ECWS-5

5th International Electronic Conference on Water Sciences

# What can we learn about hydrochemical dynamics of streamwater during flood events in a forested karstic catchment from the Pyrenees Mountains (Southwestern France)?

F. Ulloa-Cedamanos[1,2,3], A. Probst[1,2,3], V. Dos-Santos[1,2,3], J.-L. Probst[1,2,3]

[1] Laboratory of Functional Ecology and Environment, University of Toulouse, CNRS, Toulouse, France

[2] LTSER Zone Atelier Pyrénées-Garonne, CNRS, University of Toulouse, France

[3] LTER Bassin versant du Baget, SNO Karst, IR OZCAR, CNRS, University of Toulouse, France

Laboratoire écologie fonctionnelle et environnement

Zones Ateliers LTSER FRANCE PYRÉNÉES GARONNE

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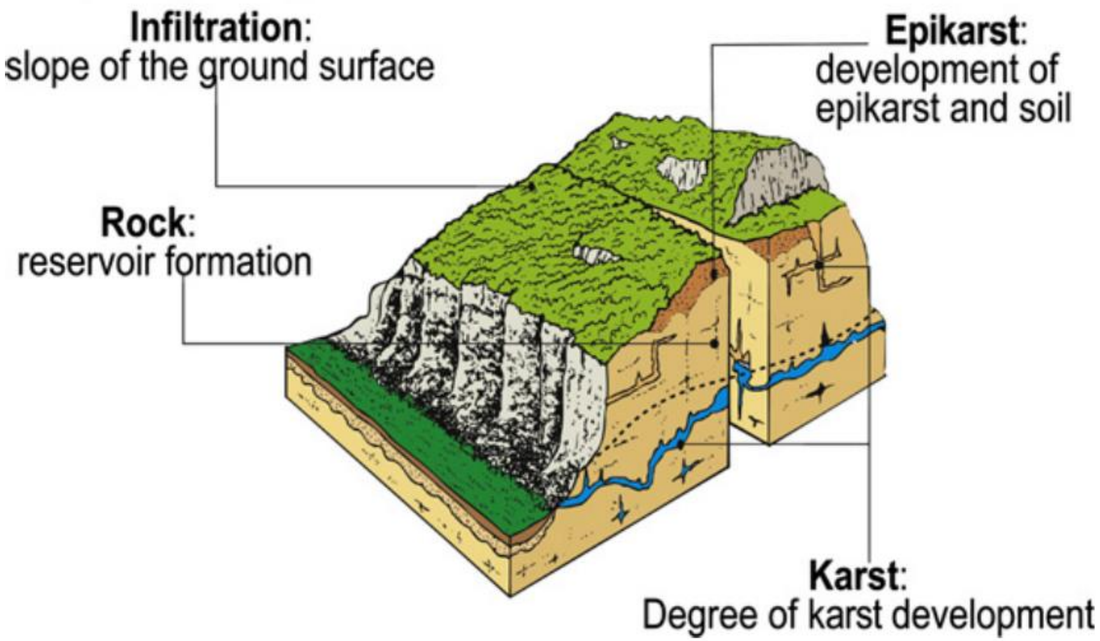
KARST

@Ulloa-Cedamanos

## Karst systems




*Daher et al., 2011*

**Sensitive to climate change and to environmental perturbations**

- ❑ Very fast water and contaminant transfer times
- ❑ Low filtering role of the infiltration zone
- ❑ Limited contaminant removal processes

## Nutrient source

Their chemical alteration: 45 - 60% of the dissolved elements transported to the ocean (80% for $Ca^{2+}$)

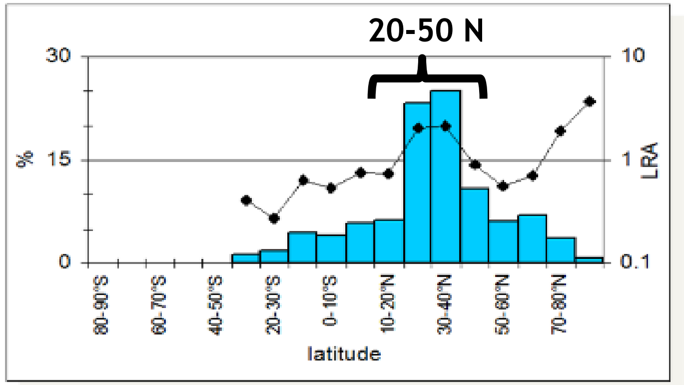
*Gaillardet et al., 1999*

## Water resources

25% of the water used for drinking water supply

*Ford and Williams et al., 2007*

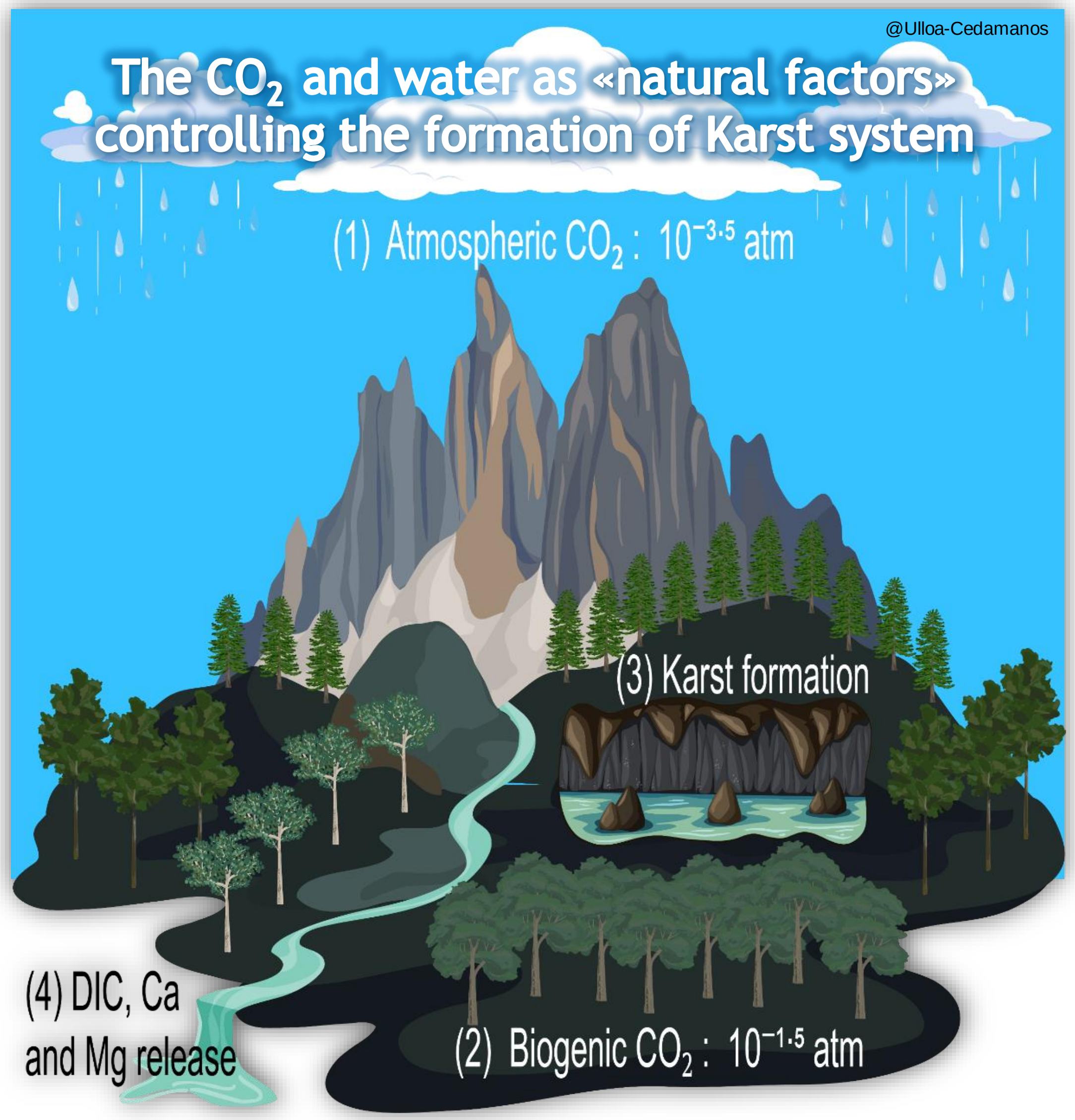
## Global karst distribution




*Amiotte Suchet et al., 2003*

Carbonates: 10-14% of the continental surface area

*Chen et al., 2017*




$$CaCO_3 + CO_2 + H_2O \Leftrightarrow Ca^{2+} + HCO_3^- + HCO_3^-$$

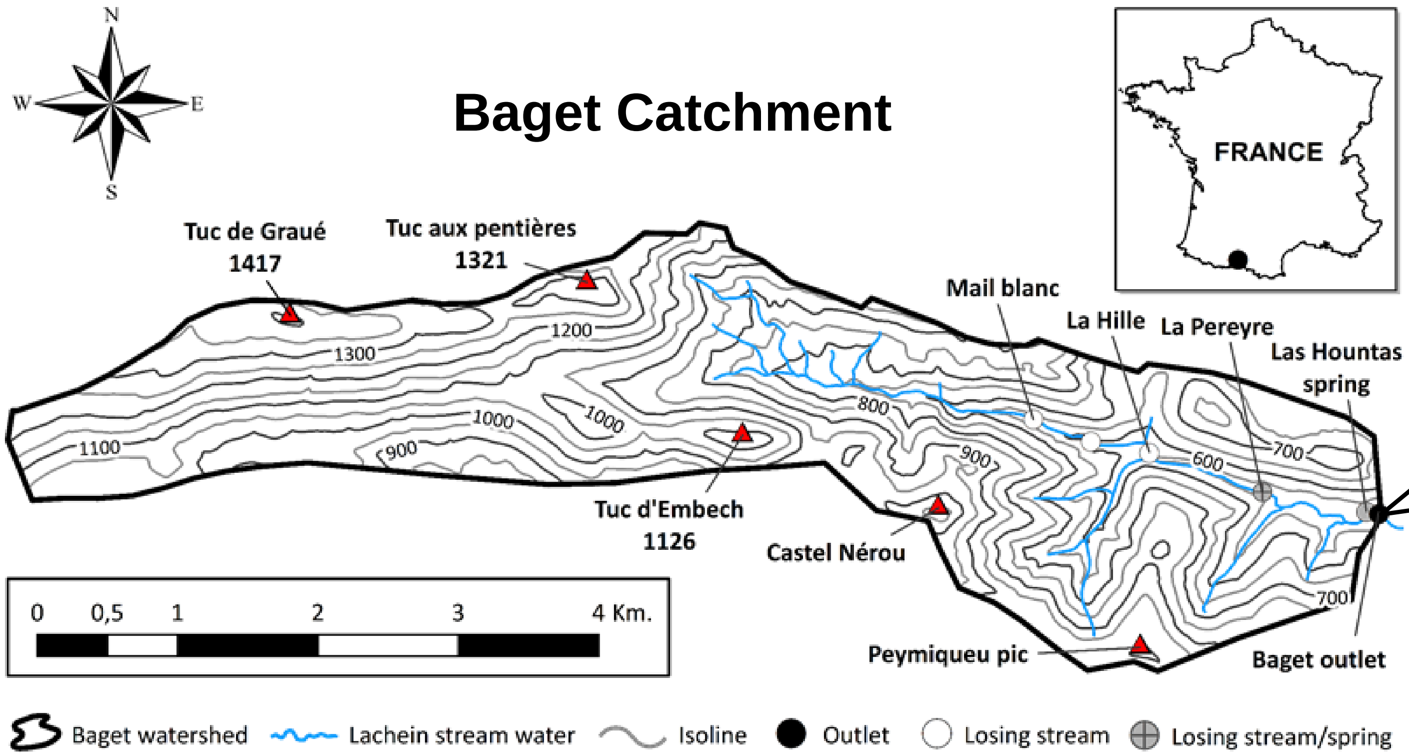
## Flood events

Variations in hydrological conditions → Chemodynamic and hysteresis behaviors of major element concentrations

*Musolff et al., 2015*

## OBJECTIVES

1. **Investigate the sensitivity of water chemistry to sudden hydrological variation**
2. **Quantify each flow component of the runoff under rainstorm conditions**
3. **Understand the hysteresis behaviors**
4. **Elucidate the dominant controls on changes in hydrochemistry during rainstorm events**

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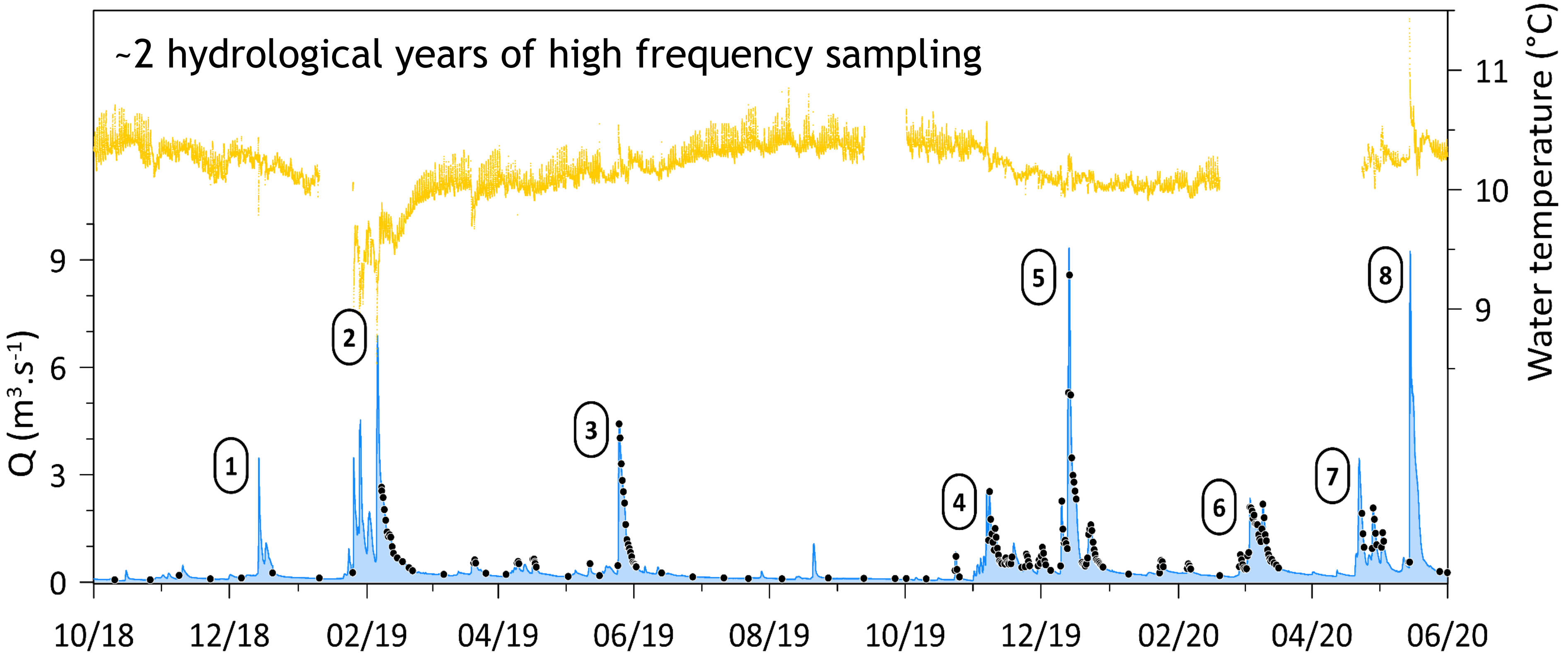
- ❑ Small (13 Km$^2$) karstic watershed
- ❑ Quasi-pristine (not polluted)
- ❑ Rainfall regime : early winter and late spring
- ❑ Predominant forest land cover (67% in 2019)
- ❑ Multilithological basin, mainly carbonate rocks

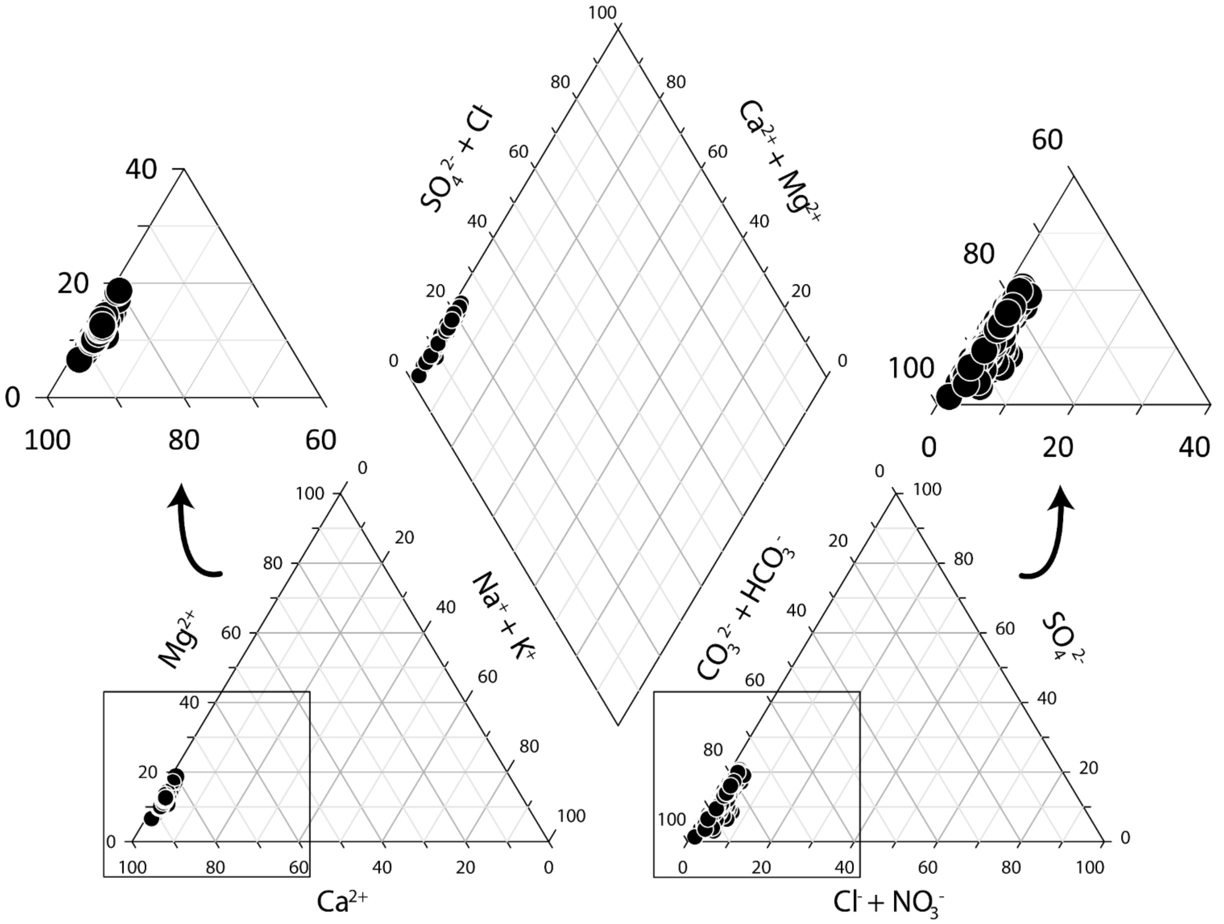
# Hydrochemical characteristics

How about some results ?




Water temperature (T) and discharge (Q) exhibited a clear seasonality, with a higher variability for discharge.

# Hydrochemical characteristics




*Ulloa-Cedamanos et al., 2020*

The water chemistry exhibited the following pattern:

**Cations:**

$Ca^{2+}$ (89%) >> $Mg^{2+}$ (10%) >> $Na^+$ (1%) > $K^+$ (0.4%)

**Anions:**

$HCO_3^-$ (93%) >> $SO_4^{2-}$ (5%) > $Cl^-$ (1%) > $NO_3^-$ (1%)

## Carbonate Lithology

*water* MDPI

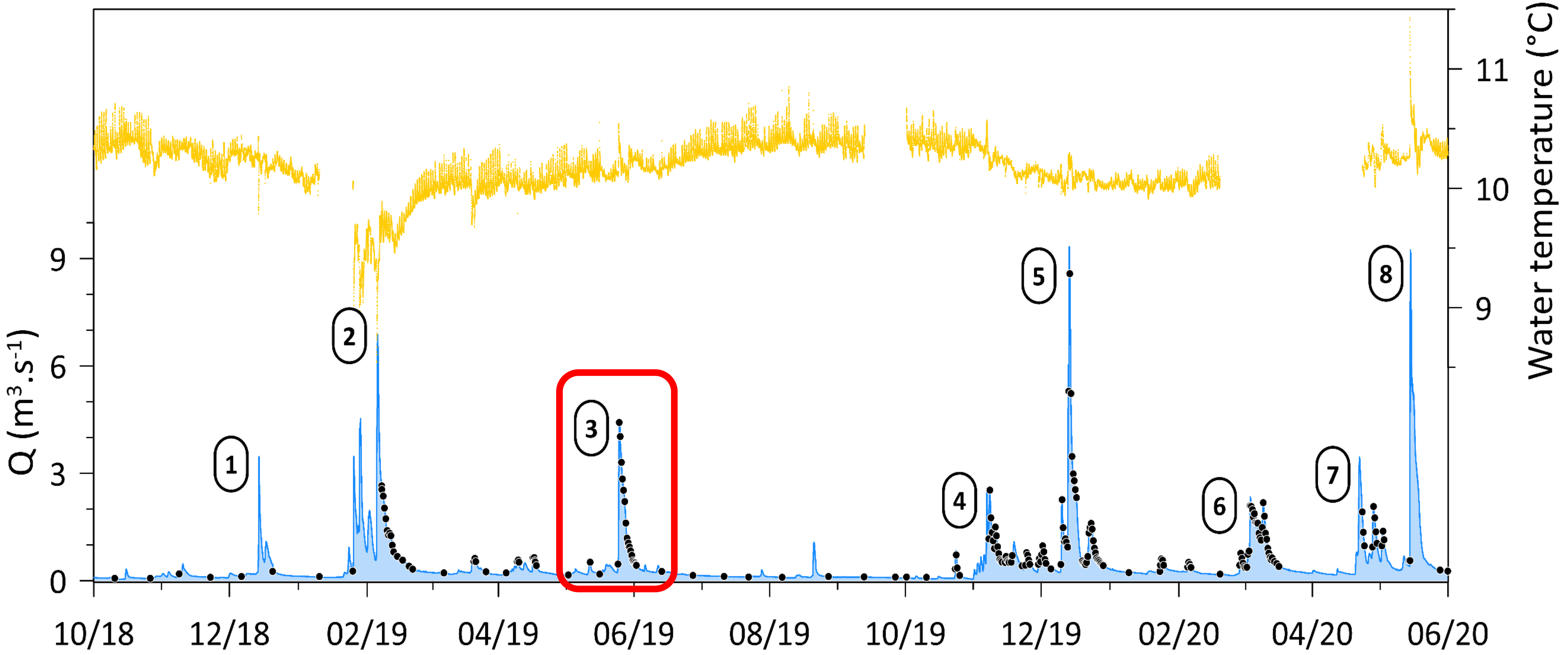
*Article*

**A Forty-Year Karstic Critical Zone Survey (Baget Catchment, Pyrenees-France): Lithologic and Hydroclimatic Controls on Seasonal and Inter-Annual Variations of Stream Water Chemical Composition, $pCO_2$, and Carbonate Equilibrium**

Francesco Ulloa-Cedamanos [1,2,3,*], Jean-Luc Probst [1,2,3], Stephane Binet [1,4], Thierry Camboulive [1,2,3], Virginie Payre-Suc [1,2,3], Corinne Pautot [1,2,3], Michel Bakalowicz [5], Sandra Beranger [6] and Anne Probst [1,2,3,*]

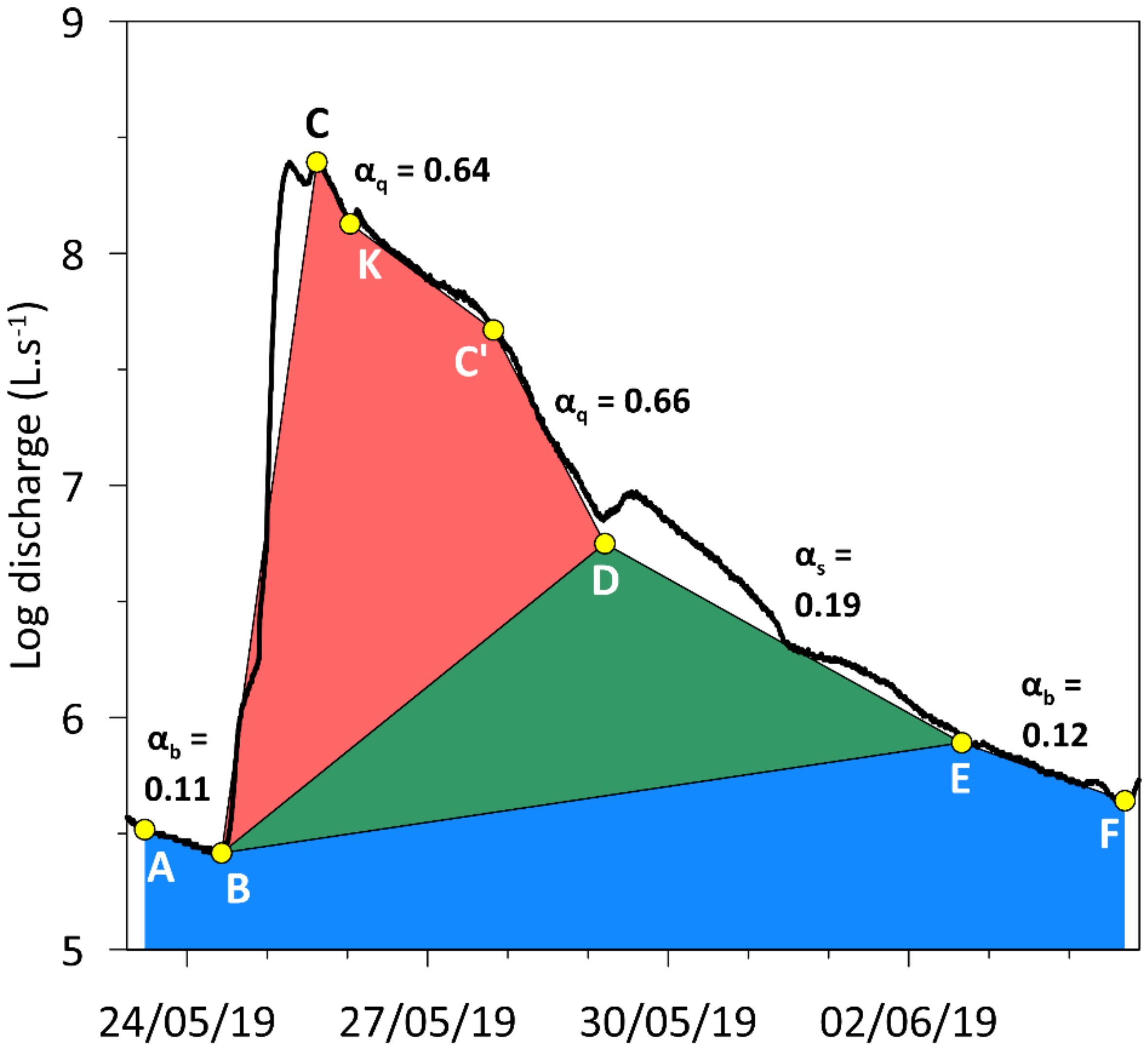
# Separation of the flood flow components

Focus on the flood event No. 3




"Representative" intensity/magnitude + Not influenced by past and/or successive floods + Recession period is not disturbed

# Separation of the flood flow components




Hydrograph separation of the flood event No.3

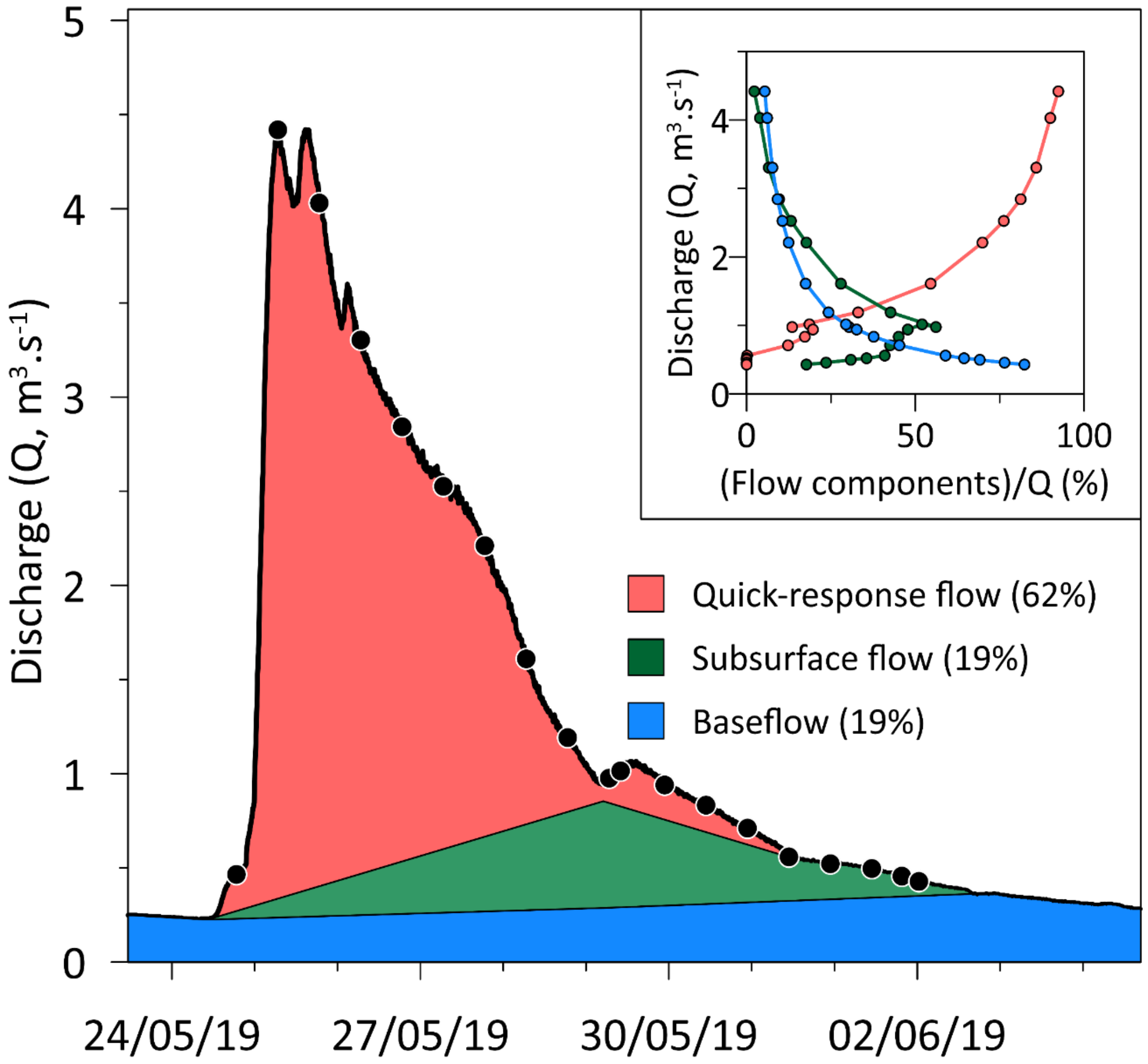
**Three distinct recession coefficients**

- The quick-response flow ($\alpha_q$ : 0.64 – 0.66)
- The subsurface flow ($\alpha_s$ : 0.19)
- The baseflow ($\alpha_b$ : 0.11 – 0.12)

**Analysis of the other flood events**

- The quick-response flow ($\alpha_q$ : 0.80 – 0.40)
- The subsurface flow ($\alpha_s$ : 0.20 – 0.10)
- The baseflow ($\alpha_b$ : 0.12 – 0.04)

# Separation of the flood flow components




**Dominant flows:**

- ❑ The quick-response flow

  up to discharges higher than 1.5 $m^3.s^{-1}$

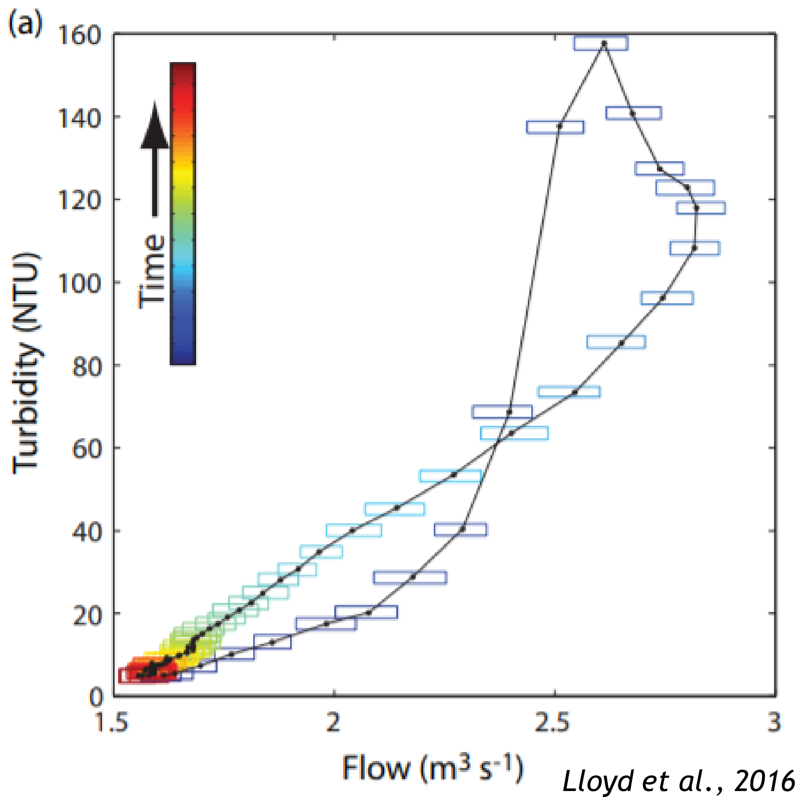
- ❑ The subsurface flow

  discharges close to 1 $m^3.s^{-1}$

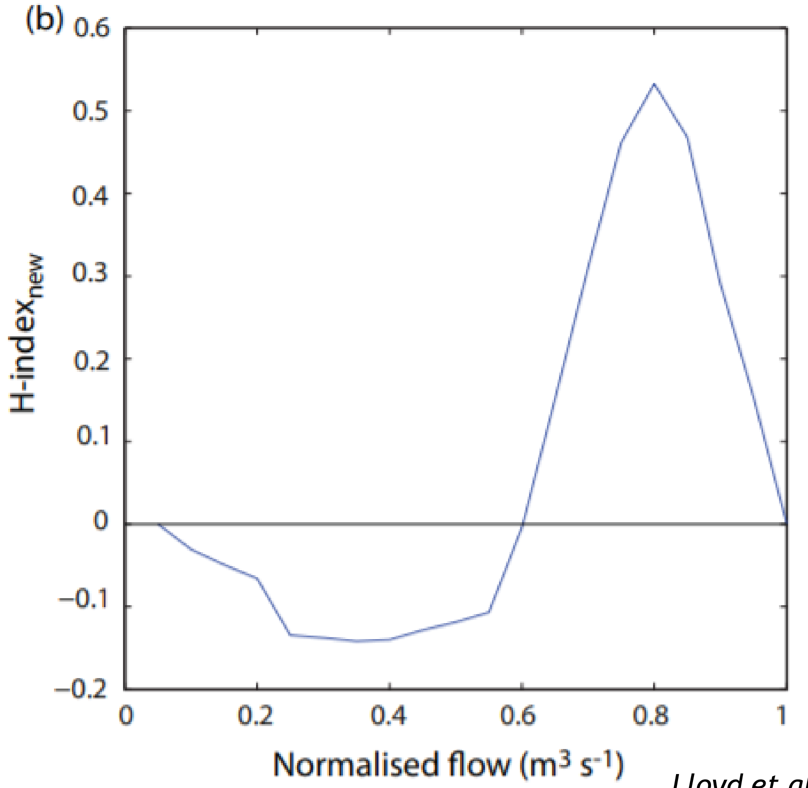
- ❑ The baseflow

  discharges lower than 0.65 $m^3.s^{-1}$

# C-Q relationships : Hysteresis analysis



*Lloyd et al., 2016*



*Lloyd et al., 2016*

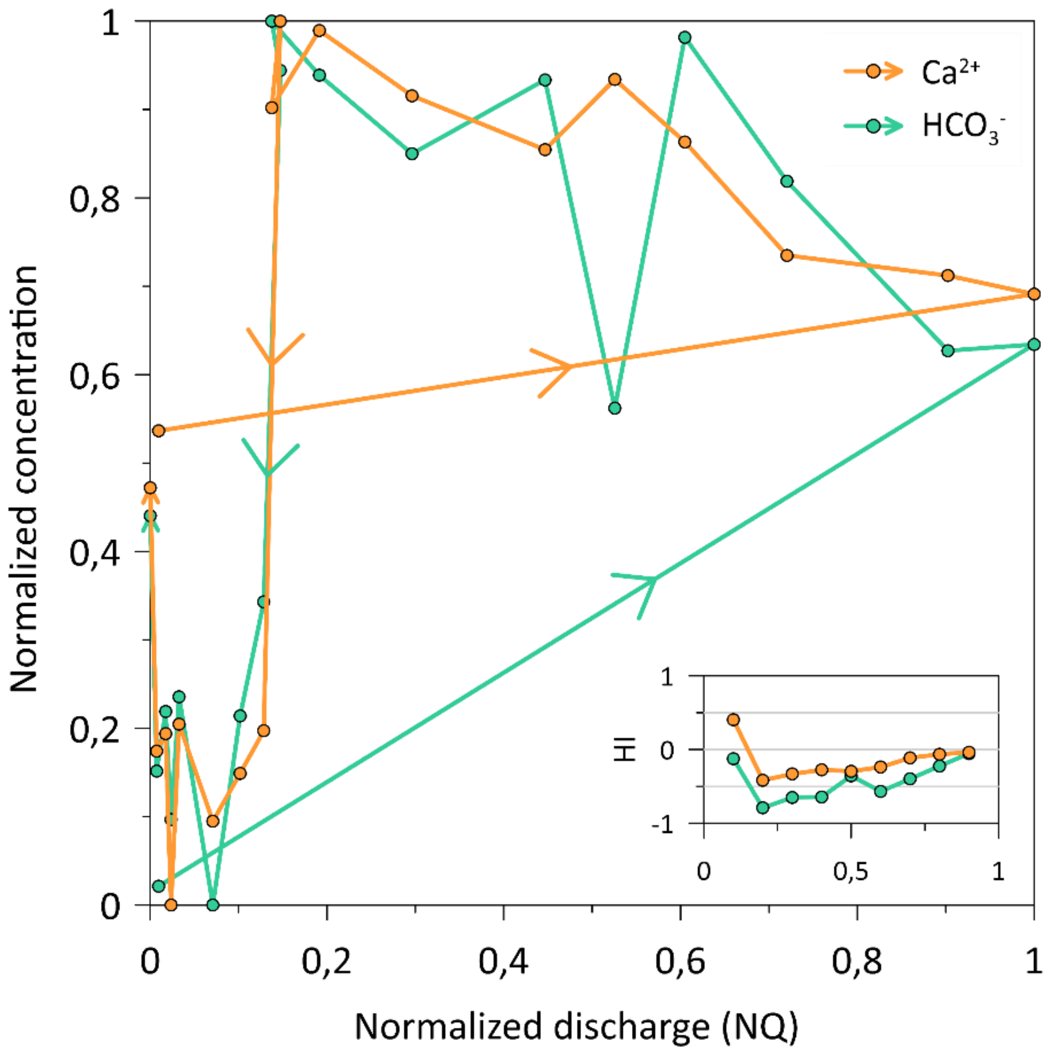
**Data Normalization**

$$\text{Norm.}\, Q_i = (Q_i - Q_{min})/(Q_{max} - Q_{min})$$

**Hysteresis Index (HI)**

$$HI = \text{Norm.}\, C_{i-Rising\ Limb} - \text{Norm.}\, C_{i-Falling\ Limb}$$

# C-Q relationships : Hysteresis analysis



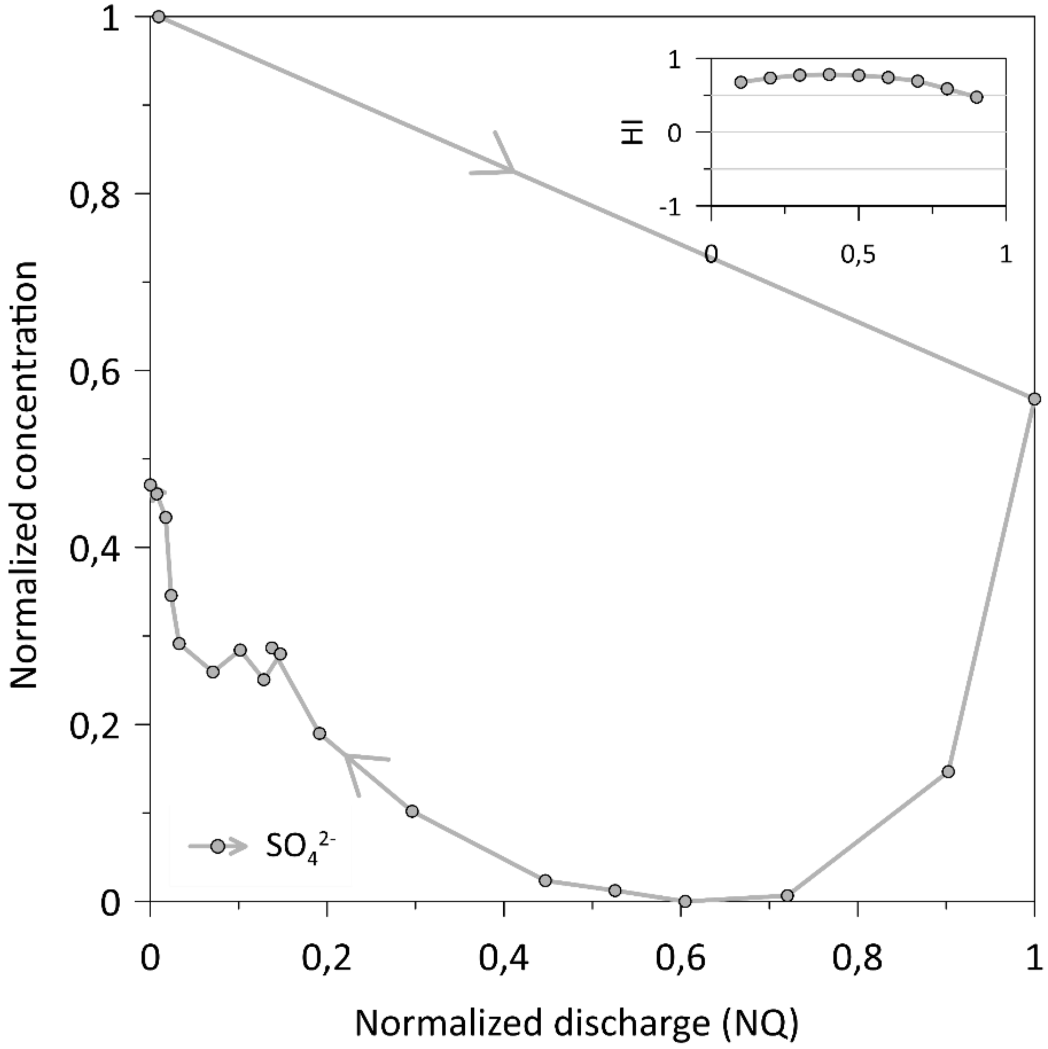

- ❑ $Ca^{2+}$ and $HCO_3^-$ displayed an overall **chemostatic behavior**.

Low-concentration in rainwater input ⟷ counterbalance ⟷ Rapid kinetic of carbonate dissolution with biogenic $CO_2$

- ❑ Only $Ca^{2+}$ and $HCO_3^-$ exhibited **counterclockwise** trajectories.

- ❑ $Ca^{+}$ and $HCO_3^-$ showed an upward trend until the end of the quick-response flow composed by the **karst flow.**

# C-Q relationships : Hysteresis analysis



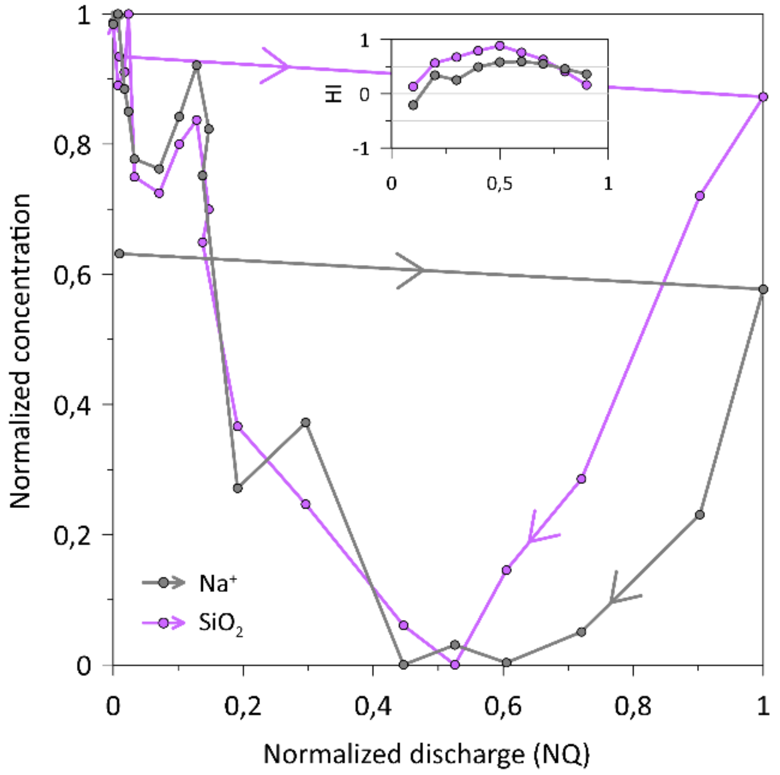

- Sulphate comes from the **gypsum dissolution** ($CaSO_4$), and to a lesser extent from pyrite oxidation ($Fe_2S$) and atmospheric contribution.

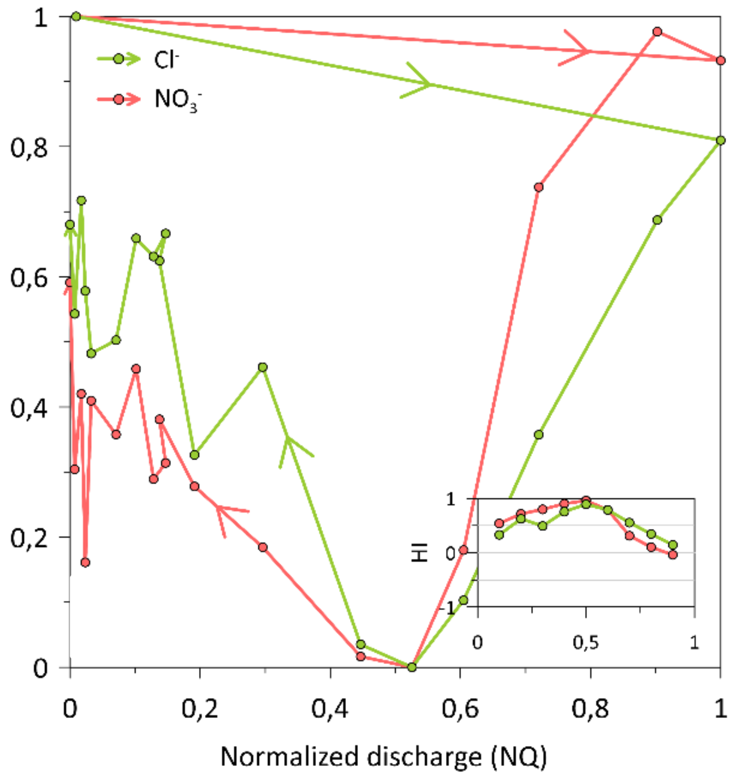
Ulloa-Cedamanos et al., 2020

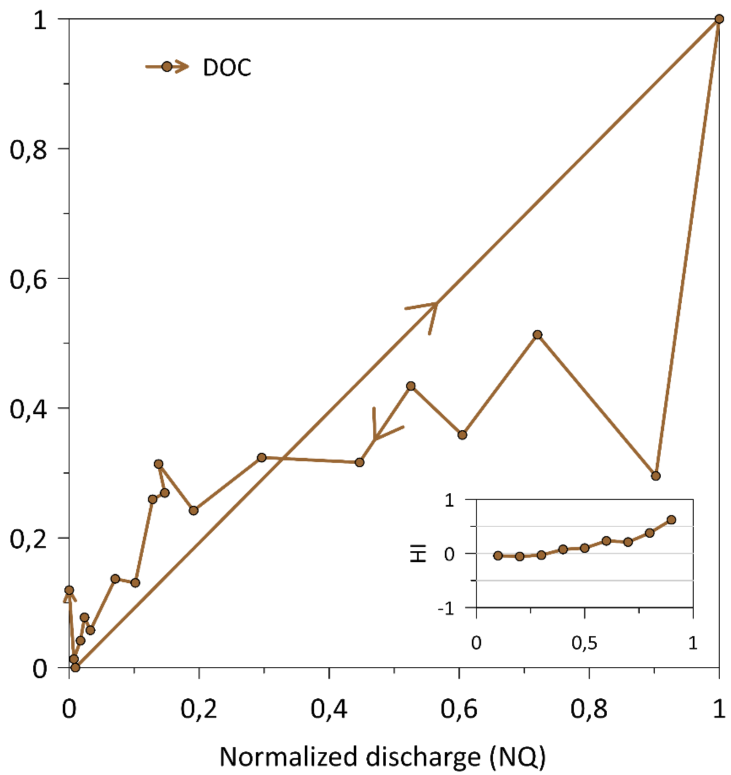
- Sulphate exhibited a **strong dilution effect**.

- The analysis of C-Q relationship revealed **slower outputs** or **reduced amounts** of this anion in the catchment.

# C-Q relationships : Hysteresis analysis




Similarity of the hysteresis pattern between $SiO_2$ and $Na^+$ suggest the weathering of **silicate rocks** as a **source** of $Na^+$.

Leaching of the fir and beech forest, a quick access source of $NO_3^-$, would **compensate** the **sudden increase** in **discharge**.

**Source** of DOC mobilized during flood events (**surface of soils** : plant litter) and a regulation by a **transport-limited regime**.


- $Ca^{2+}$ and $HCO_3^-$ exhibited an **chemostatic behavior** based on a control by **process-limited regime**.
- $Ca^{2+}$ and $HCO_3^-$ increase during the quick-response flow due to the **karst flow contribution**.
- $SO_4^{2-}$ displayed a **strong rainwater dilution**, linked to a slower outputs and/or reduced amount sources.
- A **source** of DOC is mobilized during flood events (**surface of soils**) and it is regulated by a **transport-limited regime**.
- The fast mobilization and the antecedent hydrological conditions **deplete** the **reserves** of dissolved elements and **delay** a **quick return** to the **initial conditions**.

# Thank you for your attention

Does anyone have any questions?

Ph.D. student Francesco Ulloa-Cedamanos
fulloace@inp-toulouse.fr