We would like to thank the referees for taking the time to carefully review our manuscript and for providing valuable comments and suggestions. We have made the necessary changes to improve the paper and our responses to their comments are provided below.
Referee's comments are shown in bold and the authors' responses in blue.

RC1

Suggestions

1) I would like to see more detailed hydrogeology (karstification types), groundwater movement, and catchment delineation because this information is the base used to validate the TTi results.

As regards karstification types :

- Fontaine de Vaucluse outlet was probably set up as a chimney-well in the Messinian period, concomitantly to the unification of drainage of the whole current impluvium towards a paleo-outlet in the Rhône valley (Gilli and Audra, 2004). The main mechanism is thus epigenetic karstification but there are evidences of hypogenic karstification at the southern edge of the basin. The last sentence of this comment was added to the paper, in the "study site" part.
- No speleogenesis study was performed on Millet, St Trinit and Nesque springs.

As regards catchment delineation :

- Fontaine de Vaucluse impluvium was missing. We added it to figure 1 based on Ollivier (2020) proposal.
- Millet, St Trinit and Nesque springs catchments were delineated on the basis of geology and mass balance; we completed Fig.1 legend accordingly.

As regards groundwater movements, to our knowledge there are no wells reaching the saturated zone on Millet, St Trinit and Nesque catchements. Fontaine de Vaucluse unsaturated zone is several hundred thick and (apart from at its borders) saturated water table is reached at only one point which is the final part of a 750m-deep cave. General drainage direction is in the direction of the outlets which is inferred by the reader, and we cannot provide a detailed map of drainage directions within each subsystem. This is why this information is not present in the paper.
We added the following sentence to the section 2.1 study site:
"The main karstification mechanism is epigenetic but there is evidence of hypogenetic karstification at the southern edge of the Fontaine de Vaucluse system (Audra et al., 2011)."
We also modified the Fig. 1 by adding the delineation of Fontaine de Vaucluse catchment, and we replaced its title by:
"Figure 1: Location of monitored flow points on a 1:50000 geological map (BD-CHARM) from BRGM and spring catchments delineation (based on geology and mass balance for Millet, St Trinit and Nesque springs; from Ollivier, 2020 for Fontaine de Vaucluse)."

Audra, Philippe, Bigot, Jean-Yves, Camus, Hubert, Gauchon Christophe, Michel Wienen. La grotte-mine du Piei (Lagnes, Vaucluse), paléokarst hypogène à remplissage de minerai de fer oxydé. Karstologia, 2011, vol. 58, no 1, p. 1-14. https://www.persee.fr/doc/karst_0751-7688_2011_num_58_1_2701

Éric Gilli, Philippe Audra, Les lithophages pliocènes de la fontaine de Vaucluse (Vaucluse, France). Un argument pour une phase messinienne dans la genèse du plus grand karst noyé de France, Comptes Rendus Geoscience, Volume 336, Issue 16, 2004, Pages 1481-1489, ISSN 1631-0713, https://doi.org/10.1016/j.crte.2004.09.007.

Ollivier, C.: Caractérisation et spatialisation de la recharge des hydrosystèmes karstiques: Application à l'aquifère de Fontaine de Vaucluse, France, Ph.D. thesis, Université d'Avignon, 2020.

[Question 3 and Question 2 are related ; Question 3 is answered beforehand for improved consistency]

3) Double-check the positive correlation between electrical conductivity (CE) and spring discharge, which is very unusual compared to other karst springs.

Correlation between electrical conductivity and discharge is still 0.42 after check, as it appears in Fig. 5(a). Visual assessment of the time series in Fig. 4 is consistent with this positive correlation as important peaks of electrical conductivity are observed during flood events.
The following explanation was added to the section 3.2.1 Hydrodynamic and hydrochemical functioning of Millet spring, and PCO_2 was added to Fig. 4:
"Electrical conductivity correlates well with discharge and highest conductivities are reached during high discharge with a 2 to 4 days delay. This positive correlation between electrical conductivity and discharge is less usual but it has also been observed in other karst springs of the Fontaine de Vaucluse system (Notre-Dame-des-Anges spring in Emblanch et al., 2006), others Mediterranean karst systems such as the Lez spring (Bicalho et al., 2012), or in Europe at Podstenjšek spring, Slovenia (Ravbar et al., 2011). This phenomena may result from dilution of deep flows with recent water like in the Lez spring (Bicalho et al., 2012), or a change in the catchment delineation that captures old water stored outside the usual catchment area (Ravbar et al., 2011).
At Millet spring, electrical conductivity is mainly carried by Ca^{2+} and HCO_3^- contents. Its increase at the beginning of flood events is caused by HCO_3^- increase which betrays the arrival of water characterized by higher pCO_2 (see Fig. 4). pCO_2 has higher content in soil water because of biological respiration and organic matter decomposition. A pCO_2 increase in a spring involves (i) a stronger influence of soil water which may be stored in the unsaturated zone or epikarst, or (ii) a very fast infiltration supply. Case (i) is the most likely because case (ii) involves high organic matter content (TOC) while the increase of TOC corresponds to less than 0.6 $mg.L^{-1}$."

In the section 3.2.2 Relation between TTi components and other variables, the description of the second dimension interpretation was modified as following:
"The second dimension is positively scored with electrical conductivity, discharge and humic-like organic matter (component 1). These variables evolve at low frequency (monthly to seasonal scale) mainly due to the alternance of low/high flow periods. Positive correlation between humic-like organic matter, electrical conductivity and discharge, while unexpected, may stem from the fact that as TOC, humic-like organic matter results from a mix of stored and fresh water. Increase in humic-like organic matter can be caused by the arrival of (i) fresh water with high content of all types of organic matter and thus TOC content; or (ii) of stored water with high relative humic-like organic matter content compared to the other organic compounds. Case (ii) seems the most likely because at Millet, the increase of humic-like is associated with a steady TOC content. This second dimension therefore seems to indicate a seasonal variation of humic-like organic matter content due to seasonal storage dynamics, which may induce a seasonal variation of TTi."

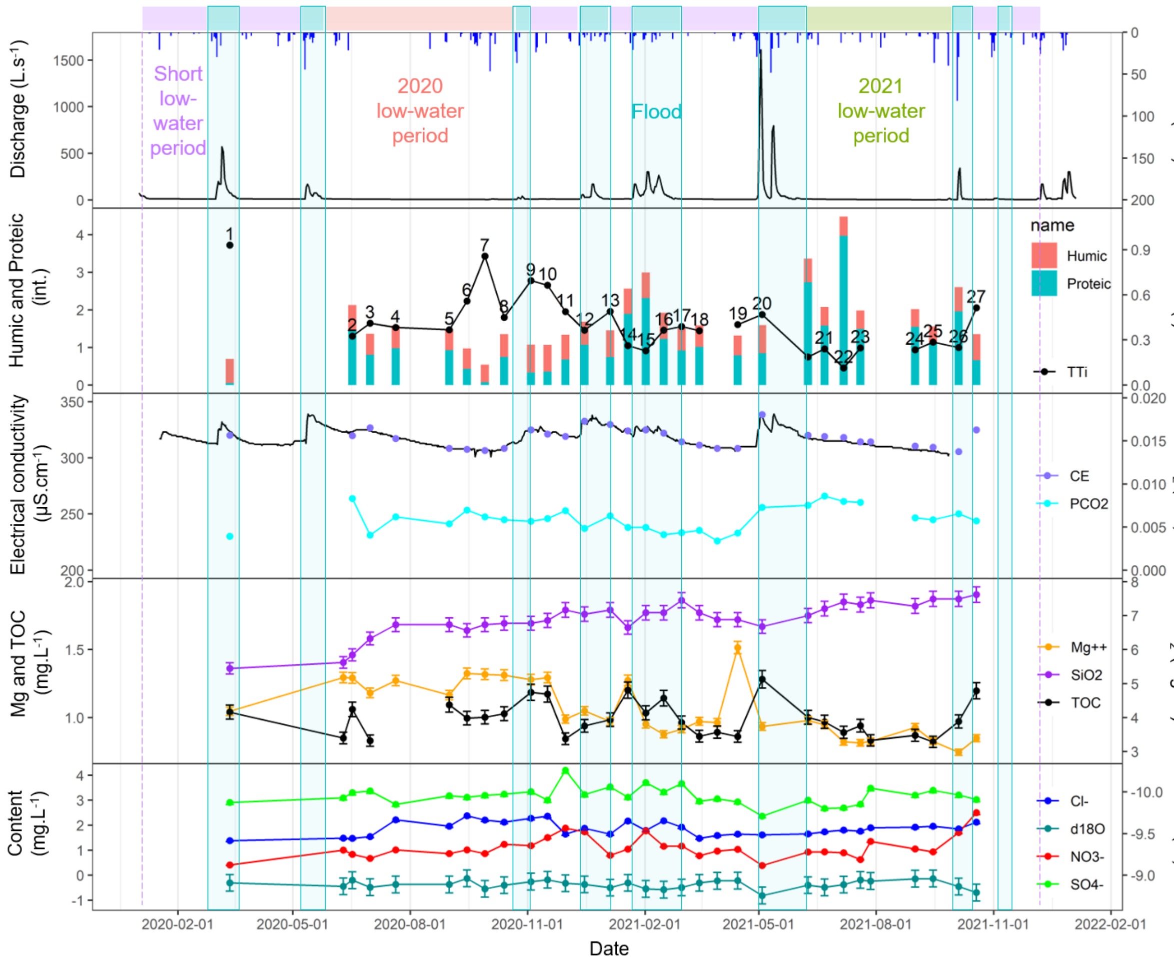


Figure 4: Millet spring time series of rain, discharge, TTi, humic-like (component 1) and protein-like (sum of components 2, 3 and 4) fluorescent organic matter, continuous & punctual electrical conductivity, **δ**18O, pCO2, magnesium, silica, chlorides, nitrates and sulfates contents over the period from june 2020 to october 2021 period. Colors above the discharge plot and numbers on TTi curve correspond to Figure 6 (b).

Bicalho, C. Caetano, Batiot-Guilhe, C., Seidel, J. L., et al. Geochemical evidence of water source characterization and hydrodynamic responses in a karst aquifer. Journal of Hydrology, 2012, vol. 450, p. 206-218.

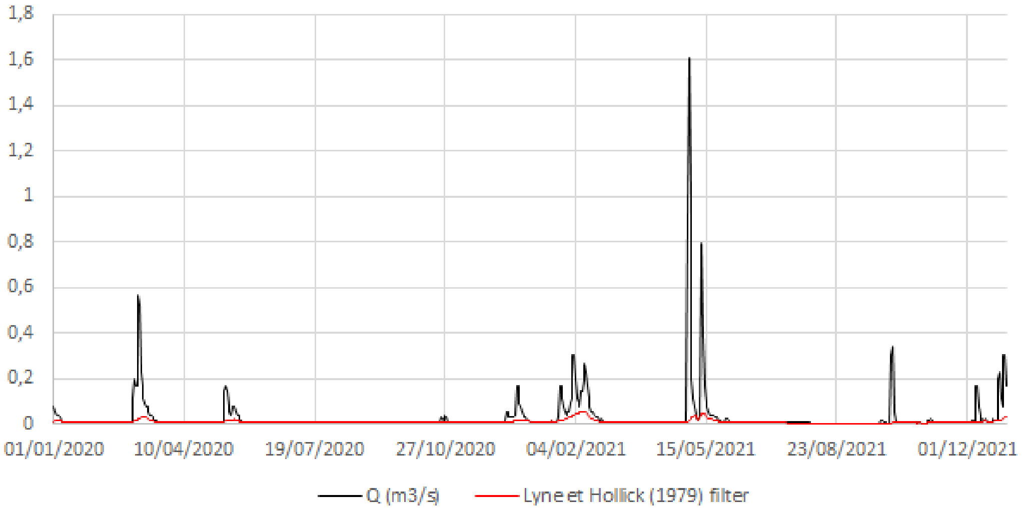
Emblanch, C., Charmoille, A., Jimenez, P., Andreo, B., Mudry, J., Bertrand, C., Batiot-Guilhe, C., Lastennet, R.: Variabilité du type et de la qualité de l'information issue du traçage naturel en fonction des caractéristiques des systèmes étudiés. Quelques exemples français et espagnols. In : Proceedings of the 8th Conference on Limestone Hydrogeology. Neuchâtel. 2006. p. 101-104.

Ravbar, N., Engelhardt, I., & Goldscheider, N.: Anomalous behaviour of specific electrical conductivity at a karst spring induced by variable catchment boundaries: the case of the Podstenjšek spring, Slovenia. Hydrological Processes, 2011. 25(13), 2130-2140

2) Perform hydrograph separation to quantify the storm flow and base flow for the storm events in different seasons, because this information is also helpful to interpret the TTi results.

Shape of the hydrograph suggests fast reactivity and thus fast circulations within the hydrosystem which is confirmed by hydrograph separation (see below).

However flash flow to baseflow separation based on hydrograph can not be directly related to TTi as they inform about pressure transfer while TTi mainly bears information about mass transfer. Moreover, this separation does not allow to determine whether fast water is coming from fast infiltration or if it was stored and mobilized thanks to the reconnection with the karstic network.



4) I would also like to suggest that the authors conduct the artificial tracer tests for the springs investigated in this manuscript and validate the TTi with the artificial tracer test results. However, this suggestion is not required for accepting this manuscript for publication.

Thanks for this suggestion. A new section (3.4) was added to the paper to discuss the limits and perspectives of TTi quantification.

About artificial tracer we added the following explanation:

"To make TTi a quantitative natural tracer of transit time, several avenues have to be explored, such as artificial tracer test, use of radiogenic isotopes, or the study of organic matter degradation kinetics.

Artificial tracer test consists in injecting a tracer in a place known for its strong and rapid connectivity with the hydrosystem, and in monitoring its restitution at a presumed outlet. It thus informs about the existence of a path between the injection point and the outlet, and provides an estimate of the transit time between the two. A set of several artificial tracer tests may provide enough transit time values to quantitatively connect TTi with transit time. However, to compare TTi with artificial tracer tests it is necessary to check that they provide the same information. An artificial tracer test with uranine, tryptophan and humic-like organic matter performed by Frank et al. (2020) in a karst system shows that uranine has the same transport properties as tryptophan but not as humic-like organic matter. It therefore seems that artificial tracer tests may not correctly illustrate the behaviour of all the organic matter compounds involved in TTi. Moreover, not all artificial tracers may be compatible with simultaneous analysis of natural fluorescence of organic matter. For example, widely-used uranine may overlay the natural fluorescence of many protein-like compounds (P1, Tyrosine-like). Indeed, the quantification of artificial tracers in a sample is performed by spectrofluorescence, exactly like the quantification of fluorescent organic matter compounds needed to calculate TTi. Some artificial tracers have emission and excitation wavelengths in the same area of the EEM of some organic compounds, and may thus hide the natural signal of organic matter. Use of such tracers would not be compatible with quantification of TTi. Furthermore, some organic matter compounds have the ability to adsorb themselves to artificial tracers molecules, which would interfere with the TTi signal. Selection of an artificial tracer in such experiment will therefore have to be taken with caution. A more fundamental remark is that TTi is related to residence time of a mix of water originating from different paths within the aquifer, while artificial tracers only trace the fastest circulations due to injection through well-connected conduits. This observation raises the question of the comparability of transit time evidenced by both methods. In addition, the presence of possible injection points is not guaranteed for all hydrosystems. For example, no possible injection point could be identified at Millet spring for now. As a conclusion, artificial tracage may be a good candidate to identify fast infiltration, as long as no interference is possible (fluorescein usage), and obtain transit time is not mistaken for residence time."

Frank, S., Goeppert, N., & Goldscheider, N.: Field tracer tests to evaluate transport properties of tryptophan and humic acid in karst. *Groundwater*. 2021, *59*(1), 59-70. doi: 10.1111/gwat.13015

Comments

RC1 - Line 47 **- Define "DOM" -** Line 47
DOM = Dissolved organic matter. Definition of this acronym was added to the manuscript.

RC1 - Lines 72-73 **- It is not clear whether the water samples are from unsaturated zones that are not groundwater or the water samples are soil water from vadose zone or unsaturated zones.**
Water samples are from unsaturated zones, they do belong to groundwater. The misleading initial sentence was changed into (modification in bold) : " Based on the critical analysis of these previous studies, we first analyzed water fluorescence on 289 **ground**water samples from 4 springs and 10 flow points located in the unsaturated zone of the Vaucluse karst system".

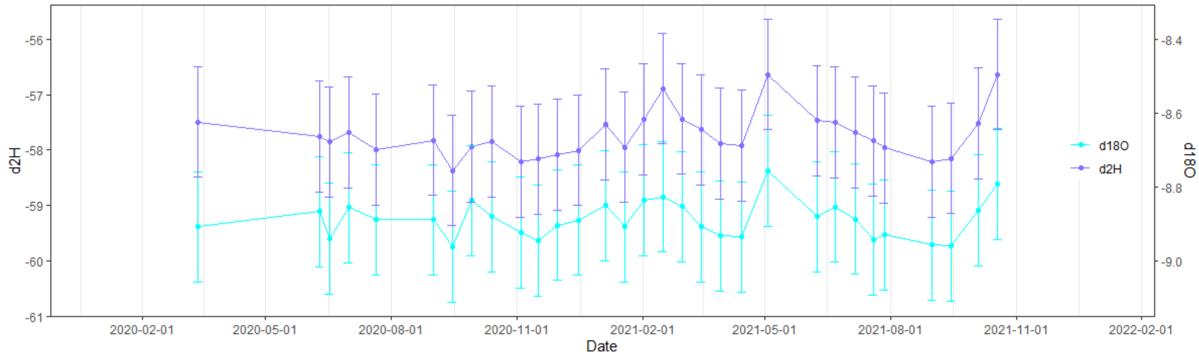
RC1- lines 84, 135, 208, 209, 227 and table 1 **- This "," should be ".". This comment is applied to many places in this manuscript.**
Comas were replaced by points.

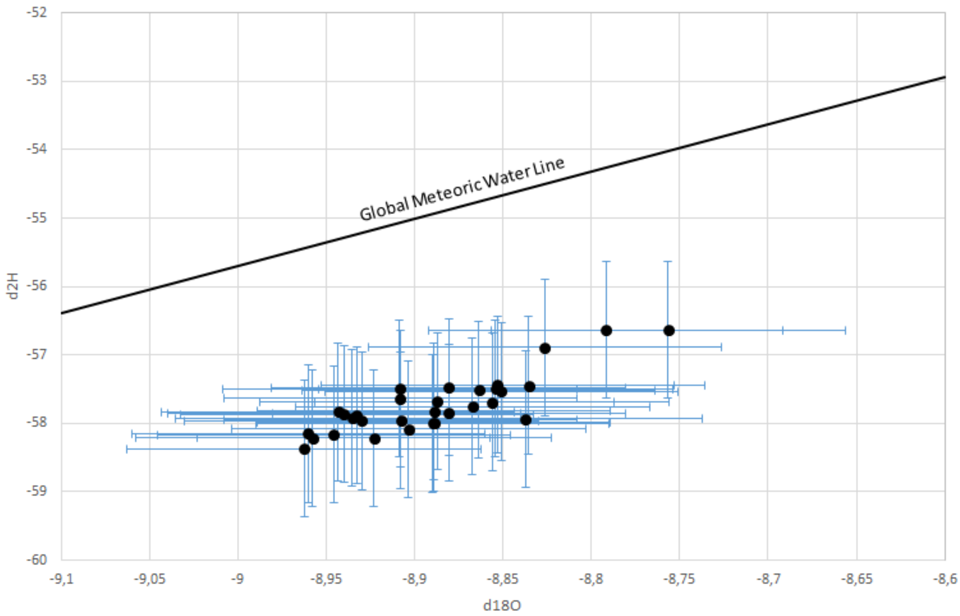
RC1 - Figure 1 **- I suggest adding some land surface or groundwater table elevation information on this map because it is a key to visualize the groundwater flow direction. There is no information how the springs catchment was delineated, which is the base to explain the TTI in 3.3 Comparison of average TTi values of Vaucluse karst springs. Please add the information how the springs catchment was delineated in the reversion.**
See answer made to suggestion 1).

RC1 **-** Figure 2 **- These two samples were taken from different dates, which are two months away. It is suggested that the comparison is better between the two samples sampled on the same day.**
These two samples were chosen for their 2D spectra showing peaks far from the L and H boxes of Ohno (2002) and different from one sample to another, with the aim to exemplify the inadequation between L and H boxes, and some of our sample's spectra. Samples from the same day do not show as many differences.

RC1- Line 164 **- It is suggested making a comparison of delta O-18 between the spring water and local precipitation. It is also suggested including deuterium data if possible.**
Deuterium was analyzed but deuterium and delta O-18 time series are similar, both are very stable with variations within the uncertainty range (see first figure below). We chose to show ^{18}O only to limit redundancy.

d18O versus d2H graph (see second figure below) illustrates the absence of evaporation process. Our data lies far from the global meteoric water line but seems to have the same tendency, probably corresponding to the local meteoric water line. No isotopic data from local precipitation is available.



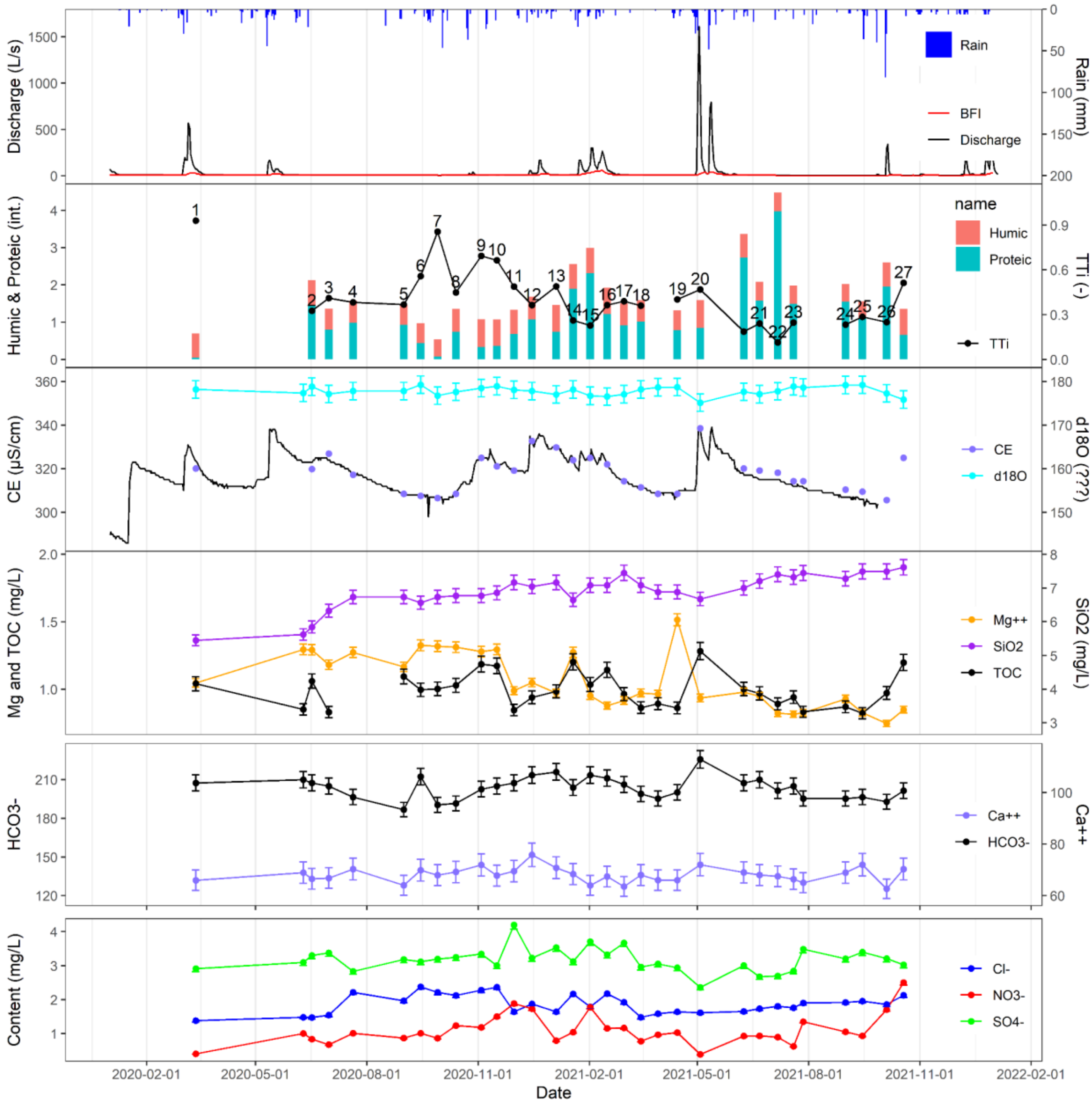


RC1- Lines 168-170 - **The positive correlation between EC and discharge is unusual on the quick recharge response karstification system. Most similar studies show some weak to good negative correlation between EC and discharge. Unless the contribution from immobile pores is significant or high EC soil water is flushed out. However, the latter case may be significant in arid vadose zone, which is not a case for this study area. In order to explain this unusual phenomena, it is suggested performing a hydrograph separation to quantify the contribution of the base flow and the storm flow. This information is also helpful to explain the Ca2+, Mg2+ and HCO3, d18O and mixing.**

See answer made to suggestion 3).

RC1- Line 170 - **Ca2+ and HCO3- of karst aquifer groundwater are generally from aquifer rocks-limestone and dolomite. The recharge water from precipitation generally has much lower Ca2+. However, the precipitation passing thick vadose zone or unsaturated zone may have elevated Ca2+. It is unlikely the case here because the fast response discharge to precipitation was observed.**

As seen in the graph below, Ca^{2+} and HCO_3^- vary almost exactly like electrical conductivity. The link with discharge is answered in the previous suggestion 3).



RC1 Lines 171-173 - **These two sentences are conflicting with each other. Please revise them.**
The first sentence was replaced by another interpretation according to previous comments. The second one "Arrival of water associated with short residence time is usually also evidenced by TOC (Batiot et al., 2003)" is an introductory sentence for what comes later, interpretation of TOC variations.
A return to the line was omitted so reading led to a misleading understanding of the second sentence. To be sure that it can't be misunderstood anymore, we removed "also" from the second sentence and added a return to line after the first sentence.

RC1 - Lines 176-178 - **This statement is not consistent with the discharge presented in Fig. 4. The base flow is about 100 L/s but the storm discharge is twice to 15 times of the base flow, which means that the fresh water during floods at millet is very high.**
The sentence concerned by your comment was deleted with the review from previous comments.

RC1- Figure 4 - **CE should positively correlate with Mg2+ and SO42- but Fig. 4 shows opposite correlation. Please double-check the time of the data. The CE has the second lowest CoV of 3% in Table 2 and the range of CE in Fig. 4 is approximately from 310 to 340 for point data and 285 to 340 for the continuous line. There are some discrepancies between Table 2 and Figure 4.**
Figure 4 was checked and no trouble was identified. Mg is not correlated with electrical conductivity, as shown in Fig. 5(a).
CE data from Table 2 was calculated based on point (field) data to be consistent with other data, this is why it doesn't perfectly match the line (automated in-situ monitoring) data.
The beginning of the curve is out of the selected time range. Its goal was to show the context. It appears that an unexplained gap of 31µS/cm was identified on the curve. It is probably due to a problem with the prob. To provide only accurate data, the beginning of the curve was removed in Figure 4.

RC1- Figure 5 - **The correlation coefficient between Component 2 Trp and P1 (Comp. 3) is 0.76 in Fig. 5 (a), not 0.94.**
Thanks for this observation, it was corrected on line 207.

RC1- Line 205 - **The dimension reduction using factor analysis appears better to group the factors related to TTi, especially the factor analysis with rotation, because the grouping from the factor analysis can have better statistic support than PCA.**
Thanks for this indication. We checked the scope of application of both analyses. As long as PCA provides dimensions with a high explained variance, and important dimensions decrease, it is already a major step forward in the understanding and description of the data (Joliffe and Morgan, 1992). It is the case in our PCA because the 3 first dimensions represent more than 70% of the total explained variance. It also appears that "PCA includes correlated variables with the purpose of reducing the numbers of variables" while factor analysis "estimates factors, underlying constructs that cannot be measured directly" (Suhr, 2005). Our dataset includes a lot of correlated variables because they were chosen for their ability to be connected with transit time in precedent studies. It therefore seems that in our case, PCA is more adapted than factor analysis.
Rotation is also possible with PCA and we wondered whether to do it or not. We finally didn't because this kind of rotation is likely to destroy differences between categories of individuals (https://sites.google.com/site/rgraphiques/4--stat/machine-learning-biostatistiques-analyse-de-donn%C3%A9es/analyse-en-composantes-principales/la-rotation-varimax).

Joliffe I, Morgan B. Principal component analysis and exploratory factor analysis. Statistical Methods in Medical Research. 1992;1(1):69-95. doi:10.1177/096228029200100105

SUHR, Diana D. Principal component analysis vs. exploratory factor analysis. 2005; SUGI 30 proceedings, 2005, vol. 203, p. 230.
https://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.444.2964&rep=rep1&type=pdf

RC1- Line 220 - **Should be "than" replaced with "as"?**
The commented sentence was deleted according to previous comments.

RC1- Lines 221-222 - **This explanation is not supported by the discharge hydrograph. Please check this statement with the information presented in Fig. 4.**
The commented sentence was deleted according to previous comments.

RC1 - Lines 253-254 - **Is it possible that TTi is also affected by the seasonality and land use on catchment?** and - Lines 258-259 - **Seasonality?**

The TTi difference presented in these sentences refers to the same season with one year delay. Land use or vegetation development are thus comparable which allows to state that differences in TTi between these two low flow periods stem from transit time variation.

We added a discussion about seasonality of TTi in the new section 3.4 of the paper as follows:

" Transferability of TTi in different pedoclimatic and anthropogenic contexts may also be questioned. Indeed, anthropic activities and seasonality may affect TTi through organic matter production and degradation :

- Fluorescent organic matter is mainly coming from vegetation related to plant cycle. As the vegetation changes with the seasons, the organic matter supply changes as well, at least in terms of quantity. Seasonality does not significantly affect organic matter composition, as exposed in Musadji et al. (2020). Anthropic activities such as land use or wastewater infiltration within the hydrosystem can affect both quantity and types of organic matter compounds because they involve input of external organic matter to the system. The influence of anthropic activity on the type of organic matter compounds may be significant and may vary over time. Moreover, the anthropic activities and the vegetation may vary from one site to another due to different pedo-climatic conditions and complicate the transposition of a quantitative TTi.

  As TTi is a ratio of different organic matter compounds, it is made independent from the absolute amount of organic matter. Possible bias may appear when very low input of a specific type of organic matter results in DOM content below the detection limits. In this case, degradation is overestimated which may impact the quantitative relation between TTi and transit time. Overall, we expect TTi to be little affected by seasonal variations of productivity even if it is quantitatively linked to residence times. As TTi is a ratio, a regular and constant supply of anthropic organic matter may not impact its variation. But in contrast, a punctual supply of humic or protein-like organic matter may result in an over or underestimation of TTi.
- The degradation of organic matter involves interactions with biocenose. Degradation occurs at different rates depending on the type of organic matter compounds and on the biodiversity and microbial activity of the soil. The latter may vary throughout seasons and with anthropic activities because of varying factors such as sunlight duration, moisture rate, temperature, climate or pesticides use.

Variation in space and time in organic matter composition and degradation rate may thus stem from either anthropic or natural factors. Influence of anthropic compounds can be circumvented by careful identification and separation of PARAFAC components. Variation in organic matter composition and degradation kinetics in different pedoclimatic contexts is not an obstacle to the qualitative use of TTi, but may be a serious limitation to the transferability of a quantitative link between TTi and residence time. Variation in organic matter degradation kinetics with time on the same hydrosystem throughout the year is questionable but it begins to be studied as shown by McDonough et al. (2022). A detailed study of composition of organic matter source in soil and of its becoming in groundwater through lab tests may provide valuable elements to estimate the lifetime of fluorescent compounds in hydrosystems, and thus to quantitatively link TTi with transit time."

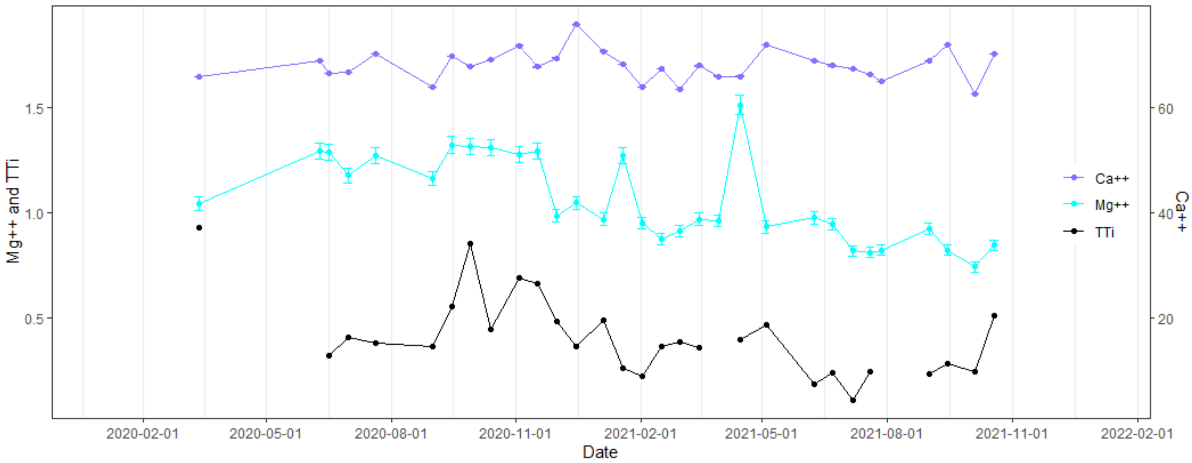
McDonough, L.K., Andersen, M.S., Behnke, M.I. *et al.* A new conceptual framework for the transformation of groundwater dissolved organic matter. *Nat Commun* 13, 2022. https://doi.org/10.1038/s41467-022-29711-9

N.Y.Musadji, L.Lemée, L.Caner, G.Porel, P.Poinot, C.Geffroy-Rodier. Data for dynamics analysis of soil dissolved organic matter. Long term amendment effect. Data in Brief, Volume 27, December 2019, Pages 104665, https://doi.org/10.1016/j.chemosphere.2019.124808.

RC1 - Line 267 - **Dreiss (1989) presented a study to quantify the storm-derived water in the spring flow hydrographs with Ca2+ and Mg2+, so these natural tracers could be additional evidence to TTi.**

Thank you for this comment/suggestion. As seen in the following graph, correlation between Ca^{2+} and Mg^{2+} is quite low for this spring.

- The Relationship between Mg^{2+} and TTi is already discussed in the paper.
- Range of Ca^{2+} variations is low so this element provides limited additional information about the spring's dynamics, this is the reason why it wasn't considered in the paper.



RC1- Line 281 - **But the discharge hydrograph in Fig. 4 does show rapid response, which may not support this assumption.**

Thanks for your comment, the sentence was modified to be a comparison between Millet and St Trinit springs (modification in bold):

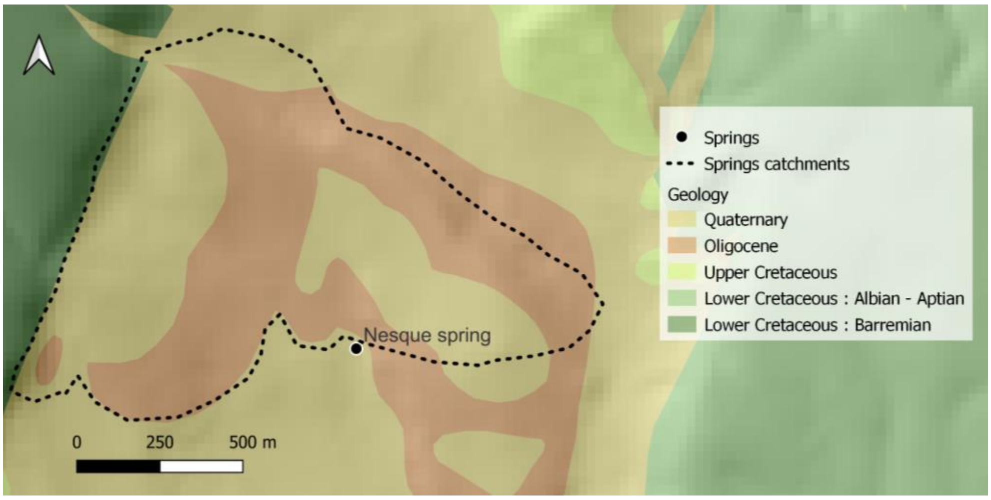
"We thus suppose that this system is **less** affected by fast infiltration **than st Trinit**".

RC1- Line 282 - **The catchment of this spring in Fig. 1 is covered by the alluvial deposits but the authors didn't provide whether the source of this spring is from carbonate aquifer or alluvial aquifer. It is also not clear how the catchment was delineated. It looks that the upper gradient area of this catchment is not different from other spring catchments. Because the karstification or quick conduit is a key to explain the TTI, more information about this spring catchment should be provided.**

It is true that Nesque catchment seems to be covered by the Quaternary in Fig. 1. But Oligocene deposits are actually also widely outcropping, as seen in the map zoom below. Furthermore Quaternary deposits are thin and the aquifer is developed within Oligocene deposits, as mentioned in Table 1. Oligocene carbonates are different from Cretaceous carbonates from other spring catchments : they correspond to lake deposits, are more marneous, and the karstification is less developed.

Karstification-related information is provided in Table 1.

Response to other parts of this comment is provided in our response to Suggestion 1).



RC1- Line 292-293 - **The mixing is common for many springs with their sources from carbonate aquifers and is also a challenge to determine the residence time of the spring water. However, detailed hydrogeology, groundwater movement and better delineation of spring catchment should enhance the interpretation of the TTi results, which is relatively weak for this manuscript. Furthermore, artificial tracers have been widely applied to the karst system to get groundwater flow paths, residence time and velocity. The TTi presented in this manuscript provides a new approach that is likely cost-effective compared to the artificial tracer but it is still necessary to validate the TTi results against the artificial tracer results before it can be applied to other karst springs.**

See answer made to suggestions 1) and 4).

RC1- Line 299 - **The cosmogenic radionuclide beryllium-7 with a 53.2 day half-life is available for this time range but it likely costs more.**

Thank you for this comment, we added a paragraph into the new section 3.4 discussing about how making a link with quantitative transit time :

"A second approach to establish a quantitative link between TTi and residence time is the use of radiogenic isotopes like beryllium-7, radium or radon-222. Price taken apart, the use of radiogenic isotopes may be problematic because of the volume of water needed for analysis which reaches several hundred of litters (e.g 500 L for Beryllium-7, Frey et al., 2011) which reserves its use for water flow points with sufficient discharge for sampling to be performed within a sensible time scale. The sampling time for radiogenic isotopes from some flow points in our study can be several days. Even quite important springs may reach low discharges that prevent such analysis during low flows. Nevertheless, radiogenic isotopes can be relevant for linking TTi to transit time values for samples from springs and flows having a sufficient discharge. "

Frey, S., Kuells, C., et Schlosser, C. New Hydrological Age-Dating techniques using cosmogenic radionuclides Beryllium-7 and Sodium-22. 2011