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Spatio-temporal variability of groundwater hydrochemical features in different hydrogeological settings in Piedmont and Campania regions (Italy), a comparative study

Variabilità spazio-temporale delle caratteristiche idrochimiche delle acque sotterranee in differenti contesti idrogeologici in Piemonte e Campania (Italia), uno studio comparativo

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Riassunto

L'interesse per l'evoluzione spazio-temporale delle caratteristiche chimiche delle acque sotterranee è aumentato a livello globale nell'ultimo decennio. Identificare e distinguere le fonti dei composti naturali ed antropici ed i processi idrochimici attuali, così come la loro evoluzione, è essenziale per supportate una pianificazione sostenibile per la gestione e protezione delle risorse idriche sotterranee, nel presente e nel futuro. Il principale obiettivo di questo studio è il confronto tra due aree di studio in Italia (Regioni Piemonte e Campania), differenti per contesti geografici e geologici e condizioni climatiche, per evidenziare similitudini e differenze nel comportamento idrogeochimico delle acque sotterranee nello spazio e nel tempo. Sono stati considerati tre ioni principali (NO_3^-, SO_4^{2-}, Na^+) ed analizzati per identificare le fonti ed i processi idrochimici responsabili della loro distribuzione spaziale nel periodo 2015-2020 e valutare l'esistenza e le potenziali cause di trend nelle loro concentrazioni nel periodo 2000-2020. I risultati evidenziano fattori e processi specifici che caratterizzano la distribuzione spaziale e la variabilità temporale delle concentrazioni degli ioni nelle aree di studio in Piemonte e Campania. Questi processi sono principalmente legati alle caratteristiche geologiche e geografiche delle aree di studio. In entrambe le aree si osserva un impatto significativo delle pressioni antropiche sia nella distribuzione spaziale e sia nell'evoluzione temporale, con cospicui aumenti delle concentrazioni di NO_3^- nel tempo. In conclusione, alcuni fattori e processi sono risultati sito-specifici, principalmente legati agli aspetti geologici e ai processi idrochimici naturali, mentre altri sono comuni alle due aree di studio (i.e., impatti antropici); ciò, rafforza il vantaggio del condurre studi di confronto tra aree geografiche differenti.

Abstract

The spatio-temporal evolution of groundwater chemistry has seen an increase in interest over the last decade at a global level. Identifying and discerning the sources of the natural and anthropogenic compounds and the actual hydrochemical processes, as well as their evolution, is essential to support a sustainable planning for managing and protecting groundwater resources at the present time and in the future. The main objective of this study is the comparison of two study areas in Italy (Piedmont and Campania Regions), different in their geographical and geological contexts and climate conditions, to highlight the similarities and differences in the hydrogeochemical behavior in space and time. Three main ions were considered (NO_3^-, SO_4^{2-}, Na^+) and analyzed to identify the sources and hydrochemical processes responsible for their spatial distribution in the 2015-2020 period and evaluate the existence and the potential causes of trends in their concentration for the 2000-2020 period. Results highlight specific factors and processes distinguishing the spatial distribution and temporal variability of ion concentrations in Piedmont and Campania study areas. These processes are mainly related to the geological and geographical features of the study areas. In both areas, a significant influence of anthropogenic pressures emerges for both spatial and temporal evolutions, with remarkably increasing trends in NO_3^- concentrations. In conclusion, some factors and processes emerge as site-specific, mainly related to the geological aspects and natural hydrochemical processes, whereas others are in common (i.e., anthropogenic impacts); thus, reinforcing the advantage of making comparative studies.

Introduction

International regulations, such as those implemented by the European Union (Groundwater Directive; European Commission, 2006), require the determination of groundwater quality status as well as its evolution. This is necessary to ensure the short and long-term provision of accessible and safe freshwater to meet the societal needs (i.e., drinking, agriculture, farming and industrial needs) as well as to preserve the functionality of groundwater-dependent ecosystems and aquifer ecosystems (Becher et al., 2022; Dwire et al., 2018; Kumar, 2015). In particular, recognizing the sources of the natural and anthropogenic compounds and the actual hydrochemical processes, as well as their evolution, is essential to support a sustainable planning for managing and protecting groundwater resources at the present time and in the future. Groundwater quality may result in heterogeneous hydrochemical facies distribution and variable temporal evolution thanks to the combined presence of (Kresic, 2009; Madene et al., 2023; Voudouris et al., 2000): i) different geological formations (e.g., crystalline vs sedimentary rocks), ii) diversified ecosystems (e.g., wetlands), iii) particular geographical patterns (e.g., enclosed by mountainous ranges, along the coastline, etc.), iv) highly developed human activities (e.g., agricultural and farming activities, urban areas). The temporal evolution of groundwater chemistry has seen an increase in interest in recent years at a global level (e.g., Jutglar et al., 2021; Liu et al., 2022; Ortmeyer et al., 2023). Three main purposes frequently found in research studies can be summarized: i) the impact of climate changes, ii) anthropogenic influences and the effectiveness of adopted measures and iii) seasonal variations. These studies use variable time series with data ranging from few months to over half a century. Among the various physico-chemical parameters, a predominant interest about NO_3^- trends is present, being NO_3^- an effective indicator of groundwater contamination thanks to its high mobility and multiple sources (Batlle Aguillar et al., 2007; DHLGH, 2021; Musacchio et al., 2020). Also other parameters, such as Na^+, Cl^- and SO_4^{2-} were considered to quantify the threat of pollutants to present and future groundwater quality (Visser et al., 2009; Urresti-Estala et al., 2016). In the European context, different trends for NO_3^- and SO_4^{2-} emerged, i.e., increasing (Stuart et al., 2007; Wang et al., 2016) and decreasing concentrations (Hansen et al., 2017; Mendizabal et al., 2012) over time. In these studies, trend reversals were identified and attributed to the national regulations and their application in the limitation of nitrogen compounds used in agricultural practices. Indeed, the change points correspond approximately to when limitations were introduced and, therefore, the Authors suggest that the currently increasing trends are due to non-virtuous agricultural practices (Baran et al., 2009; Hansen et al., 2017; Mendizabal et al., 2012).

The main objective of this study is the comparison of two study areas, different in their geographical and geological contexts and climate conditions, to highlight the similarities and differences in the hydrogeochemical behavior in space and time. The two study areas are located in northern and southern Italy. Specific objectives regard i) the identification of sources and hydrochemical processes responsible for the spatial distribution of the considered compounds (NO_3^-, SO_4^{2-} and Na^+) and ii) the evaluation of the existence of trends in the concentration of nitrates, sulfates and sodium, and the potential causes. These ions were chosen considering their primary importance for defining the groundwater processes (natural and anthropogenic influences) in the two study areas. The comparative study highlights the importance of geological, hydrogeological and land uses features to define the evolution of groundwater chemistry, spatially and temporally. This study makes use of public data. Therefore, the comparison of the two study areas is not only of scientific interest, but also highlights the advantages, limits and challenges of the current groundwater monitoring network and sampling methods. This is particularly useful for the assessment of groundwater quality status and evolution, and the compliance of EU requirements by Member States. The maintenance of efficient and optimal groundwater monitoring networks (i.e., in terms of coverage and sampling frequency) is of utmost importance also in the framework of data sharing aimed at the preservation and protection of groundwater resources at the national and international level (Sistema Informativo Nazionale per la Tutela delle Acque Italiane (SINTAI), https://www.sintai.isprambiente.it/; Global Groundwater Monitoring Network (GGMN), https://ggis.un-igrac.org/view/ggmn/).

Materials and Methods

Study areas

Geological and hydrogeological framework

To identify the main ongoing processes and to compare the spatio-temporal hydrogeochemical variations, two different study areas in Italy have been selected (Fig. 1): an alluvial plain at the foothills of the Alps relief in Piedmont Region (Northern Italy) and a coastal alluvial-pyroclastic plain in Campania Region (Southern Italy).

The first area of interest is located in the south-western sector of the Piedmont Region and corresponds to the Turin and Cuneo plain, covering an area of approximately 1800 km^2. This sector is bordered by the Alps on the southern and western sides and the Langhe Hills on the eastern side. On the hydrographic left side to Stura di Demonte river several fluvial terraces subdivide the plain.

The geological setting of the Piedmont Po Plain generally consists, from bottom to top, of (Fig. 2a): i) Pliocene marine deposits (Pliocene) that host a confined aquifer, ii) Villafranchian transitional deposits (late Pliocene–early Pleistocene) that host a multilayered aquifer and iii) Quaternary alluvial deposits (early Pleistocene–Holocene) that host a shallow, unconfined aquifer (Barbero et al., 2007; De Luca et al., 2020; Forno et al., 2018; Lasagna et al., 2020b). The alluvial deposits consist of coarse gravel and sand of fluvial or fluvio-glacial origin, with subordinate silty-clayey intercalations. These deposits have a thickness generally

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ranging between 20 and 50 m (De Luca et al., 2020).

Sedimentary rocks of the Tertiary Piedmont basin (Eocene–Miocene) generally consist of clay, silt, limestone, conglomerate, sandstone, and gypsum. These rocks have low permeability and permit only a limited groundwater circulation along fractured zones. Crystalline rocks of the Alps are mostly impermeable or slightly permeable for fracturing (granite, gneiss, serpentinite) whereas the carbonate rocks are permeable thanks to the presence of extensive karst conduits and caves.

The shallow unconfined aquifer hosted in the alluvial deposits represents an important aquifer in which the water table is directly connected to surface water. The groundwater depth in the shallow aquifer is very variable: the water table is generally less than 5 m deep in the low plain and close to the rivers, whereas it shows depths between 20 and 50 m close to the Alps. The recharge area of the shallow aquifer is the entire plain due to infiltration of precipitation and, secondly, of surface waters, mainly in the high plain sectors. The groundwater flow direction is variable: from SW-NE to S-N in the Cuneo plain while W-E direction in the Turin plain. In the south-eastern sector, the terraced areas influence the direction and elevation of groundwater flow.

The Piedmont plain has a strong agricultural vocation; the prevalent crops in irrigated arable areas are cereals and legumes. Livestock farming is highly developed in the Cuneo area, particularly cows and pigs (Lasagna & De Luca, 2016). Industrial areas are mainly located in the surrounding of urban centers. The wells capturing the shallow aquifer have depths usually less than 30 m and are used mainly for irrigation activities.

The second area of interest is located in the northern sector of Campania Region and covers an area of about 1630 km^2. It is constituted by a coastal alluvial-pyroclastic plain (Volturno and Napoli plains) close to an active volcanic zone (Phlegrean Fields). It is surrounded by Meso-Cenozoic carbonate and terrigenous mountains of the Southern Apennines (E), by adjacent plains and the volcanic edifices of Roccamonfina and Somma-Vesuvius (N and SE), and by the Tyrrhenian Sea (W and S). The plain corresponds to a structural depression: a marine environment followed by the aggradation and progradation and the development of the alluvial plain characterized the Plio-Pleistocene Epoch (Amorosi et al., 2012; Corniello et al., 2010). The recent landscape of the Phlegrean Fields and the deposits filling the Volturno and Napoli plains were mainly related to the occurrence of two main eruptions of the Phlegrean Fields: the Campanian Ignimbrite (CI; ~39 ky, De Vivo et al., 2001) and the Neapolitan Yellow Tuff (NYT; ~15 ky, Deino et al., 2004). Moreover, eruptions of the Somma-Vesuvius and Roccamonfina volcanoes contributed to the deposition of pyroclastic deposits in the plains.

From the younger to the older units, the hydrogeological succession comprises (Fig. 2b; Corniello et al., 2010; Corniello & Ducci, 2014): i) Quaternary alluvial, pyroclastic and marine deposits. Alluvial, marshy and lacustrine deposits of coarse to fine grain size are mainly related to the Volturno River and minor streams. Peat levels interbedded within the alluvial deposits are often present, especially along the Volturno River. The pyroclastic deposits are related to the eruptions subsequent to those of the CI and the NYT, which are loose to soft pyroclastics, mainly from fallout (e.g., pumice, ash, lapilli), with a prevalent medium to fine grain size. Sandy to clayey-silt deposits of marine origin are present along the coastline. ii) NYT, mainly present in the Phlegrean Fields area. These tuffs are associated with the ~15 ky eruption of the Phlegrean Fields. iii) CI, greyish cinerites associated with black scoriae and lava shreds associated with the ~39 ky eruption of the Phlegrean Fields. The CI is characterized by a variable thickness ranging from 40-50 m along the margins of the plain 10-30 m in the central sectors. The CI is absent or very thin along the Volturno River due to its erosion. iv) Plio-Pleistocene alluvial, pyroclastic and marine deposits, prevalently coarse-grained sandy sediments. The pyroclastic deposits are silt to sandy volcanic sediments related to volcanic eruptions older than the CI. The marine deposits are mainly clays with sandy layers.

Two porous aquifers are present (Allocca et al., 2007; Corniello & Ducci, 2014): a shallow phreatic and discontinuous one and a main deeper semi-confined (or confined) one (in the following defined as main aquifer), which are separated by the Campanian Ignimbrite tuff. Besides the recharge from rainwater infiltration, this aquifer is fed directly by groundwater from the adjacent reliefs (Mesozoic limestone mountains, Roccamonfina and Somma-Vesuvius Volcanoes). The groundwater flow direction of the main aquifer is mainly E-W, from the Apennines ridge towards the Tyrrhenian Sea (De Vita et al., 2018).

Thanks to land reclamation in late 1800 – early 1900 (Ruberti & Vigliotti, 2017), the Campanian plain developed a strong agricultural vocation, with agricultural areas covering about 70% of the study area (CLC, 2018). The main crops in the irrigated arable areas are cereals, legumes and horticultures, followed by permanent crops of fruit trees and vineyards. Livestock farming is highly developed in Caserta area, particularly buffalos (Regione Campania, 2013). Residential and industrial areas occupy about 27% of the study area. Most of the urban areas are located in the south and south-western sectors of the study area. Natural forests and wetlands occupy the remaining 3% of the study area (CLC, 2018).

Groundwater hydrochemical features

From a hydro-chemical point of view, the shallow aquifer of Piedmont plain shows mainly calcium and/or magnesium bicarbonate facies (Lo Russo et al., 2011). In the Campania plain, the main aquifer reflects the geological characteristics of the study area, showing waters of calcium-bicarbonate type to sodium-bicarbonate type from the mountains to the seacoast, along the main groundwater flow direction (Corniello et al., 2010; Corniello & Ducci, 2014).

NO_3^- derives from human activities (fertilizers, manure, leakages from sewage systems) and shows exceedances of

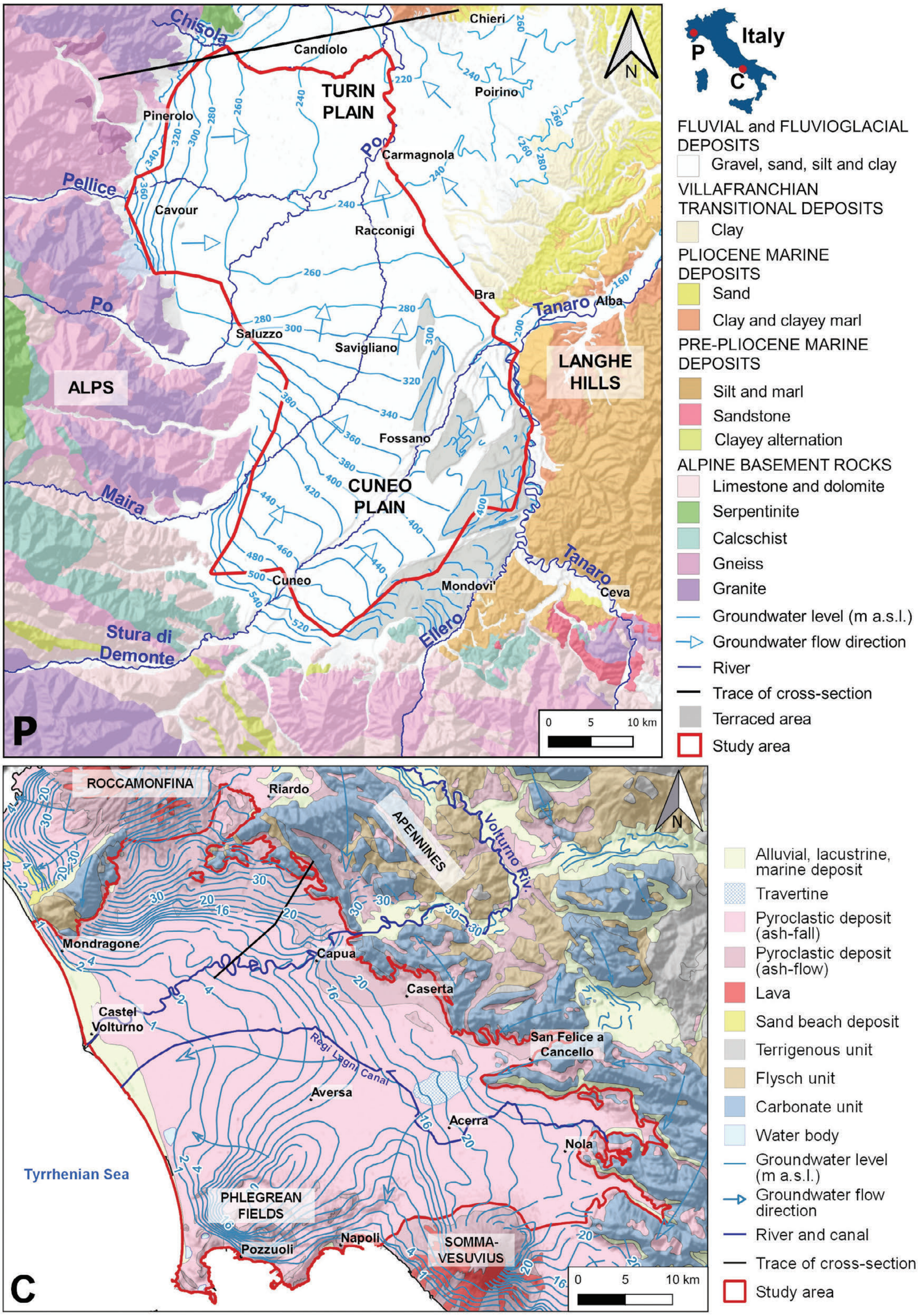

Fig. 1 - Hydrogeological map of the study areas in Piedmont (P) and Campania (C) Regions, Italy, and location of the hydrogeological cross-sections shown in Fig. 2. Piedmont Region: geological units modified from Piana et al. (2017) and piezometric levels from De Luca et al. (2020). Campania Region: piezometric levels and hydrogeological units from De Vita et al. (2018).

Fig. 1 - Carta idrogeologica delle aree di studio in Regione Piemonte (P) e Campania (C), Italia, e ubicazione delle sezioni idrogeologiche mostrate in Fig. 2. Per la Regione Piemonte, le unità geologiche sono ottenute da Piana et al. (2017) e i livelli piezometrici da De Luca et al. (2020). Per la Regione Campania, le unità idrogeologiche ed i livelli piezometrici sono ottenuti da De Vita et al. (2018).

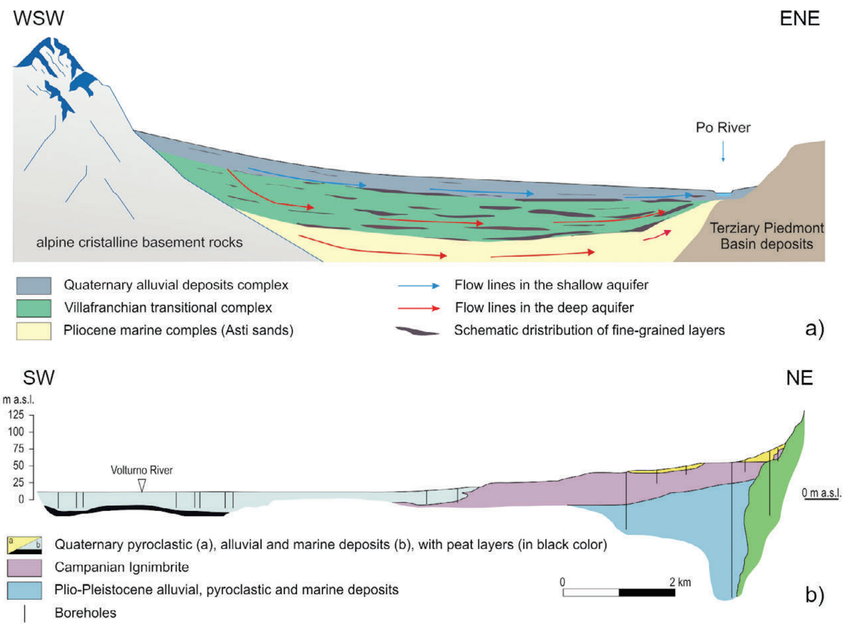

Fig. 2 - Simplified hydrogeological cross-sections of the Cuneo-Turin Po plain (a, modified from De Luca et al., 2020) and of the Campanian Plain (b, modified from Corniello & Ducci, 2014). The cross-sections are marked by the black lines on the maps in Fig. 1.

Fig. 2 - Sezioni idrogeologiche esemplificative della Piana del Po cuneese e torinese (a, modificata da De Luca et al., 2020) e della Piana Campana (b, modificata da Corniello & Ducci, 2014). Le sezioni sono rappresentate con una linea nera nelle carte in Fig. 1.

regulatory limits in both study areas, where active Nitrates Vulnerable Zones (NVZ) have been identified (https://environment.ec.europa.eu/topics/water/nitrates_en). In the Piedmont plain, several studies have identified high NO_3^- concentrations in the shallow aquifer related to intense agricultural activities (Cocca et al., 2024a; Debernardi et al., 2008; Lasagna & De Luca, 2019; Lasagna et al., 2016a,b; Martinelli et al., 2018) with a great spatial and temporal variability for NO_3^- (Cocca et al., 2024b; Civita et al., 2007). Also in the study area in the Campania Region, studies have identified high NO_3^- concentrations in the main aquifer due to intense agricultural activities (Corniello & Ducci, 2014; Cuoco et al., 2015b; Ducci et al., 2019b; Ducci et al., 2020). SO_4^{2-} has mainly a natural origin in both study areas (Civita et al., 2011; Corniello & Ducci, 2014). Na^+ shows low concentration in Piedmont and high concentrations along the coastal areas in the Campania Region due to seawater intrusion phenomenon, especially in correspondence of the Volturno River delta (Busico et al., 2021; Corniello et al., 2010; Mastrocicco et al., 2021).

Data

The hydrochemical characteristics of groundwater in Piedmont and Campania Regions are monitored by the Environmental Protection Agencies with a six-month frequency, in spring (March-June) and fall (October-December). Physico-chemical data are freely available on the web (https://www.arpa.piemonte.it/, https://www.arpacampania.it/). The databases include monitoring point coordinates and sampling date, main physico-chemical parameters (temperature, electrolytic conductivity, pH), major anions and cations, minor elements (e.g., metals) and contaminants (e.g., solvents, pesticides). Groundwater sampling and hydrochemical analyses are conducted by the Environmental Protection Agencies in compliance with the European Directives (European Commission, 2000; 2006; 2014) and the Italian Legislation (MATTM, 2016; Repubblica Italiana, 2006; 2009).

The hydrochemical datasets include data from public and private wells used for drinking purposes, agricultural, industrial and other (e.g., garden irrigation) activities. We used wells intercepting the shallow aquifer or the main aquifer for the Piedmont and Campania study areas, respectively. We considered the datasets covering the 2000-2020 and 2002-2020 periods for Piedmont and Campania Region, respectively. The main physico-chemical parameters (electrolytic conductivity, pH, Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-) were analyzed. The alkalinity, expressed as mg/L of HCO_3^- was used as an alternative to HCO_3^-. The Simple Substitution method was applied to NDs (Non Detected values); the values were set equal to the DL (Detection Limit) (SNPA, 2018).

Methodology

Spatio-temporal analyses were performed in both study areas by applying the same approaches, as far as possible according to the available data. The methodology applied in this study followed the steps: 1) data pre-processing (Quality Assurance and Quality Control; Hudson et al. 1999; Refsgaard et al. 2010); 2) data processing for the identification of the hydrochemical facies; 3) data processing for the identification of processes and factors influencing groundwater chemistry and its evolution; 4) evaluation of factors and processes potentially responsible of the distribution and evolution of Na^+, NO_3^- and SO_4^{2-}. Steps 3 and 4 focused on Na^+, NO_3^- and SO_4^{2-}, which were chosen considering their primary importance for defining the groundwater processes in the two study areas (see “Groundwater hydrochemical features” chapter).

1) Pre-processing

Data has undergone a pre-processing phase for the identification of errors and missing data. Outliers connected to transcription errors were identified and excluded. Their identification was performed through the coefficient of variation (CV) calculation for each parameter in individual monitoring points. In the data series with CV values higher than 0.40, anomalous data statistically correlated to outliers were excluded. We define "completeness of the series" (Braca et al., 2013; Estévez et al., 2022) as the ratio between the number of available data for a specific parameter and the optimum number of analyses over the selected period, expressed in percentage. The optimum number of analyses is two multiplied by the number of years over the selected period, although it could be possible that further analyses could be done.

The major ions were used for analytical quality control based on anion-cation charge balance. An anion–cation charge balance error within ±10 % was deemed acceptable for samples potentially affected by seawater intrusion (Güler et al., 2002; Parisi et al., 2023).

Following the European Guidelines for the assessment of the current status and evolution (i.e., trend) of groundwater quality (Annex 4, European Commission, 2006; Frollini et al., 2021; Grath et al., 2001), monitoring points meeting these requirements were used:

- Monitoring points with a completeness of at least 50 % in the period 2015-2020 i.e., at least six analyses over the six years, were selected for the realization of the Piper Diagram and for the "spatial variability" assessment. Therefore, 68 and 20 monitoring points were selected for the Piedmont and Campania study areas, respectively. The 2015-2020 period was chosen because it constituted the most recent monitoring period (Grath et al., 2001) and had high data completeness.
- Monitoring points showing a completeness of at least 70% for NO_3^- and SO_4^{2-} and 50% for Na^+ in the period 2000-2020 for the Piedmont study area and a completeness of at least 50% for Na^+ and SO_4^{2-} and 40% for NO_3^- in the period 2002-2020 for the Campania study area were selected for the calculation of the descriptive statistics and for the "temporal variability" assessment. Therefore, 68 and 27 monitoring points were selected for the Piedmont and Campania study areas, respectively.

2) Data processing, Piper Diagram

The Piper Diagram (Piper, 1944) was generated for the visualization and identification of hydrochemical facies. The arithmetic means of recent data (2015-2020) of the major ion concentration for each monitoring point (Grath et al., 2001) was used. The WQChartPy open-source Python package (Yang et al., 2022) was used for generating the Piper Diagram.

3) Data processing, focus on Na^+, NO_3^- and SO_4^{2-}

Descriptive statistics over the 2000/2002-2020 period for Na^+, NO_3^- and SO_4^{2-} concentrations for the two study areas were performed (i.e., all monitoring points for each study area): n° observations, minimum, arithmetic mean (i.e., average), median, maximum, standard deviation, coefficient of variation (CV) and completeness. The arithmetic mean of Na^+, NO_3^- and SO_4^{2-} concentrations over 2015-2020 was calculated for each monitoring point (Grath et al., 2001). The nonparametric Mann-Kendall trend test (Kendall, 1975; Mann, 1945) was employed to verify the existence of statistically significant positive or negative monotonic trends of the concentration of NO_3^-, SO_4^{2-} and Na^+ for each monitoring point over the 2000/2002-2020 period (Grath et al., 2001; Urresti-Estala et al., 2016). For the Mann-Kendall test, when the null Hypothesis H_0 (i.e. absence of trend) is rejected at the level of significance α (0.05), the data present a statistically significant trend. A confidence level equal to 95% was applied. The quantification of variation over time was determined through OLS regression slope (Ordinary Least Square) and Theil-Sen slope, respectively for Piedmont and Campania areas. The trend analysis was performed using ProUCL 5.1. (U.S. EPA, 2015) and the EnvStats library (Helsel et al., 2020) for R programming language (https://www.r-project.org/) for the study areas in Piedmont and Campania Region, respectively.

4) Spatio-temporal assessment

The evaluation of factors and processes potentially responsible of the distribution and evolution of Na^+, NO_3^- and SO_4^{2-} was conducted through the realization of maps of spatial distribution of the average ion concentrations ("spatial variability") and of the existence trends (increasing, decreasing, no trend) of ion concentrations ("temporal variability") for each study area. The spatial distribution maps of average ion concentrations and trends were realized in a Geographic Information System environment (QGIS, https://qgis.org/en/site/). The spatial and temporal results were compared with the natural and anthropogenic features characterizing the study areas to identify the factors potentially responsible of their distribution and evolution, such as land use and land cover, lithological composition of the surroundings mountainous chains and the various local phenomena (e.g., seawater intrusion). Average concentrations over the 2015-2020 period and trends over the 2000/2002-2020 period were compared in order to identify sectors where in the near future thresholds exceedances linked to increasing trends could occur. Finally, results from the two study areas were compared to recognize similarities and differences in groundwater characteristics.

Results and discussion

All the monitored points show an anion-cation charge balance error < ±10% and widely < ±5%. The Piper diagram (Fig. 3) shows the prevalence of the bicarbonate-calcium facies for most of the monitoring points. Water samples collected in the Campania study area show a transition from bicarbonate-calcium facies to alkaline-facies moving from the mountain range to the coast.

An interesting aspect regarding the differences between the two study areas is the higher variability of the concentration of Na^+, NO_3^- and SO_4^{2-} in the Campania study area as compared to the Piedmont study area (Table 1). The hydrochemical variability reflects the geological uniformity of the porous aquifer of the Piedmont study area, constituted of coarse sand and gravel deposits of fluvial and fluvio-glacial origin mainly coming from crystalline and sedimentary rocks, and subordinary of carbonate rocks. Instead, the porous aquifer in the Campania study area reflects the various geological units surrounding the plain (terrigenous-carbonate units and volcanic districts) affecting groundwater quality, including the influence of active volcanic areas characterized by deep-fluids upwelling (i.e., Phlegrean Fields, Mondragone and Roccamonfina areas).

A right-skewed distribution of concentration values is present in both study areas for all three selected ions. However, it is more evident for the study area in the Campania Region (mean values >> median values) rather than for the one in the Piedmont Region (mean values ≈ median values). This aspect is particularly evident for Na^+, which shows a median concentration value in the Campania study area of eight times the median concentration value in the Piedmont study area. This evidence reinforces the influence of the geological contexts on groundwater quality, as expected. The main source of Na^+ in groundwater in the Piedmont study area is the salt used for deicing roads in winter, being the outcropping rocks and alluvial deposits less prone to release Na^+ in solution. On the other hand, more sources of Na^+, which can justify the high concentrations in groundwater, are present in the Campania study area: presence of volcanic rocks and deposits, occurrence of seawater intrusion phenomenon and upwelling of deep fluids of volcanic origin. Excluding the high outlier values, NO_3^- and SO_4^{2-} median concentrations are similar for the two study areas. SO_4^{2-} in groundwater may be natural – due to ion exchange (e.g., pyrite) or dissolution (e.g., gypsum) of minerals/rocks/grains constituting the aquifer – or anthropic – wastewaters or gas emissions (Hem, 1985; Torres-Martínez et al., 2020). Thus, their presence in groundwater in the two study areas will be further investigated in the following. Instead, NO_3^- in groundwater are of anthropogenic origin (Stein & Klotz, 2016; Wick et al., 2012) and their presence may suggest an apparent similarity in the influence of contaminants on groundwater quality in the two study areas. Further speculations will be discussed in the following.

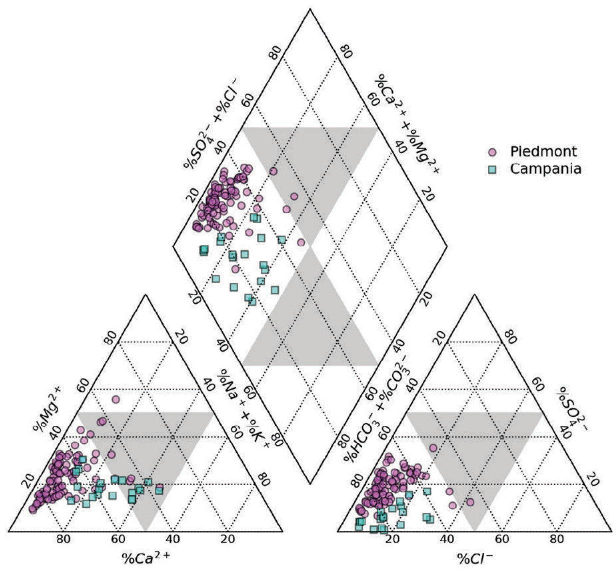

Fig. 3 - Piper diagram, average values over the 2015-2020 period.
Fig. 3 - Diagramma di Piper, valori medi sul periodo 2015-2020.

Spatial variability

As it concerns the study area in the Piedmont Region (Fig. 4), Na^+ concentrations range from 2.3 to 43.6 mg/L, showing increasing values along the groundwater flow direction, with the minimum values in the plain sector close to the Alps (<5 mg/L) and higher values in the central plain (5-20 mg/L). This increase can be attributed to the progressive natural contribution of dissolution processes (e.g., albite widespread in the gneiss and granite of Alpine sector) and to anthropic contributions (urban and agricultural). In the fluvial terraces area close to the Langhe Hills values higher than in the other areas exist (>20 mg/L). These values can be influenced by the low transmissivity of the aquifer resulting in a low dilution (Lasagna et al., 2013). A similar phenomenon appears in the area between Chisola River and Pinerolo. Monitoring points with high Na^+ value in Bra and Saluzzo can be attributed to anthropogenic influence in relation to the similar content of Na^+ and Cl^-. Ion exchange processes are to be excluded in relation to the absence of anomalous behaviors between Na^+ and Ca^{2+}.

Tab. 1 - Descriptive statistics of the three selected ions over the 2000/2002-2020 period.
Tab. 1 - Statistiche descrittive dei tre ioni selezionati sul periodo 2000/2002-2020.

Statistics	Piedmont study area			Campania study area		
	Na^+	SO_4^{2-}	NO_3^-	Na^+	SO_4^{2-}	NO_3^-
N	1716	2735	2602	730	784	717
Min (mg/L)	<1.00	<1.00	<1.00	5.00	0.10	<0.01
Mean (mg/L)	9.29	51.53	31.52	259.92	106.47	39.58
Median (mg/L)	8.00	51.00	31.00	64.00	46.00	24.00
Max (mg/L)	465.00	829.00	182.00	7,690.00	2,210.00	632.00
Standard deviation (mg/L)	4.13	7.95	8.88	1,114.95	281.30	54.52
Coefficient of Variation	0.31	0.18	0.32	4.29	2.64	1.38
Completeness (%)	60	96	91	57	61	55

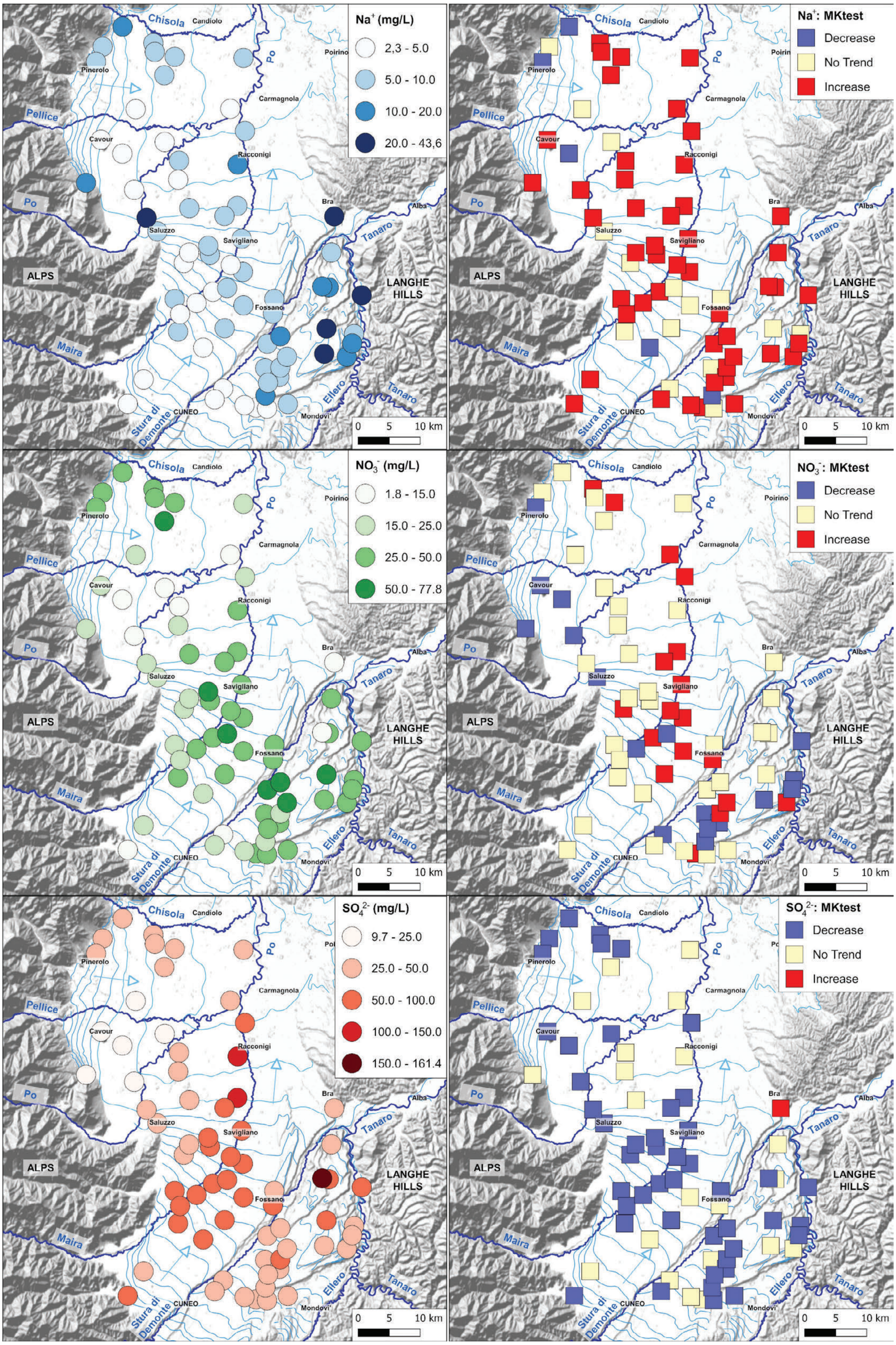

Fig. 4 - Distribution of average concentrations in the period 2015-2020 and of Mann-Kendall trend test results over the period 2000-2020 of Na^+*,* NO_3^- *and* SO_4^{2-} *in the study area in Piedmont Region.*

Fig. 4 - Distribuzione delle concentrazioni di Na^+, NO_3^- and SO_4^{2-} nel periodo 2015-2020 e dei risultati del test sui trend di Mann-Kendall sul periodo 2000-2020 dei medesimi ioni nell'area di studio nella Regione Piemonte.

NO_3^- concentrations range from 1.8 to 77.8 mg/L, showing increasing values along the groundwater flow direction, with low values in the plain sector close to the Alps (<15 mg/L) and high values in the central plain (25.0-77.8 mg/L). The high NO_3^- values (>25 mg/L) in the central plain between Mondovì and Racconigi are related to the intense agricultural practices (fertilizers, manure). Similar concentrations and land use are present in the area between Chisola River and Pinerolo and on the fluvial terraces, also favored by the low permeability of the unsaturated zone. In the plain sector closest to the relief between Cuneo and Cavour the different land use with mainly orchard contributes to the low concentrations. The contribution from precipitation, with nitrates concentrations lower than 10 mg/L (Cocca et al., 2023a), is to be considered negligible. Also the low NO_3^- concentration (<5 mg/L; Vigna et al., 2010) measured in Alpine springs confirms the low input from precipitation to groundwater.

SO_4^{2-} concentrations range between 9.7 and 161.4 mg/L showing concentrations along the Maira River higher than 50 mg/L and lower concentrations elsewhere. These concentrations are related to gypsum minerals originally present in the dolomite rocks in the alpine Maira Valley and the correlated lithological composition of the plain aquifers. The natural origin is also confirmed by the SO_4^{2-} concentrations in the Maira spring that shows similar values (Balestra et al., 2022). In other areas where gypsum minerals are not present or frequent, lower concentrations were found. For example, in the Saluzzo-Cavour area serpentinite rocks mainly contribute to low natural values whereas, in other areas, the low natural input could depend on occasional evaporite levels, clays and micaschist. As seen for Na^+ and NO_3^-, a greater SO_4^{2-} concentrations in the area between Chisola River and Pinerolo and on the fluvial terraces up to 161 mg/L, favored by the aquifer characteristics, exist. In these latter areas, a greater anthropic contribution related to agricultural practices exists. The contribution from precipitation, with concentrations below 5 mg/L (Cocca et al., 2023a), is to be considered negligible.

An upwelling of less mineralized deep waters with related dilution processes in the shallow aquifers occurs in the plain close to Alps between Cuneo and Mondovì and, partially, in the plain near the Po River, due to the interruption or absence of impermeable layers between shallow and deep aquifers (Armando et al., 1988; Cocca et al., 2023b; Lasagna et al., 2015, 2016b). As regards the agricultural pressures, the intense irrigation fed by rivers favors the transport of substances in the aquifers and oxidizing conditions. The chemical compositions of rivers, and therefore the irrigation waters, reflect the lithological composition of the mountainous relief.

In the Campania Region study area (Fig. 5), the Na^+ concentration distribution shows low values (15-30 mg/L) in correspondence of the border with the mountainous reliefs, in accordance with the carbonate nature of the reliefs. High values (> 100 mg/L) are mainly located close to the coastline and along the Volturno River. Na^+ and Cl^- are linearly correlated, showing a Pearson's coefficient equal to 0.80 (p-value < 0.05). These results can be related to the seawater intrusion phenomenon, which occurs not only close the coastline, but also along the river, through the ingression of saltwater along the river, and favored by the medium-high permeable sediments constituting the river channel itself or buried paleochannels. The seawater intrusion phenomenon has also been recognized in previous studies referring to groundwater samplings in 2006 (Corniello et al., 2010) and 2016 (Busico et al., 2021; Mastrocicco et al., 2019). According to Corniello et al. (2015) and Cuoco et al. (2015a), the peculiar chemical composition of groundwater in the area of Mondragone (NW sector), with high Na^+ concentration (about 150-200 mg/L), high Ca^{2+}, Mg^{2+} and HCO_3^- content and high electrolytic conductivity (>2200 µS/cm), can be related to water–gas (i.e., hydrothermal fluids) and water–rock (i.e., seawater intrusion, carbonate/volcanic aquifer) interactions. Anomalous high Na^+ concentrations are located in the central and SE sectors of the study area (close to Aversa, Acerra and San Felice a Cancello) and along the Regi Lagni Canal. Two of these wells are located close to water treatment plants and show anomalous high values of Na^+, K^+, HCO_3^- and Cl^-. Thus, these points could be affected by point sources of contamination. Instead, the anomalous high value located close to San Felice a Cancello may be due to alkaline metals leaching and/or ion exchange processes enhanced by local CO_2 upwelling through extensive fault systems along the border between the Campanian Plain and the Apennines (Corniello, 1996).

In six out of 21 monitoring points NO_3^- concentration exceed the regulatory threshold of 50 mg/L. These wells are located in the central sector, mostly along the Regi Lagni Canal. NO_3^- sources in groundwater are related to fertilizer use in agriculture, in the countryside and suburban areas, manure from livestock activities and sewers leakage (Busico et al., 2018; Ducci et al., 2019a). NO_3^- concentrations in the range 10-20 mg/L are present along the border with the mountainous reliefs, revealing that groundwater flowing from the surrounding mountainous ranges towards the contiguous plain is not severely affected by nitrate contamination. Low NO_3^- concentrations, below 10 mg/L, are present along the Volturno River. This peculiar aspect has also been recognized in previous studies referring to groundwater samplings in 2003-2006 (Corniello et al., 2010; Corniello & Ducci, 2014) and 2009-2012 (Cuoco et al., 2015b) and it is due to the occurrence of the denitrification process in the aquifer around the river (Corniello et al., 2010): this process is favored by a reducing environment, which is established by the confined/semi-confined nature of the aquifer and the enrichment in organic matter in the subsoil due to the presence of clay and peat layers.

SO_4^{2-} distribution almost overlaps NO_3^- distribution. The two compounds are linearly correlated, showing a Pearson's coefficient equal to 0.73 (p-value < 0.05). SO_4^{2-} concentrations higher than 50 mg/L are present in the central sector, from the mountainous range to the coastal area, mostly along the Regi Lagni Canal. SO_4^{2-} concentrations in the range 30-40 mg/L are present in the northern sector, on

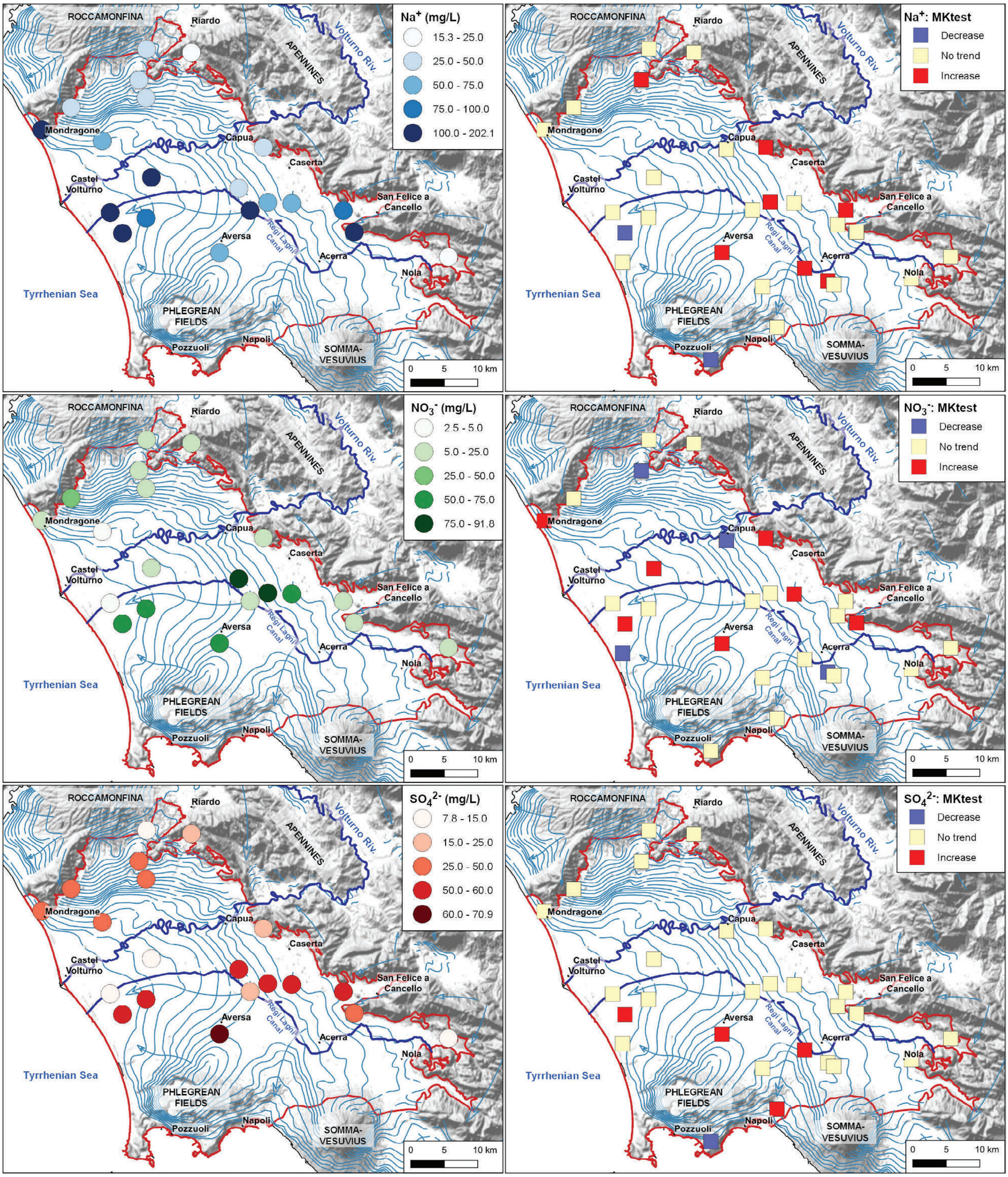

Fig. 5 - Distribution of average concentrations in the period 2015-2020 and of Mann-Kendall trend test results over the period 2002-2020 of Na^+, NO_3^- and SO_4^{2-} in the study area in Campania Region.

Fig. 5 - Distribuzione delle concentrazioni di Na^+, NO_3^- and SO_4^{2-} nel periodo 2015-2020 e dei risultati del test di Mann-Kendall sul periodo 2000-2020 dei medesimi ioni nell'area di studio nella Regione Piemonte.

the right side of Volturno River. In both cases, an increase in SO_4^{2-} concentrations appears along the main groundwater flow directions. Low SO_4^{2-} (< 10 mg/L) are located either close to the NE and SE corners of the plain (Nola, Acerra) or along the Volturno River. A similar SO_4^{2-} distribution in the plain has been observed also in previous studies (Corniello & Ducci, 2014; Cuoco et al., 2015b). The presence of high SO_4^{2-} concentrations in groundwater could be due to anthropogenic sources, such as domestic wastewaters, industrial wastes and wastewaters, or anthropogenic emissions (Torres-Martínez et al., 2020). Otherwise, their presence in groundwater could be due to water-rock interaction processes in aquifers constituted of material of igneous origin (i.e., enriched in pyrite minerals; Hem, 1985). Low SO_4^{2-} are related to i) the absence of natural (e.g., gypsum) or anthropogenic sources of SO_4^{2-} contamination along the border with the mountainous reliefs and ii) the presence of a reductive environment along the Volturno River, which provokes the reduction of SO_4^{2-} (as well as the denitrification process).

Atmospheric emissions of NO_3^- and SO_4^{2-} in the study area could be represented by (Nunziata, 2023): vehicular traffic, industries, agricultural emissions, illegal fires. According to Nunziata (2023), who collected rainfall samples in four sites located in the central sector of the study area in 2016-2017, maximum NO_3^- concentrations in rainfall were in the range 6-50 mg/L and maximum SO_4^{2-} concentration in 14-20 mg/L. However median values were about 2 and 1.1 mg/L for NO_3^- and SO_4^{2-}, respectively. Such amounts could be considered negligible in affecting groundwater contamination.

In summary, the spatial assessment of Na^+, NO_3^- and SO_4^{2-} highlights: i) the differences in groundwater circulation within the porous aquifers and due to the recharge from the mountainous ranges bordering the plain areas, ii) the occurrence of natural geogenic processes (e.g., dissolution, reductive and oxidizing processes) and natural phenomena (e.g., seawater intrusion, upwelling of deep fluids), iii) the influence of anthropogenic sources to groundwater quality.

Temporal variability

In the study area in Piedmont Region (Fig. 4, Table S1), heterogeneous behaviors between ions emerge with a greater presence of monitoring points with trends compared to those without trends (Fig. 6a,b,c); in particular, only one monitoring point shows no trends for all the three studied ions. Na^+ presents a prevalence of increasing trend (71% of the monitoring points). The few decreasing trends (7%) of Na^+ concentrations are located in the plain areas closest to reliefs, as well as, the monitoring points without trends. This behavior suggests a possible effect of land use, where the relevant agricultural pressures existing in the central area of the plain could induce an influence. The predominant increasing trends of Na^+ could be related to the road salt dissolution and its accumulation in the unsaturated zone, as confirmed in areas with a same trend (Perera et al., 2013).

Decreasing trends of NO_3^- concentrations in the plain areas closest to the reliefs (Alps and Langhe Hills) are observed (corresponding to 25% of the monitoring points) while, in the central plain area, increasing trends exist (26%). This distribution reflects the land use differences, with intensive farming area and increasing NO_3^- trends in the central plain as compared to irrigated arable and orchard uses with mainly decreasing NO_3^- trends in the plain closest to reliefs. In particular, for the monitoring points with high concentrations above the threshold value of 50 mg/L (Annex 1, European Commission, 2006) and in the range 25-50 mg/L (e.g., Fig. 6c), increasing trends are dominant. This behavior highlights the failure of the measures taken over the last two decades to reduce NO_3^- contamination in this area.

SO_4^{2-} presents a prevalence of decreasing trends (e.g., Fig. 6a), detected in 68% of monitoring points, with only one monitoring point with an increasing trend. The peculiarity of this ion is the extreme spatial uniformity of the trends, suggesting a large-scale process not connected to local factors. For this reason, limitations in the agricultural practices of recent years cannot be held for the observed decrease, due to the similar trends also highlighted in areas where measures were not applied. The monitoring point showing increasing SO_4^{2-} concentrations could be influenced by the sedimentary rocks of Langhe hill or by local anthropogenic contamination. As it concerns the decreasing trends, a complex and not completely known process emerges. Few changes in the land use occurred in the last 20 years, with a slight expansion of urban and industrial areas, which cannot explain the observed behavior. A potential reason could be the increase in the redox processes, also in relation to the decreasing trends of NO_3^- in the area close to the Alpine reliefs.

In the study area in Campania Region (Fig. 5, Table S2), a general stationarity of the concentration of Na^+, NO_3^- and SO_4^{2-} is present, with more than 70% of monitoring points (i.e., water wells) showing no trend for all the three studied ions (e.g., Fig 6e). Increasing Na^+ concentration trends have been recorded in wells located in the innermost sectors of the study area. Peculiarly, wells located along the coastline show decreasing or no trend (e.g., Fig. 6d), despite these wells showing average concentrations higher than 100 mg/L (average over the period 2015-2020). As previously observed, coastlines are affected by seawater intrusion, and this phenomenon is neither worsening nor improving. In the Phlegrean Fields and Mondragone areas this phenomenon may be masked by deep fluids upwelling (enriched in alkaline elements, metals) and water-rock interaction in the volcanic aquifer (e.g., Mastrocicco et al., 2021; Sellerino et al., 2019).

Increasing NO_3^- concentrations affect seven cases out of 27 monitoring points (e.g., Fig. 6f). Three of these points show average NO_3^- concentrations over the period 2015-2020 higher than the drinking water threshold value of 50 mg/L (European Commission, 2006; WHO, 2022), whereas the other four points show average NO_3^- concentrations in the range 10-20 mg/L. The other wells with average concentrations higher than 50 mg/L show no trend over the 2002-2020 period. Only four monitoring points show decreasing concentration trends, and their average

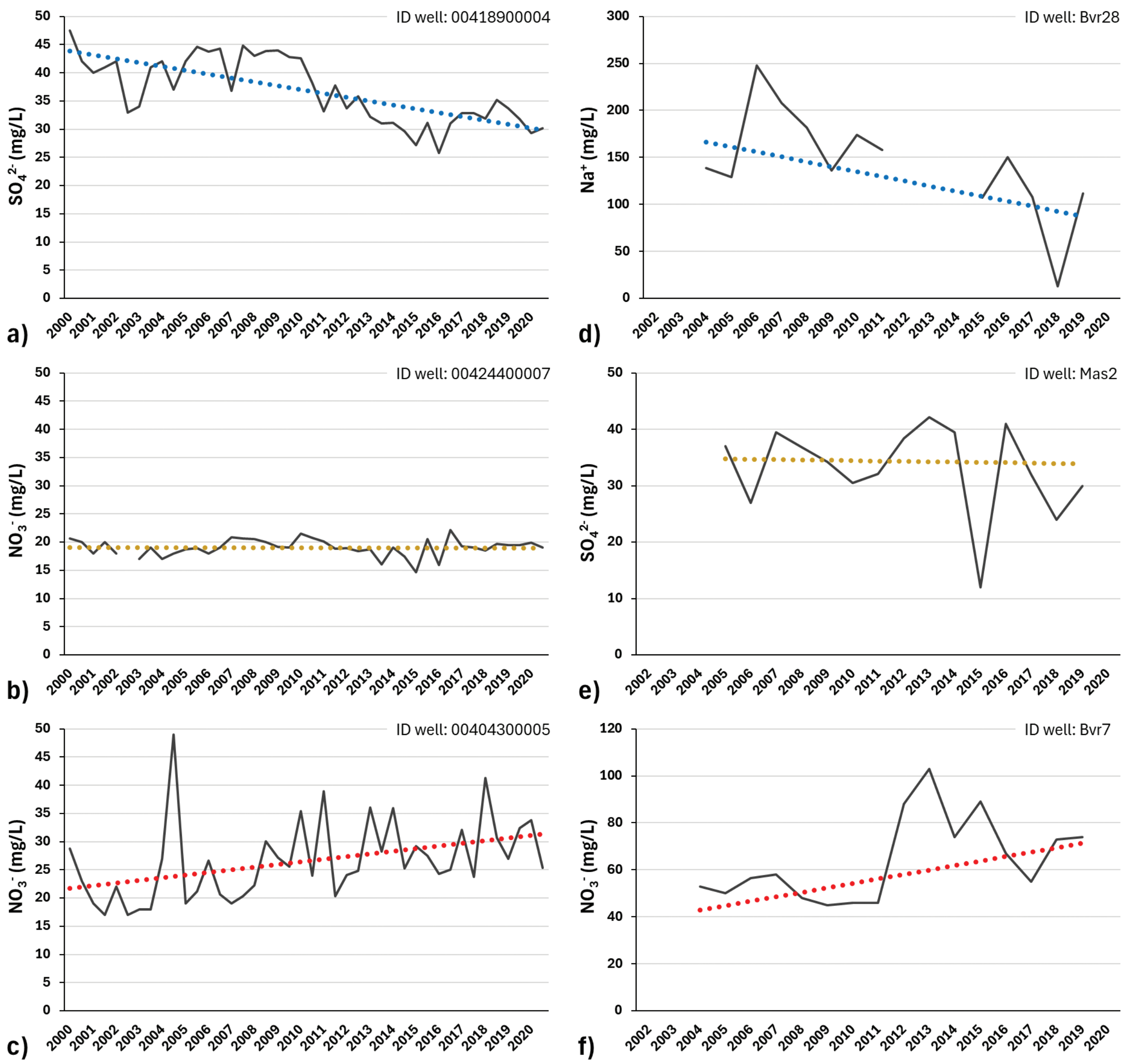

Fig. 6 - Examples of ion concentration trends in Piedmont (a, b, c) and Campania (d, e, f) study areas. Refer to Table S1 and S2 for the details of the Mann-Kendall trend test results of the selected monitoring points.

Fig. 6 - Esempi di trend nelle concentrazioni di ioni nelle aree di studio in Piemonte (a, b, c) e Campania (d, e, f). Si faccia riferimento alle Tabelle S1 ed S2 per i dettagli dei risultati dei test di Mann-Kendall dei punti di monitoraggio selezionati.

NO_3^- concentrations over the 2015-2020 period are much below the regulation threshold. Thus, NO_3^- contamination in the study area is mostly stable or worsening. Between 2000 (CLC, 2000) and 2018 (CLC, 2018), a few changes in land use occurred mainly as: i) expansion of urban areas (+4%), ii) reduction of agricultural areas (–3.5%), iii) changes in crops and pastures, and iv) reduction of natural and forested areas and wetlands (–0.5%). The pattern of NO_3^- concentration trends probably reflects non-virtuous agricultural practices which are still present in the study area or inherited from the decadal agricultural vocation in the study area. The very low filtration velocity in the tuff and in the fine-grained pyroclastic deposits may also cause the persistence of NO_3^- in the aquifer (Kim et al., 2006). Moreover, settlements with incomplete sewer coverage, outlying homes without sewerage system and treatment plants at low efficiency are still present in the study area (Ducci et al., 2019b).

Four cases out of 27 monitoring points show increasing concentration trends of SO_4^{2-}. These monitoring points are located in the southern sector of the study area: three of them are located on the right side of the Regi Lagni Canal, in the Volturno Plain, whereas the last one is in the city of Naples. Two monitoring points also show the highest average SO_4^{2-} concentration over the period 2015-2020. These two wells are also affected by increasing nitrate concentration trends and recent average NO_3^- concentrations above the regulation threshold. Instead, gaps in the monitoring activity did not allow to obtain recent hydrochemical data for the other two monitoring points. As for NO_3^-, increasing SO_4^{2-} concentrations may be related to the presence of domestic wastewaters or low efficient wastewater plants. Only one monitoring point shows a decreasing SO_4^{2-} concentration trend, and it corresponds to the same well located in the Phlegrean Fields showing a decreasing Na^+ concentration trend. It is not possible to compare trends with recent hydrochemical data because this well was excluded by the monitoring network since 2015. For this peculiar case, it is possible to assume that the decreasing trend depends on the superposition of more phenomena, as the mixing of a wide range of water types (thermal water, seawater, precipitation water), gas–water–rock interaction processes and ion exchanges, which are difficult to clearly quantify or detect (Aiuppa et al., 2006; Sellerino et al., 2019).

The analyses on temporal evolution of Na^+, NO_3^- and SO_4^{2-} reveal: i) trends with different behaviors among the selected parameters, ii) a significant spatial variability highlighted by a few opposite trends between monitoring points close to each other and, at the same time, also homogeneous behaviors for large sectors, iii) the influence of anthropogenic pressures to groundwater chemistry evolution. Furthermore, the observation of time series plots does not highlight significant seasonality. Groundwater levels variation could represent a relevant factor in controlling the hydrochemical characteristics in groundwater, resulting in a succession of biogeochemical processes (e.g., leaching or dilution processes) regulating the transport and fate of chemicals, nutrients and pollutants in the subsurface environment (e.g., Chen et al., 2022, Fan et al., 2023).

Conclusions

Specific factors and processes influence the spatial variability of the selected ions, both in terms of spatial distribution and magnitude of their concentrations in the two study areas. In particular, we observed: gypsum levels influence, road-salts contamination, upwelling of less mineralized water (Piedmont plain), seawater intrusion, water–gas interaction, denitrification processes (Campania plain). Despite these differences, common features can be recognized such as the relevant agricultural vocation and anthropogenic pressures that affect groundwater chemistry and quality, water–rock interaction processes and an increase of ion concentrations along the main groundwater flow directions.

As previously reported, for the temporal variability, both study areas highlight a relevant spatial variability, where homogeneous behaviors for large sectors with the coexistence of monitoring points close to each other with opposite trends are present. Comparing the two study areas, a higher number of monitoring points with trends appear in the Piedmont area compared to the Campania area. In the individual study area, different trends between ions emerge due to the different origin and processes. Thus, also comparing the temporal evolution of specific ions between the study areas, a different temporal evolution emerges. The same processes that influence both areas can be appreciated, such as the existence of agricultural and urban anthropic pressures affecting groundwater nitrates concentrations and the worsening of nitrate contamination. In fact, few changes in the land use occurred in the last 20 years in areas close to monitoring points with average values above the regulation threshold, highlighting the scarce effectiveness of adaptation measures to contrast nitrate contamination in groundwater. In both areas, therefore, a significant influence of anthropogenic pressures emerges for both spatial and temporal evolutions. Potential influences on the observed variabilities from groundwater level variation and irrigation practice (Liu et al., 2022; Rotiroti et al., 2023) cannot be excluded.

In conclusion, the two areas are characterized by different spatio-temporal distributions of Na^+, NO_3^- and SO_4^{2-} mainly related to the geological aspects, anthropogenic impacts, natural hydrochemical processes. Some processes are site-specific, whereas others are in common; thus, this reinforces the advantage of making comparative studies.

The limits of the present study can be identified in the sampling frequency and in some gaps in the data series, in the non-homogeneous distribution of the sampling points, in the often scarce knowledge on the sampling point characteristics (e.g., well filter depth).

For this reason, our future challenges are the collaboration with the Agencies in the groundwater sampling planning and the comparison of the groundwater quality data with groundwater levels to individuate different and preferential flows influencing groundwater quality at local level. Finally, an in-depth analysis of the role of the modification in precipitation regimes due to climate change and climate variability in the study areas (as highlighted e.g., by Lasagna et al., 2020a and Mancini et al., 2022) could be useful to emphasize potential impacts on groundwater quality.

Supplementary Materials

ANNEX 1: Table S1 and Table S2
online on: https://acquesotterranee.net

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Competing interest

All authors, declare no competing interests.

Author contributions

Collection of data, D.C. and S.S.; data processing, D.C. and S.S.; interpretation of results, D.C., S.S., D.D., D.A.D.L., M.L.; writing-original draft preparation, D.C. and S.S.; writing-review and editing, D.D., D.A.D.L., M.L.; visualization, D.C. and S.S.; supervision, D.D., D.A.D.L., M.L.. All authors have read and agreed to the final version of the manuscript.

Additional information

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