

Identification of geochemical tracers for mesoscale water paths: Field and experimental laboratory constraints with major, trace elements and Sr isotopes (Peyne, Hérault, S. France)

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While geochemistry applied to hydrology has up to now essentially dealt with large scale studies for erosion quantification, it is now also turning towards the study of small scale phenomena. This study is part of French National Research Program in Hydrology (PNRH) whose main questions are: How can geochemistry contribute to mesoscale modelling? If geochemistry is to be coupled to hydrology what are the geochemical tracers suitable to identifying the water paths in small catchments?

Site location and geochemical tools

The studied site is the Payne watershed in its lower part. The Payne is a sub-basin of the Hérault watershed. The lower basin measures 70 km² (Fig. 1). The catchment presents many various and complex lithologies which includes Triassic gypsiferous marls, Miocene sandy marls, limestones, sandstones and Villafranchian gravels.

The study focuses on two geologically and hydrologically independent and distinct parts of the lower part of the Payne watershed (Villafranchian

and Miocene + evaporites). Both rocks (soils) and waters have been sampled through three water sampling campaigns in low (Nov-96, Feb-97) and high (Nov-97) flows. The water samplings have been performed in very small brooks draining restricted monolithologic parts of the basin. Fifteen soil samples have been taken from these two parts.

Various geochemical tools are used: major and trace elements (especially alkalis and alkali-earths) were analysed by Capillary Ion Electrophoreses and ICP-MS respectively. Strontium isotopes have been analysed, after chemical separations on resin, by Mass Spectrometry. Analyses have been performed on the dissolved phase after filtration on PVDF 0.2 µm clean filters.

Results and discussion

The different waters in contact with lithologies were geochemically characterized through leaching experiments in immersion. This experiment was performed with deionized water¹, pH=5 similar to local rain, in a clean room under class 100 laminar flow. Small quantities of water were sampled after 4 hours² of water-soil contact, 24 hours and 1 week. All geochemical analyses were done on the dissolved phase (<0.2 µm). Of course, we are aware of the limits of this method which does not exactly reproduce the natural conditions. However, each soil water sample is clearly identified by specific concentration ratios and Sr isotopic signature. Large variations are observed for major and trace concentrations but also for Sr isotopic ratios which, surprisingly, extend from $^{87}\text{Sr}/^{86}\text{Sr} = 0.7088$ to 0.7137. The highest ratio is obtained for the triassic gypsiferous marls settled in an epicontinental zone: it contains some sandy banks from continental origin

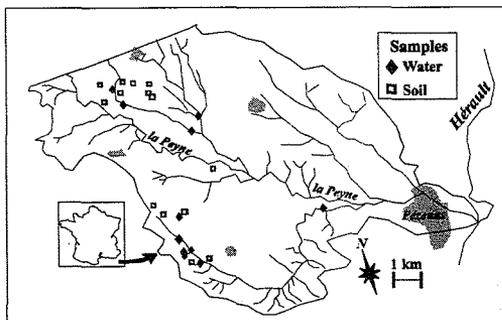


FIG. 1. The Payne watershed and sampling location.

which could explain such a radiogenic value. Differences due to alteration are also observed for lithologic formations of the same type and age but at various depths in vertical profiles.

In order to better approach the natural field leaching conditions, we have done a leaching experiment by percolation³ on one of the villafranchian soil samples. This preliminary experiment was done to compare geochemical characteristics of waters obtained in static and dynamics modes. This soil is mainly composed of Quartz with small amounts of muscovite and illite. The leaching was done in a Plexiglas column ($\phi 20 \times 120$ cm) with deionised water (pH 5), we have simulated the annual local rain over a 6 months period with an input of 5 mm/day. Sampling was done every day in a first stage, then 3 times/week and finally once a week. A second experiment was conducted after drying the material. Analyses are done on the dissolved phase. When compared to the immersion experiment results, percolation experiment values present different absolute concentrations, but also different concentration ratios (Fig. 2). These observations indicates that concentration of elements are mainly controlled by kinetic dissolution of minerals and the importance of the saturation conditions of the porous medium.

Nevertheless, as it was unrealistic in this study to perform 15 percolation leaching experiments, the field water data are compared with immersion soil leachates. Comparison is done in graphs based on element ratios because they are less dependent on fluxes: those could not been measured; moreover, concentration ratios are probably more characteristic of rock endmembers than concentrations only. Results show that both sampling campaigns in low flows present quite similar geochemical signatures for the various concentration ratios as well as for Sr isotopic compositions, this implies same water geochemical characteristics for same hydrological conditions. It seems that in both studied parts of the basin, the 'at depth' lithologies and not the surficial

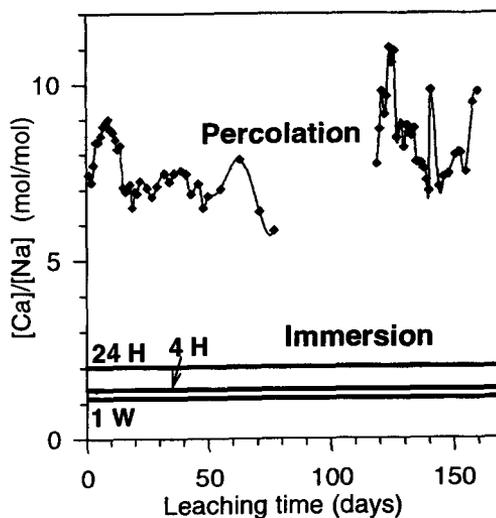


FIG. 2. Comparison between percolation and immersion leaching experiments with Ca/Na molar ratio.

ones influence the water signatures, suggesting water path at depth around one metre.

Some appropriate tracers seem to emerge from this study (in progress). In this way, we can say that Ca/Na ratio is a discriminant ratio between high and low flows (Na increases in high flows) as well as Na/Sr ratio. At the opposite, Mg/Na and Ca/Sr ratios don't vary with the flow and can be considered as suitable tracers for the corresponding soils.

References

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