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DOES THE RECHARGE AREA OF A SPRING VARY FROM YEAR TO YEAR? INFORMATION FROM THE WATER ISOTOPES

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EXTENDED ABSTRACT

Il lavoro ha come obiettivo principale l'individuazione dettagliata dell'area di ricarica della sorgente di Gorgovivo (ubicata nella regione Marche, nella parte più interna della provincia di Ancona), mediante interpretazione dei risultati geochimici ed isotopici e alla nuova caratterizzazione idrogeologica effettuata mediante indagini in sito negli ultimi anni. La sorgente è una delle più importanti dell'Italia centrale, sia per portata complessiva, sia per quantità di acqua captata e sia per numero di abitanti equivalenti serviti. La sua emergenza è ubicata in destra idrografica del Fiume Esino, nella zona più esterna e orientale dell'Appennino umbro marchigiano e nella parte esterna della dorsale umbro marchigiana. L'area in studio appartiene geologicamente alla dorsale umbro-marchigiana, caratterizzata da numerose e diffuse pieghe e faglie, e vede in affioramento i termini della cosiddetta successione carbonatica umbro-marchigiana (dal Calcare Massiccio alla Scaglia), tamponati ad Est e Ovest dai sedimenti terrigeni eocenici e miocenici. I principali complessi idrogeologici sono rappresentati dall'acquifero basale (Calcare Massiccio), sede di importanti sorgenti in tutta la regione, caratterizzate da alta salinità ed alta portata, l'acquifero della Maiolica (sorgenti a media portata, salinità più bassa) e quello della Scaglia, spesso sospeso sui precedenti e sede di piccole sorgenti a rapida circolazione idrica e tasso di rinnovamento veloce.

Diversi autori hanno individuato nelle sorgenti alimentate dal flusso di base della struttura idrogeologica umbro marchigiana una circolazione idrica caratterizzata da un duplice percorso coesistente e sovrapposto, uno più lento e profondo, caratterizzato da valori più alti di salinità, ed uno più superficiale e veloce. Tale peculiarità è riscontrabile anche nella sorgente Gorgovivo, con la presenza documentata di tale duplice circuito. Data la sua importanza, anche strategica, essa è stata oggetto di alcuni studi geologici e tecnici volti a capire le potenzialità di sfruttamento della risorsa e la sua protezione, avendo come prima preoccupazione quella di risolvere il problema dell'individuazione del suo bacino di alimentazione. Diversi autori hanno proposto negli anni una delimitazione dell'area di ricarica, per lo più limitandola alle zone immediatamente a Nord del Monte S.Vicino, individuando però aree troppo poco estese per giustificare la così alta portata della sorgente.

Nel presente lavoro si è riassunto il contributo che le analisi chimiche ed isotopiche (eseguite sulle acque della sorgente, delle sorgenti più superficiali, di piezometri limitrofi all'area di captazione, di acque superficiali e delle acque di pioggia dell'area) hanno dato alla ricostruzione più attendibile dell'area di ricarica della sorgente Gorgovivo, valutando anche le variazioni temporali di tali dati, dovute allo sfruttamento della sorgente ed alle inevitabili variazioni climatiche occorse a scala mondiale e locale negli ultimi 20 anni. Per tale operazione si è fatto ricorso al metodo isotopico che consente (misurando i valori di ossgieno-18 e deuterio periodicamente nelle acque di pioggia e nelle acque della sorgente) di ricavare l'altezza di infiltrazione media delle acque meteoriche in un'area.

I dati ottenuti evidenziano una variazione del gradiente isotopico da -0.2 a -0.23‰ / 100 m, mentre nella sorgente la variazione dell'ossigeno-18 si è attestata a valori di poco superiori a -0.1‰ VSMOW; tali dati portano ad una variazione nella quota media di ricarica che passa da un valore stimato di 1120 m s.l.m. nel 2000-2004 ad uno di 1180 m s.l.m. nel 2011-2014, con variazioni più marcate nel periodo 2007-2009. Tale lavoro si è posto quindi anche l'obiettivo di rispondere ad una domanda fondamentale: le variazioni riscontrate negli isotopi sono tali effettivamente da giustificare una variazione spaziale e temporale dell'area di ricarica o si tratta piuttosto di un fenomeno legato al cambiamento del clima che si riflette più lentamente a livello di acque sotterranee? La risposta a tale domanda ha consentito da una parte di allargare la zona di ricarica precedentemente individuata (considerando anche porzioni molto più a sud rispetto alla sorgente) dall'altra di riflettere sulla necessità di un monitoraggio isotopico piuttosto esteso nel tempo e nello spazio, in modo da tener conto delle inevitabili e frequenti variazioni nei valori isotopici tra un anno idrologico e l'altro. Tale estensione porta a considerare aree più congruenti con l'alta portata registrata nella sorgente. Ulteriori studi (che coinvolgano anche altre metodologie) potranno confermare la presenza di un collegamento tra le acque del flusso di base che si origina nella zona sud delle Marche e la sorgente Gorgovivo.

ABSTRACT

This study presents the characterization of the recharge zone and the water renewal mechanisms of the Gorgovivo spring, which feeds the aqueduct of the Ancona province and represents one of the most important water resources in central Italy. Measurements of chemical, isotopic and tritium contents were taken to get a detailed understanding of the hydrogeological setting and water circulation features. The isotopic investigation carried out in this study was performed thanks to the presence of different gauging stations for measuring rainfall heights and isotopic contents in precipitations, which allowed us to draw the altitude gradient that correlates the oxygen-18 content in groundwater with the isotopic height of infiltration. This value changed over time (from -0.23‰ to -0.2‰/100 m) indicating the intake altitude for the Gorgovivo spring at a height ranging from 1030 to about 1200 m a.s.l. Tritium contents (about 8-13 TU for shallow springs present in the area, 6-8 TU for the Gorgovivo spring) and the different isotopic compositions confirm the supposed presence of a double pathway in the groundwater: the first one being shallow and very ast - the small springs in the area studied belong to this pathway - while the second is slower and deeper, reaching the bottom part of the basal aquifer. The groundwater recharging the Gorgovivo spring is therefore a combination of these two pathways. Isotopic composition and tritium contents have also allowed the recharge area and recharge mechanisms of this spring to be investigated, by comparing the results with surface water and shallow spring waters. As a result, the present study introduces the likelihood of the recharge area of the Gorgovivo spring extending to more distant places in the Umbria-Marche ridge, thus confirming the suitability of isotopic techniques as a remarkable tool for recharge area evaluation.

Keywords: *groundwater flowpath, recharge area, tritium, stable isotopes,altitude gradient, central Italy*

INTRODUCTION

The area studied is located in the Marche Region, 50 km west of the Adriatic Sea, central Apennines (Fig. 1). The Gorgovivo spring is one of the most important sources of potable water in central Italy, with a very high total discharge rate (around 3 m^3/s), only half of which is tapped for drinking purposes; it emerges in an area of deep erosive incision near the bed of the Esino River. Several other springs, with a lower discharge rate, recharged by shallow aquifers at different elevations with rapid flowpaths exist in this area (Fig. 1). Various authors (Boni *et alii*, 1986; Caprari *et alii*, 2001; Ciancetti *et alii*, 1992; Mosca & Tazioli, 2006; Nagni *et alii*, 1995) have suggested the presence of a double pathway in the limestone ridge: the first one being extremely rapid (as happens for macro fractures and small karst ducts), the second, slower (as occurs in micro fractures in the saturated aquifer zone). The first pathway concerns the shallow catchments, with limited water volumes and a high rate of withdrawal, and is fed by direct meteoric supplies of local origin, often superimposing on the slower and deeper pathway, in which the recharge is not local and happens at different elevations. The Gorgovivo spring is the result of the combination of these two types of waters, on a large scale. Some hypothesis have been made about its hydrogeological basin, the latest include the area between the Mt S. Vicino peak and the spring outlet (Fig. 1), but this is out of line with the high discharge values of the spring and the isotopic values, which suggest a higher level of mean elevation. In addition, climate change, recorded in several rain gauge stations around the world, has modified both the rainfall amount and distribution, with appreciable changes in the isotopic content. This is also true in the investigated area, yielding different recharge inputs from year to year, and suggests the need to re-evaluate the extent of the recharge area depending on the input/output values of isotopes in the precipitations and groundwater, and the suspicion that this area could vary in its size in relation to the isotope changes.

The main objective of this study is therefore to stress the importance of monitoring groundwater resource and to investigate the properties of flow over a long period of time by means of isotope techniques, in order to assess the recharge areas and to control the time evolution of some parameters necessary to define the spring recharge mechanisms. Some studies in the central and northern Apennines propose the validity of the so-called isotopic gradient for a specific area that is more or less extended (Conversini & Tazioli, 1993; Barbieri *et alii*, 2005; Tarragoni, 2006; Tazioli *et alii*, 2012; Nanni *et alii*, 2013; Mussi *et alii*, 2017), with very variable values ranging from -0.1‰ to -0.24‰ VSMOW. These studies took into consideration isotopic values measured both in shallow springs (groundwater) and in pluviometers (rainwater) and presented isotopic gradients valid for the Gran Sasso massif (central Italy) area, the Mt Sibillini area (among the Marche, Lazio, Umbria and Abruzzi regions), the Mt Conero landscape (near Ancona, Marche region) and included the area from the Gorgovivo spring to central Umbria.

Isotopes are, in fact, a useful tool for evaluating the recharge areas of aquifers (Gat, 2010; Cervi *et alii*, 2015; Cervi *et alii*, 2016), and are often used in hydrogeological applications and hydrological studies, involving water balance analyses, climate change surveys, the development of groundwater models of recharge and transit time distribution (Herrmann et alii, 1986; Harum *et alii*, 2000; Klaus *et alii*, 2015; Gray & Troch, 2016). Given the isotopic distribution of precipitations and groundwater over time it is possible to identify the range of elevations at which rain and snow infiltrate into the soil and recharges the aquifers giving rise to springs, or tapped with wells for drinking or other purposes (MAZOR, 1997; GAT *et alii*, 2001; HSIN-FU *et alii*, 2014; GONZÀLEZ-TRINIDAD *et alii*, 2017). Recharge area evaluation of aquifers, springs and wells remains, however, one of the widespread functions of isotope techniques in hydrogeology. This essentially consists of finding the relationship between isotopic contents and elevation and consequently estimating the recharge elevation of a spring (or well) by applying this relationship to the measured data. In practice, however, some problems arise, one of them being the weighted mean process and the determination of the actual amount of rain that infiltrates the soil and effectively recharges the aquifers. The choice of actual values needed for the weighting procedure is crucial, notably affecting results, and is often undervalued in the process of recharge evaluation. Furthermore, evaporation losses and the effects of transpiration reflect on the effective amount of rainwater available for groundwater recharge (DOYLE *et alii*, 2015); land use is also considered an important element in the isotopic composition of groundwater (DARLING & BATH, 1988).

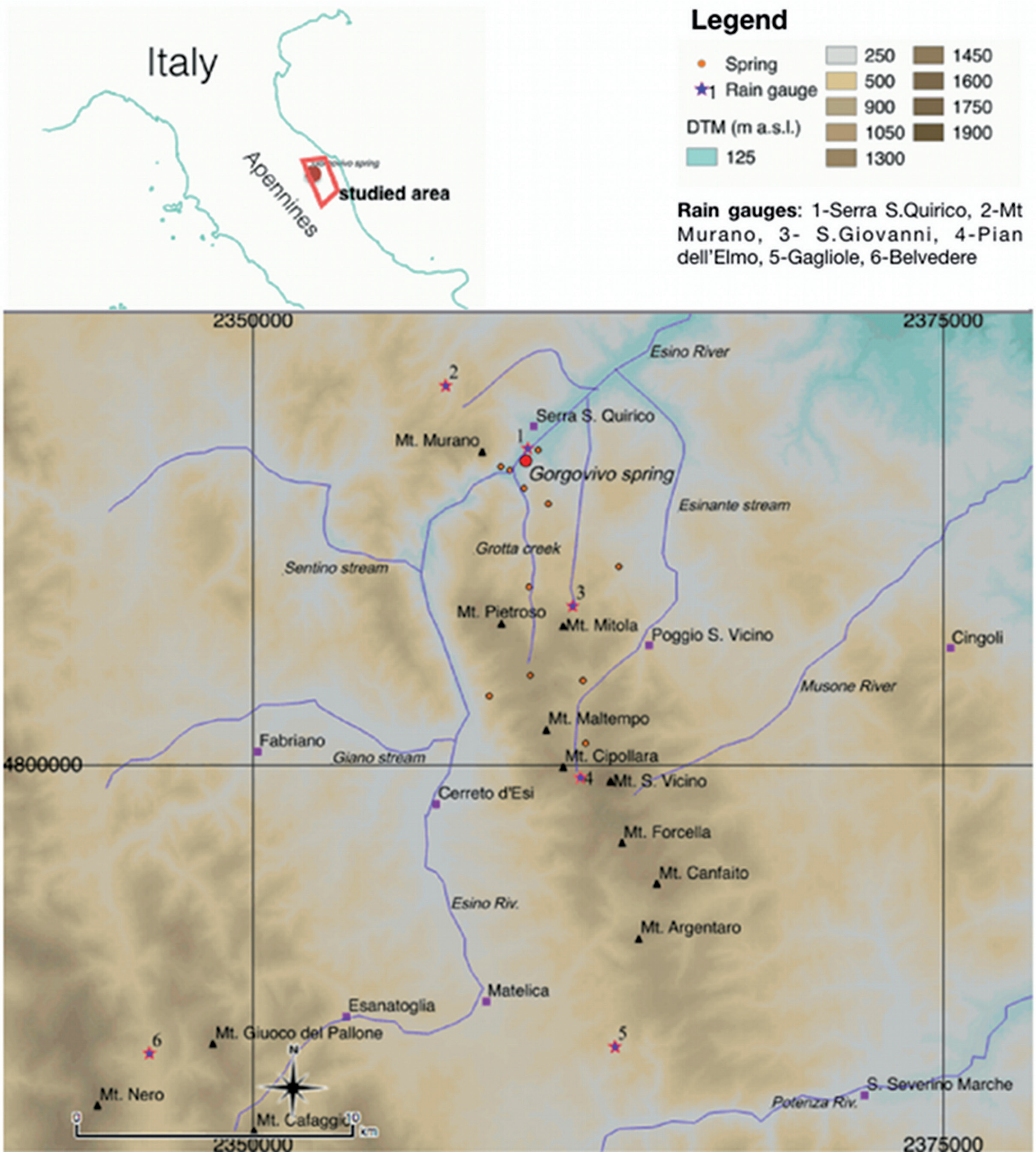

Fig. 1 - Location of the investigated area with the position of the Gorgovivo spring (great circle), the shallow springs (small circles) and the rain gauge stations for isotopic sampling (star). Rain gauging station key: 1- Serra S. Quirico, 2- Mt. Murano, 3- S. Giovanni, 4- Pian dell'Elmo, 5- Gagliole, 6- Belvedere

The overall outcome is that we do not know exactly which and how much rainfall actually recharges the aquifer, thus an averaging method is more advisable and leads to more reliable values (Clark & Fritz, 1997; Hager & Foelsche, 2015).

In the present investigation, new isotopic and chemical data of the spring have been proposed to match the objective and a comparison of the existing isotopic gradient of precipitation including different years of research is also given. The observation of chemical and isotopic contents and their time fluctuations at the different investigation points, allowed the hydrogeological basin to be identified with more confidence.

AREA DESCRIPTION

Climate, geology and hydrogeological features

The investigated area has a low-mountain climate with considerable maritime influence. At a low elevation (200 m a.s.l.) maximum precipitations are in October, November and December, while at a higher elevation (1400 m a.s.l.) maximum rainfall heights are in December and January (Centamore *et alii*, 2000; Tazioli *et alii*, 1990). The amount of precipitation increases with altitude, with average annual height of about 1000 mm (St Giovanni gauging station, 500 m a.s.l.), and about 1500 mm (Pian dell'Elmo gauging station, 940 m a.s.l.) calculated over the last 25 years. The Gorgovivo spring arises in a depressed, incised zone nearby the right bank of the Esino River, at about 170 m a.s.l. (Fig. 1). In the nearby lands, but at higher elevations, there are several small springs having shorter circuits of flow and a lower discharge rate.

The investigated area belongs to the external part of the Umbria-Marche limestone ridge, which is characterised by folds and thrusts in both an Apennines direction and secondarily anti-Apennines direction. The lithology is determined by the Umbria-Marche carbonate sequence, starting from the Calcare Massiccio Formation (platform and whitish dolomitic limestone, about 800 m thick, upper Triassic-lower Jurassic) already described by Aquilanti *et alii* (2016) and Nanni *et alii* (2013). Above it the complete series can be found only in the more depressed areas, where the Corniola Fm. (whitish micritic limestone, up to 150 m thick, lower Jurassic), the Rosso Ammonitico Fm. (marls and red calcareous marls, with ammonites, lower Jurassic), the Calcari e Marne a Posidonia Fm. (marly limestones and marls, middle Jurassic), the Calcari Diasprini and the Bosso Fm. (limestone with chert strata, middle-upper Jurassic) are placed on the Calcare Massiccio Fm. In the structurally high areas (bordered by numerous faults) the condensed series is present, with thicker sediments and/or a lack of some marly levels, thus presenting a total thickness of about 60 m (Caprari *et alii*, 2001). In these areas the sediments are mainly the Bugarone Fm. (nodular limestone and green marls, middle-upper Jurassic), the Marne del Sentino, Calcari Diasprini and Bosso Fms. (marls, limestone, middle-upper Jurassic).

Above them the sequence continues with the Maiolica Fm. (whitish micritic limestone with black chert, up to 600 m thick, upper Jurassic-lower Cretaceous), Marne a Fucoidi Fm. (marls and calcareous marls, 100 m thick, lower Cretaceous), Scaglia Bianca Fm. (whitish micritic limestone, up to 65 m thick, upper Cretaceous), Scaglia rossa Fm. (pinkish limestone with chert nodules, 70-450 m thick, upper Cretaceous-middle Eocene), Scaglia variegata Fm. (marly limestone and calcareous marls, middle-upper Eocene), Scaglia cinerea Fm. (marly limestone and grey calcareous marls, upper Eocene-Oligocene). The Bisciaro and the Schlier Fms. (marls, calcareous marls and marly limestone, Miocene) are the basis on which the terrigenous Miocene sediments lie.

From a tectonic point of view, the Marche ridge is the external portion of the Umbria-Marche limestone ridge, and overlaps the Tertiary sediments in the whole Marche region, as indicated by the occurrence of the Mt Sibillini thrust (to the south) and by normal faults lowering the back-thrust in the northern areas (Calamita *et alii*, 1991). Barchi *et alii* (1998) indicated an overthrust (Apennines direction) nearby the spring emerging area with normal faults dislocating the limestone ridge in a transverse direction, thereby creating a very complex structural setting in the ridge zones (Nanni et alii, 2013; Aquilanti *et alii*, 2016; Tazioli *et alii*, 2016).

Figure 2 provides a schematic hydrogeological map with a simplified outline of the tectonic setting. The main aquifers are represented by the Calcare Massiccio, Maiolica and Scaglia Fms., recharging several springs characterised by widely varying discharge rates (Nagni *et alii*, 1995); the regional baseflow occurs in the Calcare Massiccio, which is the principal aquifer in the Umbria-Marche ridges. The groundwater movement takes place mostly in fissures, fractures and karst conduits, which are well developed and widespread in the central part of the Marche region. In this area, the Maiolica Fm. is often in hydraulic contact with the Calcare Massiccio aquifer, sometimes forming a single hydrogeological complex (especially in areas of structural high) sealed by the Triassic aquiclude of the Anidriti di Burano (at the bottom) and by the Marne a Fucoidi aquiclude at the top (Fig. 2). Springs with a discharge rate of some hundred l/s are quite frequent in this aquifer. In the Scaglia aquifer permeability is due to micro fractures and fissures, and it is often suspended on the Calcare Massiccio or the Maiolica aquifer, sealed by the aquiclude of the Marne a Fucoidi, thus giving origin to many springs with low discharge rate and quick renewal time.

Chemistry

The shallow springs arising from the "Scaglia" aquifer have salt contents of 200-270 mg/L, are of a calcium-bicarbonate type with a concentration of chlorides and nitrates usually

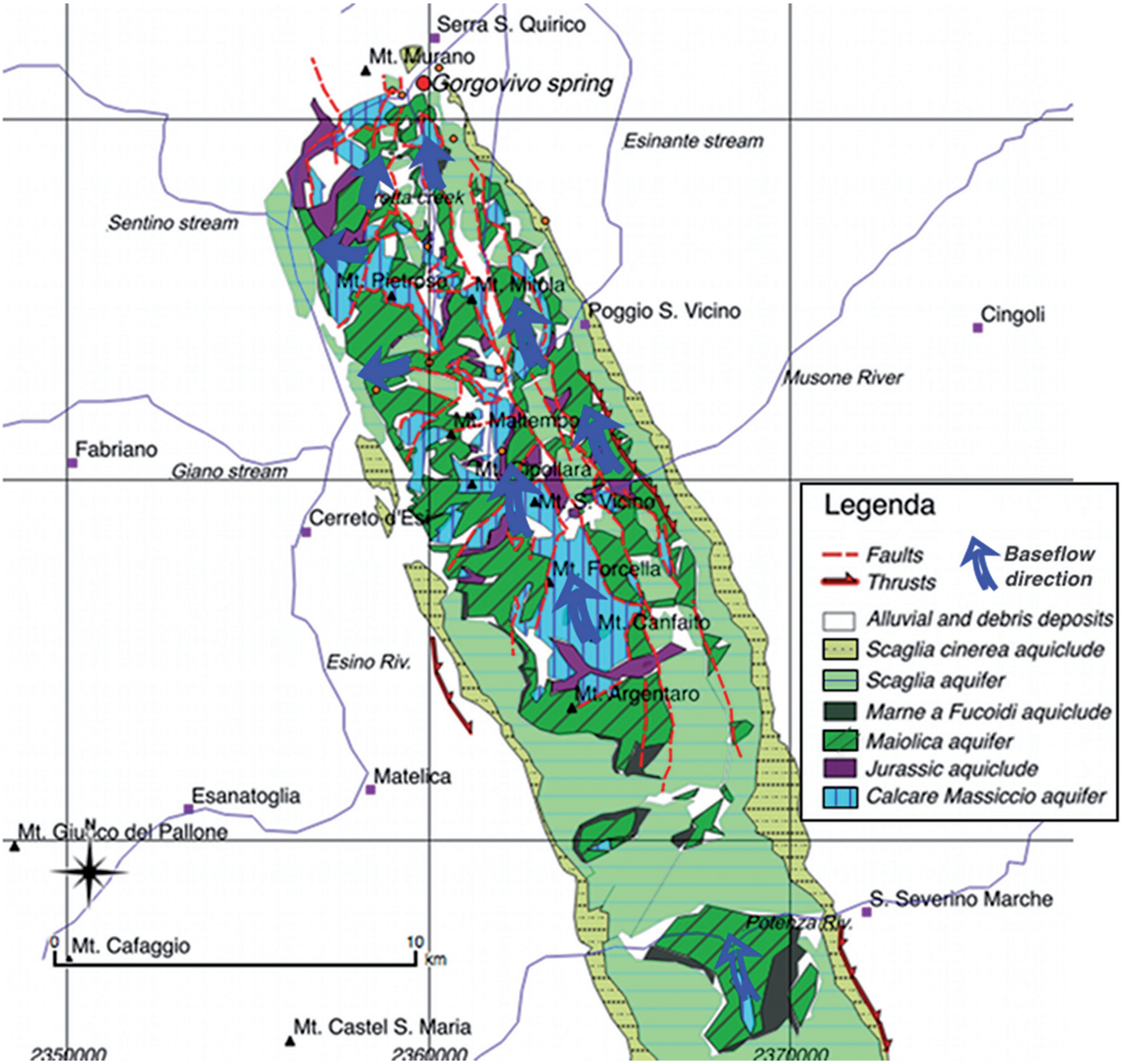

Fig. 2 - Schematic hydrogeological map of the studied area, with the indication of main aquifer complexes and aquicludes

higher than the springs from the "Maiolica" (having a similar salt content). Waters arising from the "Calcare Massiccio" are in general different from the others owing to the presence of a higher salt content, with enrichments of sulphates, magnesium and chlorides (Fig. 3). All the springs generally exhibit homogeneous chemical characteristics, with very similar chemical ratio values. The relationship rMg^{++}/rCa^{++}, for example, is in the range of 0.01- 0.02, the only exception being the Gorgovivo spring, in which the aforesaid ratio is much higher (0.25). This is mainly due to water leakage in the basal part of the Calcare Massiccio Fm., probably interesting also the evaporites of the Anidriti di Burano Fm. Magnesium (13-14 mg/L), and sulphate (60-80 mg/L) values are higher in the Gorgovivo spring in respect to the other springs in the area. The temperature of the shallow springs changes during the year, going from a minimum of 8°C to a maximum of 13°C, while the Gorgovivo spring shows a constant temperature of about 12.3°C throughout the year.

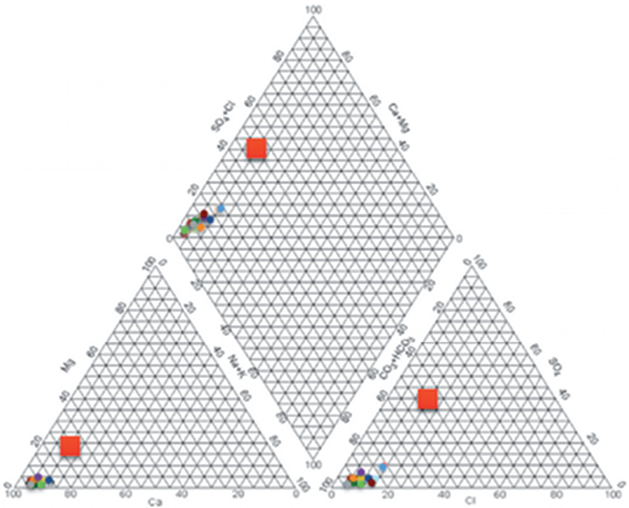

Fig. 3 - Piper diagram illustrating the chemistry of the Gorgovivo spring (red square) and shallow springs (multi-coloured circles)

MATERIALS AND METHODS

The isotopic method (Celico *et alii*, 1984; Clark & Fritz, 1997; Nanni *et alii*, 2013; Kendall *et alii*, 2014; Lauber & Goldscheider, 2014; Pang *et alii*, 2017) was used in the studied area with the aim of: assessing the hydrological cycle, investigating the behaviour of the Gorgovivo spring and, especially, evaluating the recharge area of the aquifers involved. In particular, the altitude effect (Clark & Fritz, 1997; Mezga *et alii*, 2014) has been used to estimate the recharge elevation of the spring, by using the relationship existing between the temperature of cloud formation and the altitude of formation. The input data are based on the precipitations, the isotopic content which was measured in samples collected periodically in rain gauge stations; in addition, measurements of the spring level and isotopic contents were performed in the Gorgovivo spring, in small springs located in the area, in piezometers and in the Esino river. The collection of samples was undertaken during three different sampling campaigns: from 2000 to 2003, from 2007 to 2009 and from 2011 to 2014.

Regarding the sampling activities, several rainfall totalizer devices were installed at certain points in the investigated area (Fig. 1) at different elevations (ranging from 170 m to 940 m a.s.l.), with the aim of applying the so-called altitude effect, a signature of the isotopic composition of the local precipitation in an area, obtained by measuring isotope values over time in rain gauge stations located at different heights above sea level. The devices are similar to those used by Mussi *et alii*, 2017: an insulated PoliVinilChloride tank containing a plastic flask insulated from the external environment (with polyurethane foam and neoprene strip) and attached to a tipping bucket rain gauge by means of a rubber pipe. The tanks allow for the accumulation of rainfall in plastic flasks; to prevent evaporation, a small quantity of light paraffin oil was put inside the flask. Water samples were collected on a monthly or bi-monthly basis and the accumulated rain samples were maintained at room temperature in a dark place before analysis. From each period a 100 ml PE bottle was filled with water extracted after mixing the entire amount of water. Springs, piezometers and river waters were sampled by means of a sampling pump and manual sampler. Also in this case samples were kept in 100 ml PE bottle with a sealing plug. Samples for tritium analyses were collected and kept in 500 ml PE bottles.

Laboratory measurements and data processing

In the laboratory all the samples were prepared for analysis after oil and impurity removal using a separation funnel and filtration with 0.45 μm glass filter. Tritium content (expressed as Tritium Unit, TU: 1 TU corresponds to 0.11919±0.00021 Bq/kg) was determined in the Università Politecnica delle Marche laboratory by a liquid scintillator Packard 2550, showing a standard error of 0.4 TU. Electrolytic enrichment was previously performed using 400 ml stainless steel cells to improve the sensitivity of the measures. Oxygen-18 and Deuterium were measured by means of Mass Spectrometry Finnigan MAT252 and the Europa Scientific GEO 20-20 at the Stable Isotopes Laboratory of National Research Council (CNR-Pisa, Italy). The analytical precision is around 0.10‰ on $\delta^{18}O$‰ and 1.5‰ for $\delta^{2}H$. Isotope results are reported as permil (i.e. the ratio to the international standard V-SMOW, Vienna-Standard Mean Oceanic Water, as described by Rozanski *et alii*, 1993).

After the analyses, as a preliminarily step the altitude gradient was drawn for the studied area, by weighting the isotopic contents measured in the precipitations with the rainfall amount in each gauging station. This operation was performed for each sampling period (i.e. one month or two, depending on the sampling campaign). As regards the relationship linking the altitude of infiltration to the value of oxygen-18, the quantities measured and their relative errors were considered, including the instrumental error and the error connected with the weighted mean. These errors are in the range 0.15÷0.25‰. After this, the isotopic gradient was used to calculate the recharge elevation of the shallow springs, piezometers and the Gorgovivo spring, by analysing the dependent variable h (altitude of infiltration, meters) on the independent variable $\delta^{18}O$ (‰ VSMOW), with the least squares method. In order to evaluate the uncertainty, the standard error of the dependent variable (altitude) on x (oxygen-18) was considered. The standard error of estimate of y on x was about 130 m. The standard deviation on the slope - reciprocal of the altitude gradient - is about 40, while the standard deviation on the intercept is about 330. These values result in an approximate uncertainty of about 10%.

RESULTS

Tritium data

A long-term series of monthly (or bi-monthly) tritium values in precipitations was available for the investigated area owing to the presence of a rain gauge station, equipped with an insulated PVC sampler, managed by a research group from the Università Politecnica delle Marche since 1986, situated on the north slope of Mt. San Vicino, 940 m a.s.l. and included in the IAEA-GNIP network for several years (IAEA/WMO, 2012). Figure 4 reports the tritium trend in rainwater from 1986 to 2007 (dotted black line). Periodical tritium analyses were performed monthly in the Gorgovivo spring from 1999 to 2006, whereas in the shallow springs sporadic samplings were done in the period 2002-2006.

Tritium contents of small springs rising from the Scaglia and the Maiolica Fms., characterized by low and variable discharges throughout the year, are generally high (about 8-13 TU) and follow the trend of meteoric waters, with a 1-2 month delay in the peak (Tab. 1). Tritium contents of the Gorgovivo spring showed a more homogeneous trend, with less variability and lower values

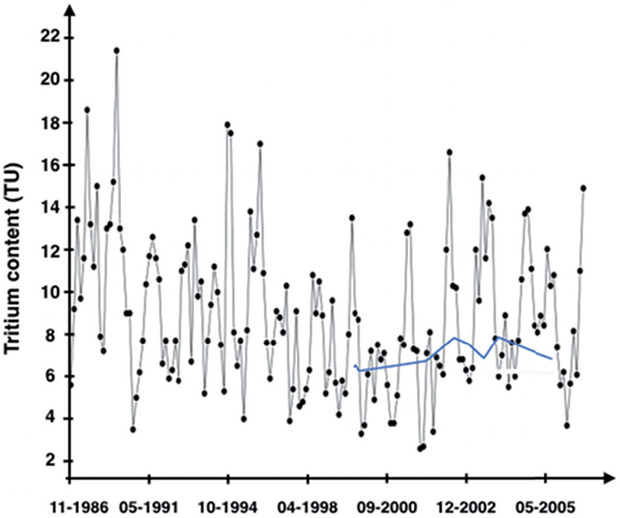

Fig. 4 - Tritium trend of the Pian dell'Elmo gauging station (940 m a.s.l., the station is represented as the no. 4 in Fig. 1). The black line with circles represents the tritium content in precipitation, the blue line represents the tritium content in the Gorgovivo spring

Monitoring point	Tritium (TU)	δ^{18}O (‰ VSMOW)	δ^{2}H (‰ VSMOW)
Gorgovivo spring	5.9/7.8	-9.13/-9.62	-59.1/-69.2
Shallow springs	7.8/13.1	-7.63/-9.21	-50.1/-66.3
Piezometers near the Gorgovivo spring	7.4/11.1	-7.14/-8.89	-43.5/-62.5
Esino riv.	7.5/12.4	-7.71/-8.86	-52.8/-60.8

Small springs		**Gorgovivo spring**		**Rivers**		**Piezometers**	
01/04/00	4.7	16/05/00	6.9	23/02/00	7.4	07/03/00	8.3
01/04/00	4.9	19/06/00	6.8	18/05/00	6.5	03/04/00	6
02/05/00	5.1	22/11/00	6.4	02/02/01	6.4	03/04/00	6.7
02/05/00	4.8	13/02/01	7.8	02/02/01	6.4	15/11/01	9.6
12/06/00	9.4	14/05/01	7.1	23/02/01	7.5	21/11/01	13.2
26/07/00	12.3	12/07/01	6.4	14/05/01	7.4	06/12/01	8.3
08/08/00	4.1	21/09/01	5.9	14/05/01	7.1	19/12/01	6.1
08/08/00	4.3	17/12/01	7.1	29/06/01	7.4		
22/09/00	5.8	18/12/01	7.4	25/05/04	8.4		
22/09/00	5.0	22/07/02	8.8	20/09/04	8.7		
10/10/00	10.0	22/07/02	9.2				
22/10/00	10.0	18/11/02	7.6				
21/11/00	11.3	18/11/02	8.4				
28/11/00	10.0	17/03/03	6.7				
10/05/01	11.7	17/03/03	7.4				
06/11/01	9.9	14/07/03	9.1				
14/11/01	2.5	17/07/03	8.8				
14/11/01	11.8	25/05/04	8.1				
14/11/01	10.3	25/05/04	8.2				
14/11/01	7.4	25/05/04	8.5				
15/11/01	19.1	20/09/04	6.5				
15/11/01	9.1	20/09/04	6.1				
15/11/01	13.9	20/09/04	6.9				
15/11/01	9.4	21/12/04	6.2				

Tab. 1 - Results of tritium analysis (expressed as Tritium Units, TU±1) for the entire set of data taken into consideration in groundwater and surface water (shallow springs, Gorgovivo spring, rivers and piezometers) (about 6-8 TU). Such values are in the range of the lower values of precipitations, which refer to the winter periods, thus suggesting a predominant recharge from November to May (Fig. 4).

Stable isotope data

In stable isotope studies involving groundwater recharge and rain waters, a plot of oxygen-18 average value versus deuterium average values is useful to better understand the hydrological behaviour of water involved in the cycle and to assess the relation existing between waters of different origins. The isotopic composition of the waters investigated in this study (complete set of data reported in Table 2, 3, 4) can be appreciated by observing the plot in Fig. 5, which represents the relationship between δ^2H and $\delta^{18}O$ for groundwater (springs and piezometers) and surface water; these groups of waters were compared to the Global Meteoric Water Line (GMWL, Rozanski *et alii*, 1993) and the Local MWL obtained by all the precipitations of the studied area. These lines represent the distribution of rain water isotopes around the world and in a local or regional area respectively; the equation of GMWL was determined to be equal to $\delta D = (8.17 \pm 0.08)\ \delta^{18}O + (10.56 \pm 0.64)$, normally the equation of LMWL differs more or less from this. The current equation of LMWL obtained for the investigated area is $\delta D = (7.31 \pm 0.11)\ \delta^{18}O + (6.23 \pm 0.59)$, with a slightly lower slope in respect to the GMWL and a somewhat smaller intercept. In Fig. 5 all the waters investigated in this study have been reported with different symbols; as can be seen, the difference between these waters is marked: the Gorgovivo spring shows an isotopic composition which is very different to the shallow springs, oxygen-18 and deuterium being considerably depleted with respect to the other water bodies, while the surface water of the Esino River is slightly enriched in comparison to the groundwater. The slope of the local meteoric water line (about 7.3) is almost the same as that found by other authors (Longinelli & Selmo, 2003; Tazioli *et alii*, 2012; Mussi *et alii*, 2017) for central and northern Italy. Table 5 reports the entire set of rain water isotope data for the investigated area. To gain a fully comprehensive understanding of the trend of isotopes in

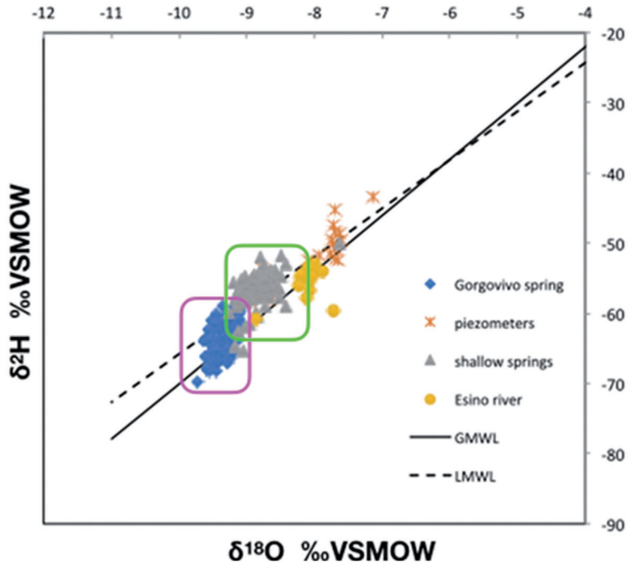

*Fig. 5 - Relationship between $\delta^{18}O$ and δ^2H values for groundwater of the Gorgovivo spring, the piezometers and the shallow springs, surface water (Esino river) and rain water. The Local Meteoric Water Line (LMWL) is plotted by the rain gauging stations isotopic values. GMWL is the Global Meteoric Water Line (*Rozanski *et alii, 1993)*

Date	$\delta^{18}O$	δ^2H	Date	$\delta^{18}O$	δ^2H
DD/MM/YY	(‰ VSMOW)		DD/MM/YY	(‰ VSMOW)	
16/05/00	-9.21	-65.6	17/03/03	-9.42	-65.3
16/05/00	-9.24	-64.8	17/03/03	-9.44	-65.3
18/05/00	-9.31	-65.6	27/03/08	-9.28	-61.3
18/05/00	-9.28	-65.6	27/03/08	-9.13	-58.1
18/05/00	-9.4	-65.2	27/03/08	-9.37	-62.1
18/05/00	-9.43	-64.4	29/04/08	-9.35	-63.3
18/05/00	-9.39	-63.8	29/04/08	-9.22	-65.7
17/06/00	-9.46	-66.5	29/04/08	-9.63	-63.9
17/06/00	-9.41	-63.6	01/03/11	-9.13	-61.2
19/06/00	-9.5	-67.5	01/03/11	-9.35	-59.0
19/06/00	-9.44	-67	01/03/11	-9.51	-61.1
19/06/00	-9.5	-66	01/03/11	-9.22	-60.6
19/06/00	-9.32	-64.4	01/06/11	-9.10	-59.7
14/05/01	-9.57	-67.4	01/06/11	-9.31	-60.4
14/05/01	-9.46	-66.6	01/06/11	-9.46	-60.7
14/05/01	-9.42	-66.1	01/06/11	-9.22	-62.2
14/05/01	-9.34	-65.1	26/09/11	-9.15	-60.7
14/05/01	-9.29	-65.1	26/09/11	-9.45	-60.1
14/05/01	-9.49	-64.9	26/09/11	-9.48	-62.3
14/05/01	-9.13	-62.4	26/09/11	-9.16	-59.0
17/12/01	-9.54	-68.1	12/12/11	-9.09	-61.7
17/12/01	-9.48	-65.3	12/12/11	-9.30	-61.8
18/12/01	-9.29	-67	12/12/11	-9.44	-61.2
18/12/01	-9.45	-65.4	12/12/11	-9.14	-60.2
18/12/01	-9.49	-64.6	04/03/12	-9.11	-61.2
18/12/01	-9.37	-64.4	04/03/12	-9.25	-61.6
19/12/01	-9.28	-66.5	04/03/12	-9.40	-62.3
19/12/01	-9.54	-66.3	04/03/12	-9.16	-60.1
19/12/01	-9.34	-63.6	04/06/12	-9.27	-62.2
20/12/01	-9.53	-65.7	04/06/12	-9.15	-59.4
22/07/02	-9.73	-69.8	04/06/12	-9.40	-61.5
22/07/02	-9.44	-68.1	04/06/12	-9.20	-59.2
22/07/02	-9.6	-68	25/09/12	-9.14	-61.7
22/07/02	-9.59	-67.7	25/09/12	-9.35	-61.3
22/07/02	-9.53	-66.8	25/09/12	-9.52	-63.5
22/07/02	-9.45	-66.8	25/09/12	-9.25	-62.2
22/07/02	-9.45	-65.4	21/12/12	-9.24	-60.5
22/07/02	-9.12	-63.7	21/12/12	-9.54	-63.1
22/07/02	-9.22	-63.7	22/12/12	-9.58	-63.9
22/07/02	-9.33	-63.5	23/12/12	-9.28	-61.4
22/07/02	-9.39	-63.5	15/03/13	-9.13	-60.2
17/03/03	-9.44	-67	15/03/13	-9.56	-62.4
17/03/03	-9.48	-66.6	15/03/13	-9.45	-61.5
17/03/03	-9.23	-65.9	15/03/13	-8.96	-56.7
17/03/03	-9.46	-65.7	10/06/13	-9.13	-60.8
17/03/03	-9.38	-65.7	10/06/13	-9.48	-61.4

Tab. 2 - Stable isotope content of the Gorgovivo spring for the investigated period (values measured in wells, expressed as ‰ VSMOW)

Date	$\delta^{18}O$	$\delta^{2}H$	Date	$\delta^{18}O$	$\delta^{2}H$
DD/MM/YY	(‰ VSMOW)		DD/MM/YY	(‰ VSMOW)	
14/11/01	-9.18	-64.7	25/01/11	-9.26	-59.8
14/11/01	-8.51	-57.6	25/01/11	-9.03	-57.05
10/05/01	-8.87	-59.9	25/01/11	-8.87	-56.7
15/11/01	-9.21	-67.4	25/01/11	-8.58	-53.8
15/11/01	-9.12	-62.5	24/03/11	-9.09	-57.0
15/11/01	-8.85	-60.3	03/02/11	-8.86	-55.9
15/11/01	-7.63	-50.0	24/03/11	-8.76	-55.0
15/11/01	-9.03	-61.9	24/03/11	-9.06	-56.6
15/11/01	-9.06	-65.2	24/03/11	-8.79	-54.8
21/11/01	-9.02	-65.6	24/03/11	-8.71	-54.1
21/10/10	-8.73	-55.1	24/03/11	-8.98	-55.8
21/10/10	-8.77	-54.3	24/03/11	-9.12	-58.4
21/10/10	-8.9	-56.1	24/03/11	-8.98	-56.5
21/10/10	-8.65	-53.7	24/03/11	-8.75	-54.9
21/10/10	-8.89	-55.0	24/03/11	-8.43	-52.9
21/10/10	-9.15	-59.0	24/03/11	-9.08	-55.9
21/10/10	-9.03	-56.75	24/03/11	-9.12	-56.6
21/10/10	-8.82	-57.5	17/05/11	-9.02	-57.1
21/10/10	-8.72	-56.6	17/05/11	-8.78	-55.6
25/11/10	-8.52	-56.5	17/05/11	-8.74	-55.5
25/11/10	-8.73	-53.9	17/05/11	-8.93	-55.4
25/11/10	-8.48	-54.7	17/05/11	-8.79	-54.4
25/11/10	-8.75	-55.4	17/05/11	-9.03	-56.0
25/11/10	-8.76	-54.8	17/05/11	-9.05	-56.8
25/11/10	-8.91	-57.9	17/05/11	-8.99	-56.2
25/11/10	-8.69	-56.4	17/05/11	-8.68	-55.0
25/11/10	-8.86	-56.3	17/05/11	-8.62	-53.9
25/11/10	-9.02	-56.9	17/05/11	-9.08	-55.8
25/11/10	-9.04	-57.9	17/05/11	-9.11	-56.4
25/11/10	-8.72	-55.55	28/06/11	-8.83	-55.3
25/11/10	-8.59	-55.9	28/06/11	-8.87	-56.2
23/12/10	-8.68	-56.8	28/06/11	-8.70	-54.4
23/12/10	-8.83	-56.1	28/06/11	-8.96	-56.0
23/12/10	-8.68	-57.7	28/06/11	-9.08	-56.7
23/12/10	-8.72	-56.5	28/06/11	-9.00	-56.1
23/12/10	-8.84	-57.3	28/06/11	-8.74	-55.3
23/12/10	-8.80	-54.1	28/06/11	-8.64	-54.9
23/12/10	-8.73	-59.0	28/06/11	-9.05	-55.4
23/12/10	-8.99	-56.6	28/06/11	-9.20	-55.5
23/12/10	-9.17	-57.9	08/09/11	-8.78	-55.3
23/12/10	-9.01	-58.3	08/09/11	-8.94	-55.2
23/12/10	-8.64	-56.3	08/09/11	-8.71	-54.5
25/01/11	-8.81	-54.25	08/09/11	-9.00	-56.1
25/01/11	-8.79	-51.9	08/09/11	-9.13	-57.1
25/01/11	-8.75	-55.9	08/09/11	-8.92	-55.4
28/01/11	-8.98	-56.9	09/09/11	-9.12	-57.8

Tab. 3 - Stable isotope content of the shallow springs in the investigated period. The values are expressed as ‰ VSMOW

rain water, Figure 6 illustrates the rain isotope profile for the Pian dell'Elmo gauging station (940 m a.s.l.), the highest station in the area, which exhibits very different behavior for each analyzed period. On the left, rapid and recurring changes in values can be observed, with particularly negative values during the winters of 2002 and 2004; at the center, a classical seasonal variation of isotopes has been recorded, with enriched values during summer and depleted values in winter. On the right side, a more linear behavior leads to values around -10 in May and shifts the negative peak with more enriched values.

Piezometers			Rivers		
Date	$\delta^{18}O$	$\delta^{2}H$	Date	$\delta^{18}O$	$\delta^{2}H$
DD/MM/YY	(‰ VSMOW)		DD/MM/YY	(‰ VSMOW)	
27/03/08	-7.94	-51.8	18/05/00	-8.24	-56.1
27/03/08	-7.77	-51.5	16/06/00	-7.71	-59.6
27/03/08	-8.72	-56.5	02/02/01	-8.08	-55.3
29/04/08	-8.66	-60.5	02/02/01	-7.88	-54.1
29/04/08	-8.68	-60.9	10/05/01	-7.99	-54.3
29/04/08	-8.71	-61.3	10/05/01	-7.99	-52.8
01/03/11	-8.58	-56.0	10/05/01	-8.12	-57.8
01/03/11	-8.76	-56.3	10/05/01	-8.05	-54.7
01/03/11	-8.76	-57.3	10/05/01	-8.10	-53.3
01/03/11	-8.73	-57.1	14/05/01	-8.18	-54.4
01/06/11	-7.69	-52.1	14/05/01	-8.86	-60.8
01/06/11	-7.66	-52.5	29/06/01	-8.21	-55.0
01/06/11	-7.69	-50.9	29/06/01	-8.15	-54.7
01/06/11	-8.66	-58.1	02/10/01	-8.06	-56.6
26/09/11	-8.60	-57.3	02/10/01	-8.00	-53.6
26/09/11	-8.81	-62.0	27/03/08	-8.27	-56.12
26/09/11	-8.82	-62.6	27/03/08	-7.74	-59.62
26/09/11	-8.77	-61.3	27/03/08	-8.11	-55.32
12/12/11	-8.10	-52.4	29/04/08	-7.91	-54.12
12/12/11	-8.78	-55.3	29/04/08	-8.02	-54.32
12/12/11	-7.60	-49.6	29/04/08	-8.02	-52.82
12/12/11	-8.93	-58.6	01/03/11	-8.02	-56.56
04/03/12	-8.72	-55.1	01/03/11	-7.96	-53.56
04/03/12	-7.62	-48.7	01/03/11	-8.23	-56.08
04/03/12	-7.71	-50.2	01/03/11	-7.70	-59.58
04/03/12	-7.70	-45.3	01/06/11	-8.07	-55.28
04/06/12	-8.81	-55.0	01/06/11	-7.87	-54.08
04/06/12	-8.81	-55.8	01/06/11	-7.98	-54.28
04/06/12	-8.71	-58.7			
04/06/12	-8.83	-62.4			
25/09/12	-8.79	-61.5			
25/09/12	-7.14	-43.5			
25/09/12	-7.74	-49.4			
25/09/12	-7.72	-47.4			
21/12/12	-7.69	-48.4			
22/12/12	-8.76	-53.5			
21/03/13	-8.73	-59.9			
22/03/13	-8.93	-62.55			
10/06/13	-7.14	-43.5			

Tab. 4 - Stable isotope content of the piezometers and rivers in the investigated area. The values are expressed as ‰ VSMOW

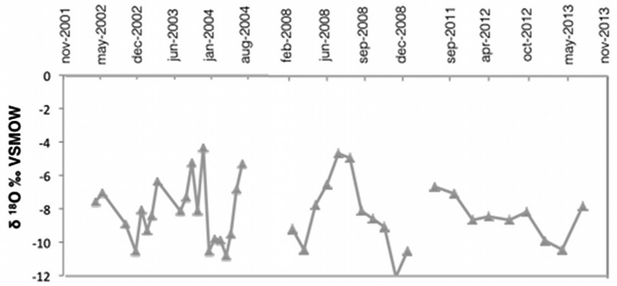

Fig. 6 - δ18O trend of rain water of the Pian dell'Elmo gauging station (940 m a.s.l., the station is the no. 4 in Fig. 1) for the entire investigated period

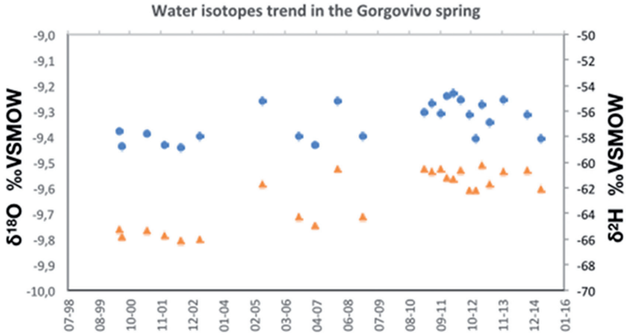

Fig. 7 - Water isotopes ($\delta^{18}O$ and δ^2H) trends of groundwater in the Gorgovivo spring, expressed by permil VSMOW

A closer look at the behavior of oxygen-18 and deuterium in the Gorgovivo spring (data available from 2000 to 2014) is very interesting as it allows for a comparison between the rainfall and the groundwater trends (Fig. 7); the enrichment trend of both the isotopes in the last years is apparent (mean values of -9.41 and -65.7 in 2000-2004, -9.33 and -62.8 in 2007-2009 and -9.29 and -61.1 in 2011-2014 for oxygen-18 and deuterium, respectively), with values increasing by 1.3% and 7% respectively with limited variability within the same sampling campaign. This increasing trend is more apparent in groundwater than in rain water, as seen by the results comparing Fig. 6 and 7.

Date	S. S. Quirico (1)		S.Giovanni (3)		P. d.Elmo (4)		Gagliole (5)		M. Murano (2)		Belvedere (6)	
DD/MM/YY	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H
02/05/02	-5.55	-36.0	-6.48	-39.6	-7.60	-49.3						
04/06/02	-4.30	-26.5	-3.52	-18.1	-7.02	-39.4						
05/09/02			-7.87	-55.4	-8.87	-44.2						
30/11/02	-6.25	-43.3	-11.99	-82.9	-10.57	-38						
30/12/02	-10.93	-76.3	-10.24	-72.6	-8.09	-53.9						
30/01/03	-9.76	-67.9	-9.05	-63.9	-9.28	-67.8						
28/02/03	-13.12	-93.1	-8.70	-59.3	-8.44	-47.3						
31/03/03	-6.80	-44.9	-6.41	-44.8	-6.31	-61.5						
01/08/03	-6.15	-46.3	-5.38	-41	-8.14	-26.8						
01/09/03	-4.86	-32.1	-8.11	-57.8	-7.30	-43.5						
01/10/03	-7.19	-52.5	-8.08	-56.8	-5.25	-18.8						
01/11/03	-7.79	-52.5	-7.52	-50.8	-8.17	-65.5						
01/12/03	-7.23	-49.8	-8.29	-54.8	-4.32	-57.7						
01/01/04	-7.61	-52.1	-9.78	-70.0	-10.52	-66.8	-11.37	-77.80	-11.78	-81.70	-9.03	-61.40
01/02/04	-9.27	-65.5	-9.95	-68.1	-9.80	-74.8	-11.22	-77.65	-11.66	-81.55	-8.88	-61.25
01/03/04	-9.48	-64.6	-10.16	-69.7	-9.84	-64.1	-11.07	-77.50	-11.54	-81.40	-8.73	-61.10
01/04/04	-8.27	-60.6	-9.39	-63.2	-10.82	-40.8	-6.84	-43.57	-6.02	-39.37	-6.82	-47.47
01/05/04	-8.94	-62.2	-6.17	-42.0	-9.54	-25.3	-5.84	-34.37	-5.98	-36.27	-5.59	-31.57
01/06/04	-4.74	-34.9	-6.84	-52.0	-6.84	-51.5	-3.09	-21.34	-4.96	-22.67	-3.08	-11.07
01/07/04	-6.22	-46.4	-5.22	-33.3	-5.34	-40.8	-4.20	-26.87	-3.27	-20.07	-3.05	-15.17
31/08/04	-3.85	-27.3	-5.32	-40.3	-6.11	-48.8	-7.18	-45.07	-7.71	-48.47	-5.37	-32.07
01/04/08	-8.15	-50.0	-9.33	-58.5	-9.20	-54.4	-8.51	-58.3	-8.41	-48.7	-8.43	-54.5
28/04/08	-5.60	-32.5	-10.38	-72.3	-10.40	-47.1	-11.44	-81.8	-9.39	-63.5	-7.65	-54.6
29/05/08	-5.49	-34.0	-6.00	-39.4	-7.71	-52.7	-6.87	-43.6	-6.05	-39.4	-6.85	-47.5
01/07/08	-4.82	-28.8	-4.67	-25.4	-6.46	-39.4	-5.87	-34.4	-6.01	-36.3	-5.62	-31.6
28/07/08	-4.78	-27.7	-4.64	-25.2	-4.60	-20.9	-1.01	-2.2	-4.99	-22.7	-3.11	-11.1
09/09/08	-3.43	-23.0	-3.15	-12.6	-4.87	-23.9	-4.23	-26.9	-3.30	-20.1	-3.08	-15.2
07/10/08	-7.27	-44.8	-8.88	-55.3	-8.55	-48.4	-7.21	-45.1	-7.74	-48.5	-5.40	-32.1
05/11/08	-3.41	-18.2	-4.36	-29.5	-9.01	-66.5	-5.51	-29.2	-4.29	-25.2	-9.16	-56.2
09/12/08	-9.02	-59.6	-9.49	-59.5	-12.55	-79.2	-8.86	-53.6	-8.91	-58.7	-8.98	-60.7
02/01/09	-11.13	-76.3	-11.68	-78.8	-10.47	-71.1	-11.32	-77.8	-11.73	-81.7		
02/02/09	-8.80	-58.2	-9.19	-56.1					-9.08	-57.0		
01/07/11	-5.02	-30.1	-5.20	-30.6	-6.64	-39.3						
05/10/11	-6.58	-35.2	-6.85	-36.4	-7.02	-43.7						
11/01/12	-8.22	-48.6	-8.18	-52.8	-8.63	-55.9	-10.24	-76.66	-10.70	-80.64	-8.47	-55.10
28/03/12	-10.45	-67.6	-8.72	-55.8	-8.39	-49.1						
13/07/12	-6.66	-32.9	-7.39	-50.1	-8.65	-42.7	-5.84	-34.37	-5.96	-36.23	-5.58	-31.55
09/10/12	-6.35	-39.7	-7.87	-45.9	-8.13	-48.5						
08/01/13	-8.61	-53.2	-9.26	-61.4	-9.84	-65.9						
04/04/13	-10.31	-66.1	-10.40	-69.9	-10.40	-70.0						
17/07/13	-6.06	-45.5	-4.85	-19.0	-7.77	-44.3						

Tab. 5 - Oxygen-18 and deuterium values measured in rain water over the different sampling campaigns in the investigated area. The values are expressed as ‰ VSMOW. Numbers in the first row indicate the rain gauge station located in Fig. 1

Altitude gradient and recharge area

Oxygen-18 and the elevation of the recharge are in relation according to the so called “isotope altitude effect”; as a general rule, the higher the elevation, the lower the isotopic content, since the temperature of the cloud formation is directly linked to the elevation a.s.l. As a consequence, the relationship between oxygen-18 content in precipitations and the altitude of infiltration can give useful information about the most likely areas of recharge of the Gorgovivo spring. This relationship (Fig. 8) has allowed for altitude gradient estimation for each investigated period: 2000-2004, 2007-2009 and 2011-2014; these values have then been used to evaluate the mean recharge elevation and therefore to estimate likely areas of recharge, also by analysing the hydrogeological setting and features of aquifers present in the Gorgovivo spring zones.

The calculated gradients obtained in this study are quite different from others (Zuppi *et alii*, 1974; Longinelli & Selmo, 2003; Tarragoni, 2006), computed for the southern zones of Umbria Marche Apennines, but very similar to those by Conversini & Tazioli (1993), Barbieri *et alii* (2005), Mussi *et alii* (2017), proposed for some areas of the middle Apennines in Central Italy. Table 6 summarizes the results, showing both the differences with literature data and the variation across the investigated period.

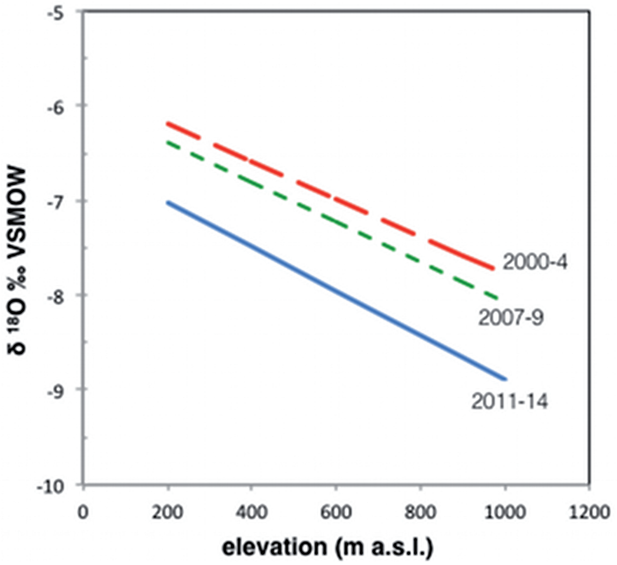

Fig. 8 - Relationship between $\delta^{18}O$ and altitude in the investigated area for each period of investigation. The isotopic gradient is equal to -0.21‰ / 100 m (red line), -0.2‰ / 100 m (green line) and -0.23‰ / 100 m (blue line)

DISCUSSION

In the general analysis of the results, the isotopic values of precipitation are worth considering due to the probable impact of climate change on the Italian peninsula. The distribution of rainfall, concentration of rain in specific periods (often far from the recharge season), and a general drop in the rainfall amount especially in certain areas, are only a few aspects of the effect of climate change at these latitudes. The climate and precipitation pattern in the area has modified notably in the last twenty years, thus also affecting the isotopic contents in rainfall. As a general rule, a comparison between isotopic content in rainfall and groundwater allows the groundwater dynamics and properties to be determined.

Firstly, tritium provides an indication of the transit time and the length of flow paths in groundwater; the high, values in the shallow springs emerging from the Scaglia and Maiolica Fms. usually indicate recharge from perched aquifers with high renewable rates and fast circuits. The lower values of the Gorgovivo spring, conversely, are probably due to the presence of a wider reservoir and the combined effect of the occurrence of both more recent waters (coming from the shallow pathway) and groundwater from the deeper circuit. Figure 4 depicts the tritium trend in the rain water, showing a decrease until the beginning of 2000’s, when the impact of nuclear test effects has completely disappeared, followed by a new increase affecting the mean values, that was probably due to climate change. The highest values (usually registered in the winter months) are however continually decreasing.

As for the stable isotope data, Fig. 6 reports the rain isotope profile for the Pian dell’Elmo gauging station (940 m a.s.l.), the highest rain-gauge station in the area, which exhibits very different behavior for each analyzed period, often depending on the distribution of rainfall and/or the specific hydrologic

Years	Altitude gradient (‰ / 100 m)	Estimated elevation (m a.s.l.)	Spring $\delta^{18}O$ (‰ VSMOW)	(1)	(2)	(3)	(4)	(5)
2000-2004	-0.21	1120	-9.41	1307	1369	1378	777	2531
2007-2009	-0.2	1030	-9.33	1275	1340	1342	715	2473
2011-2014	-0.23	1190	-9.29	1258	1326	1323	685	2444

Tab. 6 - Estimated altitude of infiltration of the Gorgovivo spring in the studied periods, calculated from the annual weighted values of oxygen-18. On the right part: (1) Conversini & Tazioli, 1993; (2) Zuppi et alii 1974; (3) Tarragoni, 2006; (4) Barbieri et alii, 2002; (5) Longinelli & Selmo, 2003

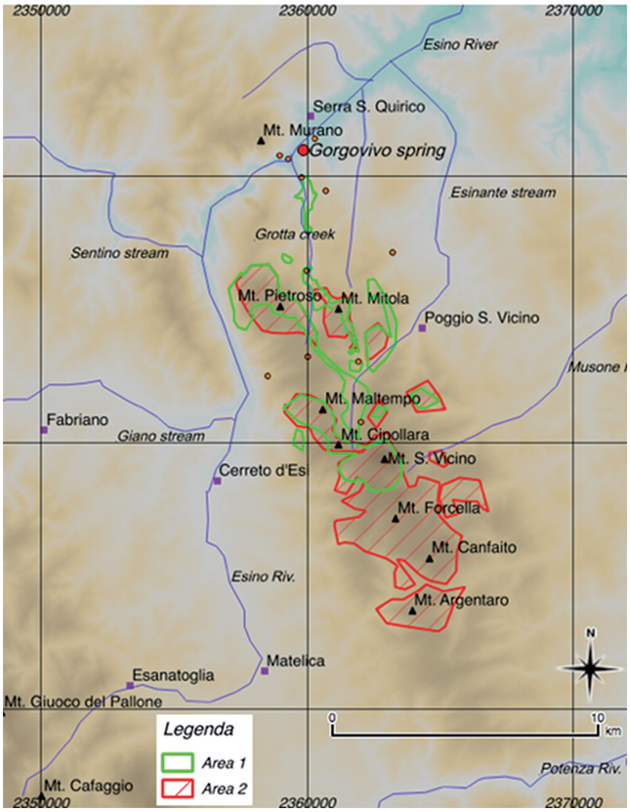

Fig. 9 - Recharge areas of the Gorgovivo spring (identified in the present study): Area1: all the outcrops of the Maiolica and Calcare Massiccio Fms. from Mt. S. Vicino and the spring. Area2: all outcrops of aquifers included between the Potenza and the Esino river

year (sometimes characterized by a large amount of snow, or intense rainfall in the summer season or a drastic increase in the temperature and lowering precipitation). An enrichment trend of both the isotopes of the Gorgovivo spring is evident in recent years (mean values of -9.41 and -65.7 in 2000-2004, -9.33 and -62.8 in 2007-2009 and -9.29 and -61.1 in 2011-2014 for oxygen-18 and deuterium, respectively), probably due to climate change and the continuous exploitation of the water resource (Fig. 7). Table 6 and Fig. 8 summarize the altitude gradients obtained in the present investigation, compared to others from literature, and the estimated altitude of recharge. As can be seen, the calculated gradients are rather different from others (Zuppi *et alii*, 1974; Longinelli & Selmo, 2003; Barbieri *et alii*, 2005; Tarragoni, 2006), computed for the southern zones of Umbria Marche Apennines, but similar to those by Conversini & Tazioli (1993) and Mussi *et alii* (2017) proposed for areas in the middle Apennines in Central Italy. Table 6 summarizes the results, showing both the differences with the literature data and the variations across the investigated period.

These calculations allow specific attention to be given to the recharge area evaluation of the spring, which is also the main aim of this article. Previous studies in fact (Cantelli, 1989; Caprari *et alii*, 2001) identified the zone included between the northern slope of the Mt. San Vicino and the spring outlet as the most likely catchment area for the spring, corresponding to a mean elevation of about 650 m a.s.l. calculated merely on the basis of the orographic profile. In this work, a more detailed calculation has been made considering the actual average height of aquifer outcrops both in the proposed area of recharge and in a more extended one (Fig. 9), compared to the value of the elevation obtained from isotopes. In the first case (area 1 in Fig. 9), the mean elevation of the Calcare Massiccio and Maiolica outcrops (supposing that they are in hydraulic contact for the entire zone) is 770±180 m a.s.l.; a higher mean altitude (930±130 m a.s.l.) has been obtained considering a wider area (area 2 in Fig. 9), also including the outcrops of the southern zones (about 11 kms towards the South). In addition, a second type of estimation involved only the Calcare Massiccio aquifer outcrops, thus resulting in higher calculated altitudes: 840±190 m a.s.l. for the smallest area and 965±170 m a.s.l. for the most extensive one. The values obtained from the analysis of the hydrogeological setting suggest that the presumed area could be extended, since the calculated altitude does not match that attained from the isotopic analysis (the latter being a little higher even if within the range of variation).

In addition, the coupled effect of the enrichment of the spring isotopes (Fig. 7, Tab. 2) and the rise of the precipitation gradient over the last 15 years (from 0.2 to 0.23‰/100 m) is remarkable, resulting in an increase of the estimated recharge height of about 160 m. Despite the isotope changes, the average altitude of the recharge area seems to vary less than expected in respect to the variation of the isotope data of precipitation and groundwater. This change in the altitude value of recharge is more limited if we consider only the periods 2000-2004 and 2011-2014 data (altitude differing by only 70 m); the hydrologic behaviour in 2007 being very peculiar (total amount of precipitation lower than the average and a summer with limited rainfalls), it might make sense to analyse the trend from 2000 to 2014 without considering the intermediate values. This would lead to a limited (but well detectable) increasing effect on isotopes both of precipitations and groundwater, yielding to a slight shift in the average elevation of the recharge area of the Gorgovivo spring. In any case, a change in the recharge area boundary could be observed over the investigated years, but mostly due to the variation of the isotopic values (connected to climate change) and to the complexity of the hydrogeological setting leading to a less than perfect identification of the areas contributing to aquifer recharge (connected to a lack in hydrogeological surveys, owing to the extent of the supposed area as well). This change is however rather small and much less important than the fact of having extended the former supposed area notably towards the south.

To summarize, based on the isotopic results presented in this study, the recharge area of the Gorgovivo spring mainly includes the highest outcrops of the Calcare Massiccio Fm. and the Maiolica Fm., in a more extended zone in respect to what was previously thought (Fig. 9). Since, in general, higher elevation aquifer outcrops (which contribute to the spring recharge) even in southern-most areas cannot be excluded, the actual recharge area of the spring is to be updated by including the contribution of the basal flow coming from more distant points (even tens of kilometres towards the south).

CONCLUSIONS

The abovementioned considerations and the experimental data gathered throughout the investigated period, overall through isotopic techniques has allowed us to reach new conclusions with regards to the recharge area and mechanism of the Gorgovivo spring. The innovative contribution of this research is connected to the evidence (from isotope values) of contact between the different aquifers, and provides evidence for the actual recharge area of the spring. In addition, the study confirms the hypothesized recharge mechanism, as it is mainly fed by the basal circulation in the Calcare Massiccio Fm., which is slow and characterized by long flow paths. However, at the same time, it also shows some typical elements of shallow circulation, which is characterised by very fast circulation with limited flowpath length. Even the shallow circulation was identified in this research through the observation of chemical and isotopic data measured in different shallow springs in the area, which are directly recharged by local meteoric waters (with isotopic contents that are higher than those in the Gorgovivo spring), and therefore characterized by greater variability in discharge and temperature. In these kinds of springs, the chemical and isotopic parameters reflect the different composition of the rock reservoir and the difference in pathways. The shallow path can reach the basal aquifer in the more depressed areas, mixing in various proportions with the slower deep flow. This occurs in the emerging zone of the Gorgovivo spring, and results in groundwater with peculiar chemical properties and a constant temperature throughout the year, with short but well-defined isotopic variations, and with a tritium content lower than that of shallow springs and rainwater. Tritium and stable isotopes contents gained during the present investigation allowed these chemical and hydrological features to be validated. The isotopic investigation (performed over a long period of time, from 2000 very recently) allowed for an extension of the recharge area, leading to the consideration of other outcrops zones, outermost with respect to those supposed in previous studies. The additional inputs from the present work lead to an increase in the zones potentially interested in the spring hydrogeological basin; in fact, it is likely that also the southernmost sectors of the Umbria Marche ridge contribute to the discharge of the spring, which is exceptional, and would make the Gorgovivo spring one of the most important groundwater resource in the Apennines as regards importance and quality. Further investigations (to be performed also using other methodologies, like artificial tracer technique) could help in quantifying the groundwater flow by separating the contribution of the basal flow occurring in southernmost parts of the Marche region.

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This work represents a tribute to the memory of my father, prof. Giulio Sergio Tazioli, who studied the Gorgovivo spring using isotopes as a useful tool to identify the recharge area of aquifers; he died few months ago, leaving a big hole in the heart of who knew him. May you rest in peace, my great mentor and life coach!

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