

# Conceptual Model of Iodine Behavior in the Subsurface at the Hanford Site

**September 2015**

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*operated by*  
BATTELLE  
*for the*  
UNITED STATES DEPARTMENT OF ENERGY  
*under Contract DE-AC05-76RL01830*

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Prepared for  
the U.S. Department of Energy  
under Contract DE-AC05-76RL01830

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## Summary

Isotopes of iodine were generated during plutonium production within the nine production reactors at the U.S. Department of Energy (DOE) Hanford Site. The short half-life  $^{131}\text{I}$  was released from the fuel into the atmosphere during the dissolution process (when the fuel was dissolved) in the Hanford Site 200 Area, is no longer present at concentrations of concern in the environment. The long half-life  $^{129}\text{I}$  generated at the Hanford Site during reactor operations was 1) Stored in single-shell and double-shell tanks, 2) Discharged to liquid disposal sites (e.g., cribs and trenches), 3) Released to the atmosphere during fuel reprocessing operations, or 4) Captured by off-gas absorbent devices (silver reactors) at chemical separations plants (PUREX, B-Plant, T-Plant, and REDOX). Releases of  $^{129}\text{I}$  to the subsurface have resulted in several large, though dilute, plumes in the groundwater. There is also  $^{129}\text{I}$  remaining in the vadose zone beneath disposal or leak locations. The fate and transport of  $^{129}\text{I}$  in the environment and potential remediation technologies are currently being studied as part of environmental remediation activities at the Hanford Site. A conceptual model describing the nature and extent of subsurface contamination, factors that control plume behavior, and factors relevant to potential remediation processes is needed to support environmental remedy decisions. Because  $^{129}\text{I}$  is an uncommon contaminant, relevant remediation experience and scientific literature are limited. Thus, the conceptual model also needs to both describe known contaminant and biogeochemical process information and to identify aspects about which additional information needed to effectively support remedy decisions.

There are three basic components of the conceptual model: Inputs, Source Flux to Groundwater, and Plume Behavior. Inputs include information about  $^{129}\text{I}$  discharges to the subsurface and other boundary conditions (e.g., recharge from precipitation) that influence  $^{129}\text{I}$  fate and transport. Information is available from several sources to define the important input parameters. The source flux to groundwater component identifies factors important to consider in defining the nature of sources to historical, current, and future groundwater plumes. This information is needed to provide a context for examining fate and transport and remediation of groundwater plumes, which are the risk driver for remediation activities. Some analyses have been completed to quantify potential source flux to the groundwater. However, additional evaluations using recently developed approaches will be needed to refine these estimates. Prediction of plume behavior associated with  $^{129}\text{I}$  fate and transport is needed for risk assessment and to support remedy decisions and remedy design and implementation. Recent information describing the relative quantity of three primary iodine chemical species present in the groundwater (iodide, iodate, and organic-iodine complexes) is pertinent to predicting plume behavior because each chemical species has different transport characteristics and may be subject to transformation reactions. The transformation reactions can change the relative quantity of chemical species, result in accumulation as a solid phase, or promote volatilization of iodine. Thus, transformation reactions are relevant to plume attenuation and for application of remediation technologies. Existing data describing iodine species transport properties and transformation reactions have been compiled. In addition, technical gaps were identified associated with the need to refine this information in support of future remedy decisions.

Because there are uncertainties in the iodine species transport parameters and transformation reactions with respect to plume behavior at the Hanford Site, alternative conceptual models were developed based on potential outcomes of ongoing research. The first two alternatives describe scenarios with different iodine chemical species controlling the overall transport behavior of  $^{129}\text{I}$  for a condition where no significant species transformation reactions are occurring. The other two alternatives describe scenarios where different types of transformation reactions are important. These alternative conceptual models provide a structure to guide development of studies that will help distinguish the alternative that best describes plume behavior as part of refining the iodine conceptual model for the Hanford Site and providing an appropriate technical basis for fate and transport analyses and remediation decisions.



## **Acknowledgments**

This document was prepared by the Deep Vadose Zone – Applied Field Research Initiative at Pacific Northwest National Laboratory. Funding for this work was provided by the U.S. Department of Energy (DOE) Richland Operations Office. The Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the DOE under Contract DE-AC05-76RL01830.





## Acronyms and Abbreviations

BBI	Best Basis Inventory\
CFB	<i>Cytophaga-Flexibacter-Bacteriodes</i>
DOC	Dissolved organic carbon
DOE	U.S. Department of Energy
DPMAS	Direct-polarization magic-angle spinning
DWS	Drinking water standard
EXAFS	Extended X-ray absorption fine structure spectra
Eh	Oxidation/reduction potential
ID	Identification (number or name)
KAPL	Knolls Atomic Power Laboratory
K <sub>d</sub>	Linear equilibrium adsorption coefficient
LMCO	Laccase-like multicopper oxidase
MCL	Maximum contaminant level
NMR	Nuclear magnetic resonance
NNDC	National Nuclear Data Center
NOM	Natural organic matter
OC	Organic carbon
OI	Organo-iodine (Organo-I)
OM	Organic matter
OU	Operable unit
pH	Negative of the base 10 logarithm of the hydrogen ion activity in solution
SAC	System Assessment Capability
SAM	S-adenosyl-L-methionine
SOM	Soil organic matter
SRS	Savannah River Site
ROD	Record of decision
TI	Total iodine
TOC	Total organic carbon
VL	(Hanford) Virtual Library
VZ	Vadose zone
WMA	Waste Management Area
XANES	X-ray absorption near-edge structure



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# 1.0 Introduction

At the U.S. Department of Energy (DOE) Hanford Site, there are large dilute iodine-129 ( $^{129}\text{I}$ ) groundwater plumes. A conceptual model describing the nature and extent of these plumes, factors that control plume behavior, and factors relevant to potential remediation processes is needed to support remedy decisions. Because  $^{129}\text{I}$  is an uncommon contaminant relevant remediation experience and scientific literature are limited. Thus, the conceptual model also needs to both describe known contaminant and biogeochemical process information and to identify aspects about which additional information needed to effectively support remedy decisions. Because there is an ongoing research program at the Hanford Site to address identified conceptual model gaps, it is anticipated that this conceptual model document will be updated periodically to represent the evolving state of knowledge for the  $^{129}\text{I}$  plumes.

## 1.1 Global Radioiodine Context

Radioiodine (i.e., radioactive isotopes of iodine) is produced primarily from neutron-induced fission of uranium and plutonium in nuclear reactors, but also is produced naturally in small quantities from spontaneous fission of natural uranium and by interaction of high-energy particles with xenon in the upper atmosphere (note that medical isotopes are not included in this document). Nuclear reactions form a variety of fission products, including 19 iodine isotopes (Kantelo et al. 1990). However, only the  $^{129}\text{I}$  isotope is of long-term concern. Worldwide, chemical separation or reprocessing of nuclear fuel has resulted in the release of radioiodine into the environment. The  $^{129}\text{I}$  isotope has also been released to the environment by nuclear weapons testing (Muramatsu et al. 2004). The Hanford Site was one of the major contributors to worldwide release of the  $^{129}\text{I}$  isotope to the environment (Table 1). Table 2 shows the radiochemical properties of  $^{129}\text{I}$  and  $^{131}\text{I}$  (an isotope of short-term concern).

Sources of  $^{129}\text{I}$  and  $^{127}\text{I}$  (stable, non-radioactive iodine) and the ways in which these species are introduced into the global iodine cycle must be considered to understand the fate of  $^{129}\text{I}$  in the environment. Stable iodine is distributed in the environment in water and in other materials (Fehn 2012; Muramatsu and Wedepohl 1998; Muramatsu et al. 2004; Whitehead 1984). Solid sources of iodine in the environment include pelagic clays, shale, limestone, igneous rocks, algae, and gas hydrates. A large amount of iodine is sequestered in geological media and would not interact with the global (surface) iodine cycle. Fluid sources of iodine include seawater, freshwater, volcanic fluids, pore waters, and oil field brines associated with drilling. Igneous rocks, such as basalts, hold the least amount of iodine, by weight, along with freshwater and seawater. Some of the primary reservoirs for iodine are marine sediments and sedimentary rocks. By weight, algae (including seaweed) contain the highest amount of iodine. Volcanic and geothermal activity can release some iodine into the surface environment as volcanic fluids and in water. Likewise, the human pursuit of various energy sources has released iodine to the surface iodine cycle in brines from oil and natural gas production and from fracking (Harkness et al. 2015). The quantity of natural  $^{129}\text{I}$  is quite small compared to the amount of natural  $^{127}\text{I}$ . Generation of  $^{129}\text{I}$  as a byproduct of the nuclear energy industry and weapons testing is the largest anthropogenic source (Table 1).

**Table 1.** Major sources of  $^{129}\text{I}$  in the environment.

Source	$^{129}\text{I}$ Mass Released (kg)
Fuel reprocessing at La Hague (France)	3800 <sup>(a)</sup>
Fuel reprocessing Sellafield (UK)	1400 <sup>(a)</sup>
Hanford Site	266 <sup>(b)</sup>
Natural hydrosphere and atmosphere	100 <sup>(c)</sup>
Atmospheric weapons testing	50 <sup>(b)</sup>
Savannah River Site	32 <sup>(d)</sup>
Nevada Test Site underground nuclear testing	10 <sup>(b)</sup>
Chernobyl	1-2 <sup>(b)</sup>
Fukushima	1.2 <sup>(e)</sup>

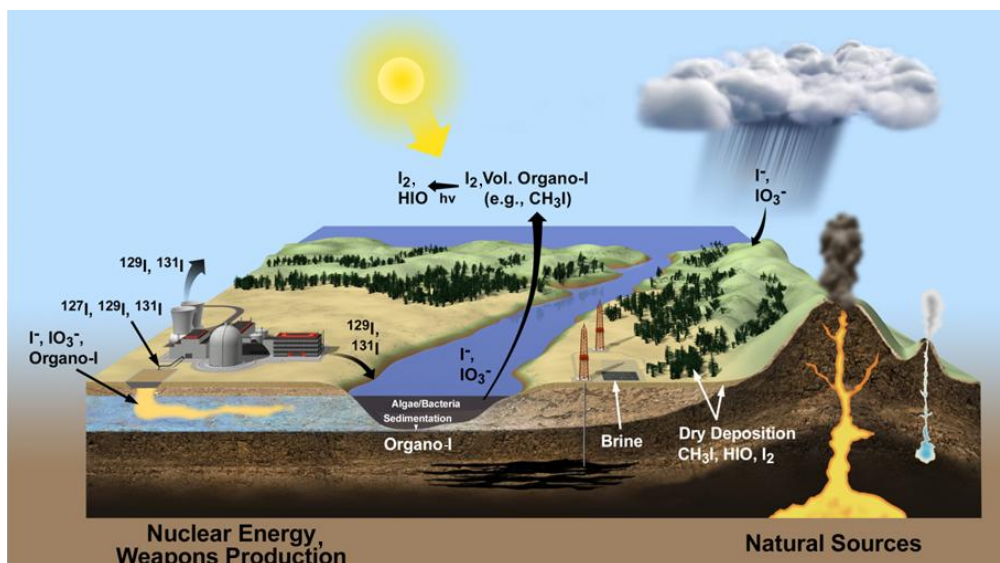
<sup>(a)</sup> Hou et al. 2009  
<sup>(b)</sup> Raisbeck and Yiou 1999  
<sup>(c)</sup> Bustad et al. 1983  
<sup>(d)</sup> Kantelo et al. 1990  
<sup>(e)</sup> Hou et al. 2013

**Table 2.** Radiochemical properties of  $^{129}\text{I}$  and  $^{131}\text{I}$ .

Property	$^{129}\text{I}$	$^{131}\text{I}$	Reference
Half-life	$1.57 \times 10^7$ y	8.0252 d	KAPL 2010
Number of Neutrons	76	78	KAPL 2010
Number of Protons	53	53	KAPL 2010
Main Radiation Emissions <sup>(a)</sup> (energies and intensities [%])	$\beta^-$ 0.15 MeV (100%) $\gamma$ 39.6 keV (7.5%)	$\beta^-$ 0.606 MeV (90%) $\gamma$ 364.5 keV (82%)	KAPL 2010; NNDC 2015
Decay Reaction	$^{129}_{53}\text{I} \rightarrow \beta^- + ^{129}_{54}\text{Xe}$	$^{131}_{53}\text{I} \rightarrow \beta^- + ^{131}_{54}\text{Xe}$	KAPL 2010

(a) X-ray, electron, and minor beta/gamma emissions are not shown.

Sources and sinks of the global iodine cycle are divided into three primary pools: marine, terrestrial, and atmospheric (Figure 1). Sources of natural iodine (mostly  $^{127}\text{I}$ ) are shown on the right of Figure 1, while anthropogenic sources (including  $^{129}\text{I}$  and  $^{131}\text{I}$ ) are shown on the left. Surface and atmospheric movement of iodine within the cycle occurs by deposition in rainfall, dry deposition (including uptake by plant leaves), volatilization, suspension of dust, suspension of marine aerosols, uptake by plant roots, decomposition of plants, runoff, irrigation, leaching, weathering, combustion of fossil fuels, nuclear fuel reprocessing, and weapons production. Iodine at the surface and in the atmosphere can also be affected by biogeochemical and solar processes that cause transformations between different iodine chemical species. Biogeochemical and physical processes relevant to subsurface fate and transport of  $^{129}\text{I}$  contamination are presented in Section 2.



**Figure 1.** Global iodine cycle, showing natural and anthropogenic sources of iodine isotopes and cycling of multiple iodine species in the environment.

## 1.2 Hanford Site Context

In 1943, construction began on the first of nine nuclear reactors at the Hanford Site to produce plutonium for the development of atomic weapons for the Manhattan Project during World War II and throughout the Cold War. Over a production period lasting from 1944 to 1987, approximately 110,000 tons of nuclear fuel was processed (Gephart 2003). During the production period, billions of gallons of liquid nuclear waste and millions of tons of solid waste were produced. Isotopes of iodine were generated during plutonium production within the nine production reactors at the Hanford Site. The short half-life  $^{131}\text{I}$  was released from the fuel into the atmosphere during the dissolution process (when the fuel was dissolved) in the Hanford Site 200 Area, is no longer present at concentrations of concern in the environment.

Much of the contamination observed in groundwater at the Hanford Site, including iodine, resulted from planned releases of process liquid wastes and wastewater to the soil via discharge to engineered structures (cribs, trenches, ditches, ponds, leach fields, or injection wells). Unplanned releases of the same or similar waste materials resulted in contaminant discharges from tanks, pipelines, or other waste storage or conveyance components to the subsurface.

The total amount of  $^{129}\text{I}$  generated at the Hanford Site during reactor operations is well known: 49.4 Ci of  $^{129}\text{I}$  was produced during reactor operations according to ORIGEN2 fuel activity estimates (Watrous et al. 2002). However, the distribution of that well-defined inventory to storage or environmental releases is very uncertain. The inventory has been distributed among the following mechanisms:

- Stored in single-shell and double-shell tanks
- Discharged to liquid disposal sites (e.g., cribs and trenches)
- Released to the atmosphere during fuel reprocessing operations
- Captured by off-gas absorbent devices (silver reactors) at chemical separations facilities (PUREX, B-Plant, T-Plant, and REDOX)

Table 3 summarizes current estimates for these mechanisms. This table does not include the  $^{129}\text{I}$  inventory that may have been disposed at the Hanford Site from receipt of offsite waste.

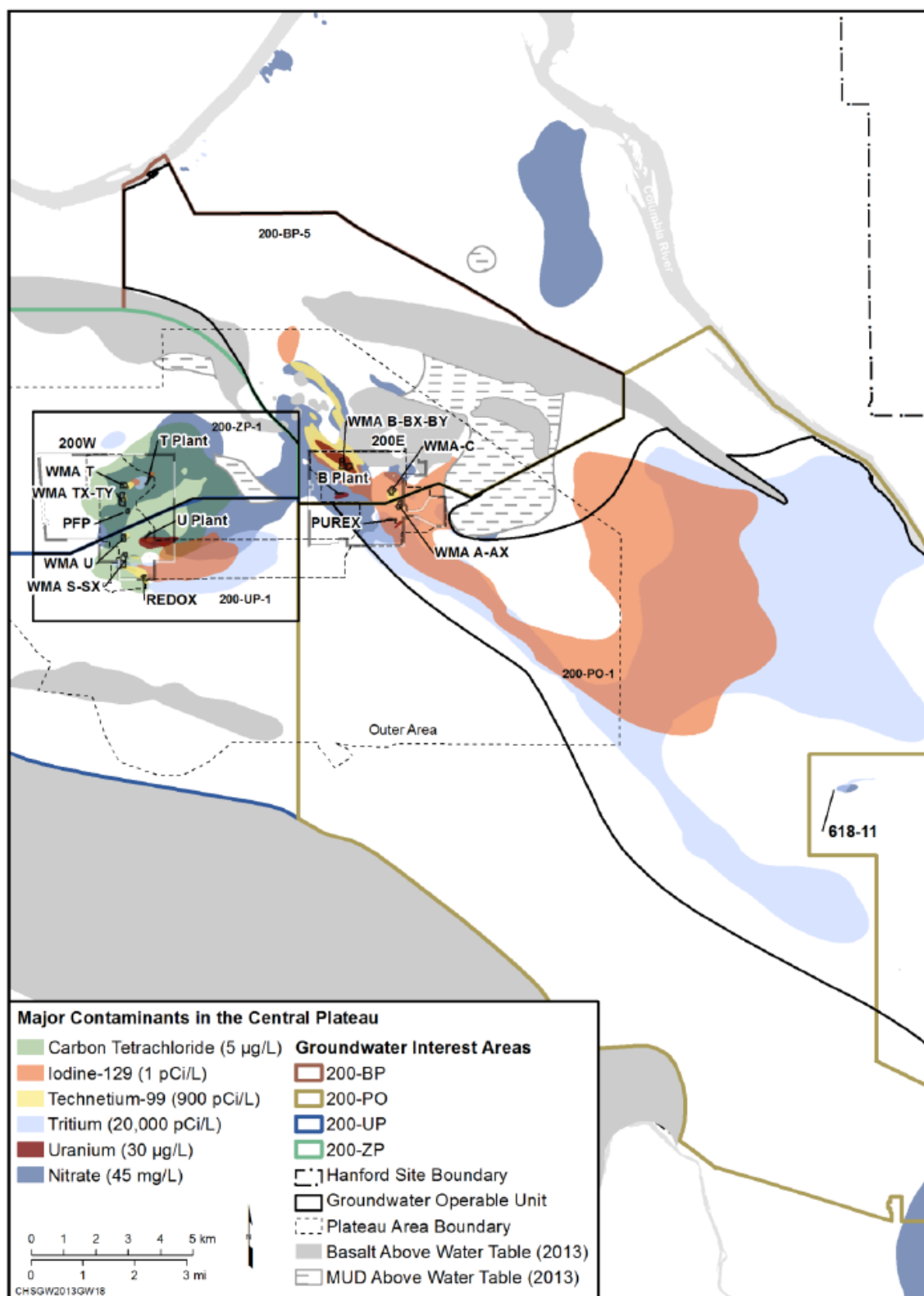
**Table 3.** Current estimates of  $^{129}\text{I}$  distribution at the Hanford Site.

$^{129}\text{I}$ Inventory Category	Estimate	Discussion and References
Total generated by production reactors	49.4 Ci	Based on calculation using the 2002 ORIGIN2 fuel activity estimate (Watrous et al. 2002). This estimate is well known and based on fuel irradiation histories.
Stored in single-shell and double-shell tanks	29.0 Ci <sup>(a)</sup>	Best Basis Inventory (BBI) obtained from the Tank Waste Information Network System (April 23, 2015) ( <a href="https://twins.labworks.org/twinsdata/default.htm">https://twins.labworks.org/twinsdata/default.htm</a> ). Significant uncertainty remains with this estimate.
Discharged to liquid disposal sites	4.7 Ci	From Hanford's Soil Inventory Model (Corbin et al. 2005). Uncertainty estimates were developed for individual waste sites that ranged from 20% to almost 400%.
Released to the atmosphere	Unknown	Estimates of magnitude of these potential releases are not available. This remains one of the main uncertainties limiting development of a true mass balance for Hanford $^{129}\text{I}$ .
Captured by off-gas absorbent devices	Unknown	Devices known as "silver reactors" were used to capture iodine at chemical separations plants (PUREX, B-Plant, T-Plant, and REDOX). The $^{129}\text{I}$ inventory captured in this manner is not known. Some of these devices remain at the canyon facilities and some are in solid waste burial grounds.

(a) The BBI underwent a significant update in 2004 (Higley et al. 2004), which reduced the tank inventory estimate from 48.2 to 31.8 Ci based on improved models of separations processes. This change removed the previous conservative assumption that essentially all of the  $^{129}\text{I}$  sent to the separations plants exited those plants in waste streams sent to tank farms. Subsequent revisions to the BBI have replaced generic estimates for specific waste streams with sample-based estimates from the tanks.

Once  $^{129}\text{I}$  and other mobile contaminants reach the aquifer, they spread, producing large-scale plumes (Figure 2). Three  $^{129}\text{I}$  plumes in groundwater originate in the Hanford Site Central Plateau (marked as the "Plateau Area Boundary" on Figure 2) cover an area greater than 50 km<sup>2</sup>. In general, the plume emanating from the 200 East Area is larger because of differences in subsurface geology. The water table beneath the 200 East Area and extending to the Columbia River is within more-permeable sediments. In the 200 West Area, the water table is primarily within the lower permeability Ringold Formation. This results in faster groundwater flow and shorter travel times in the 200 East Area than in the 200 West Area (Freshley and Graham 1988). The largest  $^{129}\text{I}$  plume extends toward the southeast from the 200 East Area. A smaller arm of the plume has moved toward the northwest between Gable Mountain and Gable Butte. The largest  $^{129}\text{I}$  plume associated with the 200 West Area is in the 200-UP-1 operable unit (OU).





**Figure 2.** <sup>129</sup>I and other contaminant plumes associated with the 200 East and 200 West Areas on the Hanford Site. Figure adapted from DOE 2014.

The  $^{129}\text{I}$  plumes in the Hanford Site Central Plateau are very large and dilute. The lengths of the leading edges of the plumes are on the scale of kilometers. The  $^{129}\text{I}$  concentrations are all less than 50 pCi/L, with most less than 10 pCi/L, though above the drinking water standard (DWS) of 1 pCi/L. Furthermore, natural stable iodine ( $^{127}\text{I}$ ) is also present in the aquifer at much greater concentrations than  $^{129}\text{I}$ . The presence of  $^{127}\text{I}$  is important because most remediation technologies are not specific for a particular iodine isotope (e.g., Kaplan et al. 2012). In addition,  $^{127}\text{I}$  and  $^{129}\text{I}$  have the same chemical behavior in the subsurface so that the presence of  $^{127}\text{I}$  will influence the biogeochemical processes for  $^{129}\text{I}$ .

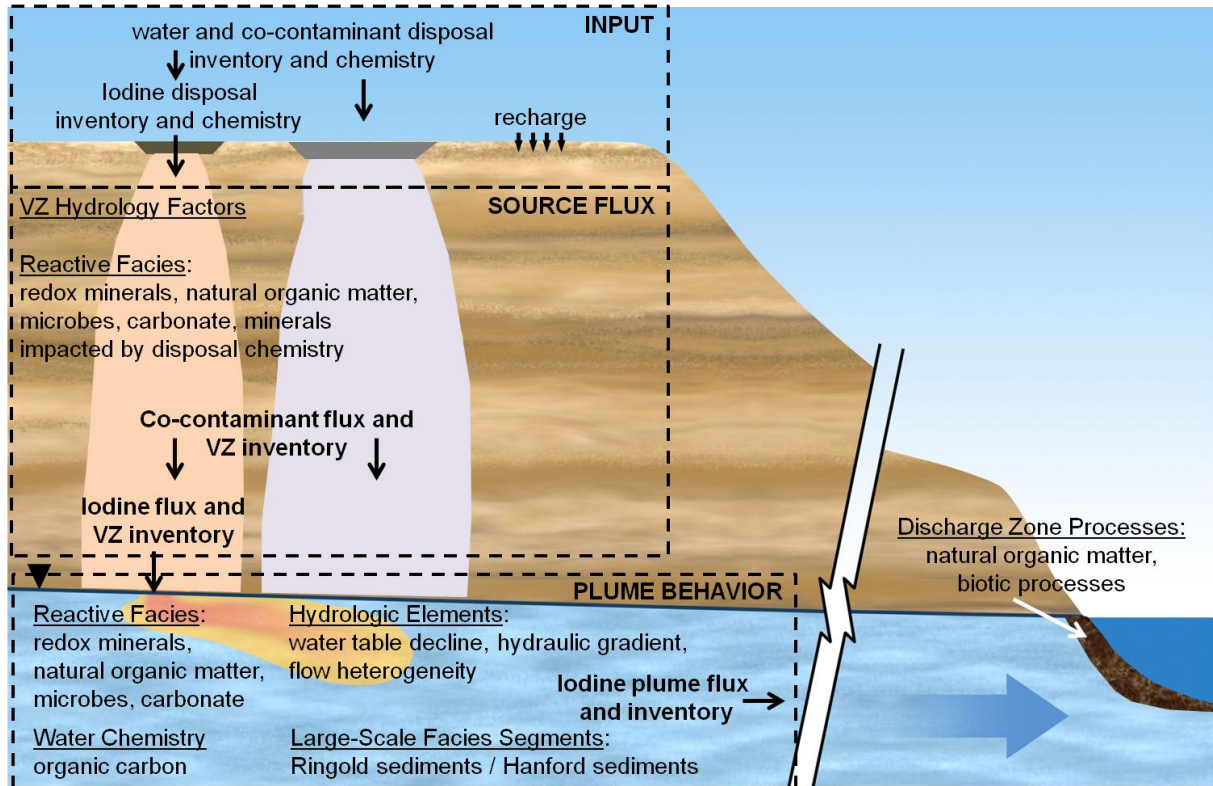
Inorganic iodine chemistry under conditions associated with most  $^{129}\text{I}$  environmental plumes suggests that the primary aqueous species that would be present are iodide ( $\text{I}^-$ ), iodine ( $\text{I}_2$ ), and iodate ( $\text{IO}_3^-$ ). Considering the ranges of pH and Eh found in groundwater,  $\text{I}^-$  should be the dominant species present in groundwater at the Hanford Site, with a small fraction of  $\text{IO}_3^-$  and an inconsequential amount of  $\text{I}_2$ . However, analysis of groundwater samples taken from numerous monitoring wells within the 200 West Area presented by Zhang et al. (2013) show that, on average, about 70% of the iodine is present as  $\text{IO}_3^-$ , about 26% is organo-iodine, and a small amount (about 4%) is  $\text{I}^-$  (see Table 4). While  $^{129}\text{I}$  was also evaluated in this study by Zhang et al., only iodate was detected when measuring radioactive  $^{129}\text{I}$  species because of limits of analytical detection. The observed iodine speciation is important input for evaluating the fate and transport of iodine in the subsurface.

**Table 4.** Chemistry and  $^{127}\text{I}$  speciation of filtered Hanford Site groundwater (Zhang et al. 2013)

Well	pH	Eh (mV)	DOC ( $\mu\text{M}$ )	Ca (mg/L)	Si (mg/L)	Iodide ( $\mu\text{g/L}$ )	Iodate ( $\mu\text{g/L}$ )	Organo I ( $\mu\text{g/L}$ )	Total I ( $\mu\text{g/L}$ )	Iodide (%)	Iodate (%)	Organo-I (%)
299-W14-11	7.7	250	50.2	59.4	7.5	0.35	59.50	15.18	75.03	0.5	79.3	20.2
299-W14-13	7.7	249	63.0	81.9	7.4	0.33	42.72	17.01	60.05	0.6	71.1	28.3
299-W14-15	7.9	220	25.5	35.4	5.6	0.43	32.63	5.66	38.72	1.1	84.3	14.6
299-W11-43	7.6	150	37.2	78.8	7.0	0.36	6.66	2.76	9.78	3.7	68.1	28.3
299-W11-88	7.8	321	15.6	22.1	15.0	0.17	7.08	2.08	9.33	1.8	75.9	22.3
699-36-70B	7.8	334	35.3	19.4	10.7	0.23	5.87	2.28	8.38	2.8	70.0	27.2
699-38-70B	7.8	125	21.5	29.7	8.9	1.38	4.18	3.68	9.24	15.0	45.2	39.8
Average	7.8	236	35.5	49.5	8.9	0.46	22.66	6.95	30.08	3.6	70.6	25.8

## 2.0 Conceptual Model

This section presents a conceptual model description, highlighting factors important to remediation technology evaluation for iodine contamination at the Hanford Site and information relevant to key elements of the conceptual model. As an overview, Figure 3 is a system-level depiction of elements affecting iodine fate and transport from waste sites in the Hanford Central Plateau. The following subsections summarize information about the three components of the conceptual model: Inputs, Source Flux to Groundwater, and Plume Behavior.

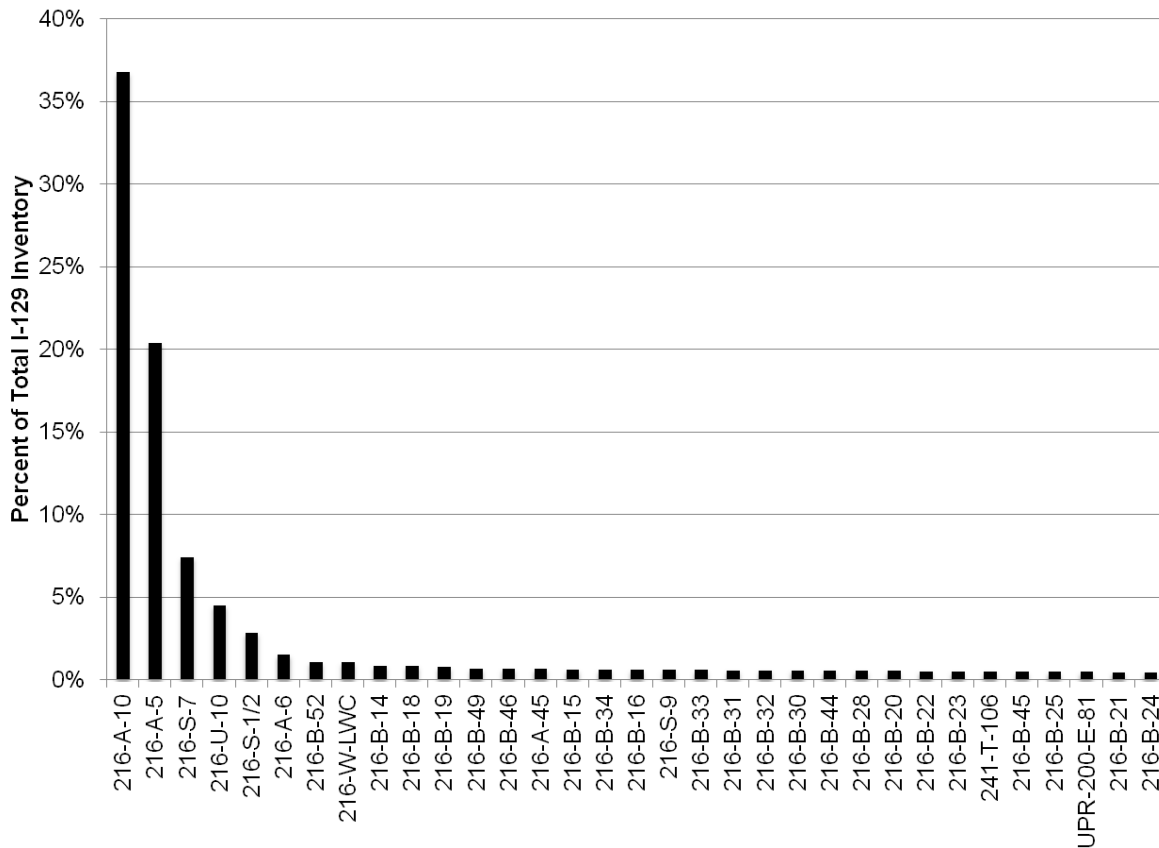


**Figure 3.** System-level depiction of elements affecting iodine fate and transport.

### 2.1 Inputs

Inputs (Figure 3) consist of waste disposal inventories, water disposal volumes, waste disposal chemistry, facility design (e.g., a specific retention trench versus a waste storage tank), and recharge. These items are discussed in turn below.

Corbin et al. (2005) indicates that a total of about 4.7 Ci of  $^{129}\text{I}$  was released to waste sites at the Hanford Site. This inventory does not include the  $^{129}\text{I}$  inventory believed to be retained in underground storage tanks. Two of these sites (216-A-10 and 216-A-5 in the 200 East Area) received 1.7 and 1.0 Ci of  $^{129}\text{I}$  (accounting for 57% of the total  $^{129}\text{I}$  disposed or otherwise released to waste sites). Four other waste sites (216-S-7, 216-U-10, and 216-S-1&2 in the 200 West Area and 216-A-6 in the 200 East Area) account for another 16% of the inventory, while 27 other sites account for another 18%. Together, these 33 sites account for 91% of the  $^{129}\text{I}$  inventory released to the subsurface. Figure 4 shows the relative percent of the overall  $^{129}\text{I}$  inventory released at each of these 33 waste sites.



**Figure 4.** Relative percentage of the total  $^{129}\text{I}$  inventory released to individual waste sites based on data from the Soil Inventory Model (Corbin et al. 2005) for sites with greater than 1% of the total (the 216-U-1/2 sites associated with part of the 200-UP-1 OU plume had less than 1% of the total).

Truex and Carroll (2013) examined predicted groundwater concentrations from the System Assessment Capability (Eslinger et al. 2006). They used a DWS factor (the maximum predicted groundwater concentration divided by the DWS) to categorize sites based on their potential impact to groundwater relative to three different timeframes: up to the year 2100, up to the year 3100, and up to the year 12,000. Table 5 lists those sites with predicted groundwater concentrations exceeding the DWS for  $^{129}\text{I}$  (i.e., a DWS factor > 1) and the relative timing of those concentrations. Sites relevant to the 200-UP-1 OU are highlighted in this table.

In addition to the inventory of  $^{129}\text{I}$  received by each facility, another important factor to consider is the volume of liquid disposal. The disposed liquid provides the primary driving force for initial distribution of contaminants in the subsurface, with large volumes generally leading to more extensive migration and in some cases, current breakthrough observed in the groundwater. Over the long term, recharge becomes a controlling factor in the flux of contaminants from the vadose zone to the groundwater.

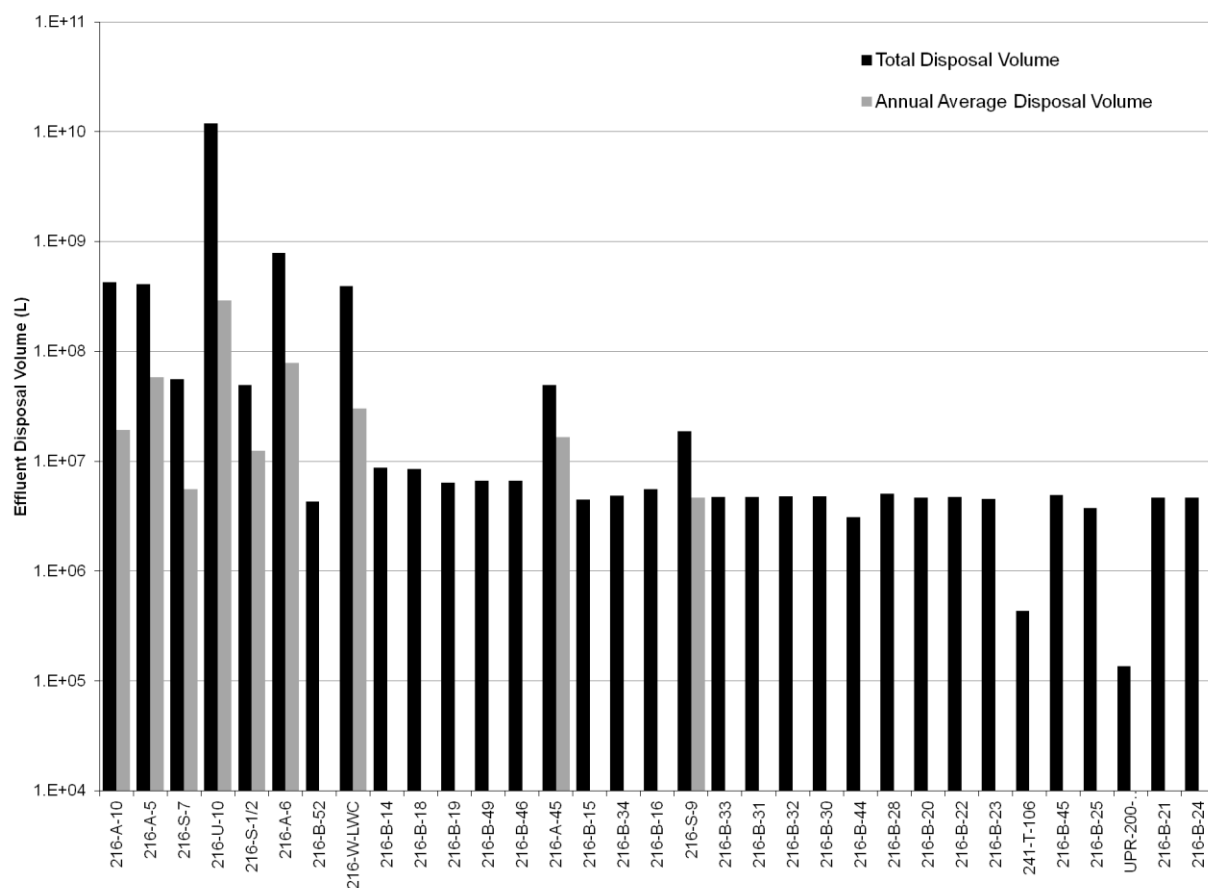
Figure 5 shows the total and annual average disposal volumes for the 33 sites with the largest  $^{129}\text{I}$  inventories (Figure 4). Many of these waste sites were either cribs (9) or trenches (13) that received process effluent for only a short amount of time (< 1 year). Figure 6 illustrates the average concentration of  $^{129}\text{I}$  received by each of the sites.

**Table 5.** Categorization of waste sites based on potential impact to groundwater for three time intervals: up to year 2100, 2100-3100, and after 3100 (adapted from Truex and Carroll 2013). Sites with predicted groundwater concentrations less than the DWS are not shown (~300 sites). Black text is for simulated results. Red text indicates values based on observed groundwater data.

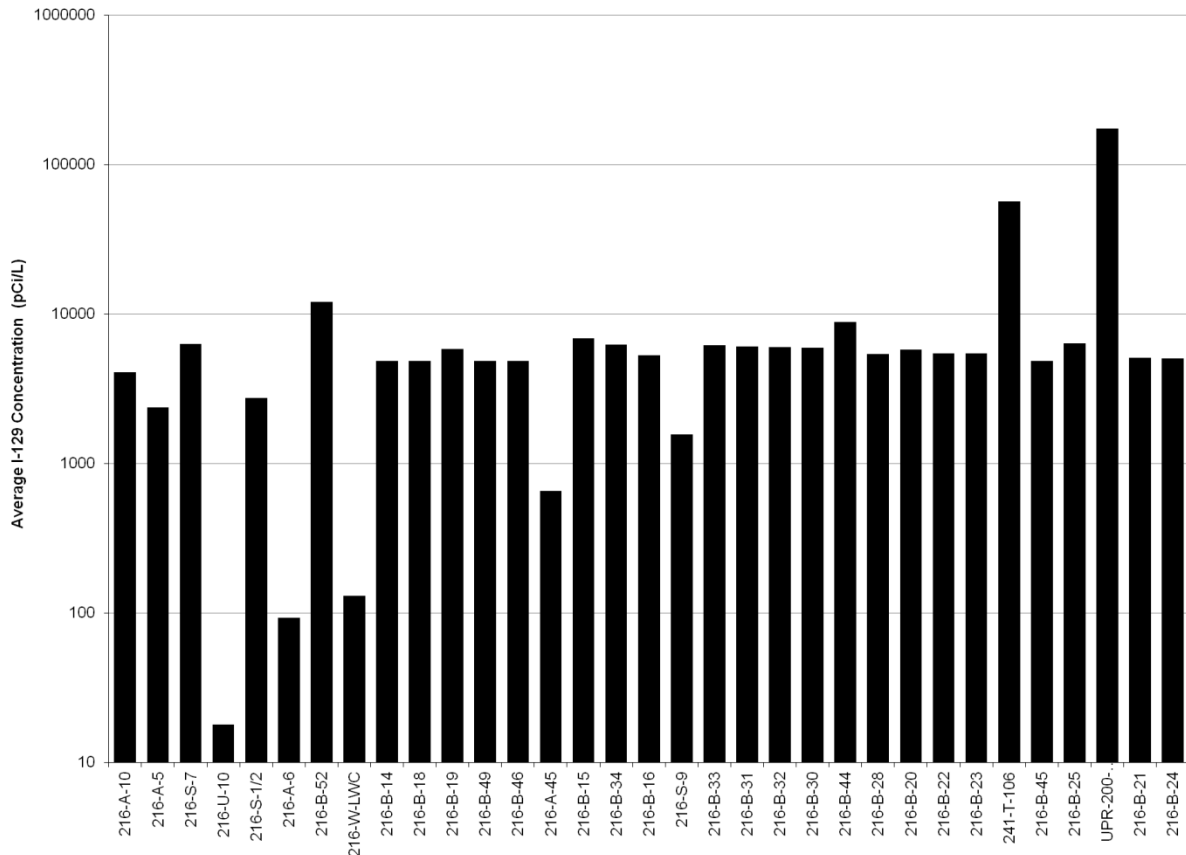
Site Name	Site ID	<sup>129</sup> I DWS Factor <sup>(a)</sup>		
		Up to Year 2100	2100-3100	After 3100 <sup>(b)</sup>
REDOX Cribs	216-S-1&2	9 (37)	14	14
	216-S-7	82 (37)	30	11
	216-S-9	—	—	3
S/SX Tank Farms	241-SX-104, 108, 109, 110, 111, 112, 113	—	1-10	1-10
	241-SX-107	—	17	—
	241-SX-108	—	53	—
	241-SX-115	—	17	—
T Tank Farm	241-T-101	—	1	—
	241-T-103	1	2	—
	241-T-106	—	57	1
Solid Waste – 200-ZP-1	218-W-4B	—	—	17
TX/TY Tank Farms	241-TX-107	23	11	—
	241-TY-101	—	2	—
	241-TY-103	—	6	—
	241-TY-105	—	2	—
TX Trenches	216-T-22	—	2	—
	216-T-23	—	2	—
	216-T-24	—	2	—
	216-T-25	6	2	—
B, BX, BY Tank Farms	241-BX-102	4	—	—
BY Cribs	Multiple	2	—	—
U Cribs	216-U-1/2	3	—	—
U Tank Farm	241-U-101	—	3	—
	241-U-104	—	10	—
	241-U-110	—	2	—
	241-U-112	—	4	—
TY Cribs and Vicinity	216-T-18	—	—	3
	216-T-26	8	2	2
A/AX Tank Farms	241-A-103	—	7	—
BC Cribs	Multiple	—	—	1-9
BC Trenches	Multiple	—	—	1-9
Laundry Waste Crib	216-W-LWC	7	1	—
PUREX Cribs	216-A-5	6 (9)	3	2
	216-A-10	5 (9)	1	—
C Tank Farm	UPR-200-E-81	—	—	3

(a) Maximum predicted groundwater concentration divided by the DWS. Only DWS Factors equal to or greater than 1 are shown.

(b) Simulations were conducted through year 12,000



**Figure 5.** Estimated total liquid waste disposal volumes for sites with greater than 1% of the disposed  $^{129}\text{I}$  inventory (Figure 4) with average annual disposal shown for sites having more than one year of disposal. Note that the 216-U-1/2 sites associated with part of the 200-UP-1 OU plume had less than 1% of the total and are, therefore, not shown here. Also, note the log-scale on the y-axis. Based on data from the Virtual Library, Effluent Volume to Soil Disposal Site module.



**Figure 6.** Calculated average  $^{129}\text{I}$  concentration for sites with greater than 1% of the disposed  $^{129}\text{I}$  inventory (Figure 4). Note that the 216-U-1/2 sites associated with part of the 200-UP-1 OU plume had less than 1% of the total and are, therefore, not shown here. Also, note the log-scale on the y-axis and that the DWS is 1 pCi/L for  $^{129}\text{I}$ .

The waste disposal chemistry can be important because the presence of co-contaminants can affect subsurface and remediation biogeochemistry. In addition, acidic or basic conditions in the disposed fluid can lead to neutralization reactions affecting contaminant fate and transport in the vadose zone, thereby influencing the contaminant flux to groundwater (Truex et al. 2014). Table 6 lists the co-contaminants for the major iodine disposal sites. Note that this assessment focused on waste disposal sites, but releases from waste storage tanks would have a unique chemistry that may need to be considered.

**Table 6.** Co-contaminants in relative rank order based on the Soil Inventory Model inventories (Corbin et al. 2005).

<b>Disposal Facilities</b>	<b>Dominant Chemicals</b> (in relative rank order by weight percent)
PUREX Cribbs (216-A-10, 216-A-5, 216-A-6, and 216-A-45)	NO <sub>3</sub> , CO <sub>3</sub> , Cl, K, Na, PO <sub>4</sub> , SO <sub>4</sub> , Fe, Ca, U-Total, Si (acidic except 216-A-6 is neutral/basic)
REDOX Cribbs (216-S-7, 216-S-1&2 and 216-S-9)	NO <sub>3</sub> , Na, Al, U-Total (acidic)
BC Cribbs (216-B-14, 216-B-15, 216-B-16, 216-B-18, 216-B-19)	NO <sub>3</sub> , Na, SO <sub>4</sub> , PO <sub>4</sub> , F, Cl, K, Si, CO <sub>3</sub> , Cr, Ca, Ni, Fe, Bi, NO <sub>2</sub> , U-Total, Zr, Ag, Hg, NH <sub>3</sub> , butanol (neutral/basic)
BC Trenches (216-B-20, 216-B-21, 216-B-22, 216-B-23, 216-B-24, 216-B-25, 216-B-28, 216-B-30, 216-B-31, 216-B-32, 216-B-33, 216-B-34, 216-B-52)	NO <sub>3</sub> , Na, SO <sub>4</sub> , PO <sub>4</sub> , CO <sub>3</sub> , NO <sub>2</sub> , F, Cl, K, NH <sub>3</sub> , Si, Al, Cr, Ca, Ni, Fe, Bi, U-Total (neutral/basic)
BY Cribbs (216-B-44, 216-B-45, 216-B-46, 216-B-49)	NO <sub>3</sub> , Na, SO <sub>4</sub> , PO <sub>4</sub> , F, Cl, K, Si, CO <sub>3</sub> , Cr, Ca, Ni, Fe, NO <sub>2</sub> , Ni, Bi, U-Total (neutral/basic)
216-U-10 Pond	CO <sub>3</sub> , NO <sub>3</sub> , SO <sub>4</sub> , K, NO <sub>2</sub> , Na, Ca, PO <sub>4</sub> , Si, Cl, TBP, NH <sub>3</sub> , Fe, CCl <sub>4</sub> , F, Al, Pb, Cr, U-Total
Laundry Waste Crib (216-W-LWC)	Na, PO <sub>4</sub> , Si, Ca, NH <sub>3</sub> , SO <sub>4</sub> , Cl, K, Fe, Al, NO <sub>3</sub> , F, Pb, Mn, Ni, Cr, U-Total
241-T-106 (UPR-200-W-148)	Na, NO <sub>3</sub> , NO <sub>2</sub> , Al, CO <sub>3</sub> , SO <sub>4</sub> , Cl, Cr, K, PO <sub>4</sub> , NH <sub>3</sub> , Fe, Si, Ca, Ni, F, Pb, U-Total
UPR-200-E-81	NO <sub>3</sub> , Na, Al, NO <sub>2</sub> , SO <sub>4</sub> , Cl, CO <sub>3</sub> , Cr, Ca, Pb, Fe, K, Ni, U-Total

Though not a waste site or contaminant input, recharge from precipitation is an important factor in transport of contaminants through the vadose zone. Recharge is the portion of water from precipitation that infiltrates into the ground and continues migrating downward toward the groundwater (recognizing that some water that infiltrates does not continue moving toward the groundwater because of processes like transpiration). Fayer and Keller (2007) reported long-term recharge rates ranging from < 0.01 to 9.2 cm/yr for various combinations of soil and surface vegetation conditions across the Hanford Site. For operational areas generally devoid of well-established shrub vegetation, the long-term drainage estimates are generally in the range of 0.8 to 9.2 cm/yr.

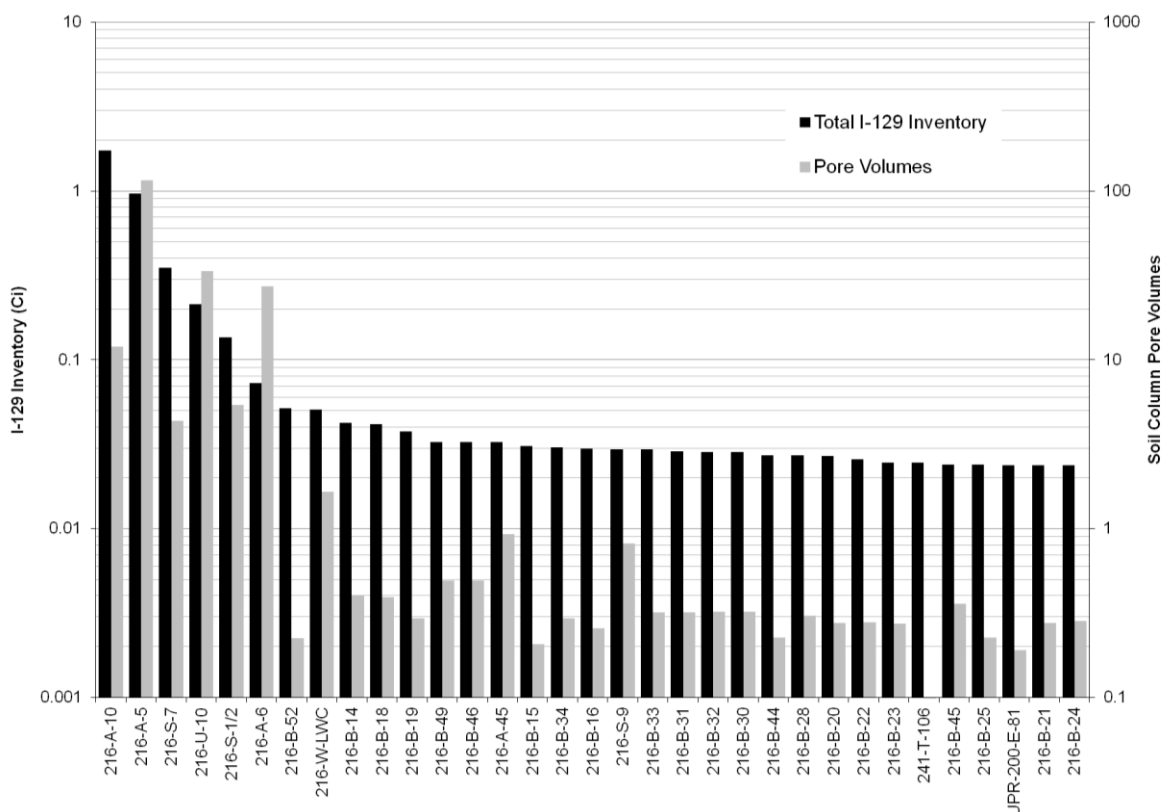
## 2.2 Source Flux to Groundwater

A combination of water disposal volume and rate, recharge, subsurface hydraulic properties, and contaminant transport characteristics (as influenced by vadose zone reactive facies and disposal chemistry) control the flux of contaminants through the vadose zone to the groundwater (Figure 3). Source flux may need to be considered in groundwater remediation if it is expected that the source flux will continue to contribute significantly to the groundwater plume.

This conceptual model evaluation does not examine source flux in detail. However, for context, Figure 7 shows the approximate number of soil column pore volumes of effluent received by each site (based on the waste site footprint and an estimated porosity of 35%) relative to their total <sup>129</sup>I inventory



(information from Last et al. 2006a and b). While this assessment does not account for lateral spreading in the vadose zone, those sites that received more than one soil column pore volume are likely to have caused a near-term impact to groundwater (e.g., as demonstrated in the groundwater monitoring data for the 216-A-10 and 216-S-7 cribs). All sites would be expected to have some longer-term contaminant flux controlled by the recharge rate. However, those sites with a higher pore volume estimate may have contaminants deeper in the vadose zone and therefore may affect groundwater sooner than sites with a lower pore volume estimate. Additional information relevant to evaluating the source flux is provided by Truex and Carroll (2013).



**Figure 7.** Total  $^{129}\text{I}$  inventory and relative number of soil column pore volumes of effluent received for sites with greater than 1% of the disposed  $^{129}\text{I}$  inventory (Figure 4). Note that the 216-U-1/2 sites associated with part of the 200-UP-1 OU plume had less than 1% of the total and are, therefore, not shown here. Also, note the log-scale on the y-axes.

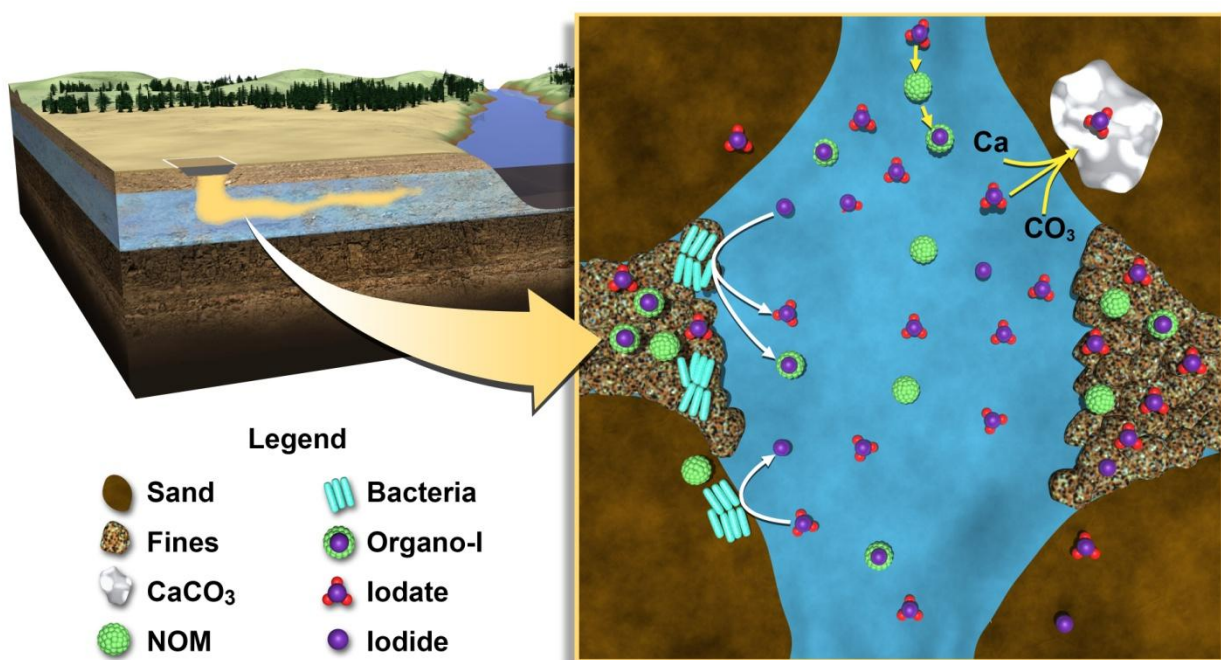
Iodine speciation will affect the iodine source flux to the groundwater because different iodine species have different transport characteristics. Other than the hydrologic features and processes, the controlling features and processes for iodine transport in the vadose zone are the same as those in the groundwater and are presented in the next section.

## 2.3 Plume Behavior: Controlling Features and Processes

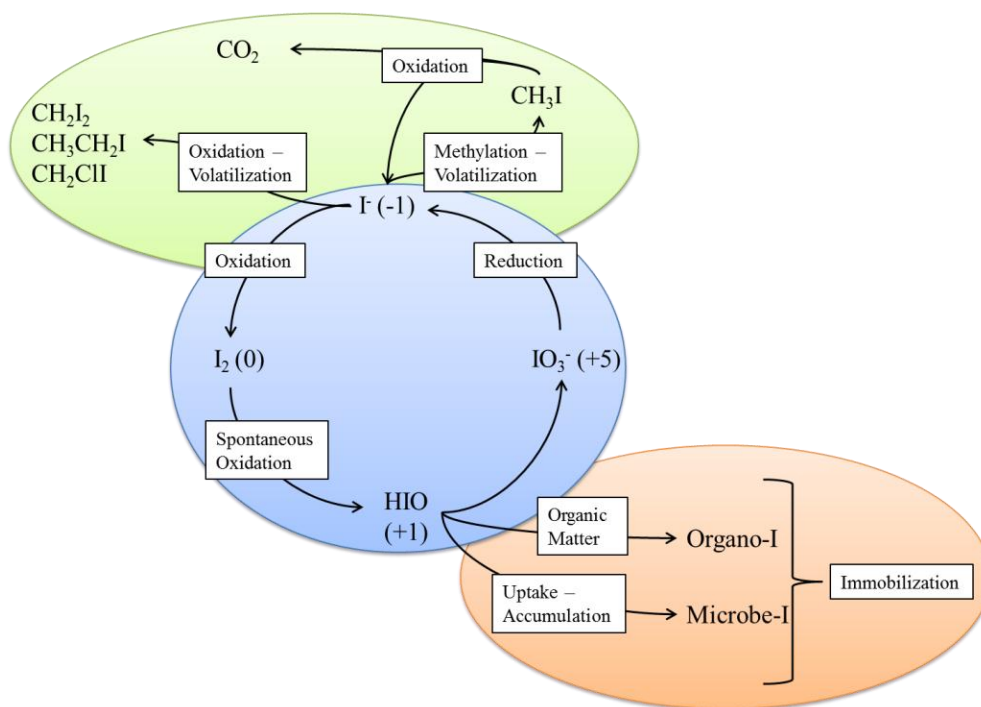
Hydrologic features are important with respect to water movement in the subsurface and, therefore, affect iodine transport and plume behavior. In addition to the groundwater information in the annual report for the Hanford groundwater monitoring program (DOE 2014), information on subsurface flow and transport parameters has been compiled in a number of documents (e.g., DOE 2005, DOE 2012a, Fayer

and Keller 2007, Last et al. 2006a, 2009). However, iodine transport is also influenced by reactive facies related to reactions (e.g., oxidation/reduction transformations) and physical interactions (e.g., sorption). The general facies of importance are redox minerals, organic material, carbonate, and microorganisms. Water chemistry components such as dissolved organic matter and pH influence transformation reactions and transport. In addition, co-contaminants, such as nitrate or other compounds that participate in redox reactions, may influence iodine transformation reactions and sorption. Both  $^{129}\text{I}$  and  $^{127}\text{I}$  concentrations should be considered when evaluating plume behavior and reactive facies.  $^{127}\text{I}$  and  $^{129}\text{I}$  are found in Hanford Site groundwater at  $^{127}\text{IO}_3^-/^{129}\text{IO}_3^-$  ratios ranging from 100 to 300, indicating much higher  $^{127}\text{I}$  concentrations in the groundwater. The source of  $^{127}\text{I}$  is not known, but iodine commonly exists as a trace constituent of nitric acid. Therefore, the enormous volumes of nitric acid used during operations are a likely contributing source for the groundwater  $^{127}\text{I}$ .

As shown in Figures 8 and 9, adsorption, transformations between species, associations with organic compounds, and precipitation are all important for iodine fate and transport. Figure 8 shows an overview of biogeochemical processes that can affect the fate of iodine in the subsurface. Categories of microbially mediated reactions are shown on Figure 9. Information about these processes are summarized below, with a more in-depth analysis provided in 0.



**Figure 8.** Conceptual overview of subsurface biogeochemical processes that affect the fate and transport of iodine. The figure does not distinguish between  $^{129}\text{I}$  and  $^{127}\text{I}$  because these processes are the same for both isotopes. The three primary aqueous iodine species are iodate ( $\text{IO}_3^-$ ), Organo-I, and iodide ( $\text{I}^-$ ). Processes include biotic (Bacteria) transformations between iodine species as shown and potential transformations to other species, as illustrated in Figure 9. Iodate reduction may also occur abiotically (not shown) (e.g., by reactions with sediment-associated iron/manganese). Iodine species adsorb to sediment surfaces (e.g., on iron oxide deposits or phyllosilicates), with greater adsorption expected in fine-textured sediment zones (Fines). Natural organic matter (NOM) may facilitate sorption and accumulation of iodine or, as a dissolved organic compound, may form mobile Organo-I. Iodate may co-precipitate with calcium carbonate.



**Figure 9.** Biological transformations associated with iodine cycling in the environment. The blue ellipse represents predominantly aqueous-phase iodine species. The orange ellipse represents predominantly solid-phase species of iodine associated with organic compounds (Organo-I) or accumulated in microbial biomass (Microbe-I). Some types of Organo-I may also be mobile in the aqueous phase. The green ellipse represents predominantly gas-phase volatile Organo-I compounds. Figure 8 provides context for some of these processes within the subsurface biogeochemical environment.

Iodine adsorption is important to quantify for predicting iodine fate and transport. Iodine is generally characterized as a mobile contaminant in groundwater, and the observed large plumes at the Hanford site are consistent with this generalization. However, iodine transport behavior differs for each species. Studies for  $\text{I}^-$  and  $\text{IO}_3^-$  have observed a low  $K_d$ , in the range of 0 to 5.64 mL/g for  $\text{I}^-$  and 0.83 to 7.56 mL/g for  $\text{IO}_3^-$  (Xu et al. 2015). In the study by Xu et al.,  $\text{IO}_3^-$   $K_d$  values were always higher than values for  $\text{I}^-$  for the same sediments. Other studies have suggested that partitioning of iodine to Hanford Site sediments may be partially related to sediment OC content (Table 7), even at the very low organic carbon (OC) concentrations in the tested Hanford Site sediments (0.04 to 0.15 wt% OC) (Xu et al. 2015). These studies showed greater sorption in the sediments with higher OC and greater sorption of  $\text{IO}_3^-$  than  $\text{I}^-$  to these sediments. Hanford Site sediments (particularly gravel-dominated sediments) typically have low OC concentrations of less than 0.1 wt% (Serne et al. 1993), with the observed range being 0.01 to 0.22 wt% (DOE 1994; MinChem Database [Mackley et al. 2010] – unpublished). Adsorption of Organo-I,  $\text{I}^-$ , and  $\text{IO}_3^-$  to iron-oxides and phyllosilicate mineral surfaces is expected to differ, with a likely highest-to-lowest ranking of sorption being  $\text{Organo-I} > \text{IO}_3^- > \text{I}^-$ , although experiments are required to test this hypothesis.

**Table 7.** Iodide and iodate  $K_d$  values for composite sediments recovered from 200 West Area borehole cores (Xu et al. 2015).

Composite Sediment <sup>(a)</sup>	Organic Carbon (%)	Inorganic Carbon (%)	Total Sediment Iodine ( $\mu\text{g/g}$ )	Total DOC <sup>(b)</sup> ( $\mu\text{M}$ )	Iodide-spiked $K_d$ <sup>(c)</sup> ( $\text{mL/g}$ )	Iodate-spiked $K_d$ <sup>(c)</sup> ( $\text{mL/g}$ )
H1	0.12	0.92	4.79	$284 \pm 33$	0.08	1.78
H2	0.04	0.01	0.68	0	0.00	0.83
H3	0.15	0.18	2.10	$94 \pm 17$	3.38	3.94

(a) H1 – 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.

H2 – composite from different depths within one well (299-W11-92).

H3 – composite of saturated zone sediments of two different wells: 299-W11-92 and 299-W15-226.

(b) Total dissolved organic carbon (DOC) is the total OC released from the sediment to the aqueous phase ( $< 0.45 \mu\text{m}$ ) after 21 days of contact during the sediment/groundwater batch iodine uptake experiment.

(c) Suspensions were spiked with either iodide or iodate (as  $^{125}\text{I}$ ). However, the spiked species transformed to other species during the contact period. Consequently, these are not species-specific  $K_d$  values.

Earlier studies had focused on  $\text{I}^-$  partitioning, with reported  $K_d$  values ranging from 0 to 2  $\text{mL/g}$ , but most frequently between 0 and 0.2  $\text{mL/g}$  (Cantrell et al. 2003). These earlier studies also assumed a reversible anion exchange sorption mechanism where sorption and desorption occurred at equal rates (Kaplan et al. 2000, Um et al. 2004). More recent studies have shown that there was a strongly bound iodine fraction that did not desorb under chemical conditions conducive to anion exchange. Using subsurface sediments, desorption  $K_d$  values were much higher than the iodine adsorption  $K_d$  values, indicating that sorption was only partially reversible (Xu et al. 2015). In these studies, similar trends were noted for  $\text{I}^-$  and  $\text{IO}_3^-$ , but results indicated that  $\text{IO}_3^-$  sorption to Hanford Site sediments was greater than  $\text{I}^-$  sorption.

Microorganisms and/or their cell exudates can mediate many important processes associated with iodine transformations between species, associations with organic compounds and adsorption. Results from sediment traps incubated at locations within the Hanford Site 200-UP-1 OU plume with background, low, and high levels of  $^{129}\text{I}$  show the presence of microbial families that include *Pseudomonads* and *Actinobacteria* (Lee et al. 2015), which are taxa that have shown the ability to both oxidize  $\text{I}^-$  and reduce  $\text{IO}_3^-$ . Microbes have been shown to be involved in iodine accumulation (Microbe-I, Figure 9) and formation of Organo-I compounds (Organo-I, Figure 9), including volatile compounds such as methyl iodide ( $\text{CH}_3\text{I}$ ) (Amachi et al. 2003; Amachi et al. 2004; Fuse et al. 2003; Muramatsu et al. 1996), although these processes have not been evaluated for the Hanford Site. Microbial processes can also affect the subsurface geochemistry and may, thereby, affect sediment adsorption and redox capacity relevant to iodine fate and transport. The above microbial processes need to be considered in the context of the biogeochemical system in terms of the microbial ecology and presence of conditions conducive to potential microbial activity within the Hanford Site  $^{129}\text{I}$  plumes.

Minerals that participate in redox reactions (e.g., iron and manganese) may mediate iodine transformation processes, either directly or coupled with microbial processes. Reduction of iodate in Hanford Site sediments was observed as part of partitioning experiments (Xu et al. 2015) and could have been driven by sediment-associated ferrous iron or microbial reactions. Data from the 200 Area suggest that  $\text{Fe(II)}$  concentrations in Ringold materials could be on the order of 3.4 to 6.9 wt% (MinChem Database [Mackley et al. 2010] – unpublished). Thus, ferrous iron incorporated in minerals may be a reactive

facies (as iron sulfide, if present, or other ferrous minerals) that needs to be considered relative to iodine fate and transport.

Organic materials in the subsurface may interact with iodine and affect its fate and transport through 1) formation of immobile sediment-associated Organo-I compounds, 2) formation of mobile soluble Organo-I compounds, 3) formation of volatile Organo-I compounds, 4) providing electron donors for microbially mediated reduction reactions that directly or indirectly affect iodine speciation, and 5) providing adsorption capacity for iodine species. Formation of Organo-I is important because iodine forms extremely strong bonds with some organic compounds.

There has been recent evidence of  $\text{IO}_3^-$  co-precipitation with calcium carbonate (Zhang et al. 2013). This finding may have important implications related to iodine partitioning near the source terms, where extreme chemical conditions may promote calcite dissolution/precipitation that can facilitate co-precipitation of  $\text{IO}_3^-$ . Co-precipitation of  $\text{IO}_3^-$  with calcium carbonate may also have important implications related to the long-term fate of iodine in the far field, where natural calcium carbonate dissolution/precipitation cycling may occur.



## 3.0 Description and Interpretation of Major $^{129}\text{I}$ Plumes

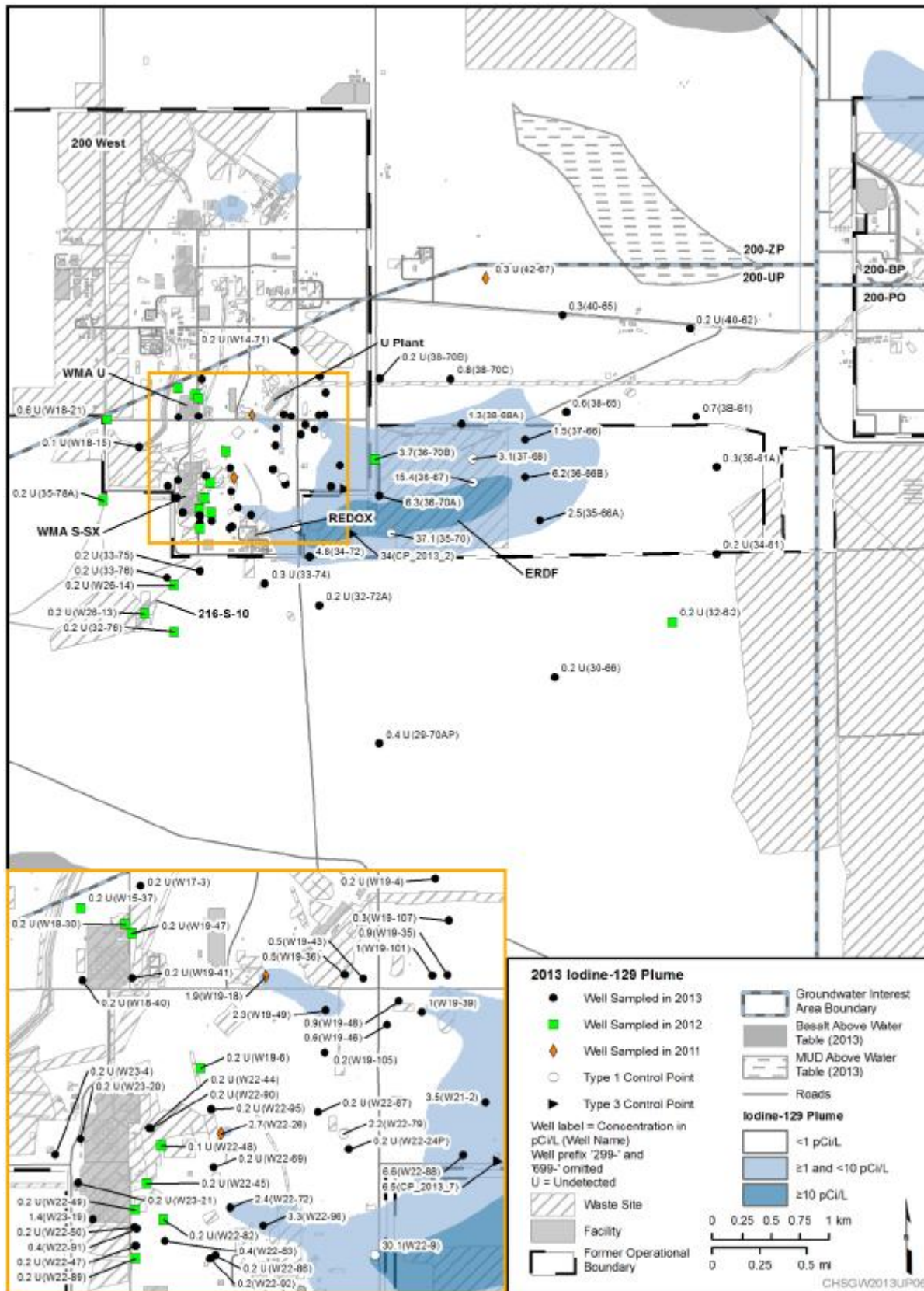
### 3.1 200 West Area

In the 200 West Area,  $^{129}\text{I}$  plumes are present in the 200-UP-1 and 200-ZP-1 operable units (Figure 10). For the 200-UP-1 OU,  $^{129}\text{I}$  plumes in southern 200 West Area originated from U-Plant and REDOX Plant waste sites, with the latter being the primary sources (DOE 2014). These plumes, one from the 216-U-1 and 216-U-2 cribs near U-Plant and a second from the REDOX Plant waste sites (e.g., 216-S-1&2, 216-S-7, and 216-S-9) in the southern portion of the 200 West Area, merge downgradient, becoming one indistinguishable groundwater contaminant plume. For the 200-ZP-1 OU (DOE 2014), sources of  $^{129}\text{I}$  include past leaks from single shell tanks and liquid waste from chemical processing at T-plant.  $^{129}\text{I}$  contamination is present near the 241-T, -TX and -TY Tank farms (Waste Management Areas [WMA] T and TX-TY).

Plume maps over a 20-year period beginning in 1993 (Figure 11) show that the 200-UP-1 plume (the primary plume in the 200 West Area) has oscillated, but declined, in areal extent, although the plume core area above 10 pCi/L has not declined. The overall plume extent (as defined by the 1 pCi/L contour) is large and the plume thickness is up to tens of meters, although there is uncertainty in this estimate. The recent  $^{129}\text{I}$  concentration results range from 1 pCi/L (MCL) to 10+ pCi/L within the 200-UP-1 plume. The 90<sup>th</sup> percentile  $^{129}\text{I}$  concentration is 3.5 pCi/L, meaning that 90% of the data for  $^{129}\text{I}$  in the plume falls below this value (DOE 2012b). However, there are a few recently recorded groundwater concentrations that exceed 10 pCi/L. The temporal concentration profiles for seven wells within the central portion of the plume (Figure 12) are shown in Figure 13. These data indicate stable to declining trends in most portions of the plume and some increases in a downgradient portion of the plume where concentrations are above 10 pCi/L. These data, in conjunction with the plume maps (Figure 11), are consistent with influences from 1) historical pulses of iodine into the groundwater that have now diminished in magnitude and 2) declining hydraulic gradients from dissipation of the historical 200 West Area groundwater mound that existed during processing operations. Thus, the current plume was generated from a historical source that has diminished and a discrete plume is now migrating in the aquifer. The overall declines in plume area (Figure 11) and concentration are consistent with natural attenuation processes affecting the plume. Increases in concentrations for discrete locations in the central portion of the plume are consistent with movement of a higher concentration core along a flow path. A higher concentration core may still be attenuating, but temporal data at individual wells may be showing the progression of a plume core past the location of the well. In addition,  $^{129}\text{I}$  currently in the vadose zone may still be a future source for groundwater contamination, even though the existing plume appears to be in a stable to declining condition.

Several co-contaminants are present within the  $^{129}\text{I}$  plumes, including chromium, nitrate,  $^{99}\text{Tc}$ , uranium, and tritium. Chromium, nitrate, uranium, and technetium may be present in forms that could interact with the same reactive facies as  $^{129}\text{I}$ . These co-contaminants will be addressed by a pump-and-treat remediation approach for the 200-ZP-1 and 200-UP-1 operable units. The pumping operations will also affect the  $^{129}\text{I}$  plumes because of the altered hydraulic gradients and by displacement of  $^{129}\text{I}$  that is extracted and re-injected.





**Figure 10.**  $^{129}\text{I}$  groundwater plumes emanating from the 200 West Area (adapted from DOE 2014).

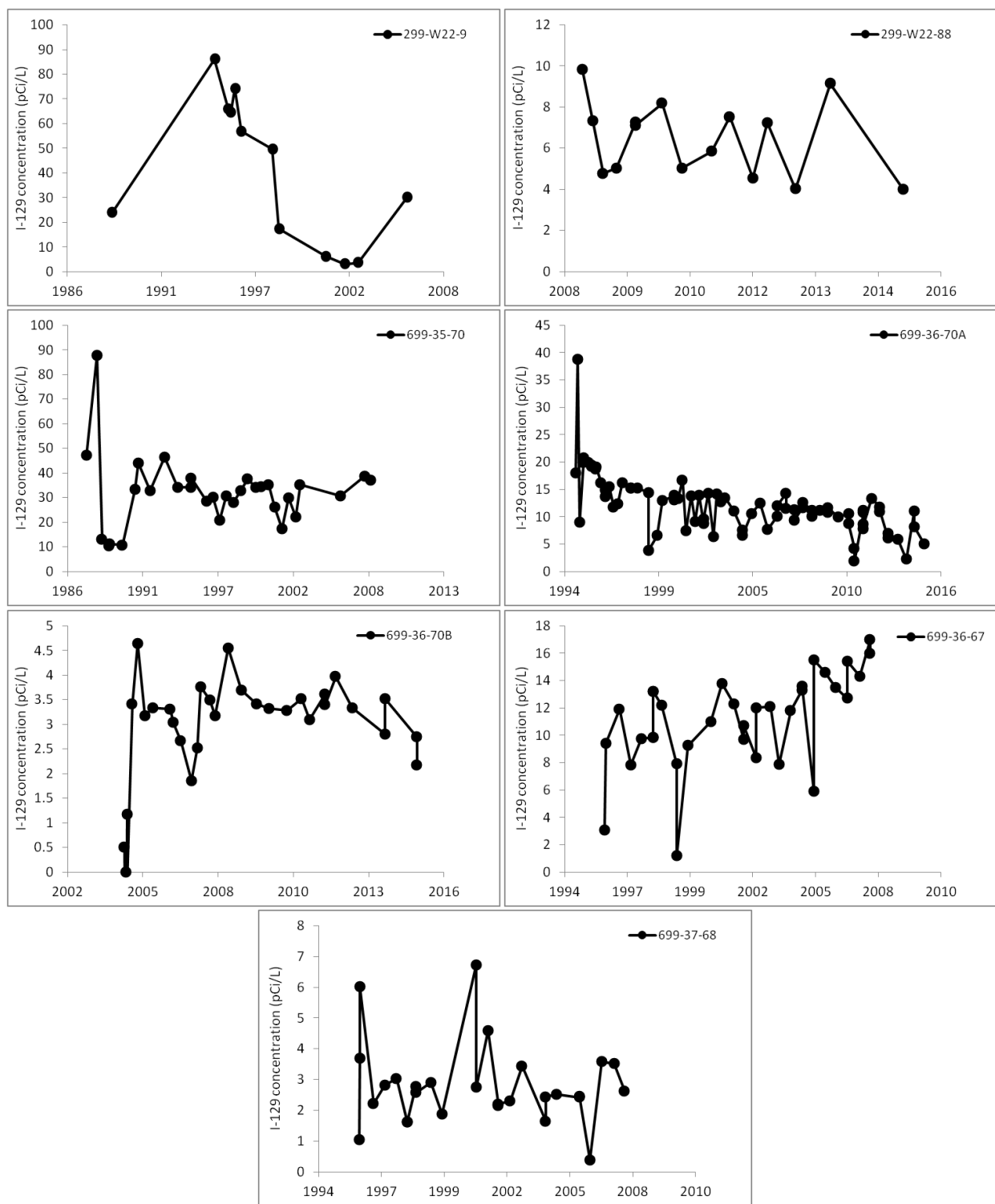




**Figure 11.**  $^{129}\text{I}$  plume depictions over a 20-year period for the 200-UP-1 OU. Plume images were obtained using the Plume Status feature of the PHOENIX web-based data tool for the Hanford Site (<http://phoenix.pnnl.gov/apps/plumes/index.html>, accessed on 8/18/2015). Note that the set of wells used for plume contouring has varied over time.



**Figure 12.** Wells selected for plotting temporal data (yellow circles). Well locations are shown with a background of the 2013  $^{129}\text{I}$  plume contours, where light blue is 1 to 10 pCi/L and darker blue is greater than 10 pCi/L. Image was obtained using the PHOENIX web-based data tool for the Hanford Site (<http://phoenix.pnnl.gov/>, accessed on 8/18/2015).



**Figure 13.** Temporal  $^{129}\text{I}$  concentration profiles in seven wells within the central portion of the 200-UP-1 OU. Data were obtained using the PHOENIX web-based data tool for the Hanford Site (<http://phoenix.pnnl.gov/>, accessed on 8/18/2015).

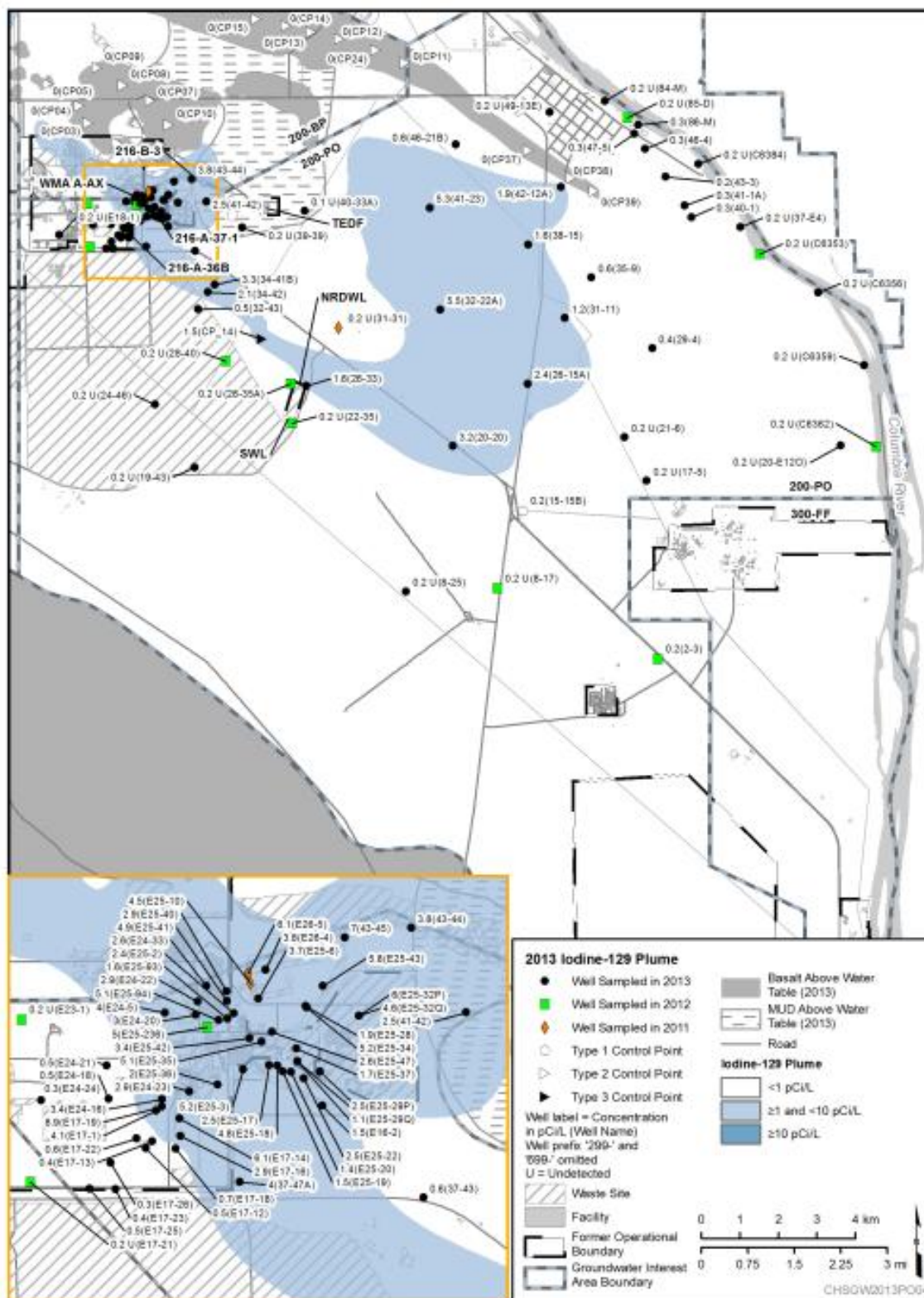
Future plume behavior depends on fate and transport factors, including natural attenuation, and the nature of the continuing iodine contamination flux from the vadose zone. There are several potential alternative conceptual models for future plume behavior. Section 4 describes these alternative conceptual models and the type of data that can be used to select the one will best describe future plume behavior in support of remedy decisions.

### 3.2 200 East Area

In the 200 East Area,  $^{129}\text{I}$  plumes are present in the 200-PO-1 and 200-BP-5 operable units (Figure 14). In the 200-PO-1 OU (DOE 2014), high current and historical concentrations of iodine in the groundwater detected near the PUREX cribs and trenches (e.g., 216-A-10, 216-A-5, 216-A-6, and 216-A-45) and near the 216-A-29 ditch, 216-B-3 Pond, and the 241-A and AX Tank Farms (WMA A-AX) point to this area as a primary source of the  $^{129}\text{I}$  plume.  $^{129}\text{I}$  in the northern portion of 200 East Area primarily migrated into the 200-BP-5 OU from the 200-PO-1 OU in the late 1980s and early 1990s (DOE 2014). Other potential sources of  $^{129}\text{I}$  are the BY cribs, an unplanned release at 241-BX-102, and the 216-B-8 Crib.

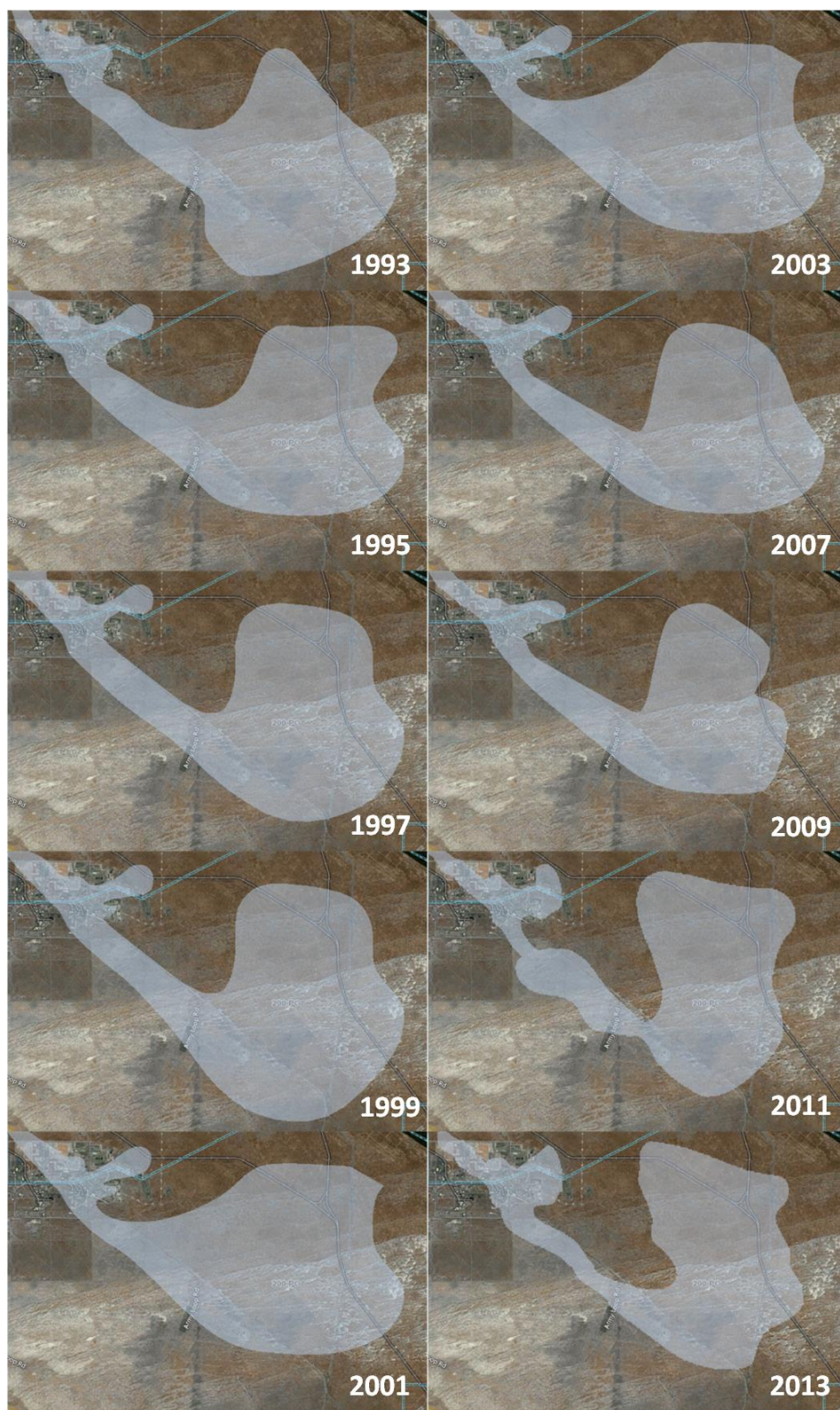
Plume maps over a 20-year period beginning in 1993 show that the 200-PO-1 plume (primary plume in the 200 East Area) has oscillated in areal extent, but has remained of similar size (Figure 15). The overall plume extent (as defined by the 1 pCi/L contour) is very large and the plume thickness is up to tens of meters, although there is uncertainty in this estimate. The recent  $^{129}\text{I}$  concentrations are all below 10 pCi/L. The temporal concentration profiles for the nine wells with historical  $^{129}\text{I}$  concentrations above 15 pCi/L are shown in Figure 16. These data show generally declining trends (though some show an initial increase followed by a decline), indicating a diminishing source. These data, in conjunction with the plume maps (Figure 15), are consistent with influences from historical pulses of iodine into the groundwater that have now diminished in magnitude. Because of the variations in groundwater flow direction, and a potential continuation of some contaminant flux from these source areas, the plume is still present beneath the former source areas. The recent plume map trends and declining plume concentrations are consistent with natural attenuation processes affecting the plume. However,  $^{129}\text{I}$  currently in the vadose zone may still be a future source for groundwater contamination, even though the existing plume appears to be in a stable to declining condition.

Several co-contaminants are present within the 200 East Area  $^{129}\text{I}$  plumes, including nitrate,  $^{99}\text{Tc}$ , uranium, and tritium. Nitrate, uranium, and technetium may be present in forms that could interact with the same reactive facies as  $^{129}\text{I}$ .

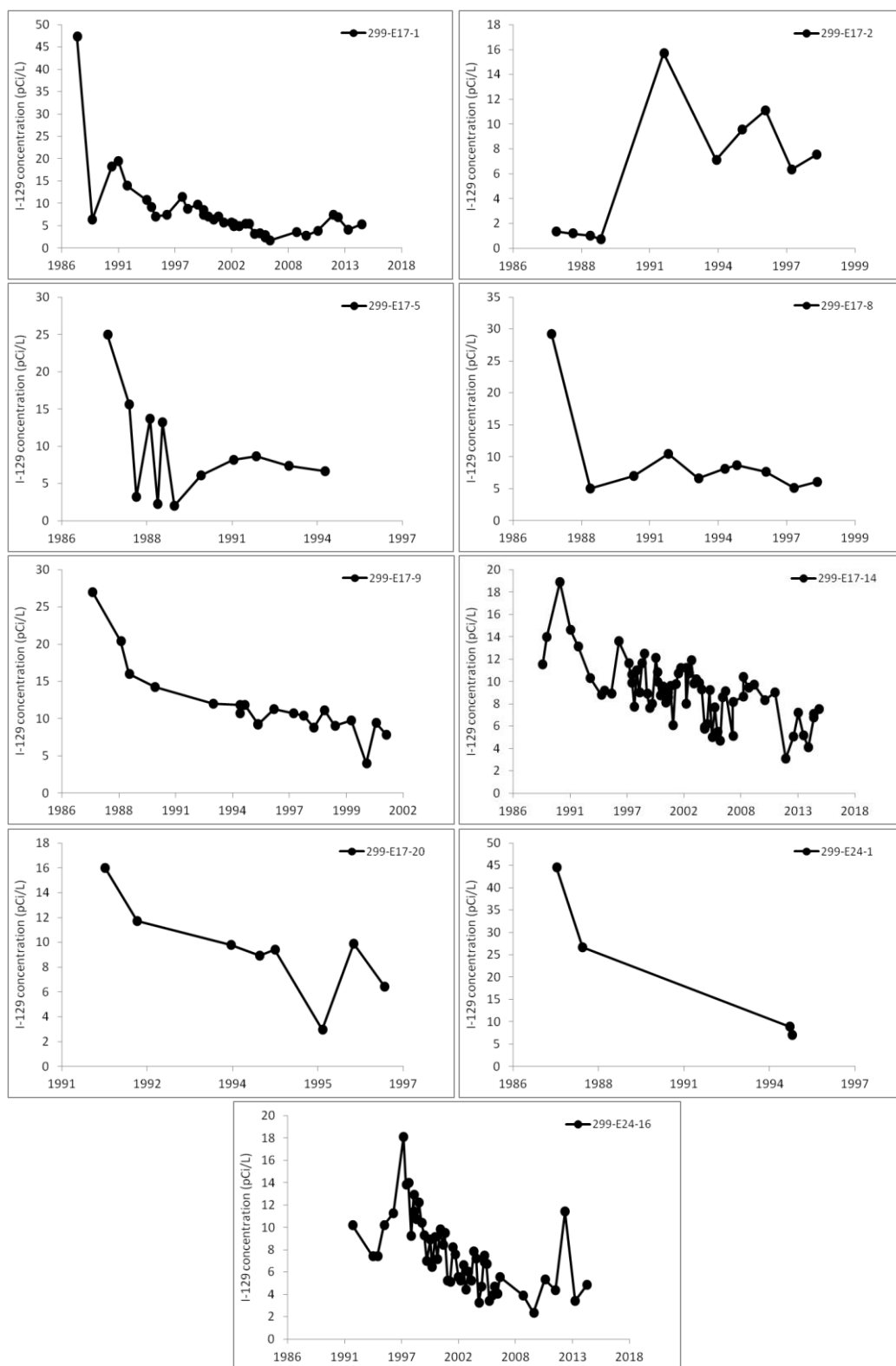


**Figure 14.**  $^{129}\text{I}$  groundwater contamination emanating from the 200 E Area (adapted from DOE 2014).





**Figure 15.**  $^{129}\text{I}$  plume depictions over a 20-year period for the 200-UP-1 OU. Plume images were obtained using the Plume Status feature of the PHOENIX web-based data tool for the Hanford Site (<http://phoenix.pnnl.gov/apps/plumes/index.html>, accessed on 8/18/2015). Note that the wells used for plume contouring has varied over time.



**Figure 16.** Temporal  $^{129}\text{I}$  concentration profiles in nine 200-PO-1 OU wells for which concentrations were historically greater than 15 pCi/L. Data were obtained using the PHOENIX web-based data tool for the Hanford Site (<http://phoenix.pnnl.gov/>, accessed on 8/18/2015).

Future plume behavior depends on fate and transport factors, including natural attenuation, and the nature of the continuing iodine contamination flux from the vadose zone. There are several potential alternative conceptual models for future plume behavior. Section 4 describes these alternative conceptual models and the type of data that can be used to select the one will best describe future plume behavior in support of remedy decisions.



## 4.0 Alternative Conceptual Models for Future Plume Behavior

Several alternative conceptual models were developed to represent variations in the controlling factors for future iodine plume behavior. These alternatives are related to the type of groundwater iodine species present, whether or not specific transformation reactions are significant within the aquifer, and whether or not a significant flux of contaminants from the vadose zone will occur. The next section describes the alternative conceptual models. The following sections then describe supporting data/research needs and recommendations for continued monitoring and characterization activities to help select the most valid conceptual model in support of future remedy decisions.

### 4.1 Alternative Conceptual Models

Four alternative conceptual models are described below. Current data are not sufficient to identify the most valid conceptual model, but suggest that Alternative 2 is more valid than Alternative 1 and that Alternatives 3 and 4 are potential refinements to Alternative 2 that will have some additional effect on future plume behavior, especially in relation to ability of natural attenuation to meet remediation objectives.

Alternative Conceptual Model 1. This conceptual model was used in the 200-UP-1 feasibility study for evaluating potential  $^{129}\text{I}$  remedies and led to the 200-UP-1 ROD stating that additional evaluation of  $^{129}\text{I}$  remediation was required to support a final decision for  $^{129}\text{I}$  remediation. In this conceptual model, iodine was considered to be present only as iodide with no transformation of iodide occurring over time. Thus, iodine transport was based on a  $K_d$  value of 0.1 mL/g and numerical model simulations showed the plume continuing to migrate as a detached plume over long distances and for a long timeframe prior to dissipating. New information from samples of 200 West Area groundwater (including samples within the 200-UP-1 OU) shows that iodine is present as a mix of iodide, iodate, and organo-iodine species. Thus, this alternative conceptual model is inconsistent with the existing iodine speciation data. Relative to the 200-UP-1 OU, this conceptual model also assumed that there is no future flux of  $^{129}\text{I}$  from the vadose zone that would cause a continuing source of contamination above clean-up levels. This aspect of Alternative Conceptual Model 1 is consistent with current observations of the 200-UP-1 groundwater plume, which is essentially detached from the disposal sites. However, the significance of continued vadose zone contaminant sources still needs to be verified for all of the  $^{129}\text{I}$  disposal sites in the Hanford Central Plateau. If vadose zone  $^{129}\text{I}$  contributions were found to be significant, this alternative would be updated to recognize this type of source flux.

Alternative Conceptual Model 2. This conceptual model is based on the current information from samples of 200 West Area groundwater (including samples within the 200-UP-1 OU) that show iodine is present as a mix of iodide, iodate, and organo-iodine species. For this alternative, plume behavior would be impacted by differential transport of iodine species due to their different sorption characteristics (Section 2.3). These sorption characteristics would result in greater plume attenuation than with Alternative 1. This alternative is for conditions where there is no significant transformation between species over time. Thus, there would be only sorptive attenuation, not accumulation or other losses of iodine. It will be important to evaluate the iodine species distribution throughout the plume and to assess transformation rates as part of evaluating the validity of this alternative. As with Alternative 1, this conceptual model would be based on a

condition with no future flux of  $^{129}\text{I}$  from the vadose zone that would cause a continuing source of contamination above clean-up levels. This aspect of the alternative is consistent with current observations of the 200-UP-1 groundwater plume that is essentially detached from the disposal sites. However, the significance of continued vadose zone contaminant sources still needs to be verified for all of the  $^{129}\text{I}$  disposal sites in the Hanford Central Plateau. If vadose zone  $^{129}\text{I}$  contributions were found to be significant, this alternative would be updated to recognize this type of source flux.

Alternative Conceptual Model 3. This conceptual model is the same as Alternative 2 (based on data that show iodine is present as a mix of iodide, iodate, and organo-iodine species), but considers the case where transformations occur over time and result primarily in shifting the relative percentages of iodide and iodate species in the subsurface. These transformations would then affect the plume behavior because of differential transport of iodine species (Section 2.3). Although some transformations are active for this conceptual model, the only loss mechanism included would be co-precipitation of iodate with calcium carbonate. These conceptual model characteristics would result in greater plume attenuation than with Alternative 1. It will be important to evaluate the iodine species distribution throughout the plume and to assess transformation rates as part of evaluating the validity of this alternative. As with Alternative 1, this conceptual model would be based on a condition with no future flux of  $^{129}\text{I}$  from the vadose zone that would cause a continuing source of contamination above clean-up levels. This aspect of the alternative is consistent with current observations of the 200-UP-1 groundwater plume that is essentially detached from the disposal sites. However, the significance of continued vadose zone contaminant sources still needs to be verified for all of the  $^{129}\text{I}$  disposal sites in the Hanford Central Plateau. If vadose zone  $^{129}\text{I}$  contributions were found to be significant, this alternative would be updated to recognize this type of source flux.

Alternative Conceptual Model 4. This conceptual model is the same as Alternative 3 (based on data that show iodine is present as a mix of iodide, iodate, and organo-iodine species and that transformation can occur over time), but considers the case where transformations include significant formation of organo-iodine species. These transformations would then affect the plume behavior because of differential transport of iodine species (Section 2.3). However, significant transformation to organo-iodine species also creates additional loss mechanisms through accumulation as functionally immobile organic deposits or through production of volatile organo-iodine species (Figure 9), in addition to losses from co-precipitation with calcium carbonate. These conceptual model characteristics would result in greater plume attenuation than with Alternative 1. It will be important to evaluate the iodine species distribution throughout the plume and to assess transformation rates as part of evaluating the validity of this alternative. As with Alternative 1, this conceptual model would be based on a condition with no future flux of  $^{129}\text{I}$  from the vadose zone that would cause a continuing source of contamination above clean-up levels. This aspect of the alternative is consistent with current observations of the 200-UP-1 groundwater plume that is essentially detached from the disposal sites. However, the significance of continued vadose zone contaminant sources still needs to be verified for all of the  $^{129}\text{I}$  disposal sites in the Hanford Central Plateau. If vadose zone  $^{129}\text{I}$  contributions were found to be significant, this alternative would be updated to recognize this type of source flux.

## 4.2 Supporting Data and Research Needs

The supporting data and research needs to help select the most valid conceptual model in support of future remedy decisions are described below in four categories.

- Environmental Data
  - Groundwater samples need to be analyzed to quantify the iodine species distribution throughout plumes (i.e., with distance from sources) using  $^{127}\text{I}$  and  $^{129}\text{I}$  data, as appropriate.
  - Improved measures of organo-iodine are needed to identify the organic ligand associated with iodine.
- Evaluation of Transformation Reactions
  - The biogeochemical conditions required for each type of transformation need to be determined to support interpretation of their importance for the Hanford Site  $^{129}\text{I}$  plumes.
    - ♦ Redox reactions associated with iodide and iodate.
    - ♦ Transformations to organo-iodine species and their stability with respect to transformation back to iodide or iodate.
    - ♦ Co-precipitation processes for iodate with calcium carbonate need to be quantified.
  - Rates of relevant transformations need to be evaluated under Hanford-specific conditions.
  - Indicators of transformation reactions or conditions (e.g., microbial probes) are needed for potential use in support of characterization and monitoring.
  - The fate of transformation products (e.g., organo-iodine accumulation, solubility, volatility) needs to be determined for key species that are expected end products of reactions.
  - The effect of co-contaminants on the above transformation reactions needs to be evaluated.
- Fate and Transport Parameters
  - Improved sorption parameters for relevant iodine species and Hanford Site sediments are needed to support selection of appropriate parameter values for numerical models.
  - Stability of precipitated iodine materials with respect to dissolution is needed to define how to model the interaction with aqueous iodine species.
  - The effect of co-contaminants on the above sorption and dissolution processes needs to be evaluated.
  - Interpretation of transformation data as fate and transport parameters for application at the field scale is needed to support numerical model configuration.
- Vadose Zone Evaluation
  - Evaluation of each iodine disposal site using the approach outlined by Truex and Carroll (2013) and Truex et al. (2015) is needed to evaluate the potential for continuing or future sources to groundwater. Data from 200-DV-1 (and other characterization data) can be used to support these evaluations.

## 4.3 Monitoring and Characterization Implications

$^{129}\text{I}$  plume behavior in the 200 West Area will be influenced by current and planned P&T operations for up to 25-40 years. Thus, monitoring of plume concentration trends to assess fate and transport will be difficult. However, sampling to include snap-shots of iodine speciation across the plume over time at a

consistent set of monitoring wells would support 1) conceptual model evaluation and refinement in conjunction with laboratory testing of transformation and 2) development of better define fate and transport parameters. In addition to iodine speciation, indicators of transformation that should be monitored include groundwater geochemistry, microbial indicators identified from ongoing research, <sup>127</sup>I speciation, and co-contaminant concentrations.

<sup>129</sup>I plume behavior in the 200 East Area may be partially influenced by potential P&T operations in the 200-BP-5 OU. However, a large portion of the plume will remain unaffected by the P&T operations and monitoring of plume concentration trends to assess fate and transport will be useful. As for the 200 West Area, 200 East Area sampling should include “snap-shots” of plume concentrations over time at a consistent set of monitoring wells within the plume as a means to assess plume trends. In addition, this snap-shot sampling should include evaluation of iodine speciation to support conceptual model evaluation and refinement in conjunction with laboratory testing of transformation and to better define fate and transport parameters. In addition to iodine speciation, indicators of transformation should be monitored, as described above for the 200 West Area.

Collection and analysis of characterization data to support estimating the future flux of <sup>129</sup>I from the vadose zone, as described by Truex and Carroll (2013) and Truex et al. (2015), is also needed to as input for refining the conceptual model with respect to future plume behavior.

## 5.0 Recommendations and Conclusions

There are three basic components of the conceptual model: Inputs, Source Flux to Groundwater, and Plume Behavior. Inputs include information about  $^{129}\text{I}$  discharges to the subsurface and other boundary conditions (e.g., recharge from precipitation) that influence  $^{129}\text{I}$  fate and transport. Information is available from several sources to define the important input parameters. The source flux to groundwater component identifies factors important to consider in defining the nature of sources to historical, current, and future groundwater plumes. This information is needed to provide a context for examining fate and transport and remediation of groundwater plumes, which are the risk driver for remediation activities. Some analyses have been completed to quantify potential source flux to the groundwater. However, additional evaluations using recently developed approaches will be needed to refine these estimates. Prediction of plume behavior associated with  $^{129}\text{I}$  fate and transport is needed for risk assessment and to support remedy decisions and remedy design and implementation. Recent information describing the relative quantity of three primary iodine chemical species present in the groundwater (iodide, iodate, and organic-iodine complexes) is pertinent to predicting plume behavior because each chemical species has different transport characteristics and may be subject to transformation reactions. The transformation reactions can change the relative quantity of chemical species, result in accumulation as a solid phase, or promote volatilization of iodine. Thus, transformation reactions are relevant to plume attenuation and for application of remediation technologies. Existing data describing iodine species transport properties and transformation reactions have been compiled. In addition, technical gaps were identified associated with the need to refine this information in support of future remedy decisions.

Because there are uncertainties in the iodine species transport parameters and transformation reactions with respect to plume behavior at the Hanford Site, alternative conceptual models were developed based on potential outcomes of ongoing research. The first two alternatives describe scenarios with different iodine chemical species controlling the overall transport behavior of  $^{129}\text{I}$  for a condition where no significant species transformation reactions are occurring. The other two alternatives describe scenarios where different types of transformation reactions are important. These alternative conceptual models provide a structure to guide development of studies that will help distinguish the alternative that best describes plume behavior as part of refining the iodine conceptual model for the Hanford Site and providing an appropriate technical basis for fate and transport analyses and remediation decisions.

Recommended additional efforts include 1) collecting appropriate environmental data, especially in relation to iodine chemical speciation, 2) determining what types of transformation reactions are relevant to iodine fate and transport and remediation approaches and then quantifying these transformation reactions for use in future remediation-related analyses, 3) refining the values of iodine transport properties, especially considering the iodine chemical speciation and Hanford Site sediment characteristics, and 4) evaluating the potential for continuing or future sources to groundwater from vadose zone sources. In conjunction with these efforts, monitoring and characterization efforts in  $^{129}\text{I}$ -contaminated zones should be designed to support the above studies and to provide enhanced information about plume behavior through collection of plume trend information.

Because there are identified data gaps and several potential alternative conceptual models for  $^{129}\text{I}$  behavior at the Hanford Site, it is recommended that a periodic update to the conceptual model be published as the conceptual model is refined.



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## **Appendix A**

### **Summary of Current Biogeochemical Process Information**



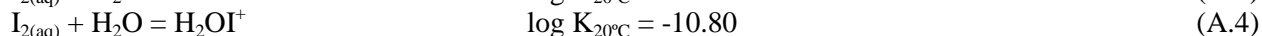
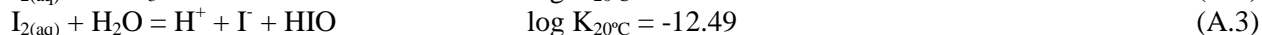
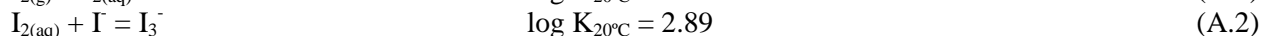
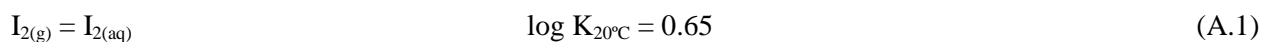
## Appendix A

### Summary of Current Biogeochemical Process Information

#### A.1 Aqueous Iodine Conversion

##### A.1.1 General Aqueous Iodine Chemistry

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 with a vapor pressure of  $4.1 \times 10^{-4}$  atm (Lauterbach and Ober 1996). Henry's Law constant at 25°C for  $I_2$  is estimated to be 381 g /L·atm (Parsly 1970). Thermodynamic data from HSC Chemistry® (Outotec, Espoo, Finland) indicates a value of 483 g/L·atm, assuming ideal behavior for both the vapor and solution. Iodine hydrolyzes in water by four main reactions (Parsly 1970):



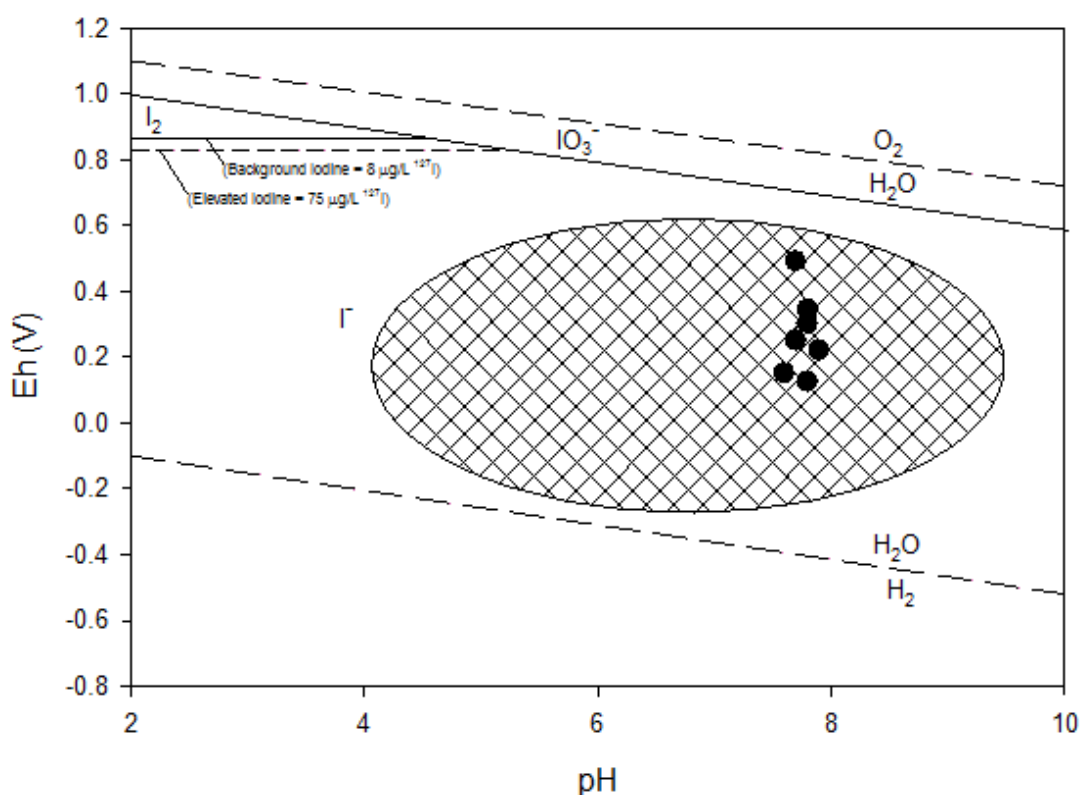
The reactions for several species are shown in Table A.1, with iodide ( $I^-$ ) as the reactant species. Under conditions prevalent in groundwater and surface water, only the -1, 0, and +5 valence states are common. Additional species may occur in natural waters because iodide forms aqueous complexes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

**Table A.1.** Reactions of log K association constants of selected aqueous iodine species (Kaplan et al. 2014).

Reaction	log $K_{20^\circ\text{C}}$
$I^- + H^+ = HI$	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

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 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., Malinauskas and Bell 1987, Paquette et al. 1986, Skulski 2000, Taghipour and Evans 2002, Wren and Ball 2001).

Inorganic iodine chemistry under conditions associated with most  $^{129}\text{I}$  environmental plumes is somewhat simplified because the only stable aqueous species that are common are  $\text{I}^-$ ,  $\text{I}_2^0$ , and  $\text{IO}_3^-$ . Figure A.1 shows the relation of these species to pH and Eh and was calculated using the background  $^{127}\text{I}$  concentrations measured at the site;  $8\text{ }\mu\text{g/L}$   $^{127}\text{I}$  (Zhang et al. 2013). Also included in the figure is the range of common pH/Eh conditions found in unimpacted natural systems, as estimated by 6200 pH/Eh-paired measurements (Baas-Becking et al. 1960). These calculations predict that iodide should be the dominant species under the groundwater conditions at the 200 West Area. However, because the lines in the pH/Eh plots identify the conditions where two species exist at 50%, it is also expected that there would be a small fraction of  $\text{IO}_3^-$  and an inconsequential amount of  $\text{I}_2$ .  $\text{I}_2$  is the only species expected to change appreciably with total iodine concentration; it was also modeled at the highest stable  $^{127}\text{I}$  concentrations measured by Zhang et al. (2013),  $75\text{ }\mu\text{g/L}$ . As expected, the  $\text{I}_2$  region increased, but still indicates that  $\text{I}_2$  will not be a significant species in this system.



**Figure A.1.** pH-Eh diagram of aqueous iodine speciation in the 200-UP-1 OU; total iodine concentration =  $8\text{ }\mu\text{g/L}$  (background) and  $75\text{ }\mu\text{g/L}$  (plume impacted) (Geochemist's Workbench® [Aqueous Solutions LLC, Champaign, Illinois]; Bethke and Yeakel 2013). Points identify pH-Eh conditions measured in groundwater in the 200-UP-1 OU (Zhang et al. 2013). The hatched zone shows the general pH-Eh limits common in the environment (based on 6200 paired measurements (Baas-Becking et al. 1960). Organo-iodine species were not considered in these calculations.

An important omission in these calculations is the consideration of 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-iodine 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-iodine (and iodate) have also been detected recently in 200 West Area groundwater (Zhang et al. 2013). Other potential contributing reasons for why thermodynamic speciation calculations do not predict actual  $^{129}\text{I}$  speciation distributions are (1) contaminant plumes may not be in steady state, and (2) thermodynamic models do not consider processes involving microbes, well known to accumulate and alter iodine speciation.

## A.1.2 Aqueous Iodine – Dissolved Natural Organic Matter Interactions

The coexistence of inorganic and organic iodine species has been reported in various environments (Arah and Kirk 2000, Baker et al. 2001, Couture and Seitz 1983, Muramatsu et al. 1989, Santschi and Schwehr 2004, Xu et al. 2011a, Xu et al. 2011b, Xu et al. 2012, Yuita 1992, Yuita and Kihou 2005). 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-iodine compounds comprise up to 40% of total iodine in aqueous samples from estuaries, rivers, and rain (Santschi et al. 2012). Organic carbon interactions with  $^{129}\text{I}$  are discussed in more detail below.

## A.1.3 Aqueous Iodine Speciation at the Hanford Site

One reason why little is known about  $^{129}\text{I}$  at U.S. Department of Energy sites is because the analytical chemistry techniques to assay the extremely low ambient  $^{129}\text{I}$  concentrations ( $10^{-7}$  to  $10^{-11}$  M) have either not been readily available or the procedures are arduous (Kaplan et al. 2014). By combining recently developed analytical techniques (Schwehr et al. 2005, Zhang et al. 2010) applicable to iodine (both  $^{127}\text{I}$  and  $^{129}\text{I}$ ) with existing spectroscopic techniques for natural organic matter, it has become possible to address applied and basic geochemistry problems.

The only characterization of groundwater iodine speciation at the Hanford Site was by presented by Zhang et al. (2013). They measured both stable  $^{127}\text{I}$  and radioactive  $^{129}\text{I}$ , but only  $^{127}\text{I}$  had sufficient concentrations to permit full speciation measurements. The results from seven samples (two from the 200-UP-1 OU and five from the 200-ZP-1 OU) that were characterized in the work by Zhang et al. are presented in Table A.2.

**Table A.2.** Chemistry and  $^{127}\text{I}$  speciation of filtered Hanford Site groundwater (Zhang et al. 2013).

Well	pH	Eh (mV)	DOC (μM)	Ca (mg/L)	Si (mg/L)	Iodide (μg/L)	Iodate (μg/L)	Organo-I (μg/L)	Total I (μg/L)	Iodide (%)	Iodate (%)	Organo-I (%)
299-W14-11	7.7	250	50.2	59.4	7.5	0.35	59.50	15.18	75.03	0.5	79.3	20.2
299-W14-13	7.7	249	63.0	81.9	7.4	0.33	42.72	17.01	60.05	0.6	71.1	28.3
299-W14-15	7.9	220	25.5	35.4	5.6	0.43	32.63	5.66	38.72	1.1	84.3	14.6
299-W11-43	7.6	150	37.2	78.8	7.0	0.36	6.66	2.76	9.78	3.7	68.1	28.3
299-W11-88	7.8	321	15.6	22.1	15.0	0.17	7.08	2.08	9.33	1.8	75.9	22.3
699-36-70B	7.8	334	35.3	19.4	10.7	0.23	5.87	2.28	8.38	2.8	70.0	27.2
699-38-70B	7.8	125	21.5	29.7	8.9	1.38	4.18	3.68	9.24	15.0	45.2	39.8
Average	7.8	236	35.5	49.5	8.9	0.46	22.66	6.95	30.08	3.6	70.6	25.8

The groundwater samples studied by Zhang et al. (2013) had an extremely narrow range of alkaline pH values, from pH 7.6 to 7.9, which is consistent with the fact that the system is highly buffered to  $\text{CaCO}_3$  phases. The iodine plumes clearly have elevated levels of total OC and stable  $^{127}\text{I}$ . DOC in the groundwater ranged from 20 to 63  $\mu\text{M}$  with an average of 35  $\mu\text{M}$ . These DOC concentrations are similar to those recently reported in the humid region of the Savannah River Site (SRS) in Aiken, South Carolina: 10 to 60  $\mu\text{M}$  (Otosaka et al. 2011). The two wells closest to the disposal source, 299-W14-11 and 299-W14-13, had the greatest DOC concentrations and a relatively high calcium concentration. Si, as one of the most abundant trace elements in groundwater, had a concentration range between 6 and 15 mg/L.

Iodate was the dominant species for  $^{127}\text{I}$  in all the groundwater samples analyzed by Zhang et al. (2013), accounting for 45% to 84% of total iodine (Table A.2). Organo-iodine ranked second in abundance, comprising 15% to 40% of the total iodine. Iodide was generally the least abundant in the groundwater, accounting for < 4% of the total iodine, except for well 699-38-70B, where iodide accounted for 15%. On average, iodate accounted for 70.6%, organo-iodine accounted for 25.8%, and iodide accounted for 3.6% of the total aqueous iodine (Table A.2). For comparison, the average  $^{129}\text{I}$  speciation distribution at the F Area plume at the SRS was 31% iodide, 34% iodate, and 35% organo iodine (Otosaka et al. 2011). The two wells in the 200 West Area enriched in DOC, 299-W14-11 and 299-W14-13, did not have unusually high organo-iodine levels. In fact, the percentage of organo-iodine remained relatively stable regardless of the variation in DOC concentration.  $^{127}\text{I}$  concentrations were much greater near source terms (e.g., wells 299-W14-11, -13, and -15) than farther from the source terms. The source of the stable iodine is not known, but iodine commonly exists as a trace constituent of nitric acid. Therefore, the enormous volumes of nitric acid disposed during site operations are a likely contributing source for the groundwater iodine. There did not appear to be trends in the observed speciation with respect to either distance from the sources or whether the groundwater sample was collected from the high or low concentration portions of the plume, although only a limited number of samples were collected.

For radioactive  $^{129}\text{I}$ , Zhang et al. (2013) only detected iodate (Table A.3). If organo-iodine or iodide were present, they were below the analytical detection limit of 0.2 nM  $^{129}\text{I}$ .  $^{129}\text{I}$  concentrations decreased with distance from the source. Based on thermodynamic consideration, iodide was expected to be the dominant species in this system. However, it is possible that iodide and iodate, as opposed to only iodide, may have been the dominant species introduced into the cribs. One of the dominant operations that took place at T-Plant and B-Plant involved the use of hot, strong acids to remove cladding from spent fuels. To provide some insight into these conditions, Zhang et al. (2013) prepared 10 mg/L iodide in 1 M  $\text{HNO}_3$ , heated the solution at 80°C for 2 hours, then measured the speciation as: 4.5 mg/L iodide; 2.2 mg/L iodate; and below detection limit concentrations of  $\text{I}_2$ . These results showed a 55% decrease in iodide concentrations and 22% increase in iodate concentrations. Zhang et al. (2013) acknowledged that the lack of  $\text{I}_2$  detection may have been the result of gaseous  $\text{I}_2$  escaping the test vials. This test indicates that the existence of iodate in the system, as opposed to iodide, may, in part, be due to the nature of the process operations that generated the disposed liquids.



**Table A.3.**  $^{129}\text{I}$  speciation in filtered groundwater from the 200 West Area (Zhang et al. 2013).

Well	Iodide ( $\mu\text{g/L}$ )	Iodate ( $\mu\text{g/L}$ )	Iodate ( $\text{pCi/L}$ )	Organo-I $\mu\text{g/L}$	$^{129}\text{IO}_3^-/^{127}\text{IO}_3^-$ Ratio
299-W14-11	< DL <sup>(a)</sup>	0.22	42.5	< DL	0.004
299-W14-13	< DL	0.21	40.6	< DL	0.005
299-W14-15	< DL	0.13	25.9	< DL	0.004
299-W11-43	< DL	0.02	3.6	< DL	0.003
299-W11-88	< DL	0.02	4.1	< DL	0.003
699-36-70B	< DL	0.05	9.3	< DL	0.008
699-38-70B	< DL	0.02	3.0	< DL	0.004

(a) DL = detection limit; the detection limit for  $^{129}\text{I}^-$  and  $^{129}\text{IO}_3^-$  is 0.08 nM (2 pCi/L) and for organo- $^{129}\text{I}$  is 0.2 nM (5 pCi/L)

However, the introduction of  $^{129}\text{I}$  primarily as iodate into the subsurface environment would only partially explain the observed groundwater speciation (Table A.3) because stable iodine ( $^{127}\text{I}$ ) also exists predominantly as iodate. This fact suggests that there are natural biogeochemical drivers promoting the existence of iodine in the oxidized iodate state. The presence of iodine in multiple oxidation states and species within a given aqueous sample is consistent with previous reports of radioiodine and stable iodine speciation measurements at other DOE sites (Kaplan et al. 2014, Otosaka et al. 2011), an oligotrophic lake (Gilfedder et al. 2008, Gilfedder et al. 2009), and in marine systems (see references in Schwehr et al. [2005]). There are no iodine speciation studies reported for arid region groundwater similar to that at the Hanford Site. The  $^{129}\text{I}$  plume at the SRS is appreciably more acidic (pH 3.1 to 6.0) and more oxidized (as estimated by Eh) than the Hanford Site. All of the SRS groundwater samples had varying percentages of iodide, iodate, and organo-iodine that changed as a function of the plume's pH, Eh, and DOC conditions. Schwehr et al. (2005) reported that marine samples (that tend to have a pH of ~8, which is closer to the pH 7 to 8.5 of Hanford groundwater, but with relatively higher DOC concentrations) also tended to have even distributions of iodide, iodate, and organo-iodine. Gilfedder et al. (2009) reported monthly iodine speciation in an oligotrophic freshwater lake in the Alps. The lake had a pH between 8.0 and 8.5 and the DOC concentrations were very low (< 2 mg/L). Organo-iodine, iodide, and iodate concentrations varied greatly during the year, but organo-iodine was clearly the dominant species, generally accounting for > 80% of the iodine pool.

## A.2 Iodine Sorption to Sediments

Sorption information in this section considers the potential affect of iodine speciation on sorption. Previous Hanford sorption studies have been conducted exclusively with introduced iodide (Gee and Campbell 1980, Kaplan et al. 1996, Kaplan et al. 1998, Serne et al. 1993, Um et al. 2004).

### A.2.1 Iodine Speciation on the Solid Phase

In this appendix, the term “sorption” is used to describe iodine partitioning from the aqueous phase to a solid phase. It is meant to include adsorption, absorption, complexation, precipitation, co-precipitation, and covalent bonding between iodine and OC (especially aromatic moieties). When specific sorption processes are identified by one of the terms above, more specific mechanisms are implied.

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 include the use of X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure spectra (EXAFS) (Fuhrmann et al. 1998, Kodama et al. 2006, Schlegel et al. 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. This is because environmental samples tend to have iodine concentrations that are appreciably lower than the detection limits of this method. The detection limit of XANES is on the order of  $> 10 \mu\text{g } ^{129}\text{I} / \text{g soil}$  (Hou et al. 2009). Shimamoto and Takahashi (2008) conducted XANES studies on soils amended with  $55 \mu\text{g I/g soil}$ . 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  $\text{IO}_3^-$  to  $\text{I}_2$  (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 iodide but not iodate from solution (this is contrary to popular understanding that iodate sorbs more strongly than iodide to mineral surfaces due to iodate's strong Lewis base characteristic) and that biotite sorbed iodate but not iodide from solution. XANES was also used to independently determine  $K_d$  values of iodate and iodide uptake by a soil (Kodama et al. 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, OM, and residual) or sorbed by a specific process (e.g., ion 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 extraction designations are operationally defined parameters and, as such, do not carry mechanistic interpretations. In practice, interpretation of sequential extractions suffer a number of pitfalls that are especially important with contaminants that are more prone to complex change oxidation, or precipitate, such as phosphate or plutonium (Nirel and Morel 1990, Scheckel et al. 2003, Tessier and Campbell 1988). However, the sequential extraction method continues to be used, and in the absence of more sophisticated analytical tools, may provide useful insight into how strongly iodine sorbs to the solid phase.

Hou et al. (2003) used a water-soluble  $\text{NH}_4\text{OAC}$  exchange, carbonate ( $\text{NH}_4\text{OAC}$  [pH 5]), Fe-oxide ( $\text{NH}_2\text{OH}$ ,  $\text{HCl}$ , pH 2,  $80^\circ\text{C}$  to  $100^\circ\text{C}$ ), organic ( $\text{NaOH}$   $80^\circ\text{C}$  to  $100^\circ\text{C}$ ), and residue (remaining) fractionation scheme. Schmitz and Aumann (1995) analyzed soils collected from a reprocessing plant in Germany and reported that 39% to 49% of the  $^{129}\text{I}$  was associated with the water soluble fraction, whereas only 4% to 15% was associated with the organic fraction and 7% to 13% was associated with the residual fraction. However, a different distribution of stable iodine,  $^{127}\text{I}$ , 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 biological as well as geochemical factors. In the coastal and estuarine area of Sellafield, most of the  $^{129}\text{I}$  was associated with the oxides (53% to 66%) and organic (23% to 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  $^{129}\text{I}$  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).

### A.2.2 Influence of Sediment Organic Matter on Iodine Sorption

Several studies of sorption in shallow soils indicate that the OM is a primary control on iodine sorption (Assemi and Erten 1994, Bird and Schwartz 1997, Emerson et al. 2014, 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 United States, with natural OM 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 species became important only in sediments with low OM contents. Similarly, Whitehead (1973) demonstrated that iodine 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 by Bors et al. (1988), sorption of iodide correlated with OC content of samples that ranged from 6.2 to 0.06 wt% OC. Similar results were reported in studies involving different heating regimes (Muramatsu et al. 1990a, Muramatsu et al. 1990b). When all OM was removed by oxidation at 500°C, sorption of iodine was reduced substantially, but the decrease in sorption was much less when carbon remained as charcoal after heating to 500°C under a nitrogen atmosphere (Muramatsu et al. 1990a).

Another approach to demonstrating the importance of OM 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. Assemi and Erten (1994) compared sorption of iodine on a soil that was 70% OC to sorption onto various minerals and found that sorption was much stronger to the soil. They also found that iodine soil sorption decreased substantially when it was heated to 180°C or irradiated. Yu et al. (1996) demonstrated the importance of OM 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.

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 and Hawkins 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). Iodine  $K_d$  values were approximately seven times greater 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- to 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. Emerson et al. (2014) conducted identical sorption experiments under oxidizing (lab bench) and reducing (inside an inert atmosphere glovebox) environments using SRS sediments. They measured significantly lower  $K_d$  values when either iodide or iodate was added to the soil suspension under reducing conditions. They attributed this trend to the greater percentage of aqueous iodide under the reducing conditions. They also observed that, especially under oxidizing conditions, steady state was not obtained until after 8 weeks.

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 through abiotic, biotic, or both types of processes; (3) why iodine sorption to OM occasionally appears to enhance or have no effect on transport; (4) the potential for abiotic iodide oxidation; and (5) the role of naturally occurring sediment microbes in accumulating iodine and promoting iodide oxidation. Much of this uncertainty arises from the fact that humic substances are inherently heterogeneous and complicated. Natural OM has been described as 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 forces, such as hydrogen bonding, hydrophobic interactions, and electrostatic interactions.

Iodine bonding with soil organic matter (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). Studies conducted using SRS sediments indicated that the 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, and (3) iodine incorporation into the SOM (or iodination) is via covalent aromatic carbon-iodine bonding. The nature of the iodine bond to OM was further evaluated using various proton and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) techniques (Xu et al. 2012). Quantitative structure analyses by  $^{13}\text{C}$  direct-polarization magic-angle spinning (DPMAS) NMR and solution state  $^1\text{H}$  NMR of 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.,  $\text{NH}_2$ ), or hemicellulose-lignin-like complex with phenyl-glycosidic linkages.

The concentration of stable iodine bound to the fulvic acid fraction ( $519 \mu\text{g } ^{127}\text{I/g-carbon}$ ) was approximately an order of magnitude greater than the concentration of stable iodine bound to humic acid fractions ( $62 \mu\text{g } ^{127}\text{I/g-carbon}$ ) (Xu et al. 2011a, Xu et al. 2011b). 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 number of reactive binding sites. This difference may be the result of differences in the micro-molecular environment of the SOM that play additional key roles in the interactions between

iodine and OC. These micro-environments can influence the hydrophobic aliphatic periphery hindering the active aromatic cores and the hydrophilic polysaccharides favoring iodine accessibility toward hydrophilic iodine species.

It is indeed very important to study iodine speciation under ambient conditions (Schwehr et al. 2009, Zhang et al. 2011). Using an SRS subsurface wetland sediment and ambient iodine ( $10^{-8}$  M) consisting of 29% iodide, 4% iodate, and 67% organo-iodine, Schwehr et al. (2009) showed that by incrementally adding more total iodide, incrementally less organo-I and more iodide was detected in the aqueous phase of sediment suspensions at steady state. At 1000  $\mu$ M, only 3% of the iodine existed as organo-iodine. They attributed this change in iodine speciation to the added iodine swamping out the existing SOM binding sites in the soil. Similarly, Zhang et al. (2011) 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 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).

The SRS 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  $^{129}\text{I}$  concentrates in the riparian zone rose to extraordinarily high levels, > 1000 pCi/L (unfiltered samples) (Kaplan et al. 2013). Studies were undertaken to identify the process/mechanism responsible for the  $^{129}\text{I}$  concentration, and in particular to quantify and understand the role of OM and microbes (Xu et al. 2011a, Xu et al. 2011b, Xu et al. 2012). Laboratory studies using SRS solid and groundwater materials showed that between 72% and 77% of the newly introduced iodide or iodate could not be readily exchanged from 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 was likely covalently bound to aromatic structures within the SOM. Under very acidic conditions, abiotic iodination of SOM was predominant, whereas under less acidic conditions ( $\text{pH} > 5$ ), microbial enzymatically assisted iodination of SOM was predominant. It was concluded that although trace amounts of SOM-bound  $^{129}\text{I}$  could enhance transport, in general the SOM in the riparian zone immobilized the  $^{129}\text{I}$ .

Iodide added to a subsurface sandy 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, a portion 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 and was 23.89 mL/g for a desorption tests. Similarly for iodate, the (ad)sorption  $K_d$  value was 5.16 mL/g, and for a desorption test, the  $K_d$  value was 9.75 mL/g. By the end of these  $K_d$  measurements, portions of the iodide or iodate spikes had transformed to other species; hence, 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 an SRS groundwater and subsurface sediment with high OM concentrations, 10.8 mg/kg. At ambient concentrations ( $10^{-8}$  to  $10^{-7}$  M), iodide and iodate were significantly retarded ( $K_d$  values as high as 49 mL/g), whereas at concentrations three orders of magnitude greater, iodide traveled predominantly at the same rate as 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 to iodide and proceeded to migrate through the sediment in a similar manner as the iodide spike system.

#### **A.2.2.1 Influence of Inorganic Sediment Properties on Iodine Sorption**

Sorption of iodine on organic-poor soils is influenced primarily by mineralogy and pH, but complicated by aqueous iodine speciation (Dai et al. 2004, Dai et al. 2009, Kaplan et al. 2000, Mishra and Srinivasu 1992, Neal and Truesdale 1976, Sazarashi et al. 1994, Whitehead 1973, Whitehead 1974, Yoshida et al. 1992). 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 reported 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.

Monomineralic studies of iodine sorption show similar results as those using bulk soils, but provide an additional level of uniformity, permitting greater interpretation of the data. 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 and Seitz 1983, Neal and Truesdale 1976, Ticknor and Cho 1990). Fuhrmann et al. (1998) observed an exception to the general iodide-iodate sorption relationship, whereby 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) reported that iodate sorption to hematite increased with increased total dissolved solids. Their experiments were done in a synthetic groundwater with high concentrations of  $\text{Na}^+$ ,  $\text{Ca}^{+2}$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{-2}$  (2000, 2170, 6176, and 985 mg/L, 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 to 3 mL/g 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 OM. 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  $10^{-7}$  M sorbed to  $\text{TiO}_2$  powder. Yet organo-clays show even stronger sorption of iodide (Bors et al. 1994).

### A.3 Iodine Geochemistry at the Hanford Site

A review of stable and radioiodine geochemistry at the Hanford Site was recently completed by Kaplan et al. (2012). Since then, the first two studies dealing with radioiodine speciation as it relates to the Hanford Site, specifically the 200 West Area, were published: Xu et al. (2015) and Zhang et al. (2013). This section summarizes this previous review and incorporates the findings from these latest studies.

In a compilation of iodine sorption studies using Hanford sediments, Cantrell et al. (2003) concluded that the likely range of iodine  $K_d$  values was 0 to 2 mL/g and that the most common range of values was between 0 and 0.2 mL/g. The tests they reported were almost exclusively designed to measure the extent to which radioiodine sorbed under Hanford subsurface conditions, i.e.,  $K_d$  value measurements, and were not designed to understand iodine speciation or sorption mechanisms (Gee and Campbell 1980, Kaplan et al. 1996, Kaplan et al. 1998, Serne et al. 1993, Um et al. 2004). Among the underlying assumptions in each of these laboratory  $K_d$  measurements was that iodide was the primary species in Hanford groundwater (an assumption motivated by Figure A.1) and that it sorbed to sediments through the reversible anion exchange process (meaning iodine adsorbs and desorbs at equal rates). The recent results shown in Table A.2 and Table A.3 contradict the assumption that only iodide exists in the Hanford subsurface environment.

The reversibility of iodine sorption to Hanford sediments has also been questioned. 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. 2000, Um et al. 2004). Yet, there was a more-strongly binding radioiodine fraction that did not desorb under chemical conditions conducive to anion exchange. Using a subsurface sediment, (ad)sorption iodide  $K_d$  values were  $< 0.3$  mL/g (depending on iodide spike concentrations), whereas desorption  $K_d$  values using the same sediments were 1.41 to 4.15 mL/g. 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, but the desorption  $K_d$  was 1.4 mL/g. Hu et al. (2005) made similar observations in studies of iodine sorption to Hanford sediments. Xu et al. (2015) also reported significantly greater desorption  $K_d$  values than sorption  $K_d$  values in three 200 West Area sediments. When iodide was added, the sorption  $K_d$  values ranged from  $< 0.05$  to 5.64 mL/g and the desorption  $K_d$  values ranged from 11.9 to  $> 30$  mL/g. When iodate was added, the sorption  $K_d$  values ranged from 0.83 to 7.56 mL/g and the desorption  $K_d$  values ranged from 12.3 to 29.8 mL/g.

A geochemical process that describes strongly sorbing iodine is iodine partitioning to sediment OM. Xu et al. (2015) recently conducted studies related to this issue (Table A.4). Using three composite sediments recovered from the 200 West Area, iodate  $K_d$  values were on average 89% greater than iodide  $K_d$  values. These studies showed greater sorption in the sediments with higher OC and greater sorption of iodate than iodide to these sediments. It is especially noteworthy that this trend existed at the very low OC concentrations that naturally exist in the Hanford sediments (0.04 to 0.15 wt% OC). Additional measurements are needed to confirm this trend of  $K_d$  values with the extremely low OC levels existing at Hanford.

**Table A.4.** Iodide and iodate  $K_d$  values for composite sediments recovered from 200 West Area borehole cores (Xu et al. 2015).

Composite Sediment <sup>(a)</sup>	Organic Carbon (%)	Inorganic Carbon (%)	Total Sediment Iodine ( $\mu\text{g/g}$ )	Total DOC ( $\mu\text{M}$ ) <sup>(b)</sup>	Iodide-Spiked $K_d$ ( $\text{mL/g}$ ) <sup>(c)</sup>	Iodate-Spiked $K_d$ ( $\text{mL/g}$ ) <sup>(c)</sup>
H3	0.15	0.18	2.10	$94 \pm 17$	3.38	3.94
H1	0.12	0.92	4.79	$284 \pm 33$	0.08	1.78
H2	0.04	0.01	0.68	0	0.00	0.83

(a) H1 – 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.  
H2 – composite from different depths within one well (299-W11-92).  
H3 – composite of saturated zone sediments of two different wells: 299-W11-92 and 299-W15-226.

(b) Total DOC is the total OC released from the sediment to the aqueous phase ( $< 0.45 \mu\text{m}$ ) after 21 days of contact during the sediment/groundwater batch iodine uptake experiment.

(c) Suspensions were spiked with either iodide or iodate (as  $^{125}\text{I}$ ), but during contact period the spiked species transformed to other species. Consequently, these are not species-specific  $K_d$  values.

Another geochemical process that may result in the strong sorption of radioiodine to sediments is the co-precipitation of  $\text{IO}_3^-$  as a trace impurity in  $\text{CaCO}_3$  phases. Carbonate minerals in subsurface systems are constantly forming and dissolving. The size of the  $\text{IO}_3^-$  ion is the same as the  $\text{CO}_3^{2-}$  ion and can substitute for it in carbonate phases. It was shown that recently precipitated carbonate phases (formed by degassing  $\text{CO}_2$  from Hanford groundwater samples) scrubbed iodine from the aqueous phase and incorporated the iodate into the precipitated phase (Zhang et al. 2013) (Table A.5). The implications of this finding may provide a mechanism by which iodine is strongly bound to Hanford sediments, explaining why desorption is often found to be much slower than sorption (i.e., why desorption  $K_d$  values are greater than sorption  $K_d$  values).

**Table A.5.** Suspended particles formed by  $\text{CO}_2$  degassing from 200 West Area groundwater samples (Zhang et al. 2013).

Wells	Particle concentration (mg/L)	Total carbon (wt%)	Total $^{127}\text{I}$ ( $\mu\text{g/g}$ )	Total $^{129}\text{I}$ ( $\mu\text{g/g}$ )	Particulate $^{127}\text{I}$ (wt%) <sup>(a)</sup>	Particulate $^{129}\text{I}$ (wt%) <sup>(a)</sup>
299-W14-11	113.0	7.62	96.67	0.14	12.7	6.8
299-W14-13	114.3	6.69	80.68	0.20	13.3	10.0
299-W14-15	99.5	6.5	88.84	0.18	18.6	11.8
299-W11-43	133.5	7.99	54.64	0.08	42.7	37.5
299-W11-88	85.7	8.56	84.97	0.17	43.8	41.2
699-36-70B	87.1	7.44	63.57	0.18	39.8	24.9
699-38-70B	120.2	7.81	48.59	0.07	38.7	35.4
Average	107.6	7.5	74.0	0.15	29.9	23.9

(a) Particulate iodine percentage is defined as the percentage of iodine in particles vs. that the bulk groundwater (particulate & dissolved), expressed as:

$$[\text{particle concentration}] \times \text{TI}(\text{particle}) / ([\text{particle concentration}] \times \text{TI}(\text{particle}) + \text{TI}(\text{dissolved/filtered}))$$



Iodine speciation changed once the spike solution came into contact with the sediments, indicating that Table A.4 is not reporting species-specific  $K_d$  values, but instead represents  $K_d$  of a suite of iodine species. The importance of evaluating a species-specific approach to describing radioiodine speciation is that it may provide an  $^{129}\text{I}$  fraction that is nearly irreversibly bound to the sediment and may provide a more accurate representation of  $^{129}\text{I}$  transport.

The significance of the data in Table A.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  $^{129}\text{I}$   $K_d$  values, albeit conservative, adequately represent the sorption anticipated by the more strongly sorbing iodate and organo-iodine species. The presence of multiple iodine species would not influence the expected extent of a Hanford plume, as the presence of the fastest moving species, iodide, would not change. However, the presence of iodate or organo-iodine would be expected to move slower, thereby changing the distribution of the total  $^{129}\text{I}$  concentrations within the plume.

Chang et al. (2014) developed an integrated model describing multiple physiochemical and enzyme catalyzed reactions based on detailed iodine speciation data obtained from laboratory experiments using organic-rich and organic-poor soils from SRS. The model accounted for iodine speciation, inter-conversion kinetics ( $\text{I}^-$ ,  $\text{IO}_3^-$ , organo-I, and colloidal-I), reversible partitioning to soil organic matter and mineral surfaces, irreversible covalent bonding to SOM, and abiotic and biotic (enzymatic/catalyst-type) reactions. Modeling results strongly supported the assertion that iodine-SOM interactions dominate iodine geochemistry; the iodine uptake coefficient for SOM ( $K_d$ ) was an order-of-magnitude greater than that for mineral surfaces. The proposed model simulated well the iodine partitioning among the soil, colloid, and solution phases. The model revealed that during the first 14 days of contact, most iodine in soil was comprised of  $\text{I}^-$  or  $\text{IO}_3^-$  associated with mineral surfaces and reversibly bound to SOM. After 14 days, the continued uptake of iodine by soil was attributed primarily to the irreversible bonding of organo-iodine to SOM. Finally, the model was successfully validated using an independent experimental data set. This biogeochemical modeling study underscores the importance of capturing the dynamic nature of iodine speciation transformations and the importance of treating SOM as a sink (irreversible covalent bonding) and a source (colloidal- and organo-iodine mobile species) for subsurface iodine.

## A.4 Biological Iodine Conversion

### A.4.1 Overview

Biological cycling of iodine is an important process that likely affects fate and transport of iodine in the Hanford subsurface. Iodine can be present in the environment in the form of iodide ( $\text{I}^-$ ), molecular iodine ( $\text{I}_2$ ), iodate ( $\text{IO}_3^-$ ), and organic-iodine (Org-I) compounds, including volatile compounds, such as methyl iodide ( $\text{CH}_3\text{I}$ ). Understanding the different biological processes involved in cycling of iodine between the different species will allow for (1) better prediction of biogeochemical impacts related to transport, (2) development of better informed bioremediation strategies to control transport, and (3) processes driving current speciation in Hanford groundwater.

Microorganisms are important catalysts for the cycling of iodine in the environment, and can affect partitioning of iodine between water, soil, and air through redox transformations. Much of the existing knowledge about iodine biogeochemistry in the environment has been generated from studies looking at

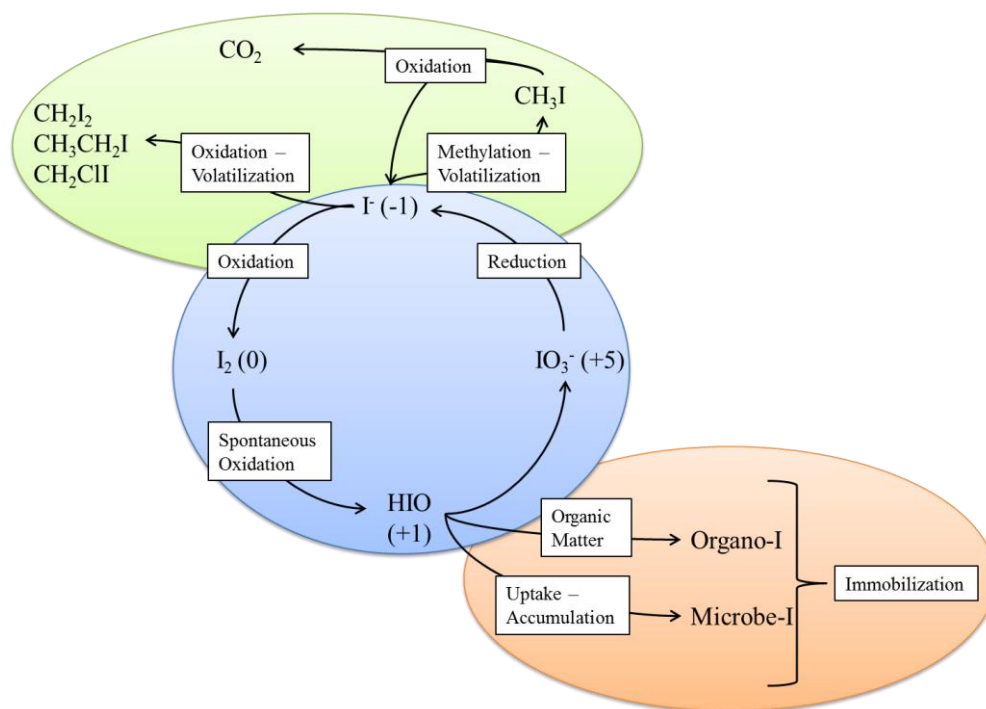
cycling of iodine, both  $^{127}\text{I}$  and  $^{129}\text{I}$ , in marine and freshwater environments (Gilfedder et al. 2009). Speciation of iodine in marine systems depends on geographical location, as well as depth in the water column (Chance et al. 2014). These differences are postulated to be related to the presence of oxygen and effects of redox on iodine oxidation and reduction. In oxic seawater, iodine speciation is dependent on where in the water column the samples are taken. Water from deep in the ocean contain low levels of  $\text{I}^-$  (~10 nM), while  $\text{IO}_3^-$  dominates, accounting for greater than 95% of the iodine present (Žic et al. 2008). Water samples at the surface and in some shelf seas have roughly equal distribution of  $\text{I}^-$  and  $\text{IO}_3^-$ . Reduction of  $\text{IO}_3^-$  near the surface has been hypothesized to occur in association with primary productivity, which is defined as the conversion of inorganic carbon to organic carbon by photosynthetic single (prokaryotes) and multicellular (algae) organisms (Finkel 2014). Many phototrophs have been characterized for their ability to reduce  $\text{IO}_3^-$  in these oxic environments through the activity of nitrate reductase enzymes. These enzymes are typically responsible for reduction of nitrate to nitrite by microorganisms. Concentrations of Org-I can approach 100 nm in near-shore environments. In contrast, in anoxic ocean environments, such as deep sea trenches, oxygen minimum zones, and the Black Sea,  $\text{I}^-$  is the dominant form and  $\text{IO}_3^-$  is absent. These results suggest that where oxygen is present,  $\text{I}^-$  oxidation to  $\text{IO}_3^-$  occurs and in the absence of oxygen,  $\text{IO}_3^-$  reduction to  $\text{I}^-$  is the dominant process.

More recently, due to accidents like Fukushima and subsurface contamination at DOE sites, such as Hanford, increased interest in understanding the effects of microbial transformation of radioiodine on fate and transport has been established (Hou et al. 2013, Kincaid et al. 2006, Zhang et al. 2013). Major pathways of iodine cycling affected by microbes, include volatilization of organic iodine compounds into the gas phase, oxidation and reduction of inorganic iodine species, accumulation of iodine species by microorganisms, and microbially mediated sorption of iodine into soil organic matter (Amachi et al. 2005a, Amachi 2008, Hu et al. 2009, Hu et al. 2012, Kaplan et al. 2013, Küpper et al. 2011). While these processes are discussed individually, there is often connectivity between the processes (e.g., iodide oxidation leading to volatilization and formation of organic iodine compounds). In addition, there are microbially catalyzed processes, such as iron and sulfate reduction, that indirectly influence iodine speciation.

The iodine cycle as proposed for the subsurface is shown in Figure A.2. One primary difference between the iodine cycle in the subsurface and in a marine system would be the absence of iodine conversion reactions catalyzed by phototrophs, as well as photo-oxidation of volatile iodine species in the atmosphere. Speciation of iodine, especially radioiodine, is important because speciation of iodine will affect interaction with geological media, which will in turn affect fate and transport.

When considering ex situ treatment strategies for iodine-contaminated groundwater, the complete iodine cycle, including phototrophs and photooxidation of volatile organic iodine species, must also be considered. Interconversion between iodine species will affect interaction with sorption technologies.

This section looks at biotransformation on iodine speciation, in a broad sense, and proposed effects on iodine fate and transport. While iodine species in the Hanford subsurface are predominantly iodate and organic iodine, understanding all aspects of iodine cycling is important and will help to determine how this species distribution was formed. Since both in situ and ex situ processes are relevant for remediation of iodine, all aspects of iodine cycling are discussed.



**Figure A.2.** Biological transformations associated with iodine cycling in the environment. The blue ellipse represents predominantly aqueous-phase iodine species. The orange ellipse represents predominantly solid-phase species of iodine associated with organic compounds (Organo-I) or accumulated in microbial biomass (Microbe-I). Some types of Organo-I may also be mobile in the aqueous phase. The green ellipse represents predominantly gas-phase volatile Organo-I compounds.

#### A.4.2 Iodide Oxidation

While iodide concentrations in Hanford groundwater are below 5% of the total iodine, waste knowledge indicates most iodine in the liquid waste should be in the form of iodide. For this reason, understanding oxidation of iodide is important to understanding the current species distribution in the Hanford groundwater. Bacterial oxidation of iodide has been recognized as an important part of the iodine cycle in marine environments for decades (Tsunogai and Sase 1969). Elucidation of an iodide oxidation mechanism based on an extracellular oxidative enzyme produced by *Pseudomonas iodooxidans* was first discussed in the 1970s (Gozlan and Margalith 1973, Gozlan and Margalith 1974). Iodide in an aquarium was oxidized to iodine, causing fish mortality; an extracellular peroxidase system, in the presence of polysaccharides, was shown to catalyze the reaction.

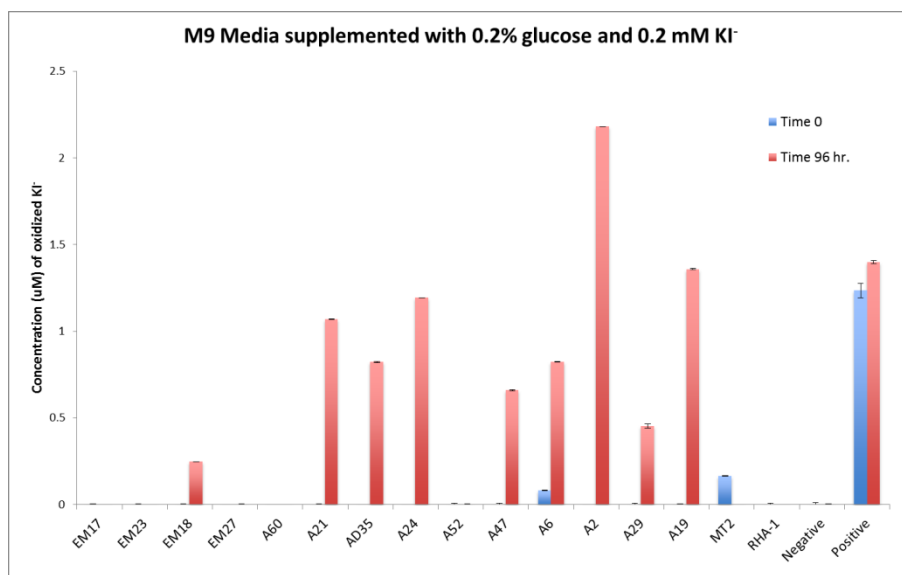
Two environments in which iodide-oxidizing bacteria have been found include natural gas brines and marine environments (Amachi et al. 2005b, Arakawa et al. 2012, Žic et al. 2008). Iodine-oxidizing bacteria have also been isolated from corroding pipes at an iodine production facility in China (Wakai et al. 2014). *Roseovarius tolerans* is an iodide-oxidizing bacterium that was isolated from natural gas brines, where populations of iodide-oxidizing bacteria were up to  $10^5$  colony forming units per milliliter of water (Amachi et al. 2005b). The oxidation of iodide to molecular iodine was catalyzed by an extracellular enzyme that required oxygen. Two bacteria closely related to *R. tolerans* have also been isolated from marine samples, and were able to produce free iodine from iodide (Fuse et al. 2003). Three

*Roseovarius* species capable of iodide oxidation to iodine were also isolated from water and biofilms collected from a natural gas plant. The marine bacterium *Roseobacter* species AzwK-3Gb, which has been characterized as a manganese-oxidizing bacterium, has also been shown to oxidize iodide to iodine (Li et al. 2014). Iodide oxidation was catalyzed by production of superoxides in the growth medium.

A number of bacteria from the *Firmicute* family, isolated from the F Area at SRS, were also shown to oxidize iodide to iodine (Li et al. 2012b). Hydrogen peroxide-dependent iodide oxidation was enhanced by the addition of organic acids, indicating that peroxy carboxylic acids were a strong oxidant for iodide oxidation. The effect of acids on iodide oxidation improved as the pH of the growth medium decreased from 9 to 4.

Production of the enzyme laccase, or other laccase-like multicopper oxidase (LMCO) enzymes produced by fungi and bacteria, has also been shown to catalyze the oxidation of iodide (Ihsen et al. 2014, Kulys et al. 2005, Suzuki et al. 2012). Iodide oxidation by *Roseovarius* species discussed above is thought to be catalyzed by a LMCO enzyme (Amachi et al. 2005b, Arakawa et al. 2012). An  $\alpha$ -Proteo-bacteria designated strain Q-1 that was isolated from iodide-rich natural gas brine water was shown to oxidize iodide to iodine using an oxidase-like enzyme (Suzuki et al. 2012). Characterization of the enzyme showed similarity to multicopper oxidase enzymes. Laccases and other LMCO enzymes have also been shown to catalyze addition of iodine to organic matter during the iodide oxidation process, yielding volatile organo-iodine species or more complex organo-iodine species. This function is discussed in a later section.

Microbial oxidation of  $I^-$  to  $I_2$  and  $IO_3^-$  is another important process that could affect iodine speciation in the Hanford groundwater. While  $I^-$  concentrations in Hanford groundwater are below 5% of the total iodine, the potential for biological  $I^-$  oxidation will provide insight into current speciation, and prevalence of  $IO_3^-$ , in the 200 West Area groundwater. A number of bacterial isolates from the Hanford groundwater have been shown to oxidize  $I^-$  to  $I_2$  (Figure A.3 and Table A.6). While not all bacterial species tested were able to oxidize  $I^-$ , most species tested appeared to have this physiological ability. Analyses are currently being performed to determine whether complete conversion to  $IO_3^-$  is occurring.



**Figure A.3.** Hanford isolates capable of oxidizing  $I^-$  (see Table A.6 for identity).

**Table A.6.** Identity of bacterial species isolated from Hanford groundwater that were tested for the ability to oxidize  $I^-$  to  $I_2$  and  $IO_3^-$ .

Strain	Affiliation (accession number)
EM17	<i>Ralstonia</i> sp. PNP11 (DQ887520.1)
EM23	<i>Pseudomonas frederiksbergensis</i> strain DSM 13022 (NR_117177.1)
EM18	<i>Pseudomonas</i> sp. PAMC 26822 (KF011696.1)
EM27	<i>Pseudomonas mandelii</i> strain NF22-1 (KF151354.1)
A60	<i>Cupriavidus necator</i> strain N-1 (NR_028766.1)
21	<i>Arthrobacter ilicis</i> strain ICMP 2608 (NR_104950.1)
AD35	<i>Agrobacterium tumefaciens</i> strain IAM 12048 (NR_041396.1)
A24	<i>Pseudomonas mosselii</i> strain CFML 90-83 (NR_024924.1)
A52	<i>Lysobacter niastensis</i> strain GH41-7 (NR_043868.1)
A47	<i>Shinella kummerowiae</i> strain CCBAU 25048 (NR_044066.1)
A6	<i>Pseudomonas mosselii</i> strain CFML 90-83 (NR_024924.1)
A2	<i>Bacillus thuringiensis</i> strain IAM 12077 (NR_043403.1)
A29	<i>Enterobacter hormaechei</i> strain 0992-77 (NR_042154.1)
A19	<i>Microbacterium invictum</i> strain DC-200 (NR_042708.1)
MT2	<i>Pseudomonas putida</i>
RHA1	<i>Rhodococcus jostii</i>

#### A.4.3 Iodine Bioaccumulation

Iodine is an element that accumulates in biological material, including vertebrates, algae, coral, sponges, lobworms, and shellfish. Accumulation of iodine is important from a health perspective because radioiodine concentrates in the thyroid gland in mammals. Most studies of iodine accumulation have been performed on thyroid tissue and in brown algae. More recently, iodine accumulation by bacteria, as well as other phototrophs, has been studied.

*Laminaria digitata* is a brown algae (kelp) that has been shown to accumulate iodine to levels ranging from 0.4% to 4.7% of the organism's dry weight, depending on the stage of growth (Küpper et al. 1998). This yields an accumulation of 30,000 times the iodine levels found in seawater (Colin et al. 2003, Küpper et al. 1998). X-ray absorption spectroscopy studies have shown that the accumulated form of iodine in *L. digitata* is iodide and that the purpose of iodide in this organism is to act as an inorganic antioxidant (Küpper et al. 2008). In this function, iodide scavenges reactive oxygen species, leading to efflux of the iodide into the external environment in the form of iodide and volatile iodocarbons (discussed in a later section). Iodine uptake and formation of iodo-organic compounds has been shown to be catalyzed by vanadium-dependent haloperoxidases, specifically iodoperoxidases (Colin et al. 2003, La Barre et al. 2010). These enzymes oxidize iodide to iodine ( $I_2$ ), hypiodous acid (HIO), which is then taken up into the cell, where it spontaneously reverts to iodide, which can be associated with cellular material (Verhaeghe et al. 2008).

Accumulation of iodine in other algal species and diatoms has also been demonstrated (Manley 2009, Osterc and Stibilj 2012, Shimura et al. 2012, Thorenz et al. 2014, van Bergeijk et al. 2013). Regardless of the species, uptake appears to occur through the mechanism of a haloperoxidase, with or without hydrogen peroxide.

Until recently, only a few instances of bacterial accumulation of iodine could be found. More recently, a number of aerobic bacteria have been found that are able to accumulate iodine (Amachi et al. 2005c, Amachi et al. 2005d, Fournier et al. 2014, Li et al. 2011, MacLean et al. 2004). Similar uptake of iodine has not been demonstrated in anaerobic bacteria, indicating that iodide uptake in bacteria may occur through oxidative processes. A vanadium iodoperoxidase from *Zobella galactanivorans* has been demonstrated (Fournier et al. 2014). Amachi et al. (2005c) demonstrated iodine uptake in a number of bacteria common to marine and terrestrial environments. One bacterium, *Arenibacter troitsensis* strain C-21, was able to accumulate 80% of a 0.1  $\mu\text{M}$  iodide solution. Uptake by this bacterium appeared to be catalyzed by hydrogen peroxide produced by a glucose oxidase enzyme (Amachi et al. 2007a). A proposed haloperoxidase enzyme then oxidizes the iodide using hydrogen peroxide as the oxidant, yielding iodine or hypoiodous acid, which then diffuses into the cell. These two species of bacteria are of particular interest because they are both members of the family *Flavobacteriaceae*, which have been found in groundwater at Hanford. Iodine accumulation by bacteria is more pertinent to the subsurface of Hanford, where bacteria are the dominant organism that may possess this ability.

Experiments have not been performed to understand the ability of Hanford bacteria to accumulate stable or radioiodine.

#### A.4.4 Iodine Volatilization

Methyl iodide is a volatile iodine compound that plays a large role in carrying iodine from terrestrial and marine environments to the atmosphere. Many examples of iodine volatilization can once again come from looking at the activity of algae and microalgae in oceans and other freshwater bodies of water. Likewise, some terrestrial environments harbor bacteria that catalyze methylation of iodide, yielding volatile iodine species. As mentioned previously, organic iodine compounds are commonly produced during the oxidation of iodide to iodine, while in other bacteria, iodide is directly methylated by the enzymatic activity of microbes. During oxidation of iodide to iodine, a range of organic compounds are produced, while direct methylation produces methyl iodide. Once in the atmosphere, methyl iodide is broken down by sunlight and the iodine produced is deposited back to terrestrial or marine environments with precipitation. While there is potential for volatilization of iodine in the subsurface, photolysis would not be expected.

On a global level, phototrophs in marine environments have been shown to produce up to  $10^6$  to  $10^{10}$  g of methyl iodide ( $\text{CH}_3\text{I}$ ) per year (Stemmler et al. 2014). In addition,  $\text{CH}_3\text{I}$  is known to play a significant role in the global iodine cycle (Klick and Abrahamsson 1992).  $\text{CH}_3\text{I}$  has been demonstrated by microalgae, phytoplankton, and cyanobacteria (Hughes et al. 2011, Karlsson et al. 2008, La Barre et al. 2010, Thorenz et al. 2014). In most cases, methylation of iodide is thought to be catalyzed by the activity of the enzyme S-adenosyl-L-methionine (SAM) methyltransferase (Ohsawa et al. 2001, Toda and Itoh 2011).

In-depth analysis of bacterial involvement in volatilization of iodine from soil was part of a study looking at cycling of iodine in rice paddy soil (Muramatsu et al. 1996). Likewise, volatile iodine production was noted in soil, seawater, and bacterial cell suspensions (Amachi et al. 2000). Analysis of volatile fractions recovered in silver mesh or granular activated carbon indicated that volatile species were primarily organo-iodine, rather than volatile  $\text{I}_2$ . Involvement of soil bacteria in the volatilization of iodine was further supported in a study comparing iodine emissions from rice paddy, upland field, forest, and wetland soil (Amachi et al. 2003). Microbial catalysis of volatile iodine species was further supported when iodine emissions ceased when soils were autoclaved or when antibiotics were added to inhibit

bacterial activity. Interestingly, iodine emission was not affected when fungal inhibitors were added, showing the prevalence of bacteria in iodine volatilization from soils. Molecular characterization of bacteria isolated from the soil showed that iodine-volatilizing bacteria are widespread and not confined to a specific group of bacteria. Bacteria were distributed in Proteobacteria ( $\alpha$ ,  $\beta$ , and  $\gamma$  subdivisions), *Cytophaga-Flexibacter-Bacteriodes* (CFB) Group, and high G+C Gram-positive bacteria.  $\text{CH}_3\text{I}$  was the primary volatile iodine species found during these studies.

A similar study was performed using samples of seawater to determine whether bacteria were involved in volatilization of iodine in marine environments (Amachi et al. 2004). Similar groups of bacteria,  $\alpha$ - and  $\gamma$ -Proteobacteria, and the CFB group were isolated and shown to volatilize iodide to  $\text{CH}_3\text{I}$ . Experiments also showed that iodate was not converted to  $\text{CH}_3\text{I}$ . When samples were autoclaved, filtered to remove bacteria, or antibiotics were added, little volatilization of iodide was shown. One of the bacteria isolated during these experiments was able to volatilize up to 2% of the total iodine added to the growth medium to  $\text{CH}_3\text{I}$ .

Bacteria isolated from brackish water were shown to methylate a range of halides, including iodide (Fujimori et al. 2012). Five genetically distinct species belonging to the genera *Erythrobacter* or *Pseudomonas* were able to produce  $\text{CH}_3\text{I}$  when grown in the presence of iodide. These bacteria represent species of  $\alpha$ - and  $\gamma$ -Proteobacteria. Analysis of the headspace of the vials showed primarily  $\text{CH}_3\text{I}$  and not other iodinated volatiles.

Recent research has shown that a wide variety of marine and terrestrial bacteria also volatilize iodine through the methylation of iodide (Amachi et al. 2001). Six out of ten terrestrial bacteria tested were shown to methylate iodide, while seven out of ten marine bacteria were shown to methylate iodide. In these same studies, anaerobic bacteria (*Clostridia* and methanogens) did not appear to methylate iodide. The cell extract from a *Rhizobium* species was shown to methylate iodide when SAM was used as the methyl donor, indicating that bacteria may use a similar mechanism to phototrophs.

Along with  $\text{CH}_3\text{I}$ , a number of other volatile organo-iodine compounds can be formed during oxidation of iodide. Two bacterial species closely related to *Roseovarius tolerans* that were isolated from marine samples were able to produce  $\text{CH}_2\text{I}_2$  and  $\text{CH}_2\text{ClI}$  from constituents in the growth medium (Fuse et al. 2003). Molecular iodine was also a product of iodide oxidation by these bacteria. Bacteria that produced the volatile organic compounds were grown in media containing yeast extract and peptone.

Since volatilization of iodine has been shown to be linked to  $\text{I}^-$  oxidation, this process may occur in Hanford groundwater since  $\text{I}^-$  oxidation was demonstrated by Hanford bacterial isolates. Formation of volatile organo-iodine species during the  $\text{I}^-$  oxidation process is currently being tested.

#### **A.4.5 Iodination of Organic Material**

In addition to volatile organic compounds, oxidation of iodide can also lead to the generation of more complex organic iodine compounds, including iodinated soil organic matter. This process becomes very important for soils that contain large amounts of organic material. Some of the peroxidase enzymes discussed in the iodide oxidation section also catalyze iodination of other organic compounds. Laccases are involved in a process called “humification,” in which polyaromatic humic acid structures become linked through phenoxy-free radical catalyzed polymerization (Chefetz et al. 1998). In terrestrial ecosystems, such as peatlands, this process is thought to be key in storage of iodine in these environments (Keppler et al. 2003). Iodine bound to the humic fraction of peat material can be stable for thousands of years.

In a study using nine organic soils, experiments showed that iodide removal was increased in soils with microbial activity (Koch et al. 1989). In soils that were fed with glucose, iodide decreased, while in soils that had been treated with thymol or gamma irradiation, iodide removal was depressed. While microbial iodide removal was thought to be the dominant process in these soils, some residual iodide removal activity occurred, indicating some abiotic factors may have been responsible. Specific mechanisms of iodine removal were not determined, only iodide removal with organic containing soil and microbial activity was determined.

A microbial enzyme that is responsible for the breakdown of lignin and other aromatic-containing compounds has also been shown to catalyze iodination of soil organic matter. These enzymes are copper oxidase enzymes commonly known as laccases. Laccases are produced by fungi and bacteria and are commonly found in many soil microorganisms. As discussed above, laccases have also been implicated in the oxidation of iodide. Formation of organo-iodine is thought to occur when iodide is transformed into more reactive species such as  $I_2$ , HIO, or  $I_3^-$  (Moulin et al. 2001). Similar results were demonstrated using the radioactive iodide tracer  $^{125}I^-$ . Soils with high laccase activity showed positive correlation to enhanced sorption of iodide (Seki et al. 2012). Treatment of soil by autoclaving, gamma-irradiation, or heat significantly inhibited iodide sorption. Likewise, the addition of laccase to autoclaved soils partially restored iodide sorption to the soils. Laccase oxidation to  $I_2$  or HIO was thought to drive iodide sorption to the soils.

A study of soils from Chiba, Japan, indicated that in the soil column, pore-water contained organo-iodine and iodide species, while analysis of the soil fraction indicated only organo-iodine (Shimamoto et al. 2011). As with previous studies, laccase activity in these soils was high and was likely driving the process.

Similar results have been demonstrated in organic-rich soils at SRS. Analysis of  $^{127}I$  and  $^{129}I$  in surface soils near the F Area of SRS indicated that the humic acid fraction of the soil organic matter accounted for up to 56% of the iodine in the soil (Xu et al. 2011b). Iodination of the soils appeared to be affected by molecular size of the soil organic matter fraction, composition, and availability of iodine binding sites. In soil resuspension experiments, to simulate surface runoff and stormwater flow, newly added iodide and iodate appeared to be irreversibly bound to organic-rich riparian soil (Xu et al. 2011a). The remainder of the iodine appeared to form complexes that represent a truly mobile organo-iodine fraction. Soils from a wetland zone adjacent to the F Area was enriched for microbes capable of iodide oxidation (Li et al. 2012a). Results showed that when microbes were active in some soils, organo-iodine was the dominant species, with iodide being the second most abundant. As demonstrated in other studies, removing microbial activity by autoclaving stopped the organo-iodine formation process.

Since iodination of organic material has been shown to be linked to  $I^-$  oxidation, this process may occur in Hanford groundwater since  $I^-$  oxidation was demonstrated by Hanford bacterial isolates. Understanding this process will be important since approximately 25% of the iodine species in Hanford groundwater is organo-iodine.

#### **A.4.6 Iodate Reduction**

Iodate can be used as an alternate electron acceptor for growth, and is converted to iodide under anaerobic or microaerobic conditions. To date, nitrate-reducing, iron-reducing, and sulfate-reducing bacteria have been found to reduce iodate. Likewise, a number of phototrophs, such as diatoms and

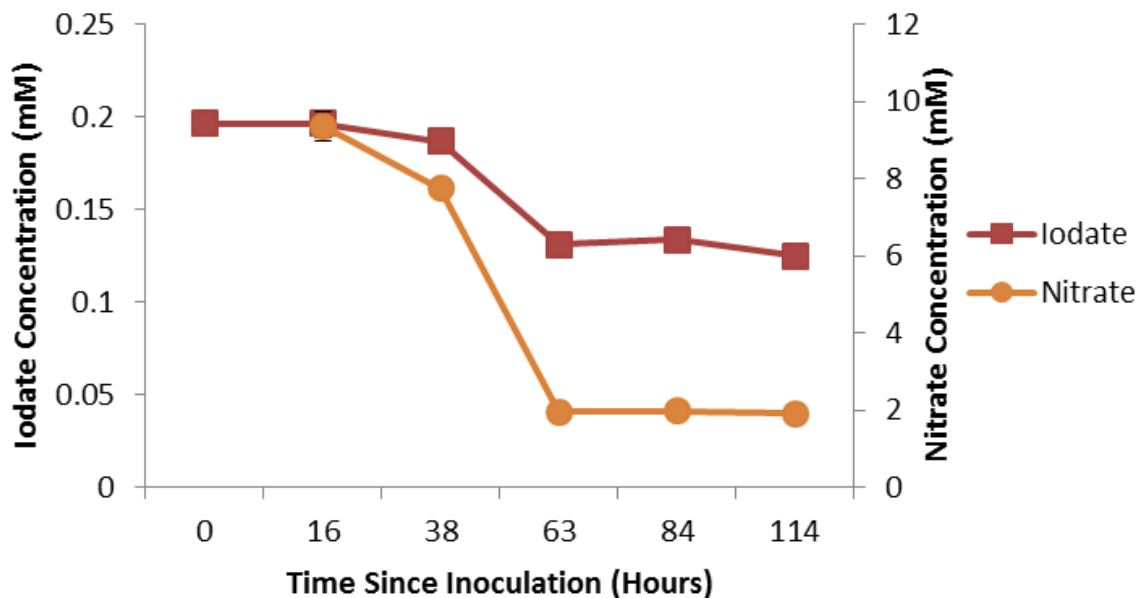


algae, have been shown to reduce iodate (Bluhm et al. 2010, Chance et al. 2007, Chance et al. 2009, Hung et al. 2005). Few studies have demonstrated the bacterial reduction of iodate. Amachi et al. (2007b) demonstrated the dissimilatory iodate reduction by *Pseudomonas* sp. SCT, isolated from marine sediment slurry, in the presence of nitrate under anaerobic conditions. During these experiments, cells pre-grown without iodate did not reduce it, nor could they reduce iodate aerobically (Amachi et al. 2007b). The iodate-reducing enzyme, which was called an iodate reductase, was found in the periplasmic space, which is located between the inner and outer membranes of this bacterium.

Tsunogai and Sase (1969) reported several marine laboratory strains of nitrate-reducing bacteria to reduce iodate aerobically, concluding that iodate is reduced in a coupled mechanism by nitrate reductases (Tsunogai and Sase 1969). Other studies have shown microbial reduction of iodate with anaerobic cell suspensions of *Desulfovibrio desulfuricans* and marine bacterium *Shewanella putrefaciens* (Counsell et al. 1997). In addition to these two bacterial species being able to directly reduce iodate to iodine, soluble ferrous iron and sulfide, as well as iron monosulfide produced by the metabolism of these microbes, were shown to abiotically reduce iodate to iodide. Likewise, *S. putrefaciens* strain MR-4 was shown to reduce iodate to iodide (Farrenkopf et al. 1997).

Reduction of  $\text{IO}_3^-$  has also been demonstrated by the perchlorate respiring bacterium strain GR1 (Kengen et al. 1999). An enzyme that was isolated from the periplasm of this bacterium was shown to reduce perchlorate, chlorate, nitrate, iodate, and bromate.

Sediments from traps incubated in iodine-contaminated groundwater at the Hanford Site have yielded a number of bacterial isolates that can oxidize or reduce different iodine species. Since the dominant iodine species in 200-UP-1 groundwater has been shown to be  $\text{IO}_3^-$ , experiments were performed to determine the ability of various Hanford isolates to reduce  $\text{IO}_3^-$  in the presence of nitrate, a common co-contaminant in the 200-UP-1 groundwater. One isolate designated AD35, which is most closely related to *Agrobacterium tumefaciens*, has been shown to reduce  $\text{IO}_3^-$  to  $\text{I}^-$  in the presence of nitrate (Figure A.4). Iodate reduction occurred under both anaerobic and microaerobic conditions. When the culture was spiked with nitrate,  $\text{IO}_3^-$  concentrations continued to decrease in the culture medium.



**Figure A.4.** Iodate reduction in the presence of nitrate by an *Agrobacterium* species isolated from sediment traps that were incubated within an iodine plume in the 200 West Area.

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