



# Assessment of the groundwater recharge processes of a shallow and deep aquifer system (Maggiore Valley, Northwest Italy): a hydrogeochemical and isotopic approach

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## Abstract

The Maggiore Valley well field plays a fundamental role in supplying drinking water to a large territory of the Piedmont Region (northwestern Italy) and has been intensively exploited since the early twentieth century. This water resource is hosted in a deep, multilayered aquifer system. The main purpose of this study was to characterize the recharge processes of the deep aquifer through hydrochemical and isotopic assessments, as well as the water quality in the recharge and drainage areas. For this purpose, 128 physical–chemical analyses (major ions) and 50 isotopic analyses ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) were carried out on samples collected in shallow and deep aquifer complexes in two sampling campaigns in 2021. From the results, a hydrogeological conceptual model of recharge processes was developed. The chemical data confirm the presence of bicarbonate–calcium facies in most samples of the shallow and deep aquifer complexes. Clear hydrochemical differences were observed among the investigated sectors. The recharge areas were identified as (1) far zones, namely the shallow aquifer complex of the Cuneo Plain, and (2) the shallow and deep aquifer complexes with groundwater mixing in the riverside sector of Po Plain in the Turin area. The mixing of waters from the Cuneo Plain and Turin Plain was verified in the well field area. The isotopic values of the artesian well water also confirmed contributions from the Turin and Cuneo Alps. This study clarified the recharge processes, thereby defining potential pollutant pathways, and the results provide additional support for groundwater resource management and protection.

**Keywords** Groundwater recharge · Stable isotopes · Hydrochemistry · Deep confined aquifer · Italy

## Introduction

Groundwater resources constitute 84% of the water supply in Italy (Ambrosetti 2021). In the Piedmont Region (Northwest Italy), 82% of the drinking water supply comes from groundwater, with the percentage rising to 100% in Asti Province (Regione Piemonte 2020). Globally, anthropogenic

activities—namely, industrialization and the extensive use of agrochemicals (chemical fertilizers, herbicides and pesticides, etc.)—have resulted in the deterioration of freshwater quality (Saturday et al. 2021). The presence of anthropogenic pollutants in confined aquifers exploited for human consumption worldwide has also been ascertained by the scientific community (Lapworth et al. 2019).

For these reasons, it is essential to establish the recharge processes of aquifers exploited for human consumption, by defining the interactions of aquifers with precipitation, irrigation and watercourses. It is especially important to define the interactions of shallow aquifers, which are typically more severely affected by anthropogenic contamination (Viaroli et al. 2022).

The origin of aquifer recharge is among the most studied topics in human water supply research (Kinzelbach et al. 2002). Chemical and environmental isotope analyses can be used to determine aquifer recharge processes in plains and

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mountains (Haji et al. 2021; Noyes et al. 2021; Gourcy et al. 2022; Hernandez Perez et al. 2022; Machida et al. 2022; Reda et al. 2022; Catania and Reading 2023), as well as groundwater and river interactions (Vituri Santarosa et al. 2021; Modie et al. 2022) and groundwater interactions with saline fluids (Larsen et al. 2021; Mayo and Tingey 2021). These techniques have been used in several case studies in the Italian context, to evaluate the recharge processes of deep plain aquifers (Bortolami et al. 1983, 1996; Pennisi et al. 2006; Quaranta et al. 2020) and fractured aquifers (Petitta et al. 2022; Lorenzi et al. 2023), as well as to evaluate the precipitation composition (Grappein et al. 2021), the effects of drought conditions and natural and anthropogenic variations in the Po River (Marchina et al. 2015, 2016, 2019), and irrigation influences (Rotiroti et al. 2019, 2023). The aim of this study is to define the recharge processes of the deep aquifer exploited by the Maggiore Valley well field using a hydrogeochemical and isotopic approach.

Deep aquifers represent a strategic resource because their water quality is generally better than that of rivers and shallow aquifers. More specifically, in the Piedmont Region of Italy, deep aquifers represent a key source of drinking water and therefore must be protected from qualitative and quantitative degradation (De Luca et al. 2019a, b).

The Maggiore Valley well field, in the Piedmont Region, plays a fundamental role in supplying drinking water to this part of the territory, as it serves 43 municipalities with ~76,000 inhabitants. The exploited deep aquifer is the only water source for human consumption in the area and is characterized by intense groundwater abstraction that began in the early twentieth century. Evidence of overexploitation includes the drawdown of the piezometric levels, subsidence, well damage and a progressive reduction in the artesian area (De Luca et al. 2018; Lasagna and De Luca 2019). In the last century, a piezometric-level drawdown of ~50 m has been observed (Sacco 1924; Beretta et al. 1999; Caviglia 2011).

The recharge areas of the deep aquifers of this region are not completely known, and only a few studies have been performed (Beretta et al. 1999; Vigna et al. 2010; De Luca et al. 2018); although isotopic and chemical methods are commonly used in recharge-area studies, such approaches have not been applied exhaustively in the study area until now. Furthermore, a peculiarity of the study area is the existence of multiple elements that can potentially affect the rate of deep aquifer recharge (Alps contribution, shallow and deep aquifer mixing in the plains sector, groundwater and river interactions, irrigation effects, saline-sulphurous water upwelling). Consequently, hydrochemical and isotopic approaches were used in this study to better identify the recharge areas of this important aquifer, as well as the potential interactions between this aquifer and shallow aquifers threatened by anthropogenic pressures, and thus to

protect the water resources. The identification of recharge areas will contribute to controlling and managing groundwater resources, with a consequent increase in the effectiveness of environmental protection.

## Study area

### Geological and hydrogeological setting

The study area is in the southwestern sector of the Piedmont Po Plain, covering an area of almost 2,900 km<sup>2</sup>. This sector, bordered by the Alps to the south and west and by hilly relief to the east (De Luca et al. 2020), can be divided into various geographic areas, including the Cuneo and Turin Po Plains, the Poirino Plateau and the Roero Hills (Fig. 1), characterized by different geological and hydrogeological features.

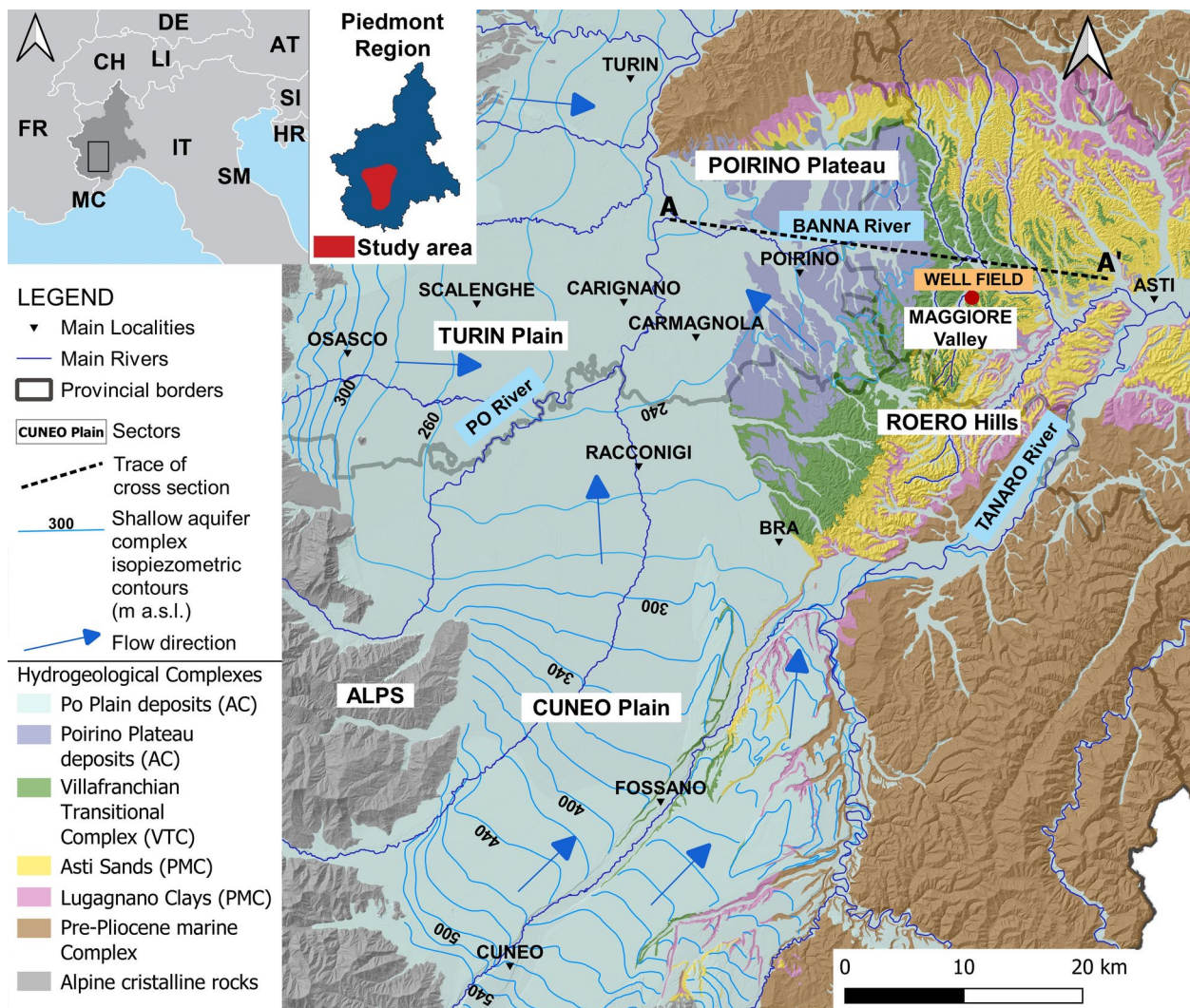
Regarding the geological setting of the study area, the Piedmont Po Plain generally consists, from bottom to top, of (1) Pliocene marine deposits (Pliocene) that host a confined aquifer, (2) Villafranchian transitional deposits (late Pliocene–early Pleistocene) that host a multilayered aquifer and (3) Quaternary alluvial deposits (lower Pleistocene–Holocene) that host a shallow, unconfined aquifer (Barbero et al. 2007; Forno et al. 2018; Lasagna et al. 2018, 2020a; De Luca et al. 2020).

In particular, the Poirino Plateau and the Maggiore Valley, which represent the central region of the study area, have been analysed in many previous geological studies (Forno 1982; Carraro 1996; Boano and Forno 1999; Doglione et al. 2011; Forno et al. 2015; Gattiglio et al. 2015, 2018).

The geological formations within these sectors can be grouped into six hydrogeological complexes (Figs. 1 and 2), distinguished based on the permeability and grain size of the deposits (Bortolami et al. 1978; Carraro 1996; Bove et al. 2005; De Luca et al. 2014; Lasagna and De Luca 2016); these complexes, from bottom to top, are briefly described in the following.

The pre-Pliocene marine complex (Eocene–Miocene) consists of silty–clayey sediments (conglomerates of the Cassano Spinola and the Gessoso-Solfifera Formations and marls of St. Agata Fossili) with very low permeability.

The Pliocene marine complex (PMC) (lower–middle Pliocene) is represented by Lugagnano clays and Asti sands. The Lugagnano clays consist of sandy–marly clays with very low permeability and represent an aquitard under the overlying Asti sands. The Asti sands are permeable sandy deposits with alternating lenses of fine sands, sandy gravels, clayey sands, silty sands and silty clays. The overlapping permeable and impermeable sediment layers make this complex a multilayered aquifer system in which the various aquifer layers can interconnect through semipermeable layers. The Pliocene sandy complex reaches thicknesses ranging from



**Fig. 1** Map of the study area in the Piedmont Region (NW Italy), hydrogeological complexes and piezometric surface of the shallow aquifer in the Cuneo and Turin Plains (summer 2016) (modified from

De Luca et al. 2020). The cross-section is shown in Fig. 2. Country codes are from ISO (2023)

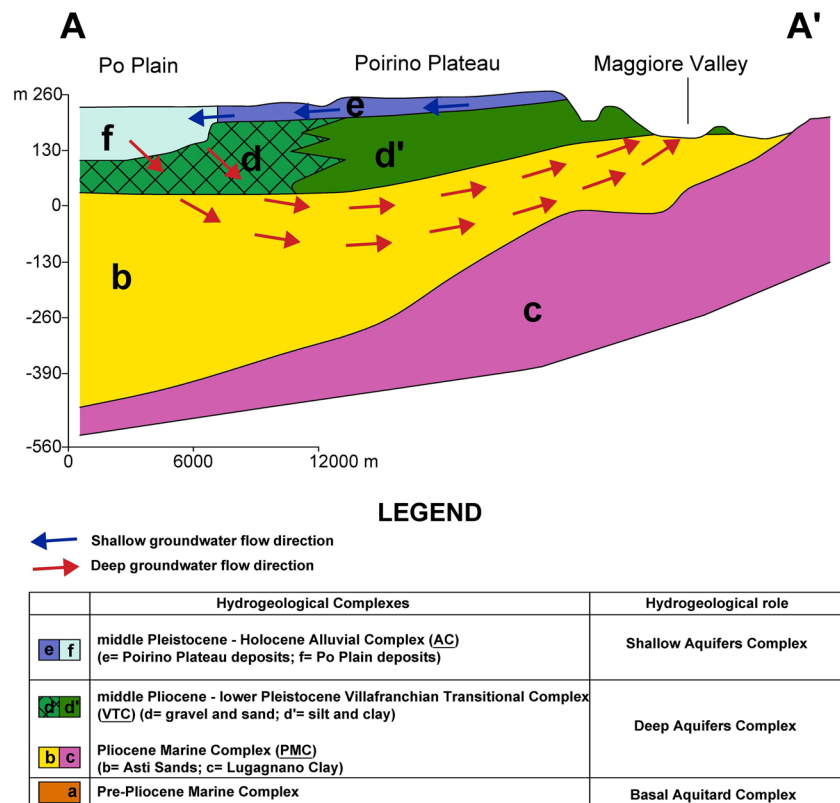
150 to 200 m in the Maggiore Valley, while eastwards and southwards, it becomes progressively thinner; conversely, this complex thickens under the Poirino Plateau (westwards), deepening below the overlying Villafranchian complex. The artesian aquifer comprises the Traversola, Triversa, Stanavasso and Maggiore valleys, hosted in the Pliocene sandy complex, and was later defined as a deep aquifer.

The Villafranchian Transitional Complex (VTC) (middle Pliocene–lower Pleistocene) consists of a sequence of silty–clayey layers of very low or low permeability with alternating sandy and gravelly permeable layers; it almost continuously covers the Pliocene sandy complex, although it is eroded and absent in the Maggiore Valley. The Villafranchian complex reaches its maximum thickness (~200 m) in the central part of the Poirino Plateau, where it hosts a multilayered aquifer system; its thickness and continuity

increase from east to west towards the Po River. In the studied hilly area of the Maggiore Valley, the Villafranchian complex, where present, consists mainly of silty–clayey sediments with limited interbedded sandy gravel layers; it comprises relatively coarse layers in the western sector of the Poirino Plateau and is relatively fine in the eastern sector (Fig. 2). The prevalence of low-permeability sediments as well as the reduced distribution and lateral continuity of permeable deposits make the Villafranchian complex less productive in this sector.

The alluvial complex (AC) (middle Pleistocene–Holocene) includes the terraced fluvial deposits of the Poirino Plateau and the Turin–Cuneo Plain deposits. The Poirino Plateau is characterized by silty or silty–clayey, sandy and gravelly bodies with overall thicknesses between 10 and 30 m. The gravelly, sandy deposits of the Turin–Cuneo

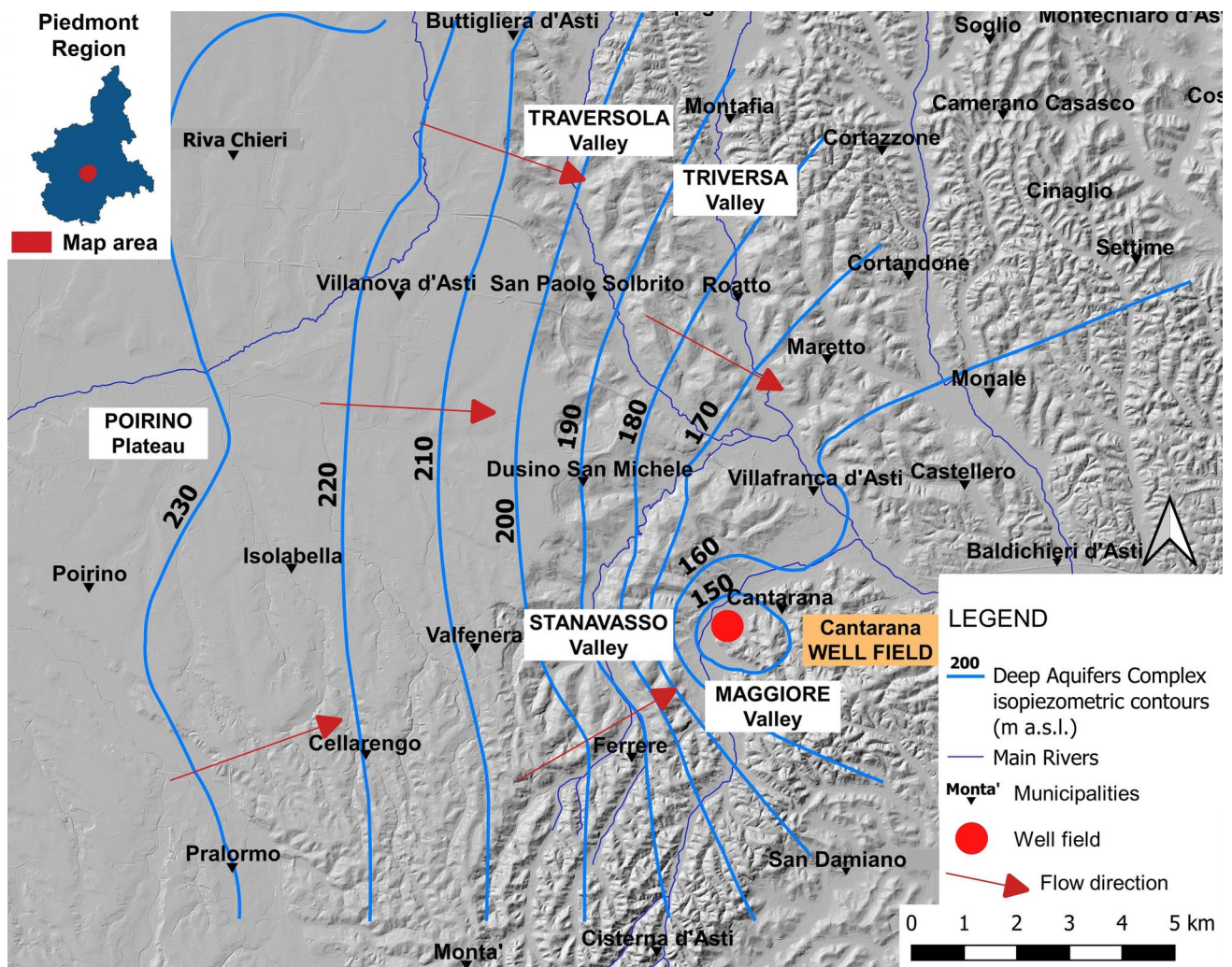
**Fig. 2** Schematic cross-section of the hydrogeological complexes located between the Po Plain and Maggiore Valley and the groundwater flow direction—trace of the cross-sections described in Fig. 1 (modified from De Luca et al. 2018)



Plain constitute a highly permeable unconfined aquifer and are directly connected with the hydrologic network; moreover, along the Po River, this complex reaches its greatest thickness. In general, the shallow aquifer complex corresponds to the middle Pleistocene–Holocene alluvial complex. The deep aquifer complex corresponds to the middle Pliocene–lower Pleistocene Villafranchian Transitional hydrogeological Complex (VTC) and the Pliocene Marine hydrogeological Complex (PMC), containing a series of confined and semiconfined aquifers (Fig. 2).

A piezometric map of the deep aquifer complex exploited by the well field of the Maggiore Valley is shown in Fig. 3, which refers to the period spanning from April to June of 2013 (De Luca et al. 2018). The piezometric level is between 230 m above sea level (asl), corresponding to the Poirino Plateau, and 142 m asl in the Maggiore Valley well field; the groundwater level of the deep aquifer complex ranges from +5.60 m (above ground level) in the artesian area to −65.20 m (below ground level) on the Poirino Plateau (Bove et al. 2005). The piezometric surface forms a pronounced depression cone in the Maggiore Valley well field and an evident underground drainage axis that directs the flow towards the Traversola and Triversa valleys can be identified (Vigna et al. 2010); additionally, artesian phenomena occur in the Traversola, Triversa, Stanavasso and Maggiore valleys.

In the Poirino Plateau sector, the main groundwater flow direction in the deep aquifer complex is from west to east, while the groundwater flow direction of the shallow aquifer complex is the opposite, generally flowing from east to west (Fig. 2; Bove et al. 2005). On the Poirino Plateau, wells are drilled in the VTC; here, the PMC deepens rapidly, so it is not reached by these perforations (De Luca et al. 2018), according to a previous study (Beretta et al. 1999), moving from W to E, the groundwater flow passes from the shallow aquifer complex to the PMC, passing through the VTC. On the Cuneo Plain, the shallow and deep main groundwater flow directions trend nearly south to north (De Luca et al. 2020; Vigna et al. 2010; Fig. 1). Previous studies that have analysed the flow lines direction have hypothesized that a deep aquifer complex recharge area exists in the Quaternary deposits of the Po River, with potential recharge directly from the Po River waters (Canavese et al. 1999; Bove et al. 2005; Lasagna et al. 2014; De Luca et al. 2018). According to Vigna et al. (2010), the VTC aquifers are supplied in part by direct recharge (precipitation) in the hilly area of the Roero Hills, where the Lower Villafranchian deposits outcrop, and in part by groundwater coming from the Turin-Cuneo Plain shallow aquifer complex, which is in Quaternary alluvium deposits overlying the Villafranchian succession (Vigna et al. 2010; Regione Piemonte 2007).



**Fig. 3** Piezometric surface of the aquifer exploited by the well field in the Maggiore Valley (April–June 2013) (modified from De Luca et al. 2018)

### Hydrochemical setting

From a hydrochemical point of view, the shallow aquifer complex of the Poirino Plateau shows a calcium, magnesium sulphate and/or chloride facies and a calcium and/or magnesium bicarbonate facies, whereas the deep aquifer complex is characterized by more carbonatitic components (Vigna et al. 2010). The low chloride concentrations measured in the deep aquifer complex do not lead to supposed mixtures with marine fossil waters; in particular, the PMC waters belong to bicarbonate calcium facies and are depleted in sulphates, indicating deep-water circuits in chalky evaporites (Bortolami et al. 1988), while the increased sodium contents measured here with respect to calcium are evidence of longer residence times and ion exchange processes. The groundwater coming from the PMC remains protected from anthropogenic pollutants (Beretta et al. 1999); in contrast,

several studies have identified high nitrate concentrations in the shallow aquifer complex of the Poirino Plateau and Cuneo-Turin Plain linked to intense agricultural activities (Bortolami et al. 1988; Bortolami et al. 1989; Canavese et al. 1999; Lasagna et al. 2005; Debernardi et al. 2008, 2015, 2016a, b, 2020b; Lasagna and De Luca 2016, 2019; Martinelli et al. 2018; Vigna et al. 2010). Actis Giorgetto (1991) analysed the isotopic composition of groundwater in the study area. The  $\delta^{18}\text{O}$  values were lower than  $-11\text{‰}$  in the groundwater of the Maggiore Valley well field and artesian wells. Moreover, the Po River sector also had isotopic values lower than  $-11\text{‰}$ ; thus, the author assumed that this was a recharge area of the aquifers in the Po River sector. In other groundwater samples from the shallow aquifer complex of the Poirino Plateau, the  $\delta^{18}\text{O}$  values were always higher than  $-9.5\text{‰}$ . The difference between the chlorine–alkaline imbalance index values measured in the

groundwater of the PMC aquifer of the Triversa and Traversola valleys suggested higher residence times in the aquifer, therefore indicating more distant recharge areas than that of the aquifer in the Maggiore Valley. On the Poirino Plateau, the wells that intercept the deep aquifer complex hosted in the VTC (used for irrigation and industrial activities) can reach depths exceeding 100 m and often interconnect this aquifer with the shallow aquifer (Vigna et al. 2010).

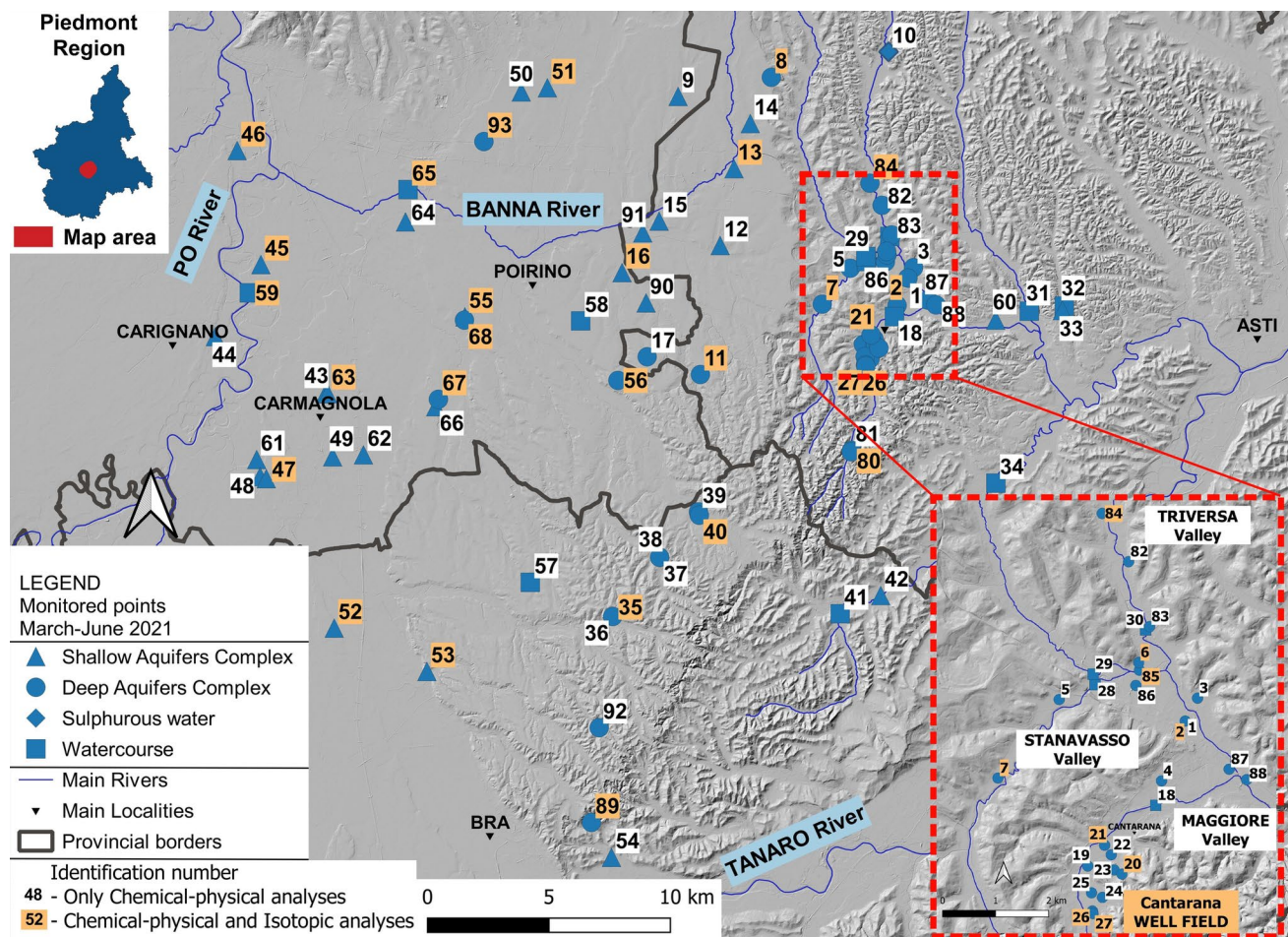
## Materials and methods

For this study, two sampling campaigns were carried out to collect water samples from the different water compartments in the study area delimited between the Po River to the west, the Maggiore Valley to the east, the hilly relief to the north, and the Tanaro River to the south (Fig. 4). These two campaigns were carried out in March–April of 2021 (60 samples) and in June of 2021 (68 samples); a total of 128 samples were collected from 82 different monitoring points (Fig. 4). In total, 34 deep aquifer complex wells, 19 artesian

wells in the Maggiore, Stanavasso, Traversola and Triversa valleys, 43 shallow aquifer complex wells, and 18 watercourses were sampled. The sampled aqueduct wells (33) in the study area are managed by three entities—the ASP (Asti Servizi Pubblici), Acquedotto della Piana and Egea Acque (Table 1). The differences in the sampling points in the two sampling campaigns were related to the inaccessibility of some points sampled in the first campaign (14 samples) that were substituted in the second campaign with new points (22 samples).

During the sampling activities, the parameters temperature, electrical conductivity (EC), pH and total dissolved solids (TDS), measured using a Hanna water tester HI98130, were recorded. The measurements were subsequently repeated in the laboratory—resolution and accuracy of the temperature samples 0.1 and 0.5 °C; EC 0.01 mS/cm, 2% F.S. (full scale); pH 0.01 and 0.05; TDS 0.01 g/L, 2% F.S. Water level depth was measured during the sampling activities.

The temperature differences between different points were compared to distinguish the deep aquifer complex



**Fig. 4** Locations of the 82 monitoring points that were included in the sampling campaigns in March–April and June of 2021

**Table 1** Monitoring point information divided by sector and aquifer type (- not measured)

Site ID	Sector	Type	Aquifer type	Well depth (m)	Sampling Date
1	Triversa Valley	Deep aquifer	Pliocene sandy complex	-	01/03/2021
2	Triversa Valley	Deep aquifer	Pliocene sandy complex	-	01/03/2021–21/06/2021
3	Triversa Valley	Deep aquifer	Pliocene sandy complex	-	01/03/2021–21/06/2021
4	Maggiore Valley	Deep aquifer	Pliocene sandy complex	-	01/03/2021–21/06/2021
5	Stanavasso Valley	Deep aquifer	Pliocene sandy complex	-	01/03/2021–18/06/2021
6	Traversola Valley	Deep aquifer	Pliocene sandy complex	-	01/03/2021
7	Stanavasso Valley	Deep aquifer	Pliocene sandy complex	-	01/03/2021–18/06/2021
8	Poirino Plateau	Deep aquifer	Villafranchian complex	112	01/03/2021–18/06/2021
9	Poirino Plateau	Shallow aquifer	Alluvial complex	-	01/03/2021
10	Triversa Valley	Sulphurous water	Pliocene sandy complex	-	01/03/2021
11	Poirino Plateau	Deep aquifer	Villafranchian complex	100	08/03/2021–18/06/2021
12	Poirino Plateau	Shallow aquifer	Alluvial complex	-	08/03/2021–18/06/2021
13	Poirino Plateau	Shallow aquifer	Alluvial complex	17	08/03/2021–18/06/2021
14	Poirino Plateau	Shallow aquifer	Alluvial complex	18	08/03/2021–18/06/2021
15	Poirino Plateau	Shallow aquifer	Alluvial complex	18	08/03/2021–18/06/2021
16	Poirino Plateau	Shallow aquifer	Alluvial complex	30	08/03/2021–18/06/2021
17	Poirino Plateau	Deep aquifer	Villafranchian complex	70	08/03/2021–18/06/2021
18	Maggiore Valley	River	-	-	18/03/2021–21/06/2021
19	Maggiore Valley	Deep aquifer	Pliocene sandy complex	200	18/03/2021–21/06/2021
20	Maggiore Valley	Deep aquifer	Pliocene sandy complex	124	18/03/2021–21/06/2021
21	Maggiore Valley	Deep aquifer	Pliocene sandy complex	-	18/03/2021–21/06/2021
22	Maggiore Valley	Deep aquifer	Pliocene sandy complex	200	18/03/2021–21/06/2021
23	Maggiore Valley	Deep aquifer	Pliocene sandy complex	116	18/03/2021–21/06/2021
24	Maggiore Valley	Deep aquifer	Pliocene sandy complex	154	18/03/2021–21/06/2021
25	Maggiore Valley	Deep aquifer	Pliocene sandy complex	112	18/03/2021–21/06/2021
26	Maggiore Valley	Deep aquifer	Pliocene sandy complex	145	18/03/2021–21/06/2021
27	Maggiore Valley	Deep aquifer	Pliocene sandy complex	145	18/03/2021
28	Stanavasso Valley	River	-	-	18/03/2021–18/06/2021
29	Traversola Valley	River	-	-	18/03/2021–18/06/2021
30	Triversa Valley	River	-	-	18/03/2021–21/06/2021
31	Monale Valley	River	-	-	18/03/2021
32	Monale Valley	River	-	-	18/03/2021
33	Monale Valley	Shallow aquifer	Alluvial complex	25	18/03/2021
34	Borbore Valley	River	-	-	18/03/2021
35	Roero sector	Deep aquifer	Pliocene sandy complex	125	08/04/2021–24/06/2021
36	Roero sector	Deep aquifer	Pliocene sandy complex	120	08/04/2021–24/06/2021
37	Roero sector	Deep aquifer	Pliocene sandy complex	117	08/04/2021–24/06/2021
38	Roero sector	Deep aquifer	Pliocene sandy complex	150	08/04/2021–24/06/2021
39	Roero sector	Deep aquifer	Pliocene sandy complex	100	08/04/2021–24/06/2021
40	Roero sector	Deep aquifer	Pliocene sandy complex	95	08/04/2021–24/06/2021
41	Borbore Valley	River	-	-	08/04/2021–24/06/2021
42	Borbore Valley	Shallow aquifer	Alluvial complex	-	08/04/2021–24/06/2021
43	Turin Plain	Shallow aquifer	Alluvial complex	7	05/03/2021
44	Turin Plain	Shallow aquifer	Alluvial complex	8	05/03/2021–16/06/2021
45	Turin Plain	Shallow aquifer	Alluvial complex	-	05/03/2021–15/06/2021
46	Turin Plain	Shallow aquifer	Alluvial complex	20	05/03/2021–16/06/2021
47	Turin Plain	Shallow aquifer	Alluvial complex	12	09/03/2021–16/06/2021
48	Turin Plain	Shallow aquifer	Alluvial complex	8	09/03/2021
49	Turin Plain	Shallow aquifer	Alluvial complex	-	09/03/2021–24/06/2021
50	Poirino Plateau	Shallow aquifer	Alluvial complex	13	09/03/2021–16/06/2021

**Table 1** (continued)

Site ID	Sector	Type	Aquifer type	Well depth (m)	Sampling Date
51	Poirino Plateau	Shallow aquifer	Alluvial complex	30	09/03/2021–16/06/2021
52	Roero sector	Shallow aquifer	Alluvial complex	6	09/03/2021–24/06/2021
53	Roero sector	Shallow aquifer	Alluvial complex	12	10/03/2021–25/06/2021
54	Roero sector	Shallow aquifer	Alluvial complex	10	14/03/2021–01/07/2021
55	Poirino Plateau	Shallow aquifer	Alluvial complex	20	12/03/2021–24/06/2021
56	Poirino Plateau	Deep aquifer	Villafranchian complex	66	12/03/2021–16/06/2021
57	Roero sector	River	-	-	10/03/2021
58	Poirino Plateau	River	-	-	12/03/2021
59	Turin Plain	River	-	-	18/04/2021–15/06/2021
60	Triversa Valley	Shallow aquifer	Alluvial complex	10	18/04/2021
61	Turin Plain	Shallow aquifer	Alluvial complex	6	15/06/2021
62	Turin Plain	Shallow aquifer	Alluvial complex	7	15/06/2021
63	Turin Plain	Shallow aquifer	Alluvial complex	30	15/06/2021
64	Poirino Plateau	Shallow aquifer	Alluvial complex	20	15/06/2021
65	Poirino Plateau	River	-	-	24/06/2021
66	Poirino Plateau	Shallow aquifer	Alluvial complex	20	25/06/2021
67	Poirino Plateau	Deep aquifer	Villafranchian complex	60	25/06/2021
68	Poirino Plateau	Deep aquifer	Villafranchian complex	80	25/06/2021
80	Maggiore Valley	Deep aquifer	Pliocene sandy complex	52	21/06/2021
81	Maggiore Valley	Deep aquifer	Pliocene sandy complex	22	21/06/2021
82	Triversa Valley	Deep aquifer	Pliocene sandy complex	-	21/06/2021
83	Triversa Valley	Deep aquifer	Pliocene sandy complex	85	21/06/2021
84	Triversa Valley	Deep aquifer	Pliocene sandy complex	-	21/06/2021
85	Traversola Valley	Deep aquifer	Pliocene sandy complex	-	21/06/2021
86	Traversola Valley	Deep aquifer	Pliocene sandy complex	-	21/06/2021
87	Maggiore Valley	Deep aquifer	Pliocene sandy complex	-	21/06/2021
88	Maggiore Valley	Deep aquifer	Pliocene sandy complex	-	21/06/2021
89	Roero sector	Deep aquifer	Pliocene sandy complex	150	24/06/2021
90	Poirino Plateau	Shallow aquifer	Alluvial complex	20	18/06/2021
91	Poirino Plateau	Shallow aquifer	Alluvial complex	9	18/06/2021
92	Roero sector	Deep aquifer	Pliocene sandy complex	150	24/06/2021
93	Poirino Plateau	Deep aquifer	Alluvial complex	50	01/07/2021

wells from the mixing wells, as the latter have higher temperatures; the results were later confirmed through physical–chemical analyses.

At each sampling point, two samples were collected in polyethylene bottles (250–500 ml) for chemical and isotopic analyses. Chemical–physical analyses were performed at the Hydrochemistry Laboratory of the Earth Sciences Department of the University of Turin, Italy. For the laboratory analyses, the pH measurements were performed with a Hanna Instrument H2211 pH/ORP metre calibrated with pH standards of 4.00, 7.00 and 10.00; the EC was measured with a Mettler Toledo Five Easy that was previously calibrated with a standard solution of KCl at 1,462  $\mu\text{m}$  and 25 °C. Both instruments were equipped with automatic temperature compensation abilities. The determination of alkalinity ( $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ) was performed with the acid–base

titration method with a Metrohm 665 Dosimat titrator using 0.1 N HCl as the titrating solution and a 100-ml sample; the colour indicator used herein was methyl orange. The anions and cations were determined by ion chromatography, in particular, chemical suppression ion chromatography was used for anions. Metrohm IC883 and Metrohm 863 Autosampler systems equipped with Metrosep A-Supp4 250 and Metrosep C4 250 separation columns were used for anions and cations, respectively.

Furthermore, isotopic analyses ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) were carried out for 50 selected samples (21 selected during the first campaign and 29 selected during the second campaign at 31 different monitoring points, Fig. 4). The analyses were conducted at the Forest Hydrology Lab of the Department of Land, Environment, Agriculture and Forestry, University of Padova (Italy) and at the Department of Physics



and Earth Sciences, University of Ferrara (Italy). For this analysis, the off-axis integrated cavity output spectroscopy method was applied using a DLT-100 analyser (ABB- Los Gatos Research Inc., USA) at the University of Padova and a CRDS Los Gatos LWIA 24-d isotopic analyser at the University of Ferrara. The analytical procedure is reported in Zuecco et al. (2021). The analytical uncertainties, as indicated in Marchina et al. (2020), were lower than 1.0 and 0.20‰ for  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ , respectively, whereas the average standard deviations of 2094 samples were 0.08‰ for  $\delta^{18}\text{O}$  and 0.5‰ for  $\delta^2\text{H}$ . Some water samples were also analysed at the laboratory of the Earth Sciences Department, University of Turin, with the aim of excluding laboratory differences and errors.

Finally, two rainfall collectors were built and installed in the September 2021–September 2022 period at two points (the Turin Plain and Roero Hills sector). The collectors consisted of two 5-L containers that were buried and joined to a funnel at each monitoring point; Vaseline oil was added to the collector intended for isotopic analyses to limit the evaporation process.

Further isotopic data collected for other studies carried out in the northwestern sector of Italy during the 2021–2022 period were used to define the local meteoric water line (LMWL) with the OLSR method (ordinary least squares regression; Hughes and Crawford 2012); this dataset was named “LMWL NW Italy” and contained data from a total of 23 analyses, reported in the electronic supplementary material (ESM). A total of four rainfall samples were collected, and the same analyses described previously were performed on these samples.

The physical–chemical and isotopic analyses conducted in this study made it possible to characterize the groundwater bodies in the various sectors and to mutually compare them. In particular, the main classification diagrams—i.e., Piper (1944) plot,  $\text{EC}/\text{HCO}_3^-$ ,  $\text{Ca}^{2+}/\text{Mg}^{2+}$ ,  $\text{Cl}^-/\text{Na}^-$ ,  $\text{NO}_3^-/\text{Cl}^-$ ,  $\text{NO}_3^-/\text{SO}_4^{2-}$ , and  $\text{Cl}^-/\text{SO}_4^{2-}$ —were created using DIAGRAMMES software (Laboratoire d’Hydrogéochimie, Université d’Avignon) to define the ongoing processes; moreover, an elevation– $\delta^{18}\text{O}$  correlation diagram was created (Clark and Fritz 1997).

Furthermore, hydrochemical and isotopic information from previous studies was collected, located on a map and used to assist with hydrogeochemical interpretations (Olivero et al. 1987; Campigotto 1989; Actis Giorgetto 1991; Albanese et al. 2008; Franchino 2016; Sangiovanni 2016) along with watercourse (Marchina et al. 2015, 2016, 2019) and precipitation information (Giustini et al. 2016; Quaranta et al. 2020; Fig. 5). Compared to previous studies, the area of interest was expanded here to include the Cuneo and Turin Plains due to the potential influence of these plains on the recharge processes of the investigated aquifers. The isotopic data were compared while focusing on the fact that these

data corresponded to different seasons and years from those considered in this study. All data were used to create three schematic sections covering the Cuneo Plain, Roero sector and Turin Plain to confirm and quantify the spatial variability in the isotopic composition of groundwater, as well as to define the ongoing processes of interest.

## Results

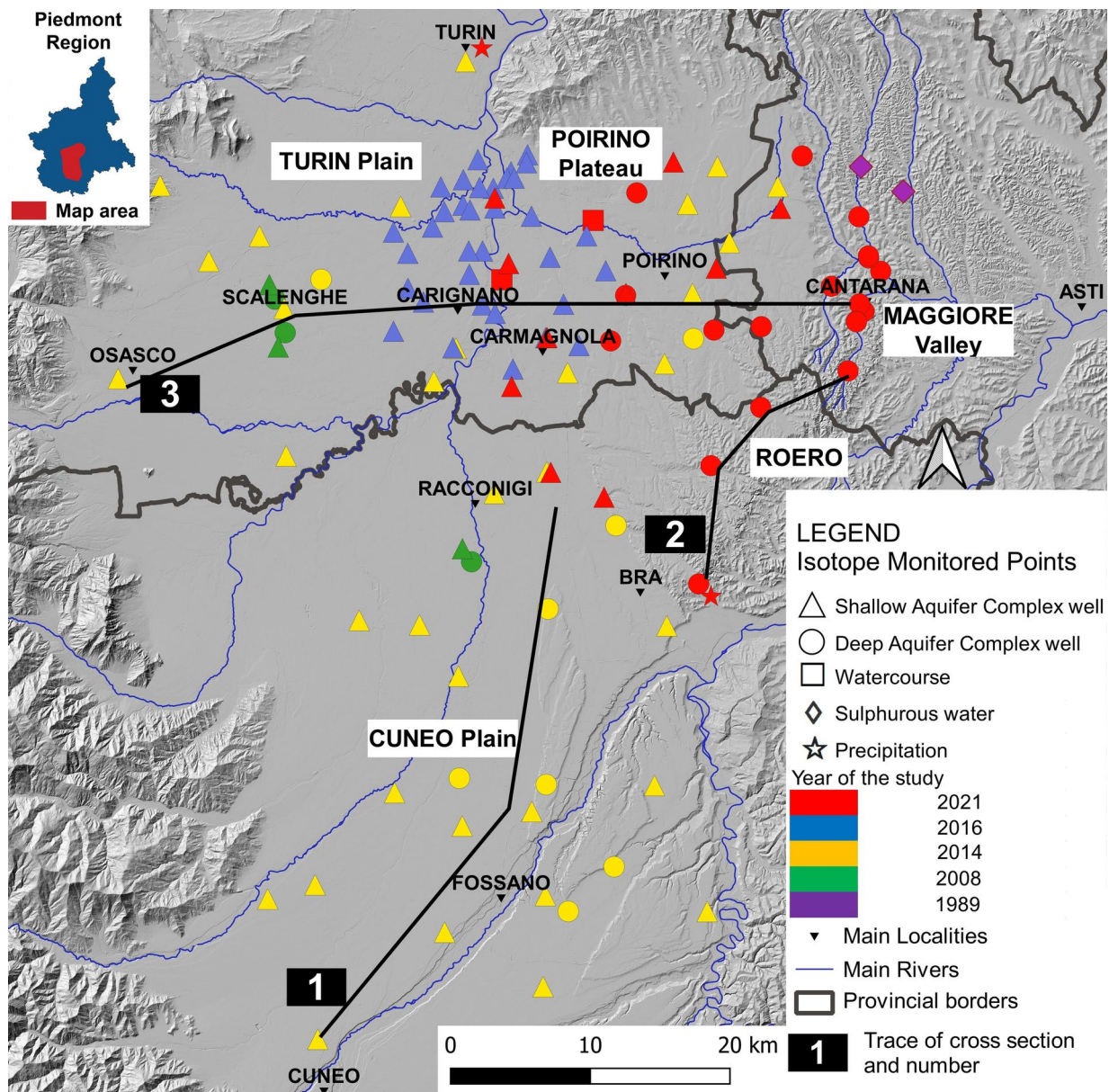
The results of the physical–chemical and isotopic analyses are reported in Tables S1, S2 and S4 of the ESM. The physical–chemical analyses did not reveal significant differences between the two sampling campaigns. Among the field parameters, only the temperature showed seasonal variation. For the isotopic analyses, temporal differences existed; however, the observed variations were uniform and similar between all sectors, without new differences in the relationships between the groundwater bodies.

For these reasons, as concerns chemical–physical data, Fig. 6 contains data from both campaigns, while the correlation diagrams (Fig. 7) are related to the second sampling campaign, which had a greater number of monitoring points and a better spatial distribution. Concerning isotopic data, Figs. 8 and 9 contain data from both campaigns. Regarding interpretation, all the chemical, physical–chemical and isotopic data were used.

## Hydrochemical characterization results

Hydrochemical results highlight differences in the mineralization conditions of the investigated groundwater bodies. The PMC aquifer wells in the Roero sector and the Maggiore, Stanavasso, Triversa and Traversola valleys showed lower mineralization than the VTC aquifers in the Poirino Plateau sector. The highest electrical conductivity (EC) values were found in the shallow aquifer complex wells of the Poirino Plateau [297–1,315  $\mu\text{S}/\text{cm}$  (min–max values)], except for two points with relatively high values in the Asti hilly area. Points related to the PMC aquifers in the Maggiore, Stanavasso, Traversola and Triversa valleys showed values between 375 and 998  $\mu\text{S}/\text{cm}$ . The pH values showed a heterogeneous distribution: in the PMC of the Maggiore, Stanavasso, Triversa and Traversola valleys, basic waters were found (essentially between pH 7.5 and 7.9), whereas values lower than 7 were found exclusively in the shallow aquifer complex of the Poirino Plateau.

The temperatures measured in groundwater and surface water during the sampling operations were higher in the summer sampling campaign than in the spring sampling campaign. The watercourses and shallow aquifer complex wells showed greater temporal minimum–maximum variations (I campaign, 10.7–16.8 °C; II campaign, 5.8–23.8 °C) than



**Fig. 5** Locations of the monitoring points where samples were obtained for isotopic analysis in this study and previous studies. Traces of the schematic sections are also shown: schematic sections

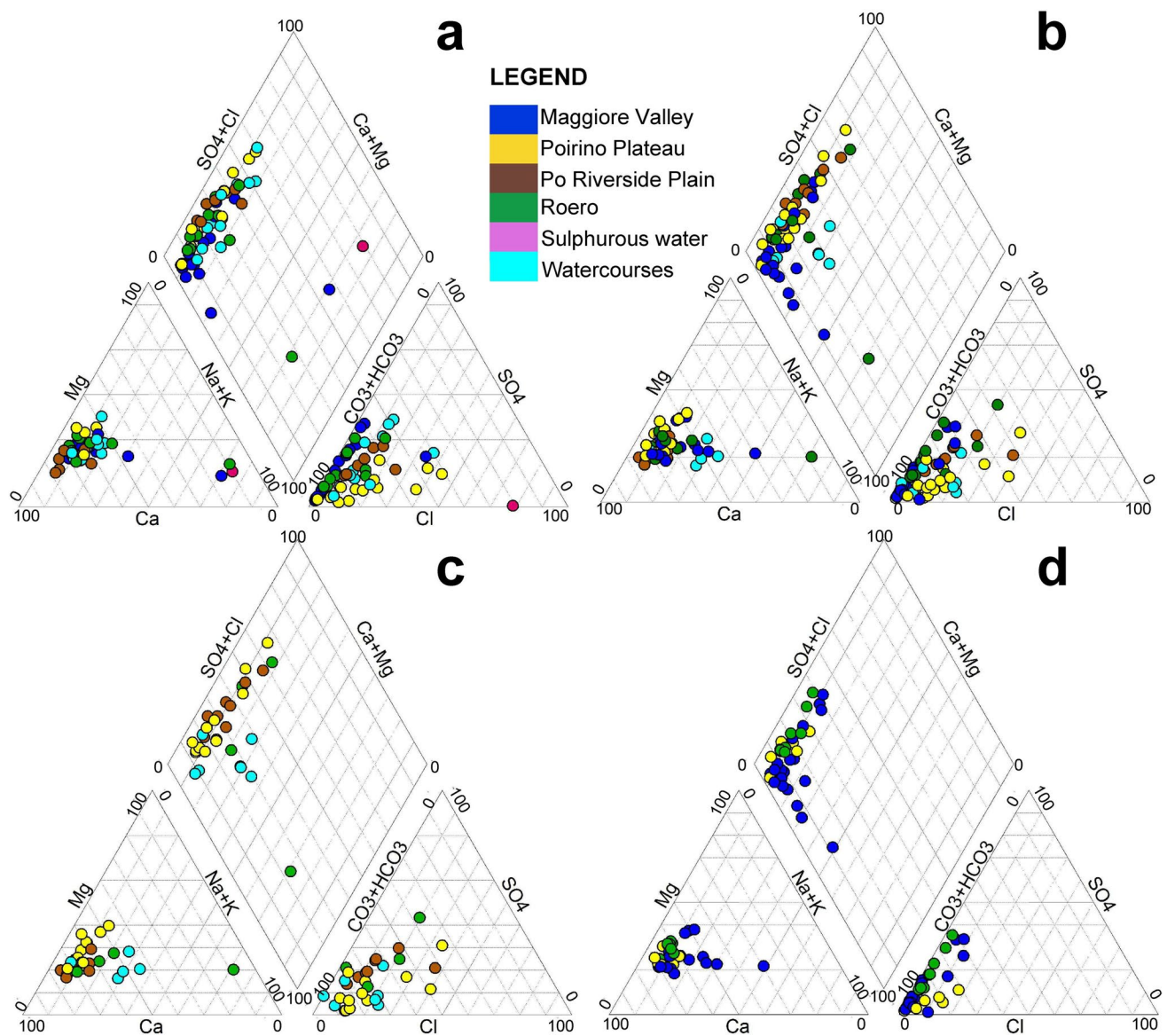
are shown in Figs. 10, 11 and 12 (Campigotto 1989; Albanese et al. 2008; Franchino 2016; Sangiovanni 2016)

the deep aquifer complex wells (I campaign, 13.2–17.3 °C; II campaign, 13.4–18.9 °C). The Piper diagrams of the two campaigns are very similar (Fig. 6a,b)—a large number of the sample points plotted within the calcium bicarbonate facies, while a small number plotted within the calcium chloride sulphate facies, corresponding to some of the shallow aquifer complex wells in the Poirino Plateau. The Poirino Plateau and the “Po riverside” sectors, which corresponded to the plain sector closest to the Po River, were similar. The samples from the Maggiore Valley sector, including from the wells in the Maggiore, Stanavasso, Triversa and Traversola

valleys, differed from the previous group due to their lower nitrate and chloride concentrations.

Comparing the shallow and deep aquifer complex wells of the second sampling campaign (Fig. 6c,d), the chemistry in the shallow aquifer complex samples exhibited greater variability than the deep aquifer complex samples, with the latter exclusively belonging to the calcium bicarbonate facies.

The highest chloride concentrations were found in watercourses on the Poirino Plateau and in the Po riverside plain, with a maximum value of 588 mg/L, while concentrations lower than 5 mg/L were found in the PMC aquifer wells in



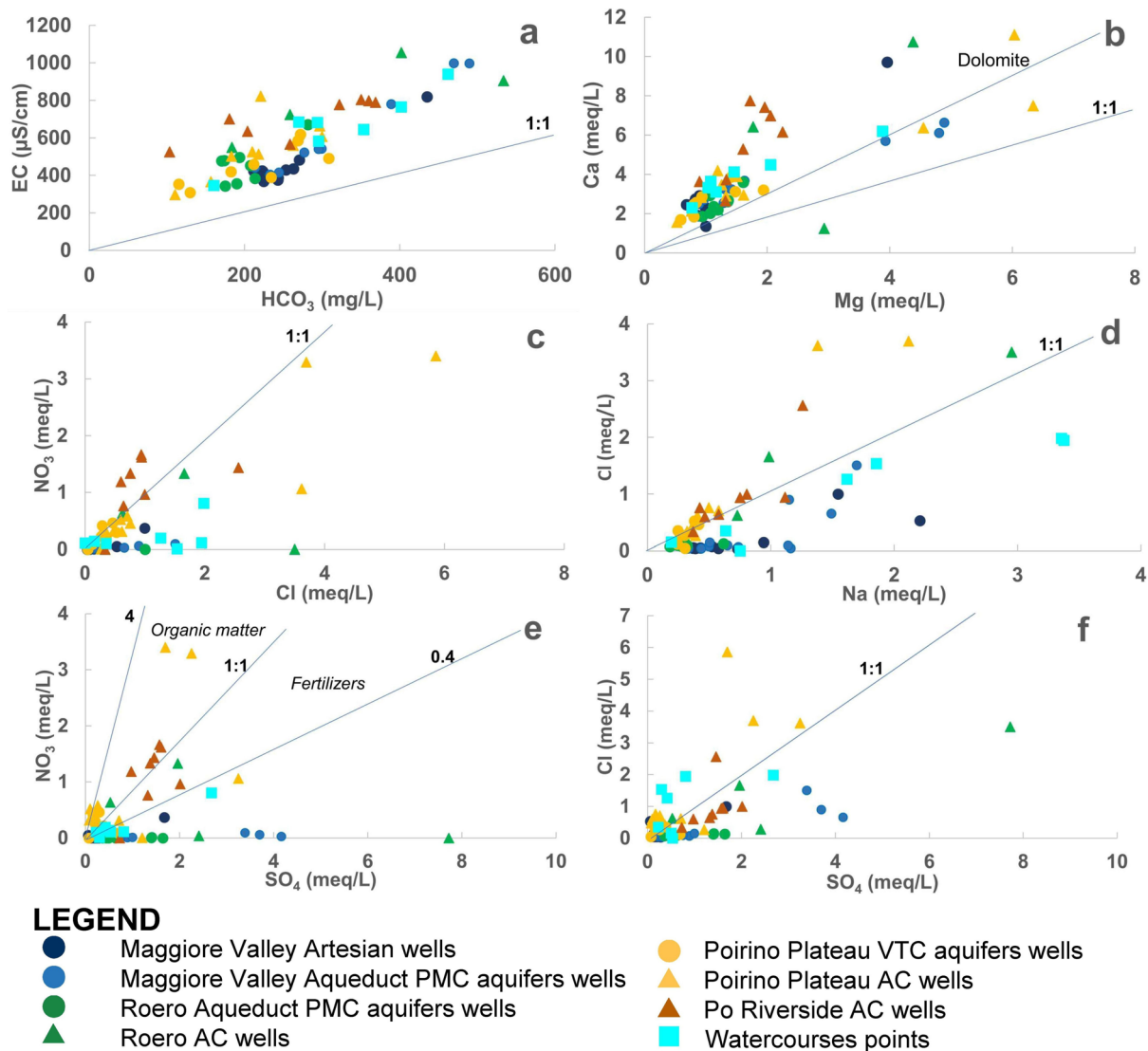
**Fig. 6** Piper diagrams. **a** March–April 2021, **b** June 2021, **c** Shallow aquifer complex and watercourses (June 2021). **d** Deep aquifer complex (June 2021)

the Roero and Maggiore Valley sectors. Regarding nitrate, high concentrations were highlighted in the shallow aquifer complex on the Poirino Plateau, with a maximum value of 208 mg/L, while low concentrations were observed in the VTC aquifers (with a maximum value of 30 mg/L); the PMC aquifer wells in the Maggiore Valley and Roero sectors showed concentrations lower than 5 mg/L. The  $EC/HCO_3^-$  diagram (Fig. 7a) shows good proportionality between the parameters. In the molar ratio diagram of  $Ca^{2+}/Mg^{2+}$  (Fig. 7b), the ratios were high (indicating higher concentrations of calcium than magnesium) at the monitoring points in all sectors.

The molar ratio diagram of  $NO_3^-/Cl^-$  (Fig. 7c) highlights the existence of some monitoring points in the exploited

shallow aquifer complex region with high nitrate and chloride concentrations. The shallow aquifer complex and VTC aquifer wells of the Poirino Plateau, which were mutually similar, showed a ratio of  $\sim 1$ , whereas the shallow aquifer complex wells in the Po riverside plain had high ratios in favour of nitrate. Conversely, the PMC aquifer wells of the Maggiore Valley and watercourses had low ratios favouring chloride.

The molar ratio diagram of  $Cl^-/Na^+$  (Fig. 7d) highlights the existence of some monitoring points with ratios varying from 1:1, while, some PMC aquifer wells showed low ratios in favour of sodium. Shown in the molar ratio diagram of  $NO_3^-/SO_4^{2-}$  (Fig. 7e), low ratios favouring sulphates were observed in the PMC aquifer wells in the Maggiore Valley



**Fig. 7** Correlation diagrams of the second sampling campaign: **a** EC vs  $\text{HCO}_3$ , **b** Ca vs Mg, **c**  $\text{NO}_3$  vs Cl, **d** Cl vs Na, **e**  $\text{NO}_3$  vs  $\text{SO}_4$  and **f** Cl vs  $\text{SO}_4$

area. In the molar ratio diagram of  $\text{Cl}^-/\text{SO}_4^{2-}$  (Fig. 7f), the PMC wells in the Maggiore Valley sector had low ratios, favouring sulphates; in contrast, some points relating to the shallow aquifer complex of the Poirino Plateau showed a high ratio, favouring chloride.

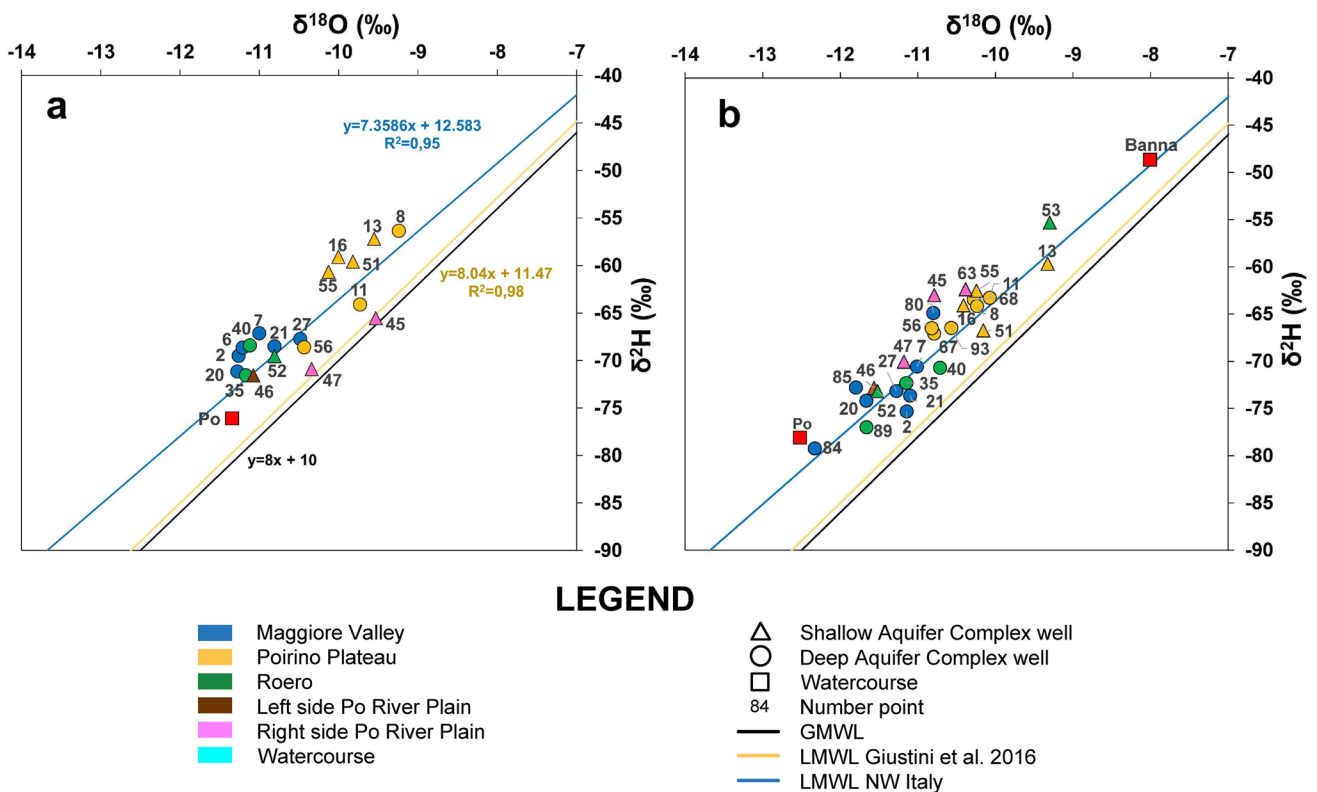
### Isotopic results

The  $\delta^{18}\text{O}$ – $\delta^2\text{H}$  diagrams (Fig. 8a,b) highlight the isotopic composition differences among the investigated sectors. The shallow and deep aquifer complexes of the Poirino Plateau showed the most enriched heavy isotope compositions among the groundwater resources [ $\delta^{18}\text{O}$  (min/max)  $-10.4/-9.3\text{‰}$ ;  $\delta^2\text{H}$  (min/max)  $-66.7/-59.7\text{‰}$ ]. The reverse situation was observed in the Maggiore Valley sector [ $\delta^{18}\text{O}$

(min/max)  $-12.3/-10.8\text{‰}$ ;  $\delta^2\text{H}$  (min/max)  $-79.2/-64.8\text{‰}$ ], and similar isotopic values were also found in the Roero well fields [ $\delta^{18}\text{O}$  (min/max)  $-11.7/-10.7\text{‰}$ ;  $\delta^2\text{H}$  (min/max)  $-77/-70.7\text{‰}$ ].

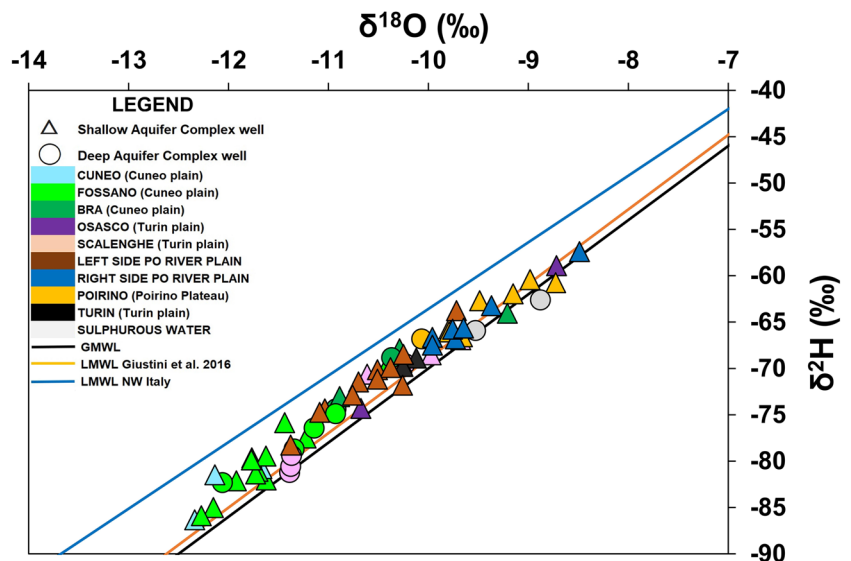
The shallow aquifer complex wells located in the Po riverside plain constitute two distinct groups: the group on the hydrographic right (east) side was more enriched in heavy isotopes and was similar to the Poirino Plateau sector [ $\delta^{18}\text{O}$  (min/max)  $-11.2/-9.5\text{‰}$ ;  $\delta^2\text{H}$  (min/max)  $-70/-62.4\text{‰}$ ]; the group on the hydrographic left side was less enriched in heavy isotopes [ $\delta^{18}\text{O}$  (min/max)  $-11.6/-11.1\text{‰}$ ;  $\delta^2\text{H}$  (min/max)  $-72.8/-71.6\text{‰}$ ].

The VTC aquifers of the Poirino Plateau showed isotopic values very similar to those observed in the shallow aquifer complex in the same area [ $\delta^{18}\text{O}$  (min/max)



**Fig. 8**  $\delta^{18}\text{O}$  vs  $\delta^2\text{H}$  diagrams corresponding to **a** March–April 2021 and **b** June 2021

**Fig. 9**  $\delta^{18}\text{O}$  vs  $\delta^2\text{H}$  diagram of isotopic monitoring points from previous studies subdivided by sector. The locations are shown in Fig. 5. The LMWL “NW Italy” was made with data acquired for this study, while the LMWL “Giustini et al. 2016” is relative to previous studies (valid also for Fig. 8)



$-10.8/-10.3\text{‰}$ ;  $\delta^2\text{H}$  (min/max)  $-67.1/-63.5\text{‰}$ ]. The Po and Banna rivers corresponded to the least and most enriched heavy isotope compositions in the dataset, respectively [ $\delta^{18}\text{O}$  (min/max)  $-12.5/-8\text{‰}$ ;  $\delta^2\text{H}$  (min/max):  $-78.1/-48.7\text{‰}$ ]. The isotopic values obtained for the

Po River in this study were similar to those indicated in the literature for this sector (Marchina et al. 2015, 2016). In Fig. 9, the data are shown divided by sector, and the figure includes data from previous studies (data shown in Table S3 of the ESM).

## Cuneo plain

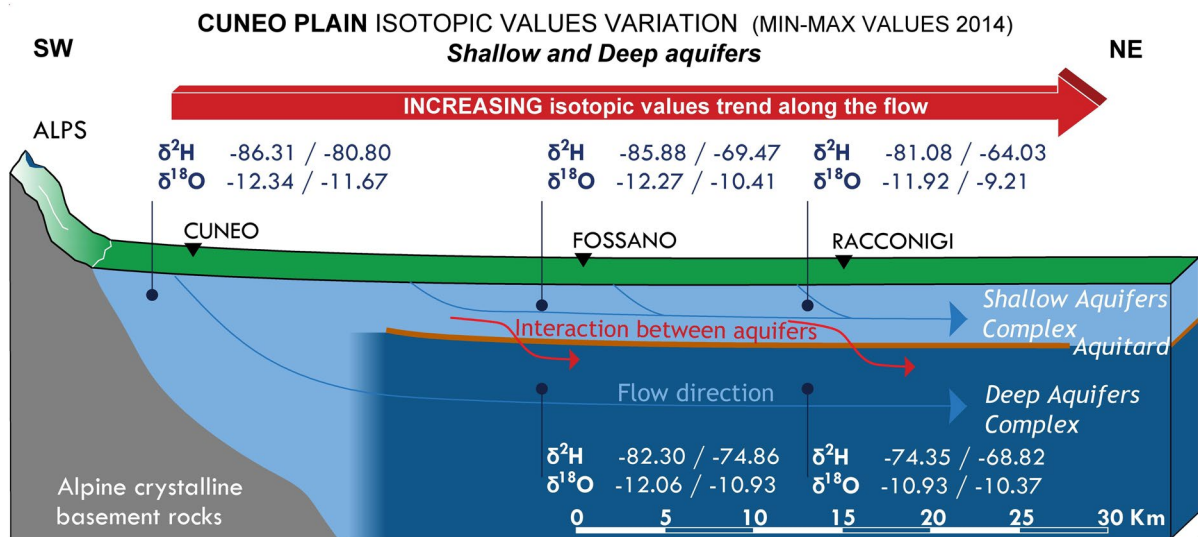
Considering the spatial distribution in the shallow and deep aquifer complexes, the stable isotopes of groundwater are spatially distributed according to the flow direction. In particular, an increasing spatial trend (more enriched in heavy isotopes) of isotopic values was observed along the groundwater flow direction in the shallow and deep aquifer complexes (Fig. 10). For the shallow aquifer complex, Cuneo:  $\delta^{18}\text{O}$  (min/max)  $-12.3/-11.7\text{‰}$ ,  $\delta^2\text{H}$  (min/max)  $-86.3/-80.8\text{‰}$ ; Bra:  $\delta^{18}\text{O}$  (min/max)  $-11.9/-9.2\text{‰}$ ,  $\delta^2\text{H}$  (min/max)  $-81.1/-64\text{‰}$ . For the deep aquifer complex, Cuneo:  $\delta^{18}\text{O}$  (min/max)  $-12.3/-11.7\text{‰}$ ,  $\delta^2\text{H}$  (min/max)  $-86.3/-80.8\text{‰}$ ; Bra:  $\delta^{18}\text{O}$  (min/max)  $-10.9/-10.4\text{‰}$ ,  $\delta^2\text{H}$

(min/max)  $-74.4/-68.8\text{‰}$ . These data were selected by Franchino (2016).

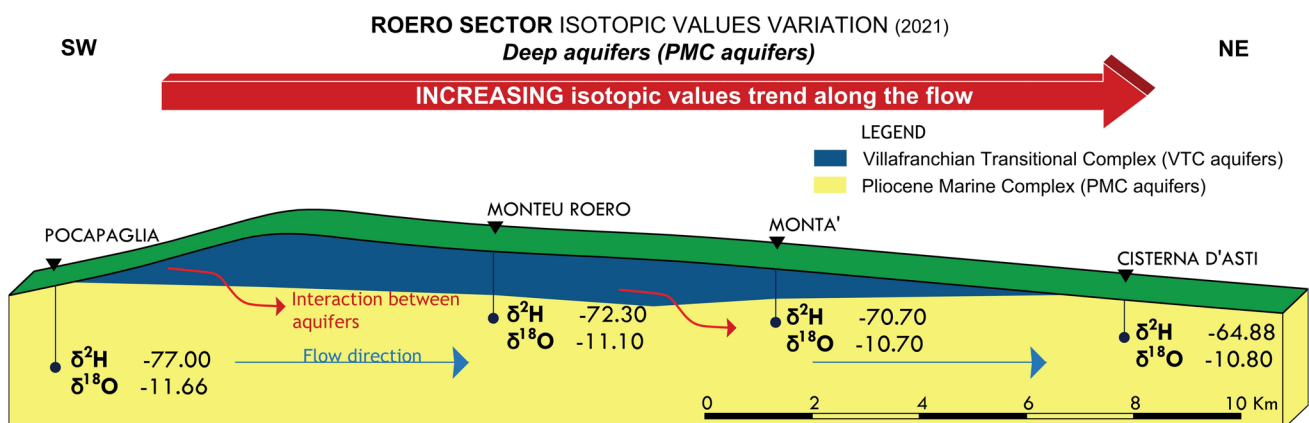
An increasing spatial trend in isotopic values was also found along the PMC aquifer flow direction in the Roero sector [Pocapaglia:  $\delta^{18}\text{O}$  (min/max)  $-11.7\text{‰}$ ;  $\delta^2\text{H}$  (min/max):  $-77\text{‰}$ ; Cisterna d'Asti:  $\delta^{18}\text{O}$  (min/max)  $-10.8\text{‰}$ ;  $\delta^2\text{H}$  (min/max)  $-64.9\text{‰}$ ] (Fig. 11).

## Turin plain

A distinction in the isotopic composition was observed between the shallow aquifer complex wells located on the right and left hydrographic sides of the Po River—left:  $\delta^{18}\text{O}$  (min/max)  $-11.4/-10.4\text{‰}$ ,  $\delta^2\text{H}$  (min/max)  $-78.2/-69.9\text{‰}$ ; right:  $\delta^{18}\text{O}$  (min/max)  $-10.0/-7.6\text{‰}$ ,  $\delta^2\text{H}$  (min/max)



**Fig. 10** Schematic section 1 (trace of the cross-section shown in Fig. 5) of the variation in the isotopic composition (‰) along the flow directions of the shallow and deep aquifer complexes in the Cuneo plain



**Fig. 11** Schematic section 2 (trace of the cross-section shown in Fig. 5) of the variation in the isotopic composition (‰) along the flow direction of the PMC aquifers in the Roero sector

-66.8/-56.5‰; Sangiovanni 2016). In particular, the wells on the hydrographic left side were less enriched in heavy isotopes than those on the hydrographic right side.

An initially increasing spatial trend in isotopic values was observed along the shallow aquifer complex flow direction in the section between Osasco and Scalenghe [Osasco:  $\delta^{18}\text{O}$  -10.7‰,  $\delta^2\text{H}$  -74.3‰; Scalenghe:  $\delta^{18}\text{O}$  (min/max) -10.6/-9.7‰,  $\delta^2\text{H}$  (min/max) -70.6/-66.9‰], followed by a decreasing spatial trend (with a decreased heavy isotope composition) between Scalenghe and Carignano [Scalenghe:  $\delta^{18}\text{O}$  (min/max) -10.6/-9.7‰,  $\delta^2\text{H}$  (min/max) -70.6/-66.9‰; Carignano:  $\delta^{18}\text{O}$  (min/max) -11.0/-10.3‰,  $\delta^2\text{H}$  (min/max) -74.4/-69.4‰ (Franchino 2016)] (Fig. 12).

The VTC aquifer wells in the Scalenghe well field ( $\delta^{18}\text{O}$  -11.8‰;  $\delta^2\text{H}$  -82.0‰) had isotopic compositions that were less enriched in heavy isotopes than those sampled from the shallow aquifer complex wells in the Scalenghe area (Albanese et al. 2008). Furthermore, the isotopic composition of the VTC was less enriched in heavy isotopes than that in the Maggiore Valley well fields [ $\delta^{18}\text{O}$  (min/max) -11.7/-11.1‰;  $\delta^2\text{H}$  (min/max) -74.2/-73.1‰].

**Poirino Plateau**

A decreasing trend in the spatial isotopic values was observed along the shallow aquifer complex flow direction between the Poirino-Villanova d’Asti area and Carmagnola [Poirino:  $\delta^{18}\text{O}$  (min/max) -10.4/-9.3‰,  $\delta^2\text{H}$  (min/max) -66.7/-59.7‰; Carmagnola:  $\delta^{18}\text{O}$  (min/max) -11.2/-10.4‰,  $\delta^2\text{H}$  (min/max) -70.0/-62.4‰].

The isotopic value ranges of the shallow aquifer complex wells in the Po riverside plain and of the VTC aquifer wells in the Poirino Plateau were very similar (Fig. 12). The isotopic values of the VTC aquifer wells were similar [ $\delta^{18}\text{O}$  (min/max) -10.8/-10.1‰,  $\delta^2\text{H}$  (min/max) -66.8/-66.5 ‰].

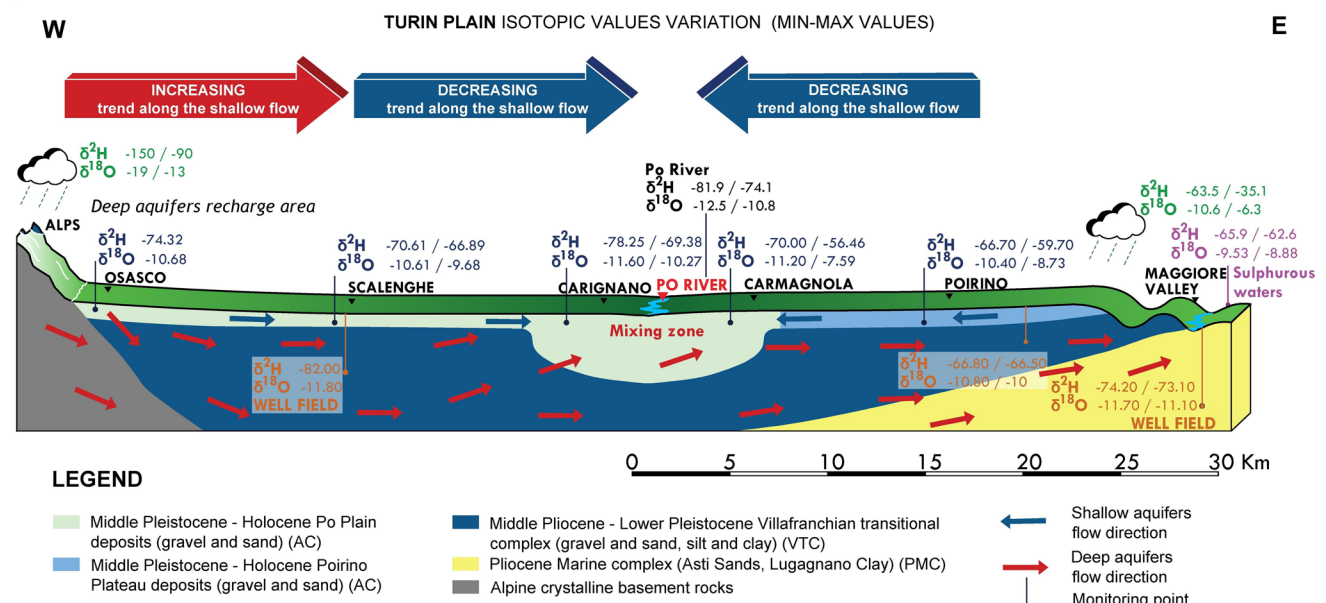
**Maggiore, Stanavasso, Triversa and Traversola valleys**

The depression cone centred in the Maggiore Valley well field is characterized by three main groundwater flow directions (S, W, and NW) coming from the Cuneo sector and the Poirino Plateau. The artesian well in the Triversa Valley, located furthest from the Maggiore Valley well field (site no. 84), was the monitoring point with the least enriched heavy isotope composition [ $\delta^{18}\text{O}$  (min/max) -12.3‰,  $\delta^2\text{H}$  (min/max) -79.3‰] in the sector containing the Maggiore, Stanavasso, Triversa and Traversola valleys. The Maggiore Valley well field had a slightly less enriched heavy isotope composition and less variability [ $\delta^{18}\text{O}$  (min/max) -11.7/-11.1‰,  $\delta^2\text{H}$  (min/max) -74.2/-73.1‰] than the artesian wells closest to this region [ $\delta^{18}\text{O}$  (min/max) -11.1/-10.7‰,  $\delta^2\text{H}$  (min/max) -75.3/-70.6‰].

**Discussion**

**Hydrochemical characterization**

The absence of relevant variations in the groundwater facies between the two sampling campaigns observed in the Piper



**Fig. 12** Schematic section 3 (trace of the cross-section shown in Fig. 5) of the variation in the isotopic composition (‰) along the samples from the shallow and deep aquifer complexes in the Turin Plain, Poirino Plateau and Maggiore Valley regions

diagrams, suggests a stationarity of natural and anthropic processes that is not influenced by seasonal variations. The greater variability of the concentrations in the shallow aquifer complex compared to the deep complex was probably the result of anthropogenic inputs (Fig. 6c,d).

The Poirino Plateau and Po riverside plain sectors showed high nitrate and chloride concentrations related to the intense agricultural activities that notoriously impact these sectors, showing evident pressure in the shallow aquifer complex and, in part, in the VTC aquifers. The  $EC/HCO_3^-$  and  $Ca^{2+}/Mg^{2+}$  diagrams (Fig. 7a,b) confirm that calcium and bicarbonate are the ions that most affect the EC. The molar ratio diagrams of  $NO_3^-/Cl^-$ ,  $Cl^-/Na^+$ ,  $NO_3^-/SO_4^{2-}$ , and  $Cl^-/SO_4^{2-}$  (Fig. 7c–f) and their concentrations confirm the influence of human activities in the Poirino Plateau (shallow aquifer complex and VTC aquifer wells) and in the Po riverside plain (shallow aquifer complex wells). In particular, the  $NO_3^-/SO_4^{2-}$  diagrams show affinities to organic matter and fertilizers (Raco et al. 2021; Rufino et al. 2022; Celico 1986). Conversely, the PMC aquifer wells of the Maggiore Valley and watercourse concentrations suggest a natural origin of chloride, sulphates and sodium, this latter linked to ion exchange processes due to their long residence times.

### Isotopic characterization

In the  $\delta^{18}O$ – $\delta^2H$  diagrams (Fig. 8a,b), the shallow and deep aquifer complexes of the Poirino Plateau showed the most enriched heavy isotope composition among the groundwater resources in relation to the low elevation of the sector (maximum elevation of 360 m asl). The reverse situation was observed in the Maggiore Valley and Roero sector, where the less enriched heavy isotope composition was due to recharge processes from higher-elevation sectors (average elevation of 1,300 m asl). The Po River was influenced by recharge from the upper part of the catchment, as well as by snowmelt inputs (Marchina et al. 2015, 2016); in contrast, the Banna River supply basin is located at relatively low elevations (with a maximum elevation of 715 m asl).

The  $\delta^{18}O$  vs  $\delta^2H$  plots (Figs. 8 and 9) report two different local meteoric water lines. The first one, NW Italy LMWL, represents the site-specific covariation of hydrogen and oxygen stable isotope ratios. The NW Italy line is site-specific and reflects the local climatic conditions and meteoric inputs (rain, snow) to that location. LMWLs can vary from one site to another due to local climate influences, topography, and meteorological factors. The differences between the two lines are probably related to the different data used for their construction (differential spatiotemporal monitoring, different numbers and intensity of sampling).

In the *Cuneo plain*, the increasing spatial trend of isotopic values observed along the groundwater flow direction in the shallow and deep aquifer complexes (Fig. 10) corresponds to

the progressive contribution of precipitation to the Piedmont plain, which had a more enriched heavy isotope composition than the shallow aquifer complex (Giustini et al. 2016; Quaranta et al. 2020), and to the progressive contribution of the overlying shallow aquifer complex to the deep aquifer complex, as characterized by the most enriched heavy isotope composition.

In the *Roero sector*, an increasing spatial trend of isotopic values was also found along the PMC aquifer flow direction in relation to the progressive contribution from the overlying VTC aquifers, which were confirmed to have a more enriched heavy isotope composition (Fig. 11).

In the *Turin plain*, the shallow aquifer complex wells on the hydrographic left side of the Po River were less enriched in heavy isotopes than those on the hydrographic right side, which was attributable to a feed derived from the alpine sector characterized by particularly less enrichment in heavy isotopes. The decreasing spatial trend in isotopic values along the shallow aquifer complex flow direction in the section between Scalenghe and Carignano and the decreasing trend in the spatial isotopic value between the Poirino–Villanova d’Asti area and Carmagnola on the Poirino Plateau were due to mixing with the underlying deep aquifer complex. In particular, in this sector, the continuity of the impermeable layers was interrupted by partial erosion from a Po River palaeo-riverbed (Fig. 12). With regard to the deep aquifer complex, there are not sufficient data to make spatial interpretations in relation to the few wells containing this complex on the hydrographic left side plain of the Po River. Furthermore, the isotopic composition of the deep aquifer complex of the Turin plain was less enriched in heavy isotopes than that in the Maggiore Valley well fields, suggesting a feed from the shallow aquifer complex along the flow direction.

On the *Poirino Plateau*, the similar range of isotopic values of the shallow aquifer complex wells on the Po riverside plain and of the VTC aquifer wells on the Poirino Plateau (Fig. 12) suggest that mixing between aquifers on the Po riverside plain constitutes the VTC aquifer feed in the Poirino Plateau sector. These observed variations in the isotopic composition confirm the connection between the shallow aquifer complex of the Turin Plain and the deep aquifer complex of the Maggiore Valley.

One factor complicating the comparison between the shallow and deep aquifer complex samples was the irrigation activities that exploit the VTC aquifers. Irrigation constitutes a component in the shallow aquifer complex recharge process, influencing the isotopic values of these samples and making them less enriched in heavy isotopes. Some previous studies have studied irrigation effects on groundwater (e.g. Rotiroti et al. 2019, 2023), defining local recharge by irrigation channels for the deep aquifers. For this reason, the shallow aquifer complex isotopic composition variability



was not attributable to the location, depth, or chemistry of the monitoring points.

In the *Maggiore, Stanavasso, Trivera and Traversola valleys*, the artesian well in the Trivera Valley (site no. 84) with the least enriched heavy isotope composition in the sector can be correlated with an origin in the alpine sector as follows:

- Similar isotopic values were observed in the Po River in the Carignano sector [ $\delta^{18}\text{O}$  (min/max)  $-12.5\text{‰}$ ,  $\delta^2\text{H}$  (min/max)  $-78.1\text{‰}$ ] and in the Cuneo Plain area close to the alpine reliefs.
- The waters hosted in the other sectors (the Poirino Plateau and Roero sectors) showed a more enriched heavy isotope composition than those sampled from the Cuneo Plain and Po River.
- The Turin Hills can be excluded as the origin, given the low elevation of this sector.
- The difference in the chlorine–alkaline disequilibrium index between the Maggiore Valley and the Traversola and Trivera valleys suggested longer residence periods of the groundwater in the latter sector and, therefore, a more distant feeding zone (Actis Giorgetto 1991).

In the Maggiore Valley well field, the slightly less enriched heavy isotope composition and less variability than the closest artesian wells are the result of interactions with particularly less-enriched heavy isotope waters in the well fields and the greater depths of aqueduct wells than artesian wells. However, a relevant interaction with deep sulphurous waters can be excluded, in relation to their more-enriched heavy isotope composition compared to the well field.

### Mixing definition in the Maggiore Valley well field

With the aim of defining mixing processes corresponding to the Maggiore Valley well field, a comparison was made

between the average  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ , chloride concentration and nitrate concentration values obtained for the well-field aqueduct wells and the average values obtained for the three components of the deep-flow directions (S, W, and NW). The wells representing these three deep-flow directions correspond to the wells without nitrate values closest to the well field.

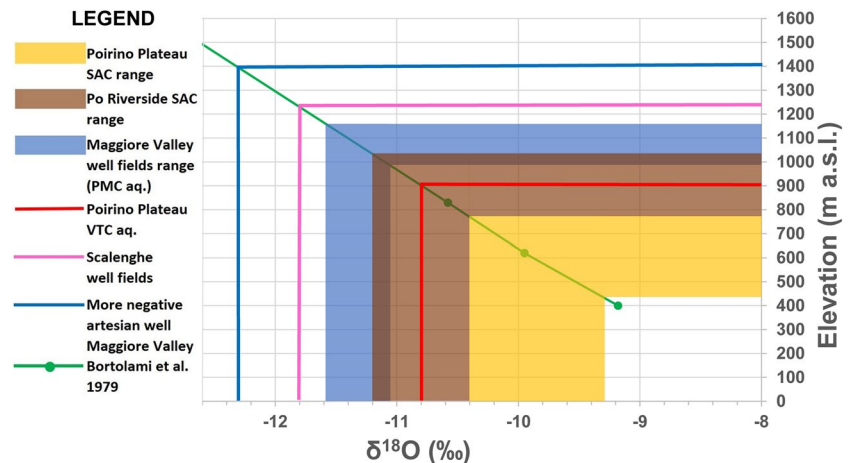
In the Maggiore Valley well field, the deep-flow rate obtained herein is comparable to the least-enriched heavy isotope composition observed in the area (at artesian well no. 84); this rate was therefore added to the three deep-flow components. The comparison results show remarkable similarity between the average  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  and chloride concentration values (Table 2); therefore, mixing among these four components in the Maggiore Valley well field is thus confirmed.

### Average recharge elevation

The elevation- $\delta^{18}\text{O}$  correlation diagram (Fig. 13) supports several previous interpretations, which are summarized as follows:

- The Maggiore Valley aqueduct wells (blue band) are located at average recharge elevations between approximately 1,000 and 1,150 m asl. This confirms the contribution of the alpine relief region, as this is the only sector with such elevations.
- The shallow aquifer complex wells in the Po riverside plain (brown band) are located at average elevations between approximately 775 and 1,025 m asl. This confirms the interaction of this shallow aquifer complex with a less-enriched heavy isotope component, in relation to the elevation of shallow aquifer complex sector  $<300$  m asl. Moreover, the wells in the brown band are located between the shallow aquifer complex wells in the Poirino Plateau sector (yellow band) and the VTC aquifers on

**Fig. 13** Diagram showing the  $\delta^{18}\text{O}$  vs recharge elevation area correlation. Correlation line from Bortolami et al. 1979



**Table 2** Comparison of the average  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ , chloride concentration and nitrate concentration values in the well field and in the 4 flow components

Campaign II flow component	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	Chloride (mg/L)	Nitrate (mg/L)	Well reference no.
South	-10.70	-70.70	4.653	<0.050	40
West	-11.00	-70.60	1.702	<0.050	7
Northwest	-11.10	-75.30	1.509	0.098	2
Deep-flow rate	-12.33	-79.24	1.502	<0.050	84
Average among four components	-11.28	-73.96	2.340	0.020	40, 7, 2, 84
Average well field	-11.36	-73.63	2.350	<0.050	20, 21, 27

the hydrographic left side of the Po River (pink line). This finding validates the existence of mixing between the shallow aquifer complex and VTC aquifers on the Po riverside plain. A mechanism of influence linked to irrigation cannot be excluded.

- The shallow aquifer complex wells in the Poirino Plateau sector (yellow band) are located at elevations between approximately 775 and 450 m asl. This elevation range overlaps the real elevation of the feeding basin (with a maximum elevation of 715 m asl).
- The artesian well least enriched in heavy isotopes (blue line) shows an average recharge elevation of 1,400 m asl. This finding validates the origin from the alpine relief region and the existence of a water component derived from distal sectors in the Trivera Valley; in addition, a very much less-enriched heavy isotope composition compared to the neighbouring sectors is conserved here. The influence of the Po River can thus be excluded, as this river is draining in this region.

However, the use of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  isotopes alone did not allow the groundwater recharge to be quantitatively estimated or the percentage contribution of different groundwater bodies to be determined, as shown also in previous studies (Ma et al. 2021). Only joint use with other tracers, such as Cl, Br and  $\delta^3\text{H}$ , could help in quantitative studies of groundwater recharge (Rotiroti et al. 2019; Larsen et al. 2021). However, the important anthropogenic contamination in the shallow aquifers of the study area, and the almost absence of Br in the analysed waters, did not permit the use of these isotopes in this study. A similar case study with a complex hydrogeological system and anthropogenic influences was performed in the Tuscany region (Pennisi et al. 2006), where the B and Sr isotopic compositions were determined and the percentage contribution of surface water and precipitation was estimated. However, in this study, the analysis of the differences in the isotopic composition and the spatial evolution of a robust conceptual model permitted one to define what water resources contribute more to the recharge of deep aquifers, even without the use of other tracers.

## Conclusions

The hydrochemical and stable isotope data of different groundwater bodies were used to determine the groundwater recharge processes of the deep aquifers used by the Maggiore Valley well field. The study has made it possible to obtain a large-scale vision never obtained before, by also using individual previous investigations that were not alone able to provide a complete and comprehensive picture of the processes. Indeed, the results of this study have allowed the kilometric flow of shallow and deep aquifers in a very complex hydrogeological system to be defined.

The *hydrochemical analyses* highlighted the differences in groundwater body mineralization among different geographical sectors. The Poirino Plateau and Po riverside plain sectors are associated with the intense agricultural activities that impact the shallow aquifer complex and, partially, the deep aquifer complex of these sectors. In the deep aquifer complex wells in the Roero sector and the Maggiore, Stanavasso, Trivera and Traversola valleys, natural contributions of sulphates, sodium and chloride exist.

The *isotopic data* revealed isotopic value differences among the investigated groundwater bodies. In particular, the main elements potentially influencing the deep aquifer recharge system have been considered (deep aquifers, shallow aquifers, rivers, local precipitation, alpine precipitation, and sulphurous waters), identifying a reference isotopic composition for each one. The isotopic composition of the shallow aquifer complex of the Poirino Plateau clearly reveals a recharge area at a low altitude compared to the deep aquifer complex of the Maggiore, Stanavasso, Trivera and Traversola valleys and the Roero sector, which have isotopic compositions reflecting a higher elevation of the recharge areas. The main recharge area of the deep aquifers, providing the major contribution, is in the Alps sector and in the foothills plain, while the plain sector provides a secondary and minor contribution. In the plain sectors, the spatial variations in isotopic data confirm that the recharge area is represented by the entire plain, in relation to the geological features that do not allow complete confinement between the shallow and deep aquifers. The

Po riverside plain confirms the interaction between the shallow and deep groundwater bodies, due to the absence of confinement and in relation to less enrichment in heavy isotopes in the shallow aquifers with respect to other sectors, while the VTC aquifer data of the Poirino Plateau confirm a feed by the shallow aquifer complex. Furthermore, an anthropogenic influence given by the probable presence of mixing wells and irrigation practices cannot be excluded in the Poirino Plateau. Lastly, a direct feed of the deep aquifer complex by the Po River in the investigated sector must be excluded given the predominantly draining condition of this watercourse.

According to these new findings, the recharge area of deep aquifers is wider than previously proposed, forcing a redefinition of actions to protect groundwater resources exploited for human consumption, also given the strong presence of anthropogenic pressures. However, the methods used have not allowed this study to quantify the contribution to the recharge from the different areas (e.g., differentiated contribution from alpine valleys); this evaluation will have to be addressed by future studies.

Finally, this study highlighted the need for a robust conceptual model in which physical–chemical and isotopic analyses represent an important aid to understanding processes and to recognizing local anomalies. The improvement in the conceptual model of the recharge processes and the interaction between groundwater bodies constitutes an extremely useful tool for local authorities to preserve drinking water resources for future generations. This research represents a successful application of hydrochemical and isotopic data in a large and complex hydrogeological setting, which is useful for hydrogeologists working in comparable settings and for local authorities to increase the effectiveness of environmental protection.

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## Declarations

**Conflict of interest** On behalf of all authors, the corresponding author states that there is no conflict of interest.

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