Processes Affecting Iodine-127,129 Speciation and Mobility in Two Contaminated DOE Plumes

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Background: ^{129}I is among the key risk drivers at all DOE nuclear disposal facilities. In our on-going SBR project we developed several highly sensitive iodine speciation techniques and one of our key findings was that sediment bacteria are capable of influencing the chemical behavior of iodide, the most common form of iodine found in groundwater, via accumulation and oxidation to iodate. In turn, sediment bacteria, as well as reduced metals in the aquifer, are capable of reducing iodate to organo-iodine via iodide. Based on this conclusion and others, we proposed the following **hypotheses** and objectives. **H1:** Despite its thermodynamic stability, iodide is readily transformed to organic iodine and iodate, a transformation that is facilitated by biotic (e.g., non-specific oxidative enzymes) and abiotic (e.g., redox reactions by Mn(IV,II), Fe(III,II), or hydroquinone/quinone moieties in humic acids) factors. **H2:** Microbial mediated oxidation of iodine species irreversibly transfers I into natural organic matter, of which aromatically bound iodine is the most stable. **H3:** I mobility is dependent on physico-chemical speciation, which decreases from iodide to iodate to organic iodine, and from low molecular weight to high molecular weight to particulate organic I species. Our **approach** will determine how microbial activity, concentrations and chemical speciation (iodide, iodate, and organo-I) of ^{129}I and ^{127}I, as well as redox reactive metals and organic carbon, affect I mobility and isotopic fractionation in groundwater samples from contaminated SRS and Hanford site locations.

Highlights: A sensitive and rapid method was developed which enabled us to determine isotopic ratios (^{129}I/^{127}I) of speciated I via GC-MS [*1*]. The fact that I occurs in multiple oxidation states leads to complex biogeochemical cycling of I. We demonstrated that the mobility of I species greatly depends on the I concentration used [*2*], mostly due to covalent binding of I to a limited number of aromatic C moieties of the particle surface and in solution [*3-5*]. Bacterial accumulation of I^- followed by iodination of cellular organic molecules was demonstrated, but likely plays a minor role in the formation of organic I in the subsurface [*6*]. First-order calculations indicate that the modest increase of 0.7 pH units detected in the study site groundwater over the last 17 years since closure of the basins may be sufficient to produce the observed increased groundwater ^{129}I concentrations [up to 1 nCi/L; [*7*]. Removal of I from the groundwater through the formation of high molecular weight organo-I complexes is modified by the release of more mobile organo-I species [*8,9*]. Extracellular, enzymatic oxidation of I^- and organic acid production by bacteria significantly contribute to organo-I formation [10,11].

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