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Research Article

Groundwater Quality Assessment in a Karst Coastal Region of the West Aurunci Mountains (Central Italy)

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This paper presents the results of a groundwater quality assessment carried out in the karst coastal region of the West Aurunci Mountains (Central Italy). 55 spring and 18 well water samples, collected from 2016 to 2018, were analysed to study the main processes controlling the hydrogeochemical evolution and groundwater quality properties. In the study area, groundwater samples are mostly characterized by a Ca-HCO_3 facies, indicating that the groundwater hydrogeochemical evolution is mainly controlled by the carbonate mineral dissolution/precipitation. The cationic and anionic concentrations confirm that groundwater samples belong to the order of $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$ and $HCO_3^{-} > Cl^{-} > SO_4^{2-}$, respectively. Well water samples show, over time, an increasing mineralization with respect to the spring water samples. In more detail, the enrichment of Ca^{2+}, Na^{+}, and Cl^{-} in well water samples is mainly due to the dissolution of calcite, dolomite, and halite minerals and secondly to a probable ion exchange related to seawater intrusion. Seawater intrusion, probably affecting the chemical composition of well water samples, was studied using ionic ratios, graphical approaches, and specific indices, such as the BEX index. Results suggest that carbonate weathering, ion exchange, and seawater intrusion in this karst coastal region are the major factors controlling groundwater geochemistry. This study shows that groundwater quality assessment, based on hydrogeochemical investigation techniques, has been a useful tool to characterize and model carbonate aquifers in Central Italy, with the aim of achieving proper management and protection of these important water resources.

1. Introduction

Karst aquifers cover more than 30% of the European land mass [1], where carbonate lithologies occupy about 35% of the territory. Groundwater resources coming from karst aquifers give, in some countries, up to 50% to the drinking water supply [2]. For a large part of the Mediterranean region, karst springs play an essential role in the water supply. During the Mediterranean long dry summer months, karst springs provide fresh and high-quality water, which has been an important resource for human development in this region since antiquity [3]. Specifically, in Italy, the karst carbonate aquifers of the Central Apennines represent the larger groundwater resource. These aquifers are very complex systems: each one has its own distinctive characteristics. Karst aquifer peculiarities make them strategic resources which, however, are not yet properly exploitable, because of objective difficulties that are found in their study [4]. The use of groundwater resources is increasing due to population rise, economic growth, intensified agricultural development, and the loss of surface water due to contamination [5]. In those countries with an extensive coastline, such as Italy, the high drinking water demand can lead to an uncontrolled groundwater exploitation of coastal aquifers [6, 7]. Coastal aquifers are major sources for freshwater supply in many countries around the world, especially in arid and semiarid zones and particularly because almost 70% of the world population lives in coastal areas [8, 9]. The main consequence of this groundwater overexploitation is seawater intrusion and, because of it, water salinization, which has become the most widespread form of groundwater contamination both in the Mediterranean regions of Europe [10–13] and in lots of coastal areas of the world [9, 14–18].

The quality of coastal aquifers is controlled by the variations of hydrochemical processes like seawater intrusion, geogenic process (weathering, ion exchange, and water-rock

Table 1: The location of the spring and the well water sampling survey.

Sample codes	Name	Location of sampling survey	Latitude	Longitude	Elevation (m a.s.l.)
TUL	Tulliola well	Formia	41°15′8.21″	13°35′2.23″	20
TER	Terenzia well	Formia	41°15′8.04″	13°34′59.06″	20
MAZ	Mazzoccolo Spring	Formia	41°15′44.10″	13°36′50.83″	18
CAP	Capodacqua di Spigno Spring	Spigno Saturnia	41°17′36.46″	13°42′42.18″	35

interaction), and anthropogenic activities (agriculture, industry, and urbanization). The salinization is the result of concomitant processes related to both seawater intrusion and water-rock interaction, which in some cases are virtually indistinguishable [19]. Hence, several studies usually combine the hydraulic and the hydrogeochemical approach, because understanding the hydrochemical characteristics of coastal groundwater could provide guidance for sustainable groundwater management [20]. In the present work, the karst coastal region of the West Aurunci Mountains has been chosen as the study area for the groundwater quality assessment.

73 groundwater samples were collected from 2016 to 2018 and analysed to evaluate the main geochemical processes controlling the groundwater evolution in this hydrogeological system. With the aim of identifying the potential seawater intrusion in this coastal region, several water quality indicators and some diagrams, which use hydrochemical parameters, have been applied in this case study [21–30].

2. Study Area

In this study, two main karst springs of the West Aurunci Mountains and 2 wells (Table 1), belonging to the "25 Ponti" wellfield, which is going to be exploited for drinking purposes, were examined based on the physical-chemical data availability. The study area is located in Italy, in the Southern Latium Region, and involves the competence territory of the Formia, Gaeta, and Spigno Saturnia municipalities, for a total of about 10 ha (Figure 1).

The Mazzoccolo Spring comes out inside the inhabited area of the Formia municipality less than 1 km from the shoreline (Figure 1). The Capodacqua di Spigno Spring is on the other hand at the base of the La Civita Mountain slopes, about 2 km away from the city and about 4 km from the shoreline. The new "25 Ponti" wellfield, at last, is out of the Formia city centre, about 500 m from the coast.

3. Geological and Hydrogeological Setting

The Aurunci Mountains, together with the Lepini and Ausoni Mountains, belong to the pre-Apennines of Latium and form the carbonate platform of the Volsci Ridge, separated from the Apennine ridge by the Latina Valley. The Aurunci Mountains mostly consist of massive dolomitic limestone and dolomite layers, deposited on the carbonate platform with a thickness of about 3000 meters [31]. The stratigraphic succession of the carbonate platform, from the bottom to the top, is generally characterized by a calcareous-dolomitic series and by a carbonate series with detrital-organogenic limestone, in which Pliocene sea deposits overlap (Figure 2) [32]. Above these deposits, marine lagunal subtidal limestone (Middle Liassic-Upper Jurassic) rarely and poorly dolomitized occurs.

The presence of layers containing rubble stones and oolitic deposits suggests the occurrence of a depositional environment. In the same way, the lower Cretaceous deposits suggest the onset of a carbonate platform depositional system ranging from a tidal flat to a lagoon. The analysis of textural parameters and vertical organisation of the lithofacies allows the recognition a cyclic organisation, arranged in shoaling upward sequences [33]. The Volsci Ridge is a structure in the Apennine direction, which on the northeastern edge is overthrust on the terrigenous deposits of the Latina Valley, while on the south western edge, it is characterized by direct faults that lower towards the Tyrrhenian Sea. The overthrust presents an Apennine trend up to Esperia, where it changes direction and follows the edge of the Western Aurunci.

Downstream of the Mazzoccolo Spring, geognostic data indicated the presence of a direct fault, which cuts the outcrop of the Pliocene calcarenites, with the presence (between the coast and the spring) of clayey silts with Quaternary piroclastite. As for the Capodacqua di Spigno Spring, a direct fault cuts the high part of the Spigno Saturnia area. In the Miocene formations, in contact with the carbonates, there are direct faults with an anti-Apennine direction, which delineate a mild Quaternary tectonic pit, characterized by extensive alluvial deposits. In addition, next to the spring, there is a circular shape of alluvial deposits, with a diameter of about 200 meters, which suggests a past phenomenon of a sinkhole, which most likely originated from the collapse of a large karst cavity in the buried carbonate substrate [32].

Karst depressions (superficial and subsurficial) originate from chemical processes related to the contact between rainwater and some types of carbonate rocks, i.e., the limestone, the dolomitic limestone, and the dolomites, which are part of the carbonate series previously described. Although dolomite has a lower solubility than calcite, in the series, the two minerals alternate, so in the studied area, the superficial karst forms are widespread in the hydrogeological basin, except in those areas with high slopes, usually associated with the fault lines. The Western Aurunci area is a karst area without a true hydrographic network, and therefore, the genesis of the existing valleys, within the relief, appears more affected by the faults than the runoff. Surface hydrology is reduced by many absorption points, which rapidly drain rainwater into the subsoil. The Aurunci Mountains are composed of two distinct hydrogeological units: the Western

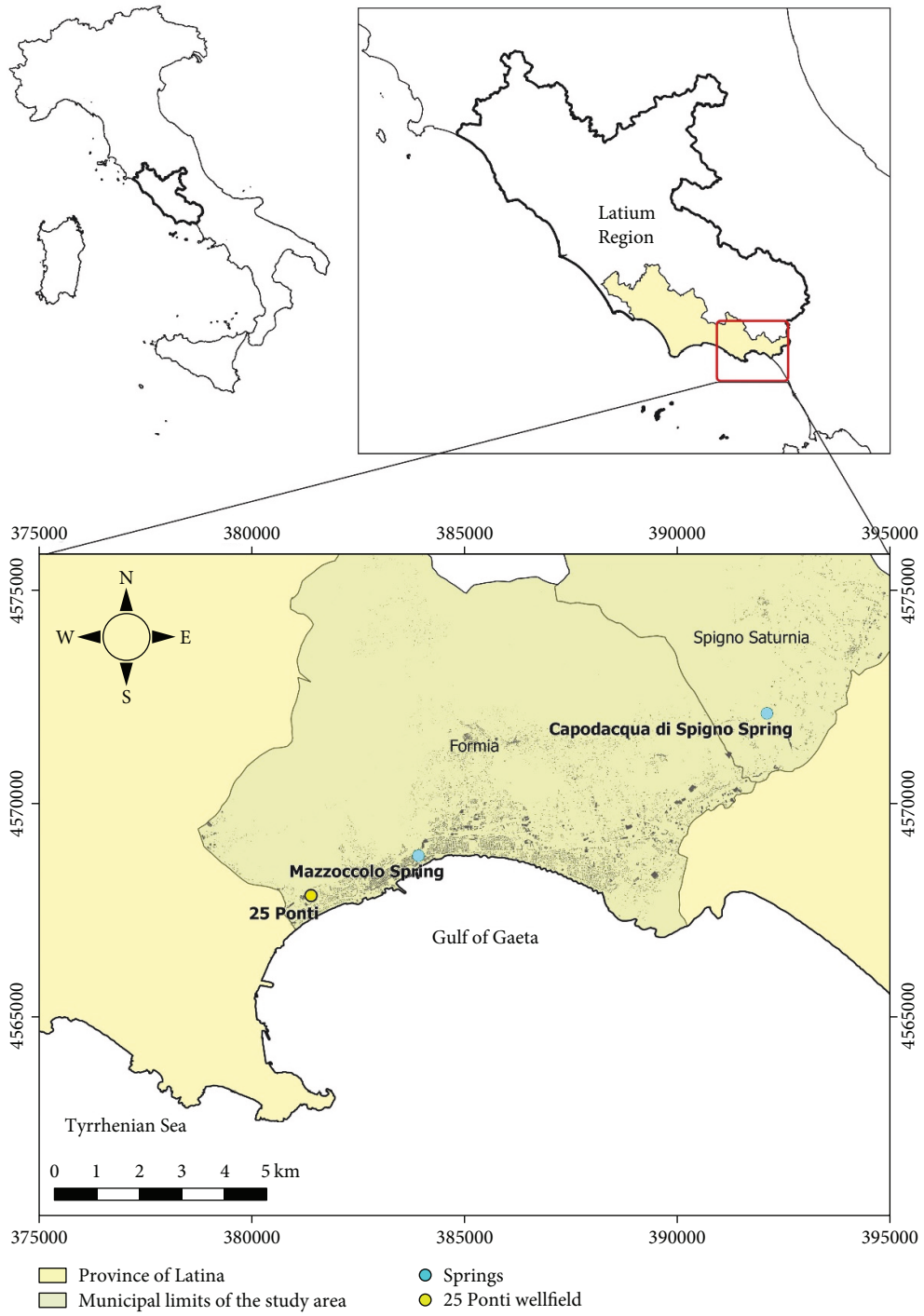

Figure 1: Geographical framework of the study area.

Aurunci Unit, belonging to the Ausoni-Aurunci system, and the Eastern Aurunci Unit, separated from the western one by a marly-arenaceous flysch complex [32]. The Western Aurunci hydrogeological unit, as previously described, is made up of dolomitic limestone and dolomites of the Jurassic and Cretaceous ages, which houses an important karst aquifer, giving rise to springs. The most important ones are the Mazzoccolo and Capodacqua di Spigno (Figure 3), which show, respectively, an active recharge of about 17 and 37 m^3/year, averaged over 40 years of observations, whereas feeding areas have been estimated at about 30 km^2 and 60 km^2, respectively [34]. The Eastern Aurunci hydrogeological carbonate structure is surrounded by relatively less-permeable sediments, including the Frosinone flysch, the Roccamonfina vulcanite, and the Garigliano Plain alluvial deposits [32, 35]. The Mazzoccolo Spring flows from the base of Pliocene conglomerates, which is tectonically in contact with the limestone. This spring is located at an altitude of

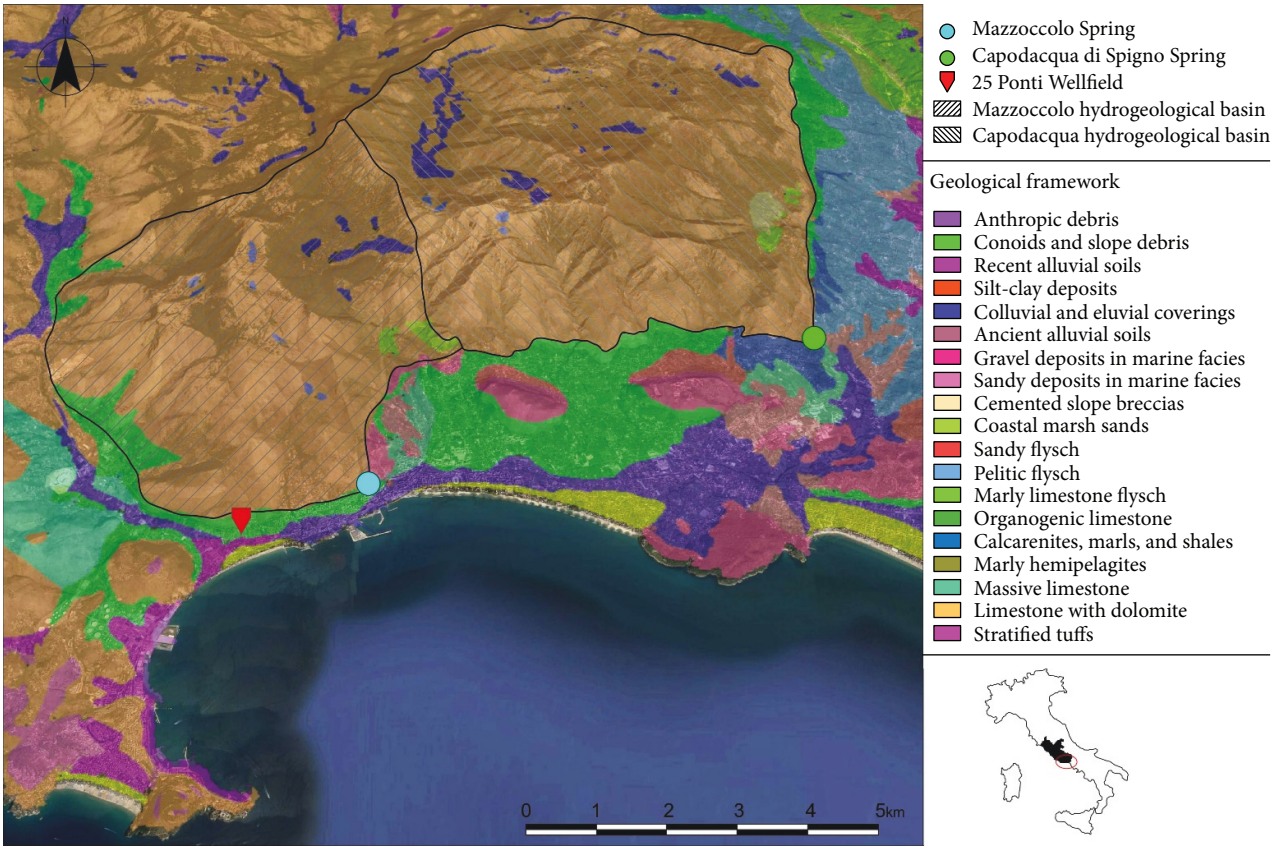

Figure 2: Geological framework of the study area.

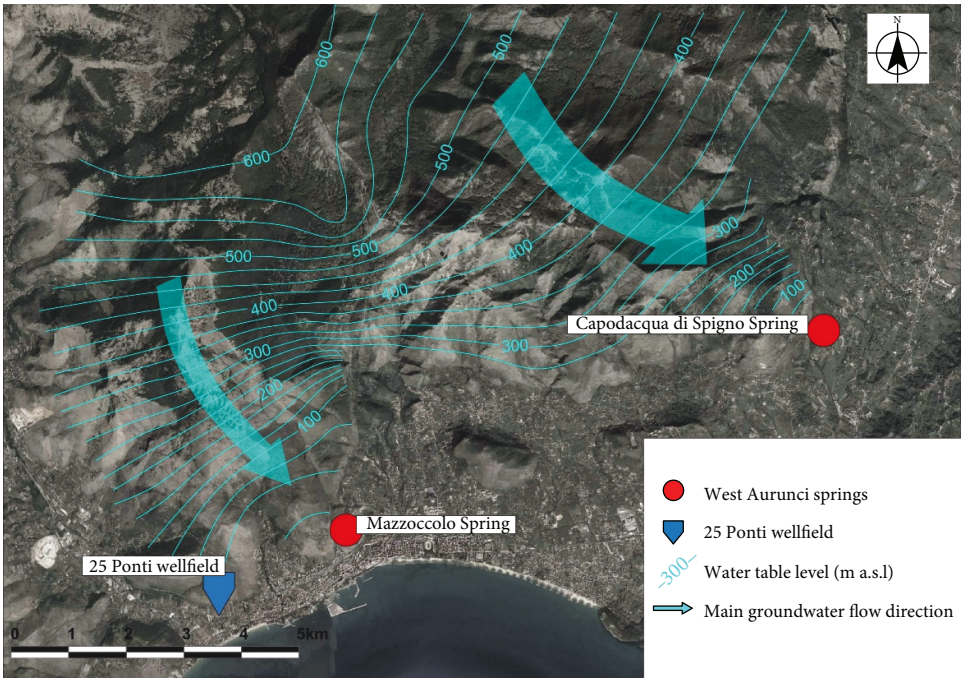

Figure 3: Subsurface hydrology of the West Aurunci karst aquifer (modified from [32]).

11.5 m a.s.l., where rocks present fractures due to the intersection of numerous faults [36]. The local geological setting of the study area is characterized by conglomeratic limestone on the hills (Mola Mountain), surrounded by clayey sands and alluvial deposits of debris. The abundance of groundwater is due to the permeability of the limestone (highly

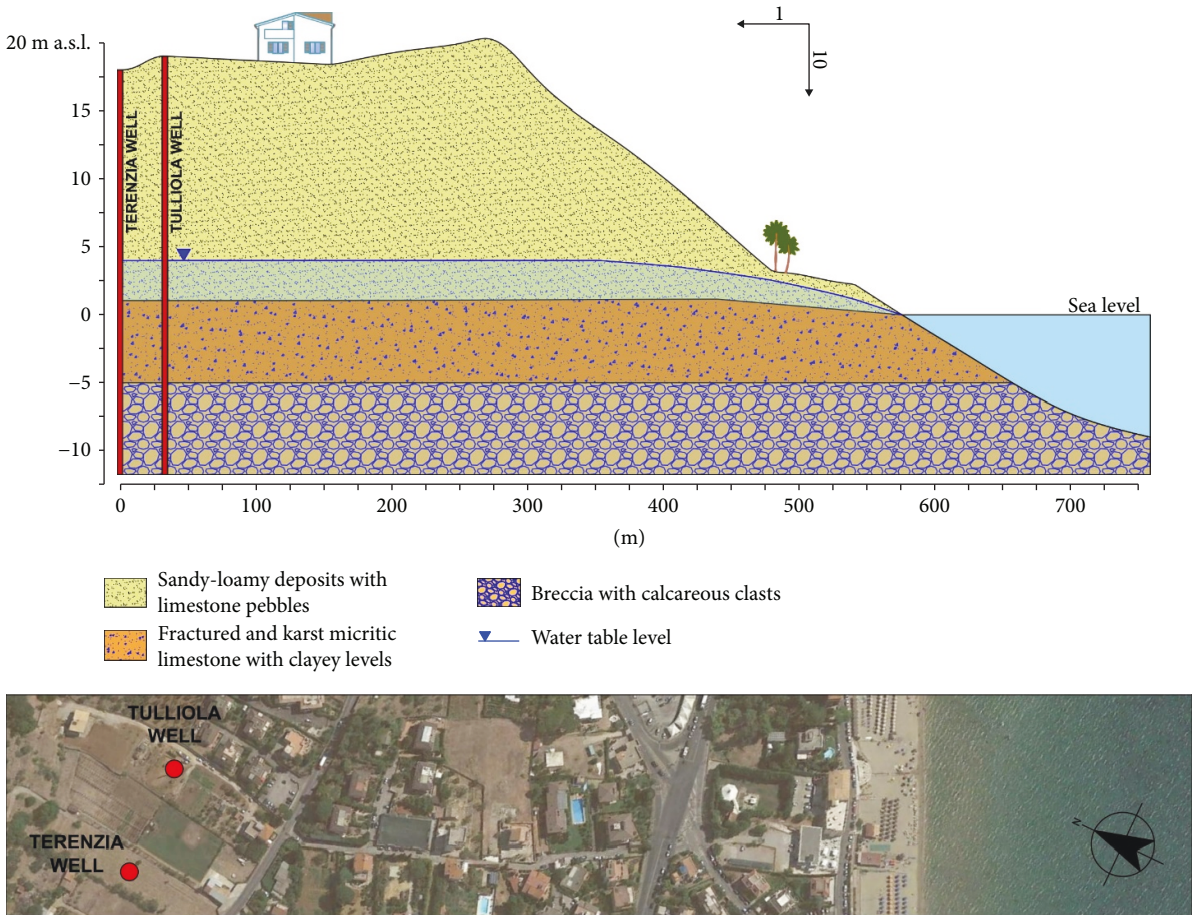

Figure 4: Geological cross section from the "25 Ponti" wellfield to the coastline.

fractured and deep karst), which stores a significant quantity of groundwater. In this area, the top of the saturated zone presents considerable differences in the level (Figure 3) [4, 32].

The Capodacqua di Spigno Spring is located at an altitude of about 35 m a.s.l., on the eastern edge of the Aurunci Mountains. The spring water comes out from the permeable limestone of the La Civita Mountain and the Castello Mountain and flows above the upper Miocene clays, at the lowest point of the limestone-clay contact [37, 38].

The general groundwater flow direction of the aquifer is towards the SE, but there are also important local flows along the two faults that delimit the carbonate series outcropping, especially the one to the east, which seems to represent the main water conduit towards the spring.

The "25 Ponti" area, where the Tulliola and Terenzia wells are located, is about 1 ha. The geology is locally characterized by the presence of a top layer made of silty-sandy deposits (about 17 m), a central layer made of fractured and karst micritic limestone (about 8 m), and a bottom layer made of breccia with calcareous clasts (more than 50 m). The bottom layer consists of the saturated part of the aquifer, since the water table level is about 4 m a.s.l. and the wells are about 500 m away from the coastline (Figure 4).

In this area, the hydrogeological context allows huge groundwater drainage towards the sea, estimated in flow rates of about 3-4 m^3/s and confirmed by the presence of several small submarine springs.

4. Materials and Methods

The monitoring activities were conducted from 2016 to 2018. 73 groundwater samples were collected from 2 karst springs and 2 wells, extensively used for drinking purposes (Table 1). Descriptive statistics of the analysed parameters in water samples are reported in Table 2. The Mazzoccolo (28 samples) and Capodacqua di Spigno (27 samples) springs have been monitored monthly from January 2016 to January 2018. The Tulliola well was realized in July 2017; for this reason, water samples have been collected monthly only from August 2017 to December 2017 (16 samples). In fact, during this period, the well has been used at increasing flow rates to monitor the effects of groundwater exploitation on the karst coastal aquifer quality (Table 3). The Terenzia well has been completed in June 2018, and the related water samples have been collected during a slug test made in July 2018 (2 samples). As regards chemical analyses, bicarbonate was determined in the lab by titration with 0.1 N HCl. The chemical composition was determined using standard analytical methods [39]. All the analyses of major cations and anions were carried out by the laboratory of the local water supply agency, using a Dionex

Table 2: Descriptive statics of analysed parameters in the groundwater samples.

Sample codes	Parameters	EC (μS/cm)	Na^+ (mg/l)	K^+ (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Cl^- (mg/l)	SO_4^{2+} (mg/l)	HCO_3^- (mg/l)
TUL	Minimum	607.00	16.70	0.30	62.90	9.80	42.80	27.20	244.00
	Maximum	858.00	36.70	12.40	120.60	17.80	137.30	32.30	475.80
	Mean	728.13	26.44	2.08	95.57	13.94	78.14	29.98	371.34
	STD	87.83	6.57	2.85	17.49	2.29	37.64	1.21	70.01
TER	Minimum	1102.00	55.00	1.40	133.30	32.90	196.00	69.20	573.40
	Maximum	1146.00	58.00	2.00	140.10	34.10	218.30	69.60	597.80
	Mean	1124.00	56.50	1.70	136.70	33.50	207.15	69.40	585.60
	STD	31.11	2.12	0.42	4.81	0.85	15.77	0.28	17.25
MAZ	Minimum	280.00	2.10	0.10	31.10	1.00	6.60	2.90	97.60
	Maximum	313.00	5.10	8.20	59.40	11.90	11.80	4.30	244.00
	Mean	302.50	3.91	0.95	48.55	7.48	8.08	3.56	185.61
	STD	6.89	0.89	1.68	7.14	2.60	1.26	0.36	30.50
CAP	Minimum	258.00	2.00	0.10	33.60	1.00	5.30	2.50	109.80
	Maximum	325.00	4.20	8.50	59.30	10.00	9.30	3.80	219.60
	Mean	290.89	3.34	0.82	47.52	7.22	6.75	3.13	181.19
	STD	17.71	0.65	1.58	7.71	2.59	1.15	0.34	28.45

TUL: Tulliola well; TER: Terenzia well; MAZ: Mazzoccolo Spring; CAP: Capodacqua di Spigno Spring.

Table 3: Average flow rates and cumulated water volumes exploited in the Tulliola well.

Date	$Q_{average}$ (l/s)	V_{cum} (m^3)
September 2017*	17.00	22032
October 2017	36.68	98246
November 2017	37.74	97822
December 2017	36.96	98997

*Exploitation start date: 18/09/2017.

ICS-1000 Ion Chromatograph, calibrated through repeated analysis of five working cation and anion standards, with concentrations within the range of analyses.

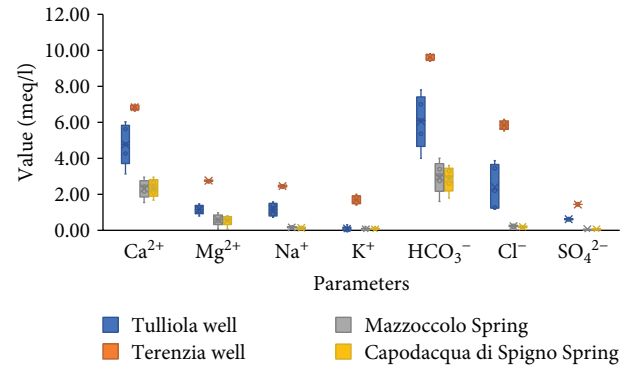

Figure 5: Boxplot of the major composition in the spring and well water samples.

5. Results and Discussion

5.1. Hydrogeochemical Facies. Results coming from analyses show that the Mazzoccolo and Capodacqua di Spigno spring water samples are characterized by a cationic composition mainly dominated by Ca^{2+} and Mg^{2+}, with the abundance order of $Ca^{2+} > Mg^{2+} > Na^+$ (meq/l). This water composition reflects the geological nature of the hydrogeological basins to which both springs refer. The Tulliola and Terenzia well water samples are more mineralized, with the abundance order of $Ca^{2+} > Mg^{2+} \approx Na^+$ (meq/l) (Figure 5). The anionic composition order is $HCO_3^- > Cl^- > SO_4^{2-}$ (in meq/l), suggesting the potentially different nature of the groundwater and related flow paths. A high variability between minimum and maximum values is specific for the Tulliola well (Figure 5). As shown in Table 2, the electrical conductivity (EC) of the Mazzoccolo and Capodacqua di Spigno springs ranges between 280 μS/cm and 313 μS/cm and between 258 μS/cm and 325 μS/cm, respectively. The lowest value of EC was recorded for both springs in April 2017, at the end of the rainy season. The EC values of the Tulliola well water range between 607 μS/cm and 858 μS/cm, respectively, at the beginning and at the end of the water withdrawal, whereas the Terenzia well shows a higher EC value, beyond the value of 1100 μS/cm.

In Figure 6, the Cl^- concentration in the Tulliola well water samples is represented, with respect to the operating flow rates from September 2017 to December 2017. The comparison between the increase of the Cl^- content and the total water volume extracted from the well, starting from 18th September, clearly highlights the flow rate influence on groundwater quality changes (Figure 6). The Piper diagram [40] shows that Ca^{2+} and HCO_3^- are the dominant ions in the study area (Figure 7). All spring and well water samples show a Ca-HCO_3 facies, due to the carbonate dissolution process, related to the presence of limestone and dolomitic limestone outcropping in the study area. The Na-Cl water

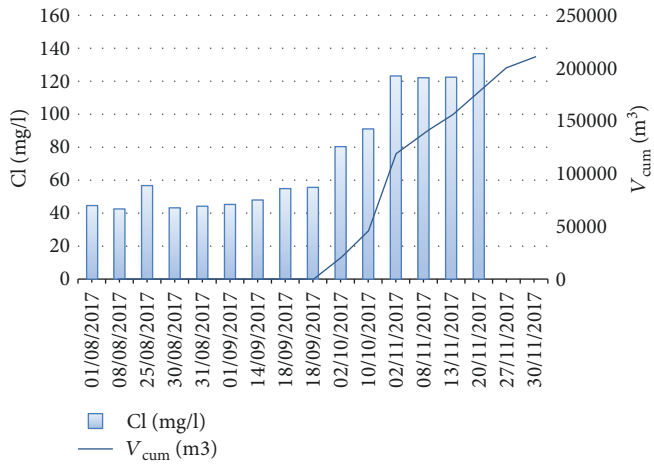

Figure 6: Comparison between the Cl concentration and water cumulated volume of the Tulliola well.

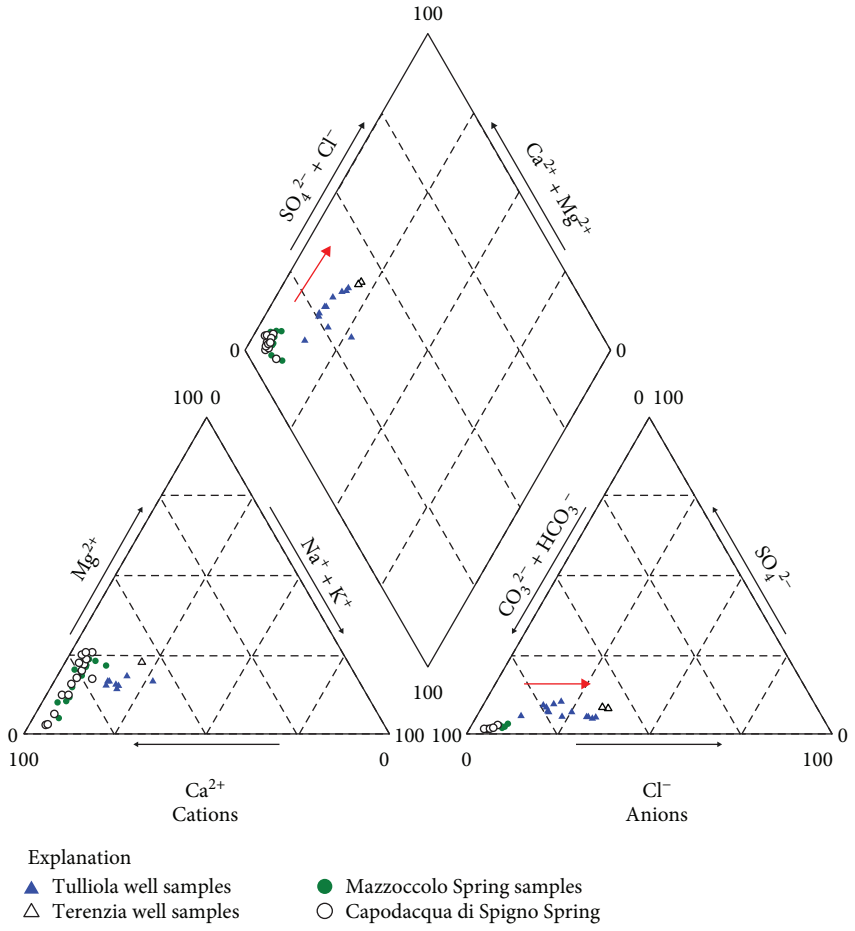

Figure 7: Piper trilinear diagram showing hydrogeochemical facies of the groundwater.

types are majorly present in the coastal aquifers where groundwater salinity is high. The sample distribution in the Piper diagram shows that the wells' groundwater (the Tulliola and Terenzia wells) slightly moves from freshwater (the Mazzoccolo and Capodacqua di Spigno springs) to Na-Cl facies, which represented the saline water type (Figure 5). The different hydrochemical facies between these different water resources may reflect on the higher Cl^- concentrations in the coastal area, due to seawater intrusion. When seawater intrusion occurs, the seawater undergoes chemical changes due to the cation exchange reactions.

5.2. Geochemical Modeling. Groundwater geochemistry is controlled by water-rock interactions [41, 42]. To identify

Table 4: Statistical summary of saturation indices of minerals in groundwater using PHREEQC. BEX index and some ionic ratios of interest in the study area.

Sample codes	Parameters	Calcite	Dolomite	Halite	Na/Cl (meq/l)	Cl/HCO_3 (meq/l)	BEX (*BEX_d)
TUL	Minimum	-0.030	-1.250	-7.690	0.400	0.155	-1.393
	Maximum	0.440	-0.300	-6.880	0.942	0.553	1.083
	Mean	0.203	-0.752	-7.333	0.583	0.353	-0.012
	STD	0.134	0.269	0.306	0.164	0.126	0.810
TER	Minimum	0.450	-0.030	-6.560	0.410	0.588	-2.825*
	Maximum	0.720	0.500	-6.490	0.433	0.628	-2.419*
	Mean	0.585	0.235	-6.525	0.421	0.608	-2.622*
	STD	0.191	0.375	0.049	0.016	0.028	0.287*
MAZ	Minimum	-0.290	-1.770	-9.360	0.450	0.051	-0.028
	Maximum	0.530	0.530	-8.860	1.092	0.118	1.111
	Mean	0.229	-0.661	-9.058	0.751	0.077	0.565
	STD	0.216	0.571	0.142	0.171	0.015	0.250
CAP	Minimum	-0.180	-1.670	-9.490	0.533	0.065	0.047
	Maximum	0.600	0.220	-8.950	1.109	0.553	0.083
	Mean	0.229	-0.714	-9.204	0.772	0.428	0.065
	STD	0.201	0.504	0.137	0.155	0.205	0.010

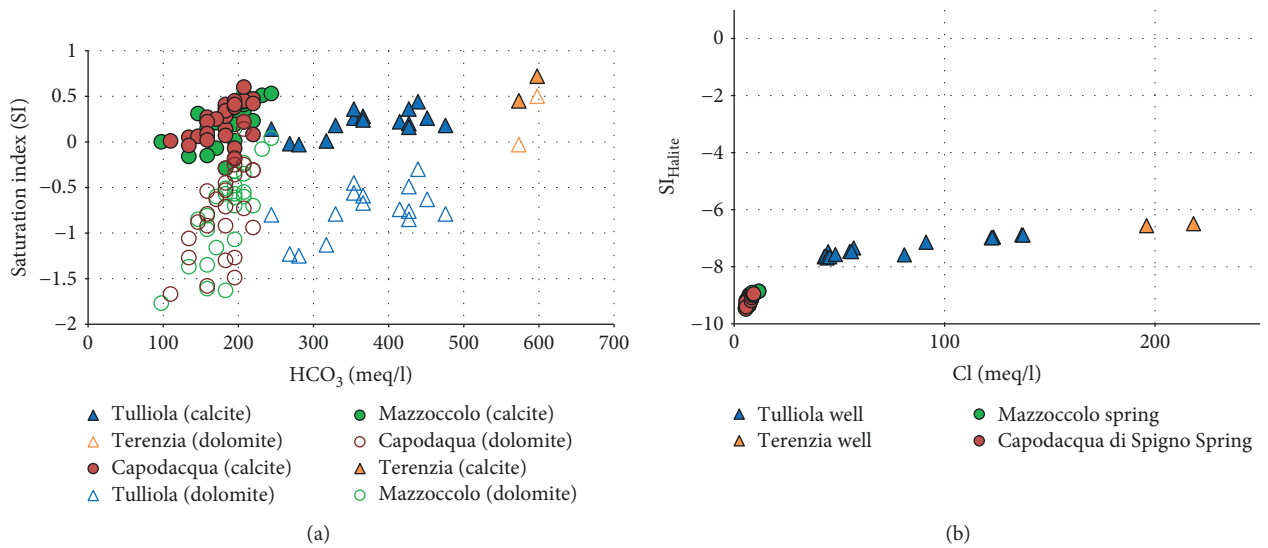

Figure 8: Saturation index (SI) values for the carbonate and evaporite minerals for the spring and well water samples. Calcite and dolomite saturation indices versus HCO_3^- (a); halite saturation index versus Cl^- (b).

these processes, geochemical modeling and the saturation index of spring and well water samples were studied, in order to investigate groundwater interaction with carbonate rocks. The saturation indices (SI) referring to groundwater samples, with respect to different mineral phases (i.e., calcite, dolomite, and halite), were calculated using the geochemical software PHREEQC [43] (Table 4). The positive and negative SI values represent the thermodynamic potential for precipitation and dissolution, respectively. Equilibrium is indicated when SI = 0; the groundwater is supersaturated when SI > 0, which shows that precipitation is needed to achieve equilibrium. If s, the groundwater is undersaturated: this fact indicates that dissolution is required to reach equilibrium. Groundwater saturation with respect to calcite suggests that this carbonate mineral is the main component in the host rock. However, the lower calcite saturation has influenced groundwater chemical composition. All water samples are undersaturated in the halite mineral, indicating that groundwater dissolves most likely the halite along the flow paths, hence leading to an increase of Na^+ and Cl^- concentrations [44].

The results of the geochemical model suggest that more than half of the spring water samples are saturated with respect to calcite and undersaturated with respect to dolomite (Figure 8(a)). The saturation with respect to calcite and dolomite reflects a great dissolution and strong

mineralization along groundwater flow paths. The high dissolution rate for carbonate rocks allows for waters close to saturation with respect to the calcite and dolomite and evaporite mineral halites to remain undersaturated, resulting in continued dissolution along the flow paths. This indicates that the groundwater is able to dissolve gypsum and halite along the flow paths; hence, the concentrations of Ca^{2+}, SO_4^{2+}, Na^+, and Cl^- in the solution would increase.

Spring water has great variability in calcite and dolomite saturation indices. The calcite and dolomite saturation indices of samples coming from both springs present great variability, instead of those related to well water (Figure 8(a)). The Terenzia well water samples are saturated with respect to both calcite and dolomite, whereas the Tulliola well water samples are saturated with calcite and undersaturated with dolomite. The diagram representing the halite saturation index with respect to Cl^- (Figure 8(b)) highlights that all the groundwater samples are undersaturated with halite, with saturation index values that generally show a growing trend related to the increasing concentration of Cl^-. This trend is clear both in the Tulliola well samples, with the flow rates increasing, and in the Terenzia well samples, but not in the groundwater spring samples. The effects of seawater encroachment in the well water have been evaluated studying different ionic ratios and relationships. For example, the Na/Cl ratio values, lower than the seawater value (0.88), generally suggest seawater encroachment [24, 25, 45].

The Na/Cl ratios for the analysed samples range from 0.40 to 0.94 in well water and from 0.45 to 1.11 in spring water (Table 4). For the well water samples, the Na/Cl ratios show a decreasing trend as the Cl^- concentration increases (Figure 9). In the Tulliola well, the Na/Cl ratios clearly decreased along the period of the well exploitation, proportionally to the extracted flow rate, suggesting first evidence of a seawater intrusion in this system as a consequence of the well exploitation. This hypothesis is confirmed by the Na/Cl ratio of the Tulliola water sample, collected before the pumping (01/08/2017), which has a value higher than the Mediterranean seawater ratio (0.88). In spring water samples, the Na/Cl ratios show high variability, which is not related to a Cl^--increasing concentration. The lower values of the Na/Cl ratios in well water samples, with respect to the Mediterranean seawater ratio, are also due to the deficit of Na^+ resulting from the cation exchange process with Ca^{2+} occurring during seawater intrusion [24].

This is quite evident examining Figures 10(a) and 10(b), where Na^+ and Ca^{2+} clearly deviated (respectively, with a negative and a positive trend) from their conservative expected values indicated by the freshwater-saline water mixing line.

The Cl/HCO_3 ionic ratio is useful to characterize the origin of salinity in the groundwater and to classify the rate of seawater intrusion [14, 23, 41]. The Cl/HCO_3 ratio ranges from 0.16 to 0.63 in well water and from 0.05 to 0.55 in spring water (Table 4). According to the classification shown in Figure 11, all groundwater samples fall in the "not affected" field, with higher values for the Terenzia well samples, close to the "slightly affected" one. As regards samples collected in the two springs, they fall far from the line that separates

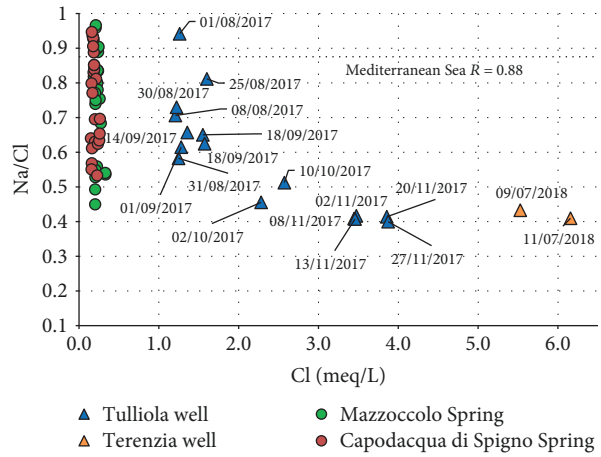

Figure 9: Scatter plot of Cl vs. Na/Cl.

the "not affected" from the "slightly affected" area. It is interesting, however, to note how the samples of the Tulliola well are approaching this line with the progress of time, i.e., with the increase of the flow rate.

5.3. Seawater Intrusion Assessment. The Base Exchange Index (BEX) is frequently used in regional hydrochemical surveys in order to indicate whether an aquifer is salinizing or freshening or it has been freshened or salinized in the past [22]. In this study, the BEX index has been calculated to investigate if well water samples were affected by seawater intrusion.

According to Stuyfzand, using the relation between sodium, potassium, and magnesium to chloride, the process of salinization and freshening of groundwater can be identified with the help of a positive or negative value of the BEX index [46, 47] according to

$$\mathrm{BEX} = \mathrm{Na} + \mathrm{K} + \mathrm{Mg} - 1.0716 \cdot \mathrm{Cl}\,(\mathrm{meq/L}). \quad (1)$$

For dolomitic aquifers, Stuyfzand [46] has suggested another index (BEX_d) which is expressed by the following:

$$\mathrm{BEX_d} = \mathrm{Na} + \mathrm{K} - 0.8768 \cdot \mathrm{Cl}\,(\mathrm{meq/L}). \quad (2)$$

These parameters represent the difference between principal marine cations, which are found in one water sample, and the expected values of these for seawater. The BEX represents the trend of groundwater salinization or freshening: a positive value represents freshening, a negative value indicates salinization, and a value equal zero represents no base exchange [46–48]. The BEX index was calculated according to equation (1) for all groundwater samples, except for the Terenzia well water samples, saturated in the dolomite mineral, for which equation (2) has been applied (Table 4). All spring water values are positive, confirming the absence of seawater intrusion (Figure 12). Tulliola well BEX indices point out a salinization trend ($BEX < 0$) from the half of September 2017, due to the extensive pumping which caused a slight seawater intrusion (Figure 12). The Terenzia well water samples show the most negative value of the BEX_d indices, confirming the seawater intrusion in the study area.

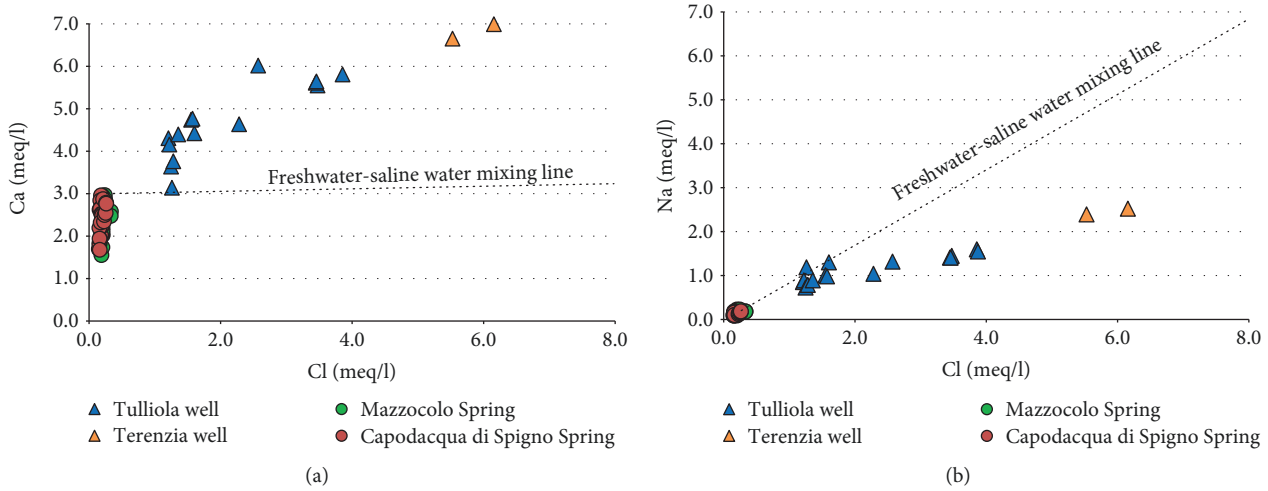

Figure 10: Scatter plot of Cl vs. Ca (a) and Na (b).

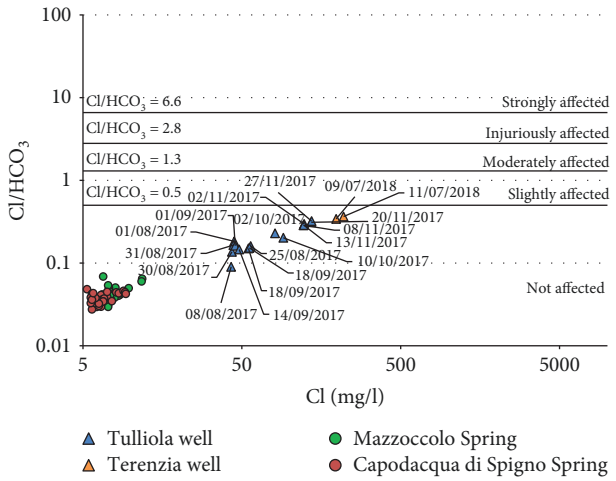

Figure 11: Scatter plot of Cl vs. the Cl/HCO_3 ratio.

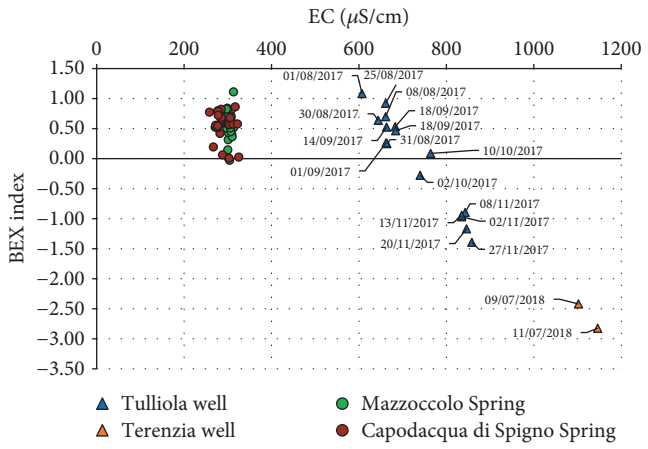

Figure 12: Scatter plot of electrical conductivity (EC) vs. the BEX index.

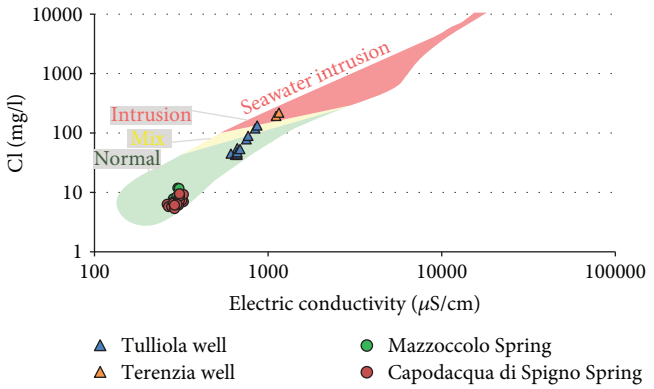

Figure 13: Chloride-EC bivariate plot to define mixing and seawater intrusion (based on Kelly approach, (2006)).

Similar considerations can be made using some graphical representations, specific for groundwater analysis, which allow to better understand the ongoing processes in the aquifer. Figure 13 shows a plot based on the approach outlined by Kelly [27], in which the correlation between chloride concentrations and the electrical conductivity of groundwater samples collected is represented.

All groundwater samples, collected in the Mazzoccolo and Capodacqua di Spigno springs, fall in the green area, which delimits the "normal" conditions, showing no trend related to the sampling date. On the contrary, for groundwater samples collected in the Tulliola well, the proportional increase of both values suggest a slight seawater intrusion in the area. In particular, water samples collected before the Tulliola well exploitation (August 2017) fall into the green area, whereas those collected during October 2017 and November 2017 fall in the yellow and red areas, respectively, confirming the slightly negative effect of the pumping to groundwater quality. The two water samples collected in the Terenzia well, before and after the slug test, fall into the red area, which defines the "intrusion" conditions.

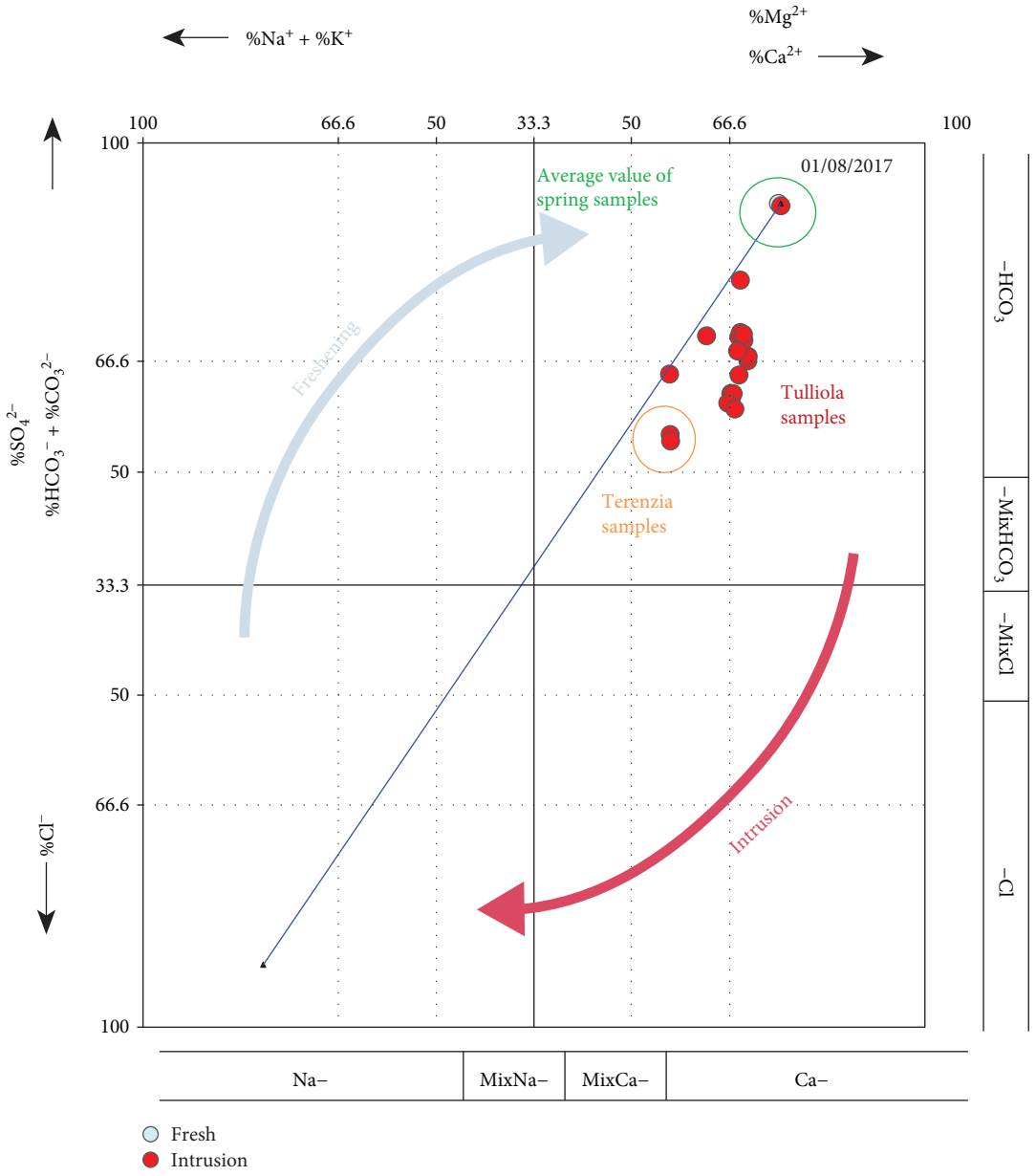

Figure 14: Hydrochemical Facies Evolution Diagram (HFE-D) for groundwater samples.

The negative effect of the pumping to groundwater quality is also confirmed plotting the Hydrochemical Facies Evolution Diagram (HFE-D), proposed by Giménez-Forcada and Sánchez San Román [49]. This diagram has been specifically created in order to better highlight the main processes occurring in coastal aquifers, involving seawater intrusion evolution, through a detailed study of the groundwater hydrochemical facies evolution [49].

The abscissa represents, separately, the percentages of Na^+ and Ca^{2+} in meq/l. In the diagram setup, in order to identify direct and reverse ion exchange reactions, for water samples containing a percentage of Ca^{2+} greater than that of Na^+, only the Ca^{2+} percentage is represented and vice versa. Calcium and sodium percentage values, between 0% and 33%, are not represented with the aim to draw the lines of evolution facies, and Mg^{2+} is not integrated into the diagram due to its irregular behaviour in exchange processes. The ordinates represent the percentage of anions. In particular, the chloride percentage characterizes seawater, and the bicarbonate or sulphate percentage (depending on their dominance in freshwater) characterizes the recharge water.

Freshwater generally corresponds to the heterotopic facies Ca-HCO_3/SO_4, whereas the Na-Cl facies identify saline or seawater. Seawater intrusion is suggested by an early increase in salinity and a reverse exchange of Na-Ca, which is recognized by the characteristic Ca-Cl facies. Finally, this type of water evolves towards facies that are closer to seawater (Na-Cl).

To build up this diagram, an excel macro, courtesy of the same authors [49], was applied. In Figure 14, data

related to the Tulliola and Terenzia well water samples are represented in the Hydrochemical Facies Evolution Diagram (HFE-D).

The blue line represents the binary mixing of freshwater with seawater. Data, coming from collected water samples, appear on the right and beneath the mixing line, falling in the field of Mg-Ca-HCO_3 facies (Figure 14). In order to investigate the possible seawater intrusion into the "25 Ponti" area, a single point, given by the mean values of all spring water samples, was added to the HFE-D. This point (blue colour) represents groundwater not affected by saline intrusion (i.e., freshwater), but in the plot, it is not easily recognizable due to the closeness to the Tulliola well sample collected in 01/08/2017. This evidence confirms that, before the pumping, the Tulliola well groundwater chemical characteristics were similar to the spring water characteristics. The other water samples collected in the Tulliola well during August 2018 fall along the mixing line. On the contrary, the rest of the Tulliola water samples show a tendency toward Ca-MixHCO_3 composition (Figure 14), highlighting an increase in salinity, maybe due to the development of reverse exchange reactions, related with the groundwater exploitation. Water samples collected in the Terenzia well are plotted below the mixing line, closer than those of the Tulliola well, suggesting a more mineralized water.

6. Conclusions

Results coming from a groundwater quality assessment, carried out in the karst coastal region of the West Aurunci Mountains (Central Italy), have been presented here, as these karst carbonate aquifers well represent some typical hydrogeological frameworks in the southern part of the Latium Region.

Groundwater samples, collected from two springs and two wells, exploited for drinking purposes, were analysed to study the main processes controlling the hydrogeochemical evolution and water quality properties.

The geochemical modeling shows that all groundwater samples belong to the Ca-HCO_3 hydrogeochemical facies, highlighting a different mineralization between spring and well water samples.

The Mazzoccolo and Capodacqua di Spigno springs present similar geochemical characteristics, related to the carbonate dissolution process occurring in the aquifer.

On the contrary, the proximity to the coastline of the "25 Ponti" wellfield and the higher values of EC, Na^+, and Cl^-, measured in well water samples, suggest a potential seawater intrusion phenomenon.

In order to evaluate its severity, ionic ratios, graphical approaches, and specific indices have been used. In the Tulliola well, all the geochemical parameters analysed clearly change over time, proportionally to the flow rate exploited from the well, approaching the values obtained for the Terenzia well samples. In fact, the two water samples collected in the Terenzia well, before and after the slug test, show the highest mineralization most likely related to seawater intrusion.

The results obtained confirm that carbonate coastal aquifers are very vulnerable; therefore, they require continuous and systematic monitoring, in order to achieve a sustainable groundwater exploitation even in times of emergency.

Data Availability

The data used to support the findings of this study have been included within the supplementary information file.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper. The authors' employer is the Department of Civil, Building and Environmental Engineering (DICEA), Sapienza University of Rome.

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Supplementary Materials

Supplementary 1. Supplementary Table 1: analysed parameters in the groundwater samples: Tulliola well (TUL), Terenzia well (TER), Mazzoccolo Spring (MAZ), and Capodacqua di Spigno Spring (CAP). The Mazzoccolo (28 samples) and Capodacqua di Spigno (27 samples) springs have been monitored monthly from January 2016 to January 2018. The Tulliola well water samples have been collected monthly only from August 2017 to December 2017 (16 samples). The Terenzia well water samples have been collected in July 2018 (2 samples). Supplementary 2. Supplementary Table 2: the groundwater sample saturation indices (SI), with respect to different mineral phases (i.e., calcite, dolomite, and halite). The SI were calculated using the geochemical software PHREEQC. *(Supplementary Materials)*

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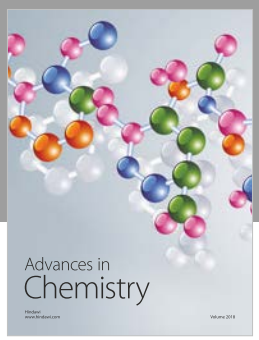

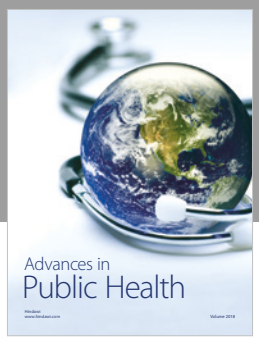

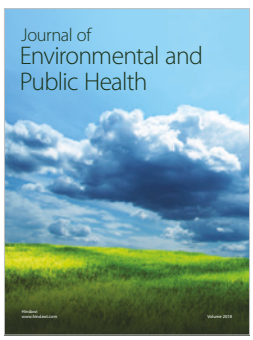

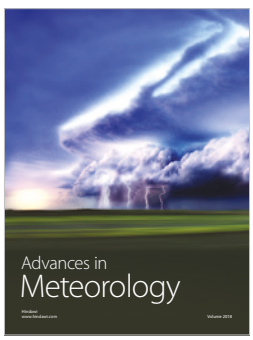

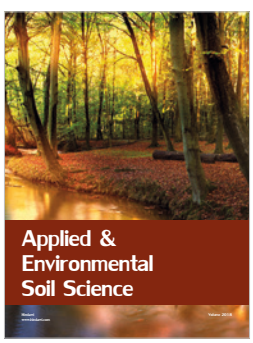

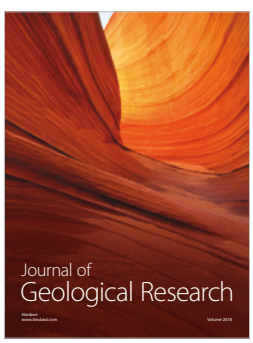

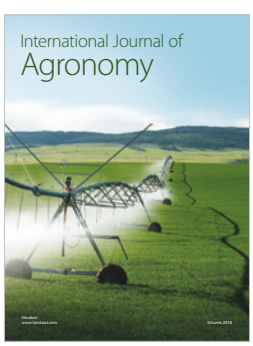

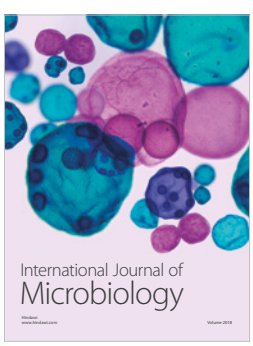

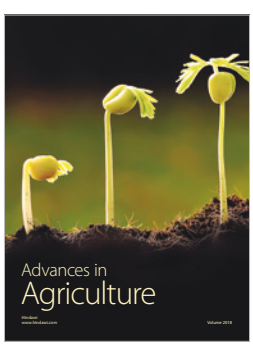

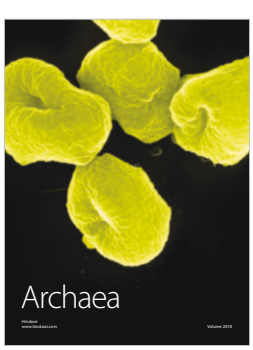

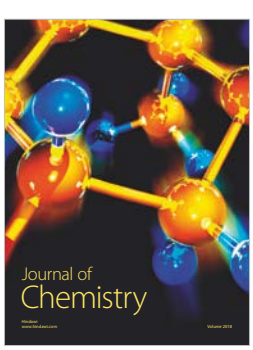

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