

Geochemical evolution of groundwater in carbonate aquifers of southern Latium region, central Italy

Evoluzione geochemica delle acque sotterranee in acquiferi carbonatici del Lazio meridionale, Italia centrale

Giuseppe Sappa, Sibel Ergul, Flavia Ferranti

Riassunto: E' stata analizzata la composizione chimica di numerosi campioni di acque sotterranee provenienti da sorgenti e pozzi, appartenenti ad acquiferi carbonatici del Lazio meridionale, al fine di definire i processi idrogeochimici che governano la evoluzione di queste acque. La maggior parte dei campioni provenienti da scaturigini nei Monti Lepini, Monti Ausoni e Monti Aurunci presenta una composizione HCO_3^- alcalino terrosa, mentre alcuni di essi mostrano una composizione Cl^- - SO_4^{2-} alcalino terrosa. I campioni di acqua sotterranea provenienti dalla Pianura Pontina presentano tre differenti facies: una HCO_3^- alcalino terrosa, una Cl^- - SO_4^{2-} alcalino terrosa ed una Cl^- - SO_4^{2-} alcalina. La modellizzazione geochemica ed il calcolo dell'indice di saturazione dei campioni esaminati, mostrano, in generale, l'interazione con litologie calcaree e calcareo-dolomitiche. La maggioranza dei campioni provenienti dalle sorgenti e dai pozzi analizzati è risultata

cineticamente satura rispetto alla calcite ed alla dolomite; e tutti i campioni sono sottosaturi rispetto al gesso. Ciò indica che queste acque sotterranee sono in grado di dissolvere gesso durante il proprio percorso sotterraneo. I valori della conducibilità elettrica e le concentrazioni in Cl^- delle acque campionate mostrano un incremento con la diminuzione della distanza dalla costa dei punti di campionamento, evidenziando così un progressivo avanzamento dell'intrusione salina. In base ai risultati delle analisi chimiche ed alla modellizzazione geochemica condotta, i fattori che governano le proprietà idrogeochimiche delle acque sotterranee esaminate sono: (i) interazione con rocce calcareo-dolomitiche; (ii) intrusione marina nelle aree costiere; (iii) dissoluzione e/o precipitazione di carbonati (calcite e dolomite) e di minerali evaporitici (gesso) determinate dall'indice di saturazione; (iv) processi di degradazione meteorica (elevato rapporto Mg/Ca dovuto all'alterazione della dolomite ricca in Mg).

Parole chiave: idrogeochimica, modellazione idrogeochimica, salinizzazione, carsismo, acquifero

Keywords: hydrochemistry, hydrogeochemical modeling, salinization, karst, aquifer

Giuseppe SAPPA 

Dipartimento di Ingegneria Civile, Edile ed Ambientale,
Sapienza - Università di Roma,
Via Eudossiana, 18, 00186, Rome.
Tel: +39-0644585010 Fax: +39-0644585016
giuseppe.sappa@uniroma1.it

Sibel ERGUL

Dipartimento di Ingegneria Civile, Edile ed Ambientale,
Sapienza - Università di Roma,
Via Eudossiana, 18, 00186, Rome.
Tel: +39-0644585010 Fax: +39-0644585016
ergul.sibel@gmail.com

Flavia FERRANTI

Centro Reatino di ricerche di Ingegneria per la Tutela e la Valorizzazione
dell'Ambiente e del Territorio, Sapienza - Università di Roma,
Via A. M. Ricci, 35 A, 02100 Rieti.
Tel: (+39) 0746 201473 Fax: (+39) 0746 270767
ferrantiflavia@gmail.com

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Abstract: Spring and well water samples, from carbonate aquifers of Latium region, have been characterized to determine the hydrochemical processes governing the evolution of the groundwater. Most of the spring samples, issuing from Lepini, Ausoni and Aurunci Mts., are characterized as alkaline earth HCO_3^- waters, however, some samples show a composition of Cl^- - SO_4^{2-} alkaline earth waters. Groundwater samples from Pontina Plain shows three different hydrochemical facies: alkaline earth HCO_3^- type, Cl^- - SO_4^{2-} alkaline earth type and Cl^- - SO_4^{2-} alkaline type waters. Geochemical modeling and saturation index computation of the sampled waters show an interaction with calcareous and calcareous-dolomitic lithologies. Most of the springs and wells was kinetically saturated with respect to calcite and dolomite, and all the samples were below the equilibrium state with gypsum. This indicates that the groundwater has capacity to dissolve the gypsum along the flow paths. The electrical conductivity and Cl^- concentrations of the sampled waters show a positive trend with the decrease in the distance from the coast, highlighting seawater intrusion in the coastal area. According to hydrochemistry results and geochemical modeling, the dominant factors in controlling the hydrochemical characteristics of groundwater are: (i) water rock interaction with calcareous and calcareous-dolomitic lithologies; (ii) seawater intrusion in the coastal area; (iii) dissolution and/or precipitation of carbonate and (i.e. dolomite and calcite) evaporate minerals (gypsum) determined by saturation indexes; (iv) mineral weathering process; (the high Mg/Ca ratio due to the weathering of Mg-rich dolomite).

Introduction

In southern part of Latium region groundwater in karst aquifers is the principal source of drinking water supply for the communities within this region. Karst aquifers are important natural resources; worldwide, more than one in four people obtain their drinking water from the karst aquifers (Ford and Williams, 1989; Hess and White, 1993). Improved understanding of geochemical processes can contribute to effective management and utilization of groundwater resources by clarifying relations between groundwater quality and aquifer lithology (Azzaz et al., 2008). Locally, many stakeholders have an interest in the groundwater quality of the water from karst aquifers. Despite the importance of groundwater in southern Latium region, little is known about the natural processes or the factors that presently affect the chemical composition of groundwater. The purpose of this study is to characterize spring and well waters, by investigating major ion chemistry, to determine the hydrochemical processes governing the evolution of the groundwater in this area.

Geological and hydrogeological setting

Lepini, Ausoni and Aurunci are three different groups of mountains belonging to the pre-Appennines of Latium: they occupy a well-defined geographic area, called "Volscian mountain range" (Fig 1). The Lepini Mts. are located in the northern part of Pontina Plain and hosts an important karst aquifer. The aquifer in the Lepini massif may be classified as "unconfined with an undefined bottom surface". The Pontina Plain, is a coastal plain developed along an extensional ma-

rine boundary. This Plain is positioned between the Lepini-Ausoni mountains of the Central Appennines and the Tyrrhenian Sea. In Pontina Plain, much of the groundwater comes out in springs near the boundary between the plain, and the carbonate massif, joining a series of streams and canals that drain to the Tyrrhenian Sea. Two aquifers are present in Pontina Plain: one is an unconfined aquifer lying under the Quaternary deposits covering the limestones at the south-western margin of the Lepini complex; the second one is a confined aquifer where the water is discharged from the calcareous aquifer of the Lepini massif and flows to the sea (Sappa and Rossi, 2007). The Ausoni Mts. rise in southern Latium and extend to close to the coastline, starting immediately after the middle Amaseno valley. The Ausoni hydrogeological unit is mainly composed of limestones with interbedded dolomitic limestones. Most of the springs lie along all of its borders but with no sharp separations between their recharge areas. The Aurunci Mts. represent the southeastern part of the Volscian range and are oriented more or less parallel to the Apennine range. The Aurunci Mts. are made of two distinct hydrogeological units: the western Aurunci, belonging to the Ausoni-Aurunci system, and the eastern Aurunci, which is separated from the western ones by a marly-arenaceous flysch complex (Boni, 1975). The Western Aurunci hydrogeological unit consists of dolomitic limestones and dolomites of Jurassic and Cretaceous age. The springs are supplied by groundwater derive from these geological formations. The groundwater is directly discharged into the Liri river through the narrow al-

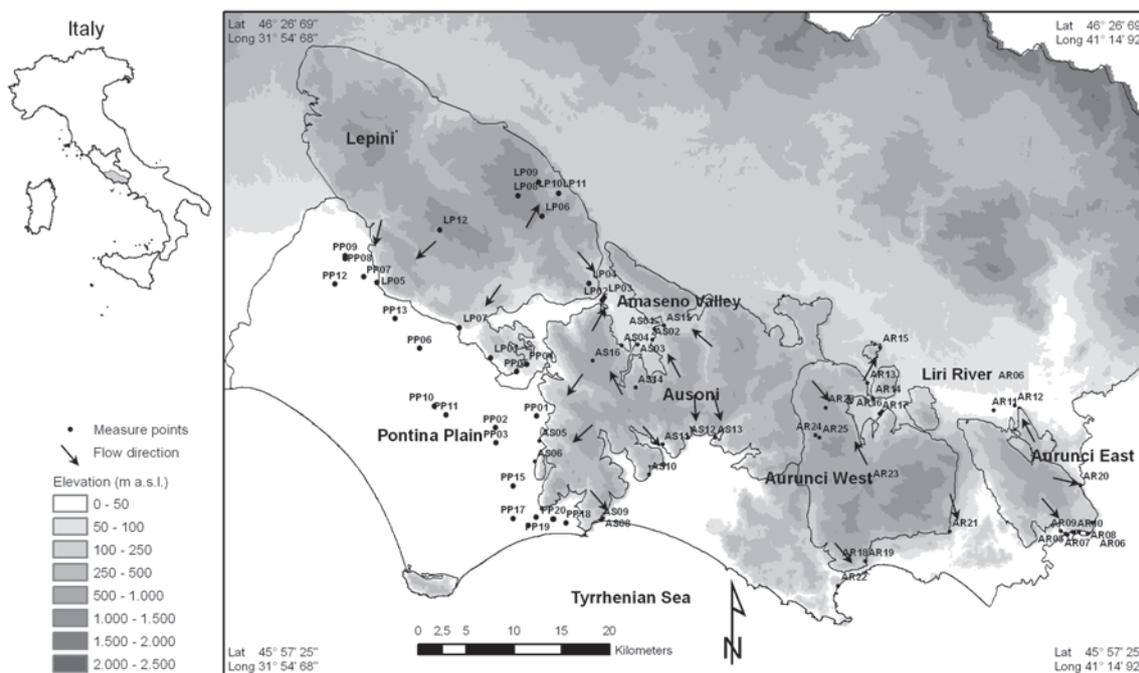


Fig. 1 - Site study area, location of springs and wells and the main directions of groundwater flow paths (LP: Lepini springs, AS: Ausoni springs, AR: Aurunci springs, PP: Pontina Plain).

Fig. 1 - Area di studio, posizionamento dei campioni e principali direzioni del deflusso sotterraneo (LP: Sorgenti Lepini, AS: Sorgenti Ausoni, AR: Sorgenti Aurunci, PP: Pozzi Pianura Pontina).

luvial belt separating the unit from the river. The unit holds multiple hydrogeological basins, whose boundaries match important tectonic lines that caused the outcropping of the calcareous-dolomitic Jura (Accordi et al., 1976). The Eastern Aurunci hydrogeological carbonate structure is surrounded by relatively less-permeable sediments, including the Frosinone flysch, the Roccamonfina volcanites and the Garigliano plain alluvia (Celico, 1978).

Material and Methods

Physico-chemical parameters (such as temperature, electrical conductivity and pH values) of spring and well waters were determined in the field using PC 300 Waterproof Hand-held meter. Bicarbonate content was measured by titration with 0.1 N HCl. Chemical analyses were carried out at the Geochemical Laboratory of Sapienza-University of Rome, using Metrohm 761 Compact IC ion chromatograph (reproducibility $\pm 2\%$). The geochemical PHREEQC software, version 2.10.0.0 (Parkhurst and Appello, 1999), coupled with the thermodynamic dataset wateq4f.dat, was employed to evaluate the saturation status of minerals (i.e. calcite, dolomite and gypsum) in spring and well water samples. The SI (Saturation Index) indicates the potential for chemical equilibrium between water and minerals and the tendency for water-rock interaction (Wen et al., 2008). If undersaturated (Saturation Index < 0), this phase could be dissolved by the groundwater and, thus, could be a potential source of constituents. Similarly, if supersaturated (Saturation Index > 0), that phase feasibly could precipitate, thus limiting the constituent concentrations.

Tab. 1 - Summary statistics of major ion concentrations and physico-chemical parameters of sampled waters.

Tab. 1 - Statistica riassuntiva delle principali concentrazioni ioniche e dei parametri chimico-fisici delle acque campionate.

Sampling Locations		T °C	pH	EC ($\mu\text{s}/\text{cm}$)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	Cl (mg/l)	HCO ₃ ⁻ (mg/l)	SO ₄ ⁻² (mg/l)	TDS (mg/l)
Lepini Springs	Mean	13	7,69	517	64,3	13,7	37,4	2,9	55,4	239,8	16,4	430
	Median	13	7,7	400	67,3	6,6	6,75	1,2	9,6	235,9	4,3	334
	Min	10	6,91	138	15,4	1,4	2,9	0,1	3,9	67,1	1,7	101
	Max	15	8,12	1540	111	44,7	221	15,8	338,4	448	85,4	1264
Ausoni Springs	Mean	13	7,69	826	65,2	18,2	73,5	3,5	128,4	234,2	27,2	550
	Median	12	7,7	404	61,6	9,2	8,6	0,8	13,3	232	5,8	324
	Min	12	6,91	315	41,5	3,8	4,1	0,2	7,5	176,9	3,8	255
	Max	15	8,12	2310	89,2	47,8	293,1	15,4	524,9	305,1	110,9	1320
Aurunci Springs	Mean	12	7,73	545	70,7	25,6	10,6	2,9	12,7	316,5	34,6	479
	Median	12	7,79	429	63,6	9,9	7,6	1,1	9,8	244,1	5,3	338
	Min	3	7,1	311	44,5	1,5	4,2	0,3	4,5	170,9	2,7	245,7
	Max	31	7,98	1217	197,3	93,4	50,5	21,6	46,7	805,5	195,8	1150
Pontina Plain Wells	Mean	15	7,73	1901	124	43,1	232,6	17,7	445	297,2	117,2	1277
	Median	14	7,73	1449	125,6	38,9	58	17,2	397,8	284,5	55,6	970
	Min	12	7,73	412	50,2	15,1	10,3	1,1	9,4	92	6,1	336
	Max	18	8,15	4180	198,1	76,5	705,6	41,5	1220	610	348,7	2790

concentrations of the sampled waters show varieties (Table 1). The electrical conductivity (EC) levels and Cl concentrations of the springs and wells range from 138 to 4180 $\mu\text{S}/\text{cm}$ and 3.9 to 1220 mg/l with the minimum and maximum values, respectively. Generally, the electrical conductivity of most fresh waters ranges from 10 to 1000 $\mu\text{S}/\text{cm}$ but may exceed this value (Chapman, 1992), however high levels of Cl and EC are most simply indicative of seawater intrusion or salinization. Low water levels (above sea level) generally correspond to high Cl concentrations and EC values (Lee and Song, 2007). Figures 3a and 3b show variations in EC levels and Cl concentrations versus discharge elevations of monitored springs and wells. It is clearly seen that the chloride concentrations show a trend of decrease with the increase in discharge elevations. Some groundwater samples from Pontina Plain showed the highest values of SO_4^{2-} -Cl⁻ and Na^+ concentrations according

to the Lepini, Ausoni and Aurunci springs due to their proximity to the coastline (Tab.1). Considering these high concentrations, it is noticeable that the groundwater from Pontina Plain was influenced by seawater in this area. Besides, springs discharges at lower elevations from Lepini and Ausoni Mts. showed also higher concentrations of Na^+ and Cl⁻ concentrations due to their proximity to the coastline and Pontina Plain which is affected by seawater intrusion. Spring samples from Aurunci Mts. show the lowest Na^+ and Cl⁻ concentrations, however they show high Mg, Ca and SO_4 concentrations due to enhanced weathering along groundwater flow paths.

The predominance of Na^+ and Cl⁻ indicates strong saline water impact, thus the effect of seawater intrusion has been evaluated by studying a series of some ionic ratios. Figures 4a and 4b show ratios of Na/Cl and SO_4/Cl versus Cl con-

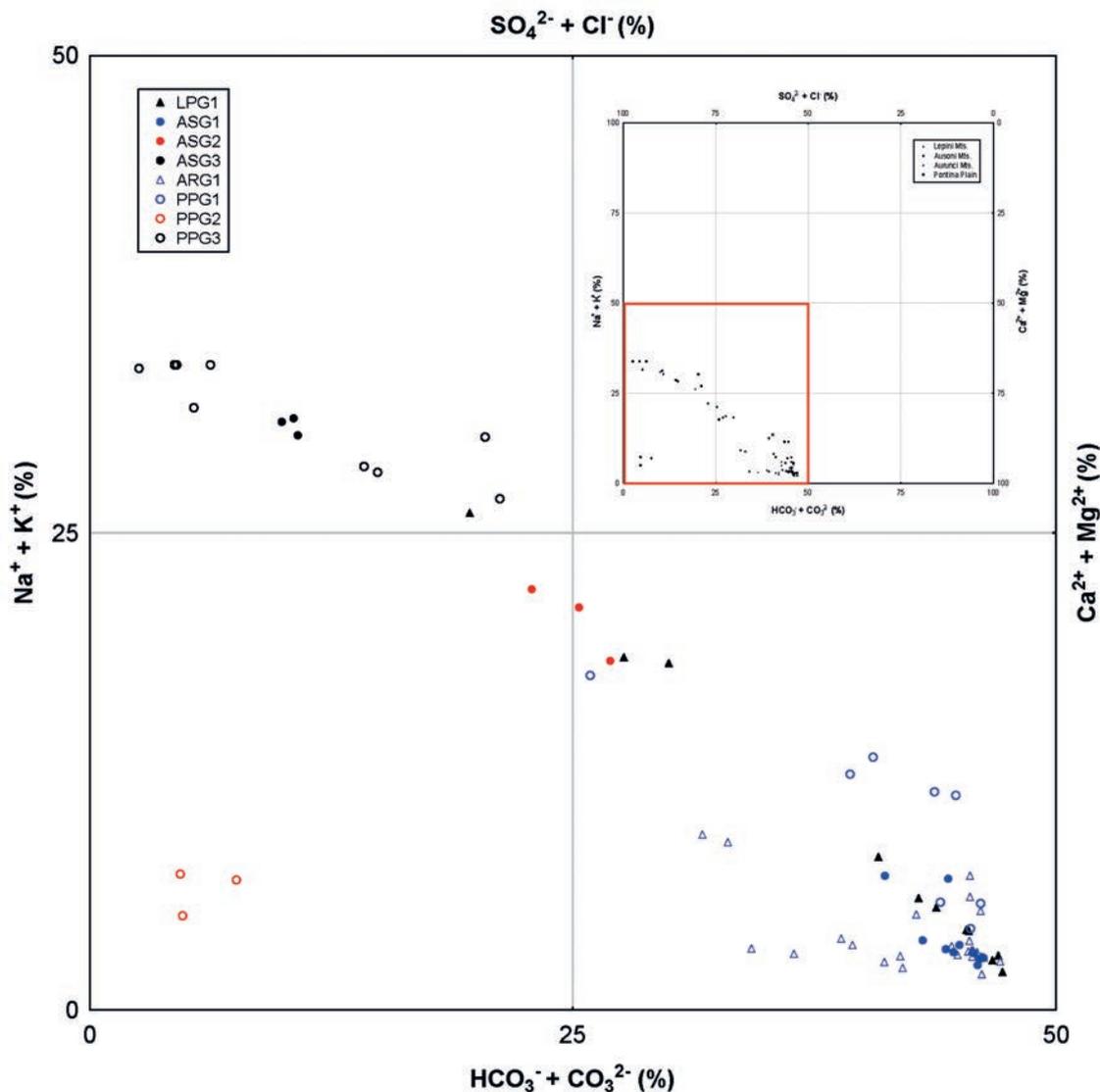


Fig. 2 - Chebotarev plot of major anions and cations of all sampled springs and wells.

Fig. 2 - Diagramma di Chebotarev per i principali anioni e cationi delle acque campionate.

centrations. Both Na^+ and SO_4^{2-} are semi-conservative and, therefore, potentially useful tracers of solute transport. As it can be seen in Figures 4a and 4b the Na/Cl and SO_4/Cl ratios increase with reduced salinity and vary between water types. Changes in these ratios show an overall trend of depletion with increased salinity. Most of the groundwater samples from the carbonate aquifers of the southern Latium region show different Na/Cl ratio. The lower values of this ratio may be attributed to depletion of Na probably caused by cation exchange through clastics (mainly clays and marly limestone). Generally, this process is associated with seawater intrusion in coastal aquifers.

Geochemical Modeling

The results of geochemical modeling suggest that most of the spring samples from Lepini, Ausoni, Aurunci Mts.

and groundwater samples from Pontina Plain are saturated with respect to calcite. Moreover, some samples are saturated or oversaturated both with respect to calcite and dolomite, which implies to a great dissolution and strong mineralization along groundwater flow paths (Fig. 5a). The addition of calcium and bicarbonate gives rises to oversaturation with respect to calcite and its subsequent precipitation. This phenomenon is related to the dissolution of calcareous-dolomitic lithologies and has been described in many carbonate aquifers (Wigley, 1973). More than half of the samples are under saturated with respect to dolomite, while all the sampled waters are undersaturated with respect to gypsum (Fig. 5b). Undersaturation with respect to dolomite indicates that dolomite dissolves in this system adding Ca^{++} , Mg^{++} , and HCO_3^- to the solution. Undersaturation with respect to gypsum indicates that groundwater could feasibly dissolve gypsum and hence,

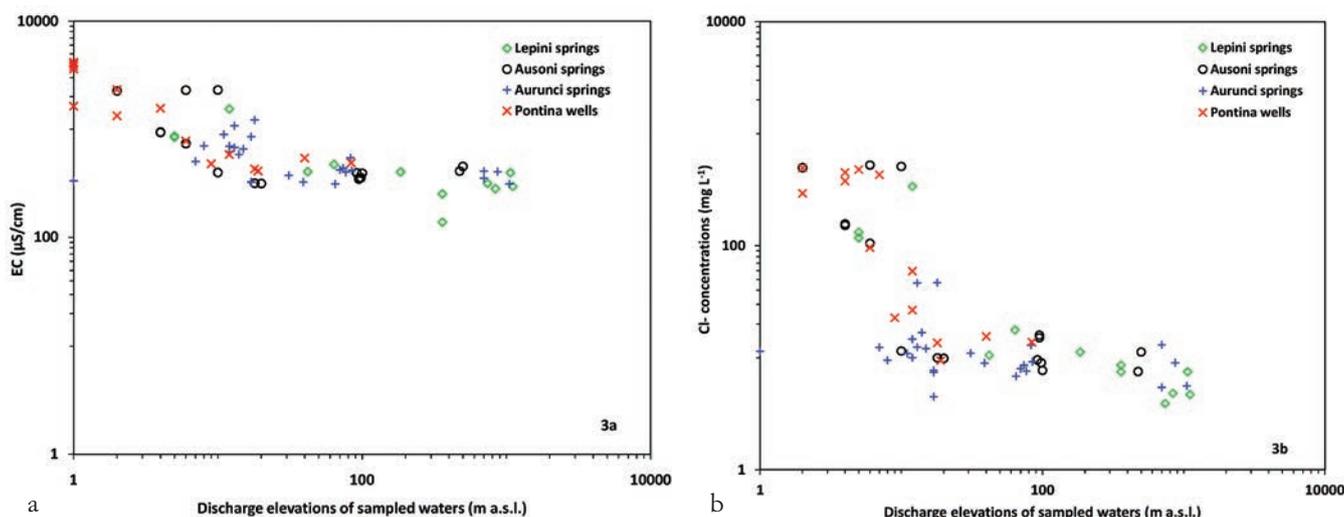


Fig. 3a, b - Levels of EC (a) and chloride (b) versus discharge elevations of sampled waters.

Fig. 3a, b - Livelli di EC (a) e cloro (b) in rapporto alla quota di discarica delle acque campionate.

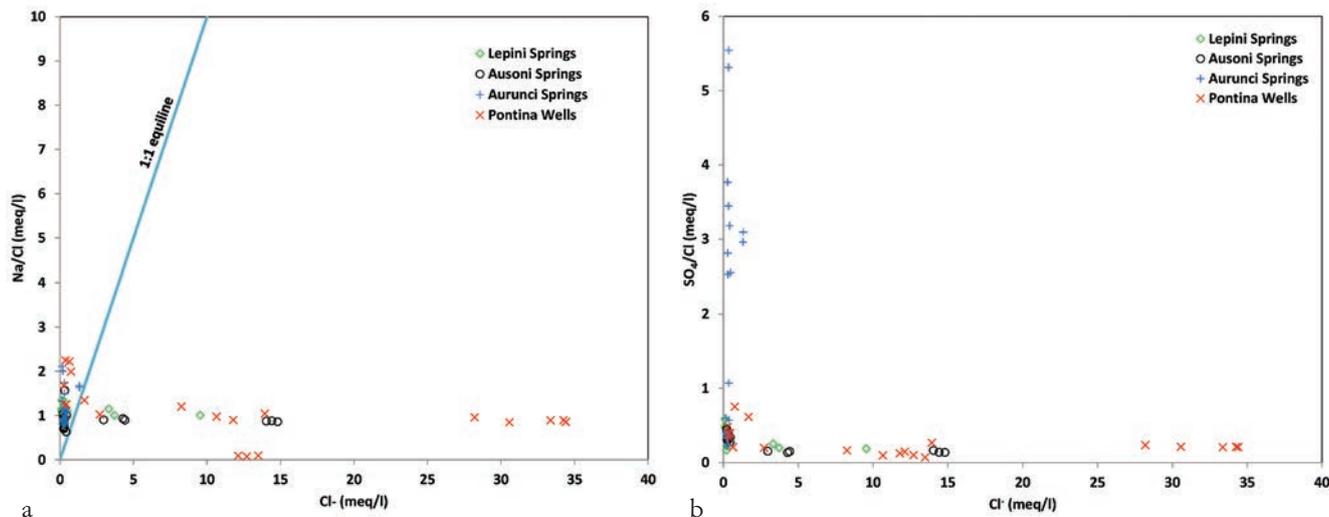


Fig. 4a, b - Ratios of Na/Cl (a) and SO_4/Cl (b) versus Cl^- concentrations.

Fig. 4a, b - Rapporto Na/Cl (a) e SO_4/Cl (b) in relazione alla concentrazione di Cl^- .

the concentrations of Ca^{++} , and SO_4^{--} in the solution would increase (Stumm and Morgan, 1996). A plot of the saturation indexes with respect to gypsum versus $\text{Ca} + \text{SO}_4$ (mg/l) concentrations gives a high correlation coefficient of 0,93, thus the dissolution of gypsum can produce exponential increases in Ca and SO_4 (Fig.5b). Some samples are saturated or oversaturated both with respect to calcite and dolomite, which implies to a great dissolution and strong mineralization along groundwater flow paths.

The low and high concentrations of major ions in the groundwater may probably due to short and long residence times along the flow paths to interact with the host rocks and possible seawater intrusion in the coastal area. Generally, the degree of hydrochemical evolution is largely determined by the residence time of the water within the aquifer, i.e., by the duration of the water-rock interaction. The influence of residence time based on Mg/Ca ratio is commonly used in carbonate aquifers (Langmuir, 1971). This ratio only depends on the dissolution/precipitation reaction of calcite and dolomite, however other dissolution reactions and ion exchanges can also influence the chemistry of groundwater. The Mg/Ca ratios of sampled waters plotted versus HCO_3^- -concentrations (Fig.6). The compositional changes in Mg and Ca concentrations are controlled by the distance from the recharge area. In the study area, springs that emerge at lower discharge elevations (i.e. farther from the recharge area) tend to present higher concentrations of magnesium, and hence show increasing in the Mg/Ca ratio. The increase in magnesium concentrations, probably, related to the kinetics of the dissolution of the dolomite. The highest Mg/Ca ratios (> 1) were found in Aurunci springs highlighting long residence time and flow paths. In Lepini Mts., only LP01, LP05 and LP07 spring samples show high Mg/Ca ratio (0.6). For the spring samples from Ausoni Mts, located near the coast, the Mg/Ca ratio ranges from 0.88 to 0.55. Groundwater samples from Pontina Plain, taken from different depths, are also show high Mg/Ca ratios (up to 0.78).

Conclusions

The preliminary results of chemical characterization of springs, allowed us to advance realistic assumptions about the main processes controlling the evolution of groundwater in the study area. The geochemical characterization of spring and well water samples, from the carbonate aquifers of Southern Latium, show different types of groundwater evolution consisting of modifications of chemical composition because of different water-rock interactions along the flow paths as well as possible manifestation of seawater intrusion. The electrical conductivity (EC) values and Cl^- concentrations of the sampled waters show a trend of increasing with a decreasing trend of discharge altitudes. The dissolution of carbonate rocks allows for waters close to saturation with respect to calcite and dolomite and gypsum to remain undersaturated, resulting in continued dissolution along flow paths; this fact indicates that the groundwater has capacity to dissolve gypsum along the general flow direction adding Ca^{++} and SO_4^{--} . Other geochemical process is the high Ma/Ca ratio. The sam-

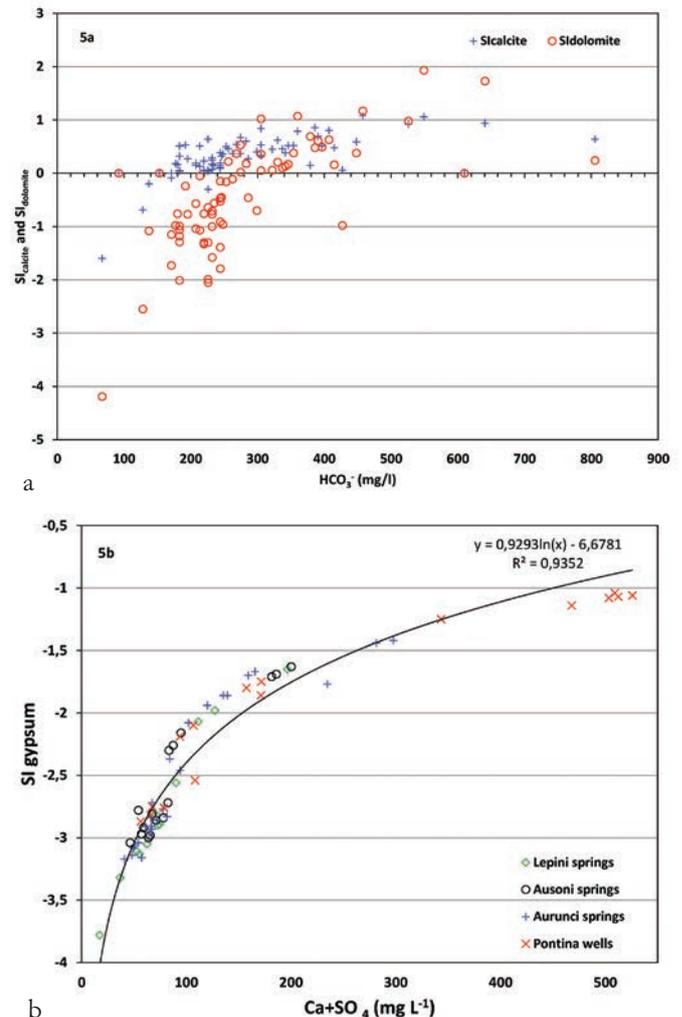


Fig. 5a, b - Saturation indices (S.I.) with respect to calcite, dolomite and gypsum.

Fig. 5a, b - Indice di saturazione (S.I.) rispetto a calcite e dolomite (a) e gesso (b).

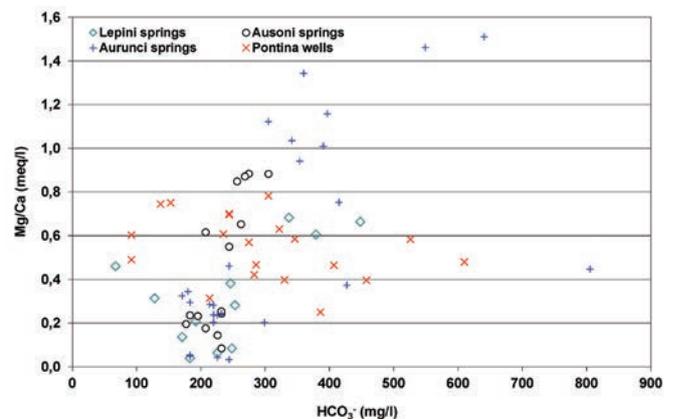


Fig. 6 - Mg/Ca ratios versus HCO_3^- concentrations.

Fig. 6 - Rapporto Mg/Ca in relazione alla concentrazione di HCO_3^- .

ples collected farther from the recharge areas show high Mg/Ca ratio due to the weathering of Mg- rich dolomite, which is common in calcareous and calcareous-dolomitic lithologies. The samples with high Mg/Ca values indicate intense water–rock interaction, reflecting longer residence times in the aquifers and/or deeper hydrogeological flow paths.

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