# Use of natural organic matter fluorescence to illustrate transit time differences in the unsaturated zone of karst hydrosystems

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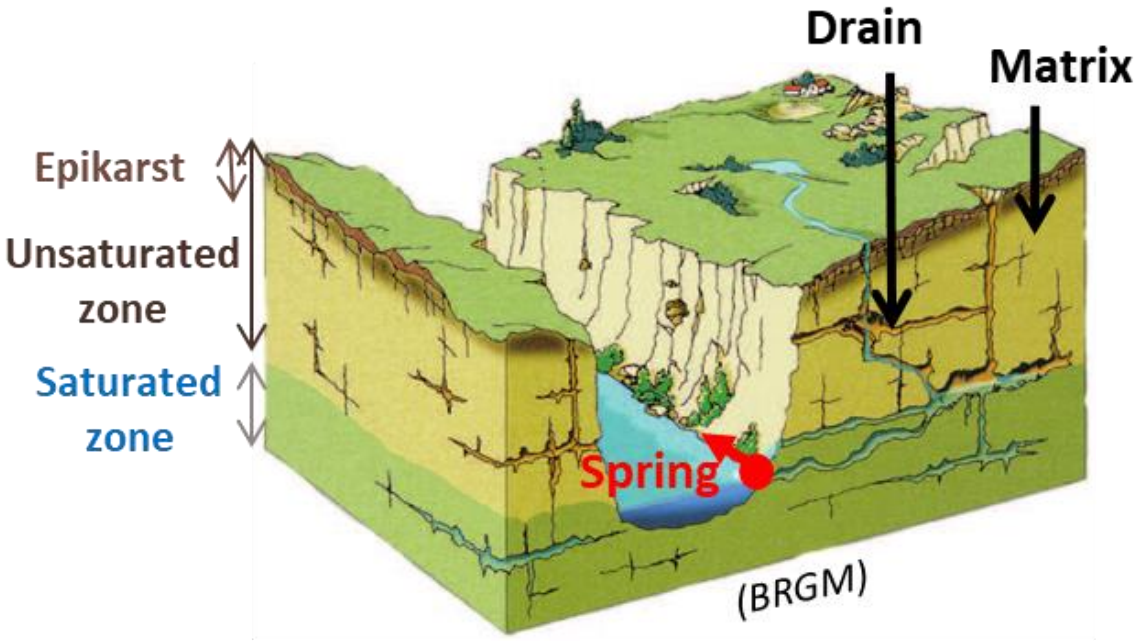
# Transit time issues in karsts




## Fast (<6 months) flows in karst

- Complex and fast recharge through hierarchized network
- Quantity and quality issues

→ Essential to trace short transit time (< 6 months)

## Natural tracers

- Few available on the 0-6 months range
- High potential of natural organic matter (life duration < 6 months, *Batiot, 2002*)
- Use of fluorescence of organic matter in this purpose by *Serène et al., 2022*

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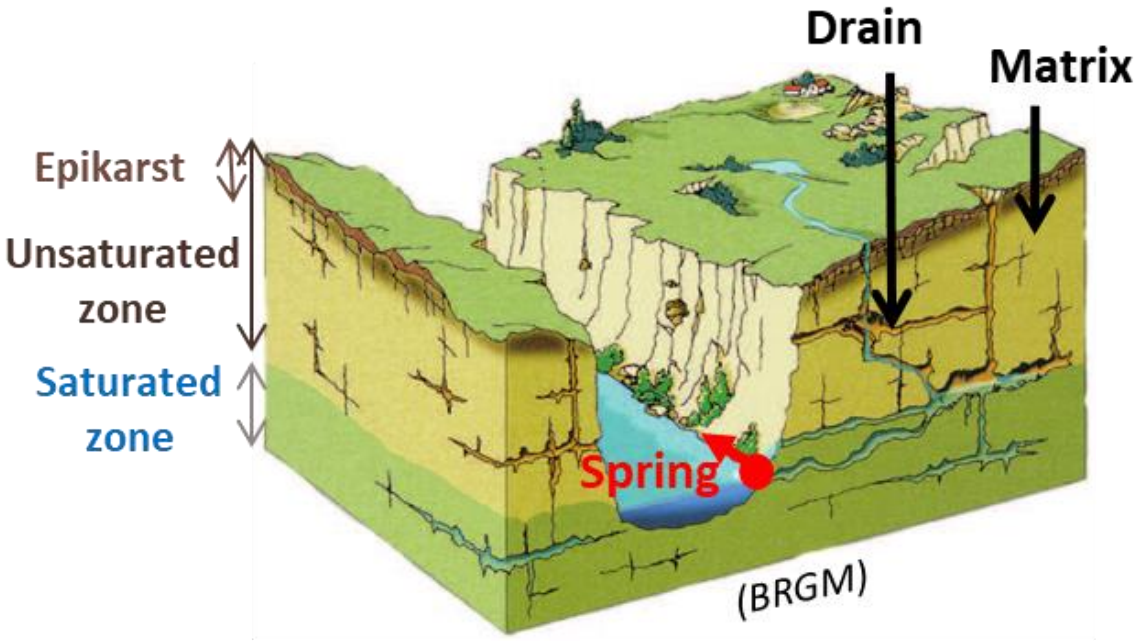


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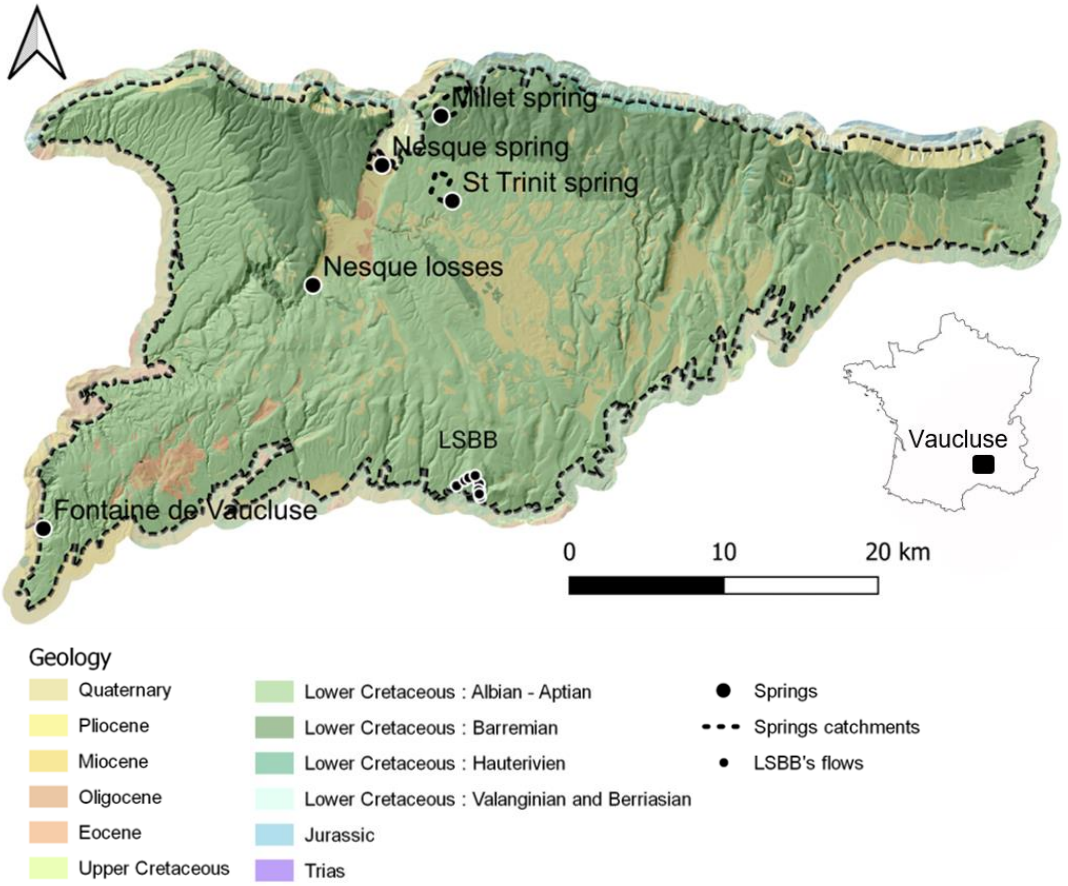
**Objective**

Use of fluorescent organic compounds as natural tracer of short transit time to improve LSBB flows knowledge

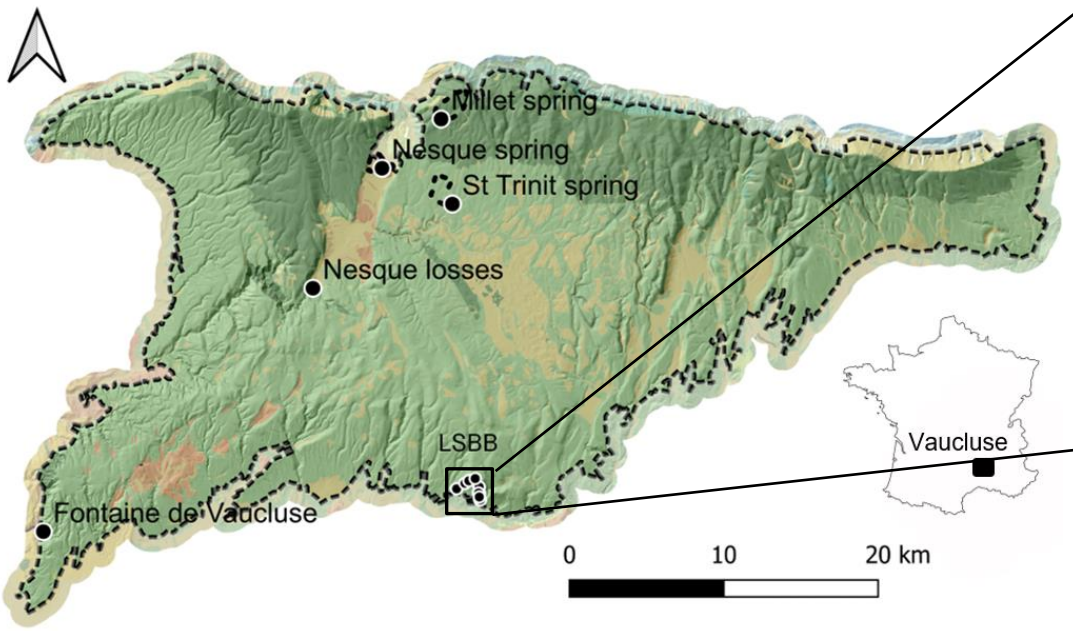
# Study site & sampling




## Fontaine de Vaucluse karstic system

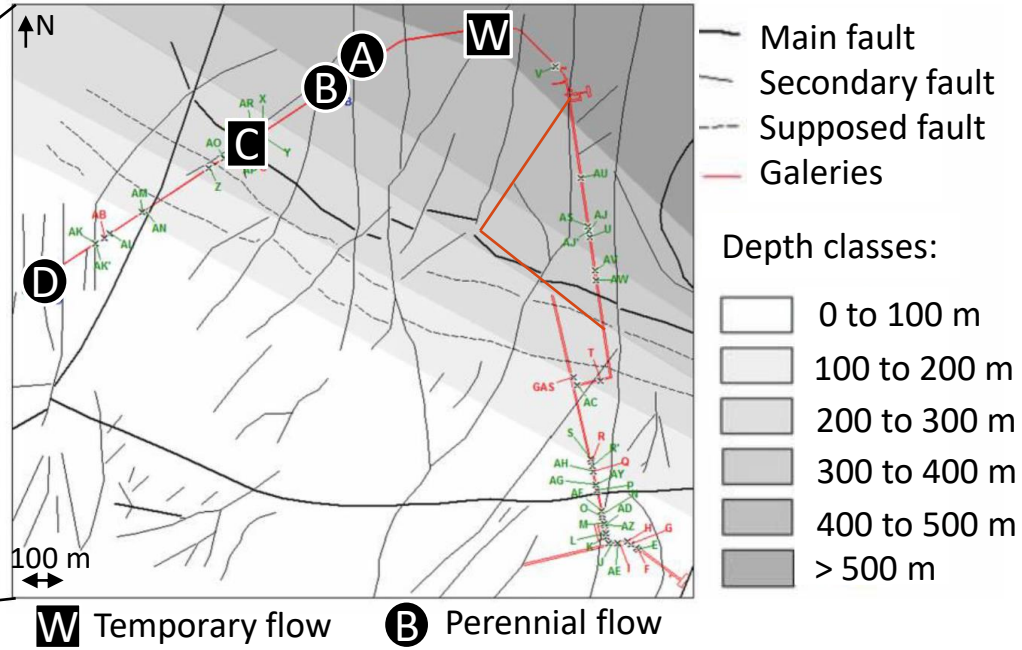
- Catchment of 1160 km² *Ollivier, 2020*
- Mean flow rate 23,3 m³/s *Cognard-Plancq et al., 2006*
- Aquifer thickness up to 1500m
- Unsaturated zone average thickness 800m

# Study site & sampling




Geology

- Quaternary
- Pliocene
- Miocene
- Oligocene
- Eocene
- Upper Cretaceous
- Lower Cretaceous : Albian - Aptian
- Lower Cretaceous : Barremian
- Lower Cretaceous : Hauterivien
- Lower Cretaceous : Valanginian and Berriasian
- Jurassic
- Trias
- Springs
- Springs catchments
- LSBB's flows




## Sampling test

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

# Organic matter in natural waters

**Organic matter of natural water** = Hydrogen + Oxygen + Nitrogen + Phosphorus + Organic Carbon (TOC)

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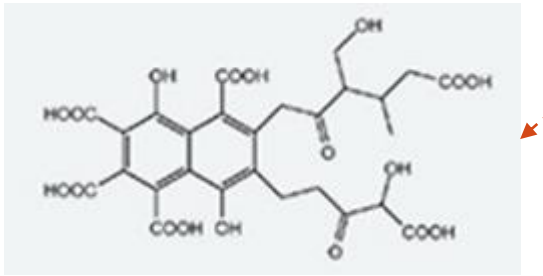
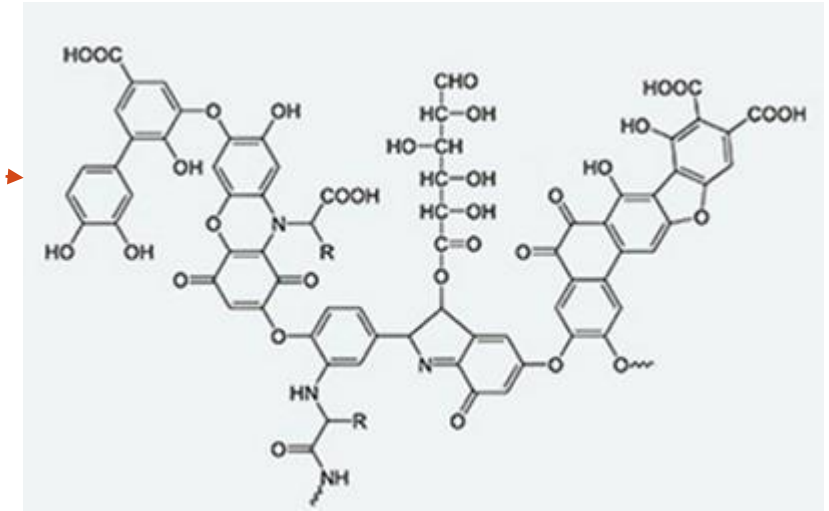
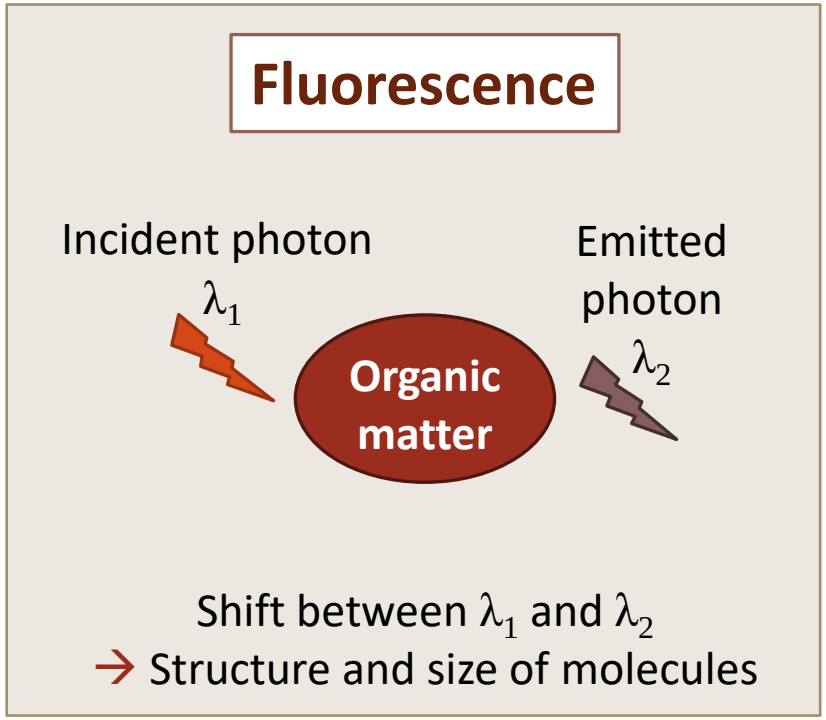
- Living components
- Dead components
  - Particulate organic matter
  - Dissolved organic matter
    - Protein-like → High digestibility
    - Humic-like → Low digestibility

*Coble,1996*





# Fluorescent organic matter at the Fontaine de Vaucluse system



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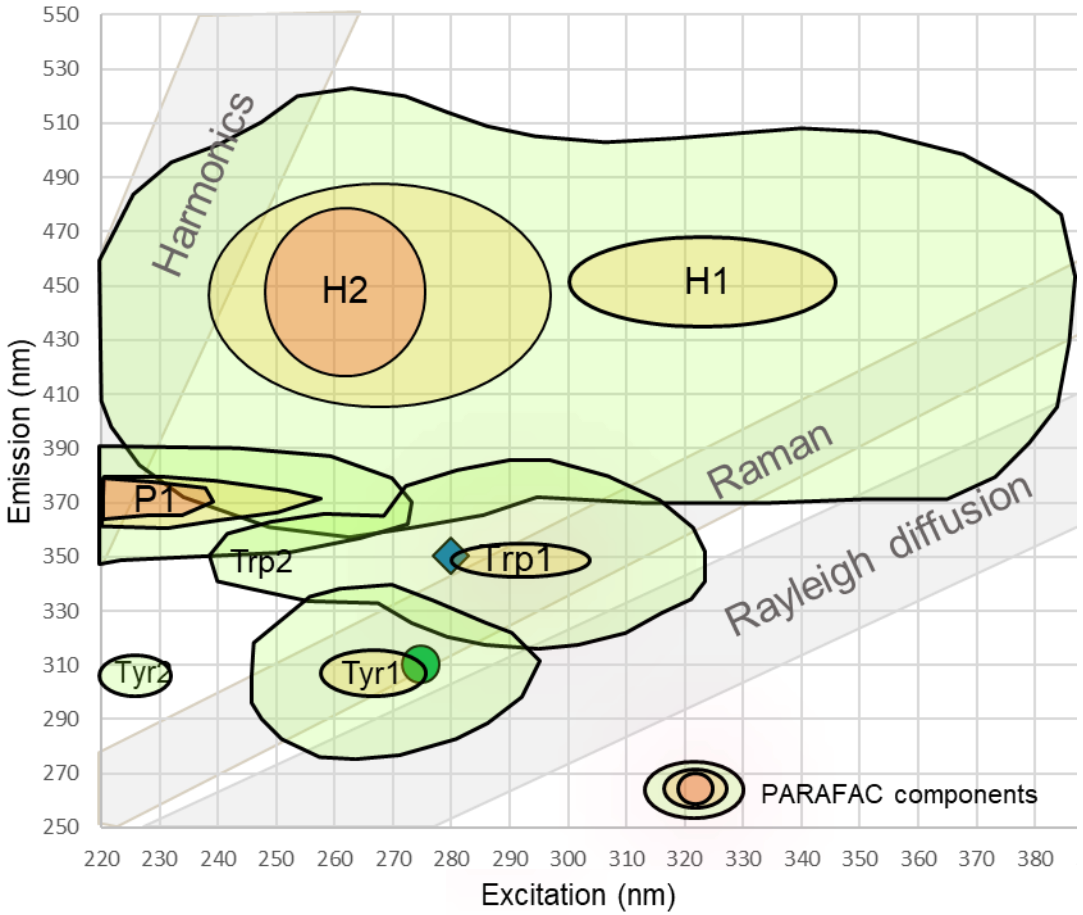



## Dissolved organic matter dataset

- PARAFAC modeling
- Identification of fluorescent compounds

**Fluorescence**

Incident photon $\lambda_1$

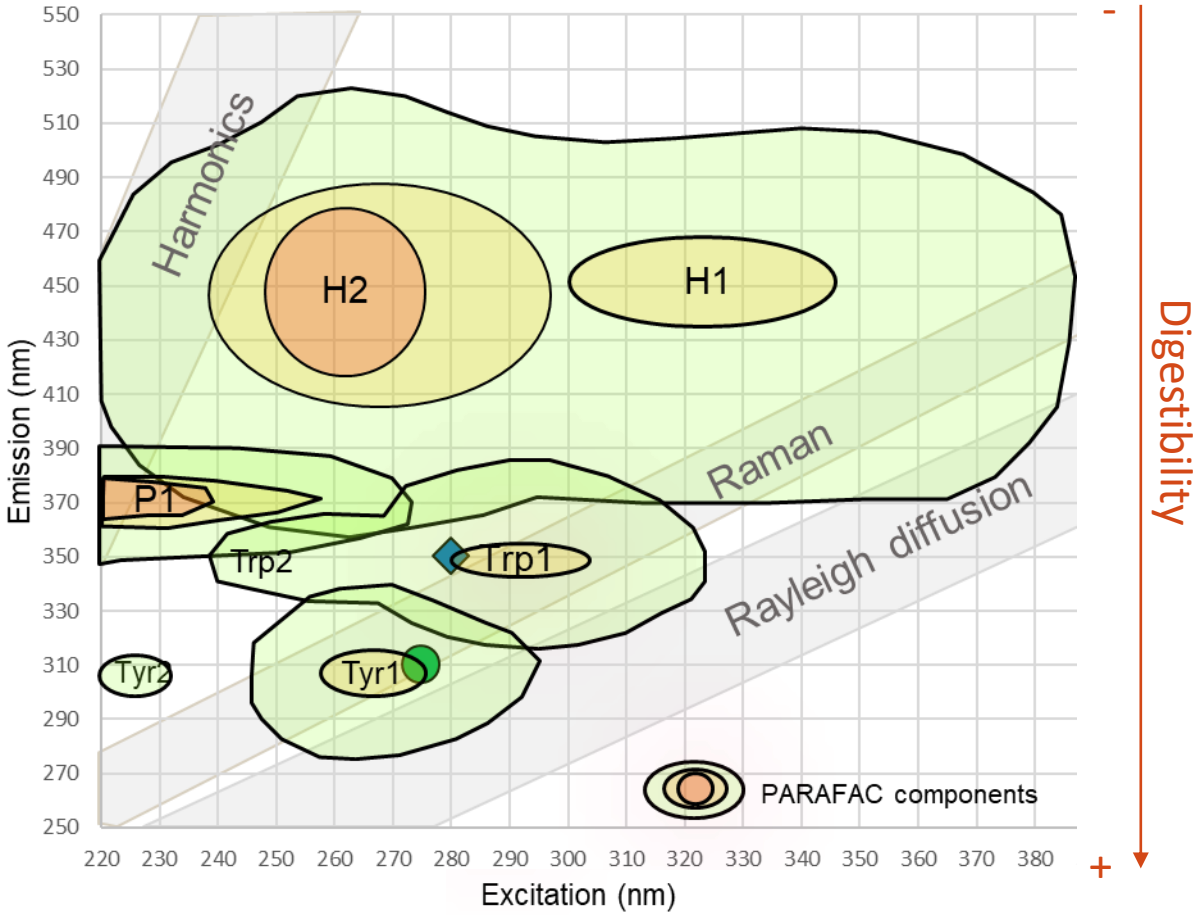
Emitted photon $\lambda_2$

Organic matter

Shift between $\lambda_1$ and $\lambda_2$

→ Structure and size of molecules

# Fluorescent organic matter at the Fontaine de Vaucluse system




## Correlation between compounds

- Soil = source of fluorescent compounds
  → Correlation between all compounds for very recent water
- Tyr is the most digestible, Trp and P1 have almost the same digestibilty
  → Correlation of Trp and P1 for recent water (Tyr is digested)
- Much more P1 than Trp

→ No correlation at all between Trp and P1 for « old » waters, most of fluorescent compound are digested

# Correlation between fluorescent compounds

| | W | | | A | | | B | | | C | | | D | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | H | P1 | Trp | H | P1 | Trp | H | P1 | Trp | H | P1 | Trp | H | P1 | Trp |
| P1 | **0.86** | | | 0.07 | | | -0.07 | | | -0.03 | | | 0.03 | | |
| Trp | **0.9** | **0.97** | | **0.79** | 0.37 | | 0.5 | **0.76** | | 0.16 | **0.82** | | 0.59 | **0.63** | |
| Tyr | **0.64** | **0.87** | **0.88** | -0.01 | 0.43 | 0.21 | 0.04 | 0.35 | 0.23 | 0.24 | 0.38 | 0.58 | 0.12 | 0.23 | 0.36 |

Correlation > 0.8 | 0.7 > Correlation > 0.8 | 0.6 > Correlation > 0.7 | Correlation < 0.6

# Correlation between fluorescent compounds

Good correlation between every compounds:
Very short transit time ?

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Correlation between H and Trp: Particular case, mix of waters?

Good correlation only between Trp and P1 : Short transit time ?

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
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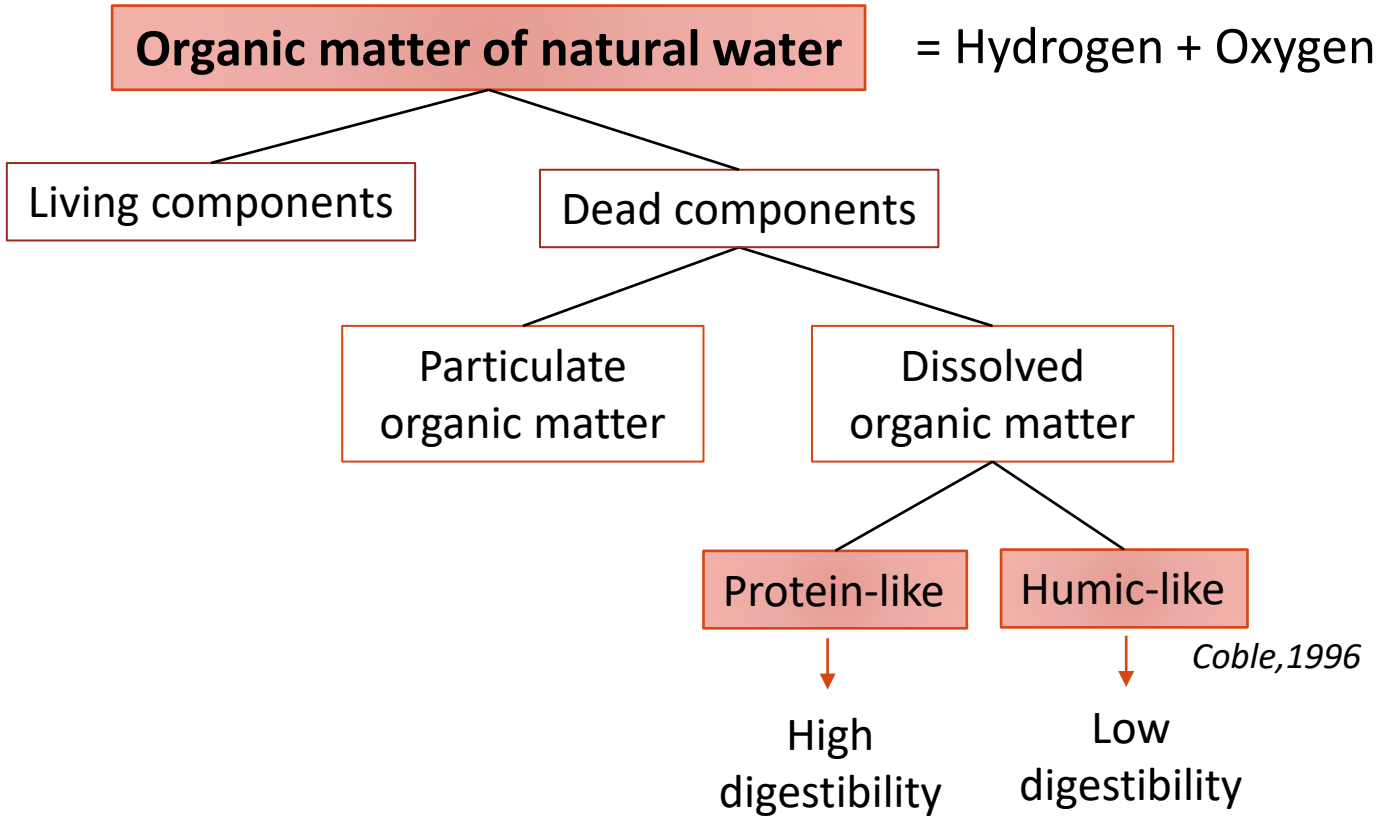


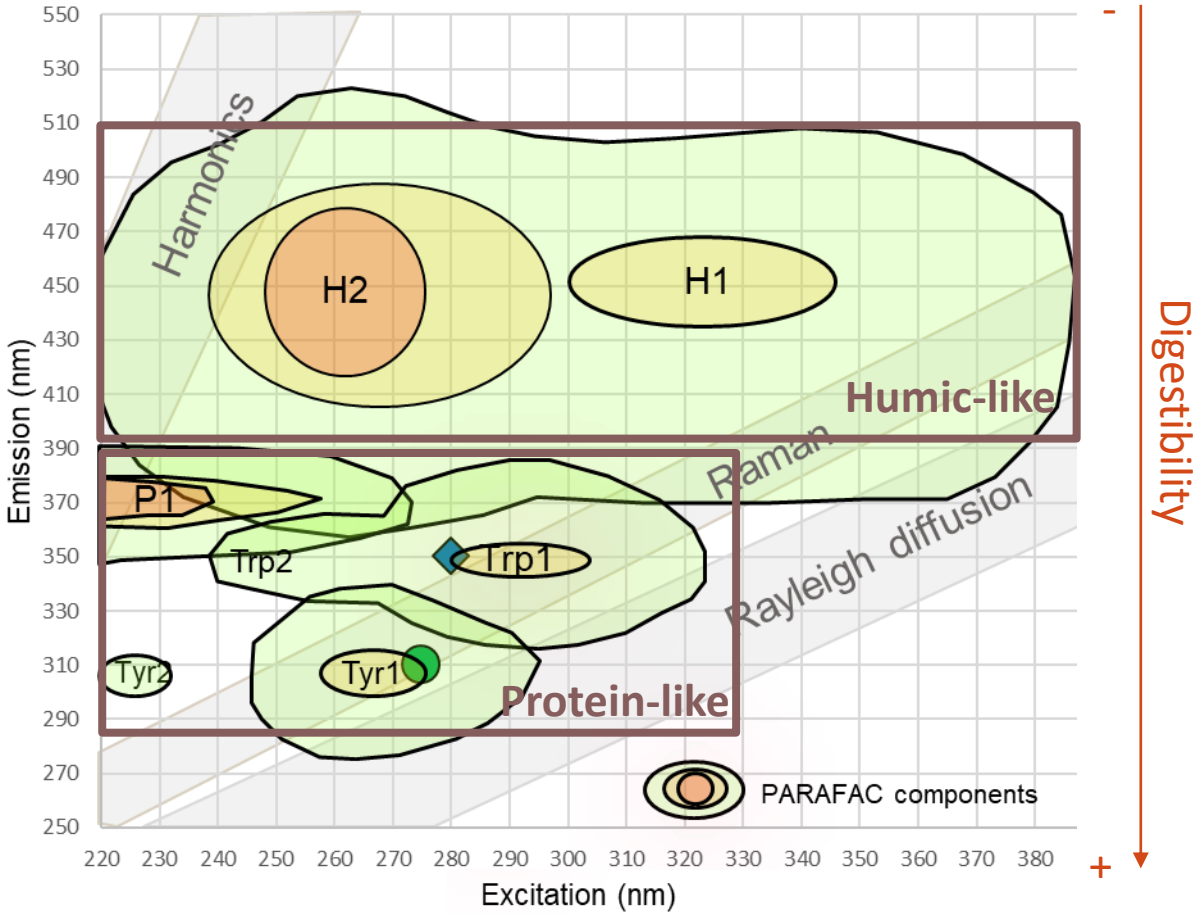

## Transit Time index (TTi)

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

TTi ≈ 1 → « long » transit time
TTi ≈ 0 → short transit time

*Serène et al., 2022*

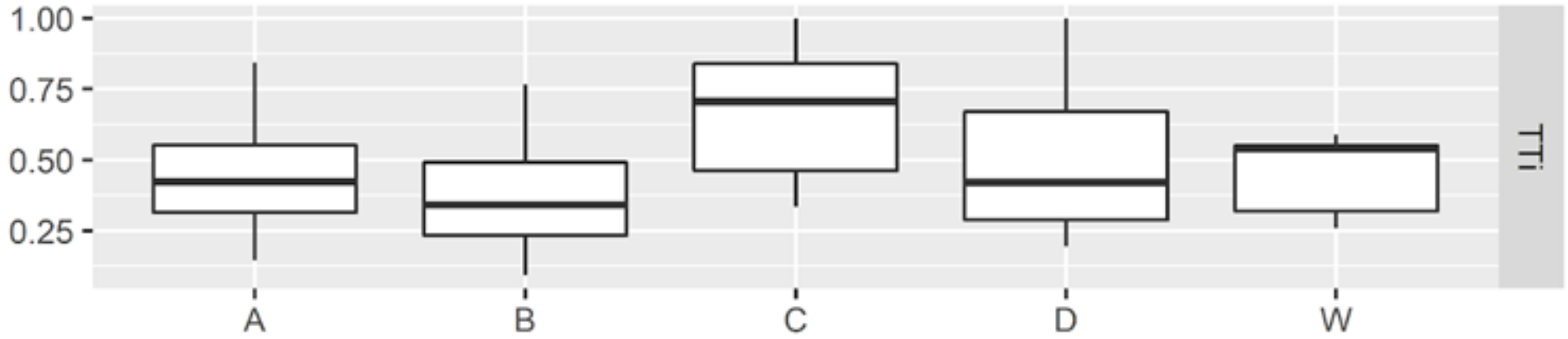
# Transit Time index (TTi)




## TTi calculation in our water samples

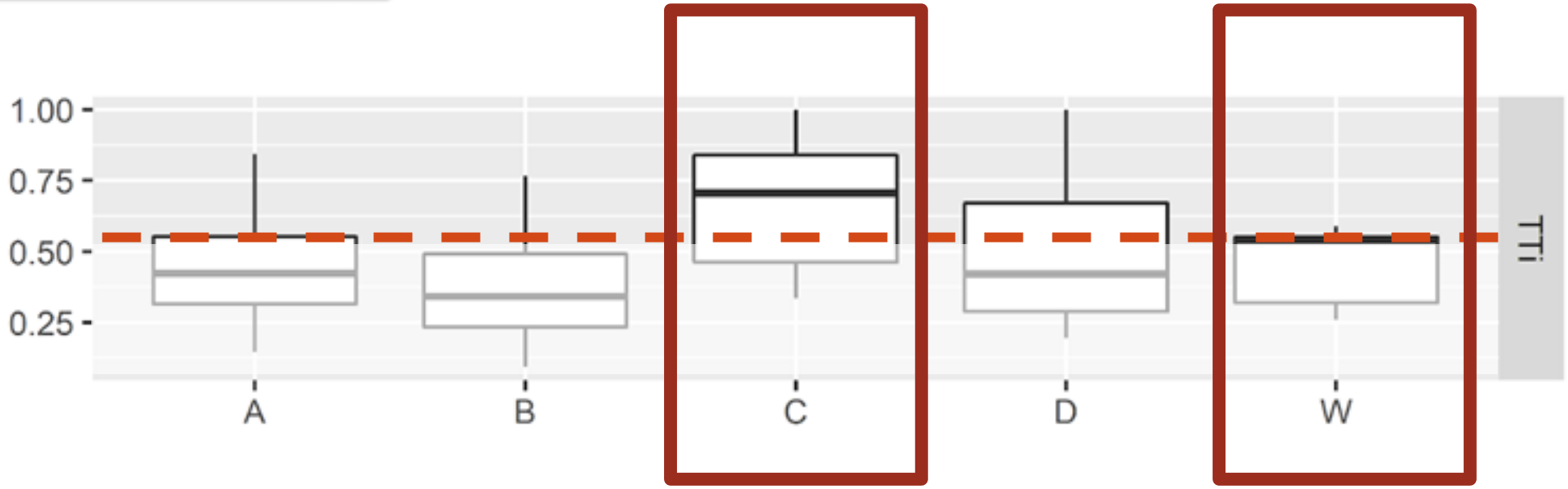
$$TTi = \frac{Humic\ (H1\ \&\ H2)}{Humic\ (H1\ \&\ H2) + proteic\ (Tyr, Trp, P1)}$$

# Transit Time index (TTi)



# Transit Time index (TTi)

Longer transit time for C, W while they are temporaries



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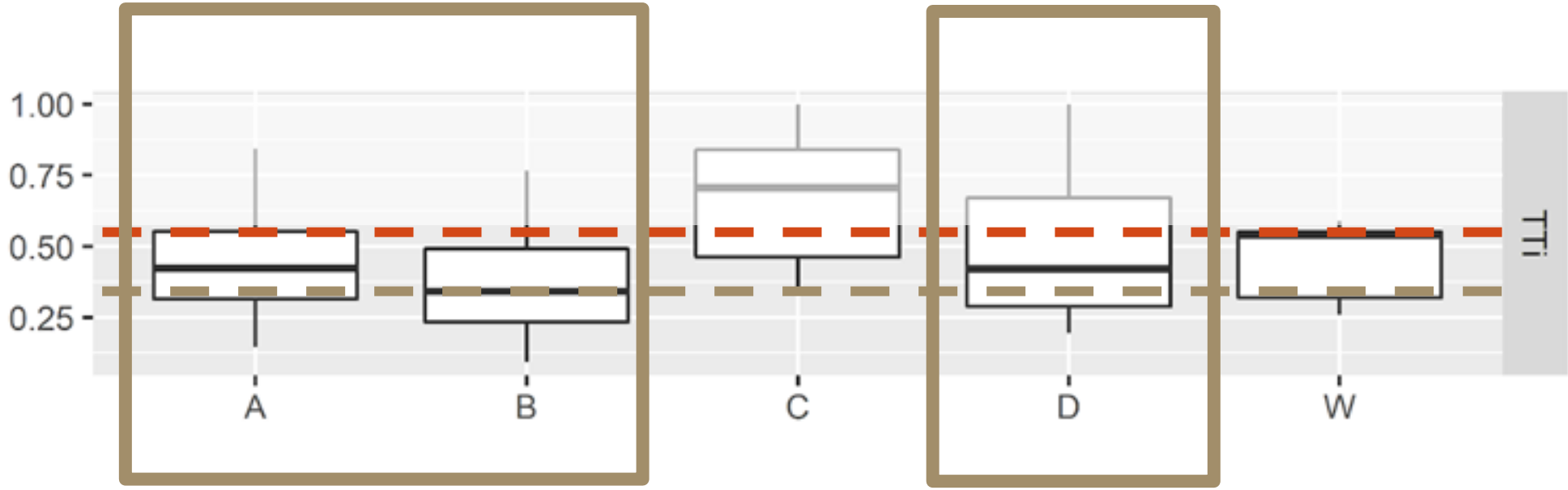


Shorter transit time for B, A and D while they are perenials

# Correlations & Tti : is there a match?

| | W | A | B | C | D |
|---|---|---|---|---|---|
| **TTi** | 2nd Longer transit time | Mid transit time | Shorter transit time | Longer transit time | Mid transit time |
| **Correlations** | All correlated: Very short transit time | H and Trp correlation: Mix of waters? | Trp and P1 correlation : Short transit time | | |

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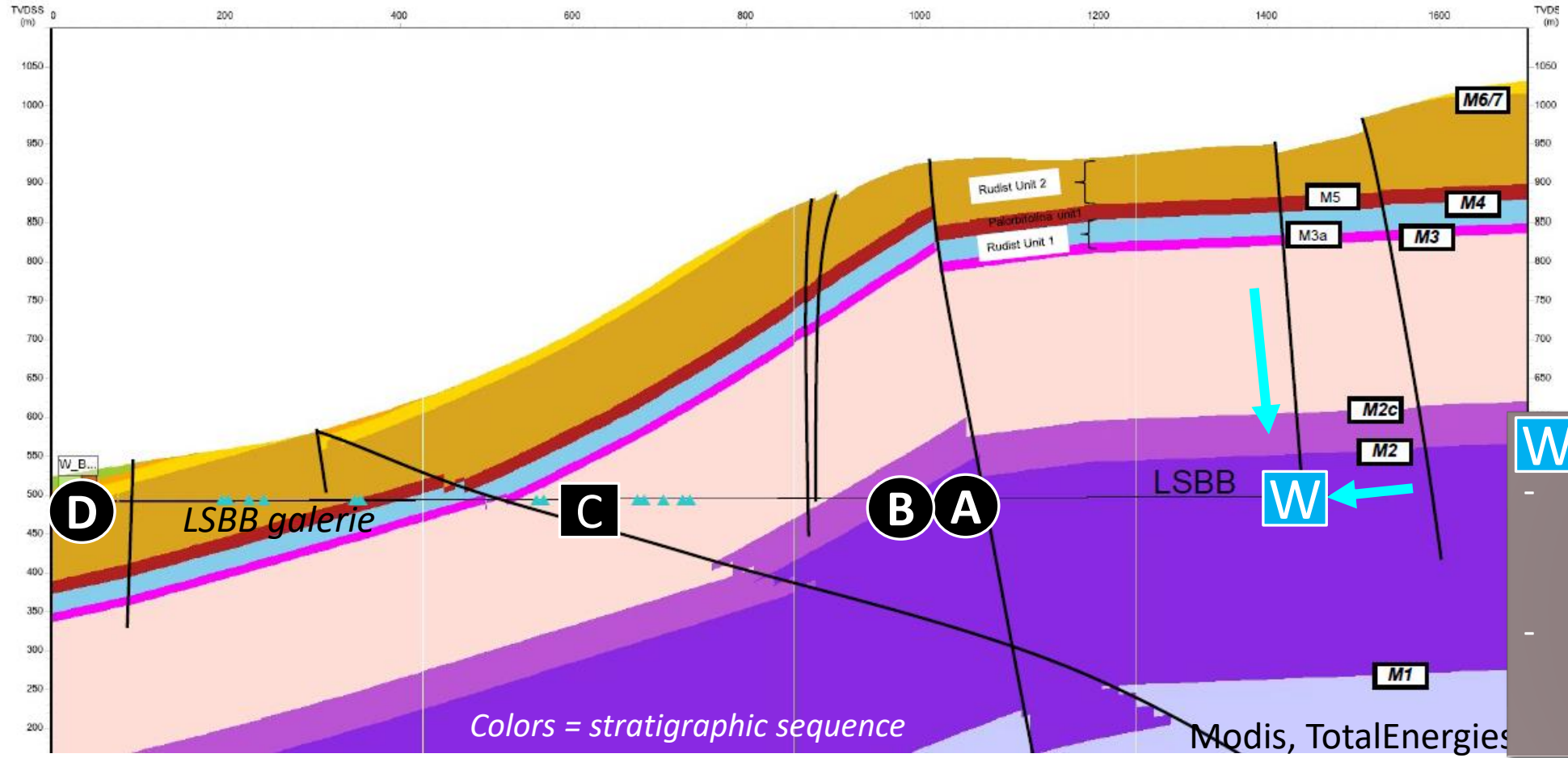
**Opposite characteristics for temporary flows**

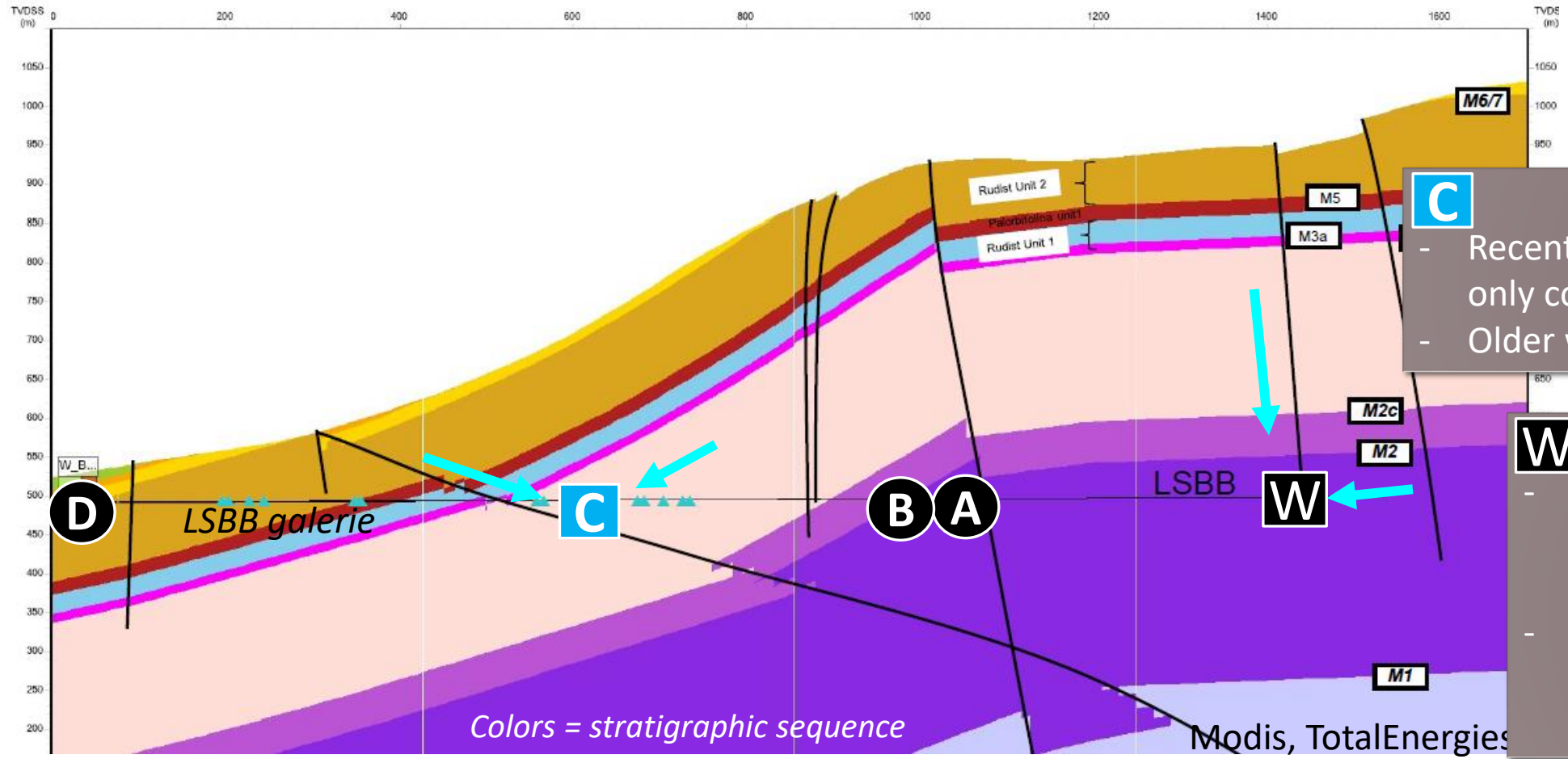
# Hydrodynamic model of flows




**W** Mix between:

- Fast flows coming by the fault → high correlation between compounds
- Old water stored → High TTi because high humic proportion

# Hydrodynamic model of flows




**C**

Mix between:

- Recent water coming by the fault → only correlation between Trp and P1
- Older water stored → highest TTi

**W**

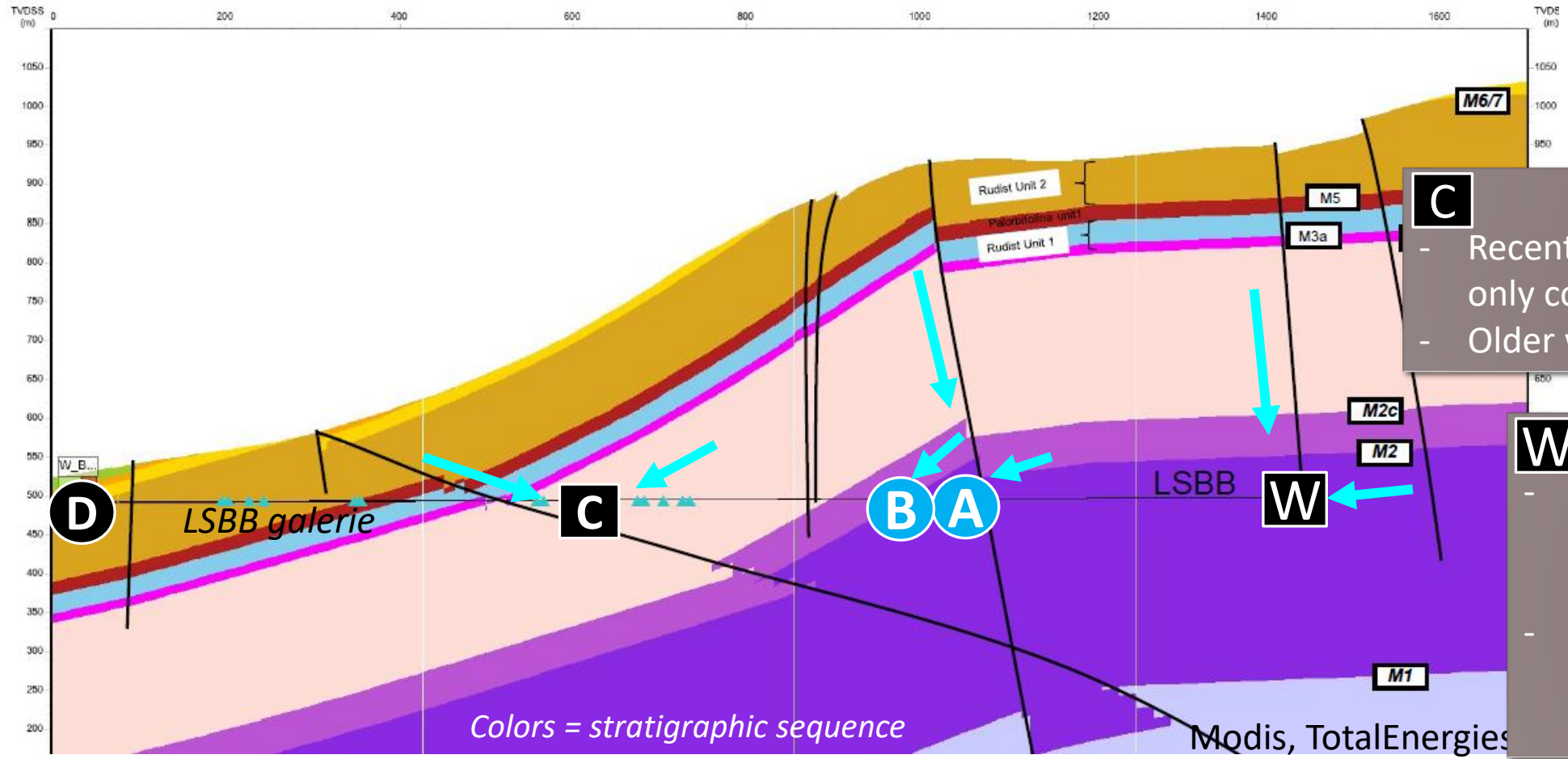
Mix between:

- Fast flows coming by the fault → high correlation between compounds
- Old water stored → High TTi because high humic proportion

# Hydrodynamic model of flows

**B** Mix between:
- Fast flows coming by the fault → Lowest TTi
- Older water stored → only correlation between Trp and P1

**A** Mix between:
- Fast flows coming by the fault → Low TTi
- Older water stored → only correlation between Trp and P1

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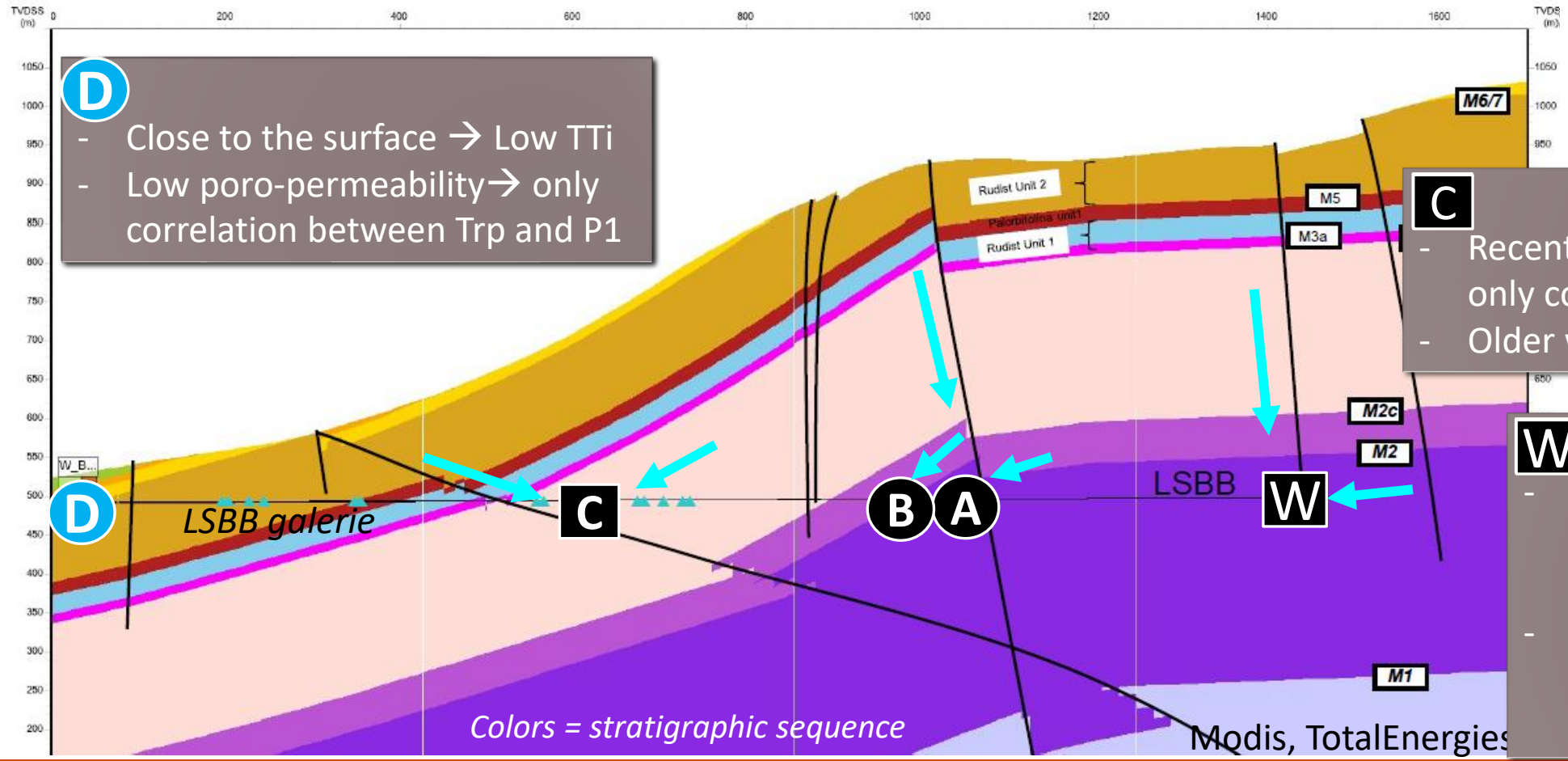


**D**
- Close to the surface → Low TTi
- Low poro-permeability→ only correlation between Trp and P1

**C** Mix between:
- Recent water coming by the fault → only correlation between Trp and P1
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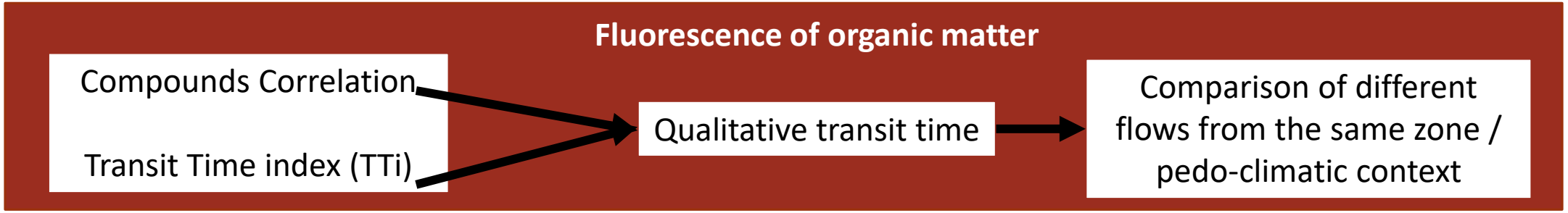
# Conclusions & perspectives



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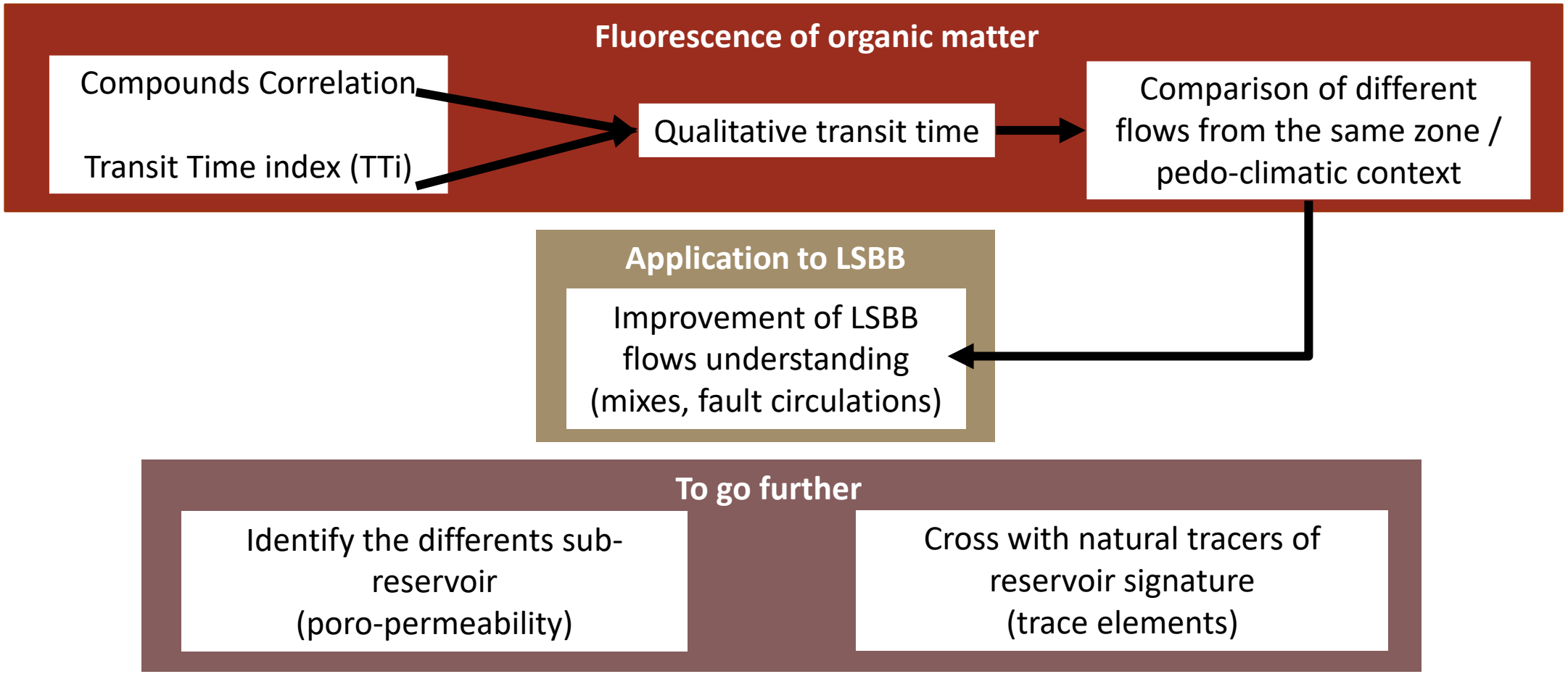

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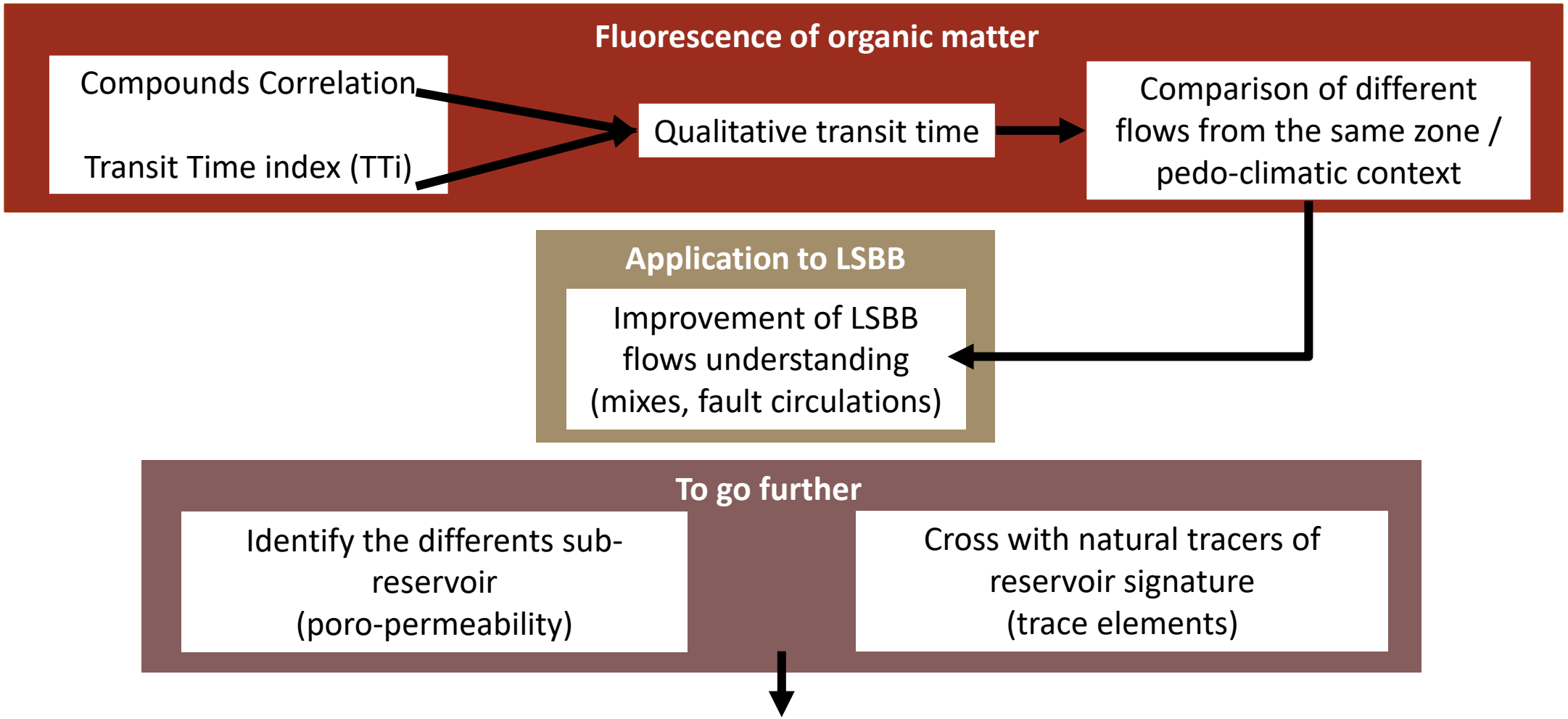

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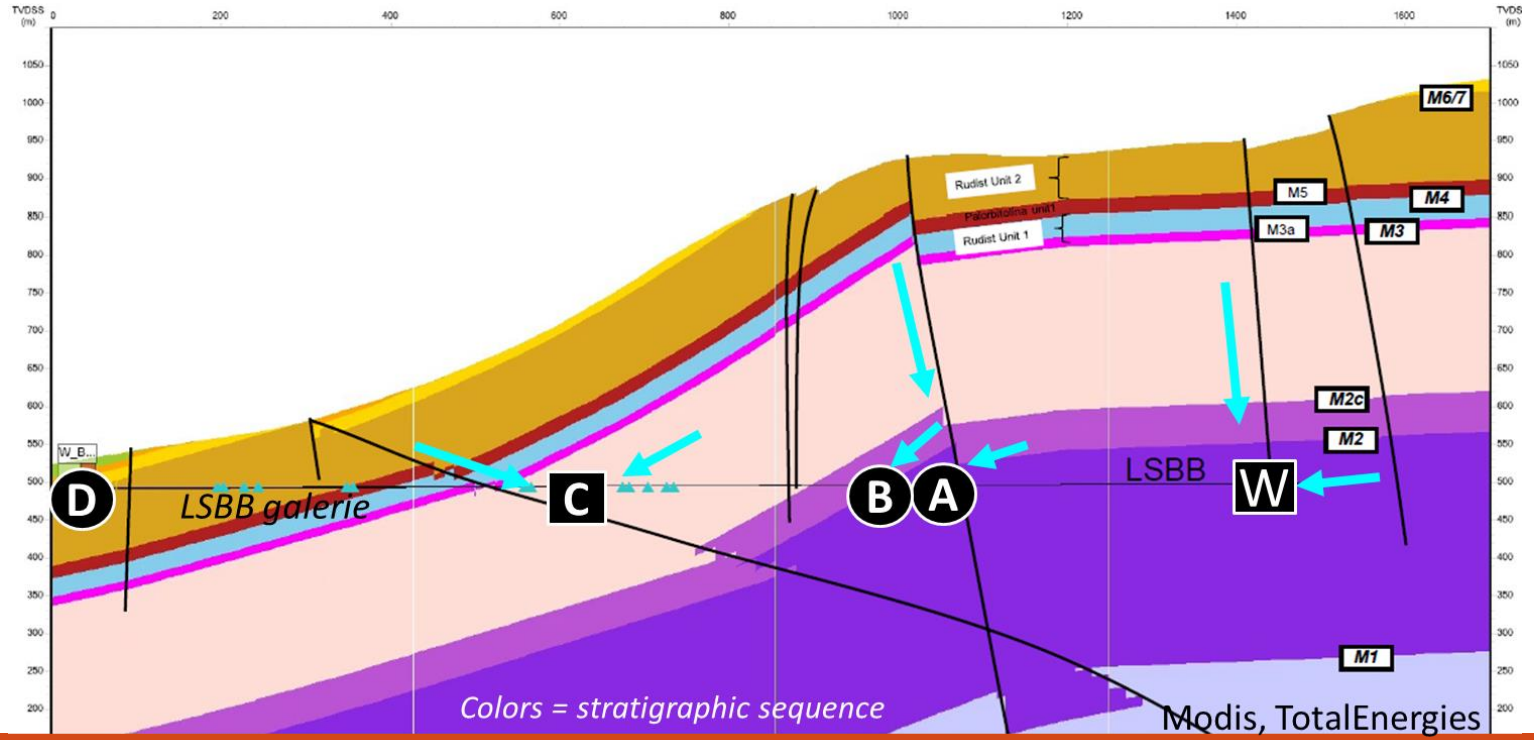


TTi and fluorescent correlation compounds

→ Qualitative transit time

→ Improvement of LSBB's flows characterization