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Assessing background values of chloride, sulfate and fluoride in groundwater: a geochemical-statistical approach at a regional scale

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Abstract

The Sardinia island (Italy) is one of the European areas least affected by potentially anthropogenic impacts, such as spreading urbanization, intensive agriculture and regional atmospheric contamination. Such characteristics allow to consider Sardinia a good site for testing an approach that integrates geochemical tools, hierarchical cluster and geographical information system, aimed at estimating background concentrations of chloride, sulfate and fluoride at the regional scale.

Analytical data were obtained from several hydrogeochemical surveys and from the groundwater-monitoring program established by the Sardinian Regional Government. Groundwater samples were grouped according to their circulation in the predominant hydrogeologic complex: Quaternary sediments, Quaternary basalts, Tertiary sediments, Tertiary volcanic rocks, Mesozoic carbonatic rocks, Paleozoic carbonatic rocks, granitic rocks and metamorphic rocks.

Samples surely affected by anthropogenic inputs, thermal waters, waters collected at wells with unknown construction details and poor quality analyses were excluded. The resulting dataset included 1414 groundwater sampling sites distributed over an area of 24,090 km² (All data). Another dataset comprised of 641 sampling sites (Selected data) was derived by All data excluding the groundwater with NO₃⁻ > 10 mg/L. Hierarchical clustering analysis was performed on both datasets considering Ca²⁺, Mg²⁺, Na⁺, K⁺, Cl⁻, HCO₃⁻, SO₄²⁻, NO₃⁻ and F⁻. The values of total dissolved solids (TDS) were a major distinguishing factor among clusters, but distinct signatures related to the median nitrate and fluoride concentrations were also recognized. The geographic distribution of clusters reflected the role of geological and geographic characteristics on the geochemistry of groundwater.

Background ranges of the regulated parameters chloride, sulfate and fluoride in each cluster, identified either using All data or Selected data, were calculated using the median±2MAD. Although results were found in general agreement, the threshold using the median+2MAD was calculated using the Selected data only, because the Selected data better represents near pristine conditions. Chloride threshold values above the drinking water limit were mainly observed in groundwater located in western Sardinia, where sediments and volcanic rocks prevalently outcrop, and also in some coastal areas. Threshold values of sulfate and fluoride above the limit were related to local conditions. Specifically, high threshold values of sulfate were observed

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