Rare earth elements as process indicators for metal and metaloid contaminated groundwater

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Diffuse sources of polluted groundwater from contaminated industrial sites account for 21% of surface water bodies that fail to achieve a 'good quality' status in the Tawe catchment, South Wales, UK. This study has used the rare earth elements (REE) as a hydrogeological tracer at one such site, with the aim of characterising the origin and transport of elements including Ni, Cu, Se, and As in a shallow, unconsolidated aquifer. Surface water was characterised by its low ∑REE concentration and a depletion of light REE (LREE) relative to medium and heavy REE (MREE and HREE). The deepest groundwater at the site exhibited a caret-shaped REE pattern with MREE enrichment, which was in congruence with local sandstone bedrock. Using LREE:HREE and MREE:HREE ratios, it was found that most surface and groundwater samples shared a common evolutionary pathway which was effectively controlled by depth. A negative sloped REE pattern, unique to a previously unidentified refinery process waste (slag), was found in shallow groundwater from the centre of the refinery site; these waters had a distinctive evolution according to LREE:HREE and MREE:HREE ratios. The Ce anomaly of waters (Ce- $[La+Pr]^{0.5}$) was used to identify areas more or less affected by sorption processes, and where reductive dissolution of Fe/Mn OOH's was occurring. Our results provide an important insight into the source of contaminants into the aquifer as well as the geochemical factors controlling their fate. This is a critical step required prior to forward geochemical modelling.