



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

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Author reply on 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

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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 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.

RESPONSE: We thank the reviewer for the supportive comments. We followed most of the suggestions in the revised manuscript to improve the document.

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?

RESPONSE: We explained further the information regarding to the preliminary exploratory and residual analysis, which is a relatively new approach to identify the correctly geochemical tracers. We have added the EMMA explanation step by step to inform this point in the methodology.

A Spearman correlation analysis was the next analysis, once we identified the main end-members contributions (water source origins). With the Spearman correlation we correlated nitrate concentrations with the principal sources of water to the streamflow.

A description of EMMA and statistical analysis used in the study is provided below: The end-member mixing analysis or EMMA model was developed by Christophersen and Hooper (1992). Concisely, this analysis entails a mixing model for identifying potential water flowpaths (end-members) that contribute to the streamflow generation (Mulholland, 1993). However, before EMMA we included exploratory analyses of a mixing model, (Liu et al., 2008b) to determine the correct numbers of geochemical tracers to use and identification of end-members. It consisted to develop a residual analysis, between observed and predicted chemical values, from the main principal components of a principal component analysis (PCA) and to examine the appropriate rank of streamflow chemistry and determine the dimensions of the data in orthogonal dimensions and also the use of p probability. The aim was to use this successive analysis combination, instead the assumptions of a simple mixing model. This was done to reduce the uncertainty, particularly in choosing the number of end-members and conservative tracers, a known weakness in original EMMA. We structured the analysis according to these following steps: (1) We use a database of two stable isotopes $\delta^{2}\text{H}$, $\delta^{18}\text{O}$ and four solutes Cl^- , SO_4^{2-} , Na^+ and K^+ as geochemical tracers, obtained from 77 samples of stream water, soil pore water and wells and additional chemistry data from precipitation at the 352 ha catchment during 2008–2009; With this data we developed a new EMMA results as follow:

(2) A principal component analysis (PCA) was performed to obtain eigenvectors using a correlation matrix of geochemical tracers (eq.1), determined by using exploratory tools of mixing models as residual analysis and p probability.

(3) Residual analysis from this PCA and p probability were used to determine the number of end-members and conservative tracer to be used in EMMA model, without using common assumptions of a mixing model (Hooper, 2003). These tools were used to

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examine the appropriate rank of streamflow chemistry through a PCA and determine the dimensions of the data in orthogonal dimensions, refer to eq. 2 and 3.

(4) After the exploratory analysis we chose the end-members in an EMMA model to obtain the flowpaths proportional contribution. The determination of end-members was evaluated using distance between original chemical compositions and U-space projections (PCA scores). The first U-space projection was used to select the end-members and examine if the projections of end-members were different from streamflow (eq. 4 and 5).

(5) Finally, the verification of end-member contributions (flowpaths contribution) was done calculating the distance of end-members, showed as percentage by dividing it by the original chemical composition. The shorter the distance the better fit of an end-member to EMMA.

(6) Then, to obtain the percentage of the proportional contribution we used hydrograph separation using the first U-space projection (U1) in a two-end-member solution (Liu et al., 2008b) instead of one tracer for two components in a simple mixing model.

eq (1) eq (2) eq (3) eq (4) eq (5) (Equations were attached as a supplement zip format)

2.3.4 Exploratory data analysis of Mixing Models Hooper (2003) defined that exploratory data analysis as exploratory or diagnostic tools are developed to identify the approximate rank of the data and to evaluate lack of fit of the data. These tools consider the fit of the chemistry of one sampling point into the mixing subspace of a different site, thus allow an appraisal of the reliability of controlling end-members across sampling points (Liu et al., 2008b). According to it, residual analysis can be used to check the accurate ranking of water chemistry data using a principal component analysis and thus identify the number of end-members and conservative tracers for EMMA, using streamflow chemistry.

Exploratory plots can be made by plotting the residuals against the observed concen-

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tration for each chemical (stable isotopes and ions). A well-posed model is indicated by a random pattern in the residuals; any structure in this plot suggests a lack of fit in the model, which can arise from the violation of any of the assumptions inherent in the mixing model (Liu et al., 2008b).

2.3.5 Sources of nitrate Once EMMA was completed, we used the Spearman's rank correlation coefficient (r_s) to investigate if there was a relation between stream NO_3^- concentrations and the percentage contribution of different end-members to the streamflow.

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 $0.6 \text{ m}^3 \text{ s}^{-1}$ 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.

RESPONSE: Certainly some inaccuracies occurred in this small section, which we corrected. We also changed the monthly time interval of Figure 2 to decade (10-day), illustrating better the rainfall stream flow relationship of the catchment. This figure clearly illustrates the seasonality of the rainfall regime and stream flow response of the catchment.

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 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

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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?

RESPONSE: Regarding paragraph 3.2, we organized the water isotopes part in the results section and we focused the results in concordance of this analysis with the EMMA. We considered this analysis and interpretation of water isotope signatures in the area a support for our results, e.g. for comparison purposes, etc. We reformulated and abridged however the section as follows:

The stable water isotope composition revealed systematic differences in the streams and wells, especially during autumn sampling in 2008 (Table 1). For the entire period (2008-2009), in the streams and wells, $\delta^{18}\text{O}$ values ranged from 10.2‰ to -3.65‰ and 36.6‰ to -21.4‰ and $\delta^2\text{H}$ values scoped from 36.6‰ to -24.8‰ and 10.2‰ to -3.4‰ respectively. Isotopic composition ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) was lowest during March (i.e., late winter-early spring) probably due to the input of rainfalls with low $\delta^{18}\text{O}$ and $\delta^2\text{H}$. The isotope composition increased afterwards and reached the highest values in September-October.

In Fig. 4, according to the distribution of stream water in the space of $\delta^{18}\text{O}$ versus $\delta^2\text{H}$, most of the stream water sample points were located below the local meteoric water line (LMWL) ($\delta^2\text{H} = 7.6\delta^{18}\text{O} + 10$), although some of them were more approaching the LMWL. Isotopic measurements of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in shallow groundwater from wells remain near the mean of -2.4 ‰ and -13 ‰ respectively (VSMOW scale). Isotopic composition of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are enriched in surface water compared to shallow groundwater. The LMWL and LEL are shown along with regressions. The LEL connects samples from stream water, shallow groundwater and roxo reservoir to precipitation samples. Low water flow is shown to be enriched in the heavy isotopes in streams and shallow groundwater, and depleted in the case of rain.

Paragraph 3.3: Axes of Figure 5 are difficult to read. Make more clear which graphs

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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)?

RESPONSE: We edited this Figure 5, (Fig.5a, Fig. 5b and Fig 5c) to show more clarity for the reader. In the legend is indicated the meaning of symbols representing concentration average and the standard deviation of the geochemical tracers. We included every number of sampling point to the legend following the same order in the graph. The standard deviation shows the differences for the three studied periods.

Fig. 5. a) Average (square) and standard deviation of the chemical composition in stream flow sites (A4, A7, A22, A23, A24, A25, A26, A28, A29, A33, A35, A36, A39) for the three studied periods: October, 2008, March 2009 and September 2009. b) Average (circle) and standard deviation of the chemical composition in shallow groundwater from wells sites (W2, W8, W13, W14, W16, W17, W18, W19, W20) for the three studied periods: October, 2008, March 2009 and September 2009. c) Average (triangle) and standard deviation of the chemical composition in soil pore water at 5, 10 and 20 cm for the three studied periods: October, 2008, March 2009 and September 2009

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.

RESPONSE: The idea to mention the absence of two sampling points was to show that these two points are important focus of diffuse sources. In the previous section (Hydrochemistry) we now mentioned about these and also in the discussion section. But we did not ignore this information in EMMA; we included all data to estimate our main water source contributions to the streamflow.

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p. 2302, line 8: slopes in figure 6 are all negative. RESPONSE: We corrected this in the text. It is not clear to me what Figure 6 illustrates.

RESPONSE: Fig. 6 show the residual analysis, basically with this figure we are showing the relation between residuals and measured concentration, if the relation is low (low R²) means that residuals are explained better that tracers. This point is well described in comment 2 about exploratory analysis and EMMA.

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

RESPONSE: we explained the codes in the methodology The end of paragraph 3.4.1: what do these distances mean?

RESPONSE: This term refers to Euclidean distance using in a principal components analysis (PCA) and is the straight line distance between two points. PCA analysis uses Euclidean distance calculated from the end-members as the measure of dissimilarity among the different tracers.

Paragraph 3.4.2: How exactly were the different contributions determined (line 5)?

RESPONSE: We verified that end-member contributions (water contributions) were calculated with the distance showed as percentage by dividing distance by the original chemical composition. The shorter the distance the better fit of an end-member to EMMA. Then, we used a hydrograph separation analysis which depended of the numbers of end-members that we found with EMMA. More details are showed in comment 1 (Paragraph 2.3.3).

What is the meaning of the sentences in line 5-8 (Stream : : cases.)? RESPONSE: It means the estimated concentrations were always satisfactorily similar to the measured concentrations in groundwater, soil pore water, precipitation in relation to the streamflow.

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, as streams are mainly fed by groundwater.

RESPONSE: We followed the same rational you are giving. However our aim was to estimate the proportional contributions (percentage) of the sources: shallow groundwater, soil pore water and precipitation to stream flow.

On the other hand, I would expect that the waste water treatment plant would also contribute to nitrate in the streams. Is this considered?

RESPONSE: The nitrate signal in the streamflow downstream the WWTP could be observed as an outlier.

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 nonpoint sources of nitrate. Has an attempt been made to identify the spatial distribution of diffuse nitrate sources?

RESPONSE: We already specified and showed in a new table the results from the spearman correlation for every end-member vs. nitrate in the streamflow.

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.

RESPONSE: We suggest keeping the results and discussion separate to illustrate clearly and guide the reader through the analysis.

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).

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RESPONSE: We suggest calling this section: Water isotope abundance in Roxo catchment. We clarified this paragraph to show the importance of spatial variation of the isotopes.

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.

RESPONSE: We added more discussion about isotopes and solutes. Considering the chemistry of the solutes and isotopes is possible to differentiate the mechanism associated with it.

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.

RESPONSE: The point to be made is to explain the source contributions to generate streamflow and nitrate flows in the catchment.

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 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

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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.

RESPONSE: The main objective of this paragraph is to show the relation of nitrate sources with the main flow path contributions to the generation of streamflow. We also have improved and explained the hydrological components and terms used in the paper in EMMA and residual analysis of streamflow against possible contributions from precipitation, soil pore water and shallow groundwater.

We included a new way of data analysis using different data scenarios to elucidate the potential proportional contributions. We incorporated to a new EMMA analysis four scenarios, with mainly 4 solutes and available stable isotopes for shallow groundwater, soil pore water and precipitation. With these sources, we studied the proportional contributions to the generation of streamflow.

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

RESPONSE: We elaborated more on the main conclusions of this work, which are summarized below: - We present a data analysis sequence and investigate how seasonal and spatial sampling campaigns can be used in combination with residual analysis, EMMA and other statistical techniques to elucidate on water and nitrate source contributions to stream flow in a medium-sized catchment. - We elaborate on the preliminary analysis using PCA and residuals plotting and analysis (preceding the EMMA and hydrograph separation for the contributions). - We research if the method can point to pollution source origins (using nitrate as example) in a catchment, an issue of much concern to land and water management in general throughout the world today.

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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) - 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 difficulty 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

RESPONSE: All suggestions and technical and editing errors have been implemented in the original manuscript.

Please also note the supplement to this comment:

<http://www.hydrol-earth-syst-sci-discuss.net/8/C3798/2011/hessd-8-C3798-2011-supplement.zip>

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

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8, C3798–C3818, 2011

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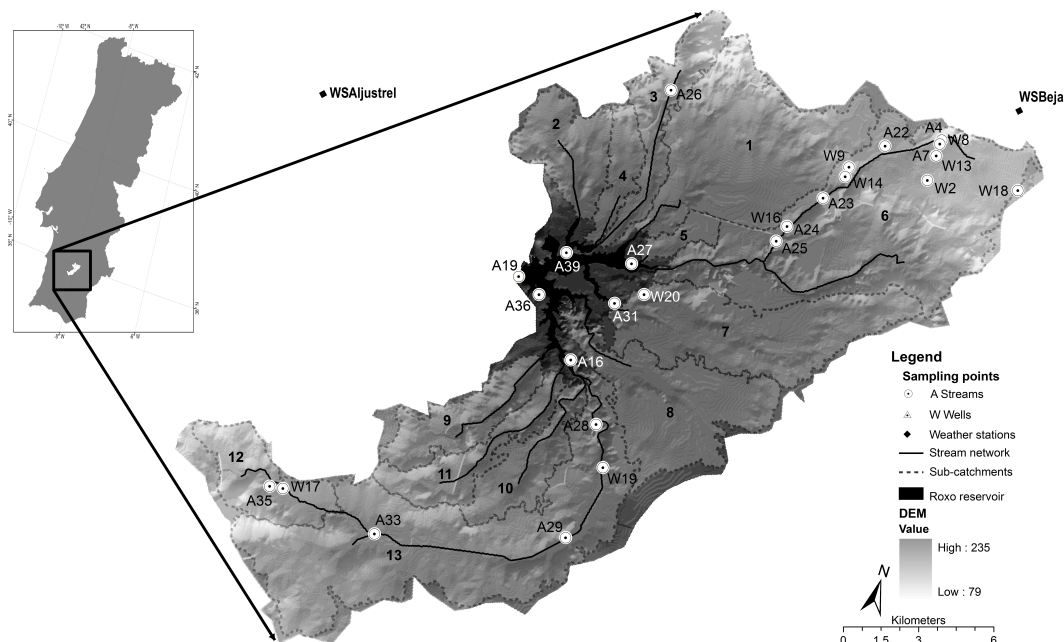


Fig. 1. Map of the study area of Roxo catchment. Stream water (A) and shallow groundwater well samples (W) are included.

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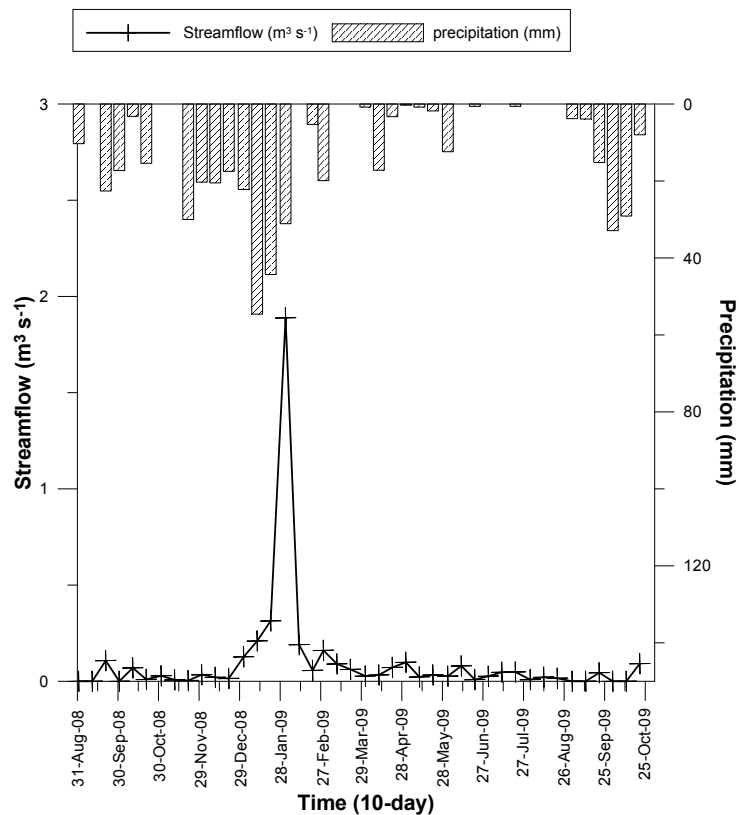


Fig. 2. Fig. 2. Rainfall and streamflow of Roxo catchment for the study period (2008-2009).

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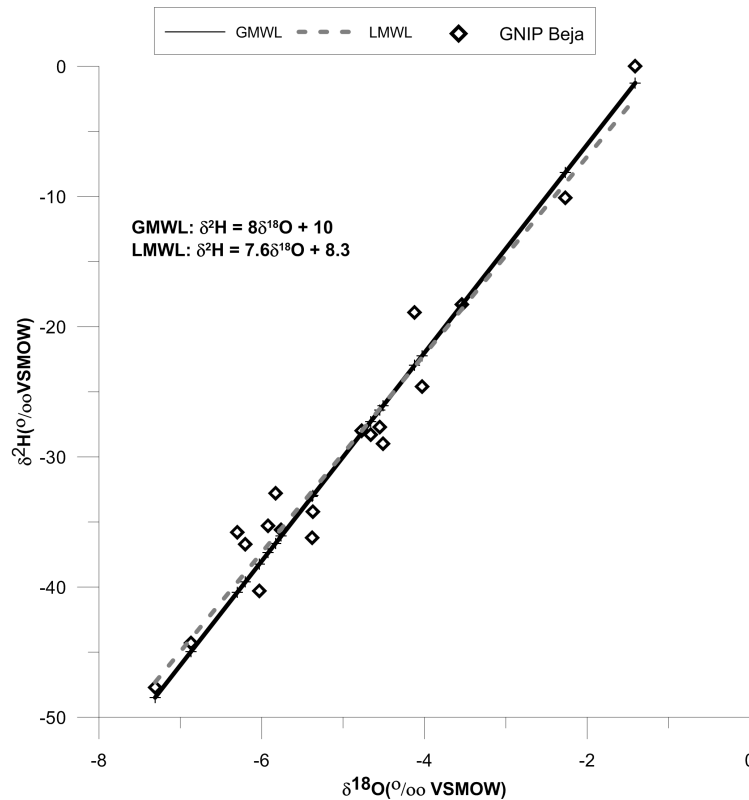


Fig. 3. Fig. 3. Distribution of stream water isotope chemistry along the global (GMWL) and local meteoric water lines (LMWL). The local meteoric line during the wet and dry periods.

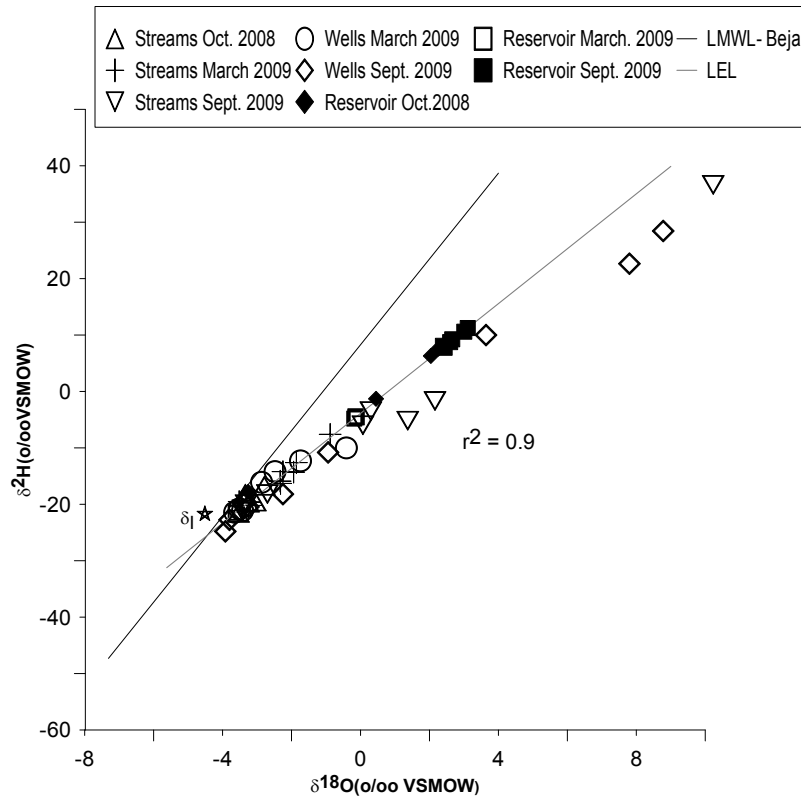


Fig. 4. Fig. 4. Local meteoric water line and Local evaporation line of streamflow water and Roxo reservoir at wet period (October 2008 and March 2009) and dry period (September 2009).

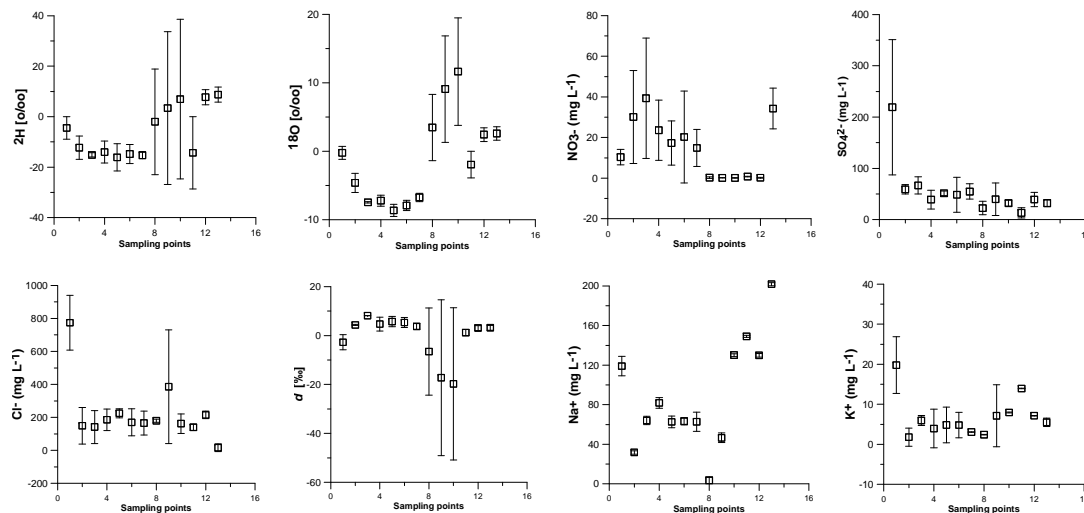


Fig. 5. Fig. 5a: Mean (square) and standard deviation of the chemical composition in stream flow sites (A4, A7, A22, A23, A24, A25, A26, A28, A29, A33, A35, A36, A39) for the studied period.

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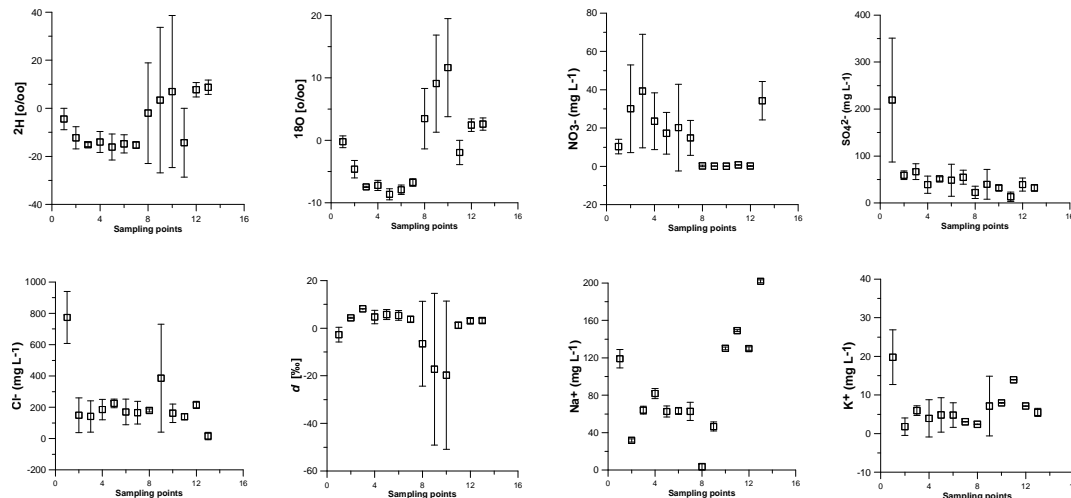


Fig. 6. Fig. 5b. Mean (circle) and standard deviation of the chemical composition in shallow groundwater from wells sites (W2, W8, W13, W14, W16, W17, W18, W19, W20) for the studied period.

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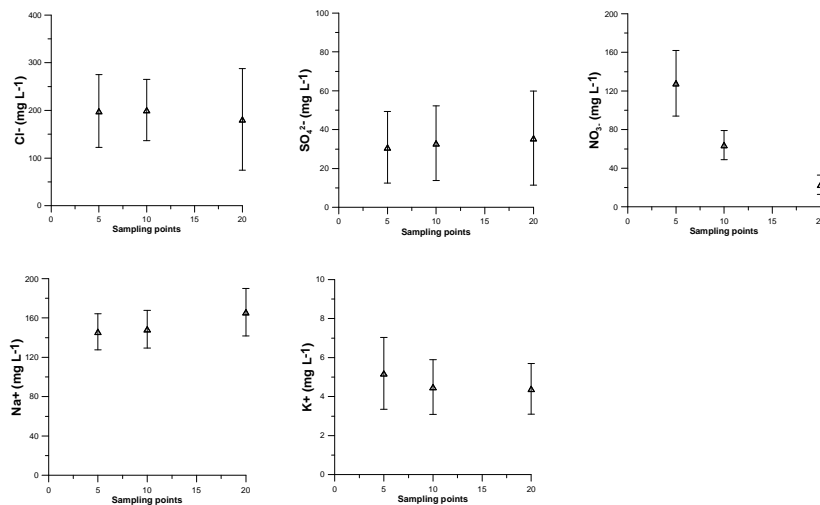


Fig. 7. Fig. 5c. Mean (triangle) and standard deviation of the chemical composition in soil pore water at 5, 10 and 20 cm for the three studied periods: October, 2008, March 2009 and September 2009.

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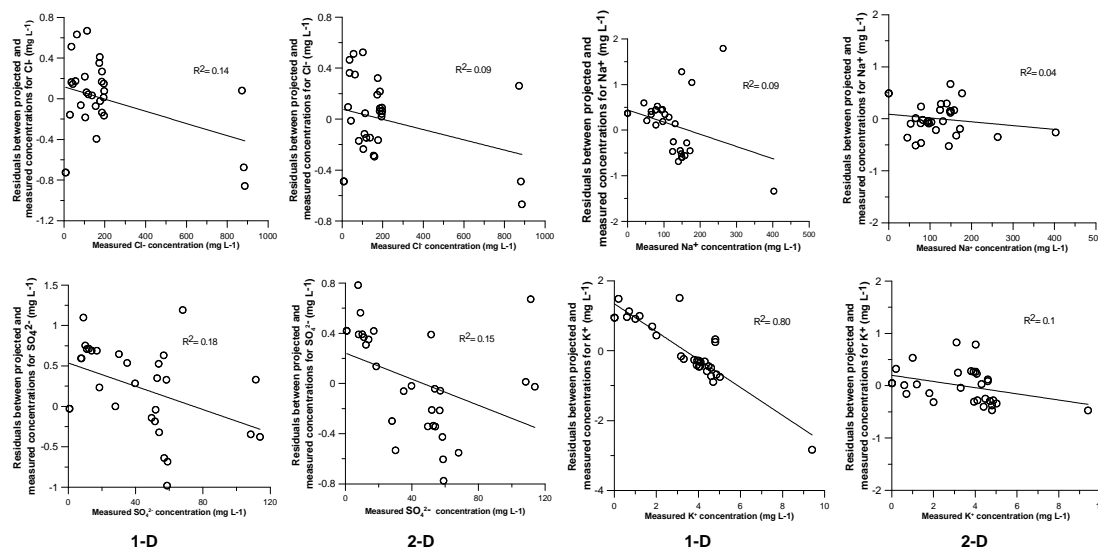


Fig. 8. Fig. 6a. Scenario B1. Plot of Residuals versus original concentrations of solutes for wet period from the 1-D mixing space and 2-D mixing spaces.

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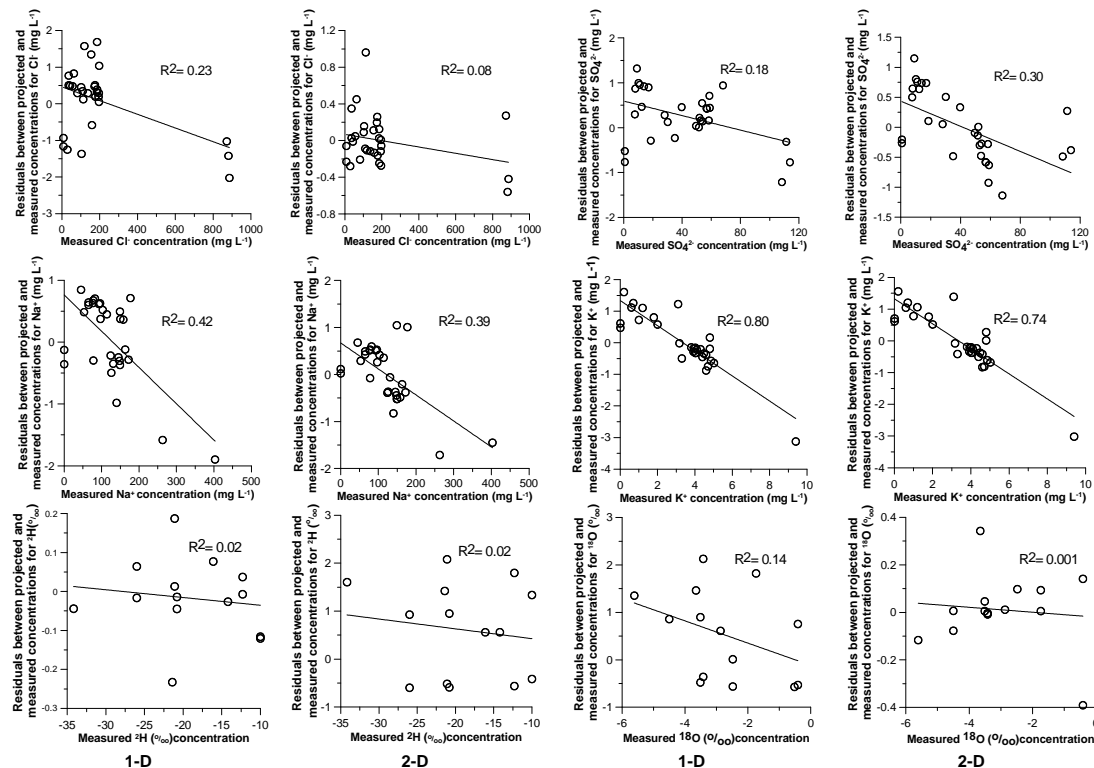


Fig. 9. Fig. 6b. Scenario B2. Plot of Residuals versus original concentrations of solutes and isotopes for wet period from the 1-D mixing space and 2-D mixing spaces.

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