Regional vs local isotopic gradient: insights and modelling from mid-mountain areas in central Italy

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Keywords: water isotopes, $\delta^{18}O$ precipitation gradients, local meteoric water lines, isotopic modelling, hydrogeological applications, Apennines ridges

Abstract

Mountainous zones are often characterized by complex orography and contacts between different aquifers that usually complicate the use of isotope hydrology techniques. The Apennine chain (Italy) and ten mountain and mid-mountain areas belonging to it are the objective of this study. An original isotopic data treatment, able to identify the most probable recharge area for several springs/springs' groups/wells, has been developed. The method consists of a two-step approach: a) the determination of the spring/wells computed isotope recharge elevation; b) an advanced $\delta^{18}O$ precipitation distribution model over the study area supported by statistical and GIS-based procedures implemented by two processes: first, the clipping of precipitation $\delta^{18}O$ values (depicted from the $\delta^{18}O$ – elevation relationships obtained for each study area) over a most probable recharge area for each analyzed spring or well and, second, the calculation of the overlapping distribution between the spring/well mean $\delta^{18}O$ values ± σ and the precipitation $\delta^{18}O$ content for each outcropping aquifer. A new regional $\delta^{18}O$ gradient covering 150 km latitudinal length of central Italy has been defined. Seven LMWL and $\delta^{18}O$ – elevation relationships able to represent the local precipitation isotopic composition have been obtained. The mean elevation of the springs and wells recharge areas have been assessed by a comparison between the obtained gradient with nine $\delta^{18}O$ gradients available in the literature and those

obtained at a local scale. The new isotopic modelling approach can stress whether the mere isotope modelling based on the stable isotope of oxygen agrees with the hydrogeological setting of the study areas.

Introduction

The very first insights in isotopic hydrology appeared in the scientific community during the '50s (Aggarwal et al., 2005). In the early years the water isotopes were mainly used to evaluate streams filtration and exfiltration zones, and the incorporation in water research studies was very slow (Aggarwal et al., 2005). Over the following decades, naturally occurring stable isotopes of water have been extensively used in hydrological investigations and the advances in isotope hydrology permitted to use them to trace both the groundwater movement and the water mixing from different sources (Clark and Fritz, 2013). Many studies deal with the application of water isotopes in small catchments usually located in headwater areas (Zhao et al., 2011; Stets et al., 2010) and most of the applications to groundwater studies have been performed in the northern hemisphere (Jasechko, 2019). Nowadays, isotopes are used to identify springs recharge areas (even in drinking purposes studies), to evaluate the mixing ratio between different water types and to study the infiltration processes that occur in the unsaturated zone as part of the so-called Critical Zone (National Research Council, 2001; Sprenger et al., 2017). In this context many authors highlighted the importance of coupling hydrogeological studies with isotope investigations to better characterize the aquifers hydrodynamic and geometry (Ozyurt and Bayari, 2008; Tziritis et al., 2017; Binet et al., 2017, among others). A lot of research papers deal with the water isotopic composition to evaluate groundwater-surface water interaction trying to perform hydrograph separation (Criss and Davisson, 1996; Hunt et al., 2005; Liu et al., 2008; Carucci et al., 2012; Klaus and McDonnell, 2013, among others). In all the applications of water isotopes hydrology, aiming at evaluating the water cycle components and their interactions, the first step is usually to define a local meteoric water line (LMWL, Crawford et al., 2014) and an isotopic gradient starting from rainfall/snowfall collected samples (Gonfiantini et al., 2001; Hürkamp et al., 2019). Indeed, many scientific works focus on LMWLs and local gradient acquisition, and, afterward, a comparison to global ones (Rozanski et al., 1993) or obtained at national or regional scale is then performed (Stumpp et al., 2014; Li et al., 2012; Hatvani et al., 2020). However, in contrast to all the previous advantages obtained by the isotopic investigation methods, the problematic employment of the isotopic data is recognized in all those areas characterized by a scarce knowledge of the geo-structural context or when the hydrogeological setting is complicated by the presence of hydraulic contacts between different aquifers, which are often responsible for water mixing from several sources (Mussi et al., 2017). A recent study (Khayat et al., 2019) tried to understand the geo-structural control of recharge and flow dynamics by mapping groundwater stable isotopes values, and at the same time affirms that recharge mechanisms, flow direction, and groundwater resident time are generally quite difficult to measure if not multiple techniques such as water budgets, tracers, geophysics, and simulation models are not applied simultaneously. The application of conventional isotopic investigation is also difficult in the cases in which different hydro-structures are in contact each other and a regional groundwater flow, external to the hydro-structures, feeds the aquifers. The knowledge of how mountain catchments capture and store meteoric water and then release it through surface and subsurface flow paths is still weak (Penna et al., 2017). In this context, some authors indicated that in high mountainous areas the application of traditional isotopic investigations is a challenging issue (Nanni et al., 2013; Tazioli et al., 2019) because the sites are characterized by the presence of steep slopes, intramountain basins, deep topographical incisions, or depressions. At the same time, environmental tracers have been positively applied to groundwater investigation in mountainous aquifers, where orography and hydrogeological setting is very complicated (Andreo et al., 2004). However, it must be underlined that the complex orography may be responsible for biased meteoric isotopic sampling and the location of sampling points should be selected considering all the meteorological phenomena (i.e., shadow effects or snow-drift effect among others) and atmospheric dynamics that characterize the isotope fractionation processes (Craig, 1961; Rozanski and Sonntag, 1982; Sharp, 2017). Since in mountainous regions the natural variability of recharge is frequently unknown, an effort is required to enhance the spatio-temporal characterization of recharge through the integration of interdisciplinary approaches (Andreu et al., 2011). A pivotal role of the scientific community is to increase the knowledge of fundamental hydrological processes, such as the origin of water sources which is a key step in improving water resource management strategies in mountain regions (Penna et al., 2017). In light of the previous considerations, the present work aims at performing advanced isotopes applications and data treatment involving $\delta^{18}O$ and $\delta^{2}H$, regarding several mid-mountain areas of central Italy in which tectonic and stratigraphic contacts between aquifers and hydro-structures have been demonstrated (Aquilanti et al., 2016). This study highlights how the isotopic methodology can be conveniently applied to define the hydrogeological features of the relief domains, helping to identify the aquifers recharge areas. To do so, twelve (12) study sites (characterized by different hydrogeological setting and different orography) and twenty-one (21) springs, spring groups/wells (used for drinking purposes) have been selected. Twenty-three (23) meteoric monitoring points have been installed and sampled between 2008 and 2019. They are located among Marche, Abruzzo and Umbria Regions, and they cover a linear latitudinal length of about 150 km. A new regional Meteoric Water Line and $\delta^{18}O$ - elevation gradient have been obtained for the whole area and the local ones are reported for each study site. At first, a statistical comparison has been performed to verify if the $\delta^{18}O$ gradients available from the scientific literature, the regional $\delta^{18}O$ gradient (obtained from this study for the entire analyzed area) and the local $\delta^{18}O$ gradient (obtained from this study for each site), allowed realistic indications on the studied hydrogeological framework. Then, a further approach, involving a GIS-based method has been applied to determine possible springs and wells recharge area. The applicability of the most used isotopic approach based on the determination of groundwater recharge areas starting from $\delta^{18}O$ - elevation gradient (Jeelani et al., 2010; Petitta et al., 2022, Jasechko, 2019), namely Computed Isotope Recharge Elevation (CIRE, Petitta et al., 2010, Petitta et al., 2022) applied to the selected springs/well isotopic data are discussed towards a comparison between the novel proposed approach, confirming that this method cannot always lead to results in accordance with the hydrogeological setting. In some study areas this procedure can mislead about the hydrogeological features, while in other cases it provides a warning signal that suggests a deepening in the study, since the isotopic modelling indicates a water mixing coming from different aquifers or underestimated aquifers recharge area extension or elevation. The refined isotopic modelling proposed in this study, represents a novel approach to investigate and determine possible groundwater recharge areas in mid-mountain and mountainous regions characterized by multi-layers aquifers systems (separated or not). Besides, the new local and regional meteoric water lines, together with the regional and local $\delta^{18}O$ - elevation gradients obtained from this study, can constitute an updated dataset and a starting point for more detailed research works focused on each of the described study areas.

Material and methods

Geological and hydrogeological features

The selected sites are mostly (10 out of 12) located in central Italy among Marche, Abruzzo, and Umbria Regions, covering an area of about 1000 km^2 (Figure 1). From a geological point of view, they belong to the Umbria-Marche sedimentary succession (U-M). Its deposition started in the Triassic with the Anidriti di Burano Formation (Fm.), mainly composed by dolomites and evaporites (Figure 2). The sedimentation continued with the deposition of the Calcare Massiccio Fm., a platform limestone of about 600-700 m thickness. Calcare Massiccio Fm. is the oldest geological formation outcropping in the U-M stratigraphic succession. During the Lower Jurassic a well-documented tectonic phase (Boccaletti et al., 2005) was responsible for the carbonate platform disarticulation in horst and graben structures (Carminati and Doglioni, 2012). In the deepest sectors of the basin, the deposition continued with the limestones and marls of the Corniola Fm., Rosso Ammonitico Fm, Calcari a Posidonia Fm. and Calcari Diasprini Fm. In the horst structures, the Calcare Massiccio Fm. was overlied by Bugarone

Fm and in some cases the Late Jurassic - Early Cretaceous Maiolica Fm. directly overlies the Calcare Massiccio Fm. The Maiolica Fm. is a powerful stratified pelagic limestone and its thickness ranging between 150 to 450 m. The deposition continued during the Early Cretaceous with the Marne a Fucoidi Fm. The Late Cretaceous was marked by the deposition of mycritic limestones and marly limestones of Scaglia Bianca and Scaglia Rossa Fms. followed by the sedimentation of the marls and marly limestones of the Scaglia Variegata Fm., the Scaglia Cinerea Fm., the Bisciaro Fm. and the Schlier Fm. The latter was followed by the deposition of a thick siliciclastic sedimentation of turbidites, clay, sandy-clay and sandstones (Figure 2). The study area is characterized by a complex tectonic setting where antiformal and syn-formal folds are associated with multiple overthrust. The main folds with ENE vergence are often separated by oblique transtensive and transversal faults, bordered by normal faults. In the U-M Apennines an Inner Ridge and an Outer Ridge are recognised (Deiana and Pialli, 1994; Pierantoni et al., 2013). The two ridges converge only in the southernmost portion of the U-M domain originating the Sibillini Mts. Massif (Figure 1B).

The hydrogeological features in the study sites are strictly influenced by the stratigraphic and tectonic setting. In fact, the main springs of the U-M domain emerge near stratigraphic limits of permeability between different geological formations or near important tectonic lineaments (Boni, 2010; Boni and Petitta, 2007; Mastrorillo and Petitta, 2014). As far as stratigraphy concerns, the Calcare Massiccio and Corniola Fms. host the Regional Basal aquifer (BAS) (Figure 2) characterized by high permeability, high karstification and high infiltration rate (Banzato et al., 2013). The BAS is underlined by the Anidriti di Burano Fm. acting as a lower regional aquiclude. In agreement with the horst and graben structures, Rosso Ammonitico, Calcari a Posidonia, Calcari Diasprini and the Bugarone Fms. act as an aquiclude complex at local scale separating BAS from the above Maiolica aquifer complex (MAI). Only at regional scale, BAS and MAI can be stratigraphically in contact, constituting a single regional aquifer. The MAI aquifer and the SCA aquifer, hosted in the Scaglia Bianca and Scaglia Rossa Fms., are separated by the Marne a Fucoidi aquiclude. The SCA aquifer represents the upper aquifer of U-M carbonate domain (Figure 2), and it is characterized by a medium-high permeability due to a well-developed fissures system. The tectonic lineaments, such as folds and faults, deeply influence the groundwater circulation, and the role of faults, even if still debated in some areas of the U-M domain, can put in contact different aquifers (Nanni, 1991; Nanni and Vivalda, 2005) or can act like no-flow barrier in accordance with its kinematics and degree of activity. Magnification of the study sites belonging to the U-M domain (from 1 to 10) are reported in the supplementary material (S1).

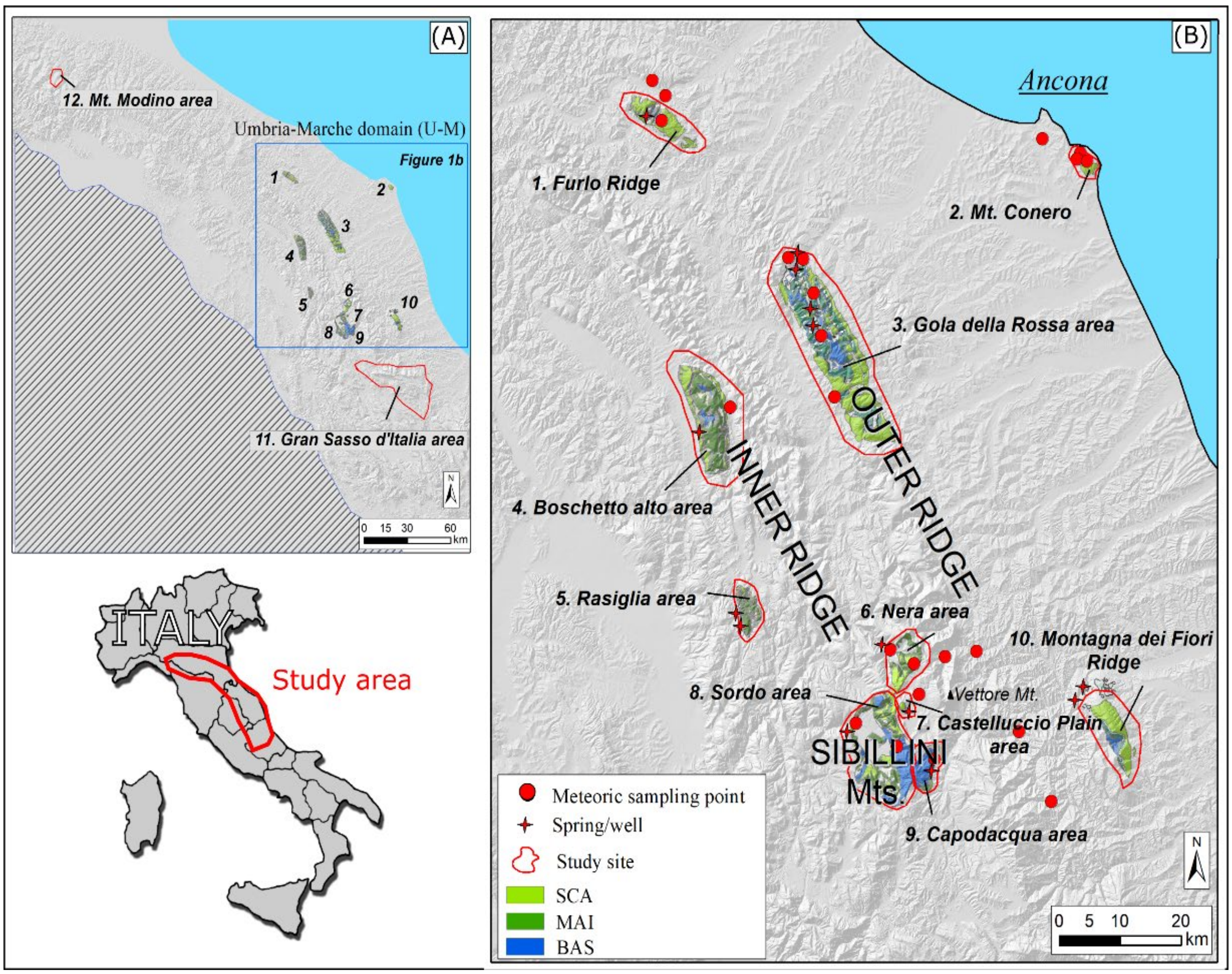

Figure 1. (A) Location of the hydrogeological study sites (from 1 to 12), (B) Magnification of Figure 1A with outcropping of the geological formation hosting the main U-M aquifers, reported as follow: BAS (blue), MAI (dark green), SCA (light green) with meteoric water samplers and springs/wells position.

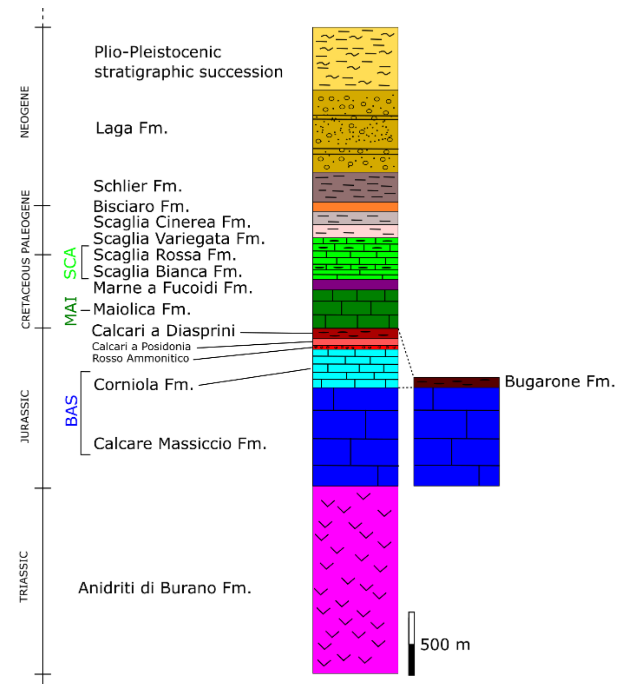

Figure 2. Schematic stratigraphic column of the U-M geological formations with detail of the main carbonate aquifers (BAS, MAI and SCA), target units of this research.

Climatic and meteorological features

In terms of climatological conditions, there is no difference between the Inner and the Outer Ridges, although in the Sibillini Mts. area, the more complex orography and the higher elevations determine a more continental climate. In both ridges there are pluvio-thermometric differences between the external Est side (Adriatic side) and the inner West side (Tyrrhenian side). The Est side is rainier while the West side, especially for the Sibillini area, is characterized by less rainy interior basins with continental thermal regime. In the purely mountain area, the thermometric annual average ranges from 6 to 11° C (3-4°C in January and 14-20°C in July). The rainfall is affected by altitude with a very strong gradient up to 1200 meters above sea level (a.s.l.) (Gentilucci et al., 2018). A relationship between morphology and annual average rainfall has been noted, reaching values about 1400-1500 mm in the higher reliefs. Concerning snowfall, it is more abundant above 1200 meters in the Sibillini Mts. massif. Seasonally, 120-220 cm of snow falls in 20-28 days, with a gradient of 8.7 cm/100m. The snowpack remains on the ground from 50 to 170 days, from November to May. Around 1500-1800 m, snowfall is constant in winter while at lower elevation the snow regime is variable (data freely available from http://app.protezionecivile.marche.it). Analysing the historical pluviometric and thermometric data of different stations managed by Marche Region Civil Protection Agency (data freely available from http://app.protezionecivile.marche.it), the climatic characteristics of the area are defined according to the Koppen classification (Lohmann et al., 1993), as sublittoral wet up to 1200 meters; then it becomes subalpine with cool summers and only on the peaks of the Sibillini Mts. the climate is boreal with moderate rainfall. From a dynamic synoptic point of view, it is clear that the more abundant rainfall is related to the frontal flows of zonal type or to southern flows moving eastward recalled by the depressions located on the north. They provide uniform rainfall on both sides of the ridge, despite the presence of a minimum in the basins of the upper Nera area (Site 6 in Figure 1) caused by the "rain shadow". The most intense rainfall events are caused by advection of continental polar air of Central European origin in late summer; they occur with intense rain most significantly affecting the external side of the two mountain alignments. In winter conditions, in the presence of a cyclonic circulation on the southern Mediterranean, fed by continental polar air or intermediate, widespread phenomena are observed mainly on the Adriatic side of the mountain, often snowy down to low altitudes.

Isotopic data collecting strategy and laboratory analysis

An isotopic sampling system has been settled up with the aim of obtaining a new regional meteoric water line, a local meteoric water line for each study area and the correlation between $\delta^{18}O$ and the elevation (at regional and local scale). In particular, 23 precipitation samplers located between 16 m and 1800 m a.s.l. were instrumented by standard precipitation gauges with a funnel diameter of 5" (12.72 cm) and connected, through an externally insulated PVC pipe, to a buried totalizer constituted by 20 L volume tank fitted between polystyrene panels surrounding all its sides as anti-evaporation technique. To further minimize the evaporation processes during the summer period (May-September), a layer (~1 cm) of pure paraffin oil was inserted in the tank (IAEA/WMO, 2004). All the rain gauges located at an altitude > 1000 m a.s.l. were supplied with an electric heating device powered by a 12 Volt battery connected to a solar panel and equipped with a temperature sensor that activates the heater when the air temperature dropped less than 2° C. This equipment permitted to slowly melt the precipitation aliquot that fell in solid form (i.e., snow). The meteoric periodic sampling was performed in multiple collection campaigns, each of one covering at least one hydrologic year (some of which are no consecutive) within the time span reported in detail in table 1. The frequency of sampling varies from 1 to 3 months depending on the accessibility of the study sites and the possibility of reaching the areas at certain times of the year, some of which are characterized by permanent snow cover on the ground during the winter period. In any case, since the precipitation samples are cumulative (depending on the sampling frequency), the sample was always retrieved and the whole precipitation sample (even if it included more than one month) was collected, adopting, as mentioned before, anti-evaporative techniques. Precipitation amount recorded by the rain gauges was compared with the amount of water measured manually for each sampling period. The precipitation average $\delta^{18}O$ and $\delta^{2}H$ values were determined by weighting the single isotopic values with the amount of water collected by the tank at each sampling respect to the total precipitation of the corresponding period of observation following the equation:

$$\delta = \frac{\sum \delta_i P_i}{\sum P_i}$$

where: δ is the weighted average of isotopes; δ_i is the isotopic value of a single sample and P_i is the corresponding precipitation amount.

As concerns the Sibillini Mts. massif, a more detailed isotopic meteoric investigation has been performed, as this area is characterized by topographical elevations among the highest in central Italy, whith steep reliefs frequently exceeding 2000 m a.s.l. (maximum altitude of about 2500 m a.s.l. for

Vettore Mt.) alternating with large hollows at medium altitude. This peculiar morphological setting is responsible for different precipitation regime between the eastern (Adriatic) and western (Tyrrhenian) side of the massif.

Therefore, both $\delta^{18}O$ gradient and meteoric water lines has been determined in the Tyrrhenian and in the Adriatic side, and compared to the ones obtained for the whole massif, to investigate whether the precipitation regime on the two sides of the massif (Tyrrhenian and Adriatic) may also influence the precipitation isotope signature. The choice of the location of the precipitation samplers was made following a careful assessment of the local topographical and meteorological conditions, trying to detail and characterize as much as possible the effects of local precipitation fractioning effects due to the presence of shaded areas or to avoid the snow-drift effect at higher altitudes due to windy conditions. Therefore, for example, precipitation samplers were placed in areas sheltered from the wind in both narrow valleys and open areas.

A water sampling field work has been performed in 8 springs and 2 wells used for drinking proposes with the aim to characterize their mean recharge elevation, by computing the isotope recharge area elevation (CIRE, Petitta et al., 2010, Petitta et al., 2022) and to set up a refined recharge isotopic model. The $\delta^{18}O$ and $\delta^{2}H$ values of some precipitation sampler and springs have been integrated by the data published by Mussi et al., 2017; IAEA/WMO, 2004; Tazioli, 2017; Conversini and Tazioli, 1993; Tazioli et al., 2019; Barbieri et al., 2005 and Cervi et al., 2015 as shown in table 1. In the same table the specifications about the number of samples and the locations of the meteoric water samplers, springs/spring groups and wells are reported.

50 mL high-density polyethylene bottles were used to collect water samples for isotopes analysis; they were tightly sealed to avoid evaporation in sample. Isotopic analyses of oxygen of the water were performed at the Stable Isotopes Laboratory of National Research Council (CNR-Pisa, Italy) through

the analysis of gaseous CO2, previously equilibrated with water at 25°C (Epstein and Mayeda, 1953) with a mass spectrometer FINNIGAN MAT252 showing analytical precision less than ±0.10‰. The δ^2H value was measured by means of the Europa Scientific GEO 20-20 mass spectrometer, by reducing the water to elemental hydrogen (Coleman et al., 1982) with magnesium instead of zinc. The analytical error is ±1.5‰. The "permil" notation is used to represent the isotope results, indicating the water sample ratio respect to the international standard V-SMOW (Vienna-Standard Mean Oceanic Water) as reported by (Rozanski et al., 1993).

Isotopic investigations and modelling

The first step to identify the mean recharge area elevation for a spring, using its $\delta^{18}O$ value, consists in the application of the $\delta^{18}O$ gradient, obtained by the linear regression of $\delta^{18}O$ precipitation values vs elevation, to the spring isotopic data (CIRE, Petitta et al., 2010). In this case for each analysed spring/well, the $\delta^{18}O$ gradients available in literature for central Italy (Conversini and Tazioli, 1993; Tarragoni, 2006; Desiderio et al., 2005; Longinelli and Selmo, 2003; Tazioli et al., 2007; Zuppi et al., 1974; Bono et al., 2005; Giustini et al., 2016) were applied and compared to the regional and local ones obtained in this study.

The computation started by applying the regional $\delta^{18}O$ - elevation linear regression to the Digital Terrain Model (DTM 20x20m cell size) with the aim to spatialize the $\delta^{18}O$ precipitation value at regional scale as a raster format. Secondary, by applying the same methodology used to obtain the regional $\delta^{18}O$ raster, a $\delta^{18}O$ precipitation values map for each study area was determined by using the local $\delta^{18}O$ - elevation linear regression. Finally, a comparison between the spatialized regional $\delta^{18}O$ precipitation values (clipped for each study area) and the spatialized local one was performed to assess if the distribution of the local isotope precipitation composition in each study area, with respect to the one determined at regional scale, was significantly different. This hypothesis has been assayed by exploiting the one-way ANOVA test via MATLAB®. The $\delta^{18}O$ precipitation value distributions were then shown as boxplot graphs.

Isotope hydrology applications, aimed at computing the mean recharge elevation of groundwater (CIRE, Petitta et al., 2010), are usually based on the average value of groundwater isotopic composition. However, the isotopic composition of groundwater is the result of various precipitation inputs from different recharge areas (Petitta et al., 2022), which may involve different recharge elevations and different outcropping aquifers.

Given these limitations, a second step has been implemented attempting to make the CIRE slightly more "hydrogeological-based". This step was performed operating in a GIS environment, integrating (over the DTM used in the first step) the geological information for each study site. Starting from the 1:10.000 Regione Marche and the 1:10.000 Regione Umbria official geological maps, a hydrogeological complexes map was obtained for each study area, by combing the geological units into appropriate complexes with similar hydrogeological features (Viaroli et al., 2021). The conceptual aggregation of different geological units into hydrogeological complexes was supported by the available literature not considering specific or detailed in-situ hydrogeological characterization. For each study area, the main outcropping aquifers (BAS, MAI and SCA) were used to clip the local spatialized $\delta^{18}O$ values. Therefore, the $\delta^{18}O$ meteoric values distribution, clipped over each single outcropping aquifer, was plotted in a bar graph to highlight the distribution of $\delta^{18}O$ for each aquifer and develop the isotopic recharge model for the analyzed spring. In fact, subsequently, the average $\delta^{18}O$ value $\pm$ σ of the analyzed springs and wells has been overlapped to the $\delta^{18}O$ aquifers distribution (Figure 3) calculating the individual contribution of each aquifer (expressed as relative percentage to the total) that can potentially feed the analyzed springs or wells as follow:

$$\%BAS = \frac{\int_{\delta^{18}O-\sigma}^{\delta^{18}O+\sigma} BAS}{\int_{\delta^{18}O-\sigma}^{\delta^{18}O+\sigma} (BAS + MAI + SCA)} \; [\%]$$

$$\%MAI = \frac{\int_{\delta^{18}O-\sigma}^{\delta^{18}O+\sigma} MAI}{\int_{\delta^{18}O-\sigma}^{\delta^{18}O+\sigma} (BAS + MAI + SCA)} \; [\%]$$

$$\%SCA = \frac{\int_{\delta^{18}O-\sigma}^{\delta^{18}O+\sigma} SCA}{\int_{\delta^{18}O-\sigma}^{\delta^{18}O+\sigma} (BAS + MAI + SCA)} \; [\%]$$

where: BAS, MAI and SCA are the cells (20x20 m) distributions of the examined outcropping aquifers (see Figure 3).

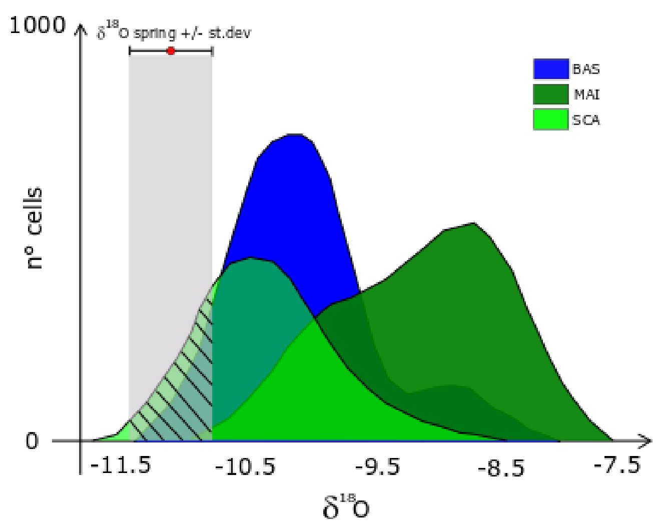

Figure 3. Graphical example of geo-isotopic modelling. The graph shows the precipitation $\delta^{18}O$ distribution for each aquifer obtained by the GIS clipping procedure for each study area. The relative percentage to the total can be calculated by overlapping the average spring or well $\delta^{18}O$ value ± σ.

Concerning the first step, is important to remark that sites 1, 2, 3, 4, 6, 7, 8 and 9, display the presence of precipitation samplers within them, and sites 5 and 10 are characterized by the presence of precipitation collector outside but in close proximity of the study area. Hence, the applicability of the obtained gradients in the uncovered areas has been tested by using the nearest meteoric network (i.e., Sibillini Mts. for study site n° 5, and Acquasanta, Ceppo, and Vallefiume rain gauges for study site n° 10). The first step was also applied to two areas located southward and northward with respect to the precipitation monitoring points: i.e., Gran Sasso d'Italia (11 in Figure 1A) and Mt. Modino (12 in Figure 1A). These two areas were selected only to define the spatial reliability and the range of application of the new regional $\delta^{18}O$ gradient obtained from this study, outside from the U-M domain (Figure 1B). Moreover, in the Gran Sasso d'Italia area, the $\delta^{18}O$ gradient obtained for the Sibillini Mts. area (located less than 30 km far and even characterized by similar meteorological, and morphological conditions) has been applied to the springs $\delta^{18}O$ values of Barbieri et al., 2005 (see Table 1) to test its suitability for hydrogeological studies of the area.

The second step was performed only to the springs belonging to the U-M domain where, for methodological completeness, more than one aquifer emerges in the potential recharge area, and for which a more defined geological framework is available to the authors. A schematic flowchart showing the main steps of the proposed approach with the complementary elaborations useful to develop the method, is presented in Figure 4.

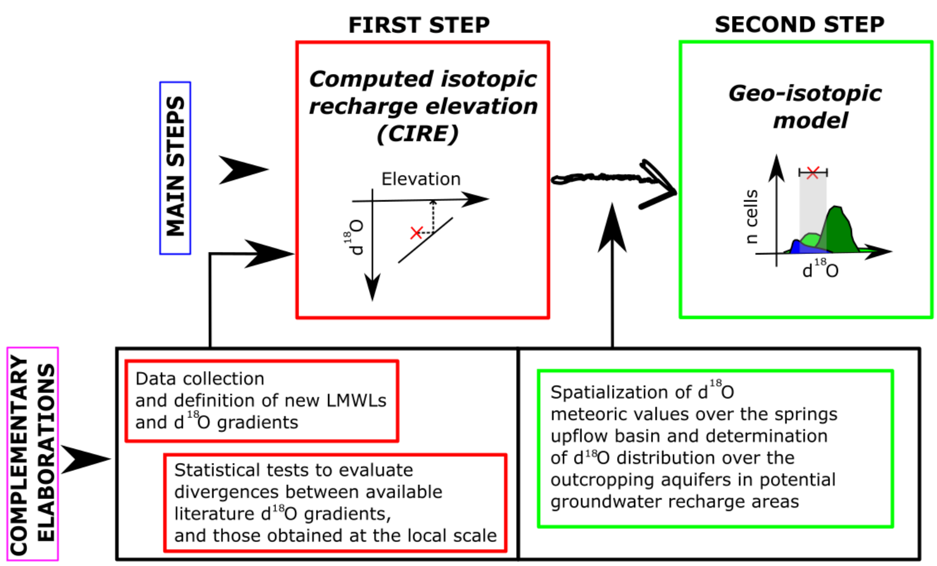

Figure 4. Main steps of the proposed approach and the complementary elaborations consequentially performed to reach the results of this research.

Results and Discussion

Meteoric water lines and $\delta^{18}O$ gradients

The meteoric precipitation sampling, performed during the years, permitted to define a new detailed regional meteoric water line and to obtain seven local meteoric water lines, one for each study area or ridge (Figure 5). Concerning the Sibillini Mts. area, for which the precipitation sampling was performed to assess potential influence on the precipitation isotope signature from the different precipitation regime recognized on the two sides of the massif, it has to be noticed that the difference in slope and intercept are 0.01 and 0.20 ‰ respectively (Figure 5G and 5H). Even if the regressions are characterized by different slopes and intercept values, they are not big enough to claim a statistically significant difference between the two sides, as suggested by the regression fitting uncertainties. This aspect is much visible by analyzing the whole massif regression (Figure 5F), which suggests that a single LMWL is sufficient to describe the meteoric isotope signature for the entire area and to prove that the precipitation regime does not influence the isotopic regime differentially on the two sides. In general, a strong correlation between the $\delta^{18}O$ and $\delta^{2}H$ meteoric values is always marked by the Pearson's coefficient of determination ($R^2 \geq 0.91$) confirming the good choice of water sampler location, installed considering the effects of orographic isotopic fractionation. The $\delta^{2}H$ / $\delta^{18}O$ slopes vary between 7.11 (Figure 5C, F and G) and 7.37 (Figure 5B), while the δ^2H -intercepts go from 0.85 (Figure 5E) to 5.96 (Figure 5C).

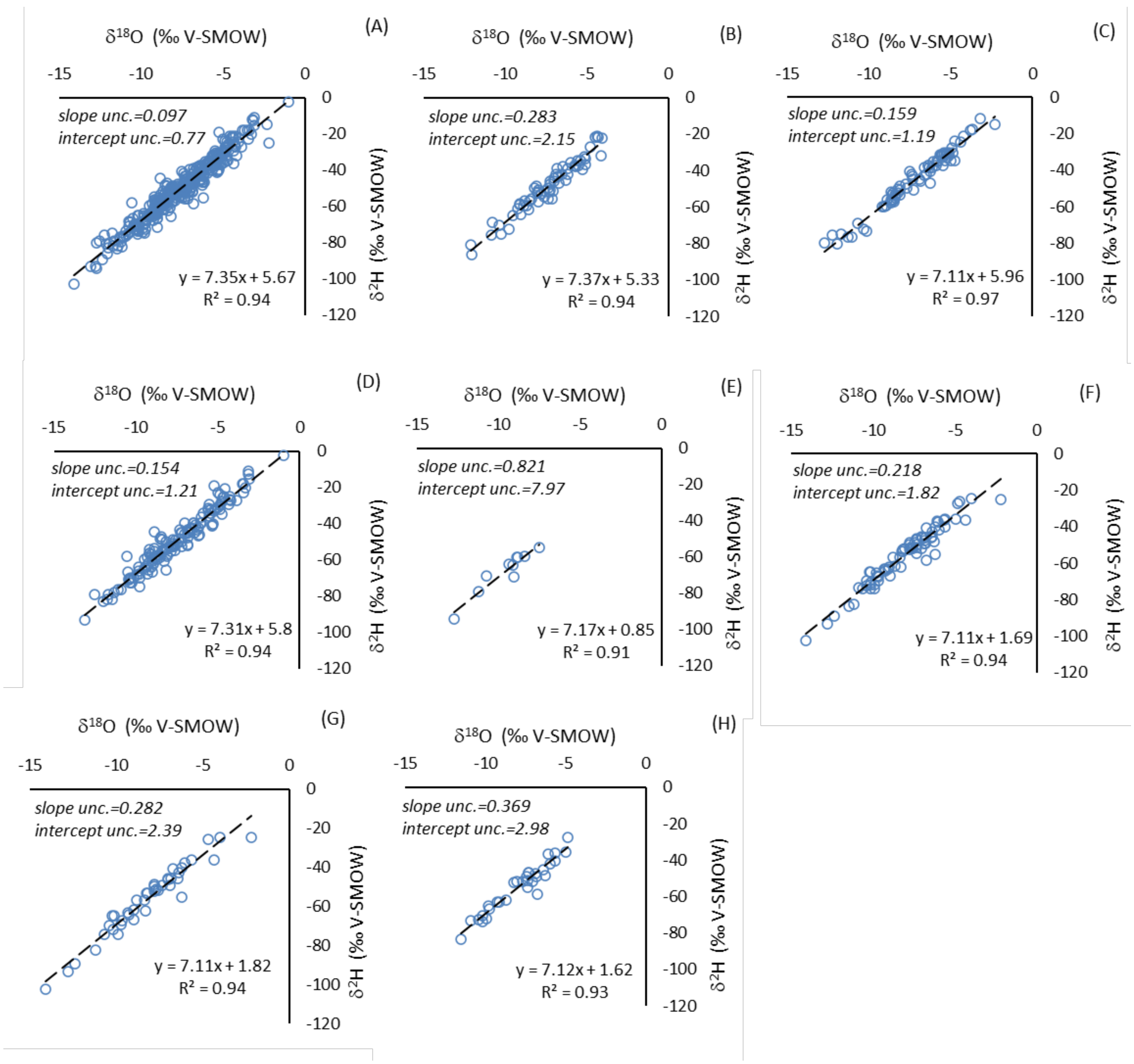

Figure 5. Meteoric water lines obtained during this study with slope and intercept uncertainties (unc.) values obtained from the linear regression between variables: (A) Regional, (B) Furlo Ridge, (C) Conero Mt., (D) Gola della Rossa area, (E) Montagna dei Fiori Ridge, (F) Sibillini Mts., (G) Sibillini Mts. Adriatic side, (H) Sibillini Mts. Tyrrhenian side.

At the same time, a new regional $\delta^{18}O$ gradient has been defined using a linear regression between $\delta^{18}O$ values and elevation showing a strong determination coefficient between data (R^2 =0.74). The new regional gradient of $\delta^{18}O$ obtained by the linear regression of 23 meteoric sampling points is equal to -0.18 ‰/100 m (Figure 6A). This outcome is similar to the one determined by Nanni et al., 2013 (-0.17‰/100 m) operating the interpolation in central Italy with 90 data coming from 9 rainfall samplers. Moreover, a more detailed $\delta^{18}O$ gradient have been defined for each study site, showing also in this case strong correlations ($R^2 > 0.75$). This suggests that the sampling points have been located in representative areas confirming the good spatial network choice of precipitation sampler within each study area. Moreover, the magnitude of the altitude effect is roughly constant in all the study sites also at regional scale. Therefore, the $\delta^{18}O$ - elevation linear regression determined for the whole Sibillini Mts. area (Figure 6F) is suitable alone to represent the $\delta^{18}O$ - elevation linear regressions determined for both the sides of the massif, even if they are characterized by different meteorological features.

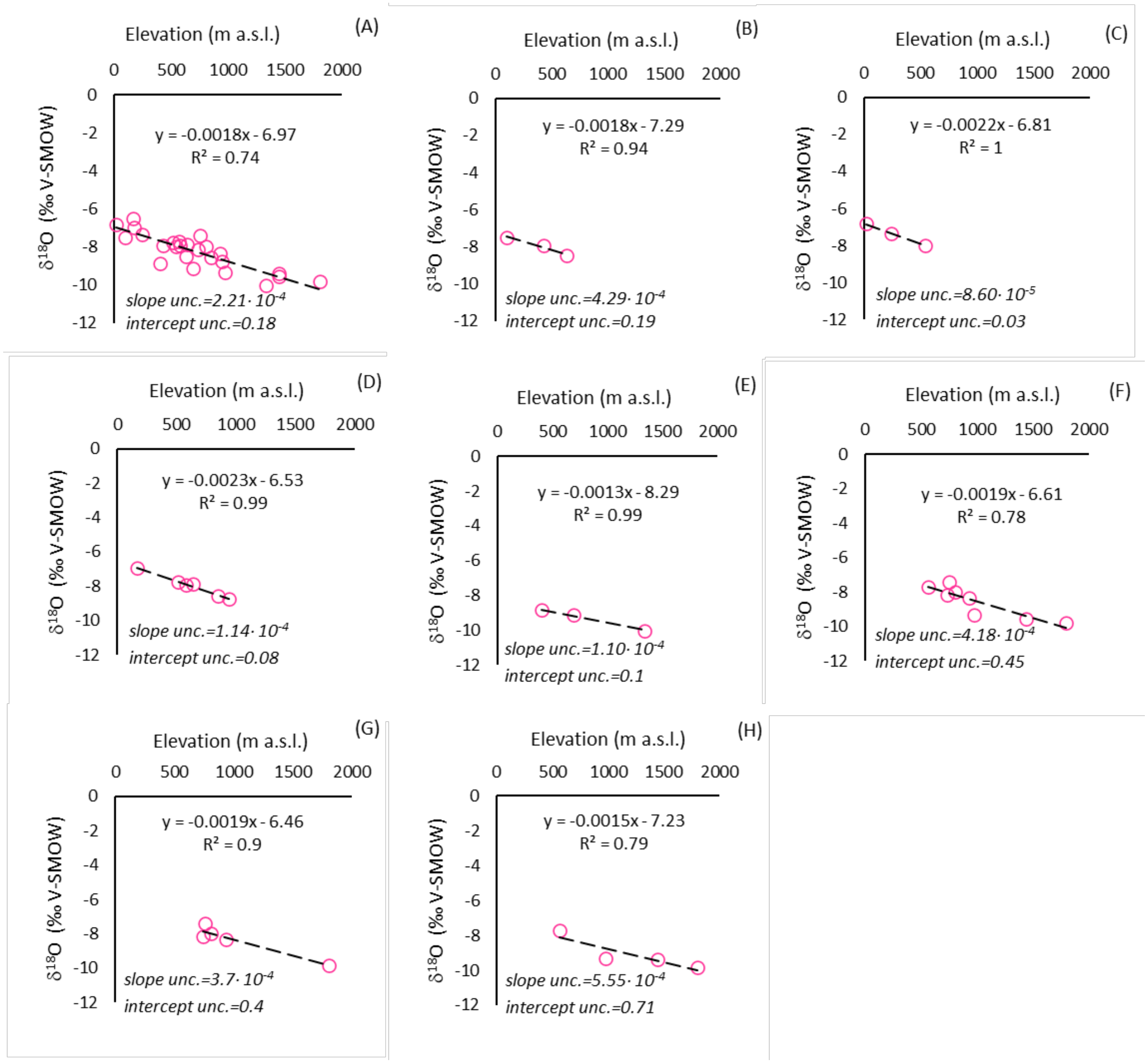

Figure 6. $\delta^{18}O$ precipitation values plotted vs elevation and linear regressions obtained during this study with slope and intercept uncertainties (unc.) values obtained from the linear regression between variables: (A) Regional, (B) Furlo Ridge, (C) Conero Mt., (D) Gola della Rossa area, (E) Montagna dei Fiori Ridge, (F) Sibillini Mts., (G) Sibillini Mts. Adriatic side, (H) Sibillini Mts. Tyrrhenian side.

The clipping procedure of the regional $\delta^{18}O$ values and the local one over each single study site made it possible to obtain two $\delta^{18}O$ distributions for each area (plotted in figure 7 as box-plot format). In all the cases the application of the one-way ANOVA test shows statistically significant different $\delta^{18}O$ values distributions over the study sites when applying the regional or local gradient with a p-value $<$ 0.05. Concerning the U-M domain, the higher differences between the regional and local $\delta^{18}O$

distributions have been observed in Montagna dei Fiori and Furlo ridges, also influencing their median values. The larger areas (Sibillini and Gola della Rossa) are characterized by a higher number of outliers. This outcome underlines the importance of preferring local meteoric gradient for detailed hydrogeological applications and for the determination of the mean spring recharge area elevation, but in cases where it is not possible, the regional gradient provides good coverage, overcoming the limits given by the orography and the location of the monitoring points. As far as the Gran Sasso d'Italia area concerns, it is characterized by a local $\delta^{18}O$ distribution (Desiderio et al., 2005) similar to the $\delta^{18}O$ distribution obtained by applying our regional $\delta^{18}O$ -elevation relationship in its minimum value (-11.25 ‰), whereas the overall $\delta^{18}O$ distributions are significantly different. The differences between the regional and the local distributions are even more accentuate moving northerly with respect to the precipitation monitoring points, in the Mt. Modino area. The latter is characterized by a completely different $\delta^{18}O$ distributions (Figure 7I) suggesting that the regional $\delta^{18}O$-elevation relationship obtained in this study lacks reliability by moving almost 200 km northwards with respect to the barycentric position of the rain gauge samplers.

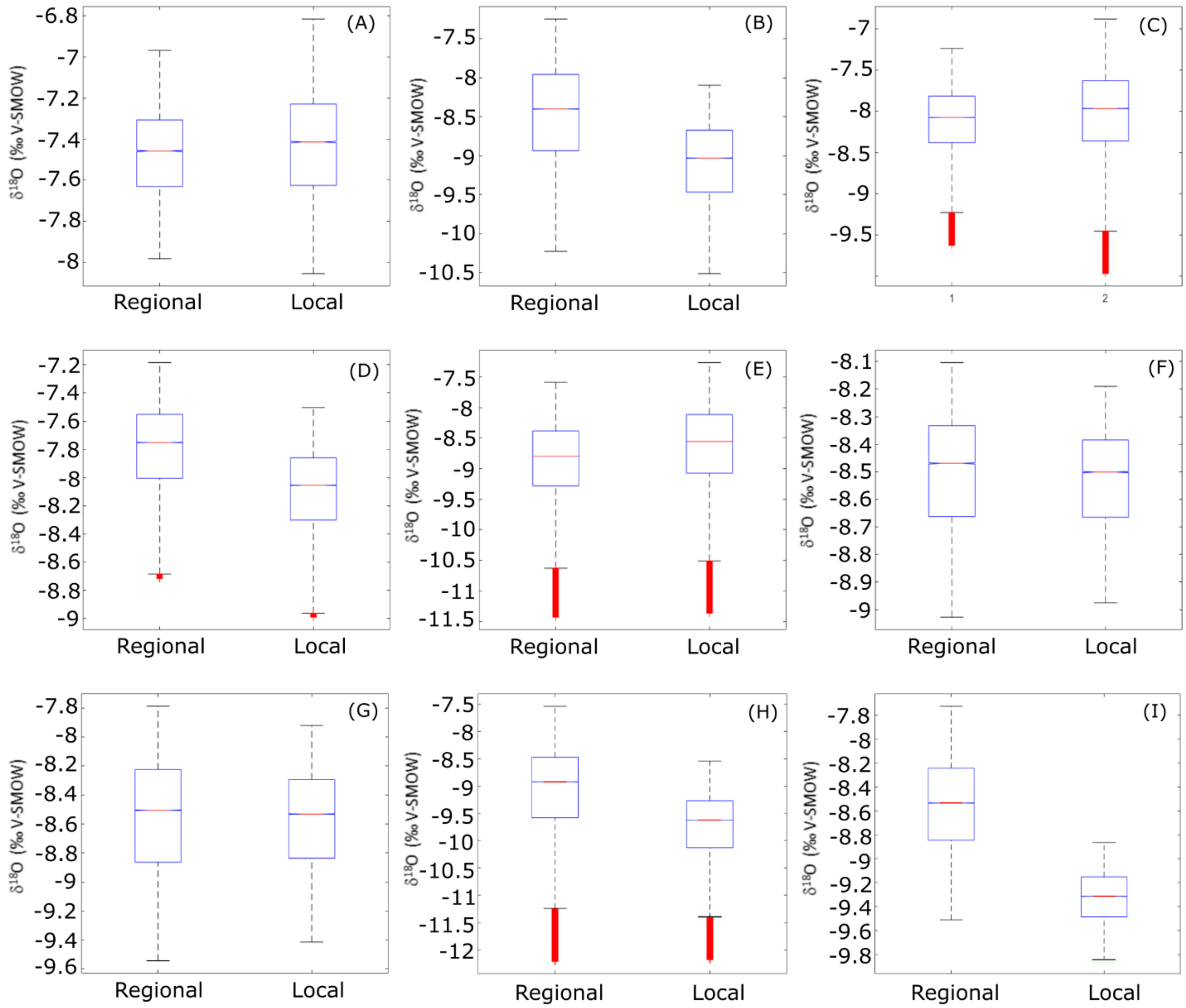

Figure 7. Regional and Local $\delta^{18}O$ values distributions as derived by applying the relative gradients by GIS analysis for: (A) Conero Mt., (B) Montagna dei Fiori Ridge, (C) Gola della Rossa area, (D) Furlo Ridge, (E) Sibillini Mts., (F) Rasiglia area, (G) Boschetto alto area, (H) Gran Sasso d'Italia area, (I) Mt. Modino area. The red bold lines in (C), (D), (E), (H) represent the $\delta^{18}O$ values distribution outliers.

According to the last result, local and regional $\delta^{18}O$ gradients have been applied to the mean $\delta^{18}O$ value for each analyzed spring and compared to the ones available in the literature (Table 2), thus computing the springs/well mean recharge area elevation (CIRE, Petitta et al., 2010; Petitta et al., 2022). In general, the application of regional and local gradients (obtained by this study) to the springs or wells data shows similar results (Figure 8). This result is much more apparent in Furlo ridge and Gola della

Rossa area, in which elevations are lower, and the low topographic gradients smooth the regional $\delta^{18}O$ distribution above the ridges with respect to other areas where the complex orography and the higher topographic gradient accentuate the differences between regional and local $\delta^{18}O$ distribution. The latter is the case of Sibillini Mts. and Montagna dei Fiori ridge. In general, the $\delta^{18}O$ gradients proposed by the available literature (Conversini and Tazioli, 1993; Tarragoni, 2006; Desiderio et al., 2005; Longinelli and Selmo, 2003; Tazioli et al., 2007; Zuppi et al., 1974; Bono et al., 2005) do not give actual indication on the spring/well mean recharge area elevation for the U-M domain. In some cases, the mean recharge area elevation is higher than the highest peak of the study area, in other cases seems to be lower than the spring elevation or shows a negative elevation value. In this context, a significant discrepancy between the Mt. Modino springs recharge area elevation obtained by the application of the regional gradient obtained in this study and the local gradient proposed by Cervi et al., 2014 can be noticed. The elevation difference is approximately 600 m, and the quote obtained by applying the regional gradient proposed in the present work is 1688 m, a value slightly higher than the maximum elevation of the study area (Cervi et al, 2014). Besides, for the Gran Sasso d'Italia area, both the regional and the Sibillini Mts. $\delta^{18}O$ gradients seem representative to estimate the springs recharge elevation pertaining to it. This aspect strengthens the evidence that the regional gradient obtained from this study fits very well for the area in which the precipitation samplers are located (U-M domain) and for the Gran Sasso d'Italia area (located less than 30 km far from the Sibillini Mts. area, and even characterized by similar meteorological and morphological conditions), while it seems not representative of the precipitation isotopic signature of external northern areas, providing an overestimation of the computed springs recharge area elevation.

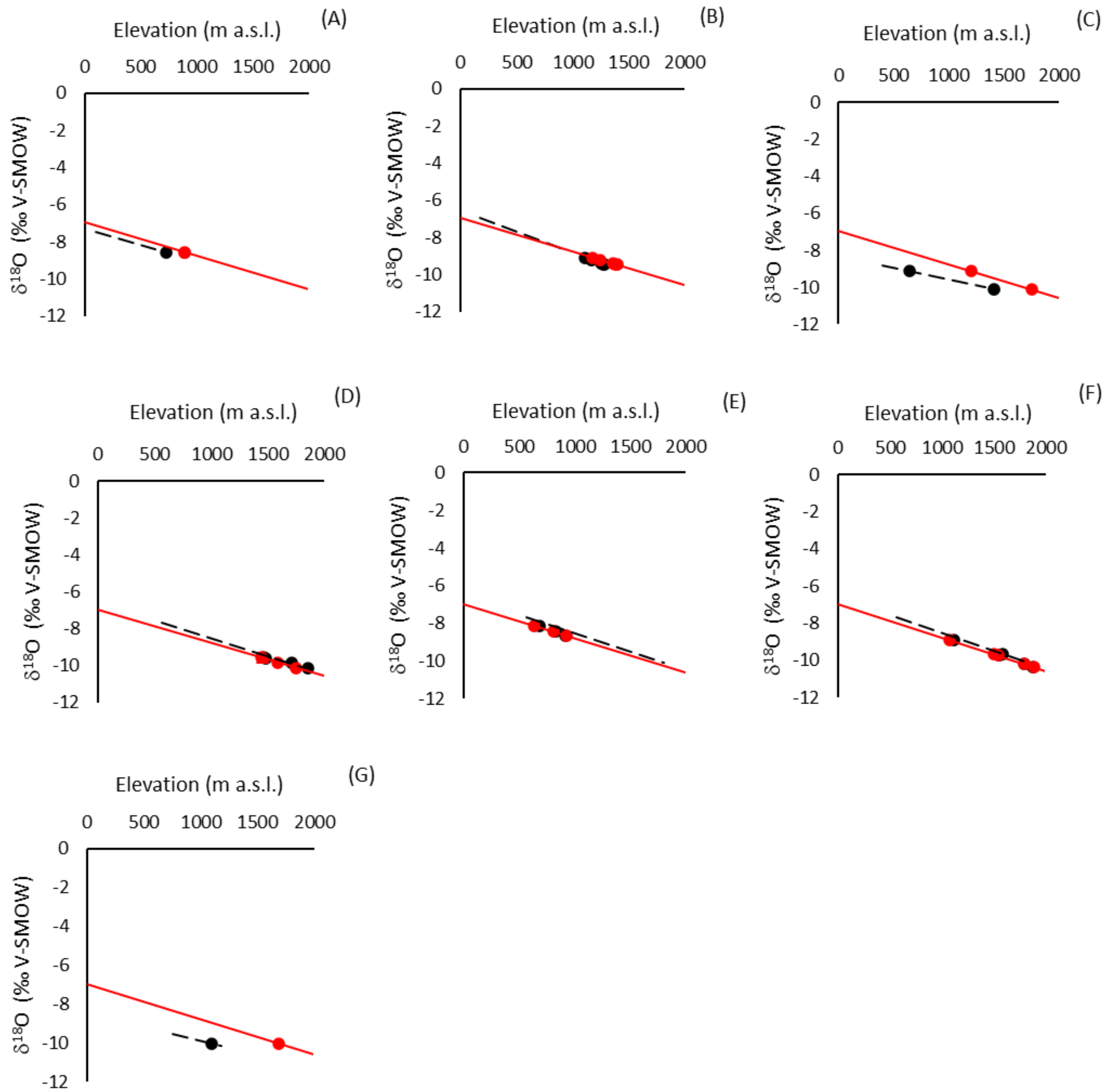

Figure 8. Application of local (black dashed line) and regional (red solid line) inverse δ^{18}O -elevation relation to the analyzed springs: (A) Furlo Ridge, (B) Gola della Rossa area, (C) Montagna dei Fiori Ridge, (D) Sibillini Mts., (E) Sibillini Mts. applied to Rasiglia and Boschetto alto areas, (F) Sibillini Mts. applied to Gran Sasso d'Italia area, (G) Mt. Modino area. The red dots represent the springs (δ^{18}O vs elevation), obtained by applying the regional δ^{18}O gradient to the spring's isotopic values, while the black dots represent the springs (δ^{18}O vs elevation), obtained by applying the local δ^{18}O gradient to the spring's isotopic values.

Observing the results reported in table 2, the δ^{18}O gradient proposed by Giustini et al., 2016 seems to provide more similar computed springs recharge area elevations to the ones (local and regional) obtained by this study. For this reason, Figure 9 shows the precipitation δ^{18}O values distribution obtained by Giustini et al., 2016 in Italy vs the new regional one proposed in this study. The maps share the same colorimetric scale, and it is possible to observe a general congruence between the $\delta^{18}O$ values distribution. The differences in the hillslopes and coastal areas can be attributed to a lack of monitoring points between the coastline and the Apennine chain or to the interpolation method used to spatializes the $\delta^{18}O$ values. Indeed, Giustini et al., 2016, generated a first map of $\delta^{18}O$ distribution of precipitation in Italy with a considerable number of data obtained from a literature review, and the Bowen and Wilkinson's method was used for spatial interpolation. As a result, the influence of latitude and altitude variables was combined. However, as declared by the authors, the map suffers from some limitations: (i) it is not based on consistent time-interval data; (ii) unverified local "bulls-eye" anomalies were observed, and this is probably related to the interpolation method. The first limitation is sharable with this study and was also reported in previous similar investigations, whereas the second limitation does not seem to invalidate the new regional map presented in this study, which only takes into account spatialization as a function of elevation since the longitudinal extent of this study is limited at about 150 km of central Italy. Other deviations of two datasets can be observed in the mountainous region, where the results obtained in the present study are more detailed as the monitoring system considers even the topographical and meteorological issues (i.e., shadow effect, snow-drift effect, etc.). Anyway, the inner parts of the map (i.e., the Apennines chain) are really those of interest for such kind of studies, and a slight difference in isotopic composition can result in a not negligible change in the understanding of hydrogeological setting. In addition, it must be stated that the study performed by Giustini et al., 2016 was successfully developed at national scale, and did not claim to achieve detailed maps to be used in specific hydrogeological applications.

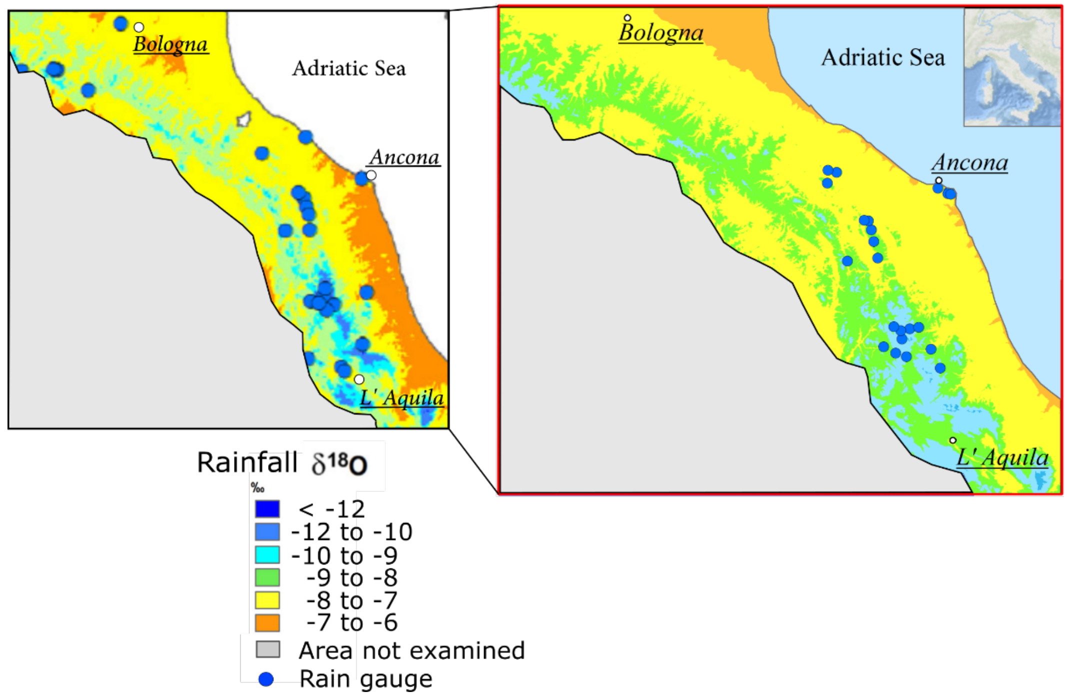

Figure 9. Precipitation δ^{18}O values distribution in the study area by Giustini et al., 2016 (left side) compared to the one obtained in this study (right side).

Geo-isotopic modelling results

The integrated approach with isotopic and geological data aimed at defining a geo-isotopic recharge model for each analyzed spring or well, highlights both realistic and unrealistic scenarios with respect to the hydrogeological settings of the study sites (Figure 10).

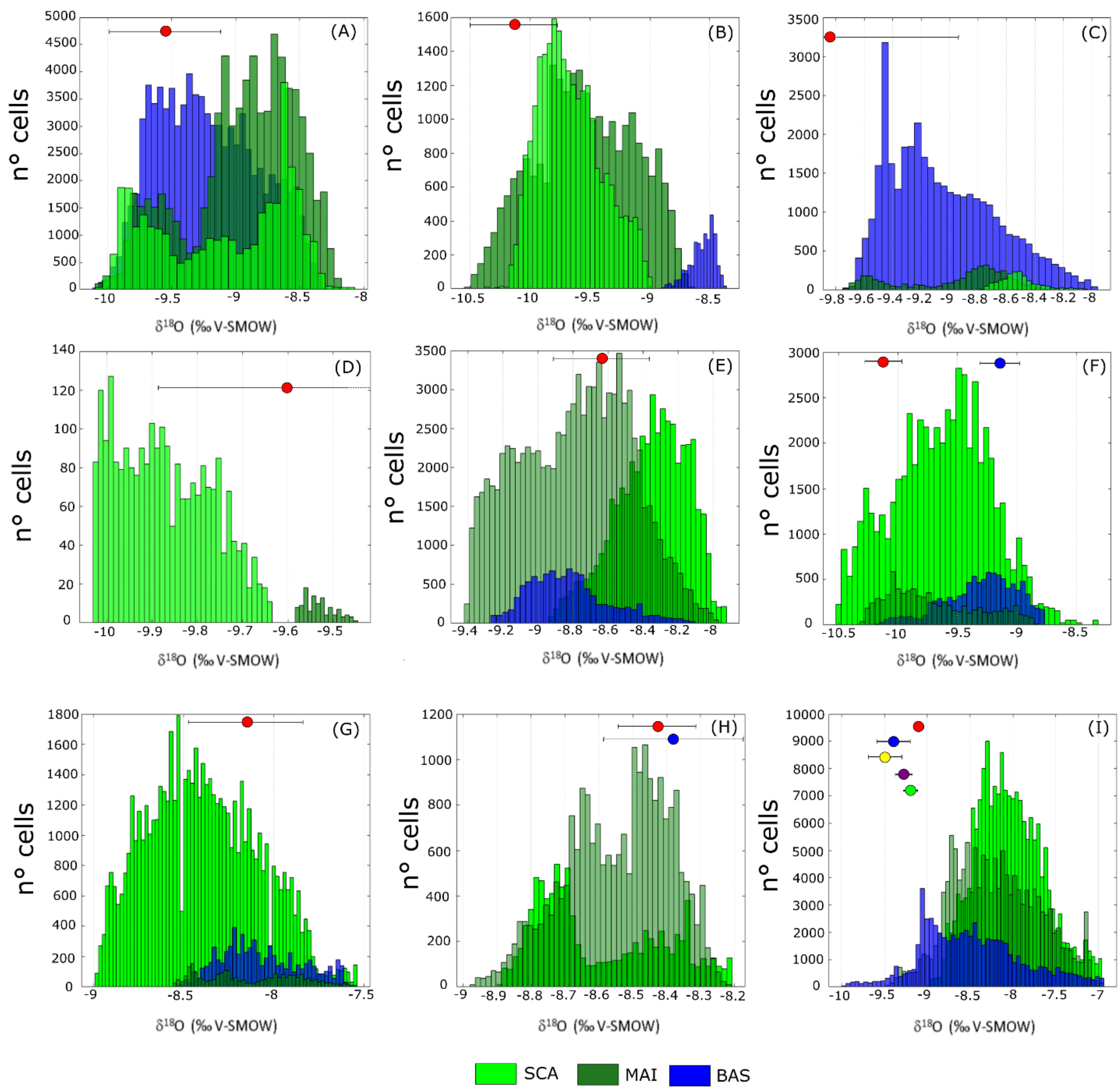

Figure 10. Precipitation $\delta^{18}O$ distribution for each aquifer (considered as outcropping of SCA, MAI and BAS geological formations) for each sudy area: A) Sordo area (B) Nera area (C) Capodacqua area (D) Conserva (Castelluccio plain area) (E) Boschetto alto area (F) Montagna dei Fiori Ridge (red dot: Castellano linear springs, blue dot: Castellano sulphur springs) (G) Furlo Ridge (H) Rasiglia area (red dot: Capovena, blue dot: Alzabove) (I) Gola della Rossa area (red dot: Montenero, blue dot: Val di Castro, yellow dot: Gorgovivo spring, purple dot: Gorgovivo new wells, green dot: Stampanata). For each domain the average springs/wells $\delta^{18}O$ value ± σ is plotted in the chart bar.

The statistically based method, performed in step two, whose outcomes are shown in table 3, gives more accurate information about the possible recharge area of a spring by including spatialized hydrogeological information on the topographical surface. This outcome can provide refined insights about the groundwater recharge areas convey to a specific spring with respect to the most used isotopic approach based on the computation of groundwater recharge areas elevation starting from $\delta^{18}O$ – elevation gradient applied to the selected springs/well isotopic data (CIRE, Petitta et al., 2010; Petitta et al., 2022). However, we stress that in few cases the geo-isotopic modelling does not provide results full in line to the geo-hydrological features. This is the case of the San Chiodo spring located in the Nera area of Sibillini Mts. (Nera area, Figure 1). The selected area used in the model computation for the San Chiodo spring corresponds to the upspring hydrological basin (Figure 11A). This selection, in fact, underestimates the actual spring recharge area. Indeed, feeding of 57.6% from SCA, 42.4% from MAI and 0% by BAS is in contrast with the results obtained by Boni and Petitta, 2007, Tarragoni, 2006 and by Nanni et al., 2020. Nanni et al., 2020 and Fronzi et al., 2021 demonstrate with artificial tracing tests a groundwater flow external to the hydrologic basin coming from Vettore Mt. - Castelluccio area (Figure 11A). Moreover, it has been recognized by Rosen et al., 2017 that the SO_4 content of about 21 mg/L makes the spring mainly fed by the BAS aquifer (Boni, 2010; Boni and Petitta, 2007; Fronzi et al., 2021).

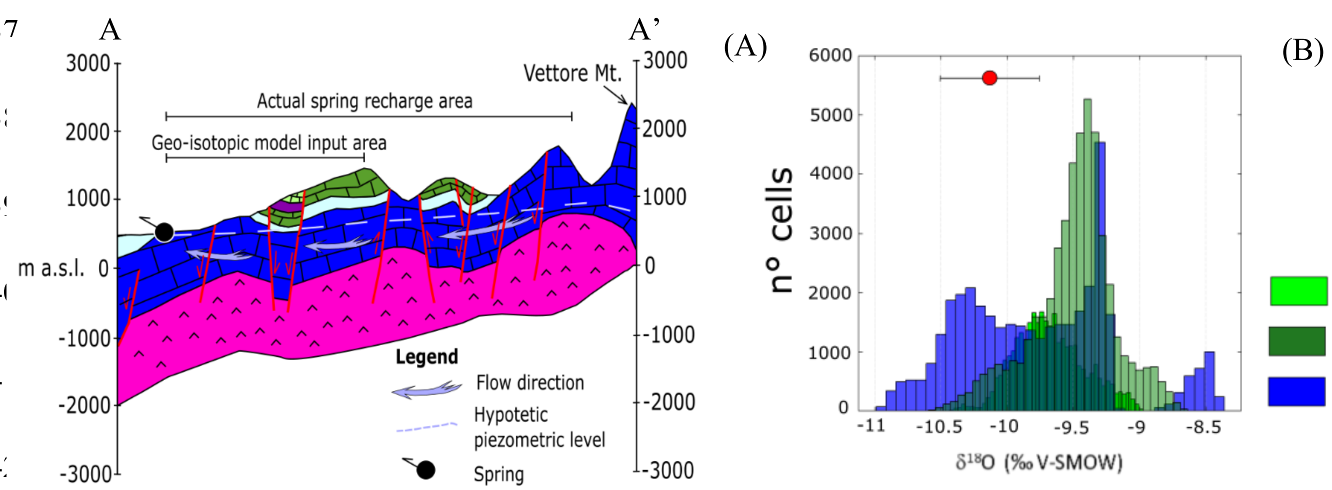

Figure 11. (A) Hydrogeological cross-section (trace reported in S1) modified from Fronzi et al., 2021 with the hypothetic piezometric level and the San Chiodo spring. The vertical scale is exaggerated to better visualize the piezometric gradient, the colors in section refers to the schematic stratigraphic column reported in Figure 2. (B) Precipitation $\delta^{18}O$ distribution for each aquifer of the new selected area and the average San Chiodo springs $\delta^{18}O$ value ± σ.

In light of these evidence, the geo-isotopic model input area was extended with the aim of making it as similar as possible to the actual recharge area by including the zone nearby the Vettore Mt. as suggested by the available literature. In this case the overlap between the $\delta^{18}O$ value ± σ of the San Chiodo spring and the $\delta^{18}O$ aquifers distribution of the new selected area (Figure 11B) permits to obtain results more comparable to the actual hydrogeological setting, with the BAS contributing to the recharge area for the highest percentage (40%) compared to SCA (36%) and MAI (24%). The results are likely still affected by the prevailing outcropping of SCA in the selected area that can biased the results. On the contrary, the minor recharge contribution due to the MAI can feeds the spring through the fault system that put in hydraulic contact MAI and BAS upstream of the spring (Figures 11A).

In all the other cases the geo-isotopic modelling gives good to excellent results in full accordance with the hydrogeological features. For instance, the springs and wells belonging to the Gola della Rossa area are mainly fed by BAS aquifer, as demonstrated by Tazioli, 2017. The Castellano linear and Sulphur springs, located in the Montagna dei Fiori ridge, show a higher BAS contribution to the Sulphur springs with respect to the linear ones located along the Castellano stream, mainly fed by SCA aquifer as reported by Tazioli et al., 2020. However, also in this case it has to be noticed that the prevailing outcropping of SCA in the study area can biased the results. In fact, Tazioli et al., 2020 suggests that the Sulphur springs in the area are mainly fed by BAS aquifer. The results obtained in the Sordo, Castelluccio and Capodacqua areas are comparable to the hydrogeological setting and this result is probably supported by the selection of a model's computation areas not far from the real springs recharge areas. As concerns the Rasiglia area (Alzabove and Capovena springs), the model results show recharge 80% from MAI and 20% from SCA, almost fully in line with the hydrogeological setting of the area.

By analyzing in detail the results obtained from the new proposed geo-isotopic model, it is possible to deduct that this approach can be satisfactory applied only if the following conditions are met:

(i) The infiltration rate of the meteoric water is fast enough to avoid fractionation processes that may alter the isotopic signal of the precipitation input within the aquifer. This characteristic is quite true for most of the analyzed springs as reported by Nanni et. al, 2020, who indicated that the infiltration processes of meteoric water in the U-M carbonate aquifers are as fast as the water movement within the fissured rock matrix constituting the same aquifers.

(ii) The standard deviation and the mean spring's isotopic value is used to calculate the overlapping distributions, because values outside this range imply the occurrence of peculiar meteoric recharge phenomena. Considering the fast groundwater movement and the relatively short lag time between precipitation and discharge increase in these hydrogeological systems (Fronzi et al., 2020b), peculiar meteoric events may in fact influence the spring isotopic signal and therefore they are treated in this research as outliers altering the significance of the mean recharge area elevation obtained by the precipitation isotopic data only.

Concerning point (ii) it should be noted that the occurrence of peculiar meteoric phenomena contributes to the recharge only as a minor component of the entire process. Moreover, a recent study of Petitta et al., 2022 states that the groundwater circulation of the carbonate aquifers of central Italy mainly involves the fractures and fissures network, and only secondarily the karst conduits. The karst features, in fact, mostly characterize the vadose zone of the aquifers and the epiphreatic region (Nanni et al., 2020 and Cambi et al., 2022). These properties made it possible to validate the choice of using the mean $\delta^{18}O \pm \sigma$ interval values of the analyzed springs and wells as representative of their recharge regime. In fact, the distribution of isotopic values falling within the mean $\delta^{18}O \pm \sigma$ interval encompasses most of the meteoric recharge contributions to groundwater. The methodological approach presented in step two actually represents an improvement of the isotopic application to hydrogeological studies, if compared to the CIRE, as it spatializes the distribution of precipitation isotopic values over the hypothetical recharge area of the analyzed springs/wells and attempts to provide quantitative information about which outcropping aquifer is involved in the recharge processes of the spring itself.

Conclusions

In conclusion, this work aims to develop a conceptual and methodological approach to define and refine the isotopic investigation in those areas characterized by hydrogeological setting difficult to interpret. A new regional-scale gradient, valid in a wide area of the central Apennines, was proposed in this study; its suitability for hydrogeological purposes, together with the application of more local gradients relative to smaller areas, was then verified by means of an advanced isotopic modelling via a two-step approach. This permitted at first to assess if the regional gradient obtained by 23 meteoric sampling points shall overcame the limits of specific isotopic studies in single hydro-structures or ridges characterized by high complexity of orography and hydrogeological setting. In general, for detailed hydrogeological studies, the local isotopic gradients are preferred to evaluate the hydrogeological features and to identify the springs recharge area. However, we stress that the new regional $\delta^{18}O$ gradient provides useful results in all the U-M domain (150 km latitudinal length) to assess springs or wells mean recharge area elevation, and in the "southern external area" those of Gran Sasso d'Italia. On the contrary, the first step of the isotopic modelling, when applied to the "northern external area" (i.e., Mt. Modino area), suggests a lack of pertinency of the new regional $\delta^{18}O$ gradient far from the precipitation sampling points. Certainly, the new updated regional $\delta^{18}O$ gradient (-0.18 ‰/100 m) is preferable to most of those available in literature that generally largely overestimate the average recharge area elevation and, only in few cases, tend to underestimate it. The comparison between the spatialized $\delta^{18}O$ precipitation values performed by Giustini et al., 2016 and the one obtained by this study stresses the importance of setting up a monitoring system taking into account all the possible meteorological features conditioned by the presence of even very inhomogeneous morphologies (steep slopes, intramountain basins), which characterize the mid-mountain and mountain areas even outside the Italian territory. For this reason, one of the main objectives of this study has been achieved presenting the new $\delta^{18}O$ gradient specifically developed for the Inner and Outer ridge of the U-M domain covering a wide area in central Italy. A more detailed isotopic investigation performed in step two permitted to evaluate with a statistic approach the belonging to a specific aquifer of springs or wells recharge areas (SCA, MAI and BAS in this case). This approach works well where the analyzed spring is not fed by regional deep groundwater flows, and if the operator selects a model area comparable to the real spring recharge area. In all the other cases a general no-agreement with the real hydrogeological setting is observed, and it would be necessary to modify the model's computation area in an iterative way. A possible future development of this approach may consist in coupling the isotopic model with a hydrogeological balance model starting from precipitation and temperature in the hypothesized spring's recharge area, obtaining the modelled spring discharge value and comparing it to the measured one (Salerno and Tartari, 2009). The importance of the presented model lies in the fact that when an operator performs a hydrological investigation starting from isotopic data only, he can notice step by step if there are inconsistencies between purely modelled results and the reality. If a difference is observed between the results obtained in the various steps and the real hydrogeological setting, the cause has often to be found in external contributions of deep regional flows into the hydro-structure; another reason can be represented by occurrence of wrong selection of the recharge area, likely to be not consistent with the real one. This may include the case of zones characterized by several aquifers in contact each other not only for stratigraphic reasons but also for tectonic lineaments and faults (also not regional faults) as demonstrated by Fronzi et al., 2021 and Mammoliti et al., 2022.

Additional improvements may benefit from detailed hydrochemical sampling and analysis on springs and wells water. Indeed, if hydrochemical data can validate the interaction between groundwater and the lithologies involved during infiltration and filtration processes (André et al., 2005), they can fill the issues related to the groundwater mixing between different aquifers by supporting the development of multi-component mixing models.

Some limitations of the method, regarding step two, may result from the large amount of isotopic data required on groundwater. However, considering that the application of isotopic techniques has been increasing over the years as it is a very effective technique to investigate recharge, storage, and discharge of groundwater (Jasechko, 2019, among others), this method can be applied in many areas, especially those exploited for drinking purposes, where isotopic data are frequently available.

Regarding precipitation isotope data availability, at first instance the available datasets (e.g., IAEA-GNIP) or available literature data could be used to derivate the distributed isotopic values in a specific area, waiting, if possible, for a more detailed definition of specific $\delta^{18}O$ - elevation relationships of the investigated areas.

As matter of fact, the proposed geo-isotopic method can be very useful to highlight a series of warnings and suggestions that, if adopted, can provide important information about the springs recharge area and therefore it can be useful to develop programs of groundwater protection and management of drinking water resources.

Acknowledgments

The authors would like to thank Mirco Marcellini for the essential help in data acquisition. This paper has been partially supported by "WAFER" project at CNR (Consiglio Nazionale delle Ricerche). The research study has been supported by some water companies: CIIP, Marche Multiservizi, and VivaServizi, to whom we extend our thanks.

Authors' Note

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Supporting Information

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding author.

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Table 1. Characteristics of monitoring sampling points. "-" data not available.

Point Name	N° Study site	Elevation m a.s.l.	Coordinates WGS 84 Projection UTM 33N East-North	Total n° of samples	Sampling periods start/end	Reference
			Precipitation samplers			
Calmazzo	1	96	323075- 4839535	22	Nov-2013/Jan-2016; Jun-2016/May-2017	This study
Cesane-Foresta	1	633	320062- 4841037	22	Nov-2013/Jan-2016; Jun-2016/May-2017	This study
Furlo	1	430	317514- 4835812	22	Nov-2013/Jan-2016; Jun-2016/May-2017	This study
Mt. Conero	2	540	387030- 4822830	34	Apr-2010/Jun-2013; Feb-2014/Mar-2017	Mussi et al., 2017
Poggio	2	241	384815- 4823568	26	Apr-2010/Jun-2013; Feb-2014/Mar-2017	Mussi et al., 2017
Portonovo	2	16	386413- 4824212	34	Apr-2010/Jun-2013; Feb-2014/Mar-2017	Mussi et al., 2017
Montedago	2	167	380187- 4827001	112	Oct-2011/Dec-2020	IAEA, GNIP
Serra San Quirico	3	170	340353- 4812312	46	Apr-2002/Aug-2004; Mar-2008/Jan-2009; Jul-2011/Jul-2013	Tazioli, 2017
San Giovanni	3	580	340952- 4806102	46	Apr-2002/Aug-2004; Mar-2008/Jan-2009; Jul-2011/Jul-2013	Tazioli, 2017
Pian dell' Elmo	3	942	342731- 4800821	46	Apr-2002/Aug-2004; Mar-2008/Jan-2009; Jul-2011/Jul-2013	Tazioli, 2017
Gagliole	3	850	344169- 4791329	26	Mar-2008/Jan-2009; Jul-2011/Jul-2013	Tazioli, 2017
Mt. Murano	3	515	337597- 4812951	26	Mar-2008/Jan-2009; Jul-2011/Jul-2013	Tazioli, 2017
Belvedere	4	635	326270- 4789533	26	Mar-2008/Jan-2009; Jul-2011/Jul-2013	Tazioli, 2017
Castelluccio	6-7-8-9	1444	353566- 4743318	21	Feb-2013/Jul-2014;	This study
San Pellegrino	6-7-8-9	974	349719- 4735689	21	Feb-2013/Jul-2014	This study
Norcia	6-7-8-9	567	343455- 4739733	21	Sept-2012/Jun-2014; Mar-2017/Oct-2019	This study
Mt. Prata	6-7-8-9	1800	353508- 4748332	32	Feb-2008/Jan-2009; Sept-2012/Jul-2014; Nov-2020/Mar-2021	This study
Vallefiume	6-7-8-9	755	362766- 4749957	7	Feb-2013/Jul-2014	This study
Foce	6-7-8-9	930	358723- 4749058	32	Oct-2012/Jul-2014	This study
Capodacqua	6-7-8-9	805	355607-4733240	32	Feb-2008/Sept-2009	This study
Castelsantangelo sul Nera	6-7-8-9	737	349249- 4750582	21	Oct-2012/Jul-2014	This study
Acquasanta	n.a.	400	370447- 4737449	17	Mar-2013/Feb-2014; Apr-2019/Jul-2021	This study
Ceppo	n.a.	1334	374443- 4725601	17	Mar-2013/Feb-2014; Apr-2019/Jul-2021	This study
			Wells			

P2 well	1	265	317905-4835531	22	Jul-2011/Jul-2013	This study
Gorgovivo new wells	3	185	339685- 4810640	36	Jan-2008/Mar-2009; Apr-2011/Aug-2013	Tazioli, 2017
			Springs			
Gorgovivo	3	185	339613- 4810533	54	Jan-2008/Mar-2009; Apr-2011/Aug-2013	Tazioli, 2017
Montenero	3	690	343498- 4794329	10	Jan-2008/Mar-2009; Apr-2011/Aug-2013	This study
Val di Castro	3	675	341767- 4803139	7	Jan-2008/Mar-2009; Apr-2011/Aug-2013	This study
Stampanata	3	765	341782- 4800485	8	Jan-2008/Mar-2009; Apr-2011/Aug-2013	This study
Boschetto alto	4	560	320515-4788550	5	Mar-2008/Mar-2009; Apr-2011/Aug-2013	This study
Capovena	5	630	325497-4758440	9	Feb-2008/Jan-2009; Apr-2011/May-2012	Conversini and Tazioli, 1993
Alzabove	5	640	325607-4758326	8	Feb-2008/Jan-2009; Apr-2011/May-2012	Conversini and Tazioli, 1993
San Chiodo	6	760	349793-4750519	16	Mar-2009/Jan-2010; May-2013/Feb-2014; Dec-2015/Jun-2020	This study
Conserva (Castelluccio Plain)	7	1511	351637-4741216	5	Mar-2009/Jan-2010; May-2017	This study
Sordo linear springs	8	605	344869-4738783	22	Apr-2013/Feb-2014; Dec-2017/Jun-2019	This study
Capodacqua	9	841	355552-4733185	56	Dec-2002/May-2009; May-2016/Apr-2017; Sept-2017/May-2019	This study
Castellano linear springs	10	310	381791-4742772	11	Sept-2016/Apr-2019	Tazioli et al., 2020
Castellano sulphur springs	10	315	381599-4742439	7	Sept-2016/Apr-2019	Tazioli et al., 2020
Spring n°17	11	1315	-	2	Jan-2001/Nov-2001	Barbieri et al., 2005
Spring n°18	11	1524	-	2	Jan-2001/Nov-2001	Barbieri et al., 2005
Spring n°19	11	900	-	2	Jan-2001/Nov-2001	Barbieri et al., 2005
Spring n°20	11	650	-	2	Jan-2001/Nov-2001	Barbieri et al., 2005
Spring n°21	11	690	-	1	Jan-2001/Apr-2001	Barbieri et al., 2005
Mt. Modino springs	12	800-1200	-	16	Jun-2005/Sept-2008	Cervi et al., 2015

Table 2. Mean recharge area elevation determined for each monitored spring or well by applying different $\delta^{18}O$ vertical gradients, (the numbers corresponds to the references from which the $\delta^{18}O$ vertical gradients are taken): 1- Local gradient lines 2- Regional gradient line 3 - Zuppi, 1974 Adriatic side 4 - Zuppi, 1974 Tyrrhenian side 5 - Conversini and Tazioli, 1993 6 - Bono et al., 2005 7 - Tazioli et al., 2007 8 - Desiderio et al., 2005 9 -Tarragoni, 2006 10 - Longinelli and Selmo, 2003 11 - Giustini et al., 2016. "*" $\delta^{18}O$ vertical gradients taken from Cervi et al., 2014.

Spring/well name (n° study site)	Mean $\delta^{18}O$ ‰ ± σ vs V-SMOW	1	2	3	4	5	6	7	8	9	10	11
P2 well (1)	-8.59±0.11	723	900	1078	1003	971	1642	968	146	1005	1939	705
Gorgovivo Spring (3)	-9.48±0.06	1282	1394	1393	1261	1335	2100	1285	829	1409	2580	962
Gorgovivo new wells (3)	-9.45±0.03	1270	1377	1383	1253	1323	2085	1275	807	1396	2559	954
Montenero (3)	-9.09±0.06	1113	1177	1138	1052	1041	1730	1028	277	1083	2062	754
Val di Castro (3)	-9.21±0.1	1165	1244	1298	1183	1225	1962	1189	623	1287	2387	884
Stampanata (3)	-9.42±0.09	1256	1361	1372	1244	1311	2070	1264	785	1383	2538	945
Boschetto alto (4)	-8.92±0.28	917	927	1195	1099	1107	1812	1086	400	1155	2177	800
Capovena (5)	-8.43±0.12	826	811	1021	956	906	1560	911	23	933	1823	659
Alzabove (5)	-8.17±0.22	648	630	929	881	799	1426	818	-177	814	1636	583
San Chiodo (6)	-10.11±0.39	1850	1744	1617	1445	1594	2426	1511	1315	1696	3037	1145
Conserva (Castelluccio Plain) (7)	-9.6±0.28	1479	1461	1436	1297	1385	2163	1329	923	1464	2668	997
Sordo linear springs (8)	-9.57±0.39	1464	1444	1426	1288	1373	2147	1318	900	1451	2647	989
Capodacqua (9)	-9.82±0.67	1712	1583	1514	1360	1475	2276	1407	1092	1564	2827	1061
Castellano linear springs (10)	-10.12±0.17	1407	1750	1621	1448	1598	2431	1514	1323	1701	3044	1148
Castellano sulphur springs (10)	-9.13±0.16	646	1200	1269	1160	1193	1921	1161	562	1251	2329	861
Spring n°17 (11)	-9.74±0.88	1552	1538	1486	1337	1443	2235	1379	1031	1528	2769	1038
Spring n°18 (11)	-10.36±0.44	1873	1883	1706	1517	1697	2555	1600	1508	1810	3217	1217

Spring n°19 (11)	-10.2±0.74	1790	1794	1649	1471	1631	2472	1543	1385	1737	3102	1171
Spring n°20 (11)	-9.68±n.a.	1583	1505	1507	1355	1467	2266	1400	1077	1555	2813	1055
Spring n°21 (11)	-8.9± n.a.	1117	1072	1188	1093	1098	1802	1079	385	1146	2163	795
Mt. Modino springs (12)	-10.01±0.32	1098*	1688	1582	1416	1553	2374	1475	1238	1651	2964	1116

Table 3. Aquifers' relative percentage to the total that can potentially feed the analyzed springs or wells, obtained by the overlapping between aquifers' $\delta^{18}O$ distribution and the average springs/well $\delta^{18}O$ value ± σ.

Spring/well name (n° study site)	%BAS	%MAI	%SCA
Gorgovivo Spring (3)	85.5	14.5	0
Gorgovivo new wells (3)	78.9	21.1	0
Montenero (3)	70.1	29.9	0
Val di Castro (3)	50.9	49.1	0
Stampanata (3)	63.9	36.1	0
San Chiodo (6)	0	42.4	57.6
Conserva (Castelluccio Plain) (7)	0	8.4	91.6
Sordo linear springs (8)	60.5	22.2	17.3
Capodacqua (9)	93.2	6.8	0
Castellano linear springs (10)	3.9	19.0	77.1
Castellano sulphur springs (10)	33.1	8.5	58.4