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# Hydrogeological Characterization of a Geothermal system: the case of the Thermo-mineral area of Mondragone (Campania, Italy)

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**ABSTRACT:** This paper deals with thermo-mineral groundwater of the Mondragone plain (Campania, southern Italy) and the possibility to use this low enthalpy geothermal resource. In the NW sector of this plain, at the bottom of Mt. Pizzuto, near the sea, there are thermo-mineral waters (50 °C) of sodium-chloride type, sulfureous and rich in $CO_2$ whose recharge is from the Mt. Pizzuto groundwater body. In the SE sector of the plain, close to the calcareous Mt. Petrino, a 80 m deep well has intercepted, in the carbonate basement of the plain, thermo-mineral groundwater (33 °C), sulfureous and rich in $CO_2$, as in the NW sector, but displaying a calcium-bicarbonate composition. The chemical and the isotopic analyses allowed to verify that these types of groundwater are due both to meteoric waters infiltration and to enrichment of endogenous $CO_2$ and $H_2S$, at fairly high temperature. In the Petrinum well, the gases involve “connate waters”, affecting upwards the groundwater body of Mt. Petrino. Moreover, the rising of the gases increases the dissolution of the carbonate aquifer, determining very high values of $HCO_3$ ions in the thermo-mineral groundwater. In the case of Mt. Pizzuto, the upwelling gas intercepts also evaporitic formation and, probably, causes saltwater intrusion. The upwelling of the gases occurs along the major fault that crosses NE-SW the plain of Mondragone. Finally, the understanding of the mineralization patterns allowed to identify in the plain the best location for a geothermal exploration well.

**Key words:** Thermo-mineral groundwater, Carbonate rocks, Geothermal energy, Mondragone, Italy

## INTRODUCTION

In the Campania region (southern Italy) there are several, well known, mineral and thermo-mineral springs at the bottom of carbonate aquifers (Lete, Telese spa, Contursi spa etc.) and many studies have pointed out the mechanisms of deep circulation and the origin of the mineralization (Celico *et al.*, 1979; Corniello, 1988; 1994; Baiocchi *et al.*, 2010). One of the most famous thermal spring’s group is located 30 km NW of Naples, in the NW sector of the coastal plain of Mondragone, at the bottom of the Mt. Pizzuto (Fig. 1). The springs there present, well known from the Roman time, when nearby they founded a town called Sinuessa (from which the springs are named), are thermal, Na-Cl type, sulfureous and rich in $CO_2$. In the SE plain sector a well, drilled a few years ago at the foot of Mt. Petrino (Fig. 1), intercepted thermo-mineral groundwater, sulfureous and rich in $CO_2$, as in the NW sector, but of Ca-$HCO_3$ type.

The plain of Mondragone is one of the pilot areas of the Italian VIGOR Project (2012). This project (Evaluation of geothermal potential in the Italian Regions of Convergence), originated from a synergy between the Italian Ministry of Economic Development

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and the Italian Council for Research (CNR), supported the exploitation of low enthalpy geothermal resources of the plain.In the framework of the Project many activities and surveys were conducted (structural-geological survey of the area, analysis of stratigraphic data, electrical tomographies, seismic profiles, chemical and isotopic analysis of groundwater etc.) in order to identify the most suitable site to drill a geothermal exploration well. The study highlights the contribution that the hydrogeological and hydrochemical surveys can give to the understanding the structural patterns that control the different mineralization observed in groundwater of the plain. Furthermore, thermo-mineral groundwater of Mondragone are close to the sea, a widespread situation in Italy (eg Baiocchi *et al.*, 2010; Petrini *et al.*, 2013) as well as in Greece (Lambrakis & Kallergis, 2005), in Turkey (Hatipoglu *et al.*, 2009; Magri *et al.*, 2012), in Syria (Charideh & Rahman, 2007) etc. and could be exposed to the seawater intrusion (Maramathas, 2006; Fleury *et al.*, 2007; Sandford *et al.*, 2007; Polemio *et al.*, 2009; Custodio, 2010). The area of interest includes the coastal plain located SW of the Massico Mountain between Mondragone and the Mts.

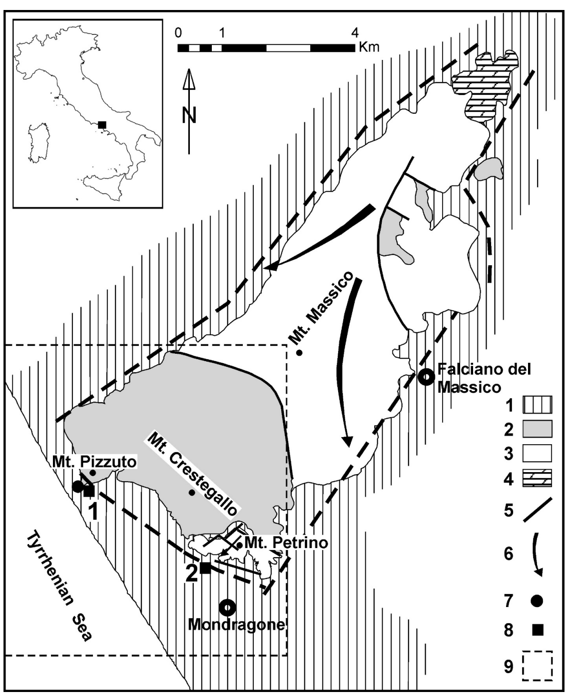


**Fig. 1. Hydrogeological schematic map of the Mt. Massico. 1) Quaternary detritic-pyroclastic-alluvial deposits; 2) Tertiary marly-arenaceous-clayey flysch deposits; 3) Mesozoic limestones; 4) Mesozoic dolomites; 5) main faults; 6) groundwater flow direction in the carbonate aquifer; 7) Sinuessa springs; 8) thermo-mineral wells: 1. Sinuessa spa, 2. Petrinum spa; 9) study area (represented in the next Figures)**

Pizzuto, Crestegallo and Petrino (Fig. 1). The Massico Mountain is a northeast trending horst typified in the eastern and central sector by carbonate rocks ranging from Trias to upper Cretaceous, while the southern sector is characterized by Miocene marly-arenaceous-clayey deposits (Vallario, 1966), which also form the Mts. Pizzuto and Crestegallo (Fig. 1). The Mt. Petrino, which is N of Mondragone town, is calcareous and in tectonic contact with the Miocene deposits above mentioned (Billi *et al.*, 1997). The raised *fault* block is bounded along the margins of the Garigliano (NW) and the Volturno depressions (SE) by NE-SW striking high-angle normal faults whereas southwestern margin is cut by a curved dipping fault that bounds the extensional coastal and probably represents the principal geothermal fault recognized in the area (VIGOR Project, 2012). Locally, near Falciano del Massico, an extensional N-S striking fault determines the contact between the carbonate rocks and the Miocene marly-arenaceous-clayey deposits (Fig. 1). Generally, the faults bounding the horst have a throw estimated at hundreds of meters and they represent the contact between the rocks of the Massico Mountain (Mariani & Prato, 1988; Billi *et al.*, 1997; Bruno *et al.* 2000) and the Quaternary sediments filling the depressions (Corniello *et al.*, 2010; Ducci *et al.*, 2010) constituted by pyroclastic-alluvial deposits caracterized by the presence of a level of grey tuff, the so-called Campanian Ignimbrite (39 ky B.P. to 37 ky B.P.: Deino *et al.*, 1994; De Vivo *et al.*, 2001). These structural boundaries have been clearly identified also by the gravimetric approach using the "enhanced horizontal derivative" (Fedi & Florio, 2001). Several data testify a recent activity of the marginal faults of the Massico Mountain during the Late Pleistocene (Romano *et al.*, 1994; Billi *et al.*, 1997). According to the geomorphological evolution of the Volturno plain between Middle Pleistocene and Holocene times, reconstructed by Romano *et al.* (1994), the tectonic lowering of the Massico Mountain toward SW has been probably active until historical times. This is also pointed out by the discovery of paved roads and harbour structures of Roman age, on the seabed near Mondragone, at a depth between 2 and 20 m below the sea level (Pagano, 1974; Cocco *et al.*, 1994).

From an hydrogeological point of view, the permeability of the Mt. Petrino limestones is high and favors the recharge by rainfalls of the unconfined, groundwater body that feeds, in turn, the deposits of the Mondragone plain through subsurface flow. In spite of this, in the Mondragone plain at the bottom of Mt. Petrino there is only one spring with relatively high flow rate (No. 20 – Tab. 1 and Fig. 2). Close to this spring, a well, drilled some years ago in the Petrinum spa (Fig. 1), intercepted an artesian groundwater, of calcium-bicarbonate type, sulfureous and rich in $CO_2$.

These wells have a depth of about 80 meters and they reach the carbonate bedrock hydrogeologically connected to the Mt. Petrino. As above mentioned, at the bottom of Mt. Pizzuto, where low permeability marly-rich deposits crop out (Allocca *et al.*, 2007), there are several thermo-mineral springs (Sinuessa), of sodium-chloride type, sulfureous and rich in $CO_2$ (temperatures ranging between 30 °C and 45 °C and total discharge of about 1.0 l/s). $CO_2$ degassing and evaporation form thin travertine deposits around the main springs. Near the springs there are also two wells of the Sinuessa Spa with discharging temperatures similar to the natural sources (T ≈43 °C).

## MATERIALS & METHODS

To investigate groundwater origin, the deep groundwater flow and the mixing processes of the termo-mineral waters of the Mondragone plain, all the physico-chemical analyses of the springs already published (Corniello, 1988; Duchi *et al.*, 1995) have been revised. Moreover, groundwater of some wells distributed in the plain of Mondragone (Fig. 2), including the wells of the Sinuessa spa, was monthly monitored from December 2001 to January 2003 for physico-chemical parameters (Cuoco, 2004). Additional data (May 2006) of the Sinuessa springs and wells, and of seawater in the nearby seashore, were also taken from the literature (Cuoco, 2008). In 2012, under the Vigor Project, many of the thermal wells and springs previously analyzed were sampled again also for several isotopic determination. In all the sampling campaigns, the water temperature, pH, Eh, specific electrical conductivity (EC) and alkalinity were measured *in situ*; in particular, alkalinity was determined by titration with 0.1 N HCl acid. All sampling materials were pre-washed using Milli-Q water generated by Milli-Q Plus Water System (Millipore, Bedford, MA, USA) and water samples were stored in PE bottles. Major and minor elements ($Cl^-$. $SO_4^{2-}$, $NO_3^-$, $F^-$, $Br^-$, $Ca^{2+}$, $Mg^{2+}$, $Na^+$ and $K^+$) were analyzed on samples unfiltered and stored at 4°C before analysis. Chloride, sulphate, nitrate, fluoride, bromide, calcium, magnesium, sodium and potassium were analyzed by ion chromatography in the laboratory of the IAMC-CNR of Taranto (Italy). All analyses show a charge balance error of less than 5%. Silica analysis was performed on samples filtered (0.45 μm) and stored in acidified solutions to prevent precipitation. Silica was determined by spettrophotometry. The $\delta\,^{18}O$ and $\delta$ D values were determined by dual inlet mass spectrometer (Finingan) using standard procedures. The analytical and isotopic data produced are shown in Table 1 and in Table 2. Regarding the average monthly temperature in the area and rainfall data, they were provided by the rain gauge network of the Centre for Weather Forecasting and Monitoring of Weather, Rainfall, Water and Landslides (*Civil Protection of the Campania region*) and integrated by the data of the meteorological network of the agricultural Council of the Campania region (http://www.agricoltura.regione.campania.it/meteo/agrometeo.htm).

During the study, five high-resolution electrical tomographies (device used: Wenner-Schlumberger, average depth of investigation: about 180 m), performed in the plain of Mondragone within the VIGOR Project (2012), have been acquired. Also, in the framework of the VIGOR Project, the results of 8 new seismic profiles were examined (recording system: 9 to 24 channels GEODE seismographs equipped with vertical geophones at 10 Hz). The seismic profiles have

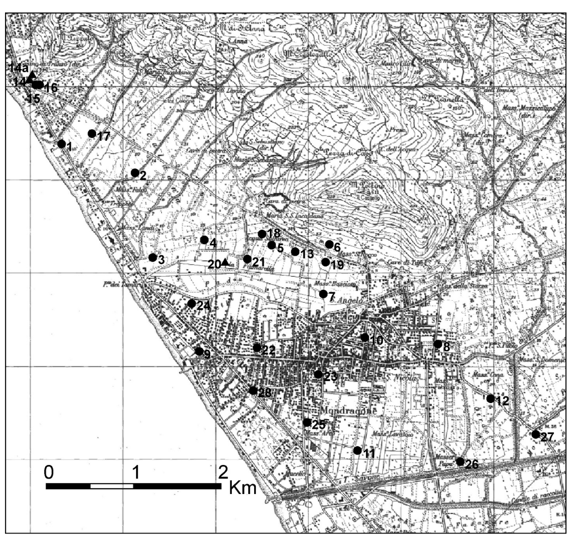


**Fig. 2. Wells (•) and springs (▲) sampled for groundwater physico-chemical (Tab. 1) and isotopic (Tab. 2) analyses**

been acquired with a "multi-fold wide-openness" geometry (Bruno *et al.*, 2010), which allows to process the data in the key of seismic reflection and refraction, as well as to obtain tomographic images. Finally, stratigraphic logs of about 50 boreholes were collected and organized, giving useful contributions to drawing up the hydrogeological map (Fig. 3) and the cross sections of the Mondragone plain (Fig 4). To plot the piezometric surface (Fig. 3), groundwater levels were measured in more than 40 wells; a pumping test (unsteady-state flow) was also performed to evaluate the hydraulic properties of the aquifer (Fig. 3).

## RESULTS & DISCUSSION

Fig. 3 shows the Hydrogeological Map of the area of Mondragone, drawn up on the basis of an *ex novo* structural-geological survey of the area and of several stratigraphic data gathered from private wells. Based

**Table 1. Physico-chemical data of sea water and groundwater sampled in springs (S) and wells; (*) analyses made for the VIGOR Project (2012), (**) from Cuoco, 2004; (***) from Cuoco, 2008; (°) from Duchi *et al.*, 1995. The location is in Fig. 2**

| No. | Well / Spring | pH | T °C | EC µS/cm | $CO_2$ mg/L | $H_2S$ mg/L | $SiO_2$ mg/L | $Na^+$ meq/L | $K^+$ meq/L | $Ca^{++}$ meq/L | $Mg^{++}$ meq/L | $Cl^-$ meq/L | $HCO_3^-$ meq/L | $SO_4^{--}$ meq/L | $Br^-$ mg/L | $F^-$ mg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | *Feb 2012 (*)* | 7,4 | 16,6 | 953 | | | 11,4 | 1,5 | 0,2 | 7,4 | 1,0 | 1,2 | 6,6 | 0,9 | 0,3 | 0,3 |
| **2** | *Feb 2012 (*)* | 7,4 | 16,2 | 890 | | | 11,5 | | | | | | 6,0 | | | |
| | *Feb 2002 (**)* | 7,3 | 16,0 | 730 | | | | 1,3 | 0,1 | 7,6 | 0,7 | 1,2 | 6,5 | 1,0 | 0,1 | 0,8 |
| **3** | *idem* | 7,4 | 15,8 | 1154 | | | 20,5 | | | | | | 6,8 | | | |
| | | 7,1 | 17,6 | 961 | | | | 1,9 | 0,2 | 7,1 | 2,4 | 2,0 | 6,1 | 1,6 | 0,2 | 0,8 |
| **4** | *idem* | 7,4 | 17,6 | 1154 | | | 22,4 | | | | | | 6,8 | | | |
| | | 7,0 | 18,3 | 934 | | | | 1,9 | 0,3 | 6,7 | 3,2 | 1,9 | 8,1 | 1,1 | 0,2 | 0,8 |
| **5** | *idem* | 6,0 | 29,6 | 2175 | | 0,2 | 27,1 | 6,1 | 0,5 | 11,7 | 5,8 | 5,2 | 18,6 | 1,5 | 1,9 | 1,3 |
| | | 6,1 | 22,0 | 2198 | | | | 7,9 | 0,6 | 14,6 | 7,6 | 8,0 | 21,8 | 1,5 | 0,7 | 0,5 |
| **6** | *Feb 2012 (*)* | 7,2 | 19,8 | 1080 | | | 23,3 | 1,9 | 0,3 | 5,5 | 3,0 | 1,7 | 8,2 | 1,0 | 0,9 | 1,1 |
| **7** | *Feb 2012 (*)* | 6,4 | 25,8 | 2081 | | 0,02 | 34,2 | 6,5 | 0,7 | 10,2 | 5,5 | 4,6 | 18,0 | 0,4 | 0,5 | 1,9 |
| | *Feb 2002 (**)* | 6,3 | 23,4 | 2144 | | | | 8,2 | 0,8 | 12,5 | 6,8 | 6,4 | 22,1 | 0,4 | 0,7 | 1,0 |
| **8** | *idem* | 7,1 | 21,0 | 1210 | | | 32,9 | | | | | | 8,9 | | | |
| | | 6,9 | 19,4 | 1056 | | | | 2,3 | 0,3 | 7,6 | 4,1 | 2,3 | 9,8 | 1,4 | 0,2 | 1,0 |
| **9** | *idem* | 7,3 | 20,9 | 1082 | | | 23,1 | | | | | | 7,2 | | | |
| | | 7,0 | 20,1 | 1024 | | | | 2,2 | 0,4 | 8,0 | 2,4 | 2,1 | 8,8 | 1,0 | 0,2 | 0,8 |
| **10** | *idem* | 7,2 | 18,6 | 912 | | | 31,6 | | | | | | 5,8 | | | |
| | | 7,0 | 19,3 | 789 | | | | 1,9 | 0,3 | 5,6 | 1,5 | 1,7 | 5,3 | 1,2 | 0,1 | 1,2 |
| **11** | *idem* | 6,9 | 20,4 | 1260 | | | 34,2 | | | | | | 9,0 | | | |
| | | 7,0 | 17,9 | 1131 | | | | 2,5 | 0,4 | 7,4 | 4,6 | 2,8 | 10,1 | 1,8 | 0,3 | 1,0 |
| **12** | *Feb 2012 (*)* | 7,2 | 20,8 | 1017 | | | 26,5 | | | | | | 7,6 | | | |
| **13** | *Mar_2012 (*)* | 6,5 | 33,0 | 5360 | 570 | 15 | 20,6 | 20,8 | 1,1 | 23,9 | 13,5 | 20,5 | 42,0 | 2,3 | 3,5 | 2,9 |
| | *Jun 2002 (**)* | | | | | | | 17,9 | 1,0 | 24,2 | 13,5 | 19,7 | 36,9 | 1,8 | | |
| **14** | *Feb 2012 (*) S* | 6,5 | | 5650 | | 70 | 28,3 | 27,4 | 1,7 | 27,5 | 7,2 | 26,5 | 23,6 | 11,5 | 2,2 | 2,8 |
| **14a** | *Feb 2012 (*) S* | 6,4 | | 5730 | 320 | | 32,2 | 28,7 | 1,8 | 25,5 | 7,4 | 27,3 | 22,9 | 12,9 | 4,7 | 0,9 |
| | *Jun 2006 (***) S* | 6,5 | 30,1 | 4565 | | | | 28,1 | 1,8 | 27,9 | 8,3 | 29,6 | 24,6 | 13,7 | 2,8 | 3,2 |
| | *Jun 2006 (***)* | 6,4 | 32,4 | 4249 | | | | 27,6 | 1,7 | 26,7 | 8,3 | 29,8 | 27,2 | 11,2 | 3,5 | 2,7 |
| **15** | *Feb 2002 (**)* | 6,3 | 31,2 | 4908 | | | | 29,4 | 1,7 | 29,3 | 8,7 | 32,2 | 29,3 | 11,5 | 2,8 | 1,2 |
| | *1995 (°)* | 6,6 | 48,0 | | | | | 28,3 | 1,8 | 24,3 | 9,8 | 26,0 | 26,5 | 13,0 | | |
| **16** | *Feb 2012 (*)* | 6,4 | 49,7 | 5840 | | 1,25 | 31,8 | 28,4 | 1,7 | 30,7 | 7,5 | 27,5 | 27,0 | 10,6 | 12,2 | 2,6 |
| **17** | *idem* | 6,9 | 17,9 | 1040 | | | 26,9 | | | | | | 4,2 | | | |
| | | | | | | | | 2,5 | 0,2 | 8,9 | 1,6 | 2,1 | 6,4 | 2,6 | | |
| **18** | *idem* | 7,7 | 14,0 | 1055 | | | 23,8 | | | | | | 5,3 | | | |
| | | | | | | | | 3,5 | 1,2 | 22,8 | 7,0 | 2,1 | 7,1 | 26,7 | | |
| **19** | *idem* | 6,5 | 25,5 | 1740 | | 0,25 | 24,6 | 4,9 | 0,6 | 9,8 | 4,9 | 3,5 | 14,9 | 0,8 | 1,9 | 1,8 |
| | | 6,3 | 25,1 | | | | | 5,0 | 0,6 | 9,7 | 5,3 | 4,3 | 15,5 | 0,8 | | |
| **20** | *Feb 2012 (*) S* | 6,3 | 23,9 | 2754 | | 0,03 | 56,4 | 5,4 | 0,6 | 23,5 | 7,4 | 3,0 | 29,3 | 1,0 | 2,0 | 0,8 |
| | *Feb 2002 (**) S* | 6,3 | 22,2 | 2380 | | | | 6,2 | 0,4 | 19,6 | 7,4 | 3,7 | 28,1 | 1,0 | 0,4 | 0,3 |
| **21** | *idem* | 6,1 | 23,0 | 1488 | | | 46,8 | | | | | | 13,3 | | | |
| | | 6,1 | 21,2 | 1421 | | | | 3,8 | 0,8 | 9,8 | 4,0 | 2,6 | 15,6 | 0,9 | 0,3 | 1,0 |
| **22** | *idem* | 6,8 | | 1404 | | | 36,3 | | | | | | 9,4 | | | |
| | | 6,8 | 19,4 | 1266 | | | | 4,4 | 0,4 | 7,6 | 3,3 | 3,9 | 9,0 | 2,3 | 0,3 | 1,2 |
| **23** | *idem* | 7,3 | 19,4 | 1551 | | | 34,3 | | | | | | 7,8 | | | |
| | | 7,1 | 18,9 | 1542 | | | | 5,5 | 1,1 | 8,1 | 3,1 | 8,1 | 7,6 | 1,1 | 0,2 | 0,8 |
| **24** | *idem* | 6,5 | 23,6 | 3010 | | | 52,1 | | | | | | 25,2 | | | |
| | | 6,4 | 21,5 | 2541 | | | | 10,4 | 0,6 | 17,6 | 8,1 | 9,9 | 24,0 | 1,7 | 0,7 | 0,5 |
| **25** | *idem* | 7,0 | 20,4 | 1433 | | | 38,2 | | | | | | 12,1 | | | |
| | | 7,0 | 17,2 | 1167 | | | | 3,6 | 0,3 | 7,4 | 3,4 | 3,3 | 8,3 | 1,7 | 0,3 | 0,8 |
| **26** | *Feb 2012 (*)* | 6,9 | 21,0 | 960 | | | 28,2 | | | | | | 4,2 | | | |
| | *Feb-Mar 2012 (*)* | 7,1 | 19,4 | 1150 | | | 25,6 | | | | | | 8,9 | | | |
| **27** | *Feb-Mar 2002 (**)* | 6,9 | 19,4 | 1159 | | | | 2,2 | 0,3 | 7,8 | 4,8 | 2,4 | 10,5 | 1,6 | 0,3 | 1,0 |
| **28** | *idem* | 7,2 | | 770 | | | 7,0 | | | | | | 7,4 | | | |
| | | 7,2 | 18,3 | 819 | | | | 1,7 | 0,5 | 6,2 | 2,2 | 1,1 | 8,5 | 0,5 | 0,1 | 0,5 |
| **29** | *Jun 2006 (sea ***)* | | | | | | | 521,8 | 11,7 | 36,4 | 60,0 | 588,2 | 3,0 | 58,1 | | |

**Table 2. Isotopic data of groundwater sampled in springs (S) and wells (analyses made for the VIGOR Project, 2012). The location is in Fig. 2.**

| No. | $\delta^{18}O$ | δD | $^{34}S/S_{tot}$ |
|---|---|---|---|
| | ‰ vs SMOW | | |
| **1** | -5,8 | -36,3 | 11,3 |
| **2** | -5,7 | -35,5 | |
| **3** | -5,8 | -35,1 | |
| **4** | -5,8 | -36,0 | |
| **5** | -6,1 | -38,0 | 15,9 |
| **6** | -6,1 | -35,8 | |
| **7** | -6,4 | -38,9 | |
| **8** | -6,2 | -37,9 | |
| **9** | -5,8 | -35,1 | |
| **10** | -6,0 | -37,1 | |
| **11** | -6,3 | -37,2 | |
| **12** | -5,8 | -35,5 | |
| **13** | -6,1 | -41,2 | 30,3 |
| **14a (S)** | -6,1 | -38,8 | 20,4 |
| **14b (S)** | -6,0 | -40,4 | 19,3 |
| **16** | -6,1 | -39,8 | 21,4 |
| **17** | -5,4 | -32,6 | |
| **18** | -5,6 | -38,9 | |
| **19** | -6,4 | -38,3 | 21,3 |
| **20 (S)** | -6,2 | -38,8 | 20,4 |
| **21** | -6,7 | -42,2 | |
| **22** | -6,1 | -36,7 | |
| **23** | -6,2 | -38,0 | |
| **24** | -6,2 | -38,5 | |
| **25** | -6,4 | -42,4 | |
| **26** | -5,6 | -35,6 | |
| **27** | -6,1 | -35,8 | |
| **28** | -6,7 | -40,6 | |

on these data, the relationship between the different lithologies are outlined in the hydrogeological cross sections of Fig. 4, whose traces are reported in Fig. 3. The stratigraphic data show the presence of a powerful bank of tuff, almost continuous across the plain, belonging to the Campanian Ignimbrite (hereinafter IC) eruption from the Phlegraean Fields Caldera, dating at 39 yr BP, that represents one of the largest late Quaternary volcanic event. This IC, with variable thickness and different degree of welding, has generally low permeability and therefore separates the above pyroclastic-alluvial deposits (often with peat, $C^{14}$ dated 4,69 ± 0.06 and 8.3 ± 0.07 ka; Amato 2006) from the underlying alluvial deposits, deeper and more permeable, making confined this lower aquifer.

The pyroclastic-alluvial deposits of the plain receive groundwater by both lateral and vertical subsurface flows from the carbonate aquifer of Mt. Petrino. This groundwater flow is shown by the piezometric contour lines (Fig. 3) of the alluvial deposits aquifer, located below the IC (Fig. 4). The piezometric pattern shows also a clear drainage area, close to N of Mondragone town, between the foot of Mt. Petrino and the coast line, which corresponds, probably, to a paleo-river bed, subsequently filled by pyroclastic materials. A groundwater divide, near Mondragone, separates this area from the remaining, flowing toward SE. The piezometric head at the bottom of Mt. Petrino is about 6 m a.s.l., while the piezometric head along the SE and the NW borders of the Massico Mountain is about 20 m a.s.l. (Corniello *et al.*, 2010; Ducci *et al.*, 2010). This piezometric difference and the geological setting of Mt. Petrino suggest the hydrogeological separation of Mt. Petrino from the remaining Massico Mountain (Fig. 1). On the other hand, the infiltration at Mt. Petrino (about 1.8 $km^2$) was assessed on the basis of climatic data in the range 25-30 l/s, which is almost equal to the amount of the subsurface flow from the Mt. Petrino aquifer toward the plain, evaluated in about 30 l/s. This value has been obtained applying the Darcy law to the piezometric pattern of the plain and using the transmissivity value of 3.8 x $10^{-3}$ $m^2/s$ obtained from a pumping test performed in unsteady-state flow (Fig. 3). The storage coefficient of 1.7 x $10^{-6}$ has also confirmed the confined conditions of the aquifer.

The groundwater flow from Mt. Pizzuto and Mt. Crestegallo into the plain is likely reduced due to the low permeability of the marly-arenaceous-clayey deposits that constitute these mounts. However, the presence of thermo-mineral groundwater at the foot of Mt. Pizzuto, indicates the existence of a small groundwater body, probably floating on seawater, due to the proximity to the coast. Geophysical data provided additional information about the subsoil stratigraphy of the plain (thickness about 400 m) at depths greater than those crossed by boreholes (max 80 m as peak depth). These data have suggested the presence of several faults affecting the carbonate bedrock; the most significant fault (Fig. 3) crosses the whole plain from NW to SE and is coupled with other sub-parallel tectonic lineaments, as stressed also by the geoelectrical tomography. Table 2 shows isotopic data of waters sampled at wells and springs in 2012, in the framework of the VIGOR Project. The maiority of determinations examines the isotopes D and $^{18}O$ (vs SMOW). The classic δD - $\delta^{18}O$ graph of Fig. 5 shows that all waters are between the line of the meteoric waters of southern Italy (Longinelli & Selmo, 2003) and the Global Meteoric Water Line (Craig, 1963). In addition, the isotopic values of the different samples differ little from the mean value (- 6.1 for $\delta\ ^{18}O$ and - 37.3 for δ D) and that makes insignificant to draw a strictly local meteoric water line, which, in other situations, can provide a useful contribution (e.g. Lihe *et al.*, 2011). These mean values are also very close to the isotopic content (period 3/

1992 - 10/2000) recorded in rainfall at Roccamonfina (Longinelli & Selmo, 2003), not far from the area of interest and with an altitude similar to those of the mounts around the plain of Mondragone. Isotopic data indicate therefore (Clark & Fritz, 1997; Drever, 1997) the meteoric origin of Mondragone thermo-mineral waters and the absence of isotopic exchanges between the fluids and the reservoir rock (probably, waters featuring fast circuits and without very high temperatures).

About the origin of the $CO_2$, that characterizes the thermo-mineral waters of Mondragone, the following considerations can be developed. For $CO_2$ of the Sinuessa springs (No. 14 and No. 14a - Table 1 and Table 2), Panichi & Tongiorgi (1976) and Minissale (2004) reported values of $\delta^{13}C$ (‰ PDB) close to 0, that are typical of an inorganic source of the gas. This source is also confirmed by the value $\delta^{13}C_{PBD}$ (11 ‰), determined for travertines near Sinuessa springs (Ascione *et al.*, 2013). The regional studies of Minissale (2004; Minissale *et al.*, 2002) also indicated the dominant source of $CO_2$ in the metamorphism of deep limestones (Rollinson, 1993), triggered by the intrusion of mantle magmas into the crust. Few years ago, in the Petrinum spa, 150 m far from the foot of Mt. Petrino, was drilled a well with a depht of 80 m that intercepted 40 meters of pyroclastic-alluvial deposits (Fig. 4) overlaying the limestone bedrock, hydraulically connected with Mt. Petrino. Confined groundwater sampled in this bedrock (No. 13 in Fig. 2 and Table 1; P1 in Fig. 4) is at 33 °C, of calcium-bicarbonate type (EC 5360 μS/cm), sulfureous and rich in $CO_2$. The Schoeller-Berkaloff graph of the chemical composition of this water is shown in Fig. 6 (a). It's noteworthy that the water sampled in the well No. 6 (Fig. 2; line b of Fig. 6), drilled on Mt. Petrinum, has, on the contrary, very low salinity (EC 1080 μS/cm, Table 1) and low thermality, although the distance from the Petrinum well is less than 400 meters. Petrinum well does not show seawater intrusion or relationships with evaporites (in fact they have low concentration in $SO_4^{-2}$), also because the $\delta^{34}S$ has a value (Table 2) higher than that characterizing recent marine waters (Clark & Fritz, 1997).

A plausible hypothesis to explain the mineralization in the Petrinum well is the mixing between shallow bicarbonate groundwater (like the well No. 6) and a very small percentage of "connate waters" ("saline formation waters" – Drever, 1997), often intercepted in the deep confined parts of sedimentary aquifers worldwide. The quite low $SO_4^{-2}$

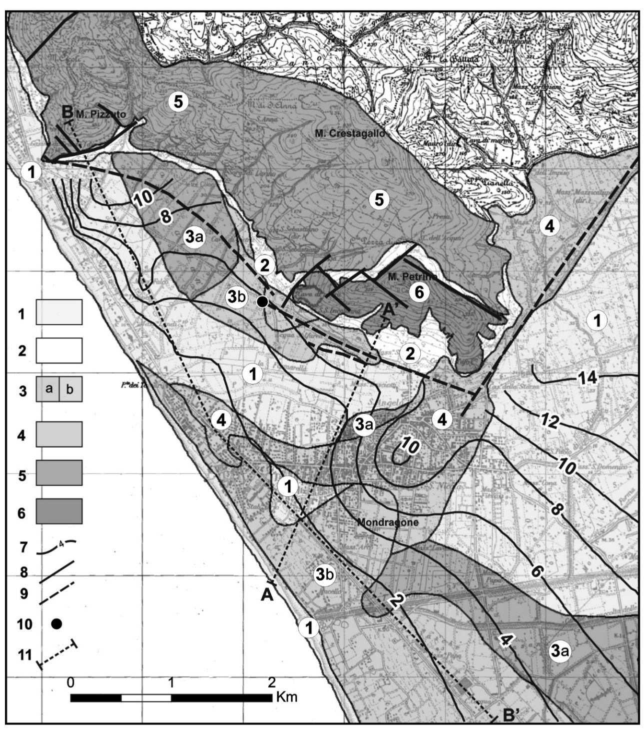


**Fig. 3: Hydrogeological Map of the Mondragone plain. 1) Quaternary marine sands and pyroclastics; 2) Quaternary debris deposits; 3) Quaternary clayey (a) or sandy (b) alluvial deposits; 4) "Campanian Ignimbrite" (39 ka B.P.); 5) Marly-arenaceous-clayey deposits (Tertiary flysch); 6) Mesozoic limestone; 7) piezometric contour (m a.s.l. January 2012), 8) faults; 9) buried faults; 10) well used for pumping test; 11) traces of the hydrogeological sections of Fig. 4**

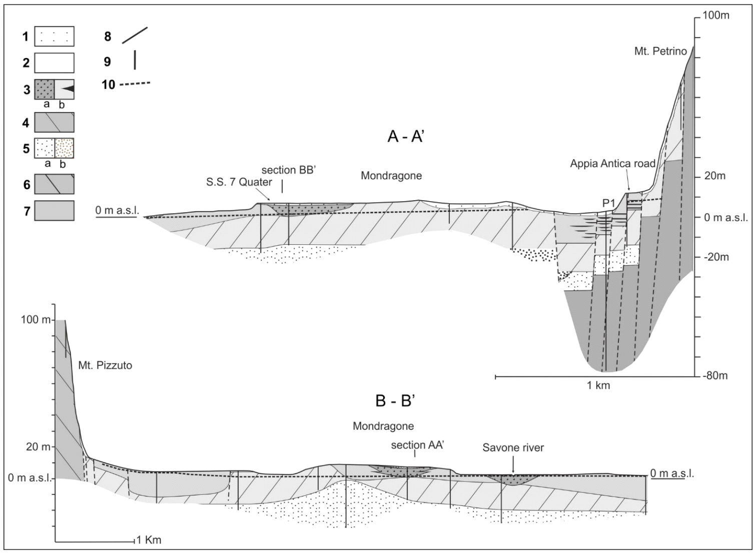


**Fig. 4. Hydrogeological Sections (traces in Fig. 3). 1) Pyroclastics; 2) Debris deposits; 3) Clayey (a) or sandy (b) alluvial deposits with peat levels (in black); 4) Campanian Ignimbrite; 5) Ancient clayey (a) or sandy (b) alluvial deposits; 6) Marly-arenaceous-clayey deposits (flysch); 7) Limestone; 8) faults (dotted if buried); 9) borehole (P1: Petrinum well); 10) groundwater level**

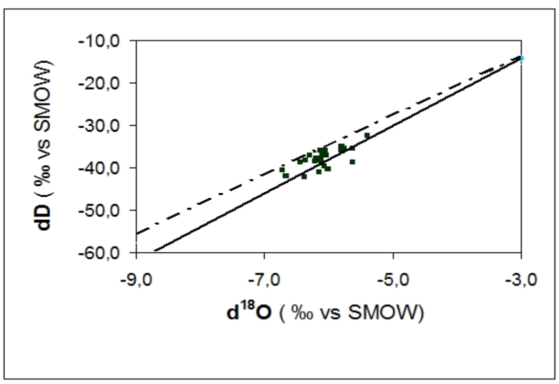


**Fig. 5. δ D - δ $^{18}$O diagram (Tab. 2); GMWL (Craig, 1963) and meteoric water of Southern Italy (dotted line; Longinelli and Selmo, 2003)**

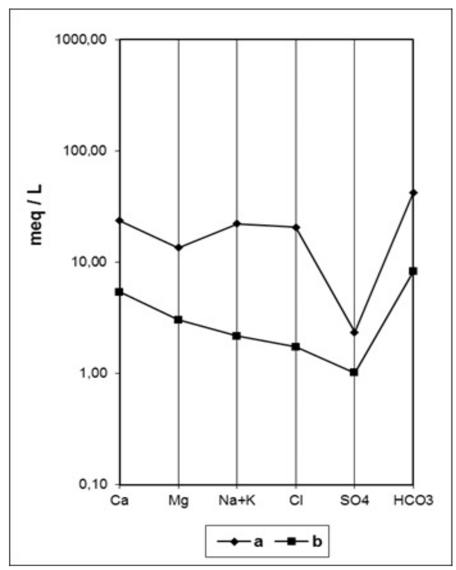


**Fig.6. Schoeller-Berkaloff graph: a) groundwater of the Petrinum well (No. 13, Tab. 1); b) groundwater of Mt. Petrino (well No. 6, Tab. 1)**

content commonly observed in connate waters (as well as in the waters of Petrinum well) is generally ascribed to sulphate reduction. Due to their high salinity ($Ca^{2+}$, $Na^{+}$ and $Cl^{-}$ are higher than in seawater, while $Mg^{2+}$ and $SO_4^{2-}$ are lower), even a small percentage of connate waters may produce a typical chemical pattern of groundwater (Figs. 6 and 8), that seems not to be affected by the lithological features of the aquifers. Indeed, the thermo-mineral waters of the Buzias spa (Albu *et al.*, 1997), resulting from a mixing with connate waters, have chemical profiles comparable with the Petrinum well notwithstanding the very different geological features. The same chemical pattern can be observed for the Sinuessa springs (see below), as well as for mineral waters sampled in a deep well in the city of Naples (Corniello & Ducci, 2014), where the aquifer is volcanic. Connate waters (often with relative low $HCO_3^-$ content; Demir & Seyler, 1999) would be transported upwards by deep gases (mainly $CO_2$ and $H_2S$) with relatively high thermality; indeed, the waters of the Petrinum well have T ~ 33 ° C and high amount of $CO_2$, responsible for high $HCO3^-$, $Ca^{+2}$ and $Mg^{+2}$, deriving from the dissolution of the carbonate

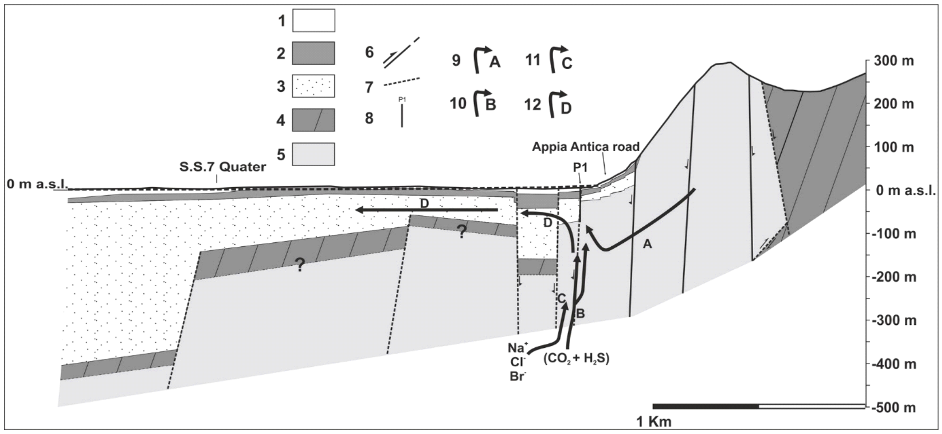


**Fig. 7. Schematic section (trace A-A' in Fig. 3) of the mineralization of groundwater around the Petrinum well: 1) Marine sands, pyroclastics and alluvial deposits (Quaternary); 2) Campanian Ignimbrite (39 ka B.P.); 3) Pleistocene alluvial deposits; 4) Marly-arenaceous-clayey (Miocene flysch deposits); 5) upper Cretaceous limestone; 6) faults (dotted if buried); 7) groundwater level; 8) Petrinum well; 9) groundwater of Mt. Petrino; 10) gas upwelling; 11) connate waters contribution; 12) mixing waters**

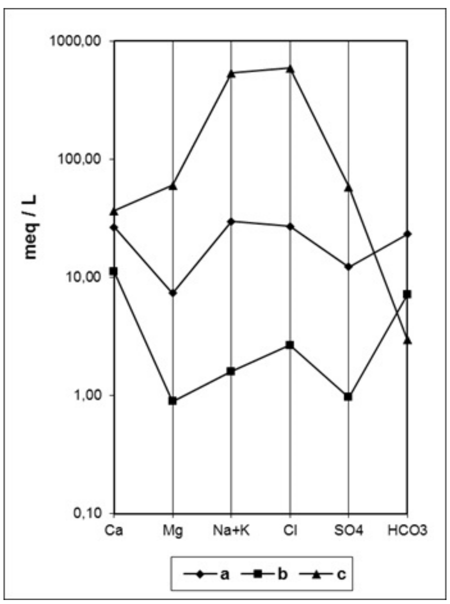


**Fig.8.Schoeller-Berkaloff graph: a) Sinuessa thermo-mineral springs (mean values in 2012); b) typical groundwater in marly-arenaceous-clayey deposits; c) sea water (Tab. 1)**

reservoir. Around the Petrinum well, the upwellig of the gases occurs through the NE-SW fault, delimiting the southern boundary of Mt. Petrino (Fig.3). This tectonic lineament, probably in connection with the major faults that limit to SE and to NW the Mt. Massico (Fig. 1), crosses the whole plain of Mondragone. However, the upwelling of gases does not occur along the whole extent of this fault but only in limited areas (Mt. Pizzuto and the sector of the plain with higher mineralization - Figs. 10b and 10c) where geophysical data indicate the intersection with other tectonic lineaments. Based on the whole results, it is possible to propose the structural hydrogeological scheme of Fig. 7. According to this model, hot gases ascend along faults of the carbonate bedrock of the Mondragone plain, involving very small fractions of connate waters; upwards, they affect the groundwater body of the carbonate bedrock. The mixing waters, coming from the bedrock, spreads into the overlying pyroclastic-alluvial aquifer; afterwards, the mineralization decreases gradually toward the groundwater flow direction (from NE to SW; see piezometric contours in Fig. 3). According to this hypothesis, the mineralization of waters is therefore closely linked to the faults, and far from these the chemistry is scarcely (or not at all) affected, especially upstream with respect to the groundwater flow. This scheme, many times observed for mineral springs emerging at the foot of carbonate aquifers in central-southern Italy (Corniello & de Riso, 1986; Corniello, 1994; Corniello *et al.*, 2013) and elsewhere (Goldscheider *et al.*, 2010), also allows to fully justify the chemical and isotopic differences between the waters of the wells No. 6 and No. 13.

At the bottom of the Mt. Pizzuto, the Sinuessa thermo-mineral springs (No. 14 and No. 14a in Fig. 2 and Table 1), with different discharges, have similar chemical characteristics, consistent in the years (Table 1). The chemistry of these thermal waters is represented on the Schoeller-Berkaloff graph of Fig 8 (a), drawn up on the basis of 2012 mean values; the line (b) refers to the composition of a typical groundwater flowing in the marly-arenaceous-clayey rocks of Mt. Pizzuto, far

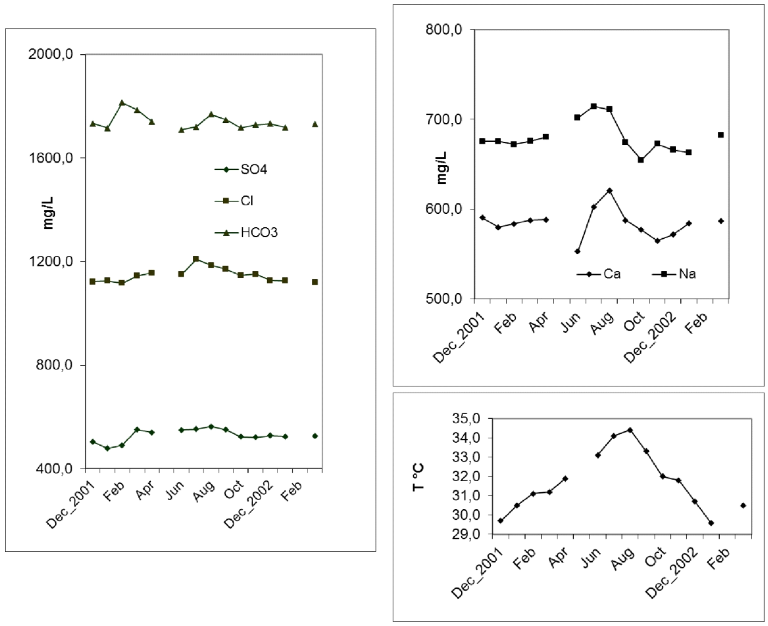


**Fig. 9. Well No. 15: Monthly variations in chemical parameters (see text)**

from the mineral springs, and the line (c) refers to the sea water composition (Table 1). The graph of Fig. 8 clearly shows the differences in chemistry between the thermal springs (a) and the more superficial waters (b). The chemical composition of the thermal springs is similar to the Petrinum well (Fig. 6), with higher values of $Na^+$, $K^+$, $Cl^-$ and, especially $SO_4^{2-}$. The origin of the Sinuessa thermo-mineral springs (and the groundwater of the neighboring wells No. 15 and 16) is similar to the Petrinum well, but in Sinuessa area the upwelling of deep gases also involves seawater and/or some water leaching evaporitic Miocene formations, as indicated by the concentration of $SO_4^{-2}$, higher than in groundwater of the Petrinum well. The values of $\delta^{34}S$ (Table 2) are anyhow in agreement with those found for present seawater and for chalks of the Miocene (Clark & Fritz, 1997). Also in the Mt. Pizzuto area the upwelling of $CO_2$ and $H_2S$ (respectively 98.11 and 1,69 % of the gases - Duchi *et al.*, 1995) occurs along the main fault that crosses the plain of Mondragone. These hot gases cause the pH lowering and the increase of the carbonate dissolution in the Mt. Pizzuto rocks.

In a wells of the Sinuessa spa (No. 15 in Table 1 and Fig. 2), groundwater has a T H” 35 °C and the same chemical composition of the springs (No. 14) and of the well No. 16 near the spa (Fig. 2 and Table 1), belonging to the same groundwater body. The hydrochemical characteristics of groundwater of the well No. 15, for which monthly analyses from December 2001 to March 2003 are available, and that are representative of all the thermo-mineral waters of Mt. Pizzuto, present the monthly variability shown in Fig. 9 that can be summarized as follow. The higher values of salinity, temperature, chloride content, sodium etc. are observed from June to September. The increase is not linear from winter to summer, except for temperature that clearly shows a typical seasonal effect: from June to September the rainfall is very low in the area and therefore the groundwater recharge is negligible reducing the dilution of the hot waters. The possible interaction between seawater and the groundwater body of Mt. Pizzuto highlights the chemical composition of these thermo-mineral waters can have severe modifications not only from geothermal exploitation but also from climate change through a reduced rainfall recharge (Holman, 2006; Tranfaglia & Ducci, 2008; Woldeamlak *et al.*, 2007; Sukhija & Dragoni, 2008; Taylor *et al.*, 2013).

The sampled wells of the Mondragone plain, tapping groundwater below the tuff, are shown in Fig. 2; groundwater analysis results are summarized in Tables 1 and 2. The data in Table 1 reveal two homogeneous groups (Fig. 10a). The first group (1) comprises waters No. 5, 7, 19, 20, 21, 23 and 24, for which the mean values of the ratios r (Ca+Mg)/ r (Na+K), r $SO_4$/ r Cl and r K/ r Na are 2.57, 0.18 and 0.11, respectively. The waters of this group have characteristics and chemical profiles (on the Schoeller-Berkaloff diagram) comparable with the water of the Petrinum well (No. 13, Fig. 6). These wells, located around the Petrinum well, identify a sector with values of electrical conductivity, temperature and salinity, higher than those of the groundwater of the remaining parts of the plain (Fig. 10b and Fig. 10c). The waters of

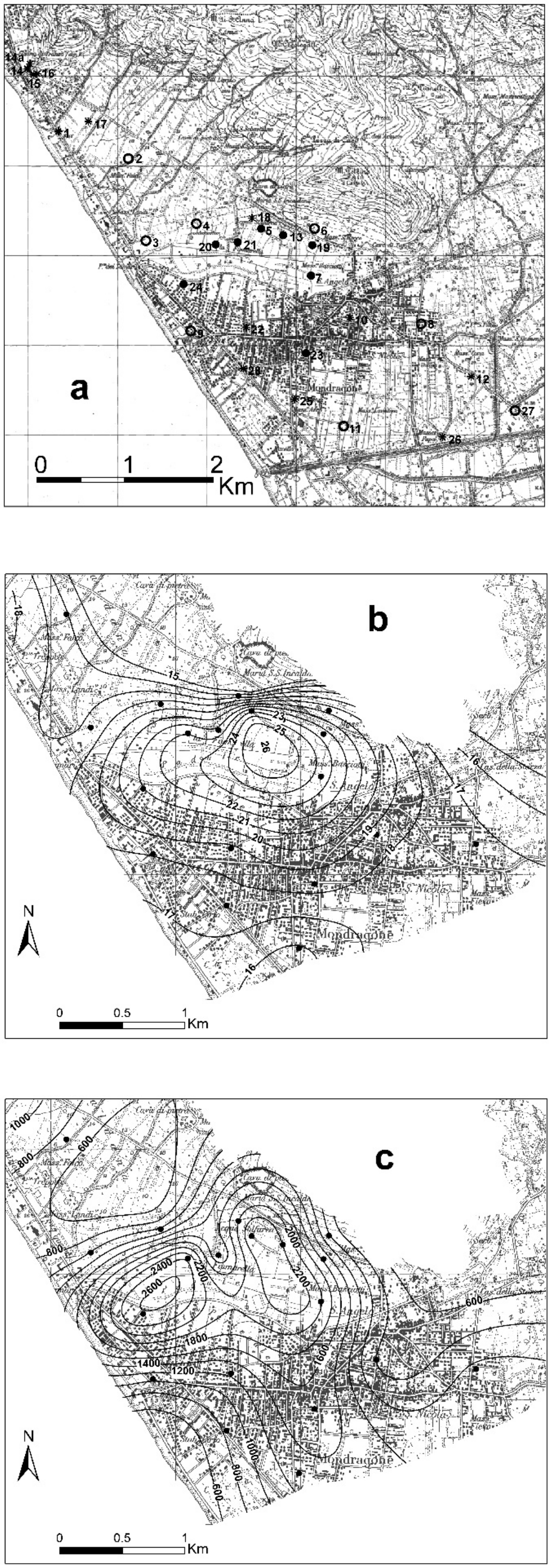


**Fig. 10. Groundwater of the Mondragone plain: a) spatial distribution of water group 1 (•) and 2 (o) (see text); b) temperature contour lines (°C); c) electrical conductivity (ìS/cm) contour lines**

the group 2 (No. 2, 3, 4, 8, 9, 11 and 27) have mean values of the ratios r (Ca+Mg)/ r (Na+K), r $SO_4$/ r Cl and r K/ r Na equal to 4.68, 0.65 and 0.13, respectively. These waters have chemical profiles similar to the groundwater of the well No. 6 (profile b in Fig. 6) and indeed, they represent the outflow from groundwater body of the calcareous Mt. Petrino, feeding the aquifers of the plain. The position of these wells are at NW and SE, with respect to the previously identified Petrinum area (see Fig. 10a).

The remaining wells of the plain have intermediate chemical characteristics, compared to those selected in the previous two groups.

## CONCLUSIONS

At the foot of Mt. Pizzuto (NW sector of the Mondragone plain) and close to sea, there are thermo-mineral waters (springs and wells) $CO_2$-rich and Na-Cl type; close to the calcareous Mt. Petrino (to SE of the plain) two wells have intercepted thermo-mineral waters $CO_2$-rich but calcium-bicarbonate type. Detailed geophysical and hydrogeological surveys allowed the definition of the origin of the mineralization in the two areas (Mt. Pizzuto and Mt. Petrino). In both areas, the thermo-mineral waters are meteoric and enriched by endogenous gases ($CO_2$ and $H_2S$) at fairly high temperature. These gases increase the dissolution of the rocks and favor the upwelling of small percentages of connate waters towards shallower groundwater. In these phenomena the role of the tectonic is crucial: in fact, the rise of the gases occurs along the main fault that crosses the plain of Mondragone and this rise is concentrated at the intersection with other tectonic lineaments; furthermore, groundwater flow upstream of this tectonic phenomenon the hydrochemical pattern is scarcely (or not at all) altered. Finally, the influence of the connate waters with high salinity on the chemical characteristics of the mixing waters results prevalent with respect to the influence of the lithological nature of the aquifers. In conclusion, between the two areas in the Mondragone plain, the area close to Mt. Petrino appears to be most suitable for drilling a geothermal well. Indeed, in the area of Mt. Pizzuto the gas upwelling would lead a moderate seawater intrusion, more pronounced from June to September, when the rainfall recharge is negligible or null; furthermore, here the groundwater body is likely unimportant to the low permeability of the cropping out marly-rich rocks and the geothermal use of the area could increase the seawater intrusion reducing the thermal levels of the resource. On the contrary, seawater intrusion does not affect groundwater close to Mt. Petrino where, besides, the more permeable rocks assure a greater percentage of thermal waters. The limit of exploitation of the resource has been estimated in approximately 20-25 l/s through a hydrogeological budget of Mt. Petrino, which represents the recharge area of the carbonate bedrock where the thermo-mineral groundwater of the plain originates. Finally, this research also contributes to the assessment and mapping of the geothermal resources of Campania (Italy) and offers a further example of the significance of the carbonate aquifers that, apart from the volcanic areas, constitute often the main geothermal reservoirs.

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