Response to the Reviewers' Comments and Suggestions — egusphere- 2025-1432

Dear editorial board of Atmospheric Chemistry and Physics,

We sincerely thank the reviewers for their careful reading and constructive suggestions. We have thoroughly considered each point, and our responses and planned revisions are detailed below. Please find below our point-by-point responses (blue) to each reviewer's comments (black).

Sincerely yours,

Dr. Chongguo Tian

Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai, 264003, China

Email: cgtian@yic.ac.cn

Tel: 86-535-2109160

Fax: 86-535-2109000

RC1: 'Comment on egusphere-2025-1432', Anonymous Referee#1, 08 Jan 2026 reply

1. The parameter t is introduced too briefly in the methodology. Is t computed from 0 until NH_3 and NH_4^+ reach equilibrium? The influence of the evolution of t on the model output is not made clear.

Response: Thank you for this comment. In the model, t represents the iteration step number, not continuous time. The model uses a discretized iterative approach to simulate the synchronous changes in NH_3 and NH_4^+ in the atmosphere, including transformation, deposition, and isotopic composition. Each iteration represents one time step (without a specific physical duration), and the process is repeated until the system reaches a steady state (i.e., when the mass fractions and isotopic compositions of NH_3 and NH_4^+ no longer change significantly).

In the lines 113-115, we have clarified: The superscript t denotes the iteration index, starting from t=1, and does not represent a specific physical duration. The model is iterated to steady state, and the resulting steady-state $\delta^{15}N_{4a\text{-}3s}$ is taken as the model output.

2. It is unclear how the $[NH_{3d}]^t$ and $[NH_{4d}^+]^t$ terms in Eq. (6) are used to calculate $\delta^{15}N_{4a\text{-}3s}$.

Response: Thank you for this comment. $[NH_{3d}]^t$ and $[NH_{4d}^+]^t$ represent the mass fractions of NH_3 and NH_4^+ deposited at iteration step t. They are used in the model for isotopic mass balance calculations (Eqs. 8-9), ensuring that deposition does not affect the $\delta^{15}N$ of the remaining NH_x in the atmosphere. Specifically:

- The isotopic composition of the deposited fraction is assumed to be the same as that in the atmosphere at that step (Eq. 9);

- The isotopic composition of the remaining atmospheric NH_x is updated via Eq. (10);
- Finally, $\delta^{15}N_{4a-3s}$ is calculated using Eq. (4).

We have added a clearer description of this computational flow in '2.1 Model Development' (lines 90-151).

3. Eq. (10) assumes that the $\delta^{15}N$ of deposition equals that of the atmosphere. How is this assumption carried into the calculation of $\delta^{15}N_{4a-3s}$ in Eq. (4)? Also, should NH_4 in the equation read NH_4^+?

Response: Thank you for this comment. Eq. (10) in the original version has been changed to Eq. (9) in the revised manuscript.

(1) The assumption in Eq. (9) is a common simplification that deposition does not cause isotopic fractionation (only gas–particle conversion fractionation is considered). This allows the deposition process to affect only the mass fractions of NH_x without additionally altering its isotopic composition, thus simplifying the model. The impact of this assumption has been assessed through sensitivity analysis (showing minor sensitivity to D_3 and D_4).

(2) You are correct; 'NH_4' should be 'NH_4^+' throughout. We will consistently use 'NH_4^+' in the revised text.

Eq. (9) does not directly modify Eq. (4); it constrains the isotope composition of the deposited fractions in the iterative mass-balance step, which in turn affects the atmospheric NH_x pool, *f*, and $\delta^{15}N\text{-}NH_x$ that are later used in Eq. (4)

We have added a clearer description of this computational flow in lines 123-151.

4. How is the $\delta^{15}N\text{-}NH_x$ value obtained from Eq. (8) passed to Eq. (4) to compute $\delta^{15}N\text{-}NH_4^+$ or $\delta^{15}N\text{-}NH_{3s}$, which is later set to 0?

Response: Thank you for this comment. Eq. (8) in the original version has been changed to Eq. (10) in the revised manuscript.

Eq. (10) yields the isotopic composition of total atmospheric NH_x at the current iteration step. It serves two purposes:

(1) it is used as the atmospheric NH_x isotopic state for the next iteration step;

(2) it is directly substituted into Eq. (4) at the current step to calculate $\delta^{15}N_{4a-3s}$.

By contrast, $\delta^{15}N\text{-}NH_{3s}$ is a prescribed value, set to 0‰ as a reference in this study, rather than being calculated from Eq. (10).

We have clarified this numerical transfer process in the iterative procedure described on lines 123–151.

5. In Eq. (6) the $[NH_{3a}]^t$ is $[NH_{3a}]^{t-1}$ times 1-G_4-D_3. Here, Are G_4 and D_3 rates or ratios?

Response: Thank you for this helpful comment. In Eq. (6), G_4 and D_3 are ratios

(dimensionless fractions) rather than kinetic rates with time units. Specifically, G_4 represents the fraction of converted to $[NH_{4a}^+]^t$ during one iteration step, and D_3 represents the fraction of $[NH_{3a}]^{t-1}$ removed by deposition during the same iteration step. Therefore, $[NH_{3a}]^t$ is calculated as the remaining fraction of $[NH_{3a}]^{t-1}$, i.e., $(1-G_4-D_3)[NH_{3a}]^{t-1}$. We have revised the manuscript to replace 'rate' with 'ratio' to avoid ambiguity.

We have explicitly stated their dimensionless nature and physical meaning in lines 111–112: where G_4, D_3 and D_4 represent the transformation ratio of NH_3 to NH_4^+, and the deposition ratio of NH_3 and the deposition ratio of NH_4^+, respectively.

6. Line 146 states that $G_4/D_3 \approx 3$ %. The subsequent sensitivity tests set G_4 to 0.5–2 × D_3, which spans one to two orders of magnitude above this ratio.

Response: We appreciate you pointing out this potential confusion. The statement '$G_4/D_3 \approx 3\%$' in the original text was a typographical error, and it will be removed in the revised manuscript. In the Supporting Information (SI), we synthesized findings from numerous previous studies to establish the parameter settings of $G_4 = 0.5\text{-}2 \times D_3$. This range was chosen to cover a wide spectrum of scenarios—from low acidic gas conditions (e.g., marine background) to high acidic gas conditions (e.g., urban pollution)—thereby extending the analysis to more extreme pollution scenarios.

In the lines 167-169, we have corrected: To evaluate the impact of varying acid-gas concentrations, we established three G_4 levels: $0.5\times D_3$ (low acid-gas content), $1.0\times D_3$ (moderate acid-gas content), and $2.0\times D_3$ (high acid-gas content).

7. In Fig. 2, which input parameters are used for the sensitivity tests? Are they the D_3, D_4, G_4, T, and ξ values shown in the figure? ξ and the molar fraction of NH_4^+/NH_x appear to be identical, so how should these parameters be assigned?

Response: Thank you for your comment. The sensitivity analysis was conducted using the independent model inputs D_3, D_4, G_4, and T. ξ denotes the molar fraction of NH_4^+ in NH_x, ($\xi = f = [NH_4^+]/[NH_x]$). In the revised manuscript, we will use the unified notation f throughout and remove ξ to avoid confusion. In practical implementation, however, f was not assigned directly; rather, it was calculated from the simulated atmospheric mass fractions of NH_3 and NH_4^+ at each iteration step using Eq. (7). Therefore, the actual independent inputs in the sensitivity test are D_3, D_4, G_4, and T, whereas f is an internally updated state variable derived from these inputs.

In the lines 233-234, we have clarified: The sensitivity coefficients of each input parameters (D_3, D_4, G_4, and T) to the $\delta^{15}N_{4a\text{-}3s}$ values at 20°C were calculated by using Eq. (11) across the six model scenarios (see Fig. 2).

8. Section 3.4 uses several datasets without citation, e.g. the $\delta^{14}N$ of NH_3 emission sources and the NH_4^+ fraction of NH_x for 2013 and 2021.

Response: Thank you for pointing this out. We agree that all observational datasets used in Section 3.4 should be explicitly cited. In the lines 300-302, we have corrected:

Four main types of NH_3 emission sources, including fertilizer use (−25.21 ± 9.43 ‰), livestock waste (−16.14 ± 7.98 ‰), vehicle exhaust (+6.62 ± 1.89 ‰), and NH3 slip (−7.12 ± 7.62 ‰) (Table S3), were considered in the model.

Table S3. Four main types of NH_3 emission sources in the Yellow River Delta.

Sources	Average	SD	Reference
Livestock waste	−16.14‰	7.98	(Freyer, 1978; Heaton, 1987; David Felix et al., 2013; Chang et al., 2016; Bhattarai et al., 2020; Ti et al., 2018)
Vehicle exhaust	+6.62‰	1.89	(Walters et al., 2020; Song et al., 2021)
NH_3 slip	−7.13‰	7.62	(David Felix et al., 2013; Bhattarai et al., 2020; Chang et al., 2022)
Fertilizer use	−25.21‰	9.43	(David Felix et al., 2013) (Chang et al., 2016; Bhattarai et al., 2020; Ti et al., 2018; Ti et al., 2019)

In the lines 412-415, we have corrected: In the MS1 case, the difference in source contributions in 2013 was significantly greater than that in 2021, which was mainly related to the change in the atmospheric f value (Zong et al., 2023). Specifically, the f value decreased from 71.9% in 2013 to 41.6% in 2021.

RC2: 'Comment on egusphere-2025-1432', Anonymous Referee #2, 24 Feb 2026 reply

This manuscript by Tian et al. presents a modeling study of isotopic fractionation effect between NH_4^+ and emitted NH_3, by considering the N deposition process (as NH_4). They corrected the partitioning of 15N between NH_4^+ and NH_3 based on modeling results from the computational quantum chemistry method, suggesting that ignoring the NH_4^+ deposition process could cause isotopic bias up to 10.7%. With the newly established method, they reevaluated the source for atmospheric NH_4 in the region of the Yellow River Delta. Overall, this work is interesting, but (1) the current study was mostly based on the ideal quantum chemistry method, without experimental data to validate. In addition, (2) radical reaction involved in the atmospheric aerosol processes is not considered, which may further complicate the isotope effect during the NH_3-to-NH_4 process. On other hand, (3) the current analysis of observations from Yellow River Delta may not be convincing enough for the application in broader scenarios, considering different meteorological and precipitation-driven scavenging effect of atmospheric NH_3. To conclude, I think the current study does not meet the requirement for publication at ACP as it is presented now.

Response and Revisions: These comments mainly consist of three questions, which we have numbered as follows:

1. Regarding the comment: ‘the current study was mostly based on the ideal quantum chemistry method, without experimental data to validate.’

Response and Revisions: Thank you for your comment. We fully agree on the importance of experimental validation for modeling studies. Previous studies were based on the 'closed system' assumption, ignoring the impact of atmospheric deposition of NH_3 and NH_4^+ on $\delta^{15}N\text{-}NH_x$. The primary contribution of this work lies in incorporating the atmospheric NH_x deposition process into the nitrogen isotope fractionation model for the first time, revealing that traditional simplified approaches (considering only gas-particle equilibrium fractionation) could lead to non-negligible biases in source apportionment. The actual verification of the relevant parameters in this model needs to take into account the influence of multiple factors such as different surface types, different weather conditions, and different atmospheric composition. This is a systematic project that cannot be validated experimentally by an article. Moreover, precisely because of this, we have conducted multi-scenario simulations and parameter sensitivity analyses based on the idealized quantum chemical method. We have systematically evaluated the variation patterns of $\delta^{15}N_{4a\text{-}3s}$ under different environmental conditions (such as the content of acidic gases, the type of underlying surface, and temperature), and constructed a fitting equation that can be used for actual source analysis. In addition, beyond the original validation using the Yellow River Delta case, we have now included an additional case study from Changsha to further evaluate the applicability of the fitted equation under a different environmental setting. Compared with the Yellow River Delta, which represents a coastal/background-influenced environment, Changsha represents a more urbanized inland atmosphere with different NH_3 source structures and chemical conditions. The inclusion of this additional case provides further support that the fitted equation is applicable across different environmental gradients rather than only under a single regional condition. Future work will further refine these model parameters.

To address the comment, we added the following sentences ('This is a systematic project that cannot be validated experimentally by an article. So, here we constructed six simulation scenarios to assess the extent to which changes in the three parameters affected the simulation results of $\delta^{15}N_{4a\text{-}3s}$ as listed in Table 1.', lines 157–159) and ('The key parameters in this model (e.g., D_3, D_4, and G_4) are currently set based on a synthesis of literature values. These parameters exhibit significant spatial heterogeneity and temporal dynamics, influenced by factors such as land surface type, meteorological conditions, and atmospheric chemical composition. Future work requires multi-site, multi-season synchronous observations combining micrometeorological methods and isotopic measurements to directly obtain parameter values under different environments. This will enhance the model's empirical foundation and regional applicability.' lines 459–464) in the revised manuscript. In addition, we have supplemented the manuscript with the Changsha case as an additional application example to further verify the robustness and broader applicability of the fitted equation.

2. Regarding the comment: 'radical reaction involved in the atmospheric aerosol processes is not considered, which may further complicate the isotope effect during the NH_3-to-NH_4^+ process...'

Response and Revisions: Thank you for your comment. We acknowledge that the

process of NH_3 converting to NH_4^+ in the atmosphere involves multiple chemical mechanisms. Currently, the isotope-based source apportionment models can be regarded as a 'macroscopic framework' based on mass balance, and the chemical mechanisms have not been systematically considered within a single system. This study is also based on this framework, focusing on the impact of atmospheric deposition processes on the isotopic mass balance, rather than detailed simulation of the chemical transformation pathways. The continuous improvement of these understandings provides a foundation for subsequently incorporating isotopic information into more complex chemical mechanism models.

To address the comment, we added the following sentences (It should be noted that the model primarily addresses the isotopic mass balance shift induced by deposition processes, rather than detailed chemical mechanisms. Line 83-85) in the revised manuscript.

3. Regarding the comment: 'The current analysis of observations from Yellow River Delta may not be convincing enough... considering different meteorological and precipitation-driven scavenging effects.'

Response and Revisions: Thank you for your comment. As mentioned earlier, the atmospheric deposition effect of NH_x on isotope values varies with changes in environmental conditions. With environmental changes, many practical cases can be formed. We chose the Yellow River Delta as a case study because this site is a typical background area with flat terrain and a single pollution source, which conforms to the model MS1 scenario (low acidic gases, flat underlying surface).

To address the limitation of relying on a single case, we have added an additional case from Changsha (lines 357-435). Compared with the Yellow River Delta, Changsha represents a typical urban inland environment with relatively flat terrain, but higher acidic gas levels and more complex anthropogenic influences. According to the scenario classification framework proposed in this study, Changsha is best categorized as the MS5 scenario. Therefore, the fitted equation developed for the MS5 scenario was applied to calculate $\delta^{15}N_{4a\text{-}3s}$, in order to evaluate the applicability of the method in a typical urban environment. By adding the Changsha case in addition to the original Yellow River Delta case, the revised manuscript now tests the proposed method under two contrasting environmental settings, namely a background/coastal-influenced environment and an urban/inland environment. This additional application improves the environmental representativeness of the analysis and further supports the broader applicability of the fitted equations.