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Constraining Long-Term Groundwater Quality Evolution in the Milk River Aquifer Through Multi-Isotope Tracers and Geochemical Modelling

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The transboundary Milk River Aquifer (MRA), covering area of ~26,000 km^2 across southern Alberta (Canada) and northern Montana (USA), faces increasing water demand and extreme events such as droughts, underscoring the need for improved understanding of groundwater quality evolution. Previous studies did not fully explain spatial variations in major ion chemistry with respect to groundwater flow distance, direction and age. The objective of this study is to propose a refined process-based hydrogeochemical conceptual model which quantifies all major geochemical processes controlling groundwater quality. We integrated 774 quality-controlled groundwater samples from 549 wells along with newly collected samples for age-dating (^{14}C, ^{36}Cl, ^{81}Kr) purposes. Inverse PHREEQC modeling combined with multi-isotope analysis ($\delta^{18}O_{Water}$-$\delta^{2}H_{Water,}$ $\delta^{13}C_{DIC}$, $\delta^{34}S_{Sulphate}$-$\delta^{18}O_{Sulphate}$, $\delta^{13}C_{Methane}$-$\delta^{2}H_{Methane}$) identified carbonate buffering, cation exchange and pyrite oxidation occurring within 50 km from the recharge zone, while bacterial sulphate reduction (BSR) and methanogenesis occurs in distal zones (>75 km). We propose four hydrogeochemical zones that explain the spatial variations in groundwater quality within the MRA. Zone 1 (<25 km) has freshly recharged Ca-Mg-HCO_3 groundwater, which rapidly changes to relatively young (<65 kyr) Na-HCO_3-SO_4 groundwater (Na^+ ~700 mg/l, SO_4^{2-} ~800 mg/l, HCO_3^- ~400 mg/l) due to ion exchange and pyrite oxidation. Zone 2 (25-75 km) represents older (65-150 kyr) Na-HCO_3-SO_4 water with low Ca^{2+} and Mg^{2+} (<10 mg/L), elevated (Na^+ ~800 mg/l, SO_4^{2-} ~1000 mg/l, HCO_3^- ~700 mg/l) resulting from progressive cation exchange and carbonate dissolution ($\delta^{13}C_{DIC}$ -13 to -10‰). Zone 3 (75-100 km) exhibits older (150-350 kyr) Na-HCO_3 type water with elevated Na^+ (>500 mg/L) and HCO_3^- (~1000 mg/L) due to organic matter oxidation ($\delta^{13}C_{DIC}$ -22‰) coupled with bacterial sulphate reduction (SO_4^{2-} <50 mg/L, $\delta^{34}S_{Sulphate}$ +10 to +15‰), and subsequently onset of methanogenesis (CH_4 30-60 mg/L, $\delta^{13}C_{CH_4}$ -76 to -72‰). Zone 4 (>100 km) represents the oldest (350-500 kyr) and most evolved Na-HCO_3-Cl and Na-Cl groundwater (Na^+ ~1000 mg/L, Cl^- ~500 mg/L, HCO_3^- ~1200 mg/L) indicating completion of bacterial sulphate reduction with ongoing methanogenesis (CH_4 ~80 mg/L, $\delta^{13}C_{Methane}$ -78 to -68‰). The proposed hydrogeochemical model provides quantitative constraints on the timing of several geochemical processes that explain the spatial variations in groundwater quality within the MRA.