

Groundwater Iodine-129 speciation and its causes for release from a subsurface burial basin

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In 1989 the F-Area Basin at the Savannah River Site (SRS) containing acidic radiological waste from plutonium extraction activities was closed by adding lime and reducing slag (containing ferrous and sulfide compounds) and backfilling the basin with sediment and covered with a low-conductivity clay cap. Since 1991, ¹²⁹I groundwater concentrations have been slowly increasing from ~180 to >800 pCi/L. During this same period, the groundwater pH has increased from 3.10 to 3.95 and tritium concentrations have declined from 27,000 to 500 pCi/mL, the latter representing primarily dilution and some decay. Laboratory studies were undertaken to understand why ¹²⁹I is releasing from the basin. SRS subsurface sediments were found to have a net positive charge within the acid plume (pH 3 to 5.5) and as such, had an anion exchange capacity for adsorbing the anionic iodine. The point-of-zero-charge of the study sediment was 4.0 to 4.2. As the pH of the sediment increased from about 3.1 to 3.95, sorption decreased by 24%, causing the release of iodine into the aqueous phase. Laboratory pH-iodine sorption trends and the field data of 47 ¹²⁹I samples over 19 years showed similar pH trends, suggesting similar processes. Additional laboratory data showed that there was a strong inverse relation to aqueous iodide concentration and degree of sorption, even down to μ molar concentrations. This finding may have uncovered previous experimental artifacts in our laboratory and elsewhere in the literature, leading to underestimation of iodine sorption. Iodate sorbed more strongly than iodide. We have quantified the presence of multiple ¹²⁹I species in groundwater samples collected in a riparian zone located ~1 km from the F-Area Basin, including: colloidal iodine, organo-iodine, iodate, and iodide. These studies underscore the importance of understanding that iodine has a complicated speciation in terrestrial environments and it is necessary to study radio-iodine environmental chemistry at ambient concentrations. Studying iodine geochemistry at more elevated, albeit more convenient concentrations, resulted in assigning erroneously low sorption constants and missing dominant aqueous species.

Influence of ionic strength on structure and redox activity of humic substances

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Humic substances (HS) are polymeric organic compounds present in soils and sediments and participate in abiotic and biotic redox processes. They can mediate electron transfer from microorganisms to poorly soluble Fe (III) minerals, but the geochemical parameters controlling these redox processes are unknown. In order to evaluate the effect of ionic strength, we incubated nonreduced and reduced HS at different ionic strength with Fe (III) compounds and quantified the amount of electrons transferred from HS to Fe (III). The amount of electrons transferred from reduced HS to Fe (III) strongly depended on ionic strength with more electrons being transferred with increasing ionic strength. This effect was observed for solid as well as for dissolved Fe (III) compounds (ferrihydrite, goethite, hematite, Fe (III) citrate) suggesting that differences in redox activity depended on changes of HS redox properties rather than on Fe (III) mineral surface effects. In contrast to HS, the quinone model compound AQDS showed no difference in redox activity at different ionic strengths, indicating that the ionic strength-dependent change in redox behaviour of HS was related to changes in HS structure. To identify the underlying mechanisms, we determined HS molecular sizes and found that nonreduced HS showed only minor changes in size at different ionic strengths, whereas reduced HS seemed to aggregate and form larger particles with particle sizes up to 4 μ m at high ionic strength. Aggregation of reduced HS at high ionic strength was probably triggered by decreasing HS charges that we quantified via zeta potential measurements. Potentiometric titration of reduced HS showed that neither identity nor quantity of functional sites exposed were influenced by ionic strength. Our results suggest that during reduction, HS molecules expand due to an increase in intramolecular electrostatic repulsion caused by increased charge densities. This process in combination with decreasing zeta potentials at high ionic strengths favours aggregation of reduced HS molecules. The resulting large, network-like HS structures may then offer an improved access of reactive sites in HS for dissolved Fe (III) and/or exhibit a facilitated electron transfer to Fe (III). The enhanced electron transfer may be caused by increased orbital overlap within HS molecules, leading to a larger extent of Fe (III) reduction at higher ionic strength.