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

Peter H. Santschi, Kathleen A. Schwehr, Saijin Zhang, Chen Xu, Hsiu-Ping Li, Yi-Fang Ho, and Russell Grandbois (all at Texas A&M Univ.-Galveston, Galveston, TX), Daniel Kaplan and Kimberly A. Roberts (both at SRNL, Aiken, SC), and Chris Yeager (LANL, Los Alamos, NM).

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 (~10^{-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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