**Programme and Proceedings** 

# **SWIM 2014**

## 23<sup>rd</sup> Salt Water Intrusion Meeting



### June 16–20, 2014 Husum, Germany

Editors Helga Wiederhold, Leibniz Institute for Applied Geophysics, LIAG Johannes Michaelsen, CONSULAQUA Klaus Hinsby, GEUS Broder Nommensen, LLUR

#### The coastal springs along the Taranto Gulf (South Italy)

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#### ABSTRACT

The Mar Piccolo (literally "small sea"), a sea internal basin which is part of the Taranto Gulf, located along the Ionian coast in southern Italy (Apulia region), represents a peculiar and sensitive environmental area and a social emergency due to the level of sea water pollution coming from the close industrial area of Taranto.

The paper describes the preliminary results to define a conceptualization of the aquifer as main support to characterize the hydrological balance of the internal sea, the geochemistry of groundwater, and the effect on the ecological equilibrium of the coastal environment.

#### **INTRODUCTION**

The aquifer occurring in the carbonate sequence of the Murgia plateau feeds numerous coastal springs and constitutes the main local source of pure fresh groundwater.

Galeso, Battentieri and Riso are the main subaerial springs located along the coast of Mar Piccolo, not far from the town of Taranto (respectively point 2, 3 and 4 in Figure 1). This area is also characterized by several submarine springs, locally called "Citri" (Cerruti,1938, Cotecchia et al., 1990).

Submarine freshwater discharge plays an important role in the hydrogeological equilibrium of the system.

#### GEOLOGICAL AND HYDROGEOLOGICAL SETTING

The area, located between the southern part of the Murgia plateau and the Ionian sea, is geologically characterized by a sequence of Mesozoic limestone (the Apulian carbonate platform) constituting the foreland of the southern Apennines chain.

The main geological units outcropping in the study area are represented by a carbonate sequence constituted by Cretaceous limestones; a Middle Pliocene-Lower Pleistocene calcarenite; a Lower Pleistocene clay; a Middle and Upper Pleistocene calcarenite and sand; a Holocene alluvial deposits and coastal deposits (Figure 1).

In the area, hydrogeological situation is characterized by a deep aquifer located in the carbonate rocks. The Mesozoic sequence is intensely fissured and karstified, and forms an important groundwater reservoir. In the sediments of Pleistocene sequence, local shallow aquifers of limited extension occur. They are located at topographically depressed areas, where Quaternary deposits, constituted by sands and calcarenites, overlie impermeable clays formations.

The base level of groundwater corresponds to the sea level. The piezometric heads (Figure 1) drop rapidly from value above 10 m a.s.l, in the inner areas, to values close to 1 m a.s.l near the shoreline. The variations of the piezometric surface are related to the permeability of the rocks. In particular, the evolution of the piezometric surface shows that the main directions of groundwater outflows are primarily focused towards Mar Piccolo, to the draining effect that coastal springs (subaerial and submarine).

The flow rate of the Galeso Spring is about 500 l/s, that of the Battentieri spring is less than 200 l/s, whereas that of the Riso spring is about di 100 l/s (Polemio et al., 2014).



Figure 1. Simplified geological and hydrogeological map. Legend: 1) coastal deposits, 2) alluvial deposits, 3) terraced marine deposits, 4) subappennine clay, 5) gravina calcarenites, 6) altamura limestone, 7) submarine spring, 8) subaerial spring, 9) piezometric line.

#### CHEMICAL ANALYSES OF WATER AND INTERPRETATION

Determination of the main constituents of waters was performed by means of ion chromatography methods, for separation of both cations and anions, with conductometric detection. Ion chromatography analyses results are shown in Table 1.

Total alkalinity values of the samples were determined by titration with 0.1N HCl, to a pH=4.5 endpoint. The location of sampling points is shown in Figure 1.

Sample	Name	pН	E.C.	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	F <sup>-</sup>	Cl.	Br	NO <sub>3</sub> <sup>-</sup>	HCO <sub>3</sub> <sup>2-</sup>	SO4 <sup>2-</sup>
1	Carbonate aquifer	7,75	0,51	< 0,05	12,5	3,19	24,2	57,9	0,27	12,9	0,05	23,7	281	7,48
2	Galeso Spring	6,98	3,83	0,03	569,0	17,64	75,0	123,0	3,68	1060,5	4,22	16,8	354	160,6
3	Battentieri Spring	7,05	5,30	0,04	824,5	30,13	98,0	141,7	3,67	1638,7	5,99	13,7	372	222,6
4	Riso Spring	7,02	3,91	0,02	575,9	22,03	77,8	125,0	2,89	1068,7	4,20	22,5	366	156,2
5	Seawater	7,33	48,3	0,15	11160	337,1	1297	408,7		21024	69,4		171	2458

Table 1. Electrical Conductivity (E.C.) in mS/cm; Concentration in mg/L

The ground water of carbonate aquifers is generally characterized by a predominance of calcium and bicarbonate ions, as a result of dissolution of the minerals calcite and dolomite. The process of dissolution and precipitation of calcite can be schematized with the following reaction:

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$$
(1)

Saturation with respect to calcite is expressed by the saturation index:

$$SI_{calcite} = \log \frac{[Ca^{2+}][CO_3^{2-}]}{K_{calcite}} = \log \frac{IAP_{calcite}}{K_{calcite}}$$
(2)

where  $[Ca^{2+}]$  and  $[CO_3^{2-}]$  are the activities of ions, calculated from the analyses; IAP<sub>calcite</sub> is the ion activity product for calcite.

Dolomite is a very poor soluble mineral, if compared with calcite. In a system containing calcite, dissolution of dolomite may be congruent or incongruent, depending on the concentration of calcium derived from calcite (Wigley, 1973b). If water is subsaturated with respect to calcite, congruent dissolution of dolomite occurs:

$$CaMg(CO_3)_2 \leftrightarrow Ca^{2+} + Mg^{2+} + 2CO_3^{2-} \qquad (3)$$

Saturation with respect to dolomite is expressed by the saturation index:



$$SI_{dolomite} = \frac{[Ca^{2+}][Mg^{2+}][CO_3^{2+}]^2}{K_{dolomite}} = \log \frac{IAP_{dolomite}}{K_{dolomite}}$$
(4)

The sample of coastal springs are subsaturation with respect to calcite and respect to dolomite (Table 2).

These waters are characterized by rather high values of electrical conductivity, high concentrations of alkaline ions (Na<sup>+</sup> and K<sup>+</sup>) and chloride ion. This water shows the chemical characteristics of fresh groundwater contaminated by seawater intrusion.

The geochemical composition of the samples (Figure 2) can be considered between that of seawater (sample 5) and the water of carbonate aquifer when not affected by the seawater intrusion (sample 1). The freshest groundwater sample was collected from an irrigation well and it is representative of local fresh groundwater.

The fraction of seawater ( $f_{sea}$ ) of each sample is calculated from the concentration of the chloride ion, considered as conservative ion in the mixing process (Appelo and Postma, 2005):

$$f_{sea} = \frac{m_{Cl^{-},sample} - m_{Cl^{-},fresh}}{m_{Cl^{-},sea} - m_{Cl^{-},fresh}}$$
(5)

The results are shown in Table 2. In particular, the water show a mixing ratio of fresh water and sea water between 5% and 8%.

The expected concentration of the different ions  $(m_{i, mix})$ , resulting from mixing between fresh water and salt water, is calculated by:

$$\mathbf{m}_{i,\text{mix}} = \mathbf{f}_{\text{sea}} \cdot \mathbf{m}_{i,\text{sea}} + (1 - \mathbf{f}_{\text{sea}}) \cdot \mathbf{m}_{i,\text{fresh}}$$
(6)

where  $m_{i,sea} e m_{i,fresh}$  are the concentration in seawater and freshwater of the species i. The enrichment or depletion ( $m_{i,react}$ ) of the species i is then obtained by:

$$\mathbf{m}_{i,\text{rect}} = \mathbf{m}_{i,\text{sample}} - \mathbf{m}_{i,\text{mix}} \tag{7}$$

where  $m_{i,react}$  may take both positive and negative value, or be equal to zero (only mixing). Table 2 shows the results of calculations. The change of the concentration of the ions, calculated from the concentration determined by analytical means, indicates the presence of additional geochemical processes that modify the water hydrochemistry compared to the composition resulting from the simple mixing.

Sample	SI <sub>calcite</sub>	SI <sub>dolomite</sub>	f %	Ca <sup>2+</sup> <sub>mix</sub>	Ca <sup>2+</sup> react	Mg <sup>2+</sup> <sub>mix</sub>	Mg <sup>2+</sup> react	HCO <sub>3</sub> <sup>2-</sup> mix	HCO <sub>3</sub> <sup>2-</sup> react
1			0						
2	-0,3	-0,30	5,0	1,9	1,2	3,6	-0,6	4,4	1,4
3	-0,2	-0,08	5,0	2,1	1,4	4,8	-0,8	4,4	1,7
4	-0,3	-0,17	7,2	1,9	1,2	3,7	-0,5	4,4	1,6
5			100						

## Table 2. Saturation indexes for calcite and dolomite; fraction of seawater; mixing; reacting.

Water samples show an enrichment of calcium and depletion of magnesium ion. These effects could be related to the dolomitization of the limestone induced by seawater intrusion, as suggested by Hanshaw et al. (1971).

#### **ACKNOWLEDGEMENTS**

The research is part of RITMARE Project (The Italian research for the Sea), coordinated by the National Research Council and funded by the Ministry of Education, University and Research.

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