



Hydrogeochemistry of regional aquifer systems from Tuscany (central Italy): the state of the art before the definition of a geochemical baseline

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European Community Water Framework Directive (WFD) and its derivative regulations have recognized the urgent need to adopt specific measures against the contamination of water bodies by individual pollutants that may significantly affect the quality of water itself. Italian regulation takes into account the EU Directives, and charges the regional authorities to create monitoring networks and produce assessment reports on the contamination of groundwater. The knowledge of "natural baseline" for various dissolved elements in groundwaters on a regional scale becomes of primary importance to distinguish natural sources and anthropogenic inputs.

The studied area includes the whole Tuscan regional district (central Italy) and covers an area of about 23,000 km². From a geolithological point of view, Tuscan territory consists of several complexes outcropping regionally, the most typical features being the Mesozoic and Cenozoic carbonate and evaporitic formations, overlain by flysch sequences, as well as granite intrusions and volcanic rocks. Moreover, two geothermal areas (Larderello and Mt. Amiata), a large number of thermal springs and CO₂-rich gas vents are mostly present in the central-southern part of Tuscany. Finally in southern Tuscany (e.g. Campiglia M.Ma, Mt. Amiata, Elba Island), mining districts, predominantly characterized by polymetallic sulphides ore deposits, were exploited since the Etruscan time.

In this work statistical distribution models are used to develop summary statistics and estimate probabilities of exceeding water-quality standards according to the National Legislative Decree 152/06. Descriptive statistics on solute concentrations are based on geochemical data from the main Tuscan aquifers and investigated by the CNR-IGG (Institute of Geosciences and Earth Resources of Pisa, Italy) and Department of Earth Sciences (University of Florence, Italy). The data processing was carried out on 4,767 water samples collected from 1997 to 2009.

According to the National Legislative, the chemical constituents were selected according to a priority interest: As, B, Cd, Cr (VI), F, Hg, Ni, Pb, Sb, Se, V, sulphate and chloride. For each species probability plots in logarithmic scale were computed and the statistical parameters were evaluated for the individual populations as resulting by the procedure of partitioning. Most of the solutes have concentrations that span within 2-3 orders of magnitude, although Ni, SO₄ and Cl concentrations show a larger variability (up to 4 orders of magnitude). All the considered variables are mainly characterized by polymodal distributions and composed by more than one population. High concentration populations, exceeding water-quality standards, are generally recognized for SO₄, As, B, Cd, Cr(VI), F, Hg, Ni, Pb and Se.