Isotopic fingerprint of Se reduction in groundwater: Results from a field experiment

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Environmental redox conditions profoundly influence the transport of essential micronutrient, and potential pollutant selenium (Se) in soil, sediments and groundwater because it is either soluble (e.g., Se(VI) or Se(IV)) or insoluble (e.g., Se(0)) in different redox conditions. For example, oxidation of Se-rich sulfides or roll-front deposits releases soluble Se oxyanions in the environment. Predicting distribution and behavior of Se in the subsurface requires a clear understanding of characteristic reactive pathways across redox interfaces. Reductive immobilization of Se can help with remediation of contaminated aquifers and controls the availability of this essential nutrient. The stable isotopes of Se may be used for accurate detection of Se-oxyanion reduction and mobility.

We present Se concentrations and aqueous speciation along $\delta^{82}$Se measurements of groundwater samples from a cross-hole test conducted at Smith Ranch-Highland uranium mine in Wyoming, USA. In this test, a slug of Se(VI) as Na₂SeO₄ solution ($\delta^{82}$Se = −0.8‰) mixed with site groundwater was injected into a reduced unmined roll-front deposit. Groundwater samples collected from an extraction well 24 m apart within the deposit show a Se(VI) breakthrough with an increase in Se(IV) above the background with time since injection. The $\delta^{82}$Se of Se(VI) smoothly increased from −0.8‰ to +0.3‰ after 47 days since Se(VI) injection. This was followed by a similar smooth increase of $\delta^{82}$Se of Se(IV) from −4.3‰ to −0.4‰ after 68 days since the injection. In each sample Se(IV) was enriched in lighter isotopes relative to Se(VI). Progressive enrichment of $^{82}$Se in both Se(VI) and Se(IV) with time as the injected slug move through the redox gradient in roll-front deposit indicate reduction of Se(VI) to Se(IV). These results demonstrate how the combined use of Se isotope and speciation measurements of groundwater can provide detailed information on Se redox processes in a natural setting.