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Hydrogeological and geochemical overview of the karst aquifers in the Apuan Alps (Northwestern Tuscany, Italy)

Inquadramento idrogeologico e geochimico degli acquiferi carsici nelle Alpi Apuane (Toscana nordoccidentale, Italia)

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Riassunto: Nelle Alpi Apuane (Toscana nordoccidentale), catena montuosa caratterizzata da una notevole complessità geologico-strutturale, sono ubicate numerose sorgenti carsiche contraddistinte da un diverso comportamento idrodinamico in funzione del particolare assetto strutturale dei sistemi acquiferi. Gli acquiferi carbonatici alimentano oltre ottanta sorgenti con valori medi di portata (Q) variabili tra 10 e 1600 L/s e temperature comprese tra 8 e 15 °C. Sono presenti alcune sorgenti termali a bassa temperatura caratteristiche di una circolazione più profonda e con maggiori tempi di residenza in acquifero. Le sorgenti carsiche più importanti (Q > 100 L/s) sono concentrate in due fasce altimetriche, la prima tra 200 e 300 m s.l.m. nel versante marino (SW-NW), la seconda tra 500 e 600 m s.l.m. nel versante interno (NE-SE). La maggior parte delle sorgenti che drenano importanti sistemi carsici, sviluppati in meta-dolomiti e marmi, è contraddistinta da bassi tempi di residenza in acquifero. Alcune sorgenti presentano un regime di portata regolare e sono alimentate da sistemi batifreatici in rocce metamorfiche o da acquiferi carbonatici non metamorfici con un maggior contributo di drenaggio fessurale. Variazioni delle caratteristiche chimico-fisiche delle acque, sia nello spazio sia nel tempo, sono conseguenza dell'eterogeneità litologica, dei processi di mescolamento e delle condizioni idrodinamiche del sistema acquifero. La maggior parte delle acque appartiene alla facies idrochimica a $Ca\text{-}HCO_3$, un minor numero di sorgenti, invece, alle facies a $Ca\text{-}SO_4$, $Na\text{-}Cl/HCO_3$ e $Na/Ca\text{-}Cl/SO_4$. I valori di conducibilità elettrica variano tra 0.1 μS/cm e 10 μS/cm. Inoltre, sono state registrate rilevanti differenze nel segnale isotopico del deflusso di base (es. $\delta^{18}O$ da -5.5 a -8.5‰) dovute ai diversi bacini di alimentazione, alla loro estensione e alla tipologia del versante. In alcuni casi, sorgenti con simile composizione chimica e ubicate nella stessa area, presentano un contenuto isotopico diverso, indicando un sistema di circolazione complesso. Infine sono presenti numerose sorgenti caratterizzate da variazioni stagionali del segnale isotopico.

Parole chiave: acquiferi carsici, flusso delle acque sotterranee, idrogeochimica, Alpi Apuane.

Keywords: *karst aquifers, groundwater flow, hydro-geochemistry, Apuan Alps.*

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Abstract: *Apuan Alps, in north-western Tuscany (Italy), have a very complex geological structure. For this reason karst springs show very different behaviours according to the geological setting of aquifer systems. More than 80 springs are fed by carbonate aquifers; flow rates (Q) range from 10 to 1600 L/s, in average, temperatures range from 8 to 15 °C. Deep and very slow groundwater flow feed some low-thermal springs (20-30 °C). Major karst springs (Q > 100 L/s) are concentrated in two altimetry ranges, one from 200 to 300 m a.s.l. in the seaward side (SW-NW) and a second one from 500 to 600 m a.s.l. on the inner (NE-SE) side of the mountain range. Most of the springs are the final destination of large karst systems developed in meta-dolomite and marbles characterized by a very rapid flow. Some springs have a regular regime and are fed by bathyphreatic systems in metamorphic rocks or by carbonate aquifers with a major contribution of fissured drainage in non-metamorphic rocks. Large physical-chemical variations, both in space and time, are observed as a consequence of lithological heterogeneity, mixing processes and hydrodynamic conditions. Most waters are of the $Ca\text{-}HCO_3$ type, but $Ca\text{-}SO_4$ and Na-Cl facies are also present. A wide range of electrical conductivity is recorded, with values between 0.1 μS/cm and 10 μS/cm. Significant differences in the average isotopic signature (e.g. $\delta^{18}O$ from -5.5 to -8.5‰) of the "base-flow" are registered due to the variability of hydrogeological basins dimension and their distribution in terms of altitude range and side. In some cases, springs with similar chemical features and located close to each other, point out very different isotopes signature, thus highlighting complicated flow path of groundwater. Furthermore, different seasonal evolutions of isotopic signatures are registered.*

Introduction

Mountain aquifers often host important water resources, either for what concerns quantity or for quality of groundwater. This is particularly true for karst aquifers, which often feed large springs that are captured by civil aqueducts. Otherwise the study of this kind of aquifers is difficult, because it cannot be performed using the conceptual models effective for homogeneous aquifers of plain areas. Furthermore, direct investigation and measure of physical and chemical parameters of groundwater are problematic due to the scarcity of wells and often they are restricted to the possibility to sample groundwater in caves. Actually, the study of non-homogeneous aquifers of karst regions can be performed mainly through a middle-long term physical-chemical monitoring of springs.

If springs fed by fissure-porosity aquifers often have all a similar physical-chemical behaviour, usually tuned with seasonal variation of rainfall, springs fed by dissolution-porosity aquifers (karst springs) can display very different dynamics, according to the development and the pattern of karst conduits and to the relationships between vadose and phreatic flow (White, 2002; Ford and Williams, 2007).

Apuan Alps, in north-western Tuscany (Italy), are a very peculiar mountain range. In an area of about 650 km^2 they display very different structural and lithological situations, in particular for what concerns carbonate rocks assemblages. For this reason they offer a wide variety of hydrogeological situations that reflect in many springs with very different hydrodynamic and hydrochemical features. Possibly, it is not a coincidence if one of the first handbook of hydrogeology written in the World, the famous "*Lezione accademica intorno alla origine delle fontane*" of Antonio Vallisneri (1715-1726), was conceived mainly through the observation of springs in this region, where Vallisneri was born more than three centuries ago.

Namely, Apuan Alps offer the possibility to study very different karst aquifers under local climatic conditions that can be considered quite homogeneous and where a single meteorological event can affect aquifers with a different hydrodynamic setting. This brief note represents a first general overview of the hydrogeological and hydro-geochemical characters of Apuan karst aquifers and has the purpose to be a background for future researches.

Geological and hydrogeological setting

Apuan Alps have a very complex geological structure that is the result of the over placing of some tectonic units mainly belonging to the Tuscan Domains. The lower tectonic units are named "Apuane" and "Massa" units and are characterized by a green-schist facies metamorphism dated from 27 to 10 Ma (Kligfield et al. 1986). The both were exhumed during a Late Miocene extensional tectonic phases (Carmignani and Kligfield 1990).

The Apuane Unit consists of a sedimentary sequence overlaying a Hercynian metamorphic basement made up of Ordovician phyllites and porphyric metavolcanics of Early Permian age (Conti et al. 1993). The sedimentary sequence consists mainly of carbonate formations deposited from Carnic to Sinemurian and made of metadolostone, dolomitic marble and marbles (among which the famous "Marmo di Carrara"). Going upward, pelagic sediments consisting of siliceous limestones and radiolarites (Pleinsbachian-Tithonian) occur. At the end of Cretaceous the sedimentation progressively changes to argillites and calcarenites followed by turbidites of Upper Oligocene. The Massa Unit has the same Hercinyan basement of the Apuane Unit, but the sedimentary sequence is limited to Triassic continental facies with some carbonate levels. The Tuscan and Ligurian Nappes overlay the both metamorphic units; the former tectonic unit has a stratigraphic sequence similar to that of the Apuane Unit, with a higher thickness of hemipelagic and turbiditic formations.

Large-scale isoclinal folds, piled one over the other and facing NE, characterize the structural setting of the metamorphic complex, which was involved in an Early-Miocene, syn-metamorphic folding phase (Kligfield et al. 1986). An extensional tectonic phase caused the uplift of the massif along fault systems with NW-SE and NE-SW strikes, which mainly affect the upper non-metamorphic units, whereas the exposed metamorphic complex is not significantly affected by important post-orogeny faulting (Carmignani and Kligfield 1990; Ottria and Molli 2000).

This complex tectonic scenery strongly reflects to the hydrogeological setting and therefore carbonate aquifers display a high variety of situations for what concerns lithology (marble, massive limestone, dolostone, cherty and marly limestones), geometry and pattern of tectonic discontinuities (Fig. 1)

Karst aquifers are usually laterally bordered by low-permeability rocks but allogenic recharge is limited to only

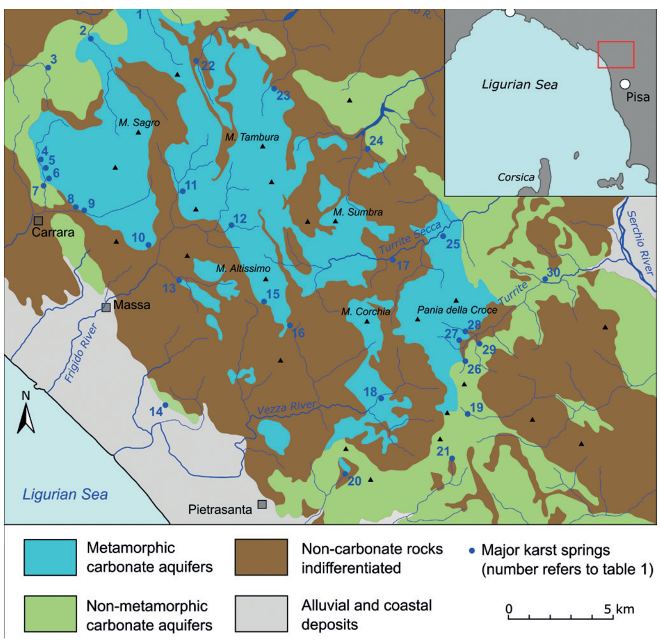

Fig. 1 - Hydrogeological sketch map of the Apuan Alps.

Fig. 1 - Carta idrogeologica schematica delle Alpi Apuane.

Tab. 1 - Major springs of Apuan Alps: Qav = mean discharge, Qmin = minimum discharge, Qmax = maximum discharge, rock type = lithology of aquifer.

Tab. 1 - Principali sorgenti delle Alpi Apuane: Qav = portata media, Qmin = portata minima, Qmax = portata massima, rock type = litologia dell'acquifero.

	Name	Municipality	Elevation m a.sl.	Qav L/s	Qmin L/s	Qmax L/s	Qmin/ Qmax	rock type	Use
1	Equi springs	Fivizzano	257	500	50	15000	0.001	metamorphic	free
2	Lucido springs	Fivizzano	260	230	55	600	0.250	metamorphic	free
3	Tenerano	Fivizzano	490	20	5	50	0.100	non-metamorphic	captured
4	Carbonera	Carrara	255	80	20	150	0.167	metamorphic	captured
5	Gorgoglio	Carrara	170	40	15	170	0.088	metamorphic	captured
6	Tana dei Tufi	Carrara	160	75	3	100	0.040	non-metamorphic	captured
7	Torano spring group	Carrara	185	95	30	110	0.273	metamorphic	captured
8	Ratto springs	Carrara	155	180	140	300	0.348	metamorphic	free
9	Martana springs	Carrara	200	90	72	170	0.424	metamorphic	free
10	Cartaro	Massa	205	400	135	800	0.204	metamorphic	captured
11	Polla di Forno	Massa	230	1600	135	8000	0.019	metamorphic	free
12	Renara	Massa	230	200	30	2300	0.091	metamorphic	free
13	Polla di Altagnana	Massa	305	60	13	180	0.072	metamorphic	free
14	Porta springs	Montignoso	10	110	70	170	0.059	non-metamorphic	free
15	Polla dell'Altissimo	Seravezza	575	60	5	100	0.063	metamorphic	captured
16	Polla del Giardino	Seravezza	400	30	5	80	0.063	metamorphic	captured
17	Pollaccia	Stazzema	545	880	40	6000	0.012	metamorphic	free
18	Fontanacce	Stazzema	176	120	60	500	0.140	metamorphic	free
19	Botronchio	Stazzema	800	50	7	100	0.070	metamorphic	free
20	Mulini di S'Anna	Pietrasanta	330	50	15	150	0.100	metamorphic	captured
21	Grotta all'Onda	Camaiore	635	70	40	260	0.267	metamorphic	captured
22	Tecchiarella	Minucciano	950	30	5	50	0.100	non-metamorphic	captured
23	Fracassata	Minucciano	775	30	15	40	0.375	non-metamorphic	captured
24	Aiarone	Vagli Sotto	575	200	60	350	0.114	metamorphic	free
25	Fontanaccio	Molazzana	430	30	6	400	0.015	metamorphic	free
26	Chiesaccia	Vergemoli	600	150	65	300	0.217	metamorphic	free
27	Tana che Urla	Vergemoli	600	30	1	1500	0.001	metamorphic	free
28	Buca del Tinello	Vergemoli	540	20	2	200	0.010	metamorphic	free
29	Battiferro	Vergemoli	525	40	10	200	0.050	non-metamorphic	free
30	Polla dei Gangheri	Vergemoli	260	300	200	800	0.250	non-metamorphic	captured

some small areas, so recharge is almost entirely provided by local precipitation. Only some minor, marginal aquifers can be drained directly to alluvial and coastal plain deposits (Fig. 1), whereas the large part of underground flow feeds springs that are the main source of surface flow in the lowermost part of streams descending from the Apuan ridge.

Due to the high development of surface and underground karst phenomena (Piccini 1998), the hydrogeological setting of carbonate formations is characterised by a high infiltration rate and by the occurrence of an underground network of conduits draining seepage water quickly to the sources (Piccini et al. 1999; Piccini 2002). These conditions are responsible for a high vulnerability of karst aquifers, which is particularly critical for metamorphic carbonate rocks, due to the absence of retention of pollutants in the epikarst zone and to the rapidity of groundwater flow in the saturated zone (Civita et al. 1991).

Carbonate rocks cover an area of about 170 km^2 and the total discharge of karst springs is roughly 7 m^3/s, the specific discharge is about 0,04 $m^3/s/km^2$, equal to an annual water blade of 1250 mm.

Despite the high topographic gradient of valleys slopes on karst areas, infiltration rate is usually more than 50% of rainfall, which is about 2500 mm in average and exceeds

3000 mm in the most elevated sectors. In these areas, epikarst, that is the upper zone where the fissures have been enlarged by dissolution and are often filled with soils and debris, has the important function of storaging water infiltration in epidermal porosity (White 2002). Below this subsurface zone, we find a vadose zone where the great number of surveyed caves testifies the occurrence of a high permeability and almost exclusively vertical percolation system, distributed in a very irregular way and with flow speeds usually higher than some m/s. Only locally a pervious basement guides the flow pattern of groundwater, whereas a thick phreatic zone often occurs at elevations close to the local base level. In the phreatic zone the water moves according to predominantly horizontal path and is mainly direct to the places where carbonate aquifers reach the lower altitudes.

By examining the metamorphic and non-metamorphic lithological succession of tectonic units, we can identify two main carbonate hydrogeological complexes characterized by high permeability due to fracturing and karst phenomena (Baldacci et al. 1993). The first one is formed by the metamorphic carbonate series consisting of marbles, dolostones and cherty meta-limestones. This complex is the main aquifer of the Apuan Alps and is delimited, at the bottom, by the impermeable rocks of the basement and, at the top, by rocks with a low permeability, especially schists, meta-sandstones and meta-jasper.

The second one is made up of the tectonic breccia (Calcare Cavernoso) interlayed between metamorphic and non-metamorphic tectonic units and of the lower carbonate sequence of Falda Toscana consisting of massive and stratified limestones, locally with shaly layers, and cherty limestones.

A third, but less important, hydrogeological complex is made of a locally thick cherty limestone (Maiolica) that usually forms perched aquifers, separated from the second and underlying hydrogeological complex by an almost continuous level of shaly-marls.

The two major hydrogeological complexes are not always well-separated and groundwater changes are locally and occasionally possible. Anyway the hydrodynamic behaviour of these aquifers is very different and springs fed by each one show dissimilar hydraulic and chemical features.

Karst springs

Springs fed by karst aquifers are several and border the Apuan massif mainly along the western side (Fig. 1) facing the Ligurian sea (Masini 1956, 1960; Piccini 2002). More than 80 springs, with volumetric flow rates (Q) ranging from 10 to 1600 L/s in average, are fed by carbonate aquifers systems with an extension up to 35 km^2.

Water temperatures range from 8 to 15 °C (Tab. 1). In particular, major springs have a temperature significantly lower than that of the emergence site, due to the mean elevation of their catchment areas, which is often around 1000 m a.s.l. and usually embracing the northern sides of the main mountain ridge, where snow persists for about 5-6 months.

Besides, deep and very slow groundwater flow feeds some low-thermal springs, with temperature of 20-30 °C, located along normal faults that delimitate the Apuan Alps on north and east margins.

The most important karst source of the Apuan Alps is the Forno spring, in the Frigido river basin and close to Massa town; its average discharge being 1.6 m^3/s. On the inner side the most important spring is named Pollaccia and has a mean flow rate of about 0.9 m^3/s. Another important spring is located just upstream the Equi Terme village, in the northernmost part of the Apuan Alps, in a small tributary channel of the Lucido creek. This spring has a mean flow rate of about 500 L/s but is characterized by impressive flood with more than 15 m^3/s (Fig. 2). At least a dozen other springs have a discharge between 400 and 100 L/s and many others have a Q more than 10 L/s.

Fig. 2 - An impressive flood at Equi spring. During exceptional events the discharge can exceed 15 m^3/s (photo L. Piccini).

Fig. 2 - Una grossa piena della sorgente di Equi. Durante eventi eccezionali la portata può superare 15 m^3/s (foto L. Piccini)

Almost all largest springs are located close to the geological contact between carbonate aquifers and impervious rock and are fed by water filled dissolution conduits, which in some cases have been explored by cave divers up to 60-100 m of depth. In fact most of the springs are "vauclusian" type sources, mainly located along deep river valleys, which have been incised during Middle-Late Pleistocene (Piccini et al. 2003)

The elevation vs. discharge graph concerning the main springs (Fig. 3) shows a general trend with Q decreasing going upward, as normally happens due to the reduction of catchment areas. Major sources are concentrated in two elevation ranges, the first one is from 200 to 270 m a.s.l. and concerns emergencies located in the seaward basins, the second one is between 540 and 600 m a.s.l. and contains springs located in the inner side (Serchio basin) of the Apuan ridge. This difference is mainly due to the different elevation of low-permeability thresholds, which were affected by a relevant incision in the seaward basins during the tectonic Quaternary uplift, in respect of inner side basins, whose base level was determined by the tectonic evolution of Serchio river (Piccini 1998, 2011). Due to the structural continuity of the largest karst aquifers, this difference in elevation of major sources favours the groundwater to flow toward the sea side basins.

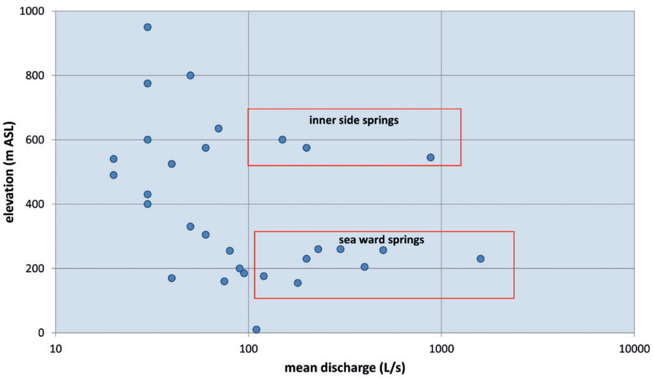

Fig. 3 - Mean flow rate vs. elevation for main karst springs reported in table 1.

Fig. 3 - Relazione tra portata media e quota per le principali sorgenti carsiche elencate in tabella 1.

Major springs (Forno, Pollaccia and Equi springs) have a very high variability of discharges and are the final destination of large karst systems, mainly developed in meta-dolomite and marbles, which are characterized by a very rapid flow and a low contribution of secondary, non-karstic porosity (Fig. 4). These springs are also particularly vulnerable to pollution and during floods they often show a high turbidity due to marble slurry produced by quarry activities (Drysdale et al. 2001).

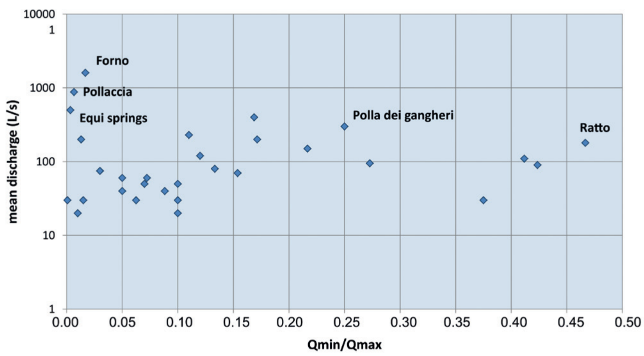

Fig. 4 - Mean flow rate vs. Q_{min}/Q_{max} for the springs of table 1.

Fig. 4 - Relazione tra portata media e rapport Q_{min}/Q_{max} per le sorgenti in tabella 1.

Most of the springs fed by metamorphic aquifers have a very irregular regime, typical of epiphreatic flow systems, and mainly for this reason most of them are not captured for civil use (see table 1 for details). Conversely, some have a more regular regime and are probably fed by aquifers with a deeper drainage due to structural factors (e.g. Ratto and Martana springs that are captured for the aqueduct of the Carrara town). Major springs fed by non-metamorphic aquifers (e.g. Polla dei Gangheri), on the contrary, have a regular behaviour due to a less development of karst conduits and a more relevant contribution of fissure porosity.

Forno spring can be considered as representative of the hydrodynamic behaviour of karst aquifers hosted in metamorphic rocks and characterized by a mainly epiphreatic drainage network. The source is covered by large collapsed blocks and it is not directly investigable, anyway the occurrence of some over-flow caves, just upstream the same valley, indicates that the water flows out from submerged conduits.

The annual hydrograph (Fig. 5) shows a rapid reply to precipitation events, which is typical of a dominant-drainage system (Vigna and Banzato 2015) where phreatic network has a reduced extension and is limited to the lower part of the aquifers close to the source.

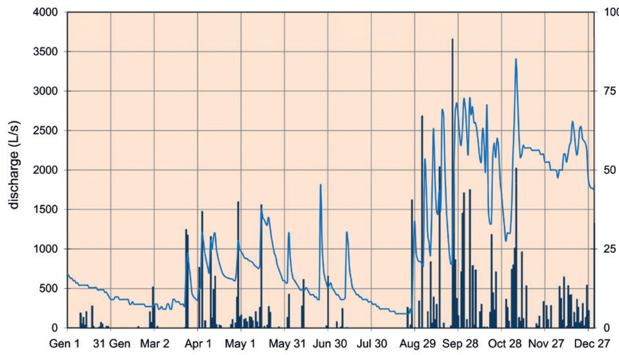

Fig. 5 - Discharge and precipitation (Casania station) diagram during the year 1993 at the Forno spring.

Fig. 5 - Diagramma di portata e precipitazione (stazione di Casania) nell'anno 1993 della sorgente di Forno.

The very rapid reply-time to rainfall events, despite the large extension of its catchment area (about 35 km^2), testifies the high development of a karst conduit network in the epiphreatic zone, and justifies the rapid decrease of discharge only after a few days from relevant precipitation (Fig. 5).

Anyway a detailed analysis of hydrographs during flood events show a complex behaviour, probably due a composite hydrogeological setting, where different sectors of the aquifer are connected through vadose or phreatic conduits. This is explained by the complex geometry of the aquifer feeding the Forno spring, which is distributed on several isoclinal folds separated by discontinuous low-permeability barriers.

Examining the relationships between discharge and electrical conductivity (EC) during flood events (Fig. 6) we can observe first a decrease, due to local infiltration of precipitation, followed by a clear increase when phreatic waters are pushed to flow out by a general rising of the water table surface. Speleological witnesses have described a rising of groundwater level up to 70-80 meters during particularly intense floods. Actually, the reply-time of the spring to the precipitation is often of only some hours and can be justified only if the effect of infiltration is that to increase the hydraulic charge in saturated zone.

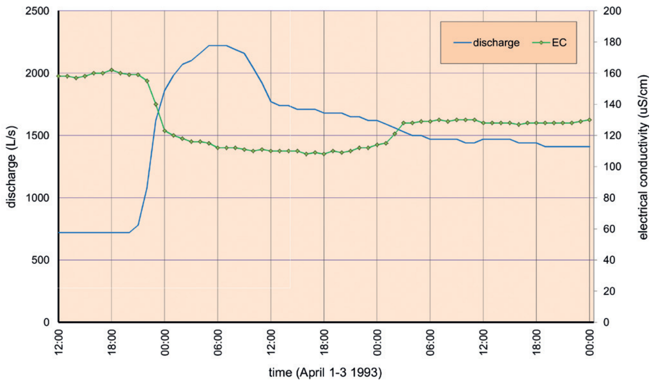

Fig. 6 - Discharge and electrical conductivity during a flood event at the Forno spring (April 1-3 1993).

Fig. 6 - Variazione della portata e della conducibilità elettrica durante un evento di piena alla sorgente di Forno (1-3 aprile 1993).

Geochemical and isotopic features

In the last years some geochemical surveys were performed in the Apuan Alps to investigate all the groundwater systems (Doveri 2000; Doveri 2004; Menichini 2012; Molli et al. 2015). In particular, geochemical and isotopic features of the main karst springs have been compared with those of other minor springs fed by different aquifers in order to characterize the different kinds of groundwater circulation.

In general, the springs show large physical-chemical and isotopic variations, both in space and time, as a consequence of lithological heterogeneity, mixing processes and hydrodynamic conditions. A wide range of EC is recorded, with values mainly in the range 100-1000 μS/cm (at 25°C). For some thermal springs with temperature > 20-30 °C, as Prà di Lama, Acqua Salata, and Acqua Sciocca springs, the EC reach values up to 7000-7500 μS/cm (Fig. 7); these springs are located in the inner side of the Apuan Alps, along some major faults delimiting the Serchio Valley.

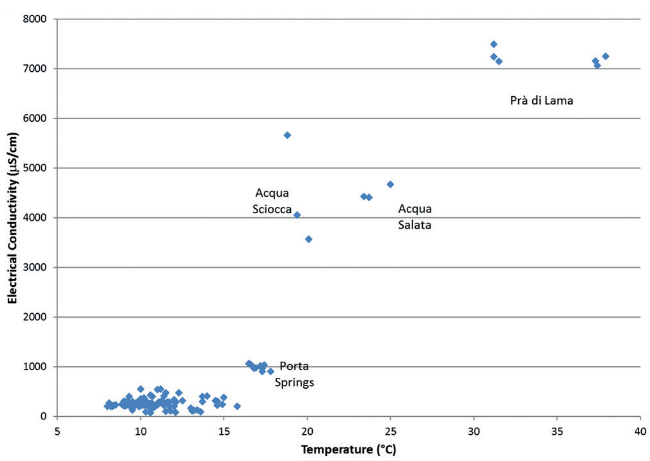

Fig. 7 - Electrical conductivity vs. temperature for some springs of the Apuan Alps.

Fig. 7 - Relazione tra conducibilità elettrica e temperature in alcune sorgenti delle Alpi Apuane.

Based on the major dissolved elements, 4 main chemical facies were identified: Ca-HCO_3, Ca-SO_4, Na-Cl/HCO_3 and Na/Ca-Cl/SO_4 (Fig. 8). The first two highlight the interaction of water with limestone and carbonate-evaporite rocks, respectively, for a time sufficient to acquire these chemical compositions and to achieve saturation/supersaturation in calcite and dolomite. The Na-Cl/HCO_3 groundwater flows out at small springs; such as composition is not very different from that of rainfall, thus indicating a circulation in rocks containing minerals not very reactive and/or a very short interaction time with carbonate rocks, and is typical of non-karstic aquifers. The waters of the Na/Ca-Cl/SO_4 type regard some of the thermal springs located in the inner side of the Apuan Alps, along the Serchio Valley; these chemical features are likely due to groundwater flow paths that interact with the Triassic evaporitic serie of Tuscan Nappe, which includes patches of halite (Molli et al. 2015).

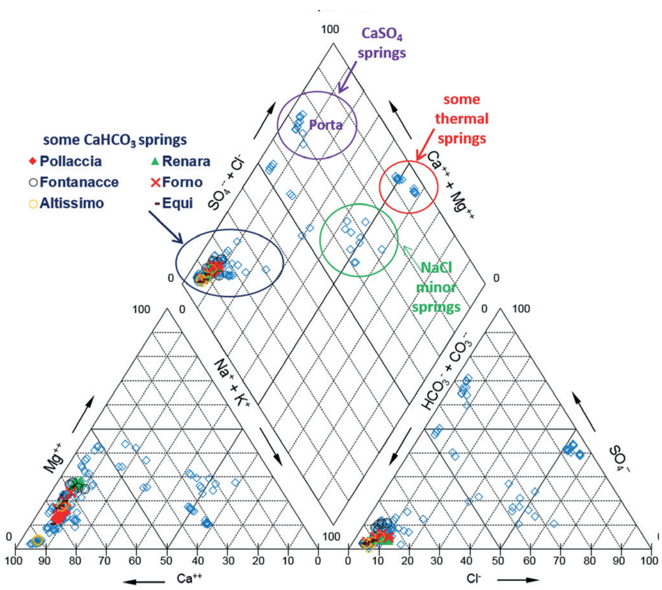

Fig. 8 - Piper diagram (Piper 1944) for some springs of the Apuan Alps.

Fig. 8 - Diagramma di Piper (Piper 1944) per alcune sorgenti delle Alpi Apuane.

Comparing the geological and hydrogeological features with the results of the geochemical characterization, it is reasonable to assume that: i) the Na-Cl/HCO_3 springs with low flow rates are representative of the shallow flow paths that mainly develop within the fracture network of siliceous rocks (e.g. phyllites); ii) the Ca-HCO_3 springs (e.g. Pollaccia, Forno and Equi springs) are representative of relatively deep circuits developed in extensive karst aquifers with high permeability, like Marmi, dolomitic marbles and meta-dolomite (Grezzoni); iii) the Ca-SO_4 springs (e.g. Porta springs) are representative of relatively deep circuits developed in extensive aquifers with high permeability, like carbonate-evaporite rocks; iv) the Na/Ca-Cl/SO_4 springs drain regional and more deep groundwater flow path that interact also with evaporite rocks.

Stable water isotopes data of the springs "base-flow" cover a wide range of values (e.g. $\delta^{18}O$ from about -5.5 to -8.5‰ and $\delta^{2}H$ from about -30 to -55 ‰ – Fig. 9), as a consequence of the variability of hydrogeological basins extension and distribution in terms of average altitude and different side of the Apuan Alps (seaward or inland).

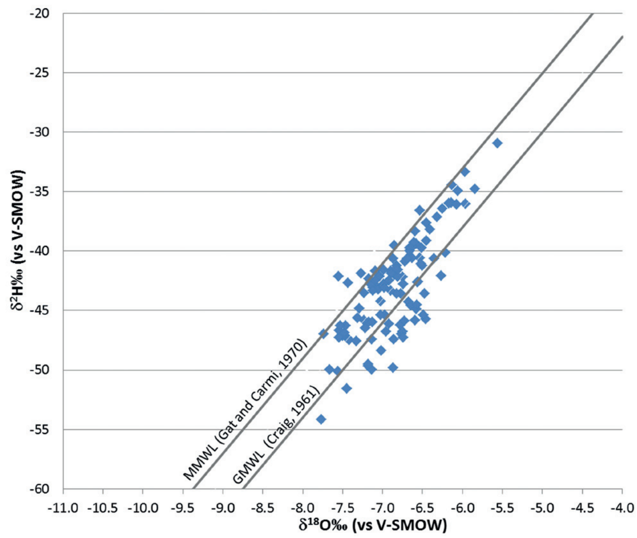

Fig. 9 - $\delta^{18}O$ ‰ vs. $\delta^{2}H$ ‰ for some springs of the Apuan Alps.

Fig. 9 - Diagramma $\delta^{18}O$ ‰ vs. $\delta^{2}H$ ‰ di alcune sorgenti delle Alpi Apuane.

The use of geochemical and isotopic data in karst aquifers, and their comparison with the hydrogeological and structural-geological ones, is also an important tool to obtain information about the hydrodynamic condition in the aquifer, to define the recharge area, and to identify different circulation systems.

In some cases, for example the case of Torano springs (Gorgoglio, Pizzutello, Carbonera, and Tana dei Tufi springs), there are karst sources, with similar chemical features and located close to each other, that point out a very different isotopes signature. The different isotopic signature highlights a very complicated arrangement of the groundwater flow paths and allows us to distinguish two main circulation systems actually separate to each other (Doveri et al. 2013).

Karst springs were sampled and analysed several times in a year in order to test their response to the isotopic variability that characterizes the meteoric waters in different seasons, thus obtaining information about the hydrodynamic conditions within the aquifer.

If we take into account the different behaviour of isotopic signature of two similar springs as regards flow rate regime, as Forno and Torano springs, it is possible to assess that the two aquifer systems are characterized by very different hydrodynamic conditions.

In particular, the Forno spring, like others karst springs of the Apuan Alps carbonate complex, is affected by isotopic variations that characterize the rainfall during the year (Fig. 10a); on the contrary, the base flow of the Torano springs shows a general stability of the $\delta^{18}O$ value over the time, despite the fact that the samplings were carried out in different flow rate conditions with differences higher than 300% (Fig. 10b). This different trend of isotopic values recorded in the two discharge areas pointed out that the circulation for the Forno spring is typical of an unconfined aquifer characterized by a relatively high flow velocity, that allows to maintain the memory of the rainwater isotopic variation in the short-medium term; whereas, the isotopic stability of the Torano springs suggests the existence of favourable conditions for the homogenization of water infiltrated during a period of one or more years (Doveri et al. 2013).

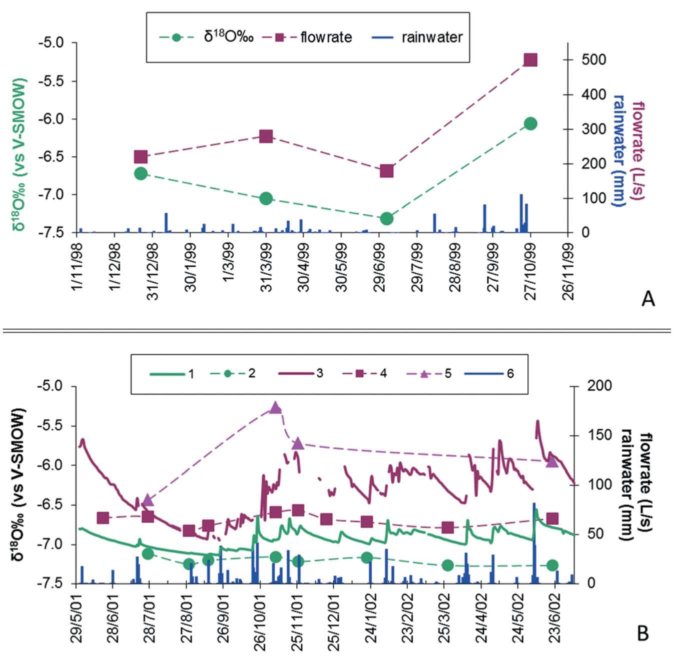

Fig. 10 - a) $\delta^{18}O$ ‰ values and flow rate of the Forno spring compared with daily rain in the November 1998 – November 1999 period (1: $\delta^{18}O$ ‰; 2: flow rate; 3: rain at the Massameasurement station, data of the Ufficio Idrografico of Pisa; modified from Doveri et al.2013).
b) $\delta^{18}O$ ‰ and flow rate of the Torano springs and $\delta^{18}O$ ‰ of the La Piastra stream compared with daily rain in the July 2001 – July 2002 period (1 and 2: respectively flow rate of the Gorgoglio-Pizzutello groundwater system and $\delta^{18}O$ ‰; 3 e 4: respectively flow rate of the Carbonera-Tana dei Tufi groundwater system and $\delta^{18}O$ ‰; 5: $\delta^{18}O$ ‰ of the La Piastra stream; 6: daily rain at the Torano rain-gauge; modified from Doveri et al. 2013).

Fig. 10 - Andamento di $\delta^{18}O$ ‰ e portata della sorgente di Forno in rapporto alle precipitazioni giornaliere nel periodo novembre 1998 – novembre 1999 (1: $\delta^{18}O$ ‰; 2: portata; 3: precipitazioni a Massa, dati dell'Ufficio Idrografico di Pisa; modificato da Doveri et al. 2013).
b) Andamento di $\delta^{18}O$ ‰ e portata della sorgenti presso Torano e del torrente La Piastra in rapporto con le precipitazioni giornaliere nel periodo luglio 2001 – luglio 2002 (1 e 2: portata e $\delta^{18}O$ ‰ del sistema sorgentizio Gorgoglio-Pizzutello rispettivamente; 3 e 4: portata e $\delta^{18}O$ ‰ del Sistema sorgentizio Carbonera-Tana dei Tufi rispettivamente; 5: $\delta^{18}O$ ‰ del torrente La Piastra; 6: precipitazione giornaliera della stazione di Torano; modificato da Doveri et al. 2013).

Conclusion

Apuan Alps aquifers have been studied by several years and they represent a very good opportunity to compare different karst flow systems under similar climate and environmental setting. Actually, in an area of about 650 km^2 they display very different structural and lithological situations in particular for what concerns carbonate rocks assemblages. For this reason, they offer a wide variety of hydrogeological situations that reflect in many springs with very different hydrodynamic and hydrochemical features.

More than 80 springs are fed by carbonate aquifers; flow rates (Q) range from 10 to 1600 L/s, in average. Major sources are the final destination of large karst systems developed in meta-dolostones and marbles and are characterized by a very rapid reply to precipitation events, with flood peaks up to ten times the mean discharge. Some springs have a more regular regime and are fed by deeper phreatic conduits in metamorphic rocks. Springs fed by non-metamorphic carbonate aquifers with a major contribution of fissured drainage have more regular regimes. Some minor springs are fed by perched aquifers and are particularly sensitive to precipitation.

The hydrogeological complexity also affects both the chemistry and isotope features of spring waters. Large physical-chemical variations, different geochemical facies, and significant differences in the average isotopic signature are observed as a consequence of lithological heterogeneity, mixing processes and hydrodynamic conditions. These geochemical and isotopic behaviour indicate different type of hydrodynamic conditions and complicated flow paths of groundwater.

This brief general overview of the hydrogeological and hydro-geochemical characters of Apuan karst aquifers has the objective to emphasize the high variety of hydrogeological conditions, where only a multi-parameter approach, concerning lytho-structural setting, hydrology, physical parameter, chemical features and isotopic geochemistry can allow characterizing a spring and the aquifers that feed it. In short, this region is a sort of natural laboratory where the different models of water circulation in carbonate-karst aquifers can be compared through the analysis of actual cases.

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