

# Preliminary hydro-geochemistry characterization of the complex geological framework of the Coreca area (Calabria, South Italy).

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**Abstract** Hydrogeochemical characterization combined with statistical methods has been used to investigate groundwater quality and related geochemical processes in the complex geological framework of Coreca (Calabria, South Italy). Coreca is characterized by a peculiar geological setting that affects the groundwater quality mainly exploited for irrigation use. Two groups of waters were identified: Ca-HCO<sub>3</sub> waters strongly controlled by the interaction with Ca-rich phases; Mg-HCO<sub>3</sub> waters related to the interaction of meteoric water with the metamorphic Units. In Mg-HCO<sub>3</sub> group was identified a good correlation between Cr and Ni (not observed in Ca waters) and a negative correlation between Cr, Ca and Al in agreement with direct interaction with ultramafic rocks characterized by low concentration in CaO and Al<sub>2</sub>O<sub>3</sub>. The concentration of major and trace elements has been compared with the Italian law limit values and the drinking water guidelines provided by the World Health Organization (WHO). Only samples S20, S25 and S29 showed Mn and Ni concentration higher than the Italian law threshold. The study allows defining how a multidisciplinary approach represents a useful tool to trace the factors controlling the groundwater evolution and quality especially in areas with an articulate geological and hydrogeological asset.

**Keywords:** Hydrogeochemistry; statistical analysis; Coreca; drinking and irrigation use; statistical elaboration.

## 1. Introduction

In areas with a complex geological-structural asset, it is not easy to discern between geochemical characteristics linked to a mere water-rock interaction from processes induced by human activity (Vespasiano et al. 2018; Apollaro, 2019). In these contexts, multidisciplinary approaches based on geological and geochemical characterization, coupled with statistical techniques, could represent a useful tool to reconstruct the groundwater evolution and

related geochemical processes (Appelo & Postma, 1996). The aim of this work is the groundwaters characterization of the complex geological framework of the Coreca area (Calabria, South Italy) through a multidisciplinary approach based on statistical methods combined with hydrogeochemical modelling and conventional data elaboration with reference to the nature of the resource and its use. Coreca is localized near the Tyrrhenian coast, in proximity of the Oliva Catchment that has been site of numerous environmental surveys with the aim to characterize the environmental matrices. As reported by Italian newspaper, previous surveys highlighted, in the main matrixes, the occurrence of several heavy metals and pollutants such as copper, mercury, zinc, manganese and other radionuclides for medical and industrial use, higher than Italian law and World Health Organization threshold limits. The complexity of the geological setting and data from historical surveys makes the Coreca area a site of high interest. Rocks and waters compositions were elaborated following (i) statistical methods, combined with (ii) hydrogeochemical modelling and (iii) conventional plots to investigate groundwater and related geochemical processes.

## 2. Geological Setting

The studied area is localized in the northern sector of the Calabria Region (South Italy), in proximity of the Tyrrhenian coast and includes the Coreca town (west side), the Gallo town (east side), the Oliva River (southern boundary) and the Coloncì Torrent (northern boundary). The area is comprised close to the Neogene-Quaternary Amantea Basin, located on the western slope of the Coastal Range. The basin developed during extensional tectonic phase and the consequent opening of the back-arc Tyrrhenian Basin (Muto & Perri, 2002), simultaneously with compression and accretionary processes developed in the eastern margin of Calabria (Van Dijk et al., 2000; Muto et al., 2014). From a geological point of view,

metamorphic units, referable to the allochthonous Alpine Liguride and Calabride Complexes, outcrop and overthrust the Mesozoic carbonate unit crop out in a fault bounded tectonic window. This latter is constituted by Triassic dolostone and dolomitic limestone (Verbicaro Unit) overthrust by the ophiolitic sequence belonging to the Frido (mainly metapelites and slates) and the Gimigliano-Monte Reventino Units (serpentinites, metabasalts, phyllites and carbonates) (Piluso et al., 2000; Iannace et al., 2007). The metamorphic units are sealed by the Miocene sedimentary sequences consisting in calcarenites, clays, marls, and Messinian limestone. Pleistocene terraced deposits outcrop at the top of the succession. The hydrogeology of the Coreca area is characterized by two different kinds of aquifers: fissured and/or karstified aquifers in the Apennine and Metamorphic units and partially in the Miocene deposits and porous multilayer aquifers developed in the Miocene/Quaternary successions. Both types present relatively high volumes of groundwater storage and circulation, with the richest amount located in pre-quaternary substratum aquifers usually subdivided in different hydrogeological complexes according to the structural, lithological and permeability features. These aquifers mainly occur in highly fractured limestones and in the fractured-altered superficial portion of the metamorphic units, both characterized by high permeability. Porous aquifers occur in gravelly-sandy permeable deposits of the quaternary succession, with flowrates variable according to annual rainfall.

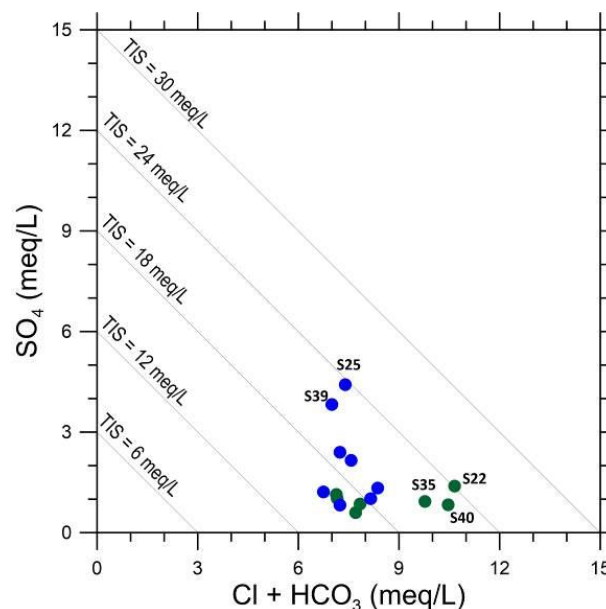
### 3. Methods and Materials

In the current study, statistical methods combined with hydrogeochemical modelling and conventional plots have been used to investigate groundwater and related geochemical processes. A total of 15 groundwater samples has been collected and analyzed in laboratory for major cations, anions, and trace elements. Furthermore, 9 representative rock samples were collected and analyzed. Chemical-physical parameters such as pH, Eh, temperature, alkalinity, and specific electrical conductivity, were measured in the field by means of portable instruments (HI9828). Total alkalinity was determined by acidimetric titration, using HCl 0.05N as titrating agent and methylorange as indicator. In the laboratory, the concentrations of F, Cl, Br, SO<sub>4</sub>, NO<sub>3</sub>, PO<sub>4</sub>, Na, K, Mg and Ca were determined by HPLC (DIONEX DX 120). During the same day was measured dissolved reactive SiO<sub>2</sub> by VIS spectrophotometry upon reaction with ammonium molybdate in acid media (and treatment with oxalic acid) to form a yellow silicomolybdate complex, whose absorbance was read at 410 nm. Trace elements were analysed by a quadrupole ICP-MS (Perkin Elmer/SCIEX, Elan DRCe) with collision reaction cell capable to reduce or avoid the formation of polyatomic spectral interferences. Data quality for major components was estimated by charge balance. Deviation between the sum of concentrations of cations and the sum of concentrations of anions, both in equivalent units, varies between -5% and +5%. Data quality for minor and trace elements was checked running the NIST1643e standard

reference solution. Deviations from the certified concentrations were found to be lower than 5%. For each sample, saturation index (SI) with respect to the mineral phases, were performed using PHREEQC Interactive software, version 3.1.1 (Parkhurst and Appelo, 2013) using the LLNL thermodynamic database. The Mineralogical associations for each main lithotype were determined using an optical microscope and by means of a Bruker D8 Advance XRD Diffractometer. The geological heterogeneity, the proximity to the coastline and the anthropic activities represents factors that can induce a high geochemical variability and favor releasing of potentially toxic constituents in solution as evidenced by the historical surveys. To evaluate the qualitative state of the resource, the water composition was then compared with the conditions set by the World Health Organization (hereafter WHO) and the Italian legislation (D.Lgs. n. 152/2006).

### 4. Results

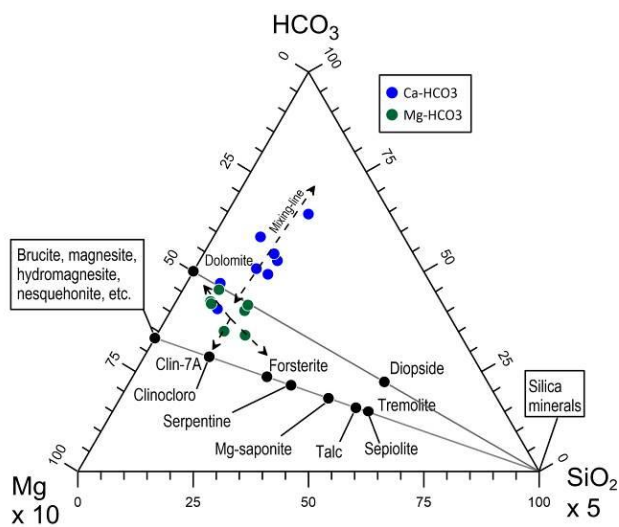
Springs and wells collected in the Coreca area have shown average temperature  $20.4 \pm 2.2$  C° that are slightly higher than the yearly mean atmospheric temperature ( $15.6 \pm 5.3$  C°). The pH and EC (electrical conductivity) values are respectively of  $7.4 \pm 0.4$  and  $980 \pm 143$  (μS/cm). In general, Eh showed a wide positive range of values, only samples S25 and S39 highlighted negative values. Triangular plots allow to identify two groups of waters: (i) a first group with a Ca-HCO<sub>3</sub> composition suggesting a chemism controlled by dissolution of Ca-rich phases and (ii) a second group with a Mg(Ca)-HCO<sub>3</sub> composition probably due to the interaction with ultramafic rocks and/or carbonate-dolomitic successions.



**Figure 1.** SO<sub>4</sub> vs. HCO<sub>3</sub> + Cl (TIS) plot. In the diagram the iso-ionic-salinity lines are drawn as reference.

Among the Ca-bearing phases, calcite, which occur both in metabasalts and carbonatic rocks, represents the phase with the highest dissolution rates. Its presence promotes Ca-HCO<sub>3</sub> waters. On the other hand, antigorite, actinolite

(in serpentinite and metabasalt) and dolomite are the local phases that can promote formation of Mg-HCO<sub>3</sub> waters (Critelli et al., 2015; Vespasiano et al., 2016). Waters were also classified using the TIS diagram of Figure 1. The correlation graph SO<sub>4</sub> vs. HCO<sub>3</sub> + Cl (TIS) shows, for the two groups of water, comparable salinity values between 12 meq/L to 24 meq/L. The values are higher than those of waters hosted in metamorphic aquifers indicating a significant role of secondary phases dissolution. Salinity values and ratios of major constituents suggest for samples S22, S40 and S35, belonging to Mg-HCO<sub>3</sub> waters, a prolonged water-rock interaction with the hosting units, increasing their salinity and Mg concentration. Furthermore, S25 and S39 (Ca - deep wells) highlight a considerable sulphate increase.



**Figure 2.** Triangular diagrams (HCO<sub>3</sub> + CO<sub>3</sub>) - Mg - SiO<sub>2</sub> where are reported the samples collected in the Coreca area.

These two samples show also high Fe (5733 and 7673 respectively) and Mn (112 and 76 respectively) concentration. S25 and S39 are representative of a third aquifer, outside the study area and hosted in the sandstone with grey calcareous cement directly in contact (tectonic contact) with the metamorphic basement (phyllites). The anomalies are probably due to repeated alternations of reducing and oxidizing conditions that can promote sulphides and Fe-Mn oxy-hydroxides dissolution. With the aim to improve the knowledge about processes and evolution undergone by the considered systems, for each sample, saturation index (SI) with respect to specific mineral phases, were performed using PHREEQC Interactive software, version 3.1.1 using the LLNL thermodynamic database. As found, most waters reach oversaturation with calcite, dolomite, clinochlore, tremolite and albite and have reached value close to the saturation with phases characterizing the main outcropping lithotypes. Furthermore, geochemical data were elaborated by using of the triangular plot (HCO<sub>3</sub> + CO<sub>3</sub>) - Mg - SiO<sub>2</sub> reported in figure 2 (Marini and Ottonello, 2002). The diagram allows to compare the observed compositions with those expected for congruent dissolution of different

magnesian minerals, such as serpentine, talc, sepiolite, brucite, magnesite (and other carbonates) and for incongruent dissolution of Mg Saponite and Clinochlore (accompanied by precipitation of Al-secondary silicates). The compositions expected for dissolution of these solid phases were represented based on the stoichiometric coefficients of the relevant reactions. Water-rock interactions with the specific phases are clearly showed in figure 2. Mg-HCO<sub>3</sub> waters are positioned between the compositions expected for dissolution of clinochlore and calcite suggesting a prevailing interaction with rocks holding these 2 phases. A shift towards phases linked to ultramafic rocks is only mildly evident. Samples S22, S40 and S35 show the highest SI values with respect to clinochlore, albite and tremolite, directly linked to metabasites, and phases characterizing ultramafic rocks (e.g. antigorite). Hydrogeological assets confirm the geochemical evidence which allow to exclude Mg compositions linked to an interaction with the dolomitic successions. Ca-HCO<sub>3</sub> falls above the dolomite-diopside line suggesting an interaction with carbonate phases.

## 5. Discussion and Conclusion

In the current study, hydrogeochemical characterization combined with statistical methods have been used to investigate groundwater quality and related geochemical processes in the complex Coreca basin (Calabria, South Italy). Geochemical data and hydrogeological evidence confirmed the existence of two group of groundwater: a) Ca-HCO<sub>3</sub> hosted in the shallow Miocene/Quaternary aquifer and b) Mg-HCO<sub>3</sub> localized in the ultramafic aquifer (serpentinites and metabasites). Calcite on the one hand and antigorite, tremolite and clinochlore on the other represent the main phases that favour the formation of Ca and Mg systems. SI calculations confirmed oversaturation with calcite, clinochlore, tremolite and albite and saturation with other phases characterizing the main outcropping lithotypes. Statistical approach allowed to define, in Mg-HCO<sub>3</sub> group, high concentrations in trace elements such as Cr and Ni and Mg replace Ca underlining a direct role pf Mg-bearing phases during water-rock interaction. Furthermore, Mg group exhibits a good correlation between Cr and Ni (not observed in Ca waters) and a negative correlation between Cr, Ca and Al in agreement with a direct interaction with ultramafic rocks (e.g. serpentinite) characterized by low concentration in CaO and Al<sub>2</sub>O<sub>3</sub>. Data confirm a multi-aquifer system. Subsequently, major and trace elements had been compared with the Italian law limit values and the drinking water guidelines provided by World Health Organization (WHO, 2004). Only samples S20, S25 and S29 have shown a Mn and Ni contents higher than the lowest threshold provided for by Italian law (50 ppb and 20 ppb respectively). The study allows to define how a multidisciplinary approach represents a useful tool to define the factors controlling the groundwater evolution and quality especially in areas with articulate geological and hydrogeological asset. From a general point of view, data highlight a good quality of groundwaters of the studied area.

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