# Relationships between natural fluorescence and organic matter content based on sampling and *in-situ* monitoring of groundwater. Application to a Mediterranean karst system

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## Get off to a good start...

The **Total Organic Carbon** (**TOC**) is the sum of dissolved and particulate organic carbon found in water.

The **Natural Organic Matter** (**NOM**) is the amount of hydrocarbon compounds, from natural and anthropogenic sources, in water. There are 2 principal groups of organic compounds: ❖**Humic-like compounds (H1, H2)**→ decomposition of plant material (1)

❖**Protein-like compounds (P1)** → microbial activity (2)

Continuous monitoring of TOC can be used to enhance the understanding of flow paths in karst systems and their vulnerability face to pollution. A better understanding of the relation between NOM fluorescence and TOC contents could define new indicators of water quality and hydrodynamic/hydrochemical responses of these hydrosystems. This study aims to characterize this relationship in the Lez karstic system (SE France) which is developed in fractured and karstified limestone formations dating from the upper Jurassic and lower Cretaceous.

## Punctual monitoring using 3D spectrofluorimetry

### Excitation/Emission fluorescence Matrix (EEM) (fig.1)

❖ Pic location → type of compound (**H1, H2, P1**)

❖ Pic intensity expressed in arbitrary units (a.u.) → concentration in sample

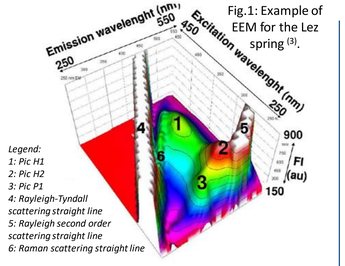



Fig.1: Example of EEM for the Lez spring (3).

### Correlation between TOC & natural fluorescence

Identification of **2 trends** (fig.2) :

1. **High fluorescence** (3000-10000 a.u.) & **low TOC concentration** (1-3 mg/L)
2. **Low fluorescence** (1000-3000 a.u.) & **high TOC concentration** (3-7mg/L)

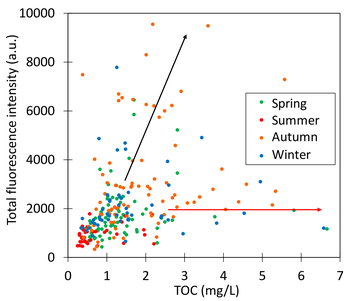



Fig. 2: Relation between total fluorescence intensity maesured by spectrofluorometer 3D SHIMADZU® RF-5301 PC and TOC (202 samples, 05/2007 to 02/2016).

**Complex relationship between NOM fluorescence and TOC, dependent on NOM seasonal variations …**

### Water characteristics constituting the two trends

**Trend 1** (fig.3) :

❖ Recovery flood

❖ Increase of turbidity and TOC concentration, drop in EC and $Mg^{2+}$

❖ Increase of fecal and total coliforms

→ **Rapid infiltration**

**Trend 2** (fig.3) :

❖ Low precipitation, low flow or recession periods

❖ Minimum EC (≈600µS/cm) and bacteriology and high concentration of non-fluorescent NOM

→ **Delayed infiltration**

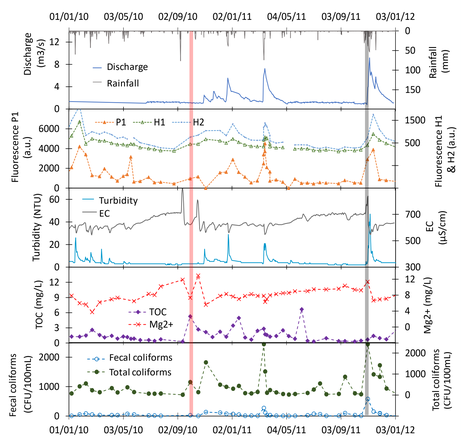



Fig. 3: Temporal variations in fluorescence and physico-chemical parameters (202 samples, 05/2007 to 02/2016). Black and red bands illustrate the most representative samples for trends 1 and 2.

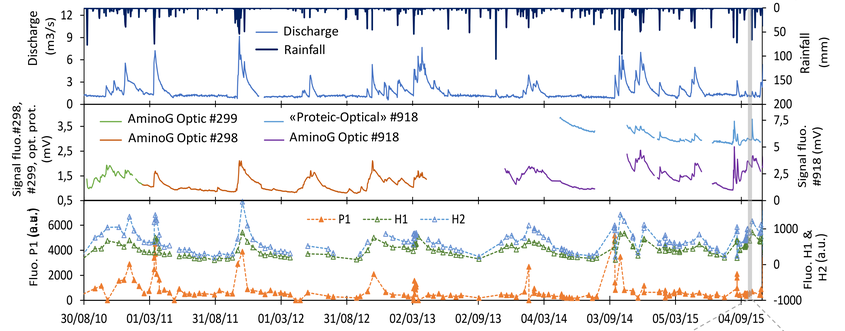
**… but also on hydrodynamic and hydrologic conditions**

## Continuous monitoring by field fluorometers

**Continuous monitoring of humic-like compounds** since April 2010 using field fluorometers (GGUN type from Albillia SARL) (fig.4a)

Fluorometer signal is correlated with the content in humic-like compounds → **Continuous monitoring of humic-like compounds (4)**

Fig. 4: Temporal variations in (a) discharge, rainfall, fluorescence signal measured by field fluorometers #298, #299, #918 and fluorescence measured in laboratory and (b) anomaly on 5/10/2015.



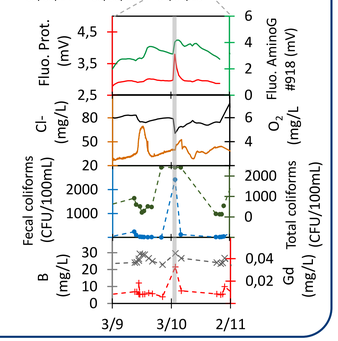

### Continuous monitoring of protein-like compounds

Test of a «proteic-optical» (λEx : 280nm et λEm : 300-400nm) → **not yet available**

**Anomaly on October 5 2016** (fig.4b), **only measured by the «proteic-optical»**

❖ Elevated fecal and total coliforms concentrations, Gd and B concentrations

❖ Increase in EC and decrease in dissolved $O_2$




## Conclusion

EEM analyses show that the relation between TOC and NOM fluorescence depends on NOM seasonal variations, the latter being likely related to hydrologic and hydrodynamic conditions. The continuous monitoring by field fluorometers allows humic-like compounds, but the continuous monitoring of protein-like compounds remains complex. However, the «proteic-optical» test used here seems able to detect some specific contaminations.

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(2) Parlanti, E. et al., 2000. Dissolved organic matter fluorescence spectroscopy as a tool to estimate biological activity in a coastal zone submitted to anthropogenic inputs. Org. Geochem. 31, 1765–1781.

(3) Batiot-Guilhe, C. et al., 2008. Characterisation of underground flows in karstic aquifers by studying DOM fluorescence. Example of two Mediterranean systems (Lez and Causse d'Aumelas, Southeastern France). Presented at the 13th IWRA World Water Congress, Montpellier.

(4) Durepaire, X. et al., 2014. Suivi en continu de la MON fluorescente à l'aide d'un fluorimètre de terrain. Implications pour le suivi des traçages artificiels. Poster présenté à la 24e Réunion des Sciences de la Terre, Pau.