Geochemical tracers and Pb isotopes in environmental matrices: natural and anthropogenic contributions of heavy metals in the Valdinievole sub-basin river system (Tuscany, Italy)

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Understanding the heavy metals distribution and their behaviour in natural systems is fundamental to protect environment and human health. In some cases, these elements are essential for life but, when present in high concentrations, they can be toxic for the ecosystems causing critical diseases. Trace and ultra-trace elements and radiogenic isotopes are a powerful tool for the characterization of natural and anthropogenic sources and related geochemical processes. The environmental matrices of fluvial systems are intimately correlated and their simultaneous investigation allows understanding the complex riverine ecosystem, which is further influenced by both geogenic and human contributions. The Valdinievole sub-basin (Tuscany, Central Italy) includes the Padule di Fucecchio, one of the most relevant Tuscan swampy zones. Besides, the Valdinievole sub-basin hosts a large number of important productive sectors such as paper mills, flora nursery farms, thermal spas, and tanning industries, thus representing an ideal study case to evaluate at which extent water, sediment and suspend solid load (SSL) respond to such anthropic burden. The water geochemistry highlighted a wide compositional variability, which ranged from Ca²⁺(Mg²⁺)-HCO₃⁻ to Na⁺-Cl⁻(SO₄²⁻) and Total Dissolved Solids up to 6,390 mg/L. The relatively high contents of the reduced N-species, which were up to 6.2 (NO₂⁻) and 23 (NH₄⁺) mg/L, suggested the presence of a fresh and diffuse pollution. A few samples of water, SSL and sediment showed Cs contents up to 170 µg/L, 57 mg/L, and 46 mg/L, respectively. The SSLs and sediments were characterized by high heavy metal concentrations, e.g., Pb, Cu, Zn and Cr up to 174, 766, 1,899 and 7,800 mg/kg, respectively, plausibly including a variable contribution from anthropogenic sources. This hypothesis is further supported by i) the Pb isotopic ratios, which allowed to identify a clear tendency from a geogenic to an anthropogenic signature and ii) the heavy metal Enrichment Factors, whose values are indicative of the significant impact exerted by local human activities on riverine environmental matrices. EFs of Pb, Cu, Zn and Cr reached values up to 12, 163, 56 and 134, respectively, confirming the influence of the enterprises situated in the Valdinievole sub-basin on the geochemical abundances of heavy metals.