EGUSPHERE-2025-1167 | Research article

Sensitivity of Simulated Ammonia Fluxes in Rocky Mountain National Park to Measurement Time Resolution and Meteorological Inputs

Naimie et al. (2025)

Anonymous Referee #3

[General comment]

The authors measured NH_3 concentrations with a high time resolution of 30-sec and estimated NH_3 flux using a bidirectional exchange model above a subalpine forest, covering a one-year period from September 2021 to August 2022. They proposed that the underestimation of NH_3 dry deposition inferred from model using biweekly basis concentrations can be improved by (i) applying a correction factor derived from the relationship with fluxes inferred using 30-min concentration, or (2) estimating the diurnal variation of the biweekly basis concentration.

Observational data on NH_3 in forest ecosystems are scarce, and long-term measurements of NH_3 concentrations with high temporal resolution are of great value. In addition, given the limited application of bidirectional exchange models in forests compared to grasslands and croplands, this study not only provides valuable information for forests but also proposes a potentially practical approach for improving dry deposition estimation with higher accuracy by utilizing the data of monitoring network such as AMoN.

The concept and overall approach in this study are excellent, and I commend the authors for their efforts for treating a large amount of observation dataset and handling long-term modeling. However, it seems that there is still room for further discussion regarding the specific aspects of the methodology and analysis of both observations and models that support the results and conclusions of this study.

[Major concerns]

1. QA & QC for measured NH_3 concentration

- Upon reviewing the dataset referenced by the authors ("Rocky Mountain National Park Ammonia Data"), I have several concerns regarding how the observational data, which is the foundation of this study, were processed and quality controlled.
- For the biweekly NH_3 measurements obtained using passive samplers, the authors mention there were 27 sampling periods, with samples collected in duplicate. From 23 August 2021 to 9 November 2021, four samples were collected per period. However, the number was reduced to two after this period. I think the authors used mean values for each period for analysis, but it is

unclear whether the authors accounted for the differing number of samples when averaging. Were the sample sizes standardized or weighted in any way?

- Additionally, there is only one valid passive sample for the period from 30 March 2022 to 14 April 2022. Moreover, the sampling period from 26 May 2022 to 21 June 2022 is approximately one month. There are also cases of overlapping sampling periods (e.g., 23 August to 6 September, and 29 August to 13 September 2021). However, the manuscript does not mention how these irregularities were addressed.
- Regarding the high temporal resolution NH_3 measurements of AirSentry, the detection limit is 0.070 ppbv. According to the raw data (RMNP_AirSentry_NH3_2021_2022.csv) from 9 July 2021 to 13 July 2022, approximately 18.6% of the total values fall below the detection limit. Surprisingly, there is even data with a concentration of "0" (approximately 10.8%). It is highly likely that a substantial portion of the data are also below the quantification limit. I am seriously wondering how the authors handled such data, as the authors state that "Only NH_3 data missing due to power outages have been removed from the AirSentry dataset".
- While missing data are understandable in long-term field observations, it is essential for the authors to clearly describe their QA/QC procedures: how sub-detection-limit values were treated, how much of the dataset exceeded the detection and quantification limits, and what criteria were used to ensure the reliability of the measurements. Without such information, the credibility of the dataset and the study's conclusions may be undermined.

2. Uncertainty in the measured NH_3 concentration

- In my opinion, the overall uncertainty of this study depends heavily on the accuracy of the measured NH_3 concentrations. The authors also state that "increasing the NH_3 concentration by 9% increased the annual deposition by 47%", highlighting the strong sensitivity of model outputs to measured concentrations. While other referees have suggested sensitivity analyses for various parameters of the bidirectional exchange model, the most critical first step is to clarify the uncertainties in the observational data. Addressing these uncertainties would not only enhance the credibility of the measurements but also improve the reliability and interpretability of the model-based analyses. Assuming proper QA/QC procedures were conducted, I offer the following specific suggestions:
- It is generally known that NH_3 exhibits strong seasonal and diurnal variability in both flux and concentration, as is evident in Figure 2. Before scaling high-resolution AirSentry data to match passive sampler, a direct comparison of the two measurement techniques should be quantitatively presented. How well do the two measurements agree? If there are systematic differences, is there any evidence of seasonal bias? In my experience, passive samplers requiring multiple lab processing can be prone to contamination, particularly during warmer seasons.

- Although the authors state that “Passive NH_3 sampling methods have been shown to have a low bias”, the raw data reveal cases where concentrations differ by more than a factor of 2 between passive samplers during same sampling period (e.g., from 10 May to 26 May 2022; 5 July to 18 July 2022; and 18 July to 2 August 2022). Given such large discrepancies in measured concentration using passive samplers, is it truly necessary to scale high resolution data from AirSentry, which is capable of detecting NH_3 at levels as low as 0.070 ppbv, by passive sampler? It also seems that Referee 2’s concerns regarding this issue have not yet been fully addressed.

3. Seasonal variation in NH_3 concentration and inferred flux

- Assuming the QA/QC procedures and the uncertainties in the observational data discussed above are adequately addressed, I offer the following suggestion concerning the seasonal variation of NH_3 concentration and fluxes. As the author described, “In practice, fluxes can change quickly and even reverse direction with changing environmental conditions.” However, the analysis and discussion about the seasonal variation in NH_3 concentration and inferred flux appear to be insufficient.
- Although direct measurements data were not presented at the forest of this study, recent long-term observations have reported that NH_3 flux in forest forests generally show emission during warm seasons and deposition during other seasons (Melman et al., 2025 https://doi.org/10.1016/j.atmosenv.2024.120976). However, the estimated fluxes are quite small level than previous studies ranging from -5 to 5 ng N m^{-2} s^{-1}, and no large seasonal variation can be seen (as shown in Figure 3). Furthermore, emission and deposition do not alternate in short-term, but in some cases show consistent deposition, particularly from late July through September in 2022. I can understand the state of "we focused on the impacts of measurement resolution to probe the impacts of time resolution and reanalysis meteorology," however, the lack of detailed discussion on the seasonal variation leaves a gap in the interpretation. As a fundamental step to enhance the methodological reliability of this study, the authors should analyze the seasonal patterns in NH_3 flux and concentration more thoroughly, and explore their potential causes, before addressing the annual deposition estimates and discussing the differences arising from the use of various concentration datasets and meteorological inputs.
- The compensation point, which determines both the direction and magnitude of the estimated NH_3 flux strongly depends on meteorological factors such as temperature as well as ambient NH_3 concentration. Despite a previous suggestion by Referee #1, the meteorological conditions at the study site remain largely undocumented. The revised manuscript includes only mean values for temperature and relative humidity, but it is not even clear over what period these values were calculated. In addition, only qualitative descriptions of rainfall and snowfall are provided. With such limited information, it is difficult to interpret the temporal dynamics of the NH_3 flux or to

assess uncertainties in the annual deposition estimates. At a minimum, the authors should clearly present seasonal variations in temperature, relative humidity, and rainfall, as well as the snowfall periods during the observation period to support their analysis.

- While the authors have conducted sensitivity analyses on parameters such as LAI and TAN in response to referee comments, I think these are relatively minor issues at this stage. The primary parameters that determine the compensation point of (χ_{z0} in the model used at this study) are temperature and emission potential of stomata and soil. In addition to temperature, the emission potential, especially for stomata, also varies seasonally (Flechard et al., 2013 https://doi.org/10.5194/bg-10-5183-2013). It is reasonable to assume a constant emission potential within a given season; however, for a one-year study such as this, it would be more appropriate to account for seasonal variation. For example, assigning higher values in summer and lower values in winter would better reflect the expected physiological and environmental dynamics. Moreover, as Referee #1 pointed out, the stomatal emission potential used in this study appear significantly lower than those reported in Zhang et al. (2010 https://doi.org/10.1029/2009JD013589) or Massad et al. (2010). Sensitivity analysis of the emission potential is a critical step when applying the bidirectional exchange model and should be prioritized. Even if the influence of emission potential on the χ_{z0} is limited under low temperature due to the high-altitude site, this feature itself could be an important characteristic worth highlighting. Accordingly, seasonal variation in temperature should be explicitly shown and discussed in this context.
- While there are still many uncertainties regarding soil processes, and I understand the difficulty in handling soil emissions in bidirectional exchange models, existing model such as Zhang et al. (2010) provide useful guidance. For example, the soil emission potential is set to zero during periods with snow cover in this model. I recommend referring to such practices in your analysis and considering whether a similar treatment may be appropriate for your study.

[Minor and technical comments]

1. Next time, please clearly indicate which parts of the manuscript have been revised in response to the referee's comments. For example, you could write: "We revised the sentence (Line: xx-yy in the Author's tracked changes version)."Additionally, **there are many typographical errors throughout the manuscript. Please perform a thorough proofreading before submitting your revised version.**
2. Figure 1: The phrase "at 7.5-arc-second spatial resolution" is difficult to immediately understand. Pleased convert it to "225 m" for clarity.
3. 2.1 Site location: According to the aerial photo at the provided coordinates (40.275903, -105.54596), there appear to be several buildings within approximately 100 meters of the NEON

tower. This suggests that the condition differs from that of a typical forest observation site. Furthermore, the spatial extent shown in Figure 1 is too large to understand the site-specific conditions. Please provide additional information, such as a photograph of the observation tower, a site map illustrating the surrounding environment, or a schematic diagram of the observation.

4. Line115 in Author's tracked changes version (same as below): Please correct the unit from "C" to "°C" and insert spaces before and after the "=" sign. Also, clarify the period over which the means of air temperature and relative humidity were calculated. At a minimum, the total precipitation and snowfall events during the observation period should be explicitly stated.
5. Line 117: Please specify the height at which these meteorological parameters (e.g., temperature, humidity) were measured. Also, indicate the temporal resolution of the measurements (e.g., 10-minute averages, hourly, etc.).
6. Line 119: Please clarify which specific product was used to determine the LAI value. A value of LAI = 0.8 is quite low for a forest site, which may be due to the coarse spatial resolution of 1km grid that includes bare land, and bulling in addition to vegetation. As the study develops, the authors should consider measuring LAI directly around the tower using a canopy analyzer or similar instrument. LAI is a critical parameter for modeling NH_3 emissions and deposition. For example, in the model by Zhang et al. (2010), the stomatal emission potential is set to zero when LAI < 0.5. Additionally, LAI is used to parameterize both in-canopy aerodynamic resistance and cuticular resistance. This is also a key issue for the authors' planned model inter-comparison paper and should be addressed carefully.
7. Line 121: Please indicate specifically which section or figure of the supplementary information readers should refer to. This comment applies to other instances of vague referencing throughout the manuscript as well.
8. Line 136: If I understand correctly, the Monin-Obukhov length (L) also must be calculate in the NEON site, and the methods for calculating L differ between Sections 2.2.1 and 2.2.2. At the NEON site, it seems that L was estimated using the sonic virtual temperature, the covariance of vertical wind and sonic virtual temperature, and the friction velocity derived from the 3D wind components measured by a sonic anemometer (Please specify the manufacturer name and model number of the instrument. Young ? or Gill?).

   In contrast, the method for calculating L from ERA5 data is unclear in the manuscript. How did you derive the surface buoyancy flux ($\overline{w'\theta_v'}$)s from ERA5? This typically requires both sensible and latent heat fluxes, along with air density. Note that ERA5 provides both "surface sensible heat flux" and "instantaneous surface sensible heat flux"; please specify which was used. To enhance transparency and allow others to reproduce your method, I strongly recommend including the equations used (e.g., L_{sonic} = …, and L_{ERA5} = …), and a table listing the specific variables used in each case. This would also help readers understand the discrepancies between

L_{sonic} and L_{ERA5} that are discussed in the supplemental information. Furthermore, since ERA5 has a 1-h temporal resolution, how was this data used with 30-min concentration data for flux calculation?

The phrase "Eq.(5.7c) from Stull (1988)" is difficult to follow. I suggest rephrasing it as: "… was calculated using Eq. (1) following Stull (1988)".

9. Line 146: Please provide the manufacturer name and model number instead of listing only a URL. The same request applies to other instruments mentioned in the manuscript, including the 3D sonic anemometer, ion chromatography system, and AirSentry.
10. Line 151-152: There are several types of denuders (e.g., annular, multi-channel, honeycomb), but I am not familiar with the term "University Research Glassware Denuders". Is this a proper noun or brand name? Please clarify or revise how this is described in the manuscript.

    And I do not agree with that the passive sampler have a low bias based on your low data.
11. Line 157: "Boulder, CO" may refer only to a location and does not specify the manufacturer or model. The correct company name is "Particle Measuring Systems." Please revise accordingly.
12. What does "1/4""means? And please correct the unit from "C" to "°C".
13. Line159: Did you perform any tests to assess potential NH_3 losses within the sampling tube? Given that NH_3 is highly soluble in water, it may be adsorbed onto the tube walls under high humidity conditions.
14. Line: 168: Please specify "the effect of NH_3 …" on what? The sentence is currently ambiguous.
15. Line: 169: The expression "30-min frequency" is potentially misleading. Since AirSentry's time resolution is already expressed as measured by "30-sec frequency", the 30-minute value generated here should be rephrase.
16. Figure 2: The labels "2021" and "2022" on the x-axis only need to appear once at the beginning of each year. Instead, it would be more helpful for readers to better illustrate seasonal trends if the figure included month labels across the full period.
17. Line 180: If my understanding is correct, the data count would exceed 3,000 if values below the detection limit or those reported as zero are also included.
18. Line 190: Please correct the formatting of "Fig (S1)" to "Fig. S1".
19. Line 202: Please specify what type of wet deposition data were used.
20. Line 203: Please use the same format for latitude and longitude notation as used for other sites to ensure consistency throughout the manuscript.
21. Line 210: The phrase "dry deposition is generated" sounds unnatural. Dry deposition is typically inferred or estimated, not "generated." Please revise this expression accordingly. The same applies to the use of "generation" in reference to V_d.
22. Line 214: The abbreviation "(V_d)" should be introduced at Line 211 when "deposition velocity" is first mentioned.

23. Line 215: Why "dry deposition velocity" is being used at here instead of V_d.
24. Line 217: Although I understand this is based on previously studies, please note that the V_d of NH_3 is not so easily defined. This may partially explain the discrepancy in annual deposition amount discussed at Line 365-368.
25. Line 219: The bidirectional flux model by Massad et al. (2010) is more complex than other models used in previous studies, and the calculation of theχ_{z0} is difficult. This is why the authors are required to conduct various sensitivity analyses. It would be better to describe the advantages behind selecting this model.
26. Line 222: If I understand correctly, the authors appear to have misunderstood the framework of the model of Massad et al. (2010). In this model, the direction of total flux is determined by the difference between atmospheric concentration (χ_a) and χ_{z0}. The canopy compensation point (χ_c) is an intermediate parameter for determining χ_{z0}, not the determinant of direction of total flux. This distinction is important because the model differs conceptually from simpler models. Please revise the explanation to ensure accuracy.
27. Figure 3: The term "surface compensation point" is incorrect; as far as I know, this terminology is not used in previous literature. χ_{z0} is the compensation point at height of ($d + z_0$). Please correct "Stomata" to "Stomatal", and "cuticle" to "cuticular". Also, "laminar" is no need for R_{bg}.
28. Line 235: Is Figure 3 showing "relationship" rather than a conceptual diagram? Please clarify and revise the description accordingly.
29. Line 239: Obukhov length, displacement and roughness length have already been defined as L, d, and z_0.
30. Line 245: Please delete "captures the aerodynamic resistance from within the canopy layer and". While this may apply to R_{ac}, it is incorrect in the context of R_g.
31. Line 247: The phrase "using Eq. 16 and Eq. 17 from equations of Massad et al. (2010)." may confuse readers, especially since the present manuscript also contains Eq.(16) and Eq.(17).
32. Line 252: Could you elaborate on how the parameter R_{bg} was determined? This parameter are not widely compiled, and your approach would provide valuable information for future studies.
33. Line 257: According to Table 1 in Zhang et al. (2003 https://doi.org/10.5194/acp-3-2067-2003), I could not find a r_{stmin} value of "225" for any land use category. Is the mistake of 250?

    Also, did you assign R_{st} at nighttime to be infinite value considering the stomatal closure following Zhang et al. (2003)? This is a critical assumption in modeling bidirectional exchange of NH_3.
34. Line258: Based on your response to Referee #1, it seems there may be a misunderstanding regarding R_w. As I understand it, this is an empirical formulation that accounts for four different vegetation types, not only for "Douglas Fir." Moreover, the effect of LAI and Temperature is

already considered at this empirical formula. It is important to avoid applying such models blindly without a full understanding of their basis.

As an additional point, changing the cuticular resistance formulation can also significantly affect NH_3 fluxes in addition to the emission potential. I recommend considering the case study of Xu et al. (2023 https://doi.org/10.1016/j.atmosenv.2023.120144) using a bidirectional exchange model in your uncertainty discussion or future sensitivity analysis.

35. Line 262: This is self-evident from Eq.(8), and Eq.(9) is unnecessary. Is there any case in which relative humidity exceeded 100% at the NEON site?
36. Line 263: Although the exclusion of HCl likely has minimal influence on the results, was there a specific reason it was not considered in the calculation? I suspect that the higher acidity ratio (AR) observed in winter may be due to extremely low NH_3 concentrations. Is it possible that a higher AR facilitated NH_3 deposition in the site? According to the study by Xu et al. (2023), R_w can be highly sensitive to this factor.
37. Line 269: The stomatal and ground compensation points have already been defined as χ_s and χ_g.
38. Line 270: Why did you not use the formula of Massad et al. (2010), which calculates Γ_s for Un-managed site based on nitrogen input? The Γ_s value calculated by this formula is about 10 times larger than the value used in this study. Do you expect this have any impact on the flux calculations?
39. Line 272: What exactly do you mean by “ratios” in this context?
40. Line 275: Same comment with comment 39 for χ_s and χ_g. Also, “Eq. (3) and Eq. (5) of Stratton et al. (2018)” could confuse readers, as the equation numbers overlap with those in your manuscript.
41. Line 281: The authors described “ground compensation points were calculated according to Massad et al. (2010)” in Line 269. However, they also described soil compensation point was calculated according to Stratton et al. (2018) in Line 275, and χ_g is not calculated follow the form of Eq. (11). If this is the mistake of Γ_g, I can understand. Which is correct?
42. Line 286: Same comment with 40 for χ_c.
43. Line 287:χ_a was already defined and explained earlier in Line 222.
44. Line 291: Same comment with 43 for d and z_0. Also, note that it is conventional to use lowercase z, not uppercase Z. Please revise accordingly.
45. Line 296: The explanation of inferred flux here is scientifically incorrect. It raises concerns about whether the authors even fully understand the resistance model framework. Also, “roughness height” is incorrect as already been pointed out by Referee #1.
46. Line 304: Please correct the section title to “Simulated bidirectional exchange flux of NH_3”.

47. Line 307-309: This explanation has already been presented in the Methods section. And I cannot agree using the word of “relative magnitudes”. Again, “Surface compensation point” is not an appropriate term; please revise all instances in the manuscript.

    I suggest adding a plot of the “difference” between χ_a and χ_{z0} in Figure 4. This “difference” directly determines the direction and magnitude of the flux and would provide valuable insight into seasonal variation.
48. Line 313: For clarity, please define the seasons as used in your study (e.g., spring = March to May). From Figure 4, it is not clear how “The largest periods of net emission occur in the spring” was concluded. It appears that the largest emissions occur from late June to July. Why are large depositions observed before and after this period (even in same summer)? What factors do you think are influencing these patterns?
49. Line 321, 323: Same comment with 28.
50. Line 324: Based on Figure 5, it is difficult to support the claim that “Winter periods of net emission (see Fig. 4b) are driven by the ground flux.” If these fluxes exhibit seasonal variation, boxplots may obscure such information, a time series plot would be more appropriate to reveal these dynamics because total flux is sum of these fluxes. Furthermore, as previously mentioned, some models assume no soil emission under snow-covered conditions. Then, why is soil emission estimated to be larger in winter when temperatures are low, and snow is present?
51. Line 325: Do you have any hypotheses or supporting information on how snow cover affects the flux?
52. Line 338: The term “surface exchange” may be more appropriate than “dry deposition” here.
53. Line 346: The phrasing should be revised to “we also observe peak deposition fluxes” for clarity.
54. Figure 6: While the discussion of diurnal variation is valuable, analyzing the full annual dataset may obscure seasonal characteristics. Do the observed diurnal patterns hold true across all seasons, for example, during winter when concentrations and air temperature are lower? Are stronger daytime emissions observed during summer?
55. Line 365-368: Is it also possible that the applied bidirectional flux model underestimates the actual amount of dry deposition? This relates to the previous question: why is dry deposition substantially higher in May and August compared to other months? Could the low dry deposition in June and July be due to large daytime emissions? Since wet deposition also become lower during these months, did less rainfall favored NH_3 emission?
56. Line 379: According to Figure 7(b), the largest NH_3 dry deposition appear in “May” and August. Please revise the text accordingly.
57. Line 380-382: Can you explain why the proportion of reduced nitrogen is so high in this area, in relation to the transport and sources mentioned above?

58. Line 389: Please be consistent in terminology. Use either “time resolution” or “time-resolution” throughout the manuscript, but do not mix both styles.
59. Line 406: Please consider expanding your discussion on the reasons for the differences in modeled flux. If I understand correctly, one key factor may be the diurnal variation in the flux: At high temporal resolution, models usually reproduce large daytime NH_3 emissions driven by increasing temperature. At night, stomatal closure and reduced turbulence lead to larger stomatal and in-canopy aerodynamic resistances, suppressing emissions from both stomata and ground. Simultaneously, elevated relative humidity and acidity ratio (AR) enhance deposition. Therefore, deposition at nighttime may largely contribute to the annual dry deposition in 30-min resolution. However, at lower temporal resolution, these diurnal dynamics are averaged out, potentially leading to overestimation of emission and underestimation of deposition.
60. Figure 10: While the overall trends of deposition and emission appear roughly consistent, there are notable differences in the magnitude of deposition fluxes in some cases. Both fluxes seem to exhibit systematic bias. What could be causing this? It is also puzzling that the annual dry deposition totals are same despite these differences.
61. Line 438: Does this mean that you applied a monthly diel pattern of each month? If so, this sentence is an insufficient explanation.
62. Line 443: Please revise “Dry deposition inferential” to “Bidirectional exchange”.
63. Line 446: Again, how did you simulate 30-min fluxes using ERA5 reanalysis data with 1-hour temporal resolution?
64. Line 451-452: This sentence is unclear and please rephrase. Figure 11 suggests that the ERA5-based flux show smaller emission compared to the NEON simulation, which could result in the higher dry deposition amount.
65. Figure 11: The title appears redundant since it merely repeats the caption.
    It may be more informative to plot by specifying season or by day/night. This could help identify reasons for the discrepancies more clearly.
66. Line 460: Same comment with 44 for R_a and χ_{z0}.
67. Line 472: Same comment with 66 for u_* and L.
68. Line 480: Same comment with 68 for L.
    If the u_* from ERA5 were corrected using NEON, would the simulation results become more consistent between the two datasets?
69. Line 481-482: Do the observed differences in R_a directly cause the discrepancies in dry deposition amount? If so, please describe. Also, it is unclear why χ_{z0} values are consistent despite significant differences in R_a (in Line 461-462).

Moreover, Figure S2(h.) shows a large discrepancy in RH (R^2 = 0.34), and ERA5 values being substantially higher than NEON. As RH is a critical input for R_w, how does this discrepancy influence fluxes? Why was this not discussed in the main manuscript?

70. Line 485: Considering the editor's comment, the phrase "best simulated" may be inappropriate at this stage.
71. Line 489: As noted previously, please use consistent terminology throughout the manuscript: either "bidirectional" or "bi-directional," but not both.
72. Line 510-514: This methodology is quite promising. If you could briefly describe its potential applicability to other sites or its utility for future research, this would enhance the academic contribution of this study.
73. Figure S7: The meaning of "calculated fractional differences" is unclear. What can be seen from this figure is that the magnitude of flux in response to the χ_a scaling factor differ considerably by season, regardless of the two time periods.