Preliminary validation of an indirect method for discharge evaluation of Pertuso Spring (Central Italy)

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Abstract: - This paper deals with the results of the first year of the Environmental Monitoring Plan, related to the catchment project of Pertuso Spring, which is going to be exploited to supply an important water network in the South part of Roma district. The study area is located in the Upper Valley of the Aniene River (Latium, Central Italy), in the outcrop of Triassic-Cenozoic carbonate rocks, and belong to an important karst aquifer. Pertuso Spring is the main outlet of this karst aquifer and is the one of the most important water resource in the southeast part of Latium Region, used for drinking, agriculture and hydroelectric supplies. Karst aquifer feeding Pertuso Spring is an open hydrogeological system aquifer characterized by complex interactions and exchanges between groundwater and surface water which influence the aquifer water budget. Thus, evaluation of groundwater discharge from this karst spring can be affected by difficulties in performing measurements because of the insufficient knowledge about water transfer processes in the hydrological cycle and geometry of drainage conduits.

The aim of this paper is to assess the interactions between karst aquifer feeding Pertuso Spring and Aniene River based on stream discharge measurements and water geochemical tracer data in order to validate an indirect method for karst spring discharge evaluation. As a matter of fact, in this paper, there are presented the results of the application of Magnesium as a reliable tracer of karst spring discharge. This indirect method is based on the elaboration of surface water discharge measurements in relationship with Mg^{2+} concentration values, determined as for groundwater, coming from Pertuso Spring, as for surface water sample, collected upstream and downstream of Pertuso Spring, along Aniene River streamflow. The application of Magnesium as an environmental tracer provides a means to evaluate discharge of Pertuso Spring, as it came up to be a marker of the mixing of surface water and groundwater. On the other hand, the Magnesium ion concentration provides information for the identification of groundwater flow systems and the main hydrogeochemical processes affecting the composition of water within the karst aquifers.

Key-Words: - Aniene River, carbonate aquifer, groundwater, karst spring discharge, Magnesium tracer, Pertuso Spring

1 Introduction

Most of part of groundwater in the southeast part of Latium Region, as in the whole Apennine Mountains chain [1] is stored in karst aquifers.

The increasing of anthropogenic activities and the impacts of climate change are identified to be responsible of karst groundwater depletion [2]-[3]. Thus, groundwater exploitation in karst aquifers requires special management strategies to prevent their quality and quantity depletion and to support decision-making for water resources management [4]-[5].

In karst aquifers, the fast underground outflow in the saturated zone [6]-[7] is due to the heterogeneous distribution of permeability, because there are many conduits and voids developed by the dissolution of carbonate minerals. Therefore, quantification of karst spring discharge and water budget formulation requires defining the karst network geometry, which is not, every time, measurable with reliability [8].

As a matter of fact, the complex hydrological behavior, on one hand, the high heterogeneity of hydraulic properties [9]-[10], on the other one, make data collection about karst networks and groundwater very difficult, and the water budget evaluation is very often too much uncertain. For this reason, environmental tracer are useful tools to provide information about groundwater flow paths and residence times in karst aquifer systems without allowing for the specification of input locations and times [11]-[12].

2 Problem Formulation

Environmental tracers are natural and anthropogenic chemical and isotopic substances that can be measured in groundwater and used to understand hydrologic properties of aquifers [13]-[14].

Environmental tracers provide information about the flow and mixing processes of water coming from different sources [15]-[16]. They are also useful to point out directions of groundwater flow and to determine origin and residence times of karst groundwater [17]-[18]. Typical natural tracers are major ions, trace elements, dissolved organic carbon and water isotopes [19]-[20]. Groundwater circulating in karst aquifer generally has great concentrations of Calcium and Magnesium as the result of bedrock weathering processes. Variations of Ca^{2+} and Mg^{2+} in groundwater chemical compositions are used very successfully as natural tracers in studies aiming to evaluate groundwater residence time within the karst aquifers [17]. The changes in Ca^{2+} and Mg^{2+} concentration values mainly depend on the residence time of groundwater in karst systems, which are controlled by the volume and mechanism of recharge, the distance from the recharge area and the dissolution of carbonate minerals [21]-[22]. The dissolution kinetics of Magnesium is longer than that of Calcium, so the increase of the Mg^{2+}/Ca^{2+} ratio implies the saturation of water with calcite, highlighting long residence time and enhanced weathering along the groundwater flow paths [22]-[23]. The Mg^{2+} content in groundwater also depends on others parameters such as chemical and mineralogical purity of limestone and presence of dolomite within the rock masses they flow across [24]. Nevertheless, the increase in Mg^{2+} concentration values, and hence Mg^{2+}/Ca^{2+} ratio not only depend on the dissolution/precipitation reaction of calcite and dolomite, but also an increase in water temperature accelerates the kinetics of the dissolution of dolomite [25]-[26]. However, it has been noticed that even in karst aquifers mainly made of limestone, the presence of slight impurities of Mg^{2+} in calcite can be responsible of significant changes in Mg^{2+}/Ca^{2+} ratio due to a high residence time of flowing waters [27]-[28]. Thus, environmental tracers and hydrochemical investigation techniques provide much information for the identification of groundwater flow systems and the main hydrogeochemical processes affecting the composition of water within the karst aquifers [28]. The analysis of the hydrogeochemical processes due to groundwater-surface water interactions let us to highlight the source of their mineralization and the influence of rock masses forming the aquifer.

2.1 Geological and Hydrogeological Framework

The karst aquifer feeding Pertuso Spring is located in the Upper Valley of the Aniene River (Latium, Central Italy), along the SW boundary of the Simbruini Mountains, in the outcrop of Triassic-Cenozoic carbonate rocks, locally covered by fluvial and alluvial deposits and, at lower altitudes, by Quaternary sediments [29]. The lithological sequence outcropping in the Upper Valley of Aniene River includes the North-West part of the Lower-Middle Miocene Latium-Abruzzi carbonate platform. The stratigraphic succession of dolomite, dolomitic limestone and limestone is distributed homogeneously from North to South and from East to West in the Valley [30]. The base of the stratigraphic series (Triassic) is widely spread among Filettino, Aniene River Springs and Faito Plateau. Dolomite is the dominant lithofacies, characterized by white and gray crystalline dolomite, with some breccia levels. Over this geological formation, limestones and dolomites, of Upper Cretaceous age (Sinemurian) are present, and their immersion is concordant with the Triassic dolomite [30]. Karst springs are numerous along the first part of the Aniene River and form in the Triassic dolomitic formations (Fig. 1). This karst system is characterized by one main outlet, Pertuso Spring, and several springs which inflow into the Aniene River, at different points (Table 1).

Spring	Altitude (m a.s.l.)	Average Discharge (l/s)
Acqua Santa	900	65
Acqua Nera	1030	80
Fonte del Forno	950	164
Cesa degli Angeli	940	200
Radica	1110	250
Pertuso	**698**	**1400**

Table 1, Elevation and average annual discharge of the main karst springs of Upper Valley of Aniene River [33]

Due to their lower solubility and their lower brittleness, in comparison with limestones, dolomites are less fracturated than these latter ones. As a consequence of it in the Aniene River Basin, almost all groundwater come out where there is a limestone-dolomite contact [29] (Fig. 1) and this latter one is below the former one. Pertuso Spring, the largest karst spring in South-East part of Latium Region, is located between Filettino and Trevi nel Lazio (FR) and belongs to the Special Area of Conservation (SAC) of Aniene River Springs (EC Site Code IT6050029) established under Directive 92/43/EEC (Fig. 2).

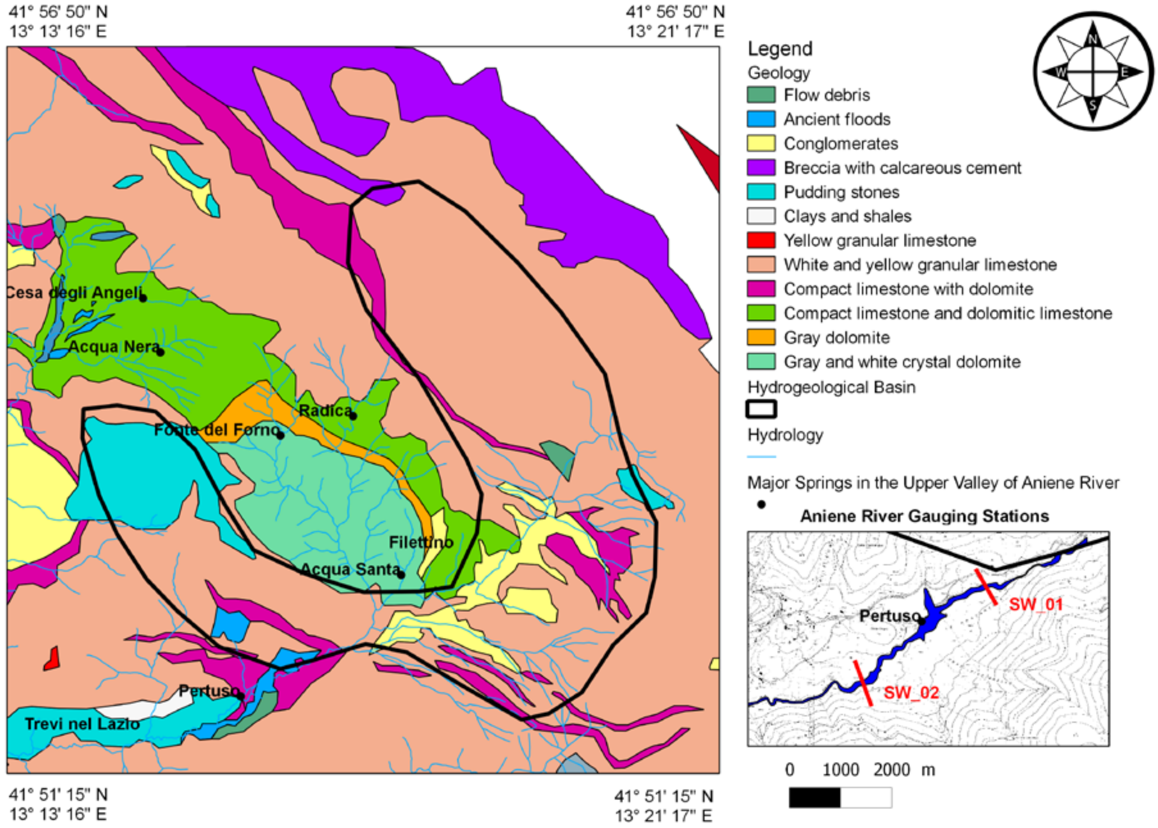

Fig. 1, Simplified geological map of Pertuso Spring hydrogeological basin and location of Aniene River gauging sections

Pertuso Spring (elevation of 720 m a.s.l.) is the main outlet of this karst aquifer and comes out about 1 km from the confluence of Fiumata Valley and Granara Valley [31].

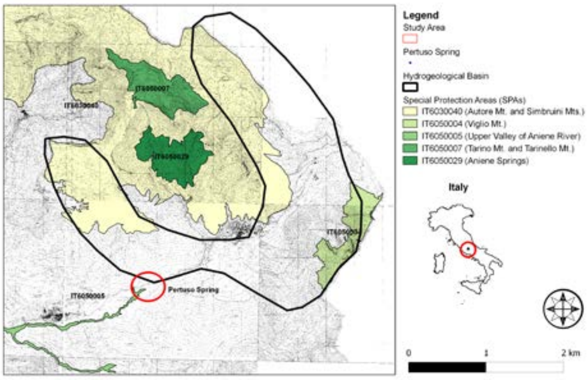

Fig. 2, Map of Special Areas of Conservation (SACs) in the Upper Valley of Aniene River

The outflow of Pertuso Spring is located in alluvial sediments, which cover a very thick layer made of Cretaceous limestone (Fig. 3). Spring water is captured for hydroelectric and drinking supplies, after which it flows into the Aniene River.

The Pertuso Spring hydrogeological basin is located between latitude 41° 51’ to 41° 56’N and longitude 13° 13’ to 13° 21’E and collect groundwater coming from a 50 km^2 catchment area [32] bounded by the Triassic dolomite to the NE (Fig. 1).

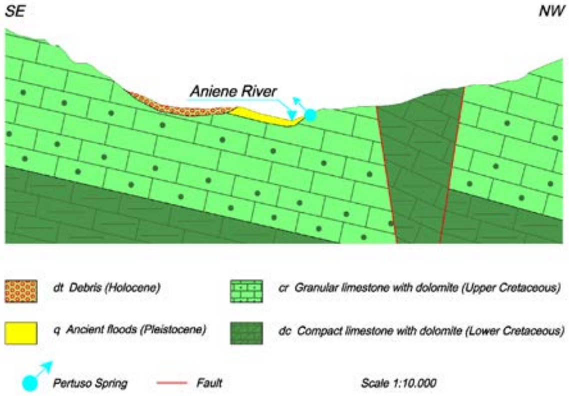

Fig. 3, Geological cross section showing the location of the Pertuso Spring

The aquifer feeding Pertuso Spring is made, for the most part, of Cretaceous karst limestone. The base of the stratigraphic series is constituted by Upper Cretaceous carbonates, made by the alternation of granular limestone and dolomites layers. Above these lie Quaternary fluvial and alluvial deposits, downward pudding and Miocene clay and shale [29] (Fig. 1).

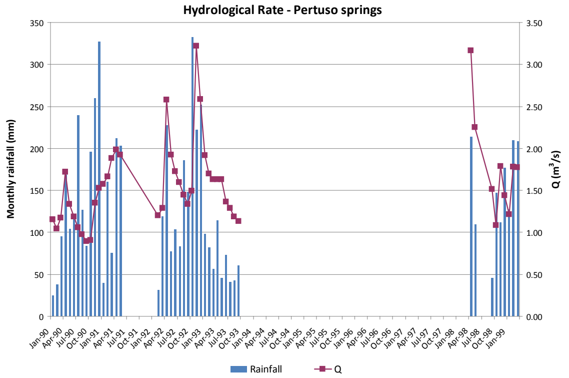

Fig. 4, Monthly rainfall and Pertuso Spring average rate in the 1990 - 1999 period (Filettino meteorological station)

Rainfall is the primary source of recharge to this karst aquifer. Most of the recharge of Pertuso Spring occurs through karst features such as sinkhole, dolines, swallows holes and fractures, which allow fast flow across the recharge zone. Pertuso Spring discharges at an annual average rate of 1400 l/s, based on the record from 1990 to 1999 [33], and responds rapidly to precipitation events, with significant increases in discharge rates which are proportional to the intensity of rainfalls (Fig. 4).

2.2 Pertuso Spring discharge evaluation aspects

Groundwater coming from Pertuso Spring, in the Upper Valley of Aniene River, are collected by a well known volume of carbonate rocks that make up the aquifer. The most distinctive feature of Pertuso karst spring is the branching network of conduits that increase in size in the downstream direction (Fig. 5).

The largest active conduit drains the groundwater flow coming from the surrounding aquifer matrix, the adjoining fractures and the smaller nearby conduits [34]-[35].

This conduit network is able of discharging large quantities of water very fastly through this karst aquifer (up to 3 m^3/s).

Karst springs are generally characterized by high and very variable discharge rate and represent the headwaters of important surface streams. These springs typically come out at the boundary of the hydrogeological basin, at a location of the minimum hydraulic head of the aquifer and sometimes next to the elevation of the base-level surface stream [22].

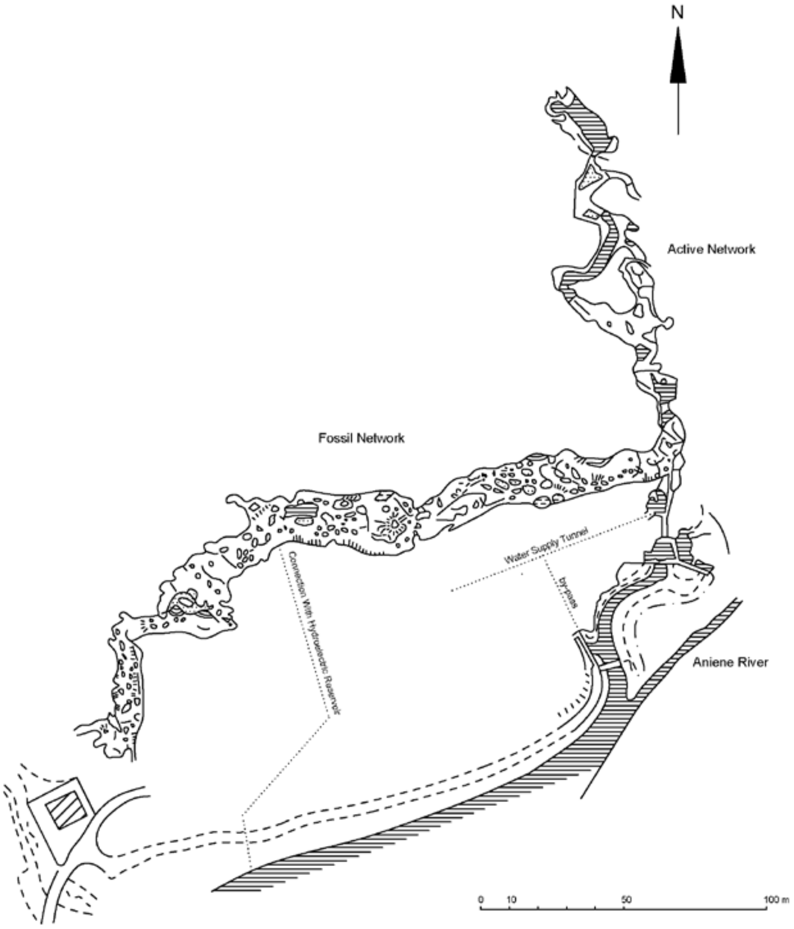

Fig. 5, Pertuso Spring drainage gallery map with plan view of the development of karst drainage network (modified from [33])

Groundwater basin boundaries are not strictly fixed, they may shift depending seasonally on the rates of recharge [7]. Many groundwater flow paths may route into adjacent groundwater basins causing difficulties to identify a single closing section. In addition, karst springs discharge is not easily measurable by standard techniques or conventional instruments. Sometimes channels are unsuitable for metering the flow, being shallow, choked with vegetation and with ill-defined banks [36]. In karst aquifers, the drainage network typically develops in a system of conduits that flows into a single trunk that discharges through the spring [6]. However, some karst aquifers may have a spread flow pattern, related to the enlargement of fractures and smaller conduits, located near the stream discharge boundary, or to the collapse of an existing trunk conduit [37].

Underflow springs are often hidden, for example by rising in the bed of the surface stream [7].

Thus, even if in this study we have identified a prevailing outlet section of the groundwater coming from Pertuso Spring, there is no chance to be sure that the whole spring contribution to Aniene River may always flow through that cross section. Consequently, the difficulty in measuring Pertuso Spring discharge makes the use of the traditional current meter method, which provides information on stream discharge in each cross section, limited and less reliable. Moreover, cross section morphology and flow regime are influenced by seasonal variations and anthropic operations, as reported in Figure 6 and 7, related to the monitoring campaign of July 2014 to December 2015.

Karst system dynamics are rapid, renewing most of the storage within a hydrologic year or less, which makes the effects of seasonal variations rapidly observable in the spring flow regime [10].

It has been noticed in dry season, at the Pertuso Spring outlet section, a reverse water inflow from Aniene River that makes unreliable the current meter measurement in that specific case. Hence, to be sure to evaluate a reliable quantification of Pertuso Spring discharge contribution to Aniene River we have decided to assess it as the difference of measured values along the river, upstream and downstream the spring [38].

In spite of being the spring, certainly, the only place where one can obtain information on the functioning of the whole system and consequently the organization of conduits and storage [10]. In this case, data coming directly from Pertuso Spring have been elaborated to set up an indirect model aimed to evaluate Pertuso Spring discharge.

Fig. 6, Pertuso Spring cross section (July 2014)

Fig. 7, Pertuso Spring cross section (December 2015)

Karst hydrology requires a mix of surface water concepts and ground water concepts [7]. For this reason, to better understand the behavior of this complex system and to validate discharge values calculated, it has been included a quali-quantitative characterization based on the Mg^{2+} contents of groundwater and surface water samples. As a matter of fact, Mg^{2+} content may generally provide information on residence time of ground waters within the aquifer [17] On the other hand, groundwater which have a longer underground flow path usually show the same properties: higher temperatures, higher Mg^{2+} concentrations and as a result a remarkable Mg/Ca ratio. However, the concentration of Mg^{2+} also depends on others parameters, such as chemical and mineralogical purity of limestone and presence of dolomite within the rock mass [24].

In this study, the Mg^{2+} ion concentration has been used as conservative water tracer, allowing us to obtain an alternative discharge calculation model based on mixing and dilution process due to Pertuso Spring and to compare the results of this model with those of traditional current meter method.

2.3 Materials and Methods

This paper presents the results of the first year of the Environmental Monitoring Plan, related to the catchment project of the Pertuso Spring, which is going to be exploited to supply an important civil water network in the South part of Latium Region, Central Italy. The experimental data, corresponding to the period July 2014 - May 2015, were obtained from field investigations and from chemical analyses performed in laboratory. Water samples were collected from three sampling points within the study area, i.e. one from Pertuso Spring, two on gauging stations located along the Aniene River, respectively, upstream (SW_01) and downstream (SW_02) the spring (Fig. 1).

Field investigations included in situ measurements of pH, temperature, electric conductivity (HANNA, Model HI9813-6) and redox and dissolved oxygen (HACH, Model LDO10101). Water samples were filtered by 0.45 µm cellulose filters and stored at 4 °C until analysis in the Geochemical Laboratory of Sapienza University of Rome [39].

Sample	**Date**	**T (°C)**	**pH**	**EC (µS/cm)**	**OD (mg/l)**	**Eh (mV)**
Pertuso Spring	July 2014	8.0	7.4	322	11.7	112
	November 2014	8.0	7.2	300	10.6	111
	January 2015	9.5	6.9	410	10.3	481
	May 2015	8.5	10.8	300	10.3	243
SW_01	July 2014	11.3	8.3	422	9.7	74
	November 2014	7.7	8.3	360	10.7	89
	January 2015	5.8	7.3	340	11.3	435
	May 2015	10.7	9.6	390	9.8	212
SW_02	July 2014	9.9	7.8	352	10.9	66
	November 2014	7.3	7.6	320	10.6	78
	January 2015	7.2	6.9	270	10.9	449
	May 2015	8.9	8.1	280	10.4	210

Table 2, Summary of T, pH, electric conductivity, dissolved oxygen and redox potential of water samples

Sample	**Date**	**Ca (mg/l)**	**Mg (mg/l)**	**Na (mg/l)**	**K (mg/l)**	**HCO_3 (mg/l)**	**Cl (mg/l)**	**NO_3 (mg/l)**	**SO_4 (mg/l)**
Pertuso Spring	July 2014	48.9	9.77	1.91	0.50	210	3.54	0.92	2.39
	November 2014	51.0	8.32	1.83	0.32	216	3.48	1.15	2.41
	January 2015	53.3	9.89	2.05	0.45	206	3.66	1.11	2.54
	May 2015	49.0	9.33	1.86	0.31	224	3.35	0.94	2.34
SW_01	July 2014	53.4	23.6	2.48	0.35	87	4.16	1.06	2.87
	November 2014	54.0	23.5	2.59	1.61	89	4.34	1.26	3.04
	January 2015	57.8	25.2	n.d.	n.d.	n.d.	4.50	1.23	3.18
	May 2015	53.9	24.6	n.d.	n.d.	n.d.	4.12	0.83	2.90
SW_02	July 2014	51.3	12.8	2.01	0.18	72	3.66	0.96	2.50
	November 2014	52.4	12.0	1.11	0.44	72	3.72	1.14	2.56
	January 2015	55.6	13.0	n.d.	n.d.	n.d.	4.17	1.09	2.73
	May 2015	51.4	12.2	n.d.	n.d.	n.d.	3.53	0.86	2.47

Table 3, Summary of major ions of water samples (n.d.= not determined)

Major ions were determined by ion chromatography (IC) by a 761 Professional IC Metrohm (reliability ±2%). A Metrosep C2-150 column was used for determining major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+), whereas major anions (Cl^-, NO_3^-, SO_4^{2-}) were determined by Metrosep A sup 4–250 column (accuracy 2-5%). Bicarbonate (HCO_3^-) was determined by titration with 0.1 N HCl (reliability ±2%).

A statistical summary of the major physico-chemical parameters is shown in Table 2 and 3.

The geochemical modeling program PHREEQC v3.0 [40], implemented with the thermodynamic dataset phreeqc.dat, was used to study mixing of groundwater and surface water to understand spatial and temporal patterns of mixing during base flow conditions.

The discharge measurements were carried out along the Aniene River, upstream (SW_01) and downstream (SW_02) Pertuso Spring, by the application of traditional current meter. According to the U.S. Geological Survey (USGS) procedure, stream discharge is calculated as the product of the cross section area by the average stream flow velocity in that cross section obtained using a current meter [41]-[42]. The main equipment needed to measure the stream flow velocity 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 [42]. This current meter method gives the local water velocity in each vertical following the application of a calibration equation between stream velocity, v (cm/s) and the number of spins, n (s^{-1}) (1).

$$v = 0.82 + 33.32 \cdot n \tag{1}$$

3 Problem Solution

In order to establish the groundwater discharge pattern, hydrochemical data and discharge measurements were used in the study.

Ca^{2+}, Mg^{2+} and HCO_3^- represent more than 80% of the dissolved solids in water samples and are influenced by the dissolution of carbonate minerals, forming limestone, which are the most dominant formations outcropping in the study area.

As a consequence of their flowing in a karst aquifer, all these water samples came out to be rich in Ca-Mg-HCO_3 as it is represented by Piper diagram (Fig. 8), but water samples coming from SW_01 gauging station present higher values of concentration in Mg^{2+}, while those coming from Pertuso Spring are definitely poorer in it, and show a clear composition of Ca-HCO_3 water type.

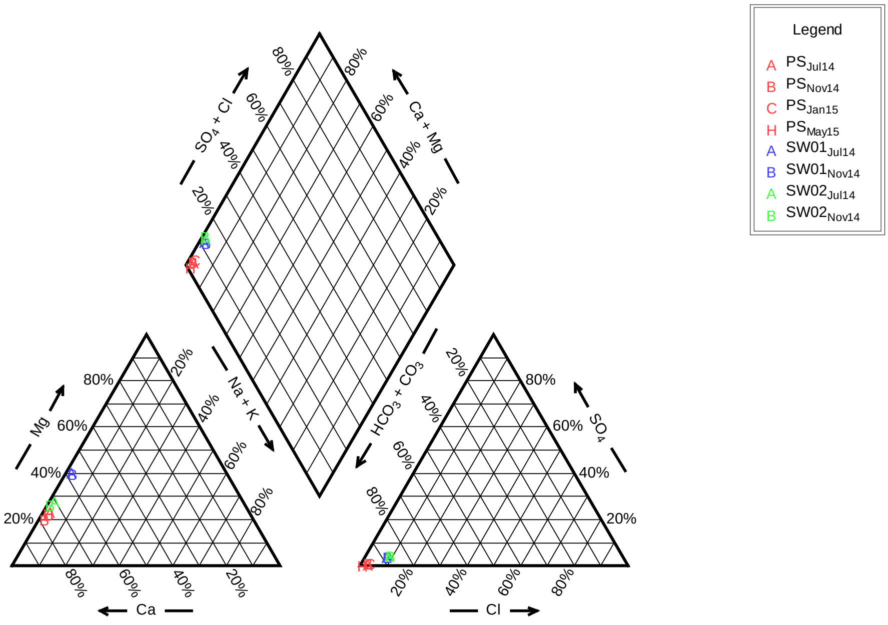

Fig.8, Piper diagram showing the hydrochemical facies of surface and groundwater in the karst aquifer feeding Pertuso Spring

These hydrochemical facies highlight that carbonate weathering processes (e.g. calcite and dolomite) are the most important factors of the observed water type.

Box plot for Mg^{2+} in groundwater and surface water is presented in Fig. 9. Following differentiation of Magnesium content along the Aniene River, we observed a 47% decrease in Mg^{2+}concentration in surface water downstream Pertuso Spring (SW_02) with respect to Mg^{2+}concentration measured in SW_01 (23.6 mg/l).

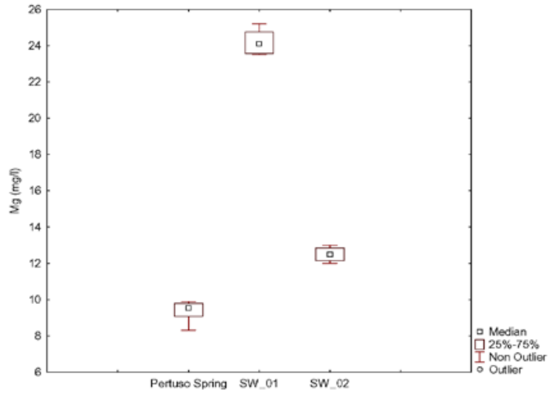

Fig.9, Box plot of Mg^{2+} concentration in groundwater and surface water

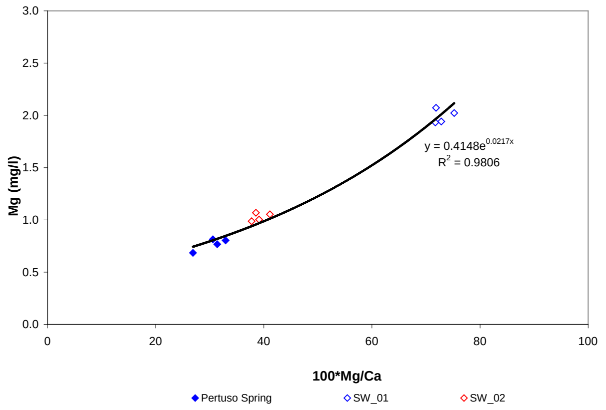

Fig.10, Mg^{2+} versus Mg^{2+}/Ca^{2+} ratio in groundwater and surface water

The scatter plots diagram for Mg^{2+}/Ca^{2+} ratio (Fig. 10) shows that the increase in Mg^{2+} concentrations in surface water, upstream the Pertuso Spring, and hence Mg/Ca ratio may be due to the weathering of Mg-rich Triassic dolomites, where dolomitic limestones and dolomites are the most dominant formations in this area. For Pertuso Spring groundwater, the high Mg/Ca ratios (~0.5) mainly depend on the residence of water in the karst system, highlighting long residence time and enhanced weathering along the groundwater flow paths of low-Mg calcite.

As a consequence of these properties water samples taken in SW_02 gauging station, downstream Pertuso Spring, present chemical composition typical of mixing of these two different kinds of waters (Fig. 11).

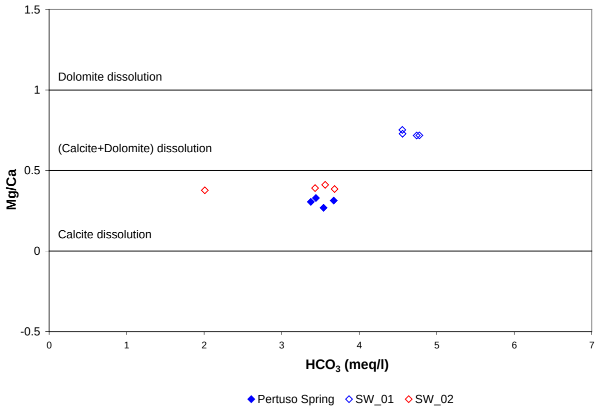

Fig.11, Mg^{2+}/Ca^{2+} ratio versus HCO_3 in groundwater and surface water

As a matter of fact, the highest Mg^{2+}/Ca^{2+} ratio in water sampled has been recorded in dolomite outcropping (SW_01: Mg^{2+}/Ca^{2+} ~ 0.7), with medium value at SW_02 gauging station (Mg^{2+}/Ca^{2+} ~ 0.4). On the other hand, the lowest value of this ratio in groundwater has been observed in Cretaceous limestone area (Pertuso Spring: Mg^{2+}/Ca^{2+} ~ 0.3) (Table 4).

Mg^{2+}/Ca^{2+}	Pertuso Spring	SW_01	SW_02
July 2014	0.329	0.728	0.411
November 2014	0.269	0.717	0.377
January 2015	0.306	0.719	0.385
May 2015	0.314	0.752	0.391

Table 4, Mg^{2+}/Ca^{2+} ratio from Pertuso Spring and Aniene River gauging station

Aniene River discharge was measured during the hydrological year 2014-2015, in order to cover the range of seasonal conditions characteristics of this complex hydrogeological system. Measurements, e.g. by current meter, were carried on in two gauging stations located upstream (SW_01) and downstream (SW_02) Pertuso Spring (Table 5).

They are represented, in Table 5, discharge values recorded in SW_01 and SW_02 gauging stations all over the hydrological year. It can be noticed that the average discharge value referred to SW_01 gauging station can be well compared with the total average discharge coming from of the most important karst springs outcropping in the Upper Part of Aniene River (Table 1). Thus, the source of

Mg^{2+} concentration values in Aniene River water upstream Pertuso Spring (SW_01) is the dissolution of Magnesium rich minerals in Triassic dolomites, sited in north-east part of the Pertuso Spring hydrogeological basin. Along the Aniene River, this decrease in Mg^{2+} concentration values is related to an increase in stream flow discharge. SW_02 surface water is the product of the confluence of groundwater coming from Pertuso Spring into the Aniene River (SW_01). As a matter of fact, Aniene River water, which is characterized by water with higher Magnesium concentration values, is affected in its chemical composition by Pertuso Spring groundwater inflowing, and this influence can be measured by Mg^{2+} concentration values variability along the river downstream.

Q (m^3/s)	SW_01	SW_02
July 2014	0.540	2.450
November 2014	0.350	1.480
January 2015	0.410	1.920
May 2015	0.501	2.747

Table 5, Results of mean discharge values obtain by current meter method, upstream (SW_01) and downstream (SW_02) Pertuso Spring

Using PHREEQC program it has been calculated the speciation of an aqueous solution of a virtual composed water sample made of the mixing of water coming from Pertuso Spring and SW_01 gauging station. To have the mixed virtual sample composition any source sample, Pertuso Spring and SW_01 gauging station, has been multiplied in its chemical component for their own contribution fraction in SW_02 gauging station discharge.

Date	Mg^{2+} (mg/l)		
	Phreeqc	SW_02	Percent difference (%)
July 2014	12.44	12.80	3
November 2014	11.61	11.80	2
January 2015	12.72	13.00	2
May 2015	11.72	12.20	4

Table 6, Magnesium concentration of SW_02 and the virtual solution made by mixing water coming from Pertuso Spring and SW_01

Figure 12 shows that the calculated values fit quite well the experimental values reported in Table 6. The results obtained by PHREEQC program fall close to the equiline of 1:1, and this fact confirms that SW_02 surface water comes from the mixing of groundwater outflowing from Pertuso Spring with surface water of Aniene River (SW_01).

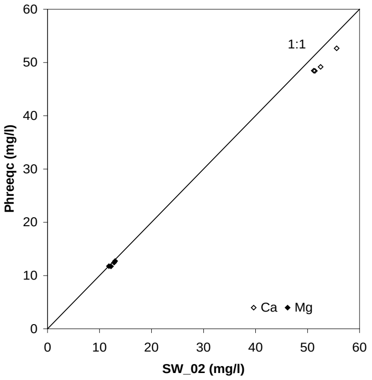

Fig. 12, Comparison between the ionic compositions of SW_02 and the virtual solution made by mixing water coming from Pertuso Spring and SW_01

The karst aquifer/river system has been studied in the aim of evaluating factors, which modify the Aniene River flow due to groundwater-surface water interactions. Three pairs of values, related, each one, to any sampling point, has been considered. The main inputs are the discharge measurements (Q_1) and the Mg^{2+} concentrations (C_1) recorded in the Aniene River upstream Pertuso Spring (SW_01). The secondary inputs are the discharge rate (Q_P) and the Mg^{2+} concentrations (C_P) recorded at Pertuso Spring. The main output is the Aniene River discharge (Q_2) and the Mg^{2+} concentrations (C_2) recorded at the SW_02 gauging station located downstream Pertuso Spring.

Thus, assuming that this is a closed system, the SW_02 gauging station discharge values, comes from the contribution of Pertuso Spring discharge (Q_P) to the original SW_01 gauging station discharge value, and so it can be represented by (2):

$$Q_2 = Q_1 + Q_P \tag{2}$$

and applying to this closed system the conservation of mass equation, it means (3):

$$Q_1C_1 + Q_PC_P = Q_2C_2 \tag{3}$$

The n parameter (Table 7), i.e. the percentage contributor of Pertuso Spring groundwater to total discharge measured at the, is defined according to (4).

$$n = \frac{Q_P}{Q_2} = \frac{(C_2 - C_1)}{(C_P - C_1)} \tag{4}$$

Thus, the discharge rate of Pertuso Spring depends on the discharge values measured in the gauging station located along the Aniene River upstream the spring (Q_1) and the Mg^{2+} concentration values recorded in groundwater and surface water samples (C_1, C_2, C_P) (5):

$$Q_P = Q_1 \cdot \frac{n}{1-n} \qquad (5)$$

Date	n	n (%)
July 2014	0.780	78.0
November 2014	0.752	75.2
January 2015	0.794	79.4
May 2015	0.812	81.2

Table 7, *n* values as percentage contributor of Pertuso Spring groundwater to total discharge measured at the SW_02 gauging

Pertuso Spring discharge values obtained by this indirect method are showed in Table 8.

The relationship between Mg^{2+} concentration and karst spring discharge values obtained with this combined Magnesium-discharge tracer approach is represented in Fig. 13.

Date	SW_01		Pertuso Spring			SW_02		
	Q^* (m^3/s)	Mg^{2+} (meq/l)	Q^{**} (m^3/s)	Q_{Mg} (m^3/s)	Mg^{2+} (meq/l)	Q^* (m^3/s)	Q_{Mg} (m^3/s)	Mg^{2+} (meq/l)
July 2014	0.540	1.94	1.910	1.922	0.800	2.450	2.462	1.050
November 2014	0.350	1.93	1.130	1.061	0.680	1.480	1.411	0.990
January 2015	0.410	2.07	1.510	1.577	0.810	1.920	1.987	1.070
May 2015	0.501	2.02	2.225	2.164	0.767	2.747	2.664	1.003

Table 8, Magnesium content and discharge values obtained by current-meter and Magnesium tracer method (Q^*: discharge values obtained by current meter method; Q^{**}: discharge values obtained by the difference between the values measured with the current meter in SW_01 and SW_02)

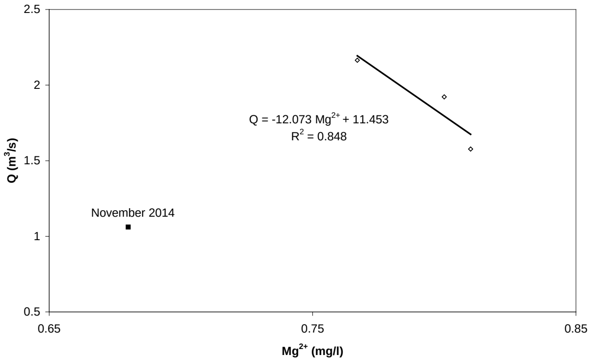

Fig. 13, Relationship between the Mg^{2+}concentration and Pertuso Spring discharge values obtain with the combined Magnesium-discharge tracer approach

The Mg^{2+} vs Q scatter plots diagram shows that all plotted points, except for November 2014 data, follow a linear trend, highlighting that the increasing contribution of Pertuso Spring flow rate is responsible of Mg^{2+} concentration values decreasing. Data, referred to November 2014 monitoring campaign, have to be considered as an outlier (Fig. 14).

This lower Mg^{2+} concentration measured at November 2014 can be related to a high precipitation rate, recorded at Trevi nel Lazio meteorological station, during the five days before the sampling date (Fig. 14), which could have influenced, lowering it, the Mg^{2+} concentration in groundwater.

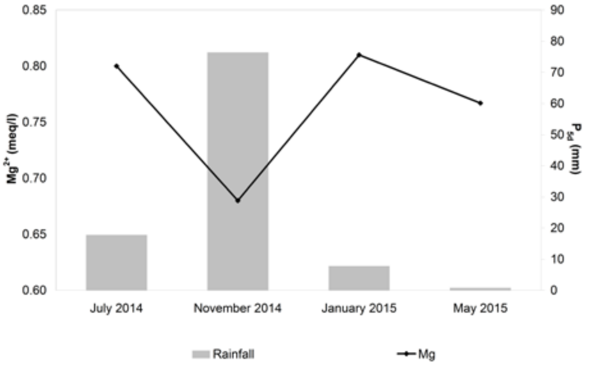

Fig. 14, Relationship between Mg^{2+} concentration in Pertuso Spring groundwater and rainfall (Trevi nel Lazio meteorological station)

4 Conclusion

This paper dealt with the assessment of the interactions between karst aquifer feeding Pertuso Spring and Aniene River surface waters on the basis of stream discharge measurements and water geochemical tracers data in the aim to set up an inversed model, which allows to estimate groundwater flow coming out from Pertuso Spring, starting from surface water discharge measurements and geochemical waters characterization. These preliminary results, carried out in a pilot area, sited in the karst aquifer, outcropping in the Upper Valley of Aniene River, show that, for this karst system, it is possible to have a reliable evaluation of Pertuso spring discharge, by the elaboration of surface water discharge measurements in relationship with Mg^{2+} concentration values, determined as for groundwater, coming from Pertuso Spring, as for surface water sample, taken upstream and downstream of Pertuso Spring, along Aniene River streaming. Although it is subject to some uncertainties, the Mg^{2+} concentration, as an environmental tracer, provides an indirect method for discharge evaluation of Pertuso Spring, due to the mixing of surface water and groundwater and, provides information on changes in water quantity and quality.

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