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Magnesium and groundwater flow relationship in karst aquifers: a tool for exploitation management of springs

La relazione tra magnesio e circolazione delle acque sotterranee in acquiferi carsici: uno strumento per la gestione della captazione dalle sorgenti

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Riassunto

Gli acquiferi carsici sono caratterizzati da diverse tipologie di circolazione idrica sotterranea, relative a differenti tipologie di permeabilità dovute alla contemporanea presenza di matrice rocciosa, fratture e condotti. La presenza di un sistema di condotti carsici ben sviluppato determina una rapida circolazione delle acque sotterranee nell'acquifero e una risposta impulsiva della portata sorgiva agli apporti pluviometrici intensi, con un potenziale rapido trasporto dei contaminanti dalla superficie del bacino idrogeologico fino in sorgente. Con l'ausilio di analisi idro chimiche su campioni di acque sorgive e singole misure di portata, è possibile impostare specifici modelli di bilancio di massa che correlino il contenuto ionico alle portate sorgive. In particolare, il magnesio (Mg^{2+}) si è rivelato un tracciante affidabile per la separazione del deflusso di base di sorgenti in ambiente carsico. Una volta impostato il modello locale, il suo comportamento conservativo, in acquiferi prevalentemente a predominanza calcarea, consente di distinguere tra il deflusso rapido nei condotti (*overflow*) dal deflusso diffuso più lento dato dall'immagazzinamento nell'acquifero (*baseflow*). In ambito carsico, la difficoltà di monitorare in continuo i valori di portata delle sorgenti, rende questa applicazione interessante per la gestione della captazione delle acque sotterranee. Questo studio mostra i risultati ottenuti per due sorgenti situate nel centro Italia, confermando che il monitoraggio della qualità delle acque sotterranee è spesso la chiave per caratterizzare le sorgenti, ma anche per valutare la disponibilità idrica quando misure dirette in sito non sono possibili.

Abstract

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 rapid circulation of groundwater within the aquifer and a pulse-type response of the spring flow to the rainfall inputs, with a potential fast transport of contaminants from the hydrogeological basin surface to the discharge zones. Supported by hydro chemical analyses of spring water samples and single discharge measurements, it was possible to develop specific mass balance models, correlating ion content to spring flowrates. Specifically, Mg^{2+} content revealed a reliable application for spring baseflow separation in karst settings. Once the local model has been set, its conservative behaviour, in mostly limestone-dominant aquifers, allows using Mg^{2+} 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 for successfully characterizing springs and assessing the total yield when direct measurements are not available.

Introduction

It is estimated that karstified rocks and aquifer systems cover 15% of the Earth's ice-free land (Bakalowicz, 2005; Hartmann et al., 2013) and 25% of the world's population is supplied partially or entirely by karst water resources (Goldscheider et al., 2020). Especially in the Mediterranean regions, karst aquifers are the primary water resources exploited for drinking water (Jarraya-Horriche et al., 2020; Lange et al., 2003; Ravbar et al., 2018).

On the other hand, the recent and forecast water scarcity in the Mediterranean basin has encouraged the authorities to find new solutions, such as the exploitation of new unconventional water resources, or to increase the exploitation of conventional ones (Balacco et al., 2022; Ducci & Lasagna, 2019; Grappein et al., 2021; Stevanović et al., 2022). However, the exploitation of karst coastal aquifers, for its strict conditions of management, should not be done from karst submarine springs but preferably onshore, where a sustainable use of conventional resources is still related to a successful approach in estimating karst groundwater potential and discharge, which is not often easy to obtain (Bakalowicz, 2018; Fleury et al., 2007; Parisi et al., 2018).

Dissolution processes involving carbonate rocks lead to a complex conduit network within low permeability fractured limestone. On a large scale, this is also called karstification and is responsible for the development of increasing of conduit network size within the aquifer (Fiorillo & Malik, 2019; Ford & Williams, 2013). Hence, karst aquifer exploitation, both coastal and inland, should consider the dual behaviour and the close relationship between the surface water and groundwater in the overall karst setting, in order to manage and protect these water resources from climate change, overexploitation and pollution (Citrini et al., 2020; Sappa et al., 2018; White, 2012).

Karst springs reflect the duality in discharge conditions: low and continuous discharge during dry periods, when rainage occurs through the matrix, and high discharge with high temporal variability during intense recharge events, when groundwater flows primarely through the conduit system (Fiorillo, 2014; Tamburini & Menichetti, 2020; White, 2002). This phenomenon influences the correlation between rainfall and spring flow. Springs with a more developed conduit network and a fast response to the hydrological input show the highest correlation coefficients in months with shortest lag time, and vice versa (Sappa et al., 2019; Sivelle et al., 2019).

In terms of water quality, the arrival of high rainwater discharge at a karst spring is frequent after a storm and shows, if checked by a continuous monitoring probe, a related change in water temperature and decreasing (total substitution flow) or increasing (piston flow) electrical conductivity (Banzato et al., 2011; Vigna, 2014). Several recent approaches have coupled hydrological and geochemical models to understand karst processes and subsurface hydrology, especially for karst conduit-systems (Koit et al., 2023; Nicolini et al., 2022). The difficulty to set up and install instrumentation at the spring outlet, costs associated with remote systems, bureaucracy and vandalism are just a few examples of the problems encountered in continuous monitoring of these resources. Considering the need for groundwater quality control for water service managers, carried out with frequent water sampling and laboratory analyses, the increasing use of artificial and environmental tracer application to assess karst spring flowrates, water sources, groundwater residence times and other hydrogeological processes can be seen as powerful tools for water management with low associated costs (Gori et al., 2023; Koit et al., 2022; Lorenzi et al., 2023; Mammoliti et al., 2023). One example is the Mg^{2+}/Ca^{2+} ratio, which is applied to assess groundwater residence time, due to the different kinetics of dolomite and calcite dissolution within the limestone. The use of both environmental tracers and spring hydrographs in mixing models has also increased, with the aim of identifying end members in complex hydrogeological systems due to groundwater-surface water interaction (Chapman et al., 1997; Chimenti et al., 2023; Nanni et al., 2020; Rovan et al., 2020). In this context, the role of Mg^{2+} has already been proved as successful in the literature, using it as a conservative tracer for spring discharge evaluation in several case studies, where mass balance techniques were applied for both surface water (Bencala et al., 1987; Schemel et al., 2006) or groundwater-surface water interaction (Sappa et al., 2017). Magnesium has already been revealed as a useful application for karst spring baseflow separation in karst settings (De Filippi et al., 2021). In this study, the results of a Mg^{2+} based method for estimation of karst spring discharge are presented for two springs located in Central Italy: Pertuso Spring and Capodacqua di Spigno Spring. Both karst springs studied are in Central Italy, in Latium Region. Capodacqua di Spigno Spring is located near the coastline, in the province of Latina, on the slopes of the western Aurunci Mountains, whereas Pertuso Spring is inland, in the Frosinone province, within the Regional Park of Simbruini Mountains, in a protected area (Fig. 1).

Fig. 1 - – Location of studied springs in Latium Region (Google Earth).

Fig. 1 - Localizzazione delle sorgenti studiate nella Regione Lazio (Google Earth).

Once the local relationship between spring discharge and magnesium content is found, it can be possible to distinguish conduit flow (overflow) and diffuse flow (baseflow) occurrence in the spring outlet. These results confirm that monitoring groundwater quality in karst environments together with a few discharge measurements allows understanding groundwater circulation mechanisms and could be a key to successfully estimate a safe yield of karst springs when continuous monitoring is not possible.

Materials and methods

Geological and hydrogeological framework

Pertuso Spring

The Pertuso Spring is one of the main water sources feeding the Aniene River (Latium, Central Italy), with high discharge rates (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 rapid groundwater flow towards the spring. The conduit network is complex and underground water pathways throughout the limestone matrix are difficult to define. Rapid increases of flow in the Pertuso Spring flow are frequent and usually related to stormy rainfall events, doubling, or even tripling the spring discharge within a few tens of hours. Nevertheless, the aquifer shows a remarkable baseflow component, with a spring depletion volume of about 25-30 Mm^3/year (Sappa et al., 2016). The hydrogeological basin of the spring extends for approx. 50 km^2 and is mostly composed of limestone and dolomite intercalations. Coupled hydrogeological water budget results and chemical analyses allow to define the boundaries, excluding the central part of the outcropping dolostone, which host a different aquifer feeding other springs (Figure 2 and 3) (Sappa et al., 2016, 2017).

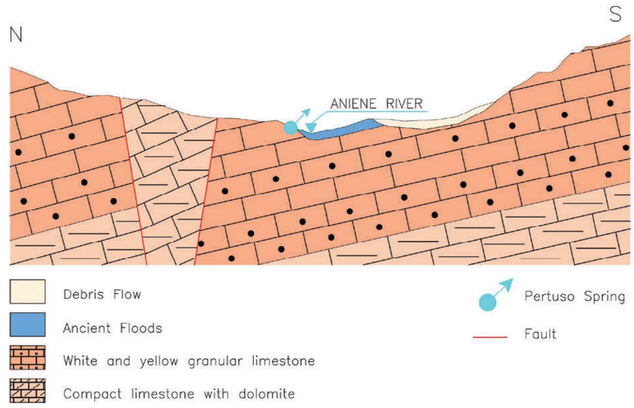

Fig. 3 - Geological cross-section near Pertuso Spring discharge.

Fig. 3 - Sezione geologica nei pressi dell'emergenza idrica della Sorgente Pertuso.

Capodacqua di Spigno Spring

The Capodacqua di Spigno Spring, located at an altitude of about 35 m a.s.l., is the natural outlet of groundwater discharging from a karst hydrogeological basin of about 60 km^2 located in the south-eastern Latium Region (Central Italy), within the Western Aurunci chain and about 6 km from the sea (Fig. 4). The spring water discharges from the permeable limestone of La Civita Mountain, whose altitude is over 1500 m a.s.l., and flows above the upper Miocene clays, at the lowest point of the limestone-clay contact (Fig. 5). Carbonate dissolution strongly influences groundwater flow and evolves into complex networks throughout the limestone matrix. According to the most recent studies, the feeding aquifer showed an active recharge of about 35 Mm^3/year, averaged over 40 years of observations, concentrated in the central part of the massif (Iacurto et al., 2021). The maximum measured discharge is about 3 m^3/s, but in high overflow conditions it was impossible to assess the total amount

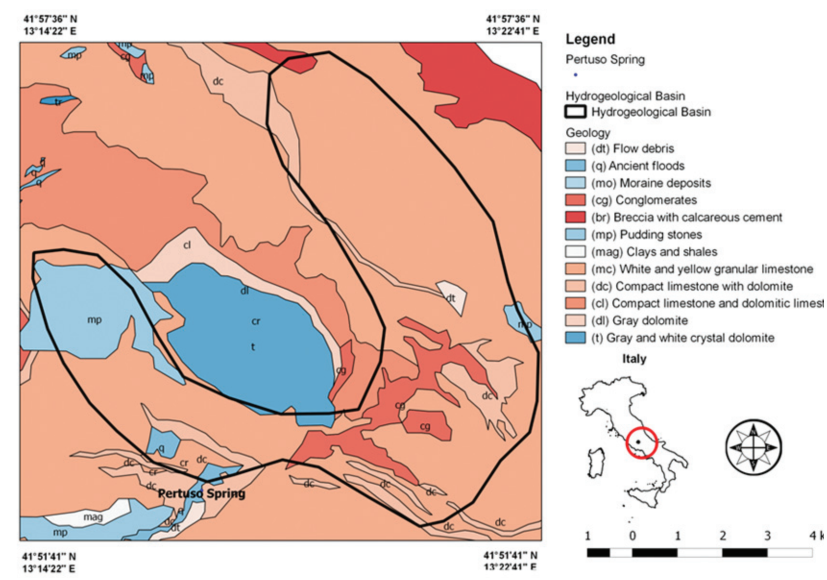

Fig. 2 - Pertuso Spring hydrogeological basin and outcropping geology.

Fig. 2 - Bacino idrogeologico della Sorgente Pertuso e geologia affiorante.

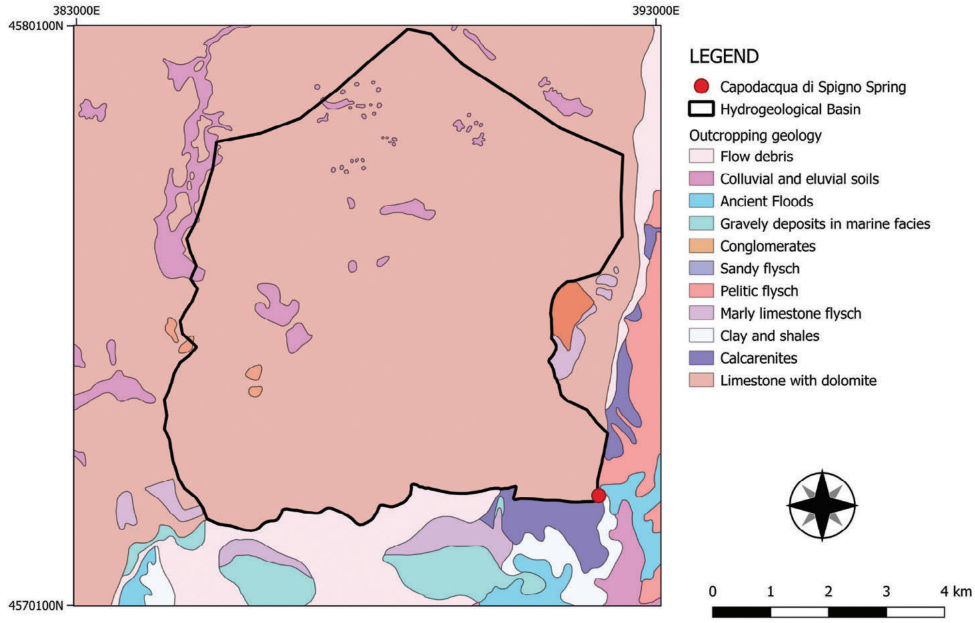

Fig. 4 - Capodacqua di Spigno Spring hydrogeological basin and outcropping geology.

Fig. 4 - Bacino idrogeologico della Sorgente Capodacqua di Spigno e geologia affiorante.

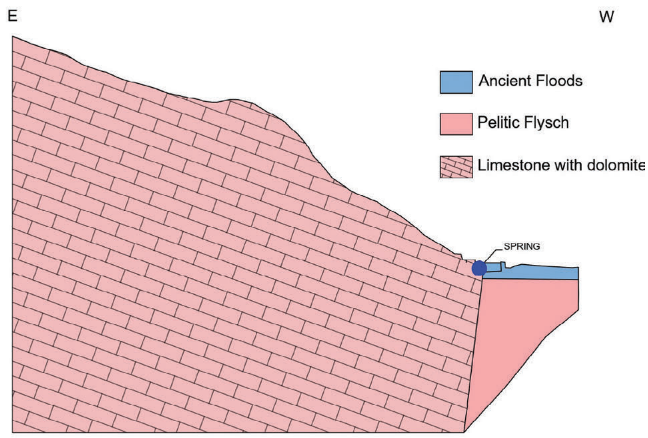

Fig. 5 - Geological cross-section near Capodacqua di Spigno Spring.

Fig. 5 - Sezione geologica nei pressi della Sorgente Capodacqua di Spigno.

with conventional instrumentation, due to the dangerous conditions at the natural cross-section.

Data and tools

For Pertuso Spring, one-time discharge measurements and water sample collections were carried out during winter and late spring months (spring minimum and maximum flow periods) from 2014 to 2022, according to the monitoring project established with the water service manager. Rainfall data were obtained from the thermo-pluviometric station of Trevi nel Lazio (http://www.centrofunzionalelazio.it/annali/).

As regards Capodacqua di Spigno, discharge measurements and water sample collection were carried out each month for more than one hydrologic year (from September 2018 to November 2019) in order to set up the total recession curve of the spring. Rainfall data refers to the thermo-pluviometric station of Esperia (http://www.centrofunzionalelazio.it/annali/).

For both, the main equipment applied to measure the stream flow velocity was a SEBA horizontal axis F1 current-meter (reliability ± 5%). Velocities were measured at 0.2, 0.6, and 0.8 m 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. Major and minor constituents were determined by ion chromatography (IC) by a 761 Professional IC Metrohm (reliability ± 2%).

Results and Discussion

Mg^{2+} content in the Pertuso and Capodacqua spring water was found to be inversely proportional to the total baseflow (BF) discharge QT (the total amount is equal to the measurements and the exploitation values by the water agency) (Table 1 and 2).

For Pertuso Spring, sixteen samples showed a data cluster around a linear trend with a good correlation (R^2 = 0.86). Maximum concentrations were detected in the same month (November/December), during the minimum seasonal spring flow, except for 2017, when a strong drought event occurred, forcing the water agency to increase the exploitation rate of the spring (Table 1 and Figure 6a) and even better is the correlation found for Capodacqua di Spigno Spring (R^2 > 0.9) (Fig. 6b).

The Pertuso Spring has a more rapid decrease in Mg^{2+} than Capodacqua di Spigno Spring. This is evident by the different slope of the regression line obtained for both springs. A possible explanation is that the Pertuso Spring aquifer presents a more developed karstification, with larger voids, fractures and conduits, allowing a different baseflow (slightly faster in time and with major recession volumes involved). The groundwater circulation is characterized by a total substitution mechanism within the aquifer (De Filippi et al., 2020), whereby an intense rainfall event (daily scale) occurring at the end of the recession limb leads to a drop in Mg^{2+} content, which was increasing during the period of diffuse flow with longer groundwater

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Tab. 1 - Results of discharge measurements and water sample Mg^{2+} contents for Pertuso Spring.

Tab. 1 - Risultati delle misure di portata e concentrazioni di Mg^{2+} nei campioni d'acqua per la sorgente Pertuso.

Month -	QT m^3/s	Mg^{2+} mg/L	$P_{3\text{-DAY}}$ cm
July 2014	2.27	9.77	20.5
November 2014	1.49	8.32	51.8
January 2015	1.87	9.89	0
February 2015	2.1	9.2	29.5
May 2015	2.61	9.3	0
December 2015	1.03	10.4	0
May 2016	1.96	9.53	33.1
November 2016	1.09	9.84	0
May 2017	1.19	10.4	19.6
June 2017	1.22	10.1	87.2
December 2017	0.75	10.7	1.8
May 2018	3.34	8.17	23
November 2018	2.52	7.43	96.7
June 2019	1.98	9.59	0
November 2020	0.86	10.9	36.1
May 2021	2.75	9.34	0.6
November 2021	0.98	10.7	27.6
May 2022	1.21	10.5	0
November 2022	1.06	7.31	116.2

Tab. 2 - Results of discharge measurements and water sample Mg^{2+} contents for Capodacqua di Spigno Spring.

Tab. 2 - Risultati delle misure di portata e concentrazioni di Mg^{2+} nei campioni d'acqua per la sorgente Capodacqua di Spigno.

Month -	QT m^3/s	Mg^{2+} mg/L
March 2018	2.51	7.6
April 2018	1.43	9.2
May-2018	1.3	9.3
June 2018	1.03	9.6
Jul-2018	0.79	9.6
August 2018	0.71	9.5
September 2018	0.66	10.4
November 2018	2.11	8.1
December 2018	2.65	7.4
January 2019	1.56	9.2
February 2019	1.33	9.4
March 2019	1.29	9.5
April 2019	0.99	9.4
May 2019	2.93	8.2
June 2019	1.13	9.3
Jul-2019	0.86	10.1
August 2019	0.64	10.3
September 2019	0.59	10.4
October 2019	0.52	10.4
November 2019	2.70	6.8

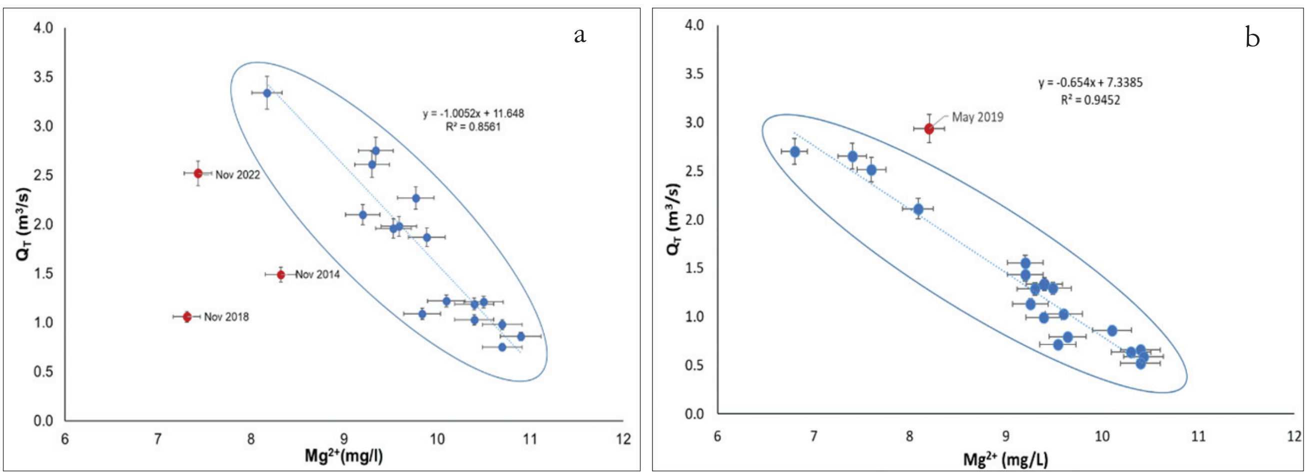

Fig. 6 - Pertuso (a) and Capodacqua di Spigno (b) spring baseflow-Mg^{2+} relationships with related measurement precision. Baseflow data are coloured in blue, whereas overflow data are in red.

Fig. 6 - Relazioni tra Mg^{2+} e flusso basale delle sorgenti Pertuso (a) e Capodacqua di Spigno (b) con precisione delle misure effettuate. Il flusso basale è colorato in blu, mentre l'eccesso in rosso.

residence times (Fig. 6a). This also highlights the role of previous saturation conditions of the hydrogeological basin on the karst spring response to different precipitation events. In comparison, after a storm event, the prevalent mechanism for Capodacqua di Spigno Spring is piston flow, due to the upwelling of the deep-groundwater reserve component and mixing with rainfall water (Iacurto et al., 2021).

The red samples in Figure 6 are not considered in the relationship because they are not related to the spring baseflow. By coupling the total amount of rainfall for a 72-hour time interval before the sampling with the magnesium content, it was possible to understand that the different behaviour

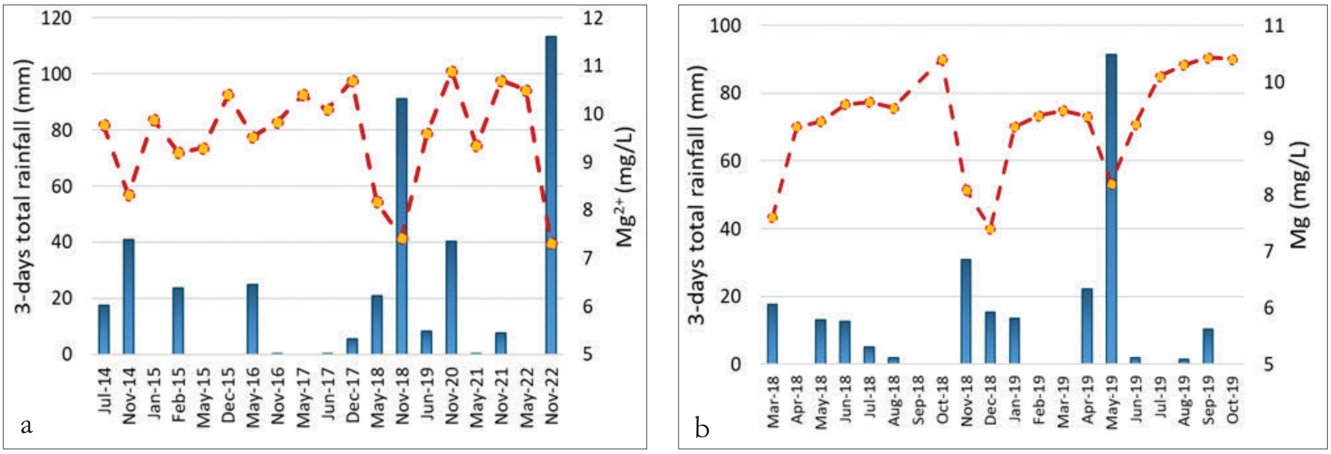

Fig. 7 - 3-day cumulative rainfall (blue bars) before sampling and Mg^{2+} content (dashed red lines) for Pertuso (a) and Capodacqua di Spigno (b) springs.

Fig. 7 - Cumulata delle precipitazioni nei tre giorni precedenti il campionamento (barre in blu) e concentrazione di Mg^{2+} (linee tratteggiate rosse) per le sorgenti Pertuso (a) e Capodacqua di Spigno (b).

of red points is due to the stormwater activating overflow through the conduit network, with a mostly pulse response of the karst springs and magnesium drop. The rainfall data used for this analysis is related to the Trevi nel Lazio thermo-pluviometric station for the Pertuso Spring and the Esperia station for the Capodacqua di Spigno Spring. Figure 7 shows this process, with remarkable drops of Mg^{2+} at intense rainfall events. Except for this, the clearest difference between the two springs is due to the frequency of sampling: twice per year (coinciding with maximum and minimum discharge) for Pertuso Spring and monthly for Capodacqua di Spigno Spring. This is highlighted by a jagged curve for the first one (Fig. 7a), where Mg^{2+} contents are the maximum and minimum values of one hydrologic year, and by a smooth-shape for the second one (Fig. 7b), where the sampling at monthly scale allows to follow the entire recession period of the spring, with a proportional increase of Mg^{2+}.

Starting from this latter result the main novelty of this study is presented. In fact, for Capodacqua di Spigno Spring, the reconstruction of the seasonal spring discharge recession for 2018-2019 highlighted a fully related increasing path of Mg^{2+} content along the linear baseline. According to the proposed model, after reaching the minimum flowrate (Oct-18 and Oct-19), the seasonal rainfall recharge occurring during late autumn/early winter returns Mg^{2+} to minimum values (Dec-18 and Nov-19), located at the top of the BF line, for a new recession period with a progressively slow increase in magnesium content (Fig. 8B).

Small deviations from the BF trend line are assumed to be related to errors of chemical analyses (± 2%) and discharge measurements (± 5%) (Fig. 5), whereas large deviations show a different discharge and hydrogeochemical response of the aquifer, highlighting the fast-spring response to storm events. The activation of the discharge overflow (OF) component leads to a mixing between long residence time groundwater and runoff water, quickly flowing through karst conduits (Fig. 9). Using the mass balance equation to separate BF and OF, it is possible to set up a model which outlines overflow drifts from the baseflow line.

Conclusion and future remarks

In this study, Mg^{2+} content in Pertuso and Capodacqua spring waters were found to be inversely proportional to the total baseflow (BF) discharge. The larger deviations from the estimated local trend lines show a different discharge and geochemical response of the aquifer, when a fast response of karst spring discharge to storm events is occurring.

Hence, the magnesium drop is activated by two different mechanisms: the seasonal recharge along the baseflow line (that usually occurs during autumn months, i.e. November, December, but sometimes until even March) and an intense and rapid storm event, which affect both the chemistry and the discharge of the spring, with a clear drift from the trendline (see the overflow in red for May 2019, Figure 8).

Future improvements of this study will assess the behaviour of springs during overflow conditions, with a three component-mixing model, in order to confirm that the direction of the overflow drift, above or below the baseflow trendline, can also be correlated to total substitution or piston-flow mechanism.

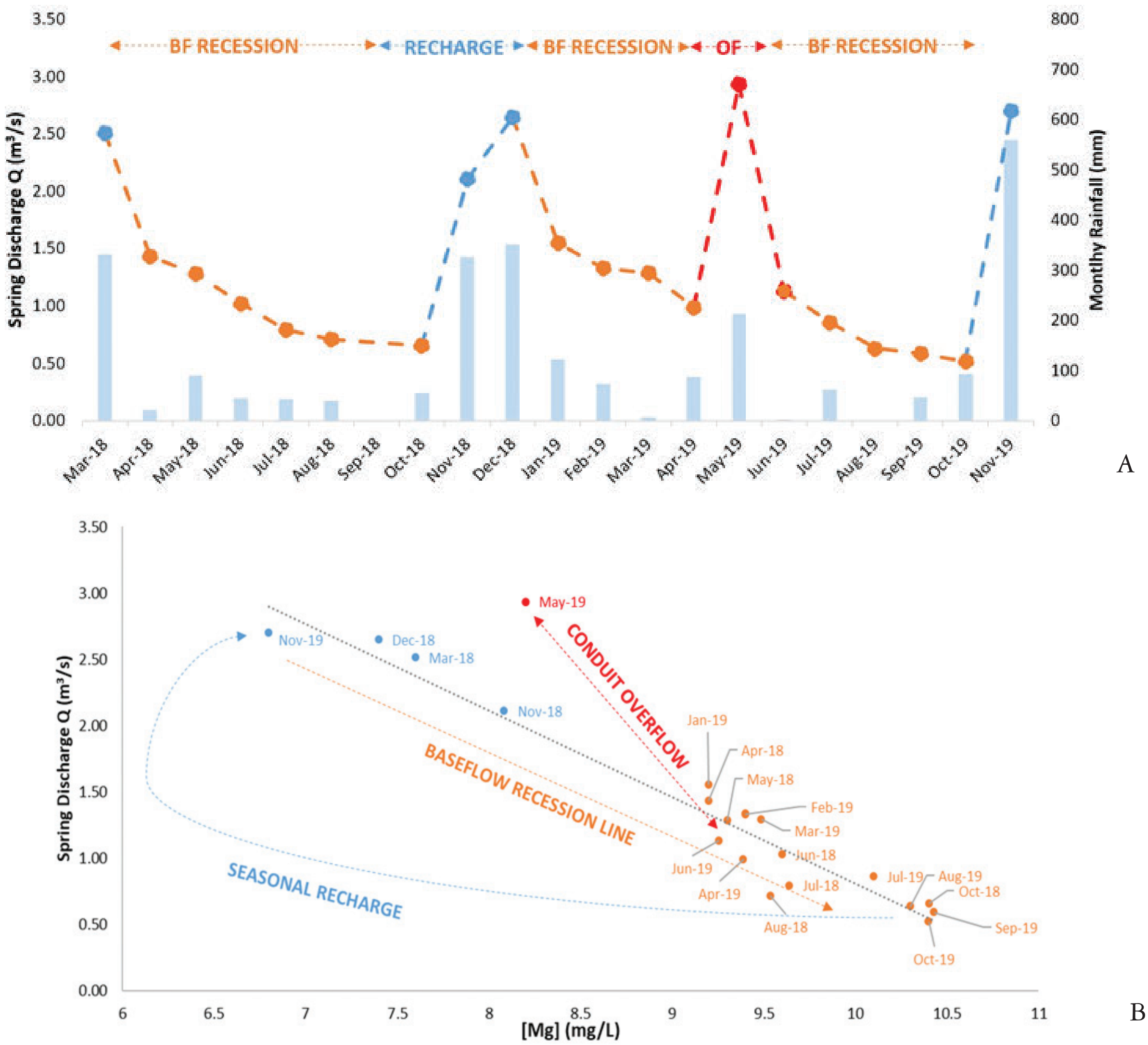

Fig. 8 - Hydrologic regime of Capodacqua di Spigno Spring (A) with monthly rainfall for the period 2018-2019 and Mg^{2+} related content paths (B).

Fig. 8 - Regime idrologico della sorgente Capodacqua di Spigno in relazione alle piogge mensili per l'anno idrologico 2018-2019 (A) e relativi percorsi della concentrazione di Mg^{2+} (B).

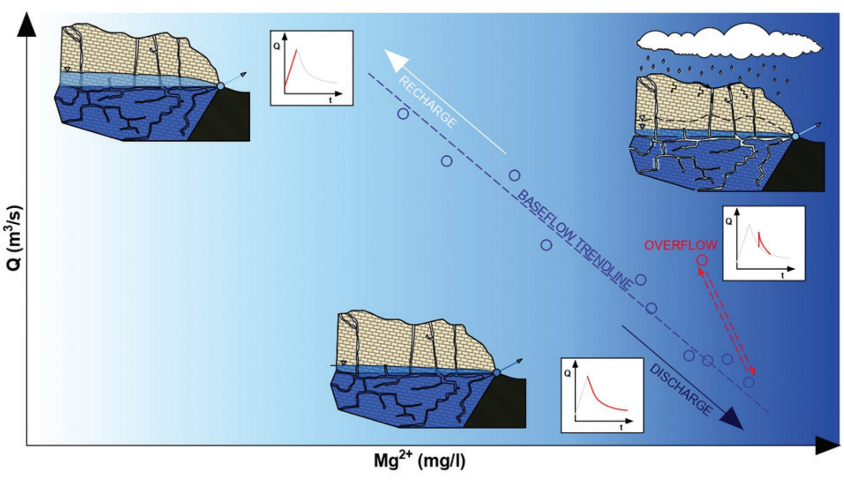

Fig. 9 - Conceptual sketch of studied karst springs' Mg^{2+} concentrations and related aquifer discharge mechanism (modified from Fiorillo et al., 2014).

Fig. 9 - Schema concettuale della relazione tra concentrazioni di Mg^{2+} nelle sorgenti carsiche studiate e il meccanismo di circolazione delle acque sotterranee nei relativi acquiferi (modificato da Fiorillo et al., 2014)

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Author contributions
Collection of data, FMDF; data processing, FMDF; interpretation of results, FMDF and GS; writing-original draft preparation, FMDF; writing-review and editing, GS; visualization, FMDF; supervision, GS; project administration, GS. All authors have read and agreed to the final version of the manuscript.

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Competing interest
The authors declare no conflict of interest.

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REFERENCES

Bakalowicz, M. (2005). Karst groundwater: A challenge for new resources. Hydrogeology Journal, 13(1), 148–160. https://doi.org/10.1007/s10040-004-0402-9

Bakalowicz, M. (2018). Coastal Karst groundwater in the mediterranean: A resource to be preferably exploited onshore, not from Karst Submarine springs. In Geosciences (Switzerland) (Vol. 8, Issue 7). MDPI AG. https://doi.org/10.3390/geosciences8070258

Balacco, G., Alfio, M. R., Parisi, A., Panagopoulos, A., & Fidelibus, M. D. (2022). Application of short time series analysis for the hydrodynamic characterization of a coastal karst aquifer: The Salento aquifer (Southern Italy). Journal of Hydroinformatics, 24(2), 420–443. https://doi.org/10.2166/hydro.2022.135

Banzato, C., Waele, J. De, Fiorucci, A., Vigna, B., Torino, P., & Duca, C. (2011). Study of springs and karst aquifers by monitoring and geochemical analysis. H2Kasrt, 9th Conference Om Limestone Hydrogeology, Besançon, France, September 1-3,2011, 45–48.

Bencala, K. E., McKnight, D. M., & Zellweger, G. W. (1987) Evaluation of natural tracers in an acidic and metal-rich stream. Water Resour. Res., 23, 827–836.

Chapman, P. J., Reynolds, B., & Wheater, H. S. (1997). Sources and controls of calcium and magnesium in storm runoff: The role of groundwater and ion exchange reactions along water flowpaths. In Hydrology and Earth System Sciences (Vol. 1, Issue 3, pp. 671–685). https://doi.org/10.5194/hess-1-671-1997

Chimenti, M., Natali, S., Giannecchini, R., Zanchetta, G., Baneschi, I., Doveri, M., Isola, I., & Piccini, L. (2023). Hydrogeochemistry and Isotopic Composition of Waters in the Renella Cave (Central Italy): New Insights into Groundwater Dynamics. Water (Switzerland), 15(9). https://doi.org/10.3390/w15091764

Citrini, A., Camera, C., & Beretta, G. Pietro. (2020). Nossana Spring (Northern Italy) under Climate Change: Projections of future discharge rates and water availability. Water (Switzerland), 12(2). https://doi.org/10.3390/w12020387

De Filippi, F. M., Iacurto, S., Grelle, G., & Sappa, G. (2021). Magnesium as environmental tracer for karst spring baseflow/overflow assessment: a case study of the Pertuso karst spring (Latium region, Italy). Water (Switzerland), 13(1). https://doi.org/10.3390/w13010093

Ducci, D., & Lasagna, M. (2019). Groundwater stress and vulnerability. In Sustainable Water Resources Management (Vol. 5, Issue 4, pp. 1379–1380). Springer Science and Business Media Deutschland GmbH. https://doi.org/10.1007/s40899-019-00356-9

Fiorillo, F. (2014). The Recession of Spring Hydrographs, Focused on Karst Aquifers. Water Resources Management, 28(7), 1781–1805. https://doi.org/10.1007/s11269-014-0597-z

Fiorillo, F., & Malik, P. (2019). Hydraulic behavior of karst aquifers. Water (Switzerland), 11(8), 10–15. https://doi.org/10.3390/w11081563

Fleury, P., Bakalowicz, M., & de Marsily, G. (2007). Submarine springs and coastal karst aquifers: A review. Journal of Hydrology, 339(1–2), 79–92. https://doi.org/10.1016/j.jhydrol.2007.03.009

Ford, D., & Williams, P. (2013). Karst Hydrogeology and Geomorphology. Karst Hydrogeology and Geomorphology, 1–562. https://doi.org/10.1002/9781118684986

Goldscheider, N., Chen, Z., Auler, A. S., Bakalowicz, M., Broda, S., Drew, D., Hartmann, J., Jiang, G., Moosdorf, N., Stevanovic, Z., & Veni, G. (2020). Global distribution of carbonate rocks and karst water resources. Hydrogeology Journal, 28(5), 1661–1677. https://doi.org/10.1007/s10040-020-02139-5

Gori, F., Paternoster, M., Barbieri, M., Buttitta, D., Caracausi, A., Parente, F., Sulli, A., & Petitta, M. (2023). Hydrogeochemical multi-component approach to assess fluids upwelling and mixing in shallow carbonate-evaporitic aquifers (Contursi area, southern Apennines, Italy). Journal of Hydrology, 618. https://doi.org/10.1016/j.jhydrol.2023.129258

Grappein, B., Lasagna, M., Capodaglio, P., Caselle, C., & De Luca, D. A. (2021). Hydrochemical and isotopic applications in the western Aosta Valley (Italy) for sustainable groundwater management. Sustainability (Switzerland), 13(2), 1–24. https://doi.org/10.3390/su13020487

Hartmann, A., Goldscheider, N., Wagener, T., Lange, J., & Weiler, M. (2013). Karst water resources in a changing world. Review of Geophysics, 2013(September), 218–242. https://doi.org/10.1002/2013RG000443.Received

Iacurto, S., Grelle, G., De Filippi, F. M., & Sappa, G. (2021). Karst recharge areas identified by combined application of isotopes and hydrogeological budget. Water (Switzerland), 13(14). https://doi.org/10.3390/w13141965

Jarraya-Horriche, F., Benabdallah, S., & Ayadi, M. (2020). Groundwater monitoring for assessing artificial recharge in the Mediterranean coastal aquifer of Korba (Northeastern Tunisia). Environmental Monitoring and Assessment, 192(7). https://doi.org/10.1007/s10661-020-08408-w

Koit, O., Mayaud, C., Kogovšek, B., Vainu, M., Terasmaa, J., & Marandi, A. (2022). Surface water and groundwater hydraulics of lowland karst aquifers of Estonia. Journal of Hydrology, 610. https://doi.org/10.1016/j.jhydrol.2022.127908

Koit, O., Retiķe, I., Bikše, J., Terasmaa, J., Tarros, S., Abreldaal, P., Babre, A., Hunt, M., Pärn, J., Vainu, M., Marandi, A., Sisask, K., Lode, E., & Männik, M. (2023). Hydrochemical signatures of springs for conceptual model development to support monitoring of transboundary aquifers. Groundwater for Sustainable Development, 21. https://doi.org/10.1016/j.gsd.2023.100927

Lange, J., Greenbaum, N., Husary, S., Timmer, J., Leibundgut, C., & Schick, A. P. (2003). Tracers for runoff generation studies in a Mediterranean region: Comparison of different scales. IAHS-AISH Publication, 278, 117–123.

Lorenzi, V., Barberio, M. D., Sbarbati, C., & Petitta, M. (2023). Groundwater recharge distribution due to snow cover in shortage conditions (2019–22) on the Gran Sasso carbonate aquifer (Central Italy). Environmental Earth Sciences, 82(9). https://doi.org/10.1007/s12665-023-10889-0

Mammoliti, E., Fronzi, D., Palpacelli, S., Biagiola, N., & Tazioli, A. (2023). Assessment of urban landslide groundwater characteristics and origin using artificial tracers, hydro-chemical and stable isotope approaches. Environmental Earth Sciences, 82(9). https://doi.org/10.1007/s12665-023-10887-2

Nanni, T., Vivalda, P. M., Palpacelli, S., Marcellini, M., & Tazioli, A. (2020). Groundwater circulation and earthquake-related changes in hydrogeological karst environments: a case study of the Sibillini Mountains (central Italy) involving artificial tracers. Hydrogeology Journal, July. https://doi.org/10.1007/s10040-020-02207-w

Nicolini, R., Di Matteo, L., Galdenzi, S., Baldoni, F., Frondini, F., & Valigi, D. (2022). Study of dilution processes of sulfidic aquifer hosted by the Fiume-Vento karstic complex, Frasassi (Central Italy). Acque Sotterranee - Italian Journal of Groundwater, 11(3), 7–17. https://doi.org/10.7343/as-2022-567

Parisi, A., Monno, V., & Fidelibus, M. D. (2018). Cascading vulnerability scenarios in the management of groundwater depletion and salinization in semi-arid areas. International Journal of Disaster Risk Reduction, 30, 292–305. https://doi.org/10.1016/j.ijdrr.2018.03.004

Ravbar, N., Kovačič, G., Petrič, M., Kogovšek, J., Brun, C., & Koželj, A. (2018). Climatological trends and anticipated karst spring quantity and quality: case study of the Slovene Istria. Geological Society, London, Special Publications, 466(1), 295–305. https://doi.org/10.1144/SP466.19

Rovan, L., Lojen, S., Zuliani, T., Kanduč, T., Petrič, M., Horvat, B., Rusjan, S., & Štrok, M. (2020). Comparison of uranium isotopes and classical geochemical tracers in Karst Aquifer of Ljubljanica River catchment (Slovenia). Water (Switzerland), 12(7), 1–30. https://doi.org/10.3390/w12072064

Sappa, G., De Filippi, F. M., Iacurto, S., & Grelle, G. (2019). Evaluation of minimum karst spring discharge using a simple rainfall-input model: The case study of Capodacqua di Spigno Spring (Central Italy). Water (Switzerland), 11(4). https://doi.org/10.3390/w11040807

Sappa, G., Ferranti, F., & de Filippi, F. M. (2016). Hydrogeological water budget of the Karst aquifer feeding Pertuso spring (Central Italy). International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM, 1. https://doi.org/10.5593/SGEM2016/B11/S02.107

Sappa, G., Ferranti, F., De Filippi, F. M., & Cardillo, G. (2017). Mg2+-based method for the Pertuso spring discharge evaluation. Water (Switzerland), 9(1), 67. https://doi.org/10.3390/w9010067

Sappa, G., Ferranti, F., Iacurto, S., & De Filippi, F. M. (2018). Effects of climate change on groundwater feeding the Mazzoccolo and Capodacqua di Spigno Springs (Central Italy): First quantitative assestments. International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM, 18(3.1). https://doi.org/10.5593/sgem2018/3.1/S12.029

Schemel, L. E., Cox, M. H., Runkel, R. L., & Kimball, B. A. (2006). Multiple injected and natural conservative tracers quantify mixing in a stream confluence affected by acid mine drainage near Silverton, Colorado. Hydrological Processes, 20(13), 2727–2743. https://doi.org/10.1002/hyp.6081

Sivelle, V., Labat, D., Mazzilli, N., Massei, N., & Jourde, H. (2019). Dynamics of the flow exchanges between matrix and conduits in Karstified watersheds at multiple temporal scales. Water (Switzerland), 11(3), 1–15. https://doi.org/10.3390/w11030569

Stevanović, Z., Stevanović, A. M., Pekaš, Ž., Eftimi, R., & Marinović, V. (2022). Environmental flows and demands for sustainable water use in protected karst areas of the Western Balkans. Carbonates and Evaporites, 37(1), 3. https://doi.org/10.1007/s13146-021-00754-1

Tamburini, A., & Menichetti, M. (2020). Groundwater circulation in fractured and karstic aquifers of the Umbria-Marche Apennine. Water (Switzerland), 12(4), 1039. https://doi.org/10.3390/W12041039

Vigna, B. (2014). Acquisizione ed interpretazione dei dati di monitoraggio delle sorgenti. Geoingegneria Ambientale e Mineraria, 143(3), 43–58.

White, W. B. (2002). Karst hydrology: Recent developments and open questions. Engineering Geology, 65(2–3), 85–105. https://doi.org/10.1016/S0013-7952(01)00116-8

White, W. B. (2012). Conceptual Models for Carbonate Aquifers. Ground Water, 50(2), 180–186. https://doi.org/10.1111/j.1745-6584.2012.00923.x