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

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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-dolomites and marbles characterized by a very rapid flow. Some springs have a regular regime and are fed by bathypetric 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-HCO₃ type, but Ca-SO₄ 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. δ¹⁸O 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 km² 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 Hercynian 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 allogetic recharge is limited to only...
Tab. 1 - Major springs of Apuan Alps: Qav = mean discharge, Qmin = minimum discharge, Qmax = maximum discharge, rock type = lithology of aquifer.

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

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

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

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 km² and the total discharge of karst springs is roughly 7 m³/s, the specific discharge is about 0.04 m³/s/km², 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 storing 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) interlayered 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 km².

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 m³/s. On the inner side the most important spring is named Pollaccia and has a mean flow rate of about 0.9 m³/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 m³/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 m³/s (photo L. Piccini).](image)

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 “vauccluse” 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.

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).

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.

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 very rapid reply-time to rainfall events, despite the large extension of its catchment area (about 35 km²), 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.
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 $\mu$S/cm (at 25°C). For some thermal springs with temperature $> 20-30 \, ^\circ C$, as Prà di Lama, Acqua Salata, and Acqua Sciocca springs, the EC reach values up to 7000-7500 $\mu$S/cm (Fig. 7); these springs are located in the inner side of the Apuan Alps, along some major faults delimiting the Serchio Valley.

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).

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. δ18O from about -5.5 to -8.5‰ and δ2H 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).

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 Tufo 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 δ18O 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).
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 km² 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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