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Hydrology and
Earth System
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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

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Author reply 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 HESSD, 8, C1285-C1291, 2011

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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.

RESPONSE: We thank the reviewer for the supportive comments. The comments below contributed to improve our paper and we followed the suggestions in the revised manuscript.

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 L11 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.

RESPONSE: Following your suggestion we have re-organized the statistical methods under section 2.3 and described their use much in depth in both results and discussion sections. The Kruskall-Wallis test was indeed not used in the final submitted manuscript, and the reference to this test was also removed.

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

RESPONSE: We have explained better the hydrological data collection and the use of it in section 2.3.1 as follows:

Daily records of rainfall data (2008-2009) were obtained from automatic weather stations located nearby Beja and Aljustrel. A daily dataset from 2008 to 2009 of precipitation, evapotranspiration, reservoir storage volume, the historical daily reservoir water levels and water abstraction data was available from Abroxo (2009). An inverted reservoir water balance method was used to estimate the total catchment stream flow into the reservoir (dam).This mass balance technique consisted of estimating the reservoir inflow from the variation over time of the storage volume of the reservoir and the total sum of outflows from the reservoir. This method proved to give reliable estimates on catchment total stream flow and inflow in the reservoir (Vithanage, 2009). Stream flow was also measured at sampling locations in the catchment during the three sampling campaigns (October 2008,March 2009 and September 2009) using the chemical dilution technique (Hershy, 1995).

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.

RESPONSE: The main productive aquifers in the upper Roxo catchment are located in the Beja-Acebuches and Beja Gabbro geotectonic complexes (Oliveira, J. T. (Coord.) 1984) consisting mainly of formations of gabbro-dioritic rocks. The altered bedrock varies locally and may reach 30 meters thickness, and creates an unconfined aquifer with a shallow water table, which naturally drains into the Roxo stream network (Paralta, 2005). The groundwater samples were taken at shallow depths ranging from 2 to 5 meter depth (since the water table range is within this depth) from several well locations, and were considered representative for the natural drainage from the groundwater aquifer towards the stream network and ultimately the Roxo reservoir.

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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):

RESPONSE: We re-structured and explained further step by step the information and importance regarding to EMMA and exploratory analysis involved in the study as we show 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) and their proportions 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 number of geochemical tracers and end-members to be used. It consisted on develop a residual analysis, between observed and predicted chemical values, from the main components of a principal component analysis (PCA). Residual analysis examines the appropriate rank of water chemistry and determines the dimensions of the data in orthogonal dimensions and also the use of p probability. The aim to use this combination of tools, instead a simple mixing model, was to reduce the uncertainty, particularly in choosing the numbers of end-members and conservative tracers.

We structured the analysis according to these following steps: (1) We use a database of two stable isotopes δ2H, δ18O and four solutes Cl-, SO42-, 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.

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(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 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-members contributions (water contributions) was calculating 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, this methodology is mathematically comparable to a common mixing model, for example, hydrograph separation using one tracer for two components while we used the first U-space projection (U1) in a two-end-member solution (Liu et al., 2008b). eq (1) eq (2) eq (3) eq (4) eq (5) (Equations are attached as a suplement zip format)

Exploratory data analysis of Mixing Models Hooper (2003) defined exploratory data analysis, as diagnostic or exploratory 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. Exploratory plots can be elaborated by plotting the residuals against the observed concentration for each chemical (stable isotopes and anions). A well-posed model is showed by a random pattern (high dispersion) in the residuals with a low determination coefficient (Liu et al., 2008b).

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 time series 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)

RESPONSE: Regarding comment number 5, we re-defined the hypothesis as follows:

The possibility to analyze water hydrochemistry on a continuous basis and for longer time periods in larger catchments requires a very significant budget and considerable time and effort, and was beyond the scope of this research. However, we accounted with historical water quality data from the area. Therefore, the aims of this study were to see whether a spatial sample-based analysis using a number of seasonal observation campaigns, can be used as data sources for conducting end-member mixing analysis using isotope and hydrochemical signatures in order to decipher the water and dissolved chemical (nitrate) contributions from different water sources (shallow groundwater, soil pore water and precipitation) to streamflow of a catchment and inflow in a reservoir.

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?

RESPONSE: Indeed, some inaccuracies occurred in this small section, which we have 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.

In comment number 2, we have already given more detailed information about determination of streamflow.

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?

RESPONSE: Regarding comment number 7, we organized the water isotopes part in the results section and we focused the results to show the concordance of this analysis with the EMMA. We considered the interpretation of water isotope signatures in the area, interesting information, using isotopes in hydrology and water resources, 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, δO18 values ranged from 10.2‰ to -3.65‰ and 36.6‰ to -21.4‰ and δ2H values scoped from 36.6‰ to -24.8‰ and 10.2‰ to -3.4‰ respectively. Isotopic composition (δ18O and δ2H) was lowest during March (i.e., late winter-early spring) probably due to the input of rainfalls with low δ18O and δ2H. 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 δ18O versus δ2H, most of the stream water sample points were located below the local meteoric water line (LMWL) (δ2H = 7.6d δ18O + 10), although some of them were more approaching the LMWL. Isotopic measurements of δ18O and δ2H in shallow groundwater remain near the mean of -2.4 ‰ and -13 ‰ respectively (VSMOW scale). Isotopic composition of δ18O and δ2H 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.

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.

RESPONSE: The standard deviations of the hydrochemical data in the previous submitted manuscript had already reported these values in Table 1. We have included this information in Figure 5a, 5b and 5c. This confirms your remark on the variations of the hydrochemistry.

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.

RESPONSE:We re-structured this section (3.3) of results and section 2.3.3 in the manuscript.

Residual and end-member mixing analysis

We generated 4 scenarios with different solutes and stable isotopes to verify the main sources and flowpaths that contribute to the streamflow generation.

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Scenario A1. We included all data from wet and dry seasons with four solutes as geochemical tracers (Cl-, SO42-, Na+, K+) from shallow groundwater, soil pore water, and precipitation.

The residual analysis using 4 solutes was highly correlated against measured concentrations in streamflow in the 1-D mixing space, with R2 usually higher than 0.3 and $p < 0.07$. The degree of randomness significantly increased in the 2-D mixing space but only for Cl- and SO4.The residuals in 2-D mixing space were however still highly correlated with streamflow solute concentrations for most tracers, with R2 near or > 0.1.

In conclusion, the use of 4 geochemical solute tracers data from both dry and wet seasons suggested one single dominating end-member, and did not permit to differentiate amongst potential sources. Further EMMA and hydrograph separation analysis was therefore not relevant with this dataset.

Scenario A2. We included all sampling data using 4 solutes as geochemical tracers (Cl, SO4, Na, K) of pore water, shallow groundwater and precipitation collected during the wet and dry seasons and we added stable isotope data (δ2H and δ18O) of shallow groundwater and precipitation.

In this scenario, the residuals of all solutes and isotopes were also well structured against measured concentrations in the 1-D mixing space, with R2 usually higher than 0.3 and $p < 0.07$. The degree of variability significantly increased in 2-D mixing space for all solutes. However, the residuals in 2-D mixing space were still highly correlated with streamflow solute concentrations for most solutes, with R2 near 0.6 with a $p > 0.1$. In conclusion, in scenario A2, as well in scenario A1, using dry and wet season data did not permit elucidation of potential source origins in streamflow and further analysis (Fig. 6b).

We therefore split the data sets and removed the dry season samples from the analysis.

Scenario (B1 and B2). Scenario B1. We used only the wet season samples gathered during October 2008 and March 2009 and we used 4 solutes as geochemical tracers (Cl-, SO42-, Na+, K+) of pore water, shallow groundwater and precipitation.

In Fig. 6a are shown the distribution of residuals between original concentrations and predicted values for the 1 and 2 dimensional mixing spaces referred to the main two principal components. This figure shows that the distributions of residuals of Cl-, SO4 and Na+ show a near random pattern in 1-D mixing space, with R2 values less than 0.3 and p>0.3. The variability increased in 2-D mixing space (m) for the four tracers with R2 less than 0.1 and p>0.4. In contrast, potassium showed a high R2 value of 0.7 and high p>0.6, which was too high to take it into account in the next analysis of determination of end-members. Therefore, according to this variability the stream flow chemistry was primarily controlled and defined by conservative 2D mixing space that means three end-members and three geochemical tracers for of Cl-, SO4 and Na+ that can give us signals of flowpaths proportional contribution. The geochemical tracers (Cl, SO4 and Na) detected with the residual analysis were used to continue with the EMMA analysis.

Therefore, a new PCA was elaborated only with Cl-, SO42- and Na+ which are conservative upon mixing, and these were employed in EMMA. PCA scores as U-space projections were made using the extracted eigenvectors from these conservative tracers using a correlation matrix indicated in the section 2.3.3 to identify the end-members.

A hydrograph separation permitted to derive the proportional contributions from the end-members: groundwater: 52%, soil pore water: 38% and precipitation: 10%

Scenario B2. We used the wet season samples of October 2008 and March 2009 and we used 4 solutes as geochemical tracers (Cl-, SO4, Na+, K+) of shallow groundwater, pore water and precipitation and available stable isotopes (δ2H and δ18O) of shallow groundwater and precipitation.

In Fig. 6d are shown the distributions of residuals between original concentrations and

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predicted values for the 1 and 2 dimensional mixing spaces referred to the main two principal components. This figure shows that the distributions of residuals of Cl-, SO4, δ2H and δ18O show a near random pattern in 1-D mixing space, with R2 values less than 0.2 and p>0.3. The variability increased in 2-D mixing space (m) for the four tracers with R2 less than 0.1 and p>0.4. In contrast, Na and K presented a high value of R2 0.7 and high p>0.6, which was high to take it into account in the next analysis. Therefore, according to this variability the stream flow chemistry was primarily controlled and defined by conservative 2D mixing space that means three end-members and three geochemical tracers for of Cl-, SO4 and Na+ that can give us signals of flowpaths proportional contribution. The geochemical tracers (Cl-, SO4, δ2H and δ18O) detected with the residual analysis were used to run a new PCA for the studied period, EMMA and streamflow separation. This data scenario analysis led to the proportional contributions from the end-members: groundwater: 56%, soil pore water: 32% and precipitation: 12%, this was similar to Scenario B1.

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).

RESPONSE: We added the information corresponding how we quantified the end-member in the comment number 4. Adding to this, we also structured further the quantification of the end-members results and discussion respectively.

Identification and validation of end-members Figure 8 indicated that the difference of the primary U-space projection (U1) and (U2) were occupied for a preliminary appraisal of end-members and look at if the projection of the end-members were different from stream flow. This analysis was done because streamflow at Roxo catchment was a mixture of end-members, according to the previous residual analysis. U1 and U2 values from shallow groundwater (wells) samples were higher than those of streamflow.

End-members were identified for each different scenarios using the orthogonal distance between their original compositions and U-space projections from the PCA. In

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Scenario B1 and B2 the distance of soil pore water, shallow groundwater and precipitation were shorter for geochemical tracers (Cl-, SO42- and Na and δ2H, δ18O, Cl- and SO42-) respectively, than other samples. As an example one orthogonal distance of shallow groundwater was only 1% for Cl-, 0% for SO42- and 1% for Na+.

In order to determine how well the calculated proportions of the end-member predicted the measured stream water chemistry, end members and chemical values obtained from hydrograph separation were used. The resulting predicted chemical and isotopic values from both scenarios were successfully re-created with a regression slope close to 1 in all the cases.

A small remark: maybe the outcome is rather logical since no data were obtained during January and February 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?

We already added a more detailed Fig. 2 with the trend of streamflow and precipitation, where effectively we can see important flows and precipitation. The percentage contribution reflected the studied period.

11. Sources of nitrogen – results: the authors observe a strong positive relationship between nitrate 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.

RESPONSE: Once we obtained the estimated water flowpaths through exploratory analysis and EMMA, then we correlated the end-members contributions with the stream nitrate concentrations. For it, we used the Spearman's coefficient to assess relations between stream nitrate concentration and the percentage of streamflow for

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the main end-members. Shallow groundwater from wells and soil pore water percentages showed a strong correlation with stream nitrate (rwell = 0.86 and rsoil pore water = 0.59 respectively). Additional information of historical nitrate in shallow groundwater (Fig.7) was included in the Spearman analysis and we found a strong correlation between shallow groundwater and stream nitrate concentrations (Table 2), suggesting that the correlated end-members were the most likely sources of nitrate in the catchment. Also Cl- hydrochemistry can help us to understand this result, mainly because major levels of chloride would indicate the provenance and residence times of water (Soulsby et al., 2007). In our data, chloride indicated synchronicity between concentrations of streamflow and shallow groundwater (Fig 5a and Fig 5b). This implies that chloride concentrations in the stream depend upon the relatively contribution from shallow groundwater and soil pore water, where Cl concentrations are more stable than the stream waters.

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?

RESPONSE: We suggest calling this section: Water isotope abundance in Roxo catchment.

We indeed removed lines 12-16 on p.2304, as they are not essential for this manuscript and purely deal with more theoretical isotope hydrochemistry, not directly adding value here.

We observed (quantified) LEL slopes between 4.6 -5.9 from the isotope analysis, which are consistent with values reported by others (Kebede et al, 2009). The LEL slope of 4 is a literature reference of a more extreme arid environment. We removed therefore the last line 28-. As it not exactly reflects and compares to our more humid semiarid environment (P=500-550 mm), and confuses the critical reader.

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.

RESPONSE: On point 13, we re-structured the hydrochemistry part:

Hydrochemistry

Table 1 shows the hydrochemistry averages and ranges of Chloride, sulfate, sodium and potassium and water isotopes for the over studied period. Stable isotopes varied simultaneously between them and showed similar variations. Thus, more enriched values for 2H and 18O isotopes were showed during September 2009 and heavier isotopic values were associated with the lower anion concentrations (Table 1). Apparently, water in streams is aerated to enhance evaporation which causes anion concentrations to increase.

Chloride and sulfate concentrations were higher in the streamflow than in shallow groundwater (Table 1), and are considered to be conservative tracers to examine the changing importance of different water sources to the streamflow over the study period. The chloride concentrations in the groundwater beneath the field are expected to be influenced by the use of fertilizer in this agricultural catchment. Potassium chloride (KCl) is a common component of agricultural fertilizers. It is highly soluble in water and readily dissociates into K+ and Cl ions. Chloride anions are repelled by the negative charge of soils; therefore groundwater recharge in agricultural areas often contributes to elevated groundwater chloride concentrations. Historical Cl values in the aquifer dos gabbros de beja located in the north of the catchment ranged concentrations from 13 to 153 mg L-1 (Paralta, 2001). Higher chloride concentrations in the stream were significantly different than those in the shallow groundwater. This can be also explained for water isotopes composition that indicated a major evaporation in the intermittent streams than in the shallow groundwater. These differences in water chemistry between the stream and wells permit the use of chloride as a tracer to determine dominant hydrologic sources at different points in the stream network.

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 build-up during 1 dry-season? Maybe there are different contributors: sediment, surface runoff? In addition, lines 4-9 of page 2307 are not clear.

RESPONSE: Information regarding EMMA methodology was already added in comment 4.

About lines 16-22 on p 2306: Definitely, concentrations in autumn-winter were lower than summer and according to EMMA results: shallow groundwater, soil pore water and precipitation contributed in different proportions to the concentration level to this period.

Regarding line 4-9 of page 2307, has been removed because has not significant contribution to the section.

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

RESPONSE:

We already provided extra information how streamflow was obtained on the methodology section. About lines 6 P 2308 precipitation was important for the wet studied period (Fig.2). However, we tested that the most important proportional contribution for the wet period was the shallow groundwater (52%) and soil pore water (38%) for scenario B1 and 56% and 32% for scenario B2.

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

RESPONSE: We added historical nitrate data in wells and applied the Spearman's analysis to clarify the link between nitrate concentration in wells and surface waters. We provided Spearman correlation's values (r) values in the Table 2 to clarify this topic. Also we compared chloride concentrations with wells and stream water to show the link between the sources.

Regarding to line 3 p 2309, even if we slightly adapted our hypothesis now we are showing data to confirm more our nitrate results.

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. C1289

RESPONSE: We reconsidered how to rephrase our conclusions due to the fact that we used data of the wet season period. We are adding statistical data and hydrochemical

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analysis to justify our results and discussion.

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

RESPONSE: We replaced this table 2 with the Spearman correlation analysis including historical nitrate in shallow groundwater, and nitrate of stream and soil pore water from our study.

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

RESPONSE: Stream network on the map has been improved.

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

RESPONSE: name has been change to streamflow.

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

RESPONSE: a new figure 4 was elaborated that included the three studied periods with their respective isotopic shift.

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

RESPONSE: Identification tags were added to each graph and data levels and points were also added to figure 1.

- figure 6: why are the residuals of chloride and sulphate so large (> 100)

RESPONSE: Because axes were placed backwards, equivalent to: axis x (measured concentration) and axis y (residual between predicted and measured values). However, we made new changes on these figures, because a new EMMA model was developed using four solutes and two stable isotopes.

- 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 explana-

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tory variable.

RESPONSE: This mistake was solved running the new EMMA model with both scenarios B1 and B2.

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 substantial evaporation 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.

RESPONSE: About the readability, if and when we reach the stage of the final revised manuscript, we will send this to an English (native language) editor to improve the language and editorial issues.

Please also note the supplement to this comment:

http://www.hydrol-earth-syst-sci-discuss.net/8/C3769/2011/hessd-8-C3769-2011-supplement.zip

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

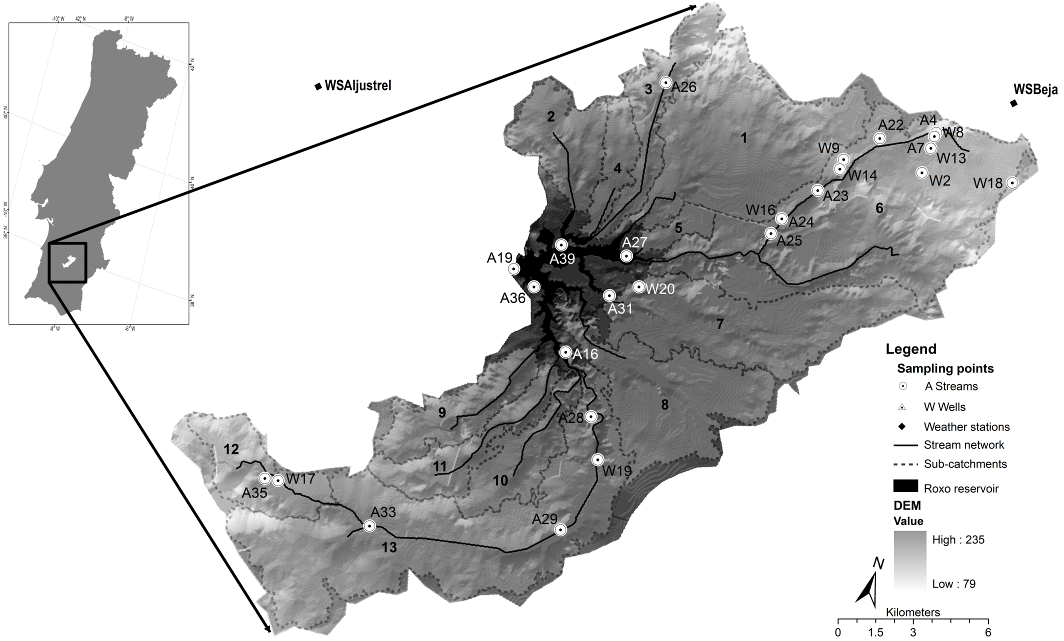

Fig. 1. Fig. 1. Map of the study area of Roxo catchment. Stream water (A) and shallow groundwater well samples (W) are included.

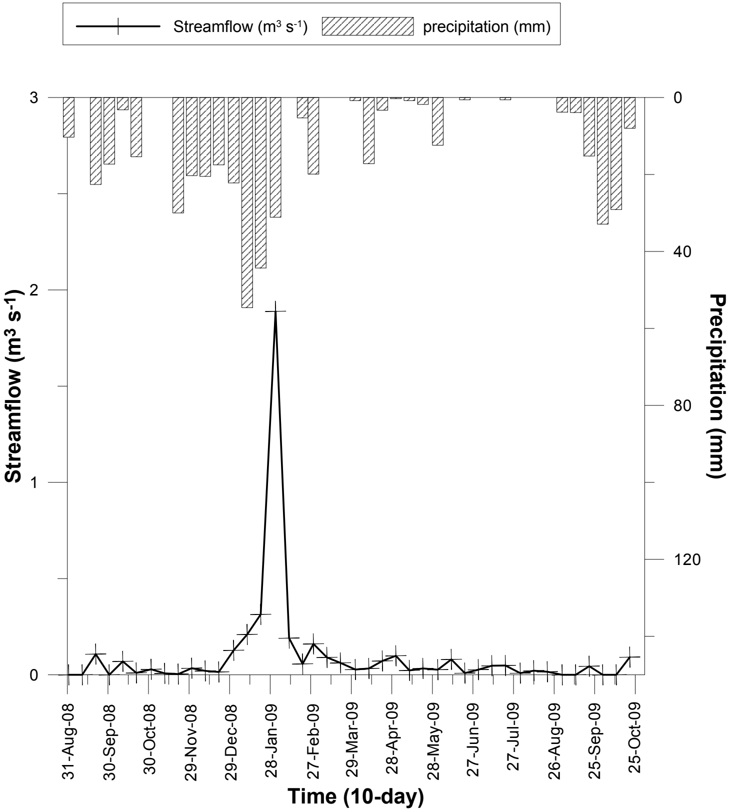

Fig. 2. Fig. 2. Rainfall and streamflow of Roxo catchment for the study period (2008-2009).

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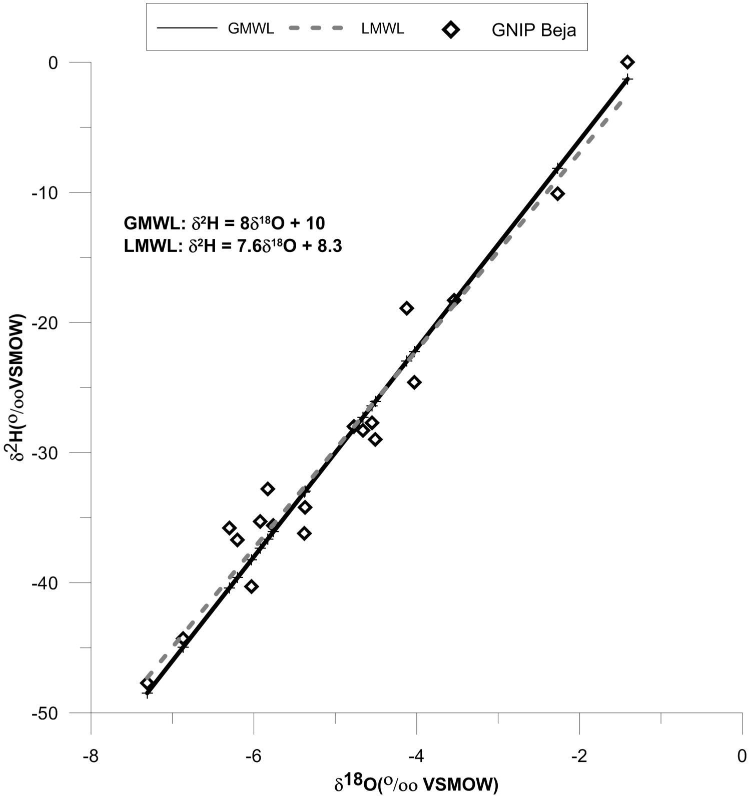

Fig. 3. Fig. 3. Distribution of stream water isotope chemistry along the global (GMWL) and local meteoric water lines (LMWL). The local meteoric line during the wet and dry periods.

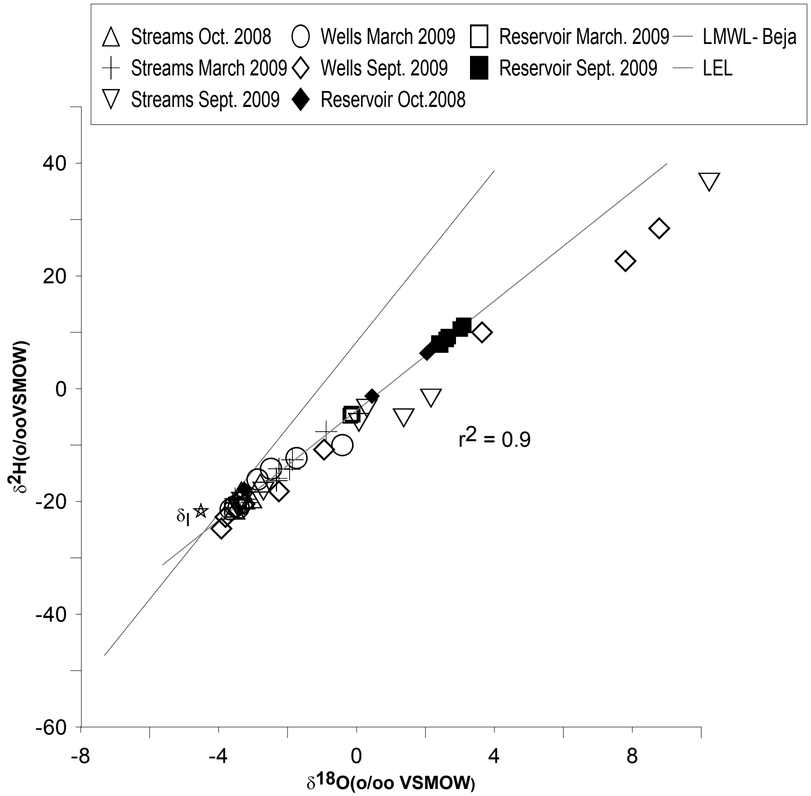

Fig. 4. Fig. 4. Local meteroric water line and Local evaporation line of streamflow water and Roxo reservoir at wet period (October 2008 and March 2009) and dry period (September 2009).

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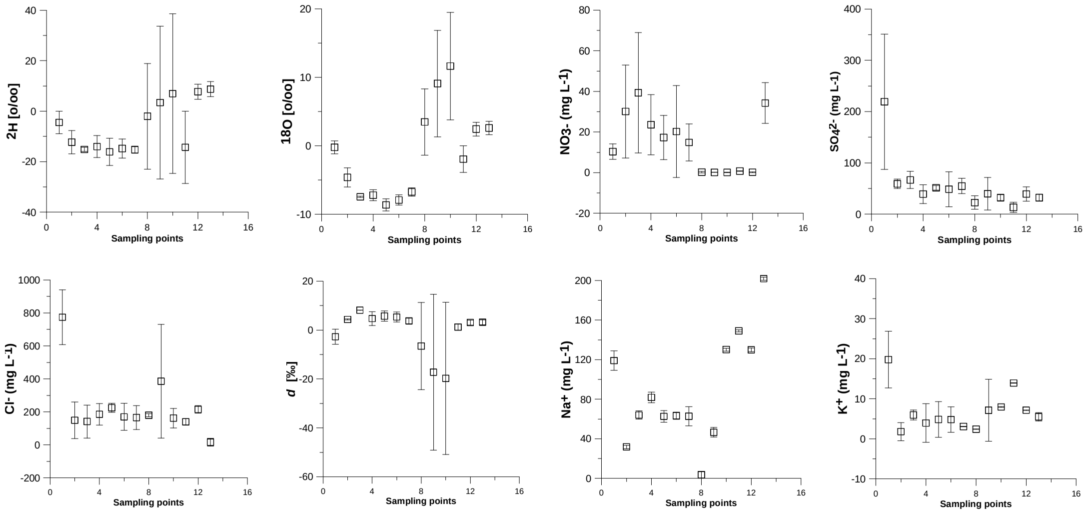

Fig. 5. Fig. 5a: Mean (square) and standard deviation of the chemical composition in stream flow sites (A4, A7, A22, A23, A24, A25, A26, A28, A29, A33, A35, A36, A39) for the studied period.

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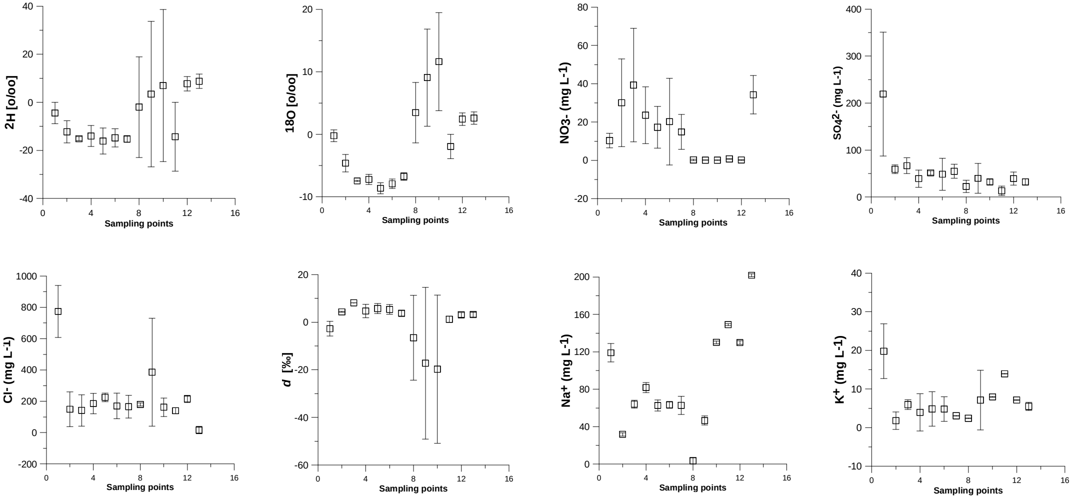

Fig. 6. Fig. 5b. Mean (circle) and standard deviation of the chemical composition in shallow groundwater from wells sites (W2, W8, W13, W14, W16, W17, W18, W19, W20) for the studied period.

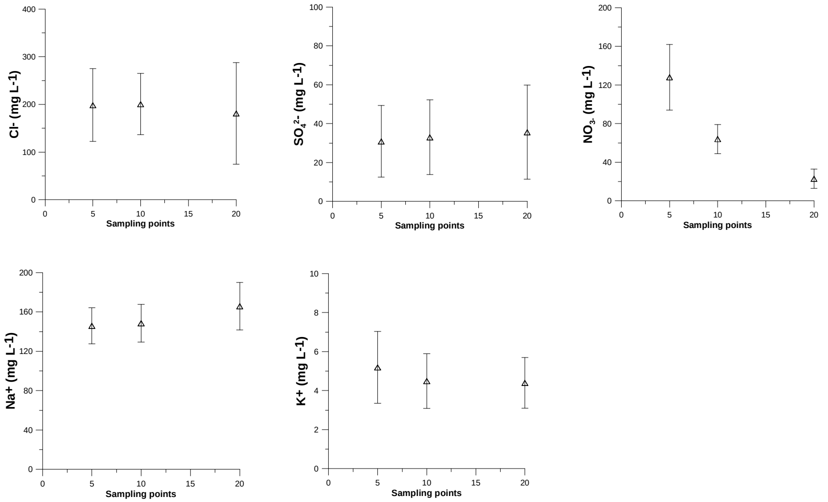

Fig. 7. Fig. 5c. Mean (triangle) and standard deviation of the chemical composition in soil pore water at 5, 10 and 20 cm for the three studied periods: October, 2008, March 2009 and September 2009.

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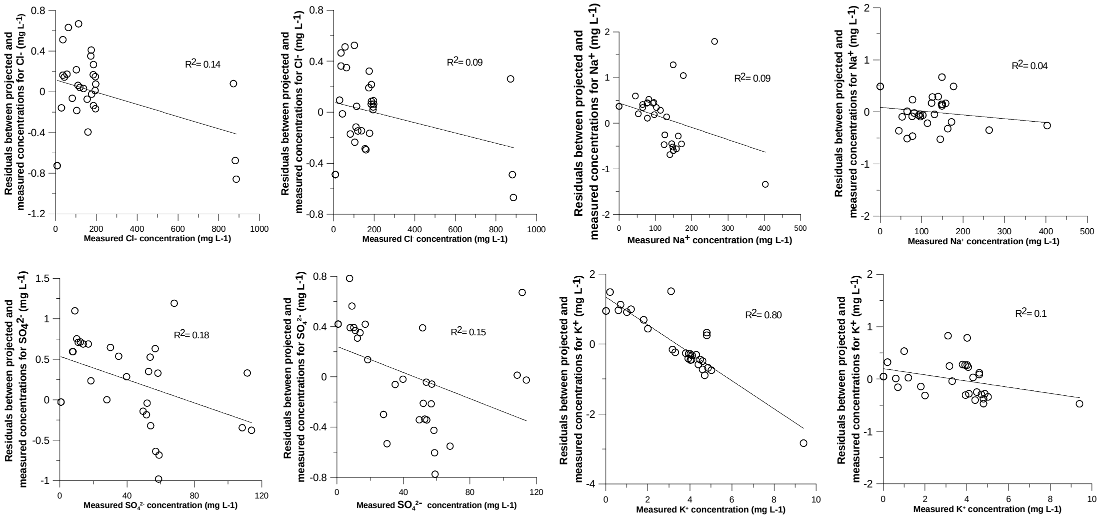

1-D **2-D** **1-D** **2-D**

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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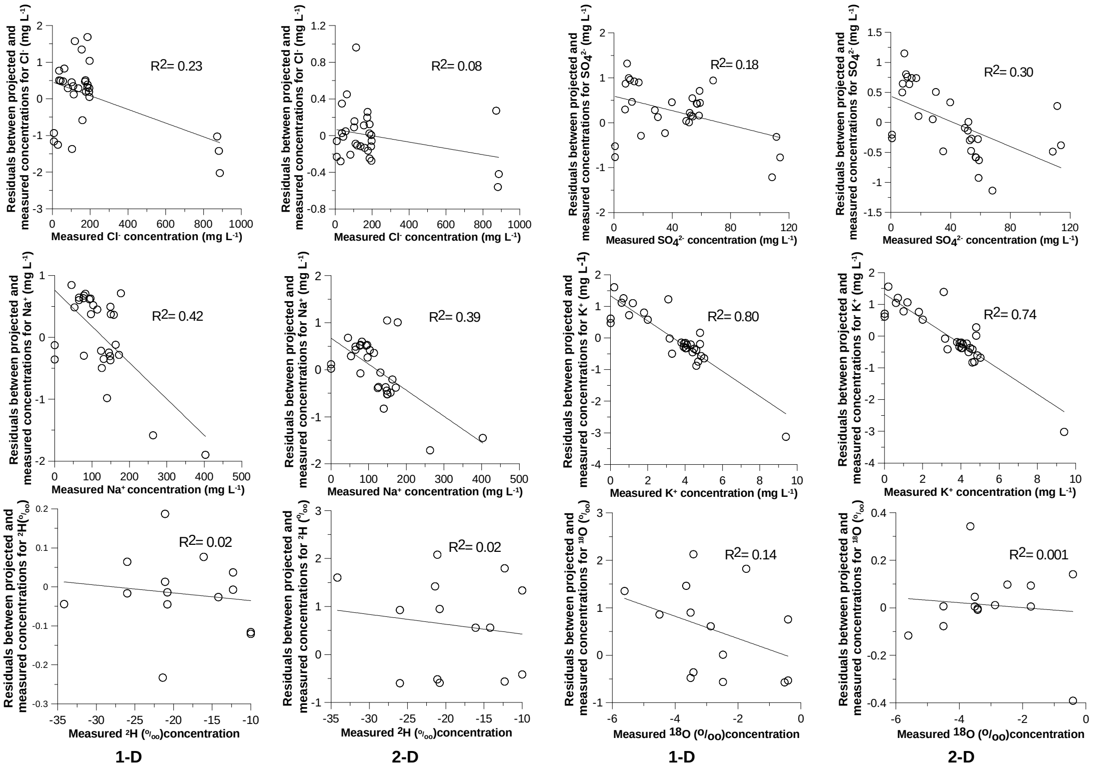

Fig. 9. Fig. 6b. Scenario B2. Plot of Residuals versus original concentrations of solutes and isotopes for wet period from the 1-D mixing space and 2-D mixing spaces.

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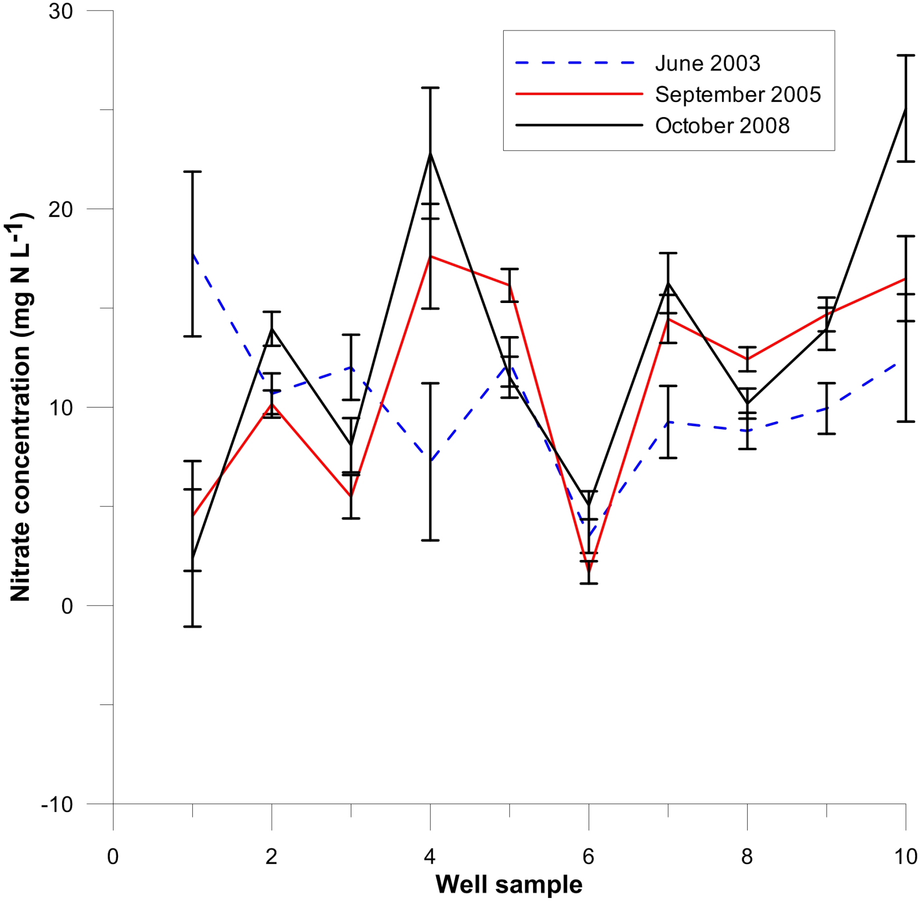

Fig. 10. Fig. 7. Nitrate concentrations in shallow groundwater of Roxo catchment.

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