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# ENVIRONMENTAL TRACING, AN INDICATOR FOR HETEROGENEITIES OF THE KARST HYDROSYSTEM

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## RESUMEN

El medio calcáreo contiene masas de agua discontinuas, yendo de las capas acuíferas casihomogéneas fisuradas a las muy carstificadas, en función de su historia geológica.

Se puede clasificar tres niveles de heterogeneidades en sectores carbonatados: la vertical, con una zona no saturada separada en el epikarst y la zona no saturada que se extiende sobre la zona saturada, spacial con bloques microfisuradas oreados por conductos y subsistemas anexo-a-drenes, en la recarga con la infiltración difusa, localmente concentrada en depresiones del karst, y finalmente la recarga puntual en ponors.

Este grande diversidad, gracias a las condiciones geoquímicas variadas producidas por las condiciones del medio ambiente (medio abierto o cerrado para oxígeno o gas carbónico, conductividad hidraulica y tiempo de residencia correlacionado,...) permite trazados especificos, visibles a los exutorios del sistema (manantiales, sondeos), a pesar del contexto litológico más bien homogéneo.

**Palabras-llaves:** heterogeneidad, karst, hidroquímica

## ABSTRACT

The calcareous media contains discontinuous groundwater bodies, ranging from fissured quasi-homogeneous aquifers to highly karstified ones, according to their geological history.

Three levels of heterogeneities can be classified in carbonate areas: vertical, with an unsaturated zone splitted into epikarst and unsaturated zone laying upon the saturated zone, spacial with microfissured blocks surrounded by conduits and annex-to-drain subsystems, in the recharge with diffuse infiltration, locally concentrated in karst depressions, and finally pin-point recharge in ponors.

This huge diversity, because of variable geochemical conditions induced by environmental conditions (open or closed media vs oxygen or carbon dioxide, hydraulic conductivity and related residence time,...) is able to set specific tracings, visible at the outlets of the system (springs, boreholes), despite the rather homogeneous lithological context.

**Key words:** heterogeneity, karst, hydrochemistry

## 1. THEORETICAL ROLE OF THE DIFFERENT HETEROGENEOUS ENTITIES IN THE KARST HYDROSYSTEM

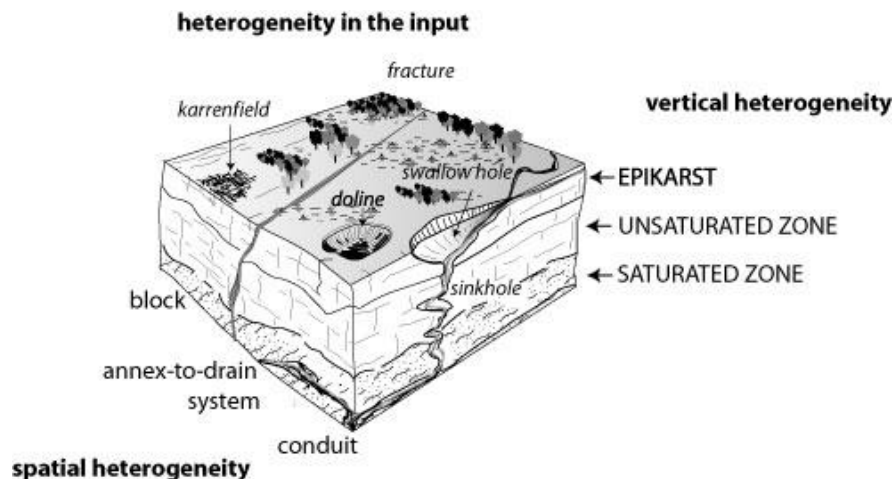


Fig. 1 : Three types of heterogeneities in the karst hydrosystem (after Gilli *et al.*, 2004)

### *1.1. Tracing the spatial heterogeneity*

The characteristics of the medium consists into (Fig. 1):

- lowly permeable fissured blocks, where the flow velocity is low and the contact between rock and water is large (months, years). We can suspect water to be supersaturated with respect to carbonate minerals, calcite and dolomite, and magnesium-rich, because of a sufficient time of contact between water and fissures. Conversely, this medium is poorly open to the gaseous phase of the soil, it then will be poorly oxidizing,
- highly conductive drains, where the residence times are short (hours, days). Water can rapidly outflow, having not time to equilibrate with carbonate minerals. The corrosive character of these waters persists through the whole system. This flow type is well aered and oxic conditions prevail in the conduits,
- annex-to-drain subsystems are voids which are poorly connected to the conduit, but as large cavities, they are open vs soil atmosphere.

### *1.2. Tracing the vertical heterogeneity*

Conversely to several porous classical aquifers, but accordingly to the aquifers which display a weathered shallow layer (basement silicate rocks, weathered marls), the unsaturated part of the aquifer consists in 2 different layers, with different hydrodynamic and geochemical properties:

- the epikarst is a well-open shallow medium, where water infiltrates rapidly. Encountering the less karstified unsaturated zone, water accumulates at its base and flows laterally, until it encounters a vertical discontinuity which enables a shortcut of this underlying layer. As the water table is open to the soil atmosphere, epikarst is a privileged site for evaporation, and then to salt concentration in water. Also epikarst is a place situated close to the pedogenetic soil CO<sub>2</sub> production, and then epikarst is the place of high pCO<sub>2</sub>, that can reach several percents. The consequence is a very active dissolution in that zone, and highly mineralized waters. But this water is not enriched in large residence time tracers (Silica, Mg<sup>2+</sup>, <sup>13</sup>C),
- the unsaturated zone sensu stricto is characterized by mainly vertical flow components, but this layer has different hydraulic and then geochemical properties, according to the spatial heterogeneity (blocks, fractures),
- the saturated zone is the flooded area, its properties are highly dependent on the spatial heterogeneity (blocks, conduits).

### *1.3. Tracing the heterogeneity in recharge*

Three recharge contexts can be observed in karst regions:

- diffuse recharge, water feeds epikarst in every place, mainly in zones devoid of vertical discontinuities. This slow entering into the limestone confers a mixing role to the epikarst. This water percolating slowly from the soil (overlying the limestone or filling the karrens) takes time to dissolve CO<sub>2</sub> and humic acids in the soil,
- locally concentrated recharge, e.g. in dolines. The difference is that these wide solutional forms are generally well connected to vertical fractures, it means that after this infiltration, water gets rapidly through the unsaturated zone towards the water table.
- concentrated recharge in ponors, is well connected to the groundwater drainage network. This surface water has generally its own tracing, due to the lithology which outcrops in the surface watershed of the brook or the river. This water can be SO<sub>4</sub><sup>2-</sup>, K<sup>+</sup> and SiO<sub>2</sub> rich in a marly context, Na<sup>+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and Ca<sup>2+</sup> rich in evaporite-rich clay context, and SiO<sub>2</sub>, Na<sup>+</sup>, Al<sup>3+</sup>, Fe<sup>2+</sup> rich in a silicated basement context. Generally, equilibrium with atmospheric pCO<sub>2</sub> (0,04 %) is observed in the calco-carbonic system.

## 2 – EXAMPLES OF OBSERVED CONTRASTS DUE TO THESE HETEROGENEITIES

### 2.1. Tracing the spatial heterogeneity

The difference of response between drainage system and fine fissures of the blocks can be reflected by the shape of the chemograph (Fig. 2).

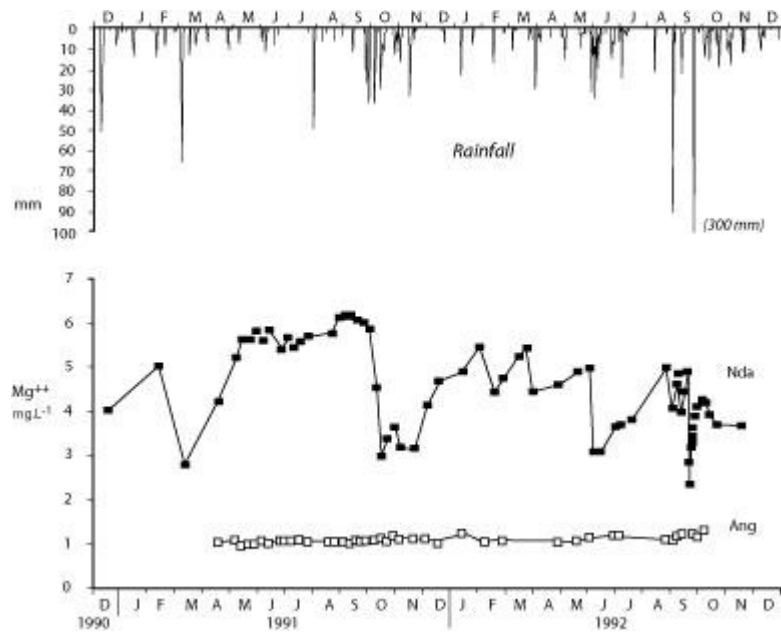


Fig. 2: Chemographs of 2 carbonate springs from Southeastern France (Lastennet, 1994)

The organization and the effectiveness of the drainage system is displayed by sharp peaks (Nda), it is able to transmit the infiltration component to the spring during a flood period. Conversely, a flat chemograph indicates a low degree of karstification (Ang), unable to transfer an input signal to the outlet. Such a system is a good mixer, consisting of a regularly distributed network of fractures with absence of conductive channels.

The frequency distribution (Bakalowicz, 1977) of  $\text{HCO}_3^-$  displays the same information. In Fig. 3, curves B has a unique high mode, a small range of values and is symmetrical. This indicates that the spring drains one water type, flowing from a lowly karstified fissured aquifer. The peaks of curves B and C reach lower frequency values and have several modes. This pattern indicates that, in this system, exist karst conduits which enable different water types to reach the spring. The dominant mode corresponds to the composition of reserves stored in the aquifer while the lower frequency modes reflect flood events where reserve water is mixed with another component.

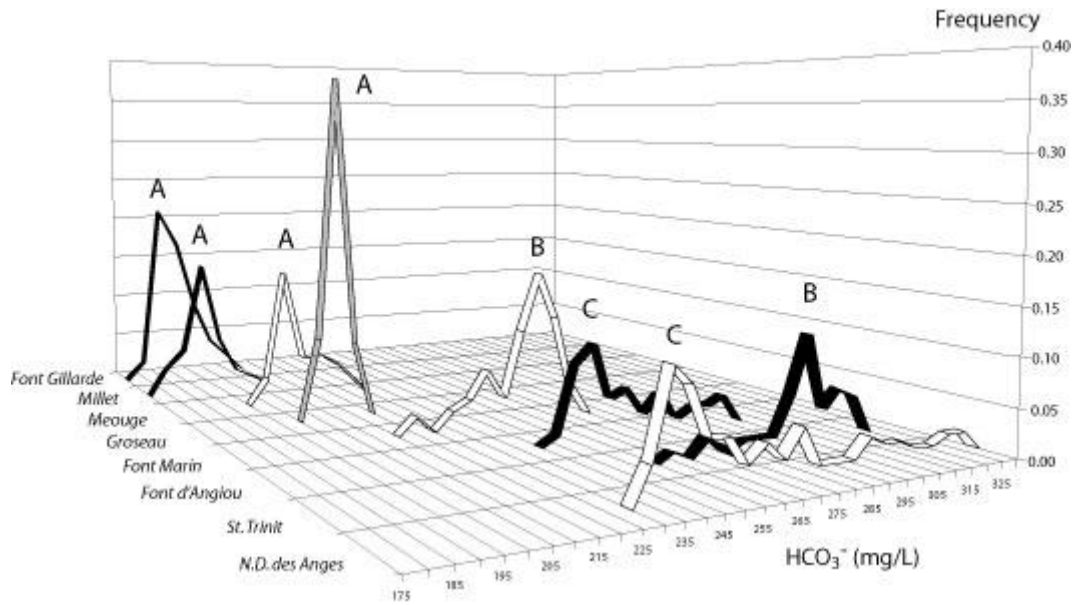


Fig. 3 : frequency distribution of hydrogenocarbonate contents of carbonate springs in Southeastern France (after Lastennet, 1993)

### 2.2. Tracing the vertical heterogeneity

In karst aquifers, water storage may take place within the saturated zone, possibly sheltered from the atmosphere, or within the unsaturated zone or epikarst, as perched aquifers. Both reservoirs can be well contrasted, due to the existence of a pedogenetic layer on top of the shallowest reservoir : water stored near the surface is enriched in tracers from the biological and agronomical activities, water from the deepest reserves is devoid of these tracers.

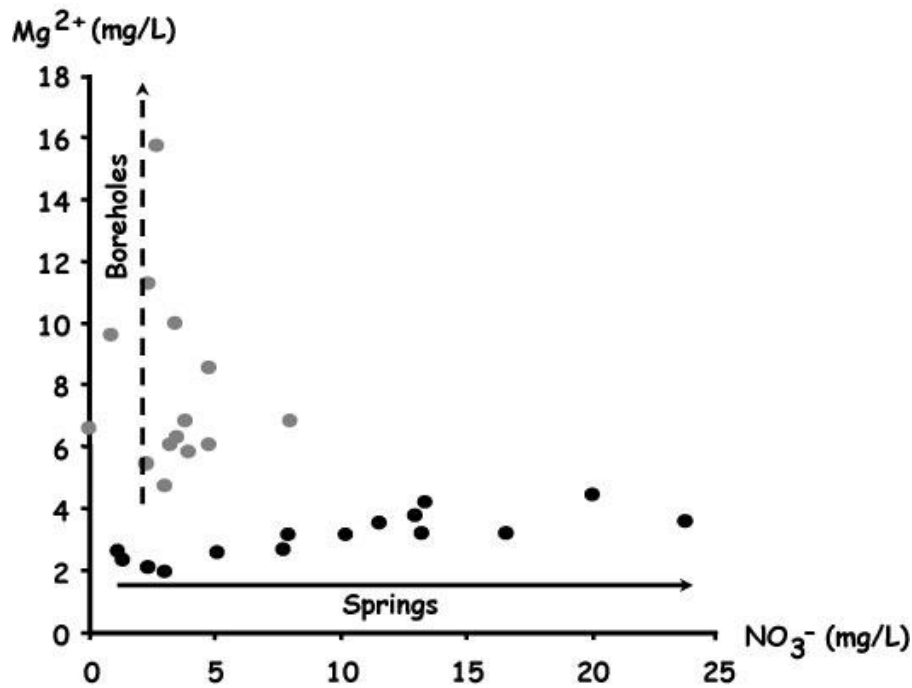


Fig. 4: Springs and boreholes of the Doubs valley, Eastern France (after Celle-Jeanton *et al.*, 2003)

Fig. 4 displays the role of outlets played by springs and boreholes in the Doubs valley karst system. The springs, enriched in nitrates and poor in magnesium, demonstrate their good connection with infiltration from the surface ( $\text{NO}_3^-$ ), and the short residence time of water flowing through the system ( $\text{Mg}^{2+}$ ). The boreholes, which nitrate have been reduced into gaseous nitrogen or ammonium, due to the reducing conditions prevailing in the more confined aquifer, contains more magnesium, due to the high interaction time between water and carbonated matrix.

Calculations of  $\text{pCO}_2$  ( $\text{CO}_2$  partial pressure of a fictitious gaseous phase in equilibrium with the solution) and measurements of  $\delta^{13}\text{C}_{\text{DIC}}$  provide indication about the storage place of the water. Water stored in the unsaturated zone is likely in contact with a gas phase containing elevated concentration of  $\text{CO}_2$ . Thus carbonate dissolution evolves under open system conditions resulting in a higher final  $\text{pCO}_2$  and more negative  $\delta^{13}\text{C}$ . In contrast, water from the saturated zone may have little contact with a gas phase. Fig. 5 contrasts karst springs mainly fed by rapid infiltration from the unsaturated zone and mixed with little long-residence time component ( $\delta^{13}\text{C}_{\text{DIC}}$  highly negative), with boreholes extracting long residence time water from the deepest part of the aquifer ( $\delta^{13}\text{C}_{\text{DIC}}$  more enriched by a long interaction time with the carbonate rock). The variable DOC concentration suggests that some springs have a longer residence time, sufficient to mineralise some of the DOC.

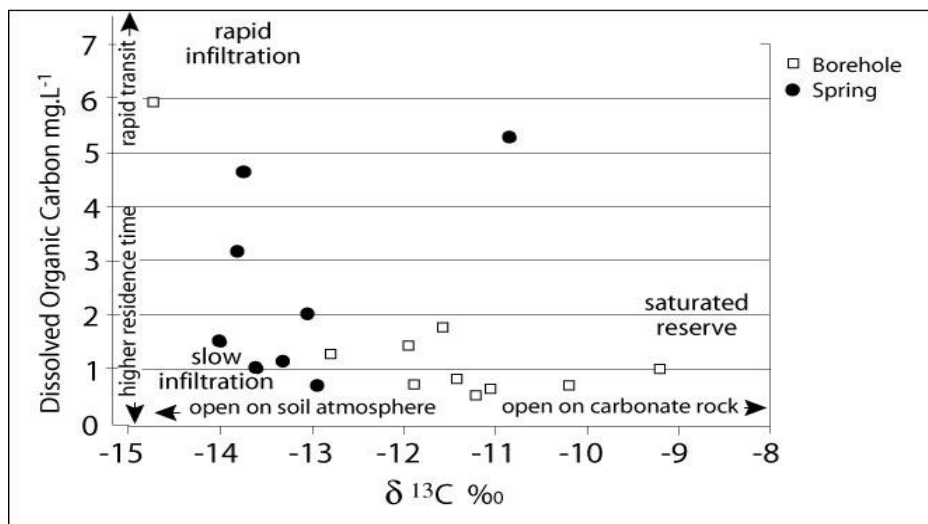


Fig. 5: Dissolved organic carbon versus carbon-13. Doubs valley karst systems, Eastern France. (data from Mudry *et al.*, 2002)

### 2.3. Tracing the heterogeneity in recharge

The heterogeneity of recharge (diffuse vs concentrated) can generally be displayed, thanks to the hydrogeochemical difference that exists between an allogenic river or a brook sinking in the carbonate rock and the diffuse infiltration water, only marked by the soil and the carbonate frameworks. Thus, for instance, the second major karst spring in France (la Touvre, near Angoulême), is recharged (up to 60%) by sinking rivers originating from the Paleozoic silicate watershed of the Limousin, rich in  $\text{SiO}_2$ , Turbidity,  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$ , ..., and (up to 40%) by local diffuse seepage in the limestones, rich in  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ , ..., (Fig. 6).

In the case of the Fourbanne system (Fig. 7), 3 spots have been monitored : the Verne swallow hole, the Fontenotte karst conduit and the Fourbanne spring. The chemographs of the same water body, traced with uranin, demonstrate a dilution of the nitrate content, when this surface water flowing from harvested surface watersheds is diluted by water seeping from the uncultivated zones in diffuse conditions.

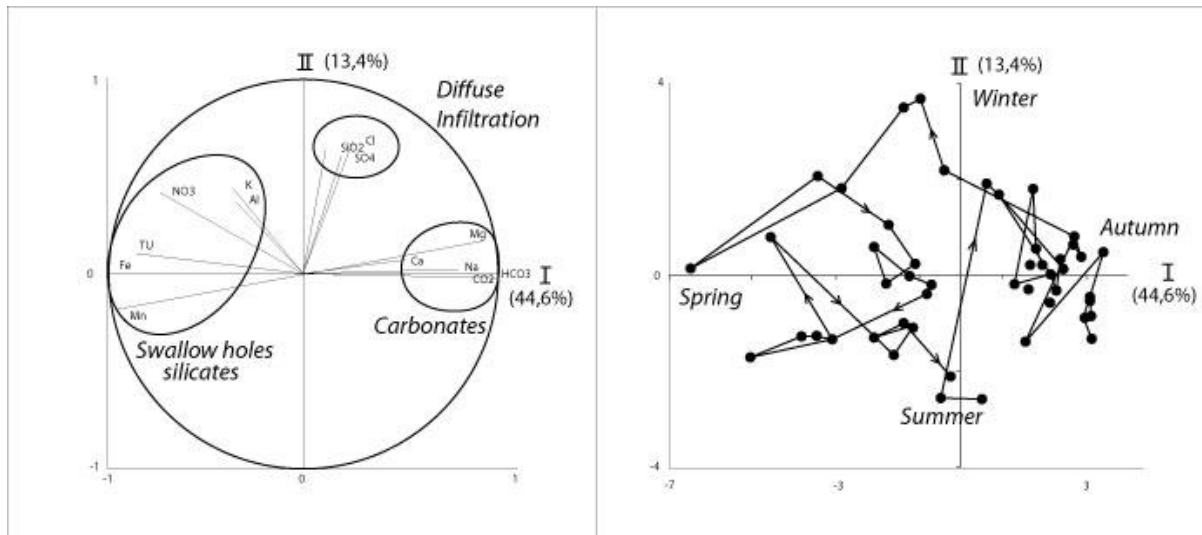


Fig. 6: Environmental tracing of water from swallow holes vs diffuse infiltration in carbonates Touvre spring (data from Rouiller, 1987)

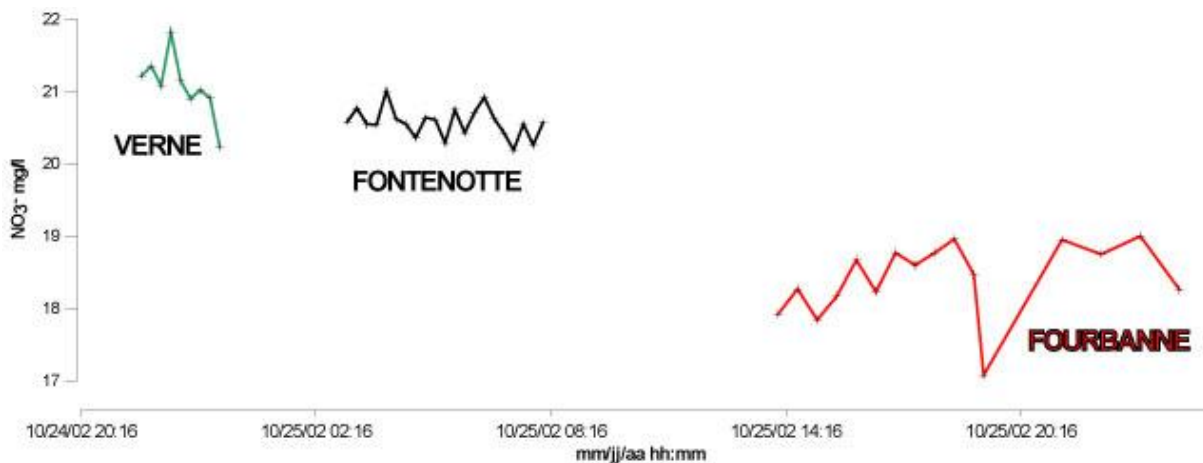


Fig. 7: Dilution of nitrates from swallow holes by water from diffuse infiltration (Charmoille, 2005)

### 3 – CONCLUSIONS

Contrarily at the other aquifers, where lithology, and then chemical contents can be more varied, carbonate rocks display a rather homogeneous geochemical framework within the same aquifer.

In spite of this little contrasted lithology, structural and genetic originality of karst aquifers induce sufficiently contrasted hydrogeochemical responses at the outlets (springs and boreholes), enabling to assign an origin to the different flows : transmissive conduits vs low permeability blocks, shallow vs deep storage, point vs diffuse recharge.

This use of environmental tracing is relevant to classify karst systems according to their vulnerability.

Moreover, this scientific step can be extended to other types of aquifers, basement fissured, alluvial, ..., where contrasts of geochemical context can be, as much or more, exacerbated.

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