Ewha, Where Change Begins

EWHA WOMANS UNIVERSITY

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Dear Editor Markus Hrachowitz,

We sincerely thank you and both reviewers for the constructive and thoughtful feedback on our manuscript entitled "Isotopic evidence for the impact of artificial snow on the nitrogen cycle in temperate regions". In revising the paper, we focused particularly on the main points raised by both reviewers, which centered on (i) the representativeness of end-members used in the mixing model, (ii) the treatment of isotope fractionation and nitrate reactivity, and (iii) the interpretation of artificial snow as a hydrological process influencing nitrogen cycling.

1. Representativeness of End-Members

Both reviewers raised concern regarding the adequacy of rainwater and artificial-snow samples used as end-members. We have now described in detail the rainfall sampling protocol (following IAEA guidelines), validated the rainwater isotopic composition using long-term data from a nearby monitoring site, and performed sensitivity tests showing that the Bayesian mixing results are robust to small variations in the rainwater end-member.

For artificial snow, we statistically confirmed its representativeness by comparing it with the source stream water (two-sample t-test, $p > 0.05$), demonstrating that their isotopic and chemical compositions are indistinguishable. These results verify that the artificial-snow end-member accurately reflects the source water used for snowmaking.

2. Isotope Fractionation and Biogeochemical Processes

Both reviewers emphasized the need to address possible isotope fractionation. We now explicitly discuss this issue using a dual-isotope ($\delta^{15}N–NO_3^-$ vs. $\delta^{18}O–NO_3^-$) comparison, which revealed no significant correlation ($R^2 = 0.03$), indicating that denitrification did not occur.

To evaluate the isotopic behavior during nitrification, we conducted a Monte Carlo simulation that incorporated uncertainties in oxygen-isotope fractionation parameters and compared the predicted $\delta^{18}O–NO_3^-$ with observed values. The observed data fall largely within the modeled range, confirming that the measured variations primarily reflect the mixing of multiple nitrate sources rather than isotopic fractionation.

Accordingly, the assumption of $\varepsilon = 0$ in the Bayesian model is justified, and the isotopic composition of groundwater nitrate is best interpreted as a mixing outcome rather than the product of active denitrification.

3. Role of Artificial Snow in Nitrogen Cycling

A recurring issue was how artificial snow, produced from natural water, could affect the nitrogen cycle. We clarified that artificial snow does not introduce new nitrate, but redistributes nitrate-bearing surface water within the catchment. This redistribution alters the timing and pathways of nitrogen transport, storing anthropogenic nitrate in high-elevation snowpacks during winter and releasing it as concentrated meltwater that infiltrates into groundwater.

From a biogeochemical perspective, the balance between storage and flux controls the residence and retention of reactive nitrogen within the hydrological system. Artificial snow prolongs the retention of nitrate rather than merely increasing water residence time, thereby enhancing nitrate accumulation in groundwater through delayed release and limited removal under cold conditions.

This hydrologically induced change in nitrogen retention and storage dynamics represents a significant alteration of the nitrogen cycle, supported by consistent trends in $\delta^{15}N–NO_3^-$, $\delta^{18}O–H_2O$, and $NO_3^-–N$ concentrations.

4. Manuscript Refinements

We have simplified the discussion to focus strictly on hydrological and biogeochemical mechanisms supported by our data, removed general statements about greenhouse-gas emissions, and rewritten the conclusion accordingly. Isotopic data are now reported to one decimal place consistent with analytical precision, and figures and terminology (e.g., LMWL, enrichment factor) have been clarified throughout.

Together, these revisions address all overlapping concerns raised by both reviewers and strengthen the conceptual and methodological consistency of the manuscript.

We greatly appreciate your consideration and the opportunity to revise our work.

In response to the reviewers' feedback, we have carefully revised our manuscript accordingly, and we provide detailed point-by-point replies to all referee comments below. We hope that our responses adequately address all concerns raised.

Reply to the comments by the reviewers

Reviewer #1: *The purpose of the submitted manuscript is to show how artificial snow in a ski resort affects local groundwater quality. In particular, the authors attempt to delineate nitrate sources and quantify the relative contributions of different sources to groundwater nitrate. Although the production of artificial snow is a local rather than a global issue, I think this is a very interesting topic. What I like very much about the manuscript is its conciseness.*

The authors build their case based on more than 60 water samples collected from groundwater, artificial snow, natural snow, rain, and surface water. Their preferred tools are nitrate isotope signatures, nitrate concentrations, and water isotope signatures.

Answer: We sincerely thank the reviewer for the thorough and insightful comments. We greatly appreciate the positive evaluation of our study's novelty and clarity. We are delighted that the reviewer found our research topic on the influence of artificial snowmaking on groundwater nitrate dynamics both interesting and concisely presented. To our knowledge, this is one of the first studies to quantitatively demonstrate how artificial snow production influences groundwater nitrate through hydrological redistribution and isotopic tracing. We believe that this novel perspective, together with the concise organization of multiple isotopic and chemical lines of evidence, enhances the clarity and scientific contribution of the manuscript. We have carefully addressed each concern and suggestion in the following detailed, point-by-point responses.

Major comments:

1. The first one is related to the representativeness of the endmembers for the mixing model. This is especially true for the rainwater samples. It is completely unclear how the rainwater samples were collected. Looking at the data points, I strongly suspect that the precipitation samples were collected as "occasional grab samples". Such a dataset might be OK for a rough estimate of the local meteoric water line. However, the use of rainwater isotope data to constrain hydrological connections and flow paths necessarily requires composite samples. This gives the opportunity to consider weighted seasonal or annual means of isotopic compositions, which are more appropriate in the given context to serve as endmembers for a mixing model.

Answer: We appreciate this valuable comment regarding the representativeness of rainwater end-members. We intended that the rainfall samples were collected following the IAEA-recommended protocol using a sampler designed to minimize evaporation after collection. This method ensures that each collected sample represents an integrated precipitation event, rather than an instantaneous grab. Sampling was conducted at both high (1,420 m) and low (770 m) altitudes during February 2021, May 2021, and August 2022, capturing distinct winter, spring, and summer isotopic signatures under different meteorological conditions. We emphasize that the samples were not collected opportunistically but through a deliberate event-based strategy designed to obtain representative isotopic compositions of seasonal precipitation.

Figure R1-1. Installation and sampling procedure of the rainwater collector at the ski resort site. The photo shows researchers collecting precipitation using a stainless-steel rain sampler designed to prevent contamination and minimize evaporation losses.

Although the number of rainwater samples is limited due to logistical constraints in the alpine environment, the collected $\delta^{18}O$–H_2O and $\delta^{2}H$–H_2O values fall along the Local Meteoric Water Line (LMWL). Therefore, they provide a robust isotopic framework for defining the rainwater end-member in the mixing model. We will add a detailed description of the rainwater collection protocol in the Methods section.

"Rainwater samples were collected using a stainless-steel rain sampler to minimize surface contamination. Sampling was conducted on an event basis, and each sample was transferred into pre-cleaned high-density polyethylene bottles immediately after precipitation and stored at 4 °C until analysis to prevent isotopic alteration by evaporation."

We also emphasize that the Bayesian mixing model is insensitive to small variations in the rainwater end-member within this isotopic range, as confirmed through sensitivity testing.

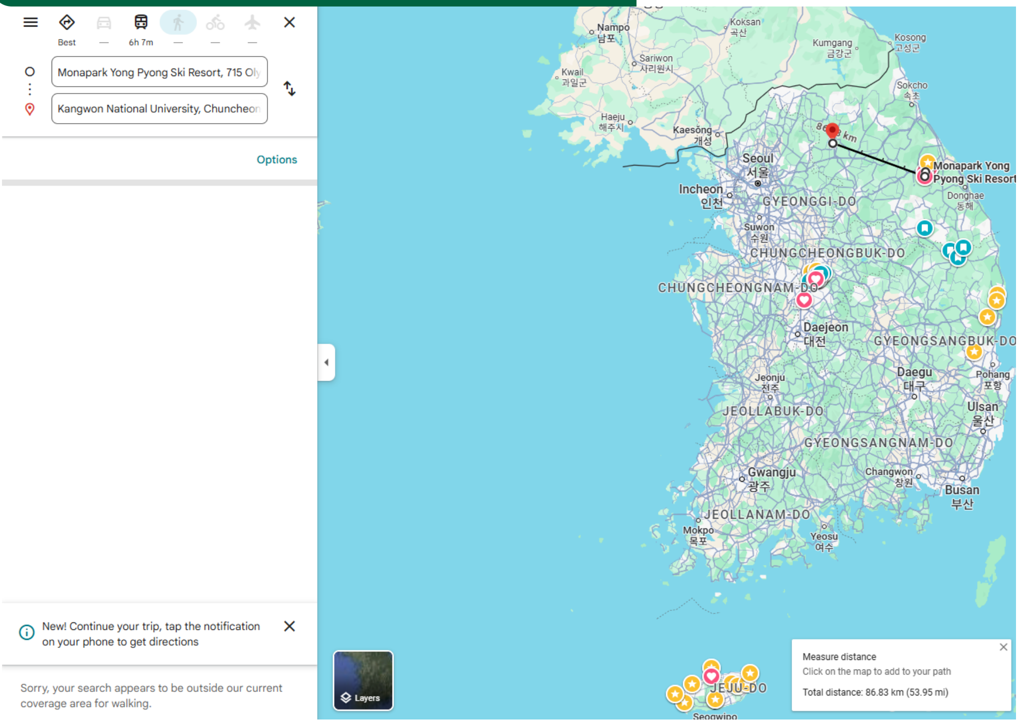

Figure R1-2. Map showing the distance between Chuncheon and the Yongpyong Ski Resort (~85.9 km).

We tested the model's sensitivity using high-resolution precipitation isotope data collected in Chuncheon, Gangwon Province (approximately 90 km from the study area) during June 2002 – April 2004, as reported by Yu et al. (2007). Although these data were not obtained during our study period, they were collected from a nearby region under comparable climatic conditions, providing an independent dataset for model evaluation (mean $\delta^{18}O = -9.5 \pm 3.3$ ‰ for summer precipitation, $n = 59$; -12.4 ± 3.7 ‰ for natural snow, $n = 17$).

The recalculated Bayesian mixing model produced results with rainwater (SP) decreasing and natural snow (NS) increasing slightly, whereas the proportion of artificial snow (AS) remained nearly unchanged.

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Summary for 1

                          2.5%    25%    50%    75%  97.5%
deviance                39.393 42.791 45.551 49.293 58.177
AS                       0.375  0.444  0.477  0.505  0.557
NS                       0.104  0.219  0.279  0.347  0.502
SP                       0.108  0.203  0.243  0.282  0.358
sd[7.0832636418570125]   0.188  0.329  0.429  0.553  0.913
sd[-10.555812119999999]  0.246  0.593  0.865  1.199  2.109
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Summary for 1

                          mean    sd
deviance                46.464 5.023
AS                       0.474 0.047
NS                       0.286 0.100
SP                       0.241 0.061
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sd[-10.555812119999999]  0.948 0.505
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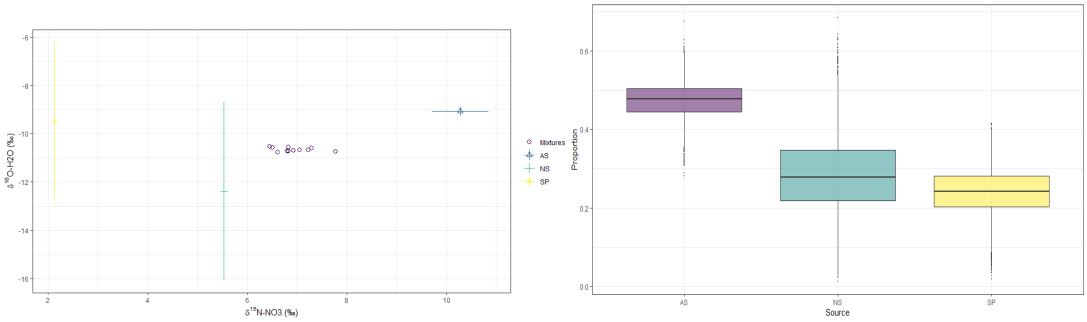


Figure R1-3. Results of the recalculated Bayesian mixing model showing the proportional contributions of artificial snow (AS), natural snow (NS), and precipitation (SP) to groundwater.

Month	Amount (mm)	mean $\delta^{18}O$ (‰)
02-Jul	24	-10.2
02-Aug	23	-9.8
03-Jun	20.8	-8.4
03-Jul	23.1	-9.6
03-Aug	23.2	-9.5

Table R1-1 Monthly mean $\delta^{18}O$ values of precipitation and corresponding rainfall amounts during the summer in Chuncheon, Gangwon Province.

We calculated the summer precipitation-weighted mean $\delta^{18}O$ value (−9.1 ‰) based on monthly precipitation amounts. This value differs only slightly (0.4 ‰) from the arithmetic mean (−9.5 ‰). Although this difference is somewhat larger than the analytical uncertainty (± 0.1 ‰), it remains negligible compared with the natural isotopic variability of regional precipitation (± 3.3 ‰). Therefore, the choice of either mean does not materially affect the Bayesian mixing model results or our overall interpretation.

Finally, we acknowledge that future work with seasonally weighted composite samples would further refine these results, but our current dataset provides an adequately constrained and defensible isotopic basis for the mixing analysis.

-Yu, J. Y., Park, Y., Mielke, R. E., & Coleman, M. L. (2007). Sulfur and oxygen isotopic compositions of the dissolved sulphate in the meteoric water in Chuncheon, Korea. *Geosciences Journal*, *11*(4), 357-367.

2. Second, I'm not convinced by the delineation of the potential nitrate sources. Strictly speaking, the authors do not exactly apply the mixing model to calculate the contribution of different nitrate sources. Rather, they use nitrate as a conservative tracer to get information about the relative contribution of different water sources to the groundwater. Artificial snow cannot be a source of nitrate. It is made from surface water and contributes the nitrate to the groundwater pool that was originally contained in the surface water. My understanding is that surface water is discharged from groundwater in the summit region so that the nitrate was originally picked up during groundwater recharge and the groundwater passage to surface water. Based on the measured nitrate isotope signatures, the authors claim that the surface water nitrate comes from manure and sewage. On the other hand, they state in lines 194/195 that "agricultural activities and sewage discharge are absent on the mountain summit". In my opinion, this is not a very conclusive scenario. If there are no agricultural activities and no sewage discharge, only two N sources remain: atmospheric deposition and natural soil N, which also comes from the atmosphere through symbiotic N-fixation and is recycled through plant uptake and plant decay. The mechanisms causing the reported positive shift in N isotope signatures certainly need to be clarified.

Answer: We partially agree with the reviewer's point, but we would like to clarify a different perspective. Artificial snow itself does not create new nitrate sources, as it is produced from surface water. Our intention is not to imply that artificial snow generates additional nitrate, but rather to highlight that the use of surface water with pre-existing anthropogenic nitrogen signatures can serve as a potential pathway for nitrate input into the groundwater system through repeated snowmaking and melting processes.

Although all forms of nitrogen may eventually return to the atmosphere through natural biogeochemical cycling, the key difference lies in their residence time and transport pathways. While nitrate transit times in shallow groundwater are typically on the order of months to a year (Radtke et al., 2024), the persistence of anthropogenic nitrogen inputs in terrestrial systems can extend over decades to centuries, forming a long-term nitrogen legacy that continues to affect groundwater quality (Canfield et al., 2010; Gruber and Galloway, 2008). Such long-term accumulation and delayed release of reactive nitrogen have been increasingly recognized even in regions with limited direct anthropogenic activity.

However, as noted in the manuscript, the NO_3^-–N concentrations observed in summit groundwater exceed the commonly accepted natural background level of 3.0 mg/L for pristine systems (Madison and Brunett, 1985), strongly suggesting the presence of anthropogenic nitrogen inputs. The ski resort located at the site has been in operation since 1975 and continues to operate, with substantial amounts of artificial snow produced over several decades. Consequently, the cumulative nitrogen load from artificial snowmaking is likely to be significant and persistent, exceeding what would result from natural deposition and short-term biogeochemical turnover.

Our results show that the $\delta^{15}N–NO_3^-$ values of both surface water and artificial snow samples are consistently enriched (mean ≈ +9.8‰), falling within the manure/sewage (M&S) domain. This isotopic signature is clearly distinct from atmospheric deposition and natural soil N, which exhibit lower δ15N values and lower NO_3^-–N concentrations. In particular, during the snowmelt period in May 2021, we observed an increase in $\delta^{15}N–NO_3^-$ values (from 6.8‰ to 7.5‰), while NO_3^-–N concentrations remained high (~4.64 mg/L), comparable to those observed in January. This points toward an input of nitrate with a manure/sewage-like signature.

Since direct agricultural or sewage discharge sources are absent in the summit region, we conclude that the nitrate was introduced via artificial snow, which was produced using surface water already impacted by upstream anthropogenic activities. Therefore, if the surface water used for snowmaking is not properly managed, it could act as a potential pollution vector that transfers anthropogenic nitrogen from surface sources (e.g., runoff influenced by agricultural or urban activities at lower elevations) to the subsurface environment.

-Gruber, N., & Galloway, J. N. (2008). An Earth-system perspective of the global nitrogen cycle. *Nature*, *451*(7176), 293-296.

-Canfield, D. E., Glazer, A. N., & Falkowski, P. G. (2010). The evolution and future of Earth's nitrogen cycle. *science*, *330*(6001), 192-196.

- Radtke, C. F., Yang, X., Müller, C., Rouhiainen, J., Merz, R., Lutz, S. R., Benettin, P., Wei, H., and Knöller, K. (2024). Nitrate and Water Isotopes as Tools to Resolve Nitrate Transit Times in a Mixed Land Use Catchment. *Hydrol. Earth Syst. Sci.* Discuss. [preprint], https://doi.org/10.5194/hess-2024-109.

3. The third concern is already implied in the section above when I said that nitrate is treated as a conservative tracer. Any potential reactivity of nitrogen species is completely neglected in the discussion. I think it is inevitable to discuss the uncertainty that is introduced into the mixing model by isotope fractionation related to biogeochemical turnover processes. The authors have the d18O-NO3 at hand, so this discussion could easily be based on nitrate concentrations and dual isotope signatures. While the authors mention denitrification as a potential process in the discussion section, they don't use of their data set to prove or disprove its occurrence.

Answer: We appreciate the reviewer's valuable comment. We agree that isotopic fractionation during biogeochemical transformations can potentially affect the interpretation of nitrate sources in the mixing model. To address this point, we first examined the relationship between $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ values (Figure R1-4) to evaluate whether denitrification occurred. Even in groundwater where denitrification could potentially occur, no significant correlation was found between $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$, suggesting that the isotopic enrichment pattern typically associated with denitrification (i.e., $\delta^{18}O–NO_3^-$ versus $\delta^{15}N–NO_3^-$ slope of 0.5–1.0; Kendall et al., 1998) was not evident in our dataset.

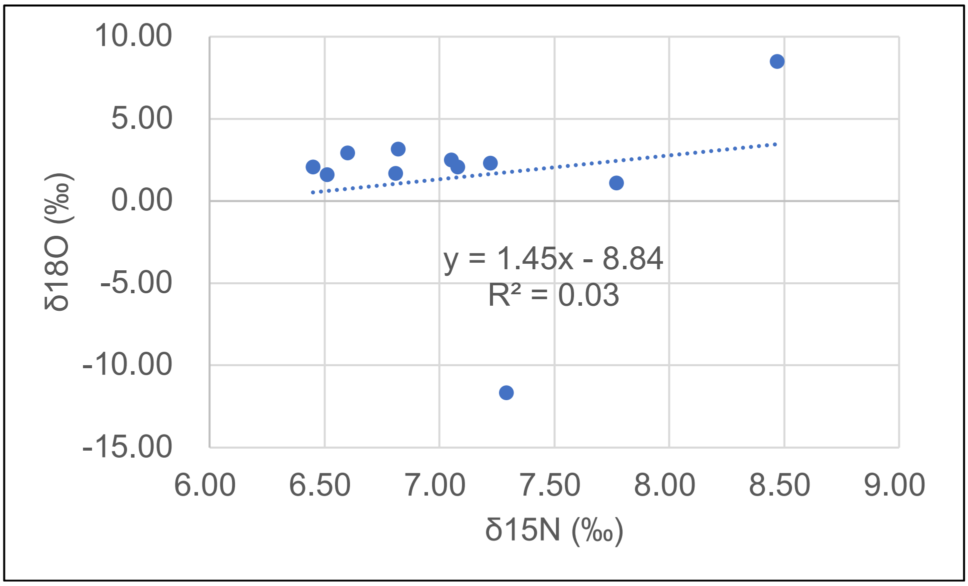


Figure R1-4. Relationship between $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ values in groundwater samples. The slope (1.45) of the linear regression indicates no clear enrichment trend between nitrogen and oxygen isotopes of nitrate (R^2 = 0.03), suggesting that denitrification was not a dominant process controlling nitrate isotopic composition.

During nitrification, oxygen atoms in nitrate are typically derived from both ambient water and atmospheric O_2 in an approximate 2:1 ratio (Andersson and Hooper, 1983; Casciotti et al., 2002). This process can be described using a dual-isotope mass balance framework that integrates contributions from $\delta^{18}O–H_2O$ and $\delta^{18}O–O_2$, as well as kinetic and equilibrium isotopic effects, associated with ammonia oxidation (Buchwald et al., 2012; Equation R1-1). Based on this framework, we performed a Monte Carlo simulation (n = 10,000) to predict the expected $\delta^{18}O–NO_3^-$ values of nitrification-derived nitrate while incorporating uncertainties in the oxygen isotope fractionation parameters (Table R1-2). The predicted values were then compared with our observed $\delta^{18}O–NO_3^-$ data (Figure R1-5).

The observed $\delta^{18}O–NO_3^-$ values generally agreed with the modeled relationship between $\delta^{18}O–NO_3^-$ and $\delta^{18}O–H_2O$ derived from the Monte Carlo simulation, although several groundwater samples exhibited slightly higher $\delta^{18}O–NO_3^-$ values than the upper limit of the 95 % confidence interval. This pattern indicates that the observed $\delta^{18}O–NO_3^-$ variations are primarily controlled by the mixing of multiple nitrate sources rather than by a single nitrification process. Considering that denitrification would be expected under the prevailing groundwater conditions but no isotope evidence for such a process was observed, the slight enrichment in $\delta^{18}O–NO_3^-$ is more plausibly attributed to mixing with nitrate derived from artificial snowmelt rather than to isotopic fractionation during denitrification.

Equation R1-1

$$\delta^{18}O_{NO_3^-} = \left(\frac{2}{3}+\frac{1}{3}x_{AO}\right)\cdot\delta^{18}O_{H_2O} + \left(\frac{1}{3}(1-x_{AO})\right)\cdot(\delta^{18}O_{O_2}-\varepsilon_{k,O_2}) - \frac{1}{3}(1-x_{AO})\cdot\varepsilon_{k,H_2O,1} - \frac{1}{3}\cdot\varepsilon_{k,H_2O,2} + \frac{2}{3}x_{AO}\cdot\varepsilon_{eq}$$

This equation models the produced $\delta^{18}O$–NO_3^- during nitrification based on oxygen contributions from water and O_2, and associated isotope effects.

Supplementary Table R1-2. Description, units, and simulation ranges for parameters used in the Monte Carlo simulation of $\delta^{18}O$–NO_3^- during nitrification.

Parameter	Description	Units	Value/Range	Reference
$\delta^{18}O$-H_2O	Oxygen isotopic composition of water	‰	-12 to -8	Measured
$\delta^{18}O$-O_2	Oxygen isotopic composition of atmospheric O_2	‰	+23.5	Kroopnick and Craig (1972)
X_{AO}	Fraction of O atoms in NO_2^- exchanged with water prior to nitrification	dimensionless	0 to +0.78	Boshers et al. (2019)
$\varepsilon_{k,O2}$	O isotope effect for O_2 incorporation	‰	+10 to +20	Casciotti et al. (2010)
ε_{eq}	Equilibrium O isotope effect between NO_2 and H_2O	‰	+14.75 (at 283.7K)	Buchwald and Casciotti (2013)
$\varepsilon_{k,H_2O,1}$	O isotope effect for H_2O incorporation during aerobic ammonia oxidation	‰	+14	Casciotti et al. (2010); Granger and Wankel (2016)
$\varepsilon_{k,H_2O,2}$	O isotope effect to H_2O incorporation during nitrifiers and anammox	‰	+12.8 to +18.2	Buchwald and Casciotti (2010)

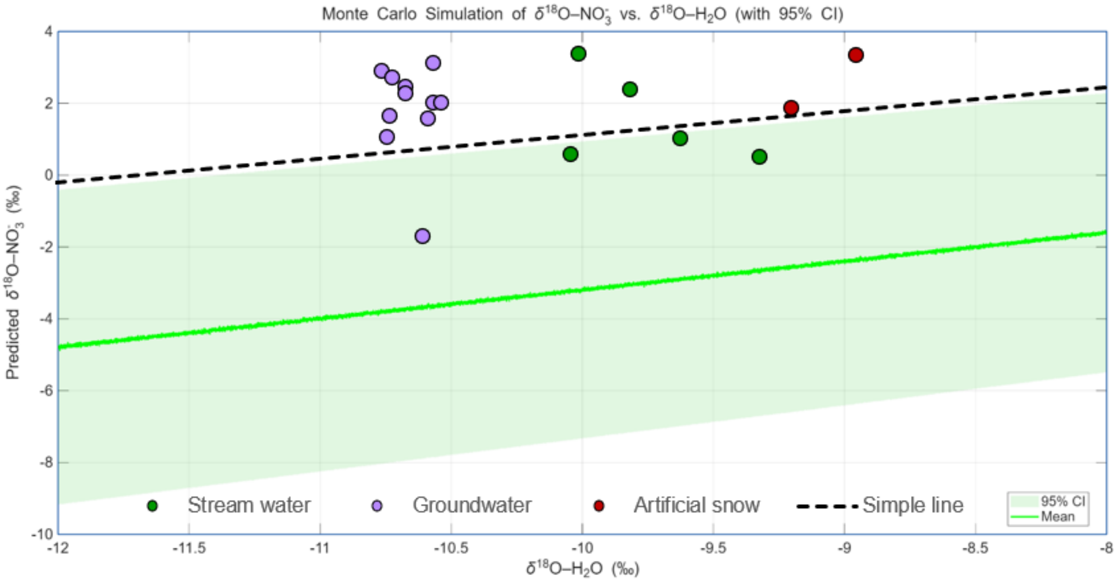


Figure R1-5. Relationship between predicted $\delta^{18}O–NO_3^-$ and $\delta^{18}O–H_2O$ for stream water, groundwater, and artificial snow. The black dashed simple line represents the theoretical relationship assuming that two-thirds of oxygen atoms in nitrate are derived from ambient water and one-third from atmospheric O_2 during nitrification. The green line and shaded area denote the mean and 95 % confidence interval (CI) of the Monte Carlo simulation results, respectively. Most samples plot above this theoretical line, indicating higher $\delta^{18}O–NO_3^-$ values than expected from nitrification. Given the absence of denitrification signals, this enrichment likely reflects the influence of nitrate mixing processes.

We will add the following at the end of Section 3.4 of the Discussion to clarify that (i) denitrification signals are not supported by the dual-isotope data, and (ii) the observed $\delta^{18}O–NO_3^-$ enrichment in groundwater likely reflects mixing between nitrified nitrate from precipitation and nitrate derived from anthropogenic sources in artificial snow.
"To further evaluate the processes controlling nitrate isotopic variation in groundwater, we examined the dual-isotope relationship between $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$. No significant correlation was observed, indicating that denitrification did not occur in the groundwater system even under conditions that would generally favor such processes. Although $\delta^{18}O–NO_3^-$ values in groundwater were slightly higher than those predicted by the Monte Carlo simulation for nitrification, this enrichment cannot be attributed to isotope fractionation associated with denitrification. Instead, the elevated $\delta^{18}O–NO_3^-$ values are more plausibly explained by the mixing of nitrified nitrate with anthropogenic nitrate derived from artificial snowmelt and with nitrate originating from precipitation. These findings suggest that biogeochemical isotope fractionation played a minor role and that the isotopic composition of groundwater nitrate largely reflects physical mixing among distinct nitrate sources. Therefore, to quantitatively assess the contribution of each nitrate source to groundwater, we employed a Bayesian mixing model in the following section."

-Andersson, K.K., & Hooper, A.B. Oxygen and hydrogen atoms in hydroxylamine, nitrite, and nitrate produced from ammonia by Nitrosomonas: 15N-NMR and 18O studies. Biochimica et Biophysica Acta (BBA) - General Subjects, 748(3), 293–303.

-Casciotti, K.L. et al. Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. Anal. Chem. 74, 4905–4912 (2002). -Buchwald, C., Santoro, A.E., McIlvin, M.R., & Casciotti, K.L. Oxygen isotopic composition of nitrate and nitrite produced by nitrifying cocultures and natural marine assemblages. Limnology and Oceanography 57, 1361–1375 (2012).

-Kroopnick, P., & Craig, H. Atmospheric oxygen: isotopic composition and solubility fractionation. Science 175, 54–55 (1972).

-Boshers, D.S. et al. Constraining the oxygen isotopic composition of nitrate produced by nitrification. Environmental science & technology 53, 1206–1216 (2019).

-Casciotti, K.L., McIlvin, M., & Buchwald, C. Oxygen isotopic exchange and fractionation during bacterial ammonia oxidation. Limnology and Oceanography 55, 753–762 (2010).

-Buchwald, C., & Casciotti, K.L. Isotopic ratios of nitrite as tracers of the sources and age of oceanic nitrite. Nature Geoscience 6, 308–313 (2013).

-Granger, J., & Wankel, S.D. Isotopic overprinting of nitrification on denitrification as a ubiquitous and unifying feature of environmental nitrogen cycling. Proceedings of the National Academy of Sciences 113, E6391–E6400 (2016).

-Buchwald, C., & Casciotti, K. L. Oxygen isotopic fractionation and exchange during bacterial nitrite oxidation. Limnology and Oceanography 55, 1064–1074 (2010).

Specific comments:

1. Lines 49/50: Here the authors state "The water used for artificial snow production was sourced from the stream located at the entrance of the ski resort". This means that any nitrate in artificial snow must come from stream water.
Answer: We agree with the reviewer's interpretation. The artificial snow was indeed produced using stream water, and our isotope results support this. The $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ values of artificial snow were within the range of stream water, confirming that the nitrate in artificial snow originated from the stream source. To clarify this point, we have revised the text as follows

Before "The water used for artificial snow production was sourced from the stream located at the entrance of the ski resort."

After "The water used for artificial snow production was sourced from the stream located at the entrance of the ski resort, indicating that any nitrate contained in the artificial snow was derived from this stream water."

2. Line 53: "natural background state…" This is unclear. What is meant by natural background state? Atmospheric deposition? On what scale (global or regional or *national) 3mg/l NO3-N are 13mg/L NO3. This number seems a bit high for a pristine mountain stream anywhere in the world.*

Answer: The value of 3 mg/L NO_3^-–N cited in the manuscript does not refer to surface water such as mountain streams but rather to groundwater concentrations, as reported by Madison and Brunett (1985) in their U.S. Geological Survey Water-Supply Paper “Overview of the Occurrence of Nitrate in Ground Water of the United States” (see highlighted excerpt in the attached figure). In that study, the authors summarized numerous regional surveys across the United States and noted that “most natural waters that are unaffected by human-related activities contain less than 10 mg/L nitrate-nitrogen … nitrate-nitrogen concentrations greater than about 3 mg/L may be indicative of human sources,” particularly in shallow aquifers.

> Most natural waters that are unaffected by human-related activities contain less than 10 mg/L nitrate-nitrogen (Feth, 1966, p. 49) though, in some arid areas, natural concentrations may be greater. As discussed later in this article, nitrate-nitrogen concentrations greater than about 3 mg/L may be indicative of human sources. A survey of relevant publications indicates that in many areas of the Nation, human sources of nitrogen have resulted in concentrations of nitrate-nitrogen that are well above 3 mg/L in ground water, especially in shallow aquifers. Freeze and Cherry (1979, p. 413) stated that dissolved nitrogen in the form of nitrate is the most common contaminant of aquifer systems. The severity of nitrate contamination on a national scale, however, has not been well documented.

Therefore, the threshold of 3 mg/L NO_3^-–N represents an empirical guideline for distinguishing natural background from anthropogenically influenced groundwater, not for pristine surface waters. Our citation of this value follows its conventional use in hydrogeological studies (Madison & Brunett 1985) to indicate the onset of potential human impact in subsurface environments. To avoid confusion, we will revise the text in the manuscript to clarify that the “natural background state” refers to groundwater unaffected by human activities, and that the 3 mg/L NO_3^-–N criterion is a groundwater-based reference rather than a global or regional surface-water standard as follows.

Before: This concentration was generally higher than 3 mg/L, which represents the natural (background) state, suggesting the presence of anthropogenic inputs (Madison and Brunett, 1985).

After: This concentration was generally higher than 3 mg/L NO_3^-–N, which represents an empirical threshold for distinguishing natural background levels from anthropogenic influence in groundwater (Madison and Brunett, 1985).

3. Lines 57/58: As it stands, this sentence is not true. There are numerous studies combining information from nitrate isotope signatures (as indicators of N cycling and N source delineation) and water isotope signatures (as hydrological tracers). However, the combination of d^{15}N-NO3 and d^{18}O in a Bayesian mixing model is not so often used. The authors should be more specific in this regard.

Answer: We appreciate the reviewer's thoughtful comment and agree that numerous studies have combined nitrate and water isotopes to interpret nitrogen cycling processes and identify pollution sources. Our intent was not to suggest that this combination is entirely novel, but rather to emphasize that this study represents one of the few attempts to integrate $\delta^{15}N–NO_3^-$ (as a source-sensitive tracer) and $\delta^{18}O–H_2O$ (as a hydrological tracer) within a Bayesian mixing model to quantitatively apportion nitrate sources. While previous studies have qualitatively interpreted the relationship between these isotopes, quantitative source partitioning using this specific isotope pairing has been rarely conducted.

To clarify this point, we will revise the text as follows in Introduction:

Before: "Although numerous multi-isotope approaches exist for identifying sources and estimating the contributions to nitrate pollution, this study is the first attempt to simultaneously utilize nitrogen isotopes of nitrate ($\delta^{15}N–NO_3^-$) and oxygen isotopes of water ($\delta^{18}O–H_2O$) as tracers. The $\delta^{15}N–NO_3^-$ reveals the contamination sources, while the $\delta^{18}O–H_2O$ offers critical insights into the hydrological processes that affect the transport of nitrate pollutants, thereby increasing the precision of source tracking."
After: "Although multi-isotope approaches combining nitrate and water isotopes are widely used to identify sources and processes of nitrate pollution, few studies have integrated $\delta^{15}N–NO_3^-$ and $\delta^{18}O–H_2O$ within a Bayesian mixing framework to quantitatively apportion source contributions. In this study, $\delta^{15}N–NO_3^-$ was used to trace the origin of nitrogen, whereas $\delta^{18}O–H_2O$ provided insights into the hydrological mixing of different water sources, allowing us to evaluate the proportional contribution of artificial snow to groundwater nitrate."

4. Line 119: "…enrichment factor for the isotope…" For which isotope? Enrichment factors are specific to individual processes that involve the separation of at least two isotopes.

Answer: The "enrichment factor" refers to the optional isotopic discrimination parameter (ε) that can be applied to the tracer isotopes used in Bayesian mixing models (Parnell and Inger, 2016). In our case, the tracers were $\delta^{15}N–NO_3^-$ and $\delta^{18}O–H_2O$. However, as discussed in Main Comment 3, the isotopic relationship indicated that biogeochemical isotope fractionation (e.g., during denitrification) played only a minor role, and that the observed isotopic composition of groundwater nitrate was mainly governed by physical mixing among distinct nitrate sources. Therefore, we assumed no isotopic enrichment ($\varepsilon = 0$) in the model.

The text will be revised accordingly as follows:

Before: “Additionally, an enrichment factor for the isotope can be added optionally (Parnell and Inger, 2016), although it was assumed to be 0 in this study.”

After: *"Additionally, an isotopic enrichment factor (ε) can optionally be applied to the tracer isotopes used in the model (Parnell and Inger, 2016), although it was assumed to be 0 in this study because isotope fractionation was considered negligible compared to mixing processes."*

5. Lines 142/143 and throughout the manuscript: It doesn't make much sense to report isotope values with two decimal places given the analytical error.

Answer: All isotope values will be rounded to one decimal place throughout the manuscript, considering the analytical precision.

6. Line 145: “amount effect” I’d rather say it’s the classic altitude effect.

Answer: We appreciate the reviewer’s suggestion. We will revise the text accordingly and replaced “amount effect” with “altitude effect” in the manuscript.

7. Line 150: “LMWL” Even though it is done in figure caption 4, spell out LMWL the first time you use it in the text.

Answer: We appreciate the reviewer’s correction. We will revise the manuscript to spell out *“local meteoric water line (LMWL)”* at its first occurrence in the main text.

8. Lines 177/178: “…The isotope values of the artificial snow were similar to those of surface water, suggesting that surface water was used to make artificial snow…” I thought it was a fact that artificial snow is made from surface water. (see line 50).

Answer: We agree that artificial snow is typically produced from surface water. Our purpose here was not to emphasize this as a new finding, but to verify that the artificial snow samples analyzed in this study indeed reflected the source water used at the ski resort. The isotopic similarity between artificial snow and surface water confirms the consistency of the snowmaking process and supports the reliability of our subsequent comparisons between natural and artificial snow.

Before “The isotope values of the artificial snow were similar to those of surface water, suggesting that surface water was used to make artificial snow.”

After “The isotope values of the artificial snow were similar to those of surface water, confirming that the analyzed artificial snow samples reflected the characteristics of the source water used for snowmaking.”

9. Line 192/193: “…The $\delta^{15}N\text{–}NO_3^-$ value increased from 6.83‰ to 7.53‰…”. When I add the error bars of +/-0.5‰ to both values, I don't see much difference anymore.

Answer: We acknowledge that the $\delta^{15}N\text{–}NO_3^-$ difference (0.7‰) is within the analytical uncertainty (±0.5‰). However, our interpretation does not rely solely on the magnitude of this change. Rather, the concurrent increase in $\delta^{15}N\text{–}NO_3^-$

values and the persistently high NO_3^-–N concentrations during the snowmelt period supports the influence of nitrate-enriched water derived from artificial snowmelt. This isotopic pattern, together with elevated nitrate levels, suggests input from anthropogenic sources (e.g., manure/sewage signature) incorporated into the artificial snowmaking water, rather than a purely natural source. We will clarify this interpretation in the revised text.

"During the snowmelt period, the $\delta^{15}N$–NO_3^- value slightly increased (from 6.8‰ to 7.5‰), coinciding with persistently high NO_3^-–N concentrations. This contrasts with the nearby stream, where NO_3^-–N concentrations markedly decreased due to dilution by meltwater. The relatively stable nitrate concentrations in groundwater may partly reflect its longer residence time and slower hydrological response compared to surface flow paths. However, unlike during the summer rainy season—when both groundwater and stream water showed a clear decrease in NO_3^-–N concentrations associated with recharge and dilution—the snowmelt period was characterized by persistently high concentrations accompanied by isotopic enrichment. This combination suggests that the snowmelt recharge carried additional nitrate inputs with an anthropogenic isotopic signature. Since agricultural activities and sewage discharge are absent on the mountain summit, the most plausible source of such nitrate-enriched recharge is artificial snow, produced from surface water already influenced by anthropogenic nitrogen."

10. Lines 235ff.: Everything in this paragraph is certainly true, but none of it is relevant to the topic of the manuscript because it does not address denitrification, greenhouse gas emissions, or other N cycling processes in any way.

Answer: We appreciate the reviewer's comment. We agree that this paragraph discussed broader environmental implications (N_2O emissions and global warming feedbacks) beyond the scope of our measured parameters. As we did not directly investigate denitrification or greenhouse gas fluxes in this study, we have revised the paragraph to focus on the implications of artificial snow primarily in terms of nitrogen cycling and water quality, which are directly supported by our data. The discussion on N_2O emissions and global feedback loops will be removed to maintain focus and relevance.

Before "The N accumulated in this way undergoes denitrification by soil bacteria, resulting in N loss and the potential release of N_2O greenhouse gas, which affects soil N availability and contributes to climate change. This underscores the dual environmental impact of artificial snow on N cycling and greenhouse gas emissions, reinforcing the need to monitor N dynamics in ecosystems affected by artificial snow. In fact, the main global source of N_2O is microbial production in soils, and N inputs from atmospheric deposition caused 51% of anthropogenic N_2O emissions from soils in 2020 (Erisman et al., 2013).

The greenhouse gas emissions will exacerbate global warming, thereby fueling a cycle that further amplifies the need for artificial snow production. This feedback loop highlights a paradox where the activities intended to mitigate the effects of climate change in winter tourism may, in turn, contribute to the broader issue of global warming. As global warming progresses, the need for artificial snow is expected to increase further than now. These persistent N source inputs can significantly impact N cycling, making long-term monitoring of their impacts crucial."

After "The nitrogen accumulated through artificial snow application can alter soil and groundwater nitrogen dynamics, potentially enhancing denitrification or nitrate leaching processes that affect N availability in local ecosystems. These findings underscore the need for long-term monitoring of nitrogen cycling in regions affected by artificial snowmaking, where persistent anthropogenic N inputs may alter both hydrological and biogeochemical processes."

11. Conclusion section: See comment above: Except for the first sentence, none of the text in the conclusion section is related to the topic of the manuscript and the data presented. This section needs to be completely rewritten.

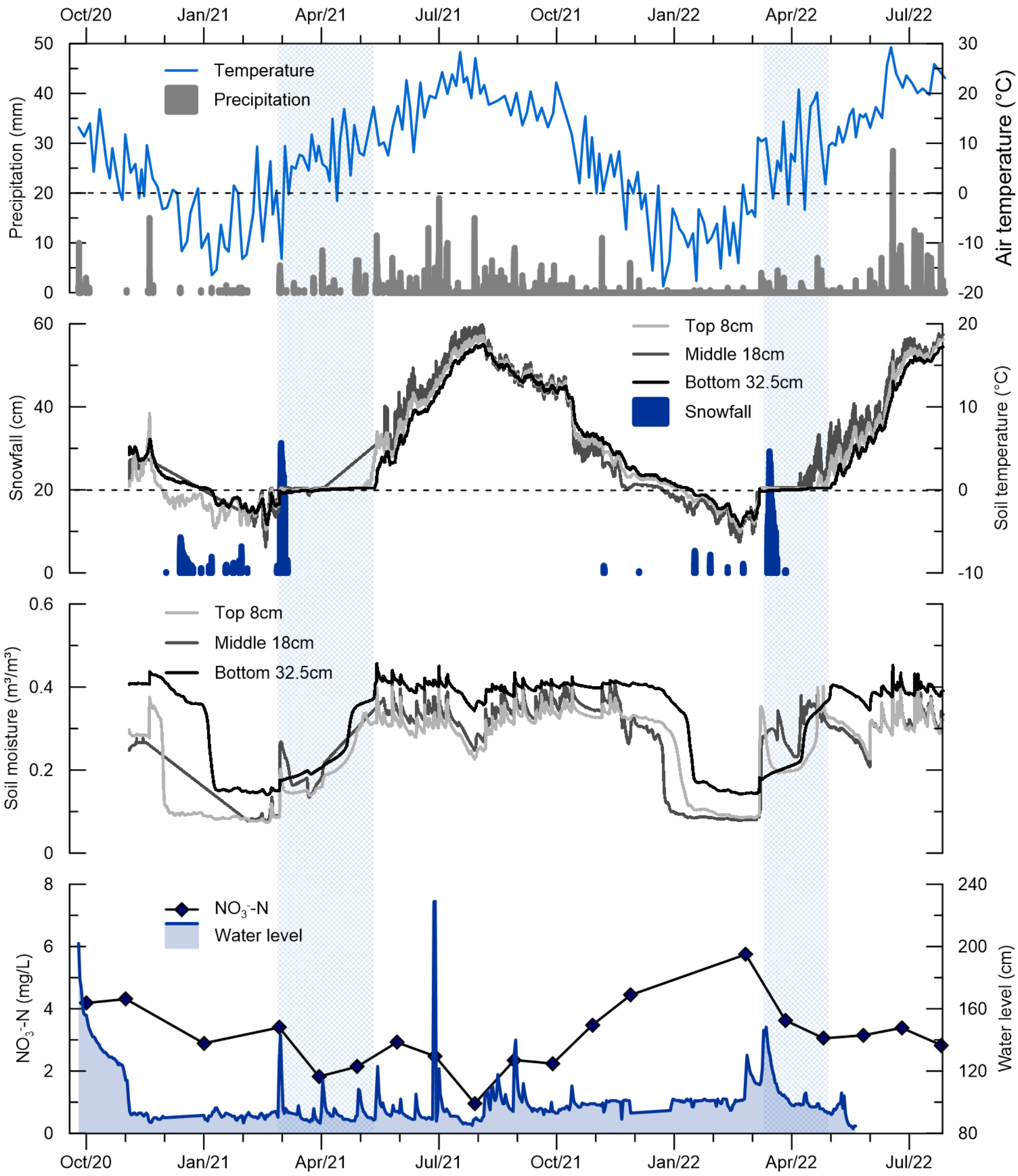
Answer: We appreciate the reviewer's helpful suggestion. We agree that the previous conclusion included general statements on greenhouse gas emissions and climate feedbacks that were not directly supported by our data. Accordingly, we have rewritten the conclusion to focus strictly on the results derived from our isotopic and mixing model analyses, emphasizing the quantified contribution of artificial snow to groundwater nitrogen and its implications for local N cycling.

Before: "We demonstrated the influence of N sources in artificial snow on the surrounding groundwater of a ski resort. Snowmaking requires large amounts of electricity, and generating this electricity requires the use of fossil fuels, which emit greenhouse gases such as carbon dioxide (CO_2). Greenhouse gas emissions from artificial snow production will accelerate further warming of the climate, in turn requiring more artificial snow and creating a positive feedback loop. In addition, denitrification reactions by soil bacteria occur as artificial snow is distributed over the soil, and the emission of nitrous oxide (N_2O) gas, which is a product of denitrification, can further intensify global warming. As a result, these anthropogenic N inputs could have important implications for nitrogen cycling. Therefore, long-term monitoring of these impacts is essential, as the use of artificial snow will continue to increase due to climate change."

After: "This study demonstrated that artificial snow significantly influences the nitrogen dynamics of mountain groundwater in a temperate alpine ski resort. Stable isotope analyses revealed that the $\delta^{15}N$–NO_3^- and $\delta^{18}O$–H_2O compositions of artificial snow and groundwater were closely related, indicating that the nitrate in groundwater was largely derived from artificial snow. Bayesian mixing model results showed that artificial snow contributed approximately 50% of the total nitrogen input to the mountain groundwater, exceeding the contributions from rainfall and natural snow. These findings suggest that artificial snow acts as an important anthropogenic nitrogen source in alpine catchments and can alter local nitrogen cycling through long-term accumulation. Continuous monitoring of nitrogen isotopes and ion concentrations in alpine groundwater is therefore essential to assess the cumulative impact of artificial snow on mountain water quality and ecosystem nitrogen balance under a warming climate."

12. Figure 4(c): What does the right y-axis in plot (c) show? It does not have the same scale as the left y-axis.

Answer: We believe the reviewer was referring to Figure 3c rather than Figure 4c. The right y-axis label and scale in Figure 3c have now been corrected for clarity. We appreciate the reviewer for pointing this out.



13. Figure 6(a): What do the red and blue arrows represent? Consider the analytical errors!

Answer: The red and blue arrows in Figure 5a represent the temporal evolution of $\delta^{15}N–NO_3^-$ values (red) and $NO_3^-–N$ concentrations (blue) during the 2021 snowmelt period. Although the enrichment in $\delta^{15}N–NO_3^-$ (from 6.8 ‰ to 7.5 ‰) is close to the analytical precision (± 0.5 ‰), this isotopic trend coincides with persistently high $NO_3^-–N$ concentrations (~4.6 mg/L) rather than the dilution expected from increased meltwater input. Such concurrent behavior indicates that nitrate was continuously supplied by the infiltration of artificial-snow meltwater. Since agricultural activities and sewage discharge are absent at the mountain summit, artificial snow is the only plausible source capable of producing the observed combination of elevated NO_3^-–N concentrations and enriched $\delta^{15}N$–NO_3^- values, consistent with nitrogen derived from manure- and sewage-related sources.

We appreciate the criticism and suggestions from the reviewers and believe that the revised manuscript will be an important asset to the hydrogeology community. We are looking forward to its publication. Thank you for handling our manuscript and your patience.

Sincerely,
Jeonghoon Lee