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Hydrogeochemistry of a wetland area of southwestern Sicily (Italy)

ABSTRACT

The “Preola” and “Gorghi tondi” lakes are the most noticeable wetlands in the Mazara del Vallo territory (south-west Sicily). There are four karst origin lakes located in a natural depression formed by gypsum dissolution and subsequent collapse of the “Calcarenite di Marsala”, a few meters above sea level.

Erosion of the depression sides and human activity has caused visible colluvial deposits, which have contributed to a natural filling process of the lakes.

A hydrogeological map of the area and the reconstruction of a water circulation model supplying the lakes have been drafted from geochemical and hydrogeological data.

It is apparent from $\delta^{18}\text{O}$ values that the well waters are mainly fed by local meteoric water circulating within the calcarenitic aquifer. However, the lake waters chemical composition are very likely controlled by evaporation processes and a complex mixing between seawater and groundwater, depending on seasonal variation in the hydrodynamic equilibrium.

SOMMARIO

I laghi “Preola e Gorghi tondi” sono le aree umide più importanti del territorio di Mazara del Vallo (Sicilia sud-occidentale). Si tratta di quattro laghi di origine carsica situati in una depressione originata dalla dissoluzione di gessi e conseguente crollo della sovrastante “Calcarenite di Marsala”, ad una quota prossima al livello del mare. L’erosione e le attività umane sono la causa della formazione di depositi colluviali che hanno contribuito al naturale processo di interrimento dei laghi. Con l’acquisizione di dati idrogeologici e geochimici è stato possibile disegnare una carta idrogeologica, linee di deflusso sotterraneo un modello di circolazione delle acque. I dati isotopici del $\delta^{18}\text{O}$ dell’acqua di falda confermano che l’alimentazione dell’acquifero calcarenitico è dovuta ad acque meteoriche locali. Tuttavia la composizione chimica dei laghi è controllata da processi di evaporazione e di miscela tra acqua di mare e di falda, sensibilmente dipendenti dalle variazioni dell’equilibrio idrodinamico.

Keywords: Hydrogeochemistry, Hydrogeology, Isotopes, Karst.

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INTRODUCTION

About two thirds of the wetland areas in the Mediterranean basin have been drained, while most of the remaining area continues to deteriorate. Aquifer overexploitation in coastal areas is a serious problem. Many coastal aquifer systems in Italy have been so seriously depleted that their piezometric surface has been lowered, causing progressive seawater intrusion [17].

The restoration of Mediterranean wetlands has become a priority. Every Mediterranean country has expressed, through participation in the Mediterranean Wetlands Initiative [6,9,19], their decision to promote studies implementing the knowledge of the delicate equilibrium controlling these areas and restoration projects.

Moreover, the evaporate sequence of the Upper Miocene is present in Italy in several regions such as Tuscany, Calabria and Sicily and many studies regarding karst processes in the evaporate sequences are also reported elsewhere [7,10].

The area investigated, located in the middle of the Mediterranean basin, is of relevant interest for both themes.

The lakes “Preola” (named in the text as “LP”) and “Gorghi tondi” (as “G1”, “G2”, and “G3”) are located in southwestern Sicily, near “Mazara del Vallo” town (Figure 1).

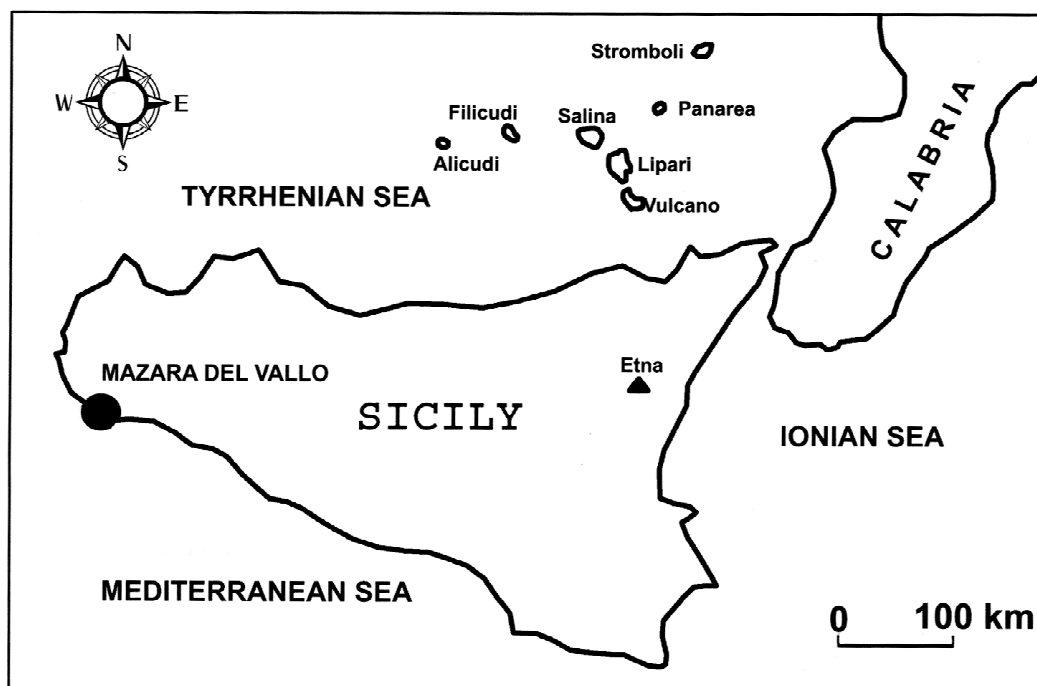
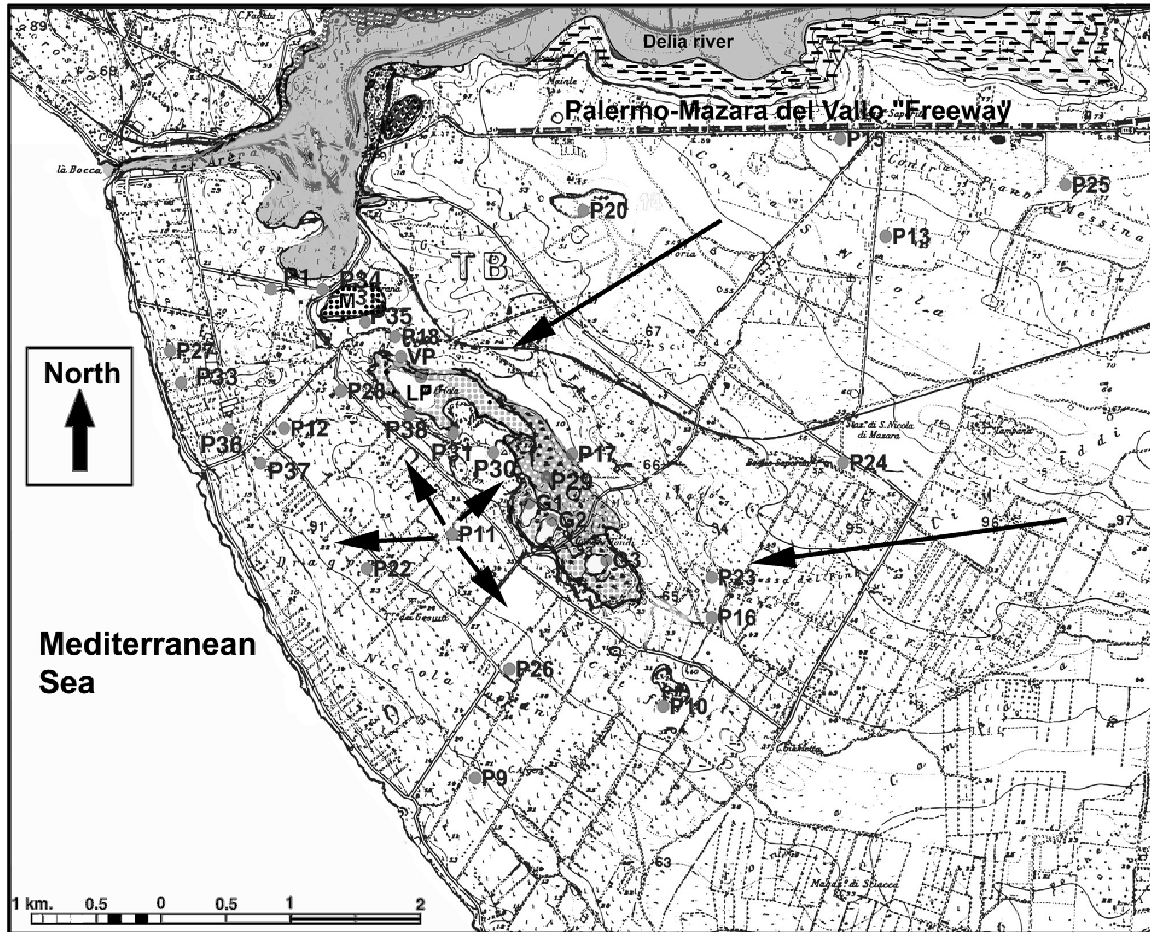


Figure 1: Location of the study area.

Today this area is a Natural Reserve managed by the WWF (World Wide Fund for Nature) Italy and represents a unique ecosystem for its great variety of fauna that flourishes in this particular wetland microclimate. At the moment, one of the most important management problems of the Natural Reserve is to restore the hydrological equilibrium in the lakes. In fact, this wetland is an ideal rest site for migratory birds, as Gray Heron (*Ardea cinerea*), Little Egret (*Egretta garzetta*), Black-winged Stilt (*Himantopus himantopus*), Eurasian Coot (*Fulica atra*), Common Moorhen (*Gallinula chloropus*) and other species from North Africa to central Europe.

Figure 2 shows the location of the field sites. It is delimited to the north by the “Palermo-Mazara del Vallo” freeway, and to the south and west by the Mediterranean Sea.



Legend

- | | |
|---|--|
| <ul style="list-style-type: none"> Dietric complex. Slope debris of varied nature and dimensions with poorly degree of cementation. Good permeability for porosity. Lacustrine deposits complex. Constituted from silty and sandy clays, the thickness in any points overcome the 6 meters. Impermeable. Eluvium and colluvium deposits complex. Deposits constituted essentially from calcarenitic elements. Medium permeability due to porosity. Alluvial complex. Terraced and recent alluvial deposits: sands, silts and polygenic gravels. Thickness varies from 1 - 10 meters. Medium to high permeability due to porosity in the multiaquifer levels. Calcarenite complex. Yellowish calcarenites, sometimes jointing with small sandy-clayey lenses, the thickness increase from north-west to south-east to reach some tens of meters. Good to high permeability due to porosity and jointing. Calclutite and marl complex. Calclutites with some marls at globigerine sometimes much jointing; maximum thickness about ten of meters. Absent permeability for porosity and very low for jointing. | <ul style="list-style-type: none"> Complex of the gypsums. Macrocrystal gypsums much jointing and karstificated, with ribbon-shaped geometries and thickness that they reach any ten of meters. High permeability for jointing and karst. Clayey and clayey sandy complex. slightly stratified reach powerful thickness up to 600 meters. Impermeable. |
|---|--|
-
- | | | |
|---------------|------------------|-----------------------|
| | P1,...,38 | Monitored water wells |
| | | Groundwater flow |
| LP | | lake "Preola" |
| G1,2,3 | | lakes "Gorghè toxdi" |
| M | | lake "Murana" |
| VP | | "Vasca Pesci" |

Figure 2: Hydrogeological map and sampling sites

The landscape morphology is essentially flat, with a slight incline towards the sea. This trend is interrupted by a karst depression, created by the subsiding calcarenitic cover. The depression is about 20 m deep and runs parallel to the coastal line for about 4 km, at an average distance of 1.7 km, marked by the presence of lakes and dolines.

For several years, the investigated aquifer, located in the extensive quaternary coastal plain, has shown signs of continuous impoverishment as a consequence of uncontrolled water exploitation. This has caused a subsequent decrease in groundwater contribution to the lakes [16]. The drastic drawdown of the hydrostatic level and modification of the delicate natural equilibrium has caused the disappearance of some surrounding wet zones (such as the nearby lake “Murana”).

The research has been focused on:

- The definition of underground lithology related to the karst lakes;
- Piezometric surface reconstruction in order to define groundwater circulation and the relationships between the aquifer, the lakes and the sea;
- Aquifer characterization and its probable recharge area, using geochemical and isotopic data.

METHODS

Well water samples were collected in three different periods: July 2000, April and October 2001. Seawater samples were also analysed. Meteoric samples were collected monthly for a period of two years by a rain gage installed within the study area. During the sample collection, some parameters were measured in situ: Temperature (thermocouple, $\pm 0,1$ °C), pH and Eh (WTW pH 315, $\pm 0,01$ mV), electrical conductivity (WTW Cond. 315, mS/cm at 20°C, $\pm 0,5\%$ of the measured value). The chemical-physical parameters in the lake waters were measured by a multi-parametric probe (Amel 396) at different points and depths to check the possible existence of a vertical gradient in the water column. Sample aliquots, collected in polyethylene bottles, were filtered through 0.45 μ m Millipore filter and acidified by HNO₃ ultra-pure at pH 2. Alkalinity was measured by HCl titration, on un-acidified aliquot, and chemical constituents by ion chromatography (Dionex Dx 1-120; Li⁺, F⁻, Br⁻; error was calculated around 3% for high concentration and 7% for low concentration; SO₄⁻, Cl⁻, NO₃⁻, Na⁺, K⁺ Mg²⁺, Ca²⁺ was 2% for high and for 5% for low concentration, respectively). Sampling techniques and chemical analyses have been carried out according to: “Standard Methods for examination of water and wastewater” [13]. $\delta^{18}\text{O}$ measurements were performed, on an unfiltered sample, using the CO₂-H₂O equilibration procedure reported the Epstein and Mayeda [8]. The reproducibility was $\pm 0,2$ ‰. The δD analyses were carried out using the H₂O-Zn reduction [4]. The reproducibility was ± 1 ‰. Isotopic analyses have been reported against the International Standard V-SMOW as defined by R.Gonfiantini [12].

RESULTS AND DISCUSSION

Hydrogeology

The area, within the neogenic basin of “Castelvetro”, is constituted by upper Miocene and Tyrrhenian terrains [1,2,3]. The Pleistocene calcarenitic successions constitute the most extensive hydrogeological unit in the zone and contain an unconfined aquifer, locally in hydraulic contact with the underlying aquifer (evaporitic complex).

The main hydrogeological units are shown in Figure 2.

The hydrostatic level was reconstructed through piezometric wells measurements and hydric levels of the lakes.

The measurements were carried out in a short period (one-week) and during periods when the wells were not being exploited for agricultural purposes.

Interpretation of the piezometric contours has revealed:

- a parallel trend of piezometric lines and the karst depression, demonstrating a water supply towards the lakes;
- a hydrogeological boundary in the sectors where the calcarenitic aquifer unconforms the clayey-sandy clayey substratum.

Hydrogeochemistry

The Piper [15] diagram was preferred to other conventional methods because it allows a more precise identification of the water samples and some dominant geochemical processes in the water chemistry (Fig. 3).

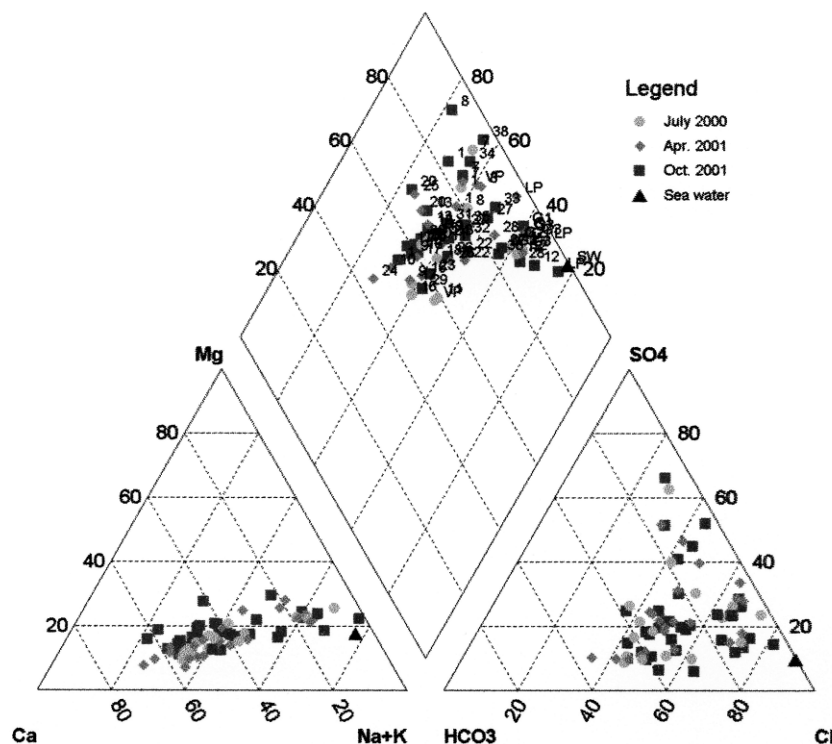


Figure 3: Piper plot showing major chemical compositions of the ground waters and lakes

The diagram also shows the seawater point (SW). At first glance one can see the presence of two main water groups: one of Na^+ , K^+ - Cl^- , SO_4^{2-} composition (essentially lake waters and well P12), and the other of Ca^{2+} , Mg^{2+} - Cl^- , SO_4^{2-} type (the remaining wells). Considering the

ternary diagrams, it can be concluded that the water chemistry is mainly controlled by Na^+ - K^+ - Ca^{2+} cations and Cl^- - SO_4^{2-} , and subordinately HCO_3^- anions. This first analysis reveals that seawater, the calcarenitic aquifer, and the presence of gypsum control the water chemistry. For instance, the Cl^- iso-concentration lines (Figure 4) point out the possible seawater intrusion direction.

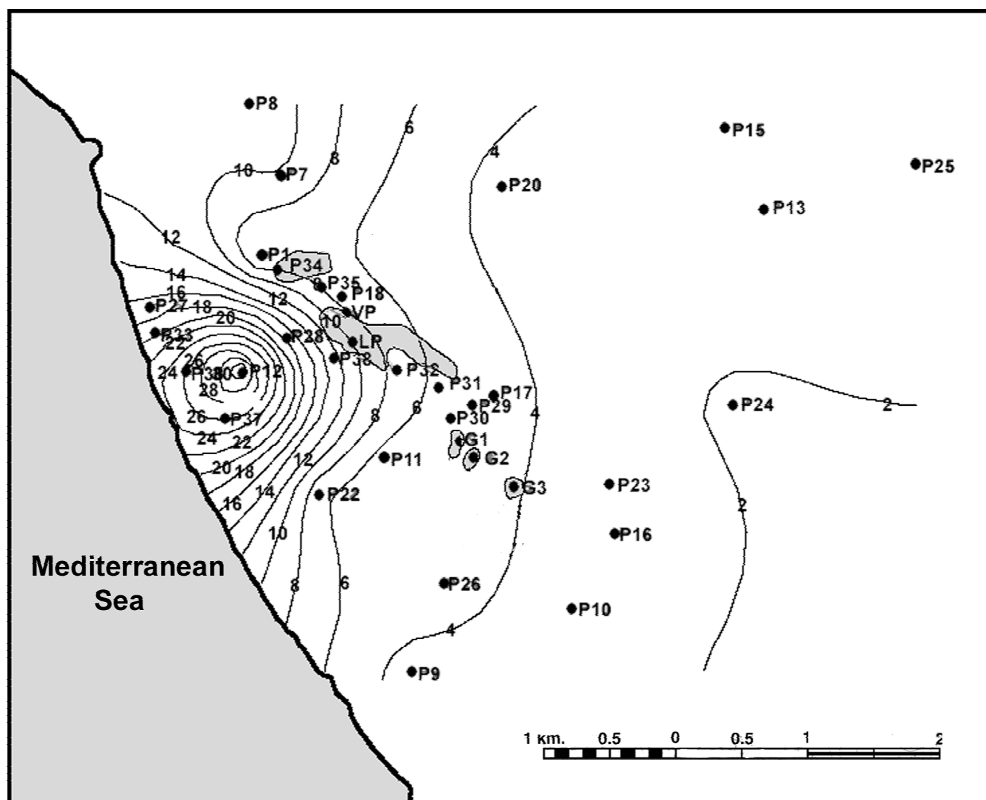


Figure 4: Cl^- iso-concentration map (concentration expressed in meq/l)

The Cl^- - Na^+ diagram (Figure 5) shows that, at low concentration, almost all samples result to be aligned along a seawater mixing line, except the lake LP points which depart from this line for all the samplings. Considering that during drought periods (Summer time) LP dries completely (to collect water samples it was necessary to drill at least 2 m beneath the lake bottom), it seems reasonable to think that last stage mineralogical phases of the evaporitic series (XRD determination performed on lake sediments showed peaks related to Kainite and Caminite) can be precipitated. When water once again reaches the lake, there is redissolution of these phases.

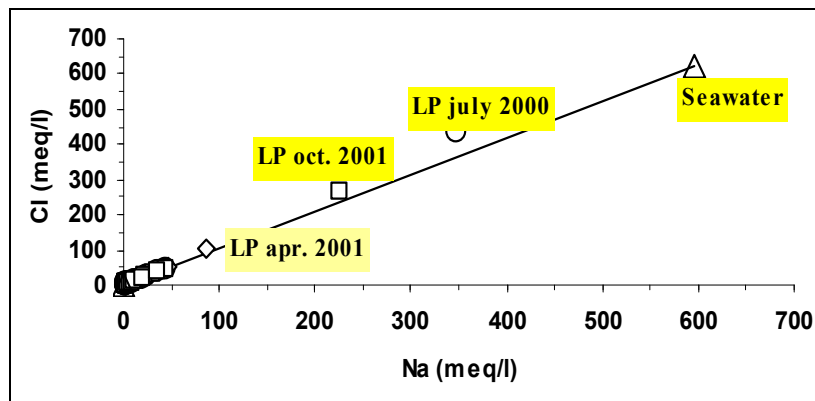


Figure 5: Cl⁻ vs. Na⁺ plot

Even Figure 6 and Figure 7 (the Cl⁻ vs. Mg²⁺ and SO₄⁼ contents) show that these two ions, which are second in abundance in the seawater after Na⁺ and Cl⁻, don't follow the seawater mixing line. Whereas the Cl⁻/Na⁺ ratio is close to 1.0 in the seawater (1.2 in the LP lake), the Cl⁻/Mg²⁺ (33.5) and Cl⁻/SO₄⁼ (9.2) ones are completely different with respect to those of LP lake (3.2, 2.5, 3.8 and 3.1, 0.9, 5.6, respectively for July 2000, April 2001 and October 2001). This means that large changes have occurred in the water chemistry of LP lake with respect to the seawater, very likely due, as previously said, to precipitation of some mineralogical phases.

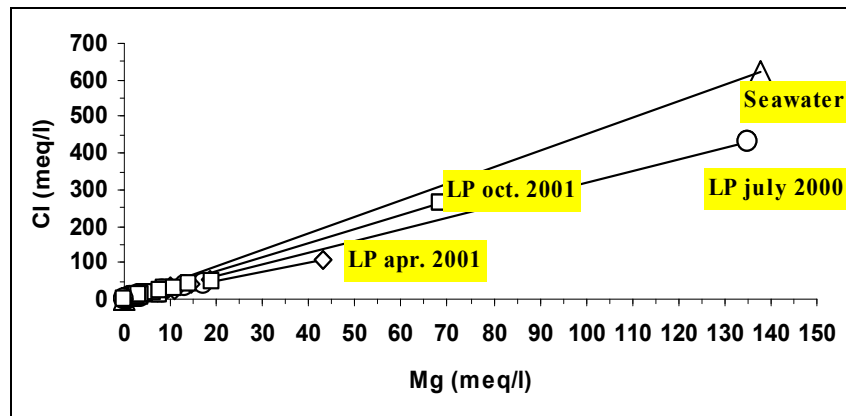


Figure 6: Cl⁻ vs. Mg²⁺ plot

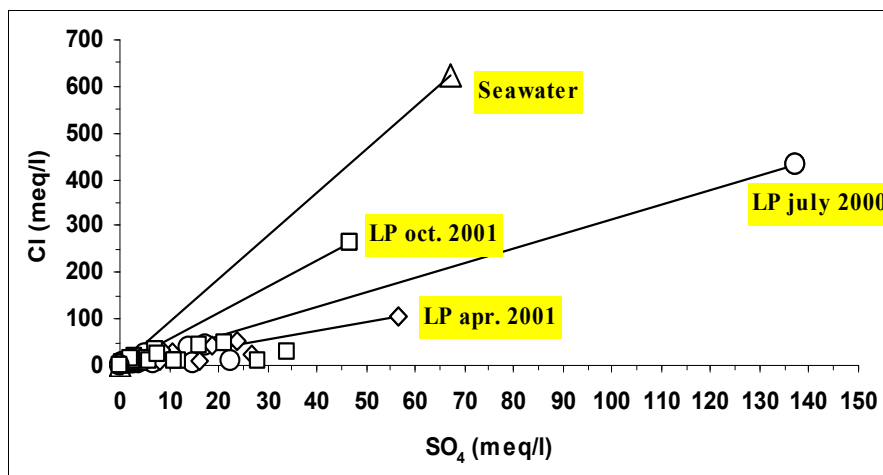


Figure 7: Cl⁻ vs. SO₄⁼ plot

The saturation index (SI) is the parameter that indicates the state of saturation of natural waters with respect to relevant minerals. It is defined as $SI = \log_{10} (Q/K_{eq})$ where Q is the reaction quotient and K_{eq} the equilibrium constant at that temperature. The activities of individual dissolved species were computed by the “PHREEQC” program [14].

The SI values reported in Table 1 considering mineralogical phases in this area such as anhydrite, gypsum, aragonite, calcite, dolomite, magnetite and fluorite, are mainly close to zero or positive, indicating oversaturation or quasi-equilibrium conditions. This agrees with the main lithotypes present in the study area.

Table 1: Saturation indexes for some selected mineralogical phases

| Date | Phase | SI | | | |
|-----------|-----------|-------|-------|-------|-------|
| | | LP | G1 | G2 | G3 |
| Jul. 2000 | Anhydrite | -0.22 | -0.98 | -1.35 | -1.10 |
| | Aragonite | 1.65 | 0.89 | 0.75 | 1.19 |
| | Calcite | 1.79 | 1.03 | 0.89 | 1.33 |
| | Dolomite | 4.31 | 2.42 | 2.06 | 3.00 |
| | Fluorite | -3.96 | -2.02 | -2.11 | -2.15 |
| | Magnesite | 1.94 | 0.80 | 0.61 | 1.11 |
| | Gypsum | -0.02 | -0.79 | -1.15 | -0.90 |
| Apr. 2001 | Anhydrite | 0.15 | -0.42 | -0.78 | -0.60 |
| | Aragonite | 0.87 | 0.41 | -0.79 | 0.19 |
| | Calcite | 1.02 | 0.55 | -0.65 | 0.34 |
| | Dolomite | 2.14 | 1.39 | -1.11 | 1.00 |
| | Fluorite | -2.12 | -2.37 | -1.73 | -2.44 |
| | Magnesite | 0.33 | 0.06 | -1.26 | -0.16 |
| | Gypsum | 0.39 | -0.20 | -0.55 | -0.38 |
| Oct. 2001 | Anhydrite | -0.87 | -0.46 | -0.93 | -0.59 |
| | Aragonite | 0.57 | 1.20 | 1.06 | 1.20 |
| | Calcite | 0.72 | 1.35 | 1.20 | 1.34 |
| | Dolomite | 2.69 | 3.01 | 2.66 | 2.97 |
| | Fluorite | -1.27 | -1.78 | -1.81 | -1.78 |
| | Magnesite | 1.20 | 0.86 | 0.64 | 0.84 |
| | Gypsum | -0.65 | -0.24 | -0.71 | -0.37 |

Comparison between the overall chemical composition of the waters of LP, G1, G2 and G3 lakes during this period of study (Table 2) shows that G1 and G3 have the same chemical composition. On the other hand, comparison of these two with the middle one (G2), highlights the presence of a more diluted water which can be explained through a preferential surface water flow towards the “Gorgo” G2. During the drought period this contribution decreases and the water composition becomes again similar to the others. Comparing the lake LP waters with one of these (for instance G1), shows that it is always more concentrated, even though some linear relationship remains (see Figure 8).

Table 2: Comparison among the chemistry of G1, G2, G3 and LP lakes. Previous chemical analyses are also reported (Consorzio di bonifica “Trapani 1”, 1969-70)

| Sample | Cond mS/cm | Na meq/l | K meq/l | Ca meq/l | Mg meq/l | Cl meq/l | SO4 meq/l | HCO3 meq/l |
|---------------|---------------|-------------|------------|-------------|-------------|-------------|--------------|---------------|
| LP 1969 | 11.0 | 65.2 | 2.4 | 2.8 | 33.2 | 94.5 | 28.0 | 7.6 |
| LP 1970 | 8.5 | 79.0 | n.d. | 3.5 | 24.7 | 85.0 | 13.1 | 7.9 |
| LP Jul. 2000 | 16.2 | 348.8 | 7.7 | 36.3 | 135.0 | 431.5 | 137.4 | 16.1 |
| LP Apr.2001 | 10.8 | 87.4 | 1.2 | 36.4 | 43.1 | 106.5 | 56.6 | 5.9 |
| LP Oct. 2001 | 26.5 | 226.7 | 5.0 | 5.3 | 68.6 | 264.1 | 46.8 | 12.5 |
| G.1 1969 | 3.1 | 16.1 | 0.9 | 4.4 | 7.6 | 21.9 | 8.0 | 5.0 |
| G.1 1970 | 2.5 | 21.5 | n.d. | 3.0 | 7.2 | 20.7 | 2.8 | 7.2 |
| G.1 Jul. 2000 | 5.7 | 43.5 | 1.7 | 11.3 | 17.1 | 43.3 | 17.5 | 6.1 |
| G.1 Apr. 2001 | 5.8 | 46.4 | 1.4 | 12.7 | 18.6 | 54.1 | 23.9 | 5.7 |
| G.1 Oct. 2001 | 5.5 | 44.7 | 1.6 | 12.7 | 19.2 | 48.2 | 21.2 | 4.6 |
| G.2 1969 | 1.7 | 7.4 | 0.4 | 4.0 | 4.8 | 11.1 | 12.0 | 4.2 |
| G.2 1970 | 1.5 | 9.6 | n.d. | 3.4 | 3.5 | 10.6 | 1.5 | 4.0 |
| G.2 Jul. 2000 | 3.1 | 20.3 | 0.7 | 6.6 | 6.1 | 21.2 | 7.6 | 4.6 |
| G.2 Apr. 2001 | 3.0 | 22.0 | 1.9 | 7.3 | 9.0 | 27.9 | 10.5 | 4.6 |
| G.2 Oct.2001 | 3.6 | 20.1 | 0.7 | 6.2 | 7.9 | 21.9 | 7.7 | 3.5 |
| G.3 1969 | 3.1 | 16.1 | 1.3 | 4.0 | 6.0 | 22.3 | 5.6 | 6.8 |
| G.3 1970 | 2.5 | 21.0 | n.d. | 2.9 | 6.2 | 21.8 | 0.8 | 6.3 |
| G.3 Jul. 2000 | 4.8 | 36.1 | 1.7 | 9.3 | 13.2 | 38.1 | 14.1 | 5.9 |
| G.3 Apr. 2001 | 4.8 | 39.1 | 1.8 | 6.7 | 14.6 | 44.8 | 18.8 | 3.6 |
| G.3 Oct. 2001 | 6.0 | 36.3 | 1.8 | 10.1 | 14.1 | 41.4 | 16.1 | 4.2 |

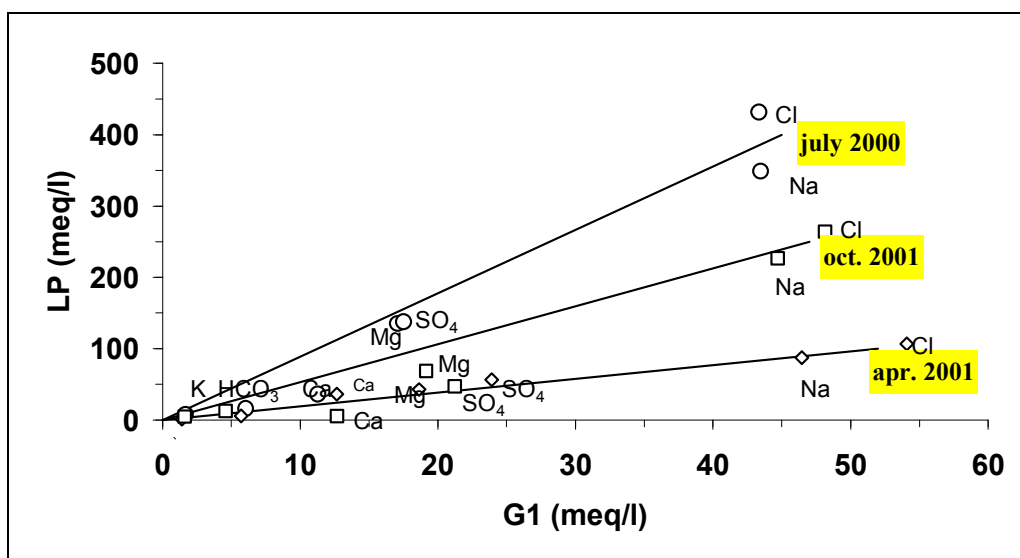


Figure 8: Comparison between the overall chemistry of LP and G.1 lakes

This may be explained with a simplified model reported in Figure 9. According to it, when the LP lake is full part of its water can pour into the other lakes modifying their chemical composition. This model also takes into account the piezometric levels measured along the karst depression. In fact, from the hydrogeological scheme it is possible to note that the lakes water levels in all the samplings evidence water flow from LP towards G1 and, at the same time, from G2 towards G1 and G3. G2 works, in somehow, as a hydrogeological watershed.

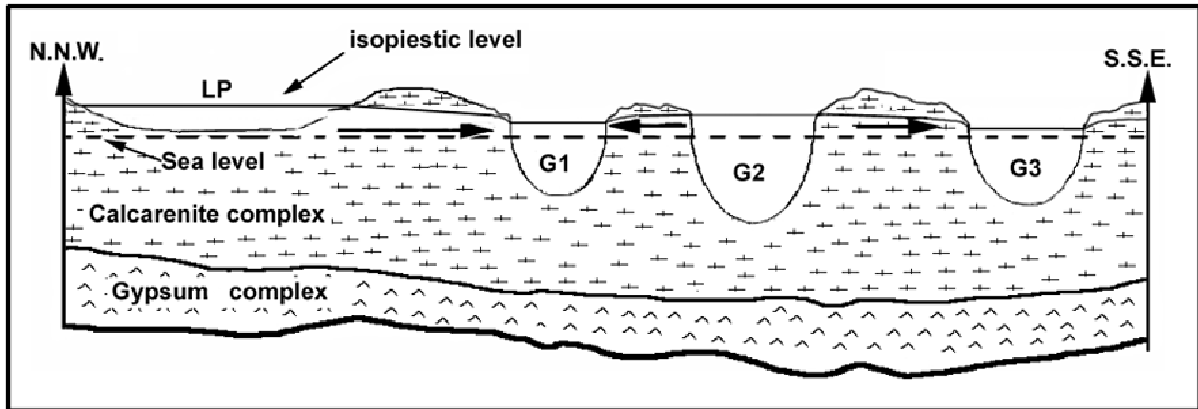


Figure 9: Water circulation model between LP and G.1, G.2 and G.3 lakes

A comparison of previous chemical analyses carried out in the same area [5,18] underlines an increase in lake water salt concentration over the time. This increase may be due to:

- over exploitation of surrounding wells during the period of major surface water contribution causing a decrease in lake input;
- decrease of average annual rainfall, with a historical minimum in 1999 (Figure 10);
- greater evaporation due to the increase of the average annual temperature (Figure 10);

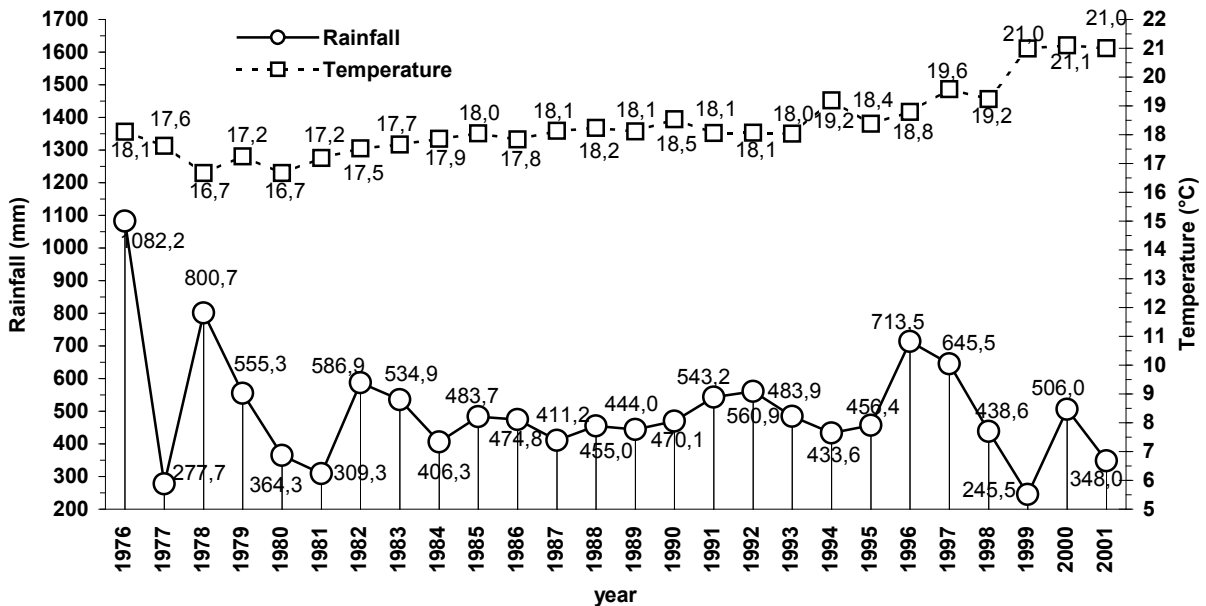


Figure 10: Precipitation and Temperature values in the last 25 years

The $\delta^{18}\text{O}$ composition of the meteoric waters is reported in Table 3. Annual weighed means resulted -6.3‰ (March 2000 - February 2001) and -6.7‰ (March 2001 – February 2002).

Table 3: $\delta^{18}\text{O}$ values for the meteoric waters. (a.w.m. = annual weighed mean; 0= no rain; n.d.= not determined)

| Year | Month | vol.(ml) | $\delta^{18}\text{O}$ (‰) | awm(‰) |
|------|-----------|----------|---------------------------|--------|
| 2000 | March | 300 | -4.4 | -6,3 |
| | April | 1,600 | -2.8 | |
| | May | 1,910 | -5.7 | |
| | June | 600 | 1.0 | |
| | July | 250 | -1.2 | |
| | August | 0 | n.d. | |
| | September | 750 | -1.7 | |
| | October | 3,900 | -6.0 | |
| | November | 1,750 | -3.6 | |
| | December | 5,550 | -6.5 | |
| 2001 | January | 7,000 | -7.9 | -6,7 |
| | February | 7,512 | -7.5 | |
| | March | 2,750 | -6.5 | |
| | April | 850 | -6.6 | |
| | May | n.d. | n.d. | |
| | June | 0 | n.d. | |
| | July | 0 | n.d. | |
| | August | 0 | n.d. | |
| | September | 450 | -1.0 | |
| | October | 650 | -2.1 | |
| | November | n.d. | n.d. | |
| | December | 4,550 | -8.0 | |
| 2002 | January | | | |
| | February | 575 | -7.5 | |
| | March | | | |
| | April | 1,900 | -4.9 | |

The second mean resulted more negative due to the absence of rains during warmer months, generally characterized by more positive values. Figure 11 shows the isotope composition of all waters analysed in this study.

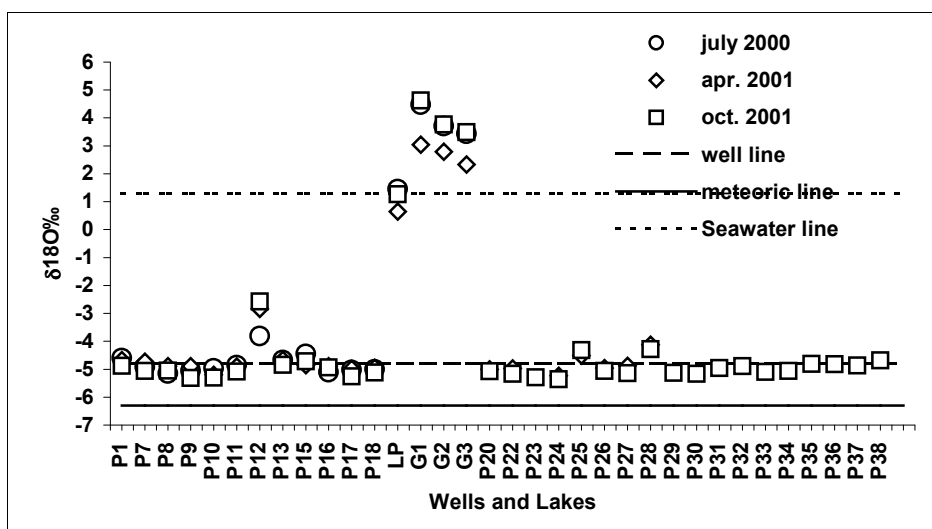


Figure 11: $\delta^{18}\text{O}$ of the waters sampled. The annual weighed mean for the meteoric water and the seawater values are also reported

Almost all well waters result quite homogenous and close to the local meteoric recharge value (around -5‰ , which is a little more positive in relation to meteoric value because of surface evaporation before the infiltration) except P12, and lake waters, which exhibit the most positive values.

Consequently, δD measurements for these samples were performed (Table 4) and the values have been reported on the $\delta D - \delta^{18}O$ diagram, along with the meteoric water line (M.W.L.) established by J. R. Gat and I. Carmi [11] for the Mediterranean area (Figure 12). The values lie along a line whose slope is typical for an evaporative process where the “Gorghetti tonidi” water lakes are the highest end-members observed.

Table 4: δD and $\delta^{18}O$ values of the lakes. Values are in ‰ vs. V-SMOW

| Sample | July-00 | | Apr.-01 | | Oct-01 | |
|----------|--------------------|------------------------|--------------------|------------------------|--------------------|------------------------|
| | $\delta D\text{‰}$ | $\delta^{18}O\text{‰}$ | $\delta D\text{‰}$ | $\delta^{18}O\text{‰}$ | $\delta D\text{‰}$ | $\delta^{18}O\text{‰}$ |
| G1 | 21 | 4,5 | 12 | 3,0 | 19 | 4,5 |
| G2 | 16 | 3,7 | 11 | 2,8 | 15 | 3,8 |
| G3 | 17 | 3,4 | 11 | 2,3 | 12 | 3,5 |
| LP | 5 | 1,4 | 3 | 0,6 | 8 | 1,3 |
| Seawater | 9,8 | 1,3 | n.d. | n.d. | n.d. | n.d. |

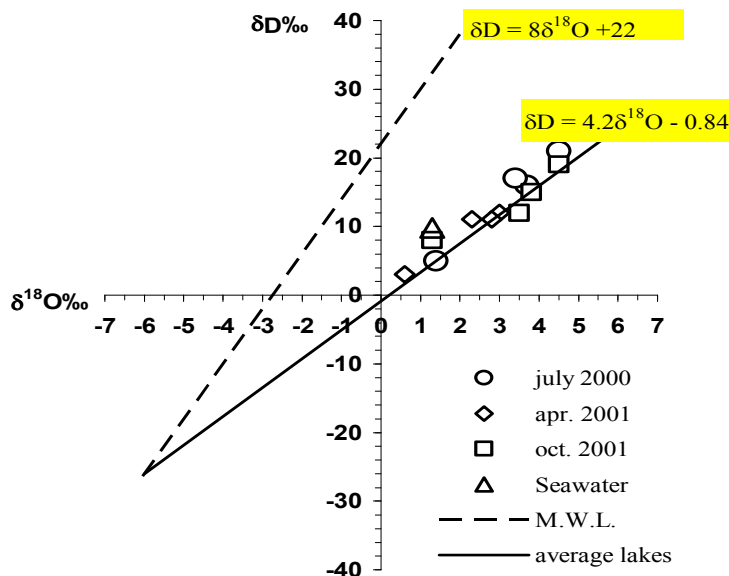


Figure 12: δD vs. $\delta^{18}O$ plot relative to lakes values. It also reported the meteoric water line (M.W.L.) defined by Gat and Carmi (1970) for the Mediterranean area. The intercept on this line, considering the mean $\delta^{18}O$ value obtained for the meteoric precipitation, gives a δD value around -30‰ , which is typical for the precipitation in this area

CONCLUSIONS

In the investigated area the main aquifer present is located in the calcarenites and is fed by local meteoric recharge.

Lakes “Preola” and “Gorghi tonidi” display salt concentrations higher than the aquifer, which supplies them, suggesting processes such as water-rock interaction, evaporation and seawater mixing. Seawater intrusion, with a west-east direction, seems more evident in lake “Preola” and in well n. 12. Considering geochemical, isotopic, and hydrological aspects, one can suppose a preferential flow path between P12 and LP with respect to P28, which may be considered as a low permeability zone and hence with a limited water exchange.

Similarities among the lakes waters may indicate that among them some mixing process takes place, depending on cyclic changes of their hydraulic loads.

The increase in salt concentration in the lakes, since 1969 to present day, is also due to other factors such as: a) reduction in average rainfall, b) over exploitation of the surrounding wells.

ACKNOWLEDGMENT

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