Characterization of the isotopic signature of effective rainfall (δ 18 O, δ 2 H) to constrain the groundwater recharge zones in a Mediterranean karst aquifer

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Characterization of the isotopic signature of effective rainfall ($\delta^{18}O$, $\delta^{2}H$) to constrain the groundwater recharge zones in a Mediterranean karst aquifer

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Abstract Carbonate aquifers are known as a major source for drinking water in the Mediterranean regions and in other part of the world. Therefore, qualitative and quantitative estimation of the groundwater resource are crucial, especially in area with densely populated areas. Stable water isotopes of surface and ground waters can be used to study water mixing, define recharge area, or identify fast infiltration in karst areas. It relies on (1) the variability of the input signal over space and time at a catchment scale, related to the rainfall isotopic signature, and (2) the flow, storage and mixing within the karst system, related to the soil – epikarst – unsaturated zone – saturated zone hydrodynamic behaviour. Mean groundwater isotopic signature can then be different from the mean total rainfall signature, depending on the effective rainfall amount. The isotopic signature of the recharge was calculated using a water balance model for two sampling sites in southeastern France. Soil and epikarst are modelled as a first compartment where evapotranspiration occurs, defined by its water capacity. An isotopic mixing balance model uses the calculated monthly effective rainfall and the analysed monthly mean isotopic water values of collected rainfall. This subsurface water capacity has a strong influence on the isotopic signature of the recharge and contributes to deplete the isotopic value of regional groundwater at the scale of a 2-year period.

Keywords stable water isotopes ● natural tracers ● effective rainfall ● recharge ● carbonate aquifers ● karst

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1. Introduction

Stable isotopes of rainwater ($\delta^{18}O$, $\delta^{2}H$), because of their conservative character- istics, are used to identify groundwater recharge zones (Clark et Fritz 1997) and thus potentially better constrain hydrogeological catchments. A global approach, by weighted isotope signatures of precipitation over relatively long periods, is often satisfactory for identifying groundwater recharge areas (Darling et Bath 1988; Prada et al. 2016). However, it is also quite common to observe a difference between rainfall and groundwater isotopic ratios (Goldscheider et Drew 2007), related to the hydrogeological functioning of karst aquifers (karst organization, reserve volume, preferential flows, ...) (Williams 2008). Soil and epikarst store a part of the precipi- tation that will never reach the saturated zone and is available for evaporation or/and evapotranspiration. Effective rainfall is the part of the precipitation that will effec- tively contribute to surface and groundwater flows. Evapotranspiration has no impact on the water stable isotopes signal but reduces the recharge to groundwater by decreasing the effective rainfall.

The goal of this study is to show how water stable isotopes of recharging ground- water can be deviated from rainfall signal, considering evapotranspiration in the soil water capacity. We used a daily water balance and a monthly isotopes balance model, to assess the impact of the effective rainfall amount on the weighted mean isotopic value of the effective rainfall in a Mediterranean case study. Considering
six usual values of soil water capacity (SWC), we computed the deviation between the average water isotopic value of collected rainfall and computed effective rain- fall. A global approach over a two-year period is first proposed and then completed with the computation over five hydrological semesters to address the seasonal var- iability. The process will help to examine the impact of recharge on groundwater isotopic signature measured at karstic springs and boreholes, and thus to better con- strain the hydrogeological catchment areas.

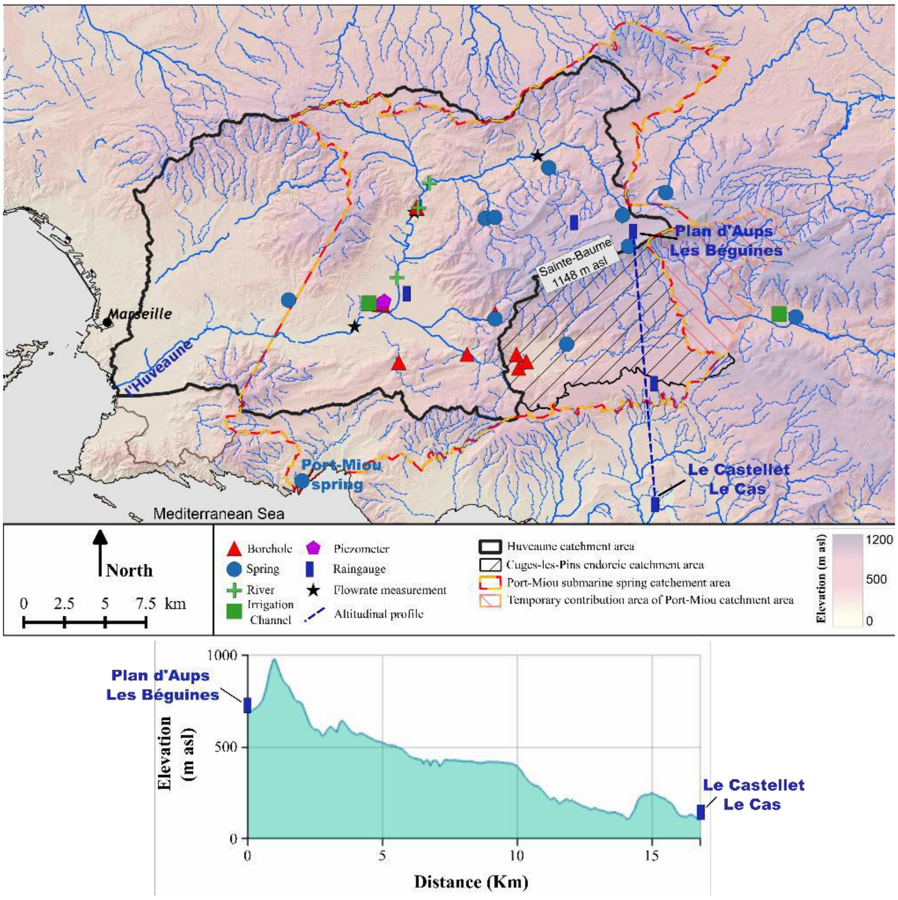


Fig. 1. Hydrogeological context of the Port-Miou spring and the Huveaune river catchment areas.

2. Case study and data

The case study is located in south-eastern France, close to Marseille city, on the Port-Miou spring and Huveaune river catchment areas (Figure 1). The 500 km² in- vestigated zone is characterized mainly by Triassic to Cretaceous carbonate rocks that have been eroded and karstified during several stages. This zone is also defined by a large range of elevation, from the sea level to 1148m asl, giving an expected significant contrast of rainfall isotopic signature. Monthly rainwater samples have been collected during two years at two sampling sites to catch the variability of the stable isotopic signature in the study area: (1) Le Castellet Le Cas station at eleva- tion 103m, south slope of the Sainte-Baume massif, 3 km from the seashore; (2) Plan d'Aups Les Béguines at elevation 682m asl, north slope of the Sainte-Baume massif (Figure 1). These two stations cover the mean elevation of the Port-Miou spring and Huveaune catchment areas (about 360 m asl). Daily precipitation are monitored by automatic rain gauges. Daily potential evapotranspiration is computed by the French National Meteorological Service using Penman-Monteith equation.

3. Method

In this study, the time step of precipitation sampling does not allow to work on the scale of one or several daily events. It is a rather global approach that is devel- oped here. An infiltration and isotopic mixing balance model is proposed to calcu- late the isotopic signature of effective rainfall over time. Figure 2 presents the work- flow. The daily effective rainfall, based on daily rainfall, potential evapotranspiration (PE) and six values of SWC, is calculated according to Thornthwaite water balance model (Thornthwaite 1948). The sum of daily effective rainfall led to monthly effective rainfall. Meanwhile, monthly rainfall is collected according to the procedure proposed by Gröning et al. (2012) to avoid evaporation of the rainwater at the two sampling sites. Water stable isotopic composition is measured by laser spectrometry (LAMA Montpellier, France) on the monthly collected rainfall. Then, an isotopic mixing balance model is used to calculate the weighted water stable isotopic composition of effective rainfall over a 2 year-period (from April 2019 to March 2021) and over 5 hydrological semesters (starting on September to August). These results can then be compared with the water stable isotopic composition of the cumulated rainfall and the groundwater samples in springs or boreholes. The computation method gives a mean value assuming that the unsaturated and saturated zones are massive waterbodies that buffer the input water geochemical signal. In this paper, we will only compare the results with the isotopic composition of the cumulated rainfall.

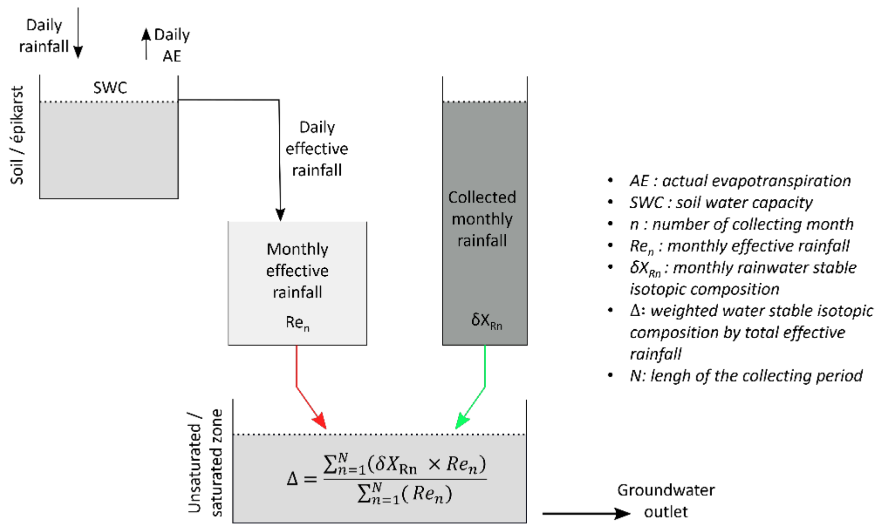


Fig 2. Conceptual infiltration model and isotopic mixing balance model

3. Results

Figure 3-A shows the isotopic signal of precipitation and effective rainfall on a 2-year period, according to six values of SWC. The difference between the isotopic signal of rainfall and effective rainfall for a SWC of 100mm is obvious with a de- crease in $\delta^{18}O$ from -6.99 to -7.96‰ and from -5.97 to -6.79‰, respectively for the sampling site of Plan d'Aups Les Béguines and Le Castellet Le Cas. Considering a near zero SWC (1mm) already implies a decrease of 0.16 and 0.19‰ in $\delta^{18}O$ for the two sampling sites. Moreover, the increase in SWC from 1 to 40mm gives a strong decrease in the

weighted isotopic signature of the effective rainfall and then a sta- bilization between 40 to 100mm. This observation is linked to the total effective rainfall, which follow this trend with a significant decrease in effective rainfall over the first 40 mm of SWC (from 1119 mm to 403 mm for Le Castellet Le Cas and from 1895 mm to 851 mm for Plan d'Aups Les Béguines).

Figure 3-B and C show the isotopic signal of precipitation and effective rainfall for 5 hydrological semesters: 3 including autumn and winter (S1-H, S3-H, S5-H) and 2 including spring and summer (S2-E, S4-E). The spring-summer semesters have a less total cumulated rainfall than autumn-winter semesters as expected in Mediterranean climate. Results given in tables below the figures 3-B and 3-C show that effective rainfall during summer (S2 and S4) is null starting from a SWC 40 mm at the Castellet station (low elevation, 103 m asl), and very low at the Plan d'Aups station (high elevation, 682 m asl). Major effective rainfall occurs during the autumn and winter seasons. Water stable isotopic composition of rainfall are more depleted during cold autumn-winter semesters than spring-summer semesters for both stations, e.g. at Plan d'Aups station $\delta^{18}O$ of rainfall equal -8.5‰ during S3 and -5.5‰ during S4. Results of effective rainfall water stable isotopic composition calculation for increasing SWC show that the mean value is depleted compared to the total rainfall (expect for the winter S5 with a decreasing slope and then an in-
creasing slope due to one event not detailed in this study). Effective rainfall amount decreases with increasing SWC, that means that only the highest rainfall events are contributing to the effective rain-fall (minor events are balance by actual evapotran- spiration). Highest events, known as Mediterra-nean events (usually higher than 50mm/day) have a strong impact on the isotopic composition of the recharging rain- fall to groundwater.

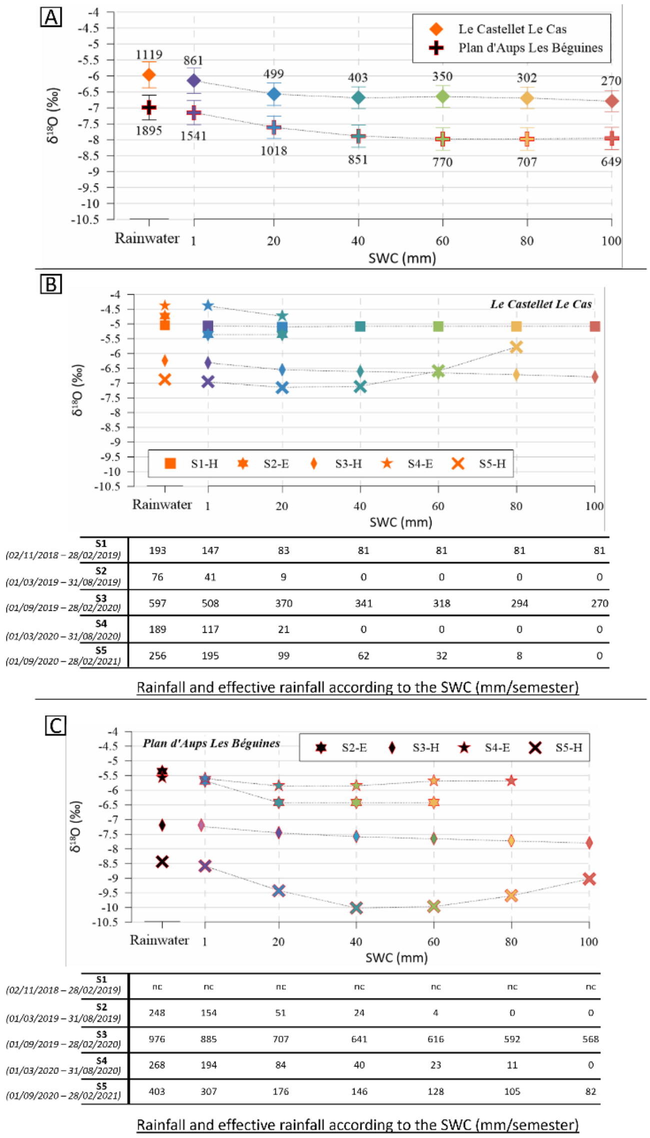
Whatever the seasons and the actual value of SWC in the case study, the effective rainfall recharging groundwater has a water stable isotopic composition depleted compared to the rainfall. The mean $\delta^{18}O$ depletions, given in Fig 3-A, are in the same range for both stations: around -0.5‰ for SWC of 20mm, and -0.8‰ for SWC of 40mm.

4. Conclusion

The approach developed here highlights:

- The monthly mean stable isotope precipitation data allow the study of the recharge water signature in a Mediterranean karst system at a pluri-annual scale
- The use of effective rainfall for the calculation of the weighted mean sig- nature leads to a deple-tion of oxygen 18 compared to the rainfall weighted mean isotopic signature

Moreover, further comparison of water stable isotope composition with ground- water samples will be used to show that groundwater recharge from effective rain- fall occurs primarily during major rainfall events, as expected by the large discharge variations observed in-situ. Depletion of the isotopic composition calculated by the balance model will be search in the groundwater isotopic composition. Small rain- fall events of a few mm to ten mm may be useful for critical zone ecosystems (soil- plant-atmosphere) but are suspected to be not effective in recharging the regional karst aquifers of the Huveaune - Port-Miou watersheds.



S1 *(02/11/2018 – 28/02/2019)*	193	147	83	81	81	81	81
S2 *(01/03/2019 – 31/08/2019)*	76	41	9	0	0	0	0
S3 *(01/09/2019 – 28/02/2020)*	597	508	370	341	318	294	270
S4 *(01/03/2020 – 31/08/2020)*	189	117	21	0	0	0	0
S5 *(01/09/2020 – 28/02/2021)*	256	195	99	62	32	8	0

Rainfall and effective rainfall according to the SWC (mm/semester)

S1 *(02/11/2018 – 28/02/2019)*	nc	nc	nc	nc	nc	nc	nc
S2 *(01/03/2019 – 31/08/2019)*	248	154	51	24	4	0	0
S3 *(01/09/2019 – 28/02/2020)*	976	885	707	641	616	592	568
S4 *(01/03/2020 – 31/08/2020)*	268	194	84	40	23	11	0
S5 *(01/09/2020 – 28/02/2021)*	403	307	176	146	128	105	82

Rainfall and effective rainfall according to the SWC (mm/semester)

Fig 3. A- Weighted mean of the $\delta^{18}O$ isotopic signature of the rainwater collected at the two collecting stations (Le Castellet Le Cas and Plan d'Aups Les Béguines) for a period of 2 years (April 2019 - March 2021), and evolution of the weighted mean isotopic signature of the ef- fective rainfall according to the six values of SWC. Labels give the total rainfall and the total effective rainfall over the studied period. B and C – $\delta^{18}O$ isotopic signature of the rainwater collected at the two collecting stations (respectively Le Castellet Le Cas and Plan d'Aups Les Béguines) for 5 hydrological semesters and evolution of the isotopic signature of the effective rainfall according to the six values of SWC. Rainfall and effective rainfall are presented in table for the two collecting stations. The hydrological semesters are defined as: S1 – 02/11/2018 to 28/02/2019. S2 – 01/03/2019 to 31/08/2019. S3 – 01/09/2019 to 28/02/2019. S4 –01/03/2020 to 31/08/2020. S5 – 01/09/2020 to 28/02/2021.

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