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Comment

## ***Interactive comment on “Untangling hydrological pathways and nitrate diffusive sources by chemical appraisal in a stream network of a reservoir catchment” by M. A. Yevenes-Burgos and C. M. Mannaerts***

### **Anonymous Referee #2**

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#### General comments

The authors present an interesting contribution in which they investigate the sources of water and nitrate input to a reservoir based on chemical traces, including hydrogen and oxygen isotopes. Although this is not a new approach, as shown by the many referenced articles, it adds valuable new experiences and case material to the practical interpretation of geochemical data in hydrological sciences. In this sense the paper has scientific significance and is worth publishing in HESS. However, the explanation of the

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methods and results is not always clear to me. The tables and figures show results, but are not presented in a way that they clearly support the conclusions. The spatial component of hydrological pathways and nitrate sources is not discussed. The system seems to be too complex to achieve useful results for management purposes with the followed research approach. The role of the waste water treatment plant is unclear. These issues need to be addressed in an improved version of the paper. Some of these aspects will be elaborated below.

#### Specific comments

Paragraph 2.3.3: The EMMA is not entirely clear to me. The purpose is to determine end members and their contribution to stream flow. How is an end member defined? What exactly is the outcome of EMMA? The end members turn out to be groundwater, precipitation and surface water. These are indeed the common sources of water. It does not require a complex analysis to conclude this. The quantification of the contribution was done by hydrograph separation. How? Is this part of EMMA? The water flow paths are estimated using a Spearman correlation. How? Is this still part of EMMA? A better explanation of EMMA is desired. What is the added value of EMMA compared to other techniques?

Paragraph 3.1: For which location is stream flow given in Figure 2? Why do you not show daily rainfall and discharge? This gives a better indication of the variability and response time of the stream flow to rainfall. Monthly discharges in Figure 2 are much lower than the daily low value of 0.6 m<sup>3</sup> s<sup>-1</sup> mentioned in the text. The monthly rainfall in March in Figure 2 seems lower than the major daily rainfall event of 34.40 mm mentioned in the text. The discharge seems shifted a month from the rainfall pattern.

Paragraph 3.2: This paragraph is not so much about the spatial variation of stable isotopes. It describes the LMWL and LELs for two different seasons (temporal variation). How do isotopes vary spatially and what does this say about the hydrological pathways? The samples for the reservoir are all alike, except one in the wet season. The

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difference between LMWL and LEL in Figure 4 is difficult to distinguish. What does the star indicate? For the wet season is in the text commonly referred to March, so refer to March instead of April in the caption of Figure 4. I would also include the year (March 2009 and September 2009). None of the two lines in Figure 4b seem to be a regression line through the data. What information can be deduced from the analyses in this paragraph other than that evaporation is important in the dry season and less in the wet season?

Paragraph 3.3: Axes of Figure 5 are difficult to read. Make more clear which graphs belong to Figure 5a and which to Figure 5b. (left 6 vs. right 6 graphs?). What do the bars indicate? Are circles averages over the three sampling periods? How do numbers correspond to sampling sites as indicated in Figure 1? In the text is stated that A4 has a high average value (line 16/17). In Figure 5 this high sulphate concentration corresponds to site 1, however, according to the text (line 10/11) A4 corresponds to site 8. How can temporal patterns be observed in Figure 5a (line 12/13)?

Paragraph 3.4: p. 2302, line 3-5: The fact that when two sampling points are ignored there would be no significant difference between seasons is an important observation. What does it mean? What are the consequences of ignoring this information in EMMA.

p. 2302, line 8: slopes in figure 6 are all negative.

It is not clear to me what Figure 6 illustrates.

p. 2302 line 26: What is meant by A28M09, W2M09, PO08? (I assume March 2009 and October 2008, but explain this in text)

The end of paragraph 3.4.1: what do these distances mean?

Paragraph 3.4.2: How exactly were the different contributions determined (line 5)? What is the meaning of the sentences in line 5-8 (Stream . . . cases.)?

Paragraph 3.4.3: This paragraph is not clearly written. What I understand is that groundwater is the main source of nitrate. This is not surprising. Streams are mainly

fed by groundwater. On the other hand, I would expect that the waste water treatment plant would also contribute to nitrate in the streams. Is this considered? Can the positive correlation between nitrate concentrations in the stream and percent groundwater contribution to the stream be illustrated by a graph? How can the negative correlations for 4 samples be explained? One of the objectives of the research is to untangle non-point sources of nitrate. Has an attempt been made to identify the spatial distribution of diffuse nitrate sources?

Chapter 4: The discussion continuous on the results in Chapter 3. The distinction between what is a result and what belongs in a discussion is not always clear. I would propose to merge chapter 3 and 4 and give a thorough explanation of the results for each of the elements in this study. A separate discussion can be reserved to comment on the shortcomings of the research.

Paragraph 4.1: Hydrological slopes is a confusing term. What is meant here are the slopes of the LELs. This paragraph does not provide much more information than paragraph 3.2 (see remark above).

Paragraph 4.2: This paragraph mainly discusses chloride. The discussion is speculative, i.e. no evidence is shown of the possible sources and processes mentioned.

Paragraph 4.3: This paragraph is not very clear to me. What is the point that is trying to be made? The first part deals with sources and processes of chloride and sulphate and therefore overlaps partly with paragraph 4.2. The second part discusses the validity of using mixing models. This is an essential discussion, however, no judgment is made about how reliable the results presented in paragraph 3.4.2 are. The last part (p. 2307, line 4-15) is poorly written.

Paragraph 4.4: This paragraph adds little to paragraph 3.4.2. It mainly compares the results to other studies that confirm the conclusion, which was also done in 3.4.2. Here I also get confused about the meaning of the term 'contribution'; contribution to what? In paragraph 3.4.2 it is stated how much the end members groundwater, precipitation

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and surface runoff contributed to the catchment stream flow and reservoir inflow. Here I interpreted surface runoff as direct runoff of water to streams by overland flow during intense rainfall (see also p. 2309, line 25), even though I wondered how the chemical composition of this end member was established. However, in paragraph 4.4 the end member surface runoff is relabeled surface water in streams (p. 2307, line 22). How do streams contribute to catchment stream flow (I would say they are the same)? (see also p. 2309, line 22) Or is only the contribution to the reservoir meant? In the latter case, a contribution of 9% by streams to the lake seems quite small. Has a water balance been calculated for the reservoir to confirm these contributions?

Paragraph 4.5: This is a somewhat unstructured paragraph. The main conclusions are given on p. 2309, line 8-11. The preceding text should clearly lead to these conclusions. Some sentences are unclear, e.g., p. 2308, line 20-22 and line 25-28.; p. 2309 line 11-13 and 13-14.

Conclusions: This section is very short and does not include all the main conclusions of the paper.

Technical corrections

To improve the article, significant changes have to be made. Therefore, I will not go into detail on the grammatical and typing errors. Some (general) comments:

- Make proper use of hyphens and use them consistently (e.g., end members is written with and without hyphen; semi-arid is spelled as semi-arid, semi arid and semiarid)
- Make proper use of capitals (e.g. North vs. south p. 2294, line 19; Local Evaporation Line vs. Local evaporation line p. 2296, line 18 and p. 2300, line 14 and 18)
- Be consistent in the use of 2H (sometimes D for deuterium is used)
- The indication of sampling sites varies (Figure 1; Figure 5; p. 2301 line 10-11; p. 2302 line 26)

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- Is EMMA analysis not redundant?
- p. 2309 line 5: two different units are used here for mineralization rate
- Axes and text in Figures 5 and 6 are difficult to read.

#### References:

- p. 2292, line 1: in reference Bothe is spelled Bothé
- p. 2299, line 22: IAEA, 2006 is not in references
- p. 2299, line 24: Paralta and Oliveira, 2005
- p. 2307, line 19 and p. 2308, line 22: Paralta et al.
- From the reference list are Ladouche et al. (2001), Perakis (2001) and Philips and Gregg (2001) not mentioned in the text.
- p. 2312, line 27: 18 and 2 should be superscripts
- Indicate Ocampo et al. (2006) a and b in reference list.
- Vithanage is in text 2008 (p. 2295, line 23) in reference list 2009

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