Biogeochemistry of redox-sensitive elements in the subterranean estuary

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The composition of submarine groundwater discharge (SGD) is determined by biogeochemical reactions that take place in the subterranean estuary (STE). Subterranean estuaries are typically characterized by steep redox gradients, which can affect the mobility of redox-sensitive elements (RSEs) such as Mo, U, V, and Cr. While the SGD volume flux is affected by factors on wave and tidal time scales, the impact of seasonality on redox chemistry in the STE is less well-understood. Seasonal variation may include meteoric groundwater recharge, reactant fluxes, and temperature-dependent reaction rates. We investigated the association and variability in redox conditions and RSE distributions in a shallow STE on the Virginia (USA) coast over two years. Advection of water through the STE and the apparent respiration of organic matter drives the formation of a “classic” redox sequence typically observed in diffusion-dominated fine-grained sediments. Porewater profiles are consistent with oxic respiration, coupled nitrification/denitrification, Fe and Mn reduction, and sulfate reduction. High concentrations of DOC lead to extensive sulfide production within 3 m of the sediment-water interface. Both Mo and U are quantitatively removed as oxic surface waters mix into ferruginous and sulfidic zones, while V and Cr show non-conservative addition across the salinity mixing gradient. Monthly trends showed that redox conditions and RSE behavior in the STE related to seasonally varying organic matter supply and oxygen consumption, both of which are higher in the summer. Seasonal differences in redox chemistry affect the role of the STE as a source or sink.