Reply to the comments of Anonymous Referee #4

This is a nice study to quantify the contributions of different formation mechanisms on nitrate at urban and suburban sites by using an observation-constrained box model. The authors found the important source of nitrate from the downwards transport of residual layer at the urban site, and a VOCs-limited chemical regime for nitrate formation, the nitrate formation was different at the suburban site. The results have important implications for future mitigation of nitrate in this region. The manuscript is overall well written, and I only have several small comments.

Reply: We would like to thank the reviewer for the insightful comments, which help us in improving the quality of our work. Please find the responses to individual comments below.

1. The measurements at the urban and suburban sites were conducted in different years? Did the author compare the meteorological differences between 2018 and 2019? Are there any influences on your conclusions?

Reply: We thank the reviewer for the valuable suggestion. The measurements at the urban and suburban sites were conducted in 2018 and 2019, respectively. Generally, the meteorological factors have important influences on the nitrate pollution. We have compared the average values of wind speed (WS), relative humidity (RH) and temperature (*T*) in the sampling periods at the urban site and suburban site as shown in **Table S6** in the revised manuscript as follows. The average wind speeds at the urban and suburban sites were generally below 2 m s^{-1}, thus, we mainly focus on the local production which simulated by the box model. The RH, *T* and photolysis frequency were set as the observation data in the simulation, which represented the actual meteorological condition. The simulated results also demonstrate the influence of meteorological condition, and showed no influence on our conclusions.

Table S6. The concentrations of chemical components (average ± standard deviation) and meteorological parameters during the investigated periods at the GIG and Heshan sites

Site	GIG	Heshan
PM_1 (μg m^{-3})	41.7±23.1	40.6 ±15.5
Organic (μg m^{-3})	16.9±9.0	21.6 ± 9.0
SO_4^{2-} (μg m^{-3})	10.1±4.6	6.9 ± 1.8
NO_3^- (μg m^{-3})	6.1±5.8	3.9 ± 3.0
NH_4^+ (μg m^{-3})	5.0±3.0	3.5 ± 1.5
Cl^- (μg m^{-3})	0.6±0.54	0.8 ± 1.3
BC (μg m^{-3})	3.2±1.1	4.0 ± 1.6
WS (m/s)	1.9±0.9	1.6±0.7
RH (%)	76.2±14.9	59.5±14.3
T (°C)	23.0±2.6	23.2±3.2

2. The urban site is approximately 80 km from the suburban site. Could the authors provide the wind rose plots during the two years to see if there is transport between the two sites. Or the authors can compare the total PM concentrations in the same year to see if the episodes occurred during the same period. This will also affect the conclusion in this study.

Reply: We agree with your comment that regional transport is also important for nitrate pollution**.** We have compared the wind rose plots at the urban and suburban sites as shown in the following Figure R5.

The wind direction at the GIG site was mainly from the north, and the wind speed was frequently lower than 4 m s^{-1}. The wind direction at the Heshan site was mainly from north and northwest, and the wind speed was lower than 4 m s^{-1}. As GIG site is in the northeast of Heshan site, the transport between the two sites was weak from the results of wind rose plots.

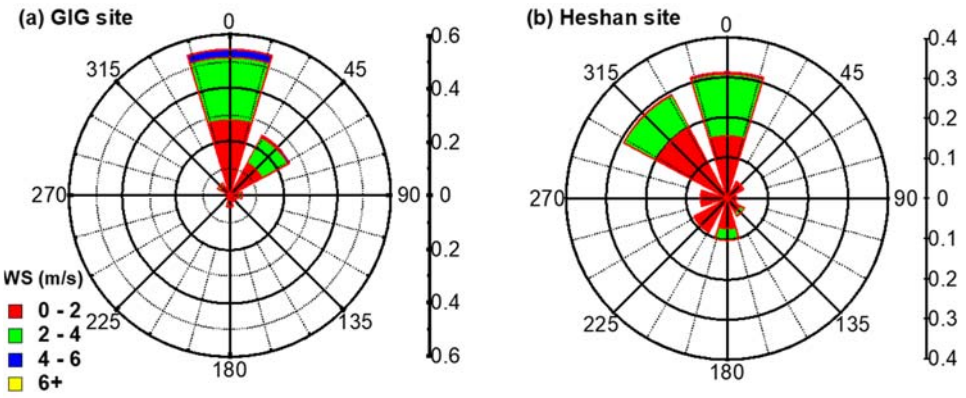

Figure R5. The wind rose plot at the urban (GIG) site and suburban (Heshan) site in the study periods.

3. “ammonia” in Figure 2 should be “ammonium”, same in Figure 3.

Reply: We have changed the legend “ammonia” to **“ammonium”** in **Figure 2 and Figure 3** in the revised manuscript as follows.

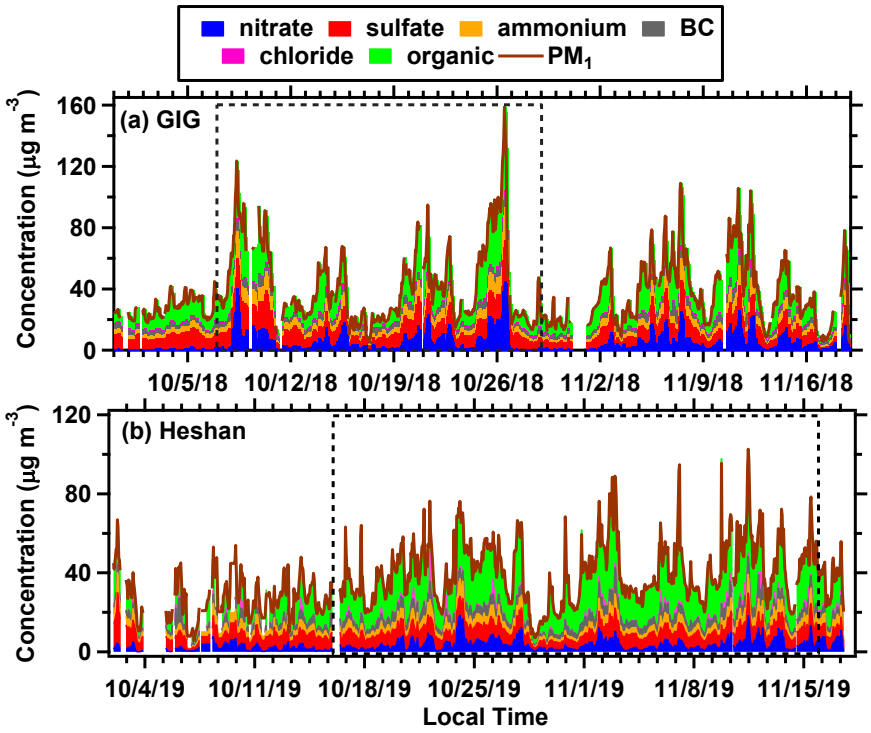

Figure 2. Temporal variations of the mass concentration of the major chemical components in PM_1 including nitrate (NO_3^-), sulfate (SO_4^{2-}), ammonium (NH_4^+), black carbon (BC), chloride (Cl^-) and organics at (a) GIG site and (b) Heshan site. The black dashed rectangle represents the investigated period which had complete set of data.

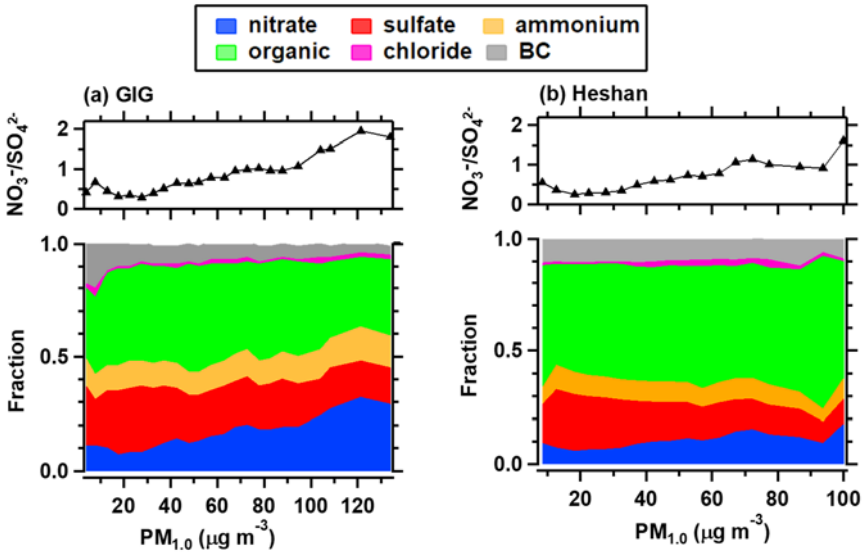

Figure 3. The mass concentration ratio of NO_3^-/SO_4^{2-} (top) and fractions of major chemical components (bottom) in PM_1 at (a) GIG site and (b) Heshan site.