Author replies are indented and italicized.

Reviewer 1:

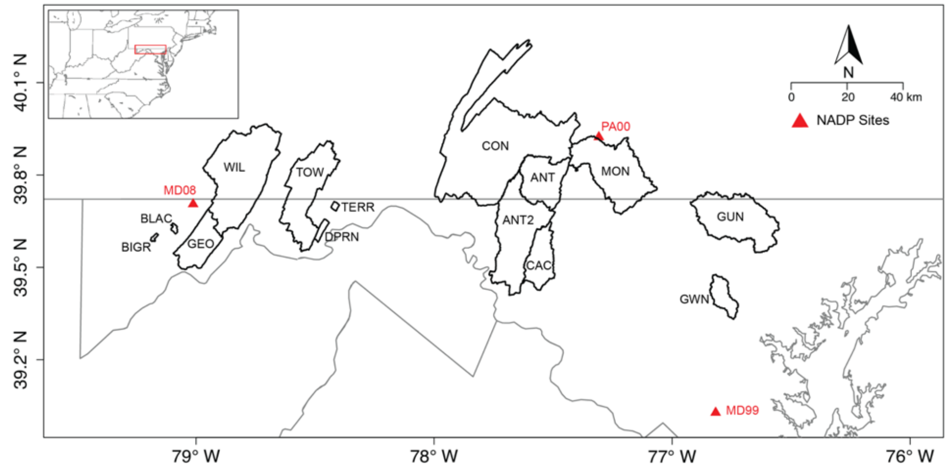
By estimating the concentration of stream nitrate (NO3-), isotopic compositions of NO3 - (δ15N, δ18O, and Δ17O), and water flux during base flow and storm events, this manuscript investigated the exportation of NO3 - terr and NO3 - atm in two different watersheds, where two watersheds have different land-use. Compared to the mixed agricultural/forested watershed, the developed urban watershed exported more NO3 - atm during storm events, which was explained by impervious surfaces that hydrologically connect runoff to channels to facilitate the export of NO3 - atm during storm events. In addition, the disproportionality factor was proposed to quantify the disproportionate effect of NO3 - terr and NO3 - atm compared to the runoff during storm events.

While the paper is nicely written, I have one major concern about the Δ17O of atmospheric NO3 - in rainfall. In the author's past study, they reported the mean value of Δ17O of atmospheric NO3 - in three nearly stations was +25.1 ‰ (Bostic et al., 2021; figures of following), which the value was in accordance with other past studies (e.g., +26.3 ± 3 ‰; Tsunogai et al., 2016, +26.1 ± 3.5 ‰; Hale et al., 2014, and +20 ~ +30 ‰; Michalski et al., 2003) in the similar latitudes. On the other hand, the mean value of Δ17O of atmospheric NO3 - in this study was +20.2 ± 2.8‰ (Table S1), which the value was seems significantly smaller than the past studies. The concern should be resolved before publication.

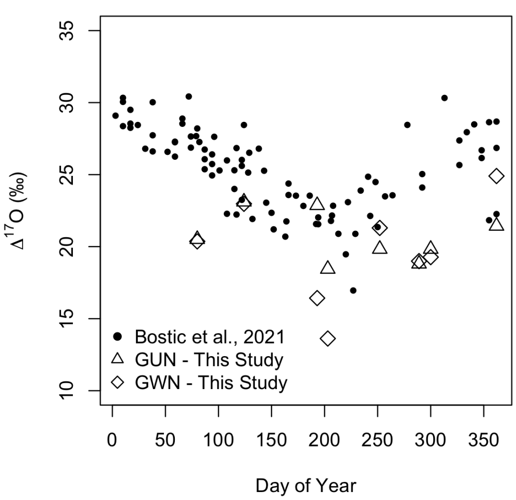
Thank you for your comments regarding D17O of our rainfall samples. The reviewer is correct that the average D17O value of NO3-Atm in rainfall (in this manuscript 20.2 per mil) is lower than that in Bostic et al., 2021 (25.2 per mil). However, both values are within measured ranges reported by studies in similar latitudes (Michalski et al., 2003; Xia et al., 2019). There is no reason to believe the different values are related to methodological/analytical issues, as the samples in both studies were analyzed in the same lab using the same methodology, and instrumental precision and accuracy of D17O-NO3 data was similar between the studies. We suspect the lower values in this manuscript relative to Bostic et al., 2021 are due to one of two most likely factors:

(1) *Samples were not collected in the same location. In Bostic et al., 2021, precipitation samples (weekly composites) were collected from three National Atmospheric Deposition Program sites from October 2016-September 2017. The locations of those sites are shown as red triangles in the figure below from Bostic et al., 2021. In the present manuscript, precipitation samples were collected (during precipitation events) at the outlet of the two watersheds (GUN and GWN on the below figure) from September 2018-October 2019. Importantly, GWN is a highly urbanized watershed. Previous work has shown that oxidation pathways of NO and NO2 can differ between urban and rural areas, resulting in lower D17O-NO3 values in urban deposition (Li et al., 2022; Nelson et al., 2018). The different sampling frequencies between studies (weekly vs event-based) could*

also potentially influence the observed differences in NO3-D17O values.



(2) Relatively few rainfall samples were collected during winter in the present study. Previous studies (list here; Xia et al., 2019; Nelson et al., 2018; Huang et al., 2020), have shown a clear seasonal pattern of D17O of NO3-Atm, with higher values in winter and lower values in summer. Six of the eight storm events sampled in the present manuscript occurred between the months of May - October. Included below is a figure of D17O of NO3-Atm for all sampled events in this manuscript, along with the samples collected from Bostic et al., 2021. Samples from the present manuscript approximately follow the seasonal pattern that was observed in Bostic et al., 2021. The combined effects of relatively more samples collected in summer than winter and differing atmospheric chemistry of urban areas likely contributed to the slightly lower average of D17O of rainfall NO3 in this study compared to our previous research in the region (i.e., Bostic et al., 2021).



Specific comments:

Line 140-147: The calculated NO3- atm Deposition should compare with similar past studies to verify the accuracy of the data.

> *We used the same procedure as previous studies (Lovett et al., 2000; Nelson et al., 2018; Huang et al., 2020) to estimate NO3 deposition (equation 1 in the manuscript).*

Line 240: Is DF=1 here?

> *Thank you for catching this incomplete sentence. This sentence has been revised to:*
>
> > *For example, an event with DF = 4 indicates that a given storm exported 4× more NO_3^- than water whereas an event with DF = 0.5 indicates that a storm exported 2× less NO_3^- than water, after both have been normalized to annual amounts.*

L370-373: The interpretation of low δ15NTerr and δ18OTerr during storm events was reasonable; the same phenomenon has also been reported by a recent study (Ding et al., 2022). However, there is another possibility, the shorter residence time of stream NO3 - during storm events could cause smaller biologically-mediated fractionation (having not enough time for bioreactions of fractionation) than normal time; thus, the exported NO3 - showed low values of δ15NTerr and δ18OTerr, rather than the addition of new NO3 -. In addition, the reason why the δ15NTerr in GUN watershed didn't show low values (and the weaker significance of δ18OTerr) also should be discussed in the manuscript. Because GUN watershed showed higher land-use of forest and agriculture (Table 1), the flushing effect should be stronger in GUN watershed.

> *Thank you for your comment regarding interpretation of δ15NTerr and δ18OTerr and your suggestion regarding the possible influence of shorter residence time of stream NO3 during storm events. We agree that reduced residence time could play a role and have added a sentence to the discussion. We have also added two new sentences further elaborating on the differences between GUN and GWN. The revised paragraph is below with additions highlighted:*
>
> > *$D^{17}O$ of NO_3^- can additionally be used to "correct" $d^{15}N$ and $d^{18}O$ values (eqs. 7 and 8) to better indicate isotope values of terrestrial NO_3^- sources (Dejwakh et al., 2012). Values of both $d^{15}N_{Terr}$ and $d^{18}O\text{-}NO_3^-{}_{Terr}$ during storm events fall within the range of values that are typical of natural "soil" and fertilizer (Kendall et al., 2007), but interestingly, $NO_3^-{}_{Terr}$ isotope values decreased during storm events relative to baseflow in both watersheds (though not significantly for $d^{15}N$ in GUN; Figure 3). This shift to lower $d^{15}N_{Terr}$ and $d^{18}O\text{-}NO_3^-{}_{Terr}$ values during storm events may reflect the flushing of less "processed" NO_3^- sources from upper soil*

horizons (Creed et al., 1996), as processing (e.g., denitrification) generally leaves the remaining NO_3^- with more positive $d^{15}N$ and $d^{18}O$ values due to biologically-mediated fractionation (Denk et al., 2017). Lower $d^{15}N_{Terr}$ during storm events relative to baseflow was not statistically significant in the mixed agricultural/forested watershed (GUN), but this was due to a single event in which $d^{15}N_{Terr}$ increased from baseflow to stormflow. Impervious surfaces in the developed watershed likely reduce flushing of this lower $d^{18}O$-$NO_3^-{}_{Terr}$ by restricting infiltration, but 30% of this watershed is not "developed" (and a higher percentage contains pervious surfaces), which likely contributes to the similarity in $NO_3^-{}_{Terr}$ isotope patterns between study watersheds. Additionally, relatively lower $NO_3^-{}_{Terr}$ isotope values in storm events could be due to reduced in-stream NO_3^- uptake (e.g., assimilation, denitrification) during periods of elevated discharge (Grimm et al., 2005). Biological NO_3^- uptake generally fractionates against heavier isotopes which increases isotope ratios of the remaining NO_3^- (Kendall et al., 2007). If in-stream NO_3^- uptake rates are reduced during high flows, the resulting effect could contribute to the lower $NO_3^-{}_{Terr}$ isotope values during storm events. Relatively lower $d^{18}O$- $NO_3^-{}_{Terr}$ values during storm events relative to baseflow, and associated insights into watershed-scale N biogeochemistry, were only realized by using $D^{17}O$ to "correct" $d^{18}O$ values. Without this correction, $d^{18}O$-NO_3^- during storm events is strongly influenced by elevated $d^{18}O$ of $NO_3^-{}_{Atm}$, as shown by the similar patterns between $D^{17}O$ and "uncorrected" $d^{18}O$ in the more developed watershed (Figure 3).

Figure 4: While other figures had 8 points, there were only 7 points in Figure 4, Figure S4 also.

Thanks for catching this mistake. A pre-storm, baseflow sample was not collected for the first event in either watershed. All figures comparing baseflow to stormflow dynamics or figures that require a baseflow sample (e.g., event water fraction) should only have 7 data points. We have added the following text to the methods for clarification:

A pre-event baseflow sample was not collected for the first storm, thus any figures or analyses that compare pre-event baseflow to event mean concentrations or event-water fractions have seven data points.

We note that this does not change the statistical significance for any results.

Figure 5: The calculation of the fraction of rainfall NO3 - exported (y-axis) should be expressed in section 2 of the manuscript. How about using the intensity of rainfall (unit: cm/h) as the x-axis?

We have added the following text and equation to the methods section:

The fraction of rainfall NO_3^- exported on an event basis was calculated as:

$$Fraction\ of\ rainfall\ NO3^{-}\ exported = \frac{NO_{3-Atm}^{-} Yield\ (g\ N\ ha^{-1})}{NO_{3-Atm}^{-} Deposition\ (g\ N\ ha^{-1})} \text{(eq. 7)}$$

where event $NO_3^{-}{}_{Atm}$ deposition was calculated using eq. 1 and event $NO_3^{-}{}_{Atm}$ yield was calculated using eq. 5. We appreciate the suggestion to use intensity of rainfall on the x-axis, but unfortunately we lack such data.

Figure S2: It seems many stream water samples were sampled during baseflow and storm periods. Did the authors analyze the isotopic compositions (δ15N, δ18O, and Δ17O of NO3 -) of all these samples? If the authors did, they can list these data in supplementary and the number of analyzed in the manuscript, not only the mean value (Figure 3; Table S3).

We did analyze the isotopic composition of all the samples shown in Figure S2. We will add a supplementary table with this data.

References

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