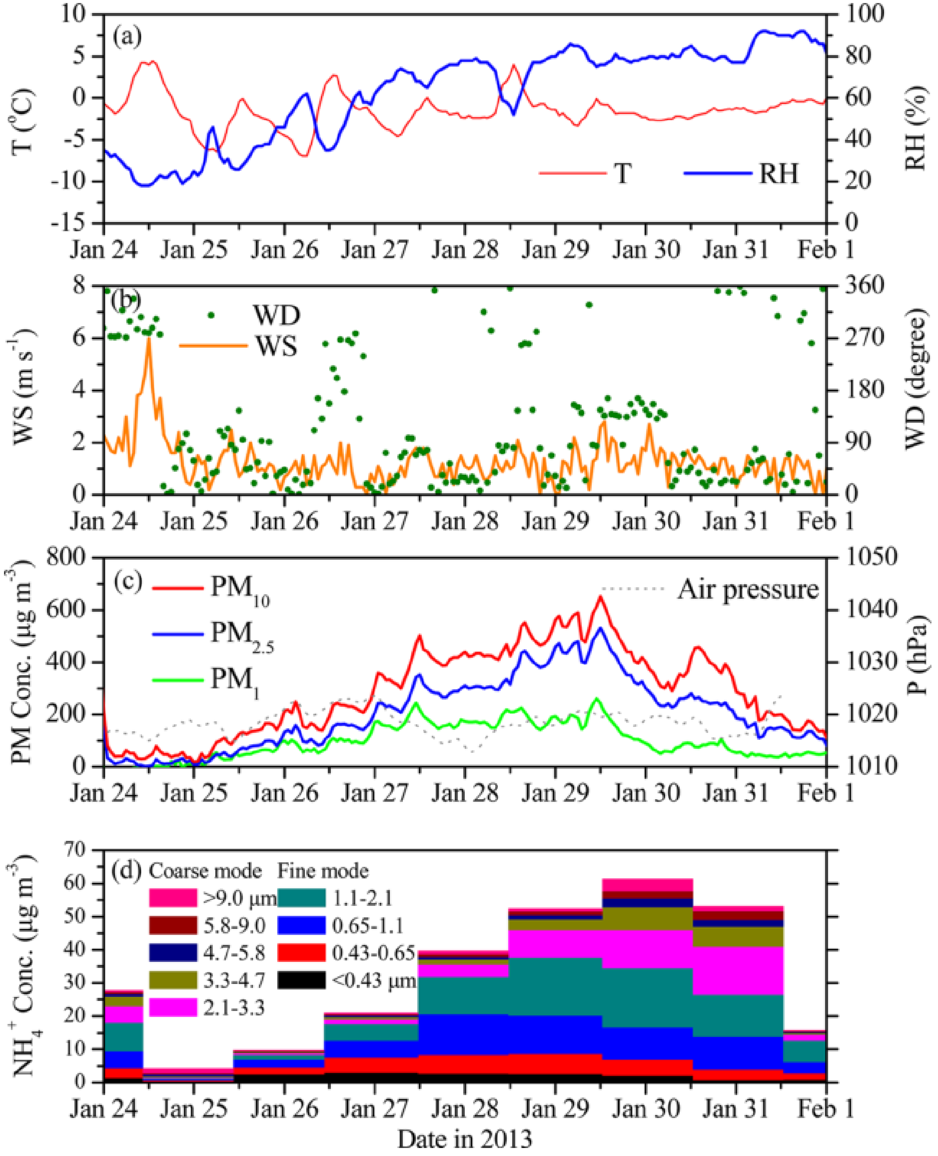


Fig. 2. Size-resolved aerosol NH_4^+ concentrations vs particulate matter and meteorological parameters.

$$\delta^{15}N(‰) = \frac{(^{15}\mathrm{N}/14\mathrm{N})_{sample} - (^{15}\mathrm{N}/14\mathrm{N})_{standard}}{(^{15}\mathrm{N}/14\mathrm{N})_{standard}} \times 1000$$

Material & Method

Calculation and Model

$$^{15}\mathrm{NH}_{3(g)} + \mathrm{NH}^{+}_{4(aq)} \leftrightarrow \mathrm{NH}_{3(g)} + {}^{15}\mathrm{NH}^{+}_{4(aq)}$$

$$\varepsilon_{\mathrm{NH}_4^+-\mathrm{NH}_3} = 33‰$$

$$\delta_{\mathrm{gas}} = \delta_{\mathrm{aerosol}} - \varepsilon_{\mathrm{aerosol-gas}}(1 - \mathrm{f})$$

Where δ_{gas} and $\delta_{\mathrm{aerosol}}$ are the isotopic composition of the initial atmospheric gas and final ion phase in aerosols, respectively, and f is the fraction of the initial gas converted to the ion phase.

- WRF-CMAQ model
- "IsoSources" isotopic mixing model

Results

The mean endmember $\delta^{15}N$ values of three main contributors to NH_3 in the urban environment:

- Agricultural sources——$-39.5‰$
- Fossil fuel sources (coal combustion and vehicle exhaust) ——$-2.95‰$
- NH_3 slip from power plants,——$-12.95‰$

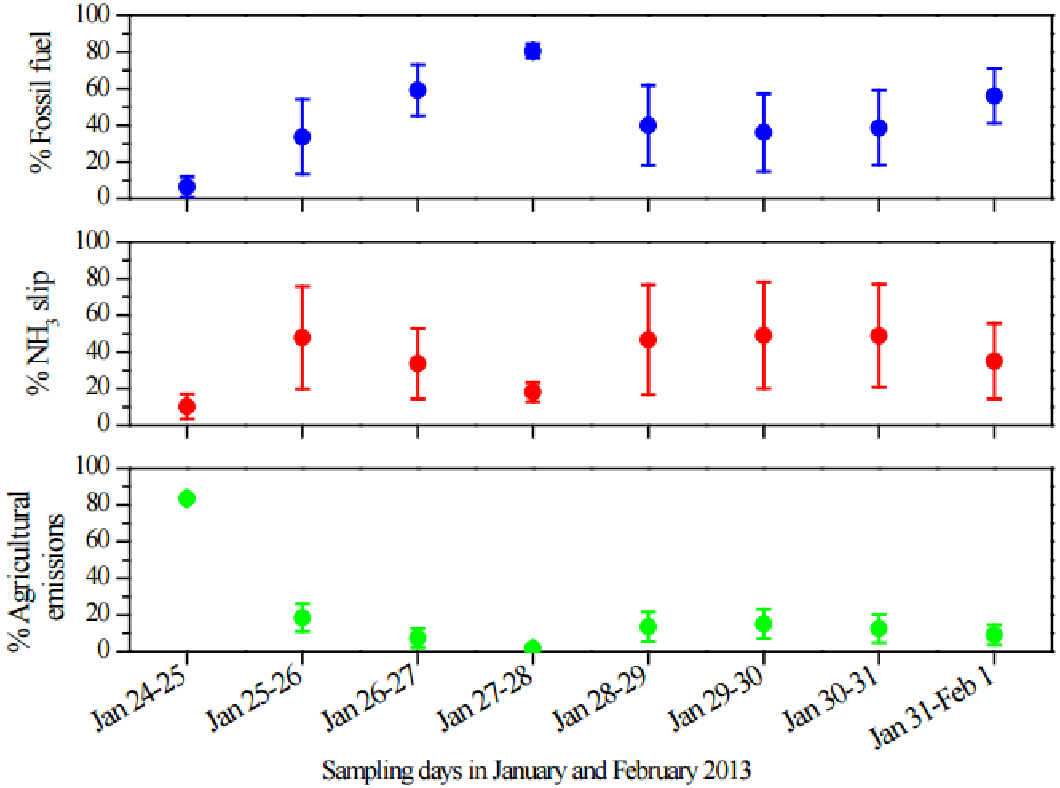
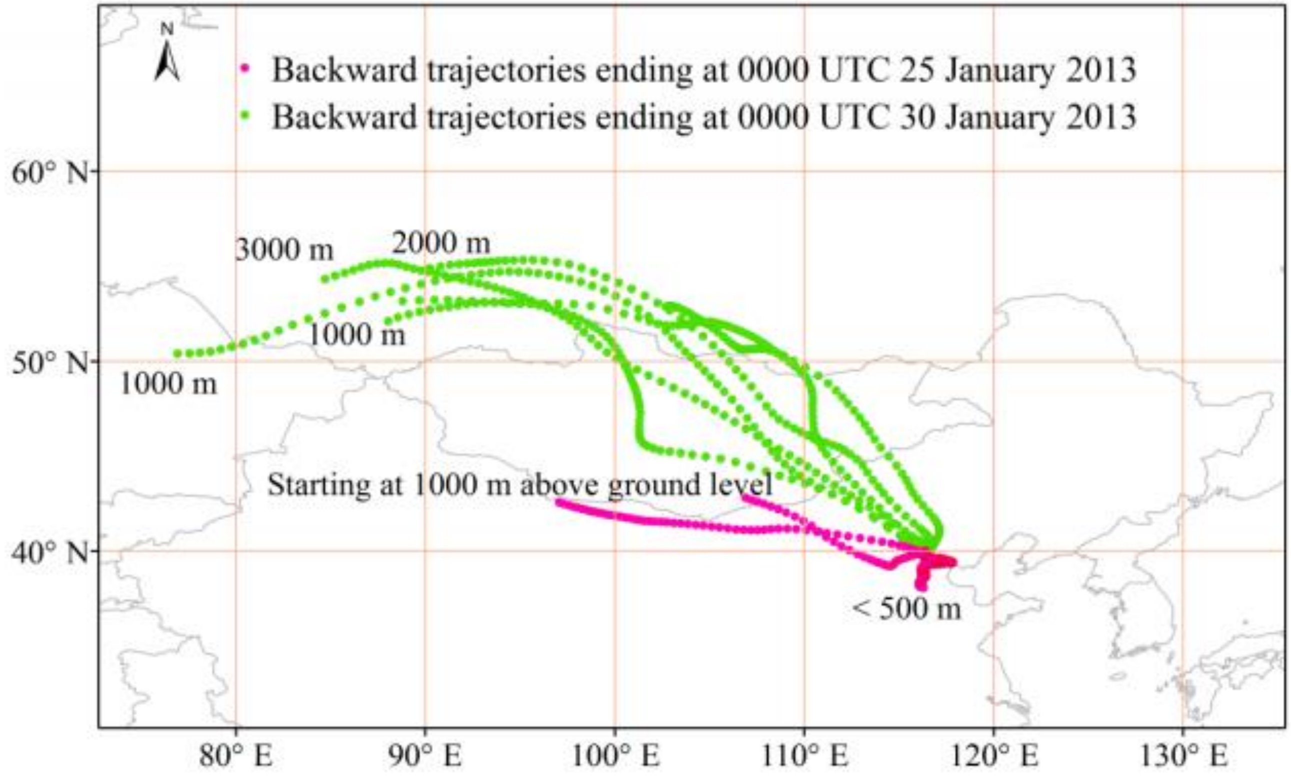


Fig. 3. Source contributions to ammonia for each sample computed using the IsoSources model presented here as the feasible solutions of the modeling results (Mean ± SD).

Results



The former air mass was from a regional scale at heights of 1000−3000 m, whereas the latter air mass was mainly from a local urban scale at heights below 500 m. The three-day back trajectories were calculated every 6 h (00:00, 06:00, 12:00, 18:00 UTC) using the HYSPLIT model .

Fig. 4. Backward trajectory showing the air mass trajectories from the NW during a clean day (January 25) and from the SE during a hazy day (January 30).

Results

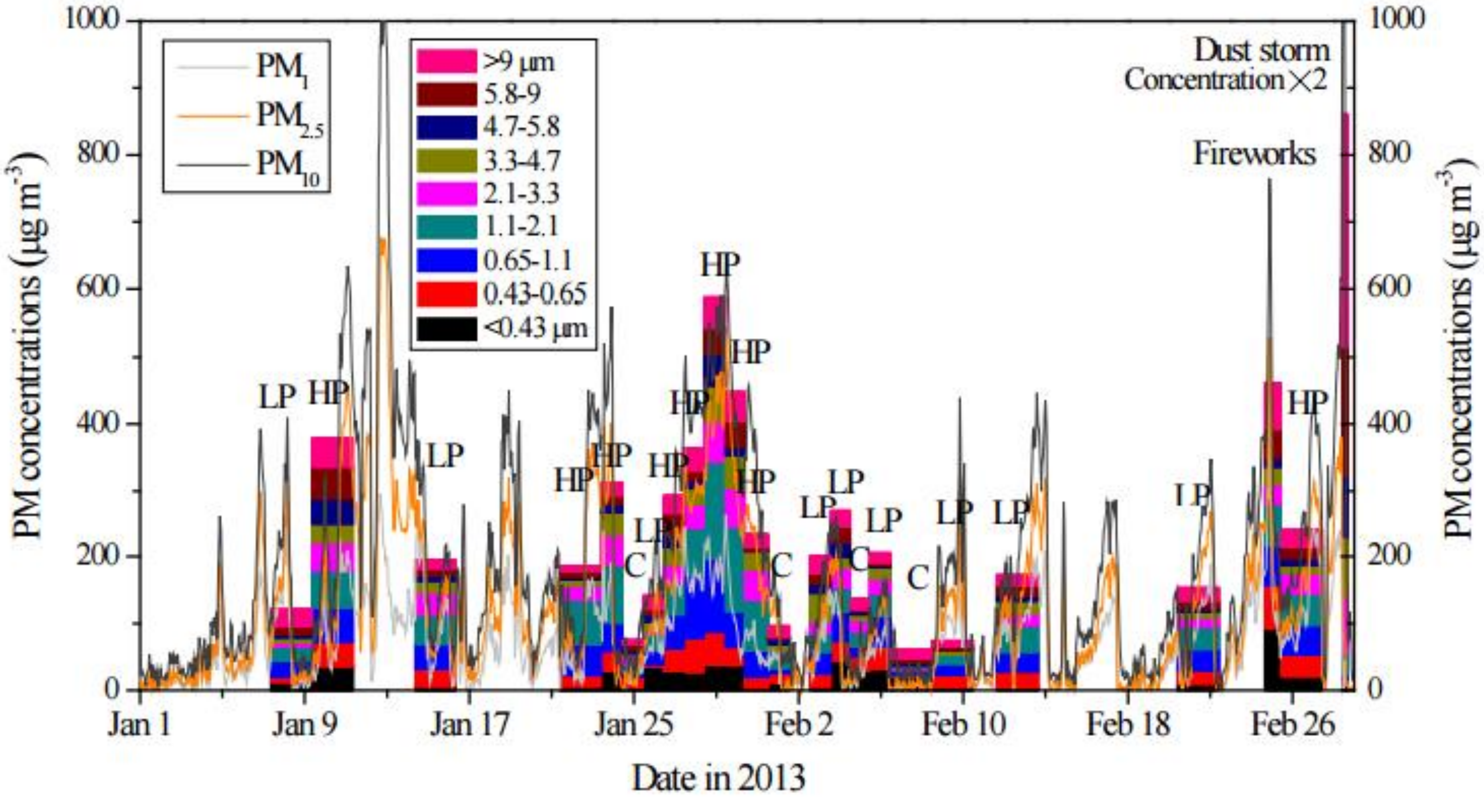


Fig. 5. Size-resolved aerosol sampling campaign conducted during the severe haze pollution episodes in early 2013 in urban Beijing.

- Sampling days marked as C, LP and HP denote clean days ($PM_{2.5} < 75\mu g m^{-3}$), lightly polluted hazy days ($75\mu g m^{-3} < PM_{2.5} < 150\mu g m^{-3}$) and heavily polluted hazy days ($PM_{2.5} > 150\ \mu g m^{-3}$), respectively .

Results

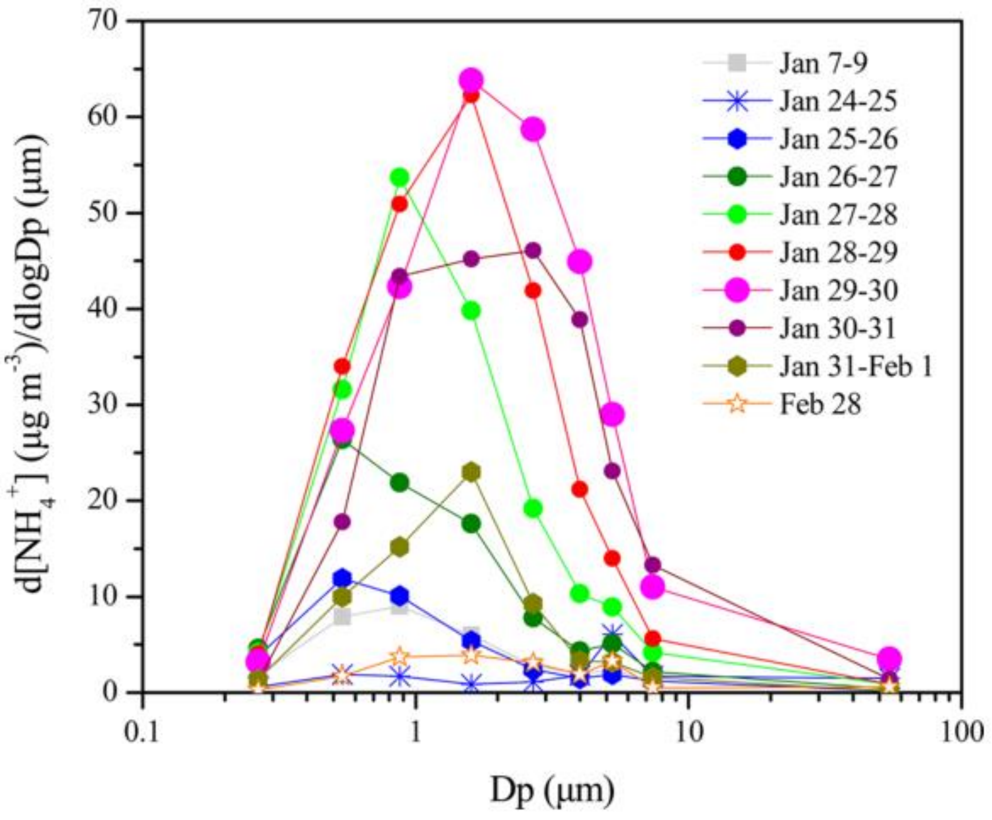
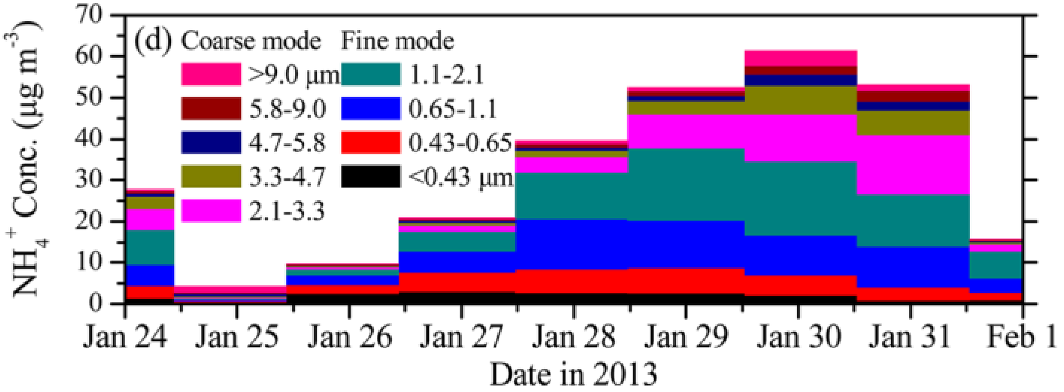


Fig. 6. Size distribution of aerosol NH_4^+ during the study period.

- Peak at 4.7-5.8 μm in clean days(Jan 24-25)
- Peak at 0.65-2.1 μm and 4.7-5.8 μm in dusty day(Feb 28)
- In the haze development stage, the main NH_4^+ particle size shifted from the submicrometer size of 0.43–0.65 μm on January 25–27 to 0.65–1.1 μm on January 27–28 and to 1.1–2.1 μm on January 28–30. (gas-particle conversion and hygroscopic growth)
- In the haze dissipation stage, NH_4^+ concentrations decreased in the fine mode (<2.1 μm) but increased in the coarse mode between 2.1 and 4.7 μm .

Results



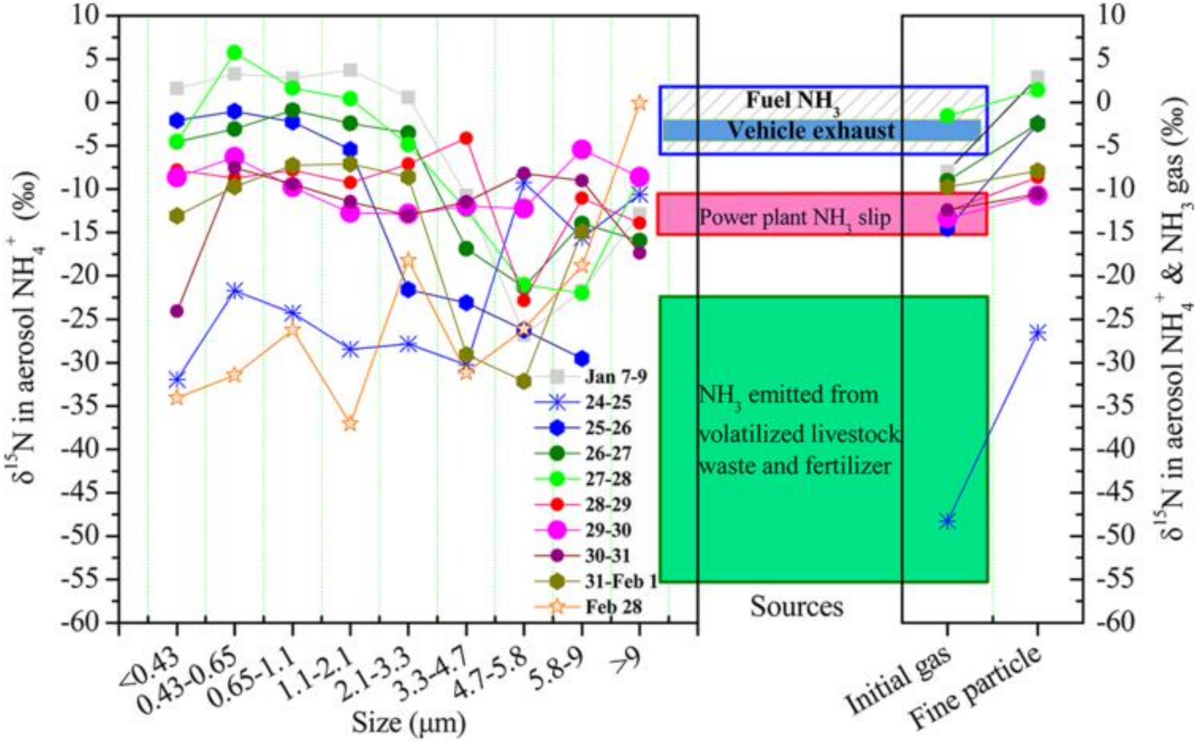


Fig. 7. Variations in the $\delta^{15}N$ values of aerosol NH_4^+ with size bins and the initial $\delta^{15}N - NH_3$ values in air against the NH_3 emission signatures of individual sources.

Fine particles

- Clean day: -26.6‰(-31.9‰~-21.7‰)
- Dusty day: -37.1‰~-26.2‰
- Haze days: from −2.7‰ on January 25−27 and to +1‰ on January 27−28. During the subsequent days, stable at approximately −10‰.

Results

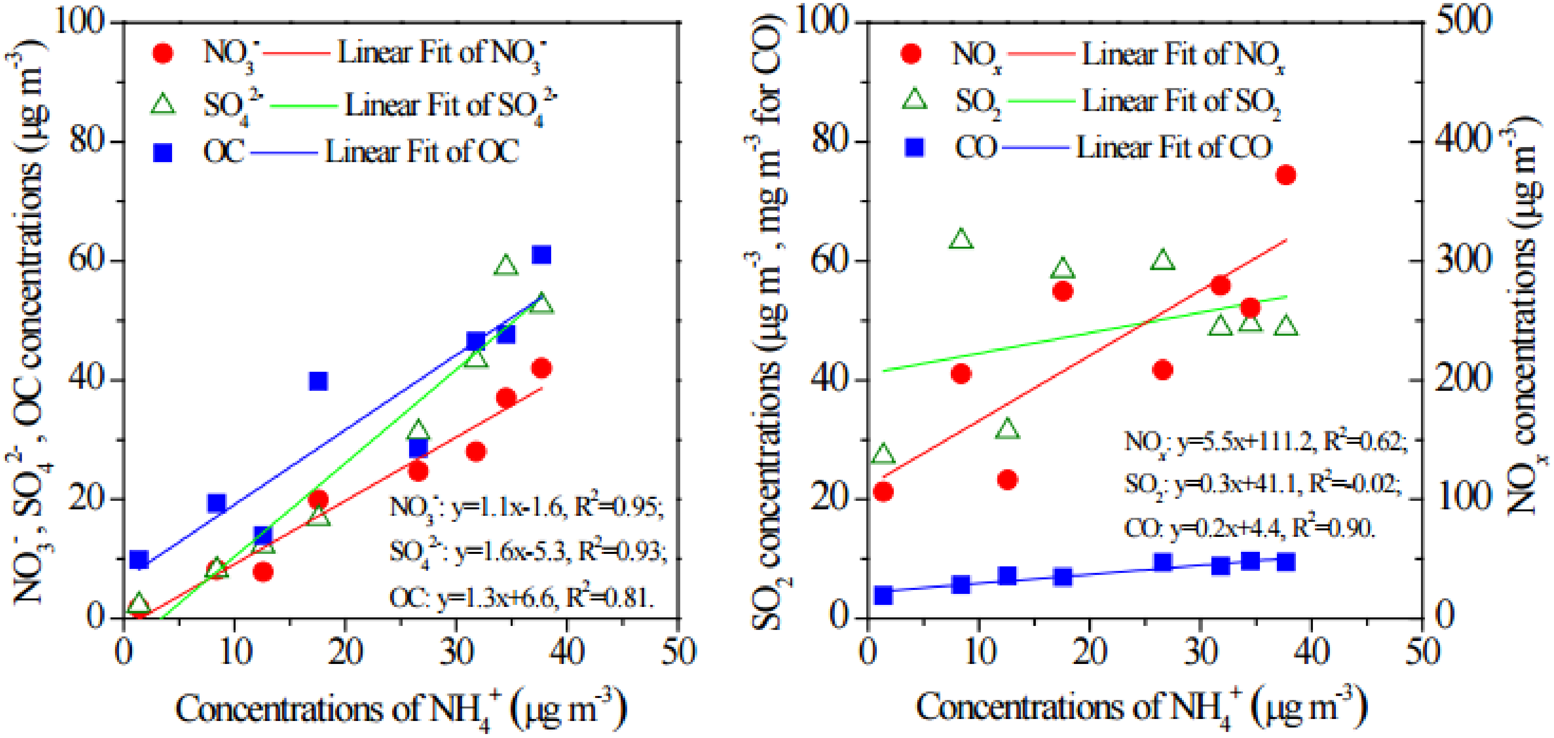


Fig. 8. Scatter plots of ammonium and other chemical components measured in this study illustrating their co-existence during haze pollution periods.

Results

Initial $\delta^{15}N - NH_3$

- Clean days: -48‰
- Remaining haze days: -1.6‰~-14.5‰(approximately -10‰)

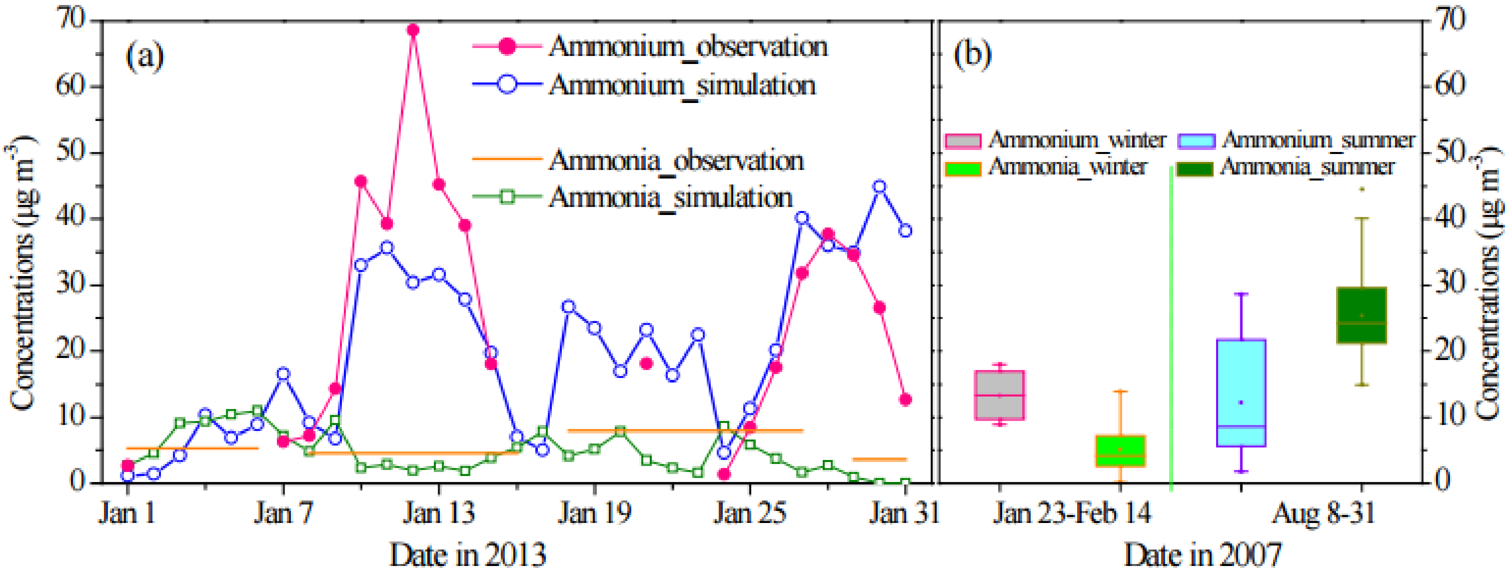


Fig. 9. Modeling results vs. observation of ammonia and ammonium in January 2013 (a) and in 2007 (b).

Results

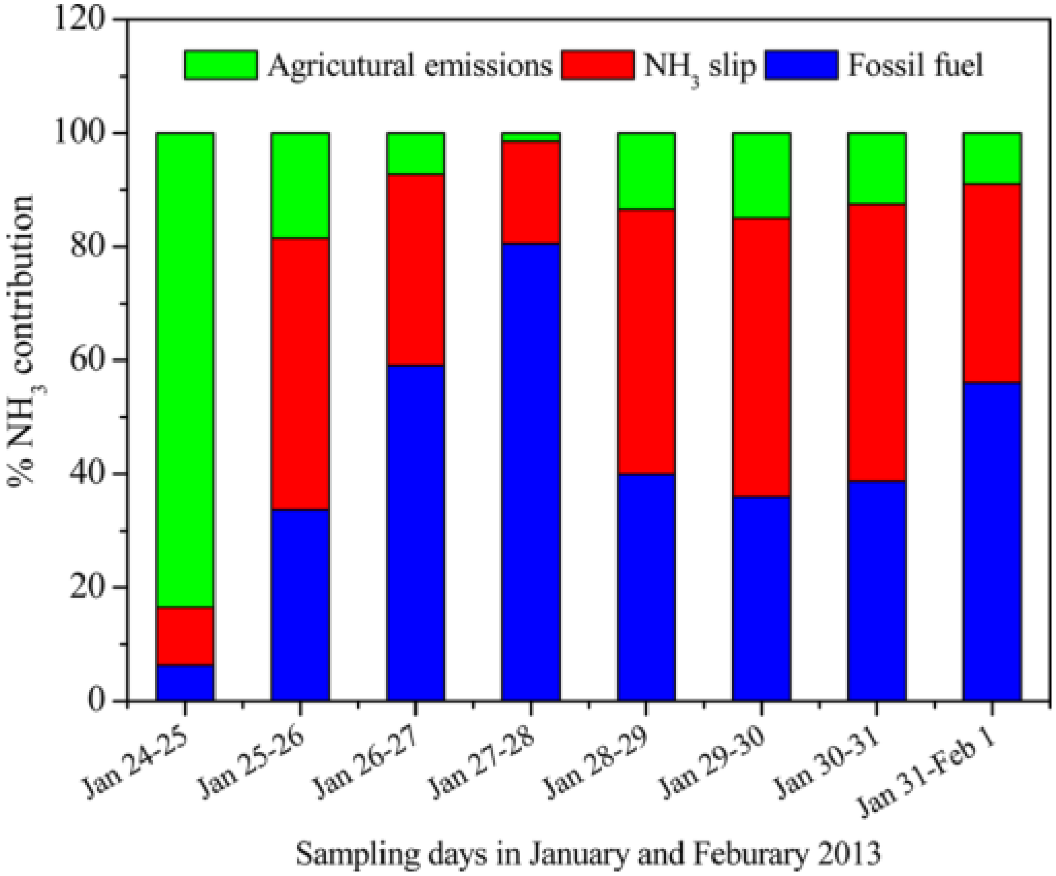


Fig. 10. Contributions of individual emissions to the atmospheric concentrations of NH_3 in urban Beijing during the haze episode.

- Clean days: agricultural 84% and nonagricultural 16%
- Haze days: nonagricultural approximately 90%
- Haze development stage: the contribution from fossil fuels increased from 34% (Jan 25−26) to 59% (Jan 26−27) and to 81% (Jan 27−28), whereas the contribution of NH_3 slip (power plants) decreased from 48% (Jan 25−26) to 34% (Jan 26−27) and to 18% (Jan 27−28)

Conclusion

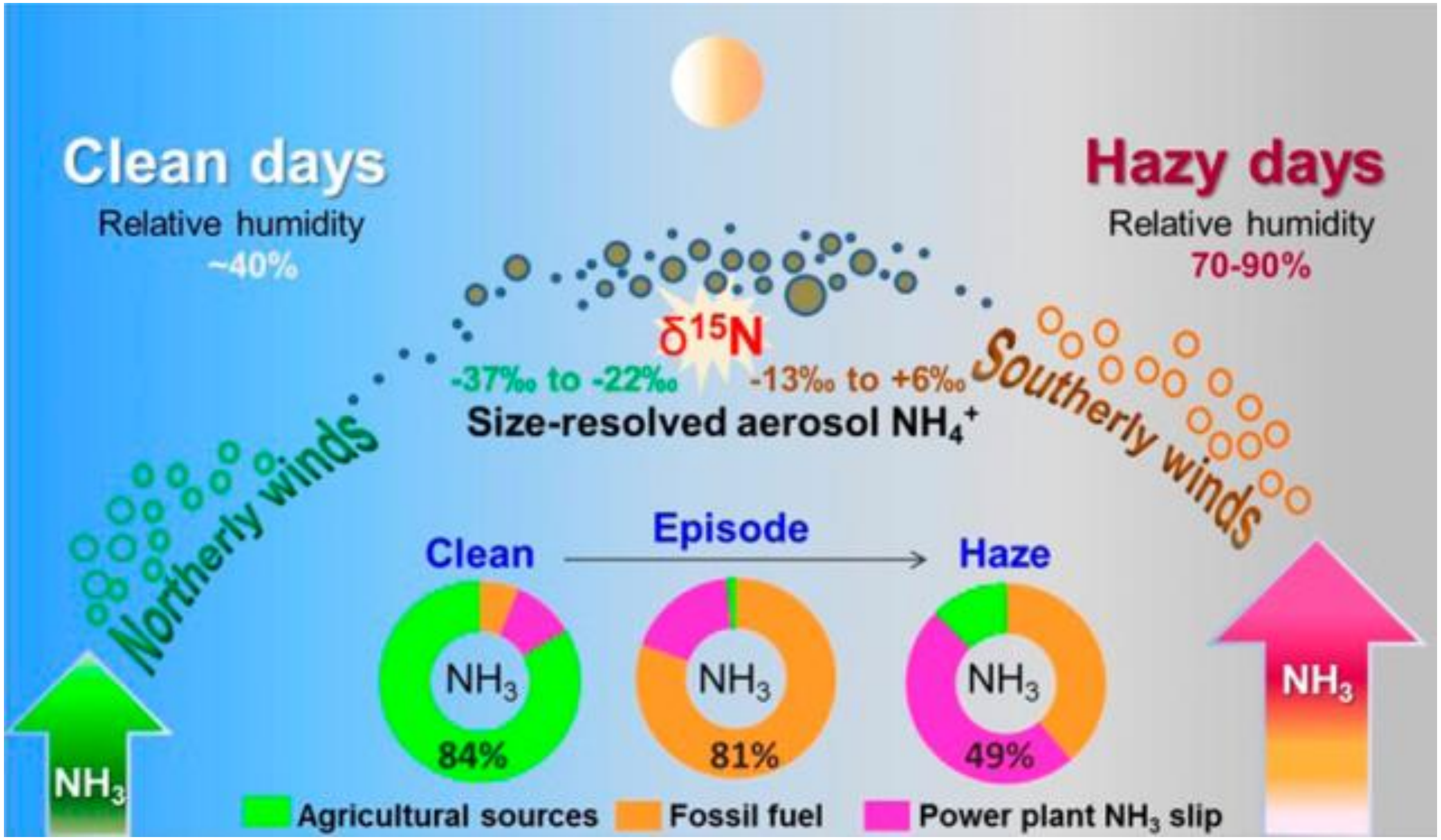


Fig. 11. NH_3 Source diagrammatic sketch

- This study presents the first isotopic evidence that fossil fuel emissions and NH_3 slip from power plants are more important than agricultural sources during haze pollution periods in urban Beijing. In contrast, agricultural sources are the major sources of NH_3 in the air during clean days when the WS is higher and the air transport is from the SW of Beijing.

Conclusion

- The ambient NH_3 that formed NH_4^+ aerosols during haze periods in Beijing was sourced at the local, urban scale rather than at the regional scale.
- In urban environments, vehicles equipped with three-way catalytic converters can be an important NH_3 source. In addition to being emitted form automobiles, NH_3 is emitted as "fuel NH_3 " from electrical generating units (EGUs) and as "NH_3 slip" from EGUs equipped with SCR and selective noncatalytic NO_x reduction (SNCR) technologies.
- The use of stable isotopes of NH_4^+ provides a powerful method to evaluate the relative contribution of fossil fuel-related and agricultural sources, allowing for better targeting of NH_3 reduction.

Thank you for listening!
Questions and suggestions are welcome.