

Response letter to Anonymous Referee #2

(Responses of authors are marked in yellow)

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 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 NO_3 found in the aquifer originated from atmospheric deposition, but they don't at all discuss where the remaining 80% originated.

2. Revised sentences in the abstract:

"Our $\Delta^{17}\text{O}_{\text{NO}_3}$ data from 0.4 to 5.0 ‰ ($n = 28$) indicate that up to $x[\text{NO}_3^-]_{\text{atm}} = 20 \text{ mol}\%$ of total dissolved NO_3^- originated from the Earth's atmosphere, where the remaining NO_3^- refers to microbial-induced nitrification in soils."

Abstract, page 20081: What is missing is the reason and importance to conduct this study. The reasons (high NO_3 in groundwater 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.

3. Revised sentences in the abstract:

Saharan paleo groundwater from the Hasouna area of Libya contains up to 1.8 mM of nitrate, which exceeds the World Health Organization limit for drinking water, but the origin is still disputed

Abstract, page 20081: much of the abstract focuses on the paleoclimatic conditions leading to the high 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 NO_3 inputs – this should be changed.

4. There are now only two sentences on paleoclimate in the abstract, which are also revised according to the comments of reviewer 1 (see also revision (2) above):

"High $\Delta^{17}\text{O}_{\text{NO}_3}$ values correspond to soils that are barren in dry periods, while low $\Delta^{17}\text{O}_{\text{NO}_3}$ values correspond to more fertile soils. Coupled high $\Delta^{17}\text{O}_{\text{NO}_3}$ and high $x[\text{NO}_3^-]_{\text{atm}}$ values are caused by a sudden wash out of accumulated disposition of atmospheric NO_3^- on plants, soil surfaces, and in vadose zones within humid-wet cycles."

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

5. Revised sentences in the abstract:

"... indicate that up to 20 mol% of total dissolved NO_3^- originated from the Earth's atmosphere ($x[\text{NO}_3^-]_{\text{atm}}$), ..."

Page 20081, line 21: Inconsistent use of chemical names and formulas throughout pa-

per (i.e. nitrate versus NO₃⁻). Chemical formula and name should be defined when first introduced and then formula should be used after. Examples include Nitrate, Sulfate, BaSO₄, Calcium, ect.

6. The text is revised accordingly (NO₃⁻, SO₄²⁻, CaSO₄, Ca²⁺, CaCO₃ etc.)

E.g. NO₃⁻ is introduced in the Introduction: "The accumulation of nitrate (NO₃⁻) in groundwater ..." and subsequently NO₃⁻ is used in the whole ms.

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?

7. Revised text: "Deciphering the source of NO₃⁻ for Saharan groundwater in Libya is highly challenging, as (i) the present arid conditions preclude appreciable recharge and (ii) groundwater is with about 90 % the main source for water supply of Libya (e.g. Salem, 1992; Edmunds, 2006; Abdelrhem et al., 2008). Several million m³ of fresh water per day are transferred to the Mediterranean for agricultural and domestic use including drinking water supply."

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 15N/14N versus δ¹⁵N versus δ¹⁵N_{NO₃} annotations).

8. All delta values are defined and delta values used exclusively in the revised text.

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 isotopic ratios.

9. Added text for explanation (further mechanisms are discussed in detail in subsequent chapters): "For instance, the discrimination of ¹⁵N versus ¹⁴N through denitrification will result in an increase of δ¹⁵N_{NO₃} values of the remaining NO₃⁻. Accordingly, a trend to higher δ¹⁵N_{NO₃} values at lower NO₃⁻ concentrations can be found in groundwater due to denitrification."

Page 20083, line 1-5: they discuss that 17O-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.

10. Added text: "This approach has never been used for ancient groundwater, and the major aim of this study is to test the applicability of Δ¹⁷O_{NO₃} values in such surroundings."

Page 20083, line 18: Change "about" to "approximately" 11. revised accordingly.

Page 20083, line 7: change "Lab" to "lab" 12. Changed to "laboratory".

Page 20083, line 13: change "analyzing the" to "analysis of" 13. revised accordingly.

Page 20086, lines 6-10. Shortly describe how the referenced methods work and are performed. 14. Isotope ratios of nitrate were measured on a Thermo Finnigan MAT 253 isotope ratio mass spectrometer, equipped with a GasBench II and coupled to an in-house-built nitrate interface. Briefly, denitrifying bacteria *Pseudomonas aureofaciens*

convert NO_3 in N_2O in anaerobic conditions. N_2O is then thermally decomposed on a gold surface heated to 900 C, producing a mixture of O_2 and N_2 which is then separated by gas chromatography and injected into the mass spectrometer for the dual O and N analysis (Erland et al., 2013 and references therein)

Isotopic data were corrected for any isotopic effect occurring during the analytical procedure by using the same approach as Morin et al. (2009) and Frey et al. (2009); international reference materials (IAEA USGS-32, 34 and 35) were prepared in an identical way and followed the same analytical procedures. This identical treatment includes the use of the same background matrix as well as the same water isotopic composition for the standards and samples. The overall accuracy of the method is estimated as the reduced standard deviation of the residuals from the linear regression between the measured reference materials ($n = 16$) and their expected values.

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

15. Revised sentence: “... at temperatures between 27 and 35°C.”

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.

16. Revised sentence: “The average deviation from electrical neutrality for the aqueous solutions is 3.6 meq% with a maximum of about 5 meq%. Values ≤ 5 meq% indicate the good quality of ion analysis by considering the individual analytical precisions (see section 3.1; Appelo and Postma, 2007).”

Page 20087, Line 14: Reword sentence, confusing

17. Revised sentence: “The dissolved ions cover a broad concentration range, but the individual ion concentrations are well correlated.”

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?

18. Revised sentence:

Comment: It is obvious from Fig.4, that all data points (red dots) fall below both solid lines (black and orange).

Revised caption of Fig. 4: “The analytic inaccuracies for $\delta\text{D}_{\text{H}_2\text{O}}$ (± 0.8 ‰) and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (± 0.05 ‰) lay within the size of the symbols.”

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

19. Revised sentence: “In accordance with the above ...”

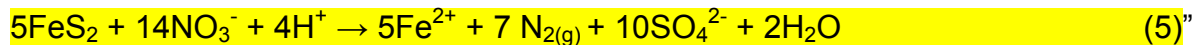
Page 20089, line 15-16: “in relation to the isotope ranges of difference sources for NO_3^- ” clarify and rephrase this sentence.

20. Revised sentence: “... and are shown in Fig. 5 in relation to the isotope ranges of different sources for NO_3^- ”

Page 20089, line 19: what is meant by “apparent”? 21. -> “... the reacting H_2O and O_2 ...”

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

22. Added sentence: "... according to the idealized overall reaction



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

23. The fit function for trend in Figure 5 is now added in the caption of Fig.5: "...where the solid green arrow displays the regression line ($\delta^{18}\text{O}_{\text{NO}_3} = -2.79 \delta^{15}\text{N}_{\text{NO}_3} + 33.8$) and an increase in NO_3^- concentration."

The Fig.5 is revised as now the calculated fit function is used for the green arrow.

The solid line in Fig.3 is not based on a regression line. It is the mixing line between the end member solution #152 and #165.

Page 20091, line 8: clarify "minor oxygen isotope" 24. Revised: " ^{17}O 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.

25. Comment: The background and use of ^{17}O -excess is already discussed in the Introduction. Thus we prefer to discuss in this sentence first the results and subsequently discuss the results. A link to the equation (1) is now given in the text to refer to the introduction for clarification. "... evaluating both the $\delta^{17}\text{O}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values (see equation (1))."

Page 20092, line 10. They conclude a high proportion of atmospherically derived NO_3 (20%), but they don't discuss at all about the origin of the remaining 80% of NO_3 . So where is the rest coming from, and why not add discussion points about the remaining sources.

26. Comment: In the following sentences of the ms the source of the remaining NO_3^- (soil NO_3) is already discussed:

Chapter 4.3 (first paragraph): "Our measured $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values are almost within the range of a microbial origin for NO_3^- (e.g. obtained by nitrification in soils), where $^{18}\text{O}/^{16}\text{O}$ is incorporated from the reacting H_2O and O_2 , and the $\delta^{15}\text{N}_{\text{NO}_3}$ value is derived from organic matter (Fig. 5)."

Chapter 4.3 (fourth paragraph): "The proportion of $\text{NO}_3^-_{\text{atm}}$ for the former reaction paths and corresponding precipitation rates can be obtained from global climate models, which finally results in $\Delta^{17}\text{O}_{\text{NO}_3,\text{atm}}$ of about +25 ‰, a value well corroborated by atmospheric observations (Michalski et al., 2003; Morin et al., 2008; Alexander et al., 2009). In contrast, microbial-induced nitrification in soils results in $\Delta^{17}\text{O}_{\text{NO}_3,\text{soil}} = 0 \text{‰}$."

To make a clear statement in the ms, the following new discussion point is now given: "The remaining NO_3^- proportion is referred to recycled NO_3^- in soil horizons, where oxygen isotopes in NO_3^- are incorporated via microbial-induced nitrification from the reacting H_2O and O_2 ."

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.

27. This section deleted.

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

28. The sentence (end of section 4.3): "At elevated NO_3^- concentrations of the groundwater, the highest concentrations of atmospheric NO_3^- , as well as the highest fractions of atmospheric NO_3^- versus the total NO_3^- concentration ($x[\text{NO}_3^-]_{\text{atm}}$) are found."

is now deleted to avoid repetition.

Page 20093, line 15: change "predicted" to "proposed" 29. Revised accordingly.

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".

30. Comment: The main statement on paleoclimatic conditions is now: "... it is proposed dry periods have alternated with periodic infiltration events during wetter climates." The authors believe that this statement can be reasonable proposed by their data and considering results from literature: (i) $\Delta^{17}\text{O}_{\text{NO}_3} > 0 \text{ ‰}$ clearly indicates that $\text{NO}_3^-_{\text{atm}}$ underwent limited biological processing as time for infiltration through soil horizons was limited (see also revision note 26) and (ii) given references in respect to just confirm past climate oscillations between wet and dry periods.

The ms is also revised in respect to paleo-climate according to the comments of review 1 (Tyler), where now additional references are given in the ms, which support our interpretation (see also revision note 1 above).

However, we agree with the reviewer that for a detailed paleoclimate reconstruction more reference data etc. are required.

Page 20093, line 18: change "coincides" to "coincide" 31. Revised accordingly.

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

32. Sentence is deleted:

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).

33. Revised sentence: "Past alternating arid periods and infiltration events are suggested, which lead to the observed isotope values."

See also revision note 1 above.

Page 20095, line 26: Reword sentence, confusing

34. See revision note 1 above (Revised Text (in Chapter 6))

Revised Figure 5

