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Arsenic – fluoride rich groundwaters in a volcanic-sedimentary aquifer in central Italy: background and anomalies

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This study explores the co-existence of arsenic and fluoride in a volcanic-sedimentary aquifer in central Italy, aiming at identifying the risk areas for human health and the most likely processes deductible at regional/groundwater body scale leading to the observed co-contamination in groundwater.
The study area is located in Latium (Central Italy) where undersaturated alkali-potassic formations largely outcrop, belonging to three different volcanic apparatus of Plio-Pleistocene age.
Geochemical data from groundwater at 398 wells or springs are analyzed through statistical methods including clustering/PCA and geostatistical analysis. 29% of the sampled groundwaters exceeds the drinking water standard for F (1.5 mg/L), while 55% exceeds that for As (10.0 μg/L). Multivariate statistics suggest a widespread process of water-rock interaction with the K-alkaline volcanic formations releasing As, F, K, Si, V, Rb and PO4 to the groundwater. As and F show a good correlation (Pearson's r = 0.61) and define a separate component, suggesting that their background in groundwater might be governed by a common process.
While in the peripheral areas of the volcanic districts, dominated by sedimentary deposits, the As-F correlation index does not present important fluctuations, Indicator Kriging shows specific As or F anomalies within the volcanic groundwater bodies and along the Tyrrhenian coastline. These anomalies seem to correspond to the zones with the highest thermal flux and/or are located near important structural lineaments. Fluoride anomalies close to mining sites (fluorite) have also been observed. We hypothesize that, unlike the regional co-contamination, these local anomalies are related to the upwelling of geothermal fluids along fracture/fault systems that mix with cold groundwater, or to the interaction with mineral deposits particularly enriched of these elements.