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Hydrology and Earth System Sciences Discussions

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 #1

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General comments: The identification of diffuse pollution sources in a river basin and the determination of the pollutant's fate in the drainage network of the river basin is an interesting topic. A lot of research has already been performed in this respect with varying success due to the multitude of uncertainties and non-linear processes that take place. The authors tackle the subject from an interesting point of view. They use a combination of hydrochemical monitoring of isotopic signatures and some main ions with a general mixing model and regression analysis. As such, the topic of the

article is worth publishing in HESS. But the authors should reconsider the background information on the methodology, the presentation of the results and the subsequent discussion since the article does not clearly convey the main message to the reader.

Specific comments:

1. P2295 Data analysis: A Kruskall Wallis non-parametric test is mentioned but this is not repeated further in the manuscript. On p 2298 L 11 the authors refer to a Spearman correlation. Please clearly elaborate the statistical analysis with proper reference in the results and discussion sections since this is an important part of the research.

2. P2295 Hydrological data: it is not clear how stream flow was determined, please explain further.

3. P2296 Isotopic framework: on line 22 the authors refer to shallow groundwater as an example of an evaporating water surface. Just how shallow is the water table located in the Roxo catchment? In addition to this remark: please identify the depth at which water samples in wells were taken and how deep the water table was located at the time of sampling. 'Shallow groundwater' is not necessarily representative of 'groundwater' and surely has different dynamics . This distinction could be important when considering the residence time.

4. P2296 End member mixing analysis: This section is not clear to an inexperienced reader. Reference is made to previous publications but these are not freely accessible. I would therefore propose a short introduction on EMMA following the steps of the methodology mentioned in these publications (if I am correct):

(1) Identification of conservative tracers & potential number of end-members using the mixing model diagram (2) PCA to derive eigenvalues and eigenvectors that can be used to determine the number of end-members (3) Screen the end-members using an orthogonal projection of the measured values into the 'end-member space' and a subsequent analysis of the Euclidian distance of the projection. (4) Use the orthogonal

projections and the generalized equations of a mixing model for hydrograph separation (5) Validate the mixing model

Figures of the mixing model diagrams should be included in the results section and a figure illustrating the orthogonal projection could be useful in this section to better illustrate the important step 3.

5. The hypothesis that is defined to present the results should be reconsidered since it implies a linear relationship between the contributor and the measured values taking into account the limited timeseries of data that also do not show a significant trend in time (see P 2302 L 4). Another approach could be: Can a sample-based analysis be used in combination with EMMA to link reactive transport to general hydrological trends in the Roxo catchment? (see p 2309 L15)

6. Rainfall and runoff data: the authors refer to table 1 but no data of rainfall and runoff are given in this table (P2298 L24). In addition, the authors mention high values in March while one would expect the highest values in January or February when examining the rainfall pattern in Figure 2 (P2298 L 24)? This remark relates to remark n° 2: how was streamflow determined?

7. Water isotopes: the authors give a lengthy presentation of the isotope data under topic 3.2. I think p 2299 and p 2300 could be summarized to a large extent by focusing on the main topic of the paper: is there a difference between potential end-members and which factors confound this analysis? Part of the text could be moved to section 2 (e.g P2300 L10 – 15). In addition, the authors refer to evaporation on lines 1-4 of page 2301 to explain some of the differences and they should include the R-square of the LEL fits to confirm this statement. Also, on lines 4-7 of that page it seems awkward to point to temperature data in addition to isotopic data as explanatory variable since isotopic data already include temperature through evaporation?

8. Hydrochemistry - results: please provide the standard deviation of measured values for stream flow and wells per time period to prove that concentrations in wells varied

less in time. This cannot be deduced from the figure.

9. End member mixing analysis - results: see comment 4. This section should be better structured. Lines 6-14 of page 2302 are not clear and I do not see the added benefit of Figure 6 taking into account the research hypothesis. The extensive PCA analysis becomes confusing if not better structured and I would consider limiting the results to the last one.

10. Please explain the quantification of the end-members to a larger extent since this is an important aspect of the research (see comment 4). A small remark: maybe the outcome is rather logical since no data were obtained during Januray and Februari with much precipitation when one would expect large flows from surface runoff (see also comment 2 and 6)? Are the % contributions on a yearly basis?

11. Sources of nitrogen – results: the authors observe a strong positive relationship between nitate in wells and surface waters (please show data) and conclude that groundwater is the main contributor of nitrate to the surface water. This is most likely true, but was it verified how these concentrations in the wells and surface waters relate to agricultural practices? I.e. is the nitrate in wells and the surface waters from old (> 1y) or new inputs? (see comment 3) Maybe the groundwater should not be identified as a 'source' but a more as a reservoir with historical pollution from other sources.

12. Hydrological slopes – discussion: I would consider a different title related to the research hypothesis: e.g. the hydrology in the Roxo catchment or other. I also do not think that lines 12-16 on p 2304 are necessary for this manuscript. And for consistency: on line 20-23 a slope of 5.2-6.4 is said to be representative while on line 1 of page 2305 the authors refer to a slope of 4?

13. Hydrochemistry – discussion: I would focus on the relation between observed values and isotopic shifts. On line 6 etc the authors mention dilution effect and other processes that were not previously mentioned (i.e. no data) and should therefore be used with care while discussing results (see also lines 14-16 p 2306). For consistency:

the authors write on line 22 that sulphate related to chloride suggesting similar evaporation/dissolution but on page 2301, line 15 one reads constant sulphate concentrations for the entire period (see also p 2306 line 10-15). Please adjust.

14. EMMA – discussion: see comment 4. A remark for lines 16-22 on p 2306: how come that concentrations in streams remain large during the entire rainy season while one would expect a faster decline due to dissolution of buid-up during 1 dry-season? Maybe there are different contributors: sediment, surface runoff. . .? In addition, lines 4-9 of page 2307 are not clear.

15. Interpretation of the source water contribution: on lines 6 P 2308 the authors state that precipitation and surface water were important during the wet season while before groundwater was said to be the largest contributor. Please provide some more data, see earlier comments on stream flow etc. Since the analysis was only performed for data from the wet season an extrapolation to the entire year should be treated with care.

16. Nitrate sources: line 20 p 2308 , see comment 11: no clear data were provided that demonstrate the link between concentrations in wells and surface waters. The authors could provide more results of the regression analysis to clarify this topic. In addition, on line 3, p 2309 the authors state that 'our study confirms this hypothesis' while this was not shown before in the manuscript. They could refer to additional studies as would be suggested by the degradation rates that are suddenly mentioned on the following lines but this information is not well documented. I would further elaborate on lines 14 to 16 of p 2309 since I see this as one of the main findings of the research

17. Conclusions: .on line 27 the authors state that groundwater was related to stream nitrate concentrations, especially during the wet season. I think this statement should be reconsidered since the authors did not provide sufficient statistical data and since only data from the wet season were taken along in EMMA, precluding an analysis of the dynamics in the dry-season.

18. Tables: The data in Table 2 do not add much to the reasoning in the manuscript.

19. Figures:

- figure 1: clearly indicate the stream network on the map.

- figure 2: Shouldn't the first Y-axes be labelled as 'streamflow' instead of 'runoff'?

- figure 4: show both figures with identical axis to clearly illustrate the isotopic shift in the dry season.

- figure 5: indicate (a) and (b) on the figure. If possible, indicate the data points on figure 1.

- figure 6: why are the residuals of chloride and sulphate so large (> 100)? In addition, it seems that chloride is worse predicted than sulphate? This should be discussed in the manuscript and kept in mind while referring to evaporation as explanatory variable.

20. Readability

Many sentences are not well structured and the authors should ameliorate this to improve the readability of the article. I will not provide an exhaustive list since the remarks above would imply a large revision of the article but here are a few examples:

- p 2293, line 6: intermittent major small streams = medium size streams?

- p 2294, line 21: using a water pump using a water collector = using a water pump with collector?

- p 2294, line 26: in situ in the field = in situ

- p 2299, line 3-4: The trend of the sum of monthly runoff was consistent with the sum of monthly precipitation, which indicates that the rainfall is the main reason of runoff variation = ?

- p 2302, line 14: ... to cross this tracer to the next analysis = to take it into account in the next analysis?

- p 2304, line 16: ...this constitution does not chase the GMWL line = the isotopic ratio differs from the GMWL line?

- p 2304, line 25: ...water resources are subjected to substantialevaporation with subsequent plotting along the LEL. = the surface waters in the Roxo catchment evaporate to a large extent yielding isotopic ratios that can be described by a LEL? Etc.

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 8, 2289, 2011.