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Study of interactions between a freshwater lake and groundwater in a Mediterranean coastal area by means of hydrochemical indicators

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Abstract

- This study is focused on a coastal water system consisting of a carbonate aquifer feeding a freshwater lake. In such a peculiar system, the geochemical interpretation of water quality data was performed to assess the relationship between groundwater and lake water quality, the potential seasonal variation of their composition, and the occurrence of seawater intrusion.
- A set of hydrochemical indicators calculated from major ion concentrations was used to understand the processes controlling groundwater composition. Lake water quality data were similarly processed for comparison. Results were also matched with the output of a K-means clustering algorithm grouping the sample points according to raw chemical data.
- Groundwater chemistry resulted mainly controlled by the dissolution of carbonate minerals, with hardly detectable contributions of cation exchange mechanisms and seawater intrusion. Variations of the calculated hydrochemical indicators resulted consistent with the distance of groundwater sampling points from the coastline, and not associated with seasonality, thus suggesting a certain influence of sea spray. Also due to this influence, lake water showed a slightly higher salinity than groundwater, while the seasonal quality variations were associated with the effect of evaporation.
- The outcomes of this study were an important starting point for potential lake water exploitation for drinking purposes.

Keywords: Coastal Aquifer, Groundwater Quality, Lake Water Quality, Hydrogeochemical Indicators, Seawater Intrusion.

1 Introduction

Most of the Mediterranean semi-arid areas are subject to increasingly severe and frequent water shortages caused by ongoing climate change. In these areas, groundwater often represents the main freshwater supply for both domestic, including drinking, and agricultural uses. Groundwater quality is frequently affected by contamination from human activities and, in coastal regions, it may undergo further deterioration due to salinization linked to marine sources, such as seawater intrusion and sea spray [1]. Contamination issues are especially severe in karst aquifers, where the conservative transport of contaminants may rapidly occur. In the above scenarios, detailed knowledge of groundwater chemistry is crucial to efficient and sustainable water management.

Multiple tools for hydrogeochemical data interpretation allow identifying the processes that control groundwater chemistry, and its variations with time and space. A convenient approach to data analysis is the calculation of hydrochemical indicators based on major ion concentrations, which reflect the interactions between water and the rock constituting the aquifer and can reveal the occurrence of saltwater contamination.

In this work, hydrochemical indicators were used to gain insight into groundwater chemistry and its correlation with the water quality of the aquifer-fed lake *Alimini Piccolo*. The study site is the *Alimini* coastal water system located in the southernmost part of Italy, on the Adriatic coast (Fig. 1). Groundwater is the main freshwater resource of the area and suffers from intensive exploitation that rises dramatically during summer. With a view to potential lake exploitation for drinking purposes, this study aimed at assessing the potential variation of lake water quality consequent to changes in groundwater composition, with special regard to the impact of seawater intrusion. Geochemical interpretation of data was complemented with statistical processing through a clustering algorithm, which revealed correlations of water quality both with the location of sampling points and with sampling seasons.

2 Data collection and methodology

Seasonal monitoring data were collected during seven sampling campaigns covering one hydrological year. *Alimini Piccolo* lake water was sampled in five points spread over the lake surface. One of them (S) was located at the main groundwater spring feeding the lake; the remaining points were those labelled, respectively, LC, RG, FE, and FS (Fig. 1). Groundwater was sam-

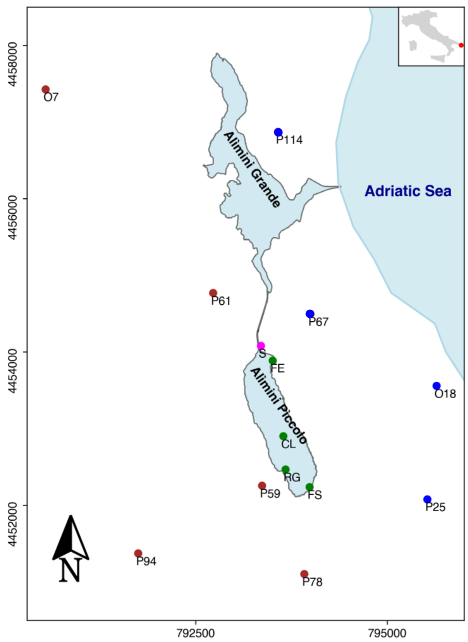

Fig. 1. Study site and positioning of the sampling points. Map projection: WGS84-UTN Zone 33N.

pled from nine surrounding wells, four of which were close to the coastline (respectively, O18, P25, P67, and P114) whereas five were inland (respectively, O7, P59, P61, P78, and P94).

Water samples were analysed for physico-chemical parameters related to drinking water production. Each sampling campaign was associated with one of two seasons, i.e., dry (D) and wet (W), and the mean values of each parameter were calculated over each season before calculating hydrochemical indicators in correspondence to each sampling point. The selected indicators were *[2-5]*:

a) the Chadha plot;
b) seawater fraction;
c) chloro-alkali indices (CAI); d) correlations between alkalinity and major cations; e) the correlation between $[(Ca^{2+}+Mg^{2+})-(SO_4^{2-}+HCO_3^{-})]$ and $(Na^{+}-Cl^{-})$; f) correlations between Cl^{-} and, respectively, the ion ratios Ca^{2+}/HCO_3^{-}, HCO_3^{-}/Cl^{-} (inverse of Simpson's Ratio), Na^{+}/Cl^{-}, and Mg^{2+}/Ca^{2+}.

Parallel data processing was performed by the Python code that employed K-means clustering to analyze the grouping patterns within the whole initial dataset without applying any data transformation. The elbow method was applied to determine the optimal number of clusters by plotting the Within-Cluster Sum of Squares (WCSS) against varying numbers of clusters.

3 Results and discussion

Generally, both groundwater and lake water quality complied with drinking standards in all seasons.

The Chadha diagram (Fig. 2) allowed the identification of the mechanisms affecting groundwater composition. All sample points (blue and brown symbols) were positioned within the subfield identifying bicarbonate-calcic freshwater, thus suggesting that other mechanisms, i.e., either saltwater mixing or ion exchange, would not affect the relative ion concentrations. Samples from either coastal or inland wells formed two distinct sub-groups within the cluster, whereas no significant separation was detectable for well samples according to seasonality. The positioning of lake water data points (green and pink symbols) at the lower edge of the cluster was consistent with higher lake salinity than groundwater.

Correlations between bicarbonate (accounting for total alkalinity) and major cations (Fig. 3a) confirmed that groundwater composition was governed by the dissolution of carbonate minerals, but also suggested a potential (although small) influence of reverse cation exchange, which could be triggered by Na^+ intake caused by seawater intrusion. However, the correlations of Ca^{2+}/HCO_3^- vs. Cl^- and $(Ca^{2+}+Mg^{2+})-(SO_4^{2-}+HCO_3^-)$ vs. (Na^+-Cl^-) confirmed the assumption that reverse cation exchange may only have a marginal role in

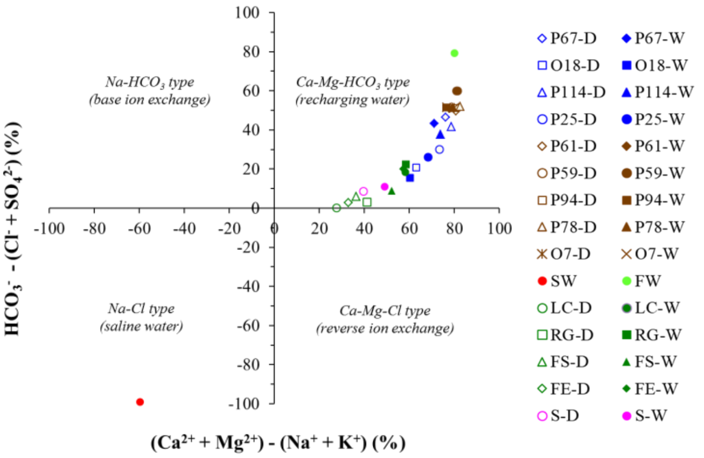

Fig. 2. Chadha diagram comparing groundwater, lake water, and the end-members seawater (SW) and fresh water (FW). Open and full symbols represent the mean values calculated over, respectively, the dry season (D), and the wet season (W). Symbol colors denote the positioning of sampling points, i.e.: blue = coastal wells; brown = inland wells; dark green = lake points, pink = spring (S). Symbols explanation applies also to Fig. 3.

groundwater. Since ion exchange cannot influence the chemistry of lake water, here the lowest concentrations of bicarbonate matched with high values of conductivity and dissolved solids and suggested the direct intake of sea salts.

Chloride concentrations relative to HCO_3^- provided information about seawater intrusion, since Cl^-, is a conservative tracer. The correlation in Fig. 3b (as well as the Na^+/ Cl^- ratio vs. Cl^-, data not shown), suggested a poor impact of seawater intrusion on groundwater. The neat separation between coastal and inland wells data points, with higher relative concentrations of chloride in coastal wells, suggested that a minimal groundwater salinization related to marine sources, such as sea spray, could affect only the area of the aquifer close to the coastline.

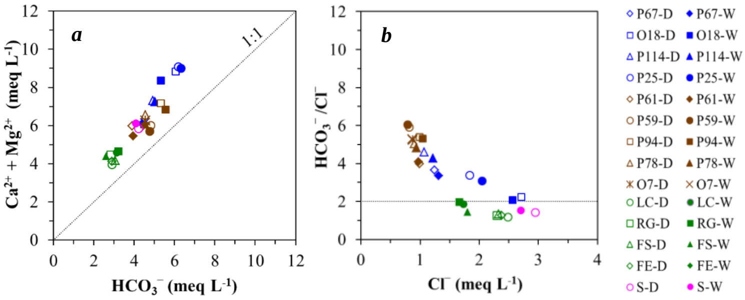

Fig. 3. Plots of ion correlations calculated for both groundwater and lake water. Symbol explanation is in Fig. 2 caption.

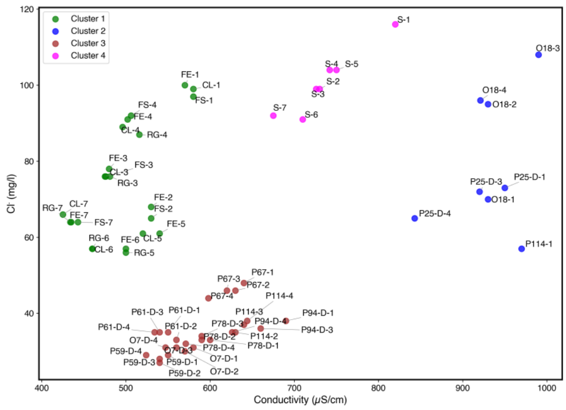

Fig. 4. Output of the K-means clustering algorithm.

Lake water data in plot 3b revealed that water quality close to the main spring resembled that of groundwater sampled in coastal wells. However, the highest values of Cl^- measured for lake water were ascribed to the direct input of sea salts (i.e., through rainfall that dissolves salt deposits on land consequent to sea spray). In addition, the grouping of lake data points into two separate clusters according to season was associated with the only effect of evaporation, without compromising drinking quality at any time.

Data clustering provided by the statistical processing through the K-means algorithm was consistent with the analysis of hydrochemical indicators for most of the sampling points. As shown in Fig. 4, four clusters were identified corresponding to, respectively, 1) lake sampling points, 2) coastal wells, 3) inland wells, and 4) the spring, with only a few exceptions. Within cluster 1, sub-groups identifying sampling campaigns confirmed the seasonal change of lake composition.

4 Conclusions

In the coastal water system under study, groundwater composition did not result significantly affected by either saline contamination or seasonal variations. Lake water quality closely mirrored that of the feeding groundwater, aside from small seasonal variations due to evaporation, and was always suitable for drinking purposes.

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