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Why molybdenum persists in groundwater: Evidence for redox-driven mineral transformations and pH-controlled mobility in a carbonate aquifer system

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Molybdenum (Mo) is a naturally occurring redox-sensitive trace element essential for humans in small quantities, but high concentrations are linked to gout, liver dysfunction, and copper deficiencies. Groundwater concentrations are typically below health-based thresholds; however, regionally elevated concentrations occur worldwide, motivating local geochemical investigations. Mo commonly associates with iron (Fe) and manganese (Mn)-oxides, organic-rich material, and/or pyrite. Under oxic conditions, Mo is retained onto Fe/Mn-oxide surfaces, while reducing conditions favor sulfide incorporation and association to organic matter. In groundwater, Mo is generally mobilized under specific redox regimes including Fe/Mn-oxide dissolution in anoxic non-sulfidic systems, pH-dependent desorption under oxic alkaline conditions, or by sulfide oxidation. However, for hotspots like eastern Wisconsin —where groundwater frequently exceeds the state's 90 µg/L health advisory level—mixed redox conditions, high sulfate concentrations, and alkaline pH complicate identification of Mo sources and release mechanisms. Here, Mo is assumed to originate from underlying organic-rich or pyrite-bearing shale units beneath a dolomite aquifer; yet no prior solid-phase analyses have evaluated Mo release to groundwater. This study investigates Mo distribution and mineralogic associations in heterogenous dolomite and shale bedrock cores using a novel sequential extraction technique coupled with groundwater geochemistry. Despite elevated groundwater concentrations (~100 µg/L average), total solid-phase concentrations are low (<3 µg/g) and vary substantially with depth. The lowest solid-phase concentrations occur in the shale, indicating that the shale alone cannot account for the regional groundwater concentrations. Conversely, the highest solid-phase concentrations occur in the shallowest intervals of the dolomite aquifer, where dominant host phases shift among exchangeable, carbonate/Fe/Mn-oxide, and sulfide fractions. Whereas sulfide-associated Mo occurs throughout the core, exchangeable-Mo diminishes with depth, and carbonate/Fe/Mn-oxide-associations exhibit interval-specific enrichment rather than a systematic trend—highlighting the heterogeneous Mo redistribution within the aquifer matrix. Our results support that redox-driven mineral transformations including Fe/Mn-oxide dissolution/reprecipitation and episodic sulfide formation/oxidation redistribute Mo among mineral hosts without generating a single dominant source. Under alkaline conditions (pH 7.4-8.9), weakened Mo sorption to oxide surfaces promotes reversible desorption, especially in shallow intervals, which sustain elevated groundwater concentrations. Together, mixed redox cycling and pH-controlled sorption-desorption processes maintain a distributed, reactive Mo reservoir within the carbonate aquifer.