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Multidisciplinary hydrogeochemical and isotopic assessment of the Pordenone Plain (Northeastern Italy) for water resources sustainability

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ABSTRACT

This study aims to comprehensively characterize the hydro-geochemical and isotopic features of the complex groundwater system in the Pordenone Plain (northeastern Italy). The area is an important industrial and agricultural area exposed to severe anthropogenic pressure and climate change, which put its water resources at risk in terms of quantity and quality, making it of high scientific and social interest. The hydrogeological setting of the Pordenone Plain has been previously simplified as a phreatic continuous aquifer in the High Plain that changes into a multilayered aquifer system towards the Low Plain. However, this study reveals significant lithological and structural heterogeneities in the High Plain that exert a strong influence on its subsurface hydrodynamics. All waters exhibit a Ca(Mg)–HCO_3 composition with relatively high Na–K values in the aquifers of the Low Plain likely related to cation exchange processes. Water stable isotopes (δ^2H–H_2O and $\delta^{18}O$–H_2O) indicate that the deep aquifers in the Low Plain are confined by impermeable geological formations, such as clays and siltstones, which entirely restrict water mixing with shallower aquifers. Concurrently, tritium analysis provides evidence of slow recharge and flow rate. Three primary groundwater flows have been identified within the plain, as follows: 1) a surface flow that affects the unconfined or semi-confined aquifers of the High Plain hosted in gravelly sediments; 2) an intermediate flow fed by the pedemontane zone, which includes unconfined deep aquifers of the High Plain, semi-confined/shallow aquifers (at a depth of 40–50 m) located near the resurgence belt area and karst springs located in eastern pedemontane of the Cansiglio Plateau; 3) a deep flow fed by the mountainous zone that affects the deep confined aquifers of the Low Plain. A reliable hydrogeochemical conceptual model has been developed to explain the compositional variability of the studied waters, providing valuable insights for the sustainable management of groundwater resources in the Pordenone Plain.

1. Introduction

In recent decades, water resources have become increasingly vulnerable to anthropogenic impacts such as pollution from agricultural and industrial activities and the effects of climate change, which have significantly altered the global water cycle (IPCC et al., 2022). Moreover, the significant decline in both the quality and quantity of water resources is further intensified by the rising demand of water for agricultural, industrial, and potable uses. To address these issues, multidisciplinary approaches that integrate geological, hydrogeological, geochemical, and geophysical investigations are often employed (e.g., Doveri et al., 2015; Vespasiano et al., 2019; Amobichukwu et al., 2020). Such approaches allow to identify, characterize and model the sources and mechanisms regulating groundwater dynamics at the catchment basin scale, providing competent authorities with effective tools for sustainable water resource management. Geochemical surveys play an important role in this context because they enable the characterization of the processes governing the chemical composition of groundwater, including water-rock interactions, residence time within the aquifer, identification of recharge areas, and mixing processes (e.g., Hem, 1985;

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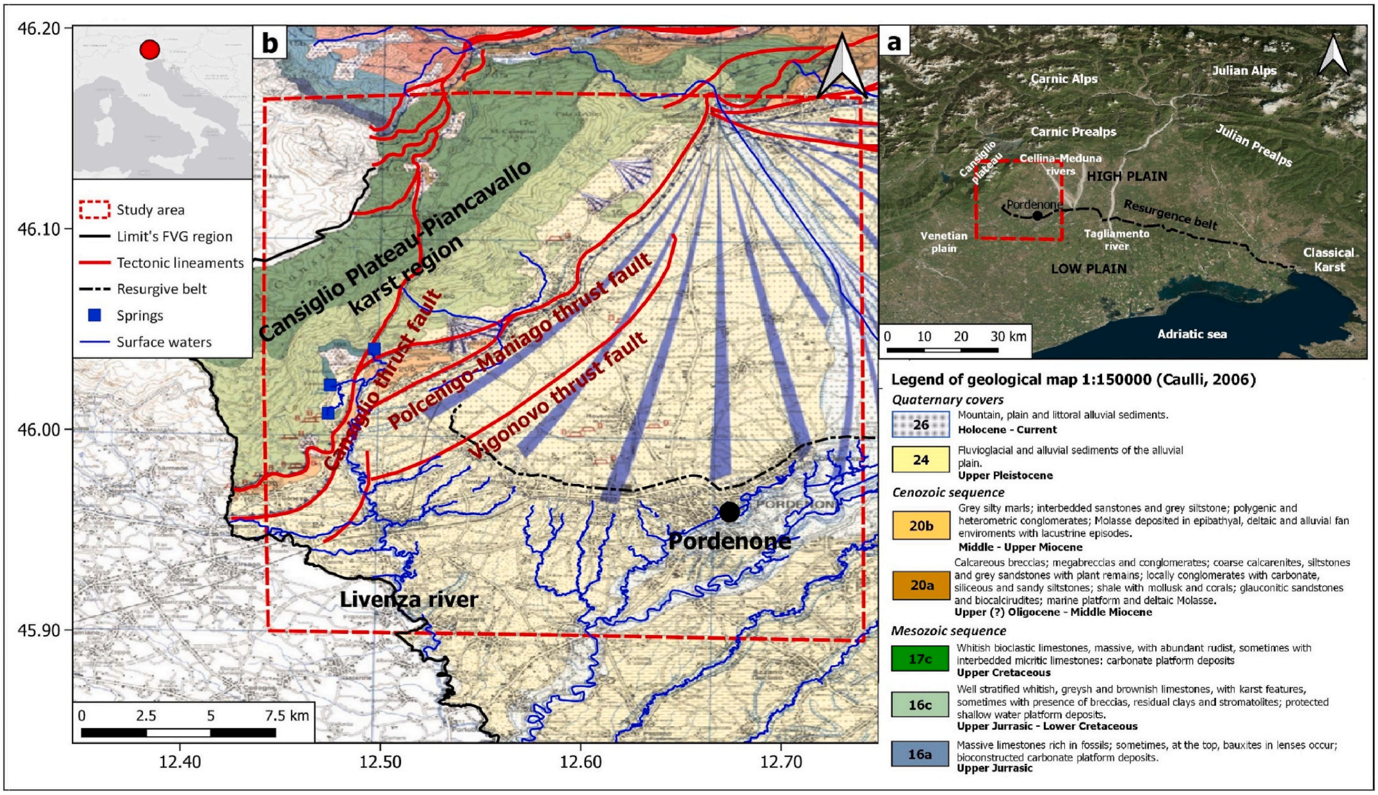

Fig. 1. Map of the study area: a) simplified map of the Friuli plain; b) geological map of Pordenone Plain (PP) modified by Carulli (2006). The main tectonic lineaments (the Cansiglio thrust fault, Polcenigo-Maniago thrust system and Vigonovo thrust fault), the karst springs and the surface water are visible on the map.

Appelo and Postma, 1996; Stumm and Morgan, 1996; Sidhu and Chandel, 2023). Understanding geochemical processes may help to provide an accurate picture of hydrogeochemical dynamics and in developing conceptual models of fluids circulation (e.g., Bundschuh and Sracek, 2012; Zanotti et al., 2022). These models may represent a valid tool for developing effective and sustainable groundwater management plans.

The Friuli-Venezia Giulia region possesses high-quality freshwater resources used for both human consumption and agricultural and industrial activities. A slightly positive water budget was reported at the regional scale (Zini et al., 2011) based on the groundwater meteoric recharge from mountain basins (233.5 m^3/s) and the volume of water emerging from the resurgence belt (134.2 m^3/s) and that deriving from withdrawals (59.3 m^3/s). However, Calligaris et al. (2010) and Zini et al. (2011) have underscored the criticality of the water budget in the region which led to tangible effects across the entire system. These effects include the gradual narrowing of the resurgence belt (Zini et al., 2011), the gradual decline in the phreatic aquifer level of the High Plains by approximately 0.1–0.4 m/year (Cucchi et al., 1999; Calligaris et al., 2010; Zini et al., 2013), and the reduced pressure in the confined aquifers of the Low Plain (Cucchi et al., 1999; Martelli and Granati, 2007; Martelli et al., 2007). These effects become particularly pronounced during the summer months due to shifts in rainfall patterns and increased water withdrawals for irrigation or domestic use (Di Renzo et al., 2023a), potentially aggravating groundwater depletion. In addition, regarding the studies of geochemical/isotopic characterization, although several previous works have been conducted, these have been primarily focused on the plain sector located on the left bank of the Tagliamento River (Martelli et al., 2007; Martelli and Granati, 2010; Teatini et al., 2015) and only on a small scale across the entire Friulian plain (Cucchi et al., 2008). Conversely, the plain sector on the right bank of the Tagliamento River, known as the Pordenone Plain (hereafter PP), has not been the subject of detailed studies. These findings suggest the need for a more comprehensive understanding of aquifer dynamics in the PP. With this aim, this research focuses on investigating the groundwater system of the PP using geochemical and isotopic approaches to enhance our knowledge of hydrogeochemical dynamics and elucidate the processes influencing groundwater chemistry and its spatial evolution. Supported by a lithological study of the subsurface, a qualitative hydrogeochemical model will be developed, which will be able to provide an accurate characterization of groundwater dynamics, thus constituting a valid help for groundwater management in the PP region.

2. Geological and hydrogeological settings

The Friuli plain (NE sector of Italy) represents the easternmost edge of the Po Valley, and it is characterized by steeper slopes and coarser sediments compared to the latter (Zini et al., 2013). It covers an area of approximately 2900 km^2 and is bordered by the Julian and Carnic Alps to the north, the Adriatic Sea to the south, the Classical Karst of Trieste to the east and the Venetian Plain to the west (Fig. 1a).

The geological and hydrogeological characteristics of the current Friuli plain derive from depositional processes occurred in the Upper Pleistocene influenced by the geological-structural evolution of the area and sea level fluctuations resulting from Quaternary glaciation events (Florineth and Schluchter, 2000; Orombelli and Ravazzi, 1996). These depositional processes resulted in the sedimentation in the plain of clastic materials of fluvio-glacial, marine, lagoon, and marshy origin. The last Würmian glaciation played a key role in shaping the plain, leading to the formation of concentric morainal arcs along the main rivers of the area. The variation in river dynamics over time resulted in the deposition of clastic materials with a decreasing grain size in the N–S direction (Fontana, 2006). This sediment distribution has led to the division of the plain into two distinct sectors, as described by Teatini et al. (2015): i) the High Plain, predominantly composed of gravelly

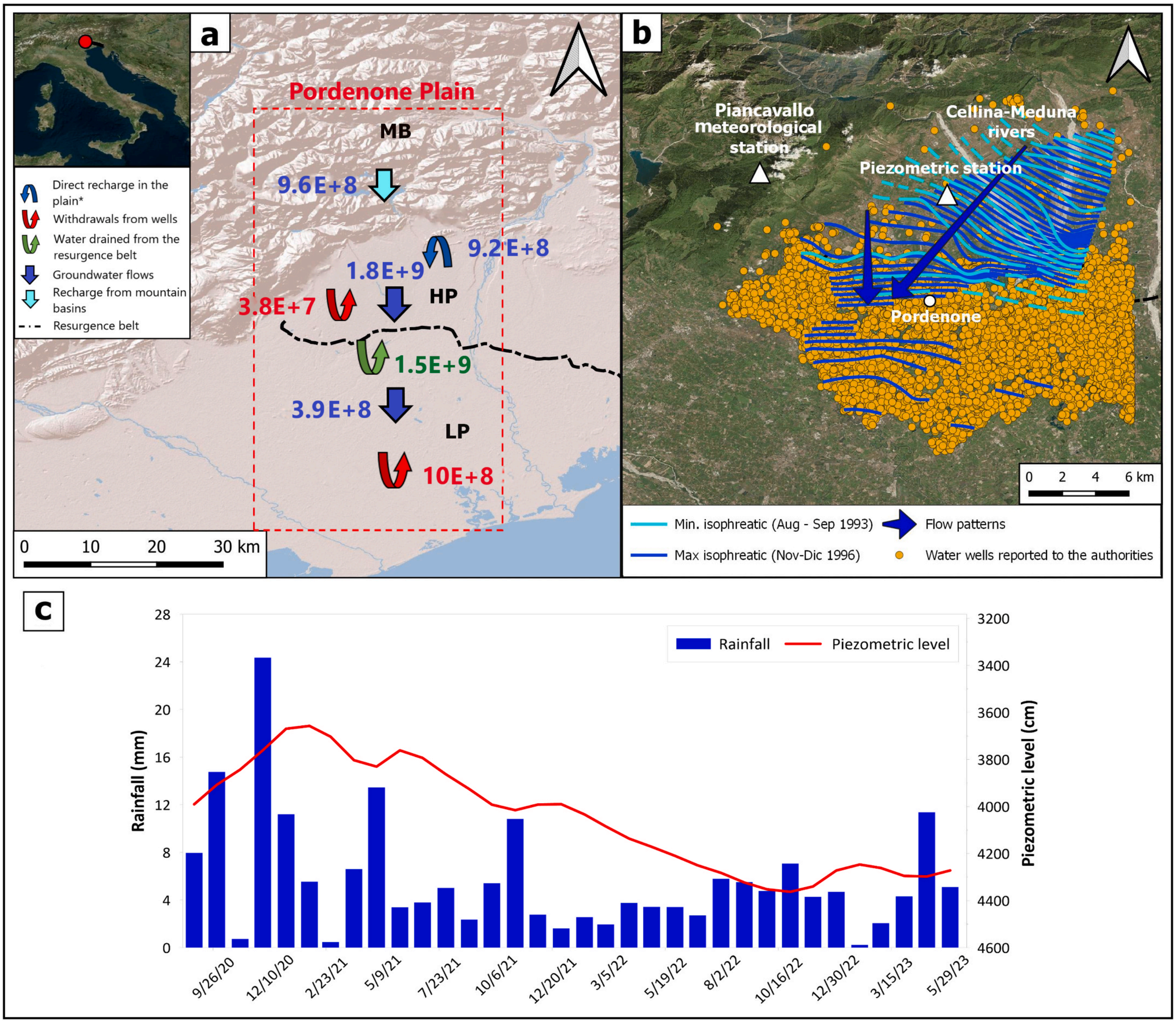

Fig. 2. a) Hydrogeological balance of the Pordenone Plain from Zini et al. (2011). MB: Mountain Basin; HP: High Plain; LP: Low Plain. b) Iso-phreatic lines representative of the maximum and minimum water tables (measured in November–December 1996 and August–September 1993, respectively) and flow patterns according to Zini et al. (2011). Wells with withdrawal authorizations are represented by orange circles. c) Comparison between rainfall in the Piancavallo meteorological station and piezometric level of High Plain aquifer temporal trends for the period September 2020–June 2023. Data from ARPA FVG - OSMER and GRN (http://www.meteo.fvg.it/), and Hydraulic Service of the Friuli Venezia Giulia Region. The locations of the Piancavallo meteorological and piezometric stations are shown in Fig. 2b.

sediments, with occasional cemented and interbedded sand and clay layers, produced from Mesozoic calcareous and dolomitic rocks (Zini e al, 2013; Martelli and Granati, 2007; Martelli and Granati, 2010) and originated from the rapid progradation of a series of megafans during the Upper Pleistocene period as a result of the last glacial maximum (Fontana, 2000, 2006), and ii) the Low Plain, which consists of clayey sediments with low permeability, occasionally interspersed with sand and gravel deposits, having a continental and marine origin related to the sea level fluctuations.

From the hydrogeological point of view, the Friuli plain hosts a multi-layered alluvial aquifer (Cucchi et al., 2000; Mosetti 1983; Stefanini and Cucchi 1976, 1977). A phreatic continuous aquifer is recognized in the high permeability loose coarse deposits of the High Plain. The High Plain aquifer is primarily fed by direct recharge, seepage from surface waters and underground sources from both the moraine hills and the Pre-Alps (Stefanini, 1978; Mosetti, 1983). Moving towards the Low Plain, the phreatic aquifer joins in a complex multi-layered aquifer system characterized by alternating gravels and sands interbedded by clayey and silty layers, which become more frequent and thicker southward direction (Zini et al., 2013; Martelli and Granati, 2007). This multi-layered aquifer system is recharged by the unconfined phreatic aquifer of the High Plain (Mosetti, 1983; Vecchia et al., 1968). The High Plain and the Low Plain are divided by the resurgence belt, a WNW-ESE oriented narrow band, where the intrinsic permeability of the sediments decreases abruptly and groundwater is forced to emerge giving rise to springs (Cucchi et al., 1999).

The PP, located in the northwestern sector of the Friuli plain, covers an area of approximately 607 km^2 and is primarily situated on the alluvial cone of the Cellina River. The study area includes, from north to south (Fig. 1b): i) the Cansiglio Plateau-Piancavallo karst region,

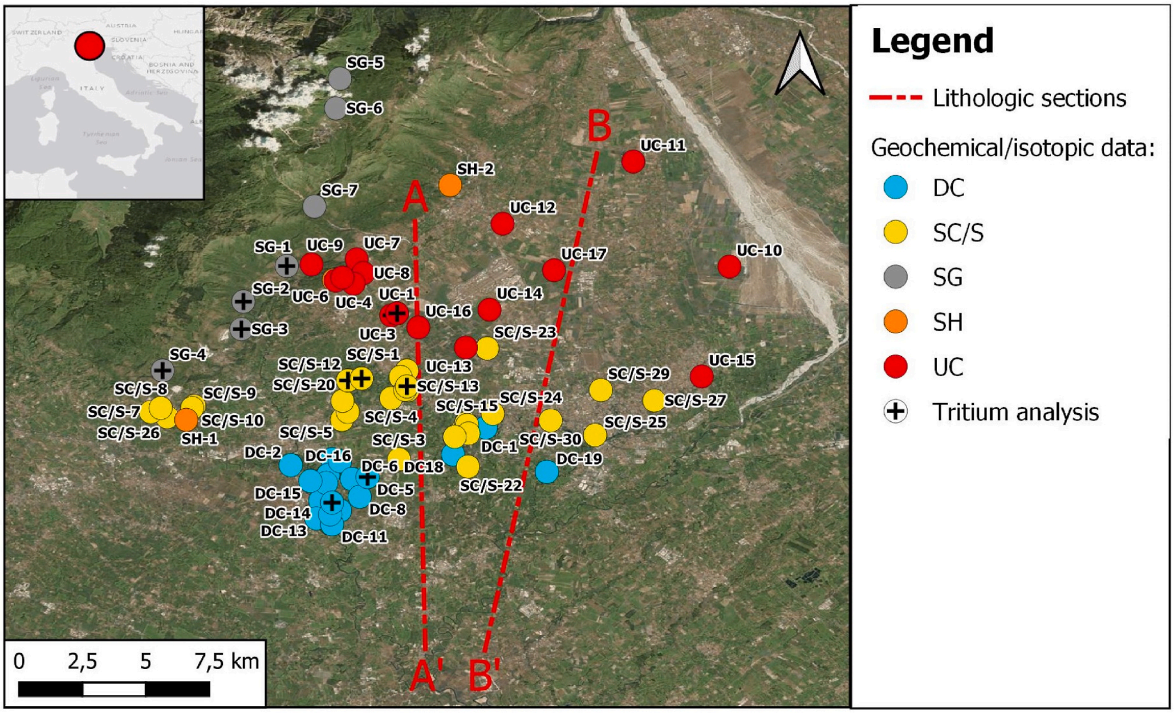

Fig. 3. Location and ID of the collected waters (DC: deep multi-layered confined aquifers; SC/S: semi-confined/shallow aquifers; UC: unconfined aquifers; SG: karst spring waters; SH: shallow waters). Red line shows the two 2D lithological sections extrapolated by model 3D.

characterized by Triassic-Miocene carbonate formations, which hosts one of the most important carbonate aquifer systems of the Southern Alps (Cavallin, 1979; Filippini et al., 2018); ii) the alluvial cone of the Cellina and Meduna rivers, situated within the High Plain, which comprises an undifferentiated phreatic aquifer characterized by high permeabilities ranging from 10^{-2} to 7×10^{-3} m/s (Cucchi et al., 2008) and iii) the deposits of the Low Plain, south of the resurgence belt, including a complex sequence of superimposed confined or semi-confined aquifer systems (Zini et al., 2011) with low permeability values ranging from 2.5×10^{-4} to 5×10^{-5} m/s (Cucchi et al., 2008).

From a hydrogeological perspective, the alluvial system of the PP is primarily fed by precipitation occurring in the mountain watersheds. In these areas, average precipitations range between 2000 and 3000 mm/year (ARPA-OSMER, 2008). The mountain watersheds supplies both the karst region of the Cansiglio Plateau-Piancavallo and the High Plain. The karst aquifer of the Cansiglio Plateau-Piancavallo feeds a series of large springs located at the base of the eastern slope of the Cansiglio Plateau (see Fig. 1b) with an average discharge ranging from 2.5×10^8 to 3.5×10^8 m^3/yr, which respond immediately to recharge inputs (Meneghel et al., 1986; Filippini et al., 2018). The undifferentiated aquifer of the High Plain is mainly recharged through the gravel beds of rivers, along with direct precipitation, with an average annual contribution estimated at about 9.6×10^8 m^3/yr (Fig. 2a). The flow in this aquifer follows N–S and NE-SW directions, creating a highly undulating piezometric surface (Fig. 2b; Zini et al., 2009), and responds synchronously to precipitation in the mountain watersheds, albeit with a delay of about 2–3 months (Fig. 2c). An additional average annual recharge of about 9.2×10^8 m^3/yr occurs directly in the plain, primarily due to effective infiltration and indirect irrigation, in contrast to the withdrawals from wells amounting to 3.8×10^7 m^3/yr (Fig. 2a). The High Plain aquifer supports both the resurgence belt and the aquifer systems of the Low Plain, with an average recharge of about 1.8×10^9 m^3/yr. Part of this recharge contribution, approximately 1.5×10^9 m^3/yr is drained by the resurgence belt, while about 3.9×10^8 m^3/yr feeds the confined multi-layer aquifer system of the Low Plain (Fig. 2a). This recharge is less than half of the estimated average annual withdrawals in the Low Plain, which are about 10×10^8 m^3/yr (Fig. 2a). This is due to the large number of private wells, especially shallow ones, used for agricultural, industrial, and potable purposes (Fig. 2c).

3. Materials and methods

3.1. Lithologic modelling of the study area

The lithologic modelling is intended to characterize the complexity of the hydro-lithographic framework of the PP and show the spatial trends and variability of thickness and heterogeneity of the aquifer system. To identify optimal sampling points for this study, 165 well logs, covering an area of approximately 400 km^2, were used (Fig. 1S; Di Renzo et al., 2023b). The first step was to standardize the log data according to the main lithological classes: gravel, gravel with sand intercalation, sand, sand with clay intercalation, clay, and clay with sand intercalation. Data were subsequently processed using lithologic modelling techniques based on the "solid modelling" concept provided by the RockWorks 2021 software package (RockWare Inc.), by means of a true three-dimensional gridding process. A "box" of regularly spaced nodes from irregularly spaced data was created by interpolating measured values of lithology types. The resolution of the model was 200 m (X) × 200 m (Y) × 5 m (Z). The resulting discretization consisted of 93 X nodes x 143 Y nodes x 163 Z nodes, thus having 2,167,737 solid model nodes. In this study, the method of inverse distance is used for interpolation of the available lithologic well log data.

The results obtained from the lithological modelling were represented by conventional 3D model and 2D lithologic sections which showed a good resolution of the model and a good direct correlation between the log well data. The traces of the 2D sections extrapolated from the model can be observed in Fig. 3.

3.2. Geochemical and isotopic characterization

The hydrogeochemical and isotopic surveys at PP were carried out in July 2021. A total of 41 sampling points from wells, surface waters, and

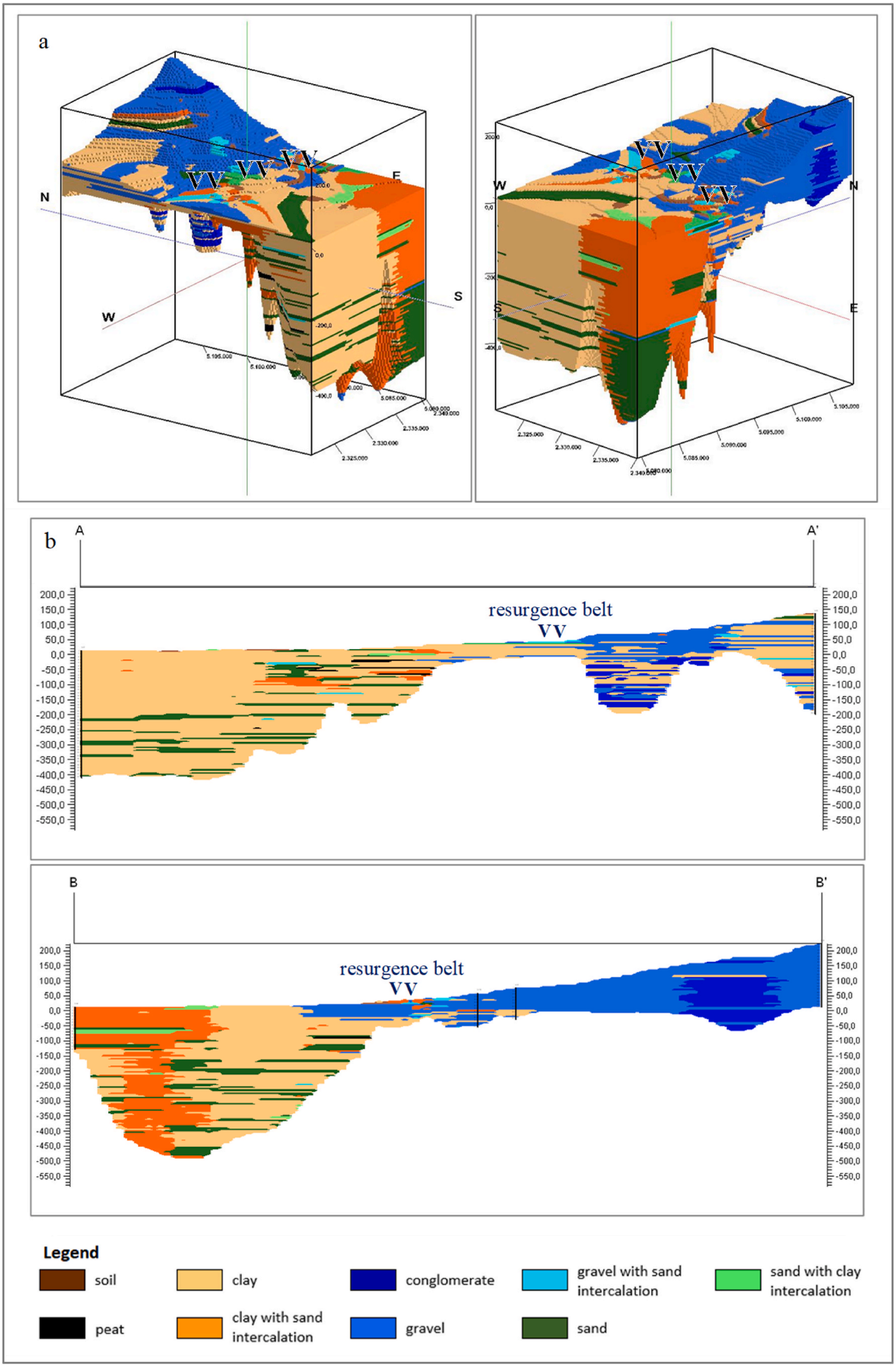

Fig. 4. Lithological model of the study area: a) 3D model (vertical exaggeration x35); b) N–S 2D section (vertical exaggeration x5). "vv" symbol refers to the resurgence belt location.

karst springs were selected for physicochemical field measurements, geochemical (major ions), and isotopic ($\delta^{18}O$ and $\delta^{2}H$) laboratory analyses. Furthermore, tritium (^{3}H) analyses were performed on selected samples (Fig. 3). The non-pressurized wells were previously purged according to international standard criteria (generally low flow and pumping of 3–4 vol of well water column). The geochemical/isotopic dataset was supplemented with additional 20 water points obtained from a survey conducted in July 2020 (Cannarsa et al., 2020) and 16 water points collected from the groundwater monitoring network of ARPA Friuli-Venezia Giulia during the period June–September 2021 (https://www.dati.friuliveneziagiulia.it/Ambiente/Acqua-Acque-di-classificazione-Sotterranee/wthn-aebz). The subdivision of the different data sources is visible in Table 1S.

Following the results of the lithological model and from the hydrogeological setting described above, the collected waters were grouped as follows (Fig. 3): 20 samples from the deep multi-layered confined aquifer (DC) located in the Low Plain, with well depths ranging from 140 to 422 m, 30 samples from the semi-confined/shallow aquifers (SC/S) located in the Low Plain near the resurgence belt zone, with well depths ranging from 7 to 80 m, 17 samples from the unconfined aquifers (UC) located in the High Plain, with well depths ranging from 10 to 280 m, 7 samples from karst springs located on the eastern slopes of the Cansiglio Plateau (SG), and 3 samples (SH) from surface waters (rivers and channels). For details on the depths of the well-screens, refer to Table 1S.

Water temperature (T), pH, electrical conductivity (EC), and oxidation-reduction potential (ORP) were measured in the field by multiparametric probes. Total alkalinity was determined by acidimetric titration using 0.05 N HCl and methyl orange as the indicator. All water samples were filtered on-site through a membrane with a pore size of 0.45 μm and stored in 100 mL polyethylene bottles that were previously washed with dilute HNO_3^- and rinsed with Milli-Q water. Water samples for anions were stored without additional treatments, while samples for cations were acidified by adding suprapur acid (1% HNO_3^-). For $\delta^{2}H$ and $\delta^{18}O$ measurements, the samples were stored in tightly sealed screwcap 50 mL polyethylene bottles without filtering. Water samples for ^{3}H analysis were collected in 1 L amber glass containers to minimize photoluminescence effects and possible sample degradation due to photochemical causes. All water samples were kept at 4 °C and in dark conditions before analysis. The main ions and stable isotopes were determined at the Department of Physics and Earth Sciences of the University of Ferrara. Specifically, the anions (Cl^-, NO_3^-, and SO_4^{2-}) were analysed using an DIONEX ICS-1000 Ion Chromatography System (Thermo Fisher Scientific). The cations (Na^+, Mg^{2+}, K^+, and Ca^{2+}) were analysed using an TQ-ICP-MS (Triple Quadrupole-ICPMS) Series iCAP-TQ spectrometer (Thermo Fisher Scientific). The water samples were acidified with 2% HNO_3^- to stabilize the sample and prevent precipitation and adsorption phenomena on the internal surfaces of vessels and pipes. The analytical error for anions and cations was less than 5% (Table 1S). Stable isotopes were analysed using the CRDS LWIA 24-d isotopic analyzer (Los Gatos Research Inc.). Based on replicate analyses of standards, the analytical precision and accuracy were better than 0.07‰ and 0.2‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively. $\delta^{18}O$ and $\delta^{2}H$ values were reported relative to Vienna Standard Mean Ocean Water (VSMOW). The ^{3}H level in the water samples was determined at the Environmental Radiometry Laboratory (FSN–SICNUC-TNMT) of the ENEA Research Centre of Brasimone using the Liquid Scintillation Counting (LSC) technique with a QuantulusTM 1220 low-background counter (Perkin Elmer, USA). Prior to measurement, all samples underwent ^{3}H preconcentration through electrolytic enrichment process as described in Östlund and Werner (1962), Taylor (1976), and Wassenaar et al. (2018a, b) as precipitation in the region are expected to have a natural abundance of 6–10 TU (Terzer-Wassmuth et al., 2022), and thus, ^{3}H values in freshwater and groundwater would be below the detectability threshold for most of the sampled areas. Detection limit for ^{3}H was estimated at 0.5 TU (tritium units).

Thermodynamic computations were employed to assess the chemical speciation of the carbonate system. The modelling process involved calculating the partial pressures of CO_2 (pCO_2) and the saturation states of calcite and dolomite ($SI_{calcite}$ and $SI_{dolomite}$) using pH, alkalinity, temperature, and main solutes as input data to the PHREEQC speciation program (Parkhurst and Appelo, 2013).

3.3. Multivariate statistical analysis (MSA)

A CoDA (Compositional Data Analysis) approach and a Principal Component Analysis (PCA) were performed to analyse hydrogeochemical data. The compositional nature of the data is considered in the CoDA, which undergoes pre-processing for statistical analysis using centred-log-ratio (clr) transformations through the CoDAPack v.2.0 program (Aitchison, 1986; Egozcue et al., 2003; Comas Cufí et al., 2011). These transformations convert the original data into new coordinates adhering to the rules of Euclidean geometry in real space. The clr transformation, developed by Aitchison (1986), is widely used for covariance-based PCA (Drew et al., 2008; Engle and Blondes, 2014).

In this study, the clr transformation was applied to the obtained CoDA matrix, x, consisting of D parts, as outlined in equation (1):

$$clr(x) = \left(ln \frac{x_i}{g(x)} \right)_{i=1,\dots,D}, where\ g(x) = \sqrt[D]{x1 * x2 * \dots * x_D} \quad (1)$$

The PCA, a statistical method widely employed for the interpretation of multi-variable data, was utilized to explore the factors influencing groundwater composition in aquifers. The data matrix consisted of major ions, and variables with a large proportion of samples below the limit of quantification were excluded. A variation matrix based on the Aitchison transformation (Aitchison, 1986) was generated to examine the data and describe the log-relationships between variables. The results were visualized using compositional covariance biplots, and interpretation followed the rules established by Blake et al. (2016). Ionic balance errors were evaluated, and samples with errors below ±5% were considered (Freeze and Cherry, 1979). The statistical analysis focused on compositional hydrochemical data, excluding temperature, pH, and electrical conductivity. A data matrix was created using major ions (Na^+, Ca^{2+}, Mg^{2+}, K^+, HCO_3^-, Cl^-), resulting in 77 observations and 6 variables. Variables with a large proportion of samples below the limit of detection (LOD) (>33% of samples below the LOD) were discarded. Each component of the variation matrix, represented by t, describes the log-relationship between two variables, xi and xj.

Overall, the study employed a robust statistical framework to explore the multivariate behaviour and relationships within the hydrogeochemical and isotopic data, enhancing the understanding of groundwater composition in aquifers.

4. Results

4.1. Lithologic modelling

The lithological model allowed a thorough delineation of the area's lithological structure and served as a valuable tool for integration with the geochemical data. The location of the lithostratigraphic logs used to create the 3D model can be seen in Fig. 1S in the supplementary material. Fig. 4a presents the 3D model illustrating a complex spatial distribution of lithological layers in the subsurface which is consistent with the characteristics of the Friuli plain (Rapti and Vaccaro, 2007; Rapti et al., 2009; Martelli and Granati, 2007; Zini et al., 2013). The vertical and horizontal variations (Fig. 4a and b) are the result of the intricate interaction between glacial deposits, piedmont fans, eustatic fluctuations, and neotectonic activity (Orombelli and Ravazzi, 1996; Florineth and Schluchter, 2000). The main lithological variability identified with the model is located within the High Plain. Here, a noteworthy presence of predominantly fractured conglomeratic deposits is observed at an approximate depth of 100 m below ground level, in agreement with

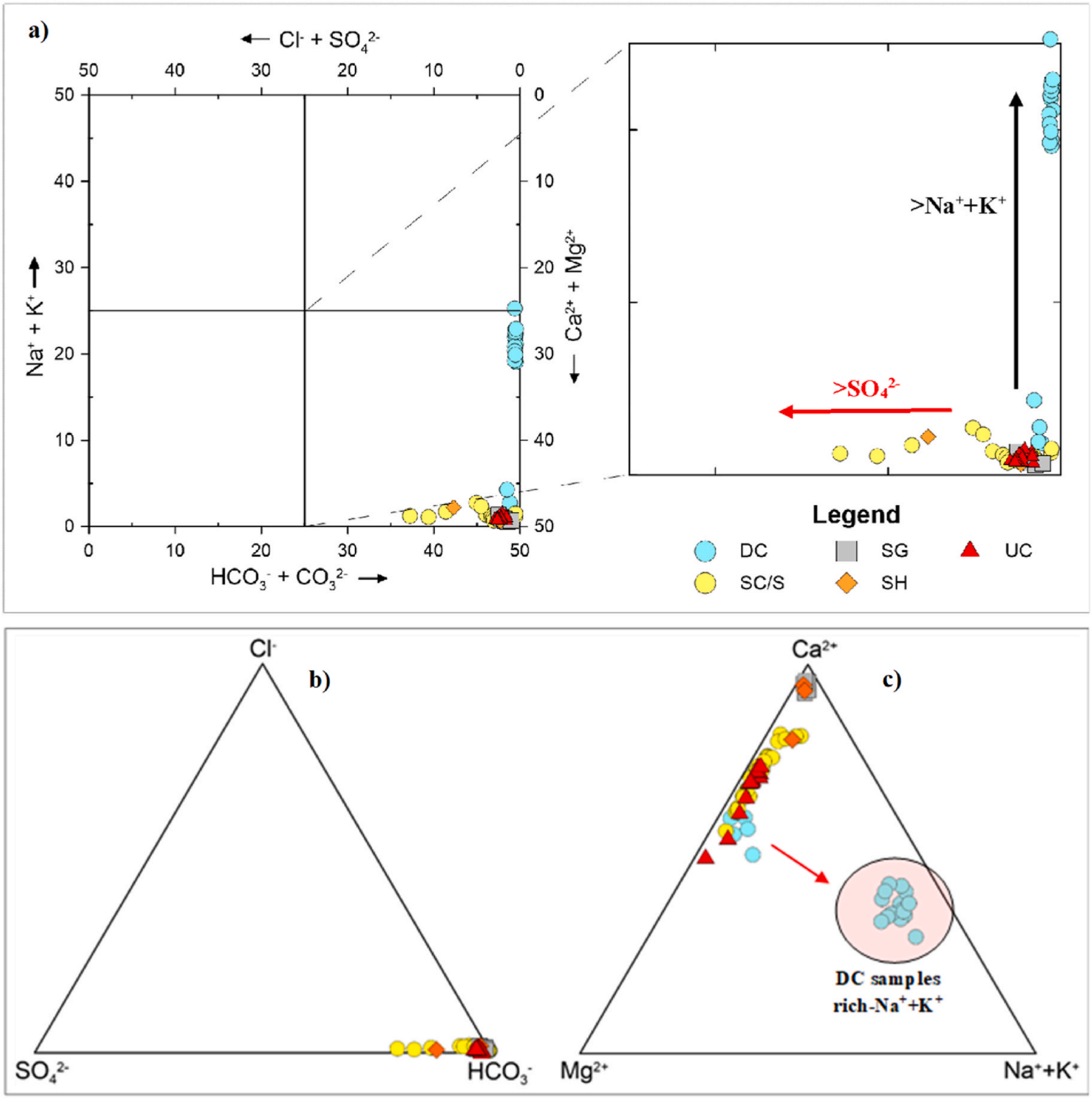

Fig. 5. a) Ludwig-Langelier plot of major anions and cations of all waters. b) Ternary plot of major anions of all sampled waters. c) Ternary plot of the major cations of all sampled waters.

previous observations (Rapti et al., 2009; Calligaris et al., 2010). This allows the partition of the High Plain into two distinct sectors with different lithological characteristics which may significantly affect the subsurface hydrological dynamics of the study area: an upper sector primarily consistent of occasionally cemented gravelly sediments and a lower sector characterized by conglomerate deposits.

4.2. *Geochemical and isotopic characterization*

Complete field and laboratory analysis are listed in Table 1S while basic statistics of the water samples are presented in Table 2S. The pH values show no significant variation among the different types of waters, ranging from 7.50 to 7.80 pH units. Water temperatures vary as follows: in DC they range from 13.0 °C to 20.0 °C, in SC/S from 12.1 °C to 25.7 °C, in SG from 8.00 °C to 15.2 °C, and in UC from 12.8 °C to 24.8 °C. The EC values range from 130 to 715 uS/cm with median values from 180 to 372 uS/cm. The ORP values are mostly negative in all the collected waters.

Among major ions, HCO_3^- and Ca^{2+} represent the most abundant species and show no significant variation among the different types of waters. On the other hand, Na^+ and K^+ exhibit higher concentrations in the DC waters (median concentrations of 45.0 mg/L and 4.60 mg/L, respectively) relative to the other groups (median concentrations of 1.30 mg/L and 0.40 mg/L, respectively). Sulfate concentrations are generally low in the DC and SG waters ranging from below the detection limit (b.d.l.) to 3.80 mg/L, while they show higher values (up to 40.0 mg/L) in the other groups. Magnesium and NO_3^- have generally lower concentrations in the DC and SG waters relative to the other groups, while Cl^- concentrations are low and show no significant variations. The SH waters were not subjected to statistical analysis due to the limited number of samples. Major ions chemistry indicated a bicarbonate-type composition for all the collected waters (Fig. 5a). Three subsets can be distinguished: i) Ca(Mg)–HCO_3 waters, which represent the majority of the analysed samples, ii) Na(Ca)–HCO_3 type waters, represented by the majority of DC waters and iii) Ca–$HCO_3(SO_4)$ waters represented by samples SC/S-8, SC/S-9, SC/S-10 and SH-1. Further indications may be provided by the ternary diagrams of Figs. 5b and c. In particular, it is evident that the SG waters exhibit an almost pure Ca–HCO_3

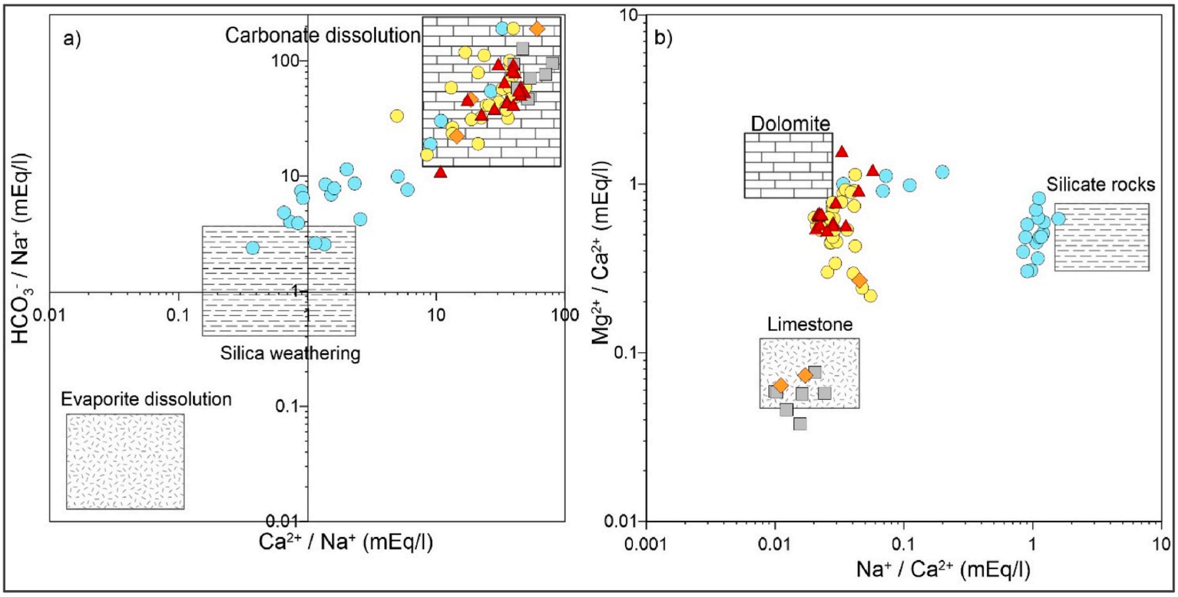

Fig. 6. Bivariate plot to classify the mineral weathering of groundwater in the study area: a) Ca^{2+}/Na^{+} vs. HCO_3^-/Na^+; the boxes characterize the ranges of estimated compositions of the three main source end members (evaporite dissolution, silicate weathering, and carbonate dissolution) without any mixing. b) Mg^{2+}/Ca^{2+} vs. Na^+/Ca^{2+}; the range of dolomite, siliceous rock and limestone in the figure is from Gaillardet et al. (1999). Symbols re the same of Fig. 5.

composition, while increasingly contents of Mg^{2+} characterize the other groups. Additionally, a significant portion of the DC waters in the Low Plain (samples from DC-2 to DC-16) display a gradual transition from a Ca-rich to a $Na^+(K^+)$-dominant composition.

Saturation indices (SI) for calcite range from −0.30 to +0.60 for SC/S, UC and SG samples, and from −0.61 to +0.47 for DC samples. Regarding dolomite, the SI values range from −4.00 to +1.10 for SC/S and UC samples, from −1.09 to +0.71 for DC samples, and from −1.60 to −0.10 for SG samples (Table 2S).

Oxygen and hydrogen isotope values range from −5.20‰ to −11.6‰ and from −39.3‰ to −75.8‰, respectively (Table 2S).

Tritium data are shown in Table 3S. The SG samples show the higher values (ranging from 6.27 to 7.67 TU) while DC samples have the lowest (from 0.82 TU to 1.58 TU). The other groups show intermediate values.

5. Discussion

5.1. Analysis and insights on the lithological model

The results of the lithological study reveal a marked distinction between the High Plain, predominantly composed of gravelly sediments of fluvioglacial origin, and the Low Plain, where clayey sediments occasionally intercalated with sandy and peaty layers prevail. However, our large-scale model allows to recognize some lithological heterogeneities within both the High Plain and the Low Plain that were not identified in previous studies. Based on these heterogeneities, the High Plains may be subdivided in two distinct sectors: the upper plain primarily consisting of gravelly sediments, and the lower plain characterized by conglomerate deposits. Additionally, in the western sector of the High Plain an alternating pattern of gravelly and clayey sediments is observed. These sediments, probably of glacio-lacustrine origin (Peresani et al., 2011; Monegato and Poli, 2015), fill the NE-trending tectonic depression originated by the Cansiglio and Polcenigo-Maniago thrust fault systems (Nicolich et al., 2004; Carulli, 2006). Within the Low Plain, the eastern sector displays a substantial proportion of sandy components relative to the western one. This increase in sandy deposits is likely linked to paleo-Livenza fluvial sediments.

5.2. The processes governing the chemical and isotopic composition of waters

The chemical composition of the collected waters is primarily controlled by the aquifer lithology. As shown in Fig. 5, the majority of the samples shows a $Ca(Mg)–HCO_3$ composition in which two main hydrochemical facies can be recognized. The first is an almost pure $Ca–HCO_3$ facies which characterizes the karst spring waters (SG group) emerging from karst aquifers hosted in the Jurassic and Cretaceous limestones from the eastern slopes of the Cansiglio plateau. The second is a $Ca(Mg)–HCO_3$ facies, which prevails in well waters from aquifers located in the plain and that can be attributed to the presence of limestones, dolomitic limestones, and dolomites in the Quaternary alluvial deposits that host these aquifers. The relative SO_4^{2-} enrichment observed in the small group of SC/S sampled geographically located in the western Cansiglio plateau area (Fig. 3) is likely related to interaction with SO_4-rich lithologies. The relative SO_4^{2-} enrichment observed in the small group of SC/S samples along the western border of the study area, on the southern slopes of the Cansiglio plateau, is likely due to mixing with $Ca–SO_4$ waters originating from interactions with SO_4-rich lithologies in the nearby western Cansiglio plateau hydrographic basin, as documented by Regione Veneto (2007), and Dal Prà (1993). In addition, the elevated average concentrations of NO_3^- in the SC/S and UC water samples, located in the High Plain and in Low Plain near the resurgence belt, is likely attributed to the intensive agricultural activities prevalent in the region. Similar observations have been documented in studies conducted in the Friuli Plain (Cucchi et al., 2008; Zini et al., 2009; Di Renzo et al., 2023a) and the Po Valley (Giuliano, 1995; Martinelli et al., 1998, 2018; Cinnirella et al., 2005; Sacchi et al., 2007, 2013; Lasagna et al., 2016; Rotiroti et al., 2019, 2023; Orecchia et al., 2022).

The Ca^{2+}/Na^{+} vs. HCO_3^-/Na^+ and Mg^{2+}/Ca^{+} vs. Na^{2+}/Ca^{+} plots (Fig. 6; Gaillardet et al., 1999) can provide further indications on the prevailing WRI processes in the study area. As explained by Gaillardet et al. (1997), the weathering is identified by the excess ions which are those not derived from the evapotranspiration of rainfall. Therefore, to accurately assess weathering processes, geochemical data must be normalized to rainfall. However, due to the lack of geochemical data from precipitations in the Friuli Venezia Giulia region, normalization of our dataset could not be carried out. Nonetheless, we can assume that

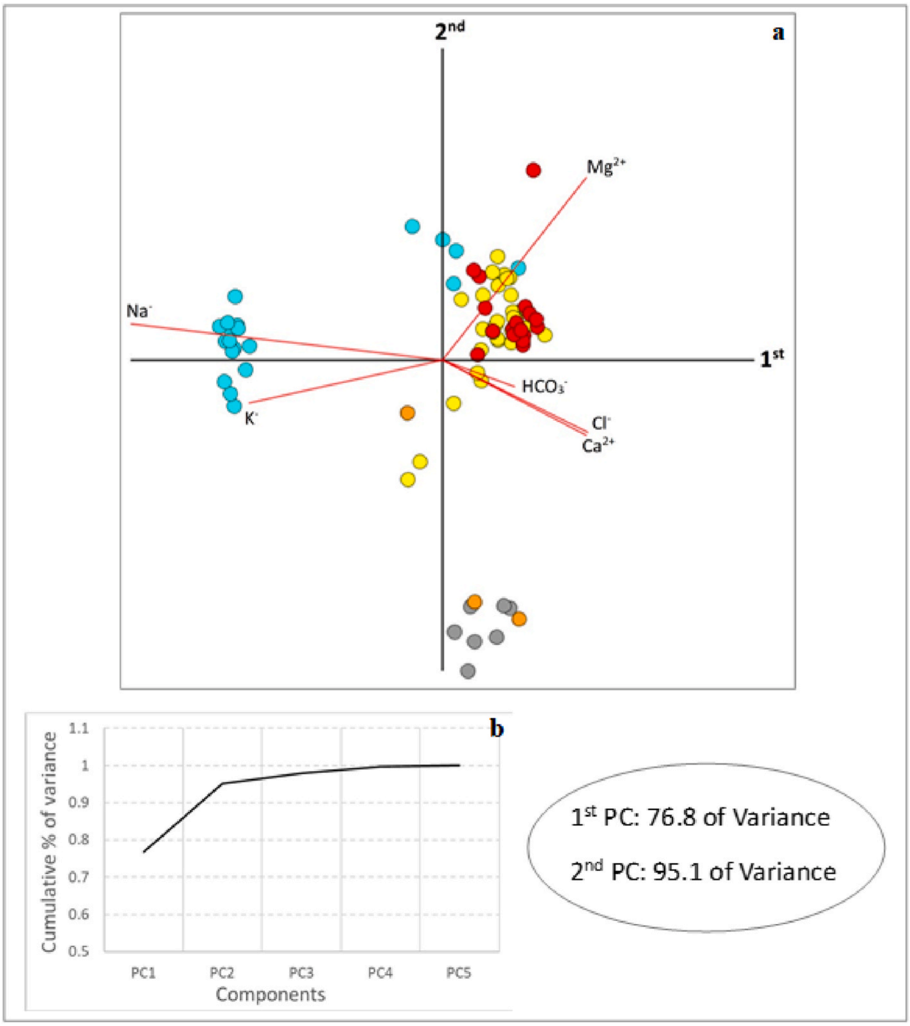

Fig. 7. Compositional PCA biplots for compositional hydrochemical data: a) a centred-log ratio (clr) biplot of data set; b) scree plot of the variance represented by each principal component for data matrix. Elaborations were conducted using the CodaPack program. Symbols are the same of Fig. 5.

the differences in ion content observed between water samples from the plain's aquifers and those from karst springs are attributable to WRI processes based on the findings of Zini et al. (2011) and Filippini et al. (2018), who identified similar recharge areas for the High Plain aquifers and karst springs, respectively. Fig. 6a confirms that most of the samples fall within the region associated with carbonate dissolution. On the other hand, waters from DC of the Low Plain shift towards the region of silicate weathering, suggesting that the composition of these waters is controlled by a combination of silicate leaching and carbonate dissolution processes. The progressive shift from Ca(Mg)–HCO_3 to Na–HCO_3 composition, in response to the gradual groundwater evolution, is the result of silica weathering through extensive cation exchange processes involving Ca^{2+} of the waters and Na^{+} released by clayey sediments. Fig. 6b shows the predominant dissolution influence of limestone and dolomite in the water samples collected within the study area.

The PCA results strengthen the hypothesis that two main geochemical processes, i.e. carbonate rocks weathering and exchange reactions, influence the chemical composition of the waters and are primarily responsible for the different geochemical evolution of the waters in the PP area (Fig. 7). The first is represented by the positive PC1 values dominating SC/S, UC, SG, SH groups and DC waters located near the resurgence belt (Fig. 7a), where the highest centred-log-ratio (clr)-variances are for Mg^{2+}, HCO_3^- and Ca^{2+}. The second process is represented by the negative PC1 values of DC waters located in Low Plain where the highest clr-variances are for K^+ and Na^+. Moreover, the trend of PC2 values from negative of SG waters to positive of the other groups agrees with the groundwater evolution from almost pure Ca–HCO_3 to more complex compositions.

Water stable isotopes confirm that the PP is characterized by a complex and heterogeneous groundwater system. The δ^2H vs. δ^{18}O plot (Fig. 8) shows that all the collected waters have a meteoric origin. However, three different clusters can be identified, as follows: i) waters with a relative enrichment of the heavier isotopes, mostly represented by the shallower UC samples from the unconfined aquifer of the High Plain, indicating a direct recharge from precipitations as they closely resemble the composition of rainfall within the plain (Michelini et al., 2012), ii) waters with a relative lighter isotopic composition, primarily represented by the DC samples from the confined aquifers of the Low Plain, from which a recharge altitude located in the mountains (from 1600 m to 2900 m) may be suggested, and iii) waters in an intermediate position relative to the previous groups, from which recharge altitude in the pedemontane sector (comprised in the range from 200 m to 1600 m) may be suggested. These waters, according to Cucchi et al. (2008) and Zini et al. (2009), are influenced by the adjacent Cellina River.

The altimetric gradient used to identify the average infiltration water levels and recharge areas is −0.17‰/100 m. This value was determined for the Friuli-Venezia Giulia region by Michelini et al. (2012) and is consistent with the value reported for the Trieste area by Longinelli and Selmo (2003), which is approximately −0.19‰/100 m.

The presence of measurable ^{3}H in groundwater samples often

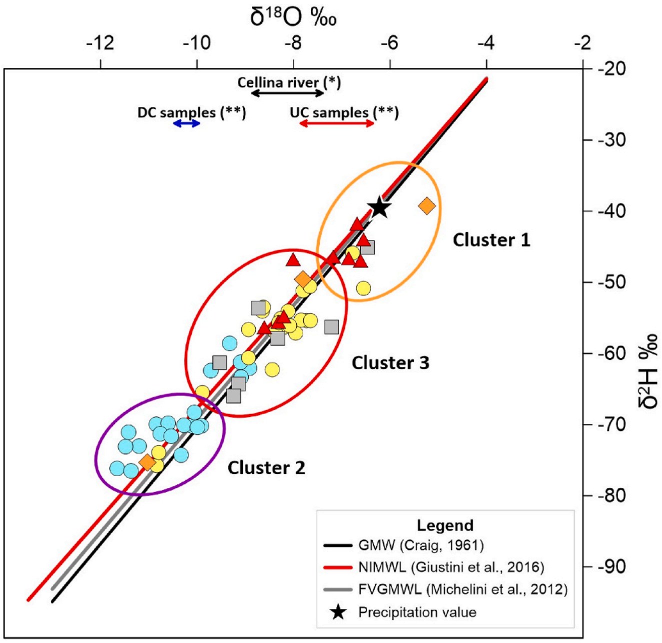

Fig. 8. Plot of δ^2H and $\delta^{18}O$ values of the collected waters. The Global Meteoric Water Line (GMWL; $\delta^2H = 8\ \delta^{18}O + 10$; Craig, 1961; Craig, 1961), the Northern Italy Meteoric Water Line (NIMWL; $\delta^2H = 8.04\ \delta^{18}O + 11.42$, Giustini et al., 2016) and the Friuli-Venezia Giulia Meteoric Water Line (FVGMWL; $\delta^2H = 7.98\ \delta^{18}O + 10.62$, Michelini et al., 2012) are also plotted. The altimetric gradient used to identify the average infiltration water levels and recharge areas is of −0.17‰/100 m (Michelini et al., 2012). (*) Isotopic signature of the Cellina stream reported by Boschin et al. (2006) and CAMI (2007); (**) average $\delta^{18}O$ values from points of interest published by Cucchi et al. (2008) and Zini et al. (2009). Symbols are the same as Fig. 5.

Table 1
Comparison between the average concentrations of ^3H, expressed in TU, detected in the water samples analysed, and the average concentration of ^3H in the precipitation recorded at the Locarno station (GNIP station network) in the period 1998–2008 (IAEA/WMO, 2022) and in period 2008–2018 (Terzer-Wassmuth et al., 2022). Min = minimum value; Max = maximum value; Std dev = standard deviation.

	Min	Mean	Max	Std dev
Karst springs (SG)	6.27	6.72	7.67	0.65
Unconfined aquifers (UC)	2.74	3.43	4.12	0.97
Semi-confined/shallow aquifers (SC/S)	2.53	3.40	4.56	1.04
Depth confined aquifers	0.82	1.20	1.58	0.54
Locarno station (1998-2008)	**5.43**	**7.90**	**11.43**	**1.72**
Locarno station (2008-2018)	**3.75**	**6.50**	**10.38**	**2.30**

indicates recent recharge; hence in this study, considering the half-life of ^3H is 12.32 ± 0.02 y, the ^3H values were used to evaluate the residence time of waters in subsoil (Schlosser et al., 1989; Clark and Fritz, 1997). The effective dating range for ^3H is strongly dependent on the pre-concentration factor and on the instrumental detection limit typically about 60 years (Kaufamn and Libby, 1954; Gleeson et al., 2016). The results obtained were compared with the concentrations of ^3H in precipitations in the Alpine area. Table 1 shows the ^3H concentrations measured in the collected water and the average annual concentrations in rainwater, recorded at the Locarno station (Global Network for Isotopes in Precipitation - network of stations "GNIP") in two different periods (Terzer-Wassmuth et al., 2022).

Based on ^3H data (Fig. 9), SG waters are indicative of recent recharge, whereas the other water types represent a mixture of both younger and older waters. Furthermore, the significant depletion of ^3H concentrations in the DC waters indicates a longer residence time in the subsurface compared to the other groups.

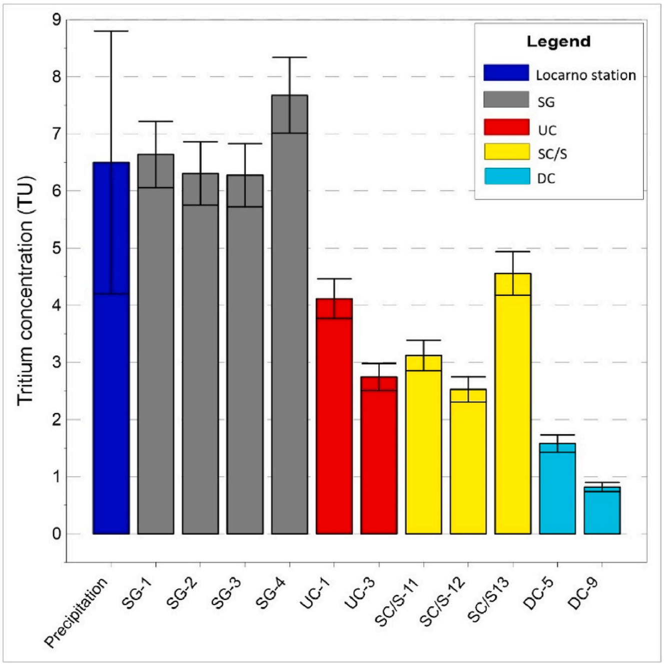

Fig. 9. Bar plot of ^3H concentrations in all analysed samples compared with the average ^3H concentration in precipitation recorded at the Locarno station during the period 2008–2018 (Terzer-Wassmuth et al., 2022).

5.3. Hydro-geochemical conceptual model of the pordenone plain

The detailed characterization of geochemical processes in the PP has enabled us to address knowledge gaps, thereby enhancing our understanding of the hydrochemical processes occurring from the recharge areas to the water flows within the plain, highlighting their influence on the chemical evolution of the waters. The integration of the hydrogeochemical processes with the lithological model and hydrogeological data has allowed us to construct a conceptual hydrogeochemical model for the study area, which is graphically represented in Fig. 10.

Three main groundwater flows have been recognized. The first flow involves the UC and SC/S waters hosted in the gravelly sediments of the upper part of the High Plain. These waters exhibit a Ca(Mg)–HCO_3 composition, attributed to the water-rock interaction involving carbonate rocks (Figs. 5–6). Stable isotope data indicate that this flow, originally fed by mountain watersheds located in pedemontane sector, is significantly influenced by the direct recharge of meteoric water into the plain (Fig. 8). This process results in substantial mixing between the two primary recharge inputs affecting the aquifers of the High Plain (Fig. 2a). Additionally, the shallow depth of the flow and the intense agricultural use of the area further contribute to its complexity, as the flow is also affected by indirect irrigation (Zini et al., 2011). The impact of human activities is evident in the elevated nitrate concentrations, which average higher than those in other flows, reaching up to 36 mg/L (Table 2S). Although these concentrations remain below legal limits, they underscore the vulnerability of this flow to anthropogenic pressures. The second flow includes the SG and UC waters hosted in the conglomerate deposits of the lower part of the High Plain, and the shallowest SC/S waters of the Low Plain near the resurgences belt. Water stable isotopes suggest that this flow is fed by a pedemontane recharge area at elevations up to 1600 m (Fig. 8). Part of this flow feeds the karst system of the Cansiglio Plateau, where its interaction with known regional faults facilitates the emergence of piedmont karst springs at the surface, as documented by Filippini et al. (2018). These karst springs (SG waters) exhibit a Ca–HCO_3 composition, resulting from the dissolution

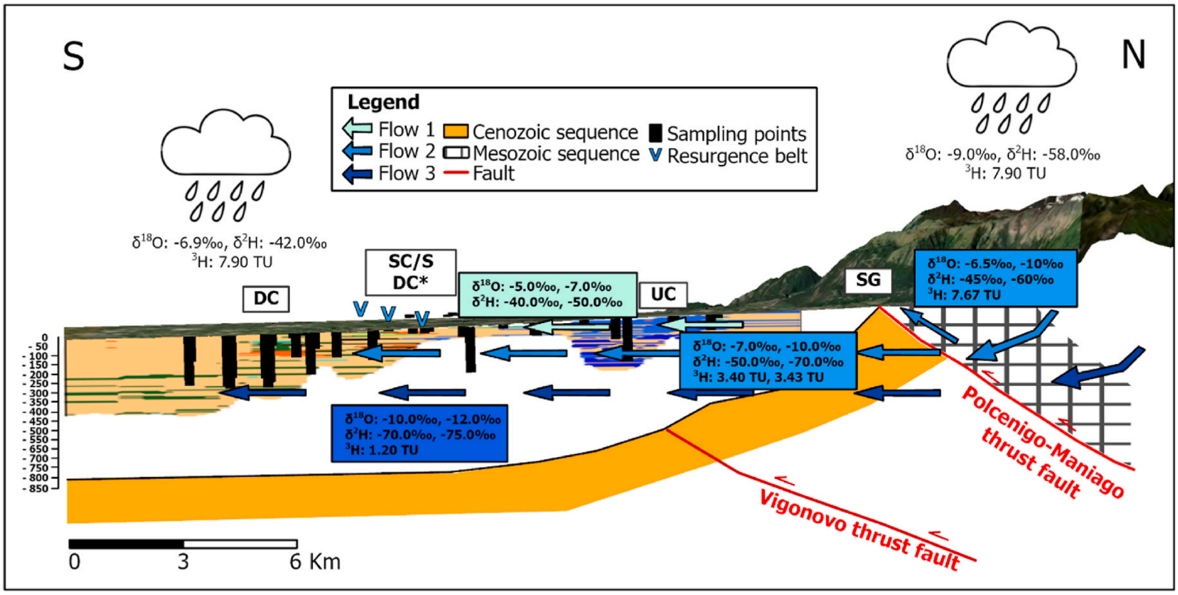

Fig. 10. Conceptual hydrogeochemical model of the PP. Section A-A′ in Fig. 2. See lithological legend in Fig. 3. Vertical exaggeration x2 and x4, respectively for the Digital Terrain Model (DTM) and the subsoil. DC* refers to DC water samples located near resurgence belt at depths ranging from −180 to −340 m from the ground level (DC-1, DC-17, DC-18, DC-19 and DC-20). “vvv” symbol refers to resurgence belt location. The isotopic data for precipitation were obtained from the multiannual arithmetic averages of two separate stations, as reported by Michelini et al. (2012).

of carbonates due to interactions with the limestone formations of the Cansiglio Plateau. These springs exhibit a rapid response to recharge events and a relatively short residence time, as indicated by tritium concentrations (Fig. 9). Considering the hydrogeological balance in Fig. 2, the remaining flow originating from the mountain watersheds moves south-southwestward (Fig. 2b), initially contributing to the UC waters in the High Plain. These UC waters subsequently recharge the more superficial SC/S waters in the Low Plain. Here, the dissolution of carbonate due to interaction with the High Plain dolomitic-rich deposits lead to the enrichment in Mg^{2+} in solution and to evolution of waters towards a Ca(Mg)–HCO_3 composition, differing from the hypothesized recharge area composition identified by the SG waters (Figs. 6–7). For these waters, stable isotopes and tritium concentrations suggest a rapid recharge rate with a modest residence time within the subsurface (Figs. 8 and 9). These findings are consistent with the synchronous response of the piezometric levels in the High Plain aquifer to precipitation events in the mountain catchments (Fig. 2c). This second part of the flow is influenced by various mixing processes that affect its geochemical evolution. It has been observed, particularly at the edges of the study area, that this flow is significantly impacted by the Cellina River to the east, as confirmed by Cucchi et al. (2008) and Zini et al. (2009), and by the western Cansiglio hydrographic basin to the west. This last contribution facilitates mixing with Ca–SO_4-type waters, which are the result of interactions with sulfate-rich lithologies (Regione Veneto, 2007; Dal Prà, 1993), leading to sulfate enrichment in the waters located in western edge (Fig. 5). Mixing between the aquifers of flow 1 and flow 2 appears not significant based on geochemical (Figs. 5–6) and isotopic (Fig. 8) results. The third flow involves the DC waters of the deep multi-layered aquifer of the Low Plain. These waters are hosted in permeable sandy lenses intercalated by low permeability clay layers, and exhibit a Na–HCO_3 composition related to silica weathering, in particular ion exchange processes between the groundwater and the hosting rocks (Figs. 6–7). Stable isotopes suggest a recharge area at high altitudes (up to 2900 m) and a slow recharge rate (Fig. 8), while the significant depletion in ^3H concentrations suggests a prolonged residence time within the subsurface (Fig. 9). The comparable chemical and isotopic composition of waters of this flow suggests that it is separated from the other flows and not influenced by more recent waters. Moreover, the very low nitrate concentrations combined with the considerable depth of the aquifer indicate that this flow is not subject to direct anthropogenic pressure.

6. Conclusion

The study conducted in the Pordenone Plain (PP) highlights how a detailed geochemical and isotopic characterization of waters, combined with hydrogeological and lithological data, may help in understanding the complex dynamics of multi-layered alluvial aquifer systems and define conceptual hydrogeochemical models of fluids circulation.

In our case study, the model allowed to identify two recharge areas in the pedemontane and mountain sectors and three distinct flows within the plain, each exhibiting different geochemical characteristics and evolution due to varying processes including water-rock interaction and mixing, and different recharge mechanism and residence times within the aquifers.

This study has highlighted the complexity of the hydrogeological system of the PP, revealing significant differences in groundwater flows within the High Plain, in contrast to the previous hypothesis of a single, continuous water body. The shallower flow has been found to be strongly influenced by local precipitation and agricultural practices, rendering it particularly vulnerable to climate change and anthropogenic pressures. The intermediate flow, though less impacted by the superficial flow, still undergoes horizontal mixing with waters of varying origins, particularly at the margins of the plain. Additionally, in the semi-confined aquifers of the Low Plain, this flow is extensively utilized for irrigation and domestic purposes, making it particularly sensitive to anthropogenic impacts, especially during drought periods. A deep flow has also been identified, characterized by high-quality water that feeds the confined aquifers of the Low Plain. Although the path of this flow in the High Plain has only been hypothesized, its existence suggests a greater complexity in the articulation of the region’s aquifers, suggesting further studies to precisely trace its patch.

In summary, this study has provided new and significant insights into the hydrogeochemical dynamics of the PP, which can be effectively integrated with other researches to develop more efficient and sustainable water resource management plans. However, to fully understand these complex dynamics, it will be necessary in the future to implement a more detailed seasonal monitoring study. This study should be based on the conceptual hydrogeochemical model developed in this study and include isotopic and chemical analyses of both groundwater and surface water, as well as precipitation, in parallel with hydrogeological monitoring. Such an approach would provide a clearer understanding of the residence time, groundwater flow paths, and recharge and discharge mechanisms of the aquifers within the PP. This integrated monitoring could also prove important for understanding the effects of intensive water withdrawals, particularly during summer periods, on groundwater quality. A detailed analysis of this kind would allow for the detection of any seasonal variations in the mixing processes between different aquifers, which could undermine the long-term sustainability of water resources. This approach would not only enable an assessment of the current quality of available water, but also allow for the proposal of safeguarding measures to protect high-quality resources and suggest remediation interventions for those already partially compromised.

CRediT authorship contribution statement

Dino Di Renzo: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Elena Marrocchino:** Writing – review & editing, Validation, Data curation. **Chiara Telloli:** Writing – review & editing, Methodology. **Daniele Cinti:** Writing – review & editing, Validation. **Lorenzo Copia:** Writing – review & editing. **Lucia Ortega:** Writing – review & editing. **Renzo Tassinari:** Writing – review & editing, Methodology. **Carmela Vaccaro:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix ASupplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2024.106161.

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