

Hydrol. Earth Syst. Sci. Discuss., author comment AC1
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Reply on RC1

Maxime Gillet et al.

Author comment on "Identification of the contributing area to river discharge during low-flow periods" by Maxime Gillet et al., Hydrol. Earth Syst. Sci. Discuss.,
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The authors applied an end-members analysis to identify and quantify stream contributions during low flow period in a headwater (<100 km²) Mediterranean catchment relatively poorly affected by human activity. The originality of the work are : (1) to focus the stream flow deconvolution to the low flow period which has been rarely done but seems relevant to understand the processes that sustain low flow in a context of global changes and of a Mediterranean climate where drought are known to increase already. (2) to compare and combine different methods for identifying the end-members: hypotheses-driven identification consists in associating an end-ember to each geological unit present in the catchments. The data-driven approach supports the first identification by applying a clustering and a principal component analyses to a set of groundwater samples collected throughout the catchments and for which concentrations in major elements have been analysed.

Four methods are conducted to infer the concentrations of each members: one use the temporally closest analyses of groundwater samples, another use the seasonal mean of these groundwater concentrations, a third uses the geographical mean of groundwater concentration by geological unit and the fourth experimentally produces a leachate of each geological unit and analyses its concentrations in major elements. The Four methods are compared in terms of end-members contributions and in terms of uncertainties.

In overall, I found the study well-designed and scientifically relevant for a publication in HESS. The result highlights the dominance for sustaining low-flow of a groundwater reservoir that has a small spatial extend and a relatively moderate/low contribution to the total flow. The approach combining different methods for end members identification and quantification (including the associated uncertainty) is applicable to other sites and seems relevant to link water contributions to potential geological reservoirs.

In details, I have some questions and several suggestions to improve the clarity of the description (please see below) that should lead to relatively minor edits of the manuscript. My major critic would be that the article should include a short overview of the limits of the EMMA approach widely discussed in the literature (such as the assumed stability of the end members chemical composition and the need for objective methods to fix the number of end-members). This would not

decrease the impact of the study as some of these limitations are either addressed here or less limiting because of the focus on low flows... I am not a native English speaker and this has to be checked with one but I think that the manuscript requires a little work for polishing the English.

The article was sent to a native English-speaking translator for correction and improvement of the English. A paragraph has been added in response to your comment in the introduction:

« In order to take into account the limitations raised in the use of EMMA, includes the assumption of the conservative behaviour of the end-member tracers in the model, and fulfil the need to implement an unbiased method to define the end-members in terms of their number and the accuracy of their signatures, the approach presented will combine different tools (Barthold 2011, James 2006, Hooper 2001, Hooper 2003).

To take into account this limitation, it will be based on an approach will include statistical classification, a leaching approach and an independent study of the end-member signature.. »

▪ **15, p1 Aubé, 2017, can you provide more references?**

7 references have been added (Bard et al., 2012; Giuntoli et al., 2015; Marx et al., 2018; Ruiz-Villanueva et al., 2014; Sauquet et al., 2015; Van Vliet et al., 2013; Vidal et al., 2016).

▪ **18, p1 add a space after "scarcity"**

Space added.

▪ **26, p2 why "However"?**

However has been removed.

▪ **31-32, p2 "due to the fact that many low flow studies work on small basins with a strong geological homogeneity": I think that the sentence is ambiguous. Studies investigating the origin of water have been rarely applied to low flow because hydrologists usually want to understand the processes of flow generation and therefore focus rather on the high flow periods or events. Water origin can be a relevant question even in catchments with homogeneous geology.**

This sentences has been removed.

▪ **79-81, p. 3, information has already be given.**

The paragraph has been removed.

▪ **88, p. 3: correct "Montpellier" and "Figure 1)**

The modification was made on the figure.

- **89, p3: I did not understand “This typical watershed of the Cévennes area”. What is typical from what?**

I remove typical which was unnecessary.

- **91, p.4: Remove “The” before “Mediterranean”**

“The” has been removed.

- **97, p. 4: Considering that altitude ranges between 250 to 1100 m is only one rain station enough? How does rainfall vary spatially?**

Precipitation varies with altitude but this remains limited. The comparison of the average annual rainfall between Barres des Cévennes (at the top of the basin) and Saint Jean du Gard (located at 160 m on a neighbouring basin) shows slight differences of less than 100 mm. Furthermore, the purpose of the sentence was only to present the climate of the catchment area in a very broad way. I have preferred to present this in a global way rather than extrapolating these dynamics only observable in the neighbouring catchment areas. Nevertheless precipitation data are presented as background information and are not further use in this paper.

- **98, p. 4: “mica schists 1”?**

« of mica schists (*Figure 1*). »

- **111-112, p.4: which type of sensor is used to monitor the stream discharge? did you use a rating curve? What is the monitoring time step?**

The following sentence has been added to the text

Pressure probes are used for limnometry measurements. Measurements are taken at a time step of 5 minutes and a rating curve is then used to calculate the flow rate from the probe measurements.

- **117, p.4 “rainfall events have a very low impact...” the authors should precise “during this low-flow period” I guess?**

During low flow period has been added.

- **130, p. 6 +L. 134, p.6: please use the standard symbol “pH” instead of “PH”**

The modification was made in the text.

- **133, p.6: why did you use a threshold of 0.25 µm for filtering? I think that usual thresholds are 0.45 and 0.20 µm used for particles and colloids respectively? Can you provide a protocol reference?**

This is a mistake, 0.45 filters were used. The change has been made in the text.

- **134, p.6: “stored until analysis” can you describe briefly in which conditions?**

The samples were stored in a cooler with ice packs.

“Tubes for the cation analysis were acidified to pH 2 with a drop of nitric acid titrated to

0.5 N and stored *in cold place* until analysis done within 24 hours"

- **135, p. 6 can you provide a reference for the analysis protocol (for major ions concentrations)?**

These sentences have been included:

« *The mobile phase was prepared in 1 L of deionized water (18.2 MOhms-cm at 25 °C) with 50 ml of Na₂CO₃ /NaHCO₃ at 64mM/20mM for the anions and 25 ml of 2.6-Pyridinedicarboxylic acid at 0.02 M and 2 ml of HNO₃ 3N for the cations. The chromatographs obtained were calibrated according to a series of standards ranging from 0.01 to 100 mg/L for the target ions. Two control samples, one with low concentrations close to water found in metamorphic waters (EC of 50 µS/cm) and the other with high concentrations close to water from sedimentary reservoirs (EC of 600 µS/cm), water, were analysed at the beginning of each series of analysis as well in order to ensure the absence of instrumental contamination or drift. A verification step was carried out on the integration of the chromatographs obtained.* »

- **137, p.6: what are the "two representative sites"? and what are "each reservoir"?**

Modifications has been added to make the sentence more understandable. "For monitoring the low-flow period *and to respond to organisational issues*, the observation site was downsized to two representative sites for each *geological* reservoir *identified as potential end-members*"

- **Table 1 p. 7: Could you report the ID of the sampling points in Map of Fig 1? (at least the stations that are monitored weekly) ?**

The modification was done in the Figure

- **140, p.7: "sites" plural**

The modification was done in the text

- **148, p.7 : " on several sections (4) " : are there four sections in the spatial analysis ?could you locate them in Fig. 1?**

The modification was done in the Figure

- **152, p. 8: "also collected for analysis (Figure 1). An additional campaign was..." instead of "for analysing (Figure 1). In addition to monitoring...."**

The modification was done in the text

- **155, p. 8: "discharge measurements WERE carried out by SALT DILUTION METHOD on the tributaries and BY exploring the velocity..."**

The modification was done in the text

- **160, p. 8 "analyses"**

The modification was done in the text

- **165, p.8: "End-memberrrs" capital mark**

The modification was done in the text

- **167, p. 8: "principal component analysis WAS applied"**

The modification was done in the text

- **173, p. 8: Please revise English "To confirm the defined hydrogeochemical end-members"... "It aimed (past) to strengthen the previous definition of the end-members by an inverse approach"?**

The modification was done in the text

- **176-177, p. 8 : present tense is used instead of past**

The modification was done in the text

- **179, p. 8: could you provide some details about the rock samples collection method?**

Modification have been done. "For this purpose, three rock samples were collected in each of the identified geological units *in different location. The rock samples were extracted from the bedrock and all had to be larger than 10 cm sized blocks. Each sample was then stored individually until analysis.*"

- **Figure 3: In title replace "experimentation " by "experiment", in legend "Granite" with "e" , add also please the number of samples for each substrates : Limestone (3), Granite (1) And add the number of replicates**

The modification was done in the Figure

- **196, p. 10, remove the point after "alkalinity"**

The modification was done in the text

- **200, p.10: "one of the objectives WAS"**

The modification was done in the text

- **202, p. 10: "the number of required tracers WAS... "**

The modification was done in the text

- **206, p. 10 "End-member..." capital mark**

The modification was done in the text

- **208, p. 10 "our approach USED..."**

The modification was done in the text

- **218, p. 10: I did not understand here? How much parameters did you use?**

The parameters have been left as defined by delsmann in his guide to using the model. Only the number of iterations has been changed.

- **222, p. 10: "The objective WAS..."**

The modification was done in the text

- **241, p. 11: I missed in this section the quick description of the software and packages used here (for PCA, clustering, EMMA and GLUE analyses)**

Two sentences has been added:

- *"The k-means analysis was done on R with stats packages"*.
- « *This PCA was done on R using FactoMineR package* ».

A description of the mixing model is already given.

"The End-Member Mixing Analysis (EMMA) was chosen to assess the contribution of the different geochemical end-members identified. Our approach used EMMA coupled with the Generalised Likelihood Uncertainty Estimate (GLUE), called G-EMMA and developed by (Delsman., et al, 2013}. This GLUE method, developed by {Beven., et al, 1992}, manages uncertainties by accepting variation in sets of input parameters. A full range of plausible results can be explored with model executions within a user-defined range by varying the input parameters. The G-EMMA method considers both the uncertainties in the conceptualisation of the model (validity of the choice of the end-members) and the measurement uncertainties related to the analytical errors. The variability accorded to the tracers chosen for the surface water is defined by the uncertainty associated with the devices used in the measurement (5 \%).

- **243 to 251, p. 11: is this paragraph new? useful? necessary?**

This paragraph was removed.

- **254, p. 11 + L. 270, p. 12: "Piper diagram" with a capital mark**

The modification was done in the text.

- **254, p. 11: "are identified" visually?**

Visually has been added.

- **256, p. 11 : "with the composition of 3 groundwater"?? the three? Which?**

It was a mistake 3 has been removed

- **276-277, p. 11 : Is there a missing end-member then?**

The granitic section has very little extension, so its contribution can only be a minor part of the whole run-off generation and it's consistent to not find its signature in the groundwater. Moreover the rare springs in the granitic section have a signature corresponding to the mixture of groundwater from the limestones and the black micaschists. Hence for all this reasons the choice was made to disregard this end member.

The followed sentence has been added to clarify this point:

"For these different reasons and the very small extension of the granitic part on the

watershed, this reservoir was not considered as an end-member."

- **279-280, p.11: Figure 5 does not show seasonal variation, does it?**

This seasonal variation can be observed in figure 5, which shows a progressive increase in the concentration of ions (Ca, Mg, Na, SO₄). The points with the lowest concentrations correspond to the beginning of summer and those with the highest concentrations to the low water period.

Arrows has been added to the figure 5 with a sentence in the caption: « *The arrows mark the seasonal variation of the different geological reservoirs.* »

- **285, p. 11 : "close to the observed signatures from groundwater samples"**

The modification was done in the text

- **Figure 6: please find a transparency or something to make the GW sample less visible compared to the leachate.**

The modification was done in the Figure. Symbols of groundwater were downsized and had made more transparent.

- **303, p. 14: not shown?**

The choice of not showing the concentrations of K and Ni ions was made to facilitate the reading of the graph and limit the number of panels.

- **Figure 7: caption : "Silhouette Values to define the optimal numbers of clusters"**

The modification was done in the text.

- **313, p. 15 : "inertia curves..on the thre classes" ?? I do not understand**

The sentences was modified: "*Inertia curves define an optimal value of 3 classes, and gives equivalent results to previous analyses on groundwater samples to characterise the end-members*".

- **Table 2 caption "clusters"**

The modification was done in the text

- **336, p. 16 "due to their low frequency of detecting..." replace by " because often below the detection limits" ?**

The modification was done in the text

- **337-339, p. 16 formulation looks strange, isn't it?**

The sentences was modified: "*Due to the low concentration of total dissolved solids in all of measured dissolved ionic elements in the groundwater from quartz mica schist reservoir, no tracers were specifically identified for this reservoir. This reservoir acts as a dilution end member for all tracers*"

- **340, p. 16 "to add tracer to the tracers chosen by the end-members" : what do you want to say here?**

The sentences was modified: " To improve the efficiency of the model and to conform *and follow the methodology developed in Barthold et al (2011)*, the choice was made *to add one additional tracer*"

- **Figure 9: more contrasted colors would be easier to read**

The Figure have been modified. The colours have remained unchanged but the size of the item has been increased

- **Table 3: "pH" instead of "PH", what is illustrated using bold characters in the column/line titles? In the table itself?**

The modification was done in the Table and bold character has been removed.

- **349, p. 18: the collection of rainfall water should be presented in the material and method section, at this stage we do not know that some rainwater has been sampled**

A paragraph has been added in the end of section sampling and analysis :

"Rainwater samples were collected using the same methodology as for groundwater. The water was collected from a rain gauge located in a neighbouring catchment area less than 10 km south of the catchment."

- **354, p. 18 precise in the subsection title "of time-window method "**

Modification was done in the title.

- **361, p. 18 what does mean "minus 10%", is it inferior to 10%?**

Minus was replaced by "under"

- **365, p. 18 "coherent with the increasing tourism activity" , I don't think so : usually WWTP rejects are constant throughout the year (unless the tourism increases drastically the population in summer?), but this constant reject is less diluted in summer low-flow period because natural stream flow is lower...**

I agree with you on the predominance of the decrease of the water flow in the increase of the contributions of the wwtp however the catchment area is very little populated and the Cevennes are a rather tourist area with a strong increase of the population in summer. I do not have the numbers but I think that the population increases by at least half during the summer. I have changed the sentence

"A more important contribution of WWTP can be observed from mid-July to the end of August, coherent with the decrease of natural stream and the increase of WWTP effluent due to the increase of population during summer but remaining nevertheless below 4 \%. "

- **Figure 10: please add the associated uncertainties, is 2018 in upper panel and 2019 in the bottom panel? If so it should be written in the caption.**

The uncertainties has been added in caption:

"The uncertainty associated with these proportions is less than 15% for WWTP and limestone waters and less than 35% for quartz and black micaschist waters."

- **Figure 11: "black represents the contribution of WWTP"? It appears "yellow" in my pdf**

"Black" has been replaced by "yellow" in the legend

- **414, p. 21: where can we see the conductivity of these higher/lower contributions?**

The average conductivity of the different reservoirs was given in the presentation of the end members (400 for the limestone waters, 100 for the black micaschists and less than 60 for the quartz micaschist waters). Modification has been done in the sentence :

"Regarding the "seasonal average" output, the results show a lower contribution of the waters with the highest low-flow electrical conductivity (*Limestone*) and a higher contribution of the waters with the lowest *electrical conductivity* (*Quartz mica schist*)."

- **417-421, p. 21 : These sentences should be in the Mat and Method section**

A paragraph present already this campaign in mat and method section. It's just a reminder, should I remove it.

"An additional campaign was carried out in 2019 to analyse the spatial contribution of tributaries to the main watercourse throughout its route. Gauging and sampling were performed on five sites distributed along the main river, and six tributaries were targeted (3 per side) using the same sampling and laboratory analysis method presented above. The discharge measurements were carried out by salt dilution method on the tributaries and by exploring the velocity field using a current meter for the main watercourse. The operation aimed to analyse the contribution of the reservoirs with a spatial approach. However, only one tributary on the northern slope could be analysed as the two others were dry."

- **426, p. 21 : "less than 0.1 l/s/km2"**

The modification was done in the text

- **Figure 12: using same colors for geological map and flow contributions is ambiguous, 7 is not readable, 3 is not numbered**

The number has been changed but I think the choice of colours is logical and understandable even if it may make the diagrams less readable on an identical background

- **450, p. 23 : what concentration does increase?**

Modification was done in the text:

« This increase of *different ion concentration* (Ca^{2+} , Mg^{2+} , SO_4^{2-} , HCO_3^{2-}) during summer observed in groundwater can be explained by a decrease in ... »

- **456-459, p. 23: Nevertheless, as here you try to identify low flow contributions it remains relevant as low flows are rather associated to the**

period where contributions are poorly diluted and residence times highest?

At the end of the low water period this is correct but the article refers to the whole summer low water period. During the beginning of this one the concentrations in ions are much lower thus more diluted and evolves gradually what justifies the assumption of a signature taken on a value close temporally and not the extreme seasonal value.

- **475, p. 23: How do you explain the increase of standard deviation here?**

This increase in uncertainty is for me linked to a lower quality of the end members definition. Taking all the measurements made, including the spring one. The groundwater signal is more diluted and therefore gives a wider range of possible concentration for the poles which gives a wider range of results and therefore a stronger standard deviation.

“(caused by a wider range of results)” has been added after standard deviation

- **497, p. 23: Precise when this specific flow calculations have been conducted (to which period are they associated)**

The modification was done in the text

- **517, p. 25 : Does “The Valat des Oules” correspond to a number provided in Figure 11?**

Yes, the number has been added in the text.

- **523-525, p. 25: then the Quartz and black micaschists reservoirs are supposed to be fissured layers of micaschists only without contribution of a weathered layer?**

This is a possibility. The contribution of the tributaries is different for quartz mica basins, which could support this hypothesis. But it can also be due to differences in the schistosity plan (allowing higher capacity) or other explanatory elements. The data do not allow us to decide on these points.

- **535, p.25 “analysis provided”**

The modification was done in the text

- **541, p. 25: “allowed us”**

The modification was done in the text

- **552, p. 25 : did you mean a higher anthropic impact on the water quantity or on the water quality?**

On the water quality.