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Transit Time index (TTi) as an adaptation of humification index to illustrate transit time differences in karst hydrosystems. Application to the karst springs of Fontaine de Vaucluse system (Southeastern France)

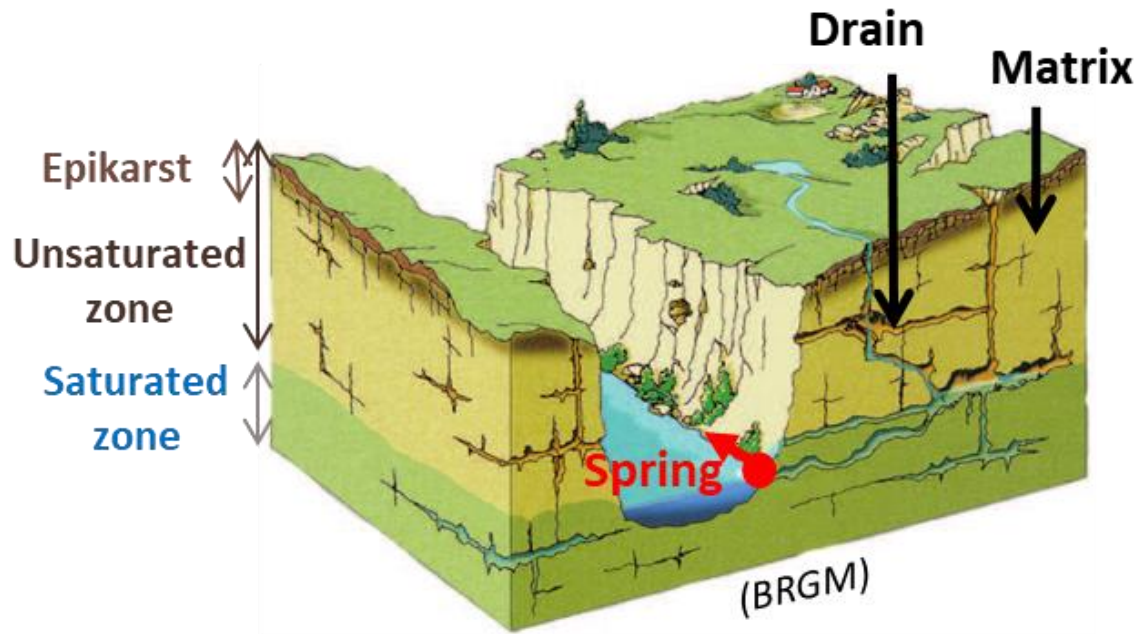
**Leïla Serène<sup>1</sup>**, Naomi Mazzilli<sup>2</sup>, Christelle Batiot-Guilhe<sup>1</sup>, Christophe Emblanch<sup>2</sup>, Milanka Babic<sup>2</sup>, Julien Dupont<sup>2</sup>, Roland Simler<sup>2</sup>, Matthieu Blanc, Gérard Massonnat<sup>3</sup>

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<sup>3</sup>TotalEnergies, CSTJF, Avenue Larribau, CEDEX 64018 Pau, France

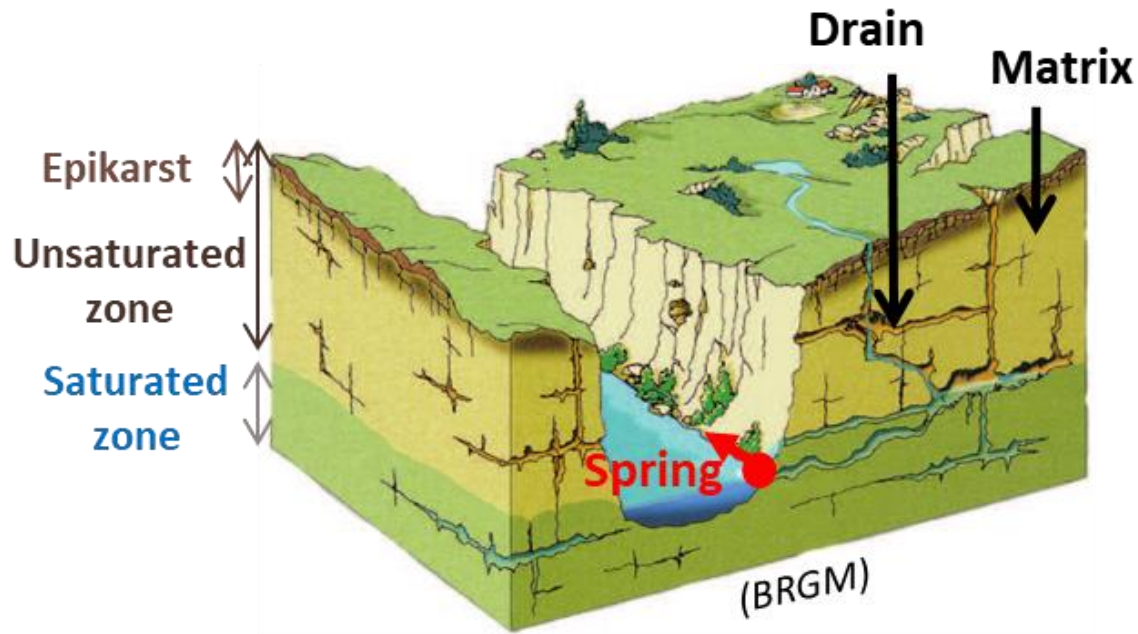
# Transit time issues in karsts



## Fast flows in karst

- Complex and fast recharge through hierarchized network
  - Quantity and quality issues
- Essential to trace short transit time (< 6 months)

# Transit time issues in karsts



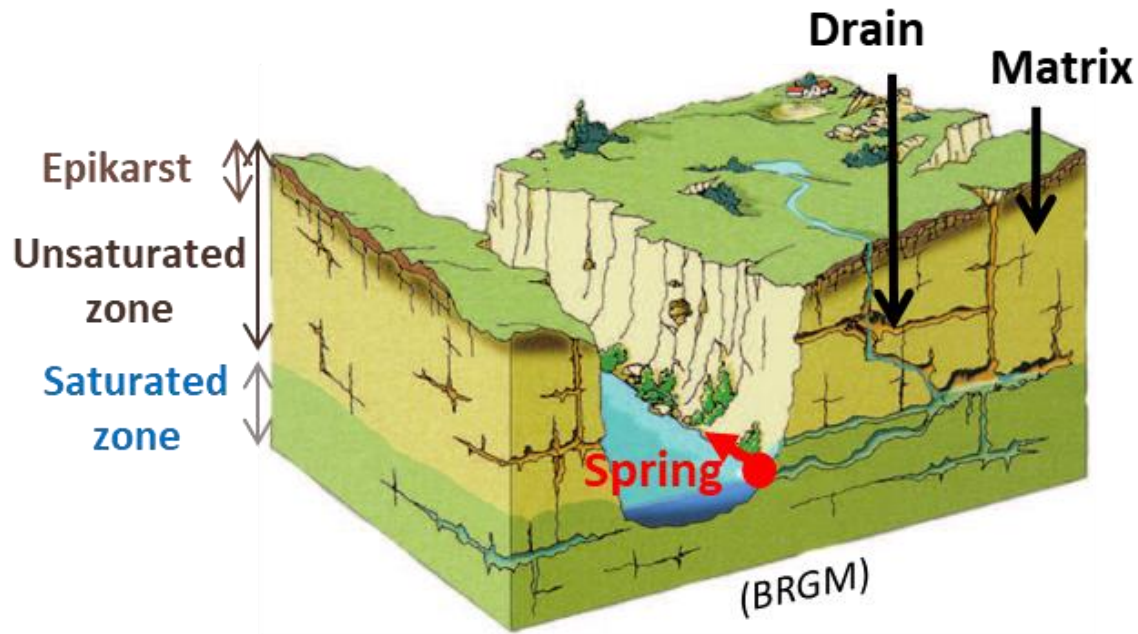
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## Natural tracers

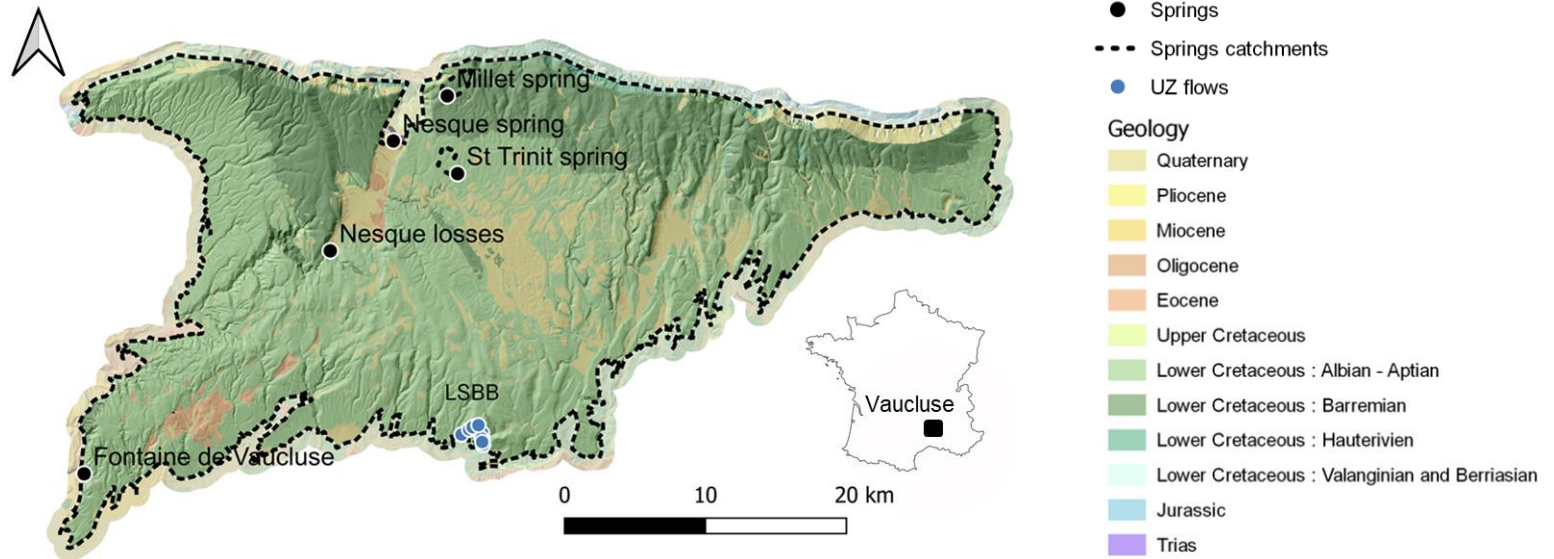
- Few available on the 0-6 months range
- High potential of natural organic matter (life duration < 6 months, *Batiot, 2002*)
- Use of Humification Index (HIX) by *Blondel et al. (2012)*

# Transit time issues in karsts



**Objective :** Analyze the potential of fluorescent organic compounds as natural tracer of short transit time (<6 months)

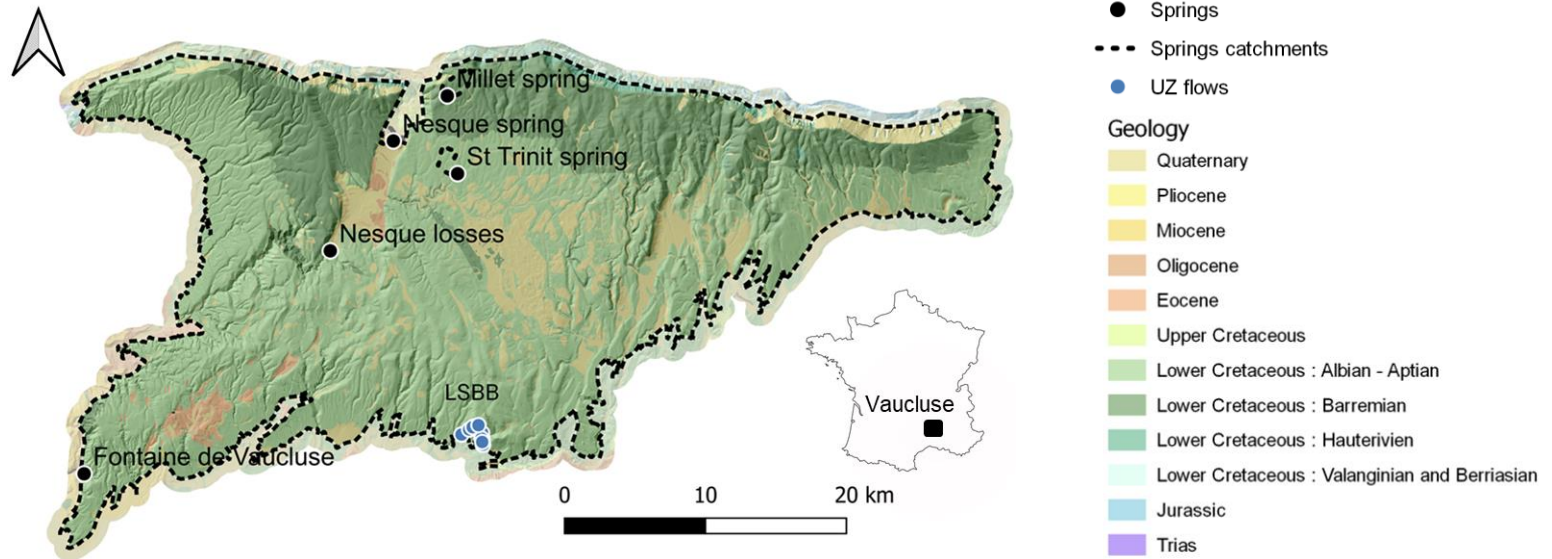
# Study site & sampling



## Fontaine de Vaucluse karstic system

- Catchment of 1160 km<sup>2</sup> *Ollivier, 2020*
- Mean flow rate 23,3 m<sup>3</sup>/s *Cognard-Plancaq et al., 2006*
- Aquifer thickness up to 1500m
- Unsaturated zone average thickness 800m

# Study site & sampling



## Fontaine de Vaucluse karstic system

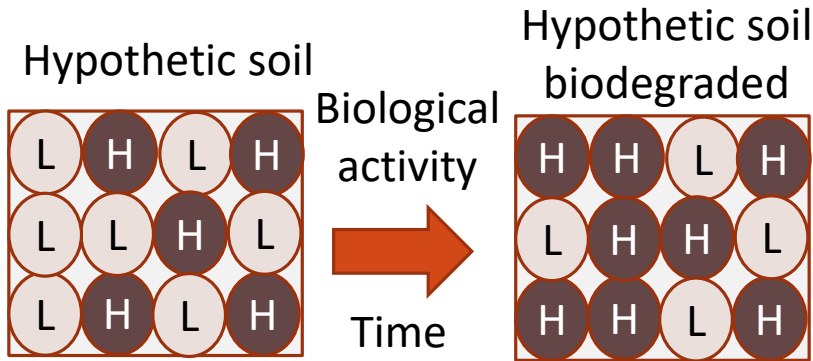
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## Sampling test

- One year bi-monthly sampling (06-2020 to 10-2021)
- Major and trace elements, TOC, water stable isotopes, fluorescence of organic matter
- 4 springs, 1 losses, flows from unsaturated zone (LSBB)

# Humification index (HIX) in brief

| $HIX = H/L$<br>$HIX = H/(L+H)$ | <b>Light organic matter</b><br><span style="border: 1px solid black; border-radius: 50%; padding: 2px;">L</span> | <b>Heavy organic matter</b><br><span style="border: 1px solid black; border-radius: 50%; padding: 2px;">H</span> |
|--------------------------------|--|--|
| Organic matter type            | Protein-like   | Humic-like   |
| Digestibility                  | high   | low  |

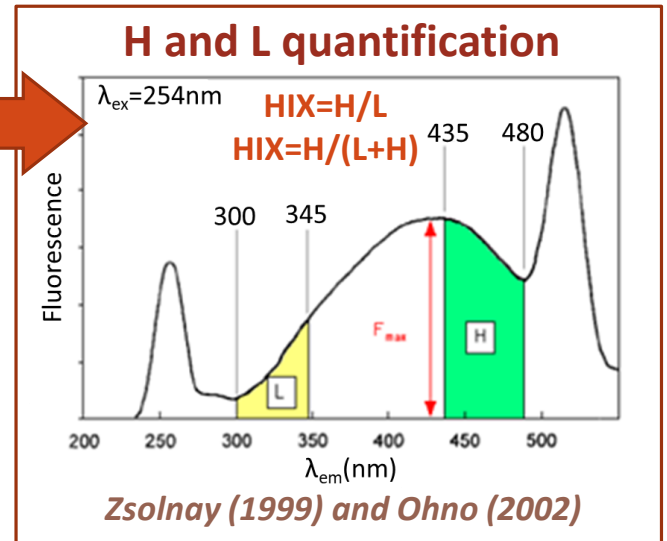


*Serène et al., 2022*

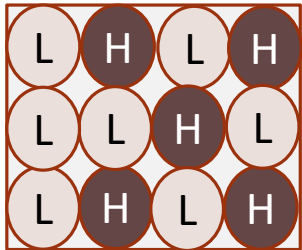
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| Organic matter type            | Protein-like                            | Humic-like                              |
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Fluorescence measurement



Hypothetic soil



Biological activity



Time

Hypothetic soil biodegraded



*Serène et al., 2022*



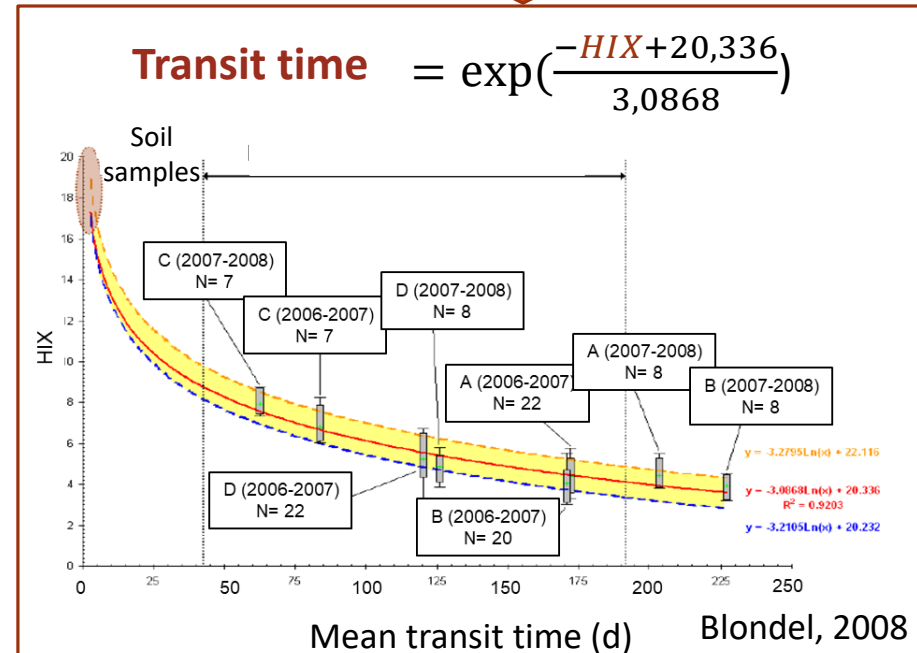
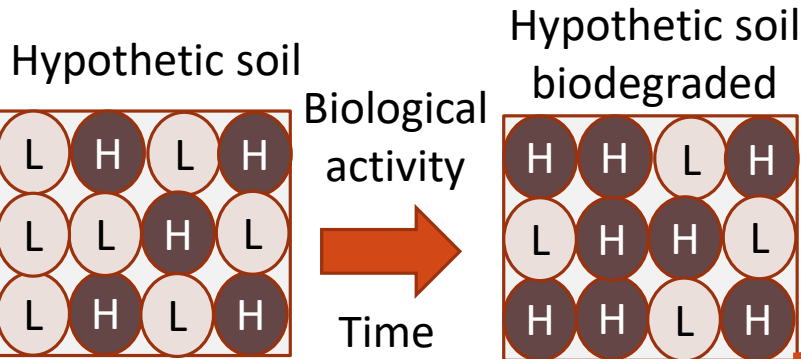
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| Organic matter type            | Protein-like                     | Humic-like                       |
| Digestibility                  | high                             | low                              |

Fluorescence measurement

H and L quantification

From HIX to transit time

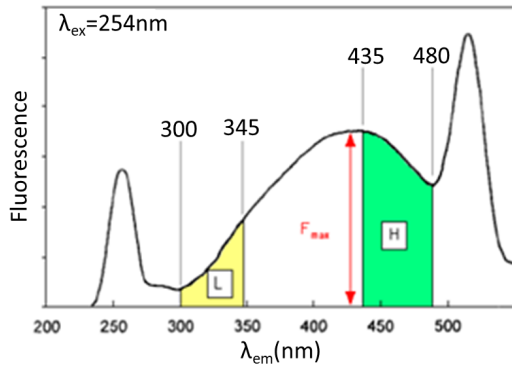


Serène et al., 2022

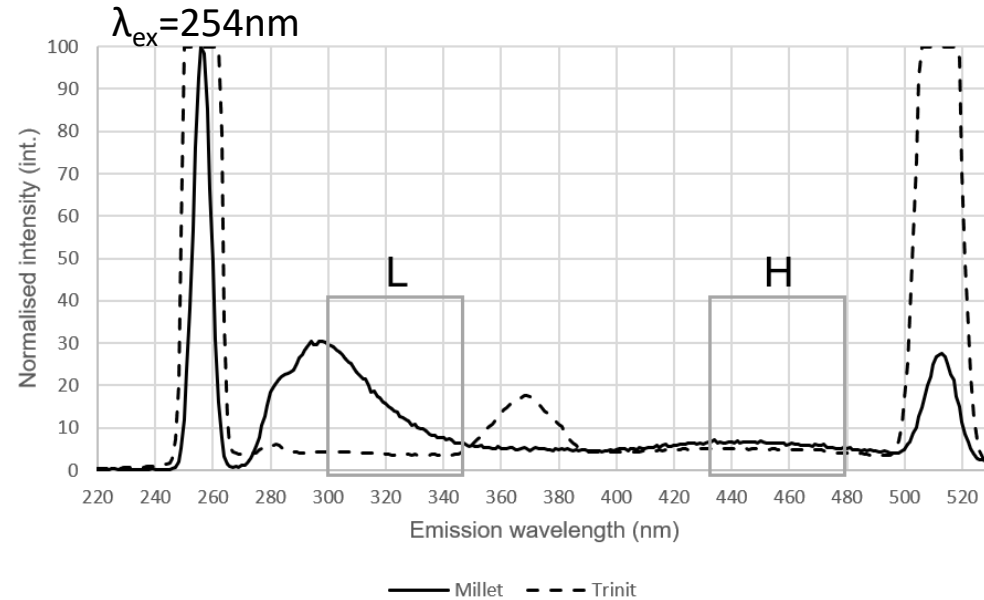
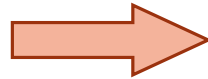
# Questioning the use of HIX in karst waters

## Previous works

H and L windows calibrated  
on soil water *Zsolnay (1999) and  
Ohno (2002)*



Application to  
groundwater  
samples

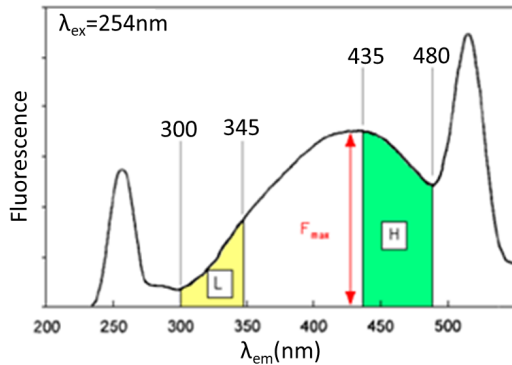


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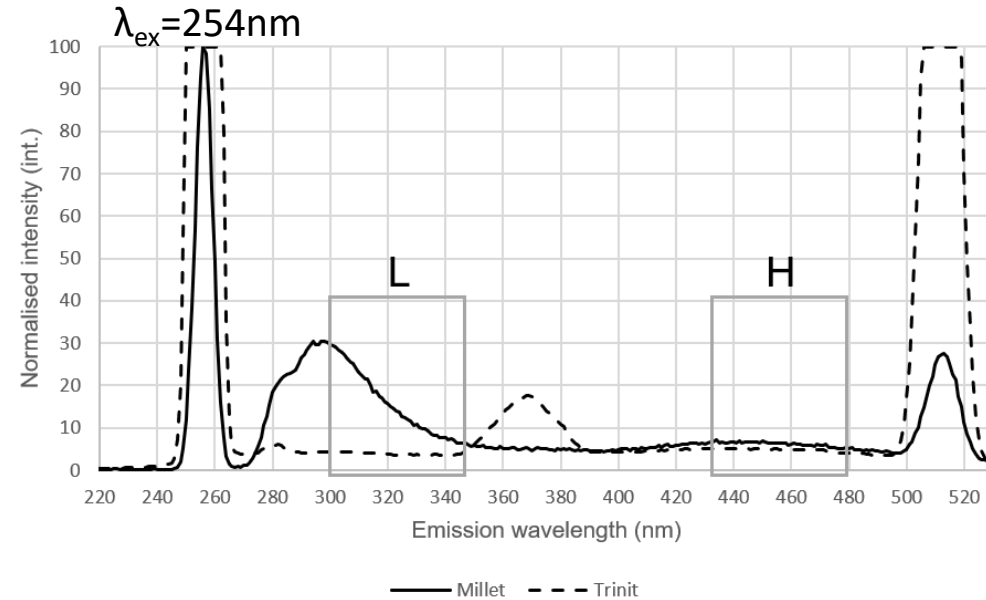
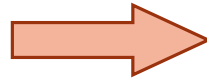
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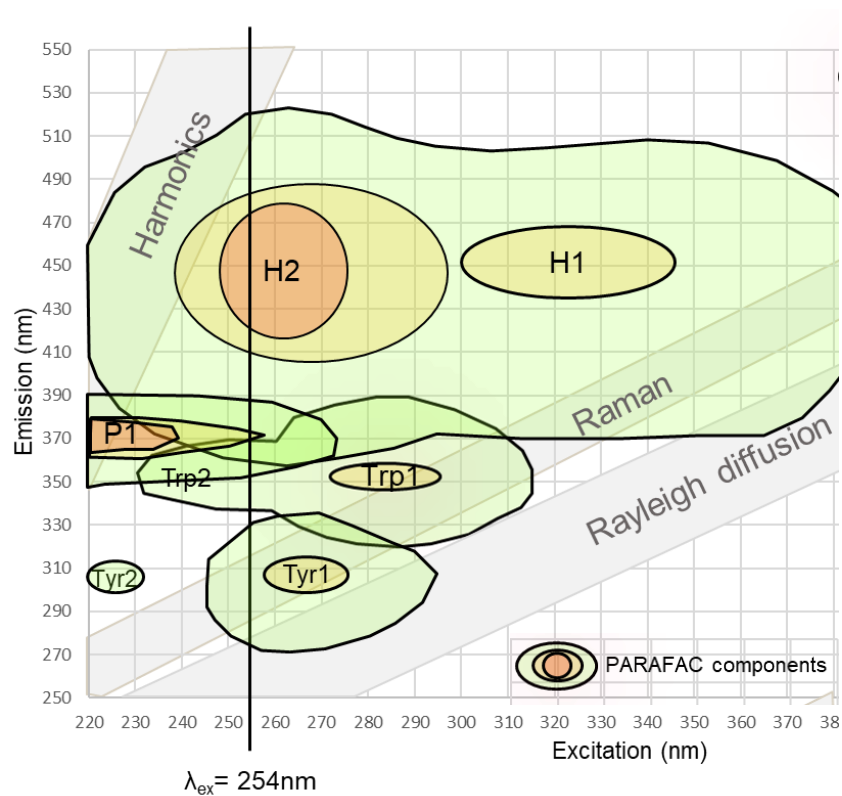


## Application results

- Mismatch of H and L windows with fluorescent peaks of groundwater samples
- Zsolnay (1999) and Ohno (2002) HIX formulas not applicable to groundwaters
- Blondel (2008) relation between HIX and transit time need to be rebuild

*Serène et al., 2022*

# From the Humification Index to the Transit Time index

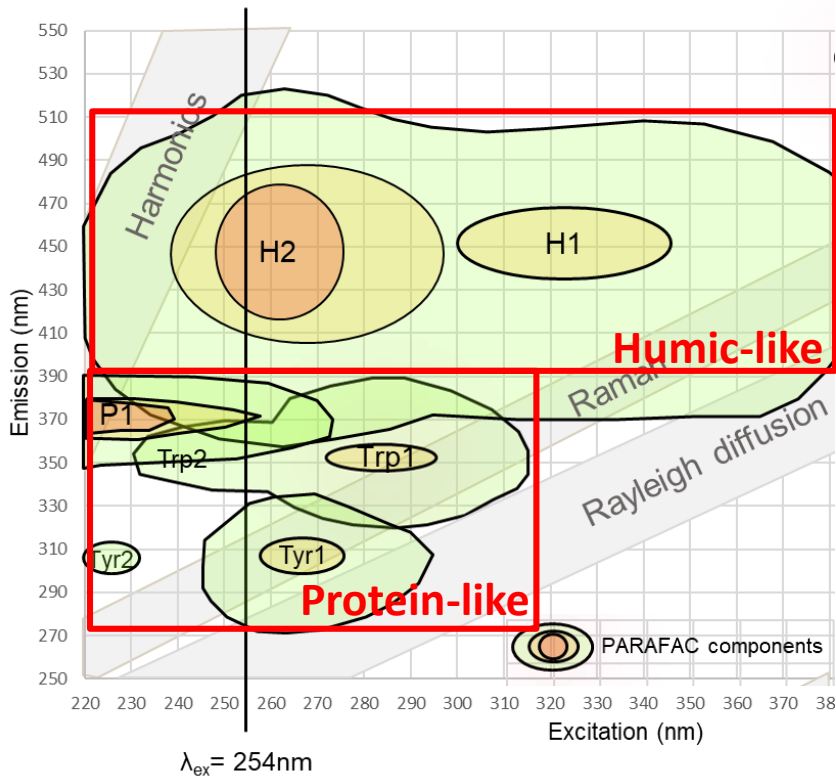


## Identification of heavy & light compounds

- 3D matrix
- PARAFAC modeling

*Serène et al., 2022*

# From the Humification Index to the Transit Time index



## Humification Index (HIX)

- 2D spectra
- H and L windows

## Transit Time index (TTi)

- 3D matrix
- PARAFAC modelling

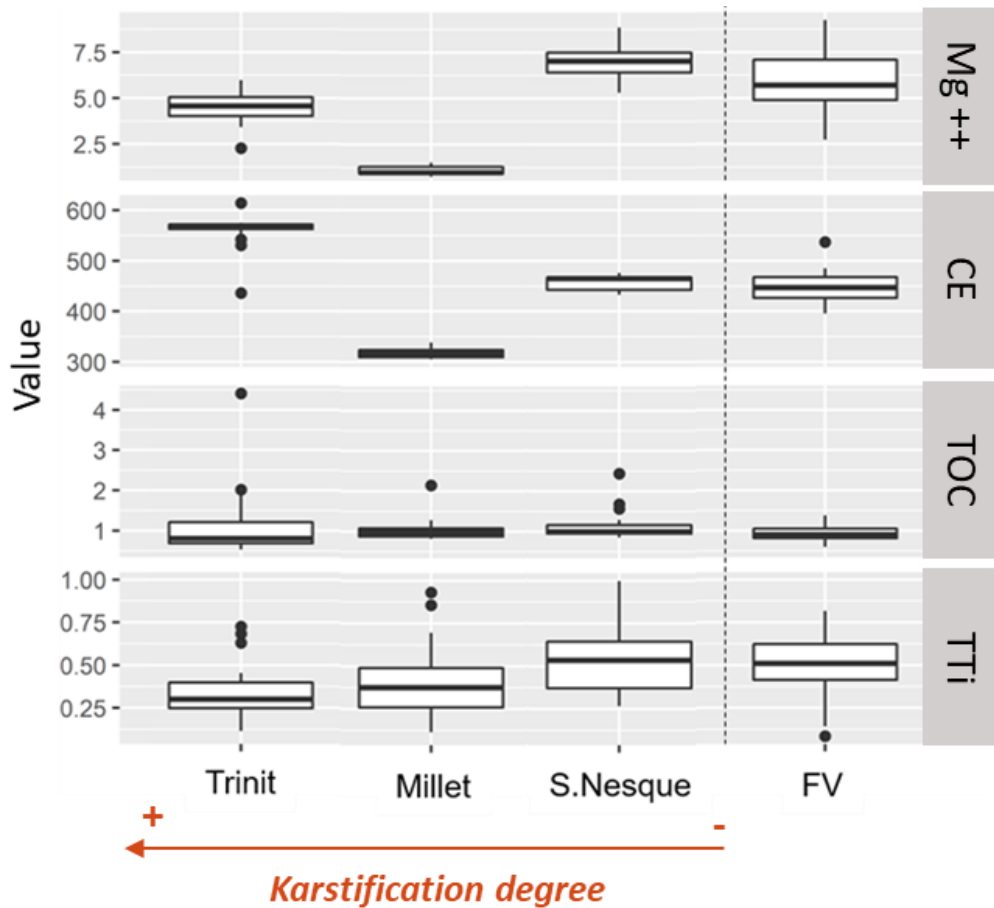
$$TTi = \frac{HIX}{H + L}$$

**HIX**
**H**  
*Humic – like*
*Humic and protein like*  
**TTi**
**H + L**

High values → « long » transit time  
 Low values → short transit time

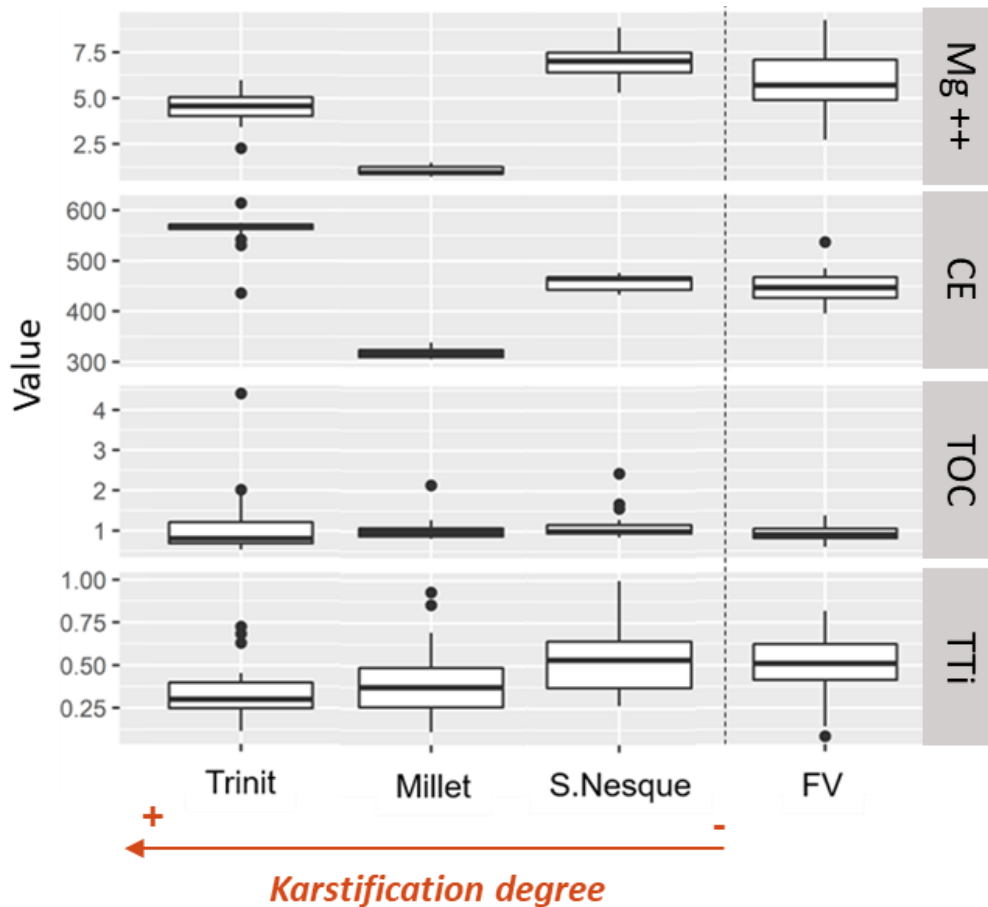
Serène et al., 2022

# Comparison of TTI between different springs



Serène et al., 2022

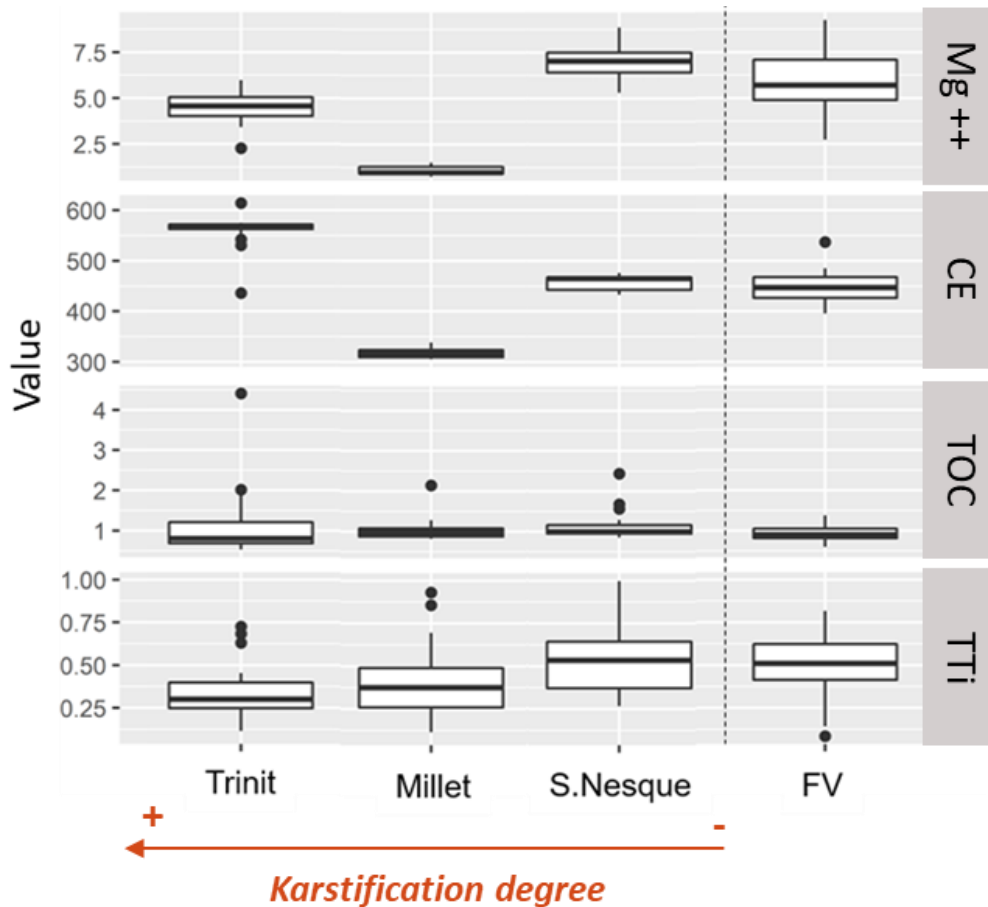
# Comparison of TTI between different springs



- Increase of TTI with decrease of karstification degree
- Consistency of mean TTI with expected transit time

Serène et al., 2022

# Comparison of TTI between different springs



- Increase of TTI with decrease of karstification degree
- Consistency of mean TTI with expected transit time
- FV TTI is similar to S.Nesque while it is the outlet of a wider system
- Limits of TTI usage in the case of mix with old waters (>> 6months)

Serène et al., 2022



# Discussion, conclusions & perspectives

## Results

### Fluorescence of organic matter as a natural tracer of transit time ?

- Methodological biases in previous work with HIX (*Blondel, 2008*)
- Adaptation of HIX to groundwater usage thanks to PARAFAC modelling → TTi
- Consistency of mean TTi with expected transit time of studied springs

*Serène et al., 2022*

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Improving qualitative approach

Seasonal variations

One site scale

Little impact  
(*Musadji et al., 2020*)

Several sites scale

Depending on hydro-pedoclimatic context

Anthropic activities

Fluorescent compounds selection thanks to PARAFAC modelling

*Serène et al., 2022*

# Discussion, conclusions & perspectives

Results

## Fluorescence of organic matter as a natural tracer of transit time ?

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Developing quantitative approach

Biodigestibility in natural groundwaters? Artificial tracer test? Radiogenic isotopes?

*Serène et al., 2022*

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Paper recently accepted for the journal HESS: <https://doi.org/10.5194/hess-2022-100>

### Transit Time index (TTi)

- 3D matrix
- PARAFAC modelling

$$TTi = \frac{\text{Humic - like}}{\text{Humic and protein like}}$$

