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UP-1 Evaluation Plan for Iodine - Draft A

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

U.S. DEPARTMENT OF ENERGY | Richland Operations Office

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Richland, Washington 99352

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H. Lee
Pacific Northwest National Laboratory

J. G. Morse
Department of Energy - Richland Operations Office

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P.O. Box 550
Richland, Washington 99352

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Prepared by Pacific Northwest National Laboratory for the U.S. Department of Energy Assistant Secretary for Environmental Managment

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Acronyms and Abbreviations

ARAR	applicable or relevant and appropriate requirement
BBI	Best Basis Inventory
BSS	Basic Safety Standards
CDI	capacitive deionization
CEDE	committed effective dose equivalent
CFB	*Cytophaga-Flexibacter-Bacteriodes*
CSM	conceptual site model
DOC	dissolved organic carbon
DOE	U.S. Department of Energy
DPMAS	direct-polarization magic-angle spinning
DWS	drinking water standard
EPA	U.S. Environmental Protection Agency
ESIX	electrochemically switched ion exchange
EXAFS	extended X-ray absorption fine structure spectra
IAEA	International Atomic Energy Agency
ICRP	International Commission on Radiation Protection
LMCO	laccase-like multicopper oxidase
MCL	maximum contaminant level
MNA	monitored natural attenuation
MZCL	mixing zone concentration limit
NBS	U.S. National Bureau of Standards
NMR	nuclear magnetic resonance
NRC	U.S. Nuclear Regulatory Commission
OC	organic carbon
OM	organic matter
OU	Operable Unit
RAO	remedial action objective
RI/FS	remedial investigation/feasibility study
ROD	Record of Decision
SAM	S-adenosyl-L-methionine
SAMMS	self-assembled monolayers on mesoporous silica
SOM	soil organic matter
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
UNSCEAR	United Nations Scientific Committee on the Effects of Atomic Radiation
WHO	World Health Organization
XANES	X-ray absorption near-edge structure

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1.0 Introduction

This document addresses a requirement in the Record of Decision (ROD) for the 200-UP-1 Operable Unit (OU) at the Hanford Site in southeastern Washington State to prepare a technology evaluation plan for remediation of iodine-129 (^{129}I) contamination in the subsurface. Currently, groundwater in the 200-UP-1 OU is contaminated with carbon tetrachloride, uranium, nitrate, chromium (total and hexavalent), ^{129}I, technetium-99 (^{99}Tc), and tritium. The preferred alternative in the ROD specifies 35 years active remediation using groundwater pump-and treat, monitored natural attenuation (MNA) for portions of the contaminated groundwater, and institutional controls until cleanup levels for unrestricted use are met (DOE 2012a). Hydraulic containment of groundwater is being performed while the treatment technology evaluation, as described in this plan, is performed and until a subsequent remedial decision for the I-129 plume is made.

From the ROD (p. 3):

> "The technology evaluation for I-129 that was completed as part of the feasibility study determined that there is no current treatment technology that can achieve the federal drinking water standard (DWS) of 1 pCi/L for the I-129 concentrations present in the 200-UP-1 OU. DOE will evaluate potential treatment options for I-129 as part of the selected remedy through further technology evaluation. If one or more viable technologies are identified, treatability tests will be conducted for those technologies."

In addition, the ROD (p. 47) states:

> "Hydraulic containment is achieved by installing injection wells at the leading edge of the I-129 plume, which provides flow path (gradient) control. Hydraulic containment of the I-129 plume would be implemented until a subsequent remedial decision for the I-129 plume is made.
>
> "Alternatives 2 through 4 [note: alternative 3 is the selected remedy] include a waiver of the federal DWS of 1 pCi/L for I-129 which is an ARAR. Alternatives 2 through 4 are for an interim remedial action which will only be part of the total remedial action for 200-UP-1 OU that will attain or otherwise waive the ARAR for I-129 upon completion of remedial action as required by CERCLA Section 121(d)(4), —Cleanup Standards,‖ —Degree of Cleanup.‖ A subsequent ROD will be needed to complete the total remedial action for the 200-UP-1 OU. In the event a viable treatment technology is not available, the use of a technical impracticable waiver under 40 CFR 300.430(f)(l)(ii)(c) may need to be considered as part of the final remedy."

The 200-UP-1 Remedial Design/Remedial Action Work Plan (DOE/RL-2013-07, Draft A) further defined the requirements for the technology evaluation as follows:

> "An iodine-129 technology evaluation plan will be prepared to outline the study approach and provide an updated feasibility analysis of potential treatment options. The feasibility analysis will evaluate available iodine-129 treatment options based on cost, effectiveness, and implementability to identify viable options. A viable option would be cost effective and implementable. The plan will also summarize relevant performance data from the

200 West Groundwater Treatment Facility, if available. The plan will be subject to review and approval by the lead regulatory agency. If one or more viable technologies are identified as a result of the feasibility analysis, treatability testing may be required to evaluate the technology or process options in more detail and would be conducted in accordance with a treatability test plan.

"The technology evaluation for iodine-129 completed as part of the feasibility study (DOE/RL-2009-122) determined that there is currently no treatment technology that can achieve the federal DWS of 1 pCi/L for the iodine-129 concentrations present in the 200-UP-1 OU. Therefore, P&T is not currently a viable remedy for this contaminant. The ROD requires that DOE evaluate potential treatment options for iodine-129 as part of the selected remedy through further technology evaluation. The approach to the evaluation will be defined in an iodine-129 technology evaluation plan to be reviewed and approved by EPA. The evaluation will include an update to the conceptual model for the plume, a review of current literature, and a feasibility analysis of potential treatment options. The feasibility analysis will evaluate available options based on cost, effectiveness, and implementability, and will serve as the basis for path-forward recommendations, such as treatability testing. If one or more viable technologies are identified, treatability testing will be conducted in accordance with a treatability test plan subject to review and approval by EPA."

This document provides the technology evaluation plan to address the above requirements and to fulfill the associated Tri-Party Agreement milestone, M-016-192, "Submit I-129 Technology Evaluation Plan Draft A to EPA as defined in the 200-UP-1 RD/RA WP," which is due June 17, 2016.

This report provides a plan for evaluation of technologies for remediating ^{129}I. Particular emphasis has been placed on updating critical biogeochemical information that was not available at the time of the 200-UP-1 feasibility study. This new information is important to understanding the fate and transport of ^{129}I and the applicability of some remediation options. This evaluation plan includes the following:

- A review of regulatory guidance for ^{129}I
- Identification of processes that control ^{129}I fate and transport in the environment
- An updated conceptual model for ^{129}I in the 200-UP-1 OU
- An evaluation of exposure risk from ^{129}I
- A review of remediation options for both vadose zone and saturated zone ^{129}I

The report incorporates information from numerous sources. Appendix A provides information to assist the reader on scientific notation, units of measure, radioactivity units, and radiological dose units.

1.1 Worldwide Sources of Iodine-129 in the Environment

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, Table 1.1). However, only the ^{129}I isotope is of long-term concern.

Worldwide, chemical separation or reprocessing of nuclear fuel is used to recover isotopes for other uses, which has resulted in the release of radioiodine into the environment. Iodine-129 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}I isotope to the environment; it has been estimated that radioiodine emissions to the atmosphere from the Hanford reprocessing operations between 1944 and 1972 were 266 kg (Raisbeck and Yiou 1999). The two largest commercial reprocessing facilities in the world are at Sellafield (UK) and La Hague (France); in 1999, a year of high discharge, their combined discharge rates were 330 kg/yr, with approximately 75% coming from La Hague. The cumulative discharges from La Hague (1975–1997) and Sellafield (1961–1997) are estimated to have been 1640 and 720 kg, respectively (Raisbeck and Yiou 1999). Both sites have authorized liquid discharge permits for treated waste to the ocean, the NE Irish Sea for Sellafield and the English Channel for La Hague. By contrast, the total amount of ^{129}I released at the Hanford Site was less than that released in a single year by these two reprocessing facilities (Table 1.2).

Table 1.1. Estimated inventory of radioiodine isotopes produced in a representative material irradiated by a production reactor (adapted from Kantelo et al. 1990). These calculations demonstrate that radioiodine total activity decreases rapidly, and after 100 days only ^{129}I and ^{131}I are present.

Iodine Isotope	Half-Life	Curies Remaining at Selected Times after Irradiation			
		Initial	24 hours	100 Days	200 Days
128	25 min	1.5×10^{4}	—	—	—
129	1.57×10^{7} y	2.3×10^{-1}	2.3×10^{-1}	2.5×10^{-1}	2.5×10^{-1}
130	12.36 h	1.4×10^{5}	3.5×10^{4}	—	—
130m	8.84 min	9.2×10^{4}	—	—	—
131	8.02 d	7.6×10^{7}	7.0×10^{7}	1.3×10^{4}	2.3×10^{0}
132	2.30 h	1.1×10^{8}	8.9×10^{7}	—	—
133	20.8 h	1.8×10^{8}	8.2×10^{7}	—	—
133m	9 s	3.8×10^{6}	—	—	—
134	52.5 min	2.0×10^{8}	1.3×10^{0}	—	—
134m	3.52 min	1.3×10^{7}	—	—	—
135	6.57 h	1.6×10^{8}	1.5×10^{7}	—	—
136	83.4 s	7.9×10^{7}	—	—	—
136m	46.9 s	5.0×10^{7}	—	—	—
137	24.5 s	7.9×10^{7}	—	—	—
138	6.23 s	4.1×10^{7}	—	—	—
139	2.28 s	1.8×10^{7}	—	—	—
140	< 1 s	4.1×10^{6}	—	—	—
141	< 1 s	8.6×10^{5}	—	—	—
142	< 1 s	1.1×10^{5}	—	—	—
Totals:		**1.0×10^{9}**	**2.6×10^{8}**	**1.3×10^{4}**	**2.5×10^{0}**

Table 1.2. Major sources of ^{129}I in the environment.

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

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

Of the 19 radioiodine isotopes in Table 1.1, only ^{129}I and iodine-131 (^{131}I) may remain in significant quantities in the environment beyond 100 days after a release. Only ^{129}I is of concern by a year after release. Table 1.3 shows the radiochemical properties of these two isotopes.

Table 1.3. Radiochemical properties of ^{129}I and ^{131}I.

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

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

1.2 Hanford Site Sources and Subsurface Distribution of Iodine-129

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}I that 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 primary sources known or suspected to have contributed to contamination in the 200-UP-1 OU include liquid process wastes and wastewater generated during historical operations of S Plant (REDOX) Plant, U Plant, S-SX Tank Farm, and U Tank Farm (DOE 2012a). The contaminants observed in groundwater within the 200-UP-1 OU resulted from planned releases of these process liquid wastes and wastewater to the soil via discharge to engineered structures (cribs, trenches, ditches, ponds, leach fields, or injection wells). Unplanned releases resulted from inadvertent releases of the same or similar waste materials from tanks, pipelines, or other waste storage or conveyance components. Most of the liquid waste and wastewater that contributed to observed groundwater contamination migrated downward through the soil column by gravity to reach the underlying groundwater. Vadose zone flux is continuing to contribute contaminants to the groundwater. Additional investigation of vadose zone contamination will be conducted before a final remedy is selected for the 200-UP-1 OU (DOE 2012a).

The total amount of ^{129}I generated at Hanford during reactor operations is well known: 49.4 Ci of ^{129}I was produced during reactor operations according to ORIGEN2 fuel activity estimates (Watrous et al. 2002). However, the distribution of that well-defined inventory 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 offgas absorbent devices (silver reactors) at chemical separations plants (PUREX, B-Plant, T-Plant, and REDOX)

Table 1.4 summarizes current estimates for these mechanisms. This table does not include the ^{129}I inventory that may be disposed at Hanford from receipt of offsite waste.

Table 1.4. Current estimates of I-129 distribution at Hanford.

I-129 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[a]	Best Basis Inventory (BBI) obtained from the Tank Waste Information Network System (April 23, 2015) (https://twins.labworks.org/twinsdata/default.htm). 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}I.
Captured by offgas 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}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}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}I and other mobile contaminants reached the aquifer, they spread, producing large-scale plumes (Figure 1.1 and Figure 1.2). Three ^{129}I plumes in groundwater at the Hanford Site cover an area greater than 50 km^2. 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}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}I plume associated with the 200 West Area is in the 200-UP-1 operable unit (OU).

The ^{129}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}I concentrations are all less than 50 pCi/L, with most less than 10 pCi/L, though above the DWS of 1 pCi/L. Furthermore, natural stable iodine (^{127}I) is also present in the aquifer at much greater concentrations than ^{129}I. The presence of ^{127}I is important because most remediation technologies are not specific for a particular iodine isotope (e.g., Kaplan et al. 2012). In addition, ^{127}I and ^{129}I have the same chemical behavior in the subsurface, so the presence of ^{127}I will influence the biogeochemical processes for ^{129}I.

1.3 Biogeochemistry of Iodine-129 in Hanford Subsurface

The subsurface behavior of radioiodine is complex because it can exist in multiple physical states (solid, liquid, or gas) and oxidation states (-1, 0, +1, +5, and +7) at environmentally relevant conditions (Kaplan et al. 2012). Initial studies to understand iodine biogeochemistry in both groundwater and on mineral surfaces was performed using groundwater and soils from the Hanford 200 West Area (Zhang et al. 2013; Xu et al. 2015). Iodine speciation and isotope analysis was performed on groundwater from seven monitoring wells (Zhang et al. 2013). Average total stable iodine-127 (^{127}I) concentrations ranged from 8.4 to 75 μg/L, with an average of 30.8 μg/L. Iodate (IO_3^-) accounted for the bulk of the ^{127}I (22.6 μg/L), followed by organo-iodine (6.95 μg/L) and iodide (0.46 μg/L). Radioiodine concentrations were orders of magnitude lower, with an average concentration of 0.1 μg/L, which was calculated from IO_3^--associated ^{129}I concentrations because organo-iodine and I^- forms of ^{129}I were below detection limits. Although the mass-based ^{129}I concentrations are low, in the seven wells tested, ^{129}I activity ranged from 3.6 to 42.5 pCi/L, concentrations above the 1 pCi/L drinking water standard. One unexpected result from these studies was the formation of $CaCO_3$ precipitates in sample bottles used during the study. These precipitates had concentrations averaging 107.6 mg/L and contained high amounts of both ^{127}I (74.0 μg/g) and ^{129}I (0.15 μg/g). These precipitates were thought to be formed during degassing of CO_2 when the groundwater was pumped to the surface. Precipitation of $^{127}I/^{129}I$-laden $CaCO_3$ could be stimulated by the addition of $CaCl_2$ and Na_2CO_3.

Aqueous-phase iodine species interact with sediments, allowing adsorption/surface complex formation, as well as transformation, depending on the geochemistry of the sediment used (Xu et al. 2015). In the study by Xu et al. (2015), sequential extraction of the three sediments showed that there were strongly bound forms of iodine on the mineral surface. Only 0.4 to 6.6 wt% of the iodine was readily released, 0% to 1.2% was associated with Fe and Mn oxides, and 2.9% to 39.4% of the iodine was associated with $CaCO_3$ on the mineral surface. Organic carbon associated with the surface of the sediments was hypothesized to account for 57.1% to 90.6% of the total iodine present. Iodine adsorption isotherms indicated that IO_3^- was more strongly sorbed to the sediments than iodide. Likewise, desorption of iodine from the sediment surface was always greater than sorption, regardless of the species tested. These studies showed that even low organic carbon on the soils appeared to control iodine binding because as organic carbon concentration increased, greater values of uptake, desorption, and residual iodine were found for these sediments. One other interesting finding for these sediments was that IO_3^- was readily reduced, meaning the IO_3^- is sorbed and then reduced, yielding I^- which would desorb.

Microbes isolated from sediment traps incubated in monitoring wells within the ^{129}I the 200 West UP-1 OU showed the ability to transform both IO_3^- and I^-. Bacteria common to groundwater were shown to reductively transform IO_3^- to I^- when grown in the presence of simple carbon sources and nitrate. Likewise, a number of bacterial isolates, as well as mixed communities isolated from these sediment traps, were able to oxidize I^- to I_2 when stimulated with a variety of carbon sources.

1.4 Health Risks Associated with Iodine-129

Iodine is an essential nutrient for humans and animals; however, it also poses a risk because it concentrates in the thyroid gland where it decays and causes damage. Twenty-three radioactive isotopes of iodine have been identified (Bustad et al. 1983), but only one stable isotope exists, ^{127}I, which is widely distributed in the ocean, rocks, and in organisms. It is generally found as iodide or iodate.

Iodine is more prevalent in marine than in terrestrial environments. Atmospheric concentrations generally diminish inland from the oceans, reducing the amount transferred to inland soils from precipitation scavenging (rainfall) and dry deposition. At 15.7 million years, ^{129}I has the longest half-life of iodine isotopes. Because it decays very slowly, any ^{129}I released to the environment represents a permanent addition to the total inventory of iodine in the biosphere (Bustad et al. 1983). The mobility of ^{129}I, its long half-life, and toxicity make it a risk driver for remediation where abundant quantities were disposed to the environment.

The risk posed by iodine can be broadly categorized as both long-term and short-term. The short-term risks result from exposure to the short-lived isotope, ^{131}I, with a half-life of 8 days. Iodine-131 decays to stable xenon-131 quickly, but the high specific activity of ^{131}I makes it an immediate threat to exposed individuals. An example of short-term risk from ^{131}I is exposure to discharges during the Chernobyl accident (Guiraud-Vitaux et al. 2008). More than 90% of stable or radioactive iodine in the human body is concentrated in the thyroid (Zaichick and Choporov 1996) and once there, beta particles (primarily 606 keV, 89% abundance) and gamma rays (primarily 364 keV, 81% abundance) bombard nearby tissue, promoting thyroid cancer. The long-term risks of iodine are those resulting from exposure to and biological uptake of the long-lived isotope, ^{129}I. By virtue of these differences in radioactivity (or half-lives), ^{129}I is a long-term risk, associated with DOE's current groundwater contamination and nuclear waste disposal.

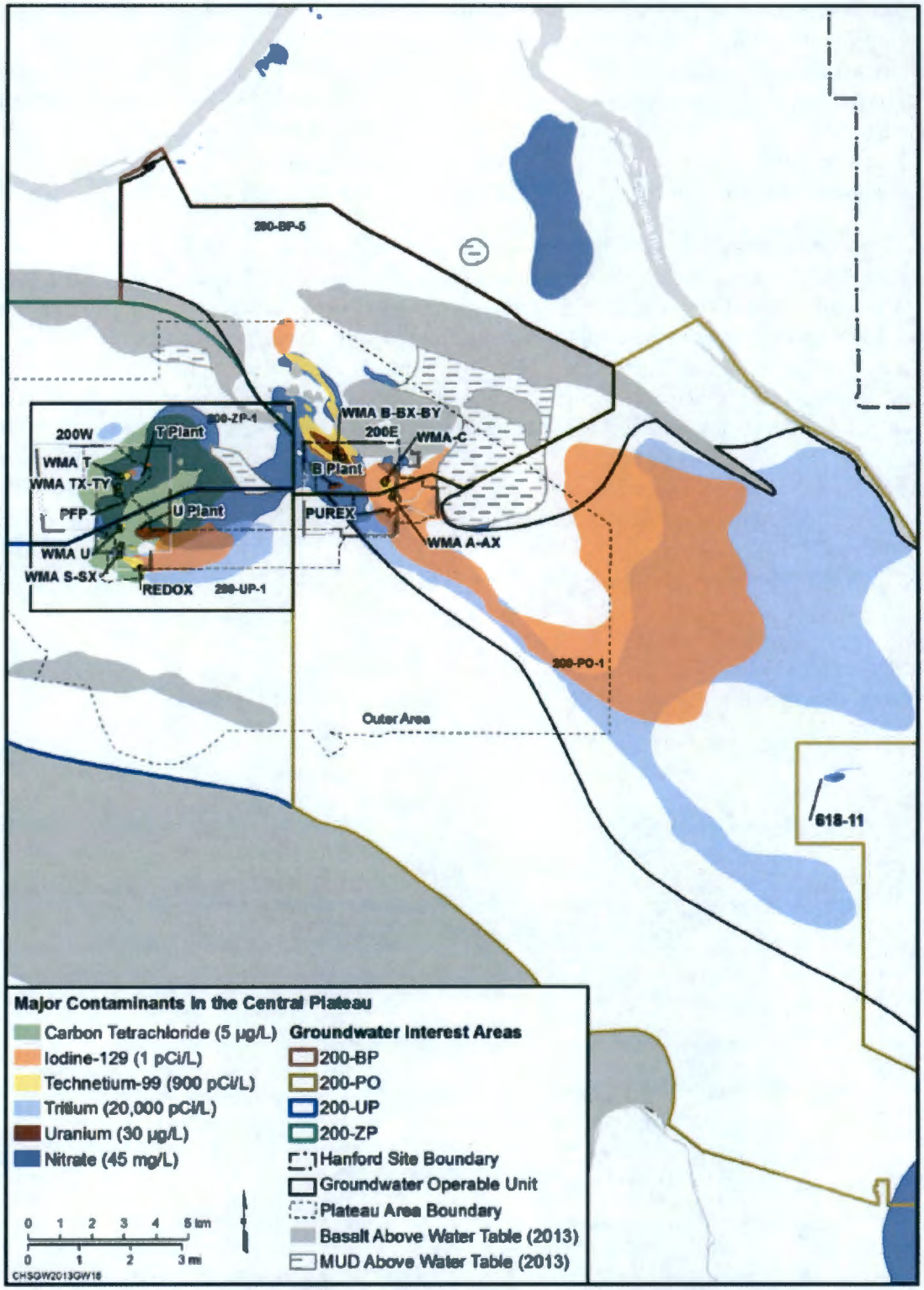

Figure 1.1. ^{129}I and other contaminant plumes associated with the 200 East and 200 West Areas on the Hanford Site. Figure adapted from DOE 2014.

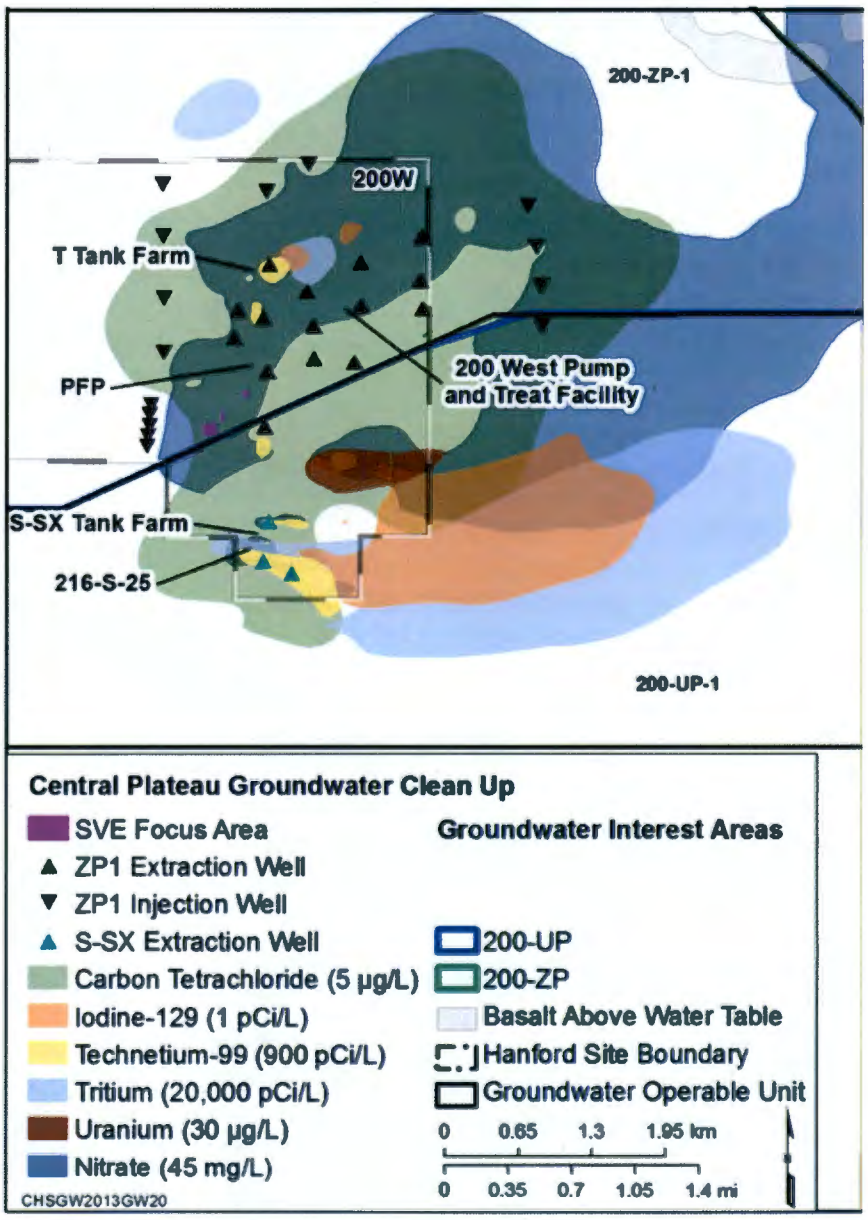

Figure 1.2. Groundwater plume map in the 200 West Area (including 200-UP-1 and 200-ZP-1 OUs). The plumes primarily emanate from disposal cribs located near U Plant and S Plant (DOE 2012b).

Among the key technical challenges associated with remediating the ^{129}I plumes in the Hanford Site Central Plateau are that the plumes are very large (~50 km^2) and dilute, and the DWS is very low. The leading edges of the plumes are several kilometers, greatly limiting implementation of a deep, permeable reactive barrier or a pump-and-treat strategy because of the large scale. Another important challenge is that the ^{129}I concentrations, while being above the DWS of 1 pCi L^{-1}, are extremely dilute. Ninety percent of the groundwater samples analyzed in this area are $\leq$ 3.5 pCi L^{-1} (DOE 2012b). Furthermore, natural stable iodine, ^{127}I, also exists in the plume and is present in much greater concentrations. In order for most strong sorbents to work effectively to lower ^{129}I concentrations, they would also have to lower

natural iodine concentrations by about two orders of magnitude (Kaplan et al. 2012). As natural iodine concentrations decrease during treatment, Hanford sediments would release more ^{127}I as a consequence of the subsurface system adjusting to the altered adsorption/desorption and solubility equilibrium. Hence, the large size of the ^{129}I plumes, the very low target concentration, and the presence of high relative concentrations of the stable isotope greatly limit practical remediation options in the Central Plateau.

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2.0 Regulatory Guidance for Iodine-129

This section provides an overview of the regulatory requirements and guidance for ^{129}I in groundwater. It summarizes the technical basis for the DWS and discusses technical issues associated with regulation of this contaminant. Regulatory decisions for ^{129}I in groundwater at the Savannah River Site (SRS) are discussed to provide examples of how national regulatory standards have been applied to ^{129}I in groundwater. This is followed by a discussion of international guidelines applicable to radionuclides in drinking water. Finally, an overview of applicable or relevant and appropriate requirements (ARARs) is provided.

2.1 Beneficial Use Standard for 200-UP-1 Groundwater

The National Contingency Plan (40 CFR 300) establishes an expectation to "return useable ground waters to their beneficial uses wherever practicable, within a timeframe that is reasonable given the particular circumstances of the site. When restoration of ground water to beneficial uses is not practicable, the EPA expects to prevent further migration of the plume, prevent exposure to the contaminated ground water, and evaluate further risk reduction" (40 CFR 300.430(a)(1)(iii)(F)). EPA generally defers to state definitions of groundwater classification provided under EPA-endorsed Comprehensive State Groundwater Protection Programs (EPA 1988). Based on the anticipated yield and natural water quality, the State of Washington has determined that the aquifer setting for the 200-UP-1 OU meets the WAC 173-340-720 definition for potable groundwater, which is the highest recognized beneficial use. Under EPA's groundwater classification program, 200-UP-1 OU groundwater would be designated Class II-B, which is groundwater that is not a current source of drinking water but is a potential future source. Consistent with the beneficial use determinations of Washington State and EPA, DOE intends to remediate the groundwater to drinking water standards. Consequently, groundwater protection is the principal focus of the regulatory discussion for the remainder of this section.

2.2 Federal Drinking Water Standard for Iodine-129

The following statements summarize the current basis for regulation of ^{129}I in drinking water, including the derivation of the maximum contaminant level (MCL) that remains in place today. ^{129}I is a beta emitter and the basis for its regulation is the same as for other beta/photon-emitting isotopes.

- For anthropogenic beta particles and photon radioactivity (e.g., gamma radiation), EPA considers an annual cumulative dose equivalent of less than 4 mrem to the total body or any internal organ to be protective of human health. This limit was established by the National Interim Primary Drinking Water Regulations (EPA 1976). The estimated concentration for selected radionuclides that would yield a 4 mrem/yr dose for 2 L per day water intake was reported in Table IV-2A (EPA 1976). This value was calculated to be 1 pCi/L for ^{129}I.

- The Radionuclides Notice of Data Availability Technical Support Document (March 2000) states:

  "It should be noted that [in 1976] EPA intended to express the MCL for man-made radionuclides in terms of the annual dose rate (millirem per year) from continuous ingestion. EPA considered, but rejected, the idea of specifying the MCL in terms of radioactivity concentrations (pCi/L) for individual beta and photon emitters in view of the short length of time such limits would be appropriate. The dose conversion factors for

ingested radioactivity available at that time were becoming obsolete and the ICRP was developing new models. ***When appropriate models for doses due to environmental contamination became available, the Agency intended to revise the Interim Regulations to permit the use of newer data. However, before the Agency could act, the 1986 Amendments to the SDWA finalized the Interim Primary Drinking Water Regulations, making them National Primary Drinking Water Regulations***." (EPA 2000a; emphasis added)

2.3 New MCLs for Anthropogenic Beta Particle and Photon Radioactivity Proposed in 1991

- In 1991, EPA proposed to retain the 4 mrem/yr dose limit for beta particle and photon radioactivity but proposed to derive MCLs for specific radionuclides using an updated method to yield a more uniform level of risk across all radionuclides. This updated method based the regulatory limit on the committed effective dose equivalent (CEDE). This method derived the concentration for a specific radionuclide based on the radiosensitivity of an individual organ. In 1976, EPA did not have an accepted method for equalizing risks. This was corrected in the 1991 proposed rule when EPA adopted the CEDE radiation protection philosophy recommended by the International Commission on Radiation Protection (ICRP 1977).
- The derived MCL for ^{129}I in the 1991 proposed rule was 21 pCi/L, increased from the 1976 derived concentration of 1 pCi/L. Using metabolically derived dose calculations, the derived concentrations for most beta particle and photon emitters increased in 1991, as compared to the values calculated in 1976 (see Table III-2, EPA 2000a).
- The proposed rule was never finalized, largely because of concerns of commenters and Congress over the most effective way to regulate radon (EPA 2000a).

2.4 Final Rule for Radionuclides under the National Primary Drinking Water Regulations

In December 2000, EPA issued the Final Rule for Radionuclides under the National Primary Drinking Water Regulations (65 FR 76708, December 7, 2000), which states:

> "Based on the need for further evaluation of the various risk management issues associated with the MCL for beta particle and photon radioactivity and the flexibility to review and modify standards under the Safe Drinking Water Act (SDWA), the current MCL for beta particle and photon radioactivity will be retained in this final rule, but will be further reviewed in the near future."
>
> "Lastly, some portions were contingent upon 1991 risk analyses, e.g., MCL revisions to the 1976 MCLs for combined radium-226 and -228, gross alpha particle radioactivity, and beta particle and photon radioactivity. The portions required under SDWA and the portions intended to make the radionuclides NPDWRs more consistent with other NPDWRs are being finalized today. ***The portions contingent upon the outdated risk analyses supporting the 1991 proposal are not being finalized today, in part based on updated risk analyses***." (EPA 2000b; emphasis added)

Table 2.1. Excerpt from Table I-1 of 2000 Final Rule (EPA 2000b)

Provision	1976 rule (current rule)	1991 proposal	2000 final rule
Beta/Photon Radioactivity MCL	• ≤ 4 mrem/y to the total body or any given internal organ • Except for H-3 and Sr-90, derived radionuclide-specific activity concentrations yielding 4 mrem/y based on NSB Handbook 69 and 2 L/d • H-3 = 20,000 pCi/L; Sr-90 = 8 pCi/L • Total dose from co-occurring beta/photon emitters must be ≤ 4 mrem/y to the total body of any internal organ	• 4 mrem/y effective dose equivalent (EDE) • Re-derived radionuclide-specific activity concentrations yielding 4 mrem/y EDE based on EPA RADRISK code and 2 L/d • Total dose from co-occurring beta/photon emitters must be < 4 mrem/y EDE	Maintain current MCL based on the newly estimated risk level associated with the 1991 MCL. This MCL will be reviewed within 2 to 3 years based on a need for further re-evaluation of risk management issues.

"Newly estimated risk level associated with the 1991 MCL" appears to refer to EPA 2000a.

2.5 Regulatory Approach to Iodine-129 Contamination in Groundwater at Other DOE Sites – Savannah River Site (SRS)

Iodine-129 is present in the groundwater at SRS from past wastewater discharges to the seepage basins in the F Area and H Area. These basins received acidic wastewater from F Area and H Area separations facilities. Both sets of basins are regulated under the Resource Conservation and Recovery Act as hazardous waste disposal facilities.

For the F Area seepage basin, a corrective action plan has been put in place to remediate the contaminated portions of the uppermost groundwater aquifer. In 1997, a water treatment system was installed to treat metals and radionuclides. An extraction/reinjection system was used to allow tritium to decay. In 2003, a small-scale pilot study was conducted to determine if a system of injecting alkaline solution into the groundwater would enable a successful passive remediation system. Because ^{129}I was not affected by the alkaline solution, in 2008 an innovative technology using silver chloride to capture ^{129}I was tested. Tests results were promising and late in 2008 the Underground Injection Control Permit Application was modified to include this remedy.

For the F Area groundwater, the compliance strategy was originally set in the 1997 ROD (WSRC 1997a) for the Old F Area Seepage Basin. A regulator-approved groundwater mixing zone application (WSRC 1997b) was used to derive mixing zone concentration limits (MZCLs) that would meet MCLs at a specified compliance point (i.e., boundary wells). The MCL and MZCL values for ^{129}I were 1 pCi/L and 48 pCi/L, respectively.

In 2000 and 2001, exceedances of up to 5.69 pCi/L at the compliance boundary were detected for ^{129}I (as well as for other contaminants). As a result, a ROD amendment was prepared (WSRC 2004) directing that further investigation and monitoring of the groundwater in this area be incorporated into the General Separations Area Western Groundwater OU. A scoping summary document was prepared in 2013 (WSRC 2013) and is updated annually to reflect new data and to review adequacy of the monitoring

systems. The current SRS groundwater management strategy (WSRC 2011) shows continued characterization under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) through about 2022, with an amended ROD to be issued subsequently.

2.6 International Standards

Most countries other than the United States use a scheme for regulation of radiation and radioactive materials based on recommendations of the International Atomic Energy Agency (IAEA). Local laws in many countries mandate the use of the IAEA recommendations. All ICRP recommendations and all IAEA Basic Safety Standards (BSS) are based on total effective radiation dose from all sources and all radionuclides. Individual radionuclides are not separately regulated or limited beyond their contribution to the total dose.

The IAEA recommendations are based on a hierarchical system of recommendations by other scientific bodies:

- The scientific understanding of human risk of radiation exposure is summarized regularly by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR). This committee was established by the UN General Assembly in 1955 to provide unbiased international consensus on the risks of radiation exposure. These radiation risk estimates provide the scientific basis for radiation protection. Governments and organizations throughout the world rely on the committee's estimates as the scientific basis for evaluating radiation risk and for establishing protective measures (UNSCEAR 2013, 2012, 2010, etc.).
- The UNSCEAR risk estimates are used by the ICRP to establish internationally accepted concepts and principles of radiation protection: i.e., justification, optimization, and limitation of radiation exposures. The ICRP is an independent, non-government, not-for-profit organization established to advance for the public benefit the science of radiological protection, in particular by providing recommendations and guidance on all aspects of protection against ionizing radiation. The ICRP establishes recommended dose limits for workers and members of the public (ICRP Publications 103 [ICRP 2007], 60 [ICRP 1991], 26 [ICRP 1977]). ICRP Publication 2 (ICRP 1959) is the basis for the current EPA requirements for drinking water MCLs; ICRP Publication 26 is the basis for current U.S. Nuclear Regulatory Commission (NRC) worker and public dose limits for nuclear operations; DOE uses a combination of ICRP Publication 30 (ICRP 1979) and Publication 72 (ICRP 1995) dosimetry models.
- The IAEA uses the UNSCEAR and ICRP recommendations as the basis for setting international radiation safety standards. These are published as the BSS. The most recent BSS was issued as General Safety Requirements Part 3 (IAEA 2014).

The ICRP recommendations as implemented in the BSS set radiation dose limits for the public. The limits are conditioned on the nature and timing of the radiation exposure:

- The basic limitation for what are called "planned exposure situations" (those for normal operation of nuclear facilities) is 1 mSv/yr (100 mrem/yr); however, this overall limit may be apportioned to different activities and "constraints" set for each activity. In addition, a level of dose so low as to be regulatorily unimportant (generally less than 0.01 mSv) may be granted "exemption" from regulatory controls.

- The BSS also sets radiation dose limits for "emergency exposure situations," which are basically responses to accidents. Emergency response workers are allowed doses of up to 20 to 100 mSv, if properly monitored and controlled.
- Finally, the BSS sets radiation dose limits for "existing exposure situations," for example, those subsequent to a nuclear accident or from *past activities that were never subject to regulatory control or that were subject to regulatory control but not in accordance with today's requirements*. This category also includes areas of high natural background, airline travel by crew members, and space flight. In addition, this category includes radiation protection strategies developed to reduce exposure when remedial actions and protective actions have been determined to be justified, such as the removal or reduction of the source giving rise to the exposure. These dose limits are also meant to apply when longer-term protective actions are needed that could include restrictions on (1) the use of construction materials; (2) consumption of foodstuffs; or (3) land use or access to land, water, or buildings. The dose limit under these circumstances is up to 20 mSv/yr.

Based on ICRP guidance, the World Health Organization (WHO) has issued guidelines for radionuclides in drinking water (WHO 2011). The current guidelines are based on the ICRP recommended approach for situations of prolonged radiation exposure of the public. According to the ICRP, in planned exposure situations, it is prudent to restrict the prolonged component of the individual dose to 0.1 mSv in any given year (ICRP 2000). Importantly, 0.1 mSv/yr is equal to 10 mrem/yr, which exceeds the EPA guidance of 4 mrem/yr given in Table 2.1.

Once a national government adopts an individual dose criterion of 0.1 mSv from 1 year's consumption of drinking water, WHO recommends an assessment methodology for controlling radionuclide health risks from drinking water that involves three steps (WHO 2011):

- Undertake initial screening for both gross alpha activity and gross beta activity. If the measured activity is below the screening levels of 0.5 Bq/L for gross alpha activity and 1 Bq/L for gross beta activity, no further action is required.
- If either of the screening levels is exceeded, the concentrations of individual radionuclides should be determined and compared with the guidance levels (see WHO 2011, Table 9.2 and Annex 6).
- The outcome of this further evaluation may indicate that no action is required or that further evaluation is necessary before a decision can be made on the need for measures to reduce the dose.

Table 9.2 of WHO 2011 provides guidance levels for common radionuclides, while Annex 6 provides guidance levels for less common radionuclides, including ^{129}I. The guidance level adopted by the WHO for ^{129}I is 1 Bq/L (27 pCi/L). This is the concentration for which annual consumption of drinking water would result in a dose of 0.1 mSv/yr (10 mrem/yr).

In Europe, ocean discharges from both Sellafield and La Hague nuclear facilities include ^{129}I resulting from nuclear fuel reprocessing operations. These discharges are regulated by the OSPAR Convention. The overall objective relative to radioactive substances is "to prevent pollution of the maritime area from ionizing radiation through progressive and substantial reductions of discharges, emissions and losses of radioactive substances, with the ultimate aim of concentrations in the environment near background values for naturally occurring radioactive substances and close to zero for artificial radioactive substances" (OSPAR 2009). Radionuclide specific targets are not defined. The Convention does not extend to groundwater protection.

2.7 Overview of Applicable or Relevant and Appropriate Requirements

The process of identifying and selecting remedial alternatives for the protection of human health and the environment involves the identification of ARARs. ARARs for an evaluation of ^{129}I in groundwater include the federal and state regulations mentioned above. A full list of ARARs is included in Appendix B; federal ARARs are listed in Table B.1 and Washington State ARARs are listed in Table B.2. The rationale for use and possible application of each ARAR are also identified in Table B.1 and Table B.2.

The requirements for the evaluations to date of 200-UP-1 OU have focused on 40 CFR 300 (National Oil and Hazardous Substances Pollution Contingency Plan) and WAC 173-340-720 (DOE 2012). Both of these requirements concern the protection of human health and support the selection of the DWS for ^{129}I. The selection of a groundwater remedy must (1) be protective of human health and the environment and (2) meet the ARARs or satisfy the criteria for an ARAR to be waived. The approach taken in the 200-UP-1 Remedial Investigation/Feasibility Study (RI/FS) is based on the MCL as established in the federal DWS (40 CFR 141) and Washington State's DWS (WAC 173-340-200).

The consideration of alternatives for remedial options for ^{129}I in groundwater requires an additional evaluation of federal and state requirements, or ARARs. Under CERCLA (40 CFR 300.430(f)(1)(ii)(C)), if an alternative is not expected to achieve compliance with a given ARAR, a waiver may be granted under the following circumstances:

1. The alternative is an interim measure and will become part of a total remedial action that will attain ARARs at the remedy completion.
2. Compliance with the requirement will result in greater risk to human health and the environment than other alternatives.
3. Compliance with the requirement is technically impracticable from an engineering perspective.
4. The alternative will attain a standard of performance that is equivalent to that required under the otherwise applicable standard, requirement, or limitation through use of another method or approach.
5. With respect to a state requirement, the state has not consistently applied, or demonstrated the intention to consistently apply, the promulgated requirement in similar circumstances at other sites within the state.

ARARs will be assessed with the development and evaluation of new remedial options.

2.8 References

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3.0 Controlling Processes

As discussed in Section 1.0, ^{129}I-containing waste produced during plutonium production at Hanford was released to the environment as liquid waste was discharged to ponds, cribs, ditches, and trenches. Once in the subsurface environment, the ^{129}I becomes part of the terrestrial iodine cycle along with any ^{127}I present in the systems. As part of the iodine cycle, biological, geochemical, and physical processes catalyze changes in iodine speciation, which in turn affects fate and transport in the subsurface. Processes affecting cycling of ^{127}I are the same for ^{129}I, so the processes discussed can be considered for both isotopes.

This section summarizes the biogeochemical processes that may affect iodine transport in the Hanford subsurface. A more exhaustive description of the global iodine cycle, as well as geochemical and biological processes affecting iodine speciation and associated reactions, is presented in Appendix C. In addition, iodine contamination at Hanford and the associated biogeochemistry are compared to conditions and biogeochemical drivers at SRS.

3.1 Aqueous Iodine Chemistry

Both stable iodine (^{127}I) and radioiodine (^{129}I) are found in groundwater beneath the 200 West UP-1 OU at $^{129}IO_3^-/^{127}IO_3^-$ ratios ranging from 0.003 to 0.008, indicating much higher ^{127}I concentrations in the groundwater. Stable iodine concentrations were much greater in monitoring wells near source terms than in wells more distal 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 used during operations are a likely contributing source for the groundwater iodine. There do not appear to be any trends in this data with respect to distance from the sources or whether the groundwater sample was collected from the highly impacted or less impacted portion of the plume. Proximity to the four primary sources, Tank T-106, T-26 Crib, S-1,2 Crib, S-7 and U-10 Crib, also did not appear to influence iodine speciation distribution.

Reactions for several iodine species are shown in Table 3.1, 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.

Table 3.1. Reactions and log K association constants of selected aqueous iodine species (Kaplan et al. 2014).

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

Various forms of iodine can also react with organic molecules, such as natural organic matter in subsurface environments. Formation of organo-iodine compounds can be driven by abiotic and biotic processes. Abiotic processes include redox reactions with minerals, or radiolytic processes that might occur during nuclear processing.

Inorganic iodine chemistry under conditions associated with most ^{129}I environmental plumes is somewhat simplified because the only stable aqueous species that are common are iodide (I^-), iodine (I_2^o), and iodate (IO_3^-). Considering the ranges of pH and Eh found in groundwater, I^- should be the dominant species present in groundwater beneath the 200 West Area at Hanford, with a small fraction of IO_3^- and a non-consequential amount of I_2. However, speciation in groundwater taken from numerous monitoring wells within the 200 West Area show that, on average, IO_3^- (70.6%) is the dominant species, followed by organo-iodine (25.8%), and then a small amount of I^- (3.6%); see Table 3.2 for summary. Formation of organo-iodine is important because iodine and organic carbon (OC) form extremely strong bonds, and soluble organo-iodine compounds can be highly mobile. Possible explanations for why thermodynamic speciation calculations do not predict actual ^{129}I speciation distributions are (1) contaminant plumes may not be in steady state, and (2) thermodynamic models do not consider processes involving microbes, well known to accumulate and alter iodine speciation (see section below).

Table 3.2. Chemistry and ^{127}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

Due to analytical detection limits, only iodate was detected when measuring radioactive ^{129}I species. As was demonstrated with ^{127}I, ^{129}I concentrations decreased with distance from the source.

Regardless of which species of iodine were present in the disposed waste, in opposition to thermodynamic constraints for Hanford groundwater, iodate is the dominant species, suggesting there are natural biogeochemical drivers promoting the existence of iodine in the oxidized iodate state.

3.2 Iodine Geochemistry at the Hanford Site

Some of the first iodine adsorption studies using Hanford sediments assumed iodide as the primary species, and 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 (Cantrell et al. 2003). These 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 more-strongly bound radioiodine fraction on Hanford sediments that did not desorb under chemical conditions

conducive to anion exchange (Xu et al. 2015). Using these same Hanford sediments, studies showed that desorption K_d values were much higher than the iodine (ad)sorption K_d values, indicating that sorption was only partially reversible. Similar trends were noted for iodate, but results indicated that iodate sorption to Hanford sediments was greater than sorption seen for iodide.

Partitioning of iodine to sediment organic matter has also been shown to be important in the overall geochemical response of iodine in the Hanford subsurface (Table 3.3). Using three composite sediments recovered from the 200 West Area, iodate K_d values were on average 89% greater than iodide K_d values. K_d values for both species increased as the amount of OC in the soil increased. 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 3.3. Iodide and iodate K_d values for composite sediments recovered from 200 West Area borehole cores (Xu et al. 2015).

Composite Sediment[a]	Organic Carbon (%)	Inorganic Carbon (%)	Total Sediment Iodine (µg/g)	Total DOC[b] (µM)	Iodide-spiked K_d[c] (mL/g)	Iodate-spiked K_d[c] (mL/g)
H1	0.12	0.92	4.79	284 ± 33	0.08	1.78
H2	0.04	0.01	0.68	0	0.00	0.83
H3	0.15	0.18	2.10	94 ± 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 µm) after 21 days of contact during the sediment/groundwater batch iodine uptake experiment.

(c) Suspensions were spiked with either iodide or iodate (as ^{125}I). However, the spiked species transformed to other species during the contact period. 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 coprecipitation of IO_3^- as a trace impurity in calcium carbonate ($CaCO_3$) phases. Carbonate minerals in subsurface systems are constantly forming and dissolving. The size of the IO_3^- ion is the same as the CO_3^{2-} ion and can substitute for it in carbonate phases. It was shown that recently precipitated carbonate phases (formed by degassing 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 3.4). The implications of this finding are far reaching. First, it 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). Secondly, this process may be useful for immobilizing ^{129}I either ex situ or in situ at the 200-UP-1 OU.

Table 3.4. Suspended particles formed by CO_2 degasing from 200 West Area groundwater samples (Zhang et al. 2013).

Wells	Particle concentration (mg/L)	Total carbon (wt-%)	Total ^{127}I (µg/g)	Total ^{129}I (µg/g)	Particulate ^{127}I (wt-%)[a]	Particulate ^{129}I (wt-%)[a]
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:

[particle concentration] × TI (particle) / ([particle concentration] × TI(particle) + TI(dissolved/filtered))

Iodine speciation changed once the spike solution came into contact with the sediments, indicating that Table 3.4 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}I fraction that is nearly irreversibly bound to the sediment and may provide a more accurate representation of ^{129}I transport.

The significance of the data in Table 3.4 is that iodate typically sorbs to sediments better than iodide. No sorption testing has been conducted with organo-iodine, but it too may sorb appreciably more than iodide to sediments. These findings bring into question whether the present Hanford ^{129}I K_d values, albeit conservative, adequately 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, iodate or organo-iodine would be expected to move slower, thereby changing the distribution of the total ^{129}I concentrations within the plume.

3.3 Biological Iodine Conversion

Microbes have been shown to be involved in numerous aspects of iodine cycling, including I^- oxidation to molecular iodine (I_2) and IO_3^-; IO_3^- reduction to I^-; iodine accumulation and formation of organic-iodine (Org-I) compounds, including volatile compounds, such as methyl iodide (CH_3I). Understanding Hanford specific 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 in situ and ex situ remediation strategies to control transport; and (3) processes driving current speciation in Hanford groundwater.

Molecular characterization of the microbial community in iodine-impacted groundwater showed a number of bacterial families with genera that have previously demonstrated iodine biotransformation capabilities (Figure 3.1). Results from sediment traps incubated in locations in the plume with

background, low, and high levels of ^{129}I show the presence of families that include *Pseudomonads* and *Actinobacteria*, taxa that have shown the ability to both oxidize I^- and reduce IO_3^-.

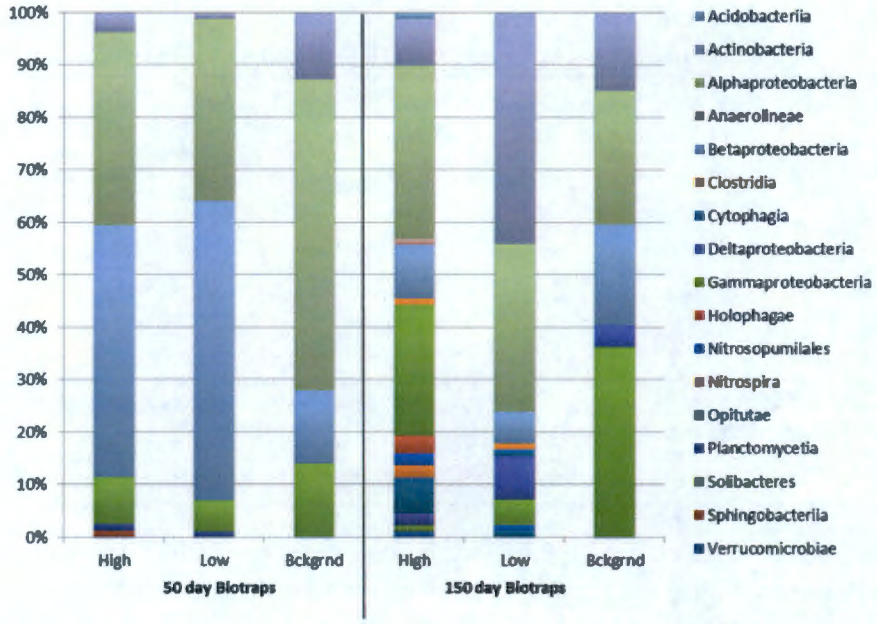

Figure 3.1. Microbial diversity in iodine impacted groundwater within the 200 West Area.

3.4 Microbially Catalyzed Iodine Redox Cycling

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 IO_3^-, experiments were performed to determine the ability of various Hanford isolates to reduce 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 IO_3^- to I^- in the presence of nitrate (Figure 3.2) (Ellis et al. In review). Iodate reduction occurred under both anaerobic and microaerobic conditions. When the culture was spiked with nitrate, IO_3^- concentrations continued to decrease in the culture medium.

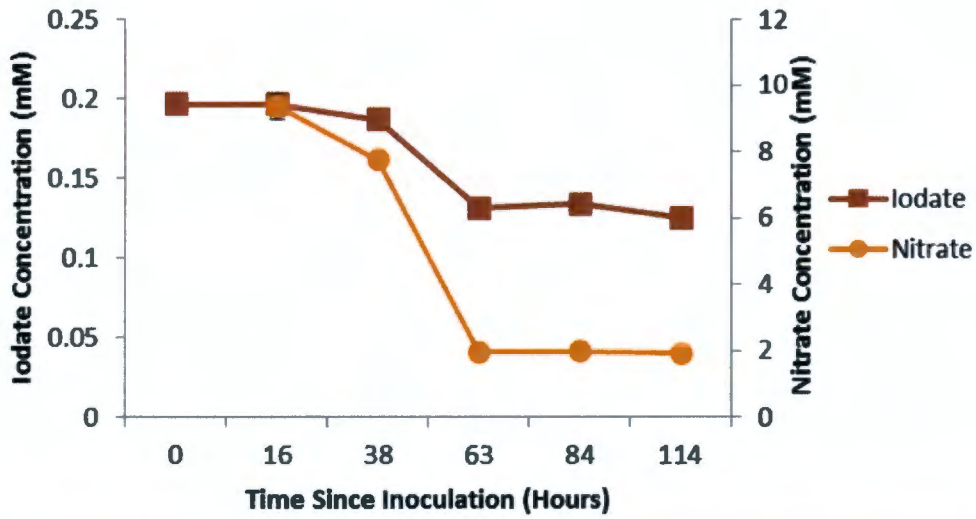

Figure 3.2. Iodate reduction in the presence of nitrate by an Agrobacterium species isolated from sediment traps that were incubated within an iodine plume in the 200 West Area.

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 to I^- to I_2. Analyses are currently being performed to determine whether complete conversion to IO_3^- is occurring.

3.5 Overview of Key Controlling Biogeochemical Processes Influencing Radioiodine Mobility

Based on this literature review of iodine biogeochemistry, a few key processes appear to be especially important in controlling radioiodine transport through the Hanford subsurface environment. The Hanford subsurface consists of gravel/sand textured sediment with layers of clay lens. These clay lens, compared to the rest of the subsurface, not only slow down flow (permitting redox and sorption reactions to occur), but also consist of greater surface areas, organic matter concentrations, and microbial populations. Aqueous ^{129}I is expected to exist as three species: IO_3^- >>> organic-I > I^-. Furthermore, stable ^{127}I concentrations in the plume are expected to greatly exceed those of ^{129}I by a factor of about 200. From a biogeochemistry point of view, the stable ^{127}I will compete with the ^{129}I in most reactions, such as anion exchange and sorption, and may facilitate other reactions, such as (co)precipitation. Therefore, the presence of a stable isotope has important implications on transport processes and the selection of remedial options.

Aqueous iodine interactions with the subsurface sediments are also expected to be strongly influenced by the trace levels of organic matter (OM) present in the system. OM has been shown to strongly influence iodine speciation and distribution in sediments through (1) irreversible covalent bonding, (2) strong complexation/partitioning interactions, (3) weak anion exchange, and (4) the release of low-molecular weight colloidal/dissolved carbon that can act as vectors for iodine transport. Microbial processes are also expected to play an important role in the ultimate fate and transport of ^{129}I by mediating

(1) surface adsorption, (2) uptake and accumulation, (3) redox processes, and (4) partitioning to and transformation by cell exudates. Bacteria isolated from Hanford sediments have been shown to reduce IO_3^- to I^- and oxidize I^- to I_2.

Iodate has also been shown to coprecipitate in $CaCO_3$, where the IO_3^- has a near identical molecular radius as CO_3^{2-}. While the precipitation and dissolution of $CaCO_3$ phases are continuous subsurface processes, the extent to which they affect ^{129}I mobility has not been demonstrated.

Iodine sorption to Fe-oxides and clay mineral surfaces has been repeatedly shown to be very weak. However the three species are expected to sorb differently, such that a ranking of species sorption is as follows: organo-I > IO_3^- > I^-, although organo-I sorption to Hanford sediments has not been tested. One important implication of the presence of these three species is that the entire ^{129}I inventory would not be expected to move identically, therefore, different species may be present at differing ratios as the plume spreads and diffuses away from disposal sources.

While these reactions are not intended to provide an exhaustive list of reactions, they appear to be among the key controlling factors. There is a reasonable understanding of how iodide binds to clay minerals and Fe-oxides (through traditional K_d studies). What remains largely unknown is the extent to which soil organic matter (SOM), at the trace levels existing in the Hanford subsurface, influences ^{129}I speciation and transport. Finally, there is a lack of quantitative data that couples hydrological considerations, such as transport through sand/gravel sediments versus clay lens and the kinetic effects on these key controlling biogeochemical processes.

3.6 References

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4.0 Conceptual Model

A conceptual model depicting the context for and behavior of iodine contamination is needed to support evaluation of remediation technologies required by the 200-UP-1 ROD. 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. Additional information about iodine behavior in the subsurface at the Hanford Site is provided by Truex et al. (2015a). As an overview, Figure 4.1 is a system-level depiction of elements affecting iodine fate and transport with respect to the groundwater. Of primary concern for groundwater remediation are the plume behavior elements, with consideration of the potential influence of vadose zone contamination from continued or future source flux. The following sections describe these conceptual model elements.

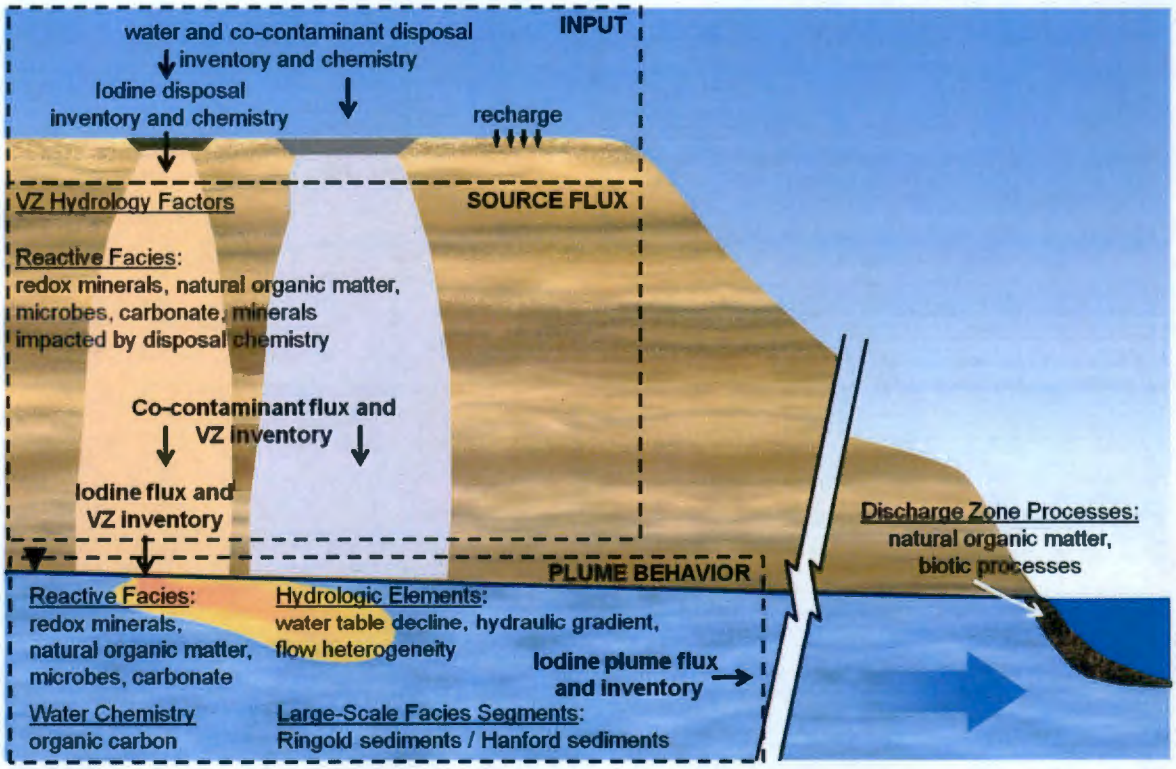

Figure 4.1. System-level depiction of elements impacting iodine fate and transport and remediation.

4.1 Inputs

Inputs (Figure 4.1) 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.

4.1.1 Waste Disposal Inventories

Corbin et al. (2005) indicate that a total of about 4.7 Ci of ^{129}I was released to waste sites at the Hanford Site. This inventory does not include the ^{129}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}I (accounting for 57% of the total ^{129}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}I inventory released to the subsurface. Figure 4.2 shows the relative percent of the overall ^{129}I inventory released at each of these 33 waste sites.

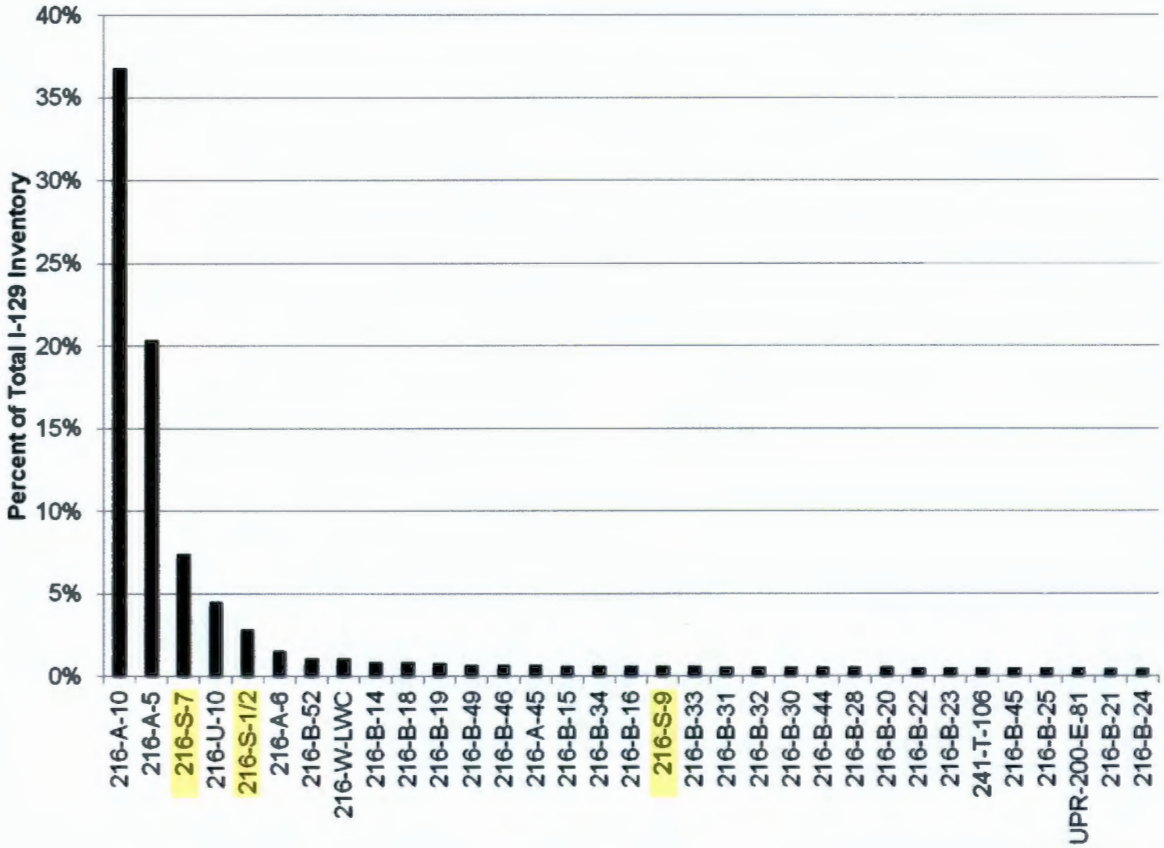

Figure 4.2. Relative percentage of the total ^{129}I inventory released to individual waste sites based on data from the Soil Inventory Model (Corbin et al. 2005) for sites with greater than 1% of the total (216-U-1/2 sites had less than 1% of the total).

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 4.1 lists those sites with predicted groundwater concentrations exceeding the DWS for ^{129}I (i.e., a DWS factor > 1) and the relative timing of those concentrations.

Table 4.1. Categorization of waste sites based on potential impact to groundwater for three time intervals: before the year 2100, 2100-3100, and 3100–12,000 (adapted from Truex and Carroll

2013). Sites with predicted groundwater concentrations less than the DWS are not shown (~300 sites). Red text indicates information based on recent groundwater plume data.

		^{129}I DWS Factor (only those >1 are shown)		
Site Name	**Site ID**	**Up to Year 2100**	**Up to Year 3100**	**Up to Year 12000**
REDOX Cribs	216-S-1&2	9 (37)	14	14
	216-S-7	82 (37)	30	11
	216-S-9	3		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	9	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

4.1.2 Water Disposal Inventories

In addition to the inventory of ^{129}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 (Section 4.1.4).

Focusing on the 33 sites with the largest ^{129}I inventories (Figure 4.2), Figure 4.3 shows the total and annual average discharge volumes for these facilities, highlighting sites relevant to the 200-UP-1 OU. Many of these facilities were either cribs (9) or trenches (13) that received process effluent for only a short amount of time (< 1 year). The facility that received the largest effluent volumes was the 216-U-10 Pond, with an estimated annual average effluent volume of 2.9E+8 L. Figure 4.4 illustrates the average concentration of ^{129}I received by each of the facilities, highlighting sites relevant to the 200-UP-1 OU.

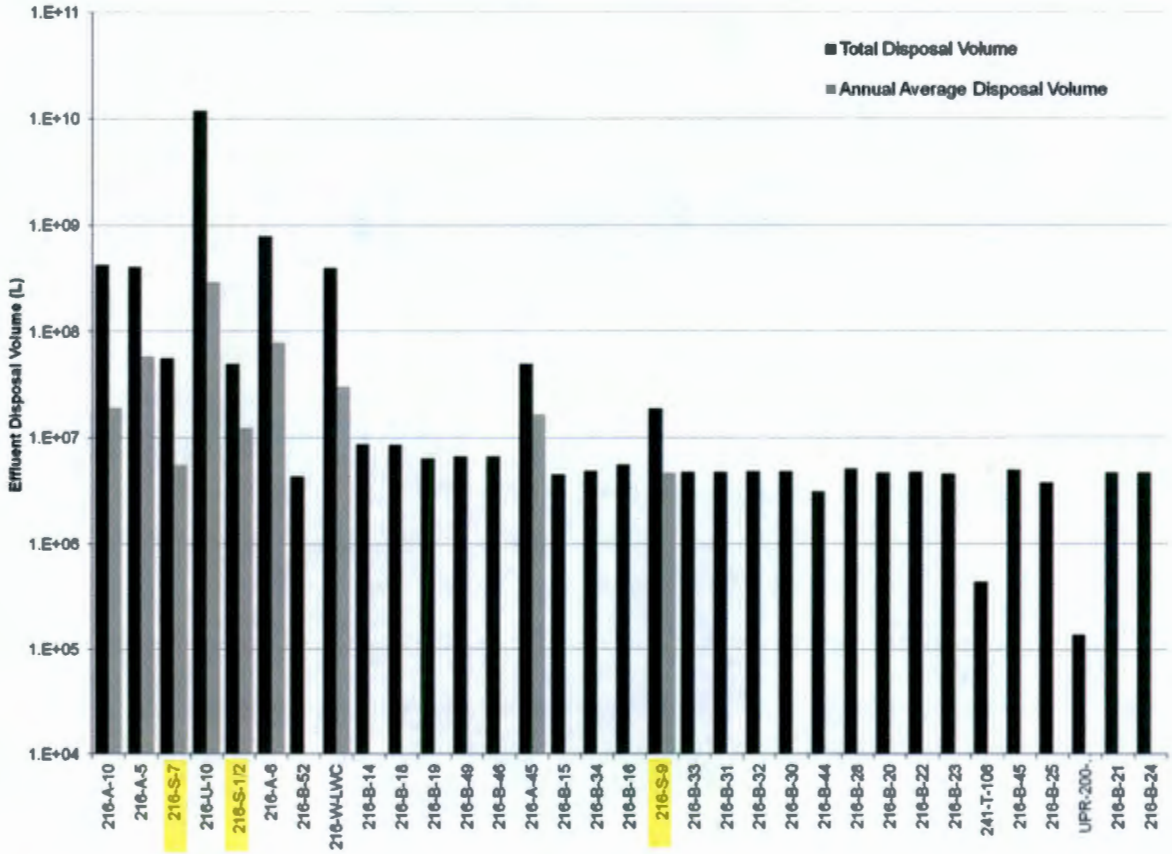

Figure 4.3. Estimated total liquid waste disposal volumes for sites with greater than 1% of the disposed ^{129}I inventory (Figure 4.2) with average annual disposal shown for sites having more than one year of disposal. Note that the 216-U-1/2 sites associated with part of the 200-UP-1 OU plume had less 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.

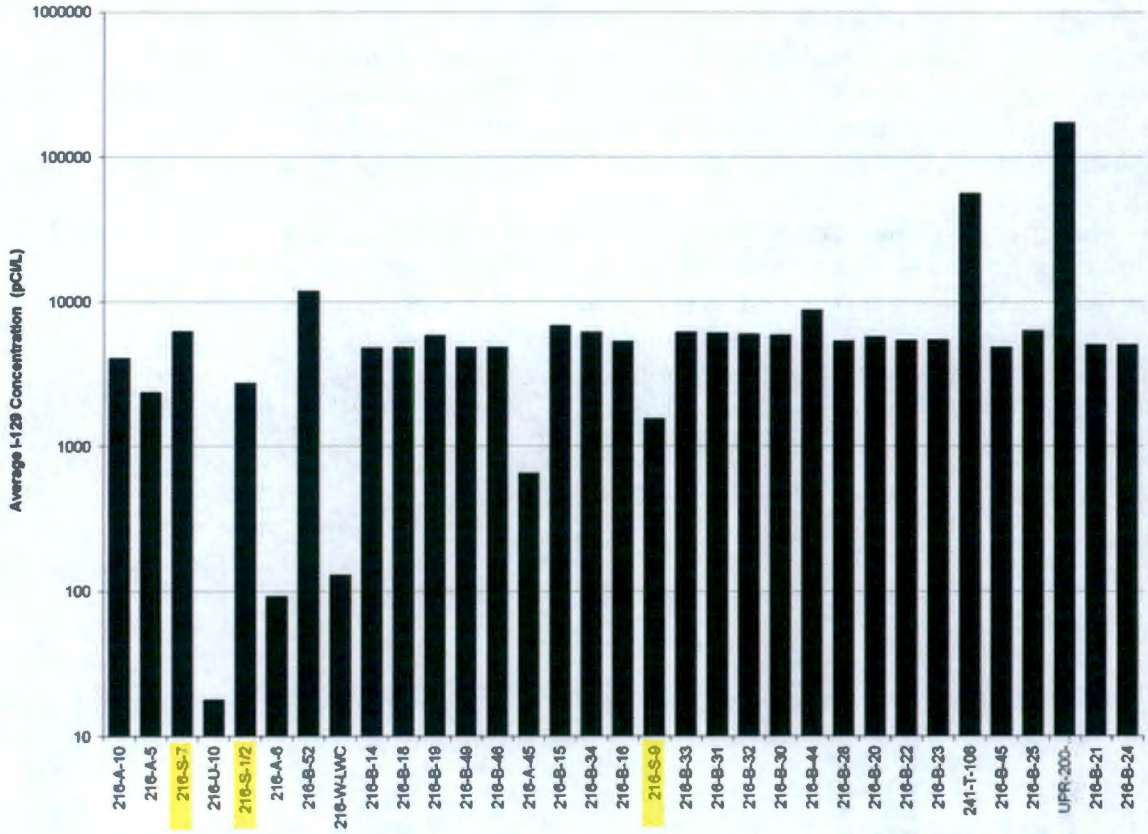

Figure 4.4. Calculated average ^{129}I concentration for sites with greater than 1% of the disposed ^{129}I inventory (Figure 4.2). Note that the 216-U-1/2 sites associated with part of the 200-UP-1 OU plume had less than 1% of the total and are, therefore, not shown here. Also, note the log-scale on the y-axis and that the DWS is 1 pCi/L for ^{129}I.

4.1.3 Waste Disposal Chemistry

The waste disposal chemistry can be important because the presence of co-contaminants can impact subsurface and remediation biogeochemistry. In addition, acidic or basic conditions in the disposed fluid can lead to neutralization reactions that can impact contaminant fate and transport in the vadose zone and thereby impact the contaminant flux to groundwater (Truex et al. 2014). Table 4.2 lists the co-contaminants for the major iodine disposal sites, highlighting sites relevant to the 200-UP-1 OU. Note that this assessment focused on waste disposal sites, but releases from tanks would have a unique chemistry that may need to be considered.

Table 4.2. Co-contaminants in relative rank order based on the Soil Inventory Model inventories (Corbin et al. 2005).

Disposal Facilities	Dominant Chemicals (in relative rank order by kg)
PUREX Cribs (216-A-10, 216-A-5, 216-A-6, and 216-A-45)	NO_3, CO_3, Cl, K, Na, PO_4, SO_4, Fe, Ca, U-Tot, Si, acidic except 216-A-6 is neutral/basic
REDOX Cribs (216-S-7, 216-S-1&2 and 216-S-9)	NO_3, Na, Al, U-Tot, acidic
BC Cribs (216-B-14, 216-B-15, 216-B-16, 216-B-18, 216-B-19)	NO_3, Na, SO_4, PO_4, F, Cl, K, Si, CO_3, Cr, Ca, Ni, Fe, Bi, NO_2, U-Tot, Zr, Ag, Hg, NH_3, 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_3, Na, SO_4, PO_4, CO_3, NO_2, F, Cl, K, NH_3, Si, Al, Cr, Ca, Ni, Fe, Bi, U-Tot, neutral/basic
BY Cribs (216-B-44, 216-B-45, 216-B-46, 216-B-49)	NO_3, Na, SO_4, PO_4, F, Cl, K, Si, CO_3, Cr, Ca, Ni, Fe, NO_2, Ni, Bi, U-Tot, neutral/basic
216-U-10 Pond	CO_3, NO_3, SO_4, K, NO_2, Na, Ca, PO_4, Si, Cl, TBP, NH_3, Fe, CCl_4, F, Al, Pb, Cr, U-Tot
Laundry Waste Crib (216-W-LWC)	Na, PO_4, Si, Ca, NH_3, SO_4, Cl, K, Fe, Al, NO_3, F, Pb, Mn, Ni, Cr, U-Tot
241-T-106 (UPR-200-W-148)	Na, NO_3, NO_2, Al, CO_3, SO_4, Cl, Cr, K, PO_4, NH_3, Fe, Si, Ca, Ni, F, Pb, U-Total
UPR-200-E-81	NO_3, Na, Al, NO_2, SO_4, Cl, CO_3, Cr, Ca, Pb, Fe, K, Ni, U-Total

4.1.4 Recharge

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.

4.2 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 from the vadose zone to the groundwater (Figure 4.1). Source flux may need to be considered in groundwater remediation if it is expected that the source flux will contribute significantly to the plume.

This conceptual model evaluation does not examine source flux in detail. However, for context, Figure 4.5 shows the approximate number of soil column pore volumes of effluent received by each site (based on the facility footprint and an estimated porosity of 35%) relative to their total ^{129}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). Sites with both high and low values for the pore volume estimate would be expected to have a longer-term contaminant flux controlled by the recharge rate. However, those with a higher pore volume estimate may have contaminants deeper in the vadose zone and therefore affect groundwater sooner than the lower pore volume estimate sites. Additional information relevant to evaluating the source flux is provided by Truex and Carroll (2013) and Truex et al. (2015b).

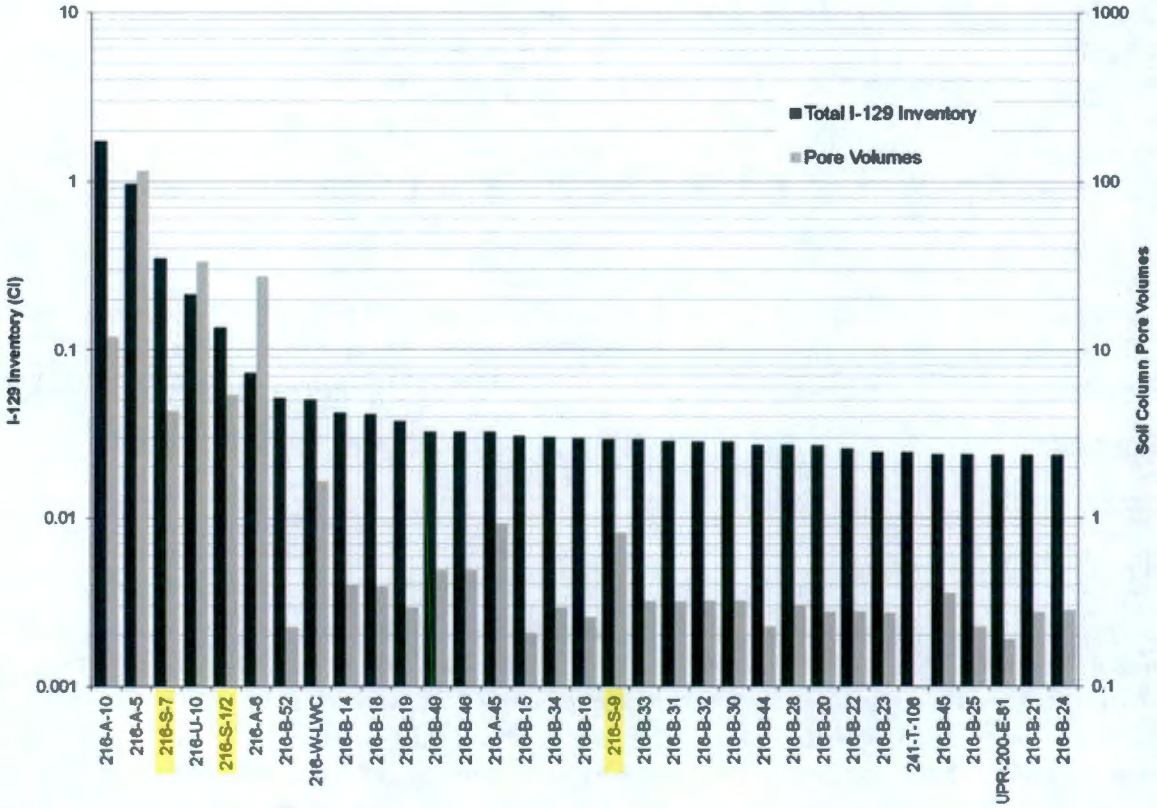

Figure 4.5. Total ^{129}I inventory and relative number of soil column pore volumes of effluent received for sites with greater than 1% of the disposed ^{129}I inventory (Figure 4.2). Note that the 216-U-1/2 sites associated with part of the 200-UP-1 OU plume had less than 1% of the total and therefore are 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. Thus, knowledge of the disposed iodine species and transformation processes in the vadose zone are important. Information in Kaplan et al. (2014) suggests that both iodate and iodide were likely present in the waste disposal fluids. While studies indicate the potential for disposed iodate to be transformed to iodide (Xu et al. 2015), iodate has been shown to be a significant fraction of the iodine species in the groundwater (Kaplan et al. 2014). In addition, transformation to organo-iodine species also needs to be considered based on laboratory observations of this transformation and data demonstrating the presence of organo-iodine species in 200 West groundwater samples. Further, recent evidence of iodate incorporation into calcite (Zhang et al. 2013) may be important in the vadose zone because of the carbonate dissolution and precipitation processes that naturally occur, as well as those induced by the disposed waste chemistry. Because of the uncertainties in source zone iodine species distribution stemming from the items discussed above, a range of scenarios

may need to be considered for evaluating remediation options. Additional laboratory studies could be applied to better bound this range of scenarios. The controlling features and processes for iodine transport in the vadose zone are the same as those in the groundwater, which are discussed in more detail in the next section.

4.3 Plume Behavior Controls

Building from information presented in Section 3.0, factors related to control of plume behavior are summarized below.

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}I and ^{127}I concentrations should be considered when evaluating plume behavior and reactive facies. ^{127}I and ^{129}I are found in Hanford Site groundwater at $^{127}IO_3^-/^{129}IO_3^-$ ratios ranging from 100 to 300, indicating much higher ^{127}I concentrations in the groundwater. The source of ^{127}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}I.

As shown in Figure 4.6 and Figure 4.7, adsorption, transformations between species, associations with organic compounds, and precipitation are all important for iodine fate and transport. Figure 4.6 shows an overview of biogeochemical processes that can affect the fate of iodine in the subsurface. Categories of microbially mediated reactions are shown in Figure 4.7. Information about these processes is summarized below, with a more in-depth analysis provided in Appendix C.

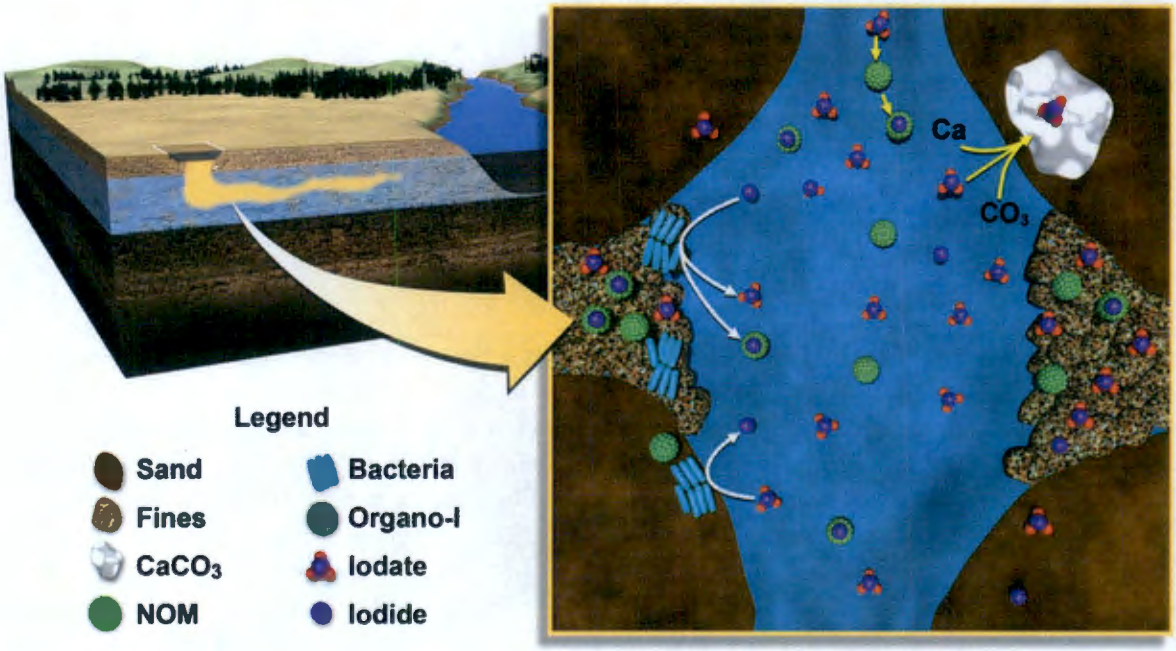

Figure 4.6. Conceptual overview of subsurface biogeochemical processes that affect the fate and transport of iodine. The figure does not distinguish between ^{129}I and ^{127}I because these processes are the same for both isotopes. The three primary aqueous iodine species are iodate (IO_3^-), Organo-I, and iodide (I^-). Processes include biotic (bacteria) transformations between iodine species as shown and potential transformations to other species, as illustrated in Figure 4.7. 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 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.

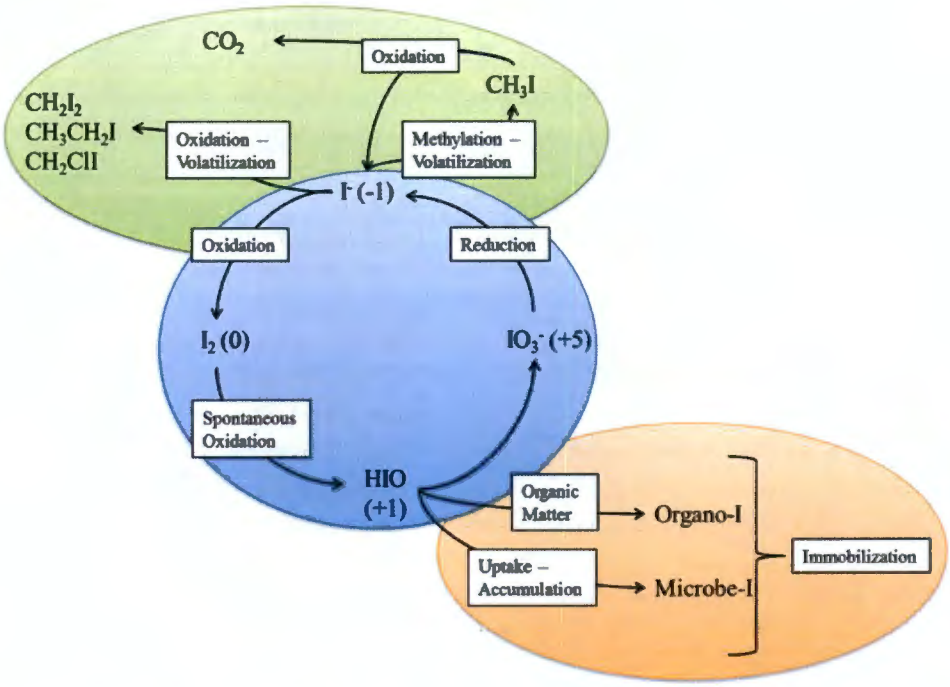

Figure 4.7. Biological transformations associated with iodine cycling in the environment. The blue ellipse represents predominantly aqueous-phase iodine species. The orange ellipse represents predominantly solid-phase species of iodine associated with organic compounds (Organo-I) or accumulated in microbial 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 4.6 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 I^- and IO_3^- have observed a low K_d, in the range of 0 to 5.64 mL/g for I^- and 0.83 to 7.56 mL/g for IO_3^- (Xu et al. 2015). In the study by Xu et al., IO_3^- K_d values were always higher than values for I^- for the same sediments. Other studies have suggested that partitioning of iodine to Hanford Site sediments may be partially related to sediment organic carbon (OC) content (Table 3.3), even at the very low 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 IO_3^- than 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, I^-, and IO_3^- to iron-oxides and phyllosilicate mineral surfaces is expected to differ, with a likely highest-to-lowest ranking of sorption being Organo-I > IO_3^- > I^-, although experiments are required to test this hypothesis.

Earlier studies focused on I^- partitioning, with reported K_d values ranging from 0 to 2 mL/g, but most frequently between 0 and 0.2 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 I^- and IO_3^-, but results indicated that IO_3^- sorption to Hanford Site sediments was greater than 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}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 I^- and reduce IO_3^-. Microbes have been shown to be involved in iodine accumulation (Microbe-I, Figure 4.7) and formation of Organo-I compounds (Organo-I, Figure 4.7), including volatile compounds such as methyl iodide (CH_3I) (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}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 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 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 IO_3^-. Co-precipitation of 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.

4.4 200-UP-1 Iodine Plume Summary

Available groundwater monitoring data can be used to evaluate iodine transport. However, it is important to consider waste discharge timing and volume, vadose zone transport, changing water tables, and the potential for differential transport of different iodine species.

For the 200-UP-1 OU, ^{129}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. Plume maps over a 20-year period beginning in 1993 (Truex et al. 2015a) 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}I concentration results range from 1 pCi/L (MCL) to 10+ pCi/L within the 200-UP-1 plume. The 90th percentile ^{129}I concentration is 3.5 pCi/L, meaning that 90% of the data for ^{129}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 wells within the central portion of the plume 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 (Truex et al. 2015a).

These data, in conjunction with the plume maps, 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 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}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 (Truex et al. 2015b).

Several co-contaminants are present within the ^{129}I plumes, including chromium, nitrate, ^{99}Tc, uranium, and tritium. Chromium, nitrate, uranium, and technetium may be present in forms that could interact with the same reactive facies as ^{129}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}I plumes because of the altered hydraulic gradients and by displacement of ^{129}I that is extracted and reinjected.

4.5 Summary

This summary includes a discussion of key conceptual model elements in relation to remedy evaluation and identification of data gaps.

Key Conceptual Model Points for Remedy Evaluation:

- The iodine plume dynamics are influenced at the large scale by the history of and projected future contaminant discharges from the vadose zone and large-scale hydrologic conditions. Plume dynamics suggest high contaminant discharge conditions in the past led to plume development and that these discharges are lower now. Future contaminant discharge from the vadose zone has not been estimated, but is likely to be lower than the historical discharge and may continue over a long duration. Large-scale hydrologic conditions for consideration are the declining water table and associated hydraulic gradient and the flow characteristics of the Ringold Formation.
- Remediation approaches will need to consider impacts of the low iodine concentration on effectiveness.
- Co-contaminants are present in some portions of the iodine plume. These co-contaminants may impact some remediation processes through competition (e.g., redox/microbial reactions) or interference mechanisms (sorption) or facilitation (co-metabolism).
- There are limited in situ geochemical sequestration mechanisms because of the solubility of most iodine species and associated complexes (exceptions being Ag, Cu, and Hg salts). However, interactions with organic materials, bacteria, or calcite precipitation may provide mechanisms for enhanced sorption and accumulation.
- As with most sites, subsurface characteristics need to be considered with respect to plume behavior controls and impact to remediation technology performance. Heterogeneities related to plume distribution and performance of amendment distribution or plume extraction efficiency need to be considered in light of the large scale of the plume.

Conceptual Model Data Gaps:

- Speciation of iodine from discharge and reactions caused by waste disposal chemistry. This information is important in defining the source term and associated source flux that is needed as part of evaluating groundwater plume behavior.
- Improved estimates of future contaminant flux from the vadose zone to the groundwater. Application of improved speciation information and methods to evaluate flux through the vadose zone are needed to improve the estimate of the source flux important to groundwater plume behavior.
- Role of abiotic reductive reactions in iodine transformation within the groundwater and vadose zone. Reduction of iodate to iodide results in greater mobility of iodine that is important to consider in fate and transport analyses or for application of remediation technologies. The role of these processes at Hanford needs to be evaluated in conjunction with the presence and distribution of reactive facies.
- Type and role of organic material and its participation in reaction, sorption, facilitated transport, and accumulation of iodine. Organo-iodine compounds are important with respect to natural attenuation and for application of active remedies, and have been shown to be present in the Hanford aquifer, even though organic content in the aquifer is generally low.

- Microbial mediation of iodine processes. As discussed in Section 3.0, microbial reactions mediate many of the important transformations of iodine that relate to its mobility and effectiveness of treatment processes. However, site-specific information about these processes is needed.
- Improved data on sorption for different iodine species and the distribution of sorbents within the subsurface. Along with fundamental knowledge of iodine speciation and reactive facies, improved transport parameters are needed to enable refined fate and transport estimates as part of natural attenuation and remedy evaluation efforts.
- Impact of co-contaminants on transformation and sorption. Multiple co-contaminants are present and may have co-metabolic or competitive impacts on biogeochemical processes as well as ion-exchange interactions that impact iodine sorption. As part of developing site-specific information for Hanford, these co-contaminants need to be considered.
- Recent information has shown the potential for co-precipitation of iodate with calcite. Site-specific information is needed on the occurrence of this process and the solubility of substituted versus non-substituted calcite to interpret the effectiveness of this process as an attenuation mechanism for iodine.

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5.0 Evaluation of Exposure Risk from Iodine-129

5.1 Health Effects from Iodine-129

Iodine is an essential nutrient for humans and other living organisms. When iodine is released into the environment, it can be directly inhaled or ingested by animals and humans as well as concentrated on or in plants and subsequently consumed by animals or humans. Since iodine is soluble in water, it can easily move from the atmosphere into the water and from the water into the food chain. Iodine is readily taken into the bloodstream from both the lungs and the gastrointestinal tract (essentially 100%) after inhalation and ingestion (EPA 2002a). When iodine enters the body, it concentrates in the thyroid and the rest is excreted from the body (EPA 2002b). Clearance of iodine from the thyroid is age-dependent, with biological half-lives (i.e., the length of time an element stays in the body) ranging from 11 days in infants to 23 days in a 5-year-old child (Peterson et al. 2007) and 100 days in adults (EPA 2012). The biological half-life also varies based on the organ. For an adult, the biological half-life of iodine in the thyroid is 100 days, bone is 14 days, and kidney, spleen, and reproductive organs are 7 days (EPA 2012).

Iodine is necessary in the body for the production of hormones in the thyroid. The risk associated with radioiodine is based on dose to the thyroid. The uptake of radioiodine by the thyroid is inversely proportional to the intake of stable iodine. At times of emergency releases of radionuclides, emergency response officials may direct individuals to ingest large doses of stable iodine, flooding the thyroid of those individuals with stable iodine and reducing the possibility of accumulation of radioiodine in the thyroid (EPA 2002a).

Iodine is an essential component of the human diet, and the major dietary sources of iodine are iodized salt and seafood. The lack of dietary iodine is a cause of mental retardation, hypothyroidism, goiter, cretinism, and varying degrees of other growth and developmental abnormalities. Excessive intake of iodine may also result in goiter as well as hyper- or hypothyroidism (CDC 2008).

Iodine radioisotopes are among the most widely used radionuclides in the medical field because several of the isotopes have short half-lives and the beta emissions are easily detectable in medical imaging and immunotherapy. Thyroid cancer is the main risk associated with radioiodine. Because iodine selectively accumulates in the thyroid, the primary health hazard from radioiodine is a thyroid tumor. Based on epidemiological studies for external radiation, children are more susceptible than adults to cancer from thyroid irradiation.

EPA has not published toxicity values for stable iodine in water (EPA 2014). However, the WHO has published health-related toxicity values for iodine in water (WHO 2003). The estimated dietary iodine requirement for adults ranges from 80 to 150 μg per day for food (based on consumption of iodized salt, seafood, and cow's milk) and 8 μg per day for drinking water (assuming consumption of 2 L of drinking water per day). Some people are hypersensitive to oral or dermal exposure to iodine. In very rare instances, short-term exposure to high concentrations of iodine can cause endocine disruption or angio-oedema (acute, transitory swelling of the face, hands, feet, or viscera) and swelling of the larynx, which may cause suffocation (WHO 2003, ATSDR 2004). Iodine is lethal to humans at oral doses of 2000 to 3000 mg. Chronic consumption of iodinated drinking water (1 mg/L iodine) has not been shown to cause adverse health effects in people. Taste and odor thresholds for iodine range from 0.147 to 0.204 mg/L in water (WHO 2003).

5.2 Dosimetry and Risk per Unit from Iodine-129

The United States has issued regulations, some still in effect, based on several different methodologies for estimating the dose from ingested radionuclides. These approaches are all based on methods published by the ICRP, which initially worked in parallel with the U.S. National Committee on Radiation Protection and Measurements. The U.S. group was later chartered by Congress as the National Council on Radiation Protection and Measurements.

5.2.1 ICRP-2/NBS-69

The commencement of industrial production of radioactive sources as part of the Manhattan Project in World War II was the impetus for development of concepts and standards related to ingestion or inhalation of radioactive materials. The U.S. National Bureau of Standards (NBS) supported the publication of the National Committee's report, Maximum Permissible Amounts of Radioisotopes in the Human Body and Maximum Permissible Concentrations in Air and Water, in 1953 (NBS Handbook 52 [NBS 1953]). This was subsequently updated in 1959 by ICRP Publication 2, Report of Committee II on Permissible Dose for Internal Radiation (ICRP 1959), which was summarized and published by NBS as Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and Water for Occupational Exposure, NBS Handbook 69 (NBS 1959). All of these documents focused on the concepts of body burden and maximum permissible concentration, but they did introduce the concept of radiation dose as the basis for these other end points.

In ICRP-2/NBS-69, radiation dose is estimated simply as the energy absorbed per unit mass. The energy absorbed is estimated as that fraction absorbed from the radionuclides as if they were a point source in the center of a spherical organ or body. These methods were used because they allowed conservative analytical solutions to the basic problem of how much energy was deposited in an organ from a radioactive disintegration.

Using the ICRP-2/NBS-69 terminology, the dose rate (DR) per unit ^{129}I activity (Q) maintained in the thyroid is given by Soldat et al. (1976) as:

$$DR/Q = 18.7\ (\varepsilon/m)$$

Where

18.7 = units conversion constant (mrem g/MeV pCi)
ε = effective energy absorbed per disintegration, MeV
m = mass of the thyroid, g.

Because the effective energy per disintegration (ε) remains fairly constant with age (ranging from 0.061 to 0.065 MeV disintegration from age 1 to adult [Soldat 1976]), the substantial decrease in dose per unit activity with increasing age results almost entirely from the rapid increase in thyroid gland mass with increasing age.

A steady dietary intake ingesting 1 pCi/day of ^{129}I would lead to an equilibrium burden of 8.7 pCi in the thyroids of 1- and 4-year-olds and 22 and 43 pCi in those of 14-year-olds and adults, respectively, leading to thyroid equivalent dose rates of 4.9, 2.1, 1.7, and 2.6 mrem/yr for the 1-, 4-, 14-year-olds, and adults, respectively. The adult thyroid dose coefficient is then 7.23×10^{-3} mrem/pCi.

The ICRP-2/NBS-69 methods were not based on risk of cancer; the primary focus was minimizing immediate effects and attempting to avoid hereditary effects. For workers, the limitations were defined in terms of annual dose, rather than committed dose.

5.2.2 ICRP 26/30

The first comprehensive system of dosimetry to be founded on the concept of "detriment" or risk was published by the ICRP in 1977 in Publication 26 (ICRP 1977). In this system, the detriment (a combination of long-term cancer risks and other adverse effects represented as a mathematical expectation of harm) was a function of the "dose equivalent." This was based on the principle that the risk should be equal whether the whole body is irradiated uniformly or there is non-uniform irradiation. This condition was met if

$$\sum_T w_T H_T \leq H_{wb,L}$$

where w_T is a weighting factor representing the fraction of the risk resulting from tissue T to the total risk when the whole body is irradiated uniformly, H_T is the total dose equivalent is the annual dose equivalent in tissue T, and $H_{wb,L}$ is the annual dose-equivalent limit for uniform irradiation of the whole body.

The organ dose equivalents H_T in this system are committed doses over a 50-year period. These were calculated using sophisticated Monte Carlo calculations of energy absorbed in a target organ from disintegrations that occurred in a source organ in which the radioactive material was uniformly distributed. The weights were developed on the basis of radiation effects as they were understood at the time. The organ-specific weights are included in Table 5.1.

Table 5.1. Organ-specific weights for use in calculation of organ dose equivalents over a 50-year period.

Tissue	w_T
Gonads	0.25
Breast	0.15
Red bone marrow	0.12
Lung	0.12
Thyroid	0.03
Bone Surfaces	0.03
Remainder	0.30

The relatively high weighting for gonads reflects the early concern about hereditary effects. Note that the weight for thyroid is 0.03. The adult thyroid ingestion dose coefficient is 9.25×10^{-3} mrem/pCi, but when weighted is only an effective dose equivalent of 2.74×10^{-4} mrem/pCi.

The values of dose per unit intake were published over several years in multiple volumes of ICRP Publication 30 (ICRP 1979). This is the system currently in use by the NRC in 10 CFR Part 20.

5.2.3 ICRP-60/72

As the understanding of radionuclide biokinetics and radiation effects has developed, the dosimetry has also advanced. In addition to various refinements in biokinetic models, the definition of detriment has also changed, resulting in refinements for the tissue weighting factors w_T. In 1990, ICRP Publication 60 updated the weighting factors (Table 5.2).

Table 5.2. Updated weighting factors based on ICRP Publication 60 (ICRP 1991).

Tissue or Organ	w_T
Gonads	0.20
Red bone marrow	0.12
Colon	0.12
Lung	0.12
Stomach	0.12
Bladder	0.05
Breast	0.05
Liver	0.05
Esophagus	0.05
Thyroid	0.05
Skin	0.01
Bone surface	0.01
Remainder	0.05

Note that in this revision, the weight for thyroid has increased from 0.03 to 0.05. The factors for radiation dose per unit intake using this system are summarized in ICRP Publication 72 (ICRP 1995). The adult ingestion effective dose coefficient is 4.1×10^{-4} mrem/pCi; which is equivalent to a thyroid dose coefficient of about 8.1×10^{-3} mrem/pCi.

Some parts of DOE now allow the application of this system of dosimetry in environmental and risk assessments. As noted in DOE Order 458.14e(7), "DOE-approved dose coefficients must be used to evaluate doses resulting from DOE radiological activities. Use of alternative dose coefficients must be approved by the Chief Health, Safety and Security Officer or by a Cognizant Secretarial Officer in consultation with the Chief Health, Safety and Security Officer." One DOE application using the ICRP Publication 60 methods that has been approved is the Derived Concentration Standards (DOE 2011), which are based not only on Publication 60 but also on age-specific effective dose coefficients, revised gender-specific physiological parameters for the Reference Man (ICRP 2002), and the latest information on the energies and intensities of radiations emitted by radionuclides in ICRP Publication 107 (ICRP 2008). The Derived Concentration Standards represent the concentration of a given radionuclide in either water or air that results in a member of the public receiving 1 mSv (100 mrem) effective dose following continuous exposure for 1 year for each of the following pathways: ingestion of water, submersion in air, and inhalation.

5.2.4 Federal Guidance Report 13

EPA has published cancer risk coefficients for environmental exposures to radionuclides as Federal Guidance Report No. 13 (EPA 2002b). This EPA document is built around the concepts of ICRP Publication 60 (ICRP 1991), with minor revisions.

EPA adult thyroid ingestion dose coefficient is 7.81×10^{-3} mrem/pCi. The risk per pCi of ^{129}I ingested for children is 8.21×10^{-11}, for teens is 6.33×10^{-11}, for adults is 8.07×10^{-12}, and averaged for chronic ingestion over an entire lifetime is 1.51×10^{-11}.

5.2.5 ICRP-103/IAEA

The Revised Recommendations for a System of Radiological Protection formally replaced the Commission's previous 1990 Recommendations in 2007. These recommendations update, consolidate, and develop additional guidance on the control of exposure from radiation sources issued since 1990. The ICRP 103 recommendations (ICRP 2007) update the radiation and tissue weighting factors in the quantities equivalent and effective dose and update the radiation detriment, based on the latest available scientific information of the biology and physics of radiation exposure. The tissue weighting factors are included in Table 5.3.

Table 5.3. Weighting factors based on ICRP Publication 103 recommendations.

Tissue or Organ	w_T
Red bone marrow	0.12
Colon	0.12
Lung	0.12
Stomach	0.12
Breast	0.12
Remainder	0.12
Gonads	0.08
Esophagus	0.05
Bladder	0.05
Thyroid	0.05
Liver	0.05
Skin	0.01
Bone surface	0.01
Brain	0.01
Salivary Glands	0.01

Note that the weight for gonads has been significantly reduced from the 1977 recommendations; this follows from the accumulated lack of hereditary effects found in human cohorts following irradiation. This allows other weights to be scaled up so that the total is 1. Note that the weight for thyroid has remained at 0.05, which actually reduces the contribution of the overall weights because the weight for

the gonad fraction has decreased. The adult thyroid ingestion dose coefficient remains at 8.1×10^{-3} mrem/pCi.

The ICRP Publication 103 recommendations are the basis of the most recent BSS issued by the IAEA.

5.3 Pathways and Dose per Unit Concentration from Iodine-129

Regulatory authority for addressing radionuclides in the environment is dispersed among various federal agencies because of the evolution of U.S. laws. EPA has the authority for determining contaminant levels in drinking water. Because radiation dose via drinking water is only a portion of the total possible dose from all environmental emissions, EPA applied a constraint on the total dose limit and arrived at a level of 4 mrem/yr for the drinking water pathway. The drinking water standards (or MCLs) for radionuclides were set using available methodologies; they have remained at the same level for many years because of public inputs to not "reduce" regulatory protection in spite of advances in radiation protection technologies.

The dose from ^{129}I depends on the exposure pathway. To help understand possible scenarios from different exposure pathways, this section breaks down the exposures to illustrate the additive portion of the scenarios.

5.3.1 Pathway from Drinking Water

In this scenario, individuals of various ages consume untreated water from the contaminated groundwater source, with no other modes of exposure. The annual consumption rates are taken from NRC Regulatory Guide 1.109 (NRC 1977). Doses and annual risks for this scenario for water contaminated to 1 pCi/L are given in Table 5.4. The MCL for ^{129}I was rounded up to 1.0, so the thyroid dose for an adult slightly exceeds 4 mrem.

Table 5.4. Dose and risk by age group for the scenario of drinking water at 1 pCi/L.

Age Group	Consumption (L/yr)	Effective and Thyroid Dose (mrem/yr)	Cancer Fatality Risk (yr^{-1})
Children	510	0.41 / 8.1	4.2×10^{-8}
Teens	510	0.26 / 5.3	1.3×10^{-8}
Adults	720	0.28 / 5.7	1.1×10^{-8}

5.3.2 Pathways from Irrigation

Radioactive contamination in water may result in radiation doses to people through various pathways not related to direct consumption of water (as represented in Figure 5.1). The primary exposure pathway for groundwater contamination is irrigation. Use of water to grow plants results in contamination of soils and plants, as well as other farm products (e.g., beef) that consume the initially irrigated crops.

- **Plants:** The primary purpose of irrigation is to grow crops in areas with insufficient rainfall. The amount of irrigation depends on the relative dearth of precipitation. In some areas, such as eastern Washington State, irrigation is the primary source of agricultural water. Assuming a unit concentration of ^{129}I in groundwater, different crops irrigated with different amounts of water would be contaminated to different levels. Some common assumptions on irrigation rate and the resulting contamination of plants are shown Table 5.5 (Snyder et al. 2013).

Table 5.5. Assumptions for calculating risk from ^{129}I based on irrigation of crops.

Crop Type	Irrigation Rate (inches per year)	Contamination Level per pCi/L
Leafy Vegetables	3.6	3.05 pCi/kg
Other Vegetables	27.6	0.73 pCi/kg
Fruits	30	0.75 pCi/kg
Grains	30	3.29 pCi/kg

- **Animals:** Many farm animals are fed from irrigated crops. Grain, feed, and forage irrigation rates applicable to eastern Washington (Snyder et al. 2013), and the resultant animal product concentrations per unit water concentration are shown in Table 5.6.

Table 5.6. Assumptions for calculating risk from ^{129}I based on irrigation of crops fed to domestic animals.

Animal Product	Feed/Forage irrigation Rate (inches per year)	Grain Irrigation Rate (inches per year)	Contamination Level per pCi/L
Meat	22.8	28.8	60.5 pCi/kg
Milk	24	--	3.67 pCi/kg
Poultry	--	22.8	0.04 pCi/kg
Eggs	--	22.8	2.22 pCi/kg

- Other pathways from irrigation include inhalation of resuspended soil and external radiation; however, the contribution of these pathways is insignificant.

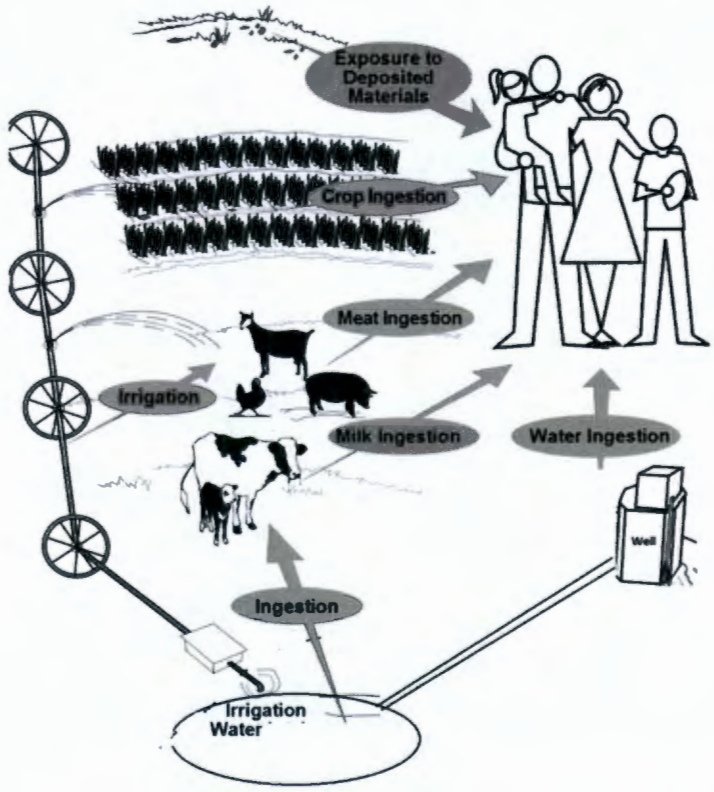

Figure 5.1. Human health exposure pathways for iodine uptake.

5.4 Uptake Modification

The radiation dose to the thyroid from ^{129}I in drinking water results from the uptake and concentration of iodine in the human thyroid. The total amount of iodine in the thyroid is about 10 mg; this amount is homeostatically regulated, so that the body takes in more iodine when it is low and takes in less iodine when it is high. It has been proposed that this mechanism could be used to limit the thyroid dose by blocking the uptake of radioactive ^{129}I by increasing the availability of stable ^{127}I.

The average concentration of stable iodine in groundwater is low. World average concentrations are on the order of 1 μg/L (ATSDR 2004, p. 238). Hanford groundwater measurements for iodine range from 8 to 75 μg/L total I, with an average of 30 μg/L total I (Section 4, Table 2, Zhang et al. 2013a). The primary source of human uptake of iodine is with foods. Daily uptake ranges from about 63 to 380 μg/day (ATSDR 2004); the average urinary excretion in the United States is about 150 μg/d. The USDA Recommended Daily Allowance of iodine is 150 μg/day.

Using the ICRP Publication 2 model of Section 5.2, it can be shown that the maximum possible dose rate for the thyroid, if 100% of the iodine in the thyroid were ^{129}I, is about 108 rad/yr.

If it is assumed that the daily intake from foods is the RDA of 150 μg per day, then additional stable iodine would reduce the uptake from drinking water (and other sources). Radioiodine in the groundwater

is a very small mass (30 pCi/L corresponds to only 0.17 µg/L). Iodine could be supplemented in the groundwater to reduce the fractional intake of iodine in the thyroid. For a drinking rate of 2 L per day, the radiation dose resulting from a water concentration of 30 pCi/L can be shown to relate to the stable iodine concentration in the water (Table 5.7 and Figure 5.2).

Table 5.7. Increasing concentrations of stable iodine in water results in dimensioning dose rate in the thyroid.

Water concentration (µg /L stable I)	^{129}I Intake pCi/d (µg/d)	Stable I Intake (µg/d)	Fraction ^{129}I in Iodine	Thyroid Activity (pCi)	Dose Rate (mrem/yr)
0.5	60	151	1.12E-03	1990	120.9
1	60	152	1.12E-03	1970	120.1
10	60	170	9.99E-04	1760	107.4
100	60	350	4.85E-04	857	52.2
1000	60	2150	7.90E-05	140	8.5
10,000	60	20,150	8.43E-06	15	0.9

Uptake modification through supplementations with stable iodine could decrease thyroid dose from radioiodine. There are no regulations limiting the concentration of total iodine in drinking water. However, the threshold for taste and smell of iodine is about 150 to 200 µg/L (WHO 2003). Iodine is used as a disinfectant of water for camping at levels of 10,000 µg/L iodine. This concentration is distinctly objectionable by taste and smell. In addition, the concentrations used for disinfection of water can lead to thyroid dysfunction in as short a period as 1 week.

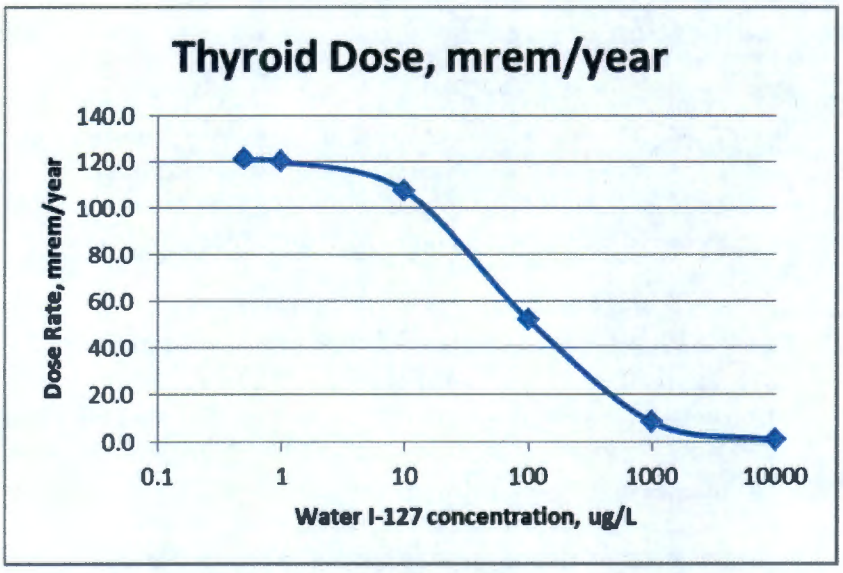

Figure 5.2. Reduction in thyroid dose rate with enhanced concentration of stable ^{127}I in groundwater.

5.5 Summary of RI/FS for the 200-UP-1 Groundwater OU (DOE 2012)

The RI/FS for the 200-UP-1 Groundwater Operable Unit (DOE 2012) included a baseline risk assessment for the use of groundwater. The exposure pathway selected for the RI/FS considered the current land use and the anticipated use of the land in the future, groundwater beneficial use, contaminant sources, release mechanisms, routes of migration, potential exposure points, potential routes of exposure, and potential receptor groups. While Figure 5.1 above shows numerous pathways, the RI/FS identified the following potential routes of exposure to groundwater contaminants:

- Ingestion of contaminated water by drinking or in food preparation
- Inhalation of contaminant vapors during showering or other household activities
- Dermal contact exposure to contaminants in groundwater
- External radiation exposure from radioactive contaminants in groundwater

The baseline risk assessment conducted as part of the RI/FS considered the contribution of not only ^{129}I but also the other beta-emitting radioisotopes in 200-UP-1 to estimate the contribution of excess lifetime cancer risk. Based on the 90th percentile current groundwater concentrations, ^{129}I contributed 4%, ^{99}Tc contributed 78%, and ^{3}H contributed 18%. As discussed in Section 2.0 and above, the international standards are based on total effective radiation dose from all sources and all radionuclides. Remediation of the groundwater in 200-UP-1 OU to meet beneficial use would require addressing more than just the ^{129}I in the groundwater.

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6.0 Remedial Options for Iodine

As discussed in previous sections, iodine is very mobile in the environment, with various forms being soluble in water and/or volatile and the iodine speciation affecting the mobility, phase partitioning, and reactivity of the iodine. Correspondingly, the nature and effectiveness of a remedial alternative will depend and/or capitalize on these chemical properties of the iodine species in the environmental media. The nature of iodine, as an element, means that remedial technologies for iodine will generally involve altering the iodine speciation, transferring iodine species to another phase, concentrating the iodine, isolating/encapsulating iodine, and/or immobilizing iodine. Radioactive decay of ^{129}I, as a destructive mechanism, is insignificant, although it could play a role in remediation of other iodine isotopes.

Radioactive isotopes of iodine (primarily ^{129}I, ^{131}I, and ^{125}I) generally either result from nuclear power or weapons production or are produced for medical applications. Thus, most technologies designed for the treatment of iodine in gas or aqueous streams originate from those industries as methods for control of iodine releases. Motivated by historical releases (for example at Hanford, SRS, and Idaho National Laboratory), a few technologies have been investigated specifically for environmental remediation of iodine. A number of generic remediation technologies (not specific to iodine) may also be useful in iodine remediation, for example, to control contaminant migration.

A comprehensive identification and inventory of potentially applicable iodine remediation technologies was conducted through a literature search and the results are summarized in this section. Potential remediation technologies are organized by the purpose of the treatment, including ex situ treatment (for media extracted from the subsurface or secondary waste streams), source removal, control of contaminant flux through the vadose zone, and groundwater plume remediation. The list of technologies is summarized in Table 6.1, with a brief description of the technology (including a list of common variations), notes on technology maturity, a rough guide to the technology cost (in terms of low, moderate, or high), and a pointer to the section in Appendix D that provides additional narrative description about the technology. Note that mature technologies have been deployed in a wide range of settings over many years, technologies at the bench scale have been demonstrated in the laboratory, while developmental technologies are innovative and are still in the initial development stages. The semi-qualitative assignment of relative cost is based on development status and historical experience; more definitive costs would only come from definition of specific remedial alternatives as part (typically) of a feasibility study.

6.1 Literature Overview

A number of articles and reports provide useful surveys or reviews of technologies for treatment of radionuclide contamination, including iodine treatment. The EPA put together a technology reference guide (EPA 2007) that discusses a range of technologies (solidification/stabilization, soil washing, capping, etc.) for radioactively contaminated media. This guide also discusses ion exchange and reverse osmosis, which are the two technologies identified as being effective for beta emitters (including ^{131}I). Truex et al. (2006) describe a range of technologies, which they screen for suitability in addressing classes of contaminants in groundwater at Hanford's 200-BP-5 OU. Watson et al. (2012) provide a good general review of halide treatment technologies, discussing membrane, electrochemical, and adsorption technologies. Rana et al. (2013) discuss liquid-phase treatment technologies in general before reviewing

membrane processes specifically, providing a long list of applications categorized by the particular membrane technology that was applied.

A number of documents have examined materials specifically for adsorption of iodine species. Mattigod et al. (2003) provide a good introduction to sorbents (so-called "getters") by discussing desired sorbent properties, several classes of iodide getters, and an approach to selecting an appropriate getter. Pierce et al. (2010) provide an extensive list of information on sorbents for iodine in liquid, and they discuss stabilization/disposal methods for silver mordenite (one commonly used type of iodine sorbent). Li et al. (2014) provide a good review (and list) of sorbents for iodine removal from water, plus they present experimental data for a suite of sorbents to compare their effectiveness. Parker et al. (2014) looked at effectiveness of iodine removal from water for multiple ion exchange resins and granular activated carbons. In a slightly different vein, though related, Haefner and Tranter (2007) discuss methods for iodine capture from fuel reprocessing off-gases, including various wet scrubbing and solid adsorbent technologies.

A couple of references provide a broader discussion of iodine in the environment and include some thoughts on iodine treatment technologies, though not a significant list and discussion of individual technologies. Denham et al. (2009) discuss radioiodine sources, exposure, biogeochemistry, and assay methods. In addition, they present a nice discussion of potential iodine remediation strategies and the issues pertaining to iodine remediation (e.g., impact of natural iodine on ^{129}I remediation, selectivity requirements for iodine treatment, stability of immobilized/sorbed iodine compounds, and iodine volatility). Expanding on the information in Mattigod et al. (2003) regarding characteristics of effective sorbents, Denham et al. (2009) also consider characteristics needed for in situ treatment in an aquifer. In their work, Kaplan et al. (2012) discuss sources of radioiodine, geochemistry of iodine, microbial processes impacting iodine, and iodine treatment challenges and strategies, mainly in the context of Hanford. They point out that Hanford has a large, dilute ^{129}I plume with coincident natural iodine at much higher concentrations. Given these conditions and the fact that removal of iodine would be expected to alter the system equilibrium and result in release of more natural iodine from the sediment, Kaplan et al. (2012) suggest that achieving the "exceptionally low" remediation target of the DWS presents significant challenges. Kaplan et al. (2012) further discuss the need to understand iodine speciation in the groundwater to obtain more accurate estimates of iodine migration and to have appropriate information to be able to select a treatment technology. The nature of the aquifer organic material and subsurface microbial activity also play a role in understanding iodine speciation and mobility. As part of their discussion on potential remediation strategies, Kaplan et al. (2012) provide some general information on various sorbents that exist or are being investigated to target capture of iodine species.

6.2 Using the Remediation Technology Information

The remedial approaches listed in Table 6.1 and described further in Appendix D, along with the conceptual site model (CSM) (Section 4.0) and regulatory context (Section 2.0), provide a basis for evaluation of suitable remedies. The site-specific context will help determine which remedial approaches are sufficiently developed and are conducive with the site conditions (iodine speciation, contaminated media, etc.) to potentially meet the remedial action objectives (RAOs). For groundwater contamination, key aspects are likely to be control of source flux to the groundwater, as well as treatment of contamination already in the groundwater. It may be important for a remedy to utilize a combination of remedial approaches to achieve remedial action goals. The process of assessing potential remedies should

also take into account other remedial actions being implemented or planned to address adjacent or co-existing contaminants. Such concurrent remedies could impact the CSM for iodine and should be integrated into the remedy for the iodine contamination.

Table 6.1. Inventory of remediation technologies for iodine.

Remediation Technology	Technology Maturity	Relative Cost	More Info
Ex Situ Aqueous-Phase Treatment			
Adsorption Water is passed through solid-phase sorbent media and contaminants are captured at active sites on the sorbent, resulting in treated water and contaminants concentrated on the solids. A variety of sorbents are applicable to one or more iodine species. • Activated carbon • Zeolite • Organoclay • Aerogels • Carbon nanotubes • Silver-impregnated carbon • Layered double hydroxides • Argentite • SAMMS • Photocatalytic adsorption	Mature (activated carbon) to developmental or bench scale (other sorbents)	Moderate	D.1.1.1
Ion Exchange Ions on solid phase media are exchanged for ions in solution in a mass transfer process that results in treated water and contaminants concentrated on the solids. Typically, media can be regenerated, resulting in a concentrated solution of contaminants and reusable media. A variety of ion exchange media is available. • Commercial ion exchange resins (Dow, Purolite, ResinTech, etc.) • ABEC ion exchange resins	Mature technology, though some resins are commercially available and some are being developed	Moderate	D.1.1.2
Membrane Separations A driving force (hydrostatic pressure, concentration gradient, or electrical potential gradient) causes selective passage of water and/or solutes through a membrane to obtain treated water and a concentrated solution with the contaminants. • Reverse osmosis Pressure-driven membrane technology to obtain clean water and a concentrated solution that contains contaminants • Electrodialysis Electric-current-driven membrane technology to separate ions in water, resulting in a treated water stream and a concentrated solution that contains contaminants	Mature	Moderate to high	D.1.1.3

Remediation Technology	Technology Maturity	Relative Cost	More Info
Electrochemical Separations Technologies to separate ions using an applied current, resulting in treated water and contaminants in a concentrated liquid or collected at an electrode. • Capacitive Deionization Uses porous activated or aerogel carbon electrodes to deionize water and capture ions in the electrodes; electrodes can be regenerated • Electrochemically Switched Ion Exchange Switched electrode potential is used to capture ions by adsorption on an electroactive film at the electrode; electrodes can be regenerated • Electrolysis Uses electrolysis to oxidize halides; has only been shown for bromide	Developmental to bench scale	Moderate to high	D.1.1.4
Co-precipitation and Coagulation Precipitation of iodine with an Ag, Cu, Hg, or Pb compound	Bench scale, though commonly used for sample preparation for iodine assay	Moderate	D.1.1.5
Ex Situ Gas-Phase Treatment			
Gas Phase Adsorption Gas is passed across solid phase materials that adsorb iodine; some sorbent materials can be densified into a durable and stable waste form. • Activated carbon • Silver impregnated alumina • Silver-loaded zeolite • Bismuth-based sorbents • Macroreticular resins • Silver exchanged mordenite • Silver impregnated silica-gel • Silver-functionalized silica aerogels	Mature, though aerogels and bismuth-based sorbents are newer developments	Moderate	D.1.2.1
Gas Phase Absorber (Scrubber) Mass transfer from gas phase to a liquid phase into which iodine preferentially partitions • Caustic solution (sodium hydroxide) • Hyperazeotropic nitric acid (Iodox) • Fluorocarbon • Molten hydroxide • Mercuric nitrate-nitric acid (Mercurex) • Electrolytic scrubbing • Polymethylsiloxane	Mature, though new scrubber solutions have been investigated (molten hydroxide is still developmental)	Moderate	D.1.2.2

Remediation Technology	Technology Maturity	Relative Cost	More Info
Ex Situ Solid-Phase Treatment			
Soil Washing Contaminant removal by ex situ scrubbing of soils using (typically) a water-based solution, though addition of surfactants and/or other additives may be used to improve contaminant recovery; results in treated soils and a contaminated liquid that requires further treatment/disposal.	Mature, but no known applications for iodine remediation	Low to moderate	D.1.3.1
Immobilization/Encapsulation and Solidification/Stabilization Processes by which contaminants are bound or enclosed within a monolithic solid; results in a solid waste (with favorable leaching characteristics, if properly developed/implemented); cement has been demonstrated for iodine treatment.	Mature, though iodine applications may require additional testing	Low to moderate	D.1.3.2
Adsorption/Vitrification Technology being developed to capture iodine from gas on nanoporous alumina, precipitate with silver or copper, then vitrify the alumina/iodine + glass formers to encapsulate the iodine.	Bench scale	Moderate to high	D.1.3.3
Low-Temperature Vitrification Iodine is captured on an adsorbent and is subsequently sequestered in low-temperature sintering glasses (e.g., bismuth-phosphate-zinc oxide, lead-boron-zinc) to make chemically durable waste forms; low temperature is intended to minimize volatilization.	Bench scale	Moderate to high	D.1.3.4
Encapsulation in Tin Involves fusing iodide that is sorbed on silver-loaded sorbents with tin in a hot-pressing process to produce a consolidated mass.	Bench scale	Moderate to high	D.1.3.5
Near-Surface / Source Zone Remediation			
Excavation Physical removal of contaminated soil for ex situ treatment or disposal.	Mature	Low to moderate	D.2.1
Vadose Zone Remediation (Control of Contaminant Flux to Groundwater)			
Surface Cap Engineered cover comprised of asphalt, clay, and/or geo-membrane materials installed at the ground surface to intercept/collect precipitation, preventing infiltration and associated contaminant migration.	Mature	Low to moderate	D.3.1.1
Horizontal Grout Barrier Horizontal infiltration barrier installed in the subsurface using either jet grouting or permeation grouting; purpose is to reduce contaminant migration (by preventing infiltration or by directly reducing contaminant mobility).	Mature	Low to moderate	D.3.1.2

Remediation Technology	Technology Maturity	Relative Cost	More Info
Lateral Desiccation Zone Subsurface horizontal infiltration barrier created by injecting dry air into a relatively permeable zone to create a desiccated layer that resists downward water (and dissolved contaminant) flux.	Pilot scale	Low to moderate	D.3.1.2
Soil Vapor Extraction Extraction of soil gas and volatile contamination from relatively permeable sediments by vapor extraction wells under vacuum.	Mature, though no applications for iodine are known	Low to moderate	D.3.2
In Situ Soil Heating Subsurface soil is heated (e.g., by resistive heating or hot air injection) to enhance contaminant volatilization; contaminants are collected via an SVE system or vapor collection hood.	Mature, though no applications for iodine are known	Moderate to high	D.3.3
In Situ Reactive Gas This technology would involve introduction of an appropriate reactive gas into a relatively permeable layer of the vadose zone to achieve reactions that immobilize iodine.	Developmental	Moderate to high	D.3.4
Saturated Zone Remediation (Groundwater Treatment)			
Monitored Natural Attenuation Natural processes such as dispersion, adsorption, and reaction (abiotic and/or biological) act to reduce the mass, toxicity, mobility, volume, or concentration of the contaminant plume; monitoring is used to track the attenuation and confirm that the remedy will meet goals.	Mature, though no applications for iodine are known	Low to moderate	D.4.1
Permeable Reactive Zone Injection of reagents or emplacement of slurry as a permeable reactive zone in the aquifer; potential reagents for iodine remediation include Ag, Hg, or Cu compounds for iodine capture and immobilization; silver chloride has been demonstrated for iodine.	Mature, though experience for iodine treatment is limited	Moderate to high	D.4.2
Microbial Facilitated Reactions Stimulation of microbes in the subsurface to increase the population count and drive specific reactive and/or sorptive processes. • Microbial Reduction/Oxidation Modify iodine redox state by enhancement of sulfate- or iron-reducing bacteria; impacts speciation, which may facilitate sorption/precipitation. • Microbial-Facilitated Volatilization Bacteria could facilitate formation of volatile methyl iodine, which could then be stripped with air sparging and collected by soil vapor extraction. • Bioaccumulation/Bioadsorption Bacteria may adsorb iodine species extracellularly or accumulate iodine intracellularly, thus reducing iodine mobility.	Developmental to bench scale	Moderate	D.4.3

Remediation Technology	Technology Maturity	Relative Cost	More Info
Air Sparging Air is injected into an aquifer to facilitate mass transfer from aqueous to gas phases; typically requires capture by soil vapor extraction.	Bench scale	Moderate	D.4.4
Extraction Wells Wells screened in the aquifer are pumped to capture the contaminant plume, preventing further downgradient migration and removing contaminant mass from the aquifer (which must be treated ex situ); may be designed to control contaminant flux from a source area, intercept the plume, or volumetrically reduce the plume extent.	Mature	Moderate	D.4.5.1
Interceptor Trench Lateral groundwater collection at a trench to control contaminant migration; applies to relatively shallow groundwater; extracted water must be treated ex situ.	Mature	Moderate	D.4.5.2
Slurry Wall Cutoff wall installed as a trench with a low-permeability slurry backfill; slurry is typically comprised of bentonite, water, and either soil or cement; a geomembrane is sometimes also installed in the trench.	Mature	Moderate to high	D.4.5.3
Grout Curtain Thin cutoff wall constructed by pressure injection of grout along a series of closely spaced borings.	Mature	Moderate to high	D.4.5.4
Sheet-pile Wall Cutoff wall comprised of interconnected sections of pre-fabricated steel or high-density polyethylene sheets driven into subsurface.	Mature	Moderate to high	D.4.5.5
Electrokinetic Remediation Electrodes installed in the subsurface cause precipitation of an iron-rich band (flow barrier), acid front generation, contaminant desorption, and ion migration (i.e., iodide migration towards the anode).	Developmental to bench scale	Moderate to high	D.4.6
Administrative / Engineered Controls			
Institutional Controls Administrative and engineered controls to prevent exposure to contamination; requires active management and periodic monitoring, inspection, and maintenance • Land use (deed) restrictions • Groundwater use restrictions • Access control (signs/fences)	Mature	Low	D.5.1

6.3 References

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7.0 Development of ^{129}I Remediation Options

This section describes the approach that will be implemented to evaluate remediation options for ^{129}I and fulfill the requirement for this evaluation included in the 200-UP-1 OU ROD. As described in the previous sections, multiple factors control ^{129}I plume behavior. These factors must be considered when evaluating remediation options. Some important biogeochemical information (Sections 3 and 4) became available after the 200-UP-1 OU RI/FS had been completed. This new information affects predictions of the fate and transport of ^{129}I and the applicability of some remediation options. Information about risk (Section 5) and regulatory guidance (Section 2) provides additional context for evaluating ^{129}I remediation options.

7.1 Technology Evaluation Process

Figure 7.1 shows an overview of the remediation technology evaluation process. This approach is consistent with the requirements for CERCLA technology evaluations (EPA 1988) and expands on the previous 200-UP-1 OU RI/FS evaluation by including treatability testing elements to adequately evaluate some of the candidate technologies. To conduct the evaluation, fate and transport simulations must be updated to incorporate new information about iodine speciation for the 200-UP-1 OU and relevant biogeochemical reactions of the various iodine species. The species of ^{129}I present (iodide, iodate, and organo-iodine) affect transport behavior along exposure pathways (Sections 3.0 and 4.0). Several alternative conceptual models were developed by Truex et al. (2015a) 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 specific transformation reactions are significant within the aquifer, and whether a significant flux of contaminants from the vadose zone will occur. The evaluation will include investigations and updated modeling developed based on the recommendations in Truex et al. 2015a to support refining the CSM and for potential reconsideration of the baseline risk assessment. Using the refined CSM, potential remediation configurations to meet the RAOs can be identified (e.g., scenarios that identify treatment volumes and concentration or flux reduction targets). This information supports the subsequent remediation technology evaluation and associated treatability testing elements.

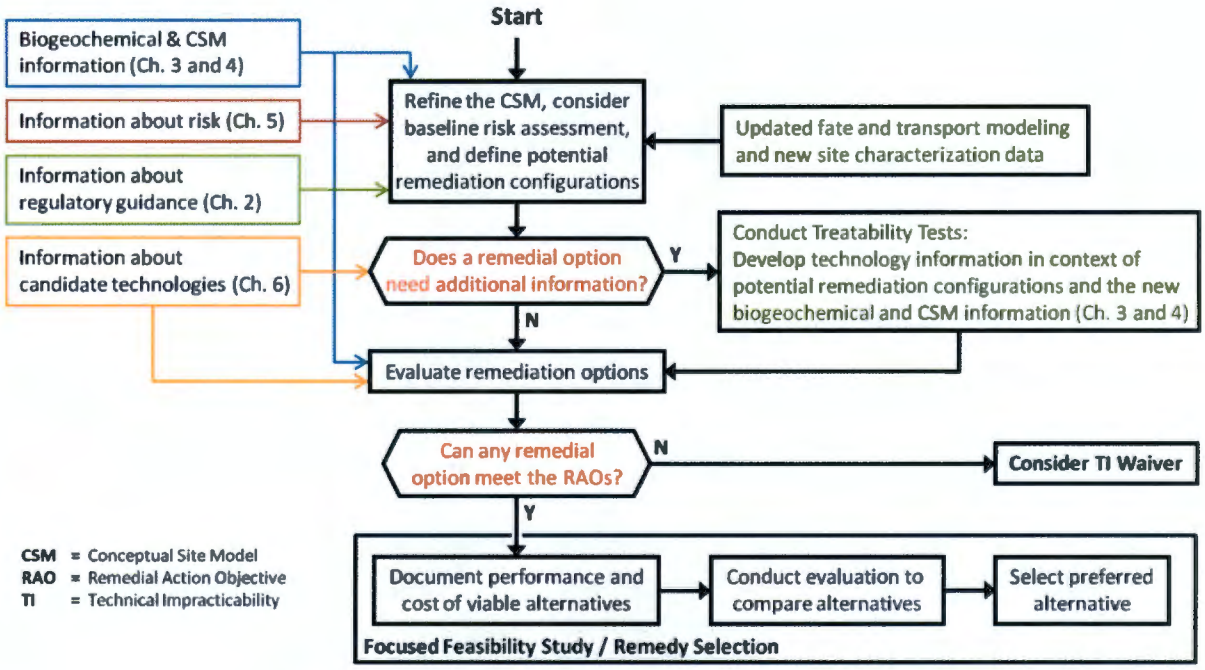

Figure 7.1. Comprehensive remedy evaluation process.

The "evaluate remediation options" portion of Figure 7.1 will be conducted in two primary steps, using an approach similar the remediation technology evaluations for the 200-BP-5 and 200-ZP-1 OUs (Truex et al. 2006a, b). The initial screening step will evaluate potential remediation options based on whether they can be effectively applied within the environmental setting of the 200-UP-1 OU. In the second step, potential remediation methods will be screened using scoping calculations to estimate the scale of infrastructure, overall quantities of reagents, and conceptual approach. Based on these estimates, each method will be screened with respect to effectiveness, implementability, and relative cost criteria of the CERCLA feasibility study screening process defined in EPA guidance (EPA 1988). In general, the effectiveness evaluation is related to (1) the estimated reliability of the process and whether it has been proven successful; (2) the expected ability of the method to treat the necessary volume of contaminated media; and (3) the potential for negative human or environmental impacts during construction and operation. Implementability is generally related to (1) the scale of effort and technical certainty that the method can be implemented at the site; (2) the availability of consumables, equipment, and services; and (3) the ability to obtain permits and administratively manage the method. The relative cost is evaluated using a conceptual design and relative cost estimates based on the relative capital and operation and maintenance required for each option. As noted previously, some candidate technologies will require treatability testing to effectively evaluate their potential for use at the 200-UP-1 OU.

The remediation technology evaluation will compile sufficient information about the technology options to demonstrate whether they are viable with respect to meeting the 200-UP-1 OU RAOs identified for ^{129}I. Based on the remedial evaluation results, the OU can either pursue a technical impracticability or other ARAR waiver, or conduct a focused feasibility study to select an ^{129}I remedy other than the hydraulic control remedy that was identified in the 200-UP-1 OU ROD.

7.2 Anticipated Technology Categories for Evaluation

The compilation of candidate remediation technologies in Section 6 serves as a starting point for evaluating remedial options for ^{129}I. Based on information in the existing 200-UP-1 OU RI/FS and the new information presented in the previous sections of this document, the evaluation of remedial options can be organized to focus on several categories of technologies.

- **Ex Situ Treatment**: The RI/FS identified pump and treat as a viable alternative for other constituents of concern in the 200-UP-1 OU, but determined that mature, demonstrated ex situ treatment processes for ^{129}I were not available. Ion exchange, silver-impregnated granular activated carbon, reverse osmosis, and electrodialysis were specifically considered in the RI/FS, but it was concluded that treatability testing would be required to evaluate potential ^{129}I treatment options. Thus, one element of the current ^{129}I remediation evaluation will focus on the ex situ treatment processes identified in Section 6, including adsorption, ion exchange, reverse osmosis, and electrochemical approaches. In particular, this evaluation will consider the new information about iodine speciation, which will affect the performance characteristics of these candidate processes.

- **In Situ Chemical Treatment:** The RI/FS identified in situ chemical precipitation of ^{129}I in the aquifer using a copper-based process as a potential remediation technology. However, the need for treatability testing and the difficulty in applying the technique over the large volume of the 200-UP-1 OU ^{129}I plume were stated as reasons to reject this technology. One element of the current ^{129}I remediation evaluation will focus on in situ chemical treatment processes. New technology information (in particular, the recent developments in the use of silver chloride as a precipitation agent) will be considered in the evaluation. In addition, the new information about iodine speciation in the aquifer and the associated change in transport behavior may render in situ treatment of targeted hot spots of the plume an effective approach for meeting RAOs. Thus, the in situ treatment evaluation may include these hot-spot treatment scenarios and will be linked to fate and transport modeling to select appropriate target treatment volumes.

- **In Situ Biological Treatment:** The RI/FS assessed in situ biological treatment options for other constituents of concern in the aquifer, but rejected these due to the large plume size. However, if treatment of smaller hot-spot zones is effective at meeting RAOs (as described above for in situ chemical precipitation technologies), then biological processes may also be viable, pending results of ongoing iodine biogeochemistry research.

- **Monitored Natural Attenuation:** The RI/FS rejected MNA for ^{129}I based on the long time frame for ^{129}I attenuation and the significant extent of plume movement (assuming that all of the ^{129}I was present as iodide) indicated by fate and transport simulations. MNA needs to be reevaluated because new speciation information shows that a significant portion of the ^{129}I is present as iodate and organo-iodine, and a smaller amount is present as iodide. The transport properties of these multiple iodine species differ and overall ^{129}I transport will be slower, allowing for more attenuation than determined in the previous fate and transport assessment. In addition, biogeochemical cycling of iodine species (e.g., the potential for formation of iodate-calcite and/or accumulation of iodine as sediment-associated organo-iodine) was not considered in the earlier assessment. A new MNA evaluation is also needed so that this new reaction information can be considered. The MNA evaluation will follow the established MNA technical protocol and will use the updated fate and transport modeling being applied to evaluate other groundwater treatment options.

- **Vadose Zone Source Control Treatment:** Treatment of the vadose zone to address future contaminant discharge into the groundwater (i.e., source control) was not addressed in the RI/FS. As part of the updated fate and transport modeling being applied to evaluate groundwater treatment options, one element of the technology evaluation will include estimating the future contaminant discharge from the vadose zone. This source control evaluation will establish the amount of contaminant flux reduction in the vadose zone that is needed to provide source control for the groundwater remedies. Potentially, no vadose zone remediation will be needed. However, if vadose zone remediation is needed, candidate technologies (i.e., those listed in Section 6) will be evaluated to provide the targeted flux reduction. Some candidate technologies (e.g., surface barriers, desiccation, grout barriers) can be evaluated based on existing information and modeled performance. Other technologies, such as in situ reactive gas treatment (e.g., a treatment like the ammonia treatment being tested for uranium sequestration in the vadose zone), will require laboratory testing to assess effectiveness for iodine contamination. While not within the 200-UP-1 OU, source control may be necessary to integrate with groundwater remediation components of a 200-UP-1 OU remedy. For instance, an MNA remedy requires evaluation of contaminant sources and source control.

7.3 Technology Evaluation Tasks

The following tasks are associated with implementing the evaluation approach described above.

1. **Conduct fate and transport analysis for the ^{129}I groundwater plume and potential (vadose zone contributions under natural conditions:** As shown in Figure 7.1, investigations and updated fate and transport modeling to evaluate alternative CSMs for future iodine plume behavior are needed as an initial element of the remedy evaluation process. The RI/FS fate and transport modeling was conducted using estimated transport parameters for iodide only. The modeling also did not include an evaluation of ^{129}I transport from the vadose zone. The simulation scenarios from the RI/FS will be repeated, with inclusion of the observed iodine species distribution and appropriate adsorption parameters for transport of these species. The investigations and modeling will also be extended using a graded approach to evaluate the impact of biogeochemical reactions and relevant solid-phase iodine compounds (e.g., iodate-calcite and/or accumulation of iodine as sediment-associated organo-iodine) on the fate and transport of ^{129}I. In addition, the continuing source term of ^{129}I from the vadose zone will be evaluated and quantified for inclusion in the modeling assessment. This set of simulations will provide the baseline plume predictions for use in subsequent risk assessment and remedy evaluation tasks.

2. **Refine the CSM and associated risk assessment and define potential remediation configurations for the remediation evaluation:** Setting a context for remedy evaluation is a key aspect of the process depicted in Figure 7.1. Results of the fate and transport analysis and complementary biogeochemical data will be incorporated into a refined CSM describing expected ^{129}I plume behavior and associated controlling factors. The refined CSM and an associated risk assessment will be used to identify potential remediation configurations to meet the RAOs (e.g., appropriate treatment volumes and concentration or flux reduction targets).

3. **Evaluate remedial options and conduct supporting treatability testing:** The remedy evaluation process is expected to include treatability testing for some potential technologies (Figure 7.1). Based on the refined CSM and potential remediation configurations developed in Task 2, remedial options

will be evaluated following CERCLA guidance for conducting feasibility studies (EPA 1988). This evaluation will include a reevaluation of an MNA remedy under the updated fate and transport and risk conditions. Information available to support performance estimates for promising remediation technology options will be assessed to identify data gaps that will then be addressed with treatability testing via laboratory experiments, modeling efforts, or field tests. The remedial options will be evaluated with respect to achieving suitable performance to meet the RAOs and the timeframe required for the remedy. The evaluation will use the model developed for Task 1, with inclusion of appropriate biogeochemical reactions and use of high-performance computing, as appropriate, to estimate remedy performance.

7.4 References

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Appendix A

Unit Conversions

Appendix A

Unit Conversions

The following information is provided to assist the reader in understanding this report. Included here is information on scientific notation, units of measure, radioactivity units, and radiological dose units.

A.1 Scientific Notation

Scientific notation is used to express very large or very small numbers. For example, the number 1 billion could be written as 1,000,000,000 or, by using scientific or E notation, written as 1×10^9 or 1.0E+09. Translating from scientific notation to a more traditional number requires moving the decimal point either left or right from its current location. If the value given is 2.0×10^3 (or 2.0E+03), the decimal point should be moved three places to the right so that the number would then read 2,000. If the value given is 2.0×10^{-5} (or 2.0E-05), the decimal point should be moved five places to the left so that the result would be 0.00002.

A.2 Units of Measure

The primary units of measure used in this report follow the International System of Units and are metric. Table A.1 summarizes and defines the terms and corresponding symbols (metric and non-metric). A conversion table is also provided in Table A.2.

A.3 Radioactivity Units

Much of this report provides data on levels of radioactivity in various environmental media. Radioactivity in this report is usually discussed in units of curies (Ci), with conversions to becquerels (Bq), the International System of Units measure (Table A.3). The curie is the basic unit used to describe the amount of activity present, and activities are generally expressed in terms of curies per mass or volume (e.g., picocuries per liter). One curie is equivalent to 37 billion disintegrations per second or is a quantity of any radionuclide that decays at the rate of 37 billion disintegrations per second. One becquerel is equivalent to one disintegration per second. Nuclear disintegrations produce spontaneous emissions of alpha or beta particles, gamma radiation, or combinations of these. Table A.4 includes selected conversions from curies to becquerels.

A.4 Radiological Dose Units

Radiological dose in this report is usually written in terms of effective dose equivalent and reported numerically in units of millirem (mrem), with the metric units millisievert (mSv) or microsievert (μSv) following in parenthesis or footnoted.

Millirem (millisievert) is a term that relates a given amount of absorbed radiation energy to its biological effectiveness or risk to humans. For perspective, a dose of 1 millirem (0.01 millisievert) would

have a biological effect roughly the same as received from 1 day's exposure to natural background radiation. An acute (short-term) dose to the whole body of 100 rem (1 sievert) would likely cause temporary radiation sickness in some exposed individuals. An acute dose of over 500 rem (5 sievert) would soon result in death in approximately 50% of those exposed. Exposure to lower amounts of radiation (10 mrem [100 μSv or 0.1 mSv] or less) produces no immediate observable effects, but long-term (delayed) effects are possible. The average person in the United States receives an annual dose from exposure to naturally produced radiation of approximately 300 mrem (3 mSv). Medical and dental x-rays and air travel add to this total. Table A.5 includes selected conversions from rem to sievert.

Also used in this report is the term rad, with the corresponding unit gray (Gy) in parenthesis or footnoted. The rad (gray) is a measure of the energy absorbed by any material, whereas a rem relates to both the amount of radiation energy absorbed by humans and its consequence. The gray can be converted to rad by multiplying by 100. The conversions in Table A.5 can also be used to convert grays to rads.

A roentgen (R) is a measure of exposure to electromagnetic radiation (i.e., gamma and x-radiation). One roentgen is equivalent to a charge release of 258 microcoulombs per kilogram of air.

The names and symbols for units of radiation dose used in this report are listed in Table A.6.

Table A.1. Names and symbols for units of measure.

Symbol	Name	Symbol	Name
Temperature		**Concentration**	
°C	degree Celsius	ppb	parts per billion
°F	degree Fahrenheit	ppm	parts per million
Time		ppmv	parts per million by volume
d	day	**Length**	
hr	hour	cm	centimeter (1×10^{-2} m)
min	minute	ft	foot
sec	second	in.	inch
yr	year	km	kilometer (1×10^{3} m)
Rate		m	meter
cfs (or ft^3/sec)	cubic feet per second	mi	mile
cpm	counts per minute	mm	millimeter (1×10^{-3} m)
gpm	gallon per minute	µm	micrometer (1×10^{-6} m)
mph	mile per hour	**Area**	
mR/hr	milliroentgen per hour	ha	hectare (1×10^{4} m^2)
mrem/yr	millirem per year	km^2	square kilometer
Volume		mi^2	square mile
cm^3	cubic centimeter	ft^2	square foot
ft^3	cubic foot	**Mass**	
gal	gallon	g	gram
L	liter	kg	kilogram (1×10^{3} g)
m^3	cubic meter	mg	milligram (1×10^{-3} g)
mL	milliliter (1×10^{-3} L)	µg	microgram (1×10^{-6} g)
yd^3	cubic yard	lb	pound

Table A.2. Conversion table.

Multiply	By	To Obtain	Multiply	By	To Obtain
cm	0.394	in.	in.	2.54	cm
m	3.28	ft	ft	0.305	m
km	0.621	mi	mi	1.61	km
kg	2.205	lb	lb	0.454	kg
L	0.2642	gal	gal	3.785	L
m^2	10.76	ft^2	ft^2	0.093	m^2
ha	2.47	acres	acre	0.405	ha
km^2	0.386	mi^2	mi^2	2.59	km^2
m^3	35.31	ft^3	ft^3	0.0283	m^3
m^3	1.308	yd^3	yd^3	0.7646	m^3
pCi	1,000	nCi	nCi	0.001	pCi
µCi/mL	109	pCi/L	pCi/L	10-9	µCi/mL
Ci/m^3	1012	pCi/m^3	pCi/m^3	10-12	Ci/m^3
mCi/cm^3	1015	pCi/m^3	pCi/m^3	10-15	mCi/cm^3
nCi/m^2	1.0	mCi/km^2	mCi/km^2	1.0	nCi/m^2
Ci	3.7×10^{10}	Bq	Bq	2.7×10^{-11}	Ci
pCi	0.037	Bq	Bq	27	pCi
rad	0.01	Gy	Gy	100	rad
mrem	0.01	mSv	mSv	100	mrem
rem	0.01	Sv	Sv	100	rem
ppm	1,000	ppb	ppb	0.001	ppm
°C	(°C × 9/5) + 32	°F	°F	(°F -32) ÷ 9/5	°C
oz	28.349	g	g	0.035	oz
ton	0.9078	tonne	tonne	1.1	ton

Table A.3. Names and symbols for units of radioactivity.

Symbol	Name	Symbol	Name
Ci	curie	Bq	becquerel (2.7×10^{-11} Ci)
mCi	millicurie (1×10^{-3} Ci)	kBq	kilobecquerel (1×10^{3} Bq)
µCi	microcurie (1×10^{-6} Ci)	MBq	megabecquerel (1×10^{6} Bq)
nCi	nanocurie (1×10^{-9} Ci)	mBq	millibecquerel (1×10^{-3} Bq)
pCi	picocurie (1×10^{-12} Ci)	GBq	gigabecquerel (1×10^{9} Bq)
fCi	femtocurie (1×10^{-15} Ci)	TBq	terabecquerel (1×10^{12} Bq)
aCi	attocurie (1×10^{-18} Ci)		

Table A.4. Conversions for radioactivity units.

aCi	fCi	fCi	pCi	pCi	nCi	nCi	µCi	µCi	mCi	mCi	Ci	Ci	kCi
27	1	27	1	27	1	27	1	27	1	27	1	27	1
1 µBq	37 µBq	1 mBq	37 mBq	1 Bq	37 Bq	1 kBq	37 kBq	1 MBq	37 MBq	1 GBq	37 GBq	1 TBq	37 TBq

New unit of quantity = Becquerel (Bq) (formerly curie [Ci]) (1 Ci = 3.7×10^{10} dps).
1 Becquerel = 1 disintegrations/sec (dps).

Table A.5. Conversions for radiological dose units.

µSv	µSv	µSv	µSv	µSv	mSv	mSv	mSv	Sv
0.01	0.1	1	10	100	1	10	100	1
1 µrem	10 µrem	100 µrem	1 mrem	10 mrem	100 mrem	1 rem	10 rem	100 Rem

Unit of absorbed dose – Gray (Gy) (formerly rad).
Unit of dose equivalent – Sievert (Sv) (formerly rem).
Table also converts Gy to rad.

Table A.6. Names and symbols for units of radiation dose or exposure.

Symbol	Name
mrad	millirad (1×10^{-3} rad)
mrem	millirem (1×10^{-3} rem)
µrem	microrem (1×10^{-6} rem)
Sv	sievert (100 rem)
mSv	millisievert (1×10^{-3} Sv)
µSv	microsievert (1×10^{-6} Sv)
R	roentgen
mR	milliroentgen (1×10^{-3} R)
µR	microroentgen (1×10^{-6} R)
Gy	gray (100 rad)
mGy	milligray (1×10^{-3} rad)

A.5 References

EPA 402-R-99-001 (1999) Cancer Risk Coefficients for Environmental Exposure to Radionuclides, Appendix G in Federal Guidance Report 13, K.F. Eckerman, R.W. Leggett, C.B. Nelson, J.S. Puskin, and A.C.B. Richardson, Office of Radiation and Indoor Air, U.S. Environmental Protection Agency, Washington, D.C.

Appendix B

Identification of Potential Applicable or Relevant and Appropriate Requirements

Appendix B

Identification of Potential Applicable or Relevant and Appropriate Requirements

B.1 Introduction

This appendix provides preliminary applicable or relevant and appropriate requirements (ARARs) and to be considered for remedial action in the 100-OL-1 Operable Unit. Federal ARARs are listed in Table B.1. Washington State ARARs are listed in Table B.2.

Table B.1. Identification of potential federal ARARs and to be considered for the remedial action sites.

Citation	Description of Requirement	Rationale for Use	Possible Application
Safe Drinking Water Act of 1974 (Public Law 93-523, as amended; 42 USC 300f, et seq.); "National Primary Drinking Water Regulations" (40 CFR 141)			
"Maximum Contaminant Levels for Organic Contaminants," 40 CFR 141.61	Establishes MCLs for drinking water that are designed to protect human health from the potential adverse effects of organic contaminants in drinking water.	Provide a starting point for establishing discharge criteria for organic compounds remaining in treated effluent water from pump and treat system. Also provides standard for extent of groundwater remedy.	Discharge criteria after treatment for water extracted and either re-injected or disposed to surface water body. Utilize in developing cleanup criteria for aquifer.
"Maximum Contaminant Levels for Inorganic Contaminants," 40 CFR 141.62	Establishes MCLs for drinking water that are designed to protect human health from the potential adverse effects of inorganic contaminants in drinking water.	Provide a starting point for establishing discharge criteria for inorganic substances remaining in treated effluent water from pump and treat system. Also provides standard for extent of groundwater remedy.	Discharge criteria after treatment for water extracted and either re-injected or disposed to surface water body. Utilize in developing cleanup criteria for aquifer.
"Maximum Contaminant Levels for Radionuclides," 40 CFR 141.66	Establishes MCLs for drinking water that are designed to protect human health from the potential adverse effects of radionuclides in drinking water.	Provide a starting point for establishing discharge criteria for radionuclides remaining in treated effluent water from pump and treat system. Also provides standard for extent of groundwater remedy.	Discharge criteria after treatment for water extracted and either re-injected or disposed to surface water body. Utilize in developing cleanup criteria for aquifer.

Citation	Description of Requirement	Rationale for Use	Possible Application
Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites (EPA/540/R-99/009)	Provides the framework and appropriateness for using the MNA as a remedy component for organic and inorganic contaminants.	Provides rationale and framework for developing a MNA alternative	Guide establishment of clean-up action plan, monitoring plan and performance criteria for a MNA remedy.
Clean Air Act of 1977; 40 CFR 60, "Standards of Performance for New Stationary Sources"			
40 CFR 60, "Standards of Performance for New Stationary Sources"	Applies to specific stationary sources that emit toxic air pollutants where construction or modification of the facility commences after the effective date of any standard promulgated in this regulation.	Defines emission limits from any active water treatment process which emits toxic air pollutants to atmosphere.	Performance criteria for design and operation of treatment processes in an ex-situ treatment or in-situ treatment remedy that emits toxic air pollutants.
Clean Air Act of 1977; 40 CFR 61, "National Emission Standard for Hazardous Air Pollutants"			
40 CFR 61.01 , "Lists of pollutants and applicability of part 61" 40 CFR 61.05, "Prohibited activities" 40 CFR 61.12, "Compliance with standards and maintenance requirements" 40 CFR 61.14, "Monitoring Requirements"	Provides general requirements for facility operations that emit regulated hazardous air pollutants. The regulation applies to any stationary source for which a standard has been prescribed.	Guide and regulate design, construction, and operation of groundwater or sediment remediation processes with regard to emission of hazardous pollutants to atmosphere.	Performance criteria for design and operation of treatment processes in an ex-situ treatment or in-situ treatment remedy that emits toxic air pollutants.
Archaeological and Historic Preservation Act of 1974			
40 CFR 6.301(c), "Applicant Requirements"	Requires that remedial actions do not cause the loss of any archaeological or historic data. This act mandates preservation of the data; it does not require protection of the actual waste site or facility.	Implementation of ex-situ or in-situ treatment remedies could modify or affect archaeological or historic assets at the site.	Adjust characterization and remedy design work plans to minimize disruption or loss of information and facilitate collection of archaeological and historic information while characterizing, constructing and operating a remedy.

Citation	Description of Requirement	Rationale for Use	Possible Application
National Historic Preservation Act of 1966			
36 CFR 800, "Protection of Historic Properties" 40 CFR 6.301(b). "Applicant Requirements" Executive Order 11593, *Protection and Enhancement of the Cultural Environment* 36 CFR 65, "National Historic Landmarks Program" 36 CFR 60, "National Register of Historic Places"	Requires federal agencies to consider the impacts of their undertaking on cultural properties through identification, evaluation, mitigation processes, and consultation with interested parties.	Implementation of ex-situ or in-situ treatment remedies could modify or affect historic or cultural assets at the site.	Conduct characterization, remedy selection, design, construction, and cleanup operation activities for selected remedies so as to mitigate or avoid damage to historic and cultural assets.
Native American Graves Protection and Repatriation Act of 1990			
43 CFR 10, "Native American Graves Protection and Repatriation Regulations"	Establishes federal agency responsibility for discovery of human remains, associated and unassociated funerary objects, sacred objects, and items of cultural patrimony. Requires Native American consultation in the event of discovery.	Site characterization and implementation of ex-situ or in-situ treatment remedies could discover or disturb cultural assets at the site.	Conduct characterization, remedy selection, design, construction, and cleanup operation activities for selected remedies so as to preserve, mitigate or avoid damage to cultural assets.
Endangered Species Act of 1973			
50 CFR 402, "Interagency Cooperation – Endangered Species Act of 1971 , as amended" 40 CFR 6.302(c), "Responsible Official Requirements"	Prohibits actions by federal agencies that are likely to jeopardize the continued existence of listed species or result in the destruction or adverse modification of habitat critical to them. Mitigation measures must be applied to actions that occur within critical habitats or surrounding buffer zones of listed species, in order to protect the resource.	Site characterization and implementation of ex-situ or in-situ treatment remedies could disturb or endanger sensitive species or their habitat at the site.	Conduct characterization, remedy selection, design, construction, and cleanup operation activities for selected remedies so as to protect sensitive species, and mitigate or avoid damage to habitat for such species.

Citation	Description of Requirement	Rationale for Use	Possible Application
Migratory Bird Treaty Act of 1918			
16 USC 703-712; Ch. 128; 40 Stat. 755	Protects all migratory bird species and prevents "take" of protected migratory birds, their young, or their eggs."	Site characterization and implementation of ex-situ or in-situ treatment remedies could disturb or endanger migratory birds and their nesting habitat, particularly if proximate to surface water.	Conduct characterization, remedy selection, design, construction, and cleanup operation activities for selected remedies so as to protect migratory birds, and mitigate or avoid damage to nesting habitat.
Floodplain Management, Executive Order 11988			
Executive Order 11988, *Floodplain Management* 10 CFR 1022, "Compliance with Floodplain and Wetland Environmental Review Requirements"	Take action to avoid adverse effects, minimize potential harm, and restore and preserve natural and beneficial values of the floodplain.	Site characterization and implementation of treatment remedies could disturb or adversely affect floodplain values depending upon location and extent.	Conduct characterization, remedy selection, design, construction, and cleanup operation activities for selected remedies so as to minimize potential harm to floodplain areas.
Clean Air Act of 1977; 40 CFR 61, "National Emission Standards for Hazardous Air Pollutants"			
40 CFR 61.05, "Prohibited Activities"	Identifies prohibited activities from stationary sources of air pollutants including operating a stationary source that is in violation of any national emission standard unless specifically exempted; or operating any existing source that is subject to national emission standards, in violation of the standards.	Construction or operation of some remedies, particularly ex-situ treatment systems for groundwater may release air emissions that could exceed a national emission standard.	Design and operate treatment processes in an ex-situ treatment or in-situ treatment remedy so as to comply with national emission standards.
40 CFR 61.12, "Compliance with Standards and Maintenance Requirements"	Requires the owner and operator of each stationary source to maintain and operate the source and associated air pollution control equipment in a manner that minimizes emissions	Ex-situ treatment equipment that release emissions to the atmosphere during operation or maintenance could have air pollution control equipment.	Maintain and operate water or soil gas treatment with off gas treatment equipment so as to minimize air emissions.

Citation	Description of Requirement	Rationale for Use	Possible Application
40 CFR 61.14, "Monitoring Requirements"	Requires the owner and operator to maintain and operate each monitoring system in a manner consistent with air pollution control practices for minimizing emissions	Where a groundwater or sediment treatment remedy involves equipment which releases emissions to the atmosphere, proper maintenance and operation is necessary.	Maintain and operate water or soil gas treatment with off gas treatment equipment so as to minimize air emissions.

CERCLA = Comprehensive Environmental Response, Compensation, and Liability Act of 1980
CFR = Code of Federal Regulations
IDW = investigation derived waste
FS = feasibility study
MNA = monitored natural attenuation
OU = operable unit
RI/FS = remedial investigation/feasibility study
RTD = removal, treatment, and disposal

Table B.2. Identification of potential State of Washington applicable or relevant and appropriate requirements and to be considered for the remedial action sites.

Citation	Description of Requirement	Rationale for Use	Possible Application
Model Toxics Control Act; WAC 173-340, "Model Toxics Control Act- Cleanup"			
"Ground Water Cleanup Standards" (WAC 173-340-720) "Method B Cleanup Levels for Potable Ground Water" (WAC 173-340-720(4)(b)(i-iii) (A)&(B)) "Adjustments to Cleanup Levels" (WAC 173-340-720(7))	Groundwater cleanup levels are based on estimates of the highest beneficial use and the reasonable maximum exposure expected to occur under both current and potential future site use conditions. Method B equations (720-1 and 720-2) to calculate groundwater cleanup levels for noncarcinogens and carcinogens, respectively, only if "sufficiently protective, health-based criteria or standards have not been established under applicable state and federal laws. Groundwater cleanup levels are established at concentrations that do not directly or indirectly cause violations of surface water, sediments, soil, or air cleanup standards.	Provides standard for extent and degree of action for planning and implementation of groundwater remedy.	Discharge criteria after treatment for water extracted and either re-injected or disposed to surface water body. Utilize in developing cleanup criteria for aquifer.

Citation	Description of Requirement	Rationale for Use	Possible Application
WAC 173-340-740, "Unrestricted Land Use Soil Cleanup Standards"	Establishes soil cleanup levels where residential land use represents the reasonable maximum exposure under both current and future site use conditions. Cleanup standards require specification of the following: hazardous substance concentrations that protect human health and the environment (clean up levels), the location of the site where clean up levels must be attained ("points of compliance"), and other regulatory requirements that apply to the clean up action because of the type of action or location of the site. These requirements are specified in the applicable State and Federal laws and are generally established in conjunction with the selection of a specific cleanup action.	Provides standard for extent and degree of action for planning and implementation of sediment remedy.	May be applicable for remedy selection and setting/guiding extent of near surface sediment remediation work.
WAC 173-340-7490, "Terrestrial Ecological Evaluation Procedures" WAC 173-340-7493, "Site-Specific Terrestrial Ecological Evaluation Procedures" WAC 173-340-7494 "Priority Contaminants of Ecological Concern"	Defines goals and procedures for determining whether a release of hazardous substances to soil may pose a threat to the terrestrial environment. Characterizes existing or potential threats to terrestrial plants or animals exposed to hazardous substances in soil; and establishes site-specific cleanup standards for the protection of terrestrial plants and animals	Provides standard for extent and degree of action for planning and implementation of sediment remedy as it may impact soils at the surface.	May be applicable for remedy selection and setting/guiding extent of near surface sediment remediation work. May be applicable for guiding disposition of stabilized or encapsulated sediment.

Citation	Description of Requirement	Rationale for Use	Possible Application
Hazardous Waste Management Act of 1976; WAC 173-303, "Dangerous Waste Regulations"			
WAC 173-303-070, "Designation of Dangerous Waste"	Establishes the method for determining if a solid waste is a dangerous waste (or an extremely hazardous waste).	A standard for determining degree of hazard or toxicity.	Classification of sediment solids, particularly if excavated or produced as a byproduct of a treatment process or well construction determines its disposition.
WAC 173-303-140, "Land Disposal Restrictions"	This regulation establishes treatment requirements and disposal prohibitions for land disposal of dangerous waste and incorporates by reference (WAC 173-303-140[2)][a], "Land Disposal Restrictions") the Federal land disposal restrictions of 40 CFR 268, "Land Disposal Restrictions," that are applicable to solid waste that is designated as dangerous or mixed waste in accordance with WAC 173-303-070(3), "Designation Procedures."	Provides standard for type and degree of treatment for planning and implementation of sediment remedy or disposition of solid byproducts from ex-situ water treatments.	May be applicable for remedy selection and setting/guiding extent of near surface sediment remediation work. Guides handling of mixed waste.
WAC 173-303-610(2), "Closure and Post-Closure"	Establishes closure requirements applicable to all dangerous waste facilities and post-closure care requirements applicable to all regulated units (as defined in WAC 173-303-040, "Definitions") at which dangerous wastes will remain after closure (including tank systems, landfills, surface impoundments, waste piles, and miscellaneous units).	Monitoring and maintenance of waste residuals and excavated, treated waste solids is necessary to prevent new contamination and control exposure to persons and the environment.	Applicable to disposal of solid waste produced from water treatment and/or excavated, treated or stabilized sediment solids.
WAC 173-303-665(6), "Dangerous Waste Regulations," "Landfills," "Closure and postclosure"	Specifies closure and post-closure requirements for landfills.	Risk control and management of landfills receiving hazardous waste from remedial actions.	Applicable to disposal of solid waste produced from water treatment and/or excavated, treated or stabilized sediment solids placed in landfills.

Citation	Description of Requirement	Rationale for Use	Possible Application
Clean Air Act; WAC 173-400, "General Regulations for Air Pollution Sources"			
WAC 173-400, "General Regulations for Air Pollution Sources"	Defines methods of control to be employed to minimize the release of air contaminants associated with fugitive emissions resulting from materials handling, construction, demolition, or other operations. Emissions are to be minimized through application of best available control technology.	Guide and regulate design, construction, and operation of groundwater or sediment remediation processes with regard to emission of hazardous pollutants to atmosphere.	Performance criteria for design and operation of treatment processes in an ex-situ treatment or in-situ treatment remedy that emit toxic air pollutants.
WAC 173-400-040, "General Standards for Maximum Emissions"	All sources and emissions units are required to meet the general emission standards unless a specific source standard is available. General standards apply to visible emissions, particulate fallout, fugitive emissions, odors, emission detrimental to health and property, sulfur dioxide, and fugitive dust.	Maintain air quality and minimize adverse effects of emissions resulting from remedial action.	Performance criteria for design and operation of treatment processes in an ex-situ treatment or in-situ treatment remedy that emit toxic air pollutants.
"Water Well Construction" (RCW 18.104, as amended); "Minimum Standards for Construction and Maintenance of Wells" (WAC 173-160)			
"How Shall Each Water Well Be Planned and Constructed?" (WAC 173-160-161)	Identifies well planning and construction requirements.	Sampling and process wells used to implement remedial actions can provide a route for unintended exposure and spread of groundwater contaminants. Also improperly constructed wells can spread contaminants in vadose zone into aquifer.	Provides guidance and specifications for construction of wells used to monitor and implement groundwater extraction and in-situ treatment technologies.
"What Are the Requirements for the Location of the Well Site and Access to the Well?" (WAC 173-160-171)	Identifies the requirements for locating a well.	Sampling and process wells used to implement remedial actions can provide a route for unintended exposure and spread of groundwater contaminants. Also improperly constructed wells can spread contaminants in vadose zone into aquifer.	Provides guidance and specifications for construction of wells used to monitor and implement groundwater extraction and in-situ treatment technologies.

Citation	Description of Requirement	Rationale for Use	Possible Application
"What Are the Requirements for Preserving the Natural Barriers to Ground Water Movement Between Aquifers?" (WAC 173-160-181)	Identifies the requirements for preserving natural barriers to groundwater movement between aquifers.	Sampling and process wells used to implement remedial actions can provide a route for unintended exposure and spread of groundwater contaminants. Also improperly constructed wells can spread contaminants in vadose zone into aquifer.	Provides guidance and specifications for construction of wells used to monitor and implement groundwater extraction and in-situ treatment technologies.
"What Are the Minimum Standards for Resource Protection Wells and Geotechnical Soil Borings?" (WAC 173-160-400)	Identifies the minimum standards for resource protection wells and geotechnical soil borings.	Sampling and process wells used to implement remedial actions can provide a route for unintended exposure and spread of groundwater contaminants. Also improperly constructed wells can spread contaminants in vadose zone into aquifer.	Provides guidance and specifications for construction of wells used to monitor and implement groundwater extraction and in-situ treatment technologies.
"What Are the General Construction Requirements for Resource Protection Wells?" (WAC 173-160-420)	Identifies the general construction requirements for resource protection wells.	Sampling and process wells used to implement remedial actions can provide a route for unintended exposure and spread of groundwater contaminants. Also improperly constructed wells can spread contaminants in vadose zone into aquifer.	Provides guidance and specifications for construction of wells used to monitor and implement groundwater extraction and in-situ treatment technologies.
"What Are the Equipment Cleaning Standards?" (WAC 173-160-430)	Identifies the minimum casing standards.	Sampling and process wells used to implement remedial actions can provide a route for unintended exposure and spread of groundwater contaminants. Also improperly constructed wells can spread contaminants in vadose zone into aquifer.	Provides guidance and specifications for construction of wells used to monitor and implement groundwater extraction and in-situ treatment technologies.

Citation	Description of Requirement	Rationale for Use	Possible Application
"What Are the Minimum Casing Standards?" (WAC 173-160-440)	Identifies the equipment cleaning standards.	Sampling and process wells used to implement remedial actions can provide a route for unintended exposure and spread of groundwater contaminants. Also improperly constructed wells can spread contaminants in vadose zone into aquifer.	Provides guidance and specifications for construction of wells used to monitor and implement groundwater extraction and in-situ treatment technologies.
"What Are the Well Sealing Requirements?" (WAC 173-160-450)	Identifies the well sealing requirements.	Sampling and process wells used to implement remedial actions can provide a route for unintended exposure and spread of groundwater contaminants. Also improperly constructed wells can spread contaminants in vadose zone into aquifer.	Provides guidance and specifications for construction of wells used to monitor and implement groundwater extraction and in-situ treatment technologies.
"What Is the Decommissioning Process for Resource Protection Wells?" (WAC 173-160-460)	Identifies the decommissioning process for resource protection wells.	Sampling and process wells used to implement remedial actions can provide a route for unintended exposure and spread of groundwater contaminants. Also improperly constructed wells can spread contaminants in vadose zone into aquifer.	Provides guidance and specifications for closure of wells used to monitor and implement groundwater extraction and in-situ treatment technologies.
"Underground Injection Control" WAC 173-218			
"UIC Well Classification Including Allowed and Prohibited Wells" (WAC 173-218-040)	Identifies what an injection well is and types of prohibited wells.	Injection wells used to implement remedial actions can provide a route for unintended exposure and spread of groundwater contaminants. Also improperly constructed wells can spread contaminants in vadose zone into aquifer.	Provides guidance and specifications for construction of wells used to implement groundwater injection and in-situ treatment technologies.

Citation	Description of Requirement	Rationale for Use	Possible Application
"Washington Clean Air Act" (RCW 70.94, as amended); "General Regulations for Air Pollution Sources" (WAC 173-400)			
"General Regulations for Air Pollution Sources" (WAC 173-400)	Defines methods of control to be employed to minimize the release of air contaminants associated with fugitive emissions resulting from materials handling, construction, demolition, or other operations. Emissions are to be minimized through application of best available control technology.	Fugitive dust emissions during remedy construction and operation, if excavation, can propagate contaminants associated with surface soil.	Provides guidance and specifications for work plans related to surface construction or excavations for remedial technologies at ground surface.
"General Standards for Maximum Emissions" (WAC 173-400-040)	Requires all sources of air contaminants to meet emission standards for visible, particulate, fugitive, odors, and hazardous air emissions. Requires use of reasonably available control technology. This state regulation is as stringent as or more stringent than the equivalent federal program requirement.	Maintain air quality and minimize adverse effects of emissions resulting from remedial action.	Performance criteria for design and operation of treatment processes in an ex-situ treatment or in-situ treatment remedy that emit toxic air pollutants.
CERCLA = Comprehensive Environmental Response, Compensation, and Liability Act of 1980 CFR = Code of Federal Regulations IDW = investigation derived waste FS = feasibility study MNA = monitored natural attenuation OU = operable unit RI/FS = remedial investigation/feasibility study RTD = removal, treatment, and disposal			

B.2 References

10 CFR 1022, Compliance with Floodplain and Wetland Environmental Review Requirements, Code of Federal Regulations.

36 CFR 60, National Register of Historic Places, Code of Federal Regulations.

36 CFR 65, National Historic Landmarks Program, Code of Federal Regulations.

36 CFR 800, Protection of Historic Properties, Code of Federal Regulations.

40 CFR 6, Subpart C, Requirements for Environmental Information Documents and Third-Party Agreements for EPA Actions Subject to NEPA, Code of Federal Regulations.

301, Applicant requirements.

302, Responsible Official Requirements.

40 CFR 60, Standards of Performance for New Stationary Sources, Code of Federal Regulations.

40 CFR 61, National Emission Standards for Hazardous Air Pollutants, Code of Federal Regulations.

61.01, Lists of pollutants and applicability of part 61.

61 .05, Prohibited activities.

61.12, Compliance with standards and maintenance requirements.

61.14, Monitoring requirements.

43 CFR 10, Native American Graves Protection and Repatriation Regulations, Code of Federal Regulations.

50 CFR 402, Interagency Cooperation- Endangered Species Act of 1973, as amended, Code of Federal Regulations.

Archaeological and Historic Preservation Act of 1974, 16 USC 469, et seq.

Clean Air Act of 1990 and Amendments, 42 USC 7401, et seq.

Comprehensive Environmental Response, Compensation, and Liability Act of 1980, 42 USC 9601, et seq.

Endangered Species Act of 1973, 16 USC 1531, et seq.

Executive Order 11593, 1971, Protection, and Enhancement of the Cultural Environment, Richard M. Nixon, May 13.

Executive Order 11988, 1977 Floodplain Management, Jimmy E. Carter, May 24.

National Historic Preservation Act of 1966, 16 USC 4 70, et seq.

Native American Graves Protection and Repatriation Act of 1990, 25 USC 3001, et seq.

WAC 173-303, Dangerous Waste Regulations, Washington Administrative Code, Olympia, WA.

173-303-016, Identifying Solid Waste.

173-303-017, Recycling Processes Involving Solid Waste.

173-303-070, Designation of Dangerous Waste.

173-303-077, Requirements for Universal Waste.

173-303-120, Recycled, Reclaimed, and Recovered Wastes.

173-303-140, Land Disposal Restrictions.

173-303-170, Requirements for Generators of Dangerous Waste.

173-303-200, Accumulating Dangerous Waste On-Site.

173-303-610, Closure and Post-Closure.

173-303-64610, Purpose and Applicability.

173-303-64620, Requirements.

WAC 173-340, Model Toxics Control Act - Cleanup, Washington Administrative Code, Olympia, WA.

173-340-740, Unrestricted Land Use Soil Cleanup Standards.

173-340-7490, Terrestrial Ecological Evaluation Procedures.

173-340-7493, Site Specific Terrestrial Ecological Evaluation Procedures.

173-340-7 494, Priority Contaminants of Ecological Concern.

WAC 232-12-292, Bald Eagle Protection Rules, Washington Administrative Code, Olympia, WA.

Appendix C

Controlling Processes

Appendix C

Controlling Processes

C.1 Global Iodine Cycle

Sources of ^{129}I and ^{127}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}I in the environment. Stable iodine is distributed in the environment in water and in geochemical materials (Fehn 2012). Solid sources of iodine in the environment include pelagic clays, shale, limestone, igneous rocks, and algae. Fluid sources include freshwater, seawater, volcanic fluids, pore waters, oil field brines, and gas hydrates (Whitehead 1984). These results show that a very large amount of iodine is sequestered in geological media and would not interact with the global (surface) iodine cycle (Muramatsu and Wedepohl 1998; Muramatsu et al. 2004). 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. This aligns with the fact that much of the iodine in marine sediments and sedimentary rocks is attributed to carbonate and limestone accumulated by sedimentation of planktonic and shallow sea organisms. Volcanic and geothermal activity can release some of the locked up iodine as volcanic fluids and pore water. Likewise, the human pursuit of various energy sources has released iodine to the surface iodine cycle through production of oil and natural gas brines, as well as fracking (Harkness et al. 2015).

Naturally occurring ^{129}I is produced, but the amount is quite small when compared to stable iodine. Anthropogenic production of ^{129}I from activities related to nuclear energy and weapons development has introduced a large amount of additional iodine to the Earth's surface, and thus into the global iodine cycle. As an example, Table 1.2 from Section 1.0 of this document shows major sources of ^{129}I from human nuclear activities and the amount in the natural hydrosphere/atmosphere. The largest nuclear industry source of iodine is from fuel reprocessing activities (i.e., the La Hague and Sellafield entries in Table 1.2), from which the produced ^{129}I is discharged into the sea and immediately becomes part of the global iodine cycle. In addition, kilogram levels of ^{129}I have also been released by both fuel reprocessing facilities into the atmosphere and the global iodine cycle.

Sources and sinks of the global iodine cycle are divided into three primary pools: marine, terrestrial, and atmospheric (Figure C.1). Sources of natural iodine (mostly ^{127}I) are shown on the right of Figure C.1, while anthropogenic sources (^{129}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.

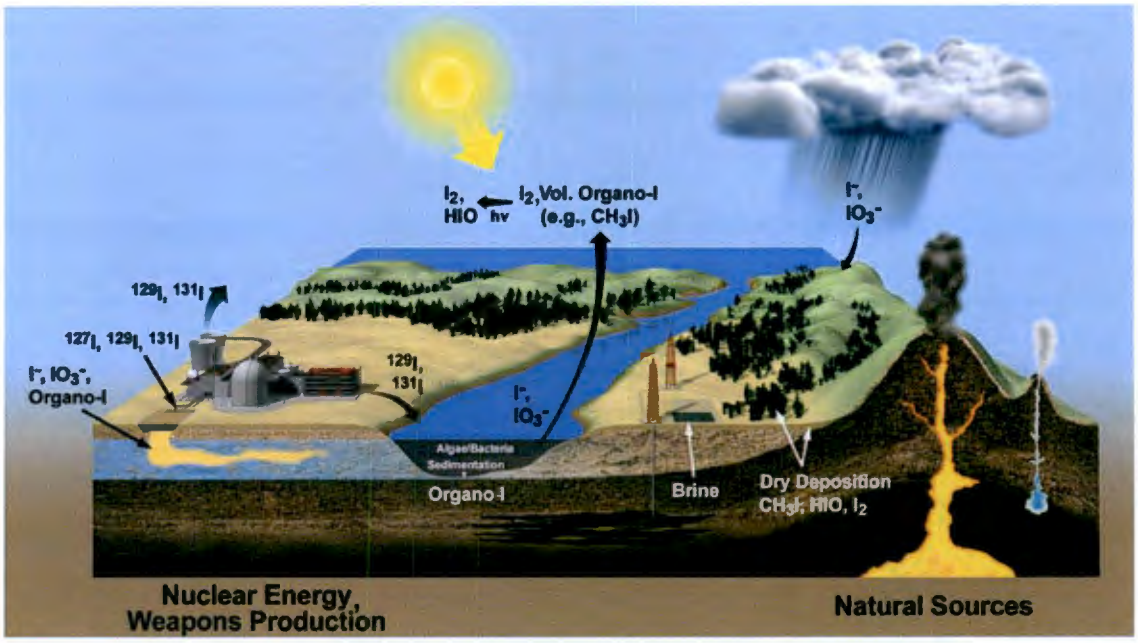

Figure C.1. Global iodine cycle, showing natural and anthropogenic sources of iodine isotopes and cycling of iodine species in the environment.

As part of the global cycle, iodine species are cycled by biological, geochemical, physical, and solar processes. Marine environments have been the primary source of experimental studies looking at the effects of each of these processes on iodine speciation. The remainder of this appendix describes the different biogeochemical reactions responsible for iodine cycling; outlining chemical and biological processes, and then summarizing by describing how these processes are coupled in the iodine cycle. For subsurface $^{129}I/^{127}I$ contamination, iodine conversion by solar processes does not need to be considered. However, the potential of capitalizing on solar processes, especially iodine conversion and uptake by algae for ex situ treatment of iodine contaminated water, may prove beneficial.

C.2 Aqueous Iodine Conversion

C.2.1 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 4.1×10^{-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):

$$I_{2(g)} = I_{2(aq)} \qquad \log K_{20°C} = 0.65 \qquad (C.1)$$
$$I_{2(aq)} + I^- = I_3^- \qquad \log K_{20°C} = 2.89 \qquad (C.2)$$
$$I_{2(aq)} + H_2O = H^+ + I^- + HIO \qquad \log K_{20°C} = -12.49 \qquad (C.3)$$
$$I_{2(aq)} + H_2O = H_2OI^+ \qquad \log K_{20°C} = -10.80 \qquad (C.4)$$

The reactions for several species are shown in Table C.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 C.1. Reactions of log K association constants of selected aqueous iodine species (Kaplan et al. 2014).

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

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}I environmental plumes is somewhat simplified because the only stable aqueous species that are common are I^-, I_2^o, and IO_3^-. Figure C.2 shows the relation of these species to pH and Eh and was calculated using the background ^{127}I concentrations measured at the site; 8 µg/L ^{127}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 IO_3^- and an inconsequential amount of I_2. I_2 is the only species expected to change appreciably with total iodine concentration; it was also modeled at the highest stable ^{127}I concentrations measured by Zhang et al. (2013), 75 µg/L. As expected, the I_2 region increased, but still indicates that I_2 will not be a significant species in this system.

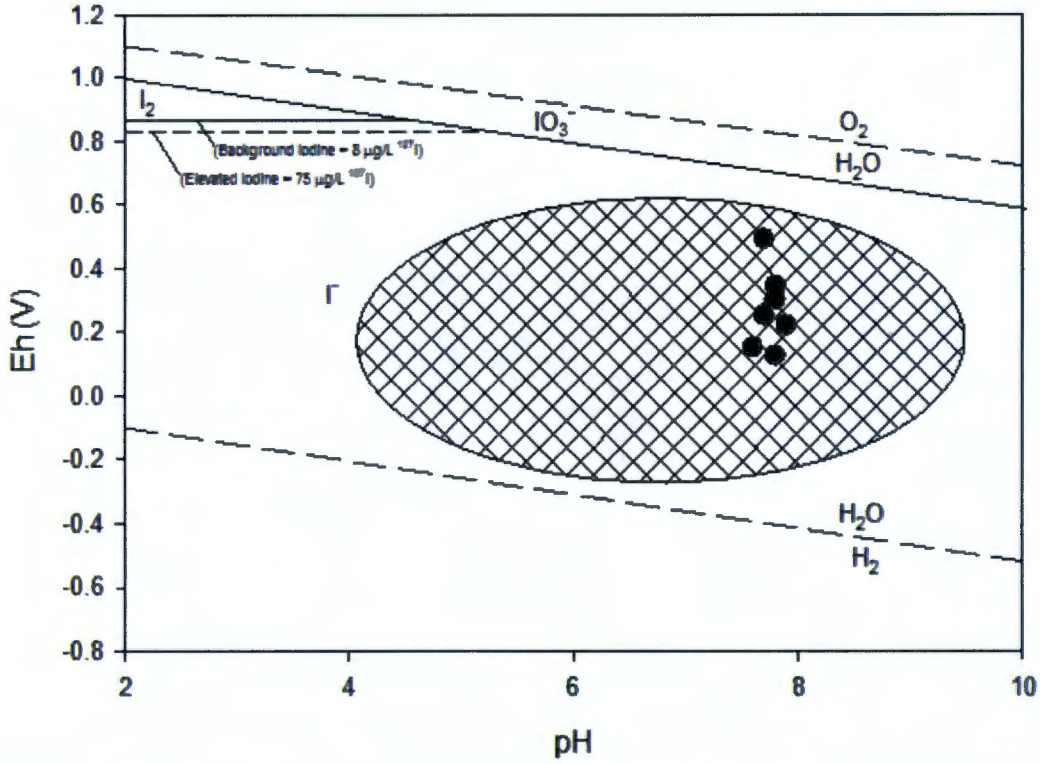

Figure C.2. pH-Eh diagram of aqueous iodine speciation in the 200-UP-1 OU; total iodine concentration = 8 µg/L (background) and 75 µg/L (plume impacted) (Geochemist's Workbench® [Aqueous Solutions LLC, Champaign, Illinois]; Bethke and Yeakel 2013). Points identify pH-Eh conditions measured in groundwater 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 significantly affect 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}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.

C.2.2 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, b; 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}I are discussed in more detail below.

C.2.3 Aqueous Iodine Speciation at the Hanford Site

One reason why little is known about ^{129}I at U.S. Department of Energy sites is because the analytical chemistry techniques to assay the extremely low ambient ^{129}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}I and ^{129}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}I and radioactive ^{129}I, but only ^{127}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 C.2.

Table C.2. Chemistry and ^{127}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 $CaCO_3$ phases. The iodine plumes clearly have elevated levels of total OC and stable ^{127}I. DOC in the groundwater ranged from 20 to 63 μM with an average of 35 μM. 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 μM (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}I in all the groundwater samples analyzed by Zhang et al. (2013), accounting for 45% to 84% of total iodine (Table C.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 C.2). For comparison, the average ^{129}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}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}I, Zhang et al. (2013) only detected iodate (Table C.3). If organo-iodine or iodide were present, they were below the analytical detection limit of 0.2 nM ^{129}I. ^{129}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 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 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 I_2 detection may have been the result of gaseous 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 C.3. ^{129}I speciation in filtered groundwater from the 200 West Area (Zhang et al. 2013).

Well	Iodide (µg/L)	Iodate (µg/L)	Iodate (pCi/L)	Organo-I µg/L	$^{129}IO_3/^{127}IO_3$ Ratio
299-W14-11	< DL[(a)]	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 $^{129}I^-$ and $^{129}IO_3^-$ is 0.08 nM (2 pCi/L) and for organo-^{129}I is 0.2 nM (5 pCi/L)

However, the introduction of ^{129}I primarily as iodate into the subsurface environment would only partially explain the observed groundwater speciation (Table C.3) because stable iodine (^{127}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, 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}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.

C.3 Iodine Sorption to Sediments

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

C.3.1 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 μg ^{129}I / g soil (Hou et al. 2009). Shimamoto and Takahashi (2008) conducted XANES studies on soils amended with 55 μg 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 IO_3^- to I_2 (Fuhrmann et al. 1998). This finding is very likely a result of using very high iodine concentrations and likely not a common process occurring in natural terrestrial environments. They also observed that magnetite sorbed 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 suffers 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 NH_4OAC exchange, carbonate (NH_4OAC [pH 5]), Fe-oxide (NH_2OH, HCl, pH 2, 80°C to 100°C), organic (NaOH 80°C to 100°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}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}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}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}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).

C.3.2 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, b). 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, b). 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}C nuclear magnetic resonance (NMR) techniques (Xu et al. 2012). Quantitative structure analyses by ^{13}C direct-polarization magic-angle spinning (DPMAS) NMR and solution state ^{1}H NMR 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., NH_2), or hemicellulose-lignin-like complex with phenyl-glycosidic linkages.

The concentration of stable iodine bound to the fulvic acid fraction (519 μg ^{127}I/g-carbon) was approximately an order of magnitude greater than the concentration of stable iodine bound to humic acid fractions (62 μg ^{127}I/g-carbon) (Xu et al. 2011a, b). 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 μM, 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}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}I concentration, and in particular to quantify and understand the role of OM and microbes (Xu et al. 2011a, b; 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 (pH > 5), microbial enzymatically assisted iodination of SOM was predominant. It was concluded that although trace amounts of SOM-bound ^{129}I could enhance transport, in general the SOM in the riparian zone immobilized the ^{129}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.

C.3.2.1 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 to 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 Na^+, Ca^{+2}, Cl^-, and 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 TiO_2 powder. Yet organo-clays show even stronger sorption of iodide (Bors et al. 1994).

C.4 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 C.2) 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 C.2 and Table C.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 C.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 C.4. Iodide and iodate K_d values for composite sediments recovered from 200 West Area borehole cores (Xu et al. 2015).

Composite Sediment[(a)]	Organic Carbon (%)	Inorganic Carbon (%)	Total Sediment Iodine (µg/g)	Total DOC (µM) [(b)]	Iodide-Spiked K_d (mL/g) [(c)]	Iodate-Spiked K_d (mL/g) [(c)]
H3	0.15	0.18	2.10	94 ± 17	3.38	3.94
H1	0.12	0.92	4.79	284 ± 33	0.08	1.78
H2	0.04	0.01	0.68	0	0.00	0.83

(a) 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 µm) after 21 days of contact during the sediment/groundwater batch iodine uptake experiment.
(c) Suspensions were spiked with either iodide or iodate (as ^{125}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 IO_3^- as a trace impurity in $CaCO_3$ phases. Carbonate minerals in subsurface systems are constantly forming and dissolving. The size of the IO_3^- ion is the same as the CO_3^{2-} ion and can substitute for it in carbonate phases. It was shown that recently precipitated carbonate phases (formed by degassing 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 C.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 C.5. Suspended particles formed by CO_2 degassing from 200 West Area groundwater samples (Zhang et al. 2013).

Wells	Particle concentration (mg/L)	Total carbon (wt%)	Total ^{127}I (µg/g)	Total ^{129}I (µg/g)	Particulate ^{127}I (wt%)[(a)]	Particulate ^{129}I (wt%)[(a)]
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:

[particle concentration] × TI (particle) / ([particle concentration] × TI(particle) + TI(dissolved/filtered))

Iodine speciation changed once the spike solution came into contact with the sediments, indicating that Table C.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}I fraction that is nearly irreversibly bound to the sediment and may provide a more accurate representation of ^{129}I transport.

The significance of the data in Table C.5 is that iodate typically sorbs to sediments greater than iodide. No sorption testing has been conducted with organo-iodine, but it too may sorb appreciably more than iodide to sediments. These findings bring into question whether the present Hanford ^{129}I K_d values, albeit conservative, adequately 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}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 (I^-, 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 I^- or 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.

C.5 Biological Iodine Conversion

C.5.1 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 (I^-), molecular iodine (I_2), iodate (IO_3^-), and organic-iodine (Org-I) compounds, including volatile compounds, such as methyl iodide (CH_3I). 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}I and ^{129}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 I^- (~10 nM), while 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 I^- and IO_3^-. Reduction of 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 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, I^- is the dominant form and IO_3^- is absent. These results suggest that where oxygen is present, I^- oxidation to IO_3^- occurs and in the absence of oxygen, IO_3^- reduction to 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 C.3. 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.

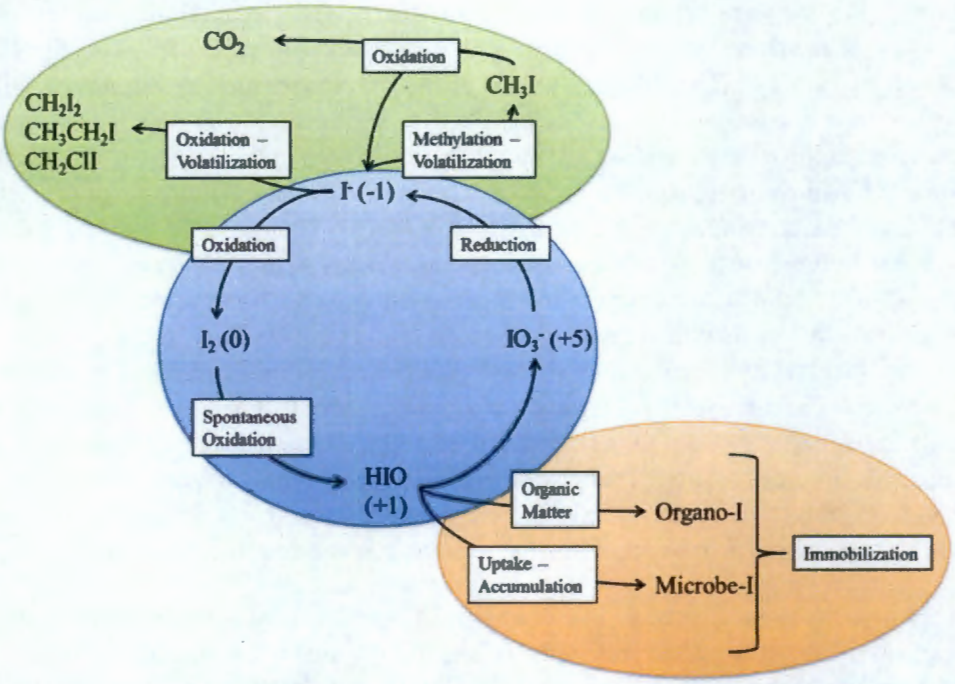

Figure C.3. Biological transformations associated with iodine cycling in the environment. The blue ellipse represents predominantly aqueous-phase iodine species. The orange ellipse represents predominantly solid-phase species of iodine associated with organic compounds (Organo-I) or accumulated in microbial 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.

C.5.2 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 (Ihssen 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 α-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 to I^- to I_2 (Figure C.4 and Table C.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.

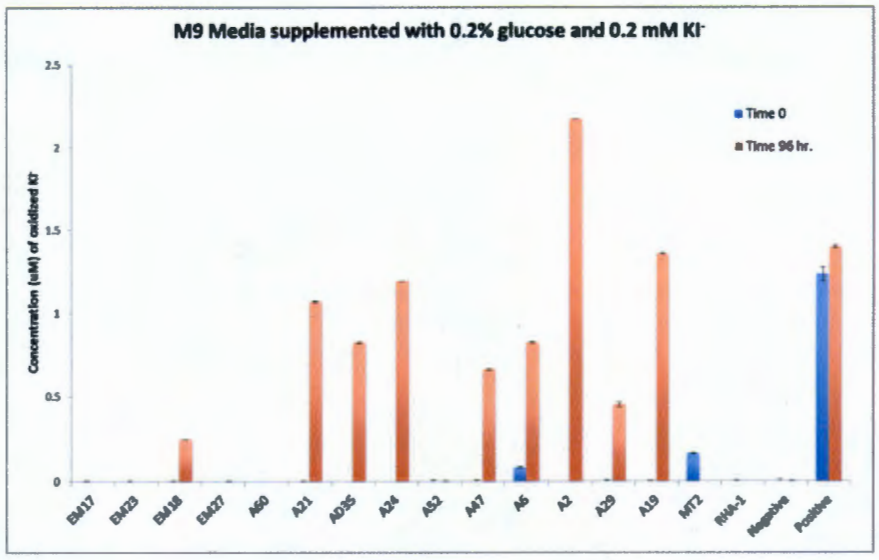

Figure C.4. Hanford isolates capable of oxidizing I^- (see Table C.6 for identity).

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

C.5.3 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), hypoiodous 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, d; 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 μM 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.

C.5.4 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 (CH_3I) per year (Stemmler et al. 2014). In addition, CH_3I is known to play a significant role in the global iodine cycle (Klick and Abrahamsson 1992). CH_3I 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 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 (α, β, and γ subdivisions), *Cytophaga-Flexibacter-Bacteriodes* (CFB) Group, and high G+C Gram-positive bacteria. CH_3I 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, α- and γ-Proteobacteria, and the CFB group were isolated and shown to volatilize iodide to CH_3I. Experiments also showed that iodate was not converted to CH_3I. 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 CH_3I.

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 CH_3I when grown in the presence of iodide. These bacteria represent species of α- and γ-Proteobacteria. Analysis of the headspace of the vials showed primarily CH_3I 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 CH_3I, a number of other volatile organo-iodine compounds can be formed during oxidation of iodide. Two bacterial species closely related to *Roseovarious tolerans* that were isolated from marine samples were able to produce CH_2I_2 and CH_2ClI 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 I^- oxidation, this process may occur in Hanford groundwater since I^- oxidation was demonstrated by Hanford bacterial isolates. Formation of volatile organo-iodine species during the I^- oxidation process is currently being tested.

C.5.5 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 were 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.

C.5.6 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. Other studies have shown microbial reduction of iodate with anaerobic cell suspensions of *Desulfovibrio desulfuricans* and marine bacterium *Shewanella putrefaciens* (Councell 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 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 IO_3^-, experiments were performed to determine the ability of various Hanford isolates to reduce 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 IO_3^- to I^- in the presence of nitrate (Figure C.5). Iodate reduction occurred under both anaerobic and microaerobic conditions. When the culture was spiked with nitrate, IO_3^- concentrations continued to decrease in the culture medium.

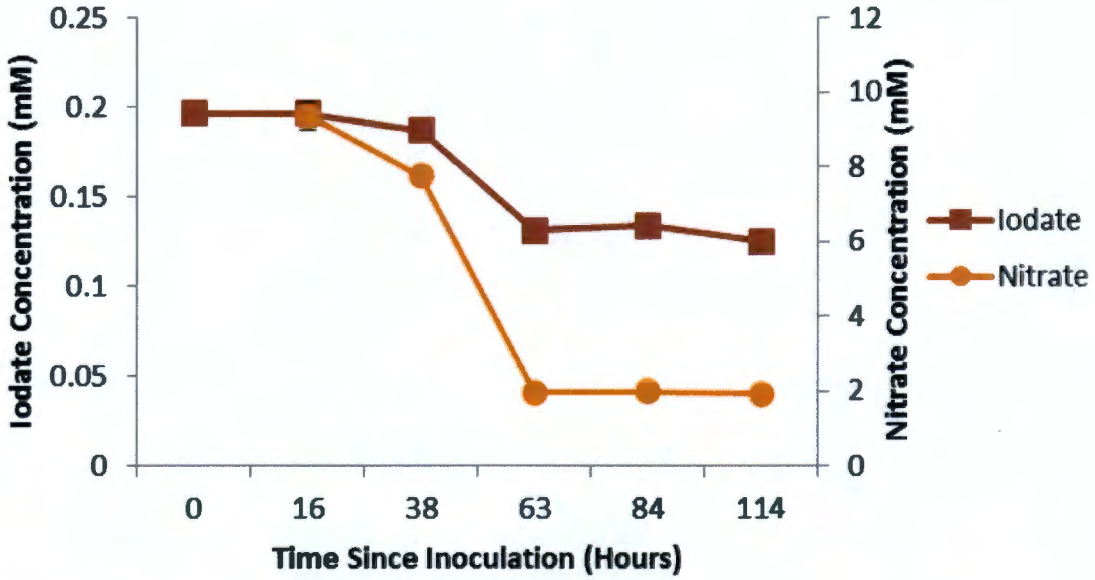

Figure C.5. Iodate reduction in the presence of nitrate by an Agrobacterium species isolated from sediment traps that were incubated within an iodine plume in the 200 West Area.

C.6 References

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Appendix D

Remediation Technologies

Appendix D

Remediation Technologies

D.1 Ex Situ Remediation

D.1.1 Ex Situ Aqueous-Phase Treatment

D.1.1.1 Aqueous Phase Adsorption

Adsorption involves the interphase accumulation or concentration of substances at a surface of a solid. Adsorption of iodine from the aqueous phase involves the mass transfer of iodine onto a solid that typically has high surface area and active sites with an affinity for one or more iodine species. Adsorption therefore concentrates iodine onto a solid-phase material from a more dilute aqueous concentration. The solids with sorbed iodine require either further processing (e.g., regeneration to give a reusable solid and a concentrated liquid) and/or disposal as a solid waste in a suitably designed landfill. The effectiveness of the adsorption is a function of the form of iodine present in the water, the sorption media, pH/alkalinity conditions, and temperature. The solid phase used as the adsorption media may be selected from a variety of substances with differing sorptive characteristics.

There is a plethora of potential adsorbents, both natural and synthetic. Sorbents include activated carbon, zeolites, layered double hydroxides, organoclays, argentite, aerogels, self-assembled monolayers on mesoporous silica (SAMMS), carbon nanotubes, and a number of other materials. Some of these adsorbents include silver impregnation (doping) to promote iodine capture and formation of immobile silver iodide when adsorbed. Several studies (Kaplan et al. 2000, Mattigod et al. 2003, Mattigod et al. 2007, Pierce et al. 2010, Li et al. 2014) have assessed the relative effectiveness of adsorbents to determine the most appropriate material to use. Pierce et al. (2010) in particular has a significant list of "getter" materials for adsorption of iodine species.

Activated Carbon

Activated carbon, most commonly utilized to adsorb and remove organic compounds from water and air streams, may also be used to treat and remove iodine from water and gas streams. Activated carbon is manufactured from charcoal derived from coal or other carbon materials such as nut shells, coconut husks, and peat using high temperature pyrolysis or carbonization in moderately high oxidizing atmospheres. Activated carbon is applied in granular or powder forms. Activated carbon is an effective adsorbent because of its extremely high degree of microporosity. When powdered activated carbon is applied to iodine in water, removal rates ranging from 30% to 40% have been reported. Chlorine addition to carbon adsorption has been reported to improve removal rates for powder activated carbon to 41% to 48% (Ikari et al. 2015). The iodine species is a factor in removal rates, organic iodine having better removal rates (Kosaka et al. 2012). Also, the efficacy of sorption by granular activated carbon is increased when dissolved iodine is in the iodide form. However, chemicals used to convert iodine in water into iodide have been shown to adversely affect the sorption of iodide (I^-) on activated carbon materials (Parker et al. 2014). Further research is suggested to determine the cause of this adverse interaction with carbon.

Silver-Impregnated Carbon

Silver-doped activated carbon is another approach to increasing the adsorption of iodine on carbon (Hoskins et al. 2002). Impregnating activated carbon with silver has been shown to increase iodine ion removal from water. Silver content, total iodine concentration, and pH were factors controlling the removal mechanisms of iodide. Iodide uptake increases with decreasing pH for both silver-impregnated carbon and virgin granular activated carbon.

Zeolite

Zeolites are microporous, aluminosilicate minerals that may be used as adsorbents. These materials occur naturally or may be synthesized. Zeolites have different types of structures with a range of characteristics for physical properties (such as hardness, acid resistance, adsorption capacity, and specificity). Synthetic zeolites pretreated with silver have been shown to be effective in removing iodine from gas streams. However, in aqueous phase iodine removal situations, removal rates tend to be much lower than those measured for organoclay and activated carbon adsorbent materials (Li et al. 2014).

Layered Double Hydroxides

Layered double hydroxides (e.g., Mg-Al (NO_3)) have been used to treat iodide and iodate in water (e.g., from optoelectronic wastewater [Kentjono et al. 2010]) and gases (Ma et al. 2014). Efficient capture of iodine is affected by several considerations, including the ratio of divalent to trivalent ions in the hydroxide composition, the charge density, and whether the material has been thermally activated. The presence of competing anions (e.g., carbonate or sulfate) can impact iodine uptake because layered double hydroxides tend to have lower affinity for monovalent anions versus anions with multiple charges (Theiss et al. 2014).

Organoclay

Organoclays are bentonite or other clay-based filtration media that are impregnated with sulfur and/or quaternary amines to facilitate adsorption and sequestration of some dissolved ionic inorganic contaminants. Batch sorption experiments have demonstrated high removal rates of iodine ($K_d \geq 2.9\times10^4$ mL/g) in water relative to activated carbon ($K_d > 6.9\times10^{-3}$ mL/g) (Li et al. 2014). The pH of the water is a controlling factor in optimizing sorption effectiveness for various types of organoclay media.

Argentite

Argentite has been assessed for iodine uptake from groundwater (Li et al. 2014, Kaplan et al. 2000, Mattigod et al. 2007). In a comparison with other cost-effective sorbents, Li et al. (2014) found that an organoclay and argentite (AgS) exhibited the best iodine sorption characteristics.

Aerogels

Silver-doped activated carbon aerogels have been investigated for iodide removal from drinking water. Aerogels are synthetic, porous, ultralight materials derived from a gel, in which the liquid component of the original gel has been replaced with a gas. When formulated with carbon, the resulting material is a solid with extremely low density and high surface area to volume ratio. Experiments with carbon aerogels impregnated with silver have demonstrated that the material has a high capacity to

remove and absorb iodine ions from drinking water. The material is regenerable with ammonia. Column tests have demonstrated iodine removal rates ranging between 60% and 90% (Sánchez-Polo et al. 2006, 2007). Iodine adsorptive capacity of silver-impregnated carbon aerogels is enhanced by activation, which increases the silver adsorption sites available to iodine ions. The use of this technology would be analogous to activated carbon adsorption, but with increased effectiveness in some situations.

SAMMS

The SAMMS nanoporous ceramic material is a novel sorbent with high surface area and tailored pore sizes. SAMMS contains monolayers of well-ordered functional groups with a high affinity for target compounds. SAMMS sorbents with Hg-thiol or Ag-thiol functionalization have been studied for iodine adsorption from groundwater and waste glass leachates (Mattigod et al. 2007, Kaplan et al. 2000). The studies found that SAMMS sorbents have very high affinities for iodine adsorption.

Carbon Nanotubes

Work has been done to investigate silver-doped carbon nanotubes for aqueous separation and sequestration of radioactive iodine from in nuclear fuel cycle wastes. Specifically, the work has examined reaction of iodide in alkaline solutions with the silver-doped carbon nanotubes (Pishko et al. 2013). Small amounts of carbon nanotubes were found to be required to sequester significant amounts of iodine from nuclear waste leachates. It was noted that a packed column approach would not work for carbon nanotubes—a thin flow-through filter was one potentially viable approach that was suggested. Carbon nanotubes currently have a higher production cost, but the higher sorption capacity (compared to activated carbon) is expected to offset those costs due to fewer sorbent change-outs and less secondary waste.

Photocatalytic Adsorption

Efficient removal of radioactive iodide ions from water by three-dimensional Ag_2O–Ag/TiO_2 composites under visible light irradiation has been investigated (Liu et al. 2015). The investigations demonstrated the ability to photocatalytically remove even trace amounts of idodide from different types of water (e.g., deionized or salt lake water) without interference from other ions. The composites could undergo a simple regeneration and be reused with effective sorption. The iodide removal process was proposed to occur by a combination of iodide adsorption, photocatalytic oxidation of iodide, and re-adsorption of iodine (I_2) by the silver.

D.1.1.2 Ion Exchange

Ion exchange is a process technology in which ions that are held by electrostatic forces to charged functional groups on the surface of a solid treatment medium are exchanged for ions of similar charge in a solution. Ion exchange is classified as a sorption process because the ion exchange involves mass transfer from the liquid phase to the solid phase (where the charged functional groups are located). The effectiveness of the ion exchange treatment is affected by the aqueous speciation of iodine in water. Conditions that favor iodide can significantly increase the sorption efficiency of ion exchange media. The EPA has identified ion exchange as an effective treatment for beta emitters such as cesium-137, strontium-89, and iodine-131 (EPA 2007).

A variety of synthetic ion exchange media, with differing degrees of effectiveness and aqueous pH applicability, are commercially available. These include Dowex 1 and Dowex 21K (The Dow Chemical Company), resins PFA600, A-530E, and A-532E (The Purolite Company), and SIR-700 and SIR-1200 (ResinTech, Inc.). Batch testing (Parker et al. 2014) of ion exchange on synthetic resin media for iodine treatment has shown adsorption rates similar to those for certain activated carbon media, on the order of 1.7 μg iodine per gram of resin. Reduction of iodine to iodide was found to more than double the loading capacity of most resins (except Dowex 21K and SIR-700).

Ion exchange media must be regenerated (resulting in a concentrated liquid waste containing the iodine) and/or sent to treatment/disposal. The radioactivity of the sorbed iodine is not mitigated in the adsorption process, so suitable handling and final disposition are required.

ABEC Ion Exchange Resins

Aqueous biphasic extraction chromatography (ABEC) resins selectively extract iodide (and pertechnetate) anions from alkaline radioactive wastes and can be regenerated by elution with water. Resin development for large-scale chromatographic equipment has been undertaken (Bond et al. 1999, Alexandratos 2009).

D.1.1.3 Membrane Separation

Several membrane separation technologies may facilitate the removal and concentration of iodine from water (Rana et al. 2013, Watson et al. 2012). A membrane is a porous material that acts as a barrier to flow of molecular or ionic species between the phases or solutions that it separates. It is either a dry solid, a solvent-swollen gel, or liquid that is immobilized. To be functional for iodine separation, the membrane must be highly selective to the passage of iodine ions. A driving force is applied on one side of the membrane to promote selective concentration of iodine and separation from the bulk water stream. The primary driving force may be hydrostatic pressure, concentration gradient, or electrical potential gradient. The membrane design and material, as well as the driving force, characterize and define the membrane separation technology. Reverse osmosis and electrodialysis are two membrane separation technologies that shown to separate iodine in water.

Reverse Osmosis

Reverse osmosis (Watson et al. 2012, Rana et al. 2013) uses pressure across a membrane (spiral-wound or hollow-fiber) to separate water from other solutes. Thus, the permeate is a clean water and the retentate is a concentrated solution of the undesirable solutes and water. The EPA has identified reverse osmosis as an effective treatment for beta emitters such as cesium-137, strontium-89, and iodine-131 (EPA 2007). One report cited a 92% removal of iodine-131 by reverse osmosis (Jeong et al. 2014).

Electrodialysis

In electrodialysis, electric current induces partial separation of the ionic components in an aqueous solution (Watson et al. 2012). The separation is accomplished by alternately placing cation anion selective membranes across the current path. Effectiveness and selectivity can be modified by adjusting the pH or using additives. Efficiency is lower in low ionic strength solutions. Electrodialysis has been shown to be effective for iodine removal (Inoue et al. 2004, Rana et al. 2013).

D.1.1.4 Electrochemical Separation

Electrochemical separation technologies (Watson et al. 2012) use an applied current to separate ions in water. Typically, these technologies collect the ion of interest at an electrode, resulting in solid phase with captured solute or a concentrated liquid phase (i.e., after electrode regeneration). Three variants of electrochemical separation technologies are described below.

Capacitive deionization (CDI) is an electrolysis technology that removes ionic species from water using porous activated or aerogel carbon electrodes (Watson et al. 2012). Water is deionized and ions are captured at the electrodes. Halide removal from solution typically occurs via electrostatic attraction within the electrode. Once saturated, the carbon aerogel electrodes can be regenerated by reversing the electrode polarity. CDI removal capacity was determined to increase in the order of $Cl^- < Br^- < I^-$, making the technology appealing for selective recovery of iodide.

Electrochemically switched ion exchange (ESIX) uses electric potential to control capture of ions by an electroactive ion exchange film on an electrode with high surface area (Lilga et al. 1997). Radioactive iodide has been separated from dilute solution (in the concurrent presence of cesium ions) using an ESIX method with polypyrrole and nickel hexacyanoferrate films on porous three-dimensional carbon felts. The applied potential significantly facilitated the adsorption efficiency and a lower pH was beneficial to the separation process. Consecutive adsorption-desorption experiments indicated that the electrodes can be effectively regenerated and are stable (Liao et al. 2015).

Electrolysis has been shown to remove bromide from water (by oxidation) on a small scale, but the feasibility of large-scale application to drinking water treatment has not been assessed (Watson et al. 2012). This process has not been shown for iodide, but may be a potential treatment technology.

D.1.1.5 Co-precipitation and Coagulation

Generally, iodine ions (primarily iodide and iodate) are soluble in aqueous solutions. But iodine ions can interact with silver, copper, mercury, or lead to form precipitates. This technique is routinely used in analytical procedures for determination of iodine (e.g., Luo et al. 2013). However, descriptions of co-precipitation/coagulation technologies for treatment of iodine in water were not found in process or environmental literature.

D.1.2 Ex Situ Gas-Phase Treatment

A range of methods exists for capture of iodine from gas streams, though they can be generally categorized as adsorption (using solid phase sorbents) or absorption (wet scrubbing) processes (Haefner and Tranter 2007). These methods were primarily developed for the nuclear industry (e.g., spent fuel reprocessing) and medical facilities.

D.1.2.1 Gas Phase Adsorption

In the gas phase adsorption process, the gas is passed through a solid phase sorbent (e.g., a packed column) and iodine is captured by adsorption at active sites on the sorbent media. Iodine adsorption can take place on a variety of adsorbents, including activated carbon, macroreticular resins, silver impregnated alumina, silver exchanged mordenite, silver-loaded zeolite, silver impregnated silica-gel,

silver-functionalized silica or carbon aerogels, and bismuth-based materials (Haefner and Tranter 2007, Jubin 1979, Deitz 1987, Mineo et al. 1999, Strachan et al. 2009, Matyáš et al. 2011, Zhou et al. 2014, Yang et al. 2015). Silica aerogels can be densified into a durable waste form through hot uniaxial pressing, hot isostatic pressing, or spark plasma sintering (Matyáš and Engler 2013).

D.1.2.2 Gas Phase Scrubber (Absorber)

A wet scrubber (absorber) is a mass transfer device designed to "scrub" target chemicals out of a gas by contacting the gas through a liquid phase into which the target chemical preferentially partitions. A variety of scrubber solutions have been used or studied for removal of iodine from the gas phase, including caustic solution (sodium hydroxide), mercuric nitrate-nitric acid (Mercurex), hyperazeotropic nitric acid (Iodox), organic liquid (e.g., polymethylsiloxane), fluorocarbon liquid, and molten hydroxide (KOH or NaOH) (Burger and Scheele 2004, Haefner and Tranter 2007, Doll et al. 2014). A variant of the technology uses a dilute nitric acid scrubber solution with electrolytic oxidation (Mailen and Horner 1976).

D.1.3 Ex Situ Solid-Phase Treatment

D.1.3.1 Soil Washing

Soil washing (EPA 1990, Khan et al. 2004) is a process for ex situ scrubbing of soils to remove contaminants, typically using an aqueous wash solution. The process would remove iodine contaminants from soils in one of two ways:

- by dissolving or suspending contamination in the wash solution for subsequent treatment of the water, or
- by concentrating contamination into a smaller volume of sediment/soil through particle size separation, gravity separation, and attrition scrubbing (similar to techniques used in sand and gravel operations).

Soil washing systems incorporating most of the removal mechanisms discussed above offer the greatest promise. Commercialization of the technology for iodine removal in sediment has not been demonstrated, though application has been demonstrated for other radionuclides (Devgun et al. 1993).

D.1.3.2 Immobilization/Encapsulation and Solidification/Stabilization

Immobilization, encapsulation, solidification, and stabilization are all related processes by which contamination is bound or enclosed within a monolithic solid (EPA 1986, 1996, 1997a, 2007, Khan et al. 2004). The intent with immobilization is to prevent movement of contaminants by chemically binding the contamination within a solid matrix. There are several variations of immobilization, including adsorption (Section D.1.1.1), thermal processes (which are discussed in subsequent subsections), and solidification/stabilization processes. Solidification is a process to treat contaminated media (e.g., excavated sediment, adsorption media, or potentially contaminated liquid) with a binder or cement to physically bind contamination within a solid mass. Stabilization uses chemical reactions between the stabilizing agent and the contamination to reduce the contaminant mobility (e.g., by changing the redox state). Encapsulation takes the approach of encompassing contamination to provide a physical barrier to

contaminant migration. An example of encapsulation is emplacement of contaminated media within a grout or epoxy resin.

For these processes, the desirable characteristics of the resultant solid monolith are a material that is durable (i.e., not subject to physical decomposition) and that has a low rate of contaminant leaching from the solid. Identification of effective solidification/stabilization/ encapsulation agents requires development and testing. This technology requires a location for long-term storage (disposal) for the monolithic solids.

Immobilization/encapsulation of iodine has been demonstrated with cement (Atkins and Glasser 1992, Nishimura 2009). The composition of the cement is important and pretreatment of adsorbed iodine to alter the speciation may be an important step. Very high rates of incorporation into the solid monolith can be achieved. Determining or confirming long-term durability and leaching characteristics for the particular cement composition and waste loading is important for evaluating treatment effectiveness.

D.1.3.3 Adsorption/Vitrification

Sandia National Laboratories is working on a process to capture gaseous iodide on nanoporous alumina, precipitate the iodide with silver or copper, then vitrify the alumina/glass formers to encapsulate the iodide (SNL 2013, Brown 2009).

D.1.3.4 Low-Temperature Vitrification

A low-temperature vitrification process is being developed (Yang et al. 2014). In this process, iodine is captured on silver-loaded zeolite (i.e., from a gas stream) and is subsequently sequestered in low-temperature sintering glasses (e.g., bismuth-phosphate-zinc oxide) to make chemically durable waste forms. The low temperature minimizes loss of iodine as volatiles. A related process (Mukunoki et al. 2009) uses $BiPbO_2$ NO_3 to capture iodine, which is then solidified into a lead-boron-zinc glass matrix using low-temperature vitrification.

D.1.3.5 Encapsulation in Tin

The volatility of ^{129}I and its high solubility make it difficult to incorporate in ceramic or glass solids for the purpose of long-term immobilization. However, iodine encapsulation can be accomplished by fusing iodide sorbed on silver-iodine sorbents with tin to produce a consolidated mass (Vance et al. 2005). This hot-pressing process uses powder metallurgy and operates at about 200°C under high pressures. The stabilized mass may be disposed in a long-term repository.

D.2 Near-Surface/Source Zone Remediation

D.2.1 Excavation

Excavation is the physical removal of contaminated sediment solids in the vadose zone and to a limited extent below the water table (ITRC 2014, EPA 2012a). Conventional earth moving equipment is used in a manner similar to open-pit mining. Contaminated soil either is treated by ex situ technologies (soil washing, immobilization/encapsulation, etc.), as discussed above, or is packaged for disposal in

lined landfills specifically designed to contain and isolate the contaminated sediments from the environment. This technology is not specific to iodine; implementation for iodine would need to consider worker/environmental exposure to volatile iodine species.

D.3 Vadose Zone Remediation (Control of Flux to Groundwater)

D.3.1 Horizontal Barriers

Horizontal barriers or engineered covers are lateral physical barriers designed to cap soil and control infiltration and surface flux of rainwater through contaminated sediments to restrict mobilization of iodine through the vadose zone and prevent continued loading of groundwater with contaminant from above. Such barriers generally are constructed on the ground surface over specified areas of sediment known to be contaminated. Horizontal barriers may also be placed below ground surface but require replacement of top soil and installation of lateral water collection systems below grade to collect infiltrating water. Such engineered barriers utilize a variety of materials installed to control infiltration. This technology is not specific for iodine treatment, but rather it impacts water movement and thus contaminant flux.

D.3.1.1 Surface Cap

A surface cap (EPA 1998, 2007) is typically installed for the purpose of eliminating (or greatly reducing) infiltration of water (precipitation) through the subsurface, although control of vapor emissions could be another objective.

Hard surface caps are constructed with asphalt or concrete using similar design and construction techniques as roadway or parking pavement. The designs of such pavement-like caps are crowned or sloped to divert rainfall runoff to collection points for disposal away from the protected area. Periodic inspection and maintenance of the cap is required to ensure integrity of the barrier.

Clay and topsoil caps consist of a low-permeability clay layer placed above contaminated sediment. Clay caps are often constructed with a thickness greater than 2 feet and overlain with topsoil and vegetated to minimize erosion. Periodic inspection and maintenance is required to verify integrity.

Geo-membrane and topsoil caps consist of a high-density polyethylene or other flexible but impermeable membrane placed over contaminated sediment. The membrane cover would require a topsoil and vegetation cover layer for protection from ultraviolet sunlight degradation. Periodic inspection and maintenance would be required.

D.3.1.2 Horizontal Infiltration Barrier

Horizontal infiltration barriers are analogous to surface caps, but are installed in the subsurface to reduce contaminant migration into groundwater (by preventing infiltration and/or by directly reducing contaminant mobility). Two basic types of barriers may be considered: grout and desiccation.

Horizontal Grout Barrier

Two categories of grouting technology may be useful for subsurface horizontal barrier formation (Truex et al. 2011a). Jet grouting uses high-energy emplacement of cement or chemical grout materials whereby sediment is displaced and mixed with grouting material. Permeation grouting is the injection of a liquid grout that fills the natural porosity and then gels to form a solid void-filling material. While both are mature technologies, some work may be required to select a grout with suitable characteristics (contaminant stabilization, shrinkage, etc.). The choice of the grouting technology will also depend on the nature of the subsurface (e.g., permeability) in the targeted area. Horizontal grout barrier technology can potentially be used to create a barrier to water infiltration, thereby reducing the driving force for downward contaminant migration. Alternately, the technology could be used to encapsulate contaminants and limit contact with infiltrating water.

Lateral Desiccation Zone

The in situ soil desiccation technology consists of removing water from a stratum in the vadose zone to create a horizontal capillary barrier (Truex et al. 2011b, 2014a). Dry air is injected and moist air is extracted via wells screened across the target interval. Vertical migration of a plume of subsurface contamination in the vadose zone to the groundwater is prevented by forming and maintaining one or more desiccation layers in the vadose zone in or above a layer of contamination. In combination with surface infiltration control, the technique can be used to prevent/reduce contaminant migration by reducing hydraulic conductivity. At the same time, desiccation could potentially also improve access for other treatments (e.g., gas-phase manipulations) by reducing water content and increasing gas-phase permeability.

D.3.2 Soil Vapor Extraction

Soil vapor extraction (SVE) is a method by which soil gas (i.e., in the vadose zone) and associated volatile contaminants are collected by vacuum extraction (EPA 2012b, Damera and Bhandari 2007, USACE 2002, Pedersen and Curtis 1991). This technology could be used to collect volatile iodine species (e.g., as a complementary technology for air sparging).

D.3.3 In Situ Soil Heating

Several approaches exist for heating in situ soil, including resistive heating and injection of hot air or steam (EPA 2012c). Such technologies have typically been applied for remediation of volatile/semi-volatile organic compounds, but may also be useful for volatilization of iodine species or to enhance other iodine remediation technologies.

D.3.4 In Situ Reactive Gas

This technology would involve introduction of an appropriate reactive gas into a relatively permeable layer of the vadose zone to achieve reactions that immobilize/sequester iodine (Denham and Looney 2007). This technology is in the developmental stage. However, laboratory-scale work has shown successful immobilization of uranium (Truex et al. 2014b) and technetium (Truex et al. 2014c) using

ammonia gas (with hydrogen sulfide in the case of technetium). Field-scale testing for uranium sequestration is being planned (DOE 2015).

D.4 Saturated Zone Remediation (Groundwater Treatment)

D.4.1 Monitored Natural Attenuation

Monitored natural attenuation (MNA) relies on natural "physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater" (EPA 1999, pg. 3). These processes include dispersion, dilution, sorption, volatilization, radioactive decay, and chemical or biological reaction (that result in contaminant stabilization, transformation, or destruction). To assess the degree/rate of attenuation, it is important to understand the processes that affect a particular contaminant and how that affects contaminant migration. Monitoring is a key component to the remedy to confirm contaminant attenuation is progressing as estimated.

Given the nature of ^{129}I, the key attenuation mechanisms for an iodine plume will be dispersion, adsorption, and reactive processes that result in either precipitation/immobilization or volatilization (radioactive decay is insignificant because of the long half-life). The speciation of iodine in groundwater (which depends on redox conditions) affects the adsorption of iodine onto aquifer materials (e.g., clay minerals, iron/manganese oxyhydrides) (EPA 2004). Iodine speciation in groundwater may be influenced by a combination of abiotic and biotic reactions, as discussed in Section 3.0. For systems in which I^- and IO_3^- are the predominant species in groundwater, it is generally observed that IO_3^- adsorbs to a greater extent (Fukui et al. 1996). The relative abundance of naturally occurring ^{127}I in the groundwater and aquifer system may limit the adsorption of radioiodine ^{129}I (Tournassat et al. 2007). A detailed outline for information requirements, characterization procedures, and an approach for development of a monitored natural attenuation remedy for radioiodine is presented in Volume 3 of Monitored Natural Attenuation of Inorganic Contaminants in Groundwater (EPA 2010).

D.4.2 Permeable Reactive Treatment Zones / In Situ Reagent-Driven Reactions

Work pertaining to the SRS F Area Seepage Basins has examined a potential remediation technology for in situ treatment of iodine based on subsurface reagent amendments. Earlier work (Denham 2002) considered injection of a univalent copper [Cu(I)] reagent, potentially enhanced by addition of non-radioactive ^{127}I, and solid copper-based reactants injected as slurries or emplaced in an aquifer as a permeable reactive barrier as potential remediation technologies. Later work identified potential injectable, iodine-selective materials for in situ groundwater treatment, including reagents involving Ag, Hg, or Cu, though the silver-based reagents were determined to have the most favorable characteristics (Denham et al. 2009). Micron-sized particles of silver chloride have been demonstrated in field tests as an injection reagent for in situ immobilization of iodine in a permeable reactive barrier at SRS (Kaplan et al. 2012). The silver chloride field demonstration has observed a 50% reduction in ^{129}I concentrations downgradient from the permeable reactive barrier. Considerations for any of these in situ reagent approaches include aquifer pH, iodine concentration (both radioiodine and natural ^{127}I), specificity for iodine (in the various ion species), adsorption capacity, and precipitation kinetics.

D.4.3 Microbial-facilitated Reactions

Microbes can facilitate changes in iodine speciation and can, in some cases immobilize iodine through bioaccumulation (intracellularly) or bioadsorption (extracellularly) (Simonoff et al. 2007, Francis 2012). Thus, stimulation of microbial activity may be one approach for iodine remediation. There are essentially three mechanisms for microbial-facilitated remediation: changes in the redox conditions, generation of volatile iodine species, and bioaccumulation/ bioadsorption.

Various microbes have been shown to alter the iodine speciation through oxidation/reduction reactions (Simonoff et al. 2007, Francis 2012). Observed reactions include oxidation of iodide (I^-) to iodine (I_2) and reduction of iodate (IO_3^-) (e.g., by sulfate- or iron-reducing bacteria). The speciation affects iodine mobility and phase partitioning. Truex et al. (2006) suggest that anaerobic bioremediation technologies may be useful for reduction of iodine species to facilitate increased adsorption of iodine. Additionally, the transition to a different predominant iodine species could enhance the performance of some other remedial technology.

Microbial conversion of iodide to methyl iodine (CH_3I) (Simonoff et al. 2007, Francis 2012) provides a volatile species that could potentially be amenable to remediation by another technology (e.g., air sparging). Additionally, redox reactions that produce molecular iodine (I_2) could be taken advantage of to strip the volatile species from the groundwater. Iodine species volatilized into the vadose zone would need to be collected with, for example, an SVE system. The gas could then be treated ex situ with a variety of technologies (Section D.1.2).

Bacterial cells may adsorb iodine species extracellularly or accumulate iodine intracellularly (Simonoff et al. 2007, Francis 2012). Either process results in accumulation/immobilization of iodine. However, the long-term effectiveness of such a process would need to be evaluated.

D.4.4 Air Sparging

Air sparging is a technology to perform in situ stripping of volatile/semi-volatile contaminants from groundwater. A gas (e.g., air) is injected into an aquifer to promote mass transfer from the aqueous phase to the gas phase. Gas is then vented through the vadose zone or collected (e.g., by SVE).

In situ iodine remediation by air sparging has been studied at Savannah River National Laboratory (SRNL). When plume conditions are acidic, iodide is the prevalent species in groundwater. It may then be possible to oxidize the iodide to elemental iodine (I_2) and subsequently apply air sparging to strip the volatile I_2 out of the groundwater. Laboratory-scale studies at SRNL have demonstrated successful removal of iodine by sparging an ozone-air mixture through iodide-containing water (Denham and Looney 2007, Denham et al. 2009).

D.4.5 Containment/Removal

Horizontal flow of groundwater may be controlled by containment technologies, either hydraulic or physical. The intent of vertical containment is to prevent groundwater flow into a contaminated zone or to prevent migration contaminants out of a contaminated zone. Physical containment does not affect the contaminant mass, but hydraulic containment may remove contaminant mass along with groundwater. Generally, containment is applied when either remediation by other methods is impractical or as an

enhancement to improve the performance of other remediation technologies. When applying physical containment, the cutoff wall must extend into a lower layer of relatively impermeable sediment (e.g., an aquitard) to prevent short-circuiting and attain full containment.

D.4.5.1 Extraction Wells

Hydraulic control (EPA 1997b) may be accomplished by using extraction wells to pump groundwater out of the aquifer (and capture contamination in the process) and/or injecting clean water into the aquifer via injection wells to create a hydraulic barrier to flow. Hydraulic control alters the natural hydraulic gradient to establish a capture zone or hydraulic barrier that prevents migration outside of the contaminated zone. Injection and extraction are often used in conjunction to achieve the desired control of the larger scale groundwater flow and thus contaminant migration. Extracted groundwater generally requires treatment at the surface using an ex situ treatment system that separates, adsorbs, or concentrates the dissolved contamination (destruction is another ex situ treatment option, but is not applicable for iodine).

D.4.5.2 Interceptor Trench for Hydraulic Extraction

Lateral groundwater collection may be accomplished by horizontal wells or drains placed within trenches excavated into sediments below groundwater level. Contaminated groundwater is pumped to the ground surface, where ex situ treatment is applied.

D.4.5.3 Slurry Walls

Slurry walls (Spooner et al. 1985, Pearlman 1999, EPA 2007) are cutoff walls constructed by trenching into the subsurface. Slurry is used in the trench as backfill to form the slurry wall and to prevent the side walls of the excavation from collapsing. A typical slurry is composed of bentonite, water, and either soil or cement, though other compositions may be used to attain the desired chemical compatibility and strength properties. In some instances, a composite slurry wall is constructed with both the slurry and a geomembrane. A slurry wall is typically 2 to 4 ft thick and extends to depths of 50 ft or less (though installation to depths of 100 ft is possible).

D.4.5.4 Grout Curtains

Grout curtains (Pearlman 1999, EPA 2007) are thin cutoff walls constructed by pressure injection of grout into the soil at closely spaced injection points, whereby the adjacent injections overlap to form a continuous barrier. Grout curtains are typically used for shallow barriers (up to 30 or 40 ft depth), but may be more useful in situations where slurry walls are impractical such as a sloped ground surface or installation in rock. Hydraulic cements, clays, bentonite, and silicates are common grout materials, though polymer grouts have advantages with respect to impermeability and resisting radiation or harsher pH conditions.

D.4.5.5 Sheet-pile Walls

Sheet-pile walls (Pearlman 1999, EPA 2007, Meuser 2013) are cutoff walls composed of interconnected sections of pre-fabricated steel or high-density polyethylene sheets. Sections are vibrated

or hammer-driven into the subsurface and adjacent sheet-pile sections are sequentially installed and connected at the joints to achieve containment. The effective depth is limited by the nature of the subsurface materials—installation is difficult in soils with boulders or cobbles. The typical maximum depth is 100 to 130 ft. Concerns include corrosion of steel sheet-pile materials and the potential for loss of integrity at section joints.

D.4.6 Electrokinetic Remediation

Electrokinetic remediation is a potential in situ iodine collection method, though it appears that few investigations of this technology for iodine have been conducted. The so-called "Ferric Iron Remediation and Stabilization" electrokinetic technique has demonstrated iodine mobilization toward the anode in a laboratory-scale test with radionuclide contamination (CL:AIRE 2003). The technology involves precipitation of an iron-rich band (as a barrier to groundwater flow), acid front generation, contaminant desorption, and ion migration. The radius of influence for field-scale implementation is not known.

D.5 Administrative/Engineered Controls

D.5.1 Institutional Controls

Institutional controls (EPA 2000, 2012d) are non-engineered instruments, such as administrative and legal controls, that help minimize the potential for human exposure to contamination and/or to protect the integrity of a remedy. Institutional controls play an important role in site remedies because they reduce exposure to contamination by limiting land or groundwater use and they guide human behavior at a site. Examples of institutional controls include groundwater use restrictions, zoning ordinances, fish consumption bans, waterway use restrictions, and access limitations (using security enforcement, barriers, or fencing). State and local police power may be employed to implement institutional controls. State registries of contaminated sites may serve as useful informational management tools and include databases, maps, or document-based inventories. The long-term stewardship of lands or water resources under institutional controls requires establishment of periodic monitoring, inspection, maintenance, and long-term management of sites with institutional controls.

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