We appreciate the reviewer for the useful comments. In the following, original reviewer comments are shown in black, our point-by-point responses are shown in blue, and updates on the manuscript are highlighted in yellow.

Reviewer: 1

General comments:

The authors investigate the transport and transformation of atmospheric reactive nitrogen (Nr), specifically particulate ammonium (pNH_4^+) and nitrate (pNO_3^-), in a mountain forest environment at Xitou, Taiwan, using size-resolved isotope measurements combined with Bayesian modeling. Samples were collected over a one-week period from April 7 to April 14, 2021, with daytime (09:00–17:00 LT) and nighttime (18:00–06:00 LT) samples analyzed separately. During this period, approximately 26 hours of fog occurred under stagnant atmospheric conditions.

Size-segregated isotope analyses were conducted on these diurnally collected filter samples, although such measurements are technically challenging because of low particle concentrations. The $\delta^{15}N$ and $\delta^{18}O$ isotope measurements were performed using gas chromatography–isotope ratio mass spectrometry (GC-IRMS), and the resulting isotope data were used to infer source contributions and nitrate formation pathways through Bayesian analysis.

Based on the observation that both $\delta^{15}N$–NH_4^+ and $\delta^{15}N$–NO_3^- decreased during the extended fog event, the authors suggest that the decreasing was associated with fog processes. They further suggest that urban plumes retain O_3-driven oxidation signatures, whereas nitrate formed locally in the mountain environment shows greater influence from RO_2-involved chemistry and biogenic contributions. Bayesian modeling further indicates that 50–83% of NH_3 emissions are combustion-related, while 42–95% of pNO_3^- is attributed to RO_2-initiated oxidation during daytime and 6–84% to heterogeneous reactions at night.

R1C1:

However, in comparison with previous studies conducted at the same site and in the same region and other locations worldwide (Fig S9, S10), Lee et al. (2025) largely corroborates earlier conclusions regarding urban influence, fog/cloud processing, and secondary oxidation involving RO_2/O_3 and isotopic dilution during transport but provides limited additional mechanistic insight.

Response:

We agree with the reviewer that additional mechanistic insight would be needed when comparing with earlier datasets. This part was updated in section 3.3.1 (Lines 241−248) and 3.4.2 (Lines 363−373) of the revised manuscript as follows:

> (Lines 241−248) "The daily concentration-weighted $\delta^{15}N$-NH_4^+ values at the Xitou site ranged from 6.31‰ to 14.69‰, with an average of 10.95 ± 2.76‰ (Fig. 2f, calculation details in Supplementary Description S5). These results are consistent with previous winter observations at this site (−3.7‰ to 21.39‰, with an average of 11.95 ± 2.65‰) (Chen et al., 2022). As shown in Fig. S5, these values fall between those typical of urban-influenced environments (19.6‰) and remote/forest sites (~5.6‰), reflecting the mixed-source characteristics of Xitou (Chen et al., 2022; Kawashima et al., 2023; Hall et al.,

2016; Kundu et al., 2010; Moore, 1977; Proemse et al., 2012; Savard et al., 2017; Ti et al., 2018; Walters et al., 2022). The isotopic signature is particularly comparable to other semi-rural receptor sites in East Asia that receive diluted urban plumes mixed with regional agricultural background."

(Lines 363−373) "The daily concentration-weighted $\delta^{18}O\text{-}NO_3^-$ ranged from 30.98 to 73.27‰, with an average value of 51.82±16.47‰ (Fig. 2h). Similar to $\delta^{15}N\text{-}NO_3^-$, these values align with measurements from other mountain regions such as 10.8−92.4‰ at Mt. Lulin (Guha et al., 2017) and 64.71±11.52‰ at the Himalayan-Tibetan Plateau (Lin et al., 2021), but are lower than previous winter observations (72.66±3.42‰) (Chen et al., 2022), as illustrated in Fig. S11. In contrast, $\delta^{18}O\text{-}NO_3^-$ at urban sites such as Changchun (68.16±9.52‰) and Beijing (83.8±13.4‰) are substantially higher, consistent with O_3-dominated oxidation under polluted conditions. The relatively lower $\delta^{18}O\text{-}NO_3^-$ values at Xitou and other mountain sites suggest that RO_2-initiated pathways contribute more substantially to nitrate formation under less-polluted conditions. A sharp decrease in $\delta^{18}O\text{-}NO_3^-$ from 70.44‰ (18D) to 33.81‰ (18N and 19D) occurred during the fog, coinciding with $\delta^{15}N\text{-}NO_3^-$ depletion. This shift from O_3- to RO_2-dominated oxidation, is likely driven by stagnant winds, suppressed urban input, and enhanced local aqueous-phase chemistry under high RH."

R1C2: The isotopic effects induced by fog/cloud aqueous-phase processing and those associated with long-range transport act in the same direction, making it difficult to disentangle their respective contributions based on the presented data.

Response: We appreciate the reviewer's point regarding the potential overlap between transport-related isotopic shifts and those induced by fog processing. We have revised the manuscript to clarify these mechanisms and address the terminology used.

For the terminology, we would like to clarify that the term "long-range transport" was used imprecisely in the original manuscript to describe the movement of air plumes from urban areas to our sampling site via upslope valley winds and sea breezes. We acknowledge that this does not align with the standard atmospheric definition of long-range transport, which typically implies distances of hundreds to thousands of kilometers. We have corrected this terminology throughout the revised manuscript.

During transport of urban air plumes, particles are expected to carry relatively elevated $\delta^{15}N$ signatures, reflecting their combustion-related origin. As the plume travels toward the site, ongoing gas-particle partitioning progressively depletes the heavier isotopes from the gas phase (NOx and NH_3), causing the $\delta^{15}N$ of both gas and particle phases to decline over transport distance. During fog events, two concurrent processes likely contribute to lower $\delta^{15}N$ values in pNH_4^+ and pNO_3^-. First, weak wind conditions suppress the advection of urban-influenced air with higher $\delta^{15}N$, reducing the contribution of combustion-derived nitrogen. Second, hygroscopic growth and wet deposition of existing particles drive the uptake of ambient NOx and NH_3 into the particle phase to maintain ionic charge balance. These gases carry relatively low $\delta^{15}N$ values, reflecting (1) their partly agricultural origin, or (2) the isotopic fractionation they have already undergone during transport. Their incorporation into the particle phase, therefore, further lowers the bulk $\delta^{15}N$ of pNH_4^+ and pNO_3^-. We acknowledge that, given the current dataset, the relative contributions of these two processes cannot be quantitatively

separated. Targeted laboratory studies on the isotopic effects of aqueous-phase reactions involving pNH_4^+ and pNO_3^- will be necessary to disentangle these mechanisms in future work. This part was updated in section 3.3.1 in the revised manuscript (Lines 251−256) as follows:

> (Lines 251−256) "[…] This decline of $\delta^{15}N$ during the fog likely results from three concurrent processes under stagnant conditions. First, stagnant conditions suppressed the transport of $\delta^{15}N$-enriched urban plumes from nearby source regions. Second, continuous exchange between gas-phase NH_3 and pNH_4^+ shifts the particle phase toward the signature of the local NH_3 pool, which is depleted in $\delta^{15}N$ due to agricultural volatilization. Furthermore, wet deposition during fog may remove ^{15}N-enriched particles, forcing the remaining pNH_4^+ to re-equilibrate with an increasingly $\delta^{15}N$-depleted gas phase. […]"

R1C3: Furthermore, the Bayesian source apportionment using MixSIAR relies on multiple layers of assumptions, including (1) the recalculation of $\delta^{15}N$–NH_3 from particulate NH_4^+ based on assumed fractionation factors ($\varepsilon(NH_3–NH_4^+)$), temperature dependence, gas–particle equilibrium, and the approximation of an open systems equilibrium, and (2) the selection of source endmember isotope signatures. Consequently, the posterior distributions are broad and show substantial overlap, between clear & foggy conditions, during both daytime & nighttime (Fig. 5 (b)). Although the modeling framework is internally consistent, it does not yield unique or well-constrained source attribution or oxidation pathway estimates.

Response: We thank the reviewer for this critical point. The influences of (1) temperature, (2) gas-particle equilibrium, and (3) the assumption of equilibrium in open systems on $\varepsilon(NH_3–NH_4^+)$ were discussed step by step as follows:

First, the influence of temperature on $\varepsilon(NH_3–NH_4^+)$ was estimated using an empirical relationship as follows (Kawashima et al., 2023):

$$\varepsilon_{\left(NH_4^+-NH_3\right)} = \frac{12.4678\times 1000}{\left(T+273.15\right)} - 7.6694,$$

where T represents temperature in °C. Since the temperature measured in Xitou ranged from 10−30°C, the resulting differences in $\varepsilon(NH_3–NH_4^+)$ ranged from 36.36 (at 10°C) to 33.46 (at 30°C), and the contribution of each emission source estimated by MixSIAR is shown as follows:

Contribution (%)	Fertilizer	Fossil Fuel	NH_3 slip	waste
ε ($NH_3–NH_4^+$) = 33 ‰	4.2 ± 3.2	66.4 ± 15.1	23.2 ± 18.3	5.2 ± 5
ε ($NH_3–NH_4^+$) = 37 ‰	4.6 ± 3.8	42.3 ± 18.7	46 ± 23	7.1 ± 6.1

The estimated contributions for fertilizer and waste at 10 and 30°C are similar. The most different part is the contribution from fossil fuel, which was estimated to decrease by ~ 20% at higher temperatures. In contrast, the contribution for NH_3 slip was estimated to increase by ~ 20% at higher temperatures.

Second, sensitivity tests on (1) nucleation with a kinetic isotope effect (KIE) of −28‰, (2) $NH_{3(aq)}/NH_{3(g)}$ chemical equilibrium during condensation (equilibrium isotope effect (EIE) of 4 ± 3‰), and (3) $NH_4^+{}_{(aq)}/NH_{3(aq)}$ chemical equilibrium during condensation (EIE of 37 ± 4‰), were

added to address the influence of gas-particle equilibrium, in additional to the original single isotope fractionation reaction ($NH_4^+{}_{(aq/s)}/NH_{3(g)}$ chemical equilibrium during condensation (EIE of 33‰)) (Chang et al., 2025). It is possible to estimate the contribution of each reaction if we know the $\delta^{15}N$ of NH_3. Unfortunately, since the values of $\delta^{15}N$-NH_3 were not measured in this study, we relied on the estimation of fractionation factors to estimate $\delta^{15}N$-NH_3. Here, we assume each reaction contributed 100% and performed several sensitivity tests. The results are organized as follows:

Contribution (%)	Fertilizer	Fossil Fuel	NH_3 slip	waste
KIE (−28 ‰)	26.6 ± 34	12.6 ± 10.4	56.3 ± 35.4	4.6 ± 4.4
EIE (4 ‰)	1.8 ± 1.9	21.1 ± 15.3	74.3 ± 15.4	2.8 ± 2.9
EIE (33 ‰)	4.2 ± 3.2	66.4 ± 15.1	23.2 ± 18.3	5.2 ± 5
EIE (37 ‰)	4.6 ± 3.8	42.3 ± 18.7	46 ± 23	7.1 ± 6.1

When assuming equilibrium, contributions of fertilizer and waste range from 1.8 to 4.6%, and 2.8 to 7.1%, respectively. For fossil fuel and NH_3 slip, the contributions range from 21.1 to 66.4%, and 23.2 to 74.3%, respectively. However, when only considering KIE, the contribution of fertilizer increased to 26.6%, fossil fuel decreased to 12.6%, while the contribution of NH_3 slip and waste is still within the range of EIE effects. Despite this sensitivity, the combined contribution of fossil fuel and NH_3 slip remains dominant (88–95%) across all equilibrium scenarios (EIE = 4, 33, 37‰), suggesting that the qualitative conclusion that anthropogenic NH_3 sources dominate particulate ammonium at Xitou is robust to the choice of fractionation factor.

The KIE scenario (nucleation-dominated) represents a physically extreme end-member. At Xitou, NH_4^+ formation is dominated by condensation under open-system conditions, where $NH_{3(g)}$ is in continuous exchange with the gas phase rather than being irreversibly incorporated. Under such conditions, isotope fractionation approaches thermodynamic equilibrium (EIE) rather than kinetic control (KIE). The KIE result is therefore interpreted as an upper bound on uncertainty rather than a likely atmospheric condition. We acknowledge that the absolute partitioning between fossil fuel combustion and NH_3 slip remains uncertain under the current framework, and this limitation has been explicitly stated in section 3.3.2 of the revised manuscript (Lines 307−310).

(Lines 307−310) "[…] Despite the sensitivity of $\varepsilon_{NH_4^+-NH_3}$ to temperature (Kawashima et al., 2023) and gas−particle equilibrium (Chang et al., 2025), the estimated $\delta^{15}N$-$NH_3{}^0$ consistently yielded MixSIAR results in which combustion-related sources accounted for 88–95% of total NH_3 emission (see Supplementary Description S3 and Table S1). […]"

"**Description S3 Sensitivity analyses on $\varepsilon_{NH_4^+-NH_3}$**

The influence of (1) temperature, (2) gas−particle equilibrium, and (3) open-system equilibrium assumptions on $\varepsilon_{NH_4^+-NH_3}$ is discussed below.

Temperature dependence. The temperature sensitivity of $\varepsilon_{NH_4^+-NH_3}$ was estimated using the empirical relationship of Kawashima et al. (2023):

$$\varepsilon_{NH_4^+-NH_3} = \frac{12.4678\times 1000}{(T+273.15)} - 7.6694, \quad \text{(S1)}$$

where T represents temperature in °C. Over the observed temperature range at Xitou (10−30°C), $\varepsilon_{NH_4^+-NH_3}$ varied from 36.36‰ (at 10°C) to 33.46‰ (at 30°C). MixSIAR source contributions estimated at these two temperature extremes are summarized in Table S1 ($\varepsilon_{NH_4^+-NH_3}$ of 33‰ and 37‰). Contributions from fertilizer and waste were insensitive to temperature. The most notable temperature effect was on fossil fuel and NH_3 slip: the fossil fuel contribution decreased by ~ 20% at higher temperature, while NH_3 slip increased correspondingly by ~ 20%.

Gas−particle equilibrium fractionation pathways. In addition to the baseline fractionation reaction ($NH_4^+{}_{(aq/s)}/NH_{3(g)}$ equilibrium during condensation (equilibrium isotope effect (EIE) of 33‰), three alternative fractionation scenarios were tested: (1) nucleation with a kinetic isotope effect (KIE) of −28‰, (2) $NH_{3(aq)}/NH_{3(g)}$ equilibrium during condensation (EIE of 4 ± 3‰), and (3) $NH_4^+{}_{(aq)}/NH_{3(aq)}$ equilibrium during condensation (EIE = 37 ± 4‰) (Chang et al., 2025). Because $\delta^{15}N\text{-}NH_3$ was not directly measured in this study, $\delta^{15}N\text{-}NH_3$ was inferred from fractionation factors rather than observation. Each scenario was therefore evaluated independently under the assumption that it contributed 100% to NH_3 formation, and the resulting MixSIAR source contributions are reported in Table S1.

Under equilibrium fractionation scenarios (EIE = 4, 33, 37‰), contributions from fertilizer and waste ranged from 1.8–4.6% and 2.8–7.1%, respectively, while fossil fuel and NH_3 slip ranged from 21.1–66.4% and 23.2–74.3%, respectively. The combined contribution of fossil fuel and NH_3 slip remained dominant across all EIE scenarios (88–95%), indicating that the qualitative conclusion that "anthropogenic NH_3 sources dominate particulate ammonium at Xitou" is robust to the choice of equilibrium fractionation factor.

Open-system equilibrium assumptions. Under the KIE scenario, the estimated fertilizer contribution increased to 26.6%, and fossil fuel decreased to 12.6%, while NH_3 slip and waste remained within the range spanned by EIE scenarios. However, the KIE scenario represents a physically extreme end-member. At Xitou, NH_3 formation is dominated by condensation under open-system conditions, where $NH_{3(g)}$ undergoes continuous exchange with the gas phase rather than irreversible incorporation. Under such conditions, isotope fractionation is expected to approach thermodynamic equilibrium (EIE) rather than kinetic control (KIE). The KIE result is therefore best interpreted as an upper bound on source apportionment uncertainty rather than a physically realistic atmospheric scenario."

Table S1. Sensitivity of gas−particle equilibrium in estimating NH_3 emission sources.

$\varepsilon_{NH_4^+-NH_3}$	Contribution (%)			
	Fertilizer	Fossil Fuel	NH_3 slip	waste
−28 ‰	26.6 ± 34	12.6 ± 10.4	56.3 ± 35.4	4.6 ± 4.4
4 ‰	1.8 ± 1.9	21.1 ± 15.3	74.3 ± 15.4	2.8 ± 2.9
33 ‰	4.2 ± 3.2	66.4 ± 15.1	23.2 ± 18.3	5.2 ± 5
37 ‰	4.6 ± 3.8	42.3 ± 18.7	46 ± 23	7.1 ± 6.1

Regarding the source endmember isotope signatures, we followed the selection of Kawashima et al. (2023), which compiled $\delta^{15}N\text{-}NH_3$ source data from 15 references with passive sampler

corrections applied. The four source categories and their $\delta^{15}N$-NH_3 values are: fertilizer (−34.1 to −22.5‰, n = 21), waste (−23.2 to −12‰, n = 51), NH_3 slip (−13.7 to −2.7‰, n = 9), and fossil fuel combustion (−1.4 to 5‰, n = 38). These four categories span a range of ~30‰ with inter-category separation consistently exceeding the within-category standard deviation, providing sufficient isotopic contrast for MixSIAR to distinguish source contributions. We acknowledge that the differences between clear & foggy conditions, during both daytime & nighttime, can be similar. We removed that original statement that "Source dynamics varied significantly with isotopic shifts", and updated it in section 3.3.2 (Lines 314−319) of the revised manuscript:

> (Lines 314−319) "[…] It should be noted, however, that the differences in source contributions between daytime and nighttime periods, or between fog and clear conditions, remain within the overlapping ranges of the posterior distributions; consequently, the current sample number precludes statistically robust discrimination between these conditions. Expanded measurements encompassing multiple seasons and contrasting meteorological regimes would be necessary to establish whether systematic diurnal or fog-driven shifts in NH_3 source apportionment exist at this site."

R1C4: In addition, the linkage between fog events and isotopic variations appears weak, based on Fig. 2. Although uncertainties are not explicitly provided, low values of $\delta^{15}N$–NH_4^+, $\delta^{15}N$–NO_3^-, and $\delta^{18}O$–NO_3^- also occur outside foggy periods. Therefore, the observed decreases in isotopic values are not unique to fog events, contrary to the authors' interpretation.

Response: We thank the reviewer for this point. We agree that low isotopic values are not exclusively restricted to foggy periods. However, while these signatures are not unique to fog, the fog period represents a period where multiple isotope-depleting mechanisms occur simultaneously. Specifically, during fog events: (1) wet scavenging preferentially removes aerosol particles that have accumulated ^{15}N-enriched nitrogen from urban areas, reducing the ^{15}N source signal in the residual particle phase; (2) the scavenged aerosol undergoes re-equilibration with gas-phase NH_3, which is depleted in ^{15}N relative to particulate NH_4^+, driving $\delta^{15}N$-NH_4^+ toward lower values; and (3) nitrate formation pathway shifted toward RO_2-initiated pathways that produce nitrate with lower $\delta^{18}O$.

In contrast, the low isotopic values observed outside fog periods likely reflect individual, single-mechanism perturbations. For instance, low $\delta_{15}N$-NH_4^+ during clear periods may occur when the source contribution shifts toward agricultural NH_3 emissions (e.g., 21D), which carry inherently lower $\delta^{15}N$ signatures. Similarly, decreases in $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- during non-fog periods are consistent with transient shifts in nitrate formation pathways or local isotope fractionation, but these may not be reinforced by the concurrent scavenging and re-equilibration dynamics that characterize fog events.

We have revised the relevant text in Section 3.3.1 (Lines 278−281) and 3.4.1 (Lines 337−342) to clarify that fog events are associated with the convergence of these mechanisms rather than being the sole condition under which low isotopic values occur.

> (Lines 278−281) "During fog, the bell-shaped distribution flattened significantly. Weakened wind suppressed the upslope transport of enriched anthropogenic pollutants, while enhanced aqueous-phase interaction promoted uniform isotopic re-equilibrium across all sizes. The high NO_3^- concentration from aqueous chemistry can also promote

the local isotopically depleted NH_3 partitioning into the particle phase, dampening the size-dependent isotopic gradient."

(Lines 337−342) "[…] During the fog, $\delta^{15}N\text{-}NO_3^-$ decreased significantly from −2.19‰ (18D) to −4.80‰ (18N), and further to −6.54‰ (19D) (Fig. 2g). This decline, contrasting with previous shorter fog events (Chen et al., 2022), reflects the combined effects of prolonged stagnation and a reduced influx of urban air. These conditions promote enhanced aqueous-phase pNO_3^- formation, predominantly driven by $\delta^{15}N$-depleted NO_x from locally derived biogenic precursors or precursors that have undergone extensive fractionation during transport (Vicars et al., 2013; Gobel et al., 2013)."

We have also added some brief discussions of the non-fog low-value occurrences to provide a more complete mechanistic picture in Section 3.3.1 (Lines 282−289) and Section 3.4.1 (Lines 343−351).

(Lines 282−289) "The flat $\delta^{15}N\text{-}NH_4^+$ size distribution was also observed on 19N and 21D. For 19N, it is likely a legacy effect of the preceding fog period (18D, 18N, and 19D). The NH_3 pool remained isotopically depleted from sustained fog-driven scavenging and re-equilibration, and regional transport had not yet replenished the accumulation-mode signal. However, high sub-micrometer NO_3^- concentration (Fig. S4) suggests that fog-like aqueous chemistry persisted, maintaining isotopic signatures similar to 18D. Conversely, the flat distribution on 21D reflects a distinct source influence. HYSPLIT back-trajectories (Fig. S7) indicate that the air parcel traveled through agricultural regions characterized by heavily depleted NH_3 (e.g., livestock waste, −28.3‰ to −17.6‰). The partitioning of this isotopically light NH_3 during transit effectively erased the characteristic accumulation-mode enrichment."

(Lines 343−351) "Relatively low concentration-weighted $\delta^{15}N\text{-}NO_3^-$ values observed outside the fog periods on 20N and 22N, likely attributable to distinct mechanisms. For 22N, the depletion is linked to enhanced local production, supported by elevated sub-micrometer NO_3^- concentration shown in Fig. S4. For 22N, the low $\delta^{15}N$ coincides with significant deposition loss, as evidenced by low total NO_3^- levels (Fig. S4b). Because HNO_3 readily reacts with coarse-mode mineral dust and sea salt, the deposition efficiency during transport is high; this preferential removal of $\delta^{15}N$-enriched species often leaves the residual nitrate pool isotopically lower. Furthermore, the thermodynamic partitioning of HNO_3, governed by ambient temperature and particle acidity regulated by sulfate and ammonium, critically influences the observed $\delta^{15}N$. Ultimately, the observed $\delta^{15}N$ at this site serves as an integrated signal of physical and chemical dynamics processes within the air parcel during its transit."

R1C5: Finally, there is room to improve the overall organization and logical flow of the manuscript. The presentation is overly dense in places and lacks clear structural connections between sections, which hinders the clarity of the scientific narrative.

Response: We thank the reviewer for this feedback. We have made substantial revisions to the organization and logical flow throughout the manuscript. Specifically, the introduction has been restructured to more clearly establish research gaps and motivate the study objectives; and the discussion has been rewritten to more explicitly connect isotopic observations to process-level

interpretations, with transitional sentences linking each subsection to the overarching scientific narrative. We believe these revisions have improved the readability and coherence of the manuscript as a whole.

R1C6: Overall, the study primarily reinforces existing understanding rather than advancing new conceptual or methodological developments in atmospheric nitrogen isotope analysis. Therefore, it may not be well suited for publication in ACP, and submission to a more appropriate journal is recommended.

We thank the reviewer for this feedback. After addressing the reviewer's comments, we believe that this study offers advances across three perspectives:

Methodological novelty. This study is among the first to apply size-resolved dual-isotope analysis ($\delta^{15}N$ and $\delta^{18}O$) simultaneously to both pNH_4^+ and pNO_3^- in a mountain cloud forest setting, where the majority of isotope-based Nr studies rely on bulk $PM_{2.5}$ or PM_{10} samples due to limited sample mass available at such sites. Size-resolved measurements provide mechanistic information on size-dependent nitrogen transformation that bulk approaches cannot resolve.

Novel observational findings. We document two previously unreported behaviors. First, a systematic flattening of the bell-shaped size-resolved $\delta^{15}N$-NH_4^+ distribution during the prolonged fog episode, attributed to aqueous-phase gas–particle isotopic re-equilibration and wet scavenging that suppressed the accumulation-mode isotopic enrichment characteristic of clear-period urban plume transport. Second, a $\delta^{15}N$–$\delta^{18}O$ analysis of pNO_3^- identifies at least two co-existing nitrate formation pathways (O_3-initiated vs. RO_2-initiated) and reveals a systematic shift toward RO_2-dominated production during fog. This transition was not previously quantified using isotopic approaches at subtropical mountain sites.

Site and process novelty. Xitou represents an under-characterized regime in East Asian Nr research: a subtropical cloud forest situated in a valley that channels urban-to-rural plume transport under persistently high-humidity conditions. By integrating size-resolved isotopes with MixSIAR Bayesian source apportionment, we quantify source contributions (combustion-related NH_3: 50–83%) and formation pathway partitioning (pNO_3^- via RO_2-initiated oxidation: 42–95% daytime; heterogeneous reactions: 6–84% nighttime) at a site where biogenic and anthropogenic Nr interact in ways not previously characterized. These results carry implications beyond the study site, suggesting that even in remote or rural environments, combustion-related sources can dominate ammonium loading, and that RO_2-initiated pathways may be systematically underweighted in current Nr budgets for mountain regions.

We believe these contributions represent new findings rather than confirmations of prior work. They directly address ACP's stated scope for aerosol process studies, specifically aerosol microphysics, chemical composition, and transformation processes. We have strengthened the framing of these contributions in the revised Introduction and Discussion.

Specific comments

R1C7: L134-L136: Please clarify the primary scale used for $\delta^{15}N$ and $\delta^{18}O$ (e.g., air-N_2, VMOW or others). It is recommended to include the weblink for both international isotope reference materials (USGS 34 and IAEA-NO3)

Response: We thank the reviewer for this point. The primary scale used for $\delta^{15}N$ and $\delta^{18}O$, as well as the weblink for the two international isotope references, were added to the introduction section of the revised manuscript (Lines 59−63) as follows:

> (Lines 59−63) "[…] Nitrogen isotope ratios ($\delta^{15}N = [(^{15}R_{sample})/(^{15}R_{air}) - 1] \times 1000‰$, where ^{15}R is the ratio of $^{15}N/^{14}N$) are used to distinguish emission sources of $p\mathrm{NH_4^+}$ and transport of $p\mathrm{NO_3^-}$ (Savard et al., 2017; Chang et al., 2018), while oxygen isotope ratios ($\delta^{18}O = [(^{18}R_{sample})/(^{18}R_{VSMOW}) - 1] \times 1000‰$, where ^{18}R is the ratio of $^{18}O/^{16}O$) in $p\mathrm{NO_3^-}$ provide insights into specific oxidation pathways, as each oxidant (O_3, OH, RO_2) imparts a unique isotopic fingerprint (Walters and Michalski, 2016). […]"

R1C8: L181-L199: The description in this section is confusing and difficult to follow.

Response: We appreciate the reviewer for pointing out the issue. We agree that the original naming of nitrate formation pathways (P1a, P2a, P3a, P1b, P2b, and P3b) was not easy to follow. We updated the naming in this section and provided explanations for these reactions in the introduction. This point was updated in the introduction (Lines 45−46, 52−54) and method sections (Lines 173−183) of the revised manuscript as follows.

> (Lines 45−46) "[…] In the presence of sunlight, NO_x undergoes rapid oxidation through ozone (O_3) or peroxy radical (RO_2) pathways (termed P_{O_3} and P_{RO_2}, respectively) before converting to nitric acid (HNO_3) via the following reactions: […]"
>
> (Lines 52−54) "[…] Under nocturnal or low-light conditions, NO_x accumulates as nitrogen dioxide (NO_2) through reaction with O_3, which then undergoes heterogeneous reactions (termed as het) to produce HNO_3 as follows: […]"
>
> (Lines 173−183) "$\delta^{18}O\text{-}NO_3^-$ is applied to evaluate the relative contributions of various HNO_3 formation. Six potential pathways were considered by combining the primary oxidants (P_{O_3} and P_{RO_2}) with three terminal mechanisms (OH1, OH2, and heterogeneous processes (het)). These pathways are characterized by their specific $\delta^{18}O\text{-}NO_3^-$ signatures (Fig. S3), calculated using a mass-balance approach assuming no kinetic isotope fractionation (Walters and Michalski, 2016). RO_2 was assigned a $\delta^{18}O$ of 23.5‰, reflecting that O in RO_2 originates from molecular O_2 (Kroopnick and Craig, 1972). O_3 exhibits elevated $\delta^{18}O$ values ranging from 90 to 122‰ (Hastings et al., 2003). OH radicals were split into OH1 (−15 to 0‰) (Dubey et al., 1997), and OH2 (38 to 61‰). Daytime mechanisms included $P_{RO_2\text{-}OH1}$ (33−49‰), $P_{RO_2\text{-}OH2}$ (50−69‰), $P_{O_3\text{-}OH1}$ (55−81‰), and $P_{O_3\text{-}OH2}$ (73−102‰). Nighttime analysis focused on $P_{RO_2\text{-}het}$ (50−69‰) and $P_{O_3\text{-}het}$ (73−102‰), while retaining $P_{RO_2\text{-}OH1}$ to account for residual daytime nitrate that persists into the night. Sensitivity analyses regarding pathway exclusion are detailed in Supplementary Description S4, Tables S3 and S4."

R1C9: L 220- L227: Please provide the uncertainty for individual measurements and individual data points shown in Fig.2.

Response: Hourly concentrations of environmental parameters (Figure 2a−e) were obtained from the Taiwan Ministry of Environment, where the analytical uncertainties are governed by national

QA/QC standards. For isotope analysis (Figure 2f–h), the uncertainties for $\delta^{15}N$ and $\delta^{18}O$ of nitrate samples are generally less than 0.1‰, which is smaller than the symbol size. We have updated the caption of Figure 2 (Lines 204–205) as follows to clarify this:

> (Lines 204–205) "[…] Uncertainties for $\delta^{15}N$ and $\delta^{18}O$ measurements are generally less than 0.1‰ and are smaller than the symbol size."

R1C10: L260-263: The content is somewhat confusing and could benefit from clarification.

Response: This part was updated in section 3.3.1 in the revised manuscript (Lines 251–256) as follows:

> (Lines 251–256) "[…] This decline of $\delta^{15}N$ during the fog likely results from three concurrent processes under stagnant conditions. First, stagnant conditions suppressed the transport of $\delta^{15}N$-enriched urban plumes from nearby source regions. Second, continuous exchange between gas-phase NH_3 and pNH_4^+ shifts the particle phase toward the signature of the local NH_3 pool, which is depleted in $\delta^{15}N$ due to agricultural volatilization. Furthermore, wet deposition during fog may remove ^{15}N-enriched particles, forcing the remaining pNH_4^+ to re-equilibrate with an increasingly $\delta^{15}N$-depleted gas phase. […]"

R1C11: L340-344: Despite the use of size-resolved isotope measurements, no clear or systematic dependence of $\delta^{15}N$ in pNH_4^+ or pNO_3^- on particle size is observed (Fig. 6a, b), which limits the interpretive value of the size-segregated data.

Response: We thank the reviewer for this comment. We acknowledge that Figs. 6a and 6b do not reveal a systematic size-dependent trend in $\delta^{15}N$ or $\delta^{18}O$ of pNO_3^-. However, we suggest that the absence of such a trend is itself a meaningful finding, indicating that isotopic fractionation during gas-to-particle partitioning across size bins is not the dominant control on $\delta^{15}N$ variability at this site during the sampling period.

The interpretive strength of the size-segregated isotope approach becomes apparent when δ15N is examined in conjunction with $\delta^{18}O$ for pNO_3^- (Fig. 6c). In this dual-isotope space, two distinct groupings emerge that would not be resolvable from bulk (non-size-resolved) measurements alone. One group, characterized by elevated $\delta^{18}O$ values, is consistent with NO_3^- formation via O_3-initiated oxidation pathways, whereas another group exhibiting lower $\delta^{18}O$ values is more consistent with RO_2-initiated oxidation, indicative of photochemically processed or locally produced aerosol particles. The size-resolved sampling framework allows these isotopic signatures to be attributed to different particle size fractions, providing insight into the size-dependent source contributions and chemical processing histories that would otherwise be obscured in bulk measurements.

We have addressed this point in section 3.4.2 (Lines 374–387) of the revised manuscript as follows:

> (Lines 374–387) "Notably, no significant systematic size-dependent trend of $\delta^{18}O$-NO_3^- on particle size was observed (Figs. 6a and 6b). The spatial heterogeneity of oxidants (O_3 and RO_2), coupled with the complex HNO_3 partitioning dynamics within the air parcel, likely erases any size-dependent isotopic pattern and daily variation (Figs. S12 and S13).

However, the $\delta^{15}N\text{-}NO_3^-$ vs. $\delta^{18}O\text{-}NO_3^-$ relationship (Fig. 6c) resolves two geochemically distinct regimes reflecting contrasting formation environments and aerosol histories. The higher $\delta^{18}O\text{-}NO_3^-$ (55−83‰) with enriched $\delta^{15}N\text{-}NO_3^-$ (−6 to 1‰) can be assigned as an urban/transported regime. Freshly emitted in metropolitan areas contributed to elevated $\delta^{15}N$, while O_3-driven oxidation leads to high $\delta^{18}O$ (Gobel et al., 2013). The observed lower $\delta^{18}O\text{-}NO_3^-$ (9−38‰) and depleted $\delta^{15}N\text{-}NO_3^-$ (−10 to −2‰) is assigned as a rural/fog regime. These signatures reflect RO_2-initiated oxidation and $\delta^{15}N$-depleted NO_x from locally derived biogenic precursors or after extensive fractionation during transport, particularly under stagnant conditions. A moderate positive correlation (r = 0.66) between $\delta^{18}O\text{-}NO_3^-$ and $\delta^{15}N\text{-}NO_3^-$ further highlights the intrinsic interplay between oxidation processes and nitrogen cycling at the site. These data demonstrate a $\delta^{18}O\text{-}NO_3^-$ and $\delta^{15}N\text{-}NO_3^-$ relationship that covers a broad isotopic range, spanning from the signatures observed at the Himalayan-Tibetan Plateau to those at regional background sites like Mt. Lulin (Fig. S14). ”

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