Collaborative Research: The Importance of Organo-Iodine and Iodate in Iodine-127,129 Speciation, Mobility, and Microbial Activity in Groundwater at DOE Sites

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Iodine occurs in multiple oxidation states in aquatic systems in the form of organic and inorganic species (iodide and iodate). This fact leads to complex biogeochemical cycling of I and its long-lived isotope, ^{129}I, a major by-product of nuclear fission [1-3]. In order to assess the distribution of ^{129}I and stable ^{127}I in environmental systems, a sensitive and rapid method was developed which enabled us to determine isotopic ratios (^{129}I/^{127}I) and speciate I via GC-MS [3] and AMS [5]. Results using this new method demonstrate that the mobility of ^{129}I species greatly depends on the type of I species and its concentration [6,7], pH [8-10], and sediment redox state [8-10], with equilibration times taking up to 12 weeks [8-10]. At ambient concentrations ($\sim10^{-7}$ M), I^- and IO_3^- are significantly retarded by sorption to mineral surfaces and covalent binding to natural organic matter (NOM), while at concentrations traditionally examined in sorption studies (i.e., 10^{-4}M or higher), I^- travels along with the water [7]. Iodate removal can also occur through incorporation into $CaCO_3$ crystal lattice, e.g., at the Hanford Site [12-14]. Iodide and iodate interactions with NOM lead to covalent binding of I to a limited number of aromatic carbon moieties on the particle surface [15-17]. Iodine association with NOM is important in sediments, even when organic carbon concentrations are very low (e.g., <0.2% at Hanford Site) [12-14]. Removal of iodine from the groundwater through interaction with NOM is complicated by the release of mobile organo-I species [15-17]. A small fraction of NOM that is bound to iodine can behave as a mobile organo-I source [15-17], a process that we were able to numerically simulate using kinetic Michaelis-Menton-type redox-reactions and kinetic uptake reactions [3]. Field [1,6,12-14,18-19] and laboratory studies evaluating the cause for steady increases in ^{129}I concentrations (up to 1000 pCi L^{-1}, 3 orders of magnitude greater than drinking water limits of 1 pCi L^{-1} ^{129}I) emanating from radiological basins at SRS indicate that an increase of 0.7 pH units in groundwater over 17 years may explain the observed increased groundwater ^{129}I concentrations [20]. Bacteria from a ^{129}I-contaminated aerobic aquifer at the F-area of SRS can accumulate I^- at environmentally relevant concentrations (10^{-7}M), but account for only a minor fraction of total added iodide (0.2-2.0%) [21-23], indicating that bacterial I^- accumulation likely does not account for the high fraction (up to 25% of total I) of measured organo-I in groundwater [6,21-23]. However, enzymatic oxidation of I^- likely plays a greater role in iodination of NOM [20-23]. The contribution of bacteria to iodide oxidizing activity likely operates via superoxide [22], and organic acid [23] production.

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