



Combining groundwater budget, hydrochemistry and environmental isotopes to identify the groundwater flow in carbonate aquifers located in Campania Region (Southern Italy)

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ABSTRACT

Study region: Carbonate mountains of Mt. Maggiore and Mt. Tifata, Campania Region, southern-central Italy, Mediterranean basin.

Study focus: The hydrogeological relationship between the carbonate massifs of Mt. Maggiore and Mt. Tifata is investigated. Archival and newly acquired data on groundwater availability, hydrochemical and isotopic data were considered. Their combined use led to the proposal of new hypotheses regarding the connection between these aquifers. The exchange of groundwater through this connection would be induced by the strong groundwater withdrawals from the well fields at Mt. Tifata; the area of possible connection was also identified. A mineralization model of some local springs showing high CO₂ and TDS values is also proposed.

New hydrological insights for the region: The carbonate rocks are widely outcropping with a mountainous morphology and host important groundwater resources in the studied region. The springs related to these carbonate aquifers have excellent chemical characteristics and, for these reasons, the major aqueducts in Campania Region rely on these groundwater resources. The well fields of the Mt. Maggiore and Mt. Tifata supply part of the metropolitan area of Naples, with 3.8 million inhabitants. The quantitative evaluation of groundwater resources and the proposed groundwater circulation scheme can support a sustainable and diversified use of the resource taking into account the presence of waters already used for drinking purposes and waters with high TDS values.

1. Introduction

The carbonate rocks occupy 15.2% of the global continental surface (ice-free), with the largest percentage in Europe (21.8%, Goldscheider et al., 2020), usually representing aquifers of significant importance (Allocca et al., 2007; Dar et al., 2014; Hilberg, 2016; Malik et al., 2021; McGibbon et al., 2022; Zeng et al., 2022). In the Campania Region (Southern Italy), the carbonate rocks are widely outcropping (about 50% of the exposed lithologies in the Region) with a mountainous morphology. Consequently, the high levels of

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rain-snow recharge and the remarkable permeability of these carbonate rocks determine the occurrence of important groundwater resources.

The water springs related to these carbonate aquifers are generally limited in number but have discharges (Q) in the order of hundreds to thousands of litres per second. The total discharge of all karstic springs in the Campania Region is approximately $70 \text{ m}^3 \text{ s}^{-1}$. Moreover, to these volumes the groundwater flow from the carbonate aquifers to the neighbouring aquifers should also be added, quantifiable in approximately $25 \text{ m}^3 \text{ s}^{-1}$ (Allocca et al., 2007; Budetta et al., 1994; Celico, 1983).

For these reasons, the major aqueducts in Campania Region rely on these springs. Moreover, the latter show excellent chemical characteristics of the waters (TDS $\sim 200\text{--}300 \text{ mg L}^{-1}$; hardness $\sim 15\text{--}17 \text{ }^\circ\text{F}^1$; Corniello 1996), and the potential pollution of the carbonate aquifers is unlikely due to their mountainous morphology limiting the human impact.

Very often, in the carbonate mountains of Campania Region, the lithological succession is quite uniform. Consequently, the infiltrating waters reach a *basal groundwater* (i.e., continuously saturated basal zone of the aquifer) that feeds the springs and the neighbouring aquifers.

On the other hand, the estimate, even within the same aquifer, of the recharge areas of the various springs located at the edge of the carbonate reliefs is, in some cases, challenging. The complexity increases when defining the relationships between neighbouring aquifers (Allocca et al., 2007; Allocca et al., 2014; Andreo et al., 2008; Petitta et al., 2022). Additionally, the hydrogeological

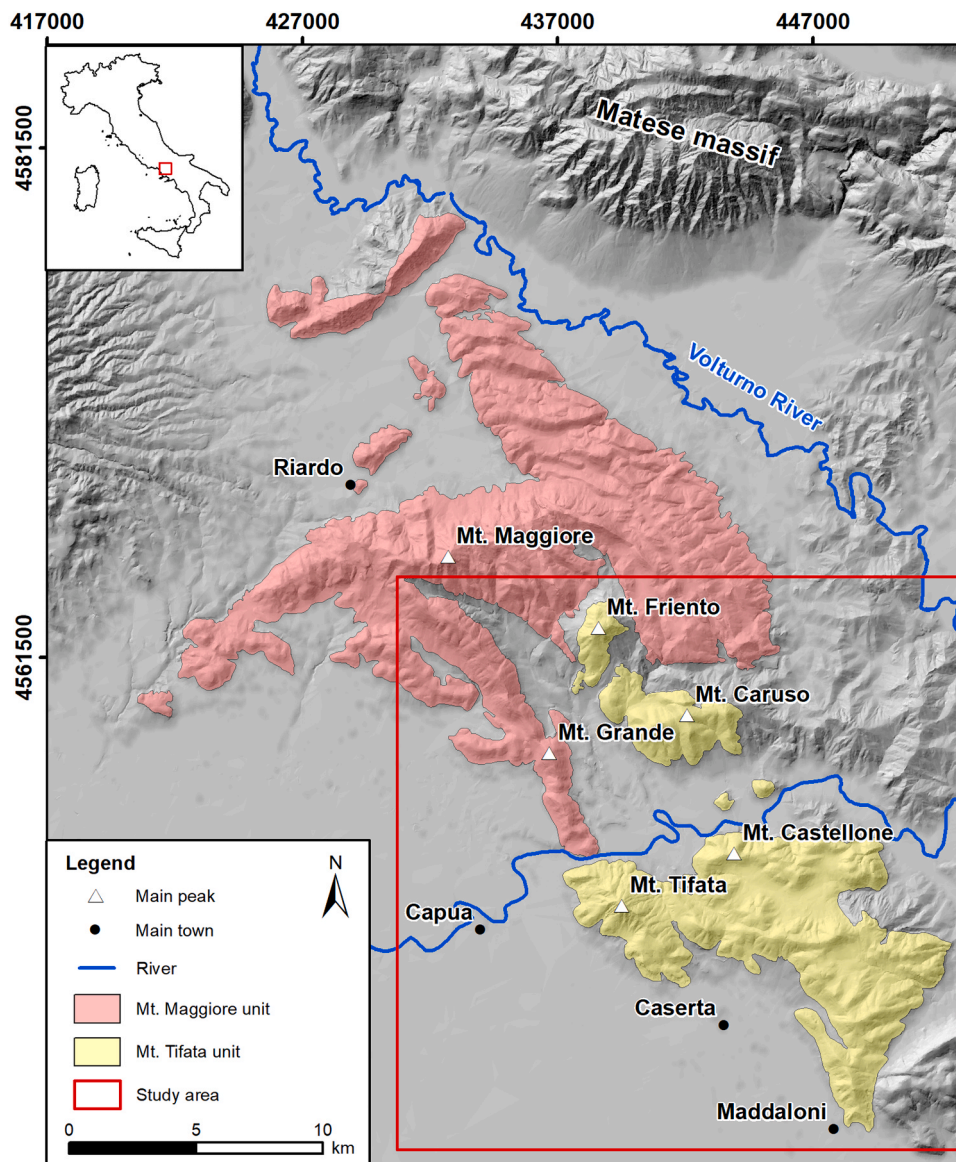


Fig. 1. Location and geographical setting of the study area, including main peaks, towns and rivers quoted in the text. Mt. Maggiore and Mt. Tifata units delineation according to DAM (2021). Basemap: hillshade derived from TINITALY digital elevation model (Tarquini et al., 2023).

relationships between different aquifers are often intricate since they are not directly observable, and are widely debated in the literature (Anderson et al., 2006; Belay et al., 2023; Le Mesnil et al., 2020; Yang et al., 2022a). However, such relationship becomes necessary for the hydrogeological budget evaluation (Allocca et al., 2014; Andreo et al., 2008; Demiroglu, 2019; Gaiolini et al., 2022; Mádl-Szőnyi and Tóth, 2015; Viaroli et al., 2018; Zhou, 2009) for the assessment of the quantitative status of groundwater, required by the European Water Framework and Groundwater Directives (EEA Report No 7/2018) through the comparison between water withdrawals and natural groundwater resources, and for a sustainable groundwater management.

In many cases, the investigation of the hydrogeological relationship between aquifers is carried out with the application of a single method (e.g., geochemical analysis, isotopic analysis, recharge/discharge imbalance). However, a multi-method investigation represents the best approach for such studies (Belay et al., 2023; Cocca et al., 2023; Zouari et al., 2024), allowing encompassing the specific limitations of the individual methods (Nelson and Mayo, 2014).

In this study, the hydrogeological relationship between two neighbouring carbonate aquifers (the mountain ranges of Mt. Maggiore and Mt. Tifata), morphologically separated by the Volturno River, is investigated. These aquifers are characterised by a strongly mountainous morphology, with the basal groundwater lying much deeper with respect to the ground level. This aspect prevents the

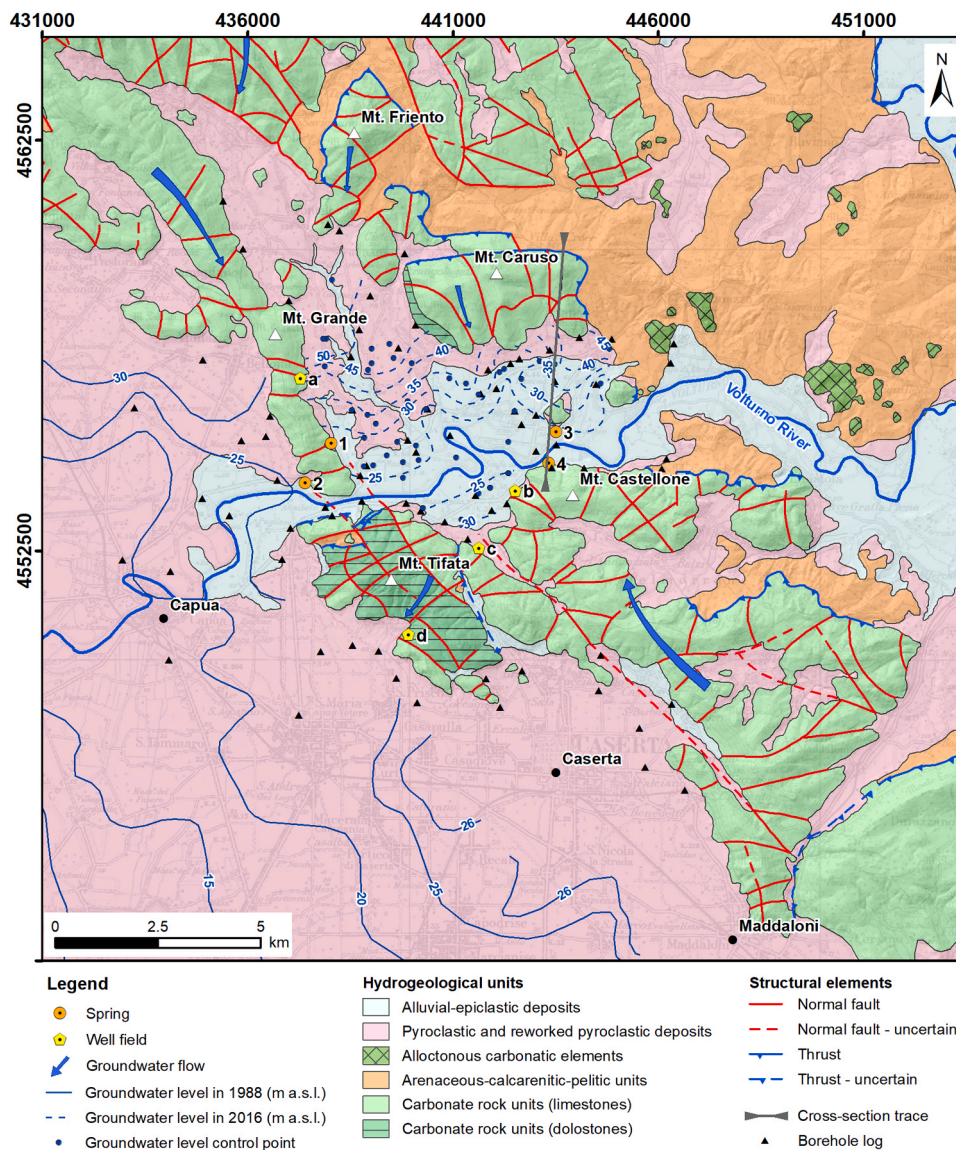


Fig. 2. Hydrogeological setting of the study area (modified after Celico et al. (1977)). Springs: 1) Pila spring; 2) Triflisco spring; 3) Murata spring; 4) S. Sofia spring. Well fields: a) Pontelatone well field; b) S. Sofia – Giglio – Baldi galleries; c) Tifata well field; d) S. Prisco well field. Groundwater flow directions modified after Piscopo (1997) and Celico et al. (1977). Groundwater levels in the porous aquifer after ASM (1988) and this work (2016). Basemap: hillshade derived from TINITALY digital elevation model (Tarquini et al., 2023) and 1:100.000 topographical map from Geoportale Nazionale (<https://gn.mase.gov.it/portale/home>).

definition of the hydrogeological relationship between the aquifers by means of the groundwater level measurement. For this reason, the investigation approach was based on the reinterpretation of archival data and the acquisition of new data (including hydrochemical and isotopic data) that enabled a comprehensive understanding of the Mt. Tifata recharge/discharge imbalance and led to the proposal of new hypotheses regarding groundwater resources and their connections. This issue is not only of scientific relevance but has also practical implications; indeed, there are important springs (with discharges in the order of several hundred litres per second) and well fields near the Volturno River, comprising a total of 35 wells with an average total flow rate of $2.2 \text{ m}^3 \text{ s}^{-1}$ in the period 2000–2015 (Corniello and Ducci, 2017).

2. Study area

The study area is located in the valley of the Volturno River, between the carbonate mountains of Mt. Maggiore to the north and Mt. Tifata to the south (Fig. 1). The geology of the area is highly diverse and complex. The valley of the Volturno River contains pyroclastic-alluvial deposits and is bordered to the north and the south by carbonate slopes belonging to two distinct tectonic Units (of Mesozoic-Cenozoic age): the Matese-Taburno-Camposauro Unit and the Lattari-Picentini-Alburni Unit (Patacca and Scandone, 2007; Servizio Geologico d'Italia, 2010).

The mountain range of Mt. Maggiore (Fig. 1) belongs to the former Unit while the latter characterises Mt. Tifata *sensu lato* (south of the Volturno River) and the Mts. Friento and Caruso to the north of the river (Fig. 1 and Fig. 2).

These Units are in contact in the valley of the Volturno River due to the Mio-Pliocene compressive tectonics and show complex and not yet completely defined relationships (Pescatore and Sgrosso, 1973; Servizio Geologico d'Italia, 2010; Vitale and Ciarcia, 2018). This tectonic phase has also involved Miocene sandy-clayey formations (of low permeability) occurring between the carbonate sectors of the two units (Pescatore and Sgrosso, 1973; Servizio Geologico d'Italia, 2010).

A successive Plio-Pleistocene extensional tectonic phase was responsible for the formation of the graben that corresponds to the valley of the Volturno River. Due to compressive tectonics and secondarily to the presence of Miocene sandy-clayey formations, the mountain range of Mt. Tifata could be hydraulically separated from that of Mt. Maggiore as well as from Mt. Friento and Mt. Caruso (Allocca et al., 2007; Celico et al., 1977; Celico, 1983). The latter are located north of the river but belong to the same unit as Mt. Tifata (Fig. 1).

More recent geological maps (Servizio Geologico d'Italia, 2010; Vitale and Ciarcia, 2018) significantly reduced the extent of the compressive faults along the northern edge of the Mt. Tifata range, clearly recognising them only in the NE and NW sectors (Fig. 2). Furthermore, numerous boreholes drilled along the Volturno River (near Mt. Castellone and Mt. Caruso) did not find any tectonic intercalations of sandy-clayey materials within the carbonate formations. On the other hand, the boreholes showed the presence of a carbonate substrate, beneath the pyroclastic-alluvial deposits of the Volturno plain, connecting the carbonate outcrops of Mts. Caruso/Friento (north) to those of Mt. Castellone (south) (Fig. 3). Towards the north, the limestones of Mts. Caruso and Friento overthrust clayey-sandy terrains (Fig. 2 and Fig. 3), determining an unlikely hydraulic continuity with the northern carbonate mountains of Mt. Maggiore.

Moreover, geo-electrical surveys (ASM, 1988) conducted between Mt. Grande and Mts. Friento and Caruso (Fig. 1) have identified a carbonate substrate approximately 200–300 m below the ground surface. This substrate probably provides hydrogeological continuity between Mt. Grande and the other reliefs.

Finally, to the south, the Maddaloni Valley (Fig. 1) separates the mountain range of Mt. Tifata from the more southern carbonate aquifers. In this case, the lack of hydrogeological continuity has been confirmed by geophysical surveys (Celico et al., 1977) and during the construction of a railway tunnel in the southern reliefs (Vitale et al., 2020; Briganti et al., 2016).

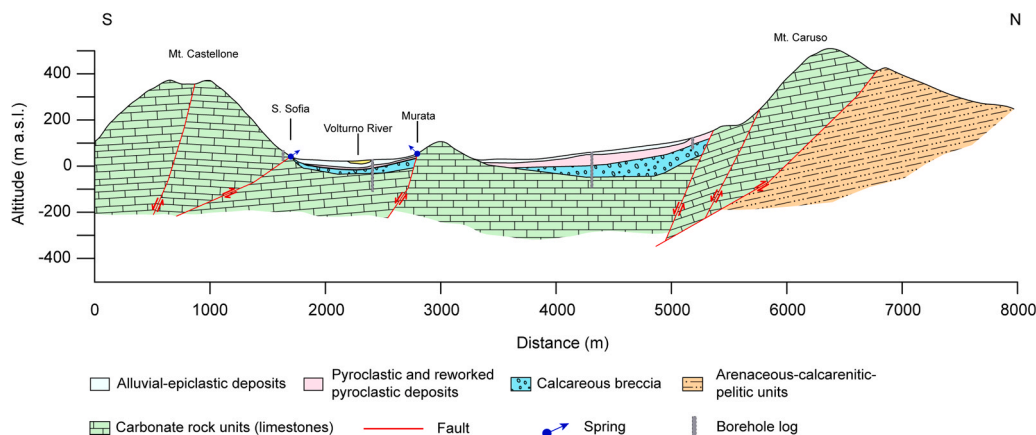


Fig. 3. Hydrogeological scheme along the N–S section marked by the grey line on the map in Fig. 2 (modified after Corniello and Ducci 2017).

3. Hydrogeological setting

The main water resources of the study area belong to the carbonate rocks, whereas groundwater in the pyroclastic-alluvial sediments of the Volturno River valley is relatively less significant.

3.1. Carbonate mountains

The permeability of carbonate rocks and the absence of relevant impervious layers in the vadose zone favour the infiltration of water from rain/snow towards the *basal groundwater*, supplying significant springs. The mountain group of Mt. Maggiore represents a large hydrogeological basin, from the Volturno River to the mountains of the Riardo plain (Fig. 1; Celico et al. (1977); Viaroli et al. (2016)). They are mainly composed of limestones, with the presence of dolomitic rocks at the base of the western slope of Mt. Maggiore. The main natural outflows of this hydrogeological basin are represented by the Pila (27–28 m a.s.l.) and Triflisco (27 m a.s.l.) springs (n. 1 and 2; Fig. 2).

In the years 1987–1988, a well field (named Pontelatone, marked as “a” in Fig. 2) was realised north of the Pila spring. Spanning from south to north and parallel to the slope, it consists of 20 wells. These wells have an average depth of 115 m and are spaced about 70 m from each other. All the wells intercept the calcareous aquifer, in which pumping tests showed transmissivity values ranging from 10^{-1} to $10^{-2} \text{ m}^2 \text{ s}^{-1}$ (Piscopo, 1997). The saturated thickness (prior to pumping) ranges between 35 and 88 m, giving a hydraulic conductivity ranging from $1.1 \times 10^{-4} \text{ m s}^{-1}$ to $2.7 \times 10^{-3} \text{ m s}^{-1}$. The wells do not reach an impermeable layer. Groundwater levels measured in the wells prior to pumping range between 30 and 33 m a.s.l. (from south to north, Piscopo 1997). From 2000–2015, the average total extraction rate from the wells was about $1 \text{ m}^3 \text{ s}^{-1}$ (Corniello and Ducci, 2017).

As a result of the withdrawal from the well field, the flow rate of the Triflisco spring decreased from an average of $3.0 \text{ m}^3 \text{ s}^{-1}$ (1983–1987 data) to approximately $1.9 \text{ m}^3 \text{ s}^{-1}$ (1990–1991 data). The reduction in flow rate was even higher for the Pila spring, which decreased from an average of $0.9 \text{ m}^3 \text{ s}^{-1}$ to around $0.25 \text{ m}^3 \text{ s}^{-1}$ in the same time interval (Fig. 4, Corniello and Ducci (2017)). These values are confirmed by more recent measurements carried out in the years 2018–2019 (Viaroli et al., 2019).

The only significant spring fed by the Mt. Tifata (south of the Volturno River) was called S. Sofia (about 30 m a.s.l., no. 4 in Fig. 2; Q_{med} : $0.8 \text{ m}^3 \text{ s}^{-1}$, from Celico (1983)). However, this spring no longer exists because of 12 wells drilled in the years 1989–1990 in the carbonate slope above the spring, distributed in three galleries (S. Sofia, Giglio, and Baldi; marked as “b” in Fig. 2). In the following we also refer to the three galleries S. Sofia, Giglio and Baldi as “S. Sofia s.l.”. All these wells reached depths of 100–115 m and penetrated limestones with different fracture intensity. As a result of the pumping, the groundwater level in the aquifer is now 10–15 m lower than the elevation of the spring.

It is worth noting that the current groundwater level is even lower than the elevation of the nearby Volturno River. Nonetheless, the consistent values of electrical conductivity, nitrates, and fluorides exclude the presence of water inflow from the river into the aquifer (physico-chemical data recorded from 2002 to 2015, Corniello and Ducci 2017).

About 2.5 km southwest of the three galleries (S. Sofia, Giglio and Baldi), there is another well field called Tifata (“c” in Fig. 2), realised in the years 1980–1982 and consisting of 5 wells (numbered from 13 to 17). These wells were drilled at the northeastern base of Mt. Tifata, encountering permeable limestones as indicated by the pumping test results (performed at constant flow rate and long duration) conducted in four of these wells (Table 1).

During the period 2000–2015, the average cumulative total flow rate of the three galleries (S. Sofia, Giglio and Baldi) and the Tifata well field was approximately $1.2 \text{ m}^3 \text{ s}^{-1}$ (data from Acqua Campania S.p.A.).

Additionally, the S. Prisco well field (“d” in Fig. 2), consisting of five wells, started working in 1990 at the southwestern base of Mt. Tifata. To the south and west of this area, an extensive flat area is present, known as the Campanian Plain. The available stratigraphic

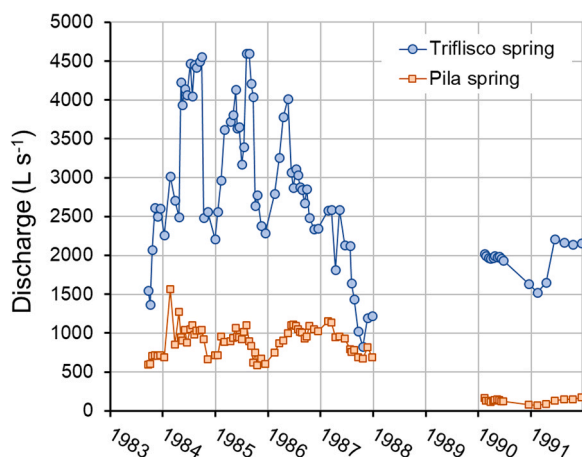


Fig. 4. Flow rate of Pila and Triflisco springs in the 1980s and 1990s.

Table 1

Results of the pumping tests conducted at constant flow rate (Q) and long duration on some of the wells (Δ is the drawdown - Corniello and Ducci (2017)).

Well	Q ($\text{m}^3 \text{s}^{-1}$)	Duration (h)	Δ (m)	Q/ Δ ($\text{m}^2 \text{s}^{-1}$)
Tifata well field: well 14	0.035	72	0.49	0.071
Tifata well field: well 15	0.040	96	1.40	0.029
Tifata well field: well 16	0.125	77	2.20	0.056
S. Prisco well field: well 1	0.035	24	0	-
	0.075	24	0	-
	0.100	24	0	-
S. Prisco well field: well 2	0.075	23	0.25	0.300

information (Acqua Campania S.p.A.) showed that the aquifer targeted by S. Prisco wells (each 120 m deep) consists of very permeable carbonate rocks (Table 1). The flow rates, recorded from 2002 to 2015, show a significant increase in withdrawals, ranging from $0.280 \text{ m}^3 \text{ s}^{-1}$ in 2002 to $0.500 \text{ m}^3 \text{ s}^{-1}$ in 2015 (Acqua Campania S.p.A.).

In Fig. 2, the contour lines of the groundwater level in the Campanian Plain are shown: these are sub-parallel to the Mt. Tifata and have higher values near it (§ 6). By comparing the current groundwater levels with those measured in 1988 (a period when the S. Prisco well field was not yet active; GEOLAB 1990), there is almost an exact coincidence of values, indicating that the significant withdrawals from the S. Prisco well field (along with those from other wells of the plain) did not alter the groundwater flowpaths in the plain.

All the previous considerations can be summarised as follows. The hydrogeological basin of the Mt. Tifata *s.l.* extends from the Maddaloni Valley to the Volturno River and, beyond the river, includes the Mts. Caruso and Friento. The groundwater outflows (natural and anthropic) from these reliefs are represented by: a) underground flows towards the deposits of the Campanian Plain, b) withdrawals from the three well fields (S. Sofia *s.l.*, Tifata and S. Prisco), and c) the small Murata spring (30 m a.s.l.; $Q \approx 0.01 \text{ m}^3 \text{ s}^{-1}$ in Celico (1983), currently almost completely dried up) located southern of Mt. Caruso (n. 3 in Fig. 2).

3.2. Volturno river valley

The Volturno Valley hosts pyroclastic deposits with significant thickness associated with alluvial deposits resulting from the widening of the Volturno River (Fig. 2 and Fig. 3). This plain area is known as Monteverna alluvial plain. The wells distributed in the plain typically show depths greater than 50–60 m, without intercepting the carbonate bedrock underlying the pyroclastic-alluvial deposits, and exploit a confined aquifer. The confined character of the aquifer is revealed by the data collected for this study which show the decrease in water levels with increasing atmospheric pressure, and vice versa, during periods characterised by a lack of rainfall (Fig. 5). This confined aquifer, which is significantly larger to the north of the Volturno River, exhibits piezometric contour lines orthogonal to the slopes of Mt. Grande (Fig. 2), and groundwater levels (30–50 m a.s.l.) higher than those measured within the mountain (28–33 m a.s.l., Piscopo 1997); this suggests the absence of connection between groundwaters of Mt. Grande and the plain, probably due to the interposition of low permeable layers. In the eastern sector of the plain, the piezometric contour lines become sub-parallel to the slopes of Mt. Caruso, indicating a likely recharge from this mountain towards the deposits of the plain.

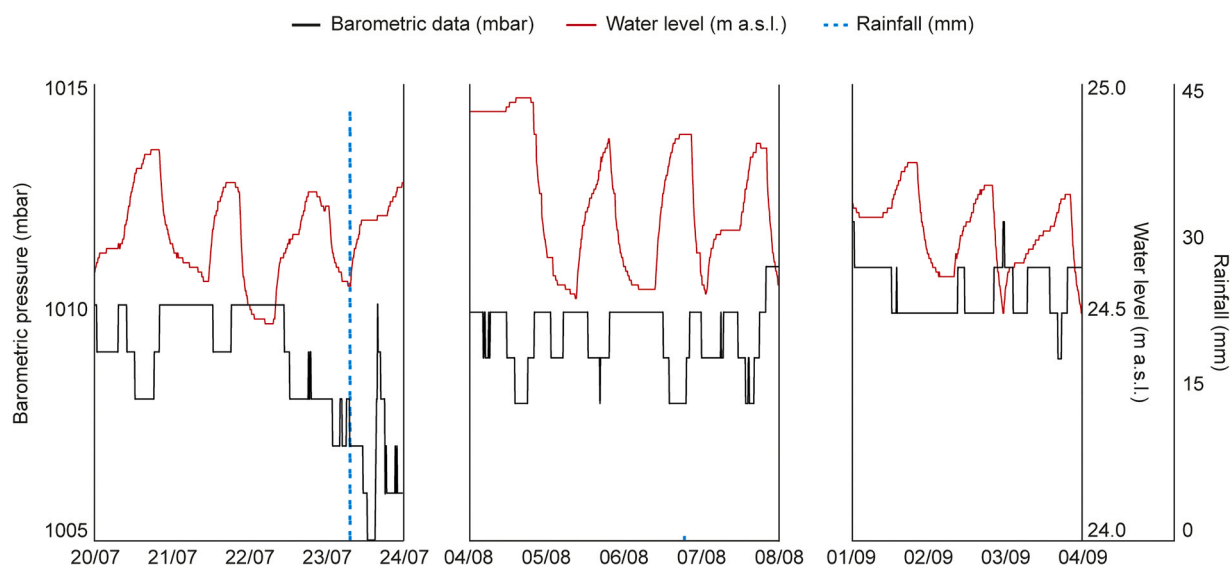


Fig. 5. Comparison between groundwater level measured in a water well in the plain east to Mt. Grande (10-minute frequency) and rainfall amount and barometric pressure measured at S. Marco Evangelista meteorological station (one-hour frequency). Data refer to summer 2015.

4. Data and methods

About 70 borehole logs were collected from local authorities, technical agencies and private companies, enabling a better understanding of the geological setting (Fig. 2).

Groundwater levels were measured in 2016 in over 50 wells, generally located in the plains surrounding the mountains. Previous data were obtained from the literature (Celico, 1983; Corniello and Ducci, 2014, 2017; Corniello et al., 2010; GEOLAB, 1990; Piscopo, 1997), providing information on the distribution and fluctuation of groundwater levels in wells of the area. Continuous groundwater level measurements from various piezometers at the Ponte Annibale dam have been provided (from 2012 to 2015) by the *Consorzio di Bonifica del Bacino Inferiore del Volturno* (Consortium for the Reclamation of the Lower Volturno Basin). Data concerning the springs and the well fields were provided by Acqua Campania S.p.A., which manages all the well fields present in the area. Meteorological data (rainfall, temperature, atmospheric pressure, wind speed and direction, solar radiation) were acquired from the rain gauge stations located in and near the study area, managed by the "Centro Funzionale Multirischi della Protezione Civile della Regione Campania" and available online (<http://centrofunzionale.regione.campania.it/>). Monthly data referring to the period 2009–2015 were considered.

Forty-four groundwater samples were collected from springs, well fields, and plain wells and were analysed by the Department of Chemical Sciences of the University of Naples Federico II (Tables S1, S2 and Fig. 7). The water samples were collected as established by the APAT-IRSA/CNR guidelines (Method 1030, Manual 29/2003). Anion and cation content was determined by ion chromatography using a Metrohm 761 Compact IC. Temperature, pH, alkalinity, and Electrical Conductivity (EC) were measured in the field using HANNA instrument meters, which were calibrated before sampling by using standard solutions. All the physico-chemical analyses available in the literature (ASM, 1988, 1990, 1991; Celico et al., 1980; Corniello, 1996; Corniello et al., 2015, 2010; Duchi et al., 1995) were also considered in this study, after verification of correctness by checking the ion balance. Samples showing an error in the ionic balance lower than $\pm 5\%$ were considered in this study. Additional chemical analyses of water collected from springs and well fields located in the study area monitored biannually since 2003–2004 by the Regional Environmental Agency of Campania Region (ARPAC) and available online (<https://www.arpacampania.it/>) were used.

Isotopic analysis ($\delta^{18}\text{O}$ and δD , as ‰ versus VSMOW) reported in Table S2 were determined by different laboratories and at various depths of the groundwater wells (see related references in the caption). The isotopic analyses for this study were performed at the Isotope Laboratory ISO4 of the University of Turin by means of an off-line cryogenic CO_2 extraction system with equilibration (Epstein and Mayeda, 1953) coupled with a Varian MAT250 mass spectrometer for $\delta^{18}\text{O}$ and by an off-line water zinc reduction line (Coleman et al., 1982) coupled with a Varian MAT251 mass spectrometer for δD . The analytical precisions were 0.1‰ and 0.5‰, for $\delta^{18}\text{O}$ and δD , respectively.

All the geographical information and numerical data were organized within a geo-database (ArcGIS-ESRI and QGIS, <https://www.qgis.org/>). The software Excel (Microsoft) was used for geochemical data visualization through graphical methods, namely the Schoeller-Berkaloff diagram and bivariate plots (e.g. $\delta^{18}\text{O}$ and δD). The Piper and Durov diagrams were generated for the visualization and identification of hydrochemical facies. The WQChartPy open-source Python package (Yang et al., 2022b) was used for generating the Piper and Durov diagrams. The software Surfer 11 (Golden Software) was used for the spatial interpolation of the hydrochemical data and groundwater budget terms. The "ET0 calculator" software developed by the Land and Water Division of FAO (Allen et al., 1998) was used for the calculation of the average reference evapotranspiration ET_0 for each month in the period 2009–2015.

5. Results

5.1. Groundwater availability

All previous studies (Allocca et al., 2014; Celico et al., 1977; Corniello and Ducci, 2017; Regione Campania, 2005) indicate that withdrawals from the Mt. Maggiore basin (mainly represented by the Pontelatone well field) are significantly lower than the recharge. The same studies highlighted an opposite situation in the mountain range of Mt. Tifata, where the Regione Campania (2005) reported cumulative withdrawals from various well fields in the study area of $68.7 \times 10^6 \text{ m}^3 \text{ year}^{-1}$ compared to a recharge of $40.7 \times 10^6 \text{ m}^3 \text{ year}^{-1}$. Therefore, it was decided to verify these situations through the calculation of a groundwater budget for assessing the recharge amount over the two areas (Mt. Maggiore and Mt. Tifata) and to compare the recharge to the groundwater withdrawals in the same period (years 2009–2015).

Precipitation data were evaluated by interpolating the cumulative monthly data from 17 rain gauge stations through the kriging technique. The air temperature (T) of the area, which is necessary for the calculation of evapotranspiration, was assessed using monthly average data from 10 weather stations. For each year in the chosen period, the average annual temperature of the stations was correlated with the elevation (z). The results led to the identification of the following equation: $T = 16.8 - 0.0059 \cdot z$ ($R^2 = 0.89$). The temperature data were correlated with the elevation using a 20-meter Digital Elevation Model of Campania Region, resulting in the maps of annual air temperature for each year. The real evapotranspiration (E_r) was derived from the reference Penman-Monteith evapotranspiration ET_0 (Allen et al., 1998). The estimation of the average ET_0 (years 2009–2015) for each month (ET_{0m} = monthly reference evapotranspiration in mm) for the various stations was then interpolated. The monthly crop evapotranspiration (ET_{cm}) was determined by applying crop coefficients (K_c) to the ET_0 values: $ET_{cm} = K_c \cdot ET_{0m}$. The crop coefficients (K_c) for each month from January to December were determined based on the vegetation-crops ratio derived from CORINE Land Cover 2006 (CLC, 2006). Finally, the annual real evapotranspiration (E_r) was obtained by calculating the soil water balance in a GIS environment, estimating the Available Water Capacity (AWC), which represents the maximum amount of water that can be retained by the soil and is usable by most crops. In this case, the AWC was estimated to be 70 mm for the entire area. This value is considered homogeneous from the point

of view of land cover, being primarily composed of 75 % of forest and seminatural areas (mainly broad-leaved forests, natural grassland, and transitional woodland/shrub), 22 % of agricultural areas (mainly heterogeneous agricultural areas) and 3 % of artificial areas.

In detail, the real evapotranspiration was calculated using an iterative process in a GIS environment, based on raster layers with a cell size of 30 m × 30 m. The calculation started from average data from the month of March, which is considered the "wet" month where the soil water reserve is assumed to be equal to the AWC. The input data for the calculation were monthly averages from the 2009–2015 period. This calculation allowed for the assessment of the monthly actual evapotranspiration (E_r), as well as the determination of excess and deficit. The former represents the difference between precipitation and real evapotranspiration, whereas the latter occurs when the real evapotranspiration (E_r) is lower than the potential evapotranspiration (E_{Tcm}). In other words, the deficit occurs when the cumulative precipitation (P_m) for the given period and the water reserve cannot meet the evapotranspiration needs of the crops.

The real evapotranspiration data (E_r) were subtracted from the precipitation layer (P) and multiplied by a Coefficient of Potential Infiltration (C.P.I.), depending on the outcropping lithologies and their characteristics of permeability (Celico, 1988; Viaroli et al., 2018), to obtain the effective infiltration: $I = (P - E_r) \cdot C.P.I.$ The adopted C.P.I. values range from 30% for the arenaceous-calcarenitic-pelitic units to 95 % for the carbonate rock units (Table S3). A C.P.I. value of 95 % was assigned to the pyroclastic deposits where they are thin and superposed to carbonate units in endoreic basins.

A spatial representation of the groundwater budget terms is shown in Figure S1 in the Supplementary Material. The groundwater budget results are summarised in Table 2.

As in Braca and Ducci (2018), to validate the approach adopted in this work, the results of the budget terms, as average annual values over the 2009–2015 period, were compared with a groundwater budget carried out at the national scale and developed through a GIS based procedure (BIGBANG 7.0—"Nationwide GIS-Based hydrological budget on a regular grid", Braca et al. 2023). The comparison between the two groundwater budgets is summarised in Table S4. In the following, the deviation (Δ) between the results obtained in this work (A) and the BIGBANG model (B) is calculated as $\Delta = (B - A)/A$ and expressed in percentage. The spatial resolution of the BIGBANG dataset is 1 km × 1 km, thus a slight difference between the extension of the considered study areas is acceptable ($\Delta < |3.4\%|$). The precipitation amounts are comparable between the two approaches and the two aquifers: deviations are -0.2 % and +1.3 % for Mt. Tifata and Mt. Maggiore aquifers, respectively. The two approaches adopted different methodologies for the calculation of the evapotranspiration term, thus the deviations are greater (+7.9% for Mt. Tifata aquifer and -6.4% for Mt. Maggiore), but within the order of magnitude of the budget error ($|10\%|$, Fekete et al. 2004). In both approaches, C.P.I. values are assigned to hydrogeological units outcropping in the study area. The infiltration amounts are always lower in the BIGBANG model respect to this work, and the deviations are -9.1 % and -30.9 % for Mt. Maggiore and Mt. Tifata aquifers, respectively. The significant deviation observed for Mt. Tifata aquifer could be due to the different spatial resolutions of the thematic layer representing the hydrogeological units and, therefore, the assignment of C.P.I. values between the two approaches, such as the high C.P.I. value assigned to the pyroclastic deposits outcropping in endoreic basins (this work).

5.2. Evidence of the groundwater flow from groundwater chemistry and isotopic data

The Piper and Durov Diagrams (Fig. 6 and S2) show that waters collected from springs and well fields belong to the bicarbonate-alkaline earths (Ca-Mg-HCO₃) hydrochemical facies, which is related to the carbonate nature of the aquifers. Despite of additional waters collected from wells located in the plain area, either west or east to Mt. Grande (grey diamonds in Fig. 6 and S2), belong to the Ca-Mg-HCO₃ hydrochemical facies, some of these waters show a higher concentration of Cl⁻ and SO₄²⁻ and do not present any dominant cation. This suggests that the hydrochemical characteristics of groundwater in the plain are influenced both by the outflow of Ca-Mg-HCO₃ waters from the carbonate aquifers, and by ion exchange processes and/or leaching of Na⁺ and K⁺ in the pyroclastic-alluvial materials of the plain (§ 6).

Pila and Trifisco springs (numbers 1 and 2 in Fig. 7) exhibit high levels of CO₂ (several hundred mg L⁻¹) that cannot be solely

Table 2

Groundwater budget terms and withdrawals for the period 2009–2015. Withdrawal data from Acqua Campania S.p.A.

Aquifer	Area (km ²)	Average precipitation (P) (mm year ⁻¹)	Average real evapotranspiration (Er) (mm year ⁻¹)	Average infiltration (I)		Wells	Withdrawals (W) (10 ⁶ m ³ year ⁻¹)	I-W (10 ⁶ m ³ year ⁻¹)
				(mm year ⁻¹)	(10 ⁶ m ³ year ⁻¹)			
Mt. Tifata (including Mts. Friento and Caruso)	88.86	1149.9	530.2	562.9	50.02	S. Sofia s.l., Tifata and S. Prisco well fields Other wells	49.90 10.00	-9.88
Mt. Maggiore	179.90	1271.5	626.4	587.1	105.62	Pontelatone well field Other wells Total	31.00 3.33 34.33	71.29

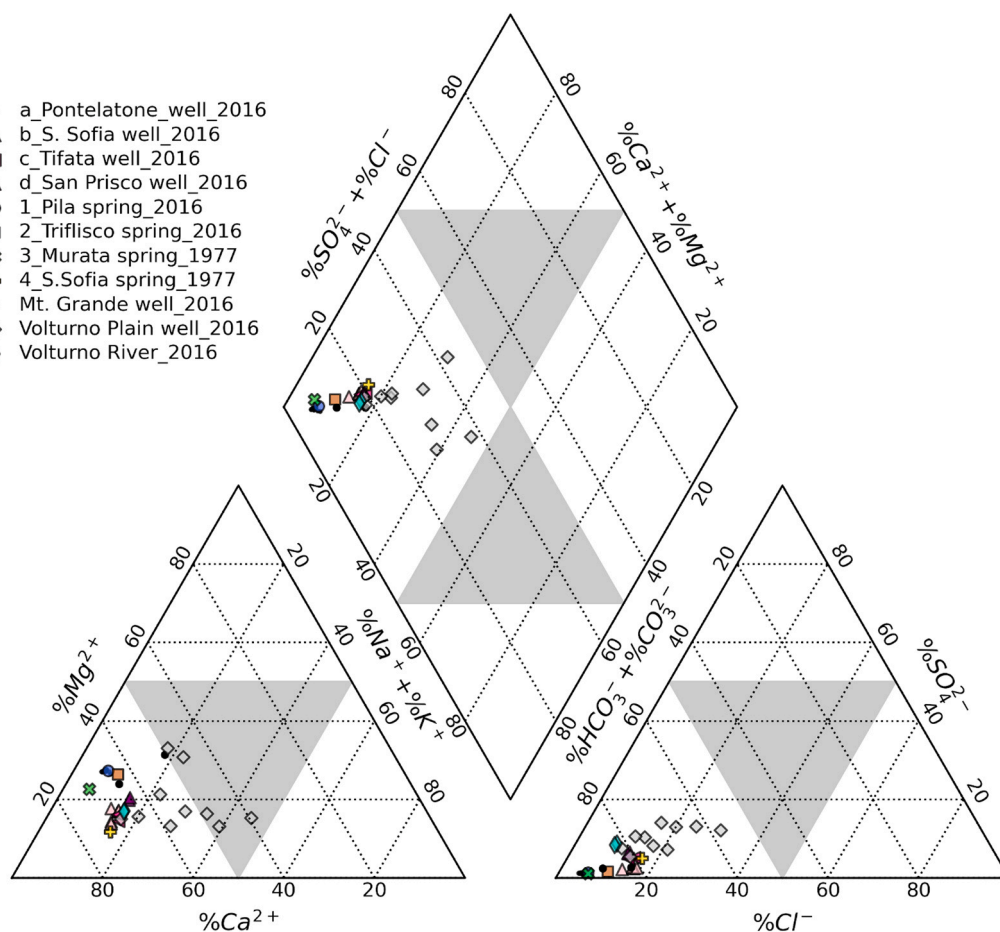


Fig. 6. Piper diagram of groundwater samples collected in this study (2016) and of Murata and S. Sofia springs (ASM, 1990). Refer to Table S1 for the aggregation of water samples as listed in the legend of this figure.

attributed to an external source of this gas (Table S1). Additionally, the waters from these springs show mineralisation and hardness values significantly higher than those typically observed in springs fed by carbonate rocks (Corniello, 1996). The chemical characteristics of the springs are similar (Figs. 6 and 8) and, considering the consistency of the parameters over time (Fig. 8), they appear to have not been affected by the realization of the Pontelatone well field (“a” in Fig. 7), which instead has significantly influenced the discharge rates (§ 3). The chemistry of the water in this well field is entirely comparable to the springs (Fig. 6). In the 20 boreholes of the well field distributed along the base of the Mt. Grande slope in a north-south direction, it is observed that the hardness and TDS values decrease moving away from the springs (Fig. 9). The Murata spring (n. 3 in Fig. 7) exhibits an isotopic content (Tab. S2) and a chemical profile comparable to the waters of the Pontelatone and Pila springs (Fig. 8).

Conversely, the chemistry of the S. Sofia spring (n. 4 in Fig. 7) is remarkably different from what observed so far (Fig. 6). The chemical profile (Fig. 10) and the values of CO₂ and TDS (Tab. S1, Fig. S2) are much lower. For the spring only the analyses from the years 1977, 1979, and 1980 are available, and show a comparable composition (Tab. S1). In the years 1989–1990, the spring dried up due to the withdrawal of water through wells drilled in the three galleries (S. Sofia, Baldi and Giglio; “b” in Fig. 7) realised in the carbonate slope near the spring site.

Therefore, the current characteristics of the spring can be considered as similar to those recorded in the wells of these galleries (Fig. 10). The water from these wells is significantly more mineralised (TDS ranging from 570 to 690 mg L⁻¹ and CO₂ from 453 to 791 mg L⁻¹) with respect to that of the spring (average TDS: 433 mg L⁻¹, average CO₂: 50.5 mg L⁻¹), as also shown in the Durov diagram (Fig. S2). The chemical profiles of the water from the various wells overlap each other and exhibit a similar shape to that of the Pila spring (Figs. 8 and 10).

To the southwest of the galleries, the water from the Tifata well field (“c” in Fig. 7) shows lower TDS and CO₂ values compared to the water from the galleries (Tab. S1). These characteristics, along with an identical chemical profile (Fig. 10), are also found in the Vaccheria well (n. 32 in Fig. 7) and in the water from the S. Prisco well field (“d” in Fig. 7; Fig. 10; Tab. S1).

The waters examined so far are clearly bicarbonate-calcium waters with a ratio $r [(Ca^{2+} + Mg^{2+}) / (Na^{+} + K^{+})]$ higher than 5. In the plain to the east of Mt. Grande, these characteristics are preserved, in addition to the Pontelatone well field, only in a few wells located at the base of the relief (wells n. 9, 6, 8 in Fig. 7). Conversely, in the other wells distributed in the plain, the waters are

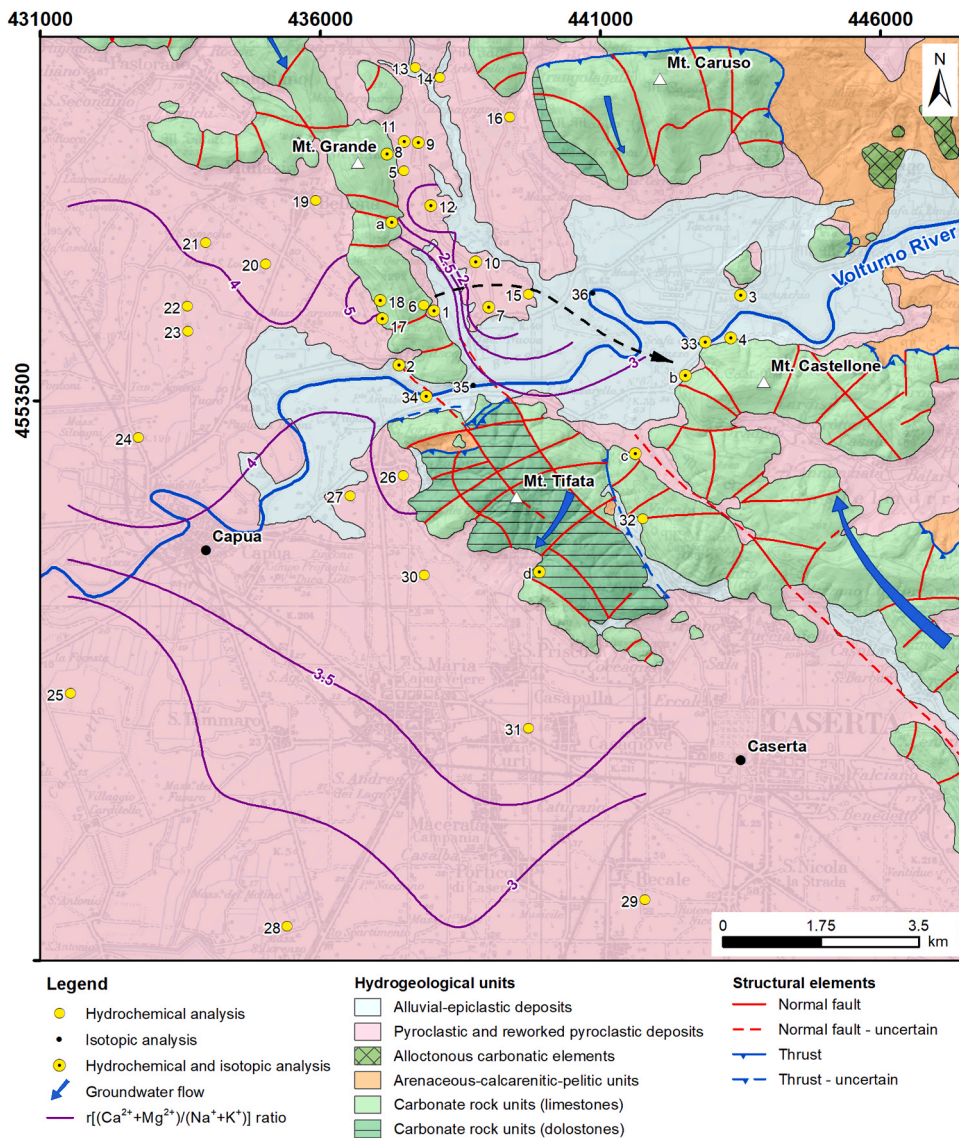


Fig. 7. Location of the sampling points for hydrochemical and isotopic analyses considered in this study. Refer to [Table S1](#) and [Table S2](#) for the identification numbers of the sampling points. Purple lines represent the contour lines derived from the spatial interpolation of $r[(Ca^{2+} + Mg^{2+}) / (Na^{+} + K^{+})]$ ratio at the sampling points. The black dashed arrow represents the possible groundwater flow connection between the carbonate units located north and south of the Volturno River. Basemap: hillshade derived from TINITALY digital elevation model (Tarquini et al., 2023) and 1:100,000 topographical map from Geoportale Nazionale (<https://gn.mase.gov.it/portale/home>).

bicarbonate-alkaline, and the HCO_3^- content is low.

To the west of Mt. Grande, the situation is different as the water in the wells remains consistently bicarbonate-calcium, and even at a few kilometres from the mount along the groundwater flowpath, the ionic ratio $r[(Ca^{2+} + Mg^{2+}) / (Na^{+} + K^{+})]$ remains relatively high (Fig. 7). The same is observed in the southern part of the Campanian Plain, which extends at the base of Mt. Tifata (Fig. 7). In both cases the greater alkaline character is highlighted in the Piper and Durov Diagrams (Fig. 6 and S2).

The measurement of $\delta^{18}O$ and δD of the water molecule can give information about the origin and the recharge processes of groundwater (Clark and Fritz, 1997), as well as mixing of water bodies (Petrella and Celico, 2013). In [Table S2](#) isotopic data measured in groundwater, springs and the Volturno River are reported. In this paper water stable isotopes measurements are reported from previous studies (Celico et al., 1980; Sacchi et al., 2022) as well as from new sampling campaigns carried out in 2017, 2018 and 2023.

The $\delta^{18}O$ and the δD values range from -7.2 to -5.8‰ and from -45.6 to -31.8‰ , respectively. The Volturno River is characterised by the most depleted values (average value: $-6.9 \pm 0.2\text{‰}$ and $-42.0 \pm 1.6\text{‰}$, for $\delta^{18}O$ and the δD , respectively) due to the average higher altitude of the recharge areas, while the agricultural and domestic wells in the Monteverna alluvial plain are characterised by the most enriched values (average value: $-6.1 \pm 0.3\text{‰}$ and $-33.6 \pm 2.0\text{‰}$, for $\delta^{18}O$ and the δD , respectively) indicating a likely local

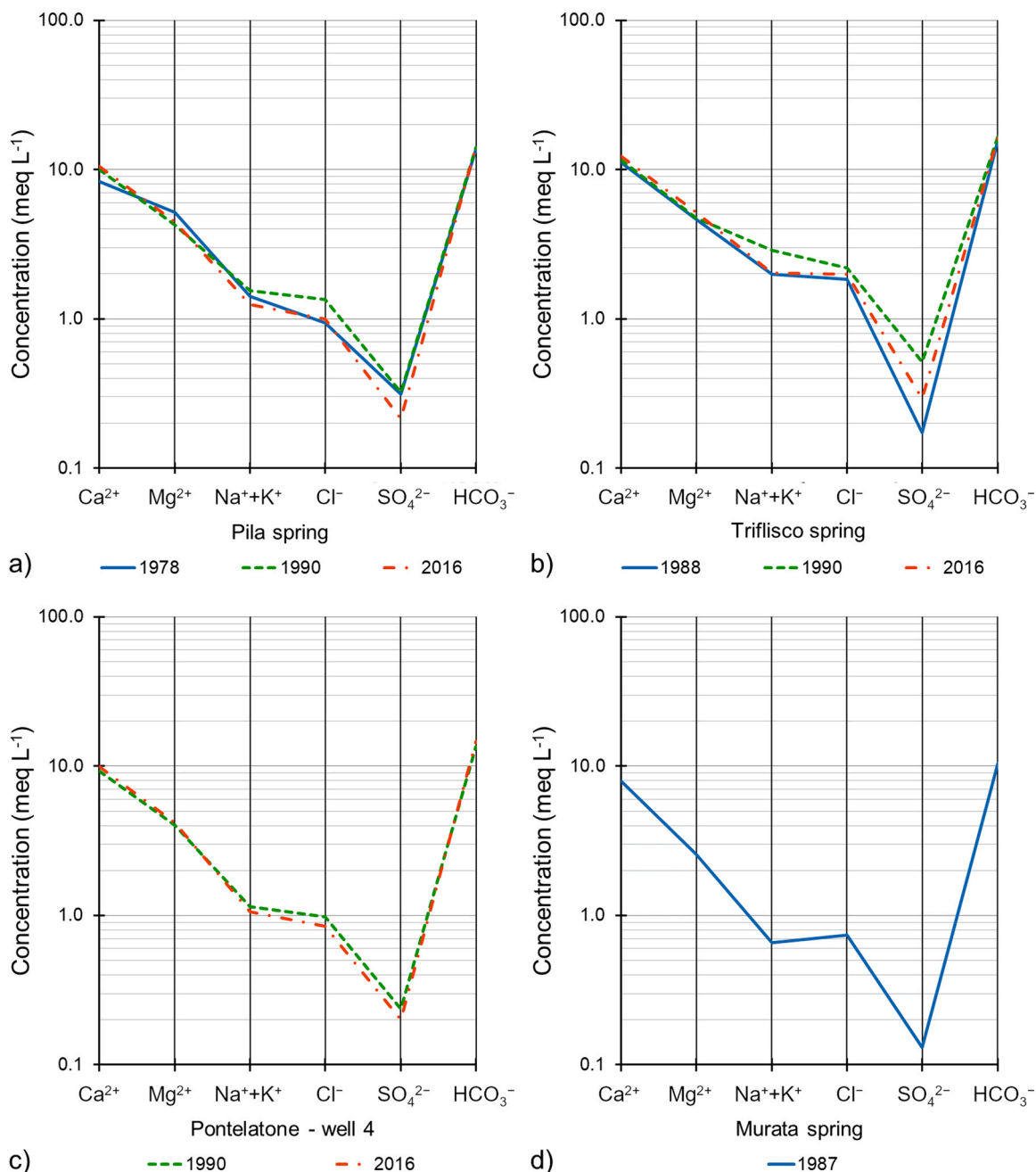


Fig. 8. Schoeller-Berkaloff diagrams of water collected in different periods from: a) Pila spring; b) Triflisco spring; c) Pontelatone well field (well n. 4); d) Murata spring.

recharge (Table S2).

In Fig. 11 the water samples are compared with the Southern Italy Meteoric Water Line (MWL, Longinelli and Selmo 2003) and the MWL of the Vesuvius Mt. (Madonia et al., 2014), which is located about 40 km to the south from the study site. The results indicate that the samples are mainly fed by rainwater with an isotopic signature typical of Southern Italy. In particular, the samples are all comprised between the two MWLs with the exception of part of the October 2017 and the December 2017 campaigns, which show much more depleted δD values (Fig. 11), likely depending on a fast recharge mechanism due to exceptionally abundant rains observed in the considered period (615 mm from September to December 2017, the average for the same period for the years 2014, 2015 and 2016 is about 380 mm) coming from air masses formed in different humidity and temperature conditions. The latter observation is also supported by the deuterium excess values. The deuterium excess ($d_{\text{excess}} = \delta D - 8 \cdot \delta^{18}O$, Dansgaard 1964) is a parameter used to infer information about water vapour formation originating the precipitation (Froehlich et al., 2002; Merlivat and Jouzel, 1979; Pfahl and

Sodemann, 2014) and in the months of October and December 2017 its mean value is $9.4 \pm 0.5\text{‰}$ ($n = 11$) versus the average d-excess of $15.8 \pm 0.8\text{‰}$ ($n = 33$) measured for the rest of the sampling campaigns.

The assessment of the mean recharge altitude of the considered water bodies is based on the application of the empirical equation for the $\delta^{18}\text{O}$ altitude gradient ($z = -512.24 \cdot \delta^{18}\text{O} - 2781$) found by Di Luccio et al. (2018) for the Matese massif, which is close to the study area (see Fig. 1), since rain water collectors or springs at different altitudes were not available. The average values of vertical isotopic gradient measured in Italy is about $-0.22\text{‰}/100\text{ m}$ elevation for $\delta^{18}\text{O}$ (Giustini et al., 2016), while in the study area the average value used is $-0.19\text{‰}/100\text{ m}$ elevation based on the data from Di Luccio et al. (2018). The mean recharge altitude of the waters of the Monteverna alluvial plain is $259 \pm 59\text{ m a.s.l.}$, indicating a local recharge, while the mean recharge for the Volturno river is $503 \pm 49\text{ m a.s.l.}$, indicating a recharge occurring in the upstream areas of the basin. The mean recharge altitude for the Pontelatone well field and the Triflisco and Pila springs is $425 \pm 37\text{ m a.s.l.}$, very similar to that of the Tifata and San Prisco well field which is $418 \pm 18\text{ m a.s.l.}$, indicating a similar recharge altitude consistent with the topography of the area even if the two aquifers, according to their hydrochemistry, can be considered disconnected. The wells of the S. Sofia spring seem to be recharged from water infiltrating at an average altitude of $363 \pm 37\text{ m a.s.l.}$, which is consistent with the altitude of the Castellone Mt. and nearby mountains.

6. Discussion

The comparison of different approaches for the assessment of the groundwater budget highlights the importance of reliable quantitative estimations of water resources in groundwater bodies for their sustainable water management. Through the comparison of two groundwater budgets with different spatial resolutions (local VS national scale) we observed that the most sensitive terms in the evaluation of the groundwater budget are the evapotranspiration and infiltration terms (i.e., recharge). The former is affected by the methodology applied for its calculation (e.g., Turc, Thornthwaite-Mather, Penman-Monteith) and by the scale resolution. The infiltration is affected by the assignment of C.P.I. values to the hydrogeological units and by the scale resolution. On the other hand, the evaluation of the precipitation term – using data collected at meteorological stations – is less influenced by the scale resolution or by the interpolation technique used for obtaining a spatial distribution of the precipitations. Therefore, local studies enable a better delineation of the groundwater bodies, hydrogeological units and land cover/land use classes, reducing inherent approximations of regional or national studies necessarily performed at coarser spatial resolutions. The results of the groundwater budget evaluation (§ 5.1) show that the annual groundwater withdrawals from wells in the Mt. Maggiore area constitutes about 30 % of the recharge, thus

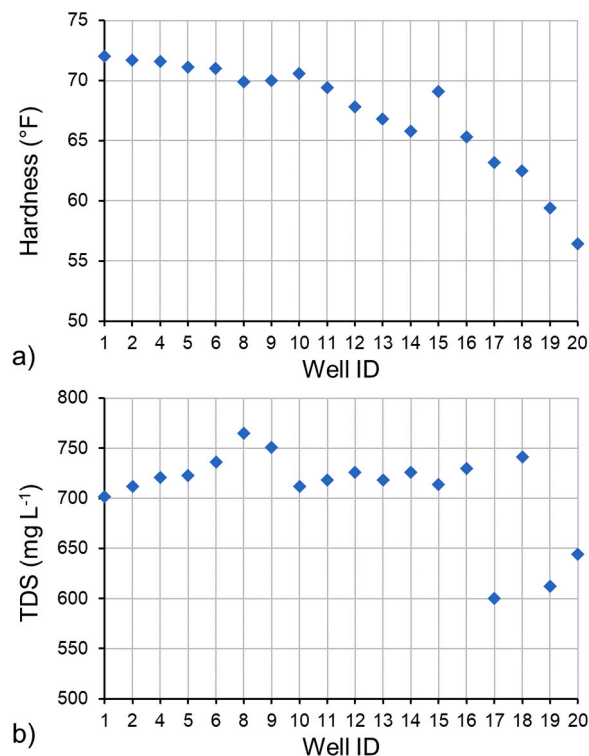


Fig. 9. (a) Hardness¹ and (b) Total Dissolved Solids (TDS) of wells belonging to the Pontelatone well field (water samples collected in 2016). Wells are named from 1 to 20, from south to north.

¹ $1\text{ °F} = 10\text{ mg L}^{-1}\text{ CaCO}_3$ (Matthess, 1982)

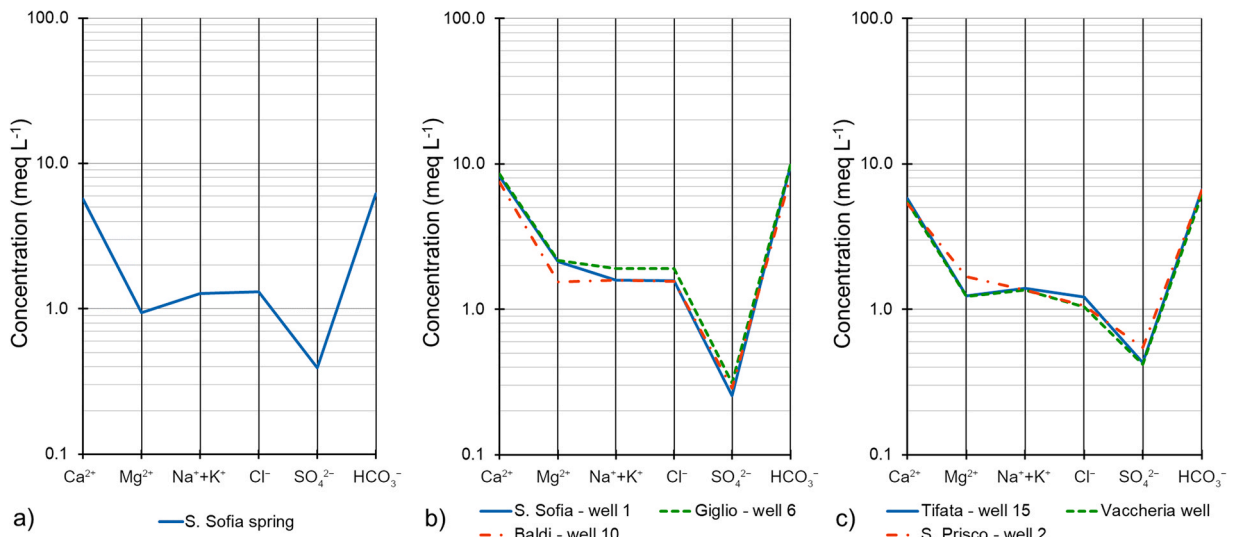


Fig. 10. Schoeller-Berkaloff diagrams of: a) S. Sofia spring; b) representative wells of S. Sofia, Giglio and Baldi galleries; c) representative wells of Tifata and S. Prisco well field, and Vaccheria well. Hydrochemical data refer to water samples collected in 1978 (a) and 2016 (b, c).

the remaining 70 % represents an important amount of water that feeds the Pila and Triflisco springs and could flow towards the neighbouring porous aquifers (Campanian and Riardo plains; [Celico et al. 1977](#); [Corniello et al. 1990](#); [Corniello et al. 2010](#); [Cuoco et al. 2020](#); [Viaroli et al. 2018](#)), as well as towards the carbonate aquifer of Mt. Tifata. On the other hand, both groundwater budgets show that the annual groundwater withdrawals in the Mt. Tifata area exceed the recharge (withdrawal exceedance equal to 20 %), though there are no clear signs of overexploitation. The evidence supporting the hypothesis of no overexploitation can be observed in the

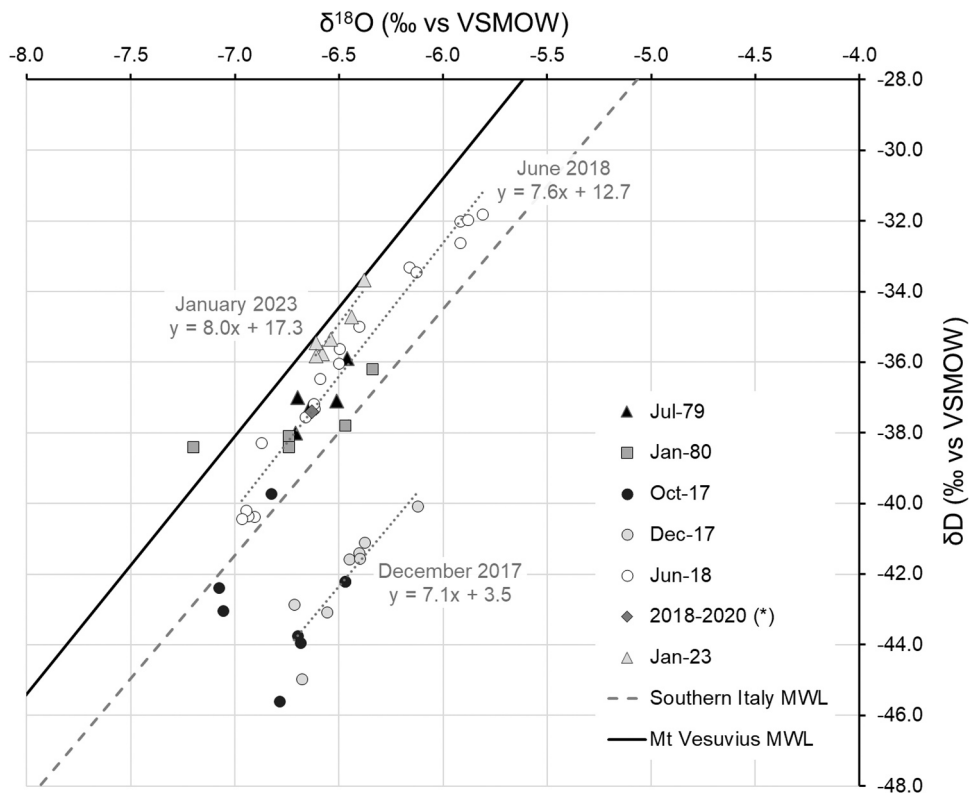


Fig. 11. δD vs $\delta^{18}O$ diagram of springs, wells and Voltorno river samples aggregated according to the sampling period. In the graph the Southern Italy and the Mt. Vesuvius Meteoric Water Lines are reported ([Longinelli and Selmo, 2003](#); [Madonia et al., 2014](#)).

following aspects:

- a) the groundwater levels in the wells of the S. Sofia, Giglio and Baldi galleries, which dried up S. Sofia spring, appear to be consistently influenced by the withdrawals. Groundwater levels decrease with increasing withdrawals and vice versa. Furthermore, there is no negative trend observed in the piezometric levels over the years (Acqua Campania S.p.A. data);
- b) in the wells of the Campanian Plain (to the southwest of Mt. Tifata), the groundwater levels measured in 2016 are comparable to those observed in 1988 (§ 3);
- c) the groundwater of the Campanian Plain is often contaminated by nitrates (also near the S. Prisco well field (Corniello and Ducci, 2014; Corniello et al., 2010); however, nitrate pollution is not present in this well field from which significant water withdrawals take place (§ 3).

However, the detailed analysis of current and past hydrochemical and isotopic data (§ 5.2) has revealed significant changes that can lead to new hydrogeological scenarios. As previously observed, the Pila and Triflisco springs show high levels of CO₂, which cannot be solely attributed to external sources (Minissale, 2004; Panichi and Tongiorgi, 1976). It is necessary to consider the contribution of endogenous inputs, likely associated with the upwelling of gases along the faults that have influenced the formation of the Volturno River graben (§ 2). This gas increases the reactivity of groundwater towards the carbonate aquifer (Albu et al., 1997; Balderer et al., 2014; Corniello, 1996; Corniello et al., 2018, 2022; Drever, 1997; Duchi et al., 1995; Goldscheider et al., 2010; Gunn et al., 2006), possibly explaining the peculiar chemical characteristics observed in the spring waters. According to this hypothesis, the mineralisation of the water occurs near the springs, indicating a local phenomenon associated with specific tectonic processes. Therefore, moving away from these areas, the water chemistry gradually becomes less altered.

Water stable isotopes allowed to identify different recharge altitudes for the considered water bodies indicating a lack of connection of the Monteverna alluvial plain wells from the rest of the groundwater bodies as well as from the Volturno river, which is mainly recharged in the upstream areas of the basin.

Mt. Grande (Fig. 7) serves as the final part of the aquifer that feeds the Pila and Triflisco springs. In this mount, groundwater flows from north to south with an average elevation of around 30 m a.s.l. (Piscopo, 1997). From Mt. Grande there is a groundwater outflow towards the plain to the west. This is evidenced by the contour lines of the groundwater in the plain (which are sub-parallel to the slope and show lower elevations with respect to groundwater levels in the carbonate aquifer; Fig. 2) and the gradual change in the ion ratio r $[(Ca^{2+} + Mg^{2+}) / (Na^{+} + K^{+})]$ (Fig. 7). This ratio is higher in groundwater close to the mount due to the prevalence of Ca²⁺ and Mg²⁺ ions, released from the carbonate aquifer, and decreases in wells located farther away from the mountain due to the progressive increase of Na⁺ and K⁺ ions for leaching and/or ion exchange processes occurring in the pyroclastic-alluvial materials of the plain. However, the magnitude of this groundwater transfer cannot be assessed due to the limited availability of transmissivity data for the plain's materials.

On the other hand, the groundwater outflow does not occur from Mt. Grande towards the plain extending to the east, as indicated by the following factors:

- a) water levels in the wells of the plain do not correspond to those of the groundwater within the mount, most probably because of the presence of low permeable layers;
- b) the bicarbonate-alkaline nature of the well waters and their higher content of δ²H and δ¹⁸O (§ 5.2);
- c) the ion ratio r $[(Ca^{2+} + Mg^{2+}) / (Na^{+} + K^{+})]$ reaches values around 1 even at a modest distance from the mountain (Fig. 7).

The hydrogeological continuity between Mt. Grande and Mt. Tifata should be excluded, as the groundwater in the latter mountain is the least mineralised among all those examined. On the other hand, the hydrogeological continuity between Mt. Grande and Mt. Caruso seems to be confirmed due to a carbonate substratum connecting both mountains (§ 2), as shown also by the chemical and isotopic characteristics of the Murata spring. The latter are comparable to those of the Pila and Triflisco springs and of the Pontelatone well field. Also the mean recharge altitudes are comparable: 418 ± 18 m a.s.l. vs 411 ± 25 m a.s.l. for the Pontelatone well field and Pila – Triflisco springs and the Murata spring, respectively.

Of particular interest is the situation that has been emerging for the areas of Mt. Tifata s.l., south of the Volturno River. As observed, these mountains fed the S. Sofia spring, which has now disappeared after being tapped by wells (§ 3). The withdrawals have significantly lowered the original groundwater table of the spring, which had an elevation of about 30 m a.s.l. Currently, in the wells the water levels are between 10 and 15 m a.s.l. (Acqua Campania S.p.A. data). Consequently, this influenced the chemistry of the well waters, which are significantly more mineralised and enriched in CO₂ with respect to the S. Sofia spring (§ 5.2).

In fact, this suggests that the significant lowering of water levels in the wells has actually drawn in the more mineralised waters from the mountain range of Mt. Maggiore located north of the Volturno River (a situation already observed elsewhere by Corniello et al. (2005)). A number of observations support this hypothesis: i) the chemical profile of the well waters tends towards the one of the Pila spring (Fig. 8 and Fig. 10); ii) the possibility that inflows from the north can compensate for the significant deficit in the water budget of Mt. Tifata (§ 5.1) considering the absence of over-exploitation phenomena and that the hydrochemical and isotopic data excludes contributions (useful for this purpose) from the Volturno River (§ 5.2), which flows at the northern edge of Mt. Tifata; iii) the water levels in the wells of the S. Sofia well field are currently around 10–15 m a.s.l., hence significantly lower than the elevations of the Pila and Triflisco springs (27–28 m a.s.l.). The potential hydraulic connection between the ridge and the well field area could develop as indicated in Fig. 7, through the identified carbonate substratum between Mt. Grande and Mt. Caruso. Other possible connections further south, involving Mt. Tifata, are not considered feasible as the waters in the Tifata well field are low in

mineralisation and do not show increases in salinity over time.

The lower salinity of the waters of the Tifata and S. Prisco well fields, as well as of the Vaccheria well (n. 32 in Fig. 7), indicates that inside Mount Tifata s.s. groundwater is poorly connected to the higher TDS groundwater intercepted by the wells which dried up the S. Sofia spring. This observation is further corroborated by the fact that the groundwater flow of the mountains west of Mt. Tifata s.s. is oriented towards north-northeast (where the S. Sofia spring was located), while the flow at Mt. Tifata s.s. is towards the southwest. Indeed, at the time of their construction, the wells in the Tifata well field had higher water levels (between 27 and 30 m a.s.l.) than those recorded in the S. Prisco well field (23–24 m a.s.l.). Therefore, the groundwater of Mt. Tifata s.s. flows into the Campanian Plain, as indicated by the groundwater contour lines (sub-parallel to the slope of the ridge; Fig. 2) and by the progressive decrease of the ion ratio $r[(Ca^{2+} + Mg^{2+}) / (Na^{+} + K^{+})]$ (Fig. 7). It is likely that this situation is determined by the hydrogeological role (groundwater divide) played by a major normal fault (Fig. 7), which consistently follows the valley that separates Mt. Tifata s.s. from the other mountains further east (Celico et al., 1977; Servizio Geologico d'Italia, 2010).

7. Conclusions

The paper presents the results of a multi-disciplinary study based on hydrogeological, hydrochemical and isotopic data in order to assess the hydrogeological relationship between two neighbouring carbonate aquifers (mountain ranges of Mt. Maggiore and Mt. Tifata), morphologically separated by the Volturno River, located in Campania Region (Southern Italy), and to formulate a new conceptual model of their inter-connections.

Previous knowledge hypothesised a lack of hydrogeological connection between the two basins.

In particular, Pila and Triflisco springs, fed by the hydrogeological basin of Mt. Maggiore, are still active while the third spring present in the Volturno River valley (S. Sofia; at an elevation of about 30 m a.s.l.), connected to the basin of Mt. Tifata, has dried up after being tapped in 1989–1990. The data here presented and discussed allow to draw several considerations:

- A. The Pila and Triflisco springs exhibit a high degree of mineralisation, which can be justified by a more pronounced dissolution of the carbonate reservoir rocks due to the uprise of CO₂ along local tectonic structures. Moving away from these faults (in the opposite direction of the groundwater flow), the mineralisation decreases until completely disappearing. In fact, at the Pontelatone well field (located upgradient with respect to the springs), the TDS, hardness, HCO₃⁻, Ca²⁺, and Mg²⁺ show a progressive and consistent reduction moving upgradient from south to north. This opens broader prospects for water utilisation, for example, a more specific use for mineralised waters (such as bottling, balneotherapy, etc.) and a potable use for the same waters in areas distant from the mineralised zone, considering, in planning the management of the resource, that it is always the same groundwater body. In the Campania Region, several examples of such water capture exist (Corniello et al., 2022).
- B. The three galleries of the S. Sofia spring have caused a significant drawdown of up to 15 m of the original water table level. This resulted in a progressive mineralisation of the local groundwater, accompanied by an increase in CO₂. The hypothesis proposed here is that the drawdown has triggered the influx of mineralised waters from the Pila and Triflisco springs (§ 6), especially considering that an underground connection pathway has been identified (Fig. 7). This hypothesis presents new scenarios compared to previous knowledge, because it could explain both the changes in chemical characteristics and the absence of the overexploitation phenomena (e.g., increasing drawdown over time) despite of the indications from past and current analyses that the withdrawals in the Mt. Tifata basin significantly exceed natural recharge (§ 5.1). In this context, it is more consistent to evaluate the recharge/withdrawal ratio not for individual basins (Mt. Maggiore and Mt. Tifata) but for the system as a whole. Furthermore, the importance of groundwater monitoring is evident from the preceding reflections. Without the ability to compare different data (such as piezometric and chemical data) from the past and present, none of the changes would have been identified.
- C. Finally, it was possible to provide a more detailed description of the groundwater circulation within the Mt. Tifata area. Piezometric, chemical and isotopic data have revealed that the groundwater in Mt. Tifata s.s. is less mineralised and flows predominantly towards southwest compared to the groundwater of the mountains extending further east, recharging at a mean altitude of 418 ± 38 m a.s.l.

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CRedit authorship contribution statement

Daniela Ducci: Formal analysis, Conceptualization, Resources, Validation, Writing – original draft. **Alfonso Corniello:** Writing – original draft, Validation, Supervision, Resources, Project administration, Funding acquisition, Conceptualization. **Elena Del Gaudio:**

Formal analysis, Data curation, Investigation, Visualization, Writing – review & editing. **Luigi Massaro**: Writing – review & editing, Visualization, Investigation, Formal analysis. **Stefania Stevenazzi**: Writing – review & editing, Visualization, Validation, Formal analysis, Data curation. **Luisa Stellato**: Conceptualization, Formal analysis, Validation, Writing – original draft.

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.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.ejrh.2024.101790](https://doi.org/10.1016/j.ejrh.2024.101790).

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