

Pertuso Spring discharge assessment in the Upper Valley of Aniene River (Central Italy)

G. Sappa and F. Ferranti

Abstract—Sustainable management of karst aquifers is an important tool for the protection of these strategic water resources. Assessing water balance in a karst aquifer can be very difficult, due to the complex interactions and exchanges between groundwater and surface water. Therefore, measurements of streamflow and spring discharges are useful to assess karst aquifers available budget. Water balance calculation requires the estimation of two main parameters: recharge (precipitation, agriculture water, surface runoff, etc.) and discharge (underground outflow) which are affected by the highly heterogeneous distribution of permeability due to conduits and voids developed by the dissolution of carbonate rocks. This paper deals with the preliminary results of Pertuso Spring groundwater discharge assessment, in the Upper Valley of Aniene River (Central Italy), where the complex hydrogeological characteristics, related to the high heterogeneity of hydraulic properties, make difficult to set up a reliable methodology of measurement. To achieve this objective, an integrated approach based on the streamflow measurements and geochemical modeling, applied to groundwater and surface water was carried out.

Because no continuous discharge measurements of Pertuso Spring were available, different methods (velocity–area using current meter and geochemical assessment) were applied to evaluate the discharge of the spring and the stream flow during the monitoring period from July 2014 to May 2015. Aniene River streamflow measurements were carried out by using the conventional current-method and the salt dilution method. For the evaluation of the Pertuso Spring discharge, as a support for traditional discharge methodology, various groundwater and surface water monitoring campaigns have been made along the Aniene River, upstream and downstream the Pertuso Spring, for the acquisition of geochemical data. The aim of this study is to present the preliminary results of an indirect method for the estimation of the Pertuso Spring discharge, based on Magnesium concentration changes in groundwater and surface water.

Keywords — Aniene River, current meter method, discharge measurement, environmental tracers, Magnesium concentration, Pertuso Spring.

I. INTRODUCTION

KARST aquifers supply more or less the 25% of freshwater worldwide [1]. Water resources assessment

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is an important tool to evaluate groundwater dynamics in the aim of to maintain high-quality drinking water in the framework of climate change effects [2]. The determination of groundwater discharge is a direct measure of the amount of water available for drinking, industrial, and agricultural purposes. Karst springs react to rainfall events by sinkhole drainage and discharge from conduits in bedrock, responsible for the subsurface outflow [3]-[4]. The estimation of karst spring discharge is affected by methodological difficulties, data deficiencies, and resultant uncertainties due to spatial variability of permeability in carbonate rocks [5], and also because the pathway of groundwater outcoming is not always the same along the year. The traditional quantitative approach for the evaluation of groundwater discharge is the application of water balance, which requires the estimation of water storage and flow. Karst systems are characterized by a highly heterogeneity due to a network of highly permeable flow features, embedded in a less permeable fractured rock matrix [6]. Thus, in these complex hydrogeological scenarios, understanding the behavior of the groundwater system and the recharge–discharge relation is required to formulate a reliable water balance [7]. In karst aquifer the presence of underground stream flows, that are not accurately measurable, makes very difficult to develop a reliable methodology that includes physical assessments of the input–output relation [8]-[9]. In this paper, an indirect groundwater model has been set up in the aim of evaluating karst spring discharge. The model drives to a reliable estimation of groundwater discharge in karst aquifers. The Pertuso Spring, located in the Upper Valley of Aniene River (Central Italy) is used for validate this model. The Aniene River basin is located in the upper part of the shallow karst aquifer, where surface water and groundwater exhibit complex interactions.

This paper presents preliminary results of discharge measurements carried out in two gauging sections along the Aniene River, upstream and downstream the Pertuso Spring, by the application of traditional current meter, in the framework of the Environmental Monitoring Plan related to the catchment project of the Pertuso Spring which is going to be exploited to supply an important water network in the South part of Roma district [10]. In the following they are presented the results obtain with the current method and the comparison with a proposed model based on Magnesium concentration changes in groundwater and surface water. As

a matter of fact the aim of the present work is to set up an indirect reliable method to estimate spring discharge in karst aquifer where the complex groundwater flows can make difficult the application of traditional quantitative approaches.

II. GEOLOGICAL AND HYDROGEOLOGICAL SETTING

The study area is located along the SW boundary of the Simbruini Mountains, characterized by the confluence of the Fiumata Valley and the Granara Valley from which starts the Valley of Aniene River [11]. In this area it outcrops an important carbonate karst aquifer, mainly made of highly permeable Cretaceous carbonate rocks, deeply fractured, locally showing distinctive karst features (Fig. 1).

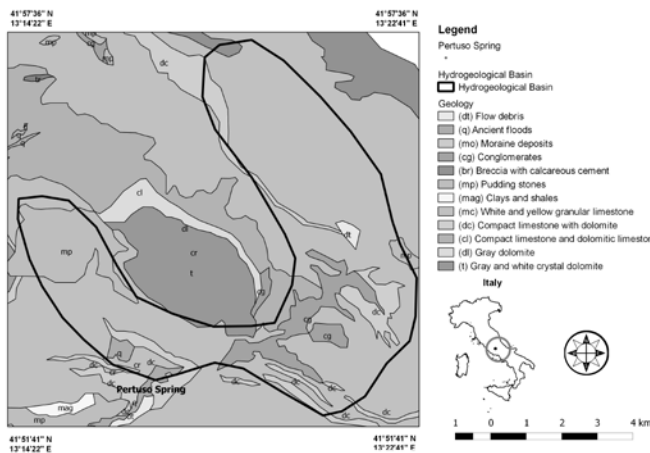


Fig. 1 simplified geological map of the study area

The alternation of carbonate rocks, limestone and dolomite, together with the epikarst, made of residual of karst activity, and some marly horizons, dating back to the Miocene age, are the main responsible for the hydrogeological system of this area [12]. The abundance of water is due to the permeability of the limestone (highly fractured and deep karst), which stores a significant quantity of rainwater feeding perennial springs located in the Upper Valley of Aniene River [13].

Table 1 main springs in the Upper Valley of Aniene River

Spring	Elevation (m a.s.l.)	Mean Annual Discharge (l/s)
Rigoglioso	1110	250
Fonte del forno	950	164
Fonte Santa	900	65
Pertuso	698	1400
Cesa degli Angeli	940	200
Cardellina bassa	955	10
Cardellina media	970	15
Cardellina alta	990	25
Acqua nera	1030	80
Zompo lo schioppo	900	1200
La Sponga	832	400
Renga	875	40
Capo di Rio	930	30

Groundwater coming out from this karst aquifer discharges from 13 small and large springs located close to the boundary of the carbonate hydrogeological system. Table 1 shows elevation and mean annual discharges of these springs. The mean annual discharge of Pertuso Springs is 1400 l/s, whereas the mean annual discharge of the other springs ranges from 10 to 1200 l/s. The catchment area of Pertuso Spring has been estimated in 50 km² [10].

The most important discharge point of this aquifer is the Pertuso Spring, located westward of Filettino (FR) at an elevation of 696 m above sea level. The spring is located in the dolomite outcrop (Fig. 2), upstream the town of Trevi in Lazio and flows into the Aniene River, close to the boundary of the carbonate hydrogeological system [12].

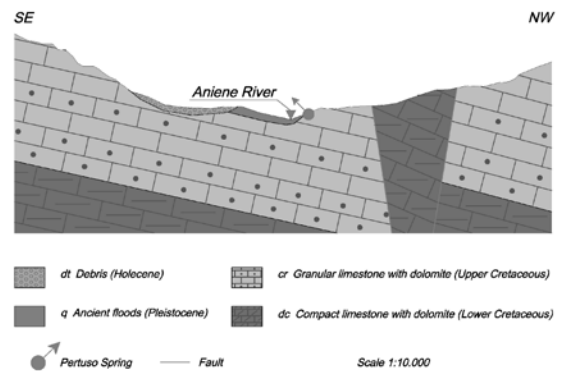


Fig. 2 schematic geological section of the Pertuso Spring

The limestones outcropping in the study area are deeply fractured and mostly soluble; karst erosion has occurred on a large scale on this area, assuming great importance in the modelling of the soil and also of the subsoil. The karst network system, located along the NS boundary, has a total length of about 311 m. This spring, with an average discharge capacity (Q) of 1.4-1.5 m³/s [13], is one of the most important fresh water springs in the South part of Latium Region and currently is feeding with a rate of 360 l/s the Comunacqua hydroelectric power plant, owned by ENEL group. The Pertuso Spring discharge almost immediately increases after heavy rainfall (from March to May) followed by a retarded decrease in discharge (Fig. 3).

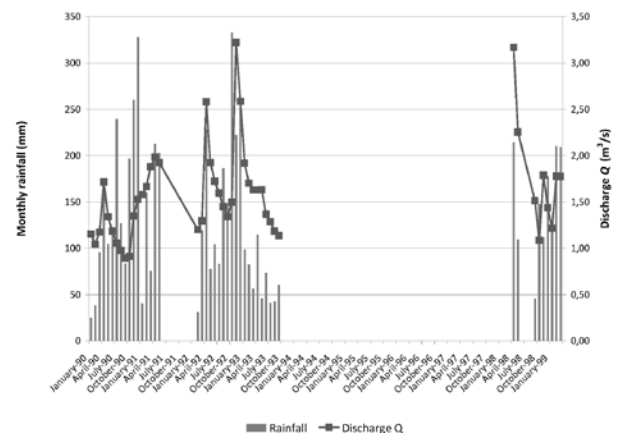


Fig. 3 hydrogeological rate of Pertuso spring in the 1990 – 1999 period (Filettino meteorological station)

This type of reaction is due to the presence of karst features, which receive water from nearby sources in a short period of time. Later, this water stored in the limestone matrix is slowly released back into the karst conduits. Unfortunately they are not available data referred to groundwater discharge more than ones represented in Fig. 3.

III. MATERIALS AND METHODS

The Pertuso Spring discharge in the karst aquifer of the Upper Valley of Aniene River was studied through the

implementation of various methods, tailored to the available set of hydrogeological data. In the framework of this work two main activities were carried out: the execution of four groundwater and surface water monitoring campaigns from July 2014 to May 2015 and six discharge measurements campaigns driven from September 2014 to April 2015, using the current meter method (Fig. 4).

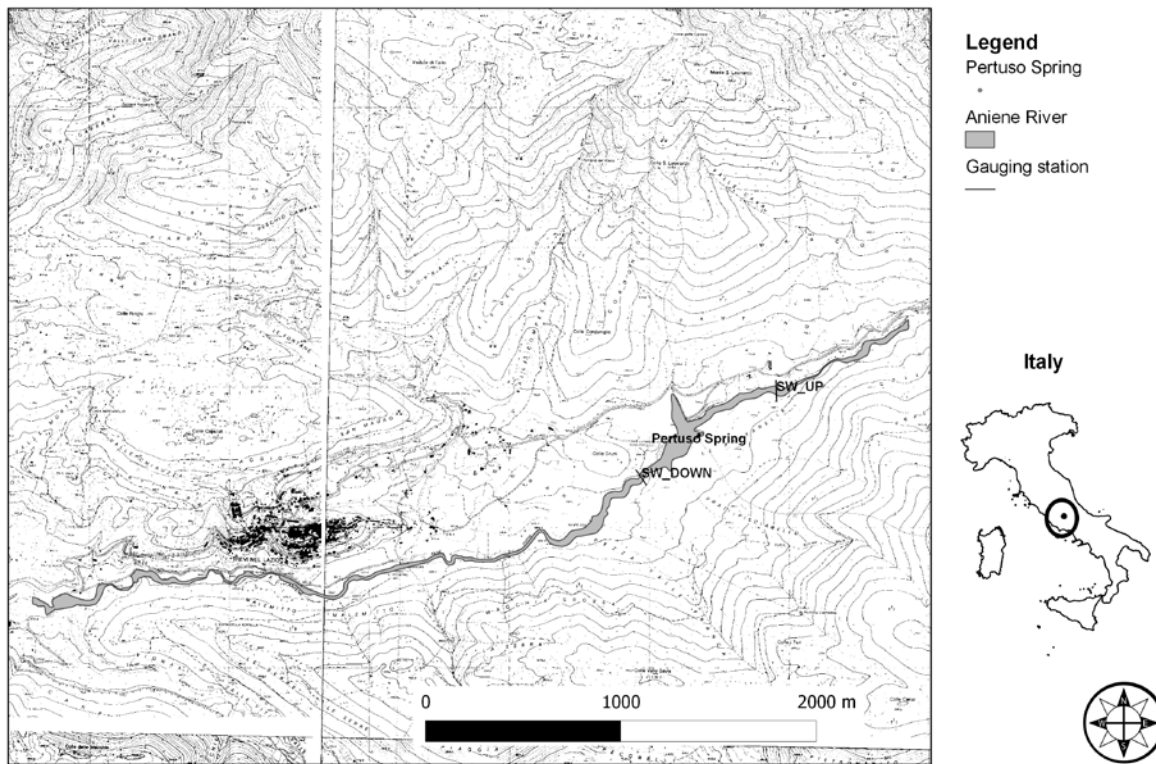


Fig. 4 study area and location of gauging sections

Table 2 main physico-chemical characteristics of water samples (n.d.= not determined)

Sample	Date	T (°C)	EC (μS/cm)	pH	Eh (mV)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	HCO ₃ (mg/l)	Cl (mg/l)	SO ₄ (mg/l)
Pertuso Spring	July 2014	8.0	322	7.4	112	48.9	9.77	1.91	0.50	210	3.54	2.39
	November 2014	8.0	300	7.2	110	51.0	8.32	1.83	0.32	216	3.48	2.41
	January 2015	9.5	410	6.9	481	53.3	9.89	2.05	0.45	206	3.66	2.54
	May 2015	8.5	300	10.8	243	49.0	9.33	1.86	0.31	224	3.35	2.34
SW_UP	July 2014	11.3	422	8.3	74	53.4	23.6	2.48	0.35	87	4.16	2.87
	November 2014	7.7	360	8.3	89	54.0	23.5	2.59	1.61	89	4.34	3.04
	January 2015	5.8	340	7.3	435	57.8	25.2	2.59	1.61	95	4.50	3.18
	May 2015	10.7	390	9.6	212	53.9	24.6	n.d.	n.d.	86	4.12	2.90
SW_DOWN	July 2014	9.9	352	7.8	66	51.3	12.8	2.01	0.18	72	3.66	2.5
	November 2014	7.3	320	7.6	78	52.4	12.0	1.11	0.44	72	3.72	2.56
	January 2015	7.2	270	6.9	449	55.6	13.0	1.11	0.44	77	4.17	2.73
	May 2015	8.9	280	8.1	210	51.4	12.2	n.d.	n.d.	70	3.53	2.47

Water samples were collected, every three months, from July 2014 to May 2015, from Pertuso Spring and from two cross section located along the Aniene River, upstream and downstream this spring. Field parameters, such as pH, conductivity (EC), water temperature (T), Redox potential (Eh), dissolved oxygen (DO) were measured on-site using a multi-parameter PC650 probe hand-held meter (Eutech Instruments) (Table 2). All samples were filtered by 0.45 μm cellulose filters and stored at 4 °C until analysis in the laboratory. Batches of 12 samples were analyzed in the Geochemical Laboratory of Sapienza University of Rome. Major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) were determined by ion chromatography (IC) using an 761 Professional IC Metrohm and Metrosep C2-150 column, whereas major anions (Cl^- , SO_4^{2-}) were determined by Metrosep A sup 4–250 column. Alkalinity was determined immediately after sampling by means titration and converted to hydrogen-carbonate (HCO_3^-) according to [14]. The saturation index of calcite ($\text{SI}_{\text{Calcite}}$) and dolomite ($\text{SI}_{\text{Dolomite}}$) in water samples were calculated by means of PHREEQC [15] with the WATEQ4F database.

The discharge measurements were carried out along the Aniene River, upstream (ST_UP) and downstream (ST_DOWN) the Pertuso Spring, by the application of traditional current meter. These cross sections have been chosen as gauging section because they are relatively straight to ensure streamlines parallel to each other and reduce errors in velocity measurements. The bed stream relatively uniform and free of heavy aquatic growth allows keeping the current meter perpendicular to the flow whereas measuring velocity, to ensure a stable relation between stage and discharge. At ST_UP and ST_DOWN gauging stations, the Aniene River surface width ranges from 3.5 to 4 meters and from 8 to 9 meters, respectively. The depth ranges from 0.3 to 0.8 meter for ST_UP and from 0.4 to 1 meter for ST_DOWN, according to the limits imposed by the type of current meter used.

According to the U.S. Geological Survey (USGS) procedure, the current meter method involves measuring the area and the velocities of a stream at a cross section, which must be perpendicular to the main flow of the river. Usually, river discharge is calculated as the product of the cross section area of flow by the average stream flow velocity in that cross section. Thus, the river cross section is divided into many vertical sub-sections, in each one the area is obtained by measuring the width and depth of the sub-section and the stream flow velocity is determined using a current meter. The sum of the products of area velocity for each segment gives the total stream discharge [16]-[17].

The preliminary step in stream flow measurements is the determination of the section width by stringing a measuring tape from bank to bank at right angles to the direction of flow. In mountain stream, where the hydraulic pattern changes monthly, more than a single measurement is needed

to characterize accurately the hydraulic profile of the cross section. For this reason it has been necessary determine the hydraulic profiles of ST_UP and ST_DOWN gauging sections for each discharge measurements campaigns (Fig. 5, 6, 7, and 8). This measuring tape is used to define the hydraulic profile of the cross section and the location of each velocity measurements. Determining the cross sectional area of a stream involves measuring water depths at a series of points across the stream and multiplying by the width of the stream within each segment represented by the depth measurement. With the aim to obtain an average velocity, each section has been divided into vertical parts, spaced by 1.00 m (Fig. 5 and 6). Along each one of these investigated verticals, up to 2 measuring points have been defined at different depths (0.2 and 0.3 m from bed stream).

The main equipment needed to measure the stream flow velocity in each verticals is a SEBA horizontal axis current meter F1, having a propeller diameter of 80 mm which, combined with SEBA Z6 pulse counter, allows to measure velocity between 0,025 m/s and 10 m/s. The SEBA current meter has been used as rod equipment with tail plane for best positioning to the flow direction. For each measurement point, flow velocity is determined counting the number of spins of the meter rotor during a fixed interval of time. Thus, in order to assess any fluctuations due to the turbulence condition and, also, to avoid accidental measurement errors, velocity has been measured for at least 60 seconds, according to EN ISO 748:2007 requirements [18].

This current meter method gives the local water velocity in each vertical following the application of a calibration equation between stream velocity (cm/s) and the number of spins (s-1) (1).

$$v = 0.82 + 33.32 \cdot n \quad (1)$$

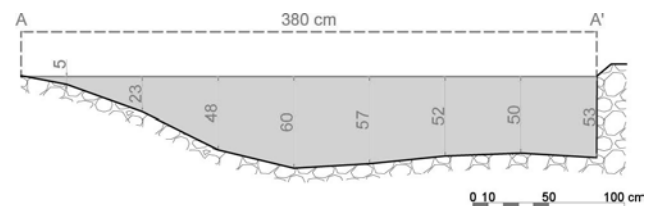


Fig. 5 ST_UP cross section illustrating sub-sections to determine discharge by current meter method (July 2014)

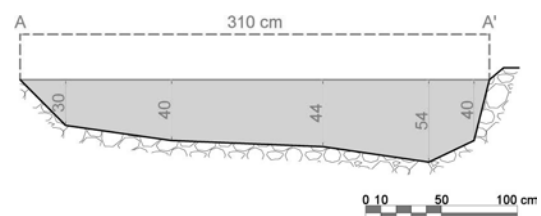


Fig. 6 ST_UP cross section illustrating sub-sections to determine discharge by current meter method (November 2014)

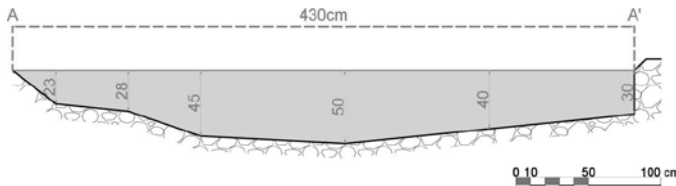


Fig. 7 ST_UP cross section illustrating sub-sections to determine discharge by current meter method (January 2015)

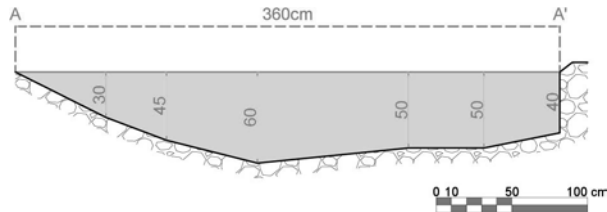


Fig. 8 ST_UP cross section illustrating sub-sections to determine discharge by current meter method (May 2015)

IV. RESULTS AND DISCUSSION

Stream discharge measurements obtained by the velocity area method are summarized in Table 3.

Table 3 mean discharge values obtained by current meter method

Date	Discharge Q (m ³ /s) ST_UP	Discharge Q (m ³ /s) ST_DOWN
July 2014	0.54	2.45
November 2014	0.35	1.48
January 2015	0.41	1.92
May 2015	0.50	2.75

Table 3 shows the discharge values coming out from four measurements campaigns, referred to the maximum height value, measured in the stream in each campaign. The average current meter streamflow for ST_UP and ST_DOWN gauging stations was 0.45 m³/s and 2.15 m³/s, respectively.

The temperature of water samples ranges between 5.8 °C and 11.3 °C. The pH of these samples is between 6.9 and 10.8 (average 8) showing neutral to slightly alkaline. The variability in pH of the springs is caused by changes in flow paths, water discharge and residence times within the aquifer [19]. The redox potential of the springs showed partially oxidizing waters (74-449 mV, with an average of 213 mV). Chemistry of groundwater coming from karst aquifer in the unsaturated zone is modified by local flow variations and changes in redox condition [20]. Electrical conductivity ranges between 270 and 422 μS/cm and generally decreases in wet seasons due to the rainfall dilution.

The hydrochemical facies of samples waters was studied by plotting the concentrations of major cations and anions in the Piper diagram (Fig. 9). Based on the dominance of major cationic and anionic species, Ca-HCO₃ water type was identified, suggesting that all groundwater and surface water come from the karst aquifer.

Calculated saturation indexes with respect to calcite, dolomite and gypsum of the spring and surface water

samples are shown in Table 4.

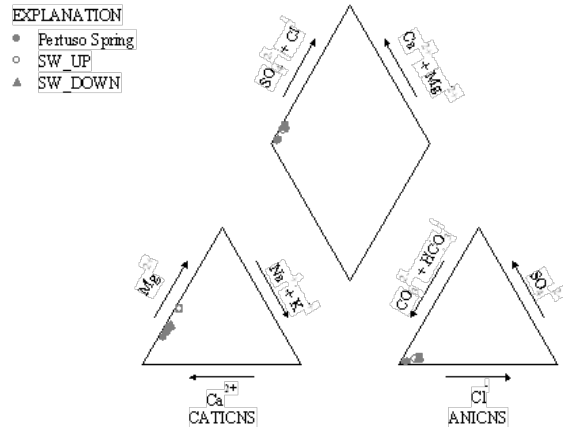


Fig. 9 Piper diagram for hydrochemical facies evolution and water classification

Geochemical modeling shows that water chemistry in the study area is affected by the interaction with carbonate minerals.

Table 4 Saturation Index (SI) values for common carbonate and evaporate minerals of spring and surface water samples

Sample	Date	SI _{calcite}	SI _{dolomite}
Pertuso Spring	July 2014	-0.25	-1.12
	November 2014	-0.46	-1.54
	January 2015	-0.71	-2.04
ST_UP	July 2014	0.35	0.48
	November 2014	0.29	0.29
	January 2015	-0.68	-1.68
ST_DOWN	July 2014	-0.22	-0.93
	November 2014	-0.49	-1.56
	January 2015	-1.14	-2.85

Figures 10 and 11 show a comparison of calcite and dolomite saturation indexes of all water samples as a function of HCO₃ concentration.

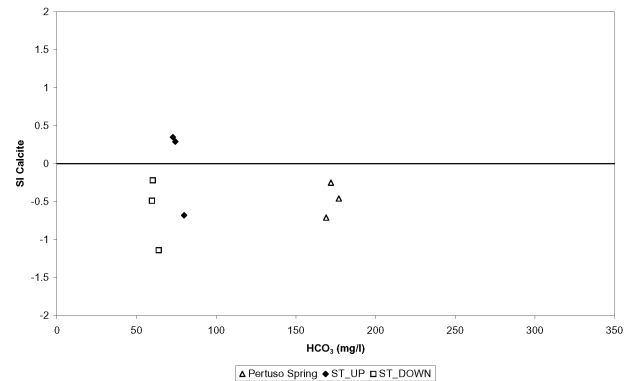


Fig. 10 calcite saturation index versus HCO₃

All samples are undersaturated with respect to calcite and dolomite, except for water samples collected upstream the

Pertuso Spring in July and November 2014, which implies a huge dissolution and high mineralization along groundwater flow paths. This indicates that the surface water is able to dissolve dolomite along the flow paths and hence, the concentrations of Mg^{2+} in the solution would increase.

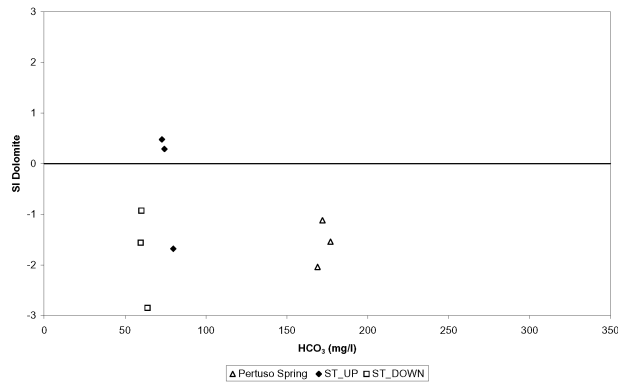


Fig. 11 dolomite saturation index versus HCO_3

The rate of hydrochemical evolution can be determined by the Mg/Ca ratios presented in Fig. 10. The changes in Mg and Ca concentrations in water samples mainly depend on the residence time of groundwater in karst systems which is controlled by the volume and mechanism of recharge, the distance from the recharge area and dissolution of carbonate minerals [21].

The Mg/Ca ratios indicate that the dissolution of carbonate minerals played a significant role in the groundwater and surface water chemistry, depending on the hydrological processes which control the groundwater residence time and chemical equilibrium in the aquifer (Fig. 12). Water samples coming from ST_UP, upstream the Pertuso Spring show the highest Mg/Ca ratios (0.5-1), whereas downstream samples and Pertuso Spring groundwater show lower Mg/Ca ratios (<0.5).

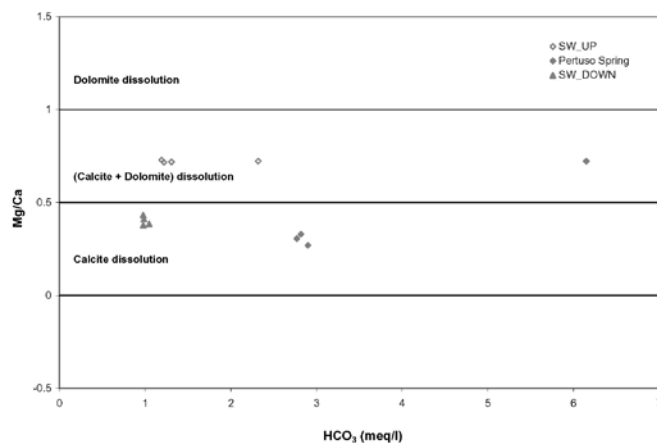


Fig. 12 saturation Index (S.I.) values for common carbonate minerals of water samples

The increase in Mg/Ca ratio, due to a larger concentration

of Magnesium upstream the Pertuso Spring (Table 5), is due to the dissolution/precipitation reaction of calcite and dolomite. The ST_UP samples are oversaturated with respect to calcite and dolomite, however, the high Mg/Ca ratio may be due to the weathering of Mg-rich dolomite, where dolomitic limestones and dolomites are the most outcropping formations in this area.

Table 5 comparison of Magnesium concentrations in groundwater and surface water

Date	Mg^{2+} (mg/l)		Pertuso Spring
	SW_UP	SW_DOWN	
July 2014	23.5	12.8	9.8
November 2014	23.5	12.0	8.3
January 2015	25.2	13.0	9.9
May 2015	24.6	12.2	9.3

We observed proportionality between the decreasing of Magnesium concentrations and the increasing of the streamflow discharge (Fig. 13). The higher the flow, the more it dilutes the tracer. For this reason it has been chosen Magnesium concentrations as tracer of dilution processes.

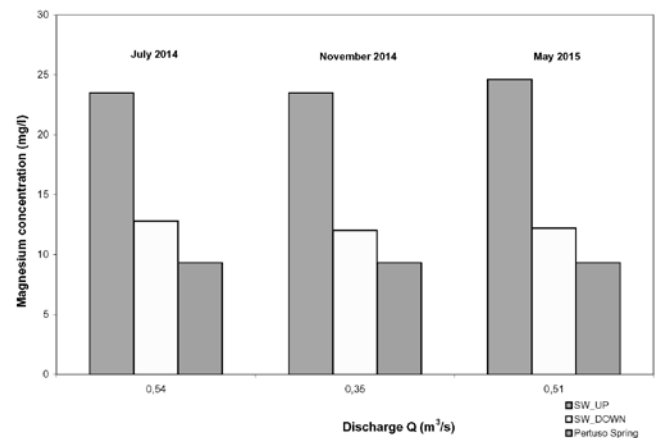


Fig 13 plot of Magnesium concentration vs. discharge in m^3/s

The Pertuso Spring discharge (Q_p) can be computed from the equation for the conservation of mass (2), using the discharge values, Q (l/s) and the Magnesium concentration, C (meq/l) upstream (C_{UP} ; Q_{UP}) and downstream (C_{DOWN} ; Q_{DOWN}) the spring.

$$Q_{UP}C_{UP} + Q_p C_p = Q_{DOWN}C_{DOWN} \tag{2}$$

Considering n the percentage contribution that the Pertuso Spring provides total discharge measured downstream, the Pertuso Spring discharge (Q_p) is defined according to (3).

$$Q_p = Q_{UP} \cdot \frac{n}{1-n} \tag{3}$$

The Pertuso Spring discharge values downstream the Aniene River, obtained by this indirect method, are definitely comparable with ones obtained by the traditional current meter method (Table 6 and Fig. 14).

Table 6 Pertuso spring discharge values obtained by Magnesium tracer method

Date	$Q_{\text{current_meter}}$ (m^3/s)	Q_{Mg} (m^3/s)	Percent difference (%)
July 2014	1.91	1.92	-1
November 2014	1.13	1.06	7
January 2015	1.51	1.58	-7
May 2015	2.25	2.16	9

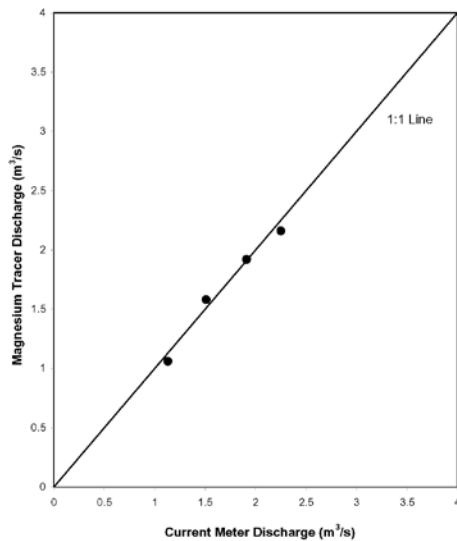


Fig. 14 comparison of current-meter and Magnesium tracer model at the Pertuso Spring

V. CONCLUSION

A combined geochemical and streamflow discharge techniques were applied to groundwater and surface water from the carbonate aquifer of the Upper Valley of Aniene River, Central Italy, which is the most important groundwater reservoir in this area, in order to set up a reliable methodology for the evaluation of Pertuso Spring discharge.

In framework of the Environmental Monitoring Plan related to the catchment project of the Pertuso Spring, physical-chemical data, in addition and streamflow discharge has been acquired from July 2014 to May 2015. In this study we presented the first results of the application of an indirect method, based on Magnesium as a tracer, with its concentration changes in groundwater and surface water, for the evaluation of karst spring discharge.

The measurements of Magnesium concentration, along the Aniene River and groundwater coming from the Pertuso Spring, has confirmed potential for using Magnesium, as a suitable aqueous tracer, to assess karst spring discharge. These preliminary results show that the dilution of naturally dissolved Magnesium ion in groundwater and surface water can give a reliable estimate of dolomite dissolution where traditional methodologies are not easily applied. This value depends on the Pertuso Spring water, which is undersaturated with respect to dolomite until it joins the main stream of Aniene River, where the magnesium content

is much higher due to the oversaturation with respect to dolomite (ST_UP). Thus, the decreasing of Magnesium concentrations downstream (ST_DOWN) the Pertuso Spring is due to this mixing with spring waters.

This method applied in the Upper Valley of Aniene River showed its reliability and indicates that such measurements can be useful to better understand groundwater movement in this karst system. In fact, the use of Magnesium, as an aqueous tracer, is well suited because it occurs naturally in the environment and it is easy to monitor and its measurements inexpensive to be performed.

REFERENCES

- [1] D.C. Ford, P.W. Williams, *Karst Geomorphology and Hydrology*, John Wiley & Sons, Chichester, England, 2007.
- [2] G. Sappa, G. Luciani, "Groundwater Management in Dar Es Salam Coastal Aquifer (Tanzania) under a Difficult Sustainable Development", WSEAS Transactions on Environment and Development, vol. 10, 2014, pp. 465-477.
- [3] M. Bakalowicz, "Karst groundwater: a challenge for new resources", *Hydrogeology Journal*, vol. 13, Springer, 2005, pp. 148-160.
- [4] M. Bakalowicz, "Management for karst groundwater resources", *Karst Management*, Springer, 2011, pp. 263-284.
- [5] B.R. Scanlon, R.W. Healy, P.G. Cook, "Choosing appropriate techniques for quantifying groundwater recharge", *Hydrogeology Journal*, vol. 10, Springer, 2002, pp. 18-39.
- [6] B. Andreo, J. Vías, J.J. Durán, P. Jiménez, J.A. López-Geta, and F. Carrasco, "Methodology for groundwater recharge assessment in carbonate aquifers: application to pilot sites in southern Spain", *Hydrogeology Journal*, vol. 6, Springer, 2008, pp. 911-925.
- [7] C. Cherubini, N. Pastore, V. Francani, "Different approaches for the characterization of a fractured karst aquifer", WSEAS Transactions on fluid mechanics, vol. 3, 2008, pp. 29-35.
- [8] J.W. Hess, W.B. White, "Storm response of the karstic carbonate aquifer of south central Kentucky", *Hydrogeology Journal*, vol. 99, Springer, 1988, pp. 235-252.
- [9] W.B. White, *Geomorphology and Hydrology of Karst Terrains*, Oxford University Press, New York, 1988.
- [10] G. Sappa, F. Ferranti, "An integrated approach to the Environmental Monitoring Plan of the Pertuso spring (Upper Valley of Aniene River)", *Italian Journal of Groundwater*, 2/136, 2014, pp. 47-55.
- [11] F. Cipollari, D. Cosentino, M. Parotto, *Modello cinematico-strutturale dell'Italia centrale*, Studi Geol. Camerti, 1995, pp. 135-143.
- [12] U. Ventriglia., *Idrogeologia della Provincia di Roma, IV, Regione orientale, Assessorato LL.PP, Viabilità e trasporti*, Roma, 1990.
- [13] Acea ATO 2 S.p.A., *Studio idrogeologico – Proposta di aree di salvaguardia della sorgente del Pertuso*, 2005.
- [14] APHA. *Standard Methods for the Examination of Water and Wastewater*, 20th ed.; American Public Health Association: Washington, DC, USA, 1998.
- [15] D. L. Parkhurst, C.A. J. Appello, *User's Guide to PHREEQC (Version 2)—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations*. US Geological Survey Water-Resources Investigations, Report 99-4259, 1999.
- [16] V.T. Chow, *Handbook of Applied Hydrology*. McGraw-Hill, New York, NY, 1964.
- [17] US EPA Region 6, *Standard operating procedure for stream flow measurement*, 2003.
- [18] BS EN ISO 748:2007, *Hydrometry. Measurement of liquid flow in open channels using current-meters or floats*, 2007.
- [19] S. Parisi, M. Paternoster, C. Kohfahl, A. Pekdeger, H. Meyer, H.W. Hubberten, G. Spilotro, G. Mongelli. "Groundwater recharge areas of a volcanic aquifer system inferred from hydraulic, hydrogeochemical and stable isotope data: Mount Vulture, southern Italy". *Hydrogeology Journal*, 2011, 19, pp. 133-153.

- [20] C. Emblanch, G. Zuppi, J. Mudry, B. Blavoux, C. Batiot. "Carbon 13 of TIDC to quantify the role of the unsaturated zone: The example of the Vaucluse karst system (southeastern France)". *Hydrogeology Journal*, 2003, 279, pp. 262–274.
- [21] D. Langmuir. *Geochemistry of Some Carbonate Ground Waters in Central Pennsylvania*. *Geochimica et Cosmo-chimica Acta*, Vol. 35, No. 10, 1971, pp. 1023-1045.