Development of a water monitoring network in the Pesaro-Urbino province (northern Marche, central Italy) aimed at seismic precursors

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INTRODUCTION

In the last decades, several studies stated that earthquakes of moderate to large magnitude ($M_w > 4$) are able to produce detectable changes in the geochemical composition of the waters circulating close to the epicentral area and/or in hydrogeological features of the aquifers involved (Cicerone et al., 2009; Wang & Manga, 2021). These variations, also called "seismic tracers" (Martinelli, 2020), may be of different nature and are generally observed before (from months to days), concurrently, or immediately after the seismic event (Thomas, 1998; Cicerone et al., 2009). Notable changes were related to discharges of springs, piezometric levels in wells, chemical and isotopic composition of waters and dissolved gases and groundwater physico-chemical parameters (Cicerone et al., 2009; Wang & Manga, 2021). These modifications are considered to be produced by the earthquake and its preparation process (*i.e.*, the seismic cycle), since several chemical and physical processes may be triggered (Doglioni et al., 2014). Precursory changes were observed in different geological and geodynamic settings characterized by intense seismic activity worldwide. However, due to the fact that these changes are often transitory and strictly site-sensitive, the identification of possible and suitable seismic precursors represents one of the major challenges for geoscientists (Franchini et al., 2021). Consequently, to improve scientific knowledge on this topic, the development of multi-parametric water monitoring networks located in seismic-prone areas is a fundamental step towards a better understanding of the underlying relationship between the seismic cycles and the seismic tracers (Franchini et al., 2021; Chemeri et al., 2024). Therefore, the aim of this research was to characterize the geochemistry of the waters (springs and wells) discharging in the Pesaro-Urbino (hereafter, PU) province, which was characterized in both past and recent history by an intense seismic activity, to define the main processes controlling the waters (and dissolved gases) composition and, later, to develop a hydrogeochemical monitoring network by applying a three-step hydrogeochemical approach: *i*) characterization, *ii*) detailed isotopic analysis and *iii*) monitoring. The outcomes can be summarized in to: (a) define the acting geochemical processes and the hydrogeological pathways, (b) investigate the possible interplay between deep-originated fluids and shallow aquifers, (c) evaluate the possible use of selected geochemical parameters as seismic tracers for this specific study area and (d) select sampling sites that should be included in a continuous water-monitoring network aimed at seismic surveillance (Franchini et al., 2021; Chemeri et al., 2024).

GEOLOGICAL AND GEODYNAMIC SETTING

The PU province is located in the northern Marche (Central Italy) within the Umbria-Marche Apennines, which represent the external part of the Northern Apennines, developed during the Miocene. The study area was recently interested by a moderate seismicity (up to 6.4 M_w), in terms of both frequency of events and magnitudes, related to the presence of two major composite seismogenic structures (DISS Working Group, 2021), located in the Umbria-Marche Apennines, along the Mt. Catria-Mt. Nerone Ridge, and on the Adriatic coast and off-shore areas, respectively (Fig. 1). The activity on the Adriatic coast and offshore is characterized by events with magnitudes usually lower than 6 (*e.g.*, the 1916 Rimini – M_w: 5.8 -, the 1930 Senigallia – M_w: 5.8 –, and the recent Marche offshore – M_w: 5.5 – seismic sequences) and related with transpressive and compressive structures. Contrarily, along the Apennine chain, the most destructive and strongest events are generally associated with extensional movements, such as the 1781 Cagli earthquake ($M_w = 6.4$) (Chemeri et al., 2025a and reference therein).

The study area features a variable topography and a complex geological-structural setting, with the outcropping geological formations spanning from Lower Jurassic to north-west to Miocene-Pleistocene deposits covered by Quaternary alluvial deposits in the coastal

area, to the east (Conti et al., 2020 and therein references). Moreover, it must be remarked that the Burano Fm, which is not outcropping in the study area, occurs at the bottom of the succession (Capaccioni et al., 2001; Conti et al., 2020), and was reached at 620 and 1550 m depth at the Nerone-Catria and Cesane Ridges areas (Fig. 1), respectively, during hydrocarbon exploration drillings.

Hydrogeological features

In the study area, three superimposed aquifers are present (Capaccioni et al., 2001). The upper aquifer is hosted in the limestone and marly-limestones belonging to the Scaglia Rossa and Scaglia Bianca Fms (*i.e.*, the Scaglia Calcarea aquifer), whilst the intermediate system is within the Maiolica Fm (Maiolica Aquifer). Eventually,

the deepest is in the Calcare Massiccio and Corniola Fms (Basal Aquifer). The latter is the major hydrogeological unit in the area, being characterized by high infiltration rates and high permeability due to extensive karstification. The Basal Aquifer is confined, at the bottom, by the Burano Fm, which acts as a regional aquiclude. Marlstones and clayey-marlstones pertaining to the Marne a Fucoidi Fm represent an aquiclude between the Scaglia Calcarea and Maiolica aquifers, whilst the Calcare Massiccio and Maiolica aquifers are separated by the Rosso Ammonitico, Calcari Diasprini, and Bugarone Fms (Capaccioni et al., 2001). Furthermore, minor and shallow aquifers can also be recognized, and they are hosted in the *i*) siliciclastic Bisciaro and Marnoso Arenacea Fms and *ii*) Quaternary and alluvial deposits.
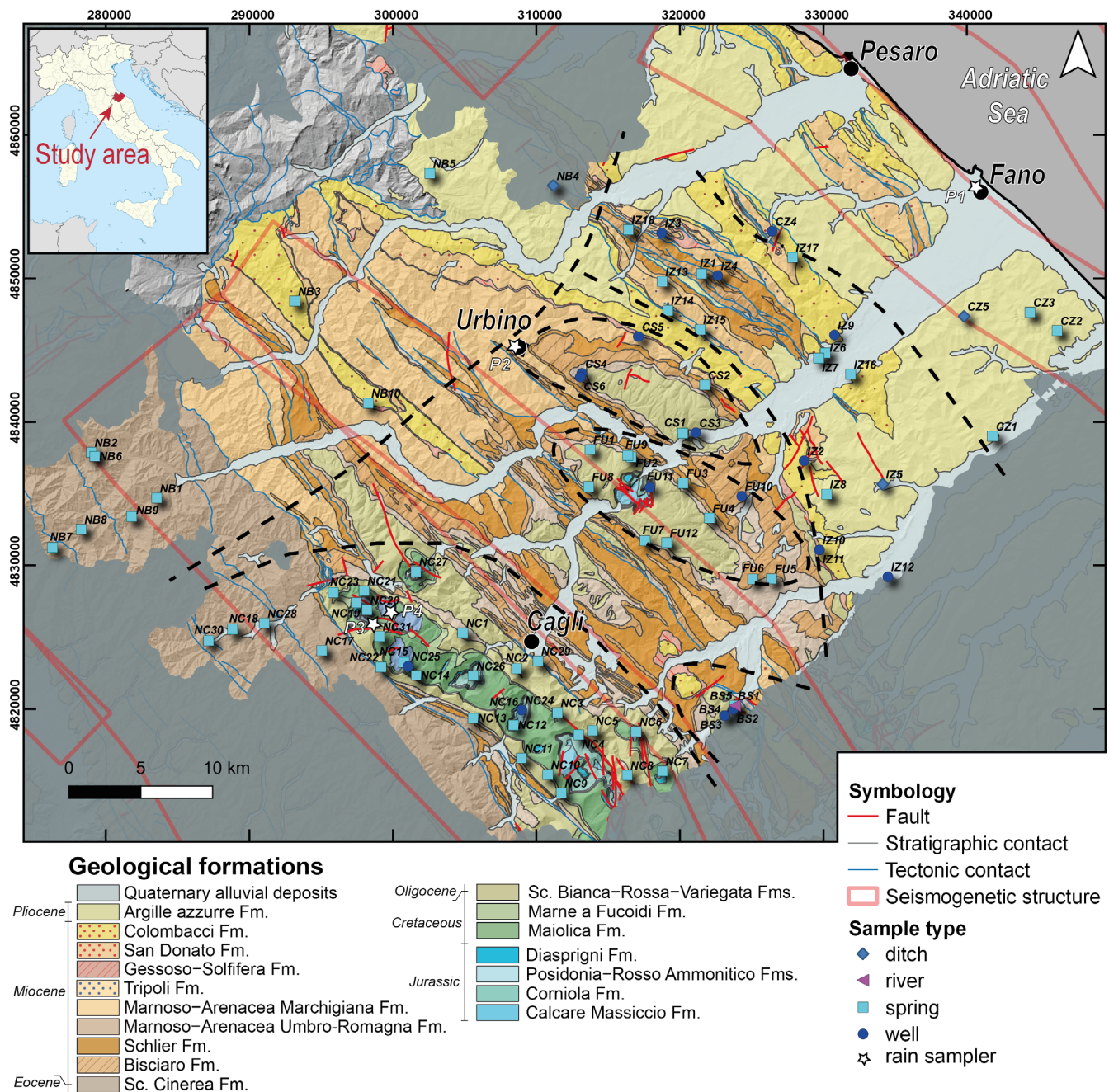

Figure 1 *Geological map of the Pesaro-Urbino (Conti et al., 2020) and location of the sampling points. Major seismogenetic structures are reported after Diss Working Group (2021). Black dashed lines represent the borders of the sampling areas: NC (Nerone-Catria Ridge), FU (Furlo Gorge), CS (Cesano-Ridge), BS (Bellisio Solfare), IZ (Internal Zone), CZ (Coastal Zone), and NB (Northern Border). For further details, please refer to Chemeri et al. (2024).*

SAMPLING STRATEGY AND ANALYTICAL METHODS

During the first step of the project, a large-scale sampling survey was performed, covering as much as possible the entire study area and its geological and topographic variability, collecting a total of 87 water samples from springs, wells and ditches, to define the main geochemical processes acting in the PU province. The survey was performed twice, during Spring and Winter 2022 (for a total of 145 analyses), in order to evaluate any possible influence related to seasonality. At each sampling sites, physico-chemical parameters were measured in situ and different aliquots were collected to determine *i*) major and minor components, *ii*) trace elements, *iii*) water stable isotopes and *iv*) the $\delta^{13}C$ in dissolved CO_2 and CH_4, this latter analysis was performed on a restricted number of sampling sites. For a detailed description of the sampling procedures and of the analytical methods deployed, I refer to Chemeri et al. (2024).

For the second step, a multi-isotopic approach was carried out, during February and November 2023, to deepen the understanding on water-rock interaction processes, reconstruct the hydrological pathways and assess sampling sites' suitability for the inclusion in a water monitoring network aimed at seismic surveillance (Chemeri et al., 2025b). A restricted number of sampling sites was selected following the results obtained from the large-scale geochemical characterization (Chemeri et al., 2024). The multi-isotopic approach involved the determination of *i*) the $\delta^{13}C$ in the total dissolved inorganic carbon (TDIC), *ii*) the $\delta^{34}S$ and $\delta^{18}O$ in the dissolved sulfate (SO_4), *iii*) the boron isotopic ratios ($\delta^{11}B$) and *iv*) those of strontium ($^{87}Sr/^{86}Sr$). Together with the isotopic determinations, major and trace components as well as water stable isotopes were also determined. The detailed description of the sampling strategy and of the different chemical and isotopic methodologies applied for the second step of the project are widely discussed and presented in Chemeri et al. (2025b).

RESULTS AND DISCUSSION

Hydrogeochemical characterization

The PU waters showed a wide compositional variability and a large variation of TDS values (230 mg/L < TDS < 4930 mg/L), thus reflecting multiple water-rock interaction processes acting at different extents and different hydrological pathways within shallow and deeper aquifers. The complete results are reported in Chemeri et al. (2024). Hence, the PU groundwaters can be classified into 5 compositional groups (Fig. 2a): (a) Ca-HCO_3 waters, including most of the samples, *i.e.*, those collected from springs and wells characterized by TDS values < 750 mg/L; (b) Ca-$HCO_3(SO_4)$ waters, which showed significant enrichment in SO_4^{2-} (up to 200 mg/L); (c) Ca-SO_4 waters, including high-TDS (>1500 mg/L) springs; (d) Na-HCO_3 waters, pertaining to waters collected from "sulfur springs" which were also characterized by alkaline pH (> 8.8) and negative Eh (< -180 meV); and (e) Na-Cl waters, those collected from ditches (Chemeri et al., 2024). The water stable isotope composition did not show any relevant correlation with the compositional groups and setting aside for Ca-SO_4 and/or Na-HCO_3 discharges (showing anomalous values in a few trace elements such as Li, B, As, Sr), most of the waters were characterized by extremely low contents in trace metals. Referring to major dissolved gases, two compositional clusters were identified: (a) N_2-dominated gases with N_2/Ar ratios similar to those of air and ASW (Air Saturated Water), mainly pertaining to Ca-HCO_3 discharges; (b) CO_2- and/or CH_4-rich gases related to Ca-SO_4 and Na-HCO_3 springs.

Based on the geochemical evidence, the Ca-HCO_3 hydrofacies includes most of the waters characterized by low-to-medium TDS values (< 1200 mg/L) and does not show any anomaly in terms of pH values and trace element contents. Therefore, the origin of Ca-HCO_3 waters results by the congruent dissolution of carbonate-bearing (*i.e.*, calcite, dolomite) rocks, in accordance with the geology of the area (Fig. 1). However, slight enrichments in Na^+ may be associated with silicate weathering. Ca-$HCO_3(SO_4)$ waters, characterized by moderate to strong enrichments in sulfate (up to 240 mg/L), are related to the dissolution of gypsum and anhydrite minerals hosted within deeper layers (i.e., Burano Fm) since these waters emerge from carbonate formations linked to the Basal Aquifer. The variable contents of sulfate likely depend on the different degrees of interaction with the anhydrite formations or dilution processes with shallower aquifers (Capaccioni et al., 2001; Chemeri et al., 2024). The Ca-SO_4-type are characterized by TDS values up to 4,900 mg/L. Their origin is related to interaction with gypsum-anhydrite lithologies, i.e., the Burano Fm or the Gessoso-Solfifera Fm, according to their geographical location and local geology (Fig. 1). The enrichments in chloride and sodium shown by a few of these waters indicate halite dissolution as another major process governing their geochemistry, which is also consistent with their Br, B, and Li contents (Chemeri et al., 2024; 2025b). These waters emerge in areas where Messinian evaporites or Triassic anhydrites do not outcrop, thus suggesting that they are related to long flow paths in deeper layers (Capaccioni et al., 2021; Chemeri et al., 2024; 2025b). The Na-HCO_3 waters show strong Na and (HCO_3+CO_3) excess relative to the stoichiometric ratio with Cl and Ca+Mg, respectively. Among minor and trace elements, these waters display high contents in F, NH_4, Li and B and relatively low values of Sr and Ba.

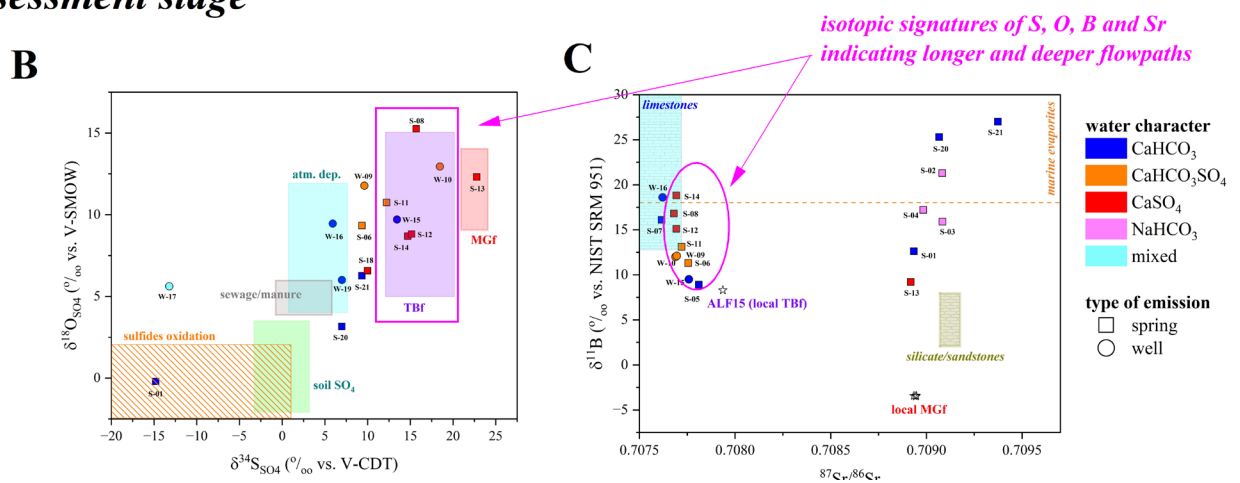## *(1) Characterization stage*
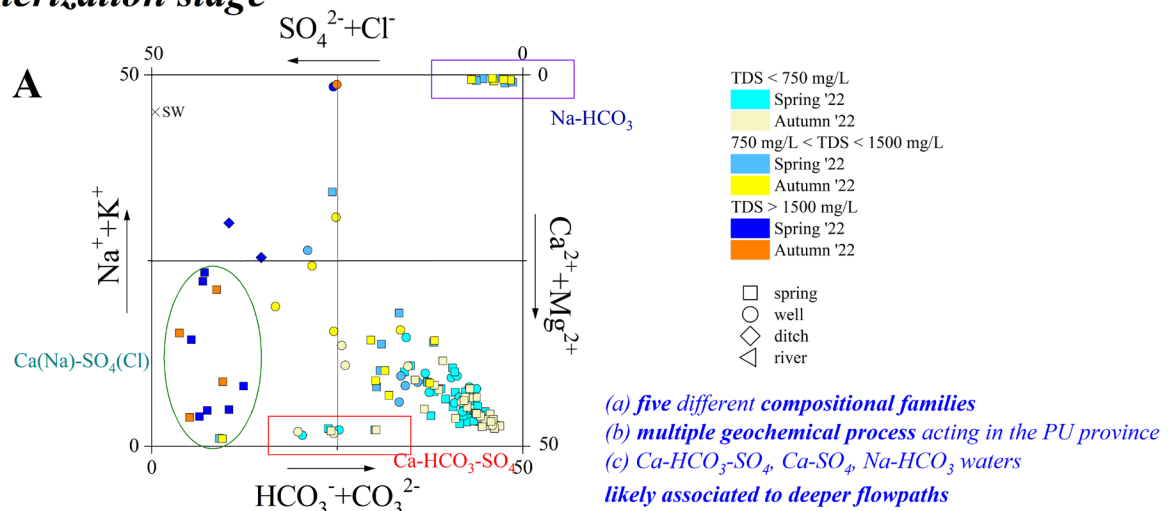
(2) Assessment stage

*Figure 2 Summary of the results obtained during the characterization and assessment stages. **a)** Langellier-Ludwig square diagram for the waters circulating within the Pesaro-Urbino province (from Chemeri et al., 2024). **b)** $\delta^{18}O_{SO4}$ (in ‰ vs. V-SMOW) vs. $\delta^{34}S_{SO4}$ (in ‰ vs. V-CDT) binary diagram. **c)** $\delta^{11}B$ (in ‰ vs. NIST SRM 951) vs. $^{87}Sr/^{86}Sr$. In plot **(b)**, the isotopic ranges for different potential sources of sulfate are also drawn according to Gori et al. (2023) and Chemeri et al. (2025b). Acronyms are: TBf (Triassic Burano Fm), MGf (Messian Gessoso Solfifera Fm), oS (organic sulfur) and ps (sulfides). In plot **(c)**, the isotopic ranges for both B and Sr in limestones and siliciclastic sediments/sandstones are reported according to Chemeri et al. (2025b). The stars indicate the $\delta^{11}B$ and $^{87}Sr/^{86}Sr$ ratios measured in local rocks TBf (Triassic Burano formation: ALF15) and MGf (Messinian Gessoso Solfifera formation). IDs as reported in Chemeri et al. (2025b).*

Moreover, the B/Cl and Li/Cl ratios in these waters are higher than those recorded in Ca(Na)-SO$_4$(Cl) discharges, indicating that the Na-HCO$_3$ waters are enriched in B and Li and Cl-poor when compared to those detected in the Ca(Na)-SO$_4$(Cl) springs. Their composition is likely acquired following prolonged weathering of Na-rich silicate rocks, thus allowing the release of sodium in solution, along with B, Li and F, due to their marked affinity with the former. This hypothesis agrees with the fact that these waters emerge from the siliciclastic Marnoso Arenacea Fm (Fig. 1), whose interaction with the circulating waters produces alkaline hydrolysis, as supported by the high pH values detected in these samples. The excess in bicarbonate species is likely associated with the CO$_{2(aq)}$ produced by the decay of organic matter trapped in the foredeep sediments, boosted by a reducing environment (negative Eh values). Eventually, Na-Cl waters were only pertaining to those samples collected from ditches, and they are likely deriving from a mixing process involving meteoric-sourced solutions and high-

ly saline (Na-Cl) connate waters, whose presence within the Adriatic foredeep clayey deposits has widely been reported (Chemeri et al., 2024 and references therein).

As far as the origin of dissolved gases is concerned, the N$_2$, Ar and O$_2$ contents in both N$_2$- and CO$_2$(CH$_4$)-dominated samples are related to the dissolution of atmospheric gases whereas CO$_2$ and CH$_4$ are biogenically derived, as confirmed by their $\delta^{13}C$ values, are probably formed following plant-root respiration processes and decay of organic matter (Chemeri et al., 2024).

Consequently, the results obtained from the first step of the project allowed to understand that Ca-HCO$_3$(SO$_4$), Ca(Na)-SO$_4$(Cl) and Na-HCO$_3$ water discharges are likely related to relatively deeper hydrogeological pathways and their emergence at surface is probably favoured by the local structures and might be interesting to monitor for seismic precursors. Following these results, these sampling sites were carefully investigated during the second phase (*i.e.*, multi-isotopic approach).

Multi-isotopic approach

Stable and radiogenic isotope composition of ground-waters has been proven to be highly effective in interpreting geochemical and hydrogeological processes in natural environments. In the present study, isotope (H, O, C, S, B, Sr) systematics were explored to disentangle different information and constraints on the characteristics of the groundwater circulating in the seismically active area of the PU province and evaluate the sampling sites' hydro sensitivity for their inclusion in a water monitoring network aimed at seismic surveillance and hazard mitigation. The full results are reported In Chemeri et al. (2025b).

The investigated waters are characterized by δ^{13}C-TDIC values < -1.67 ‰ vs. V-PDB, with less negative δ^{13}C values associated with the Na-HCO$_3$ and Ca(Na)-SO$_4$(-Cl) waters. These values are consistent with the dissolution of calcite and the interaction with biogenic soil CO$_2$ as the primary sources for the origin of dissolved carbon species (Bottrell et al., 2019) and are consistent with those of δ^{13}C$_{CO_2}$ and δ^{13}C$_{CH_4}$, which were previously mentioned (Chemeri et al., 2024; 2025b). These results clearly indicate a predominant biogenic origin for carbonate species produced at relatively shallow depths with absent or negligible contributions from deep-seated fluids. The use of sulfur and oxygen isotope systematics in the PU waters is of notable importance since some of them are characterized by either a Ca-SO$_4$ composition or a strong sulfate enrichment (Capaccioni et al., 2001; Chemeri et al., 2024). In both cases, sulfate can be derived by the interaction with the anhydrite-bearing Triassic Burano (TBf) or the gypsum-bearing Messinian Gessoso Solfifera (MGf) Fms, which lie at the bottom and the top of the Umbro-Marche succession, respectively (Conti et al., 2020 and references therein). Thus, if the chemical contribution of SO$_4^{2-}$ is isotopically different, it is possible to define and constrain the hydrological circuits. Indeed, the δ^{34}S$_{SO_4}$ and δ^{18}O$_{SO_4}$ values from TBf and MGf are characterized by different isotopic ranges (Fig. 2b). In the PU waters, the more positive δ^{34}S values (> 10 ‰ vs. V-CDT) are usually associated with those waters where the gypsum-anhydrite dissolution is predominant compared to that of carbonate-bearing minerals (SO$_4$ ≫ HCO$_3$ + CO$_3$) (Fig. 2b). Among the sulfate-enriched sampled, most of them are discharged from the Basal aquifer (setting aside for samples VLZ and PGL in Fig. 2b, c) with their sulfate isotopic values falling close, or within, the *TBf* field, indicating a likely interaction with the Burano Fm (Fig. 2b). Nevertheless, the influence of secondary processes, like "microbially-mediated" sulfate reduction, cannot be ruled out, at least for those waters characterized by strongly negative Eh values. On the other hand, the PGL water discharges from a hill where the Gessoso Solfifera Fm is largely outcropping (Fig. 1), and falls with-in the MGf field, pointing that the sole source of sulfate is related to the Messinian gypsum. Moreover, the location of VLZ contrasts with the SO$_4$ isotopic signature (Fig. 2b). This spring is located far from the carbonate anticline, where the TBf have been identified at > 1500 m depth in a deep well), thus suggesting that the interaction with TBf is unlikely. The Ca-HCO$_3$ waters tend to be positioned between or within the TBf, atmospheric deposition and soil SO$_4$ fields, therefore suggesting a mixed origin related to multiple sources contributing to different extents.

While the application of B isotopes may present some limitations since different sources are characterized by similar and overlapping ranges, the Sr isotopes provided useful clues. In fact, two groups of samples can be identified according to their ^{87}Sr/^{86}Sr ratios: *i*) ^{87}Sr/^{86}Sr ranging from 0.70762 and 0.70781 (including also Ca-SO$_4$ and Ca-SO$_4$-HCO$_3$) and falling within the TBf and limestones (*i.e.*, Calcare Massiccio and Corniola Fms) isotopic ranges; *ii*) ^{87}Sr/^{86}Sr ratios included between 0.70892 and 0.70937 (including also Na-HCO$_3$ and PGL waters), approaching the reference values of MGf and the carbonate fraction of the Marnoso Arenacea Fm. Taking into account the δ^{11}B, the distribution of the first group of samples in Figure 2c suggests that the primary source of Sr (and consequently of Ca) is represented by TBf and/or limestones, which is consistent with the main geochemical processes occurring in these waters and with the hydrogeological features of the areas where they circulate. Additionally, Sr and B values confirmed that the PGL sample is interacting with the MGf and that the origin of Na-HCO$_3$ waters is associated with the interaction with silicate lithologies, since they all show isotopic values consistent with the weathering of the local Marnoso Arenacea Fm (Fig. 2c). As previously discussed, the different contributions in Ca-HCO$_3$ may be multiple and influenced by the surroundings lithology and hydrogeology. Further details on the data discussion are reported in Chemeri et al. (2025b).
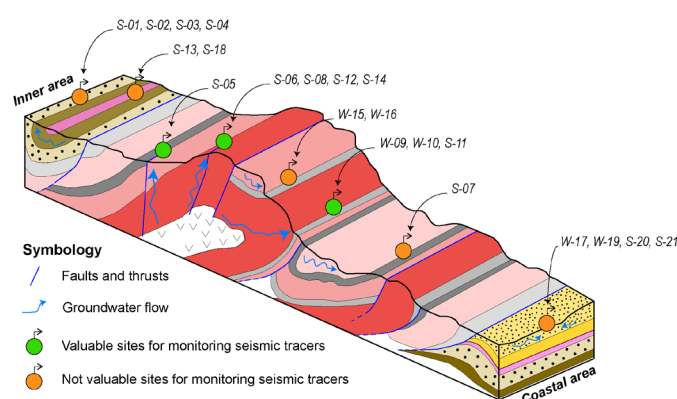

Figure 3 *Conceptual model summarizing the hydrogeological circuits of the investigated sites, which helps to define the most valuable setting to be monitored for possible seismic tracers' recognition in the investigated area of the Pesaro-Urbino Province. The sketch follows and modifies the schematic model of Nanni and Vivalda (2005). For sample IDs and colours, refer to Chemeri et al. (2025b).*

CONCLUDING REMARKS

In deploying a water geochemical monitoring network to identify possible seismic tracers, selecting the most suitable sampling sites, *i.e.*, those related to longer circulation paths and fed by deep aquifers, is a fundamental and necessary step. For this purpose, a detailed hydrogeochemical and isotopic characterization of the groundwaters circulating in the seismically active PU province was carried out. A conceptual model of the main hydrogeological, geochemical, and isotopic findings of the present work are summarized in Figure 3. In conclusion, our results suggest that (most of) the Ca-SO$_4$ and Ca-HCO$_3$-SO$_4$ waters are discharged by the Basal aquifer after long and deep flow paths that lead to water–rock interactions with the local deep-seated TBf (Fig. 3), maintaining the isotopic signature of the primary source (almost) unchanged and thus less affected by secondary processes; notably, faults can play a critical role in facilitating groundwater circulation from deep layers to the surface, especially during seismic periods, when they can act as preferential flow features (Fig. 3). Indeed, these kinds of water have been widely found to be sensitive to possible geochemical and isotopic variations in similar geological-tectonic contexts such as the Sibillini Mts. (Marche Region) or the Gran Sasso Mt. area (Abruzzo Region) (*e.g.*, Barberio et al., 2017). The results of this work make our approach applicable to other geological contexts where seismic activity is well-documented, thus taking a step further to mitigate the seismic hazard.

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