Journal of Maps

ISSN: (Print) (Online) Journal homepage: www.tandfonline.com/journals/tjom20

Hydrogeochemistry of the shallow aquifer in the western Po Plain (Piedmont, Italy): spatial and temporal variability

Daniele Cocca, Manuela Lasagna, Laura Debernardi, Enrico Destefanis & Domenico Antonio De Luca

To cite this article: Daniele Cocca, Manuela Lasagna, Laura Debernardi, Enrico Destefanis & Domenico Antonio De Luca (2024) Hydrogeochemistry of the shallow aquifer in the western Po Plain (Piedmont, Italy): spatial and temporal variability, Journal of Maps, 20:1, 2329164, DOI: 10.1080/17445647.2024.2329164

To link to this article: https://doi.org/10.1080/17445647.2024.2329164

Published online: 20 Mar 2024.

JOURNAL OF MAPS
2024, VOL. 20, NO. 1, 2329164
https://doi.org/10.1080/17445647.2024.2329164

SCIENCE

OPEN ACCESS Check for updates

Hydrogeochemistry of the shallow aquifer in the western Po Plain (Piedmont, Italy): spatial and temporal variability

Daniele Cocca, Manuela Lasagna, Laura Debernardi, Enrico Destefanis and Domenico Antonio De Luca

Earth Sciences Department, University of Turin, Turin, Italy

ABSTRACT

This paper describes the spatial and temporal variability of the hydrogeochemistry of shallow aquifer in the western Po Plains, located in Piedmont (northwestern Italy), using groundwater monitoring network data for the main chemical–physical parameters. Hydrochemical maps for the 2015–2020 period were created to identify the main natural and anthropogenic factors responsible for the remarkable spatial variability. Temporal variations in the 2000–2020 period were defined to show the existence of variabilities that were previously not investigated. The spatial and temporal elaborations show significant and various variabilities. The hydrochemical maps confirm the existence of several natural and anthropogenic factors, including the lithological compositions of aquifers, agricultural practices and pressure from urban centres. The temporal variations suggest different resilience capacities of the aquifers to the several impacting factors. The availability of this knowledge is crucial to create the basis for groundwater protection.

ARTICLE HISTORY
Received 7 June 2023
Revised 13 November 2023
Accepted 5 March 2024

KEYWORDS
Groundwater; hydrochemistry; spatial evolution; time series fluctuations; hydrodiversity

1. Introduction

The quality of groundwater resources is affected by several factors (De Giglio et al., 2015; USGS, 1999). Previous studies have confirmed the relevant role of natural processes on groundwater quality namely, water–rock interactions (Flores Avilés et al., 2022; Madrigal-Solìs et al., 2022), watercourse interactions (Uhl et al., 2022) and natural climate variability (Barbieri et al., 2023; Cross & Latorre, 2014).

In addition, various human actions can influence the hydrochemistry of aquifers such as agriculture and farms (UNESCO, 2022), irrigation and canals (Rotiroti et al., 2019; Xia et al., 2022), urban sewage leakages (Balzani et al., 2022), road deicing salt infiltration (McQuiggan et al., 2022) and industrial inputs (Aubert, 2020; Bucci et al., 2018; UNESCO, 2022).

Moreover, global interest in the temporal variability of groundwater quality in relation to meteorological variability is increasing (Frollini et al., 2021; Lasagna et al., 2020; Mohammed et al., 2022; Orecchia et al., 2022; O'Connell et al., 2022; Toller et al., 2020; Zanotti et al., 2023).

Few studies with regional hydrochemical maps are found in the literature (BGR, 2013; Schaffer et al., 2021; SGUDS, 2010); conversely, there are many studies of local hydrochemical characteristics.

In the Piedmont Region (northwestern Italy), a few groundwater quality studies have been conducted at the regional scale (Arpa Piemonte, 2006a). In this region, there are approximately 4.2 million inhabitants, predominantly concentrated in the plain sector. Here, a great number of water-dependent activities are conducted in the industrial and agricultural sectors (paddy, farms, agricultural), with an important influence on socioeconomic development. A large number of anthropogenic pressures, both from contaminated sites and from diffuse sources, exist. In addition, this region has an enormous variety of lithologies associated with the variable relief (Piana et al., 2017).

Shallow aquifers recharge rivers and wetlands and are most exploited for irrigation, farming and industrial activities. Furthermore, in a large portion of the plain, they feed the deep aquifers that are exploited for drinking purposes.

For these reasons, a regional hydrochemical overview is crucial to define and monitor the nature of the groundwater quality and main processes affecting groundwater resources, to preserve groundwater qualitative stability over time, and therefore to protect human health and human activities and appreciate 'hydrodiversity' such as natural heritage.

This study provides the first hydrochemical characterization of the shallow aquifers in the Piedmont Plain sector at the regional scale in the last decade, identifying the main natural and anthropogenic

CONTACT Manuela Lasagna manuela.lasagna@unito.it Earth Sciences Department, University of Turin, Via Valperga Caluso 35, Turin, Italy
Supplemental data for this article can be accessed online at https://doi.org/10.1080/17445647.2024.2329164.

factors responsible for the remarkable hydrochemical spatial variability observed.

At the same time, some elaborations are provided that are aimed at showing the existence of hydrochemical temporal variability that has not previously been reported.

2. Study area

The study area (Figure 1) is located in the Piedmont region in northwestern Italy. From a geomorphological and geological point of view, the Piedmont region can be divided into three macro-sectors: Alps-Apennine chains, hilly sectors and plain sector.

The Piedmont plain extends approximately 6,230 km^2, covers 27% of the regional territory and represents the westernmost part of the Po Plain (De Luca et al., 2020). This region is surrounded by Alps and Apennine chains on the north, east and south and constitutes the most important groundwater reservoir of the region (Debernardi et al., 2008).

The geological setting of the Piedmont Alps and Apennines is highly varied and widely investigated. Piana et al. (2017) summarized the geological units (Figure 2) and distinguished them from a lithological point of view:

- calcareous and dolomitic rocks (Triassic – Paleogene) with limestone-dolomitic rocks and evaporitic-carbonatic levels, characterized by karst phenomena.
- Tertiary Piemonte Basin succession (BTP) rocks (Late Cretaceous-Early Eocene) with mainly argillaceous schist, sandstone limestone, sandstone and slate schist.
- Metamorphic, volcanic and plutonic rocks (Paleozoic – Neozoic) with gneiss, mica schist, quartzite, serpentinite, amphibolite, prasinite, granite.

The alpine crystalline rocks are mostly impermeable or slightly permeable by fissuration.

In the hilly sectors, sedimentary rocks, especially marl, clay, silt, conglomerate, sandstone and gypsum, represent the Tertiary Piedmont Basin, which includes Langhe, Turin and Monferrato Hill deposits (Eocene-Miocene). These rocks have low permeability and show limited groundwater circulation.

In the Piedmont plain, the hydrogeological conceptual model consists of superimposed complexes represented, from top to bottom, by the fluvial deposits complex (lower Pleistocene-Holocene), Villafranchian transitional complex (upper Pliocene–lower Pleistocene) and marine complex (Pliocene-Eocene) (Figure 3).

More specifically, De Luca et al. (2020) recognized three different hydrogeological complexes hosting shallow unconfined aquifers in the Piedmont plain, with an overall thickness ranging between 20 and 50 m. In order from youngest to oldest, these consist of the following:

- Fluvial deposits (Lower Pleistocene-Holocene): fluvial and fluvioglacial sediments, mainly gravelly sandy and secondarily silty-clayey, located in the bottom of the valleys and in the Piedmont Plain. They mainly show permeability for porosity from high to medium.
- Glacial morainic deposits (Pleistocene): morainic amphitheater deposits of Rivoli-Avigliana, Serra d'Ivrea and Upper Novarese consist of sediments with variable grain sizes. The prevalent permeability for porosity varies from medium to low, locally high.

The water table follows the topography of the land surface, and the piezometric lines are generally parallel to the Alps relief (Figure 2). The main watercourses are generally losing rivers close to the Alps and gaining rivers in the low plain.

The water table depth shows high variability. The most frequent range is less than 5 m, while the highest values (more than 50 m) are found on high morphological terraces.

The recharge areas of the shallow aquifers are located across the entire plain due to infiltration from rainfall and surface waters in the high plain sectors. The low plain sectors are generally discharge areas, and the Po River represents the main regional discharge axis for groundwater flow (De Luca et al., 2019; De Luca et al., 2020).

In terms of the hydrochemical setting, several local studies have investigated the groundwater quality in the Po Plain (Civita et al., 2009, 2011; De Luca et al., 2006; Orecchia et al., 2022) and in the alpine sector (Balestra et al., 2022; De Luca et al., 2015). Some studies have been conducted to evaluate the temporal evolution in the hydrochemical characteristics (Arpa Piemonte, 2006a, 2006b; Lasagna et al., 2020; Raco et al., 2021), while others have characterized the high nitrate contamination linked to intense agricultural activities (Bortolami et al., 1988, 1989; Canavese et al., 1999; Debernardi et al., 2008; Lasagna et al., 2005; Lasagna et al., 2013, 2015, 2016a, 2016b; Lasagna & De Luca, 2016, 2019; Lo Russo et al., 2011; Martinelli et al., 2018; Vigna et al., 2010). Other studies were conducted to define the upwelling of salt water near hilly sectors due to the low permeability of sedimentary rocks and high residence time of the groundwater (Clemente et al., 2009a, 2009b).

In the study area, irrigated arable areas are prevalent, except in the Vercelli-Novara plain, where paddies are widely present. The main industrial areas are located close to large urban centres (Figure 4).**3.**

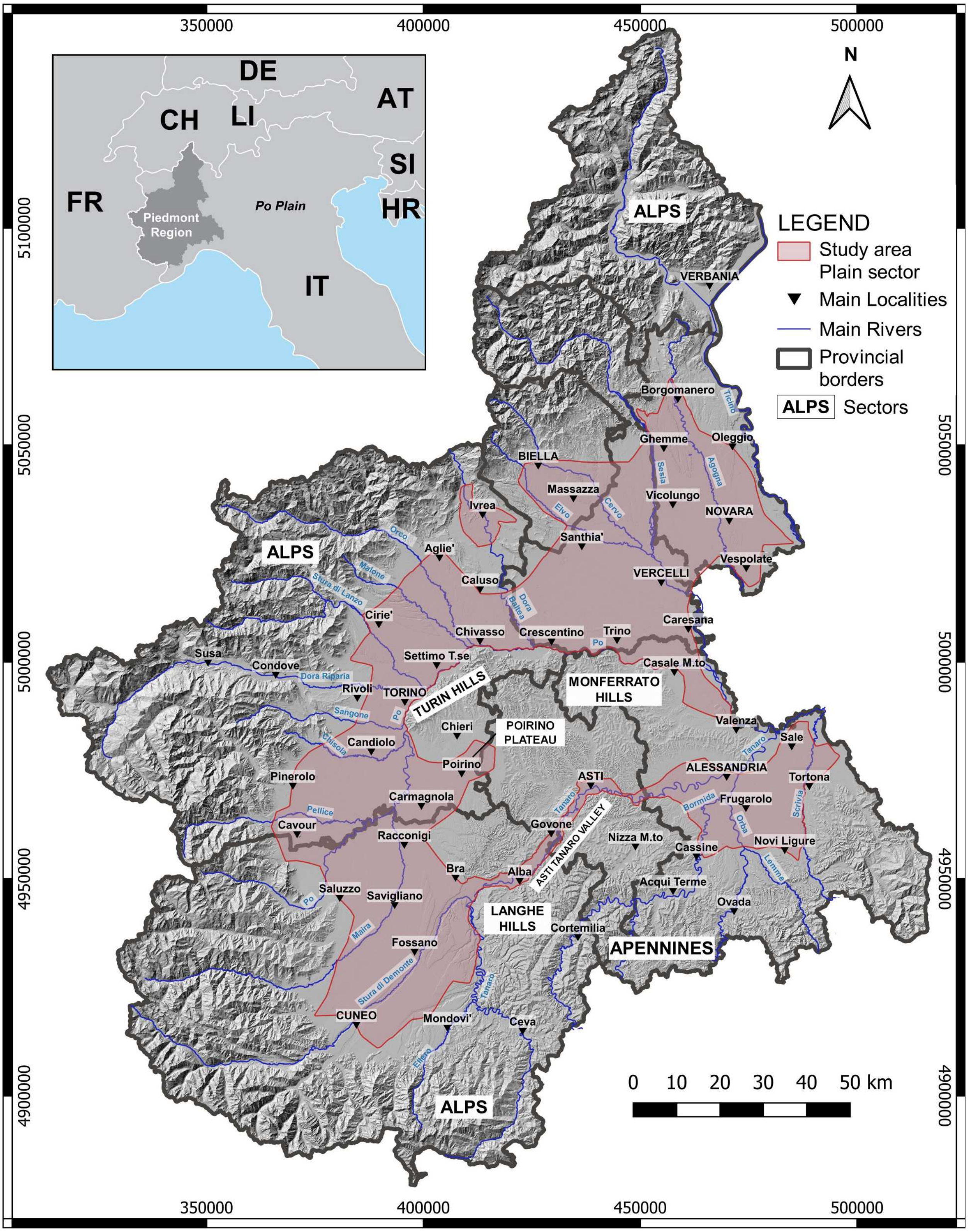

Figure 1. Location of the study area. Map coordinates refer to the metric system WGS84/UTM zone 32 N.

Materials and methods

In this paper, 42,720 groundwater chemical data from 345 shallow aquifer wells were analysed. Chemical data are referred to sampling campaigns performed by ARPA Piemonte (Regional Agency for Environmental Protection), consisting of half-yearly sampling for the period 2015–2020 (spring and autumn seasons, with two samples every year in the better condition of completeness). The chemical data are freely available at the ARPA Piemonte website (http://webgis.arpa.Piedmont.it/monitoraggio_qualita_acque_mapseries/monitoraggio_qualita_acque_webapp/, in Italian).

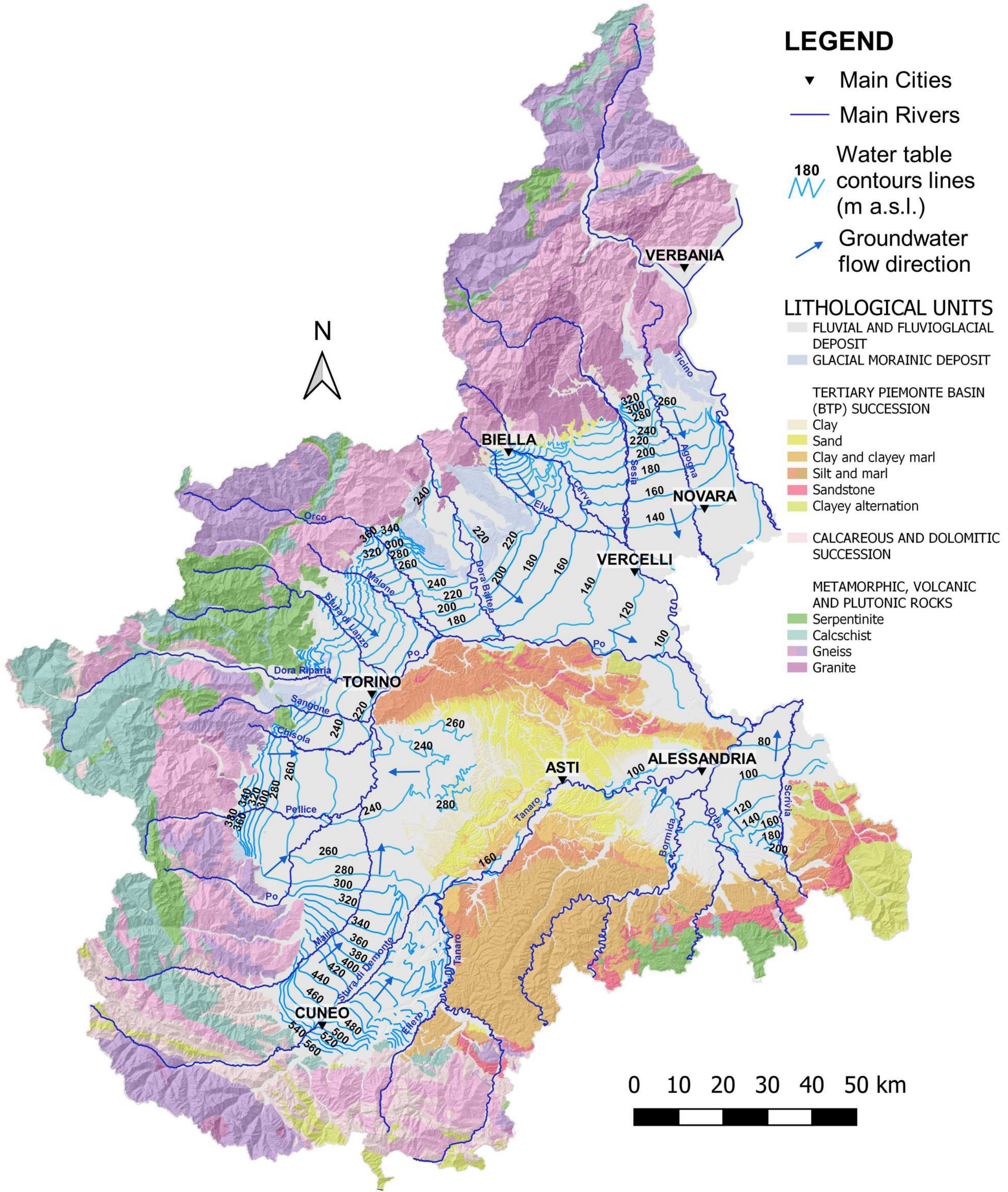

Figure 2. Geological map and piezometric surface of the shallow aquifer in the Po Plain (summer 2016) of the Piedmont Region. The simplified geological map and the piezometric map of the shallow aquifer are modified from Piana et al. (2017) and De Luca et al. (2020), respectively.

Descriptive statistics for the main chemical–physical parameters and ion concentrations (electrolytic conductivity, pH, hardness, Sodium Adsorption Ratio (SAR), NO_3, Cl, HCO_3, Ca, Mg, SO_4, Na, K) were obtained.

Data processing consisted of (i) selection of monitoring points and time periods, (ii) data suitability assessment, (iii) spatial analysis, interpolations and revisions, and (iv) temporal analysis.

3.1. Selection of monitoring points and time period

The wells drilled in the shallow aquifer with a completeness (% half-yearly chemical data available for the overall period) of at least 50% in the period 2015–2020 were selected (345 wells). The locations of the selected monitoring wells are displayed in Figure 5. The 2015–2020 period (6 years) was chosen for the

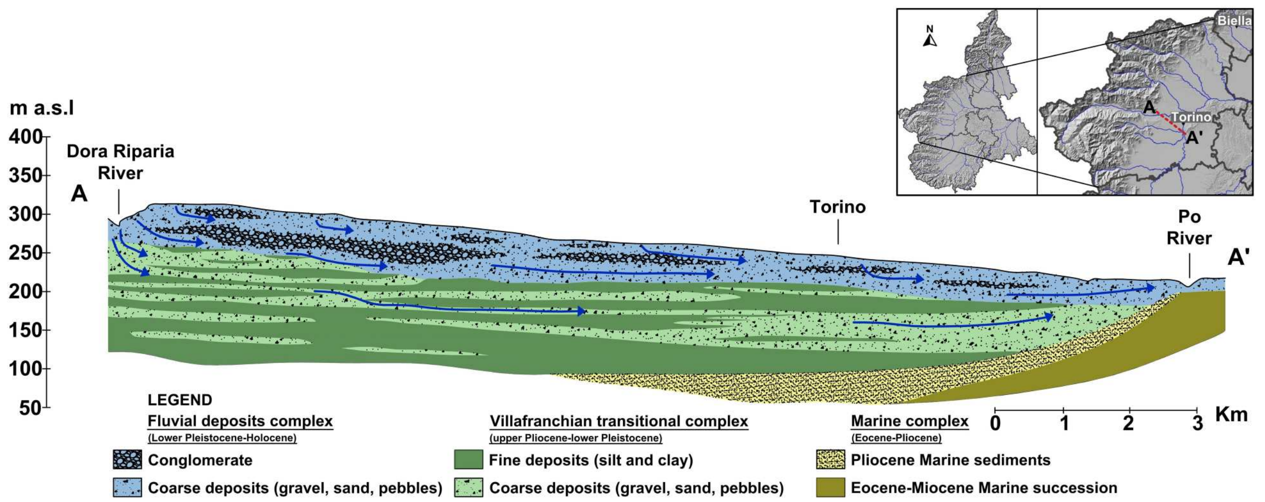

Figure 3. Simplified hydrogeological section of the alluvial Po Plain. The blue arrows represent the groundwater flow direction (modified from Canavese et al., 2004).

analyses because it constituted the most recent time period and had a high level of data completeness. A time range rather than a single year was chosen to identify and exclude temporal anomalies. For the cartographic elaborations, 5 chemical–physical parameters (electrolytic conductivity (EC), chloride (Cl), nitrate (NO_3), hardness and Sodium Adsorption Ratio (SAR)) that are considered of primary importance for defining the chemical and irrigation quality of groundwater resources were chosen.

While EC, Cl and NO_3 were directly measured, the hardness and SAR were obtained through the following formulas:

$$\text{Hardness} = 2,497 \text{ X Ca2} + + 4,116 \text{ X } Mg^{2+}(\text{mg/L } CaCO_3) \quad (1)$$

$$\text{SAR} = Na^{+}/[\sqrt{(Ca^{2+} + Mg^{2+})/2}] \quad (2)$$

The USGS classification (https://www.usgs.gov/special-topics/water-science-school/science/hardness-water) was used for hardness, while the classification proposed by the U.S. Department of Agriculture (Richards, 1954) was used for SAR.

3.2. Data suitability assessment

The main ions were employed for analytical quality control based on anion–cation charge balance.

The main descriptive statistical were reported (n° observations, minimum, maximum, average value, standard deviation, coefficient of variation (CV) and completeness).

The average values were chosen as the statistical indicator to be represented in the cartographic elaborations.

The outliers connected to transcription errors and therefore unreal values, were identified and excluded. Their identification was performed through the CV calculation for each parameter in individual wells. In the data series with CV values higher than 40, anomalous data statistically correlated to outliers were excluded (Arpa Piemonte, 2012). 'False outliers', also defined as hot spots, which corresponded to real values that were occasionally related to contamination phenomena were retained in the dataset (U.S. EPA, 2002). Their identification as contamination origin were verified observing the behaviour of other ions (e.g. Na, Cl, NO_3, SO_4) and indices showing anomalous conditions and also with previous local studies control.

The Simple Substitution method was applied to NDs (Non Detected values); the values were set equal to the DL (Detection Limit) (SNPA, 2018).

3.3. Spatial analysis, interpolations and revisions

Dataset frequency distribution was checked by means of Shapiro–Wilk, Lilliefors and Kolmogorov–Smirnov tests, using the U.S. EPA software ProUCL (version 5.1; epa.gov\land-research\proucl-software).

Geostatistical data processing was carried out using SAGA GIS 2.3.2 software with experimental variogram construction. Subsequently, spatial interpolation was performed using the geostatistical software Surfer 16.8.3-Golden Software. The kriging methodology was chosen, which is widely used for the treatment of chemical data in groundwater (Belkhiri et al., 2020) and in the Piedmont plain (Butera & Cotto, 2008).

In particular, spatial interpolations were carried out delimiting the individual hydrogeological distinct areas (n. 13). This subdivision is used to distinguish groundwater bodies that are independent of each other according to geological-morphological and hydrogeological structures, recharge–discharge processes and hydrochemical facies. In contrast to the

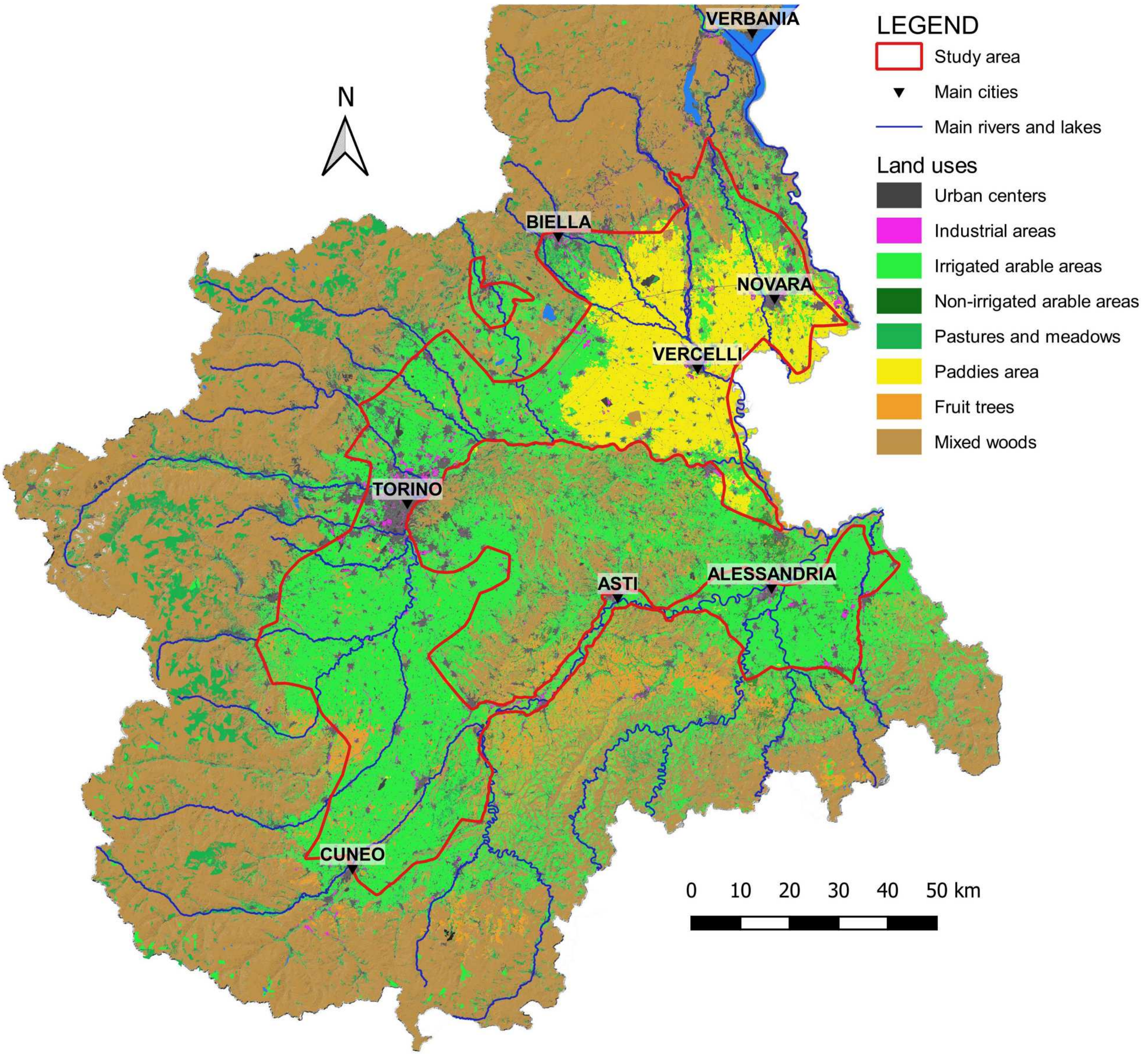

Figure 4. Land uses in the Piedmont Region. Corine Land Cover (Regione Piemonte, 2010).

proposed subdivision by Arpa Piemonte (https://www.geoportale.piemonte.it/geonetwork/srv/ita/catalog.search#/metadata/r_piemon:4ee0d274-a0c3-4cbd-b98d-77e7e2753cfc), for this study, it was necessary to merge some sectors due to the low number of monitoring points.

Furthermore, an external perimeter for the interpolations was created to avoid dataset extrapolation conditions. This perimeter delimits the area with the presence of monitoring points from the area without them.

The interpolations generated by the software were subsequently modified according to the local, natural and anthropogenic aspects that can potentially influence the distribution of chemical parameters such as main watercourses (losing or gaining conditions, watercourses hydrochemistry), geomorphology (e.g. fluvial terraces), punctual anthropogenic pressures, and areas with different monitored point densities. For this reason, previous local studies with higher monitoring point densities were analysed with the aim of identifying local spatial variability that the regional monitoring network did not characterize due to the large distances between points to confirm the hydrochemical maps created.

The previous studies consist of approximately 50 studies, mainly unpublished research carried out by the Earth Sciences Department of University of Turin, with a total of approximately 1800 monitoring points throughout the entire Piedmont Po plain. In particular, data from previous studies were not integrated with regional monitoring network data because different periods were analysed. The interpolation was only perfected where there were at least two studies indicating the same areal variability.

In some cases, the hydrochemical maps highlighted the existence of individual anomalous points, and ion concentrations were examined to identify the origin of the anomaly (natural or anthropogenic). Where the parameters clearly suggested anthropogenic origins,

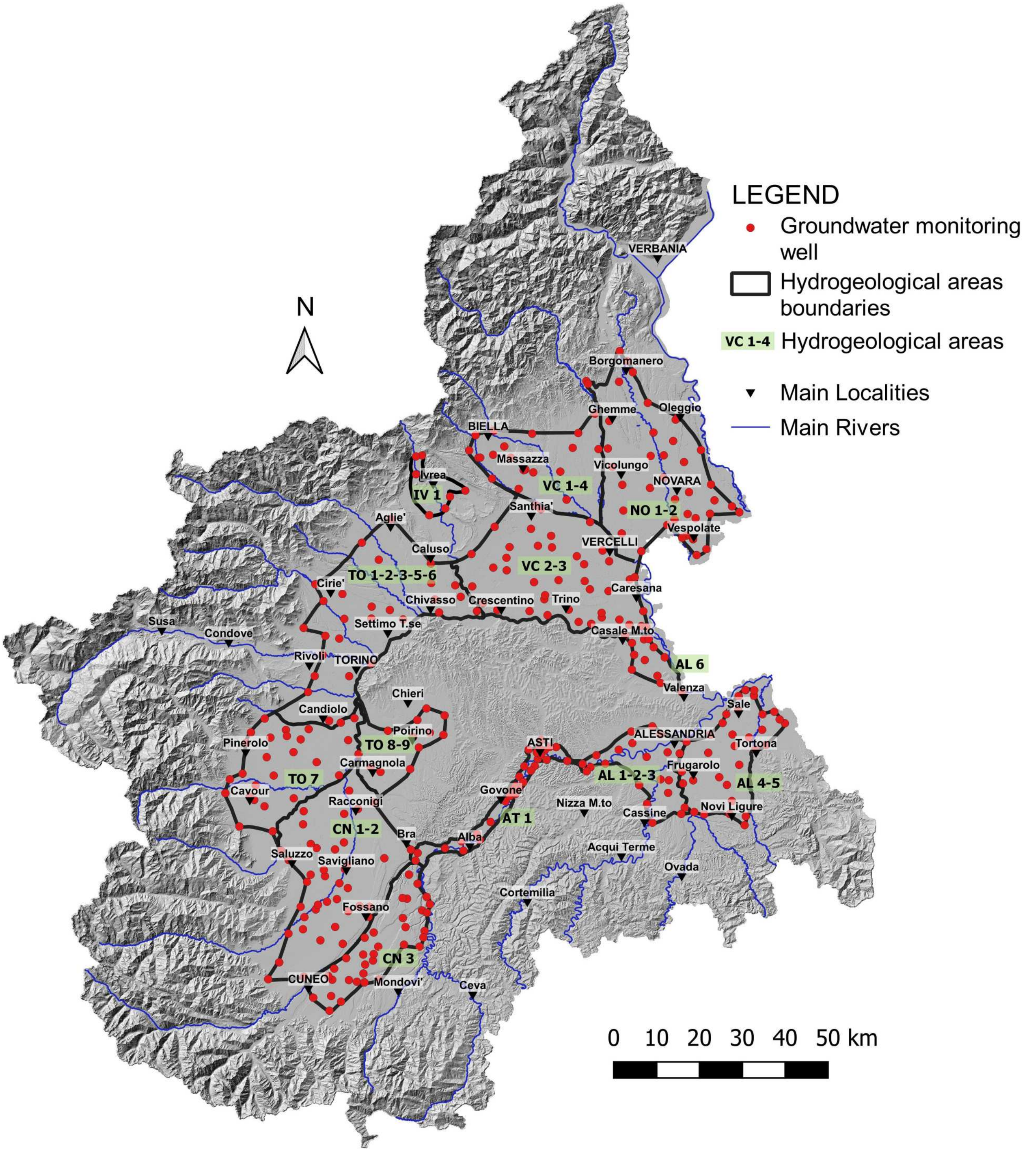

Figure 5. Locations of the 345 groundwater monitoring wells and the 13 distinct hydrogeological areas.

and previous local studies suggested the presence of hot spots, the anomaly areal size was reduced in order to minimize the exaggeration created by the interpolation method.

Moreover, to investigate geochemical processes, hydrochemical facies were defined and visualized by Piper diagrams (Piper, 1944).

For the interpretation of hydrochemical maps, the factors driving ion concentrations and their spatial variability were defined (influence of watercourses, the lithological nature of deposits hosting the aquifers, the lithological nature of alpine and hilly reliefs adjacent to the plain sectors, differences in precipitation rates, land use, irrigation channel network, irrigated areas and variation along groundwater flow). In particular, data from the same regional database for the watercourses and alpine springs were considered and compared with groundwater data as part of the analysis.

3.3.1. Hydrochemical time series fluctuations

To show hydrochemical temporal fluctuations, 15 shallow aquifer monitoring wells that were equally distributed throughout the territory were selected. The selection was made by taking into account the completeness of the data for the three chosen parameters (EC, NO_3 and Cl with minimum 80% completeness), selecting points with relevant and specific temporal fluctuations (e.g. increasing-decreasing trend, seasonal fluctuations, stationarity condition, change points). The selected monitoring wells correspond to the most representative of that area.

The time period analysed for the fluctuation analysis was 2000–2020 (21 years), characterized by half-year data (two annual data) from the spring and autumn seasons, with a maximum of 42 observations.

The nonparametric Mann-Kendall trend test (Kendall, 1975; Mann, 1945) and OLS regression slope (Ordinary Least Squares) were applied to identify statistically significant positive or negative monotonic trends in the three chosen parameters and to evaluate their magnitude.

4. Results and discussion

Table 1 shows the main descriptive statistics. All the monitored points show an anion–cation charge balance error <10% and widely <5%. Very low outlier and ND numbers were found. The completeness is on average greater than 90% for EC, NO_3 and Cl and almost 80% for hardness and SAR. The CV average changes according to parameters and sectors, with the highest values observed for NO_3 and Cl and the lowest observed for EC and hardness.

Regarding the spatial analysis, the frequency distribution analysis of data shows a mainly lognormal distribution for the majority of data. The nuggets effect suggests a monitoring network that is too sparse and is occasionally unable to highlight local variability.

In general, the changes that were made to the interpolations were necessary, they had a very low impact on the regional interpolation although. Where anomalous points were identified from anthropogenic origins, the anomaly areal size was reduced.

Previous studies are consisted with the spatial variability found by the regional monitoring network. However, in some sectors local variability was observed in previous studies but was not detected by the regional monitoring network due to low point density or the absence of network coverage (e.g. plain sector between the Stura di Lanzo and Dora Baltea River, Turin plain near the Turin Hills). Even in the presence of local natural conditions (e.g. fluvial terraces) or intense anthropogenic influences (e.g. agricultural inputs), hydrochemical spatial variability was not correctly reflected by the regional monitoring network data (e.g. Poirino Plateau). This evidences confirms the necessity to increase the monitoring points density of the groundwater monitoring network.

4.1. Hydrochemical spatial distribution

The Piper diagram confirms the prevalence of the bicarbonate-calcium facies for the majority of the monitoring points (89%). Some points belonged to the calcium-sulfate facies (11% monitoring points).

For this reason, the EC and hardness distributions are similar.

Important spatial variability in the selected parameters was identified and mapped through the constructed hydrochemical maps. More specifically, some specific factors were identified (subdivided by sectors), which are presented below.

The electrolytic conductivity values show large variability in the maps. The high values in the Cuneo and Poirino plateau sectors (>600 μS/cm) are linked to agricultural pressures due to the high values of NO_3. In the Turin-Monferrato-Langhe Hills and Apennine reliefs the sedimentary rocks affect several sectors (Asti Tanaro Valley, Alessandria Plain, Casale Monferrato-Valenza sector, the plain sector close to the Turin Hills) due to the high values of several ions (e.g. HCO_3, Ca, Mg, Na). In the Biella-Novara Plain, the plain sector between the Stura di Lanzo and Dora Baltea River and the Cuneo-Turin plain sector near the Alps low ion concentrations are presence linked to the silicate rocks of the Alpine sector that affect aquifers lithological composition due to low permeability.

In the entire Piedmont Plain, the SAR is low resulting in excellent and locally good irrigation quality (widely <1). No sectors show poor or fair conditions. Only the Asti Tanaro Valley and some points in the

Table 1. Descriptive statistics of the main chemical-physical parameters and ion concentrations (OBS: observation number, ND: Non Detected, Min: minimum, Max: maximum, Mean: average value, STD Dev: standard deviation, CV: coefficient of variation).

	OBS (n°)	ND (n°)	Completeness (%)	Min	Max	Mean	STD DEV	CV average (%)
EC [*μS/cm*]	3871	0	93.5	45	8470	569.28	80.72	13.53
Cl [*mg/L*]	3984	3	96.2	<1	1882	30.95	8.74	26.36
NO_3 [*mg/L*]	3962	237	95.7	<1	241	22.92	6.32	33.64
Hardness [*mg/L $CaCO_3$*]	3277	0	79.5	13	1294	270.96	35.42	13.62
SAR	3286	0	79.6	0.02	24.95	0.51	0.18	20.44
HCO_3 [*mg/L*]	3291	0	79.5	9	842	243.2	31.34	14.74
SO_4 [*mg/L*]	3985	6	96.3	<1	1122	53.95	14.41	24.42
Ca [*mg/L*]	3281	0	79.3	4.2	399	78.44	13.00	16.39
Mg [*mg/L*]	3282	0	79.3	1.4	83.4	18.36	2.35	13.65
Na [*mg/L*]	3283	3	79.3	<1	1325	20.06	4.90	19.26
K [*mg/L*]	3214	568	77.6	<1	71.8	3.1	1.12	33.94
pH	4004	0	96.7	5	8.4	6.97	0.27	3.83

Alessandria and Vercelli Plain have higher values (between 1-11.8) due to saline water upwelling and local anthropogenic impacts.

In the *Cuneo Plain*, the hardness values increase along the groundwater flow direction on the hydrographic right side of the Stura di Demonte River due to the progressive dissolution of $CaCO_3$ (from soft to hard water). On the hydrographic left side, higher values are present than on the right side due to the carbonate rock outcrops in the nearby alpine valleys and the correlated lithological composition of the plain aquifers (hardness range of hard waters). The high NO_3 values (>20 mg/L) are due to intense agricultural practices. Cl shows increasing values along the groundwater flow direction, with the minimum in the plain sector close to the Alps (<10 mg/L). This increase can be attributed to the progressive natural contribution of dissolution processes and to anthropogenic contributions (urban and agricultural).

On the *Turin Plain,* different conditions exist. On the Poirino Plateau, intense agricultural practices and the low permeability of aquifers are responsible for the high NO_3 and Cl concentrations. A similar condition is also found in the Pinerolo plain sector, with higher NO_3 and Cl increasing along the groundwater flow direction. Hardness shows a progressive increase along the groundwater flow direction in the Pinerolo plain, as it does in the Cuneo Plain. In particular, the soft waters between the Po and Pellice Rivers are linked to the alpine Dora-Maira unit, which is mainly constituted by gneisses. In contrast, higher hardness and Cl values near Turin Hill are correlated with the sedimentary lithologies. In Turin city and its surrounding sector, higher NO_3 and Cl values exist due to urban pressures. Moreover, the hardness of the water (hard water) is linked to the carbonate component in the aquifer reflecting calcschist outcrops in the Dora Riparia alpine basin. In the plain sector between the Stura di Lanzo and Dora Baltea Rivers, hardness (soft-slightly hard) is linked to the aquifer lithological composition reflecting the silicate rock outcrops in the nearby Alpine sectors. The lower Cl and NO_3 values (<20 mg/L) reflect the absence of diffuse anthropic impacts.

In the *Ivrea sector*, the hardness (moderately hard-hard) is linked to the carbonate component in the aquifer reflecting the carbonate rock outcrops in the Dora Baltea alpine basin. The lower NO_3 and Cl values (<20 mg/L) confirm the absence of diffuse anthropic impacts.

At the borders of the Morainic Amphitheatre, between the Turin and Vercelli Plains, a large area with NO_3 values between 20–40 mg/L is highlighted. Here, the land mainly consists of cultivated land unlike the neighbouring plain sectors.

In the *Biella-Vercelli-Novara Plains*, different conditions exist from the Cuneo and Turin Plains. On the Novara Plain and the hydrographic left side of Elvo River, Cl and hardness show lower values mainly due to recharge-induced dilution from the low-mineral waters used for paddy field irrigation. Here, the Cl shows mainly <20 mg/L values except at a few points in the Biella Plain that correlate to human impacts, while the hardness values show waters that range from very soft to moderately hard due to the absence of carbonate rocks in the neighbouring Alpine sector. Additionally, the prevalent NO_3 values <20 mg/L are due to paddy field-induced dilution. However, where land use was different (arable land such as in the upper Novara plain) or large urban centres were present (e.g. Biella and Novara cities), the concentration ranged from 20 mg/L to 50 mg/L.

In the Vercelli Plain, between the Elvo and Po Rivers, the large paddy fields induce dilution resulting in lower NO_3 and Cl values. Additionally, here, some exceptions are the urban centres (e.g. Vercelli city area) with values between 20-30 mg/L. Natural influences exist on Cl and hardness values from the sedimentary rocks and deep saline water upwellings near the Monferrato Hills, where the values are higher (Cl up to 50 mg/L; hardness is in the hard water range). The hardness in the Vercelli Plain is widely in the moderately hard water range.

Additionally, in the Casale Monferrato-Valenza sector, a clear natural influence from the Monferrato Hills is observed resulting in high Cl and hardness values (Cl up to 50 mg/L; hardness range showing hard-very hard waters).

On the *Alessandria Plain,* strong natural contributions affect the Cl and hardness values. They are influenced by both the Monferrato hills and the Apennine reliefs, both consisting of terrigenous sedimentary rocks, which are characterized by low permeability and high residence times (hardness in the moderately hard-hard range). In particular, the high Cl values near the Monferrato Hills (max 189 mg/L) are attributed to deep saline water upwelling. However, a relevant anthropic pressure also exists and affects the NO_3 and Cl values. This is evidenced by the punctual and variable distribution of NO_3 high values (maximum values of 72 mg/L).

Very similar natural phenomena occur in the *Asti-Tanaro Valley sector,* where Cl and hardness show very high values and NO_3 shows low values confirming deep saline water upwelling and low anthropogenic influences (hardness of 1054 mg/L $CaCO_3$ (max. value); Cl of 986 mg/L (max. value); NO_3 is mainly lower than 40 mg/L). In this sector, relatively high values of several ions (e.g. Cl, Na, Ca, Mg) in the Piedmont Plain are present.

In general, HCO_3 shows an almost identical distribution to EC, since it is the major ion (range 22–648 mg/L). High SO_4 values reflect the sectors of deep saline water upwelling (Alessandria and Asti sectors) and the gypsum dissolution (Cuneo and Asti sectors) (range 1.8-759 mg/L).

As concern NO_3, Cl, Na, hardness and SO_4, the values highlighted are well aligned with those found in the various local studies, and their interpretations here briefly summarized are confirmed with regional values. Moreover, the precipitation and Alpine springs concentrations are low (Cocca et al., 2023; De Luca et al., 2015). Their direct contribution in terms of ion concentrations to shallow aquifers is reduced. The influence of watercourses is low due to the predominant drainage conditions, and feeding conditions exist only in some sectors near the Alps. Leakage from canals and irrigation practices, fed by the watercourses, can lead to a general dilution of groundwater.

4.2. Hydrochemical time series fluctuations

The temporal fluctuation diagrams of EC, NO_3 and Cl show heterogeneous trends (Table 2).

Different behaviours are found between the monitoring points but also between parameters at single monitoring points.

Increasing trends, stationary trends, seasonal fluctuations, change points and heterogeneous fluctuations were observed:

- At the Cuneo and Savigliano monitoring points, good direct proportionality between EC, NO_3 and Cl exists.
- At the Salussola monitoring point, a change point with a decreases in EC, NO_3 and Cl was detected in 2008, approximately from 250 to 100 μS/cm and from 25 to 10 mg/L, respectively. Additionally, at the Asti monitoring point, a change point with an increases was detected; however, regarding only EC and Cl.
- In the Solero monitoring point, a clear increasing trend for the three parameters was observed. Additionally, at the Savigliano and Briona monitoring points, a slight increasing trend was ascertained.
- At the Casale Monferrato monitoring point, a good correlation exists between EC and Cl, with an increasing trend, and the values were not correlated with NO_3.
- Conversely, at the Poirino and Salussola monitoring points, a decreasing trend for the three parameters was observed.
- At the Carmagnola monitoring point, large seasonal fluctuations in the three parameters were observed due to agricultural inputs. Conversely, at the Briona and Borgomanero monitoring points, there were very limited fluctuations over time.
- At several monitoring points, occasional positive (e.g. San Germano Vercellese) and negative (e.g. Torino) peaks exist due to temporary anthropogenic inputs.
- Finally, at the Piverone, Airasca and Novi Ligure monitoring points, heterogeneous fluctuations exist with moderate variations.

4. Conclusions

The hydrochemical maps of the shallow aquifer in the western Po Plain at the regional scale summarize the knowledge on the main ion concentrations in this area. This knowledge is crucial as a basis for groundwater protection.

Table 2. Trend analysis of the 15 groundwater time series for the period 2000–2020. OLS regression slope and Mann-Kendall results (p value), level of significance α = 5% (HDA: hydrogeological distinct areas, MK: Mann-Kendall, OLS: ordinary least squares).

		Number observations			*P*-Value			MK trend 2000–2020			OLS Regression Slope		
Monitoring wells name	HDA	EC	Cl	NO_3	EC	Cl	NO_3	EC	Cl	NO_3	EC (μS/cm/yr)	Cl (mg/L/yr)	NO_3 (mg/L/yr)
SOLERO	AL 1-2-3	42	42	42	<0.001	<0.001	0.005	Increasing	Increasing	Increasing	10.06	1.82	0.34
NOVI LIGURE	AL 4–5	42	42	42	0.132	0.150	0.161	No trend	No trend	No trend	2.50	−0.06	0.48
CASALE MONFERRATO	AL 6	41	41	41	<0.001	<0.001	0.493	Increasing	Increasing	No trend	9.14	1.52	−0.04
ASTI	AT 1	41	40	42	0.035	<0.001	0.001	Increasing	Increasing	Decreasing	1.18	0.82	−0.76
CUNEO	CN 3	41	42	41	0.161	0.068	0.230	No trend	No trend	No trend	2.20	0.06	−0.12
SAVIGLIANO	CN 1–2	42	42	42	<0.001	<0.001	<0.001	Increasing	Increasing	Increasing	5.04	0.40	0.58
PIVERONE	IV 1	41	42	42	<0.001	0.011	<0.001	Increasing	Increasing	Increasing	5.76	0.46	0.68
BRIONA	NO 1–2	42	41	42	0.006	0.001	<0.001	Increasing	Increasing	Increasing	0.58	0.04	0.24
BORGOMANERO	NO 1–2	42	41	41	0.200	0.023	<0.001	No trend	Increasing	Decreasing	−0.80	0.04	−0.32
TORINO	TO 1-2-3-5-6	34	34	34	0.258	<0.001	0.064	No trend	Increasing	No trend	3.62	0.76	−0.02
AIRASCA	TO 7	42	42	42	0.182	0.110	0.173	No trend	No trend	No trend	0.42	0.08	0.24
CARMAGNOLA	TO 8–9	34	34	34	0.022	0.058	0.337	Decreasing	No trend	No trend	−25.88	−0.66	−0.38
POIRINO	TO 8–9	40	40	40	<0.001	0.002	<0.001	Decreasing	Decreasing	Decreasing	−8.62	−0.84	−1.12
SALUSSOLA	VC 1–4	42	42	41	0.002	0.010	<0.001	Decreasing	Decreasing	Decreasing	7.30	−0.36	−1.10
SAN GERMANO V.	VC 2–3	42	42	42	0.051	0.005	0.127	No trend	Increasing	No trend	0.92	0.20	−0.10

The spatial and temporal elaborations show significant and diverse variabilities.

Hydrochemical maps confirm the existence of several natural and anthropogenic factors, including the lithological compositions of the aquifers and related mountain supply basins and anthropogenic impacts linked to agricultural practices, farms and urban centres.

For the hydrochemical time series fluctuations, the different responses observed in the shallow aquifers as a function of the typology of chemical species, their origins and aquifer characteristics suggest different resilience capacities in the aquifers to several impacting factors (e.g. denitrification and dilution processes), which tend to change the qualitative stability of groundwater over time.

For this reason, groundwater monitoring represents a paramount activity that plays a key role in defining hydrochemical processes and serving as a valuable data resource. This study emphasizes the need to increase monitoring point density to identify localized phenomena. Furthermore, the fluctuation of ion concentrations over time makes it imperative to specify time periods for hydrochemical maps.

The next step involves a detailed characterization of hydrochemical time series evolution in shallow and deep aquifers to yield more complete knowledge and comprehension of these valuable resources.

Software

The maps were generated and realized in Surfer 16.8.3-Golden Software. Dataset frequency distribution has been checked using U.S.EPA software ProUCL (version 5.1).

Acknowledgements

We would like to thank the thorough and thoughtful comments provided by reviewers.

Disclosure statement

No potential conflict of interest was reported by the author (s).

Data availability statement

The data that support the findings of this study are openly available in ARPA Piemonte website (http://webgis.arpa.Piedmont.it/monitoraggio_qualita_acque_mapseries/monitoraggio_qualita_acque_webapp/).

References

ARPA PIEMONTE Agenzia Regionale per la Protezione Ambientale. (2006a). Progetto per la condivisione delle conoscenze e lo sviluppo di sistemi informativi e di monitoraggio su temi specifici di interesse per la pianificazione di bacino. Fase 1 Ricostruzione del quadro conoscitivo di riferimento. Tema 8 – presenza di microinquinanti nelle acque superficiali e sotterranee – Relazione tecnico-scientifica

ARPA PIEMONTE Agenzia Regionale per la Protezione Ambientale. (2006b). Progetto per la condivisione delle conoscenze e lo sviluppo di sistemi informativi e di monitoraggio su temi specifici di interesse per la pianificazione di bacino. Fase 1 Ricostruzione del quadro conoscitivo di riferimento. Tema 10 – Evoluzione storica, qualitativa e quantitativa delle risorse sotterranee – Relazione tecnico-scientifica

ARPA PIEMONTE Agenzia Regionale per la Protezione Ambientale. (2012). Definizione dei valori di fondo naturale per i metalli nelle acque sotterranee come previsto dalla Direttiva 2006/118/CE e dal Decreto Legislativo 16 marzo 2009 n.30. Arpa Piemonte - Struttura Specialistica Qualità delle Acque

Aubert, N. (2020). Evaluation de l'impact des pressions industrielles sur la qualitè des eaux souterraines du basin Rhin-Meuse – ètape 1. Rapport Final. BRGM/RP-69815-FR, 96 p., 16 fig., 17 tabl, 4 ann.

Balestra, V., Fiorucci, A., & Vigna, B. (2022). Study of the trends of chemical–physical parameters in different karst aquifers: Some examples from Italian Alps. *Water*, *14*(3), 441. https://doi.org/10.3390/w14030441

Balzani, L., Orban, P., & Brouyère, S. (2022). Protection of peri-urban groundwater catchments: A multi-tracer approach for the identification of urban pollution sources. *Advances in Geosciences*, *59*, 27–35. https://doi.org/10.5194/adgeo-59-27-2022

Barbieri, M., Barberio, M. D., Banzato, F., Billi, A., Boschetti, T., Franchini, S., Gori, F., & Petitta, M. (2023). Climate change and its effect on groundwater quality. *Environmental Geochemistry and Health*, *45*(4), 1133–1144, https://doi.org/10.1007/s10653-021-01140-5

Belkhiri, L., Tiri, A., & Mouni, L. (2020). Spatial distribution of the groundwater quality using kriging and Co-kriging interpolations. *Groundwater for Sustainable Development*, *11*, 100473. https://doi.org/10.1016/j.gsd.2020.100473

BGR. (2013). Hydrogeologische Karten für den Hydrologischen Atlas von Deutschland. *BGR*. https://www.deutsche-rohstoffagentur.de/DE/Themen/Wasser/Projekte/abgeschlossen/Beratung/Had/had_projektbeschr.html?nn=1557832

Bortolami, G., Cavallero, E., Forno, M. G., & Mosso, E. (1989). Studio idrogeologico del bacino di Asti. Caratteristiche e potenzialità degli acquiferi. International Congress of Geoengineering. 27-30 September 1989.

Bortolami, G., De Luca, D. A., Filippini, G., & Giva, P. (1988). Caratteristiche idrogeochimiche delle acque sotterranee della pianura torinese

Bucci, A., Bianco Prevot, A., Buoso, S., De Luca, D. A., Lasagna, M., Malandrino, M., & Maurino, V. (2018). Impacts of borehole heat exchangers (BHEs) on groundwater quality: the role of heat-carrier fluid and borehole grouting. *Environmental Earth Sciences*, *77*(5), 175. https://doi.org/10.1007/s12665-018-7375-9

Butera, I., & Cotto, I. (2008). Non linear kriging applied to groundwater concentration data. *L'acqua, Sezione I/Memorie*, *8*, 49–54.

Canavese, P. A., Beretta, G. P., De Luca, D. A., Forno, M. G., & Masciocco, L. (1999). Stratigrafia e distribuzione degli acquiferi nel sottosuolo del settore centrale

dell'Altopiano di Poirino (Torino). *Italian Journal of Quaternary Sciences*, *12*(2), 195–206.
Canavese, P. A., De Luca, D. A., & Masciocco, L. (2004). La rete di monitoraggio delle acque sotterranee delle aree di pianura della Regione Piemonte: quadro idrogeologico. *Prismas: Il Monitoraggio Delle Acque Sotterranee Nella Regione Piemonte, Regione Piemonte*, 175.
Civita, M. V., De Maio, M., & Fiorucci, A. (2009). The groundwater resources of the morainic amphitheatre. A case study in piedmont. *American Journal of Environmental Sciences*, *5*(4), 578–587. ISSN 1553-345X https://doi.org/10.3844/ajessp.2009.578.587
Civita, M. V., Vigna, B., De Maio, M., Fiorucci, A., Pizzo, S., Gandolfo, M., Banzato, C., Menegatti, S., Offi, M., & Moitre, B. (2011). *Le acque sotterranee della pianura e della collina cuneese*. Scribo editore.
Clemente, P., De Luca, D. A., Irace, A., & Lasagna, M. (2009a). L'origine e le caratteristiche delle acque salate nei bacini sedimentari piemontesi. *EngHydroEnv Geology*, *12*, 145–154. https://doi.org/10.1474/EHEGeology.2009-12.0-12.0263
Clemente, P., De Luca, D. A., Irace, A., & Lasagna, M. (2009b). Le acque salate del sottosuolo della Pianura Piemontese (Salt waters in the Piemonte Plain subsoil). *Rend Online Soc Geol it*, *6*, 171–172.
Cocca, D., Lasagna, M., Marchina, C., Santillán Quiroga, L. M., & De Luca, D. A. (2023). Chemical and isotopic composition of precipitation in the Piedmont Po Plain (NW Italy): preliminary evaluation of impacts on the groundwater quality. *EGU General Assembly 2023*, Vienna, Austria, 24–28 Apr 2023, EGU23-2088. https://doi.org/10.5194/egusphere-egu23-2088.
Cross, K., & Latorre, C. (2015). Which water for which use? Exploring water quality instruments in the context of a changing climate. *Aquatic Procedia*, *5*, 104–110. https://doi.org/10.1016/j.aqpro.2015.10.012
Debernardi, L., De Luca, D. A., & Lasagna, M. (2008). Correlation between nitrate concentration in groundwater and parameters affecting aquifer intrinsic vulnerability. *Environmental Geology*, *55*(3), 539–558. https://doi.org/10.1007/s00254-007-1006-1/s002539-007-1006-1
De Giglio, O., Quaranta, A., Barbuti, G., Napoli, C., Caggiano, G., & Montagna, M. T. (2015). Factors influencing groundwater quality: towards an integrated management approach. *Annali di Igiene: Medicina Preventiva e di Comunità*. https://doi.org/10.7416/ai.2015.2022
De Luca, D. A., Gisolo, A., Lasagna, M., Morelli di Popolo e Ticineto, A., Falco, A., & Cuzzi, C. (2019). Potential recharge areas of deep aquifers: an application to the Vercelli-Biella Plain (NW Italy). *Rendiconti Lincei. Scienze Fisiche e Naturali*, *30*(1), 137–153. https://doi.org/10.1007/s12210-019-00782-z
De Luca, D. A., Lasagna, M., Casaccio, D., Ossella, L., & Falco, M. (2006). *Le acque sotterranee della pianura vercellese. La falda superficiale*. Provincia di Vercelli. Edizioni Saviolo.
De Luca, D. A., Lasagna, M., & Debernardi, L. (2020). Hydrogeology of the western Po plain (Piedmont, NW Italy). *Journal of Maps*, *16*(2), 265–273. https://doi.org/10.1080/17445647.2020.1738280
De Luca, D. A., Masciocco, L., Caviglia, C., Destefanis, E., Forno, M. G., Fratianni, S., Gattiglio, M., Gianotti, F., Lasagna, M., Latagliata, V., & Massazza, G. (2015). Distribution, discharge, geological and physical-chemical features of the springs in the Turin Province (Piedmont, NW Italy). *Engineering Geology for Society and Territory*, *3*. https://doi.org/10.1007/978-3-319-09054-2_52
Flores Avilés, G. P., Spadini, L., Sacchi, E., Rossier, Y., Savarino, J., Ramos, O. E., & Duwig, C. (2022). Hydrogeochemical and nitrate isotopic evolution of a semiarid mountainous basin aquifer of glacial-fluvial and paleolacustrine origin (Lake Titicaca, Bolivia): the effects of natural processes and anthropogenic activities. *Hydrogeology Journal*, *30*, 181–201. https://doi.org/10.1007/s10040-021-02434-9
Frollini, E., Preziosi, E., Calace, N., Guerra, M., Guyennon, N., Marcaccio, M., Menichetti, S., Romano, E., & Ghergo, S. (2021). Groundwater quality trend and trend reversal assessment in the European Water Framework Directive context: an example with nitrates in Italy. *Environmental Science and Pollution Research*, *28*, 22092–22104. https://doi.org/10.1007/s11356-020-11998-0
Kendall, M. (1975). Multivariate analysis; charles Gri_n Co. LTD: London, UK; p. 210.
Lasagna, M., & De Luca, D. A. (2016). The use of multilevel sampling techniques for determining shallow aquifer nitrate profiles. *Environmental Science and Pollution Research*, *23*(20), 20431–20448. https://doi.org/10.1007/s11356-016-7264-2
Lasagna, M., & De Luca, D. A. (2019). Evaluation of sources and fate of nitrates in the western Po plain groundwater (Italy) using nitrogen and boron isotopes. *Environmental Science and Pollution Research*, *26*(3), 2089–2104. https://doi.org/10.1007/s11356-017-0792-6
Lasagna, M., De Luca, D. A., Debernardi, L., & Clemente, P. (2013). Effect of the dilution process on the attenuation of contaminants in aquifers. *Environmental Earth Sciences*, *70*(6), 2767–2784. https://doi.org/10.1007/s12665-013-2336-9
Lasagna, M., De Luca, D. A., & Franchino, E. (2016a). The role of physical and biological processes in aquifers and their importance on groundwater vulnerability to nitrate pollution. *Environmental Earth Sciences*, *75*(11), 961. https://doi.org/10.1007/s12665-016-5768-1
Lasagna, M., De Luca, D. A., & Franchino, E. (2016b). *Nitrate contamination of groundwater in the western Po Plain (Italy): the effects of groundwater and surface water interactions*. Springer-Verlag Berlin Heidelberg, Environmental Earth Sciences. https://doi.org/10.1007/s12665-015-5039-6
Lasagna, M., De Luca, D. A., Sacchi, E., & Bonetto, S. (2005). Studio dell'origine dei nitrati nelle acque sotterranee piemontesi mediante gli isotopi dell'azoto. *Giornale di Geologia Applicata*, *2*, 137–143.
Lasagna, M., Ducci, D., Sellerino, M., Mancini, S., & De Luca, D. A. (2020). Meteorological variability and groundwater quality: examples in different hydrogeological settings. *Water*, *12*(5), 1297. https://doi.org/10.3390/w12051297
Lasagna, M., Franchino, E., & De Luca, D. A. (2015). Areal and vertical distribution of nitrate concentration in Piedmont plain aquifers (North-western Italy). In G. Lollino et al. (Eds.), *Engineering geology for society and territory – Volume 3, River basins, reservoir sedimentation and water resources*, 389–392. Springer International Publishing Switzerland 2015. https://doi.org/10.1007/978-3-319-09054-2_81
Lo Russo, S., Fiorucci, A., Vigna, B. (2011). Groundwater dynamics and quality assessment in an agricultural area. *American Journal of Environmental Sciences*, *7*(4), 354–361. ISSN 1553-345X https://doi.org/10.3844/ajessp.2011.354.361
Madrigal-Solìs, H., Jiménez-Gavilàn, P., Vadillo-Perez, I., Fonseca-Sànchez, A., Calderòn-Sànchez, H., Quesada-

Hernàndez, L., & Gòmez-Cruz, A. (2022). Discriminant model and hydrogeochemical processes for characterizing preferential flow paths in four interconnected volcanic aquifers in Costa Rica. *Hydrogeology Journal*, *30*, 2315–2340. https://doi.org/10.1007/s10040-022-02557-7

Mann, H. B. (1945). Nonparametric tests against trend. *Econometrica*, *13*(3), 245–259. https://doi.org/10.2307/1907187

Martinelli, G., Dadomo, A., De Luca, D. A., Mazzola, M., Lasagna, M., Pennisi, M., Pilla, G., Sacchi, E., & Saccon, P. (2018). Nitrate sources, accumulation and reduction in groundwater from Northern Italy: insights provided by a nitrate and boron isotopic database. *Applied Geochemistry*, *91*, 23–35. https://doi.org/10.1016/j.apgeochem.2018.01.011

McQuiggan, R., Scott Andres, A., Roros, A., & Sturchio, N.C. (2022). Stormwater drives seasonal geochemical processes beneath an infiltration basin. *Journal of Environmental Quality*, *51*(6), 1198–1210. https://doi.org/10.1002/jeq2.20416

Mohammed, L. R., Kai, K. H., Kijazi, A. L., Bakar, S. S., & Khamis, S. A. (2022). The influence of weather and climate variability on groundwater quality in Zanzibar. *Atmospheric and Climate Sciences*, *12*(4), 613–634. https://doi.org/10.4236/acs.2022.124035

O'Connell, D. W., Rocha, C., Daly, E., Carrey, R., Marchesi, M., Caschetto, M., Ansems, N., Wilson, J., Hickey, C., & Gill, L. W. (2022). Characterization of seasonal groundwater origin and evolution processes in a geologically heterogeneous catchment using geophysical, isotopic and hydro-chemical techniques (Lough Gur, Ireland). *Hydrological Processes*, *36*(10), e14706. https://doi.org/10.1002/hyp.14706

Orecchia, C., Giambastiani, B. M. S., Greggio, N., Campo, B., & Dinelli, E. (2022). Geochemical characterization of groundwater in the confined and unconfined aquifers of the Northern Italy. *Applied Sciences*, *12*(15), 7944. https://doi.org/10.3390/app12157944

Piana, F., Fioraso, G., Irace, A., Mosca, P., d'Atri, A., Barale, L., Falletti, P., Monegato, G., Morelli, M., Tallone, S., & Vigna, G. B. (2017). Geology of Piemonte region (NW Italy, Alps–Apennines interference zone). *Journal of Maps*, *13*(2), 395–405. https://doi.org/10.1080/17445647.2017.1316218

Piemonte, R. (2010). *Land Cover Piemonte: Classificazione uso del suolo 2010 (raster) – storico*. https://www.geoportale.piemonte.it/geonetwork/srv/ita/catalog.search#/metadata/r_piemon:4647f5d5-ed39-428d-a84b-8916e77e8f4c

Piper, A. M. (1944). A graphic procedure in the geochemical interpretation of water-analyses. *Eos, Transactions American Geophysical Union*, *25*(6), 914–928. https://doi.org/10.1029/TR025i006p00914

Raco, B., Vivaldo, G., Doveri, M., Menichini, M., Masetti, G., Battaglini, R., Irace, A., Fioraso, G., Marcelli, I., & Brussolo, E. (2021). Geochemical, geostatistical and time series analysis techniques as a tool to achieve the Water Framework Directive goals: An example from Piedmont region (NW Italy). *Journal of Geochemical Exploration*, *229*, 106832. https://doi.org/10.1016/j.gexplo.2021.106832

Richards, L. A. (1954). *Diagnosis and improvement of saline alkali soils*. Agriculture, vole 160. Handbook 60. Washington: US Department of Agriculture. https://www.ars.usda.gov/ARSUserFiles/20360500/hb60_pdf/hb60complete.pdf

Rotiroti, M., Bonomi, T., Sacchi, E., McArthur, J. M., Stefania, G. A., Zanotti, C., Taviani, S., Patelli, M., Nava, V., Soler, V., Fumagalli, L., & Leoni, B. (2019). The effects of irrigation on groundwater quality and quantity in a human-modified hydro-system: The Oglio River basin, Po Plain, northern Italy. *Science of the Total Environment*, *672*, 342–356. https://doi.org/10.1016/j.scitotenv.2019.03.427

Schaffer, R., Sass, I., Blummel, C., & Schmidt, S. (2021). Hydrochemistry of the Tuxertal, NW Tauern Window, Austria: water use and drinking water supply in an alpine environment. *Journal of Maps*, *17*(2), 197–213. https://doi.org/10.1080/17445647.2021.1899066

SGUDS. (2010). Hydrogeochemical maps. *State Geological Institute of Dionýz Stúr*. https://www.geology.sk/maps-and-data/mapovy-portal/geological-maps/hydrogeochemical-maps/?lang=en

SNPA Sistema Nazionale per la Protezione dell'Ambiente. (2018). Linea guida per la determinazione dei valori di fondo per i suoli e per le acque sotterranee. ISPRA, Manuali e Linee Guida 174/2018. ISBN 978-88-448-0880-8

Toller, S., Giambastiani, B. M. S., Greggio, N., Antonellini, M., Vasumini, I., & Dinelli, E. (2020). Assessment of seasonal changes in water chemistry of the ridracoli water reservoir (Italy): Implications for Water Management. *Water*, *12*(12), 581. https://doi.org/10.3390/w12020581

Uhl, A., Hahn, H. J., Jager, A., Luftensteiner, T., Siemensmeyer, T., Doll, P., Noack, M., Schwenk, K., Berkhoff, S., Weiler, M., Karwautz, C., & Griebler, C. (2022). Making waves: Pulling the plug—Climate change effects will turn gaining into losing streams with detrimental effects on groundwater quality. *Water Research*, *220*, 118649. https://doi.org/10.1016/j.watres.2022.118649

UNESCO United Nations Educational, Scientific and Cultural Organization. (2022). Groundwater Making the invisible visible. The United Nations World Water Development Report 2022. ISBN 978-92-3-100507-7.

U.S. EPA Environmental Protection Agency. (2002). Calculating upper confidence limits for exposure point concentrations at hazardous waste sites. *EPA OSWER* 9285.6-10.pp.32.

USGS U.S. Geological Survey. (1999). Sustainability of groundwater Resources. U.S. Geological Survey Circular 1186. ISBN 0–607–93040–3.

Vigna, B., Fiorucci, A., & Ghielmi, M. (2010). Relations between stratigraphy, groundwater flow and hydrogeochemistry in poirino plateau and roero areas of the tertiary piedmont basin, Italy. *Mem Descr Carta Geol d'It*, *XC*, 267–292.

Xia, Q., He, J., Li, B., He, B., Huang, J., Guo, M., & Luo, D. (2022). Hydrochemical evolution characteristics and genesis of groundwater under long-term infiltration (2007—2018) of reclaimed water in Chaobai River, Beijing. *Water Research*, *226*, 119222. https://doi.org/10.1016/j.watres.2022.119222

Zanotti, C., Rotiroti, M., Redaelli, A., Caschetto, M., Fumagalli, L., Stano, C., Sartirana, D., & Bonomi, T. (2023). Multivariate time series clustering of groundwater quality data to develop data-driven monitoring strategies in a historically contaminated urban area. *Water*, *15*(1), 148. https://doi.org/10.3390/w15010148