Groundwater recharge areas of the Mt. Vulture volcanic aquifer by means of hydrogeochemical data and stable isotopic tracer

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Environmental isotope techniques and hydrogeochemical analysis were employed to identify the recharge area of Mt. Vulture hydrogeological basin placed along the external edge of the Apennine Chain (southern Italy). The groundwater in the studied area, meteoric in origin [1], derived from seepage rainwater flowing from the highest to the lowest altitude, through the volcanic leached host rock. The Vulture basin shows an altitude gradients of almost 1000 meters providing good conditions for application of water stable isotopes. Water sample were collected at 48 locations, for stable isotope ($\delta^{18}O$, δD) and major ion analysis. Seventeen springs were sampled from June 2007 to June 2008 along an altitudinal gradient between 340 masl and 1100 masl. Thirty-one groundwater samples were taken from the discharge of operating wells in the Vulture basin, located between 352 and 960 masl. Calculated recharge altitudes of studied aquifer showed that source areas of mainly precipitation recharge, estimated on the basis of the local vertical isotopic gradient (-0.17‰ $\delta^{18}O$/100; [1]), are generally located between 700 and 1200 masl. The isotope pattern of the volcanic aquifer reflects the spatial separation of different sources of recharge. Isotopic signatures in the south and north-eastern areas of the volcanic aquifer indicate a considerable recharge contribution by flow discharged from the adjacent volcanic domain and minor recharge input comes from fluvio-lacustrine deposits. The north-western sectors is the main recharge area of the most investigated sampling points. No relevant evaporation effects have been detected.

[1] Paternoster *et al.* (2008) Stable isotope ratios in meteoric recharge and groundwater at Mt. Vulture volcano, southern Italy. *Journal of Hydrology* **348**, 87 – 97.

Multivariate statistical interpretation of hydrochemistry data of bedrock groundwaters: Evaluation of geochemical backgrounds and anthropogenic contamination

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Better evaluation of the degree of anthropogenic contamination, based on determination of a natural background, is required to sustainably manage groundwater. We performed hydrochemical and statistical analyses of bedrock groundwater (N=162) collected from two suburban areas (Boeun and Naju) in Korea. This involved model-based clustering using the Expectation-Maximization algorithm and discriminant analysis. Groundwater samples can be divided into two major groups, Group I (35 samples) and Group II (123 samples) which show characteristic bimodal probability density distribution patterns. Major ion chemistry changes gradually from Na-HCO_3 type (Group I) to Ca-Cl type (Group II). Among major dissolved ions, NO_3 and F are useful variables to successfully classify (>90% confidence) polluted and unpolluted groups, respectively. Group I waters show a positive relationship between Na and HCO_3, indicating that their chemistries are mainly controlled by progressive hydrolysis of Na-silicates (plagioclase) during water-rock interaction. A negative correlation between Na and Ca ions also indicates the subordinate role of cation exchange and subordinate calcite precipitation. On the other hand, Group II waters show good correlation between the concentrations of total cations, Cl and NO_3. The hydrochemistry of Group II waters is mainly controlled by anthropogenic pollution (esp., influences from agrochemicals and domestic sewage/manure) with subordinate cation exchange and calcite dissolution. This study shows that multivariate statistical interpretation of hydrochemistry data (especially, concentrations of F, NO_3, and other variables such as HCO_3, Cl, Mg, Ca, and Na) can be successfully used to determine geochemical backgrounds and to distinguish contribution from anthropogenic pollution.