

Review of

Isotopic evidence for the impact of artificial snow on the nitrogen cycle in temperate regions

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submitted to HESS

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.

They apply a Bayesian isotope mixing model and use two independent parameters ($\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-H}_2\text{O}$) to quantify the relative contributions of different sources to the groundwater. The approach is simple and straightforward.

However, I must express three serious concerns:

(I) 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.

(II) 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.

(III) 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 $\delta^{18}\text{O-}$

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.

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.
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.
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 $\delta^{15}\text{N}$ -NO₃ and $\delta^{18}\text{O}$ in a Bayesian mixing model is not so often used. The authors should be more specific in this regard.
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.
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.
6. Line 145: "amount effect" I'd rather say it's the classic altitude effect.
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.
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).
9. Line 192/193: "...The $\delta^{15}\text{N}$ -NO₃- 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.
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.
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.
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.
13. Figure 6(a): What do the red and blue arrows represent? Consider the analytical errors!

- a. Does the paper address relevant scientific questions within the scope of HESS?
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- b. Does the paper present novel concepts, ideas, tools, or data?
Yes
- c. Are substantial conclusions reached?
No
- d. Are the scientific methods and assumptions valid and clearly outlined?
In part. See general remarks
- e. Are the results sufficient to support the interpretations and conclusions?
No (see specific comment 10 and 11)
- f. Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)?
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- g. Do the authors give proper credit to related work and clearly indicate their own new/original contribution?
Yes
- h. Does the title clearly reflect the contents of the paper?
The title is somehow misleading (see general remark (II))
- i. Does the abstract provide a concise and complete summary?
Yes
- j. Is the overall presentation well-structured and clear?
Yes
- k. Is the language fluent and precise?
I have the impression.
- l. Are mathematical formulae, symbols, abbreviations, and units correctly defined and used?
Yes
- m. Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated?
Yes: Conclusion section.
- n. Are the number and quality of references appropriate?
Basically yes, a lot of the references are a bit outdated.
- o. Is the amount and quality of supplementary material appropriate?
Yes