

Comments and Responses

Referee #1

Comments: In the manuscript, the study reported the first observations of $\text{PM}_{2.5}\text{-}\Delta^{17}\text{O}(\text{SO}_4^{2-})$ during haze events from October 2014 to January 2015 in Beijing, and use them to quantify the relative importance of different sulfate formation pathways, which is quite interesting and significant. But there are some mistakes and problem:

Responses: Thanks for your comments. We reply to your comments one by one as follows:

1. **Q:** There are some typesetting in the manuscript: such as: (1) line 1: should be sulfate production; (2) line 25: formationwith should be formation with;(3) line 30: should be NO_2 in; (4) line 84: should be round 20m; (5) line 84:should be round 60m; line 243: should be Figure 1a shows;

A: Thanks for noticing these mistakes. Some typesetting problems occurred when we used another computer to edit and upload the document in final. We corrected all the typesetting problems you mentioned. The corrected typesetting is respectively in line 1 for “sulfate production”, in line 30 for “ NO_2 in”, in line 87 for “around 20 m”, in line 87 for “around 60 km” and in line 248 for “Figure 1a shows”.

2. **Q:** Sampling site locate at a country-site (is not downtown), round 60 km northeast of downtown, and so that it is not perfect to know isotopic constraints on heterogeneous sulfate production in Beijing haze, the reason is that downtown has more information about the automobile exhaust emission, enterprise emission, and resident emission and so on. Furthermore, the sampling site is close to Yanxi lake, so that it has been probably affected by cloud liquid water content;

A: Thanks for your comments. For your concern about the sampling site, we do agree that it would be better if the sampling site was in downtown area. However, we think our sampling site is a representative site of Beijing haze for the following reasons:

(1) High concentrations of both secondary and primary air pollutants were observed at our sampling site. Figure 1 in the main text shows that 12h-averaged SO_4^{2-} concentrations at our sampling site can be up to $56.4 \mu\text{g m}^{-3}$. The 1h-averaged concentrations of primary air pollutants such as CO at our sampling site can be as high as 4025 ppb (Fig. C1), and shows similar trends and range with observations at the nearest station (Huairou station) set for estimating urban environment by Beijing Municipal Environmental Monitoring Center (BJMEMC, <http://zx.bjmemc.com.cn/getAqiList.shtml?timestamp=1513326206397>). For other air pollutants that were not observed at our sampling site but observed at BJMEMC stations (e.g., $\text{PM}_{2.5}$, SO_2 and NO_2), the comparisons between observations at Huairou station and a downtown site (Tiantan station, Fig. C2) show that the variations and range of $\text{PM}_{2.5}$ and SO_2 are very similar in these two sites. We also note that the peak concentrations of CO and NO_2 at or around our sampling site are generally lower than those observed at Tiantan station, so we do agree as you comment “downtown has more information about the automobile exhaust emission, enterprise emission, and resident emission and so on”. However, our sampling site is suggested to be a suburban site based on the above comparisons and other studies (Wang et al., 2016; Wang et al., 2017; Li

et al., 2017; Tong et al., 2015).

(2) Our sampling site is usually downwind of downtown Beijing during polluted days (PD, $PM_{2.5} > 75 \mu\text{g m}^{-3}$). Backward trajectory analysis shows that air masses from downtown Beijing can reach our sampling site within a day during PD (Fig. C3), which suggests our sampling site can reflect the main signal of downtown Beijing, especially considering the lifetime of sulfate which is 4–5 days (Alexander et al., 2012).

(3) The total area of Beijing is around 16411 km^2 while its urban area is only about 1401 km^2 . As haze in Beijing and North China Plain is a regional phenomenon (Zheng et al., 2015), it's truly important to sample at downtown area, however, it may be also necessary to sample at suburban area to have a more comprehensive understanding of Beijing haze.

(4) Our sampling site at UCAS (University of the Chinese Academy of Sciences) is a supersite set by HOPE-J³A (Haze Observation Project Especially for Jing-Jin-Ji Area). Other observations at this site have been used to discuss scientific problems in Beijing haze in previous studies, e.g., (Zhang et al., 2017; Xu et al., 2016; Chen et al., 2015; Tong et al., 2015). Especially, in the work of Tong et al. (2015), they found that the heterogeneous reaction efficiency from NO_2 to HONO is higher in suburban areas than urban areas. As our sampling site is the same as the suburban site in the work of Tong et al. (2015), we think our sampling site should be suitable, even though it may be not perfect, to discuss heterogeneous sulfate production in Beijing haze.

(5) It's true that our sampling site is close to Yanqi lake (Fig. C2). The linear distance from our sample site to the nearest edge of Yanqi lake is around 1 km and is around 3 km to the farthest edge of Yanqi lake. We note that it's difficult to give an accurate estimate of the influence of Yanqi lake on cloud liquid water in the present study as the formation of cloud is quite complicated. However, as the area of Yanqi lake is about 2.3 km^2 , the area fraction of Yanqi lake to the nearest 3 km circular area from our sample site is about 8 % ($=2.3/(3.14 \times 3^2)$), which is small. So that we expect its influence on cloud liquid water is probably small, too, especially in winter when the lake is frozen.

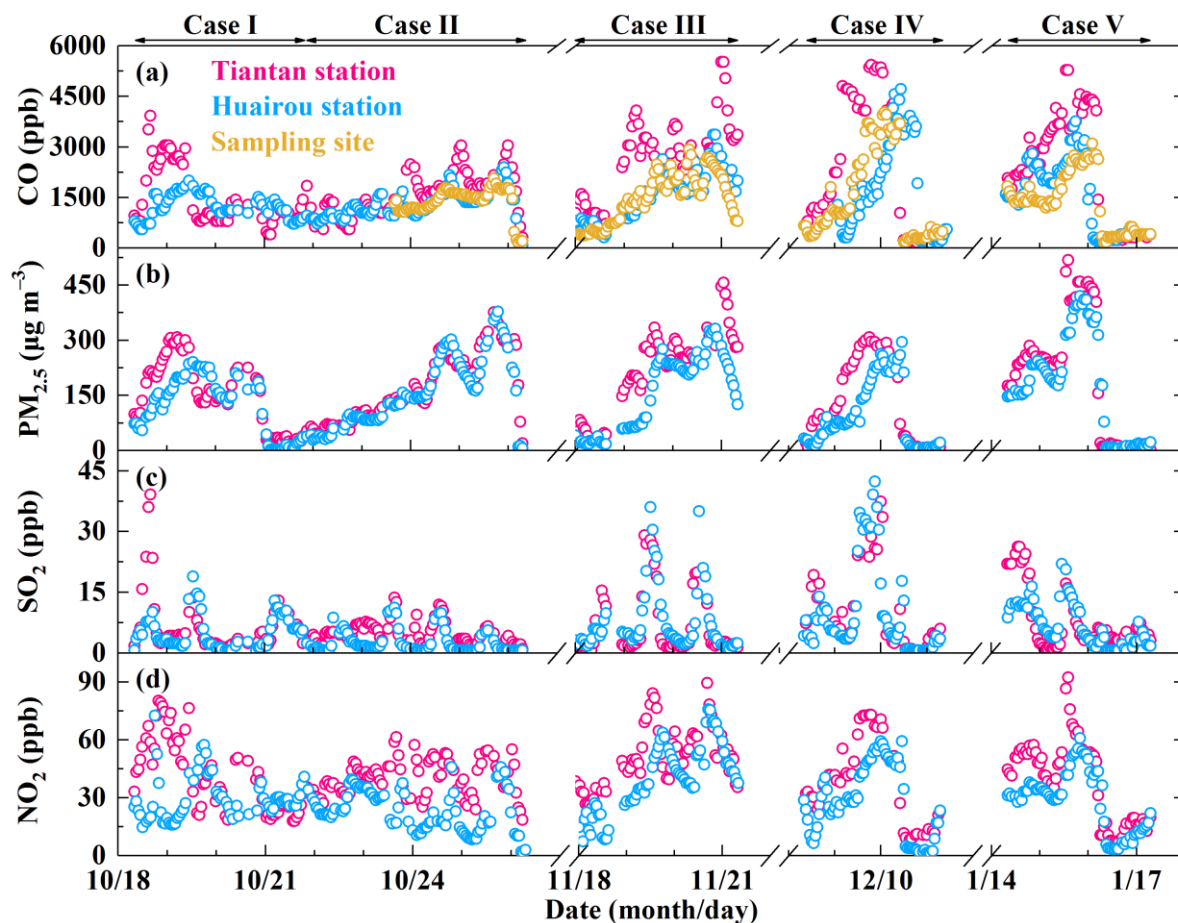


Figure C1. Comparisons of air pollutants observed at our sampling site with that observed at Huairou station and Tiantan station. The Huairou station is the nearest station (to ours) set for estimating urban environment by Beijing Municipal Environmental Monitoring Center (BJMEMC), while the Tiantan station is located in the center of downtown Beijing (please refer to Fig. C2 as below). The missing concentrations of CO at our sampling site are due to that our CO analyzer (EC9830B, Ecotech Inc., Australia) were taken away to be calibrated. Hourly concentrations of other air pollutants (e.g., PM_{2.5}, SO₂ and NO₂) were not observed at our sampling site but observed at BJMEMC stations.

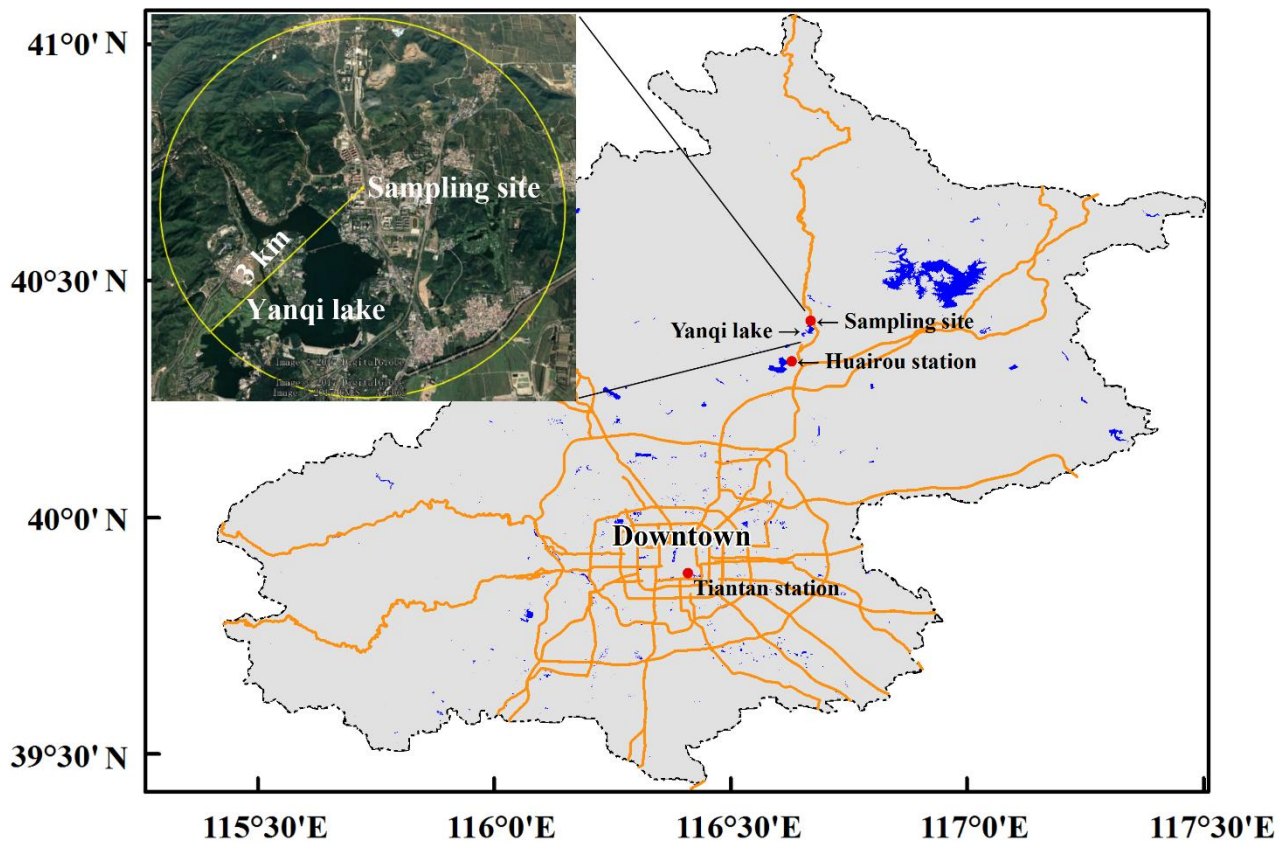


Figure C2. Map of our sampling site. The blue area on the base map represents rivers and lakes with a map scale of 1:1250000.

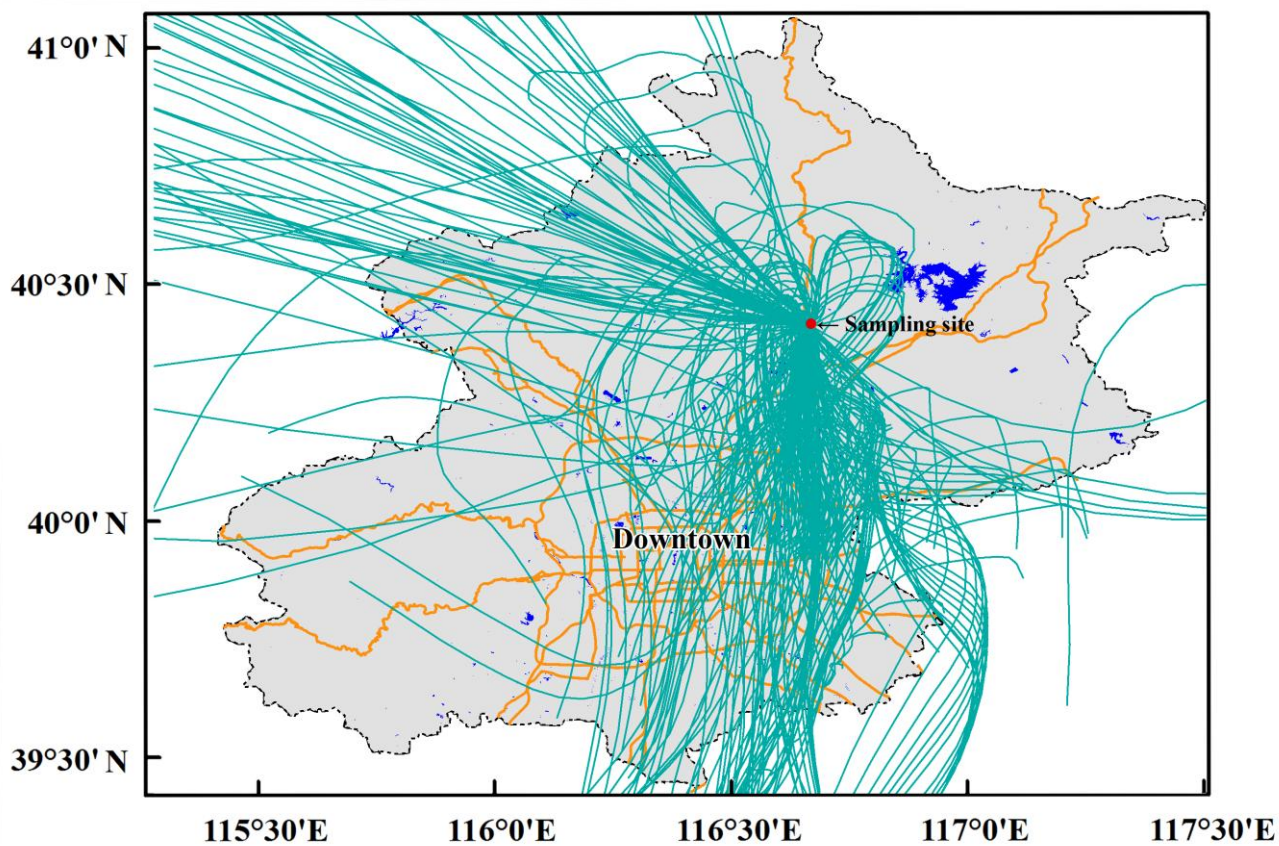


Figure C3. 1-day backward trajectories reaching our sampling site at each hour during our sampling time when $PM_{2.5} \geq 75 \mu g m^{-3}$.

3. **Q:** Method: As we know, these data are likely contaminated to various degrees by occluded nitrate isotope signal in the samples, so that we had better remove nitrate during the preparing the Ag_2SO_4 , but the manuscript has not removed the nitrate, which will effect on the sulfur isotope composition results;

A: Thanks for your comment. Actually, we removed NO_3^- before SO_4^{2-} being converted to Ag_2SO_4 . The preparation and measurements of $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ in the University of Washington have been well documented in previous studies (Geng et al., 2013; Chen et al., 2016; Alexander et al., 2012), thus we didn't describe the experimental procedures in detail in the former manuscript. Now, the description " SO_4^{2-} was separated from other anions (e.g., NO_3^-) by ion chromatography" is presented in lines 111–112.

4. **Q:** The manuscript should introduce name of laboratory, precision of the machine.

A: Thanks for your suggestions. The name of the laboratory where ions were measured now is added in lines 98–99 reading "[The measurements of ions were conducted in Anhui Province Key Laboratory of Polar Environment and Global Change in University of Science and Technology of China](#)". The description about precisions of ion measurements is added in lines 104–105 reading "[Typical analytical precision by our instrument is better than 10 % RSD \(relative standard deviation\) for all ions \(Chen et al., 2016\)](#)". The name of the laboratory where our $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ was measured now is added in lines 105–107 reading "[The preparation and measurements of \$\Delta^{17}\text{O}\(\text{SO}_4^{2-}\)\$ were conducted in Isolab \(<https://isolab.ess.washington.edu/isolab/>\) at the University of Washington, USA](#)". The precision is dependent on the instrument itself and the method. The description about precision of our $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ measurements (which includes the machine MAT253) now is added in lines 116–118 reading "[The precision of \$\Delta^{17}\text{O}\$ measurements in our method is \$\pm 0.3\$ ‰ based on replicate analysis of standards, which is consistent with previous studies \(Alexander et al., 2005; Sofen et al., 2014; Chen et al., 2016\)](#)".

References

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