KARMA

Karst **A**quifer **R**esources availability and quality in the **M**editerranean **A**rea

Stable Isotopes

Deliverable 2.3

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Executive Summary

WP2 deals with the evaluation of water availability at the five test sites in KARMA project using different methods. The previous deliverables consisted of a preliminary assessment (D2.1 Preliminary water budget) of the water balance (recharge/discharge) in individual test sites, using available data and (recent and historical) information. Thus, a first estimation of karst groundwater resources was established.

A subsequent deliverable (D2.2 Recharge evaluation) comprised the core activity of the Task 2.1 "Recharge assessment and tracer tests", and it includes an updated estimation of recharge rates in the KARMA test sites. The final goal is to provide a distributed recharge map for the studied areas at a catchment scale in a continental Mediterranean context. Therefore, a more accurate recharge assessment was performed in each study area, as described in the following chapters.

The common research approach in D2.2 consisted of the application of the APLIS method, originally developed by members of the UMA partner (Andreo et al., 2008; Marin, 2009). The application of APLIS at different test sites different from the climatic and hydrogeological contexts in which the method was originally designed also serves as a test of its robustness and reliability.

In a further step, provided results on the spatial distribution of aquifer recharge will be compared with discharge measurements for the investigated karst systems. Besides APLIS, alternative approaches (i.e. hydraulic modeling) have been performed in some individual test sites for the same purpose.

In the present deliverable, a collection of previously collected and directly performed analyses on water stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) at different test-sites is included. These data are considered useful to check and validate the water budget based on indirect method (as APLIS) applied in D2.2. Comparing collected stable isotopes data with literature correlation lines, a Computed Isotopic Recharge Evaluation for the springs included in each study area has been assessed. By this way, the consistency of the recharge area with isotope values with the groundwater flow conceptual models applied in the different karst aquifers have been confirmed.

The new stable isotope data collected in four test-sites do not show significant changes with respect to previous information. Consequently, the conceptual model of groundwater flow of studied karst springs has been confirmed. The steady isotope values reflect the stability of the recharge area contribution to the spring flow, despite to possible reduction in recharge rate. At this stage the stable isotope data confirms that the distribution of the aquifer recharge with altitude (and consequently the extension and the mean elevation of hydrogeological basins and sub-basins within the studied karst aquifers) is still not affected by possible changes in recharge rate due to different precipitation values with years.

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1 Introduction

The overarching objective of the KARMA project is to achieve substantial progress in the hydrogeological understanding and sustainable management of karst groundwater resources in the Mediterranean area in terms of water availability and quality. At karst catchment scale, the main objective is to advance and compare transferable modeling tools for improved predictions of climate-change impacts and better-informed water management decisions, and to prepare vulnerability maps as tools for groundwater quality protection.

The main objective of WP2 is the assessment of groundwater availability by investigating recharge, discharge and storage. Recharge consists of the downward flow of rainwater that reaches the water table. Recharge into karst and fissured aquifers can occur in two ways, (1) diffusely over carbonate outcrops, epikarst and soils (autogenic) or (2) from nearby non-karst areas where rainwater infiltrates through swallow holes or dolines (allogenic) (Figure 1.1).

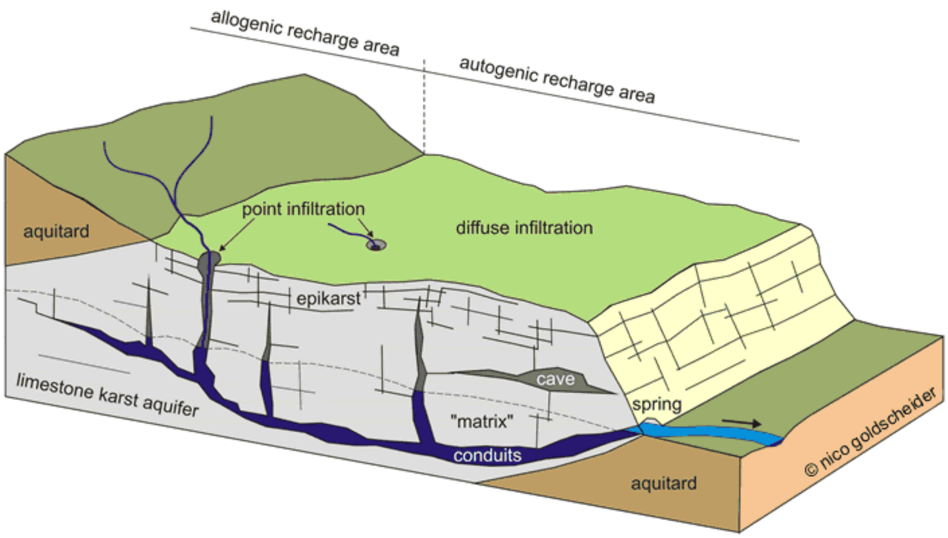


Figure 1.1. Schematic illustration of a heterogeneous karst aquifer system characterized by a duality of recharge (allogenic vs. autogenic), infiltration (point vs. diffuse) and porosity/flow (conduits vs. matrix) (Goldscheider 2019)

The available knowledge about these processes and how infiltration takes place in each KARMA test site highly influences the development of numerical models and vulnerability maps, as well as their accuracy. Therefore, in order to achieve a better hydrogeological understanding and to obtain reliable data for the calibration and validation of models and vulnerability maps, hydrological monitoring, isotope studies, and tracer tests will be carried out in addition to the recharge rate estimation.

When considering an appropriate time scale (decades), it can be assumed that the mean annual value of the recharge is equivalent to the rate of discharge. Thus, groundwater recharge over a defined area is usually equivalent to infiltration excess. Different methods are traditionally applied for groundwater recharge assessment (i.e. hydrological or numerical balance, based on hydrochemistry and environmental isotopes, etc), however none of them are free from uncertainty. The use of stable isotopes data collected at springs helps to validate proposed water budget, identifying the infiltration area (or better its elevation) to be compared with calculated recharge rate for sub-basins and for the entire study area.

2 The water stable isotopes in karst hydrogeology

As well known in literature (Doveri et al., 2013 and references herein) isotopic applications are a relevant and useful tool for the knowledge of the hydrogeological features of karst systems. The water isotopes can be considered as real natural tracers because they are not affected by water-rock interaction processes until temperatures of about 200°C and consequently they can be useful to compare stable isotope composition of rain with those of groundwater and springs. By correlating stable isotopes correlation lines with catchment elevation, a Computed Isotope Recharge Elevation can be derived for each spring water isotope composition, to validate conceptual models related to groundwater flow direction, recharge areas attribution to each spring and, possibly, to discharge measured in different seasons and different flow (low/high-) conditions. In other words, in karst aquifers it is possible to fully correlate the discharge contribution with the infiltration, by considering the variations of the isotopic values of rainwater with respect to both periods of year and precipitation elevation.

The principles of the use of water stable isotopes (namely, δ^2H and $\delta^{18}O$) can be resumed as follow (Tazioli et al., 2019). In mountainous areas, precipitation (in the form of rain and snow) is the input into hydrological processes occurring at the soil surface (i.e., evapotranspiration, runoff and infiltration). In this context, isotopic fractionation seems to be a key factor in understanding of hydrological processes connected to the entire hydrological cycle with a particular focus on precipitations. Indeed, the so-called isotopic effects are all related to the distribution of the contents and changes of the composition of stable isotopes all over the world and at different times of the year. The isotopic composition of water vapor is modified during evaporation, freezing, condensation, and melting due to isotopic fractionation. Usually, the Global Meteoric Water Line (GMWL, Craig 1961) is used to depict the relationship between the δ2H and $\delta^{18}O$ content in precipitations on a global scale.

In regional studies, a local meteoric water line (LMWL) is typically plotted, using data from local rain stations. The isotopic composition of rainfall is affected by the so-called isotopic effects, mainly dependent on the temperature of cloud formation and are followed by isotopic fractionation. The seasonal effect is the fluctuation of isotopic content related to temperature change. The continental effect is the depletion of isotopic values moving from the coast to inland areas. Moreover, latitude greatly affects isotopic values. The overall effect creates correlations between isotopic variations and the hydrological cycle on a global or regional scale. The altitude effect (i.e., isotopic depletion with increasing elevation) is likely the most important property in hydrogeology; with this property, in fact, the recharge areas of springs and aquifers can be identified in both local and regional groundwater systems, assuming that after infiltration process, no significant changes can be observed in stable isotope composition of δ2H and $\delta^{18}O$.

Craig, H. (1961). Isotopic variations in meteoric waters. Science 133, 1702-1703.

Doveri M., Menichini M., Cerrina A., 2013. Stable water isotopes as fundamental tool in karst aquifer studies: Some results from isotopic applications in the Apuan Alps carbonatic complexes (NW Tuscany, Italy). It J Eng Geol Env, 2013 (1), 33–50

Tazioli A, Cervi F, Doveri M, Mussi M, Deiana M., Ronchetti F, 2019. Estimating the isotopic altitude gradient for hydrogeological studies in mountainous areas: Are the low-yield springs suitable? Insights from the northern Apennines of Italy. Water 11 (9) 1764

3 Gran Sasso aquifer (Case Study Italy)

3.1 General description of the test site

The Gran Sasso hydrostructure is defined as a calcareous-karstic aquifer system of about 1034.4 km^2 of total extension and it is the most representative karst aquifers of the central-southern Apennines. The Gran Sasso hydrogeological system is characterised by Meso-Cenozoic carbonate units (aquifer). It is bounded by terrigenous units represented by Miocene flysch (regional aquiclude) along its northern side, and by Quaternary continental deposits (regional aquitard), along its southern side (Figure 3.1) (Barbieri et al. 2005, Amoruso et al. 2012).

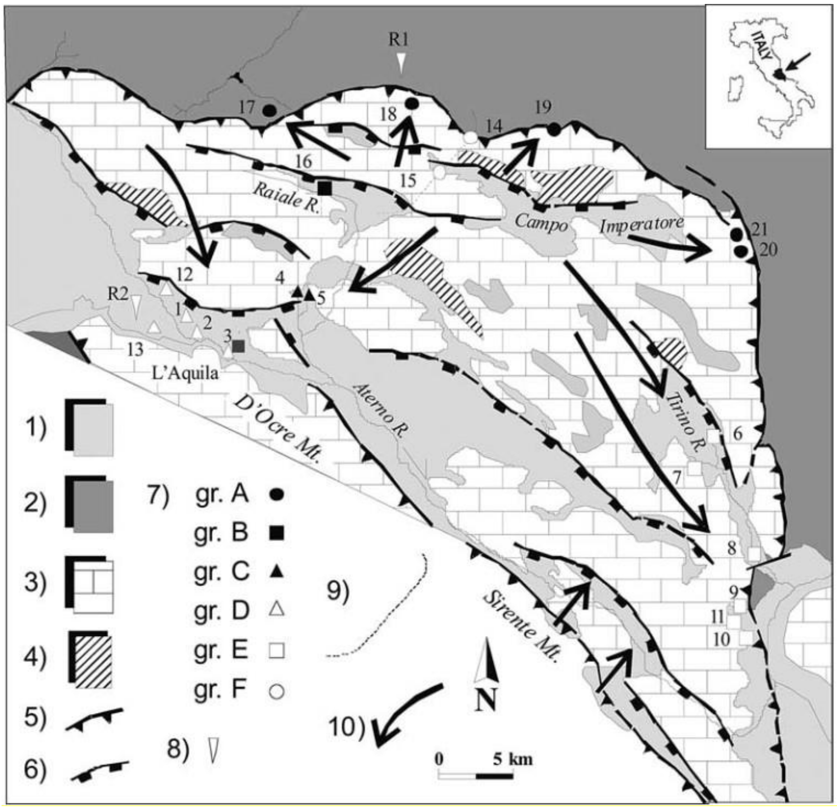


Figure 3.1-Hydrogeological map of Gran Sasso. 1 – continental deposits of tectono-karst basins (Quaternary); 2 – terrigenous deposits –pelites and sandstones – (upper Miocene); 3 – carbonate sequences of platform (including shelf), scarp to basin and ramp lithofacies (Miocene – upper Trias); 4 – dolomites (upper Trias); 5 – overthrust; 6 – extensional fault; 7 – spring group; 8 – location of rainwater sampling for isotope analyses; 9 – motorway tunnel; 10 – main directions of groundwater flowpaths. Spring and rain sampling station numbers refer to Barbieri et al., 2005.

The Gran Sasso karst aquifer hosts a unique regional-wide groundwater table. The main springs have been organized into six groups based on groundwater flow and hydrochemical characteristics Tallini et al., 2000; Barbieri et al., 2005), as illustrated in Figure 1. The aquifer has a total discharge of more than 18 m3/s from its springs (Adinolfi Falcone et al., 2008; Amoruso et al., 2012), including a highway tunnel drainage tapped for drinking water on both sides. At the massif core, an endorheic basin having tectonic-karst origin, called Campo Imperatore basin (elevation 1650 m a.s.l), acts as preferential recharge area of the Gran Sasso aquifer, fed by high rainfall and snow rate.

3.2 Isotope findings from previous studies

The Gran Sasso aquifer has been deeply investigated during time due to its relevance in terms of extension, complexity of aquifer system, amount and quality of groundwater resources exploited for drinking and other purposes, and it can be considered as one of the most representative karst aquifers of the Apennines.

Nevertheless, hydrogeological studies are sometimes not sufficient to shed light on the groundwater hydrodynamics in terms of recharge mechanisms of this carbonate karst environment, since groundwater also flows through fractures and karst conduits. In this framework many studies deal with the application of groundwater stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) to validate and fine-tune hydrogeological conceptual models. For the Gran Sasso case study different "isotopes approaches" have been followed both on local and full aquifer scales, here we summarize the main results obtained from the latest investigations.

In Barbieri et al. 2005, a comprehensive isotopes study has been carried out, sampling 21 springs and 2 rain stations, during 2001. The analysis of $\delta^{18}O$ and $\delta^{2}H$ allowed to confirm the hydrogeological classification of 6 groups of springs, to define a local water line and a vertical isotope gradient. Coupled with groundwater stable isotopes, analyses on $^{87}Sr/^{86}Sr$ ratios have been performed to understand water-rock interaction processes.

Adinolfi Falcone et al. 2008 focused their attention at the scale of underground laboratory of the Italian National Institute of Nuclear Physics (INFN), representing as defined by the authors, a "window" in the core of Gran Sasso aquifer. Specifically, groundwater isotopes analyses have been carried out in groundwater collected inside the Lab and on snow and snow-melting water from Calderone Glacier. Results highlight that recharge water in the Lab comes from high-altitude areas where a mixing between "old" and "young" snow melting water occurred. In addition, analyses on $\delta^{13}C$ and ^{222}Rn, allowed to define respectively, water-rock interaction processes and groundwater flow velocity inside the fractured network.

A more recent isotopes study carried out at Gran Sasso aquifer scale has been performed in 2014 by Tallini et al.. The aim of this study was to characterize and fine-tunes the recharge process and water–rock interactions in the Gran Sasso aquifer through groundwater and $\delta^{13}C$ (in DIC) isotope data collected between 2006 and 2010. Samples have been collected from springs, from the Underground Nuclear Physics Laboratories and results compared with isotope signal of rain and snow collected during time from different weather stations. The analysis of $\delta^{18}O$ and $\delta^{2}H$ allowed to confirm the hydrogeological conceptual model proposed by Barbieri et al. in 2005 and to obtain an update one by local water line and by vertical isotope gradient.

Another research study performed at local scale, has been conducted by Petitta et al. in 2015 on the Presciano spring system, in the south-eastern area of the Gran Sasso massif. Through the help of groundwater stable isotopes, it was possible to validate the presence of a dual flow system in two main spring sectors. Specifically, isotope analyses allowed to distinguish different recharge areas: one characterized by more depleted values indicating the existence of a flowpath influenced by a higher elevation recharge area, the second one with enriched isotope signals supporting a regional recharge area of local water infiltration. Also in this case additional effort has been added coupling groundwater isotopes with $\delta^{34}S$ and $\delta^{18}O$ analyses of dissolved sulphate in groundwater. In this paper also changes in groundwater isotopes composition due to the 2009 L'Aquila earthquake have been highlighted.

Additional insights about groundwater flow and water – rock interaction in the Gran Sasso aquifer, have been assessed in Tallini et al. 2013, through a long-term hydrochemical and ^{222}Rn radioactive isotope tracing survey. Specifically, due to its short half-life (about 3,8 days), ^{222}Rn have been used to differentiate groundwater flowpaths inside individual spring groups at the final stage, close to the outflow areas.
Results shows that springs among the same group are characterized by significant variability in ^{222}Rn content allowing to isolate the effects of seasonal water table fluctuations, karst features and marly lithology outcrops. These features make possible to fine tune the regional groundwater flowpaths previously identified by hydrogeological and hydrogeochemical studies.

3.3 Stable isotope sampling survey and results in KARMA project

Basing on the relevant findings obtained from previous isotopic studies performed on Gran Sasso aquifer, within the framework of KARMA project, to date, four isotopes sampling surveys on groundwater stable isotopes have been carried out. Additional samples for the analyses of tritium isotope have been also collected. This new isotope characterization is aimed to clarify the correlation between recharge (rainfall and snow) and discharge and consequently validate the calculated water balance; highlight possible shift and differences with historical data probably induced by climate changes (i.e. temperature and precipitation distribution); analyse seasonal variability.

Figure 3.2 shows the location of sampling points of the Gran Sasso monitoring network (springs and groundwater sampled from motorway tunnel), while the results are summarized in Table 3.1. Specifically, the monitoring network consists in 12 main springs (from GS1 to GS 13, excluding GS3) and 8 monitoring points representative of the drainage and of the groundwater collected inside the motorway tunnel (from GS14 to GS16B and GS3). Nowadays results are available for October 2020 and March 2021 surveys, we are waiting results from the lab for the June-July 2021 and August 2021 sampling surveys.

*Table 3.1- ID, name and elevation of sampling sites selected for isotopes analyses; results of October 2020 and March 2021 sampling surveys (*referred to May 2021); N.S. Not Sampled; X refer to samples running in the lab*

		Elevation	oct-20		mar-21		jun-jul-21		aug-21	
ID	Name	m (a.s.l.)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)
GS1	*Chiarino*	1315	-10.79	-69.60	-10.06*	-65.00*	X	X	X	X
GS2	*Rio Arno*	1524	-10.61	-69.30	-10.21*	-66.50*	X	X	X	X
GS3	*Esubero Alto*	960	-11.32	-73.70	-10.79	-69.6	X	X	X	X
GS4	*Ruzzo*	900	-10.14	-65.30	N.S.	N.S.	X	X	N.S.	N.S.
GS5	*Vitella D'Oro*	690	-10.74	-70.20	-10.24	-65.30	X	X	X	X
GS6	*Mortaio D'Angri*	650	-10.77	-67.70	-10.49	-67.30	X	X	X	X
GS7	*Capodacqua*	340	-10.38	-67.90	-10.22	-66.70	X	X	X	X
GS8	*Presciano*	336	-10.21	-66.80	-9.85	-65.30	X	X	X	X
GS9	*Capopescara*	270	N.S.	N.S.	-10.13	-65.90	X	X	X	X
GS10	*Tempera*	650	-10.95	-70.90	-10.62	-69.2	X	X	X	X
GS11	*Vera*	650	-10.56	-69.28	-10.65	-70.3	X	X	X	X
GS12	*Vetoio*	640	-9.13	-59.30	-9.19	-61.1	X	X	X	X
GS13	*Boschetto*	625	-9.58	-63.10	-9.43	-62.10	X	X	X	X
GS14	*Traforo Sud*	967	-11.00	-71.90	N.S.	N.S.	X	X	N.S.	N.S.
GS15A	*S13*	1000	-11.22	-73.36	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
GS15B	*S15*	1000	-11.16	-73.14	N.S.	N.S.	X	X	N.S.	N.S.
GS15C	*S17*	1000	-11.15	-73.02	N.S.	N.S.	X	X	N.S.	N.S.
GS15D	*S18*	1000	-11.11	-72.74	N.S.	N.S.	X	X	N.S.	N.S.
GS16A	*TRAFORO DX*	1000	-10.98	-71.34	N.S.	N.S.	X	X	N.S.	N.S.
GS16B	*TRAFORO SX*	1000	-11.00	-71.13	N.S.	N.S.	X	X	N.S.	N.S.

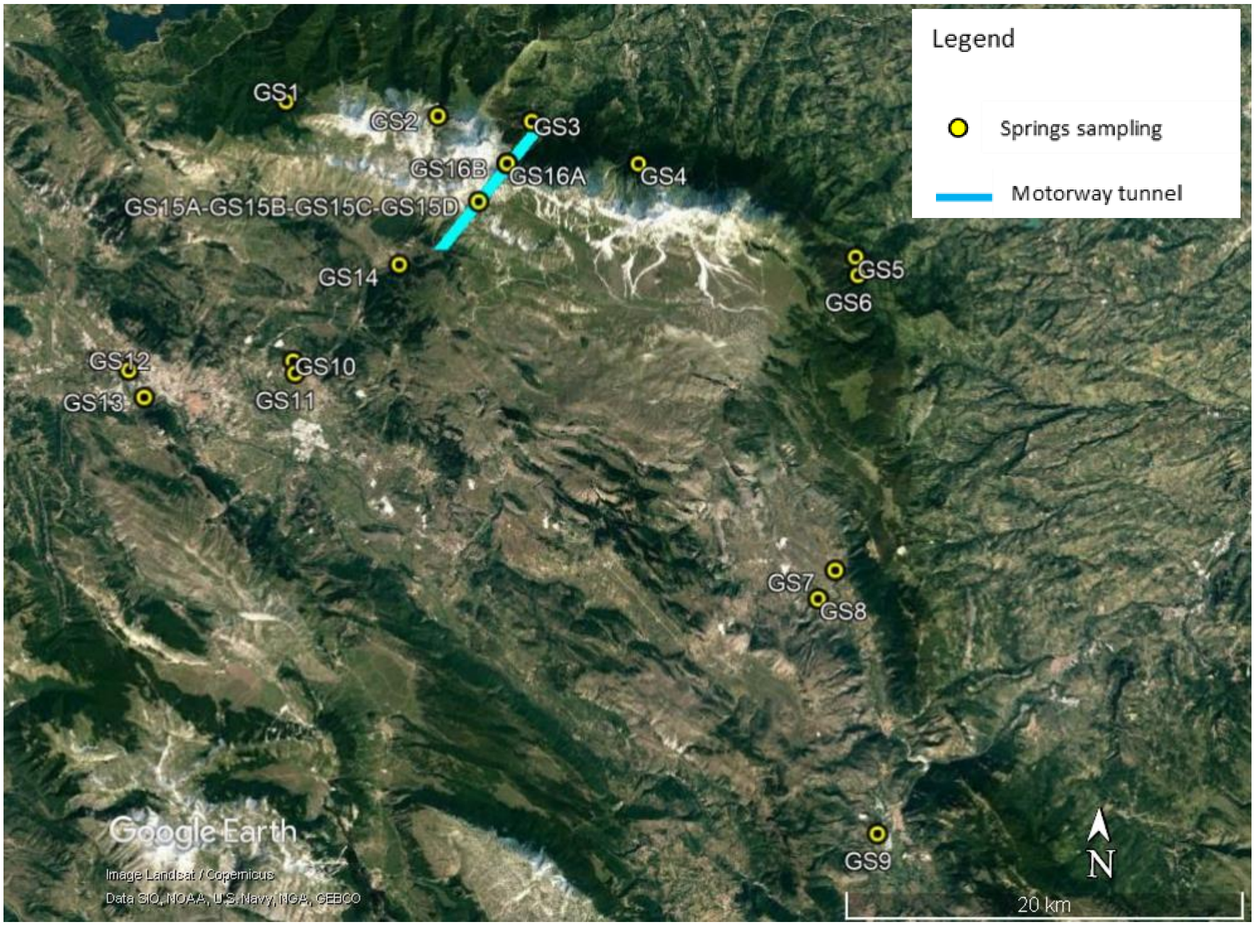
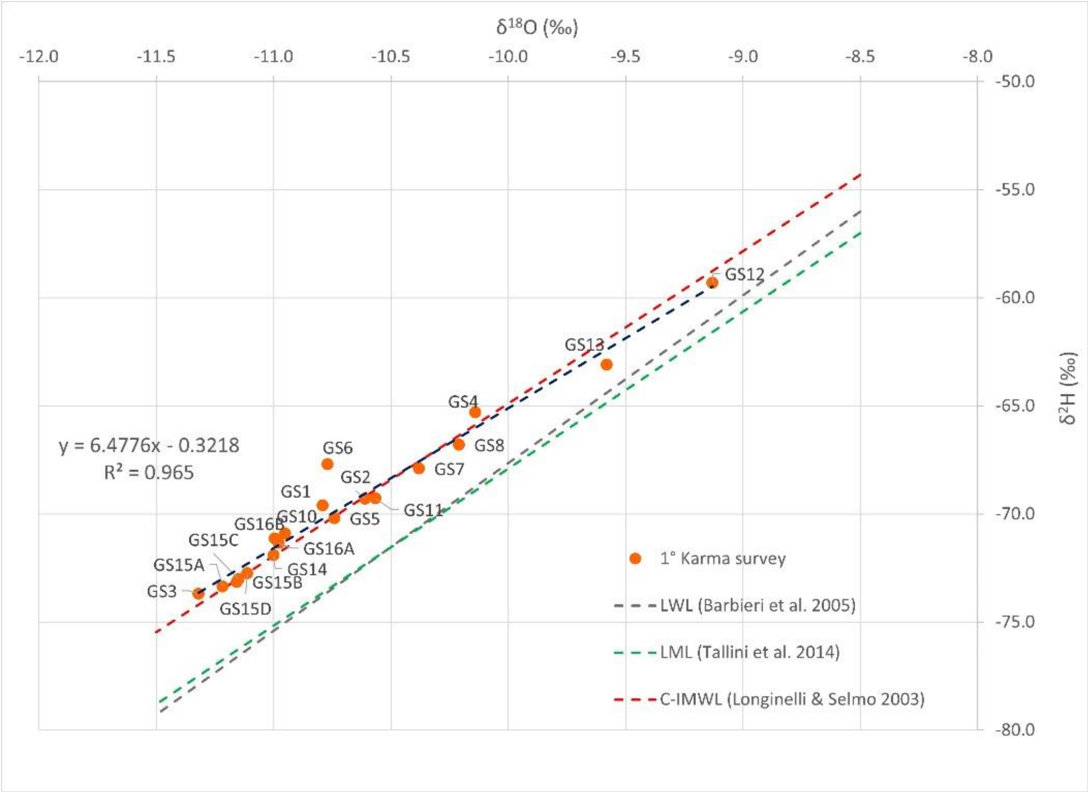


Figure 3.2. Location map of sampling sites selected for isotopes analyses.

During the October 2020 monitoring survey $\delta^{18}O$ isotopic values are ranging between -11,3 ‰ and -9,1 ‰, while $\delta^{2}H$ isotopic values between -73,7‰ and -59,3‰ (Fig.3a). Looking at March 2021 data, $\delta^{18}O$ and $\delta^{2}H$ vary respectively, between -10,8‰ and -9,2‰ and -70,3‰ and -61,1‰ (Fig.3b). The comparison between the Fall and Spring sampling surveys, which correspond respectively to the exhaustion and the end of recharge phases, shows a limited variability of isotopic signal with a maximum shift of ±0,73 for $\delta^{18}O$ and ±4.9 for $\delta^{2}H$, and absolute variability values of 0,33 and 2,27 for $\delta^{18}O$ and $\delta^{2}H$, respectively. Missing results of recent sampling surveys will be updated as soon as we get them from the lab. In addition, in both sampling surveys, GS12 (Vetoio spring) and GS3 (Esubero Alto, tunnel drainage on northern side) represent, respectively, the most enriched and the most depleted samples of the dataset. This finding is in accordance with Barbieri et al. 2005 and Tallini et al. 2014 about the isotopic fingerprint characterizing the different spring groups of the Gran Sasso aquifer.



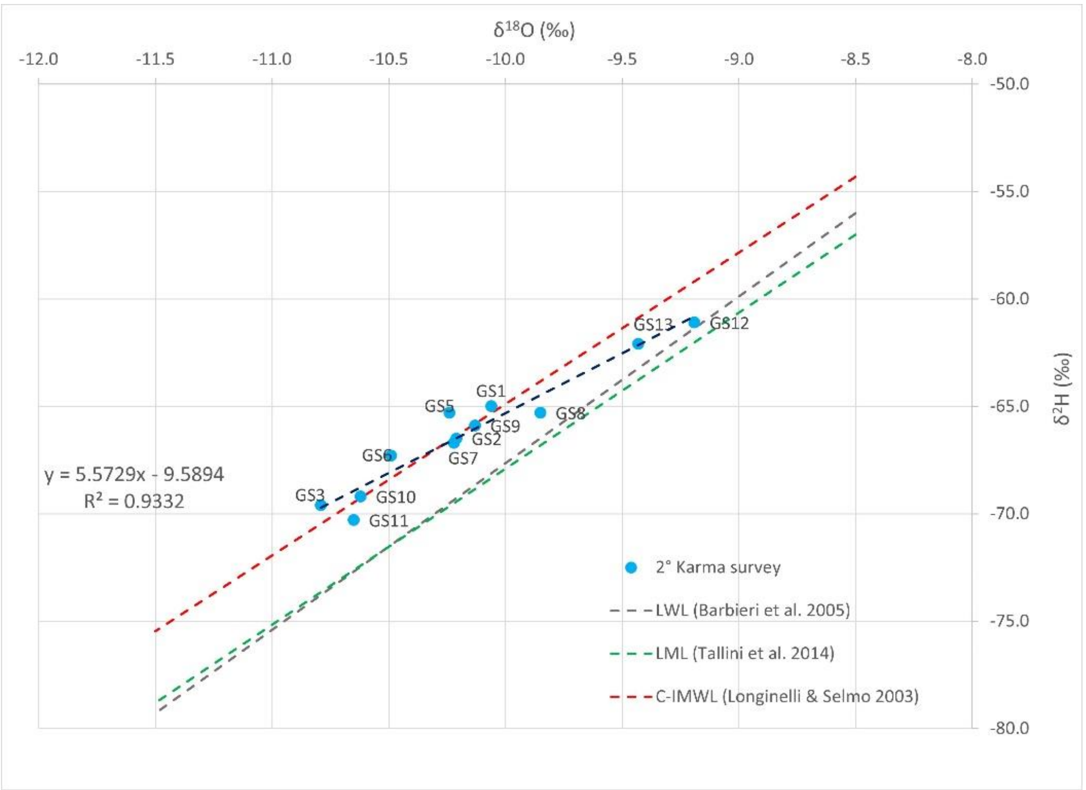


Figure 3.3 - $\delta^{18}O$- $\delta^{2}H$ plot of October 2020 (upper panel, 3a) and of March 2021 (lower panel, 3b) sampling surveys. Results for GS1 and GS2 are referred to May 2021

To better analyse the differences in isotope signals between the Fall (October 2020) and the Spring (March 2021) sampling surveys, a $\delta^{18}O$ 2020- $\delta^{18}O$ 2021 plot (Fig.3.4) has been realized with the results of common sampling points. Values are mostly aligned along the X=Y line, following a slight trend toward more enriched values recorded in March 2021 sampling survey. This effect is particularly clear for GS1 (Chiarino) and GS5 (Vitella d'Oro) springs and for GS3 (Esubero Alto) monitoring point, all located on the northern side of Gran Sasso massif having a recharge area at high elevation. The recorded slight enrichment suggests that, on the northern side of the massif at the beginning of Spring, recharge is probably attributable by rainfall comes from lower elevation areas due to snow persistence at higher elevations. In this period infiltration is still not influenced by snow-melting water contribution, the latter generally characterized by depleted isotope values, contributing to the spring discharge in late spring/summer periods.

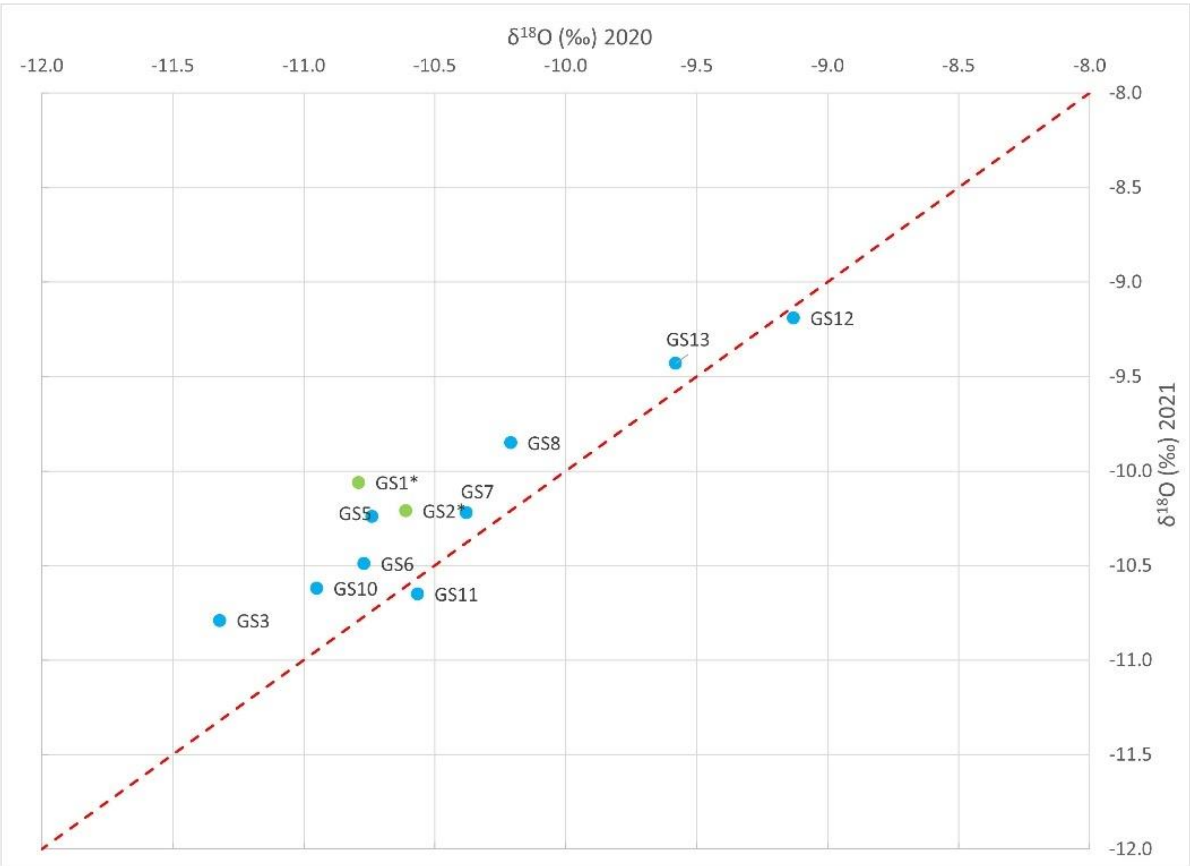


Figure 3.4. δ18O-δ18O comparison plot of October 2020 and March 2021 sampling survey (green dots are referred to May 2021)

Isotopes results of Fall sampling survey (October 2020), which is representative of the entire monitoring network and correspond to the exhaustion phase, have been also compared to isotope data coming from previous studies (Fig. 3.5). Previous and new results lie between the Central Italy Meteoric Water Line (C-IMWL) defined by Longinelli and Selmo 2003 and the Local Meteoric Line calculated by Tallini et al. in 2014, confirming the clear dependence of Gran Sasso aquifer system to meteoric recharge and ruling out the occurrence of evaporation processes during time. Not significant variations in isotope signals have been recorded between previous and new collected data.

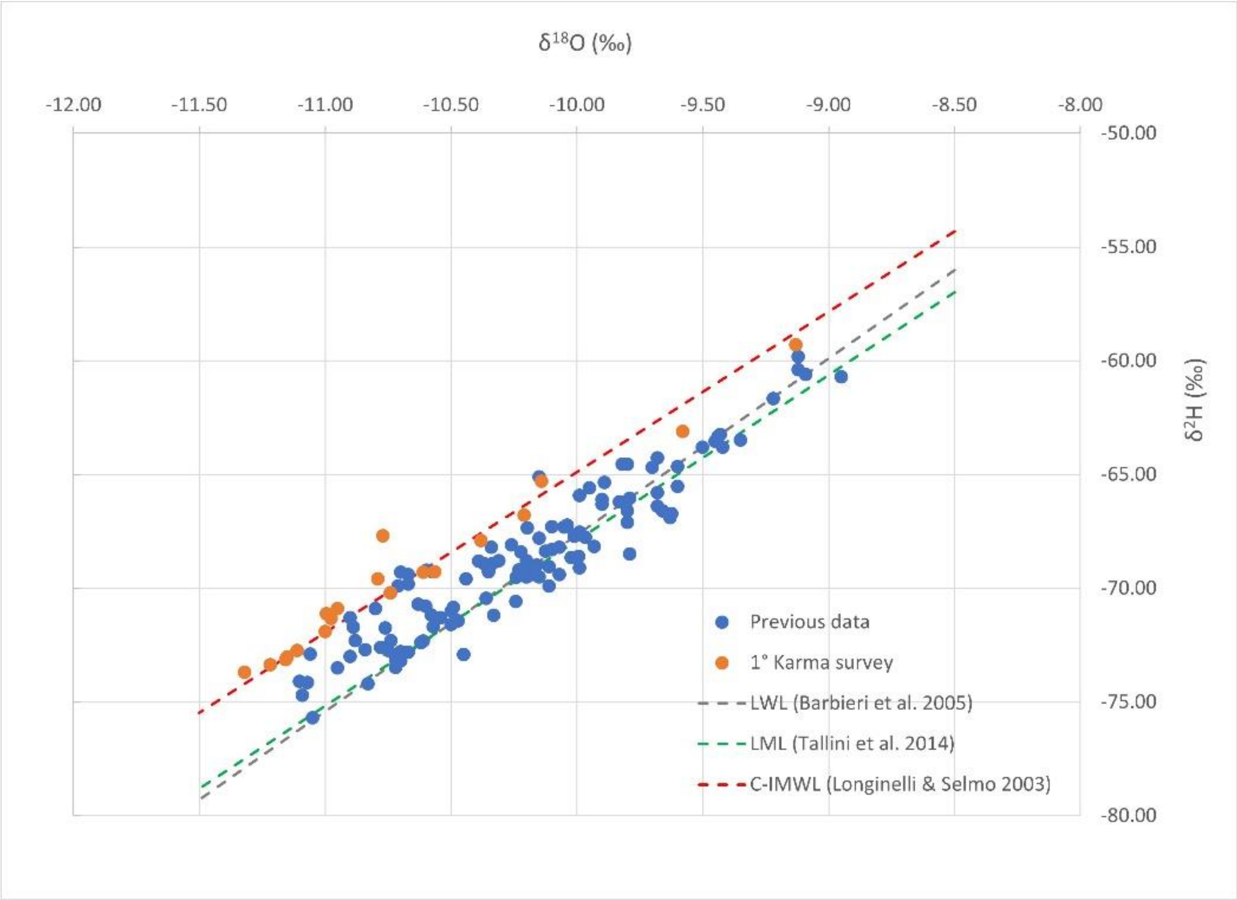


Figure 3.5. Comparison between δ18O – δD data coming from previous study and results of 1° Karma isotopes sampling survey.

As for other mountainous aquifer in Italy, and in the Mediterranean area, the distribution and type of precipitation is highly dependent on elevation of the recharge areas. For this reason, basing on the isotopic composition of rainfall water the Computed Isotopes Recharge Elevation (CIRE) for each spring and monitoring point have been calculated. CIRE values (Tab. 2), for October 2020 sampling survey, have been determined following two equations proposed in literature:

- CIRE m a.s.l. = ($\delta^{18}O$ + 6,35) /-0,0024 (Barbieri et al. 2005)
- CIRE m a.s.l. = ($\delta^{18}O$ + 5,871) /-0,00256 (Tallini et al. 2014)

Table 3.2. ID, name and elevation of sampling sites and results of CIRE values calculated through different equations for October 2020 sampling survey.

		Elevation	CIRE Barbieri et al. 2005	CIRE Tallini et al. 2014
ID	**Name**	**m (a.s.l.)**	**Oct-20**	**Oct-20**
GS1	*Chiarino*	1315	1850	1921
GS2	*Rio Arno*	1524	1775	1851
GS3	*Esubero Alto*	960	2071	2129
GS4	*Ruzzo*	900	1579	1668
GS5	*Vitella D'Oro*	690	1829	1902
GS6	*Mortaio D'Angri*	650	1842	1914
GS7	*Capodacqua*	340	1679	1761
GS8	*Presciano*	336	1608	1695
GS10	*Tempera*	650	1917	1984
GS11	*Vera*	650	1756	1833
GS12	*Vetoio*	640	1158	1273
GS13	*Boschetto*	625	1346	1449
GS14	*GSA - Traforo Sud*	967	1938	2004
GS15A	*S13*	1000	2028	2088
GS15B	*S15*	1000	2002	2064
GS15C	*S17*	1000	2000	2062
GS15D	*S18*	1000	1984	2047
GS16A	*TRAFORO DX*	1000	1928	1994
GS16B	*TRAFORO SX*	1000	1935	2002

CIRE values calculated using the two equations show a wide range of variability (> 900 m), reaching the minimum values for Vetoio Spring (GS12), and the maximum one at Esubero Alto sampling point (GS3). The generally high computed recharge elevations (> 1500 m a.s.l.), immediately suggest that the contribution of snow and consequently of snow-melting play a fundamental role in Gran Sasso aquifer recharge processes, as already highlighted during the calculation of water budget.
The latter is particularly evident for water collected from the highway tunnel (GS14÷GS16B and GS3), which is characterized by the most depleted $\delta^{18}O$ values and the higher CIRE values confirming a high-elevation recharge area (> 1900 m a.s.l.), as already assessed by Adinolfi Falcone et al. 2008 and Tallini et al. 2014.

The obtained CIRE values will represent a useful tool to validate the recharge areas, identified through water balance calculation.
CIRE estimation will be updated with results of June-July and August 2021 sampling surveys, when available.

3.4 Tritium isotope sampling results

In addition to stable groundwater isotopes, to shed more light about groundwater age and recharge mechanisms feeding the Gran Sasso aquifer, four sampling surveys for the determination of Tritium concentration (T.U.) have been carried out. Surveys have been performed during October 2020, March 2021, June – July 2021 and August 2021. Analyses have been performed in two different laboratories; specifically, the October 2020 survey has been analysed in University of Trieste Laboratory, instead the others in the IT2E Laboratory in Milan. To date, we gain results for the first two sampling surveys which are listed in Table 3.3; results will be updated with the last two sampling surveys.

*Table 3.3. ID, name, elevations and tritium concentration results for October 2020 (Trieste Lab) and March 2021 (Milan Lab) sampling surveys; *referred to May 2021; N.S. Not Sampled; X refer to samples running in the lab.*

			Oct-20	Mar-21	Jun-Jul-21	Aug-21
ID	**Name**	**Elevation m (a.s.l.)**	**Tritium (T.U.)**	**Tritium (T.U.)**	**Tritium (T.U.)**	**Tritium (T.U.)**
GS1*	*Chiarino*	1315	5.75	3.5	X	X
GS2*	*Rio Arno*	1524	7.96	4.1	X	X
GS3	*Esubero Alto*	960	5.50	3.8	X	X
GS4	*Ruzzo*	900	6.50	N.S.	X	N.S.
GS5	*Vitella D'Oro*	690	5.28	4.1	X	X
GS6	*Mortaio D'Angri*	650	7.26	2.2	X	X
GS7	*Capodacqua*	340	5.48	3.3	X	X
GS8	*Presciano*	336	6.61	1.9	X	X
GS9	*Capopescara*	650	N.S.	2.5	X	X
GS10	*Tempera*	650	7.95	2.6	X	X
GS11	*Vera*	640	5.56	3.0	X	X
GS12	*Vetoio*	625	N.S.	N.S.	X	X
GS13	*Boschetto*	967	N.S.	N.S.	X	X
GS14	*GSA - Traforo Sud*	1000	6.24	N.S.	X	N.S.
GS15A	*S13*	1000	7.13	N.S.	N.S.	N.S.
GS15B	*S15*	1000	9.07	N.S.	X	N.S.
GS15C	*S17*	1000	7.73	N.S.	X	N.S.
GS15D	*S18*	1000	6.59	N.S.	X	N.S.
GS16A	*TRAFORO DX*	1000	6.36	N.S.	X	N.S.
GS16B	*TRAFORO SX*	1315	6.02	N.S.	X	N.S.

For the October 2020 survey, values range between a minimum concentration of 5.3 T.U. (GS5 Vitella d'Oro spring) and a maximum concentration of 9.1 T.U. (GS15-B S15 monitoring well located inside the motorway tunnel). For March 2021 sampling survey, results range between 1.9 T.U. (GS8 Presciano spring) and 4.1 T.U. (GS2 Rio Arno and GS5 Vitella d'Oro springs). Data show significant variations between the two surveys analysed in different labs.

Focusing on March results, the minimum concentration values of 1.9 T.U. recorded in GS8 spring located at the southern side of Gran Sasso massif (see Fig. 3.2) at the lowest elevation (about 330 m a.s.l.), suggests a long residence time of groundwater inside the aquifer. On the contrary, the maximum values reached in GS2 and GS5, both located at the northern side of the massif at higher elevations, suggest a shorter travel time of groundwater inside the aquifer.

To compare Tritium data recorded at springs with rainfall in Central Apennine, a reference has been made to the rainfall station of Pian dell'Elmo (950 m asl), where values ranging from about 3 to 14 T.U. have been recorded in 1986-2010 period, with lowest values during wintertime and maximum values in summertime (Tazioli 2011). The comparison between rainfall data and March 2021 results, confirms what already suggested by stable isotopes data about the influence of rainfall water on aquifer recharge on the northern side of Gran Sasso. In fact, values in GS1 to GS5 water samples are comparable to tritium concentration detected in rainwater. The only one exception for the northern side is represented by GS6 spring characterized by the lowest tritium content recorded on this side of the massif.

For springs located at the southern side (GS7 to GS 11), tritium concentrations are generally lower than tritium in rainwater confirming what assessed through $\delta^{13}C$ (Tallini et al. 2014), about the relatively long residence time of groundwater characterizing this group of springs belongs to Gran Sasso aquifer.

3.5 References

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4 The Qachqouch aquifer (Case Study Lebanon)

4.1 Study Area: The Qachqouch spring

Qachqouch Spring (Figure 4.1), is located within the Nahr el Kalb Catchment and originates from the Jurassic karst aquifer at about 64 meters above sea level. During low flow periods, the spring is used to complement the water deficit in the capital city Beirut and surrounding areas. Its total yearly discharge reaches 35-55 millions of m^3 based on high-resolution monitoring of the spring (2014-2019; Dubois et al., 2020). Flow maxima reach a value of 10 m^3/s for a short period following flood events; discharge is about 2 m^3/s during high flow periods and 0.2 m^3/s during recession periods.

About 67% of the area in Lebanon consists of karstified (6,900 km^2) rock sequences (Dubois, 2017). The catchment area drained by the Qachouch spring is delimitated to the North by Nahr El Kalb River and extends for more than 55 km^2 of mountainous nature at a maximum elevation of 1650 m.a.s.l. (Dubois, 2017). Tracer experiments show a relationship between the Nahr El Kalb River and the Qachqouch Spring through a sinking stream (Doummar and Aoun, 2018b).

The spring originates from a carbonate aquifer composed of the Jurassic formation sequence of massive fissured limestone of more than 100 m in thickness. Dolostones characterized by a higher porosity (10-12%) are found in the lower part of the formation because of the diagenetic dolomitization and along leaky faults and dykes because of hydrothermal dolomitization (Nader et al., 2004). The investigated area is located in the tectonic regime of a major fault, Yammouneh Fault, causing tectonic deformation and fracturing of the catchment area. Multi-level karstification in the Mediterranean was developed during the Messinian salinity crisis and Quaternary glacial events causing deep karst systems with features such as large dissolution conduits, dolines, sinkholes, and caves (Bakalowicz, 2015; Dubois et al., 2020). The area is characterized by a duality of infiltration portrayed by the point source infiltration in preferential pathways (dolines, permeable faults) and diffuse recharge in bare fissured rocks.

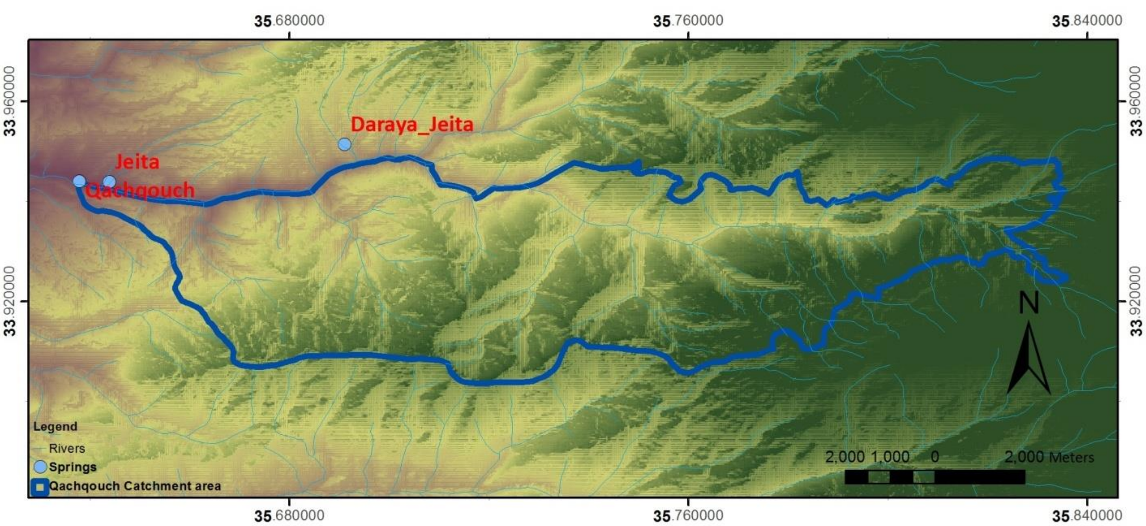

Figure 4.1. The catchment area of the investigated Spring (Qachqouch). Nahr el Kalb River acting as a boundary condition in the northern part of the catchment. Catchment tentatively delineated ecompassing authochtonous recharge occuring in Jurassic and lower createcous rock exposures.

4.2 Previous studies

Previous studies were done in the study area by Koeniger et al., 2017. The meteoric line for the catchment area of Nahr El Kalb was successfully constructed based on rain data collected at different altitudes on the catchment (yielding a correlation between both stable isotopes and elevation (z); $\delta^{18}O$= -0.0015z -4.02; R2=0.97). Additionally within the framework of the protection of the Jeita Spring (BGR), bi-monthly samples (n=55) were collected from January 2012- till April 2013 from El Qachqouch spring. The observed ranges have means of -6.82‰ and 33.3‰ for $\delta^{18}O$ and $\delta^{2}H$ respectively. Only a short record of isotopic data are available for Lebanon in general and for the study area in particular. Therefore no conclusions can be drawn on the long term variation of isotopic signatures in spring water and precipitation in Lebanon.

Another study (Elghawi et al., 2021) sampled a total of 41 springs in Lebanon and yielded a spring line ($\delta^{18}O$ and $\delta^{2}H$) for Lebanese springs and highlighted the continental and altitude effect. It also developed multi- regression models to predict isotopic signatures based on easily monitored parameters like temperature and altitude and latitude. The data obtained on the Qachqouch spring part of the data set shows that the Qachqouch spring is characterized by a large catchment area with complex processes (fast and slow flow, as well as diffuse and point source infiltration) yielding an averaged isotopic signatures from precipitation at different elevations.

4.3 Results: Isotopes collected within Karma Project

Stable isotopes $\delta^{18}O$ and $\delta^{2}H$ were collected and analyzed in the framework of the PRIMA Project between November 2019 and January 2021 every 3 days (sampling and laboratory analysis is currently ongoing). A total of 141 samples were collected and analyzed to date from the Qachqouch Spring. The samples are analyzed at the Department of Geology (American University of Beirut) using a PICARRO isotopic analyzer L2130-i cavity ring-down spectrometer (CRDS).

The correlation between $\delta^{18}O$ and $\delta^{2}H$ yields a linear relationship ($\delta^{2}H = 6.3599\ \delta^{18}O + 13.384\ R^2 = 0.8499$; Figure 4.2). Observed slopes are comparable to the Lebanese Spring lines (Elghawi et al., 2021) and the line for the Jeita spring catchment in vicinity to the Qachqouch Spring (Koeniger et al., 2017). The values of $\delta^{18}O$ and $\delta^{2}H$ vary respectively between -7.67 and -6.08‰, and -36.16 and -23.61‰ with means of 6.58 ‰ and 28.48 ‰ for n=141 samples. The distribution of stable isotopes values helps assess qualitatively the extent of the catchment, indicating altitudes ranging between 1000 and beyond 1500 m, which extends beyond the Jurassic Aquifer exposure.

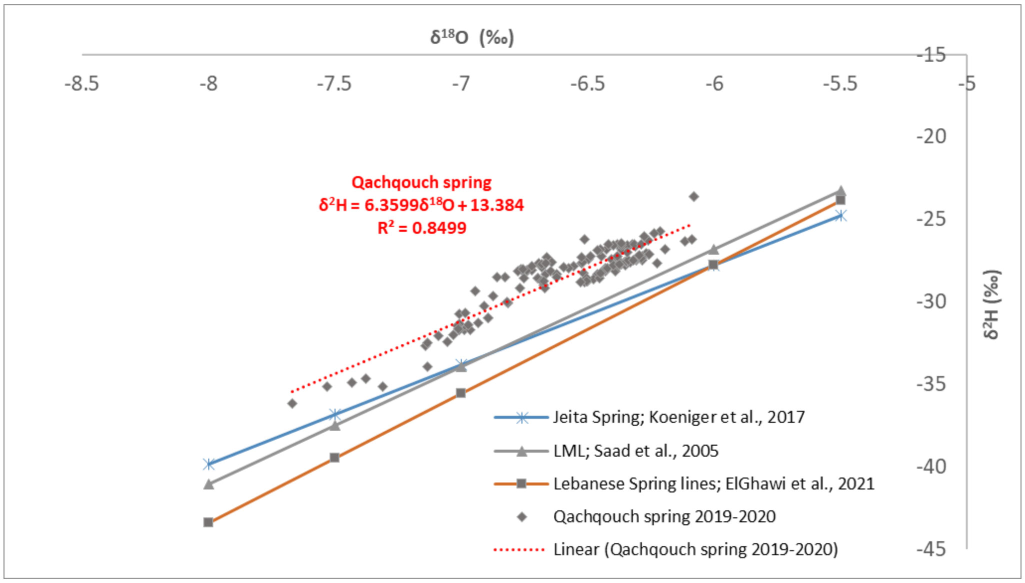

Figure 4.2. Plot of $\delta^{18}O$ and δ2H comparing regression models for the Qachqouch spring and the Lebanese meteoric, Lebanese Spring and the Jeita catchment linea

However, since the river fed by snowmelt from April to June, infiltrates into a sinking stream (Figure 4.3) in the lower parts of the catchment and influences the stable isotope signature in the spring, the differentiation between allochtonous and authochtonous discharge can be done based on the detailed analysis of isotopic time series over more than a year (Figures 4.3 and 4.4).

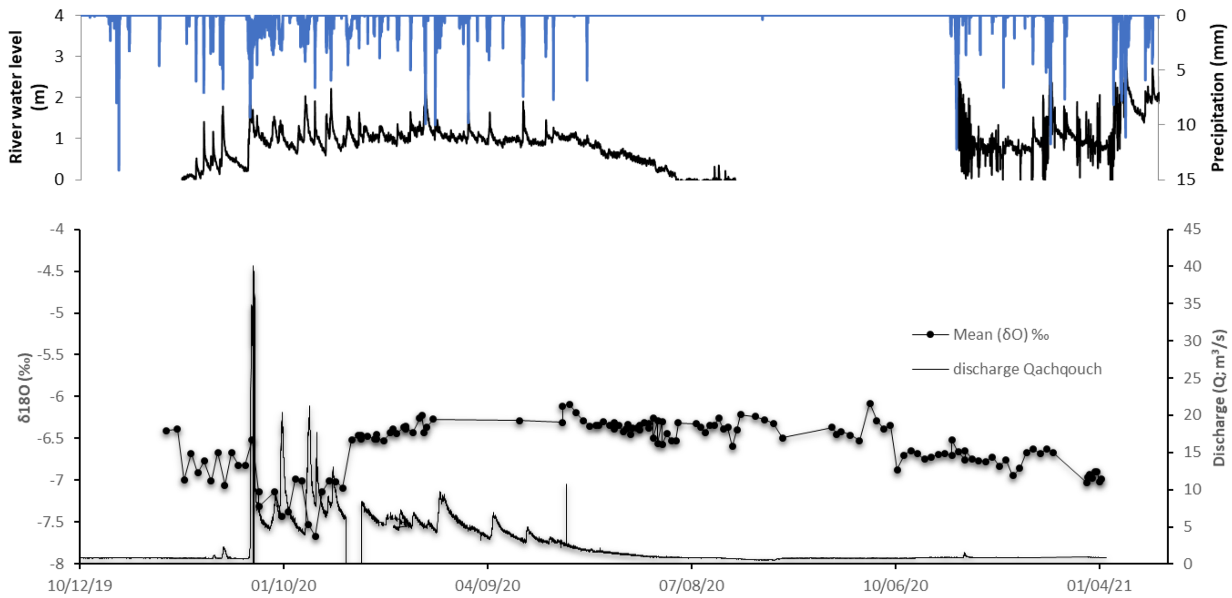

Figure 4.3 Precipitation (at 950 m), Water level in the Nahr El Kalb River (sinking stream and snowmelt from April-June), Flowrates at the Qachqouch spring as a response to precipitation events, variation of $\delta^{18}O$ (‰) values in the collected spring water.

An infiltration of overflow may also occur in the Jurassic downstream exposures allowing for a delayed recharge and an increased storage effect (Dubois et al., 2020). Similar conclusions were reached for the Jeita Spring catchment recharge area (Koeniger et al., 2017). Therefore the area of the catchment may be higher than expected, or overland flow needs to be accounted for while computing the water balance of the Qachqouch Spring. Simple mixing models based on mean values for baseflow isotopic signatures and rain isotopic signatures during a flood event can provide an indication of the mixing ratios of recharged water to baseflow waters. For example a mean value of $\delta^{18}O$ =-5.5 ‰ (800 m) of rain at lower altitudes and a value of -6.85‰ (1600 m) yield a mean value of baseflow of $\delta^{18}O$ =-6.52 ‰ at the Qachqouch spring. The later indicates that a ration of more than 75 % should be coming from high altitudes than 800 m rather from the direct catchment at lower altitudes. This is in accordance with the presence of dolostones and point source infiltration (dolines) at these altitudes.

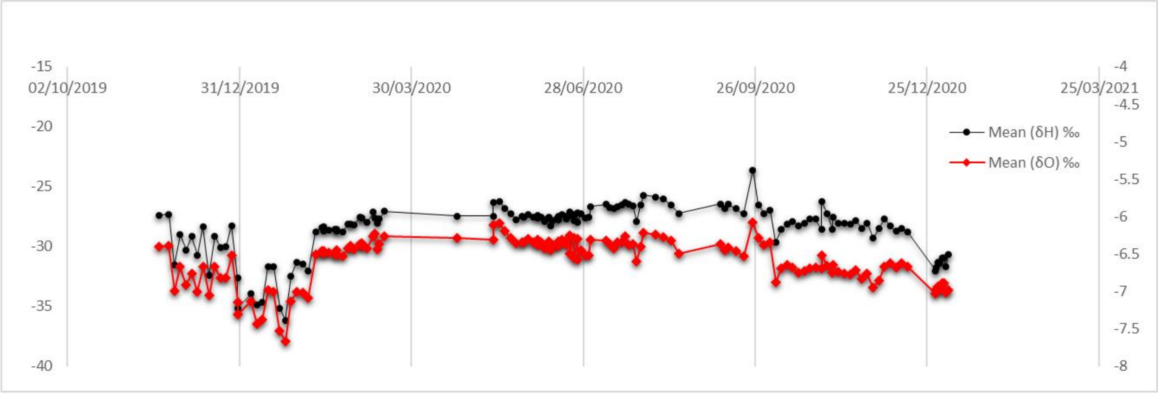

Figure 4.4 δ18O and δ2H values observed in samples collected every 3 days from the Qachqouch spring (with missing values in march 2020 during Covid-restrictions

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5 Ubrique test site (case study Spain)

5.1 General description of the test sites

The Eastern Ronda Mountains (Fig. 5.1) test site is located in southern Spain (western area of Málaga province) and it covers a total surface of around 110 km². The relief in this area presents NE-SW alignments with steep slopes that range from 800 to 1200 m.a.s.l. and the mean annual precipitation during the historical rainfall record (1964/65-2009/10) is 615 mm (Barberá, 2014). Regarding the temporal distribution of precipitation, the rainiest period in the area takes from October to February, although the highest rainfall is recorded in December, with an average of 99 mm. The spatial distribution shows a strong relationship between the rainfall and the altitude of the recharge area. In this area, the calculated rainfall gradient is 66 mm /100 m altitude (Fig. 5.2).

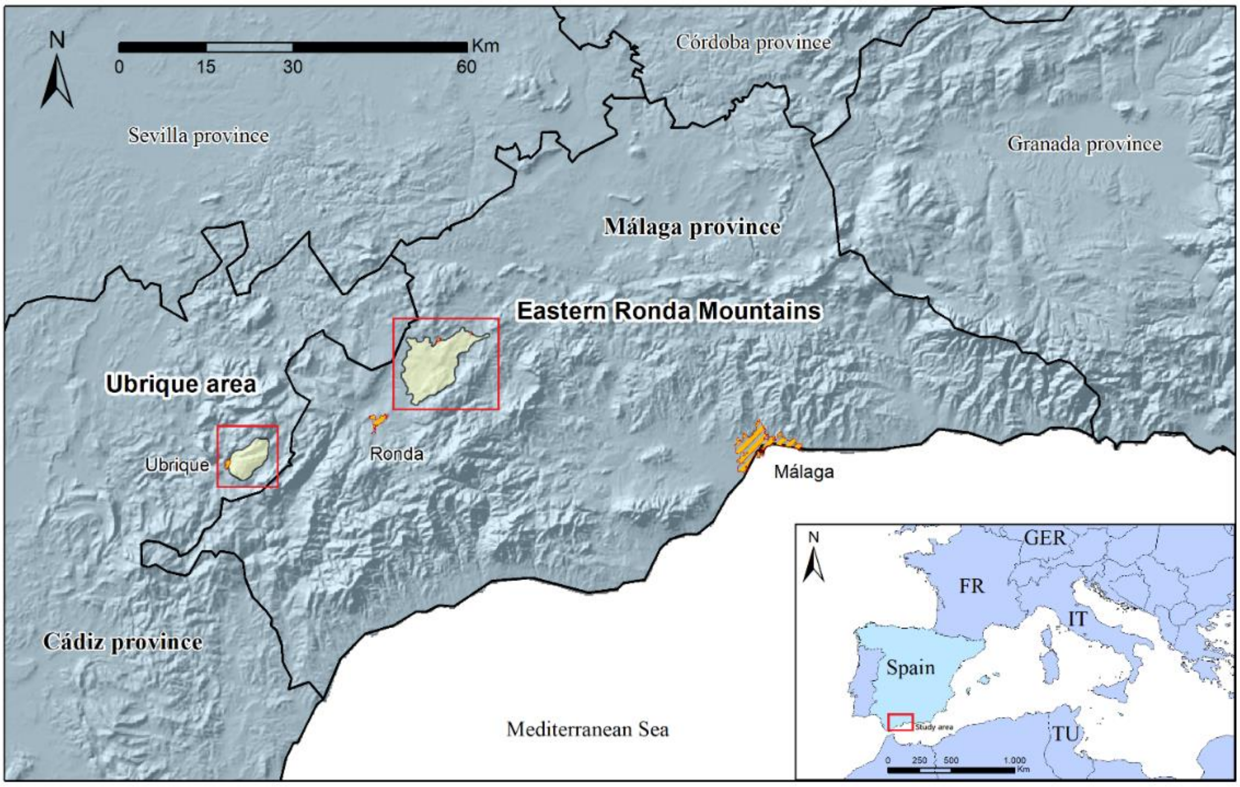

Figure 5.1. Geographical context of the Eastern Ronda Mountains and Ubrique area.

Groundwater discharge in the Merinos-Colorado-Carrasco aquifer system is produced in natural regime, mainly towards NE border, through the springs of Cañamero (540 m a.s.l.) and Carrizal (740 m a.s.l.) (Fig. 5.3) (Barberá *et al*., 2012). In addition, groundwater transference toward the porous aquifer of the Ronda basin (overlying the Jurassic aquifer) exists and the shallower (visible) discharge takes place via Ventilla spring (740 m a.s.l.).

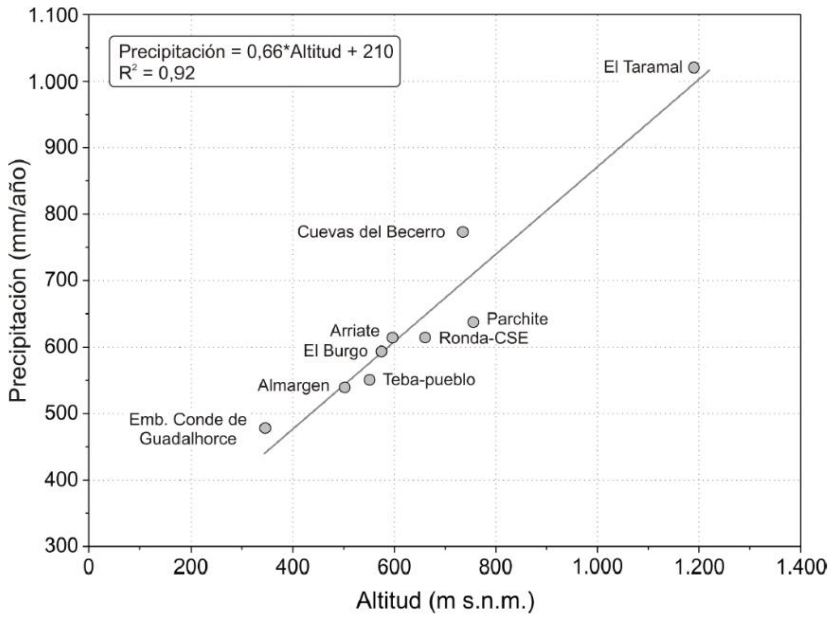

Figure 5.2. Relationship between annual rainfall and altitude at the Eastern Ronda Mountains (Barberá, 2014).

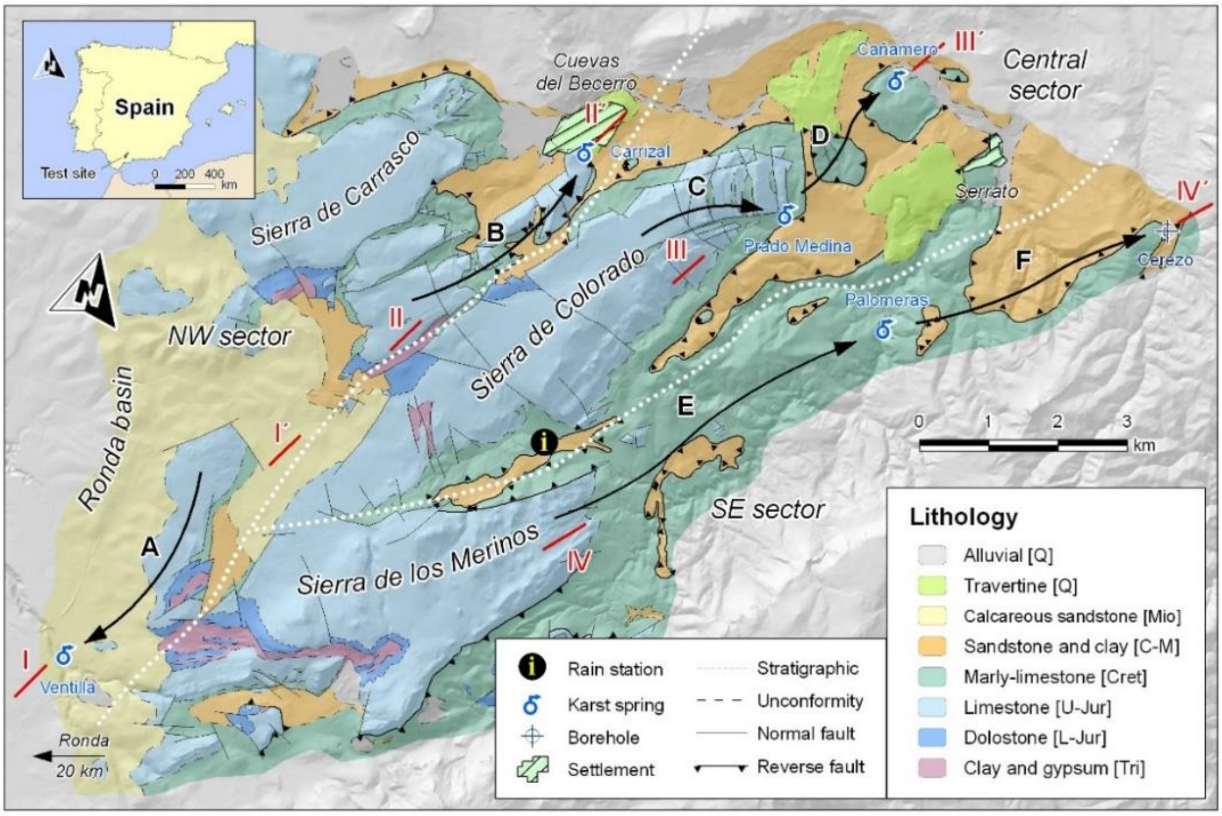

Figure 5.3. Hydrogeological setting of Merinos, Colorado y Carrasco aquifer systems and main groundwater flowpaths (Barberá et al., 2012).

On the other hand, **Ubrique test site** (Fig. 5.4) is located in the north-eastern part of Cádiz province and it covers a total surface of 25 km². This area has also been described on previous researches (Sánchez and Andreo, 2013), the relief presents an alignment NE-SW with slopes that range from 800 to 1400 m(a.s.l.). In this area, the mean annual precipitation in has been estimated around 1350 mm, however, it can variate depending on the altitude and sector from 900 mm to 1800 mm in the highest zones (Sánchez et al. 2016). Drainage mainly occurs through the springs of Cornicabra (349 m a.s.l.) and Algarrobal (317 m a.s.l.) (Fig. 4) (Martín-Rodriguez et al., 2016), located in the western border of the area. In the same way that happens in the main site, other discharge points exist (such as Garciago spring, 422 m a.s.l., an overflow type associated with the previous springs).

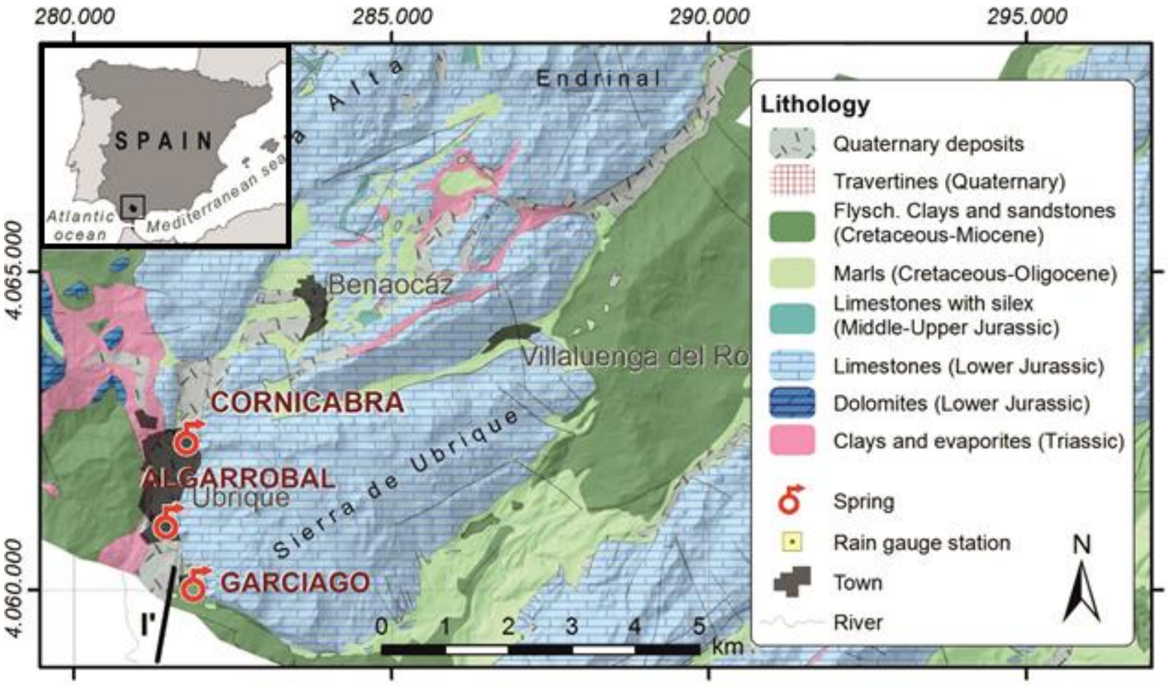

Figure 5.4. Hydrogeological setting of the Sierra de Ubrique aquifer system (modified from Sánchez et al., 2017).

5.2 Available data

The analysis of the isotopic composition of rainwater in Eastern Ronda Mountains was carried out from the sampling in six control points (Barberá, 2014) (Fig. 5.5), of which three are located within the study area of the KARMA project. Groundwater samples for isotopic analysis were taken at Carrizal, Cañamero and Ventilla springs. Regarding Ubrique test site, none of the previous rainwater sampling points are located within the KARMA study site, however the results suppose the closest approximation to the real isotopic composition of Ubrique area. The δ18O and δ2H values of the water samples have been measured with a compact isotopic analyser from the PICARRO brand (Sunnyvale CA, USA) and model CRDS L1102-i.

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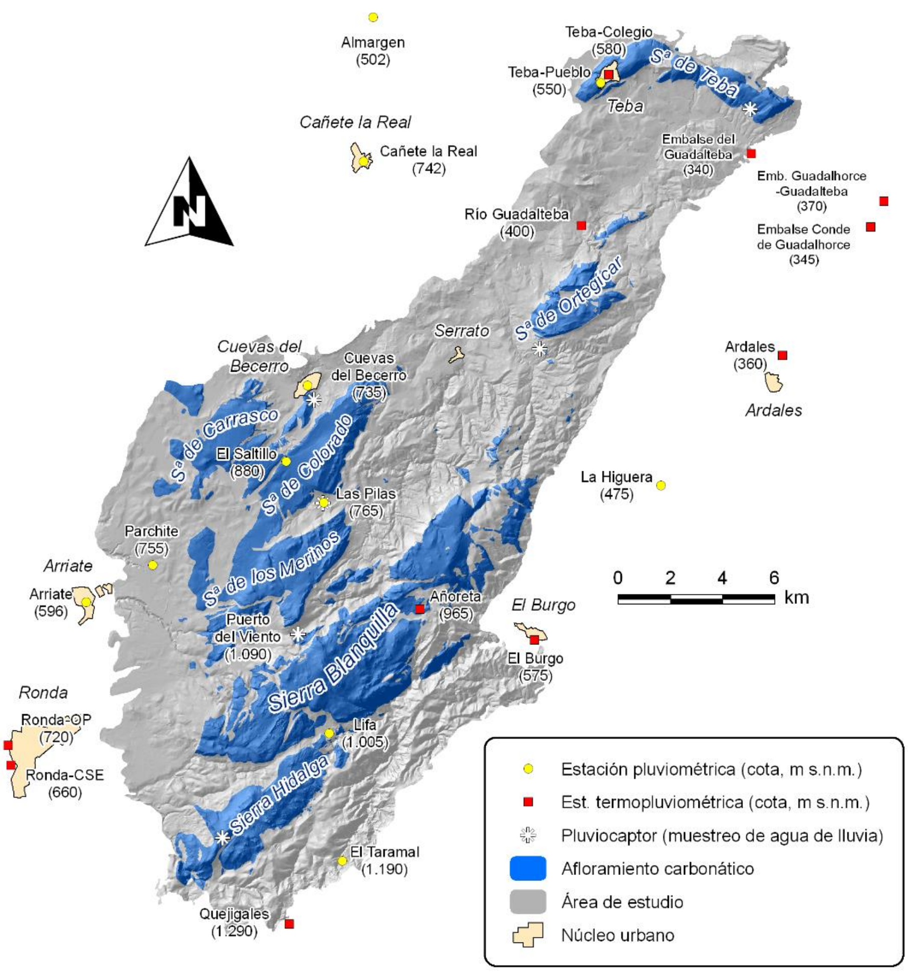

Figure 5.5. Location map of the weather station used for rainwater sampling (taken from Barberá, 2014).

5.3 Meteorological data

In Eastern Ronda Mountains (Merinos, Colorado and Carrasco), the plot of $\delta^{18}O$ versus δ2H data (Fig. 5.6) shows a large dispersion of rainwater between the Global Meteoric Line (Craig, 1961) and the Western Mediterranean Meteoric Line (Celle-Jeanton, 2000). The $\delta^{18}O$ values in the sampling point located within the KARMA study area vary between -3.66 ‰ at Cortijo de las Pilas and -12.74 ‰ at Puerto del Viento and $\delta^{2}H$ data -17.52 ‰ and -86.01 ‰ at the same points respectively. Therefore, the origin of the rainfall in the study area is mixed: it comes from both the Atlantic Ocean and the westernmost part of the Mediterranean Sea. The points represented in figure 3 define the Local Meteoric Line, defined as $\delta^{2}H = 7.7 \cdot \delta^{18}O + 12.6$, which slope shows a value slightly lower than that of the other lines represented, which is equal to 8. From this data, it can be deduced that the collected rainwater samples have undergone processes of isotopic fractioning by evaporation during the evolution of the cloudy fronts that originate the precipitations. The mean weighted deuterium excess value of the sampled rainwater is +14.79 ‰, which suggests the predominance of rainfall from the western Mediterranean, although it may also be the result of the mixture of storm fronts of Atlantic and Mediterranean origin (Barberá, 2014).

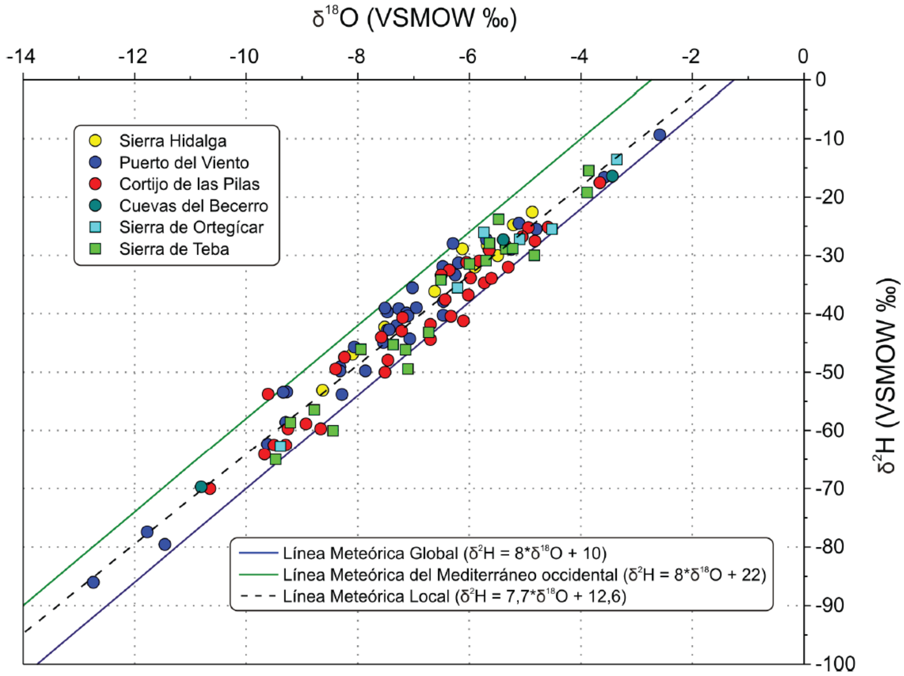

Figure 5.6. $\delta^{18}O$ values versus δ2H values of rain samples collected during the study (taken from Barberá, 2014).

In figure 5.7 the mean values of $\delta^{18}O$ and the mean recharge altitude of the main springs have been represented and it can be distinguished that the recharge altitudes in the Merinos, Colorado and Carrasco mountain ranges are included between 800-1,000 m a.s.l.. Unlike rainwater, which isotopic composition has not made it possible to specify a clear relationship with altitude, an isotopic gradient ($\delta^{18}O$ - altitude) has been established, valid, at least, for groundwater. The value obtained from this gradient is -0.15 ‰ /100m.

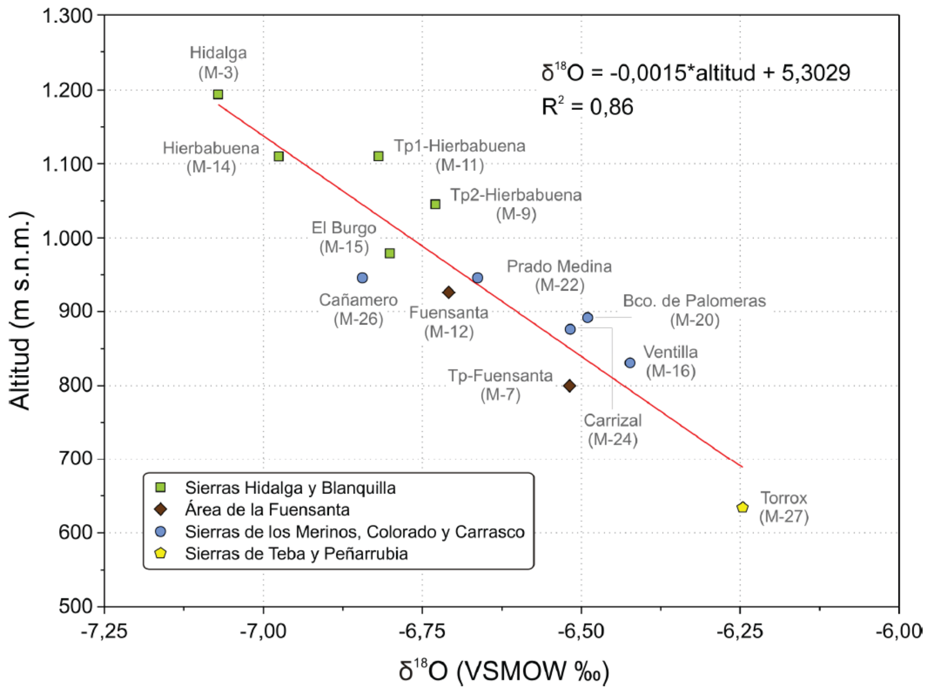

Figure 5.7. Relationship between the mean values of $\delta^{18}O$ and the mean recharge altitude of the main springs in the study area (Barberá, 2014).

In the case of Ubrique area, although the number of analyzed rainwater samples (n = 36) is not large enough to consider the results statistically significant, the data indicate that the rainwater collected in the southern area stations show isotopic values lighter than the rest (Fig. 5.8). Selection of the sampling sites was made using geographical, altitude and accessibility criteria. They are located at altitudes ranging from 338 m to >1220 m a.s.l., covering a total range of c. 880 m (Sánchez et al., 2017). This is congruent with the position that these stations occupy with respect to the direction of movement of the main humid air masses that produce rain in the Sierra de Grazalema. A tentative local meteoric water line (LMWL) drawn from the isotopic composition of the rainwater in the study area can be defined as: $\delta^2H = 8 \cdot \delta^{18}O + 13.9$ (Sánchez and Andreo, 2013).

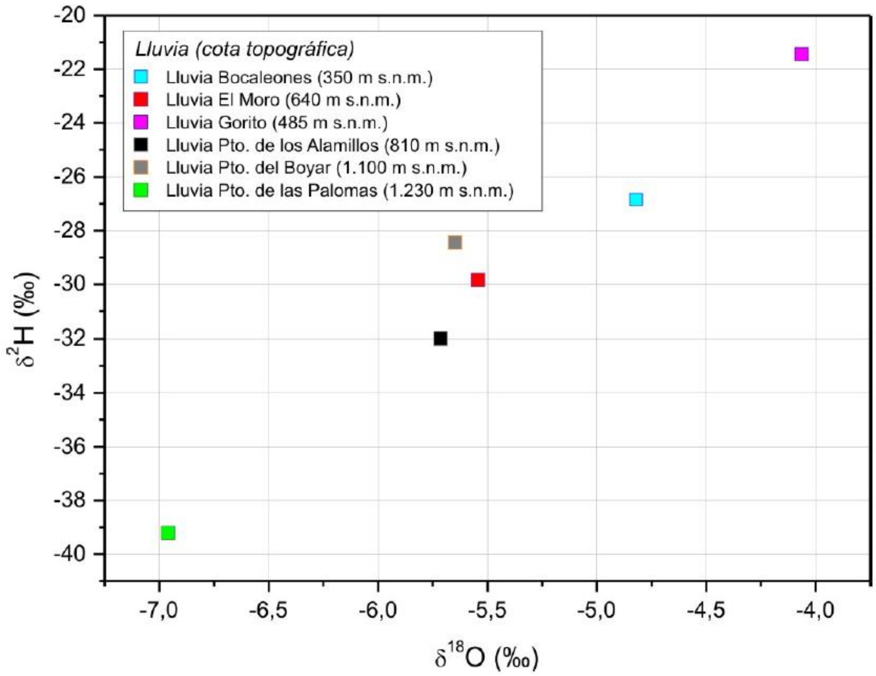

Figure 5.8. $\delta^{18}O$ values versus δ2H values of rain samples collected during the study period (taken from Sánchez and Andreo, 2013).

5.4 Groundwater data

The mean values of $\delta^{18}O$ of the groundwater sampled in springs and soundings of the Merinos, Colorado and Carrasco mountain ranges (Tab. 5.1) are between -6.84 ‰, in the Cañamero spring, and -6.42 ‰, in that of La Ventilla. The mean values of δ^2H vary between -41.68 ‰, in the overflow spring Prado Medina, and -39.69 ‰, in that of Carrizal (Fig. 5.9). The excess in deuterium (d), in general terms, presents average values between 10.04 ‰ in the borehole of Arroyo del Cerezo and 13.31 ‰ in the Cañamero spring. Table 1 summarizes the statistical parameters of the values of $\delta^{18}O$ and δ^2H, as well as the excess in deuterium (d) of the waters.

Table 5.1. Statistical parameters (number of analyzes, n; minimum, min; maximum, max; mean, med; and coefficient of variation expressed in %, cv) of the isotopic composition of the groundwater samples (Barberá, 2014).

Manantial/Sondeo	Ref.	$\delta^{18}O$ (‰)					$\delta^{2}H$ (‰)				*d*, exceso en deuterio (‰)			
		n	*mín*	*máx*	*med*	*cv*	*mín*	*máx*	*med*	*cv*	*mín*	*máx*	*med*	*cv*
Ventilla	M-16	47	-6,80	-5,42	-6,42	4	-41,48	-38,67	-40,17	2	4,73	13,59	11,21	13
Bco. de Palomeras	M-20	16	-7,01	-6,18	-6,49	3	-44,04	-38,47	-41,13	3	9,59	12,51	10,79	8
Prado Medina	M-22	15	-7,26	-5,96	-6,66	4	-44,04	-40,22	-41,68	2	7,45	14,08	11,62	14
Carrizal	M-24	23	-6,77	-6,17	-6,52	3	-40,82	-38,02	-39,69	2	10,47	14,09	12,45	9
Cañamero	M-26	65	-7,31	-5,97	-6,84	4	-44,96	-38,62	-41,44	3	8,76	16,66	13,31	11

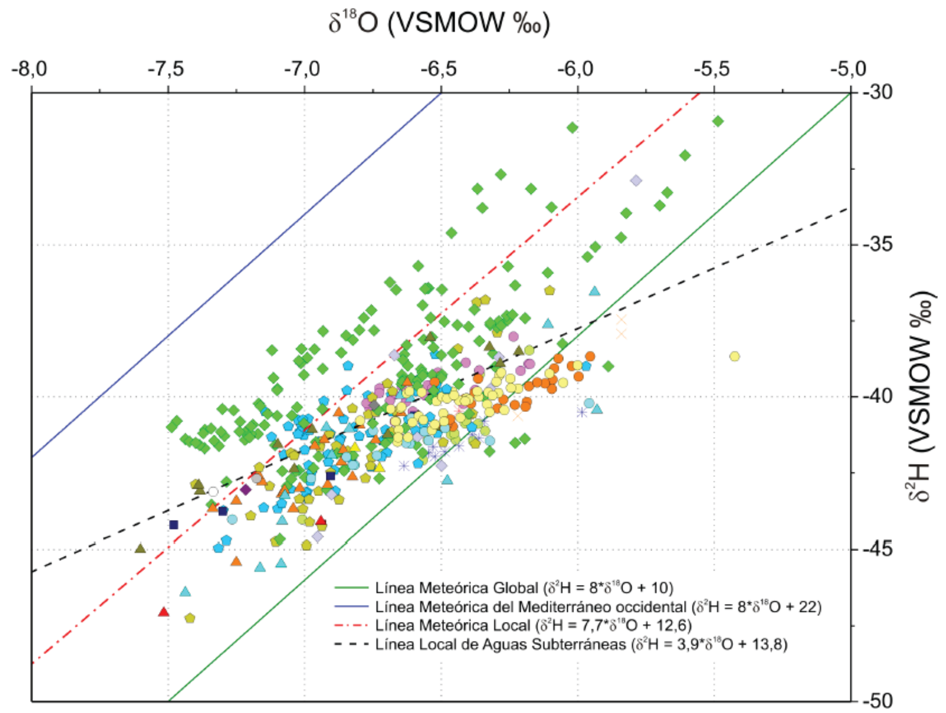

Figure 5.9. Representation of the isotopic composition ($\delta^{18}O$ vs $\delta^{2}H$) of groundwater samples (springs and boreholes) collected in the study area (taken from Barberá, 2014).

The $\delta^{18}O$ and $\delta^{2}H$ values obtained in the water samples from the springs (n = 279) in Ubrique test site have been represented in figure 5.10. The values of $\delta^{18}O$ are given between -6.8 and -4.7 ‰ and those of $\delta^{2}H$ between -39.3 and -26.9 ‰. The isotopic values of the springs are included within the field defined by the maximum and minimum values of the rainwater, which shows that the isotopic composition of the aquifer waters is the result of the mixing of the waters of all the rains. that occur throughout the year. In other words, the water in the aquifer represents an intermediate isotopic value of rainwater, which in turn depends on the time of year, temperature, altitude and the amount / intensity of precipitation, among other factors.

The Garciago spring samples are the ones with the greatest dispersion. Its isotopic composition ranges from the lightest (-6.2 and -37.2 ‰) to the heaviest (-5.0 and -26.9 ‰), with the rest of the samples positioned between these extreme values. This isotopic variability is consistent with the karst behaviour of this spring, which is reflected in its wide variations in flow and chemical composition produced in short periods of time. This suggests the existence of fast-flow paths that connect the infiltration water with the spring with little intervention from the saturated zone of the aquifer; therefore, without homogenization of the $\delta^{18}O$ and $\delta^{2}H$ values.

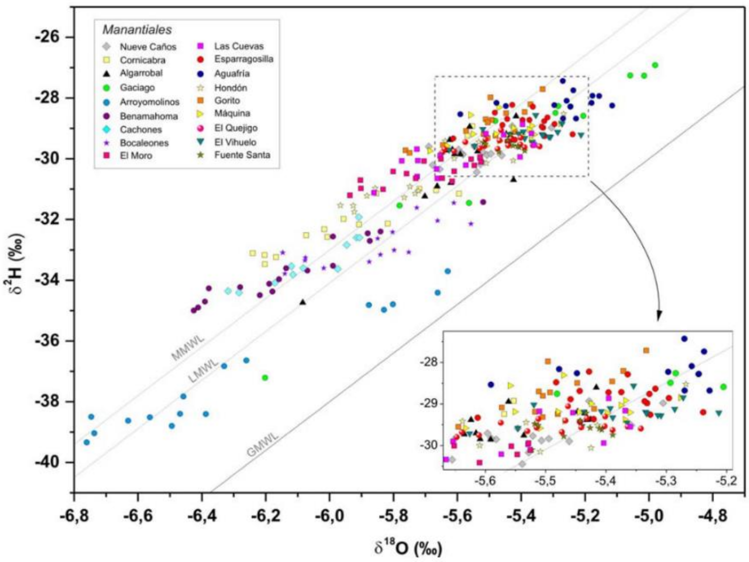

Figure 5.10. Isotopic composition of water samples from controlled springs and rainwater (GMWL: world meteoric line; LMWL: local meteoric line; MMWL: western Mediterranean meteoric line) (Sánchez & Andreo, 2013).

5.6 References

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6 The Lez Karst Catchment (case study France)

6.1 General description of the test site

The Lez spring catchment is located 15 km north of Montpellier (France). It is located between the Hérault and Virdoule river valleys. The maximum extent of the hydrogeological basin which feeds the Lez spring is estimated to be about 380 km² due to regional drawdown resulting from continuous pumping at the karst spring (Thiéry and Bérard, 1983). The lithology of the Lez karst system corresponds to massive limestone of the Upper Jurassic (Argovian to Kimmeridgian) and of the lower part of the Early Cretaceous (Berriasian), with 650 to 1,000 m thickness. The marls and marly-limestone of the Middle Jurassic (Oxfordian) constitute the lower boundary of the aquifer. The marls and marly-limestone of the Early Cretaceous (respectively Lower and Upper Valanginian) constitute the upper boundary of the aquifer. The major tectonic events that influenced the Lez aquifer were: the Hercynian/Variscan orogeny, the Pyrenees formation, and the opening of the Lion Golf.

As a large part of the hydrogeological catchment is relatively impermeable, due to the presence of marls and marly-limestones of the Valanginian, the Lez spring recharge catchment covers about 130 km² only. The main recharge area over the catchment corresponds to the Jurassic limestone outcrops located by the western and northern limits of the basin. Localized infiltration occurs through fractures and sinkholes along the basin and through the major geologic fault of Corconne-Les Matelles, in the northern part of the basin. A certain number of fractures are also known to exist only just upstream from the Lez spring. The soils on the Lez catchment are essentially leptosols, with some areas of umbrisols in the southern part of the basin. The mean altitude is 191 m. The high altitudes correspond to the Jurassic limestone outcrops in the west and north of the catchment, with the maximum being 655 m. The mean slope is 10%.

The Lez catchment is exposed to a Mediterranean climate, which is characterized by hot, dry summers, mild winters and wet autumns. Analyses by the Meteo France show that on average 40% of the annual precipitation occurs between September and November with a high variability across years. The average annual rainfall rate for the 1945-2019 period is 916 mm based on a weighted average of four rainfall stations located on the Lez basin.

6.2 Isotope sampling

Water samples were collected at the Lez spring for chemical and isotopic analysis twice a month, with daily sampling during high discharge events from August 2009 until today. At Lirou, Restinclières, and Fleurettes temporal springs, sampling was carried out during the wet season only, from 2010 to 2017 (Fig.6.1). Samples are collected in clean 15 ml amber glass bottle and kept to 4°C up to analysis. An automatic sampler with 24 bottles (1liter acid cleaned polyethylene bottles) was used for water sampling at the Lez spring during several high flows.

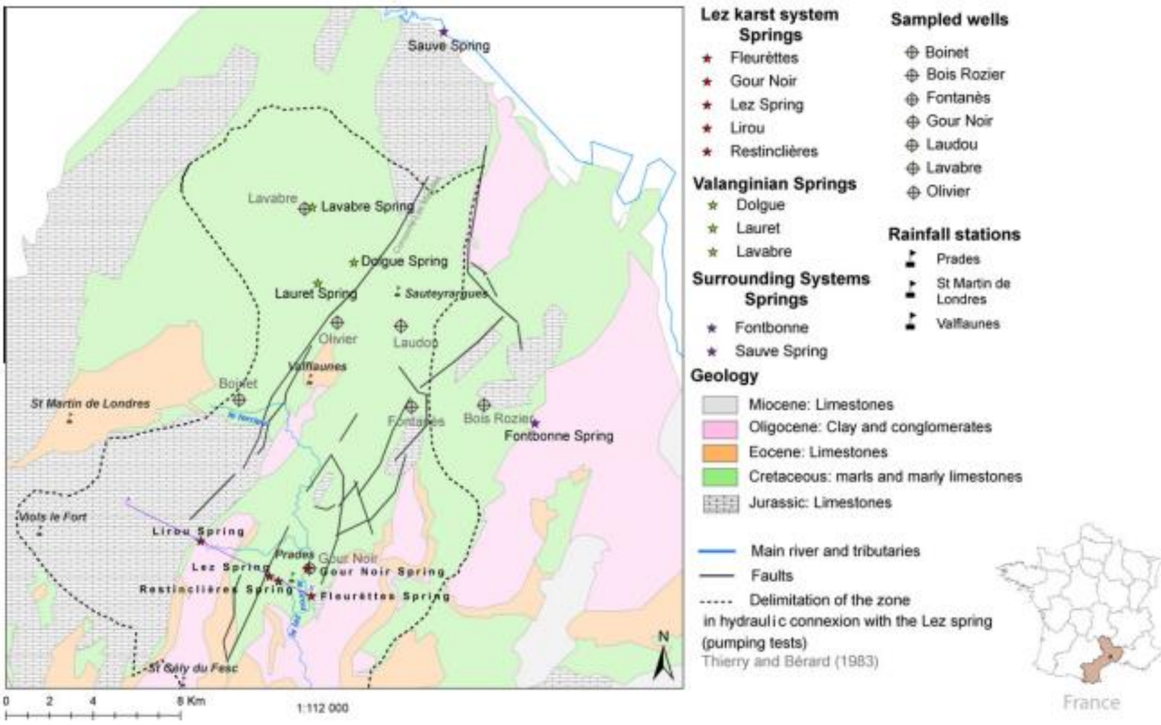

Figure 6.1. Lez karst system: sampled springs, wells and rain gauge locations (Caetano Bicalho et al., 2012)

Rain waters are regularly sampled (monthly to bi-monthly) for water isotopes analysis from an underground tank connected to rain gauges at Sauteyrargues and Boisseron stations (Fig. 6.1 and 6.2) from 2010 until today. To complete the lack of rainwater isotopic data, the monthly average rainfall isotopic composition at the Montpellier rain gauge station located 9 km downstream the Lez spring and sampled daily or weekly over the whole study period, is used as a reference for the input signal.

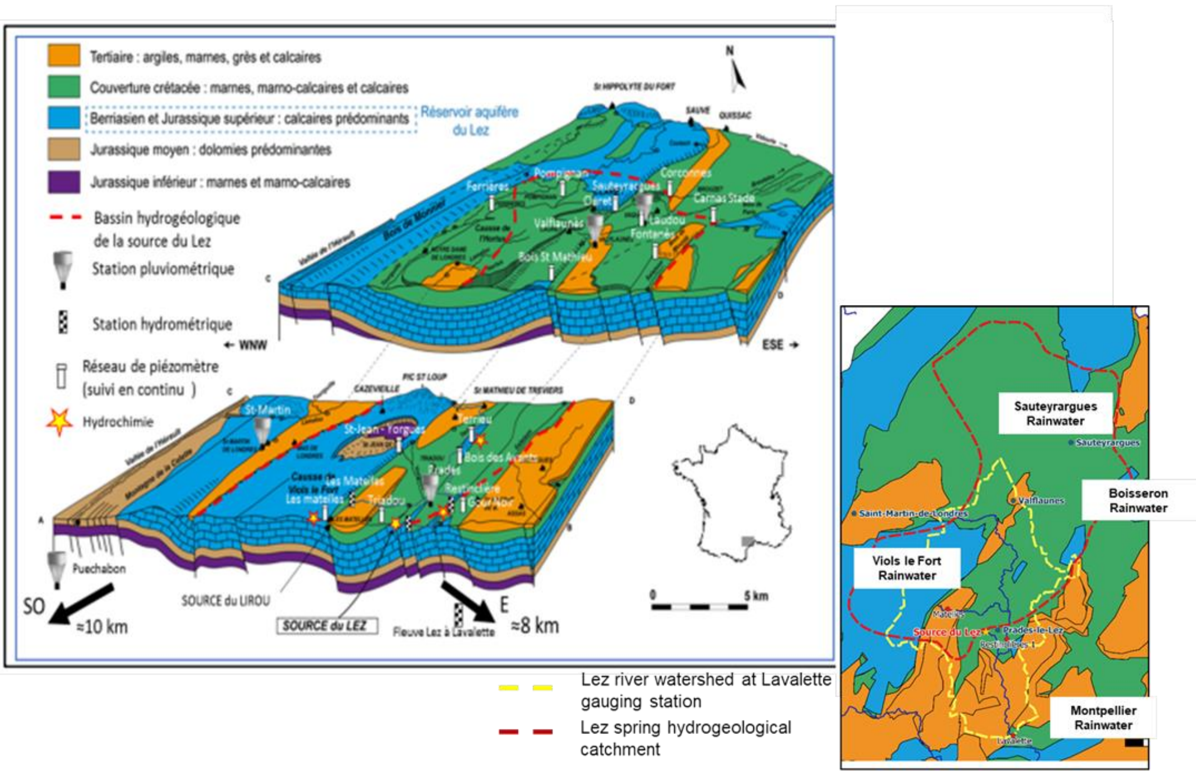

Figure 6.2. MEDYCYSS Observatory - Lez River basin monitoring network (modified from Dausse, 2015)

6.3 Analysis

Water stable isotopes ($\delta^{18}O$ and δ^2H) are analyzed at the LAMA mass spectrometry laboratory of HydroSciences Montpellier on an Isoprime mass spectrometer. $\delta^{18}O$ is measured with the classical CO_2 equilibration method, with an overall uncertainty of ± 0.1‰. δ^2H is measured in continuous-flow mode with an Eurovector Pyr-OH analyzer converting H_2O to H_2 on Cr at 1070 °C, with an overall uncertainty of ± 0.8‰. All isotopic water values are reported relative to the V-SMOW scale.

6.4 Previous available stable isotope data

Stable isotope monitoring over the Lez catchment: rain water and spring isotopic signals

For the 2009-2019 data, the water isotopic input signal was calculated from three rain gauges located at Sauteyrargues, Boisseron and Montpellier. In the δ^2H vs. $\delta^{18}O$ diagram (Fig. 6.3), rainwater showed a wide range of composition, mostly distributed along the Global Meteoric World Line (GMWL). Likewise, most groundwater samples lied about these lines, indicating that they originated as meteoric recharge (Grobe and Machel, 2002; McIntosh and Walter, 2006). We can see on the APLIS recharge map that the main Jurassic limestone outcrops (west and north-west parts of the basin) mostly contribute to the recharge of the aquifer, with a mean recharge rate of 47% for an area of 80 km². The recharge contribution from this area is about 60% of the overall recharge of the catchment.

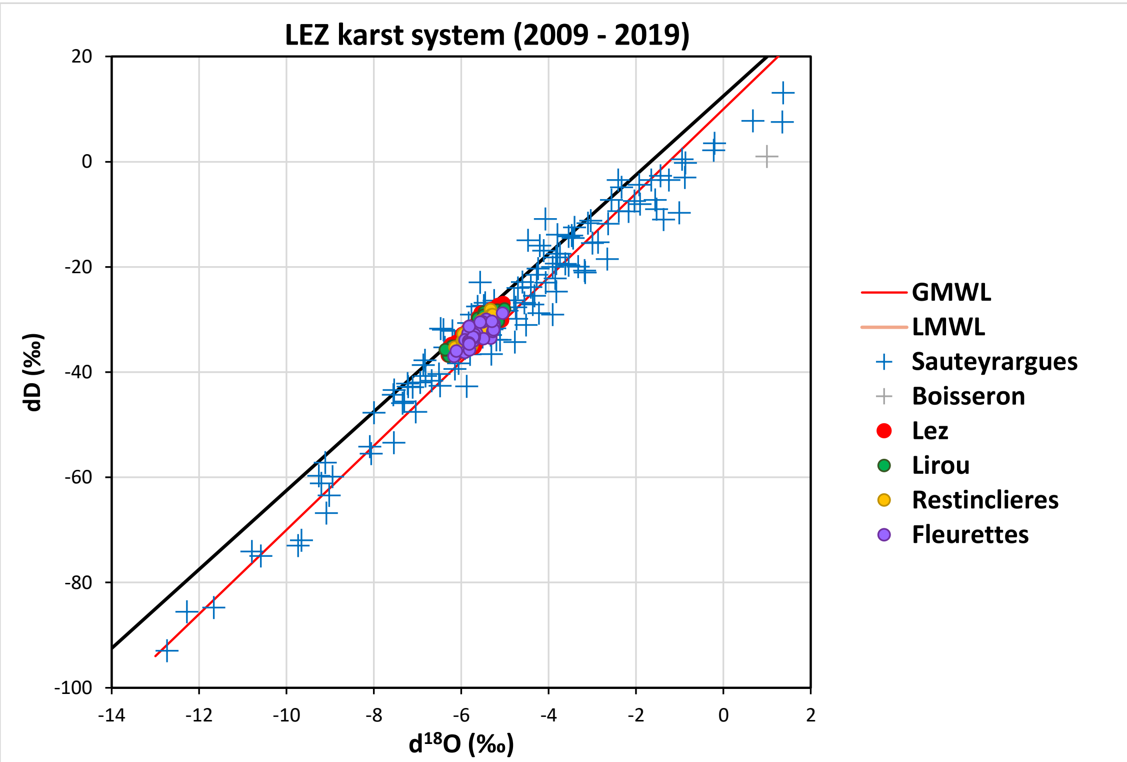

Figure 6.3: dD vs. $\delta^{18}O$ (‰) for the Lez system spring waters (Lez, Lirou, Fleurette and Restinclières) and rainwater samples from the 2 rain gauges (Sauteyrargues, Boisseron). Data from Jan. 2009 to Sep. 2019.

The local meteoric water line was calculated from 22 rainwater samples collected during a hydrological year at the Lez basin rain gauges (Sauteyrargues and Boisseron) by using linear least squares, and was $\delta^2H = 7.3 * \delta^{18}O + 7.8‰$. The relatively low slope (7.3) and intercept (+7.8‰) observed, suggest that partial evaporation of raindrops may have a measurable influence on the isotopic input signature over the area (Ladouche et al., 2009). In order to consider only the air masses origins and condensation processes that control the isotopic composition of meteoric water, and excluding fractionation linked with evaporation of water during the raindrops fall to the ground, nine evaporated rainwater samples (identified with low deuterium excess d≤8‰, with d =dD−8× $\delta^{18}O$) were removed from the previous dataset. This allowed the determination of a Local Meteoric Water Line (LMWL) of non-evaporated rainwaters: $\delta^2H = 7.5 * \delta^{18}O + 12.5‰$. The y-intercept of this LMWL is +12.5‰, indicating that rainwaters in the Lez basin typically resulted from vapor transports temporally alternated from Mediterranean (d > 22‰) and Atlantic origins (d= 10‰) (Celle-Jeanton et al., 2001; Ladouche et al., 2009).

Stables isotopes variations observed at the springs within the hydrological cycle

The temporal variability of EC and $\delta^{18}O$ shows how $\delta^{18}O$ isotopes varied during rainfall events on the monitored springs with respect to the rainfall water entry (infiltration) signal. The $\delta^{18}O$ weighted average of rainwater in the study period was about −6.2‰, while for the Lez waters the average was −5.7‰. In general, the groundwater samples showed a much-reduced variability in $\delta^{18}O$ when compared to rainwater inputs. The monthly rainwater means calculated for Montpellier station presented a relatively large $\delta^{18}O$ amplitude (−9.0‰ to +0.6‰ over the period); on the other hand, seasonal isotopic variations were strongly reduced at the springs, especially at the Lez and Restinclières springs, which showed a significant attenuation of the signal variability, typically about 1.5‰ in amplitude (Fig. 6.4).

Despite the dampening of the signal and a low variability, $\delta^{18}O$ varied as much as +1‰ during the first high flows of autumn 2009. This variation is low but is still important enough to suggest that rapid infiltration waters participated to the Lez spring discharge, considering the isotopically enriched rain waters during the same period ($\delta^{18}O$ =−3.78‰ for the corresponding 4-day long event at Montpellier station). Restinclières and Fleurette springs also presented dampening of the $\delta^{18}O$ signal which denotes a residence time at least equal to the period of the input function, i.e. one year. This indicates the existence of an important storage component and an efficient mixing of infiltrated waters with stored waters, which suggests an important autogenic recharge through diffuse percolation of precipitation waters deposited directly onto the karst landscape. Consequently, the seasonal behaviors and recharges are difficult to identify solely from the spring characteristics (Barbieri et al., 2005; Long and Putnam, 2004).

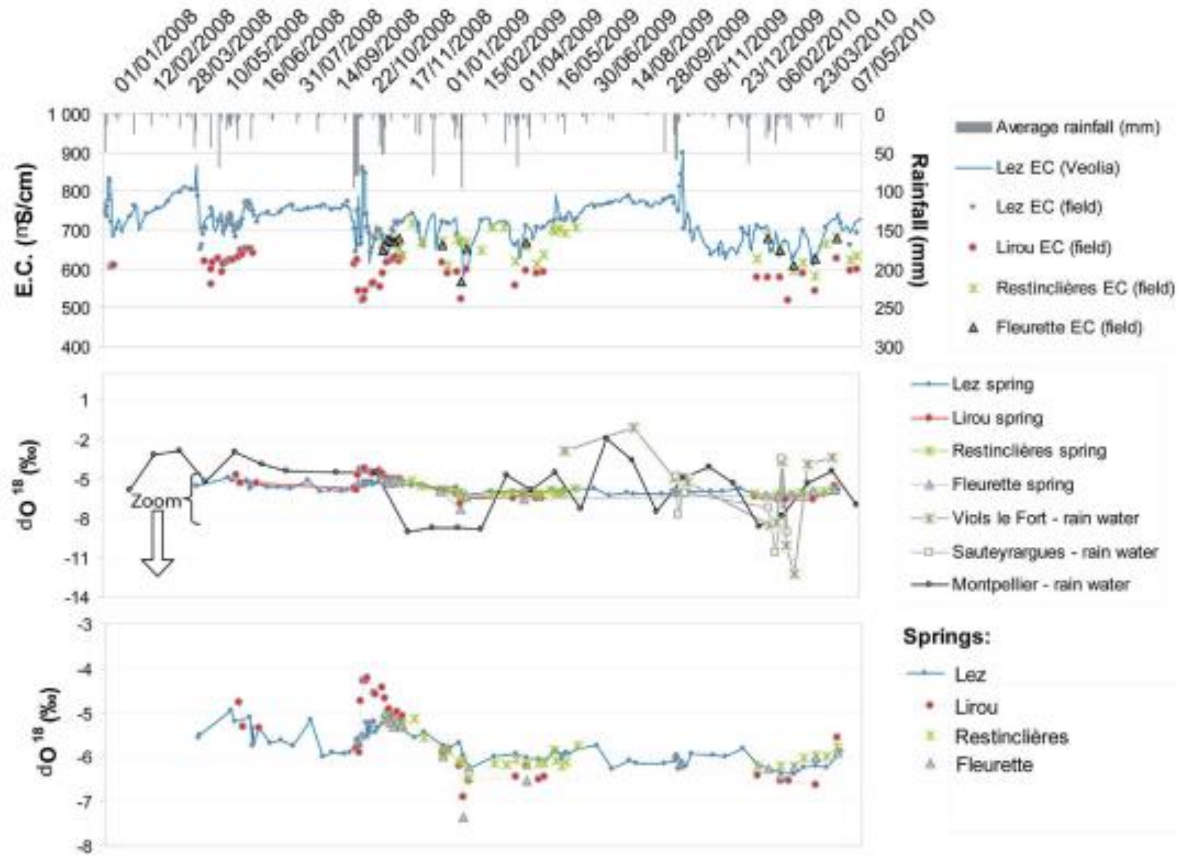

Figure 6.4. Rainfall (Montpellier, Viols le Fort and Sauteyrargues stations); E.C., δ18O (‰); zoomed δ18O (‰) and deuterium-excess for the Lez system springs (Lez, Lirou, Fleurettes and Restinclières, Bicalho et al., 2019)

Unlike the other springs of the system, the Lirou spring showed a remarkable $\delta^{18}O$ variability, especially during the storms of October 2009 characterized by a relatively large rainfall amount (121 mm registered during the first day of a storm that lasted 3 days).

This important rainfall input has triggered a large infiltration and an immediate hydrologic response of the Lirou spring, where a marked groundwater EC decrease was observed. This behaviour illustrates the great reactivity of Lirou spring compared to the other springs, indicating that it is effectively under a comparatively stronger influence of recent rainfalls, and presents short residence times through a shallow groundwater flow-path within the limestone bedrock.

6.5 Data collected in the frame of KARMA project

The samples for Lez spring, Sauteyrargues, Boisseron and Montpellier rain gauge stations have been collected from October 2019 until today (Table 6.1). The samples from 2021 are still under analysis.

The data of the Oct. 2019- Nov. 2020 survey confirmed the results obtained from Jan. 2009 to Sep. 2019 (figure 6.5). The rain water data are widely distributed between the GMWL and the LMWL along the GMWL and exhibit evaporation effect for a few samples. The Lez spring data show the dampening of the stable isotope signal with a low variability.

Table 6.1. Lez spring and Sauteyrargues rain gauge stable isotope data (Oct. 2019- Nov. 2020)

LEZ spring

DATE	$d^{18}O$	d D	d excess
18/10/2019	-5,80	-32,6	13,8
12/11/2019	-5,39	-29,8	13,3
04/12/2019	-5,81	-33,7	12,8
15/01/2020	-5,74	-33,3	12,6
05/02/2020	-5,72	-31,8	14,0
04/03/2020	-5,80	-32,3	14,1
26/05/2020	-5,67	-31,8	13,5
22/07/2020	-5,89	-32,6	14,5
28/08/2020	-5,92	-32,8	14,6
24/09/2020	-5,65	-31,7	13,5
28/10/2020	-5,65	-31,7	13,5
10/11/2020	-5,68	-32,0	13,4

Sauteyrargues rain water

DATE	$d^{18}O$	d D	dExcess
02/10/2019	-3,09	-12,0	12,7
23/10/2019	-3,99	-16,8	15,1
04/11/2019	-6,63	-37,2	15,8
15/11/2019	-5,99	-38,2	9,7
01/12/2019	-6,95	-45,1	10,5
21/12/2019	-6,58	-45,8	6,8
01/02/2020	-5,20	-28,0	13,6
23/05/2020	-4,45	-26,2	9,4
31/07/2020	-0,59	-1,1	3,6
31/08/2020	-3,09	-17,4	7,3
15/09/2020	-2,10	-9,9	6,9
30/09/2020	-6,82	-41,9	12,7
31/10/2020	-3,55	-17,8	10,6
30/11/2020	-3,48	-13,2	14,6

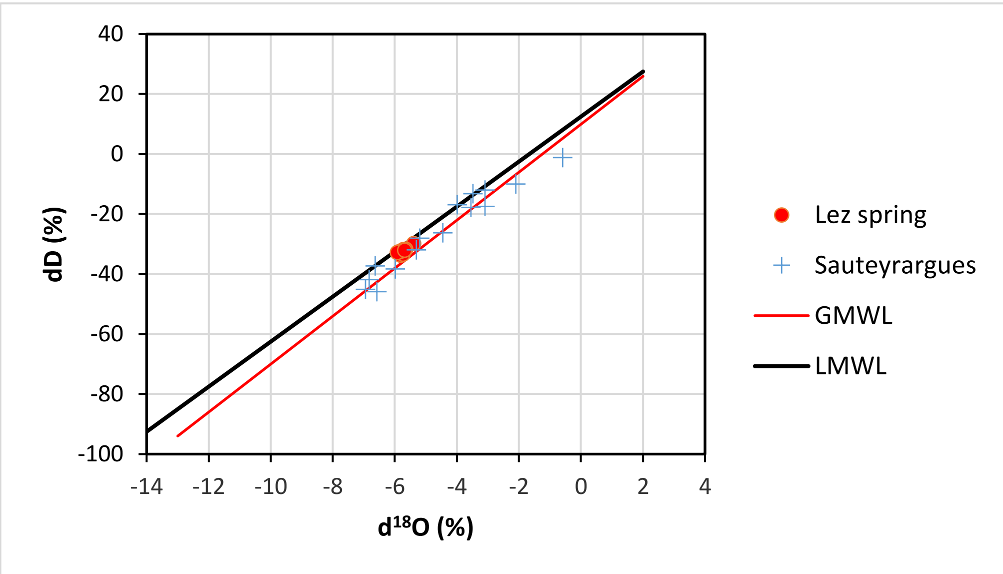

Figure 6.5. dD vs. d18O (‰) for the Lez spring waters and Sauteyrargues rainwater samples from Oct. 2019 to Nov. 2020.

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7 Conclusions

Water stable isotope data ($\delta^{18}O$ and $\delta^{2}H$) have been collected during the KARMA project in four test sites (Italy, Lebanon, Spain and France). In all these sites, previous data are available, and the conceptual model of groundwater flow was based also on isotope analysis, by local correlation isotopic lines based on rain samples.

The new stable isotope data collected during the KARMA project do not show significant changes with respect to previous information in each test site. Consequently, the conceptual model of groundwater flow of studied karst springs has been still validated by new isotope data. In some cases, the analysis frequency allows to obtain useful additional information on flow regime of karst springs.

In several cases, water samples collected in the first two years of the project duration are still in analysis. Further results can improve the conceptual model of some springs, and they will be considered in future updates of this deliverables.

The absence of significant changes at monitored springs is also a relevant signal of the stability of the recharge area contribution to the spring flow, despite to possible reduction in recharge rate. This does not mean that the renewable groundwater resources cannot be affected by climate change, but it testifies the steady conditions of groundwater flow to the springs, in terms of recharge area contribution. In other words, at this stage the stable isotope data affirms that the distribution of the aquifer recharge with altitude (and consequently the extension and the mean elevation of hydrogeological basins and sub-basins within the studied karst aquifers) is still not affected by possible changes in recharge rate due to different precipitation values with years.