Magnesium content and groundwater flow in limestone aquifers: a relationship with potential development for exploitation management of karst springs

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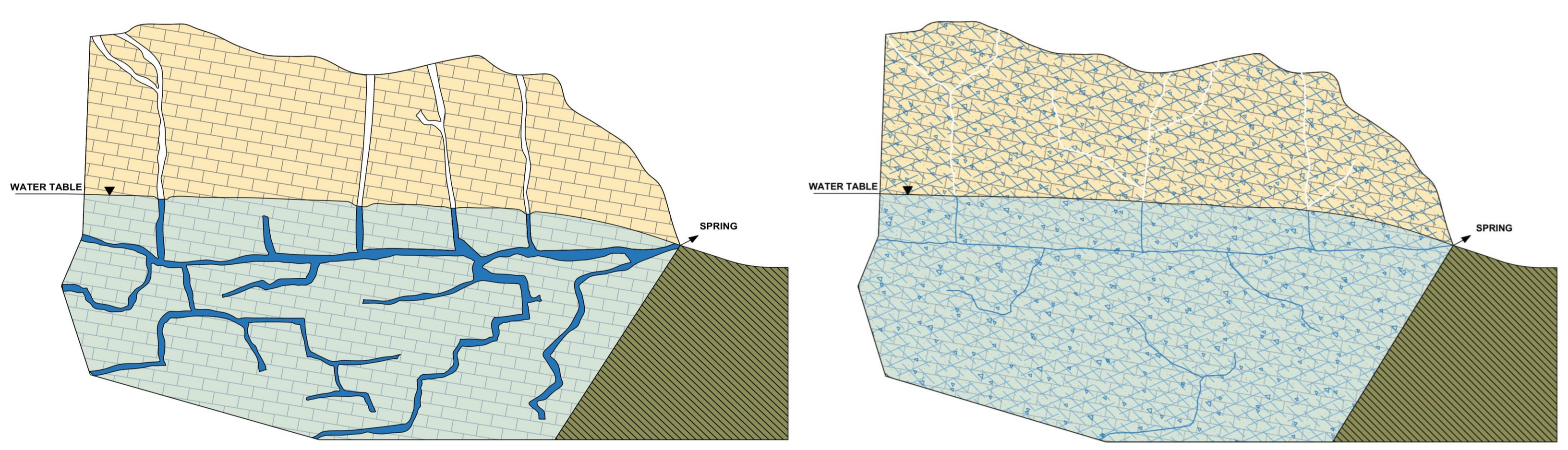
Introduction

Karst aquifers are characterized by different types of groundwater flow, related to different types of permeability due to the simultaneous presence of matrix, fractures and conduits. The presence of a well-developed karst conduit system leads to a fast circulation of groundwater, within the aquifer and an impulsive response of the spring flow to the rainfall inputs, with a potential fast transport of contaminants from the hydrogeological basin surface to the output (Fiorillo et al., 2014). With the help of hydro chemical analyses on spring water samples and single discharge measurements, it is possible to set specific mass balance models correlating ion content to spring flowrates. In particular, Mg^{2+} content revealed a reliable application for spring baseflow separation in karst settings. Once the local model has been set, its conservative behavior, in mostly limestone dominant aquifers, allows using it as a natural tracer of groundwater flow, distinguishing conduit flow (overflow) and diffuse flow (baseflow) occurrence in the spring outlet, without additional discharge measurements. In karst settings, the difficulty in continuously monitoring the spring discharge values makes this application interesting for exploitation management. This study shows the results obtained for two springs located in Central Italy, confirming that monitoring groundwater quality in karst environments is often the key to successfully characterize springs but also to assess the total yield when direct measurements are not frequent. This phenomenon influences the values of the correlation between rainfall data and spring flow values. Springs with a fast response to the hydrological input show the highest correlation coefficients in those months with shortest lag time. In terms of water quality, the arrival of large rainwater volumes at a karst spring is frequent after a storm and leads to a related change in water temperature and decreasing (total substitution) or increasing (piston flow) of electrical conductivity.

Fig. 1 – Types of groundwater circulation in karst aquifer (modified from Fiorillo et al., 2014)



(a) Karst conduit groundwater circulation (overflow) (b) Dispersive groundwater circulation (baseflow)

Materials and methods

For Pertuso Spring, one-time discharge measurements and water samples collection were carried out during winter and late spring months (spring minimum and maximum flow periods) from 2014 to 2022.

As regards Capodacqua di Spigno, discharge measurements and water samples collection were carried out each month for more than one hydrologic year (from September 2018 to November 2019) in order to set up the recession curve of the spring.

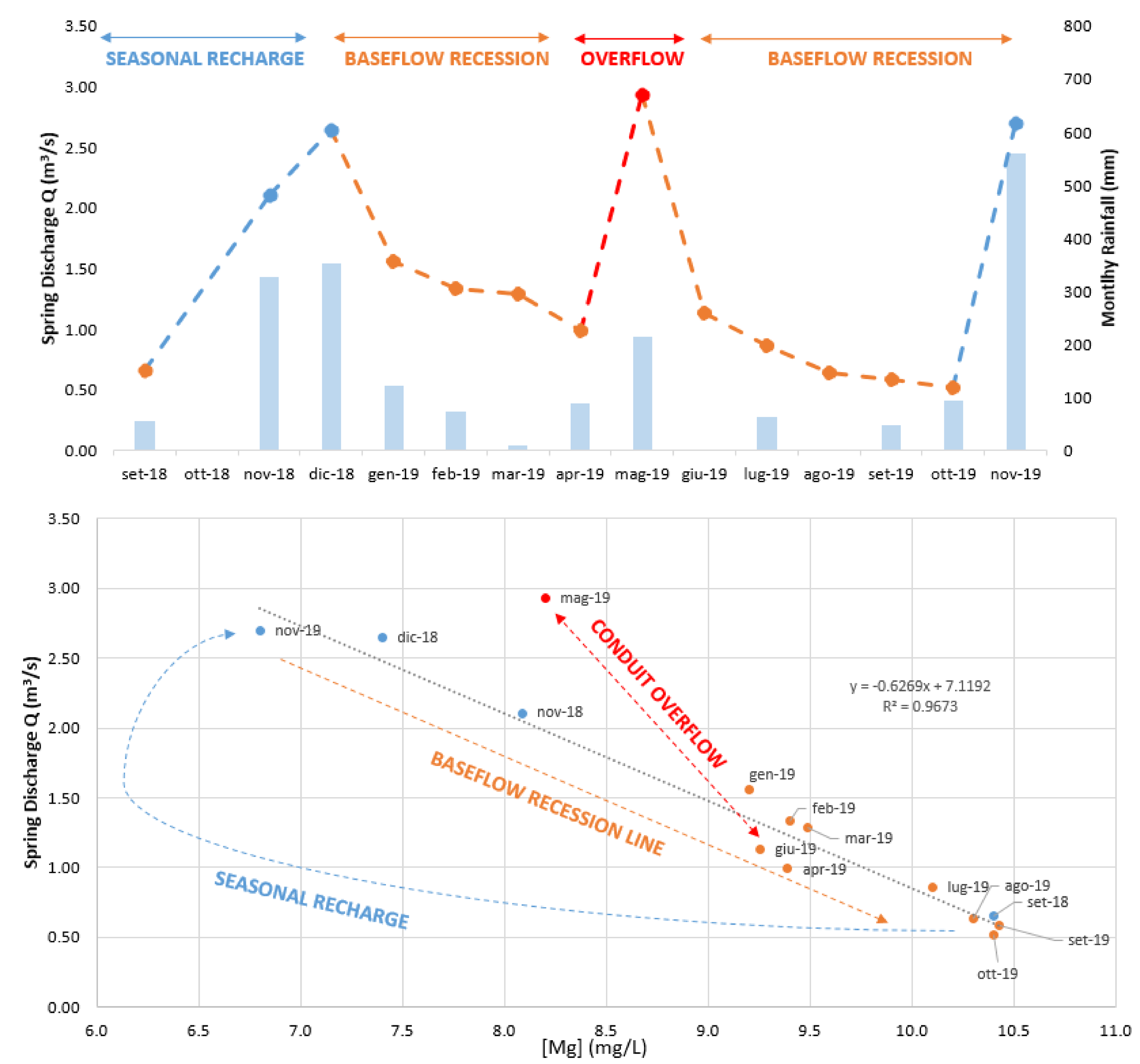
For both, the main equipment applied to measure the stream flow velocity was a SEBA horizontal axis current-meter F1 (reliability ±5%). Velocities were measured at 0.2, 0.6, and 0.8 of the depth below the water surface according to EN ISO 748:2007 requirements. Chemical analyses were carried out at the Geochemical Laboratory of Sapienza University of Rome. Water samples were filtered through cellulose filters (0.45 μm), and their major and minor constituents were determined by ion chromatography (IC) by a 761 Professional IC Metrohm (reliability ±2%). Bicarbonate (HCO_3^-) was determined by titration with 0.1 N HCl (reliability ±2%).

Capodacqua di Spigno Spring

The Capodacqua di Spigno Spring, located at an altitude of about 35 m a.s.l. (meters above sea level), is the natural outcrop of groundwater discharging from a karst hydrogeological basin of about 60 km^2 located in the South-eastern Latium Region (Central Italy) and it is about 6 km far from the sea. The spring water comes out from the permeable limestone of La Civita Mountain (Aurunci Mountains) and flows above the upper Miocene clays, at the lowest point of the limestone-clay contact.

Carbonate dissolution strongly influences groundwater flow and evolves into complex networks throughout the limestone matrix. The feeding aquifer showed an active recharge of about 35 m^3/year, averaged over 40 years of observations (Sappa et al., 2018).

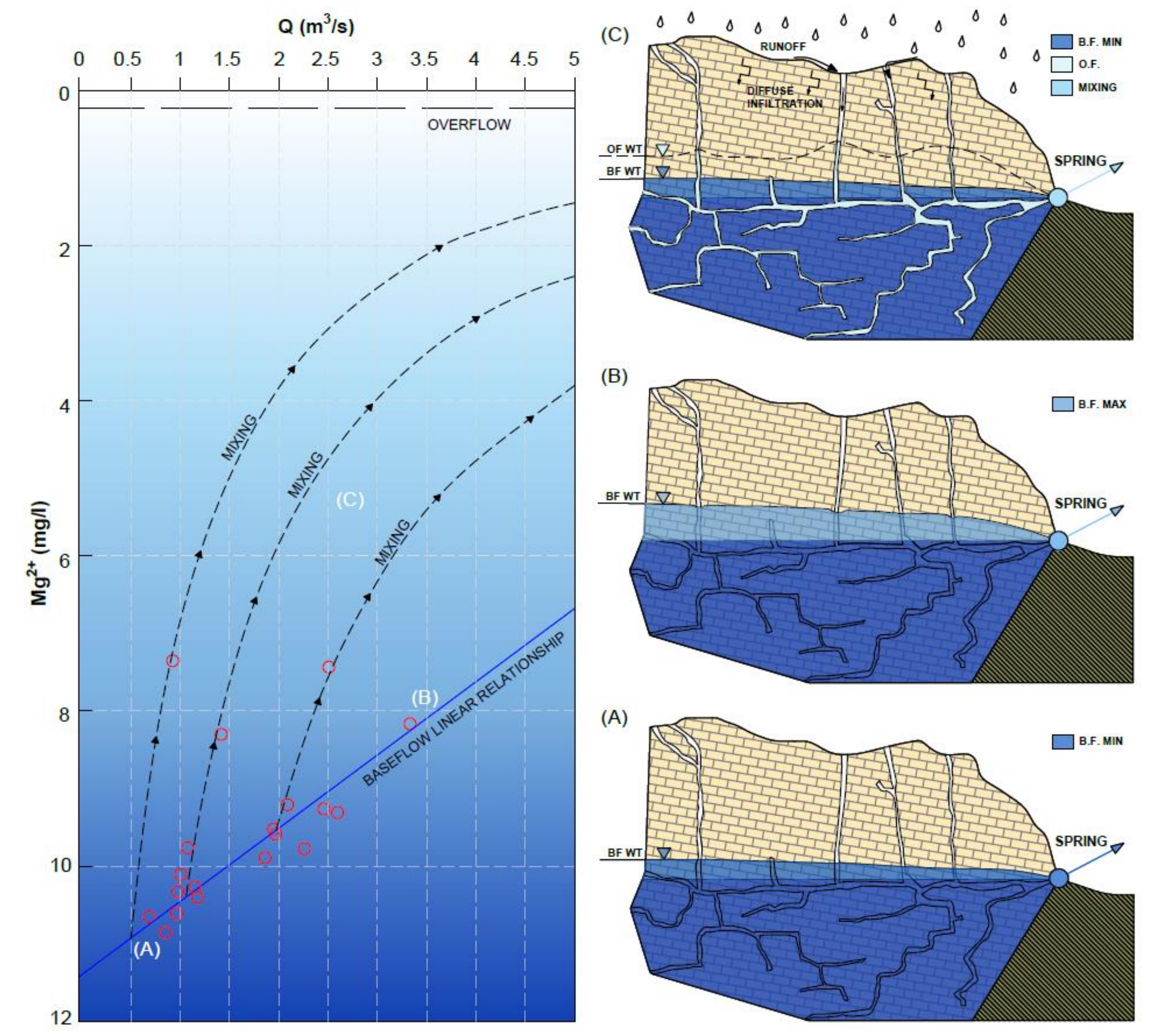
Fig. 3 – Results of monthly Capodacqua di Spigno Spring baseflow recession and Mg^{2+} related contents path



Pertuso Spring

The Pertuso Spring is the main water feeding the Aniene River (Latium, Central Italy), with high discharges (up to 4–5 m^3/s). The water outlet is next to the boundary between the carbonate hydrogeological basin, mostly made of limestone, and less permeable geological formations. Dissolution in karst conduits causes groundwater flowing very quickly towards the spring. Conduits network is complex, not allowing to identify underground water pathways throughout the limestone matrix. The rapid increasing of Pertuso Spring flow is frequent and usually related to stormy rainfall events, doubling, or even tripling the spring discharge within few tens of hours. Nevertheless, the aquifer shows a remarkable baseflow component, with a spring depletion volume of about 25 Mm^3/year (Sappa et al., 2016). The hydrogeological basin of the spring extends for approx. 50 km^2 and is mostly composed by limestone

Fig. 2 – Sketch of Pertuso Spring Mg^{2+} concentrations and karst aquifer mechanism (modified from Fiorillo et al., 2014)



Results and Discussion

Mg^{2+} content in Pertuso and Capodacqua springs' water is inversely proportional to the total baseflow (BF) discharges Q. For Pertuso Spring, sixteen samples showed a data cluster around a linear trend with a good correlation ($R^2 = 0.86$). Maximum concentrations are detected in the same month (November/December), during the minimum seasonal spring flow, except for 2017, when a strong drought event occurs, forcing the water agency to increase the exploitation rate of the spring (Figure 2).

Even better is the correlation found for Capodacqua di Spigno Spring ($R^2 > 0.9$), where the reconstruction of seasonal spring discharge depletion for 2018-2019 highlighted a related increasing path of Mg^{2+} content along the linear baseline. After reaching the minimum flow, the seasonal recharge occurring during late autumn/early winter brings back Mg^{2+} values at the top of the BF line for a new recession period (Figure 3). Small deviations from the BF trendline are comparable with errors related to chemical analyses (±2%) and discharge measurements (±5%), whereas large deviations, initially supposed to be outliers, show a different hydrodynamics-geochemical mechanism of the aquifer, tracing the fast-spring response to storm events. These latter activate the discharge overflow (OF) component and the consequent mixing between long residence times groundwater and runoff water, quickly flowing through karst conduits. In fact, the marked drop in magnesium content at equal discharges is the result of the mixing. Using the mass balance equation to separate BF and OF, it was possible to set up a model which outlines overflow drifts from the baseflow line. Sensitivity analysis starts using typical rainfall Mg^{2+} contents as C_{OF} and a couple of values coming from the linear relationship C_{BF}—Q_{BF}. Based on available literature data, rainfall average Mg^{2+} content ranges from 0.1–0.3 mg/L in mountain areas (Sapek B., 2014). The only free parameter (variable) is Q_{OF}, related to the rainfall event intensity, giving different results of C_{MIX} (Figure 2). For Pertuso Spring, characterized by a total substitution mechanism within the aquifer, an intense rainfall event occurring during the final phase of aquifer depletion immediately implies a drop in Mg^{2+} content, whose value was enriching due to the longer residence time of groundwater in the carbonate rock. This also highlights the role of previous saturation conditions of the hydrogeological basin on the karst spring response to different precipitation events.

References

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