

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.

## RC2

**1) The main goal of this work is to link the humification index and transit time in karst systems. However, the authors do not provide strong evidence about their linkage. Transit time in this work is inferred from time series of discharge and biogeochemical data (e.g., Mg) rather than being really quantified. Particularly, the authors stated that humification index can be a good candidate for karst systems with short transit times (0-6 months). I think this is a big missing if transit time is not quantified and therefore conclusions are not that convincing.**

You clearly identified the main scientific question of this work which is to link TTI and transit time in karst systems. But this work doesn't pretend to build a quantitative natural tracer of transit time. It aims to be a preliminary study to assess qualitatively the potential of TTI and fluorescent organic matter to trace transit time from 0 to 6 months. As exposed in the introduction, this range was inferred from TOC which represents the quantity of organic matter present in the water and its mineralisation (or degradation) is complete after 6 months (Batiot, 2002). Fluorescent organic matter is a small part of the total organic matter represented by TOC and will therefore also be completely degraded after a maximum of 6 months

The time series used to qualitatively assess TTI potential to trace transit time correspond to natural tracers that were the subject of former studies of springs of the same study area (answer better developed to your third comment).

To clarify the quantification aspect to your comment, we added section 3.4 of the paper. Please refer to it. We also added the following paragraph to the introduction:

“Fluorescent organic matter compounds are degraded in natural environment. The rate of this degradability is constrained by two aspects: the type of organic matter and biological activity. The influence of the organic matter type is well documented, complicated molecules of organic matter having higher emission wavelength and lesser digestibility (Zsolnay, 1999). For example, humic-like organic matter are less digestible than protein-like organic matter, and thus takes more time to be degraded.”

Batiot, C.: Etude expérimentale du cycle du carbone en régions karstiques: apport du carbone organique et du carbone minéral à la connaissance hydrogéologique des systèmes, Ph.D. thesis, Université d'Avignon et des Pays de Vaucluse, France, 2002.

Zsolnay, A., Baigar, E., Jimenez, M., Steinweg, B., Saccomandi, F.: Differentiating with fluorescence spectroscopy the sources of dissolved organic matter in soils subjected to drying, *Chemosphere* 38, 45–50, [https://doi.org/10.1016/S0045-6535\(98\)00166-0](https://doi.org/10.1016/S0045-6535(98)00166-0), 1999.

**2) This work is trying to illustrate the advantage of humification index for karst systems where other existing tracers fail. However, I don't see the authors provide this kind of comparison in terms of data in the part of results and discussions. Therefore, it is hard to believe the authors' statements. Besides, in-depth discussion about the advantage and limitation of humification index is needed.**

The main goal of this work is to assess the potential of TTI to trace short transit time. Millet spring was chosen as a challenging spring because usual natural tracers vary little and thus provide little valuable information. The comparison between TTI and other natural tracers is illustrated in Figure 4 with time series and Table 2 through variation coefficient. It thus appears that TTI varies more than other natural tracers at Millet spring which suggests that TTI has the potential to trace something which cannot be seen by other natural tracers. Then, PCA is performed to try to characterize the source of TTI signal. The comparison of mean TTI between different springs (section 3.3 of the paper) nevertheless shows the consistency of this index to qualitatively assess transit time. If you have some suggestion or answer to our response, don't hesitate.

About advantages and limitations of TTI, you are right, they are not enough discussed in the paper, this is why we added section 3.4.

**3) Since this is a karst system, how about the time series of typical species such as Ca and HCO<sub>3</sub> look like? And how they are correlated with the principal components of PCA? I don't understand why the authors chose SiO<sub>2</sub>, Cl, and NO<sub>3</sub> as the representative species here.**

**Please also clarify.**

Time series of typical species such as Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> are reported in the graphs below. They vary with the same shape, and are very well represented by electrical conductivity. To omit redundancy, we made the choice to represent only electrical conductivity. Please refer to our answer to the comment of line 171 of RC1 and suggestion 3).

For the same reason, these two elements were omitted in PCA to avoid imbalance of the result. As electrical conductivity is mainly represented by Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup>, these 3 parameters provide almost the same information which is susceptible to imbalance PCA and do not provide representative results.

SiO<sub>2</sub>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and other parameters like Mg<sup>2+</sup> were selected for their ability to distinguish flows and springs of the system Fontaine de Vaucluse in previous studies (Barbel-Périneau, 2013; Blondel, 2008; Garry, 2007).

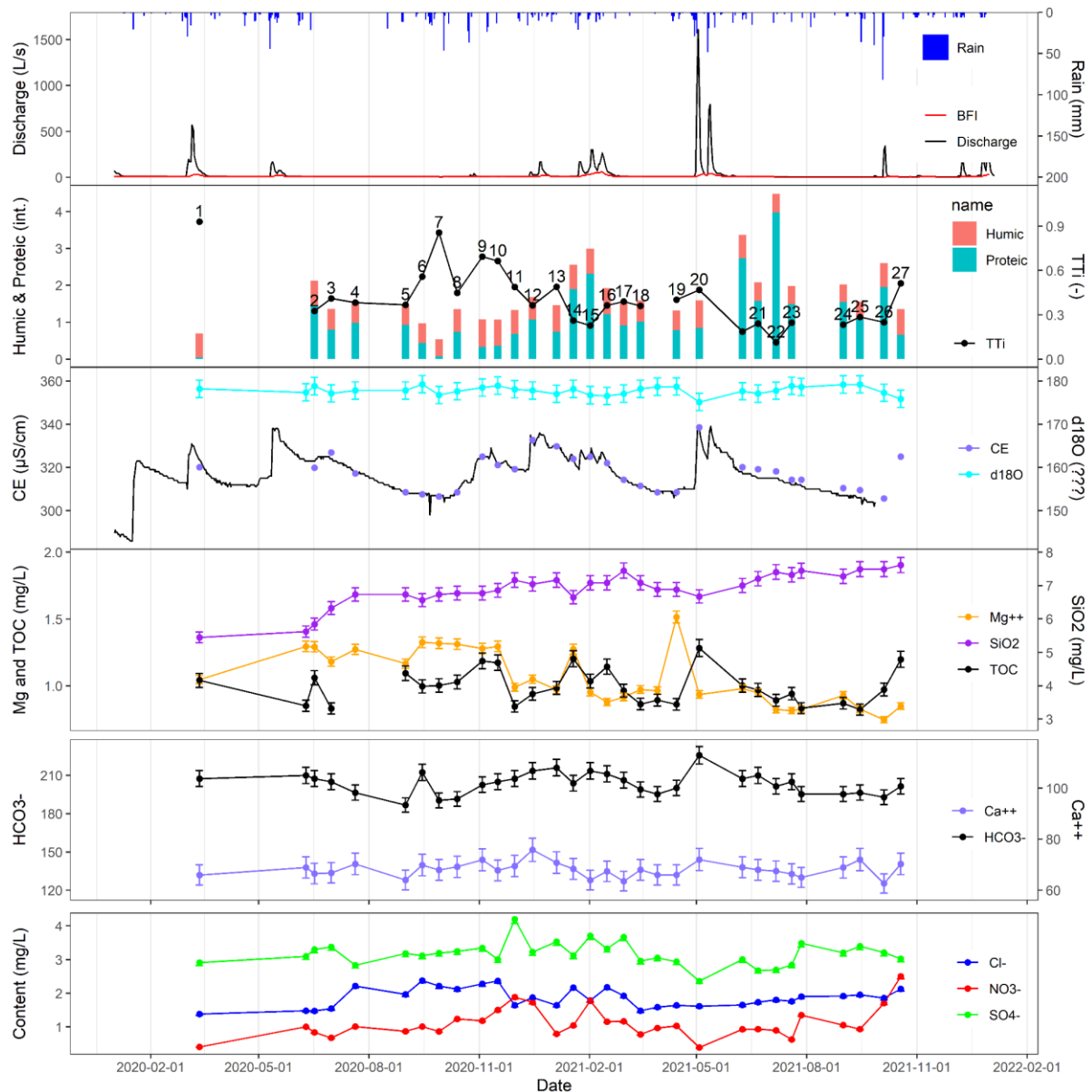
We add the following sentence at the beginning of the section 3.2.1 to clarify the choice of these parameters:

“Descriptive statistics of major ions, TOC, electrical conductivity, humic-like and protein-like organic matter, TTI, standard deviation, and coefficient of variation are available in Table 2. and represented as time series in Fig. 4. These parameters were chosen for their ability to improve recharge and transit time knowledge on flows and springs of the Fontaine de Vaucluse system (Garry, 2007, Barbel-Périneau, 2013, Blondel, 2008).”

Barbel-Périneau, A., 2013. Caractérisation du fonctionnement de la zone non saturée des aquifères karstiques: Approche directe par études hydrodynamiques et hydrochimiques sur le Bassin de Recherche, d'Expérimentation et d'Observation de Fontaine de Vaucluse – Laboratoire Souterrain à Bas Bruit de Rustrel – Pays d'Apt. Université d'Avignon et des Pays de Vaucluse (PhD).

Blondel, T., 2008. Expérimentation et application sur les sites du Laboratoire Souterrain à Bas Bruit (LSBB) de Rustrel – Pays d'Apt et de Fontaine de Vaucluse. Université d'Avignon et des Pays de Vaucluse (PhD).

Garry, B., 2007. Etude des processus d'écoulements de la zone non saturée pour la modélisation des aquifères karstiques - Expérimentation hydrodynamique et hydrochimique sur les sites du Laboratoire Souterrain à Bas Bruit (LSBB) de Rustrel et de Fontaine de Vaucluse. Université d'Avignon et des Pays de Vaucluse (PhD).



**4) The method part is too brief. Please provide more descriptions about PARAFAC modelling and PCA. For example, what is the principle and purposes? This may help the readers better understand the results.**

PARAFAC is a factorial method applied to excitation-emission matrix (EEM). It corresponds to a statistical approach model that extracts independent high intensity zones (fluorophores) from EEM (Murphy et al., 2013).

It is a frequently used method in fluorescent studies permitting the identification of the organic matter present in samples. Our modeling was performed following Anderson and Bro (2003) methodology which is a reference in PARAFAC modeling. As it is a widely used method and as the methodology references are cited, we decided to not to expand on the subject.

About PCA, here is a citation from Abdi and Williams (2010):

“Principal component analysis (PCA) is a multivariate technique that analyzes a datatable in which observations are described by several inter-correlated quantitative dependent variables. Its goal is to extract the important information from the table, to represent it as a set of new orthogonal variables called principal components, and to display the pattern of similarity of the observations and of the variables as points in maps.”

PCA is also a widely used statistical method (Abdi and Williams, 2010). As PCA is that popular, we decided to not to describe it too much in the paper. Nevertheless, we added more details in the paper:

- At the end of the section 2.2 Sampling and fluorescence analysis methods: “PARAFAC modelling was then performed to extract organic matter components thanks to the same software and package using non-negative constraints for all modes following the method described by Andersen and Bro (2003)” ;
- In the second part of the section 3.2.2, we added “To characterize the source of TTI signal, Principal Component Analysis (PCA) was performed on 27 Millet spring samples with TTI, TTI components (Tyr, P1, H1&H2)”

Abdi, H. and Williams, L.J. Principal component analysis. Wiley interdisciplinary reviews: computational statistics, 2010, vol. 2, no 4, p. 433-459. <https://doi.org/10.1002/wics.101>

Andersen, C.M. and Bro, R., Practical aspects of PARAFAC modeling of fluorescence excitation-emission data. J. Chemometrics, 2003, 17: 200-215. <https://doi.org/10.1002/cem.790>

Murphy, K. R., Stedmon, C. A., Graeber, D., Bro, R., Decomposition routines for Excitation Emission Matrices. Analytical Methods, 2013, vol. 5, no 23, p. 1-29. <https://doi.org/10.1039/c3ay41160e>

**5) There are lots of typos through the whole manuscript. Just to name a few: Line 31, “9,2%”; Line 84, “23,3”; Line 227, “10,6%”.**

Comas were replaced by points.

**6) Lots of texts repeat again and again with no changes at all. For example, the texts of the abstract are basically the same with those in the introduction and conclusion.**

As the abstract is not supposed to be new content, redundancy between it and introduction/conclusion didn't disturb us. But you are right to tell us that the different parts are too similar, we modified the beginning of the conclusion accordingly as following:

“Groundwater from karst aquifers is an important resource for drinking water supply in the world (Stevanović, 2019). Soils from carbonate aquifers are generally poorly developed which combined with the rapidity of groundwater fluxes within karsts conduits explains the vulnerability of these aquifers to contamination. To face the challenge of the protection of karst water resources, several specific hydrogeochemical tracers have been developed by the community to characterize the different types of fluxes and recharge. One of the main current challenges is to develop natural tracers able to estimate water transit times for short times ranges of the order of 0 to 6 months.”

Stevanović, Z.: Karst waters in potable water supply: a global scale overview, Environ. Earth Sci. 78, 662, <https://doi.org/10.1007/s12665-019-8670-9>, 2019.