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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 ($\delta^{15}\text{N}\text{--NO}_3^-$ vs. $\delta^{18}\text{O}\text{--NO}_3^-$) 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 $\delta^{18}\text{O}\text{--NO}_3^-$ 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 $\epsilon = 0$ 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 $\delta^{15}\text{N}-\text{NO}_3^-$, $\delta^{18}\text{O}-\text{H}_2\text{O}$, 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.

Reviewer #2: Joel Savarino

Review of Isotopic evidence for the impact of artificial snow on the nitrogen cycle in temperate regions by Hyejung Jung et al.,

The manuscript addresses an interesting and innovative idea, namely measuring the impact of artificial snow produced in ski resorts on the hydrological cycle using isotopic tools. While the basic idea is innovative and the manuscript deserves to be



published in another context, unfortunately the statistical treatment and the approach taken by the authors contain too many errors of interpretation and analysis to garanti its publication.

Answer: We respectfully disagree with the reviewer's general assessment that our manuscript "contains too many errors of interpretation and analysis to guarantee its publication." We appreciate that the reviewer acknowledges the innovative nature and scientific importance of our work; however, the assertion that our analytical and interpretative framework is flawed appears to arise from a misunderstanding of the study's scope, objectives, and methodological design.

Our study integrates hydrological, isotopic, and hydrogeochemical evidence to assess how artificial snowmaking alters the timing and isotopic signature of nitrogen delivery to groundwater systems. This interdisciplinary design necessarily combines process-based reasoning with Bayesian statistical modeling to quantify source contributions and uncertainties. The statistical framework we used follows well-established approaches in isotope hydrology and environmental geochemistry (e.g., Kendall & McDonnell, 1998; J.J. Klaus and Mc Donnell, 2013; Parnell and Inger, 2016).

Furthermore, the interpretations presented in the manuscript are not arbitrary or overextended. Each conclusion is grounded in measured isotopic gradients that exceed analytical uncertainty and in consistent hydrological patterns observed across seasons and compartments.

We fully acknowledge the limitations of our dataset (e.g., number of artificial snow samples, temporal coverage), which are clearly stated and critically discussed in the manuscript. However, these constraints do not invalidate the results; instead, they delineate the natural limits of observation-based field research in alpine environments. The reproducibility and internal consistency of our isotope and ion data support the reliability of the interpretations drawn.

In summary, we maintain that the manuscript's analytical approach and interpretations are scientifically sound, supported by robust field data, and consistent with the established literature in isotope hydrology and nitrogen cycling. The claim of "too many errors of interpretation and analysis" is therefore not substantiated by specific evidence.

- Kendall, C. Tracing nitrogen sources and cycling in catchments, in *Isotope Tracers in Catchment Hydrology* (eds. Kendall, C. and McDonnell, J.J.) 519–576 (Elsevier, Amsterdam, The Netherlands, 1998).

- Klaus, J. and Mc Donnell, J.J. (2013). Hydrograph separation using stable isotopes: Review and evaluation. *Journal of hydrology* 505, 47–64.

- Parnell, A.C. and Inger, R. (2016). Simmr: A Stable Isotope Mixing Model R Package Version 0.4.1.

Major comments:



1. The statistical approach appears to be very weak. Artificial snow was measured on only two samples, which eliminates any possibility of gaining insight into the natural variability of this artificial snow. The absence of variability thus makes it impossible to reliably determine a mixing pole. Similarly, isotopic measurements are given with accuracies that far exceed those of the analytical methods used. For example, isotopic values for nitrogen 15 cannot be given as 0.01 ‰ when the method has an accuracy of 0.5 ‰. It follows that all the variability interpreted and commented on by the authors is misinterpreted. There is also no evidence that the isotopic values of the different reservoirs remain constant over time. Not including isotopic fractionation for nitrate, which is a species that degrades, seems to be an unjustified simplification that needs to be justified beforehand.

Answer: We respectfully disagree with the reviewer's assessment that the statistical approach is weak or that our interpretations are misled by analytical precision. We clarify each point below.

(1) Number of artificial snow samples

We acknowledge that only two artificial snow samples were collected, and this limitation was explicitly stated in both the Methods and Discussion. However, these samples were not intended to statistically characterize the full variability of artificial snow, but rather to represent its isotopic and chemical composition as a hydrological end-member.

To validate the representativeness of this source, we additionally collected surface water samples from the snowmaking reservoir across multiple seasons and compared their NO_3^- -N concentrations and isotopic compositions ($\delta^{15}\text{N}$ - NO_3^-) with those of the artificial snow.

The results of a two-sample t-test showed no significant difference between the artificial snow and surface water for either NO_3^- -N concentration ($p = 0.17$) or $\delta^{15}\text{N}$ - NO_3^- ($p = 0.89$) (see Table R2-1). This demonstrates that the isotopic and chemical characteristics of artificial snow are statistically indistinguishable from its source water. Therefore, the representativeness of artificial snow as an isotopic and chemical end-member is empirically supported.

NO_3^- -N	Stream water	Artificial snow
Mean	4.2	5.3
Variance	1.9	0.1
Observations (or Sample size, n)	5	2
Hypothesized Mean Difference	0	
Degrees of Freedom (df)	4	
t Statistic	-1.66	



$P(T \leq t)$ One-tail (One-tailed p -value)	0.09
t Critical One-tail (Critical t value, one-tailed)	2.13
$P(T \leq t)$ Two-tail (Two-tailed p -value)	0.17
t Critical Two-tail (Critical t value, two-tailed)	2.78

$\delta^{15}\text{N}-\text{NO}_3^-$	Stream water	Artificial snow
Mean	10.1	10.3
Variance	4.0	0.3
Observations (or Sample size, n)	4	2
Hypothesized Mean Difference	0	
Degrees of Freedom (df)	4	
t Statistic	-0.15	
$P(T \leq t)$ One-tail (One-tailed p -value)	0.44	
t Critical One-tail (Critical t value, one-tailed)	2.13	
$P(T \leq t)$ Two-tail (Two-tailed p -value)	0.89	
t Critical Two-tail (Critical t value, two-tailed)	2.78	

Table R2-1. Results of the independent two-sample t-test comparing NO_3^- -N and $\delta^{15}\text{N}-\text{NO}_3^-$ values between stream water and artificial snow used for snowmaking.

(2) Analytical precision and significant figures

We agree that isotopic data should be presented within the limits of analytical precision. In the revised manuscript, $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ values are now reported with appropriate significant figures (one decimal place, ‰).

The reviewer seems to have misunderstood the meaning of the reported analytical precision. According to the University of Waterloo Environmental Isotope Laboratory, the analytical precision (2σ) of the reduction method is $\pm 0.5\text{‰}$ for $\delta^{15}\text{N}-\text{NO}_3^-$ (AIR) and $\pm 1.0\text{‰}$ for $\delta^{18}\text{O}-\text{NO}_3^-$ (VSMOW). These values represent the reproducibility between duplicate measurements rather than the measurement resolution. Although the reported values were given to two decimal places (e.g., 7.08‰), this



does not imply an analytical precision of 0.01‰ but simply reflects the numerical mean of duplicate analyses. The interpretation in our study is based on isotopic differences well above the analytical uncertainty, and thus remains robust.

We revised the manuscript to clarify that the reported uncertainties represent analytical precision rather than accuracy. The sentence now reads as follows:

“The analytical precision (2σ) of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ measurements was $\pm 1.0\text{‰}$ and $\pm 0.5\text{‰}$, respectively.”

This revision eliminates potential confusion between accuracy and precision and aligns with the analytical specifications provided by the University of Waterloo Environmental Isotope Laboratory.

Because nitrogen isotopes alone cannot fully discriminate among multiple potential sources, our approach integrates water isotopes that trace the hydrological transport of nitrogen-bearing water masses. Nitrate, as a highly soluble anion, readily dissolves and moves with water flow, and has therefore been widely used together with water isotopes in hydrological studies to trace the origin and flow paths of nitrogen-bearing waters. This combined isotope framework allows us to distinguish isotopically overlapping sources by linking nitrate composition to specific hydrological processes such as snowmelt infiltration and groundwater mixing. As noted in the main text, the distinct separation of isotope values among endmembers supports a robust interpretation of source contributions (Figure 6a).

(3) On isotopic fractionation of nitrate

Answer: We appreciate the reviewer’s valuable comment. We agree that isotope 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 $\delta^{15}\text{N}\text{--NO}_3^-$ and $\delta^{18}\text{O}\text{--NO}_3^-$ values (Figure R1-4) to evaluate whether denitrification occurred. Even in groundwater where denitrification could potentially occur, no significant correlation was found between $\delta^{15}\text{N}\text{--NO}_3^-$ and $\delta^{18}\text{O}\text{--NO}_3^-$, suggesting that the isotopic enrichment pattern typically associated with denitrification (i.e., $\delta^{18}\text{O}\text{--NO}_3^-$ versus $\delta^{15}\text{N}\text{--NO}_3^-$ slope of 0.5–1.0; Kendall et al., 1998) was not evident in our dataset.

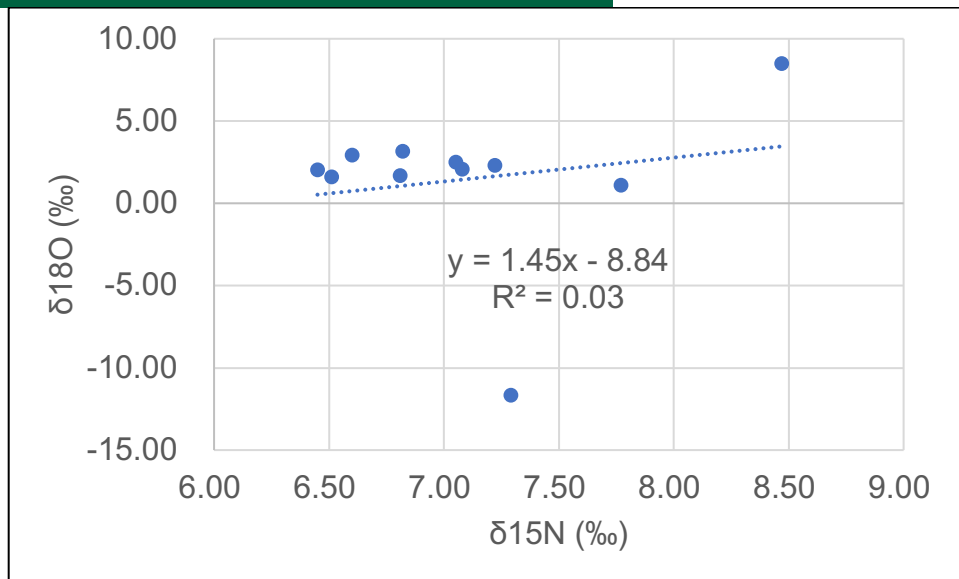


Figure R1-4. Relationship between $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ values in groundwater samples. The slope (1.45) of the linear regression indicates no clear enrichment trend between nitrogen and oxygen isotopes of nitrate ($R^2 = 0.03$), suggesting that denitrification 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 $\delta^{18}\text{O-H}_2\text{O}$ and $\delta^{18}\text{O-O}_2$, as well as kinetic and equilibrium isotope 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 $\delta^{18}\text{O-NO}_3^-$ 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 $\delta^{18}\text{O-NO}_3^-$ data (Figure R1-5).

The observed $\delta^{18}\text{O-NO}_3^-$ values generally agreed with the modeled relationship between $\delta^{18}\text{O-NO}_3^-$ and $\delta^{18}\text{O-H}_2\text{O}$ derived from the Monte Carlo simulation, although several groundwater samples exhibited slightly higher $\delta^{18}\text{O-NO}_3^-$ values than the upper limit of the 95 % confidence interval. This pattern indicates that the observed $\delta^{18}\text{O-NO}_3^-$ 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 $\delta^{18}\text{O-NO}_3^-$ is more plausibly attributed to mixing with nitrate derived from artificial snowmelt rather than to isotopic fractionation during denitrification.

Equation R1-1



$$\delta^{18}\text{O}_{\text{NO}_3^-} = \left(\frac{2}{3} + \frac{1}{3}x_{\text{AO}} \right) \cdot \delta^{18}\text{O}_{\text{H}_2\text{O}} + \left(\frac{1}{3}(1 - x_{\text{AO}}) \right) \cdot (\delta^{18}\text{O}_{\text{O}_2} - \varepsilon_{\text{k},\text{O}_2}) - \frac{1}{3}(1 - x_{\text{AO}}) \cdot \varepsilon_{\text{k},\text{H}_2\text{O},1} - \frac{1}{3} \cdot \varepsilon_{\text{k},\text{H}_2\text{O},2} + \frac{2}{3}x_{\text{AO}} \cdot \varepsilon_{\text{eq}}$$

This equation models the produced $\delta^{18}\text{O}$ – 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 $\delta^{18}\text{O}$ – NO_3^- during nitrification.

Parameter	Description	Units	Value/Range	Reference
$\delta^{18}\text{O}$ – H_2O	Oxygen isotopic composition of water	‰	-12 to -8	Measured
$\delta^{18}\text{O}$ – 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)
$\varepsilon_{\text{k},\text{O}_2}$	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)
$\varepsilon_{\text{k},\text{H}_2\text{O},1}$	O isotope effect for H_2O incorporation during aerobic ammonia oxidation	‰	+14	Casciotti et al. (2010); Granger and Wankel (2016)
$\varepsilon_{\text{k},\text{H}_2\text{O},2}$	O isotope effect to H_2O incorporation during nitrifiers and anammox	‰	+12.8 to +18.2	Buchwald and Casciotti (2010)

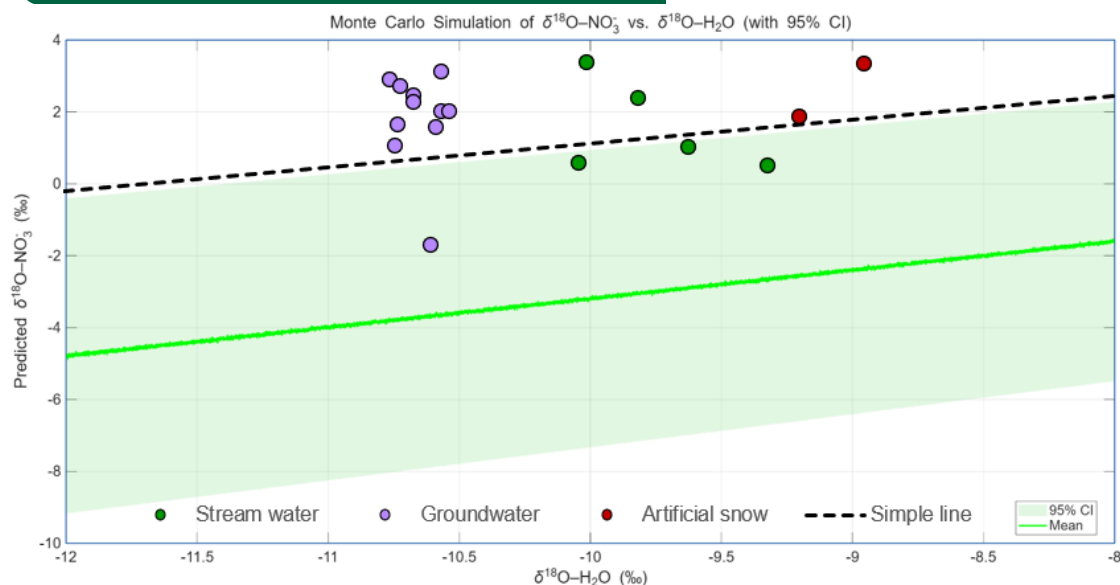


Figure R1-5. Relationship between predicted $\delta^{18}\text{O-NO}_3^-$ and $\delta^{18}\text{O-H}_2\text{O}$ for stream water, groundwater, and artificial snow. The black dashed simple line represents the theoretical relationship assuming that two-thirds of oxygen atoms in nitrate are derived from 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 $\delta^{18}\text{O-NO}_3^-$ 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 $\delta^{18}\text{O-NO}_3^-$ 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 $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$. 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 $\delta^{18}\text{O-NO}_3^-$ 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 $\delta^{18}\text{O-NO}_3^-$ 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.”



These results demonstrate that omitting isotope fractionation was not an unjustified simplification but a process-based decision, fully supported by isotopic evidence and quantitative modeling.

- Andersson, K.K., & Hooper, A.B. Oxygen and hydrogen atoms in hydroxylamine, nitrite, and nitrate produced from ammonia by Nitrosomonas: ^{15}N -NMR and ^{18}O 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).

2. The second point concerns the objective of the paper. As the reviewer rightly pointed out, the paper focuses much more on the composition of groundwater bodies than on the origin of the nitrogen in these same bodies. In this respect, the title of the article is misleading. It is not a question of determining the impact of artificial snow on the nitrogen cycle, but rather of determining the hydrological cycle of this mountain area. Like the first reviewer, I do not see how artificial snow could be a source of contamination, since it is itself produced from natural water collected in the same hydrological basin. The production of artificial snow (which is made with natural water, not artificial water) is at most a phenomenon of time lag in a hydrological load. This in no way corresponds to contamination.

It is surprising to see the paper evolve from an analysis of the nitrogen cycle to what ultimately becomes an analysis of the water cycle, where what is supposed to be



determined by a combination of nitrogen sources becomes the sources themselves for determining the origin of groundwater. Clearly, the title of the article is inappropriate.

Unfortunately, the static weakness, the overinterpretation of the data, the confusion between contamination and flow displacement, and finally the change in the scientific question throughout the paper require too much rewriting for the paper to be accepted. It requires a complete rewrite with a paradigm shift from the nitrogen cycle to the hydrological cycle.

Answer: Our objective is precisely to quantify how artificial snowmaking redistributes nitrate-bearing water masses and thereby modifies nitrogen cycling in the catchment. Although artificial snow is produced from “natural” source water, that water already carries the anthropogenic nitrate signature of the basin. By transporting and storing this water at higher elevations and releasing it as a short, concentrated melt pulse, snowmaking alters the timing, magnitude, pathways (surface runoff vs. infiltration), and residence time under which nitrogen transformations occur. In biogeochemical terms, this constitutes anthropogenic nitrate loading via hydrologic redistribution, not merely a neutral time lag.

The reviewer’s interpretation overlooks a fundamental hydrological–biogeochemical principle: even if the instantaneous nitrate flux remains approximately constant, altering the storage and residence time of water and solutes inevitably changes the system’s steady-state balance. Artificial snowmaking increases the temporary storage of nitrogen-bearing water in high-elevation snowpacks. Because natural biogeochemical turnover (e.g., nitrification, denitrification, and assimilation) proceeds at rates constrained by temperature and microbial activity, this enhanced storage effectively decouples the timing between nitrogen input and removal processes. Consequently, nitrate accumulates in the snowpack and underlying soils during winter, leading to a prolonged residence time and a delayed but concentrated release during melt. This hydrologically induced shift in storage–flux dynamics represents a clear modification of the nitrogen cycle, even when the input water itself is natural.

Our evidence supports this mechanism. First, nitrate isotopes show a distinct end-member separation (Fig. 6a): artificial-snow nitrate clusters toward the anthropogenic $\delta^{15}\text{N}\text{--NO}_3^-$ – $\delta^{18}\text{O}\text{--NO}_3^-$ band, while post-snowmelt groundwater and stream samples shift along mixing vectors toward that composition. Second, water isotopes ($\delta^{18}\text{O}\text{--H}_2\text{O}$) trace the influx and mixing of artificial-snow meltwater into groundwater, enabling us to disentangle isotopically overlapping nitrate sources by linking nitrate composition to specific flowpaths (snowmelt infiltration and groundwater mixing). The associated nitrate concentration increases during winter and early melt cannot be explained by precipitation or soil water alone.

To avoid any ambiguity in terminology, we now clarify that “contamination” in our manuscript is used in the hydrological–biogeochemical sense of anthropogenic nitrate loading relative to the natural baseline, rather than implying the addition of a



chemically “artificial” substance. We also revised the title to emphasize hydrological redistribution and isotopic mechanisms rather than contamination.

“Isotopic evidence for the impact of artificial snow on the nitrogen dynamics in a temperate mountain catchment”

Specific Comments:

1. line 29-30: If snow is artificial, the water used for it is not artificial. they should better present why N in this natural water is a problem.

Answer: Although artificial snow is produced from natural surface water, the source water itself is often already impacted by local anthropogenic activities, such as wastewater discharge and fertilizer runoff. When this nitrogen-enriched water is repeatedly used for snowmaking, it is recycled within the same hydrological system, leading to a progressive accumulation of reactive nitrogen in the catchment.

Our isotopic data clearly support this mechanism. In our study, artificial snow exhibited significantly higher $\delta^{15}\text{N}\text{--NO}_3^-$ values (9.9‰ and 10.7‰) than natural snow (6.3‰ and 5.5‰), indicating an enrichment characteristic of manure- or sewage-derived nitrogen. This demonstrates that the water used for snowmaking is not chemically equivalent to unaltered natural water but already carries an anthropogenic nitrogen signature.

2. Line 31-42: poorly connected to N cycle, more about energy consumption. Biogeochemical cycle and climate change are two separate environmental issue, even if at some point they can be connected.

Answer: We agree with the reviewer that the previous paragraph primarily emphasized the energy demand and greenhouse gas emissions associated with artificial snow production, without clearly linking these processes to nitrogen cycling. To address this comment, we will add a new paragraph explaining that the dissolved chemical components present in artificial snow can influence biogeochemical cycling by increasing solute storage and extending their residence time within the catchment.

“The dissolved chemical components present in artificial snow can influence biogeochemical cycling by increasing the temporary storage of solutes and consequently extending their residence time within the catchment. Among these, nitrate (NO_3^-) is of particular concern because of its high solubility and mobility in aquatic systems. As snowmelt acts as a diffuse source of contaminants, tracing the sources and pathways of nitrate is essential for understanding its contribution to nitrogen dynamics and potential impacts on downstream water quality.”

3. Line 49: volume of water used needs a comparison with some other human use.

Answer: We agree with the reviewer that providing a comparative context would help readers better understand the magnitude of water consumption for



snowmaking. Accordingly, we have revised the sentence to include a quantitative comparison with local domestic water use in Pyeongchang County. The revised text now reads as follows:

“From the 2017/2018 season to the 2023/2024 season, the average annual volume of water used for snowmaking was 1.15 ± 0.15 million m^3 , equivalent to approximately 15 % of the annual domestic water consumption (7.37 million m^3 in 2022; Korea Statistical Information Service, 2023) in Pyeongchang County.”

- Gangwon Special Self-Governing Province, Pyeongchang-gun. (2023). *2022 Water Supply Statistics Summary Report (in Korean)*. Available at: <https://www.waternow.go.kr>

4. Line 52: 3mg/L, need to give the variability to see how different it is from artificial snow

Answer: Although only two artificial snow samples were available, we additionally analyzed five stream water samples that served as the source water for snowmaking. The NO_3^- -N concentrations in the stream water averaged 3.95 ± 1.38 mg/L (range: 2.62–5.71 mg/L), demonstrating a variability that encompasses the concentrations observed in the artificial snow samples.

As described in response to Major Comment 1, a T-test revealed no significant difference ($p > 0.05$) between the nitrate concentrations of the artificial snow and its source stream water, confirming that the artificial snow reflects the chemical composition of the source water rather than introducing additional enrichment. Therefore, we consider the use of the surface water data sufficient to represent the variability of nitrate concentration associated with snowmaking.

5. Line 71: only two artificial samples ! This is not enough to have a clear variability

Answer: This issue has already been addressed in detail in Major Comment 1. To avoid redundancy, we refer the reviewer to our detailed explanation and data presented in response to Major Comment 1.

6. Line 101 and 105: giving the precision of the methods, all data in the paper should be consistant with these precisions. no data at 0.0x precision for water or 0.x for 18? N nitrate etc.

Answer: All isotope values have been rounded to one decimal place throughout the manuscript to be consistent with the analytical precision

7. Line 108: definition delta: remove x 1000, useless 0.006 or 6 ‰ is exactly the same number no need to x 1000

Answer: We respectfully but firmly disagree with this comment. The inclusion of the “ $\times 1000$ ” term in the delta (δ) notation is not optional but a fundamental and



internationally standardized convention in “stable” isotope geochemistry. The δ value expresses the relative deviation of an isotope ratio in per mil (‰) units. Multiplying by 1000 converts this small, dimensionless ratio difference (e.g., 0.006) into the conventional per mil scale (e.g., 6‰), as defined by the International Union of Pure and Applied Chemistry (IUPAC; Coplen, 2011, Pure Appl. Chem., 83:1459–1466).

The reviewer’s comment appears to reflect a confusion between stable isotope ratio notation (δ , per mil units) and radioisotope ratio or activity expressions, which are reported without the $\times 1000$ factor because they are expressed in absolute or decay-related units (e.g., disintegrations per second or atom ratios). In contrast, stable isotope studies universally use δ notation scaled to per mil (‰) for clarity and comparability across isotopic systems (e.g., $\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{15}\text{N}$, $\delta^{13}\text{C}$).

Removing the $\times 1000$ factor would yield dimensionless numbers inconsistent with international analytical standards and decades of isotope research. Therefore, Equation (1) in our manuscript correctly follows the established δ notation format used in all stable isotope laboratories worldwide.

8. Line 150 LMWL give the definition

Answer: We have revised the manuscript to spell out “local meteoric water line (LMWL)” at its first occurrence in the main text.

9. Line 152-153: how can exchange with all samples on the LMWL can give point off the line ?

Answer: We respectfully note that not all samples plot on the LMWL. As shown in Figure 4a, the samples from the bottom layer of natural snow (old snow) clearly deviate from the LMWL. This deviation is consistent with partial melting and refreezing within the snowpack, during which isotopic exchange occurs between ice and liquid water. Such exchange processes can locally modify $\delta^2\text{H}$ – H_2O relationships without producing a full evaporation trend, resulting in a slight offset from the LMWL in only the basal snow layer, while the overlying layers remain aligned with meteoric water signatures. This interpretation is supported by previous studies (Lee et al., 2010a; Lee et al., 2010b) that reported similar isotopic re-equilibration in melting snowpacks.

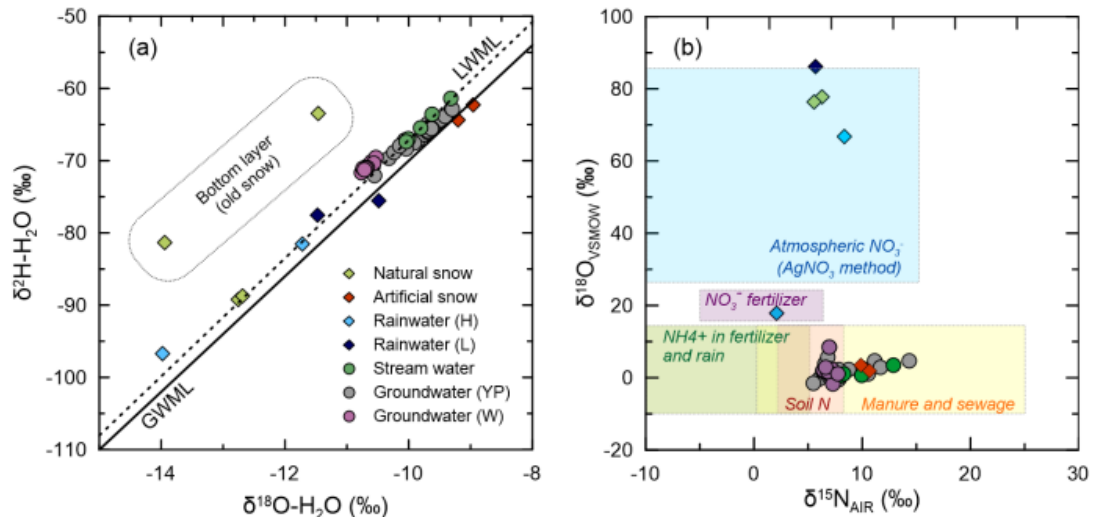


Figure 4. (a) Stable isotopic compositions ($\delta^2\text{H-H}_2\text{O}$ vs. $\delta^{18}\text{O-H}_2\text{O}$, ‰) for samples analyzed in this work alongside the global meteoric water line (GMWL; $\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10$, Craig [1961]) and the local meteoric water line (LMWL; $\delta^2\text{H} = 8.18 \times \delta^{18}\text{O} + 14.66$, Jung et al. [2023]) derived from the IAEA station in South Korea. (b) Nitrate isotopic compositions ($\delta^{18}\text{O-NO}_3^-$ vs. $\delta^{15}\text{N-NO}_3^-$, ‰) of various N sources (Kendall et al. [1998]) and isotopic values for samples obtained in our study.

- Lee, J., Feng, X., Faiia, A., Posmentier, E., Osterhuber, R., & Kirchner, J. (2010a). Isotopic evolution of snowmelt: A new model incorporating mobile and immobile water. *Water Resources Research*, 46(11).

-Lee, J., Feng, X., Faiia, A. M., Posmentier, E. S., Kirchner, J. W., Osterhuber, R., & Taylor, S. (2010b). Isotopic evolution of a seasonal snowcover and its melt by isotopic exchange between liquid water and ice. *Chemical geology*, 270(1-4), 126-134.

10. Line 168: 17 ‰ for ^{18}O nitrate rain is very low, why? This point seem to be an outlier

Answer: We agree that the $\delta^{18}\text{O-NO}_3^-$ value of 17.9 ‰ in rainfall is lower than the typical range for atmospheric nitrate (approximately +25 ‰ to +85 ‰ when measured by the denitrifier method); however, this result is not an analytical outlier. The relatively low $\delta^{18}\text{O-NO}_3^-$ value likely reflects microbial nitrification that occurred either within the precipitation system or shortly after deposition. Nitrate produced by nitrification incorporates oxygen mainly from ambient water and O_2 , resulting in lower $\delta^{18}\text{O-NO}_3^-$ values compared to purely atmospheric nitrate. Therefore, this value represents nitrification-derived nitrate rather than an anomaly, and it was retained in the dataset as a valid measurement.

Importantly, this nitrification process primarily affects the oxygen isotopic composition of nitrate, while the nitrogen isotopic composition ($\delta^{15}\text{N-NO}_3^-$) remains largely unchanged because it reflects the $\delta^{15}\text{N}$ signature of its precursor nitrogen



species (NH_4^+ or organic N). Consequently, the $\delta^{15}\text{N}\text{--NO}_3^-$ value of this rainfall sample reliably represents its nitrogen source and was appropriately used as an end-member in the mixing model.

11. Line 171-172: attribution with no discussion

Answer: We will revise the text to include a brief discussion and literature support behind the attribution.

Before: “Low summer $\delta^{15}\text{N}\text{--NO}_3^-$ values may result from depleted $\delta^{15}\text{N}\text{--NO}_x$ due to enhanced biogenic soil emissions (including nitrification of fertilizers) and lightning during warmer months, and the enriched $\delta^{15}\text{N}\text{--NO}_x$ during colder seasons can be attributed to the increased combustion of fossil fuels (Freyer, 1978; Zhang et al., 2003; Jaeglé et al., 2005).”

After: “The seasonal variability in $\delta^{15}\text{N}\text{--NO}_3^-$ can be explained by shifts in the dominant NO_x sources and their isotopic characteristics. During warmer months, enhanced biogenic soil emissions and lightning contribute isotopically depleted NO_x with $\delta^{15}\text{N}$ values typically ranging from -10 to $+2\text{‰}$, reflecting light nitrogen derived from microbial nitrification or denitrification in soils (Freyer, 1978; Williams et al., 1987) and from atmospheric N_2 oxidation by lightning (-0.5 to $+1.4\text{‰}$; Hoering, 1957). In contrast, during colder seasons, the $\delta^{15}\text{N}\text{--NO}_x$ becomes enriched ($+6\text{‰}$ to $+13\text{‰}$) due to increased fossil-fuel combustion, as the nitrogen originates mainly from ^{15}N -enriched organic compounds in the fuel (Heaton, 1990). Consequently, the $\delta^{15}\text{N}\text{--NO}_3^-$ in precipitation reflects both the seasonal transition from biogenic to anthropogenic NO_x sources (Freyer, 1978; Hastings et al., 2003).”

-Heaton, T. H. E. (1990). $^{15}\text{N}/^{14}\text{N}$ ratios of NO_x from vehicle engines and coal-fired power stations. *Tellus B*, 42(3), 304-307.

- Hoering, T., The isotopic composition of ammonia and nitrate ion in rain, *Geochim. Cosmochim. Acta*, 12, 97–102, 1957.

- Freyer, H. D., Seasonal variation of $^{15}\text{N}/^{14}\text{N}$ ratios in atmospheric nitrate species, *Tellus, Ser. B*, 43, 34–44, 1991.

- Williams, E. J., Parrish, D. D., & Fehsenfeld, F. C. (1987). Determination of nitrogen oxide emissions from soils: Results from a grassland site in Colorado, United States. *Journal of Geophysical Research: Atmospheres*, 92(D2), 2173-2179.

- Hastings, M. G., Sigman, D. M., & Lipschultz, F. (2003). Isotopic evidence for source changes of nitrate in rain at Bermuda. *Journal of Geophysical Research: Atmospheres*, 108(D24).

12. Line: 174-175: attribution with no discussion

Answer: We will add the following discussions.



“The artificial snowmaking water at the study site is stored in reservoirs that receive inputs from nearby settlements and ski facilities, where such nitrogen-enriched sources are plausible. Therefore, the isotopic signature of artificial snow reflects nitrogen originating from anthropogenic sources within the local hydrological system.”

13. Line 179-180: attribution with no discussion

Bizarre to mention sources that does not exist in theis system.

Answer: We clearly state that anthropogenic pollution sources do exist in the study area. The surface water used for artificial snow production originates from streams and reservoirs that are directly affected by nearby human activities, including wastewater discharge and runoff from residential and ski resort facilities. These inputs introduce manure- and sewage-derived nitrogen into the local hydrological system.

As a result, the snowmaking water already contains elevated nitrate concentrations and enriched $\delta^{15}\text{N}-\text{NO}_3^-$ values, which are transferred into artificial snow and subsequently into the mountain groundwater during snowmelt. This interpretation is supported by our isotopic data, showing $\delta^{15}\text{N}-\text{NO}_3^-$ values of +9.9‰ to +10.7‰ in artificial snow.

Therefore, it is not “bizarre” to mention such sources; rather, their presence and isotopic influence are empirically observed and consistent with both the site hydrology and previous literature.

14. Line 184: the seasonal pattern is not very clear on the figure and seem very weak

Answer: We respectfully disagree. The seasonal pattern of NO_3^- -N concentration is statistically significant ($p = 0.05$, one-tailed t-test), with consistently higher values during the dry season (December–February) compared to the wet season (July–September). The statistical test clearly supports the existence of a significant seasonal difference. Therefore, we maintain our interpretation as presented.

15. Line 191: ad hoc explanation?

Answer: We respectfully disagree with the reviewer’s remark that this statement is “ad hoc.”

The interpretation that nitrogen sources with relatively high NO_3^- concentrations continuously flow into mountain groundwater along with natural snowmelt is not speculative, but supported by multiple independent lines of hydrological and isotopic evidence presented in the manuscript: (i) seasonal variations in $\delta^2\text{H}-\text{H}_2\text{O}$ and $\delta^{18}\text{O}-\text{H}_2\text{O}$ clearly demonstrate snowmelt recharge to groundwater; (ii) concurrent increases in NO_3^- concentration during the snowmelt period indicate the inflow of nitrate-enriched water; and (iii) $\delta^{15}\text{N}-\text{NO}_3^-$ enrichment consistent with



anthropogenic signatures in the artificial-snow endmember reflects the transfer of anthropogenic nitrogen through recharge pathways.

These observations collectively define a hydrologically coherent mechanism in which surface water—already influenced by anthropogenic inputs—is stored in a reservoir, converted to artificial snow, and subsequently reintroduced into the subsurface as meltwater. This process establishes a dynamic surface water–groundwater interaction that facilitates the downward transfer of anthropogenic nitrate into mountain aquifers.

To correctly interpret this finding, it is essential to understand the hydrological framework of the system, particularly how groundwater recharge operates through snowmelt infiltration and surface water–groundwater interactions. This conceptual linkage between hydrological connectivity and nitrate transport underpins our process-based interpretation, which is grounded in empirical evidence rather than an ad hoc explanation.

16. Line 193: increased from 6.83‰ to 7.53‰ is it significant with a precision of ± 0.5 ‰?

Answer: Although the absolute difference in $\delta^{15}\text{N}\text{--NO}_3^-$ values ($6.8\text{‰} \rightarrow 7.5\text{‰}$) is close to the analytical precision ($\pm 0.5\text{‰}$), the interpretation is not based solely on isotopic change but on the combined pattern of isotopic and concentration data.

During the snowmelt period, the $\delta^{15}\text{N}\text{--NO}_3^-$ values slightly increased while NO_3^- –N concentrations remained nearly constant rather than being diluted. If precipitation or soil water were the dominant sources, the influx of low-nitrate water would have diluted groundwater nitrate, resulting in decreased concentrations. However, the absence of such dilution together with a modest $\delta^{15}\text{N}$ enrichment indicates a continuous input of nitrate from a source with higher $\delta^{15}\text{N}$ and comparable or higher NO_3^- –N concentration, consistent with the artificial-snow endmember.

Therefore, this pattern is hydrologically and isotopically coherent and cannot be explained by natural snowmelt or soil leaching alone. The stability of NO_3^- –N concentrations during melt confirms that artificial-snow-derived nitrate is the most plausible contributor during this period.

17. Line 200: replace M&S by manure and sewage

Answer: We have revised the term “M&S” to “manure/sewage” as suggested.

18. Line 201: what pollutants the author are talking about?

Answer: We have clarified this point in the revised manuscript. The term “pollutants” refers primarily to manure and sewage. The revised sentence now reads as follows:



“Thus, if the water from the area were used to produce artificial snow, it could potentially introduce manure and sewage as well.”

19. Line 204: replace contaminants by sources

Answer: We have revised the term “contaminants” to “sources” as suggested.

20. Line 215: now snow and rain have become sources

Answer: In this study, rainwater, natural snow, and artificial snow are treated as hydrological end-members that contribute to groundwater recharge in the alpine area. Although snow and rain are precipitation forms, they represent the main source waters that mix to form the isotopic composition of mountain groundwater. To avoid confusion, we have clarified this concept in the revised text as follows:

“In the bivariate mixing diagram (Figure 6a), mountain groundwater (W) samples plot within the mixing area defined by the three hydrological end-members—rainwater, natural snow, and artificial snow—which represent the principal recharge sources of groundwater in the study area.”

21. Line : 219-222: why then these values are reported and were used for interpretation before?

Answer: The clarification is that the samples with NO_3^- concentrations below the detection limit (<0.037 mg/L) or with low concentrations (<0.5 mg/L) were excluded only from the nitrate isotope analysis, as reliable $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ measurements were not possible at such low levels. However, these samples were still used for water isotope ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) analyses, since water isotopic composition is independent of nitrate concentration.

22. Line 244: there is no source inputs from artificial snow as it is formed from natural water.

Answer: Our statement does not imply that artificial snow introduces a new anthropogenic nitrogen source, but rather that it redistributes existing nitrogen from the source water into the alpine environment through repeated snowmaking activities. This process can alter the timing and pathways of nitrogen release during melt periods, thereby influencing local N cycling.

23. Table S2: how can artificial snow density be > 800 kg/m³ ??? strange, it is ice at this density

Answer: A bulk density exceeding 800 kg/m³ for artificial snow is physically realistic and characteristic of ski-resort snowpack conditions. Artificial snow is produced from pressurized water droplets that freeze rapidly, forming small, dense, and wet grains with an initial density often above 600 kg/m³ (Rixen et al., 2004). Subsequent



grooming, compaction, and repeated melt–refreeze cycles further increase snow density over time.

Therefore, our measured density values are fully consistent with real-world snow-management practices at ski resorts and do not represent solid ice but densely compacted, wet artificial snow typical of long-maintained ski slopes.

- Rixen, C., Haeberli, W., & Stoeckli, V. (2004). Ground temperatures under ski pistes with artificial and natural snow. *Arctic, Antarctic, and Alpine Research*, 36(4), 419-427.

24. Table S1: can we consider earth snow chemistry different that groundwater? How two analysis can be statistically representative? Same for Table S3

Answer: The chemical and isotopic compositions clearly show distinct ranges between snow and groundwater. As presented in Table S1, parameters such as EC, Ca^{2+} , Na^+ , Cl^- , and NO_3^- -N differ by more than an order of magnitude (e.g., EC = 7–129 $\mu\text{S}/\text{cm}$ and NO_3^- -N = 0.05–0.96 mg/L in snow, compared to EC = 114–976 $\mu\text{S}/\text{cm}$ and NO_3^- -N = 3.1–9.4 mg/L in groundwater). The same is true for NO_3^- -N reported in Table S3, which also clearly differ between snow and groundwater, further supporting this interpretation. These large differences far exceed analytical uncertainty and natural short-term variability, confirming that snow and groundwater represent distinct hydrological and chemical populations. Therefore, the datasets are sufficient to support the interpretations presented.

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