

## ***Interactive comment on “<sup>17</sup>O-excess traces atmospheric nitrate in paleo groundwater of the Saharan desert” by M. Dietzel et al.***

**Anonymous Referee #2**

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This study provides a comprehensive study of groundwater in a sandstone aquifer in Libya. The authors use  $^{15}\text{N}/^{14}\text{N}$  ratios, triple stable isotopes of oxygen, and other geochemical and isotopic tracers to assess the origin of high  $\text{NO}_3$  levels found in these groundwater reservoirs. I consider the methods sound, and most of the results and analysis are presented in a convincing and solid fashion. However, I think there are some clarifications needed for readers not fully aware of the complex use of all these isotopic analysis, as well as some more careful interpretation of paleo-climatic conditions. The main result of the study found that high proportions (up to 20%) of  $\text{NO}_3$  found in the aquifer originated from atmospheric deposition, but they don't at all discuss where the remaining 80% originated. Abstract, page 20081: What is missing is the reason and importance to conduct this study. The reasons (high  $\text{NO}_3$  in groundwa-

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ter exceeding drinking water standards, unclear origin) are alluded to in some degree in the introduction and later in the manuscript, but it should be clearly mentioned in the abstract what the reasons and importance of this study is.

Abstract, page 20081: much of the abstract focuses on the paleoclimatic conditions leading to the high  $\text{NO}_3$ atm recharge in the aquifer (which, to my degree, are at times somewhat speculative), rather than focusing on the results of biogeochemical and isotopic analysis that highlights the importance and contributions of atmospheric  $\text{NO}_3$  inputs – this should be changed.

Abstract, Page 20081, line 8: clarify  $x[\text{NO}_3\text{-}]_{\text{atm}}$  – the reader does not know what this is prior to reading the rest of the manuscript.

Page 20081, line 21: Inconsistent use of chemical names and formulas throughout paper (i.e. nitrate versus  $\text{NO}_3^-$ ). Chemical formula and name should be defined when first introduced and then formula should be used after. Examples include Nitrate, Sulfate,  $\text{BaSO}_4$ , Calcium, ect.

Page 20082, lines 1-5. Can you add to the importance of this study? How many people use/rely on this water, what is the health and environmental impact of this? What are the challenges in deciphering the sources so far?

Page 20082, line 12-13: clearly define all used isotopic ratios used in the manuscript and be consistent with use of terminology throughout the manuscript to facilitate reading of the manuscript (e.g., be consistent with the use of ratios  $^{15}\text{N}/^{14}\text{N}$  versus  $\delta^{15}\text{N}$  versus  $\delta^{14}\text{N}$  annotations).

Page 20082, lines 15-18. They describe how signatures can be used to evaluate/separate various processes (e.g., denitrification versus atmospheric sources), but no clear reaction and description of how to use these are given here. I realize that this is discussed in detail in Results and Discussion, but it would be helpful here to give a clear overview how the various processes lead to discrimination and changes in

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isotopic ratios.

Page 20083, line 1-5: they discuss that  $^{17}\text{O}$ -excess has been used in various settings before (Atacama, modern groundwater, lakes, etc) – they should highlight that this approach has never been used for ancient groundwater, and one/the goal of this study is to test the applicability for ancient groundwater.

Page 20083, line 18: Change “about” to “approximately”

Page 20083, line 7: change “Lab” to “lab”

Page 20083, line 13: change “analyzing the” to “analysis of”

Page 20086, lines 6-10. Shortly describe how the referenced methods work and are performed.

Page 20086, line 16: “slightly elevated temperatures”, compared to what?

Page 20086, line 21: deviation from electrical neutrality, “which verified the (good?) quality of ion content analysis” clarify for the reader what the percent deviation means and state (or reference) what levels are generally considered good quality.

Page 20087, Line 14: Reword sentence, confusing

Page 20088, lines 15-20: the isotope values fall below the GMWL and LMWL – this should be statistically supported. In figure 4, the authors state that the analytic inaccuracies lay within the size of the symbols, can you quantify these?

Page 20089, line 9; “As an analogy to the above” this seems the wrong lead-in to this sentence.

Page 20089, line 15-16: “in relation to the isotope ranges of difference sources for  $\text{NO}_3^-$ ” clarify and rephrase this sentence.

Page 20089, line 19: what is meant by “apparent”?

Page 20089, LINES 20-25. Please show reactions for clarification

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Page 20091, line 2 can you give fit of the trend in Figure 5, same for Figure 3?

Page 20091, line 8: clarify “minor oxygen isotope”

Page 20091, line 8 to page 20092, line 5: the structure of this section should be improved: currently, they first describe trends and figures of their analysis, but describe the reason for the figures and mixing models only later. It would clarify for the reader if they first clearly introduce how oxygen isotope can be used, then discuss the results of their data.

Page 20092, line 10. They conclude a high proportion of atmospherically derived  $\text{NO}_3$  (20%), but they don't discuss at all about the origin of the remaining 80% of  $\text{NO}_3$ . So where is the rest coming from, and why not add discussion points about the remaining sources.

Page 20092, line 12-15. This section is confusing and I cannot understand it. I think they say the same as in the section below, so I suggest to delete this or add to the lower section.

Page 20093, line 1-7: this is not an implication statement, but rather restating of the results before.

Page 20093, line 15: change “predicted” to “proposed”

Page 20093, line 15-25. I think the authors over-interpret their data. I don't mind that they provide a possible scenario of how nitrate could have been washed down to the aquifer and what paleo-climatic conditions may have driven this, but in my view their data cannot be used to exclude other possible processes as well. I think if they authors really want to link their results to paleo-climatic conditions, a lot more evidence of these climatic conditions need to be presented and discussed, in addition to the simple statement that their results “coincided well with results from pollen analyses”.

Page 20093, line 18: change “coincides” to “coincide”

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Page 20094, lines 3-7. This section is not clear and I am not sure what they base their statements on.

Page 20095, lines 18-30. They should state that their interpretation is that these paleo-climatic conditions possibly lead to observed patterns, rather than presenting this as a fact (see comments above).

Page 20095, line 26: Reword sentence, confusing

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