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Aqueous geochemical modeling and multivariate statistical approach for in-depth understanding carbonate drainage systems (Gran Sasso fissured aquifer, central Italy)

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The Gran Sasso carbonate aquifer is partitioned, fractured and partly karstified with a total groundwater discharge about 23 m3/s, corresponding to a net infiltration of more than 800 mm/year, very high respect to an average rainfall of 1200 mm/year. Gran Sasso aquifer is composed of Meso-Cenozoic lithologies, mainly cherty-marly-calcareous belonging to basin, slope and carbonate platform-reef lithofacies. Gran Sasso is bounded by Miocene sandstones, marls and clays (aquiclude) along its northern side, and by Quaternary fluvial and lacustrine deposits (conglomerates, breccias, sands and clays) (aquitard) along its southern side. In the Gran Sasso aquifer, groundwater flows from recharge areas (concentrated at the core of the aquifer) to the boundaries of the aquifer, and reaching remote springs located in the Tirino River Valley.

For the Gran Sasso aquifer the conceptual model of groundwater flow, formerly defined by means of hydrogeological studies, is fine-tuned with the long-term (2001-2009) spatial and temporal multi-hydrochemical spot monitoring.

Moreover the conceptual model has been validated by the analysis of the 222Rn activity in groundwater, considered as environmental tracer of different groundwater flowpaths. Indeed, considering its fast half-life (3.823 days), the average 222Rn is reflective of the final part of the groundwater flowpaths, especially of calcareous and calcareous-marly lithotypes occurring in the spring outflow areas. While, its temporal variability is dependent on the seasonal changes of the water table.

Seasonal sampling surveys were carried out to characterize the hydrogeological cycle (recharge, unsaturated and saturated zone infiltration, discharge) and water-rock interaction. About 7500 physic-chemical parameters of regional groundwater flow for about 30 monitoring surveys (2001-2009) were investigated.

Generally Gran Sasso groundwater is alkaline-earth bicarbonate type with low to medium mineralization (about 100-500 μS/cm). Currently, it is undersaturated or slightly saturated in calcite and is related to an open CO_2-H_2O-$CaCO_3$ system.

Six geochemical facies are identified in the whole system. The differences between the six groups (in terms of local hydrostructural setting and hydrochemistry) support groundwater flowpaths from the Gran Sasso core to its boundaries; these flowpaths depend on various factors, such as structural setting, karst features, outcrops of dolomite bedrock, local recharge effects and geological setting near the springs. Different geochemical evolution trends characterize the final chemical composition of discharging groundwater, based on the water-rock interaction and seasonal dilution effects.

A Factorial Analysis has been applied on the samples, considering a correlation matrix of main ion parameters: T, EC, pH, Ca2+, Mg2+, Na+, K+, HCO_3-, SO42-, Cl-, F-, Br-, NO_3-, SI calcite and SI dolomite. While a Cluster Analysis has defined 5 statistical groundwater groups. The multivariate statistical results represent the beginning of a specific geochemical modeling of evolution flowpaths. The PHREEQC v.2.16 software (Parkhurst and Appelo, 1999), was used to simulate the geochemical reaction occurring along the flowpath. The results of numerical modeling are consistent with the evolution and flowpaths derived from the preliminary hydrogeochemical conceptual model. Especially the performed inverse models generate the main geochemical processes happening in groundwater system, that are also responsible of mixing processes. Dissolution/precipitation govern water-rock interaction respect to ion exchange processes, at each evolution step, demonstrating a short time interaction of infiltrating water in the unsaturated zone and seasonal dilution effect.