Biogeochemical Considerations Related to the Remediation of ^{129}I Plumes

D. I. Kaplan,[1] C. Yeager,[2] M. E. Denham,[1]
S. Zhang,[3] C. Xu,[3] K. A. Schwehr,[3] H.-P. Li,
R. Brinkmeyer,[3] and P. H. Santschi[3]

[1] Savannah River National Laboratory, Aiken, SC
[2] Los Alamos National Laboratory, Los Alamos, NM
[3] Texas A&M University, Galveston, TX

September, 2012

SRNL
SAVANNAH RIVER NATIONAL LABORATORY

DISCLAIMER

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U.S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:
1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
2. representation that such use or results of such use would not infringe privately owned rights; or
3. endorsement or recommendation of any specifically identified commercial product, process, or service.
Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

Printed in the United States of America

Prepared for
U.S. Department of Energy

Acknowledgements

EXECUTIVE SUMMARY

^{129}I is commonly among the top risk drivers, along with ^{99}Tc, at radiological waste disposal sites and contaminated groundwater sites where nuclear material fabrication or reprocessing has occurred. It is presently among the top three risk drivers in the Hanford 200-UP-1 Operable Unit (OU). The risk stems largely from ^{129}I having a high toxicity, a high bioaccumulation factor (90% of all the body's iodine concentrates in the thyroid), a high inventory at source terms (due to its high fission yield), an extremely long half-life (16M years), and rapid mobility in the subsurface environment. As a consequence of these characteristics, ^{129}I has a very low Drinking Water Standard (DWS), which is set at 1 pCi L^{-1}, the lowest of all radionuclides in the Federal Register. By way of comparison, the DWS for the two other primary risk drivers at the 200-UP-1 OU are 20,000 pCi L^{-1} tritium and 900 pCi L^{-1} ^{99}Tc.

The three largest ^{129}I plumes on the Hanford Site are located in the Central Plateau Area and cover more than 50 km^2. Presently, no treatment technology for these ^{129}I plumes has been identified to achieve the federal DWS. The Proposed Plan for Remediation of the 200-UP-1 OU calls for hydraulic containment through the use of injection wells placed at the leading edge of the plume. The objective of this report is to provide the current state of the science of radioiodine geochemistry relevant to its fate and transport at the Hanford Site. Particular attention is directed toward identifying critical knowledge gaps necessary for successful selection, implementation, and technical defensibility to support remediation decisions.

All three ^{129}I plumes in the 200 Area have associated tritium plumes; the latter provides an excellent tracer for how groundwater moves. In all cases, the ^{129}I plumes' leading edges have not traveled as far as those for the tritium plume, suggesting the existence of ^{129}I retardation.

Existing laboratory studies have measured iodine distribution coefficients (K_d values; ratio of ^{129}I concentrations in sediments/water) in the range 0 and 2 mL g^{-1}, with most commonly in the range of 0 and 0.2 mL g^{-1}. Among the underlying assumptions in each of these laboratory K_d measurements was that iodide, I$^-$, is the primary species in Hanford groundwater and that it sorbs to sediments through the reversible anion exchange process (meaning iodine adsorbs and desorbs at equal rates). Ongoing measurements have shown that groundwater from the 200-UP-1 OU, in fact, contains primarily iodate (84 - 98%), with appreciably less iodide (1 – 2%) and organo-iodine (0 – 14%). Multiple iodine species in the same plume have been identified at other sites. In the few terrestrial environments where full iodine speciation has been conducted, all three aqueous iodine species have been detected. The significance of this finding is that iodate K_d values have recently been shown to be 89% greater than iodide K_d in Hanford sediments. These findings bring into question whether the present site-wide ^{129}I K_d values, albeit conservative, adequately represent the sorption anticipated by iodate and organo-iodine species.

Researchers have reported that a large fraction of radioiodine sorbed onto Hanford sediment readily desorbs, consistent with the reversible anion exchange mechanism (or K_d model). Yet, there was a more-strongly bound radioiodine fraction that did not desorb even under extreme chemical conditions conducive to anion exchange (desorption). A geochemical process that accounts for strongly sorbing iodine is iodine-organic matter bonding. Organic matter uptake of iodine has been commonly reported in other systems to be the single most important sediment property controlling iodine uptake. Iodine forms a covalent bond with organic carbon, especially aromatic moieties, through electrophilic substitution. It is not known whether the low organic matter concentrations in the Hanford subsurface, in the range of 100 to 2000 mg kg^{-1} organic carbon (OC) (0.01 to 0.2 wt % OC), would be sufficient to significantly influence sorption of the 0.00002 mg L^{-1} ^{129}I (3.5 pCi L^{-1} ^{129}I; 90th percentile concentration in the 200-UP-1 OU) in the groundwater. Ongoing sorption measures using three subsurface Hanford sediments showed incremental increases in iodide K_d values from 0.00 to 3.38 mL g^{-1} and iodate K_d values 0.83 to 3.94 mL g^{-1} as the total organic carbon increased from 0.04 to 0.15 wt %. The importance of evaluating this process is that it would account for a ^{129}I fraction that is nearly irreversibly bound to the sediment and may provide a more accurate representation of ^{129}I transport.

The primary reason that researchers have assumed that iodide is the only groundwater species in groundwater at Hanford (and elsewhere) is because thermodynamic modeling identified only the presence of iodide under Hanford subsurface conditions. Although several inorganic iodine species were included in the modeling, no organo-iodine species were incorporated. The other reason is analytical limitations have resulted in limited information about groundwater radioiodine or stable iodine speciation. Over the last couple years the Department of Energy (DOE) Office of Science program has produced significant advancements related to detecting iodine species at ambient groundwater concentrations, permitting a more mechanistic understanding of radioiodine biogeochemistry.

Three critical knowledge gaps were identified that would significantly enhance our capability to successfully select, implement, and provide technical defensibility in support of a treatment technology decision.

1. <u>Iodine groundwater and sediment speciation</u>: It is essential that any treatment technology effort be based on site-specific iodine speciation measurements because the various species are expected to have different chemical properties and therefore different transport rates. Furthermore, iodine species will influence the selection of many chemistry-based treatment technologies, such as the use of sequestering agents and coprecipitation processes. In these measurements/studies, it is important to work at ambient or near ambient conditions when possible. Several researchers have demonstrated the influence of iodine concentration on iodine sorption values and speciation.

2. <u>Develop a conceptual biogeochemical model</u> that identifies and quantifies controlling biogeochemical processes by iterating between site-specific experimental results and model refinement for use in a predictive reactive transport model (discussed below). The lab and field testing would evaluate the role of multiple aqueous and sorbed iodine species on transport and long-term sorption properties. There is also a related need to quantify and understand the extent that subsurface organic matter influences [129]I uptake. Much of the organic matter was placed in the subsurface during the Missoula Floods, some 14,000 years ago. As such, [129]I-bound sediment organic matter may be expected to remain bound in the subsurface for a significant duration. Finally, there is recent evidence of sediment microbial processes that promote iodide oxidation, a process that would decrease [129]I mobility. There is also recent data demonstrating the presence of microbes in the subsurface environment, especially in the Ringold formation, that may influence iodine speciation. Improved quantification of iodine redox processes and improved quantification of the role of microbes in promoting the formation of organo-iodine species will help predict iodine speciation (and therefore transport) in the subsurface environment.

3. <u>Develop a mass flux-based conceptual biogeochemical transport model</u> that integrates controlling biogeochemical and hydrogeologic processes. The predictive model would permit understanding and quantifying the mass flux of iodine to support remediation assessments and decisions. The model structure would likely have to account for the influence of subsurface silt lens where elevated natural organic matter and microbial activity may exist. Identifying and including coupled hydrological and biogeochemical processes are especially needed to improve long-term predictive capabilities. Such a model would provide a more accurate representation of [129]I transport and greater defensibility for remediation decisions.

Together the information gained from addressing these knowledge gaps will not alter the observation that [129]I is only slightly less mobile than tritium in the Hanford subsurface, but it will likely permit demonstration that the entire [129]I pool in the source term is not moving at the same rate and some may be bound to the sediment, thereby "smearing" the modeled [129]I peak and reducing maximum calculated risk.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

DOC	Dissolved organic carbon
DOE	Department of Energy
DWS	Drinking Water Standard
EXAFS	Extended X-ray absorption fine structure spectra
HEDR	Hanford Environmental Dose Reconstruction Project
IFRC	Integrated Field-Scale Subsurface Research Challenge
IOB	Iodine-oxidizing bacteria
INL	Idaho National Laboratory
K_d	Distribution coefficient
NMR	Nuclear magnetic resonance
OC	Organic carbon
OM	Organic matter
OU	Operable unit
SOM	Sediment organic matter
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
XANES	X-ray absorption near-edge structure

1.0 Introduction

The geochemical behavior of iodine is complex because it can exist in multiple physical states, as well as multiple oxidation states at environmentally relevant conditions. It readily reacts with organic compounds, further complicating its chemistry in organic-rich environments. Iodine is also an essential nutrient for animals that concentrates in the thyroid gland, greatly enhancing its toxicity. This together with its long half-life and relatively high mobility in the environment usually assures that ^{129}I is a risk driver at sites where abundant quantities were disposed.

DOE is concerned about radioiodine because it is an identified risk in groundwater on the Hanford Site and the Savannah River Site (SRS), and is abundant in nuclear waste currently being processed and disposed at these sites and in the waste that will be eventually disposed at a national repository (e.g., (DOE, 2002, 2003, 2012a; WSRC, 2008). To illustrate how the properties of ^{129}I magnify its risk, ^{129}I accounts for only 0.00002% of the radiation released offsite from the SRS, but contributes 13% of the population dose, a six order-of-magnitude magnification of risk with respect to its radioactivity (Kantelo et al., 1990).

The potential "Nuclear Renaissance" in response to global warming presents another concern regarding radioiodine. There are 16 license applications to the Nuclear Regulatory Commission to construct 18 new nuclear reactors in the U.S., increasing the total number of reactors from 104 to 122 (Parker and Holt, 2007). Similarly, India plans to construct another 20 to 30 reactors by the year 2020 (WNA, 2009). China presently has 17 reactors under construction and anticipates building another 13 by the year 2020, increasing their nuclear capacity to at least 50 gigawatts (WNA, 2009). By the year 2030, China anticipates another threefold increase in nuclear power to 120 to 160 gigawatts. Radioiodine is produced at a rate of 1 Ci (37 giga-Becquerels) per gigawatt of electricity produced by nuclear power (McKay, 1984). For example, if all 22 proposed 1-gigwatt U.S. reactors are built, an additional 22 Ci of ^{129}I will be generated annually (reactors are 98% efficient), and within seven years these reactors will generate more ^{129}I waste than currently exists at the Hanford Site (65.5 Ci; Kincaid, 2006) and SRS (26 Ci; Hiergesell et al., 2008). Thus, if only a fraction of the proposed nuclear growth from the "Nuclear Renaissance" is realized, a significant increase in world-wide radioiodine inventory will be created by the nuclear power industry. Understanding the environmental behavior of ^{129}I is critical to assessing the capability and capacity of facilities where this waste will be stored or disposed.

The risk posed by radioiodine can be broadly categorized as being long-term and short-term. The long-term risks are those resulting from exposure to the long-lived isotope, ^{129}I, with a half-life of 16 million years. The short-term risks are those resulting from exposure to the short-lived isotope, ^{131}I, with a half-life of eight days. By virtue of these differences in radioactivity (or half-lives), ^{129}I is a long-term risk, associated with DOE's current groundwater contamination and nuclear waste disposal. ^{131}I decays to stable ^{131}Xe quickly, but its high specific activity makes it an immediate threat to exposed individuals. An example of the short-term risk from ^{131}I is illustrated from the Chernobyl accident (Figure 1). The majority of the radiation emitted immediately after the Chernobyl accident was from ^{131}I. Studies show a link to thyroid cancer in exposed children that were less than five-years old at the time of the accident (e.g., (Guiraud-Vitaux, 2008)). This was attributed to the fact that more than 90% of stable or radioactive iodine in the human body is concentrated in the thyroid (Zaichick and Choporov, 1996). Once ^{131}I is taken up by the thyroid, beta particles (primarily 606 keV, 89% abundance) and gamma rays (primarily 364 keV, 81% abundance) bombard nearby tissue, promoting thyroid cancer. Thus, ^{131}I is a problem associated with large scale accidents or failures at nuclear facilities, whereas ^{129}I is a problem related to environmental remediation and long-term stewardship of disposed nuclear waste. This report focuses on ^{129}I.
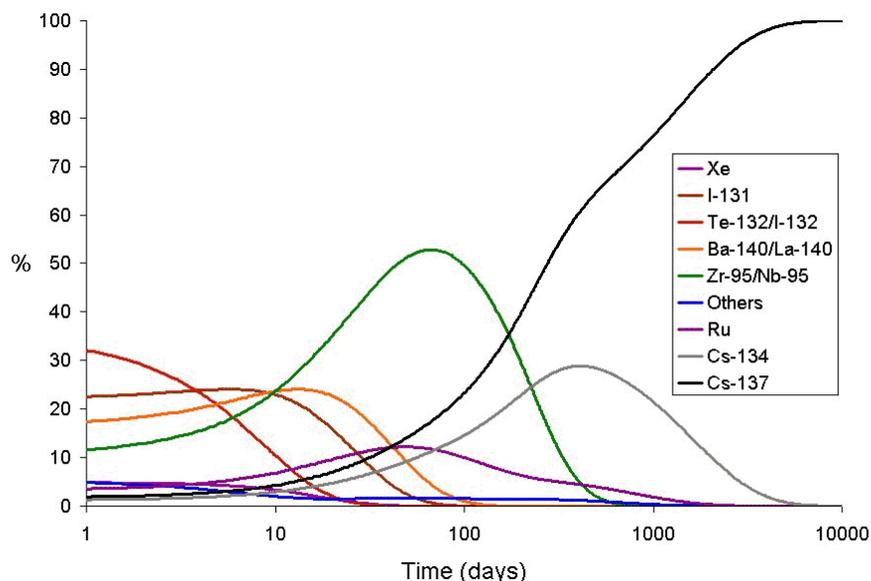
Figure 1. Relative activity emitted as a function of time after the Chernobyl accident. Note that ^{131}I accounted for most of the radioactivity during the first week (IAEA, 2006).

1.1 [129]I on the Hanford Site

Between 1943 and 1988, operations in the Central Plateau Areas of the Hanford Site, which include 200 East and 200 West Areas, were involved in Pu separation and U recovery operations. In the 200 West Area, the S and U Plant chemical separation and recovery processes generated liquid waste streams, such as process condensate, cooling water, and laboratory waste that were discharged to the ground using ponds, cribs, ditches and trenches. Mobile radiological and non-radiological contaminants, including [129]I, ^{99}Tc, and nitrate, discharged to these facilities have migrated through the vadose zone to the underlying aquifer, some 76-m below grade. Once the contaminants reached the aquifer, they spread relatively rapidly, producing large-scale plumes (Figure 2 and Figure 3). Amongst these plumes are three [129]I plumes covering an area >50 km^2. The largest plume extends toward the southeast from the 200 East Area. A smaller arm of the plume is moving toward the northwest between Gable Mountain and Gable Butte. The two smaller plumes emanate from S Plant and U Plant cribs. The 90 percentile [129]I concentration is 3.5 pCi L^{-1}, meaning 90% of the data for [129]I in the plume falls below this value. There are few recently recorded groundwater concentrations that exceed 10 pCi L^{-1}. By comparison, the [129]I Drinking Water Standard (DWS) is 1 pCi L^{-1}. Therefore, major challenges for treating 200 Area groundwater [129]I plumes is that the plumes are extremely extensive and the [129]I is extremely dilute (3.5 pCi L^{-1} = 0.00002 mg L^{-1} = 1.5 x 10^{-10} M). A technology evaluation for [129]I was completed, which identified no current treatment technology that can achieve the federal DWS (DOE, 2012a). The proposed plan for [129]I treatment at the site is hydraulic containment to be performed using injection wells placed at the leading edge of the plume(s) (DOE 2012b). DOE continues to evaluate potential treatment options for [129]I (DOE, 2012b). [129]I is among the three primary radiological risk drivers, along with ^{99}Tc and [3]H (DOE, 2012b).

All three ^{129}I plumes in this region have associated tritium plumes; the latter provides an excellent tracer for how groundwater moves. In all cases, the ^{129}I plume's leading edge has not travelled as far as that for the tritium plume. Assuming the retardation factor (R_f = velocity of water / velocity of iodine) can be represented by the ratio of the distances between the source and the plume leading edge of the tritium and ^{129}I plumes, then the apparent ^{129}I R_f may be approximated as follows:

- 200 East plume R_f = 1.44 (m yr^{-1})/(m yr^{-1}) and the associated K_d = 0.07 mL g^{-1} (assuming bulk density = 1.86 kg L^{-1} and porosity = 0.3 L L^{-1}),
- 200 West S-plant plume R_f = 1.44 (m yr^{-1})/(m yr^{-1}) and the associated K_d = 0.07 mL g^{-1}, and
- 200 West ZP-1 plume R_f = 1.25 (m yr^{-1})/(m yr^{-1}) and the associated K_d = 0.04 mL g^{-1}.

Based on these simplistic calculations, the "average" iodine species is retarded with respect to tritium. The associated K_d values are very low.

To put these plumes into perspective, the other major ^{129}I-contaminated site in the United States is at the SRS (discussed in more detail in Section 2.4). The SRS plumes are much smaller, <2 km^2, and have much greater ^{129}I concentrations, greater than 20% of the plume has ^{129}I concentrations between 50 to 100 pCi L^{-1}. Within the last ten years, ^{129}I concentration >1000 pCi L^{-1} have been measured near the disposal basins and in a riparian zone located 0.7 km downstream.

A great deal of attention has been directed to airborne emissions of ^{131}I, the short-lived isotope, from the Hanford Site. In 1987, the DOE began the Hanford Environmental Dose Reconstruction Project (HEDR), which analyzed some 19,000 pages of newly released data related to Hanford environmental releases and production (NRC, 1995). The HEDR estimated how much radiation Hanford released and how much people were exposed based on where they lived and what they consumed. For most of those exposed, the greatest part of their total dose came from drinking milk and eating food that was contaminated with radioactive materials from Hanford. Between 1944 and 1972, according to HEDR's estimates, about 2 million people were exposed either through the air or the Columbia River. ^{131}I accounted for >98% of the radiation dose they received (NRC, 1995; WSDH, 2000). The Hanford Thyroid Disease Study reported that thyroid diseases, including thyroid cancer, were not more common among people in the Hanford vicinity (Davis et al., 2007). The study screened >3,000 people for thyroid diseases. Essentially all the ^{131}I that was the subject of the Hanford Study has completely decayed, and as such, no longer poses a health threat.
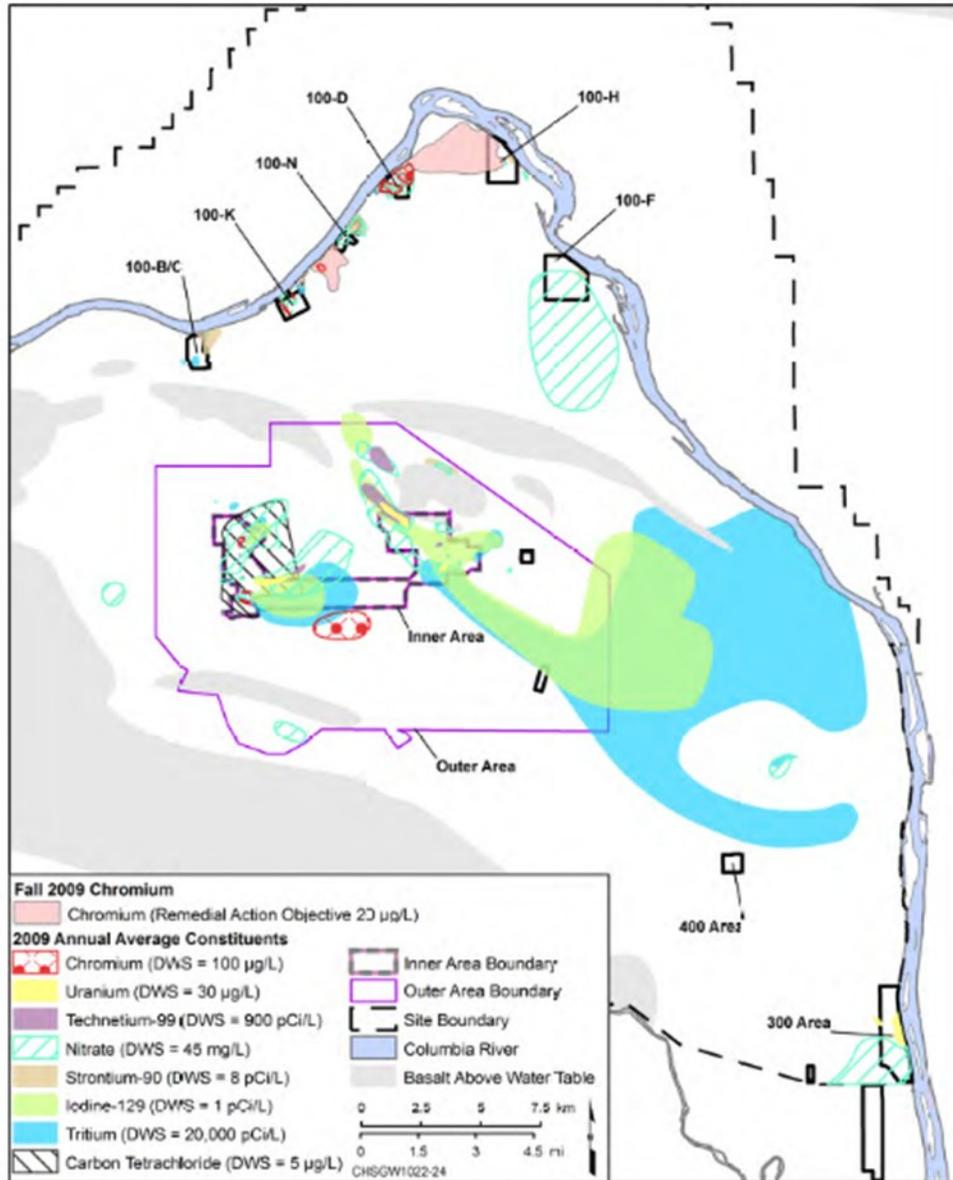
Figure 2. ^{129}I plumes in the surface aquifer of the 200 East and 200 West Areas on the Hanford Site. ^{129}I plumes coexist with other contaminants. ^{129}I, ^{99}Tc, and ^{3}H are the primary risk drivers at the site (DOE, 2012a).
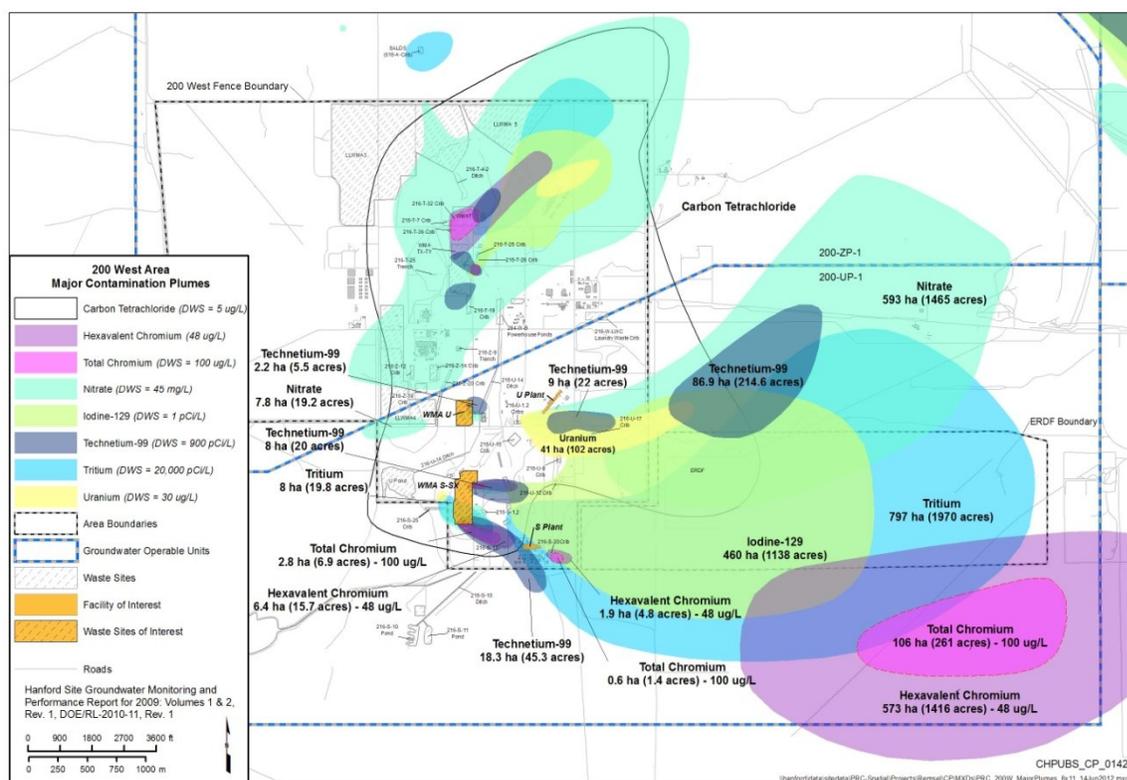
Figure 3. Groundwater plume map in the 200 West Area (including 200-UP-1 and 200-ZP-1 Operable Units). The plumes primarily emanate from disposal cribs located near U Plant and S Plant (DOE, 2012b).

1.2 Objectives

The objectives of this report were to:

1) provide a current state of the science of radioiodine biogeochemistry relevant to its fate and transport at the Hanford Site,
2) conduct a review of Hanford Site data dealing with groundwater ^{129}I, and
3) identify critical knowledge gaps necessary for successful selection, implementation, and technical defensibility in support of remediation decisions.

1.3 Summary and Relevance of the Introduction

Hanford Site:

- The three largest ^{129}I plumes on the Hanford Site are located in the Central Plateau and cover more than 50 km^2 (DOE, 2010). The primary challenge for remediation is that the plumes are extremely large, extremely dilute, and the DWS is extremely low, among the lowest of all radionuclides. ^{129}I at the 200-UP-1 OU is among the three greatest risk drivers on the site, along with ^{99}Tc and ^{3}H.

- Presently, no treatment technology for ^{129}I plumes has been identified to achieve the federal DWS (DOE, 2012a). The Proposed Plan for Remediation of the 200-UP-1 OU calls for hydraulic containment through the use of injection wells placed at the leading edge of the plume.

General:
- ^{131}I poses a very short-term risk (days to months) and ^{129}I poses a very long-term risk (years to 1000s of years).
- ^{129}I is commonly among the key risk drivers at disposal facilities (Hanford Intermediate Disposal Site, Idaho National Laboratory's Remote-Handled Low-Level Waste Disposal Facility, SRS's E-Area Low-Level Waste Disposal Facility; former Yucca Mountain Disposal Facility), and at radionuclide-contaminated plumes emanating from reprocessing facilities. The risk stems largely from ^{129}I having a high toxicity, a high bioaccumulation factor (90% of all the body's iodine concentrates in the thyroid), a high inventory at source terms (due to its high fission yield), an extremely long half-life (16M years), and perceived rapid mobility in the subsurface environment.
- As U.S. and world-wide inventories of ^{129}I increase, understanding how to minimize its release to the environment and what to do if it is released becomes increasingly important.

2.0 Radioiodine Sources

2.1 Reactor Sources of Radioiodine

The principle mechanism for radioiodine production is neutron-induced fission. Neutron-induced fission is a nuclear reaction in which the nucleus of an atom (e.g., ^{235}U) splits when bombarded with neutrons into lower atomic-weight isotopes (e.g., ^{129}I), often producing free neutrons and energy. Reactions form a variety of fission products, including 19 iodine isotopes (Table 1). Typically fission products are by-products and are not the isotopes of interest. At the Hanford Site and SRS, where most ^{129}I exists, the reactors were fueled with uranium, and part of this uranium was converted into plutonium by the reactor neutron flux.

To provide an idea of the relative contribution of the various iodine isotopes to radiation over time, Kantelo et al. (1990) calculated the decay rate of iodine isotopes from a representative irradiated material (Table 1). These calculations demonstrate that radioiodine activity decreases very quickly after reactor shutdown. By letting the irradiated material cool for 200 days, radioiodine activity decreases from 1,000,000,000 Ci to 2.5 Ci. Only two of the 19 radioiodine isotopes remain after 200 days, ^{129}I ($t_{1/2} = 1.6$ x 10^7 years) and ^{131}I ($t_{1/2} = 8$ days). Hence, of all of the radioiodine isotopes produced, ^{129}I is the only one that can last long enough to be a long-term threat in groundwater.

Table 1. Inventory of radioiodine isotopes produced in a representative material irradiated by a production reactor (Kantelo et al., 1990). These calculations demonstrate that radioiodine total activity decreases rapidly and after 100 days, only ^{129}I and ^{131}I are present.

Isotope	Half-Life	Curies Remaining at Various Times After Irradiation			
		0 sec	24 hours	100 days	200 days
128	25m	1.5×10^4	-	-	-
129	1.6×10^7y	2.3×10^{-1}	2.3×10^{-1}	2.5×10^{-1}	2.5×10^{-1}
130m	9m	9.2×10^4	-	-	-
130	12h	1.4×10^5	3.5×10^4	-	-
131	8.0d	7.6×10^7	7.0×10^7	1.3×10^4	2.3×10^0
132	2.3h	1.1×10^6	8.9×10^7	-	-
133g	9s	3.8×10^6	-	-	-
133	21h	1.8×10^4	8.2×10^7	-	-
134m	4m	1.3×10^7	-	-	-
134	53m	2.0×10^8	1.3×10^8	-	-
135	6.6h	1.6×10^8	1.5×10^7	-	-
136m	47s	5.0×10^7	-	-	-
136	83s	7.9×10^7	-	-	-
137	24s	7.9×10^7	-	-	-
138	7s	4.1×10^7	-	-	-
139	2s	1.8×10^7	-	-	-
140	<1s	4.1×10^6	-	-	-
141	<1s	8.6×10^5	-	-	-
142	<1s	1.1×10^5	-	-	-
Totals		**1.0×10^9**	**2.6×10^8**	**1.3×10^4**	**2.5×10^0**

Once the elements have cooled, the desired isotopes are recovered through chemical separation or reprocessing. It is at this step that essentially all the radioiodine is introduced into the environment. It has been estimated that radioiodine emissions to the atmosphere from the Hanford reprocessing operations between 1944 and 1972 were 266 kg (Raisbeck, 1999). The two largest commercial reprocessing facilities are at Sellafield (UK) and La Hague (France) and they have authorized liquid discharge permits for treated waste to the NE Irish Sea and the English Channel, respectively. In 1999, a year of high discharge, their discharge rates were 330 kg yr^{-1}, with approximately 75% coming from La Hague. The integrated discharges from La Hague (1975 – 1997) and Sellafield (1961 – 1997) are estimated to have been 1640 kg and 720 kg, respectively (Raisbeck, 1999). Therefore, the total amount of ^{129}I released at the Hanford Site was less than that recently released in a single year by these two reprocessing facilities (Table 2).

Table 2. Major sources of ^{129}I in the environment (compiled from Raisbeck and Yiou, 1999).

Source	^{129}I (kg)
Atmospheric testing	50
Chernobyl	1-2
Savannah River Site	32[a]
Hanford Reservation	266
Nevada Test Site underground nuclear testing	10
Yucca Mountain repository (projected)	13,300
Fuel reprocessing Sellafield (UK)	1640
Fuel reprocessing at La Hague (France)	720
Natural hydrosphere and atmosphere	100[b]

[a] Kantelo et al., 1990
[b] NCRP, 1983

Another manner in which radioiodine can enter the environment is through nuclear power plant accidents, such as the Fukushima Daiichi and Chernobyl reactor accidents. The Fukushima Daiichi accident introduced 1.5 x 10^7 kg (10^{17} Bq ^{131}I; note ^{131}I and not ^{129}I as described in Table 2), this is about 10% the ^{131}I mass released from the Chernobyl disaster (MacKenzie, 2011; von Hippel, 2011).

2.2 Natural Sources of Radioiodine

Radioiodine is also naturally produced in very small quantities, by the spontaneous fission of natural U (which contains 0.07% ^{235}U), cosmic ray spallation of trace levels of xenon (Xe) in the atmosphere, and by cosmic ray muons (high energy particles) striking tellurium-130 (Edwards, 1962). These natural processes account for trace levels of radioiodine in the environment but results in no human health risk. The ratio of stable ^{127}I to radioactive ^{129}I in the environment is more than 10,000,000 to 1. The global inventory of natural ^{129}I accumulated over the lifetime of the earth is estimated to be 10 Ci in the terrestrial environment and 30 Ci in oceans and the atmosphere (NCRP, 1983).

2.3 Radiochemistry of Relevant Iodine Isotopes

As demonstrated in Table 1, only ^{129}I and ^{131}I of the 19 radioiodine isotopes formed in reactors may be of environmental concern 100 days after a release and only ^{129}I is of concern after a year after release. Table 3 shows the radiochemical properties of these isotopes.

Table 3. Radiochemical properties of ^{129}I and ^{131}I.

	^{129}I	^{131}I
Half life	1.6×10^7 yr	8.0197 days
Neutrons	77	78
Protons	52	53
Radiation	ß 0.154 keV (100%); γ 0.0396 (7.5%), γ 0.0295 (20%)	ß 0.606 (90%) keV; γ 0.364 (82%)
Decay	$^{129}_{53}I \rightarrow \beta + {}^{129}_{54}Xe$	$^{131}_{53}I \rightarrow \beta + {}^{131}_{54}Xe$
Fission yield[a]	0.6576% per fission ^{235}U	2.8336% per fission ^{235}U

[a] Nuclear fission splits a heavy nucleus such as uranium or plutonium into two lighter nuclei, which are called fission products. Yield refers to the fraction of a fission product produced per fission.

2.4 Contaminated Sites and Groundwater Sources in the United States

As a product of uranium fission, ^{129}I occurs in the environment at several DOE facilities, but is especially problematic at the Hanford Site (Section 1.1) and the Savannah River Site (Table 2). Both of these sites have contaminant plumes that contain ^{129}I at concentrations well above the DWS of 1 pCi L^{-1} (discussed in more detail below). Maximum concentrations of 2 pCi L^{-1} in groundwater from wells at nuclear test holes at the Nevada Test Site have been reported (Hu, 2009), but concentrations well below 1 pCi L^{-1} at satellite wells located outside the chimney-cavity of the nuclear tests. Very low concentrations of groundwater ^{129}I have been reported in wells to the south of the Idaho National Laboratory (INL) boundary (Hall, 2005). The origin of the ^{129}I was tied to wells in the INL waste disposal area based on spatial concentration variations of ^{129}I to the concentrations of accompanying ^{36}Cl. The maximum concentration observed in groundwater at the West Valley Demonstration Project in 2007 was 5.6 pCi L^{-1} (WVDP, 2007). Using ^{129}I to stable iodine (^{127}I) ratios, elevated ^{129}I concentrations were detected in soil cores of western New York to atmospheric release of ^{129}I from the West Valley reprocessing plant (Rao and Fehn, 1999). It is likely that other sites that processed spent fuels, uranium targets, or other sources of uranium that underwent fission, may have some ^{129}I in their subsurface sediments and groundwater.

The SRS also has extensive ^{129}I environmental contamination (Denham et al., 2009; Kantelo et al., 1990). The ^{129}I (and ^{131}I) were produced through similar but not identical operations as existed at the Hanford Site. Radionuclides were extracted from irradiated materials at two locations, F-Area and H-Area, together known as The General Separations Area). In both F-Area and H-Area, low-level radioactive liquid waste was discharged to seepage basins. Low mobility radionuclides, such as Am, Cm, and Pu have been largely sequestered in the sediments immediately beneath the basins, but more mobile radionuclides have migrated into the groundwater and discharge into Four Mile Branch, a small stream to the south of the General Separations Area that eventually flows into the Savannah River. The F- and H-Area Seepage Basins received approximately 3 Ci of ^{129}I from 1955 to 1989. The seepage basins have since been closed and capped with a low permeability engineered cover built to Resource Conservation and Recovery Act (RCRA) specifications.

The F-Area Seepage Basins plume has the highest concentrations of ^{129}I, with numerous wells having concentrations tens to hundreds of times greater than the DWS (1 pCi L^{-1}). The highest concentration reported to date, 1060 pCi L^{-1}, was in 1996 for a well adjacent to the largest basin. Concentrations of ^{129}I in this well have been rising over the past twenty years, while concentrations of most other contaminants have been decreasing (Kaplan et al., 2011). The increase likely reflects release of adsorbed ^{129}I from vadose zone and seepage basin sediments as pH has risen with time (Denham and Vangelas, 2008; Kaplan et al., 2011). The concentrations of ^{129}I in the Four Mile Branch below the F-Area also exceed the drinking water standard, but are typically <5 pCi L^{-1}. The high concentrations within the F-Area Seepage Basins plume make ^{129}I one of the primary risk drivers at this site (along with tritium, uranium and ^{90}Sr).

The H-Area Seepage Basins plume has much lower concentrations of ^{129}I. The highest concentration observed in the first half of 2009 was 79 pCi L^{-1} in a well adjacent to the largest basin. The bulk of the plume has concentrations that are <10 pCi L^{-1}. Likewise, the small plume emanating from the Old Radioactive Waste Burial Ground contains relatively low concentrations of ^{129}I. The highest concentration measured in the plume in 2011 was 11 pCi L^{-1}. The ^{129}I plumes at both the F- and H-Areas have already travelled from the source to the nearest surface water, Four Mile Branch.

Results from an ongoing project studying the biogeochemistry at the F-Area are presented in Appendix A. A dozen manuscripts describe the results from this study, which include analytical development, iodine speciation at the study site, factors affecting the accumulation of ^{129}I in the down-gradient wetland, site-specific sediment microbial ^{129}I accumulation, microbial induced oxidation, mineral surface induced iodine speciation transformations, causes for increasing ^{129}I concentrations in the groundwater over a 19 year period, and site sediment organic matter (SOM) and dissolved organic carbon (DOC) transformations for iodine species. This discussion is relegated to Appendix A of the report because the applicability of these results to the Hanford Site may be tenuous.

2.5 Summary and Relevance of Radioiodine Sources

Hanford:
- ^{129}I is a fission product (waste product) from plutonium separation and uranium recovery operations.
- There are two radioiodine isotopes of concern, ^{131}I, which has a half-life of 8 days and is a significant dose contributor at accidental releases (e.g., Chernobyl, "down winders" at Hanford), and ^{129}I, which has a much longer half-life of 16M years and is of concerned in contaminant plumes and waste disposal.

General:
- Within the DOE complex Idaho National Laboratory, Nevada Test Site, and the West Valley Demonstration Project have released ^{129}I to the environment, but only low concentrations have been detected. The Hanford Site and the Savannah River Site have major plumes containing ^{129}I at concentrations above the drinking water standard; the former are an order of magnitude larger, whereas the latter have orders of magnitude greater ^{129}I plume concentrations.
- The largest facilities operating today and generating the most ^{129}I are in La Havre, France and Sellafield, UK.

3.0 Geochemistry of Iodine

3.1 General Iodine Chemistry Relevant to Environmental Remediation

Iodine is a complicated element because under environmentally relevant conditions, it can exist in multiple physical (solid, liquid, or gas) and oxidation states (-1, 0, +1, +5, and +7). It readily reacts with organic compounds, further complicating its chemistry in most natural environments. The solubility of elemental iodine in water at 25°C is 340 mg L^{-1} with a vapor pressure of 4.1 x 10^{-4} atm (Lauterbach and Ober, 1996). Henry's Law constant at 25°C for I_2 is estimated to be 3.0 moles/L·atm (Parsly, 1970). Thermodynamic data from HSC Chemistry® indicates a value of 3.8 moles/L·atm, assuming ideal behavior for both the vapor and solution. Iodine hydrolyzes in water by four main reactions (Parsly, 1970):

$$I_{2(g)} = I_{2(aq)} \qquad\qquad \log K_{20°C} = 0.65 \qquad\qquad (1)$$

$$I_{2(aq)} + I^- = I_3^- \qquad\qquad \log K_{20°C} = 2.89 \qquad\qquad (2)$$

$$I_{2(aq)} + H_2O = H^+ + I^- + HIO \qquad\qquad \log K_{20°C} = -12.49 \qquad\qquad (3)$$

$$I_{2(aq)} + H_2O = H_2OI^+ \qquad\qquad \log K_{20°C} = -10.80 \qquad\qquad (4)$$

The reactions for several species are shown in Table 4 with iodide (I$^-$) as the reactant species. Under conditions prevalent in groundwater and surface water only the -1, 0, and +5 valence states are common. Additional species may occur in natural waters because iodide forms aqueous complexes with various soft metals, but require high iodide concentrations to account for a significant fraction of the metal species.

Table 4. Reactions of log K association constants of selected aqueous species of iodine.

Reaction	$\log K_{20°C}$
$I^- + H^+ = HI$	0
$2I^- = I_{2(aq)} + 2e^-$	-21.33
$3I^- = I_3^- + 2e^-$	-18.44
$I^- + H_2O = HIO_{(aq)} + H^+ + 2e^-$	-33.81
$I^- + H_2O = IO^- + 2H^+ + 2e^-$	-44.53
$I^- + 2e^- = I^3$	-0.90
$I^- + 3H_2O = HIO_{3(aq)} + 5H^+ + 6e^-$	-112.56
$I^- + 3H_2O = IO_3^- + 6H^+ + 6e^-$	-113.31
$I^- + 4H_2O = IO_4^- + 8H^+ + 8e^-$	-168.10

Iodide forms low solubility salts with several metals, notably Ag, Hg, and Cu(I). Figure 4 shows the calculated aqueous concentration of the metal in equilibrium with metal salt and 10 μg L^{-1} I$^-$, assuming ideal behavior and no significant complexing by other constituents. The occurrence of natural iodide minerals containing Ag, Hg, and Cu, though rare, attests to the insolubility of these metal iodides. The solubility of metal iodates is typically much higher than iodides and thus metal iodates are unlikely to exert any control on iodate concentrations in most systems (Fuge and Johnson, 1986).
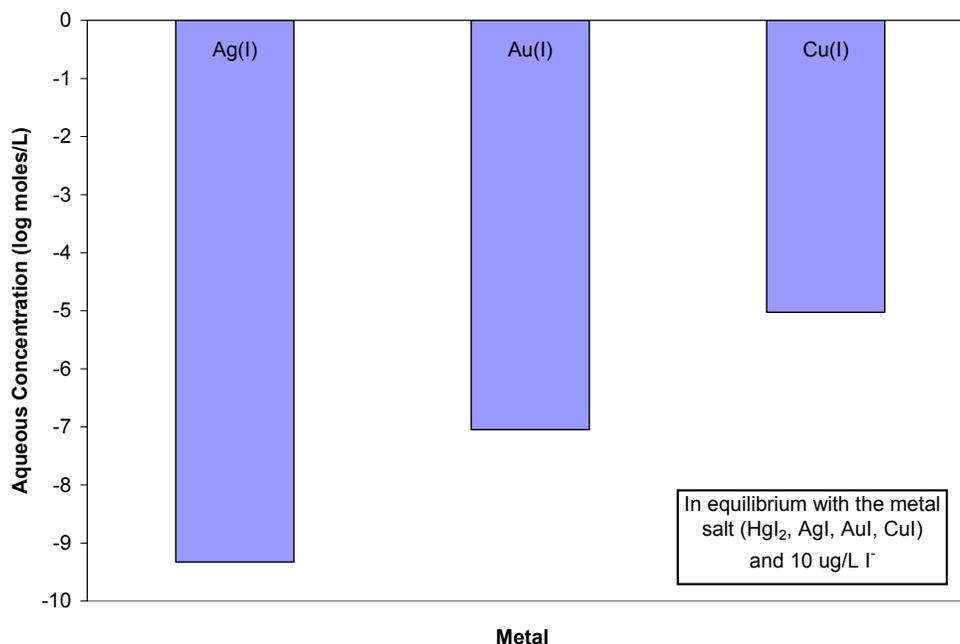
Figure 4. Solubility of various metal iodides expressed as the aqueous metal concentration (log mole L^{-1}) at 10 ug L^{-1} iodide.

Various forms of iodine react with organic molecules. Elemental iodine reacts in much the same way as chlorine and bromine, to form organo-iodine compounds. The syntheses of polyvalent organo-iodine compounds has been reviewed (Stang, 2003; Zhdankin and Stang, 2002). Skulski (2000) reviewed 10 years of research at the Medical University of Warsaw, Poland into aromatic organo-iodine compounds. Another area of research into organic-iodine reactions has been the reactions that might occur with organic substances in nuclear reactors during an accident (e.g., Skulski, 2000; Malinauskas and Bell, 1987; Paquette et al., 1986; Taghipour and Evans, 2002; Wren and Ball, 2001).

3.2 Aqueous Speciation

Inorganic iodine chemistry under conditions associated with most ^{129}I environmental plumes is somewhat simplified because the only aqueous species that are common are I$^-$, I$_2^o$, and IO$_3^-$. Figure 5 shows the relation of these species in Eh-pH space. Iodate (IO$_3^-$) is expected to be stable under very oxidized conditions across the range of pH likely to be encountered in most contaminant plumes. Elemental iodine, I$_2$, is stable at moderately oxidized, acidic conditions in which relatively high total iodine concentrations are present, such as in marine environments. Increased total iodine concentration expands the diiodine field as shown by the dotted line in Figure 5. Iodide (I$^-$) is the stable form over much of the range of conditions expected in contaminant plumes.

As will be discussed in Sections 3.4, an important omission in these calculations is to consider any organo-iodine species; these species are omitted because association constants are not available. Because iodine and organic carbon (OC) form extremely strong bonds, covalent bonds, the presence of small concentrations of dissolved OC can have significant effects on iodine speciation. Such organo-I species have been shown to account for as much as 40% of the iodine species in estuaries, rivers, and rain (Santschi and Schwehr, 2004), or as much as 80% in subsurface aquifer environments (Kaplan et al.,

2011; Otosaka et al., 2011). Low concentrations of organo-I (and iodate) have also been detected recently in Hanford groundwater (discussed in Section 3.4). Other potential contributing reasons for why thermodynamic speciation calculations do not predict actual [129]I speciation distributions are: 1) contaminant plumes may not be in steady state, and 2) thermodynamic models do not take into consideration processes involving microbes, well known to accumulate and alter iodine speciation (Section 4.0).
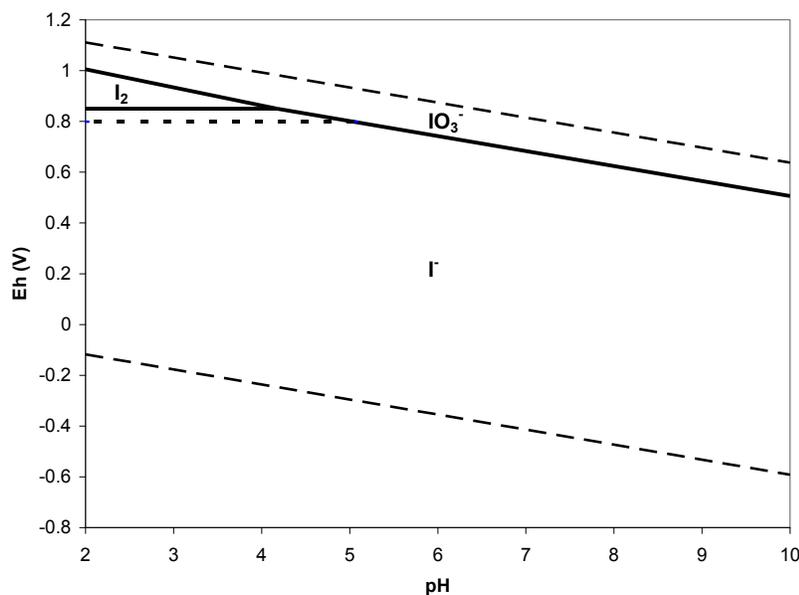
Figure 5. Eh-pH diagram of aqueous iodine speciation; solid line = total iodine concentration of 1 μg L^{-1}, a typical groundwater concentration, dotted line = total iodine concentration of 58 μg L^{-1}, a typical seawater concentration (Fuge and Johnson, 1986); dashed lines are stability limits of water (note that organo-iodine species are not included in these calculations).

3.2.1 *Aqueous Iodine – Dissolved Natural Organic Matter Interactions*

The coexistence of inorganic and organic iodine species has been reported in various environments (Couture and Seitz, 1983; Yuita, 1992; Yuita and Kihou, 2005; Muramatsu et al., 1988; Baker et al., 2001; Santschi and Schwehr, 2004; Xu et al., 2011a; Xu et al., 2011b; Xu et al., 2012). For example, methyl iodide is an important gaseous form of iodine in the marine atmosphere and in releases from nuclear fuel reprocessing facilities, while dissolved organo-I compounds comprise up to 40% of total iodine in aqueous samples from estuaries, rivers, and rain (Santschi and Schwehr, 2004). Organic carbon interaction with [129]I are discussed in more detail in Section 3.3.

3.3 Sorption to Sediment Minerals and Organic Matter

3.3.1 *Iodine Speciation on the Solid Phase*

There have been two different approaches to identifying iodine species associated with soils and sediments: direct spectroscopic methods and indirect extraction methods. Direct spectroscopic methods have been limited to the use of X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure spectra (EXAFS) (Fuhrmann et al., 1998; Kodama, 2006; Shimamoto and

Takahashi, 2008). These direct X-ray absorption spectroscopy techniques are limited to analyzing geological samples with elevated iodine concentrations added to the samples. The reason for this is because environmental samples tend to have iodine concentrations that are appreciably lower than this method's detection limits. The detection limit of XANES may be >10 μg g^{-1} ^{129}I (Hou et al., 2009a). Consequently studies must be conducted at extremely high iodine concentrations, ppm to percent concentration levels. Shimamoto and Takahashi (2008) conducted XANES studies on soils amended with 55 μg g^{-1} I. They reported that most of the iodine in the soil was in an organic form. XANES studies with a pyrite mineral isolate showed the reduction of IO_3^- to I_2 (Fuhrmann et al., 1998). This finding is very likely a result of using very high iodine concentrations and likely not a common process occurring in natural terrestrial environments. They also observed that magnetite sorbed I$^-$ from solution but not IO_3^- (this is contrary to popular understanding that IO_3^- sorbs more strongly than I$^-$ to mineral surfaces due to iodates strong Lewis base characteristic) and that biotite sorbed IO_3^- from solution, but not I$^-$ from solution. XANES was also used to independently determine K_d values of iodate and iodide sorption onto a soil (Kodama, 2006).

The second method of assessing the speciation of iodine on the solid phase is via sequential extraction or selective extraction. This technique involves adding extractants designed to remove iodine associated with a given phase (e.g., water soluble, carbonate, Fe-(oxy)hydroxide, organic matter, residual) or sorbed by a specific process (e.g., exchangeable). Sequential extractions have been carried out to investigate iodine speciation in sediments (Hou et al., 2003; Schmitz and Aumann, 1995; Stutz et al., 1999; Yuita, 1992). These are operationally defined parameters and as such do not carry mechanistic interpretations. In practice they suffer a number of pitfalls, although the application of sequential extractions to iodine is not nearly as problematic as it is with other ions that are more prone to complex, change oxidation, or precipitate, such as phosphate, or plutonium (Nirel, 1990; Scheckel et al., 2003; Tessier and Campbell, 1988). Hou et al. (2003) included a water soluble NH_4OAC exchange, carbonate (NH_4OAC (pH 5), Fe-oxide (NH_2OH, HCl, pH2 80-100 °C), organic (NaOH 80-100 °C), and residue (remaining) fractionation scheme.

Despite its pitfalls, various extractions schemes have been employed to determine which solid phase fraction sorbs the most iodine. Schmitz and Aumann (1995) analyzed soils collected from a reprocessing plant in Germany and reported that 39 to 49% of the ^{129}I was associated with the water soluble fraction, whereas only 4 to 15% was associated with the organic and 7 to 13% was associated with the residual fraction. However, a different distribution of stable iodine, ^{127}I, was observed where only <4% occurred in the water soluble fraction. This difference between the two isotopes may be attributed to the different sources of the two isotopes and underscores an important point that the fate of iodine in the environment is controlled by more than just geochemical behavior. In the coastal and estuarine area of Sellafield, most of the ^{129}I was associated with the oxides (53 to 66%) and organic (23-43%) fractions, whereas <7.5% was found in the other fractions. A similar result was also obtained from soil samples collected from near the Chernobyl accident: 30 to 40% of the ^{129}I was associated with the oxides, 40 to 48% with the organics, and only 6 to 13% with the water soluble fraction (Hou et al., 2003).

3.3.2 Influence of Sediment Organic Matter on Iodine Sorption

All studies of sorption in shallow soils that contain organic matter (OM) indicate that the OM is a primary control on sorption of iodine (Assemi and Erten, 1994; Bird and Schwartz, 1997; Fukui et al., 1996; Kaplan, 2003; Neal and Truesdale, 1976; Sheppard and Thibault, 1991; Whitehead, 1974; Yoshida et al., 1992; Yu et al., 1996). In a survey of 26 soils and sediments samples from across the U.S. with natural organic matter concentrations ranging from 0.046 to 0.5 wt % (except for one peat sample that was 28.1 wt %), Hu et al. (2009) reported that ~90% of the total iodine in soils was present as organic iodine, while inorganic iodine became important only in sediments with low organic matter contents. Whitehead

(1973) showed this by demonstrating that sorption in untreated soils was greater than in soils that were treated to destroy the OM. There was some sorption of iodine in the treated soils, primarily by iron and aluminum oxides (Whitehead, 1973). In a single soil profile studied (Bors et al., 1988), sorption of iodide correlated with organic carbon content of samples that ranged from 6.2 to 0.06 wt % organic carbon. Similar results were reported in studies involving different heating regimes (Muramatsu et al., 1990b; Muramatsu, 1990a). When all organic matter was removed by oxidation at 500ºC, sorption of iodine was reduced substantially, but the decrease in sorption was much less when carbon remained as charcoal after heating to 500ºC under a nitrogen atmosphere (Muramatsu, 1990a).

Another approach to demonstrating the importance of organic matter to iodine sorption by soils is to compare sorption onto individual components that comprise the soil. Whitehead (1974) took this approach and found that organic compost sorbed iodine more strongly than the mineral components of a soil. He also noted that drying the compost prior to the experiments greatly reduced iodine sorption. Neal and Truesdale (1976) measured sorption of iodide and iodate in riverine sediments and concluded that stronger sorption of these species occurred in peaty sediments than in freshly prepared ferric hydroxide. Sorption of iodine on a soil that was 70% organic carbon was compared to sorption onto various minerals by Assemi and Erten (1994) and sorption was much stronger to the soil. They also found that iodine soil sorption decreased substantially when it was heated to 180ºC or irradiated. Yu et al. (1996) demonstrated the importance of organic matter to iodide sorption by showing that the individual high surface area inorganic phases that make up most of a volcanic soil poorly sorb iodide relative to the bulk soil. A different approach was taken by Fukui et al. (1996) who compared iodine sorption onto a soil to sorption onto pure humic material. K_d values on the humic material were 10 times higher than on the soil.

Comparisons between iodine sorption to organic-rich soils and organic-poor soils also demonstrate the importance of organic matter to sorption of iodine. In lysimeter studies of four soils with organic contents ranging from 0.2-6.8 wt %, Sheppard and Thibault (1991) measured K_d values that were 1-2 orders of magnitude higher in the organic-rich soils relative to the organic-poor soils. Similar results were shown in comparative studies by Yoshida et al. (1992), Bird and Schwartz (1996), Sheppard et al. (1996), and Yoshida et al. (1998). Kaplan (2003) compared iodide uptake by two sediments that had similar grain-size, mineralogy, and pH values, but had very different organic carbon contents, <0.02 versus 0.14 wt %. Sorption was substantially higher in the organic-rich soil.

Sorption of iodine in oxic organic-rich sediments is greater than in anoxic organic-rich sediments (Ashworth and Shaw, 2006; Ashworth et al., 2003; Maillant et al., 2007; Sheppard, 1995; Whitehead, 1974). This was hinted at by Whitehead (1974) who found that drying organic-rich soils before measuring iodine K_d values substantially reduced the sorption. (Unfortunately, the implications of these results on experimental protocol have been overlooked by several subsequent related studies.) Sheppard and Hawkins (1995) explicitly noted this difference in iodine sorption between oxic and anoxic organic-rich sediments with experiments on bog soils. Changes in the redox state of an organic-rich soil from oxic to anoxic can also release iodide that was sorbed in the oxic state (Bird and Schwartz, 1997). The same relation was observed by Ashworth et al. (2003) and Ashworth and Shaw (2006) in column studies where they noted much lower sorption in saturated anoxic portions of their columns than in unsaturated oxic portions. Likewise, the same observation has been made in the field by Maillant et al. (2007) who returned, after 15 years, to the site of an iodide injection into bog soils documented by Sheppard et al. (1989). They found that iodine K_d values were approximately seven times higher in the surface bog soils than in the deeper anoxic bog soils. Release of soil-bound iodine has also been observed in two forest soils (9 – 56 fold increase) under flooded, anaerobic conditions (Yuita, 1992). Iodate was the dominant (86% of water soluble I) form under non-flooded, oxidizing conditions, whereas iodide was the dominant (87% of water soluble I) form under flooded conditions. In one soil type, the soil solution concentration of organo-iodine increased 2.5 fold under flooded conditions. A very extensive sampling of iodine soil water from a forest, upland field, and rice paddy field in Japan revealed a strong negative relationship

between soil Eh and soil water iodine concentrations (Yuita and Kihou, 2005). In particular, soil water iodine concentrations increase with decreasing Eh values below 200 mV. In summary, it appears that iodine uptake by sediments is largely controlled by OM concentrations and that iodine binds to surface soils under oxic conditions and is released under strongly reducing conditions. It is not clear from these studies whether the changes in redox alter the iodine speciation or the OM speciation, or both.

Although the above studies demonstrate the importance of OM controlling iodine sorption in sediments, there still remains considerable uncertainty regarding: 1) the nature of the organo-iodine bonding mechanism, 2) whether the organo-iodine bond occurs only under abiotic, biotic, or under both soil conditions, 3) why iodine sorption to OM occasionally appears to enhance or have no effect on transport, 4) the potential for abiotic I^- oxidation, and 5) the role of naturally occurring sediment microbes to accumulate iodine and to promote I^- oxidation. Much of this uncertainty arises from the fact that humic substances are inherently heterogeneous and complicated. They are supramolecular associations of self-assembling heterogeneous and relatively small molecules derived from the decomposition of dead plant and animal residues. These small molecules are held together by weak dispersive forces, such as hydrogen bonding, hydrophobic interactions, and electrostatic interactions.

The importance of studying iodine speciation under ambient conditions was demonstrated by Schwehr et al. (2009). Using a SRS subsurface wetland sediment and ambient iodine consisting of 29% I^-, 4% IO_3^-, and 67% organo-I, Schwehr et al. (2009) showed that by incrementally adding more total iodide, incrementally less organo-I and more I^- was detected at steady state. At 1000 μM, only 3% organo-I was detected. They attributed this change in detected iodine speciation to the added iodine swamping out the low system DOC concentrations. Similarly, Zhang et al. (2012) investigated the sorption, transport, and interconversion of iodine species by comparing their mobility in groundwater at ambient iodine concentrations (10^{-8} and 10^{-7} M) to those at artificially elevated concentrations (10^{-5} M). Iodine mobility greatly depended on iodine concentration, in addition to the type of species. At ambient concentrations, K_d values as high as 49 mL g^{-1} were measured, whereas at 10^{-5} M iodide, the solute traveled along with the water without retardation. Consequently, it is not possible to assess accurately natural iodine speciation using elevated spike loadings (to ease analytical detection).

3.3.3 *Influence of Other Sediment Parameters on Iodine Sorption*

Sorption of iodine on organic-poor soils is influenced primarily by mineralogy and pH, but complicated by iodine speciation. Whitehead (1973) showed that when OM was removed from a soil, some iodine still sorbed to the mineral fraction – primarily to iron and aluminum oxides. The magnitude of the sorption was inversely related to pH. In several studies sorption of iodate to the mineral fraction of soils has been greater than sorption of iodide. Neal and Truesdale (1976) observed that there was little sorption of iodide by ferric hydroxide or kaolinite, whereas iodate sorbed strongly to ferric hydroxide. Yoshida et al. (1992) concluded that the difference was that iodide sorption was likely purely electrostatic attraction, while iodate was chemically adsorbed or exchanged by the mineral allophane or sesquioxides. Nishimaki et al. (1994) observed the same behavior of iodide versus iodate sorption, with the iodate sorption showing a two-step mechanism – an initial rapid equilibrium sorption, followed by slow non-equilibrium sorption. The conclusions of Fukui et al. (1996) were consistent with Yoshida et al. (1992), except they concluded that iodide sorption seemed to be more complicated than pure electrostatic attraction. For 20 different Chinese soils, Dai et al. (2004) observed that the only strong correlation between soil properties and iodate sorption was the content of free iron and aluminum oxides.

Sorption of iodine in subsurface aquifer materials occurs as adsorption to specific mineral surfaces. Quantification of this has been approached by measuring sorption in the bulk material and by measuring adsorption onto individual minerals common to aquifer materials. Measurements of iodine sorption onto

bulk aquifer material, in general, show that sorption is weak, similar to organic poor surface soils (e.g., (Alvarado-Quiroz et al., 2002; Hu et al., 2008; Lieser, 1989; Schwehr et al., 2005b). The relationship to ionic strength is consistent with the relation to salinity observed by Lieser and Steinkopff (1989). Similar low sorption of iodine on Savannah River Site aquifer material was suggested by compilations of studies in the literature by Kaplan (2009). Their recommended K_d values for performance assessment models were 0 mL g^{-1} for sandy sediments and 0.6 mL g^{-1} for clayey sediments.

Laboratory measurements of iodine sorption on organic-poor Hanford soils by Kaplan et al. (2000) showed sorption to be relatively low, but higher than expected. For comparison, they measured sorption onto individual mineral components of the soil and found that only illite sorbed iodine significantly. Sorption onto illite was high and pH dependent, with K_d values varying from 46 mL g^{-1} at pH = 3.3 to 22 at pH = 9.4. An interesting comparison is the studies of iodine sorption onto an indurated shale by Devivier et al. (2004) and Savoye et al. (2006). They found sorption to be very low on the illite dominated shale at a pH of 8.3 with a high K_d value of 1.7 ml g^{-1} (Devivier et al., 2004). This highlights the point that natural samples are complex and mineralogy and chemistry alone cannot explain their sorption capacity for iodine. The pressures and temperatures required for induration of the shale, its relative impermeability, or other factors apparently rendered its illite much less sorptive of iodine than the samples used by Kaplan et al. (2000).

3.3.4 *Influence of Mineralogy on Iodine Sorption*

Monomineralic studies of iodine sorption show similar results to bulk soil studies, but provide an additional level of detail. In general, iodate sorbs more strongly to individual minerals than iodide and the common soil minerals that most strongly bind iodate are ferric oxides and hydroxides (Couture, 1983; Neal and Truesdale, 1976; Ticknor and Cho, 1990). Fuhrmann et al. (1998) observed an exception to the general iodide-iodate sorption relationship. Magnetite sorbed iodide more strongly than iodate. They also looked at redox changes in the sorbed iodate using XANES spectra. They observed that no reduction of iodate occurred when sorbed to the ferrous iron containing minerals biotite and magnetite, but reduction to elemental iodine did occur when iodate was sorbed to pyrite. Further reduction of the elemental iodine to iodide was not observed. Ticknor and Cho (1990) found that iodate sorption to hematite increased with increased total dissolved solids. Their experiments were done in a synthetic groundwater with relatively high concentrations of Na$^+$, Ca^{+2}, Cl$^-$, and SO$_4^{-2}$ (2000, 2170, 6176, and 985 mg L^{-1}, respectively) indicating that the presence of one or more of these ions changed the surface chemistry of the hematite to favor iodate sorption. Relatively strong sorption of iodate to freshly precipitated aluminum hydroxide has been measured, but sorption decreased as the aluminum hydroxide aged (Musić et al., 1979).

Iodide also sorbs to common soil minerals. Musić et al. (1979) observed weak sorption of iodide to aluminum hydroxide. Sazarashi et al. (1994) measured K_d values of 2-3 mL g^{-1} for sorption of iodide onto allophane, but observed no sorption to montmorillonite. Weak sorption of iodide to imogolite and ferrihydrite was observed by Yu et al. (1996), with sorption to ferrihydrite inversely related to pH. However, sorption onto these minerals was much less than onto a bulk soil containing these minerals and organic matter. Substantial sorption of iodide to common minerals has been observed by some investigators. Kaplan et al. (2000) observed strong sorption of iodide to illite, which was inversely related to pH. Titanium oxides are a common minor component of soils and Mishra and Srinivasu (1992) found that 73% of iodide at a concentration of 10^{-7} molar sorbed to TiO$_2$ powder. Yet organo-clays show even stronger sorption of iodide (Bors et al., 1994).

3.4 Radioiodine Sorption Studies at Hanford

In a compilation of iodine sorption studies using Hanford soils, Cantrell et al. (2003) concluded that the likely range of K_d values was 0 to 2 mL g^{-1} and that the most commonly range of values is between 0 and 0.2 mL g^{-1}. The tests he reported were almost exclusively designed to measure the extent that radioiodine sorbs under Hanford subsurface conditions and were not designed to understand iodine speciation or sorption mechanisms (Gee and Campbell, 1980; Kaplan et al., 1998b; Kaplan, 1996; Serne et al., 1993; Um et al., 2004). Among the underlying assumptions in each of these laboratory K_d measurements was that iodide, I$^-$, is the primarily species in Hanford groundwater and that it sorbs to sediments through the reversible anion exchange process (meaning iodine adsorbs and desorbs at equal rates). Ongoing measurements have shown that groundwater from the 200-UP-1 OU, in fact, contains not only iodide, but also organo-iodine and significant amounts of iodate, IO$_3^-$ (Table 5; personal communication with Dr. P. Santschi, Texas A&M University, Galveston, TX). Both stable and radioiodine indicate that iodate is clearly the predominant species in all samples analyzed to date. Stable ^{127}I, for which there was a sufficient concentration to conduct full iodine speciation, consisted of only 1-2% iodide and 0-14% organo-I.

Table 5. Stable ^{129}I and radioactive ^{129}I speciation in groundwater collected in March 2012 from 200 West Area (personal communication with Dr. P. Santschi, Texas A&M University).

	^{127}I					^{129}I			
	TOC μM	Total μM	Iodide μM (%)	Iodate μM (%)	Organo-I μM (%)	Total (pCi L^{-1})	Iodide (pCi L^{-1})	Iodate (pCi L^{-1})	Organo-I (pCi L^{-1})
299-W14-11	50.2	0.79	0.015 (2%)	0.707 (90%)	0.066 (8%)	31.6	<2	31.6	<5
299-W14-13	63.0	0.58	0.012 (2%)	0.481 (84%)	0.084 (14%)	35.6	<2	35.6	<5
299-W1-88	15.6	0.14	0.002 (2%)	0.141 (98%)	<0.003 (0%)	6.63	<2	6.63	<5

Based on thermodynamic considerations (Figure 5), iodide was expected to be the dominant species in Hanford groundwater. However, it is quite likely that iodide and iodate, as opposed to only iodide, may have been the dominant species introduced into the cribs that serviced facilities that used hot, strong acids to remove cladding from spent fuels, such as at T and B Plants in the 200 Areas. In a study to provide some insight into these conditions, 10 ppm iodide was prepared in 1 M HNO$_3$ and heated at 80 ^{o}C for 2 hours (personal communication, Dr. P. Santschi, Texas A&M University). The following speciation was measured:

- 4.5 ppm iodide
- 2.2 ppm iodate
- Below detection limit concentrations of I$_2$.

These results show a 55% decrease in iodide concentrations and 22% increase in iodate concentrations. Lack of detection of I$_2$ may in part be due to it escaping when the vial was opened for analysis and the analytical sample may have been overly diluted to permit measuring the iodide and iodate.

However, the likely introduction of ^{129}I in part as iodate, can only partially explain the observed speciation (Table 5) because stable iodine, ^{127}I, also exists predominantly as iodate. The presence of iodine in multiple oxidation states and species within a given aqueous samples is consistent with previous reports of radioiodine and stable iodine speciation measurements at other DOE sites (reviewed in Denham

et al., 2009; Kaplan, 2011; Kaplan et al., 2011; Otosaka et al., 2011), oligotrophic lakes[a] (Gilfedder et al., 2008), and marine systems (see references in Schwehr et al., 2005). To our knowledge there are no iodine speciation studies of arid region groundwater similar to that at the Hanford Site. The ^{129}I plume at the Savannah River Site is appreciably more acid (pH 3.1 to 6.0) and has higher DOC levels than the Hanford Site (Appendix A), all samples had varying percentages of iodide, iodate, and organo-iodine that changed as a function of the plume's pH, Eh, and DOC gradients. It was not uncommon to have about equal concentrations of all three species. Iodide concentrations tended to be greater than those reported in Table 5. Schwehr et al. (2005) reported that marine samples, which tend to have a pH of ~8, closer to that of Hanford groundwater (pH 7 – 8.5), but relatively higher DOC concentrations, tended to have even distributions of iodide, iodate, and organo-iodine. Gilfedder et al. (2010) reported monthly iodine speciation in an oligotrophic freshwater lake, Lake Constance in the Alps. Lake Constance had a pH between 8.0 and 8.5 and the DOC concentrations were very low (<2 mg L^{-1}). Organo-iodine, iodide, and iodate concentrations varied greatly during the year, but clearly organo-iodine was the dominant species, generally accounting for >80% of the iodine pool. Iodate concentrations remained fairly constant throughout the year, and iodide concentrations tended to vary. Although there are no systems for direct comparisons for the Hanford iodine speciation data presented in Table 5, the iodine speciation discussed here indicates that all three iodine species tend to exist in varying percentages in a wide range of oxidizing environments. The significance of the data in Table 5 is that iodate typically sorbs to sediments greater than iodide. No sorption testing has been conducted with organo-iodine, but it too may sorb appreciably more than iodide to sediments. These findings bring into question whether the present Hanford ^{129}I K$_d$ values, albeit conservative, adequately represents the sorption anticipated by the more strongly sorbing iodate and organo-iodine species.

Researchers have reported that a large fraction of radioiodine sorbed onto Hanford sediment readily desorbs, consistent with the reversible anion exchange mechanism (or K$_d$ model) (Kaplan et al., 2000b; Um et al., 2004). Yet, there was a more-strongly binding radioiodine fraction that did not desorb under extreme chemical conditions conducive to anion exchange (desorption). Using a subsurface sediment, (ad)sorption iodide K$_d$ values were <0.3 mL g^{-1}, depending on iodide spike concentration, whereas desorption K$_d$ values using the same sediments were 1.41 to 4.15 mL g^{-1}.   A geochemical process that describes strongly sorbing iodine is iodine-sediment organic matter bonding (Section 3.3.2). Organic carbon uptake of iodine has been commonly reported in other systems to be the single most important sediment property controlling iodine uptake. Iodine forms a covalent bond with organic carbon, especially aromatic moieties, through electrophilic substitution. It is not known whether the low OC concentrations in the Hanford subsurface, perhaps in the range of 200 to 2000 mg kg^{-1} OC (0.02 to 0.2 wt % OC), would be sufficient to significantly influence sorption of the 0.00002 mg L^{-1} ^{129}I (3.5 pCi L^{-1} ^{129}I; 90th percentile concentration in the 200-UP-1 OU) in the groundwater. Some ongoing research related to this issue is presented in Table 6. Using three composite sediments recovered from the 200 West Area, iodate K$_d$ values were on average 89% greater than iodide K$_d$ values and both species tended to increase with the amount of OC present in the sediment. It is especially noteworthy that this trend existed at the very low OC concentrations that naturally exist in the Hanford sediments, albeit there were only few samples in this early study. Another observation made by the researchers was that the iodine speciation changed once the spike solution came into contact with the sediments, indicating that Table 6 is not reporting species-specific-K$_d$ values, but instead represent K$_d$ of a suite of iodine species (personal communications with P. Santschi, Texas A&M). The importance of evaluating a species specific approach to describing radioiodine speciation is that it may provide an ^{129}I fraction that is nearly irreversible bound to the sediment and may provide a more accurate representation of ^{129}I transport.

---

[a] Oligotrophic lakes are characterized by a low accumulation of dissolved nutrient salts, supporting but a sparse growth of algae and other organisms, and having a high oxygen content owing to the low organic content.

Table 6. Iodide, I⁻, and iodate, IO₃⁻, K_d values after 21 days of composite sediments recovered from 200 West Area borehole cores (personnel communications with P. Santschi, Texas A&M).

Composite Sediment [a]	Organic Carbon (%)	Inorganic Carbon (%)	Total Sediment Iodine ($\mu g\ g^{-1}$)	Total DOC (μM) [b]	Iodide, spiked K_d ($mL\ g^{-1}$) [c]	Iodate spiked K_d ($mL\ g^{-1}$) [c]
H3	0.15	0.18	2.10	94 ± 17	3.38	3.94
H1	0.12	0.92	4.79	284 ± 33	0.08	1.78
H2	0.04	0.01	0.68	0	0.00	0.83

[a] Sediment 1 – composite of fine-grained sediments, mostly silt, from the vadose zone of borehole cores 299-W11-92 and 299-W15-226. Natural calcium carbonate cementation of the sediment was apparent.
Sediment 2 – composite from different depths within one well (299-W11-92)
Sediment 3 – composite of saturated zone sediments of two different wells: 299-W11-92 and 299-W15-226.
[b] Total dissolved organic carbon is the total organic carbon released from the sediment to the aqueous phase (<0.45um) after 21 days of contact during the sediment/groundwater batch iodine uptake experiment.
[c] Suspensions were spiked with either iodide or iodate but during contact period the spiked species transformed to other species. Consequently these are not species-specific K_d values

Um et al. (2004) noted that, although sorption of iodide was very low on Hanford sediments, the iodide was only partially reversible. The sorption K_d was 0.2 mL g⁻¹, but the desorption K_d was 1.4 mL g⁻¹. Irreversibility of iodide diffusion into shale was observed; a substantial fraction did not diffuse back out (Savoye, 2006). Glaus et al. (2008) observed little actual sorption of iodide on Opalinus Clay, but suggested that iodide was converted to an unidentified species because not all of the iodide injected could be recovered. They also noted that iodate sorption was stronger than iodide, but iodate was readily converted to iodide (Glaus et al., 2008). Hu et al. (2005) made similar observations in studies of iodine sorption to SRS and Hanford sediments. They found that the capacity for reduction of iodate to iodide in SRS sediments was greater in deeper aquifer material than in surface soil or sub-soil. A sample of Hanford sediment had a reduction capacity even greater that the SRS aquifer material. Hu et al. (2005) concluded that the reduction capacity is caused by the presence of structural Fe(II) in common clay minerals such as illite, smectite, and kaolinite.

3.5 Summary and Relevance of Geochemistry of Iodine

Hanford Site:
- Ongoing studies indicate that the 200-West contaminated aquifer contains primarily iodate and much lower concentrations of iodide and organo-iodine, consistent with iodine speciation measured in other ¹²⁹I plumes. This speciation distribution is not predicted by thermodynamic calculations because these calculations: 1) do not account for the extremely strong organic matter – I complexes (because such thermodynamic constants are not available), 2) assume the modeled system is under steady state conditions, and 3) do not account for the potential impact of microbial processes that have been shown to accumulate iodine and greatly alter iodine speciation.
- Ongoing K_d values for iodate amended Hanford sediments were 89% greater than iodide amended sediments.
- Ongoing studies indicate that iodide and iodate uptake by 200-West sediments may be correlated to the amount of organic carbon present.

- Iodine sorption to Hanford sediments is mostly reversible, but a fraction is not, suggesting a sorbed iodine fraction may be more strongly bound than the rest. Consequently, measured (ad)sorption K_d values are less than desorption K_d values.

General:
- Iodine behavior in the environment is complicated by its multiple physical states, multiple redox states, interactions with organic matter, and microbial transformations.
- Adsorption and interaction with OM are the dominant attenuation mechanisms for ^{129}I in groundwater. Precipitation is not likely to be a natural attenuation mechanism for ^{129}I because iodide forms insoluble salts with only relatively scarce metal cations – Ag, Hg, and Cu.
- Iodate is typically adsorbed more strongly than iodide; adsorption is inversely related to pH.
- Sediment organic matter generally decreases iodine mobility, especially when bound to larger organic moieties. To a lesser extent, organo-iodine complexes may increase mobility, especially when iodine is bound to smaller organic moieties.
- Radioiodine speciation studies are underway at the SRS's F-Area ^{129}I plume. Iodide, iodate and organo-iodine were measured in each of the groundwater samples containing a range of pH levels (3.2 to 6.8) and Eh levels (360 to 654 mV).

4.0 Microbial Processes Influencing ^{129}I Behavior

The activity of iodine in biota, the strong chemical bond with organic matter, the redox sensitivity, and studies of marine iodine cycling have led to the hypothesis that microbial activity is involved in iodine sorption by sediment OM. Many researchers have tested this hypothesis by comparing iodine sorption onto sterilized and unsterilized soils (Behrens, 1982; Bird and Schwartz, 1997; Sheppard, 1995; Yoshida et al., 1998). These studies have confirmed that microbial activity is involved, but the nature of that involvement is unresolved. Bors et al. (1991) showed that under specific conditions bacteria and fungi cells isolated from a soil did take up iodine, though they acknowledged that this did not resolve whether microbes are directly or indirectly involved in sorption of iodine in soils. Sheppard and Hawkins (1995) suggest that microbes exert an indirect effect on iodine sorption, perhaps just by their action of degrading OM under oxic conditions. Sheppard et al. (1996) reiterated this conclusion by showing that the organic content of seven soils correlated positively with sorption, but enzymatic activity did not. Some of the iodide in their studies was irreversibly sorbed and they suggested that this iodide had converted to elemental iodine that reacted irreversibly with OM. Results reported by Yamaguchi et al. (2006) and Yamaguchi et al. (2009) using XANES to analyze iodine speciation also demonstrated that elemental iodine was ultimately the species that reacted with organic matter. In anaerobic soils, iodate ($I^VO_3^-$) was reduced to elemental iodine (I^0) that reacted with organic matter (Yamaguchi et al., 2006). In aerobic soils, iodine reaction with organic matter involved either reduction of iodate or oxidation of iodide (Yamaguchi et al., 2010). Yamaguchi et al. (2009) also concluded that microbes were not necessary for the reduction of iodate by humic substances. Maillant et al. (2007), studying the bog samples from the 15 year earlier iodide injection of Sheppard et al. (1989) found considerably more evidence of microbial behavior in the oxic surface layers than in the anoxic layers. They also observed iodine associated with polyphenols in the humified fraction of the soils. This is consistent with the findings of Warner et al. (2000) that observed that sorption rates of elemental iodine onto solid humic material were in the range of sorption rates onto the phenolic compounds (Warner et al., 2000). Thus, the exact role of soil microbes in sequestering iodine remains unclear, though it is generally agreed they play some role.

4.1 Biological Reactions and the Global Iodine Cycle

Biological mechanisms are intrinsic to the global iodine cycle. Oceans are considered the primary source of iodine; accordingly, our understanding of biological transformations of iodine is derived largely from those processes that have been studied in marine environments. Based on thermodynamic considerations iodate/iodide levels in seawater are in disequilibrium, with iodide found at levels much higher than would be expected, especially in certain surface waters, coastal and estuary regions, deep oxygenated water, and porewater of marine sediments where I^- concentration up to 40 µg L^{-1} have been measured (Amachi, 2008; Farrenkopf et al., 1997). The conversion of IO_3^- to I^- is thought to be catalyzed primarily via microbial activity, perhaps by the enzyme nitrate reductase or release of I^- from C-I or N-I bonds upon decomposition of organic matter (Farrenkopf et al., 1997; Tsunogai and Sase, 1969; Waite and Truesdale, 2003; Wong et al., 2002) (Figure 6).
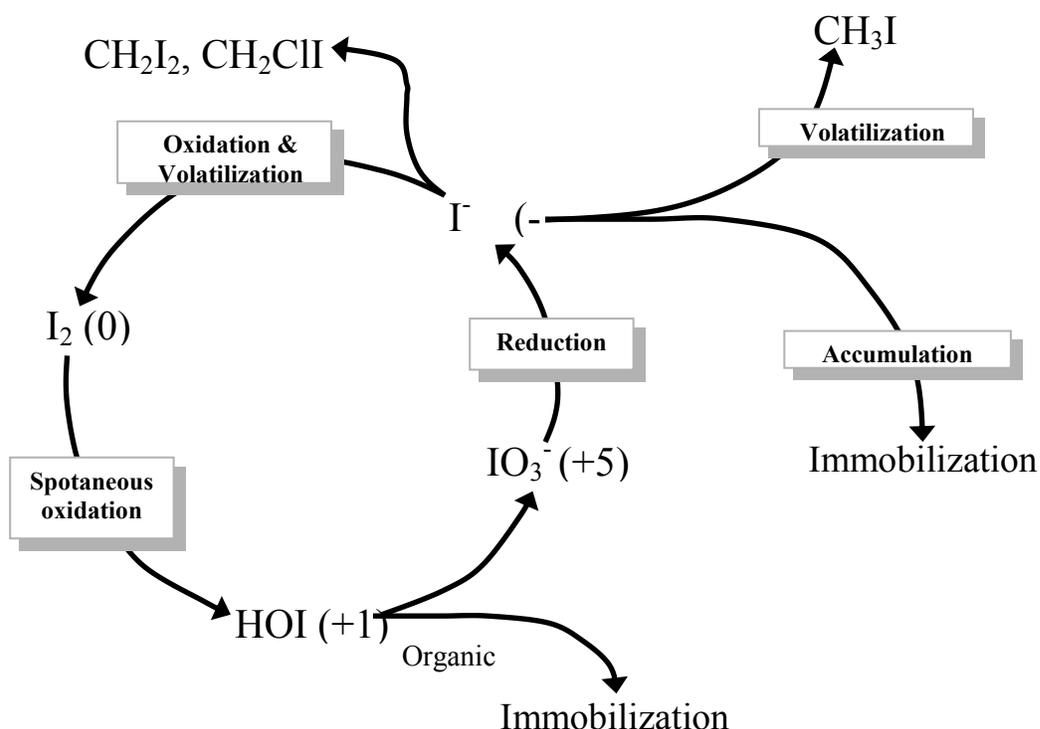
Figure 6. Biological transformations of iodine (Amachi et al., 2005a).

Organic iodine species, including CH_3I, CH_2ClI, CH_2I_2 and CH_3CH_2I, are found at relatively low concentrations (< 5% of total I) in the open ocean, but concentrations between 5-40% of total dissolved iodine are not uncommon in coastal and estuary systems (Schwehr and Santschi, 2003; Wong and Cheng, 1998; Hou et al., 2009b). Volatilization of iodine (primarily as methyl iodine, CH_3I) from the ocean into the atmosphere is a critical feature of the biogeochemical cycling of this element (Fuge and Johnson, 1986). Localized concentrations of CH_3I can be very high over seaweed beds and this may be the dominant source of gaseous organo-iodine in coastal regions, whereas microalgae, bacteria, and abiotic photochemical processes probably play a larger role in open ocean surface waters (Amachi et al., 2004; Baker et al., 2001; Moore and Groszko, 1988; Richter and Wallace, 2004; Smythe-Wright et al., 2006).

Importantly, organic-I species are thought to play a key role in the transfer of iodine to the terrestrial environment whereby organic iodine volatilizes from the ocean surface, undergoes various photolytic transformations in the atmosphere, and is transferred to the land surface via wet $(1 - 6 \ \mu g \ L^{-1}$ total I in rainwater) and dry deposition (Fuge et al., 2005; Hou et al., 2009b; Kolb, 2002). Runoff concentration of iodine in fresh waters is typically $1 - 3 \ \mu g \ L^{-1}$ (Hou et al., 2009b). Iodine concentrations in soil ranges from $0.5 - 40 \ \mu g \ g^{-1}$ with common concentrations of $1 - 5 \ \mu g \ g^{-1}$, a value much greater than that of underlying rocks $(0.05 - 0.5 \ \mu g \ g^{-1})$ (Fuge et al., 2005; Hou et al., 2009b). Within the terrestrial sphere, little research has been devoted to the participation of biological processes in iodine cycling.

4.2 Accumulation and Speciation of Iodine in Biological Samples

It has been known for centuries that marine macroalgae concentrate iodine (Rosenfeld, 2000). Brown algal species such as *Laminaria digitata* can accumulate iodine up to concentrations as high as 5% of dry weight, with tissue concentrations exceeding 50 mM (Ar Gall et al., 2004; Küpper et al., 1998b). Iodine accumulation is widespread among marine algae and ranges from $10 - 6000 \ \mu g \ g^{-1}$ for brown, red, and green algae (Hou and X., 1998). In comparison, terrestrial plants accumulate, on average, $0.2 - 0.5 \ \mu g \ g^{-1}$ (Fuge et al., 2005).

Studies examining the accumulation of iodine by microorganisms are exceedingly sparse. A number of bacterial strains capable of iodide accumulation have been isolated from marine sediment (Amachi et al., 2005a; Amachi et al., 2005b). All strains were classified within the *Flavobacteriaceae* family of the *Bacteroidetes* phylum. The maximum iodide content measured in cells was $30 \ \mu g \ g^{-1}$ dry cells, and the maximum concentration factor based on the ratio of iodide in cells to that in the media was $5.5 \ x \ 10^3$. By comparison, the brown algae, *Laminaria digitata*, has exhibited an iodide concentration factor of $1.5 \ x \ 10^5$ (Küpper et al., 1998b).

Iodide uptake by bacterial cells was stimulated in the presence of glucose and O_2, and the process was saturable (0.073 μM affinity constant; 0.55 pmol min^{-1} mg dry $cells^{-1}$ maximum velocity) (Lin et al., 2012b). Iodate was not accumulated. In a follow up study with one of these iodide-accumulating bacterial strains, it was determined that glucose stimulated iodide uptake through the action of glucose oxidase, which generated extracellular H_2O_2 (Amachi et al., 2007b). The authors proposed a model whereby extracellular H_2O_2, generated by glucose oxidase, is used to oxidize iodide to I_2 or hypoiodous acid, HIO, via an unidentified haloperoxidase. HIO is then transported across the cell membrane via a facilitated diffusion-type mechanism. Once inside the cell, HIO would be reduced to iodide or form organo-iodine species. This scenario is strikingly similar to that observed in the brown algae, *L. digitata*, where iodide is oxidized to hypoiodous acid (HIO) by an extracellular haloperoxidase, which then enters the cell via facilitated diffusion (Küpper et al., 1998a) (Figure 6). Inside the cell, iodine is stored in the iodide form and it has been posited that it acts as an inorganic antioxidant, scavenging reactive oxygen species (Kupper et al., 2008). Very interestingly, data indicated that while inside *L. digitata* tissue, I^- is surrounded by organic molecules such as phenols, carbohydrates, and proteins rather than an ordered hydration shell (Figure 7). In the presence of H_2O_2 and peroxidase activity most of the available iodine is incorporated into aromatic organic molecules that may or may not undergo nucleophilic substitution with Cl^-, Br^-, or HO^- to regenerate I^-.
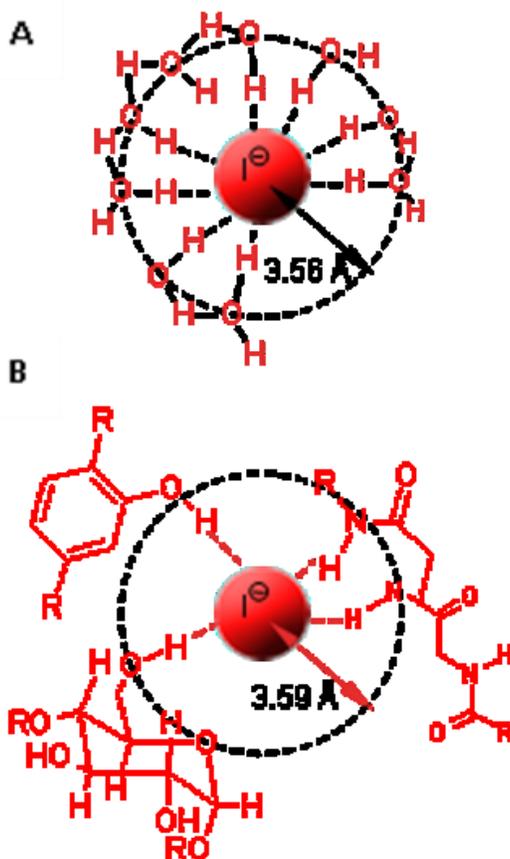
Figure 7. Iodide surrounded by A) Aqueous hydration shell; B) intracellular phenols, carbohydrates, or amines (Kropper et al., 2008).

4.3 Biological Formation of Gaseous Iodine

From early studies it was concluded that volatilization of iodine from surface soils was not a widespread phenomenon. Whitehead (1981) found that among 24 surface soils volatilization was negligible, except in an acid sandy soil where 57% of the iodine was volatilized. It was generally believed that the presence of organic matter inhibits volatilization in soils by binding available iodine.

Rice paddies have, however, been shown to be a significant source of iodine transfer to the atmosphere. It has been calculated that worldwide methyl iodide volatilization from rice paddies at 16 to 29 Gg per year or as much as 4% of the atmospheric methyl I balance (Lee-Taylor, 2005; Muramatsu, 1995). In one of the early studies examining iodine volatilization from rice paddies, Muramatsu and Yoshida (1995) determined that iodine volatilized from rice plants was mainly in the form of CH_3I. Production of CH_3I was greatest when the plants were flooded, and paddy soil incubated with increasing concentrations of iodide (0.1 – 10 mM) released increasing amounts of CH_3I (other alkyl iodides were not detected).

A survey of 53 soil samples collected from rice paddies, forests, upland fields, and wetlands yielded detectable CH_3I production from spiked iodide (0.1 µM) in samples from each of these terrestrial environments (Amachi et al., 2003). Formation of other alkyl iodides was not observed. The addition of

glucose or yeast extract could enhance CH_3I production, whereas the addition of antibiotics targeting prokaryotes (streptomycin and tetracycline) was strongly inhibitory (the fungal antibiotic, cyclohexamide had little effect). Very little methyl iodide was produced with autoclaved soils or under anaerobic conditions. These results suggest that soil bacteria (mainly, aerobic soil bacteria) may preferentially contribute to iodine volatilization from these soil environments. It is important to note that iodide methylation has been observed to occur primarily under aerobic or microaerobic conditions in other environments as well such as freshwater, seawater, brine waters, etc. (Amachi et al., 2001; Stephenson, 1995). The extrapolation of iodine methylation rates from laboratory studies with select soils to natural soil environments is, however, difficult because of the large variations in iodine levels among different soil types, the dependence of iodine availability on soil properties, and the concentration-dependent nature of methyl iodine formation (Amachi et al., 2001). Of particular interest, it has been suggested that biologically mediated iodine methylation could contribute to localized air concentrations of ^{129}I near nuclear production facilities or reprocessing plants, even after closure (Brauer and Strebin, 1982; Muramatsu, 1995).

Wide varieties of terrestrial bacteria are capable of methylating iodine including multiple taxa within the α-, β-, and γ-*Proteobacteria*, *Bacteroidetes*, and *Actinobacteria* phyla (Amachi et al., 2001; Muramatsu et al., 2004). Indeed, of 100 bacterial isolates from a variety of sources, including soils, seawater, and marine sediments, approximately 40% were observed to produce CH_3I. Rates of CH_3I production were directly correlated with iodide concentration over the range of iodide concentrations examined (0.1 μM – 10 mM), thus bacterial CH_3I production depends greatly on ambient iodine levels. Results indicated that iodine methylation may proceed via a S-adenosyl-L-methionine (SAM)-dependent mechanism in the strains evaluated. An affinity constant for iodide in cell extracts of one strain was 0.26 mM. SAM-dependent iodine methylation activity has been observed in a number of eukaryotes including marine algae, fungi, and higher plants (Amachi et al., 2001; Saini, 1995; Saxena et al., 1998; Wuosmaa, 1990). Although halide volatilization has been demonstrated for terrestrial plants, fungi, and bacteria, the relative contribution of each in soil systems has not been established.

4.4 <u>Influence of Redox Conditions on Alkyl Iodine Formation</u>

It has been observed that the Eh of soils in flooded rice paddies drops to ≤ 200 mV and that iodine is desorbed from soil to the solution phase as iodide under these conditions (Muramatsu, 1989). It was subsequently shown that high iodine desorption occurs in soils at or below a soil Eh of -100 mV (Muramatsu et al., 1996). The highly reduced conditions surrounding the roots of rice were attributed to O_2 uptake by respiratory metabolism of soil bacteria consuming organic exudates from the rice plant, and iodine desorption was enhanced by addition of organic substances such as straw and glucose to soil or cultivation of rice plants in soil. In support of this idea, it was demonstrated that iodine desorption was enhanced by addition of organic substances such as straw and glucose to soil or cultivation of rice plants in soil. It is thought that rice roots or soil microbes within the rhizosphere can oxidize iodide to I_2 under these conditions because of localized oxidizing power provided by the plants (Yamada, 2005). Muramatsu et al. (1996) propose that under low Eh conditions, the released iodide is thus available for biological methylation at oxic/anoxic boundaries found not only in rice paddies, but also in environments such as peat bogs and swamps.

4.5 Microbiological Oxidation of Iodine

The initial description of iodide oxidation by a bacterial species was elicited by the death of fish in experimental aquaria, presumably due to iodine poisoning. The marine bacterium, *Pseudomonas iodooxidans* (γ-Proteobacteria), was isolated from tank water by observing colonies that produced a blue color on seawater-agar plates containing 4% glycerol, 0.12% starch, and 0.1% potassium iodide (Gozlan, 1968). Iodine production could be detected in the presence of 8 mM but not 0.8 mM KI. The microorganism was highly resistant to iodine toxicity. Experimental evidence pointed towards the production of an extracellular haemoprotein peroxidase by *P. iodooxidans* that could oxidize iodide in the presence of H_2O_2 (Gozlan and Margalith, 1973; Gozlan and Margalith, 1974).

$$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O. \tag{7}$$

Importantly, the physiological status of the bacterial culture needed to be such that H_2O_2 was produced as a co-substrate for iodide oxidation.

Iodide oxidation has also been confirmed (used 1 – 5 mM KI) to be catalyzed by two *Roseovarius* sp. (α-Proteobacteria), one isolated from marine sediment and another from seawater (Fuse et al., 2003). Organic iodine species, including CH_3I, CH_2ClI, CH_2I_2, and CHI_3, were also produced from iodide by these strains, and it was suggested that organic acids in the media or produced by the strains could be the carbon sources for these organo-iodine products. Extracellular peroxidases were implicated in the process.

In the most exhaustive study to date prospecting for iodide-oxidizing bacteria, strains were isolated from iodide-rich (63 μM to 1.2 mM) natural gas brine waters and seawater (Amachi et al. 2005). Iodide-oxidizing bacteria were not obtained from the 22 surface soil samples that were tested. Iodine-oxidizing bacteria were isolated directly from brine waters, but were only isolated from seawater after enrichment in the presence of 1 mM iodide (however, it was shown that KI does not influence the levels of iodide-oxidizing activity in the isolates). Why iodide-oxidizing bacteria can be enriched in the presence of high I concentrations (mM) is currently unknown. Amachi et al. (2005) suggest two possibilities. First, iodide oxidation generates energy using oxygen as an electron acceptor, a thermodynamically favorable reaction ($2I^- + \frac{1}{2}O_2 + 2H^+ \rightarrow I_2 + H_2O$ ($\Delta G^{0'} = -56$ kJ/reaction). However, since the iodide oxidizing enzyme appears to be extracellular, this hypothesis is unlikely. Alternatively, iodide-oxidizing bacteria use oxidized iodine species to attack competing microbes giving them a selective advantage, especially in environments with high levels of I.

The reaction required O_2 but the addition of H_2O_2 did not stimulate iodide-oxidizing activity, thus the role of a peroxidase in iodide oxidation by these strains was not borne out by the experimental evidence. The authors suggested that an oxidase may be involved. The strains, which were most closely related to *Roseovarius* and *Rhodothalassium* spp. (α-Proteobacteria), were also shown to produce organic iodine species (CH_2I_2 and CH_2ClI) in marine broth. It was postulated that I_2 reacted with organic molecules in the media to form organo-iodine species. Bromine-oxidizing activity was not detected in these strains.

4.6 Biological Reduction of Iodine

A number of studies have demonstrated that phytoplankton (true algae and cyanobacteria) are involved in transformation of iodate to iodide in seawater (Chance et al., 2007; Wong et al., 2002). Nitrate reducing bacteria have also been implicated in biological iodate reduction in marine environments (Tsunogai and Sase, 1969). The sulfur and iron reducing bacteria, *Desulfovibrio desulfuricans* and *Shewanella oneidensis*, have been shown to reduce iodate in pure cultures, but the mechanism and enzymes involved have not been identified (Councell et al., 1997; Farrenkopf et al., 1997). Iodate was toxic to cells of *S. oneidensis* at high concentrations (20 mM), and biological iodate reduction was optimal for both organisms at or below a concentration of 250 uM. Importantly, it was observed that two primary products of microbial sulfur and iron reduction, ferrous iron and sulfide, can abiotically catalyze the reduction of IO_3^- to I^- (Councell et al., 1997). This abiotic mechanism could contribute to IO_3^- reduction in environments that support microbial iron and sulfate reduction.

Recently, an iodate-reducing bacterium (strain SCT) was isolated from marine sediments (Amachi et al., 2007a). The microorganism is closely related to the denitrifier *Pseudomonas stutzeri* and was capable of utilizing iodate (2 – 4 mM) as the terminal electron acceptor for growth in the presence of organic acids, alcohols, or sugars serving as the electron donor/carbon source. The results indicate that SCT is a dissimilatory iodate reducing bacterium that may couple iodate reduction directly to energy generating electron transport (IO_3^-/I^- ΔG^o = 3347 kJ mol^{-1}). However, nitrite reductase did not appear to be the primary mechanism behind iodate reduction in this microorganism.

4.7 Microbiology of the Hanford Subsurface

A series of recent studies have provided the most in-depth analysis of the microbial community inhabiting subsurface sediments of the Hanford Site. Subsurface cores obtained from the Integrated Field-Scale Subsurface Research Challenge (IFRC) site within the 300 Area were extensively analyzed by biogeochemical measures, high-throughput sequencing and state of the art community analysis tools (Lin et al., 2012a; Lin et al., 2012b; Lin, 2012; Stegen et al., 2012). Not unexpectedly, microbial community characteristics of the Hanford sediments were largely delineated based upon the formation from which they were retrieved, Hanford or Ringold. The Hanford formation, which is aerobic and primarily composed of unconsolidated sediments varying in size from silt to sand to large gravel, harbored moderate levels of bacterial biomass ($\sim 5 \times 10^6$ – 5 x 10^7 cells per gram of sediment) and exhibited high diversity representing 12 bacterial divisions (Lin et al., 2012a). Transitioning into the anoxic portion of the Ringold, bacterial biomass decreased approximately 50 fold ($\sim 1 \times 10^5$ – 1 x 10^6 cells per gram of sediment), and the bacterial diversity was greatly diminished and was comprised of nearly 90% *Proteobacteria*.

Because the organic carbon content of sediments from the two formations were similar it was suggested that higher hydrological flux and transmissivity of the Hanford formation enables higher advective flux of nutrients, thus supporting higher levels of biomass than observed in the less porous Ringold formation (Lin et al., 2012b); the concentration of DOC in groundwater has been measured <25 μmol L^{-1} (<0.3 mg L^{-1} C), and sedimentary organic C ranged from <42 μmol g^{-1} to 67 μmol g^{-1} (<0.05% to 0.08%) in Hanford and upper Ringold sediments though higher organic C contents have been detected deeper in the Ringold, ~850 μmol g^{-1} (1.02% C). Sequencing and culturing results indicated that anaerobic respirers were present in both formations, and it was posited that anoxic microsites or "hot spots" of electron donors are interspersed throughout the largely aerobic Hanford

sediment supporting spaces where anaerobic processes could dominate. Boulder-sized rip-up clasts of Ringold silt and clay found throughout the Hanford formation (Bjornstad et al., 2009) could also support anaerobic populations of microorganisms, adding to the complexity of the system and influencing the range of redox reactions possible.

Gaseous products of anaerobic metabolism were detected in both Ringold sediments and lower portions of the Hanford formation (Lin et al., 2012b). Indeed, it was suggested that anaerobic activity in the anoxic Ringold formation could support microbial growth in the aerobic Hanford sediments via upward fluxes of H_2 and CH_4. Yet the extent to which metabolic products of fermentation and methanogenesis support biomass formation in the Hanford formation remains untested.

4.7.1 *Relevance of Microbial Processes Influencing [129]I Behavior at the Hanford Site*

Microorganisms can catalyze the reduction, oxidation, and alkylation of iodine (Amachi, 2008; Denham et al., 2009). Within the anoxic portion of the Ringold formation or within anaerobic pockets of the heterogeneous Hanford formation, the potential for iodate reduction to iodide is high since this activity has been readily detected among microorganisms involved in denitrification and iron and sulfur reduction (Amachi et al., 2007a; Councell et al., 1997; Farrenkopf et al., 1997). It is important to note that both ferrous iron and sulfide (the two primary products of microbial iron and sulfur reduction) can catalyze the reduction of iodate to iodide (Councell et al., 1997). Evidence for denitrification and iron and sulfur reduction within the Ringold formation and at the Hanford/Ringold boundary has been reported, and relatively high proportions of ferrous iron are found even within sediments in the Hanford formation (Lin et al., 2012b). Yet, resent analyses of iodine speciation in Hanford groundwater and sediments revealed that the large majority of I exists as iodate (Table 5). Therefore, microbial reduction of iodate is either limited within this formation or oxidative processes (abiotic and/or biotic) are kinetically hindered.

Relatively high rates of iodide oxidation have been detected in environmental samples and in select bacterial isolates (a multicopper oxidase purified from the iodide oxidizing bacterium, Alphaproteobacterium Strain Q-1, had Michealis-Menton constants of K_m values of 2.64 mM and k_{cat} of 2.48×10^3 min^{-1} for iodide). However, in each case, the activity is associated with mixed cultures or isolates that have come from either: 1) environments with naturally high concentrations of iodide (~0.05 − 1 mM), or 2) enrichment cultures spiked with elevated concentrations of iodide (1 mM or higher) (Amachi et al., 2005b; Amachi et al., 2005c; Arakawa et al., 2011; Li et al., 2012a; Zhou and Chen, 2000). Attempts to isolate such "iodide oxidizing" bacteria from forest soils (Amachi et al., 2005b) or subsurface sediments of the SRS near an [129]I contaminated plume (Li et al., 2012a) have been unsuccessful (though significant levels of iodide oxidation were observed in enrichment cultures obtained from the SRS sediment). These results indicate that "iodide oxidizing" bacteria that are capable of enzymatically catalyzing relatively high rates of iodide oxidation are typically rare or non-existent in environments where ambient iodide concentrations are within the normal range of soils systems (0.01 − 1.0 μM), such as the Hanford subsurface.

Through ongoing research funded by the DOE Office of Science, several other mechanisms whereby bacteria can influence iodine speciation or transport in the subsurface were observed. Bacteria can accumulate iodine, through either electrostatic adsorption on the cell surface or via electrophilic substitution of cellular organic molecules. Strains isolated from seawater and marine sediments can concentrate iodide by a factor of 6×10^3, but efforts to identify iodine accumulating strains from soils or among anaerobic bacteria common in subsurface aquifers failed (Amachi et al., 2010; Amachi et al., 2005a). Iodide accumulation ability was tested among 136 bacterial strains isolated from sediments of an [129]I-contaminated, aerobic aquifer in F Area of the SRS and three strains were identified that accumulated low levels of iodide (0.2 to 2.0% of a 0.1 μM solution; 1 − 2 orders of magnitude less than that of the

marine strains that accumulate iodide) (Li et al., 2011). The results revealed that iodide accumulation was due to electrophilic substitution of cellular organic molecules. However, it is unlikely that iodide accumulation was responsible for the high fraction of organo-iodide (up to 25% of total iodine) present in F-area groundwater. Importantly, iodide accumulation was negligible at pH values >6.0.

An indirect mechanism has recently been identified whereby bacteria can influence iodine fate and transport in soil-water systems (Li et al., 2012c). Organic acids secreted by a subset of bacterial strains isolated from SRS's F Area enhanced iodide oxidation by (1) lowering the pH of the medium, and (2) reacting with H_2O_2 to form peroxy carboxylic acids, which are extremely strong oxidizing agents. Results demonstrated that iodide oxidation was enhanced up to three fold in the presence of environmentally relevant concentrations of organic acids (5 – 100 μM). Microniches surrounding bacterial biofilms are often more acidic than the surrounding bulk phase due to respiratory activity and organic acid secretion and could act as "hotspots" for iodide oxidation in the subsurface. It is a distinct possibility that organic acid production coupled with the production of oxygen radicals, including H_2O_2, could lead to iodide oxidation near anoxic-oxic interfaces in the Hanford subsurface, particularly at the interface between Ringold and Hanford sediments. Depending on the availability of organic carbon, the immediate product of iodide oxidation, I_2, will spontaneously transform through a series of reactive intermediates to iodate (low available organic carbon) or the reactive intermediates will covalently attach to organic moieties, particularly aromatics, forming organo-iodine.

4.8 Summary and Relevance of Microbial Processes Influencing [129]I Behavior

Hanford Site:
- Microbial activity is an important factor in iodine biogeochemical cycling, particularly in enhancing iodine binding to high-molecular-weight organic matter, which is expected to sorb strongly to sediments.
- The role of enzymatically catalyzed iodide oxidation by "iodide oxidizing bacteria" and cellular iodide accumulation on iodine speciation and transport in the Hanford subsurface is unknown.
- Indirect iodide oxidation mechanisms facilitated by bacteria, such as the production of organic acids and reactive oxygen species, likely influence iodine speciation and transport in the Hanford subsurface and this activity would be expected to be pronounced at interfaces between the Hanford and Ringold formations where products of anaerobic bacterial metabolism (i.e., organic acids, H_2, CH_4) could support aerobic activity and indirect iodide oxidation.

General:
- Microorganisms can catalyze I oxidation, reduction, accumulation, volatilization, and incorporation into organic matter.
- Iodide oxidation, albeit at very slow rates, can be supported by a variety of terrestrial bacteria. This is important because it may explain in part why the thermodynamically favored iodide is not the only phase present in Hanford groundwater (iodide may oxidize to iodate).

5.0 Technical Challenges and Review of Radioiodine Treatment Strategies

Among the key technical challenges associated with remediating the Hanford Site's Central Plateau's ^{129}I plumes are that the plumes are very large, ~50 km^2. The leading edges of the plumes are several kilometers long, greatly limiting the practical implementation of a deep, permeable reactive barrier or a pump-and-treat treatment strategy. Another important challenge is that the plumes' ^{129}I concentrations, while being above the DWS of 1 pCi L^{-1} (4 x 10^{-11} M), are extremely dilute. As stated in Section 1.1, 90% of the groundwater samples analyzed in this area are ≤ 3.5 pCi L^{-1} (≤ 1 x 10^{-10} M). Furthermore, natural stable iodine, ^{127}I, also exists in the plume in much greater concentrations, in the order of 10^{-8} M. In order for most strong sorbents (or getters), such as those based on anion exchange, irreversible complexation, and precipitation, to work effectively to lower the ^{129}I concentrations, would also have to lower the natural iodine concentrations, ^{127}I, about two orders of magnitude. Upon lowering the ^{127}I concentrations, the Hanford sediment would release more ^{127}I as the subsurface system adjusts to the altered adsorption/desorption and solubility equilibrium. Consequently, the large size of the ^{129}I plumes, the exceptionally low target concentration, and the presence of high concentrations of a stable isotope, greatly limit practical remediation options in the Central Plateau of the Hanford Site.

An in-depth evaluation of potential ^{129}I treatment technologies was conducted as part of the Remedial Investigation/Feasibility Study for the 200-UP-1 OU (DOE, 2012b). It was concluded that there are no current treatment technologies that can achieve the federal ^{129}I DWS for the 200-UP-1 Operable Unit located within the Central Plateau. Instead of suggesting a remediation treatment, the document concludes that hydraulic containment should be performed using injection wells placed at the leading edge of the plume. DOE continues to evaluate potential treatment options. Related reviews of potential ^{129}I groundwater treatment strategies have been presented for the SRS ^{129}I plume (Denham, 2002; Denham et al., 2009) and for engineered barriers for high-level nuclear waste disposal facilities (see references in Krumhansl et al., 2006; Viani, 1999).

Research on immobilizing radioiodine has predominantly been focused on the development of new materials, such as Self-Assembled Monolayers on Mesoporous Silica (SAMMS) (Mattigod et al., 2003), silver impregnated nanoparticles (Kaplan et al., 2000a), and positively charged minerals, including delafossites, spinels, and hydrotalcite (Krumhansl et al., 2006). Extraordinarily high removal efficiencies have been achieved using these synthesized materials. In most cases, their immobilizing longevity, sorption kinetics, and ion specificity has typically not been measured. Also important, is that a practical sorbent must be able to immobilize not only I$^-$, but perhaps more importantly, IO$_3^-$ and organo-iodine, which have recently been shown to be present in Hanford groundwater (Table 5). For example, copper-delafossites (CuAlO$_2$) and spinels (CuMn$_2$O$_4$) were more effective for removing I$^-$ than IO$_3^-$, whereas hydrotalcites consistently sorbed much more IO$_3^-$ than I$^-$ (Krumhansl et al., 2006).

Appreciably less expensive natural materials have also been evaluated for their effectiveness as ^{129}I getters, but they tend to have weaker sorption efficiencies (see references in Kaplan et al. 2000; Krumhansl et al., 2006). These minerals tend to rely upon iodine precipitation with soft metals (e.g., argentite, AgS; cinnabar, HgS; chalcocite, Cu$_2$S; chalcopyrite, CuFeS$_2$; galena, PbS; and stibnite, Sb$_2$S$_3$) or the substitution of iodine into the structure of phosphates (e.g., apatite; Ca$_5$(PO$_4$)$_3$(OH, F, Cl)).

Additionally, a silver chloride amendment for in situ treatment of ^{129}I contamination is being currently being developed and field tested at the Savannah River National Laboratory (SRNL). Injection of silver chloride (AgCl) particles to immobilize ^{129}I has been successfully tested at bench (Denham et al., 2010c) and field scales (Denham et al., 2010a; Denham et al., 2010b). AgCl reacts with iodide to form insoluble

silver iodide ($logK_{sp}$ = -16.1). In addition, AgCl has a low solubility, is stable in subsurface environments, and is unlikely to become occluded by microbial growth. Iodide is one of the few constituents in groundwater that reacts with AgCl and at natural iodine ([127]I) concentrations, on the order of 2 - 4 µg L^{-1}, interference with the sequestration of [129]I is minimal.

5.1 <u>Summary and Relevance of Radioiodine Treatment Strategies</u>

Hanford Site:
- An in-depth evaluation of potential [129]I treatment technologies was conducted as part of the Remedial Investigation/Feasibility Study for the 200-UP-1 OU (DOE, 2012b). It concluded that for the 200-UP-1 Operable Unit within 200 West Area there are no current treatment technologies that can achieve the federal DWS. DOE will continue to evaluate potential treatment options. Instead hydraulic containment will be performed using injection wells placed at the leading edge of the plume.
- Practical remediation options for the [129]I plumes in the Central Plateau are greatly limited because of the large size of the [129]I plumes, the exceptionally low target concentration (DWS), and the existence of much greater concentrations of naturally occurring [127]I compared to the targeted DWS concentration of [129]I.

General:
- A field demonstration of AgCl particle technology to create a permeable reactive barrier is presently underway at the SRS's F-Area. After one year, the [129]I concentrations downstream of the barrier remained 50% reduced. Not all monitoring wells demonstrated [129]I concentration reduction; this was attributed to flow heterogeneity through the permeable barrier.

6.0 Technical Knowledge Gaps

Three critical knowledge gaps were identified that would significantly enhance our capability to successfully select, implement, and provide technical defensibility in support of a treatment technology decision for the Hanford Site.

1. Iodine groundwater and sediment speciation: It is essential that any treatment technology effort be based on site-specific iodine speciation measurements because the various species are expected to have different chemical properties and therefore different transport rates. Furthermore, iodine species will influence the selection of many chemistry-based treatment technologies, such as the use of sequestering agents and coprecipitation processes. In these measurements/studies, it is important to work at ambient or near ambient conditions when possible. Several researchers have demonstrated the influence of iodine concentration on iodine sorption values and speciation.

2. Develop a conceptual biogeochemical model that identifies and quantifies controlling biogeochemical processes by iterating between site-specific experimental results and model refinement for use in a predictive reactive transport model (discussed below). The lab and field testing would evaluate the role of multiple aqueous and sorbed iodine species on transport and long-term sorption properties. There is also a related need to quantify and understand the extent that subsurface organic matter influences ^{129}I uptake. Much of the organic matter was placed in the subsurface during the Missoula Floods, some 14,000 years ago. As such, ^{129}I-bound sediment organic matter may be expected to remain bound in the subsurface for a significant duration. Finally, there is recent evidence of sediment microbial processes that promote iodide oxidation, a process that would decrease ^{129}I mobility. There is also recent data demonstrating the presence of microbes in the subsurface environment, especially in the Ringold formation, that may influence iodine speciation. Improved quantification of iodine redox processes and improved quantification of the role of microbes in promoting the formation of organo-iodine species will help predict iodine speciation (and therefore transport) in the subsurface environment.

3. Develop a mass flux-based conceptual biogeochemical transport model that integrates controlling biogeochemical and hydrogeologic processes. The predictive model would permit understanding and quantifying the mass flux of iodine to support remediation assessments and decisions. The model structure would likely have to account for the influence of subsurface silt lens where elevated natural organic matter and microbial activity may exist. Identifying and including coupled hydrological and biogeochemical processes are especially needed to improve long-term predictive capabilities. Such a model would provide a more accurate representation of ^{129}I transport and greater defensibility for remediation decisions.

Together the information gained from addressing these knowledge gaps will not alter the observation that ^{129}I is only slightly less mobile than tritium in the Hanford subsurface, but it will likely permit demonstration that the entire ^{129}I pool in the source term is not moving at the same rate and some may be bound extremely strongly to the sediment, thereby "smearing" the modeled ^{129}I peak and reducing maximum calculated risk.

7.0 References

1. Alvarado-Quiroz, N. G., Kotzer, T. G., Milton, G. M., Clark, I. D., and Bottomley, D. (2002). Partitioning of ^{127}I and ^{129}I in an unconfined glaciofluvial aquifer on the Canadian Shield. *Radiochimica Acta* **90**, 469-478.

2. Amachi, S. (2008). Microbial contribution to global iodine cycling: Volatilization, accumulation, reduction, oxidation, and sorption of iodine. *Microbes and Environments* **23**, 269-276.

3. Amachi, S., Kamagata, Y., Kanagawa, T., and Muramatsu, Y. (2001). Bacteria mediate methylation of iodine in marine and terrestrial environments. *Applied and Environmental Microbiology* **67**, 2718-2722.

4. Amachi, S., Kasahara, M., Fujii, T., Shinoyama, H., Hanada, S., Kamagata, Y., Ban-nai, T., and Muramatsu, Y. (2004). Radiotracer experiments on biological volatilization of organic iodine from coastal seawaters *Geomicrobiology Journal* **21**, 481-488.

5. Amachi, S., Kasahara, M., Hanada, S., Kamagata, Y., Shinoyama, H., Fujii, T., and Muramatsu, Y. (2003). Microbial participation in iodine volatilization from soils. *Environmental Science & Technology* **37**, 3885-3890.

6. Amachi, S., Kimura, K., Muramatsu, Y., Shinoyama, H., and Fujii, T. (2007a). Hydrogen peroxide-dependent uptake of iodine by marine *Flavobactefiaceae* bacterium strain C-21. *Applied and Environmental Microbiology* **73**, 7536-7541.

7. Amachi, S., Kimura, K., Muramatsu, Y., Shinoyama, H., and Fujii, T. (2007b). Hydrogen Peroxide-Dependent Uptake of Iodine by Marine Flavobacteriaceae Bacterium Strain C-21. *Appied Environmental Microbiol.* **73**, 7536-7541.

8. Amachi, S., Minami, K., Miyasaka, I., and Fukunaga, S. (2010). Ability of anaerobic microorganisms to associate with iodine: ^{125}I tracer experiments using laboratory strains and enriched microbial communities from subsurface formation water. *Chemosphere* **79**, 349-354.

9. Amachi, S., Mishima, Y., Shinoyama, H., Muramatsu, Y., and Fujii, T. (2005a). Active transport and accumulation of iodide by newly isolated marine bacteria. *Applied and Environmental Microbiology* **71**, 741-745.

10. Amachi, S., Muramatsu, Y., Akiyama, Y., Miyazaki, K., Yoshiki, S., Hanada, S., Kamagata, Y., Ban-nai, T., Shinoyama, H., and Fujii, T. (2005b). Isolation of iodide-oxidizing bacteria from iodide-rich natural gas brines and seawaters. *Microbial Ecology* **49**, 547-557.

11. Amachi, S., Muramatsu, Y., Shinoyama, H., and Fujii, T. (2005c). Application of autoradiography and a radiotracer method for the isolation of iodine-accumulating bacteria. *Journal of Radioanalytical and Nuclear Chemistry* **266**, 229-234.

12. Ar Gall, E., F., K., and Kloareg, B. (2004). A survey of iodine content in *Laminaria digitata*. *Botanica Marina* **47**, 30-37.

13. Arakawa, Y., Furukawa, H., Suda, W., and Amachi, S. (2011). Growth stimulation of iodide-oxidizing α-*Proteobacteria* in iodide-rich environments. *Microbial Ecology* **83**, 522-531.

14. Ashworth, D. J., and Shaw, G. (2006). Effects of moisture content and redox potential on *in situ* Kd values for radioiodine in soil. *Science of the Total Environment* **359**, 244-254.

15. Ashworth, D. J., Shaw, G., Butler, A. P., and Ciciani, L. (2003). Soil transport and plant uptake of radio-iodine from near-surface groundwater. *Journal of Environmental Radioactivity* **70**, 99-114.

16. Assemi, S., and Erten, H. N. (1994). Sorption of radioiodine on organic rich soil, clay minerals, and alumina. *Journal of Radioanalytical and Nuclear Chemistry* **178**, 193-204.

17. Baker, J. M., Sturges, W. T., Sugier, J., Sunnenberg, G., Lovett, A. A., Nightingale, P. D., and Penkett, S. A. (2001). Emissions of CH_3Br, organochlorines, and organoiodines from temperate macroalgae. *Chemosphere Global Change Science* **3**, 93-106.

18. Behrens, H. (1982). New insights into the chemical behavior of radioiodine in aquatic environments *In* "Environmental Migration of Long-Lived Radionuclides" (IAEA, ed.), International Atomic Energy Agency, Vienna.

19. Bird, G. A., and Schwartz, W. (1997). Distribution coefficients, K_ds, for iodide in Canadian Shield lake sediments under oxic and anoxic conditions. *Journal of Environmental Radioactivity* **35**, 261-279.

20. Bjornstad, B. N., Homer, J. A., vermeal, V. R., Lanigan, D. C., and Thorne, P. D. (2009). "Borehold completion and conceptual hydrogeologic model for the IFRC Well Field, 300 Area, Hanford Site," Rep. No. PNNL-18340, Pacific Northwest National Laboratory, Richland, WA.

21. Bors, J., Gorny, A., and Dultz, D. (1994). Some factors affecting the interactions of organophilic clay minerals with radioiodine. *Radiochimica Acta* **66/67**, 309-313.

22. Bors, J., Martens, R., and Kuhn, W. (1988). Studies on the Role of Natural and Anthropogenic Organic Substances in the Mobility of Radioiodine in Soils. *Radiochimica Acta* **44/45**, 201-206.

23. Brauer, F., and Strebin, R. J. (1982). "Environmental migration of long-lived radionuclides," Rep. No. IAEA-SM-257, International Atomic Energy Agency, Vienna.

24. Chance, R., Malin, G., Jickells, T., and Baker, A. R. (2007). Reduction of iodate to iodide by cold water diatom cultures *Marine Chemistry* **105**, 169-180.

25. Councell, T. B., Landa, E. R., and Lovley, D. R. (1997). Microbial reduction of iodate. *Water Air and Soil Pollution* **100**, 99-106.

26. Couture, R. A. a. S. (1983). M.G Sorption of anions of iodine by iron oxides and kaolinite. *Nuclear Chemical Waste Management* **4**, 301-306.

27. Davis, S., Kopecky, K. J., and Hamilton, T. E. (2007). "Hanford Thyroid Disease Study Final Report," Rep. No. CDC 200-89-0716, Fred Hutchinson Cancer Research Center, Seattle, WA.

28. Denham, M., Nichols, R., Whiteside, M., Bickmore, C., Millings, M., Blount, G., and Thibault, J. (2010a). In situ remediation of [129]I in a multiple contaminant plume. *In* "American Geophysical Union, Fall Meeting 2010", San Francisco, CA. .

29. Denham, M., and Vangelas, K. M. (2008). Biogeochemical gradients as a framework for understanding waste-site evolution. *Remediation* **19**, 5-17.

30. Denham, M. E. (2002). "Potential in situ remediation of [129]I and ^{99}Tc in groundwater associated with the F-area Seepage Basins," Rep. No. WSRC-TR-2002-00571, Westinghouse Savannah River Co., Aiken, SC.

31. Denham, M. E., Kaplan, D. I., and Yeager, C. M. (2009). "Groundwater radioiodine: prevalence, biogeochemistry, and potential remedial approaches." Savannah River National Laboratory, Aiken, SC.

32. Denham, M. E., Millings, M., and Noonkester, J. (2010b). "Post-Injection assessment of the silver chloride field demonstration for treatment of I-129 in groundwater at the F-area Seepage Basins. ," Rep. No. SRNL-STI-2010-00179, Savannah River National Laboratory, Aiken, SC.

33. Denham, M. E., Nichols, R., Whiteside, M., and ., M. M. (2010c). "Laboratory tests of an injectable solid silver chloride amendment for treatment of I-129 in groundwater," Rep. No. SRNL-STI-2010-00179, Savannah River National Laboratory, Aiken, SC.

34. Devivier, K., Devol-Brown, I., and Savoye, S. (2004). Study of iodide sorption to the argillite of Tournemire in alkaline media. *Applied Clay Science* **26**, 171-179.

35. DOE (2002). "Yucca Mountain site suitability evaluation " Rep. No. DOE/RW-0549, U.S. Department of Energy – Office of Civilian Radioactive Waste Management.

36. DOE (2003). "Preliminary Performance Assessment for Waste Management Area C at the Hanford Site," Rep. No. DOE/ORP-2003-11, Department of Energy, Richland Operations Office, Richland, WA.

37. DOE (2010). "Hanford Site groundwater monitoring and performance report for 2009. Volumes 1 & 2," Rep. No. DOE/RL-2010-11, Revision 1, U.S. Department of Energy, Richland Operations Office, Richland, WA.

38. DOE (2012a). "Proposed plan for remediation of the 200-UP-1 groundwater operable unit," Rep. No. DOE/RL-2010-05, Rev. 0, Deaprtment of Energy, Richland Operations Office, Richland, WA.

39. DOE (2012b). "Remedial Investigation/Feasibility Study for the 200-UP-1 Groundwater Operable Unit," Rep. No. DOE/RL-2009-122, U.S. Department of Energy, Richland Operations Office, Richland, WA.

40. Edwards, R. R. (1962). Iodine-129: Its occurrence in nature and its utility as a tracer. *Science* **137**.

41. Farrenkopf, A. M., Dollhopf, M. E., Chadhain, S. N., Luther, G. W., and Nealson, K. H. (1997). Reduction of iodate in seawater during Arabian Sea shipboard incubations and in laboratory cultures of the marine bacterium *Shewanella putrefaciens* strain MR-4. *Marine Chemistry* **57**, 347-354.

42. Fuge, R., and Johnson, C. C. (1986). The geochemistry of iodine – a review. *Environmental Geochemistry and Health* **8**, 31-54.

43. Fuge, R., Selinus, O., Alloway, B., Centeno, J., Finkelman, R., Lindh, U., and Smedley, P. (2005). Soils and iodine deficiency. *In* "Essentials of Medical Geology" (O. Selinus, ed.), pp. 417-433. Elsevier Academic Press, Amsterdam.

44. Fuhrmann, M., Bajt, S., and Schoonen, M. A. (1998). A Sorption of iodine on minerals investigated by x-ray absorption near edge structure (XANES) and ^{125}I tracer sorption experiments. *Applied Geochemistry* **13**, 127-141.

45. Fukui, M., Fujikawa, Y., and Satta, N. (1996). Factors affecting interaction of radioiodide and iodate species with soil. *Journal of Environmental Radioactivity* **31**, 199-216.

46. Fuse, H., Inoue, H., Murakami, K., Takimura, O., and Yamaoka, Y. (2003). Production of free and organic iodine by *Roseovarius spp. Fems Microbiology Letters* **229**, 189-194.

47. Gee, G. W., and Campbell, A. C. (1980). "Monitoring and physical characterization of unsaturated zone transport – Laboratory analysis," Rep. No. PNL-3304, Pacific Northwest Laboratory, Richland, WA.

48. Gilfedder, B. S., Petri, M., and Biester, H. (2008). Iodine speciation and cycling in limnic systems: observations from a humic rich headwater lake (Mummelsee). *Biogeoscience Discussions* **5**, 25-64.

49. Glaus, M. A., Mueller, W., and Van Loon, L. R. (2008). Diffusion of iodide and iodate through Opalinus Clay: Monitoring of the redox state using an anion chromatographic technique. *Applied Geochemistry* **23**, 3612-3619.

50. Gozlan, R. S. (1968). Isolation of iodine-producing bacteria from aquaria. *Antonie van Leeuwenhoek* **34**, 226.

51. Gozlan, R. S., and Margalith, P. (1973). Iodide oxidation by a marine bacterium. *Journal of Applied Microbiology* **36**, 407-417.

52. Gozlan, R. S., and Margalith, P. (1974). Iodide oxidation by Pseudomonas iodooxidans. *Journal of Applied Microbiology* **37**, 493-499.

53. Guiraud-Vitaux, F., Elbast, M., Colas-Linhart, N (2008). Thyroid cancer after Chernobyl: Is Iodine-131 the only culprit? Impact on clinical practice. *Bulletin du Cancer* **95**, 191-195.

54. Hall, F. (2005). "Concentrations of Selected Trace Metals, Common Ions, Nutrients and Radiological Analytes in Ground Water for Selected Sites, Eastern Snake River Plain Aquifer, South of Idaho National Laboratory, Idaho," Rep. No. OP-06-03, Idaho National Laboratory, Idaho Falls, ID.

55. Hiergesell, R. A., Phifer, M. A., Cook, J. R., Young, K. E., Birk, M. B., and Dean, W. B. (2008). "Inventory of residual radioactive material at the projected Savannah River Site end state," Rep. No. SRNL-STI-2008-00380. Savannah River National Laboratory, Aiken, SC.

56. Hou, X., Hansen, V., Aldahan, A., Possnert, G., Lind, O. C., and Lujaniene, G. (2009a). A review on speciation of iodine-129 in the environmental and biological samples. *Analytica Chimica Acta* **632**, 181-196.

57. Hou, X., and X., Y. (1998). Study on the concentration and seasonal variation of inorganic elements in 35 species of marine algae. *The Science of the Total Environment* **222**, 141-156.

58. Hou, X. L., Fogh, C. L., Kucera, J., Andersson, K. G., Dahlgaard, H., and Nielsen, S. P. (2003). Iodine-129 and Caesium-137 in Chernobyl contaminated soil and their chemical fractionation. *The Science of the Total Environment* **308**, 97-109.

59. Hou, X. L., Hansen, V., Aldahan, A., Possnert, G., Lind, O. C., and Lujaniene, G. (2009b). A review on speciation of iodine-129 in the environmental and biological samples. *Analytica Chimica Acta* **632**, 181-196.

60. Hu, Q., J. E. Moran, V. Blackwood (2009). Geochemical Cycling of Iodine Species in Soils. *In* "Comprehensive Handbook of Iodine" (G. N. B. V. R. Preedy, and R. Watson, ed.), pp. 93-107. Oxford Academic Press, Oxford.

61. Hu, Q. H., Rose, T. P., Zavarin, M., Smith, D. K., Moran, J. E., and Zhao, P. H. (2008). Assessing field-scale migration of radionuclides at the Nevada Test Site: mobile species. *Journal of Environmental Radioactivity* **99**, 1617-1630.

62. IAEA (2006). "Chernobyl Legacy: Health, Environmental and Socio-economic Impacts, and Recommendations to the Governments of Belarus, the Russian Federation and Ukraine. The Chernobyl Forum: 2003-2005. (Second revised version)." International Atomic Energy Agency, Vienna, Austria.

63. Kantelo, M. V., Bauer, L.R., Marter, W.L, Murphy, C.E., Jr., Zeigler, C.C (1990). "Radioiodine in the Savannah River Site Environment," Westinghouse Savannah River Company, Aiken, SC.

64. Kaplan, D. I. (2003). Influence of surface charge of an Fe-oxide and an organic matter dominated soil on iodide and pertechnetate sorption. *Radiochimica Acta* **91**, 173-178.

65. Kaplan, D. I. (2011). "Estimated Neptunium Sediment Sorption Values as a Function of pH and Measured Barium and Radium Kd Values," Rep. No. SRNL-STI-2011-00011, Savannah River National Laboratory, Aiken, SC.

66. Kaplan, D. I., Mattigod, S., Parker, K. E., and Iversen., G. (2000a). " I-129 Test and Research to Support Disposal Decisions," Rep. No. WSRC-TR-2000-00283, Rev. 0, Westinghouse Savannah River Company, Aiken, SC.

67. Kaplan, D. I., Mattigod, S. V., Parker, K., and Iversen, G. (2000b). "I-129 Test and Research to Support Disposal Decisions," Rep. No. WSRC-TR-2000-00283, Savannah River National Laboratory, Aiken, SC.

68. Kaplan, D. I., Parker, K. E., and Orr, R. D. (1998b). " Effects of High-pH and High-Ionic-Strength Groundwater on Iodide, Pertechnetate, and Selenate Sorption to Hanford Sediments: Final Report for Subtask 3a," PNNL-11964. Pacific Northwest National Laboratory, Richland, WA.

69. Kaplan, D. I., R. J. Serne, A. T. Owen, J. A. Conca, T. W. Wietsma, and T. L. Gervais (1996). "Radionuclide Adsorption Distribution Coefficients Measured in Hanford Sediments for the Low-Level Waste Performance Assessment Project," Pacific Northwest National Laboratory, Richland, WA.

70. Kaplan, D. I., Roberts, K. A., Schwehr, K. A., Lilley, M. S., Brinkmeyer, R., Denham, M. E., Diprete, D., Li, H. P., Powell, B. A., Xu, C., Yeager, C. M., Zhang, S. J., and Santschi, P. H. (2011). Evaluation of a radioiodine plume increasing in concentration at the Savannah River Site. *Environmental Science & Technology* **45**, 489-495.

71. Kincaid, C. T., Eslinger, P. W., Aaberg, R. L., Miley, T. B., Nelson, I. C., Strenge, D. L., Evans, J. C. (2006). "Inventory data package for Hanford Assessments," Pacific Northwest National Laboratory, Richland, WA.

72. Kodama, S., Takahashi, Y, Okumura, K. and Uruga, T (2006). Speciation of iodine in solid environmental samples by iodine K-edge XANES: Application to soils and ferromanganese oxides. *Science of the Total Environment* **363**, 275-284.

73. Kolb, C. E. (2002). Atmospheric chemistry: Iodine's air of importance. *Nature* **417**, 597-598.

74. Krumhansl, J. L., Pless, J. D., Chwirka, B., and Holt, D. C. (2006). "Yucca Mountain Project Getter Program Results (Year 1): I-129 and other Anions of Concern," Rep. No. SAND2006-3869, Sandia National Laboratory, Albuquerque, NM.

75. Kupper, F. C., Carpenter, L. J., McFiggans, G. B., Palmer, C. J., Waite, T. J., Boneberg, E.-M., Woitsch, S., Weiller, M., Abela, R., Grolimund, D., Potin, P., Butler, A., Luther, G. W., Kroneck, P. M. H., Meyer-Klaucke, W., and Feiters, M. C. (2008). Iodide accumulation provides kelp with an inorganic antioxidant impacting atmospheric chemistry. *Proceedings of the National Academy of Sciences* **105**, 6954-6958.

76. Küpper, F. C., Schweigert, N., Ar Gall, E., Legendre, J. M., Vilter, H., and Kloareg, B. (1998a). Iodine uptake in Laminariales involves extracellular, haloperoxidase-mediated oxidation of iodide. *Planta* **207**, 163-171.

77. Küpper, F. C., Schweigert, N., Gall, E. A., Legendre, J. M., Vilter, H., and Kloareg, B. (1998b). Iodine uptake in *Laminariales* involves extracellular, haloperoxidase-mediated oxidation of iodide. *Planta* **207**, 163-171.

78. Lauterbach, A., and Ober, G. (1996). Iodine and iodine compounds. *In* "Encyclopedia of Chemical Technology, Vol. 14" (Kirk-Othmer, ed.), pp. 709-737. John Wiley & Sons, Boston.

79. Lee-Taylor, J., and Redeker, K.R (2005). Reevaluation of global emissions from rice paddies of methyl iodide and other species. *Geophysical Research Letters* **15**, 1-5.

80. Li, H.-P., Brinkmeyer, R., Jones, W. L., Zhang, S., Xu, C., Ho, Y.-F., Schwehr, K. A., Kaplan, D. I., Santschi, P. H., and Yeager, C. M. (2012a). Iodide Oxidizing Activity of Bacteria from

Subsurface Sediments of the Savannah River Site. *In* "Interdisciplinary Studies on Environmental Chemistry Vol. 6 - Environmental Pollution and Ecotoxicology" (K. M. M. Kawaguchi, H. Sato, T. Yokokawa, T. Itai, T. M. Nguyen, J. Ono, S. Tanabe, ed.), Vol. 6, pp. 89-97, Terra Scientific Publishing Company, Tokyo.

81. Li, H.-P., Brinkmeyer, R., Jones, W. L., Zhang, S., Xu, C., Schwehr, K. A., Santschi, P. H., Kaplan, D. I., and Yeager, C. M. (2011). Iodide accumulation by aerobic bacteria isolated from subsurface sediments of a I-129-contaminated aquifer at the Savannah River Site, South Carolina. *Applied and Environmental Microbiology* **77**, 2153-2160.

82. Li, H.-P., Yeager, C. M., Brinkmeyer, R., Zhang, S., Ho, Y.-F., Xu, C., Jones, W. L., Schwehr, K. A., Otosaka, S., Roberts, K. A., Kaplan, D. I., and Santschi, P. H. (2012b). Bacterial production of organic acids enhances H_2O_2-dependent iodide oxidation. *Environmental Science & Technology* **46**, 4837-4844.

83. Li, H.-P., Yeager, C. M., Brinkmeyer, R., Zhang, S., Ho, Y.-F., Xu, C., Jones, W. L., Schwehr, K. A., Otosaka, S., Roberts, K. A., Kaplan, D. I., and Santschi, P. H. (2012c). Organic acids produced by subsurface bacteria enhance iodide oxidation in the presence of hydrogen peroxide. *Environmental Science & Technology* **46**, 4837-4844.

84. Lieser, K. H. a. S., Th   (1989). Chemistry of radioactive iodine in the hydrosphere and in the geosphere. *Radiochim Acta* **46**, 49-55.

85. Lin, X., Kennedy, D., Fredrickson, J., Bjornstad, B., and Konopka, A. (2012a). Vertical stratification of subsurface microbial community composition across geological formations at the Hanford Site. *Environmental Microbiology* **14**, 414-425.

86. Lin, X., Kennedy, D., Peacock, A., McKinley, J., Resch, C. T., and Fredrickson, J. (2012b). Distribution of microbial biomass and potential for anaerobic respiration in Hanford Site 300 Area subsurface sediment. *Applied and Environmental Microbiology* **78**, 759-767.

87. Lin, X., McKinley, J., Resch, C. T., Kaluzny, R., Lauber, C. L., Fredrickson, J., Knight, R., Konopka, A. (2012). Spatial and temporal dynamics of the microbial community in the Hanford unconfined aquifer. *ISME J* **6**, 1665-1676.

88. MacKenzie, D. (2011). Fukushima radioactive fallout nears Chernobyl levels. *New Scientist* **17**, 14.

89. Maillant, S., Sheppard, M. I., Echevarria, G., Denys, S., Villemin, G., Tekely, P., Leclerc-Cessac, E., and Morel, J. L. (2007). Aged anthropogenic iodine in a boreal peat bog. *Applied Geochemistry* **22**, 873-887.

90. Malinauskas, A. P., and Bell, J. T. (1987). The chemistry of fission-product iodine under nuclear reactor accident conditions. *Nuclear Safety* **28**, 505-514.

91. Mattigod, S. V., Fryxell, G. E., Serne, R. J., and Parker, K. E. (2003). Evaluation of novel getters fro adosrption of radioiodine from groundwater and waste glass leachates. *Radiochim Acta* **91**, 539-545.

92. McKay, A. (1984). The Making of the Atomic Age. *In* "Oxford University Press", New York.

93. Moore, R. M., and Groszko, W. (1988). Methyl iodide distribution in the ocean and fluxes to the atmosphere. *Journal of Geophysical Research* **11**, 163-171.

94. Muramatsu, Y., and Yoshida, S (1995). Volatilization of methyl iodide from the soil-plant system. *Atmospheric Environment* **29**, 21-25.

95. Muramatsu, Y., Uchida, S., Sriyotha, P., and Sriyotha, K. (1990b). Some consideration on the sorption and desorption phenomena of iodide and iodate on soil. *Water Air and Soil Pollution* **49**, 125-138.

96. Muramatsu, Y., Uchida, S. and Ohmomo, Y (1990a). Determination of I-129 and I-127 in soil and tracer experiments on the adsorption of iodine on soil. *Journal of Radioanalytical and Nuclear Chemistry* **138**, 377-384.

97. Muramatsu, Y., Uchida, S., Sumiya, M., Ohmomo, Y., and Obata, H (1989). Tracer experiments on transfer of radio-iodine in the soil — rice plant system. *Water, Air, & Soil Pollution* **45**, 157-171.

98. Muramatsu, Y., Yoshida, S., Fehn, U., Amachi, S., and Ohmomo, Y. (2004). Studies with natural and anthropogenic iodine isotopes: iodine distribution and cycling in the global environment. *Journal of Environmental Radioactivity* **74**, 221-232.

99. Muramatsu, Y., Yoshida, S., Uchida, S., and Hasebe, A. (1996). Iodine desorption from rice paddy soil. *Water Air and Soil Pollution* **86**, 359-371.

100. Musić, S., Šipalo-Žuljerić, J., and Wolf, R.H.H (1979). Radiochemical study of the sorption of iodide and iodate on aluminum(III) hydroxide precipitate. *Isotopenpraxis* **15**, 93-96.

101. NCRP (1983). "(National Council Radiation Protection Iodine-129: Evaluation of releases from nuclear power generation." National Council on Radiation Protection and Measurements, , Bethesda, MD.

102. Neal, C., and Truesdale, V. W. (1976). Sorption of iodate and iodide by riverine sediments - Its implications to dilution gauging and hydrochemistry of iodine. *Journal of Hydrology* **31**, 281-291.

103. Nirel, P. M. V., and F. M. M. Morel (1990). Pitfalls of Sequential Extractions. *Water Research* **24**, 1055-1056.

104. NRC (1995). "A Review of Two Hanford Environmental Dose Reconstruction Project (HEDR) Dosimetry Reports: Columbia River Pathway and Atmospheric Pathway." National Research Council, National Academy Press, Washington, DC.

105. Otosaka, S., Schwehr, K. A., Kaplan, D. I., Roberts, D. A., Zhang, S., Xu, C., Li, H. P., Ho, Y. F., Brinkmeyer, R., Yeager, C. M., and Santschi, P. H. (2011). Transformation and Transport Processes of ^{127}I and ^{129}I Species in an Acidic Groundwater Plume at the Savannah River Site. *The Science of the Total Environment* **409**, 3857-3865.

106. Paquette, J., Wren, D. J., Ford, B. L., and Toth, L. M. (1986). Iodine chemistry. *In* "The Three Mile Island Accident – Diagnosis and Prognosis, ACS Symposium Series", Vol. 293. American Chemical Society, Washington, DC.

107. Parker, L., and Holt, M. (2007). "CRS Report for Congress. Nuclear Power: Outlook for New U.S. Reactors," Congress Research Service, Washington, DC.

108. Parsly, L. F. (1970). "Design Considerations of Reactor Containment Spray Systems – Part IV. Calculation of Iodine-Water Partition Coefficients," Oak Ridge National Laboratory, Oak Ridge, TN.

109. Raisbeck, G. M., and F. Yiou (1999). 129I in the oceans: Origins and applications. *The Science of the Total Environment* **237/238**, 31-41.

110. Rao, U., and Fehn, U. (1999). Sources and Reservoirs of anthropogenic iodine-129 in western New York. *Geochimica et Cosmochimica Acta* **63**, 1927-1938.

111. Richter, U., and Wallace, D. W. R. (2004). Production of methyl iodide in the tropical Atlantic Ocean. *Geophysical Research Letters* **31**, 1-4.

112. Rosenfeld, L. (2000). Discovery and early uses of iodine. *Journal of Chemical Education* **77**, 984-987.

113. Saini, H., Attieh, J., and Hanson, A   (1995). Biosynthesis of halomethanes and methanethiol by higher plants via a novel methyl-transferase system. *Plant Cell and Environment* **18**, 1027-1033.

114. Santschi, P. H., and Schwehr, K. A. (2004). I-129/I-127 as a new environmental tracer or geochronometer for biogeochemical or hydrodynamic processes in the hydrosphere and geosphere: The central role of organo-iodine. *The Science of the Total Environment*, 257-271.

115. Savoye, S., Michelot, J.L., and Wittebroodt, C (2006). Evaluation of the reversibility of iodide uptake by argillaceous rocks by the radial diffusion method. *Radiochimica Acta* **94**, 699-704.

116. Saxena, D., Aouad, J., Attieh, J., and Saini, H. (1998). Biochemical characterization of chloromethane emission from the wood-rotting fungus *Phellinus pomaceus*. *Applied and Environmental Microbiology* **64**, 2831-2835.

117. Scheckel, K. G., Impellitteri, C. A., Ryan, J. A., and McEvoy, T. (2003). Assessment of a sequential extraction procedure for perturbed lead-contaminated samples with and without phosphorus amendments *Enirononmental Science & Technology* **37**, 1892-1898.

118. Schmitz, K., and Aumann, D. C. (1995). A study on the association of two iodine isotopes of natural I-127 and of the fission product I-129, with soil components using a sequential extraction procedure. *Journal of Radioanalytical Nuclear Chemistry* **198**, 229–236.

119. Schwehr, K. A., and Santschi, P. H. (2003). Sensitive determination of iodine species, including organo-iodine, for freshwater and seawater samples using high performance liquid chromatography and spectrophotometric detection. *Analytica Chimica Acta* **482**, 59-71.

120. Schwehr, K. A., Santschi, P. H., and Elmore, D. (2005a). The dissolved organic iodine species of the isotopic ratio of (129)I/(127)I: A novel tool for tracing terrestrial organic carbon in the estuarine surface waters of Galveston Bay, Texas. *Limnology and Oceanography-Methods* **3**, 326-337.

121. Schwehr, K. A., Santschi, P. H., Moran, J. E., and Elmore, D. (2005b). Near-conservative behavior of ^{129}I in the Orange County aquifer system, California. *Applied Geochemistry* **20**, 1461-1472.

122. Serne, R. J., Conca, J. L., LeGore, V. L., Cantrell, K. J., Lindenmeier, C. W., Campbell, J. A., Amonette, J. E., and Wood, M. I. (1993). "Solid-Waste Leach Characteristics and Contaminant-Sediment Interactions. Volume 1: Batch Leach and Adsorption Tests and Sediment Characterization," PNL-8889. Pacific Northwest National Laboratory, Richland, WA.

123. Sheppard, M. I., and Thibault, D. H. (1991). A 4-Year mobility study of selected trace-elements and heavy-metals. *Journal of Environmental Quality* **20**, 101-114.

124. Sheppard, M. I. a. H., J.L (1995). Iodine and microbial interactions in an organic soil. *Radioactivity* **29**, 91-109.

125. Shimamoto, Y. S., and Takahashi, Y. (2008). Superiority of K-edge XANES over L-III-edge XANES in the speciation of iodine in natural soils. *Analytical Sciences* **24**, 405-409.

126. Skulski, L. (2000). Organic iodine (I, III, and V) chemistry: 10 years of development at the Medical University of Warsaw, Poland. *Molecules* **5**, 1331-1371.

127. Smythe-Wright, D., Boswell, S. M., Breithaupt, P., Davidson, R. D., Dimmer, C. H., and Diaz, L. B. (2006). Methyl iodide production in the ocean: Implications for climate change. *Global Biogeochemical Cycles* **20**, BG 3003.

128. Stang, P. J. (2003). Polyvalent iodine organic chemistry. *Journal of Organic Chemistry* **68**, 2997-3008.

129. Stegen, J. C., Lin, X., Konopka, A., McKinley, J., and Fredrickson, J. (2012). Stochastic and deterministic assembly processes in subsurface microbial communities. *ISME J* **(in press)**.

130. Stephenson, M., Motycka, M (1995). Volatility of ^{125}I in fresh water. *Journal of Environmental Radioactivity* **28**, 295-311.

131. Stutz, J., Hebestreit, K., Alicke, B., and Platt, U. (1999). Chemistry of halogen oxides in the troposphere: Comparison of model calculations with recent field data. *Journal of Atmospheric Chemistry* **34**, 65-85.

132. Taghipour, F., and Evans, G. J. (2002). Modeling of iodine radiation chemistry in the presence of organic compounds. *Radiation Physics and Chemistry* **64**, 203-213.

133. Tessier, A., and Campbell, P. G. C. (1988). Partitioning of Trace Metals in Sediments. *In* "Metal Speciation: Theory, Analysis and Application" (J. R. Kramer and H. E. Allen, eds.), pp. 183-217. Lewis Publishers, Inc., Chelsea, MI.

134. Ticknor, K. V., and Cho, Y. H. (1990). Interaction of iodide and iodate with granitic fracture-filling minerals. *Journal of Radioanalytical and Nuclear Chemistry* **140**, 75-90.

135. Tsunogai, S., and Sase, T. (1969). Formation of iodide-iodine in the ocean. *Deep-Sea Research* **16**, 489-496.

136. Um, W., Serne, R. J., and Krupka, K. M. (2004). Linearity and reversibility of iodide adsorption on sediments from Hanford, Washington under water saturated conditions. *Water Research* **38**, 2009-2016.

137. Viani, B. (1999). "Assessing Materials ("Getters") to Immobilize or Retard the Transport of Technetium Through Engineered Barrier System at the Potential Yucca Mountain Nuclear Waste Repository," Lawrence Livermore National Laboratory, Livermore, CA.

138. von Hippel, F. N. (2011). The radiological and psychological consequences of the Fukushima Daiishi accidnet. *Bulletin of the Atomic Scientists* **67**, 27-36.

139. Waite, T. J., and Truesdale, V. W. (2003). Iodate reduction by *Isochrysis galbana* is relatively insensitive to de-activation of nitrate reductase activity--are phytoplankton really responsible for iodate reduction in seawater. *Marine Chemistry* **81**, 137-148.

140. Warner, J. A., Casey, W. H., and Dahlgren, R. A. (2000). Interaction kinetics of I^{-2}(aq) with substituted phenols and humic substances. *Environmental Science & Technology* **34**, 3180-3185.

141. Whitehead, D. C. (1973). The sorption of iodide by soils as influenced by equilibrium conditions and soil properties. *Journal of the Science of Food and Agriculture* **24**, 547-556.

142. Whitehead, D. C. (1974). The sorption of iodide by soil components. *Journal of the Science of Food and Agriculture* **25**, 73-79.

143. WNA (2009). Nuclear Power in India Vol. http://.world-nuclear.org/info/inf53.html World Nuclear Association, Washington, DC.

144. Wong, G., Piumsomboon, A., and Dunstan, W. (2002). The transformation of iodate to iodide in marine phytoplankton cultures. *Marine Ecology Progress Series* **237**, 27-39.

145. Wong, G. T. F., and Cheng, X. H. (1998). Dissolved organic iodine in marine waters: Determination, occurrence and analytical implications. *Marine Chemistry* **59**, 271-281.

146. Wren, J. C., and Ball, J. M. (2001). LIRIC 3.2: An updated model for iodine behavior in the presence of organic impurities. *Radiation Physics and Chemistry* **60**, 577-596.

147. WSDH (2000). Hanford Environmental Dose Reconstruction (HEDR) Project.

148. WSRC (2008). " E-Area Low-Level Waste Facility DOE 435.1 Performance Assessment," Rep. No. WSRC-STI-2007-00306, REVISION 0, Washington Savannah River Company, Aiken, SC.

149. Wuosmaa, A., and Hager, L (1990). Methyl chloride transferase: A carbocation route for biosynthesis of halometabolites. *Science of the Total Environment* **249**, 160-162.

150. WVDP (2007). "West Valley Demonstration Project Annual Site Environmental Report -- Calendar Year 2007." West Valley Environmental Services LLC and URS, West Valley Demonstration Project.

151. Xu, C., Miller, E. J., Zhang, S. J., Li, H. P., Ho, Y. F., Schwehr, K. A., Kaplan, D. I., Otosaka, S., Roberts, K. A., Brinkmeyer, R., Yeager, C. M., and Santschi, P. H. (2011a). Sequestration and remobilization of radioiodine (I-129) by soil organic matter and possible consequences of the remedial action at Savannah River Site. *Environmental Science & Technology* **45**, 9975-9983.

152. Xu, C., Zhang, S., Ho, Y.-F., Miller, E. J., Roberts, K. A., Li, H.-P., Schwehr, K. A., Otosaka, S., Kaplan, D. I., Brinkmeyer, R., Yeager, C. M., and Santschi, P. H. (2011b). Is soil natural organic matter a sink or source for mobile radioiodine (^{129}I) at the Savannah River Site? *Geochimica et Cosmochimica Acta* **75**, 5716-5735.

153. Xu, C., Zhong, J. Y., Hatcher, P. G., Zhang, S., Li, H. P., Ho, Y., Schwehr, K. A., Kaplan, D. I., Roberts, K. A., Brinkmeyer, R., Yeager, C. M., and Santschi, P. H. (2012). Molecular environment of stable iodine and radioiodine (^{129}I) in natural organic matter: Evidence inferred from NMR and binding experiments at environmentally relevant concentrations. *Geochimica et Cosmochimica Acta* **(submitted)**.

154. Yamada, H., Takeda, C., Mizushima, A., Yoshino, K., and Yonebayashi (2005). K Effect of oxidizing power of roots on iodine uptake by rice plants. *Soil Science and Plant Nutrition* **51**, 141-145.

155. Yamaguchi, N., Nakano, M., Takamatsu, R., and Tanida, H. (2010). Inorganic iodine incorporation into soil organic matter: Evidence from iodine K-edge absorption near-edge structure. *Journal of Environmental Radioactivity* **101**, 451-457.

156. Yamaguchi, N., Nakano, M., Tanida, H., and Fujiwara, H. (2006). Redox reaction of iodine in paddy soil investigated by field observation and I K-edge XANES spectroscopy. *Journal of Environmental Radioactivity* **86**, 212-226.

157. Yoshida, S., Muramatsu, Y., and Uchida, S. (1992). Studies on the sorption of I$^-$ (iodide) and IO$_3^-$ (iodate) onto Andosols. *Water Air and Soil Pollution* **63**, 321-329.

158. Yoshida, S., Muramatsu, Y., and Uchida, S. (1998). Soil-solution distribution coefficients, K$_d$s, of I$^-$ and IO$_3^-$ for 68 Japanese soils. *Radiochimica Acta* **82**, 293-297.

159. Yu, Z., Warner, J. A., Dahlgren, R. A., and Casey, W. H. (1996). Reactivity of iodine in volcanic soils and noncrystalline soil constituents. *Geochimica Cosmochimica Acta* **60**, 4945- 4956.

160. Yuita, K. (1992). Dynamics of iodine, bromine, and chlorine in soil II. Chemical forms of iodine in soil solutions *Soil Science and Plant Nutrition* **38**, 281-287.

161. Yuita, K., and Kihou, N. (2005). Behavior of iodine in a forest plot, an upland field, and a paddy field in the upland area of Tsukuba, Japan: Vertical distribution of iodine in soil horizons and layers to a depth of 50 m. *Soil Science and Plant Nutrition* **51**, 455-467.

162. Zaichick, V. Y., and Choporov, Y. Y. (1996). Determination of the natural level of human intra-thyroid iodine by instrumental neutron activation analysis. *Journal of Radioanalytical Nuclear Chemistry* **207**, 153-161.

163. Zhang, S., Schwehr, K. A., Ho, Y.-F., Xu, C., Roberts, K., Kaplan, D. I., Brinkmeyer, R., Yeager, C. M., and Santschi, P. H. (2010). Determination of ^{127}I and ^{129}I speciation in environmental waters using a novel gas chromatography-mass spectrometry method. *Environmental Science & Technology* **44**, 9042-9048.

164. Zhdankin, V. V., and Stang, P. J. (2002). Recent developments in the chemistry of polyvalent iodine compounds. *Chemical Reviews* **102**, 2523-2584.

165. Zhou, D.-M., and Chen, H.-M. (2000). Cr(VI) adsorption on four typical soil colloids: Equilibrium and kinetics. *Journal of Environmental Sciences* **12**, 325-329.

8.0 Appendix A: A Case Study of Radioiodine Biogeochemistry at the Savannah River Site

An active research program related to SRS groundwater [129]I (plume described in Section 2.4) has been underway for the last four years. This program has made some discoveries about groundwater [129]I geochemistry that may provide some insight to the Hanford Site [129]I plume problem. However, due to the vastly different biogeochemical conditions between SRS and the Hanford Site, differences may be expected. Perhaps the foremost difference is the pH of the two systems, [129]I concentrations, and the expected OC and sediment organic matter (SOM) in the two systems. The importance of these parameters was discussed in Section 3.0.

One reason that little is known about radioiodine at DOE sites is because very little research funding has been directed at [129]I biogeochemistry, certainly not to the extent that has been directed at Cs, Pu, Tc, and U biogeochemistry. Among the reasons for this is that the analytical chemistry at the extremely low concentrations necessary to study ambient [129]I (10^{-7} to 10^{-11} M) have not been readily available and the analytical procedures were (and still are) arduous (Denham et al., 2009). By combining recently developed analytical techniques applicable to stable iodine, [127]I, and radioiodine, [129]I (Schwehr et al., 2005a; Zhang et al., 2010) with existing spectroscopic techniques for natural organic matter (NOM), it has been possible to address applied and basic geochemistry problems. To our knowledge, the [129]I speciation geochemistry studies at SRS represent the first in the DOE complex, thereby making mechanistic interpretations possible. As explained in Sections 3.3.1, iodine speciation can greatly alter the extent that iodine partitions to the solid phase.

Groundwater [129]I and stable [127]I speciation was measured in 14 well samples in SRS F-Area, comprising gradients in redox potential (360 to 654 mV), OC concentrations (5 to 60 μmol L^{-1}; portion was anthropogenic organic contaminants), and pH (pH 3.2 to 6.8) in the F-Area plume (Otosaka et al., 2011). The [129]I in all the groundwater samples were comprised of more than one species, typically all three of the analyzed species: iodide, iodate, and organo-iodine. As would be the case at the Hanford Site, these results were not consistent with thermodynamic calculations that predict almost 100% iodide. Within these 14 groundwater samples, iodate accounted for 7% to 100% of the [129]I and 19% to 84% of the [127]I. Organo-iodine accounted for 0% to 70% of the [129]I and 8% to 75% (the source term) of the [127]I. Total groundwater [129]I concentration was 232 pCi L^{-1} immediately downstream of the seepage basins (source terms) and decreased with distance from the seepage basin. [127]I concentration decreased similarly to that of [129]I. Near the seepage basins, the majority (55 – 86%) of iodine existed as iodide for both [129]I and [127]I. Then as the iodide move down gradient, some of it transformed into iodate and organo-iodine. Significant amounts of organo-iodine (30 – 82% of the total iodine) were also observed at upstream wells, including those outside the mixing waste plume (as stable [127]I). Concentrations of groundwater iodide decreased at a faster rate than organo-iodine along the transect from the seepage basin. It was concluded that removal of iodine from the groundwater through the formation of high molecular weight organo-iodine species was complicated by the release of other more mobile organo-iodine groundwater species.

The F-Area plume flows 0.7 km before it is intercepted by a riparian zone. As part of the SRS groundwater monitoring program, it has been documented that [129]I concentrates in the riparian zone to extraordinarily high levels, >1000 pCi L^{-1} (unfiltered samples) (Kaplan et al., 2011). Studies were undertaken to identify the process/mechanism responsible for the [129]I concentrated, and in particular to quantify and understand the role of NOM and microbes (Xu et al., 2011a; Xu et al., 2011b; Xu et al., 2012). The F-Area riparian zone is much more vegetative than would be found at the Hanford Site. But an organically rich interface exists where aquifers surface with the biosphere, as would be expected for Hanford aquifers along the Columbia River. Laboratory studies using SRS solid and groundwater materials showed that between 72 and 77% of the newly introduced iodide or iodate were irreversibly sequestered into the organic-rich riparian sediment, while the rest was transformed by the sediment into colloidal and truly dissolved organo-iodine (Xu et al., 2011a). Laboratory iodination experiments indicated that iodine likely covalently bond to aromatic structures of the SOM. Under very acidic conditions, abiotic iodination of SOM was predominant, whereas under less acidic conditions (pH >5),

microbial enzymatically assisted iodination of SOM was predominant. It was concluded that although trace amounts of SOM-bound ^{129}I could enhance transport, in generally the SOM in the riparian zone immobilized the ^{129}I.

Iodide added to a subsurface sediment with very low OM concentrations (0.01 wt% OC) did not convert to iodate, but trace levels were converted to organo-iodine (Xu et al., 2011a). When iodate was added to the same sediment, it immediately transformed to about 18% iodide and 3% organo-iodine. The iodide (ad)sorption K_d value in the organic poor sediment was 0.71 mL g^{-1} and was 23.89 mL g^{-1} for desorption tests. Similarly for iodate, the (ad)sorption K_d value was 5.16 mL g^{-1} and for a desorption test, the K_d values was 9.75 mL g^{-1}. By the end of these K_d measurements, portions of the iodide or iodate spikes had transformed to other species, thereby these test do not represent "species-specific" K_d values, but were mixed-species K_d values.

In column studies, Zhang et al. (2011) investigated the sorption, transport, and interconversion of iodine species in and SRS groundwater and subsurface sediment with high OM concentrations, 10.8 mg kg^{-1}. At ambient concentrations (10^{-8} to 10^{-7} M), iodide and iodate were significantly retarded (K_d values as high as 49 mL g^{-1}), whereas at concentrations three orders of magnitude greater, iodide traveled along with the water without retardation. Appreciable amounts of iodide were retained in soils during transport due to iodination of OC. When iodate was introduced in SRS subsurface sediment columns, it quickly reduced into iodide and proceeded to migrate through the sediment in a similar manner as the iodide spike system.

Studies were undertaken to understand the role of microbes in iodine accumulation and species transformation (Li et al., 2012a; Li et al., 2011; Li et al., 2012b; Li et al., 2012c). Measurements of iodide uptake by aerobic bacteria isolates from F-Area sediments indicated that only 3 out of 136 strains could accumulate iodide and they only accumulated between 0.2 to 2.0% of the ambient aqueous iodide (Li et al., 2011). Iodide accumulation in these isolates was inversely related to pH levels, significantly increasing at pH levels <6. Spent liquid medium from 27 of 84 bacterial cultures enhanced iodide oxidation 2 − 10 fold in the presence of H_2O_2 (Li et al., 2012c). Organic acids secreted by the bacteria were found to enhance iodide oxidation by (1) lowering the pH of the spent medium and (2) reacting with H_2O_2 to form peroxy carboxylic acids, which are extremely strong oxidizing agents. H_2O_2-dependent iodide oxidation increased exponentially from 8.4 to 825.9 μM with decreasing pH from 9 to 4. As pH decreased (≤5.0), it increased H_2O_2 hydrolysis, thereby promoting iodide oxidation. However, at pH ≥ 6.0, spontaneous decomposition of peroxy carboxylic acids, generated from H_2O_2 and organic acids, contributes significantly to iodide oxidation. The results reveal an indirect microbial mechanism, organic acid secretion coupled to H_2O_2 production that could enhance iodide oxidation and organo-iodine formation in soils and sediments. Most recently, Li et al. (2012b), screened 84 strains for iodide oxidizing activity using a combination of triiodide (I_3^-) formation, radiography and a recently developed, sensitive iodine speciation assay revealed that 44 of these strains were capable of iodide oxidation. Together these results indicate that readily culturable, aerobic bacteria of the F-area aquifer do not accumulate significant amounts of iodide (Li et al., 2011). However, iodide oxidation, albeit at very slow rates, can be supported by a variety of terrestrial bacteria.

Iodine bonding with SOM is greatly influenced by not only the functionality of the SOM, but also the hydrophilic/hydrophobic forces in the SOM (Xu et al., 2011a; Xu et al., 2011b). Coincident variations in chemical composition, aromaticity, functional groups (e.g., aliphatic), hydrophobicity, and molecular weight indicated that: 1) iodine in different humic acids was bound to a small-size aromatic subunit (~10 kDa); 2) the large-size subunit (~90 kDa), determined the relative mobility of iodine bound to SOM, 3) iodine incorporation into the SOM is via covalent aromatic C-I bond is the key mechanism controlling iodine behavior in the SRS system. The amount of stable iodine bound to the fulvic acid fraction (519 μg ^{127}I/g-carbon) was approximately an order of magnitude greater than the concentration of stable iodine bound to humic acid fractions (62 μg ^{127}I/g-carbon).

The nature of the iodine bond to organic matter was evaluated using various proton and ^{13}C nuclear magnetic resonance (NMR) techniques (Xu et al., 2012). Quantitative structure analyses by ^{13}C direct-polarization magic-angle spinning (DPMAS) NMR and solution state ^{1}H NMR on these humic substances indicated that iodine was closely related to the aromatic regions containing esterified products of phenolic and formic acids or other aliphatic carboxylic acids, amide functionalities, quinone-like structures activated by electron-donating groups (e.g., NH_2), or hemicellulose-lignin-like complex with phenyl-glycosidic linkages. Fulvic acids contained appreciable more ^{127}I or ^{129}I than their corresponding humic acids for two sediments. However, the contrasting radioiodine contents among the two fractions of SOM (humic acids and fulvic acids) could not be solely explained by the difference in the amount of their reactive binding sites. This may be the result that the micro-molecular environment, such as the hydrophobic aliphatic periphery hindering the active aromatic cores and the hydrophilic polysaccharides favoring its accessibility towards hydrophilic iodine species, play additional key roles in the interactions between iodine and organic matter. The importance of this study is that it conducted its characterization using ambient levels of iodine, thereby not swamping the OM functional groups, yielding unrealistic iodine-organic matter bonding.

Because the geochemistry is very different between the F-Area SRS plume and 200W Hanford Site plumes, not all of these results are necessarily directly applicable. The two most important differences are that SRS subsurface sediments are extremely old and weathered and the pH is between 3.1 and 5.5. The Hanford subsurface sediments contain appreciably younger, less weathered minerals and the pH is appreciably more alkaline, pH 7 to 9.5. The SRS clay-size fraction consists primarily of kaolinite, goethite, hematite, and typically <5% of 2:1 clays (hydroxyl interlayered vermiculite). Mineralogy of Hanford clay-size fraction is far more diverse, containing carbonate, smectite, illite, chlorite, kaolinite, goethite, and hematite; the larger fractions tend to also contain feldspar, which is not typically found in SRS sediments. Based on the discussion in Section 3.3, the conditions at the SRS are likely somewhat more conducive to iodine sorption. The lower pH of the SRS sediments would be expected to promote greater iodine sorption due to: 1) the lack of carbonate ion, CO_3^{2-}, anion competition, 2) the lower pH increasing anion exchange capacity of the sediment of the large amount of pH-dependent charge minerals, 3) the relatively low negative permanent charge in the sediments. An important knowledge gap at the Hanford Site is the range of natural OC in the sediments. The SRS typically has subsurface sediment OC concentrations between 400 and 900 mg kg^{-1} (0.04 to 0.09 wt %). (Some of the experiments described above were conducted with wetland sediments that contained significantly higher OC concentrations, two orders of magnitude greater OC.

Distribution:

Savannah River National Laboratory, Aiken, SC 29808

B. T. Butcher, 773-43A/Rm. 211
M. E. Denham, 773-42A/Rm. 218
D. I. Kaplan, 773-43A/Rm. 215
J. J. Mayer, 773-42A/Rm. 242
K. A. Roberts, 773-43A/Rm. 225
M. Whiteside, 773-42A/Rm238

Texas A&M University, Ocean and Coastal Studies Building, 200 Seawolf Parkway, Galveston, TX 77553

R. Brinkmeyer
Y. F. Ho
H. P. Li
P. H. Santschi
K. A. Schwehr
C. Xu
S. Zhang

Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352

D. Wellman
M. Triplett
H. Lee
W. Um
J. Serne

U.S. Department of Energy Richland Operations Office, Richland, WA 99352

B. Charboneau
J. Morse