Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.29158

Arsenic Mobility in Groundwater: A Multivariate Statistical and Geochemical Approach within the Varese CARG Project

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Arsenic contamination in groundwater is a pressing environmental and public health issue, particularly in areas where natural geogenic processes contribute to elevated As concentrations. Several physicochemical features of both groundwater and sediment play crucial roles in determining As mobility, yet current research focuses on single factors individually, overlooking their effect in combination. This study addresses this gap by integrating hydrochemical characteristics of groundwater and geochemical properties of sediments in the Como aquifer and Stabio water recharge basin (Italy-Switzerland), an area known for anomalously high As levels in water (>230 µg/L). To achieve this, we conducted controlled batch adsorption/desorption experiments on sediment samples collected reflecting different geochemical facies, simulating variable physicochemical conditions of groundwater (pH, salinity, and dissolved organic carbon). Additionally, we examined sediment composition, cation exchange capacity (CEC), grain size distribution, and metal oxide content to assess their role in As species adsorption/desorption mechanisms. A novel aspect of this research is the application of chemometric statistical methods, such as Principal Component Analysis (PCA), Multilinear Regression (MLR), and Design of Experiment (DOE), robust tools in modelling trace element features, but with limited application in environmental geochemistry. The results indicate a complex interplay between sediment and water chemistry. The adsorption efficiency of As is primarily influenced by pH, with maximum retention under acidic conditions. However, non-linear interactions between salinity and dissolved organic carbon (DOC) were observed, leading to parabolic adsorption trends. Moreover, significant variations in adsorption capacities between the two sediment depths were identified, with the deeper sediment (70 m) exhibiting lower retention efficiency due to its distinct mineralogical and geochemical composition. These findings suggest that deep groundwater is more prone to As mobilization, which aligns with field observations of elevated As concentrations in deeper aquifer zones. This integrated approach provides a more accurate and predictive model of As behaviour in groundwater, offering critical insights for risk assessment and mitigation strategies. By incorporating chemometric techniques, this study introduces a novel, data-driven methodology for geochemical investigations, reinforcing the importance of multidimensional analyses in environmental contamination research.

Keywords: Arsenic mobility; Geochemical interactions; Chemometric analysis; DOE; Foglio Geologico 74 Varese; Carg project

