Groundwater Radioiodine: Prevalence, Biogeochemistry, and Potential Remedial Approaches

Miles Denham, Daniel Kaplan, and Chris Yeager

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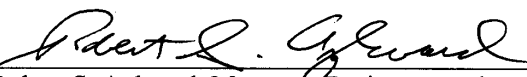
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LIST OF ACRONYMS AND ABBREVIATIONS

ALI	Annual Limit of Intake
AMS	Accelerated mass spectrometer
Bq	Becquerels (decays per second)
Ci	Curies (1 Ci = 3.7 x 10^{10} Bq)
DOE	U.S. Department of Energy
DOE-EM	U.S. Department of Energy Office of Environmental Management
EXAFS	X-ray absorption fine structure spectra
HEDR	Hanford Environmental Dose Reconstruction Project
I	Iodine
IAEA	International Atomic Energy Agency
ICP-MS	Inductively coupled plasmas mass spectrometry
INL	Idaho National Laboratory
IOB	Iodine Oxidizing Bacteria
NAA	Neutron activation analysis
RCRA	Resource Conservation and Recovery Act
rem	Unit of dose equivalent
SAMMS	Self-Assembled Monolayers and Mesoporous Silica
SRS	Savannah River Site
WVDP	West Valley Demonstration Project
XANES	X-ray absorption near-edge structure

EXECUTIVE SUMMARY

Iodine-129 (^{129}I) has not received as much attention in basic and applied research as other contaminants associated with DOE plumes. These other contaminants, such as uranium, plutonium, strontium, and technetium are more widespread and exist at more DOE facilities. Yet, at the Hanford Site and the Savannah River Site ^{129}I occurs in groundwater at concentrations significantly above the primary drinking water standard and there is no accepted method for treating it, other than pump-and-treat systems. With the potential arrival of a "Nuclear Renaissance," new nuclear power facilities will be creating additional ^{129}I waste at a rate of 1 Ci/gigawatts energy produced. If all 22 proposed nuclear power facilities in the U.S. get approved, they will produce more ^{129}I waste in seven years than presently exists at the two facilities containing the largest ^{129}I inventories, (~146 Ci ^{129}I at the Hanford Site and the Savannah River Site). Hence, there is an important need to fully understand ^{129}I behavior in the environment to clean up existing plumes and to support the expected future expansion of nuclear power production.

^{129}I is among the key risk drivers at all DOE nuclear disposal facilities where ^{129}I is buried, because of its long half-life (16 million years), high toxicity (90% of the body's iodine accumulates in the thyroid), high inventory, and perceived high mobility in the subsurface environment. Another important reason that ^{129}I is a key risk driver is that there is the uncertainty regarding its biogeochemical fate and transport in the environment. We typically can define ^{129}I mass balance and flux at sites, but can not accurately predict its response to changes in the environment. This uncertainty is in part responsible for the low drinking water standard, 1 pCi/L ^{129}I, and the low permissible inventory limits (Ci) at the Savannah River Site, Hanford Site, and the former Yucca Mountain disposal facilities.

The objectives of this report are to: 1) compile the background information necessary to understand behavior of ^{129}I in the environment, 2) discuss sustainable remediation approaches to ^{129}I contaminated groundwater, and 3) identify areas of research that will facilitate remediation of ^{129}I contaminated areas on DOE sites. Listed below are lines of scientific inquiry that would significantly advance the goals of basic and applied research programs for accelerating ^{129}I environmental remediation and reducing uncertainty associated with disposal of ^{129}I waste.

- Evaluation of amendments or other treatment systems that can sequester subsurface groundwater ^{129}I.
- Develop analytical techniques for measurement of total ^{129}I that eliminate the necessity of collecting and shipping large samples of groundwater.
- Develop and evaluate ways to manipulate areas with organic-rich soil, such as wetlands, to maximize ^{129}I sorption, minimizing releases during anoxic conditions.
- Develop analytical techniques that can identify the various ^{129}I species in the subsurface aqueous and solid phases at ambient concentrations and under ambient conditions.
- Identify the mechanisms and factors controlling iodine-natural organic matter interactions at appropriate environmental concentrations.

- Understand the biological processes that transform iodine species throughout different compartments of subsurface waste sites and the role that these processes have on ^{129}I flux.

1. INTRODUCTION

The U.S. Department of Energy's Office of Environmental Management (DOE-EM) recognizes that [129]I may be a risk in groundwater at some DOE waste sites and has requested this review of the current scientific understanding of [129]I relating to waste site closure. This review covers the reason [129]I is important, analytical methods, biogeochemistry, and potential remediation methods for [129]I in groundwater. The intent is to describe the state of knowledge of [129]I behavior at waste sites, as well as provide guidance for incorporation of research on [129]I behavior and remediation into the DOE-EM applied science and the DOE Office of Science basic research programs.

The behavior of iodine is complex because it can exist in multiple physical states, as well as multiple oxidation states at environmentally relevant conditions. It readily reacts with organic compounds, further complicating its chemistry in organic-rich environments. Iodine is also an essential nutrient for animals that concentrates in certain organs driving the toxicity levels for radioactive isotopes to very low concentrations. This together with its long half-life and relative mobility in the environment usually assures that [129]I is a risk driver at sites where abundant quantities were disposed.

DOE is concerned about radioiodine because it is an identified risk in groundwater on the Hanford Site and the Savannah River Site (SRS), and is abundant in nuclear waste currently being processed and disposed at these sites and eventually at a national repository (e.g., DOE 2002; DOE 2003; WSRC 2008). The risk stems largely from the factors noted above and the current inventory of radioiodine in nuclear waste -- 120 Ci at the Hanford Site (Kincaid et al. 2006) and 26 Ci at the SRS (Hiergesell et al., 2008). To illustrate how the properties of [129]I magnify its risk, [129]I at the SRS is a very small portion of the total radiological releases from the site, approximately 0.00002% (Kantelo et al. 1990), but contributes 13% of the offsite population dose.

The potential "Nuclear Renaissance" in response to global warming presents another concern regarding radioiodine. There are 11 applications to the Nuclear Regulatory Commission to construct 18 new nuclear reactors in the U.S., increasing the total number of reactors from 104 to 122 (Parker and Holt 2007). Similarly, India plans to construct another 20 to 30 reactors by the year 2020 (World Nuclear Association, 2009). China presently has 17 reactors under construction and anticipates building another 13 by the year 2020, increasing their nuclear capacity to at least 50 gigawatts (World Nuclear Association, 2009. By the year 2030, China anticipates another threefold increase in nuclear power to 120 to 160 gigawatts. Radioiodine is produced at a rate of 1 Ci (37 giga-Becquerels[1]) per gigawatt of electricity produced by nuclear power (McKay et al. 1984). For example, if all 22 proposed 1-gigwatt U.S. reactors get built, an additional 22 Ci of [129]I will be generated annually (reactors are 98% efficient) and within seven years these reactors will generate more [129]I waste than the 146 Ci currently at the Hanford Site and Savannah River Site (Kincaid and Eslinger, 2002;

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[1] 1 Bq = 27 x 10^{-12} Ci.

Hiergesell et al., 2008). Thus, if only a fraction of the proposed nuclear growth from the "Nuclear Renaissance" is realized, a significant increase in world-wide radioiodine inventory will be created by the nuclear power industry. Understanding the environmental behavior of ^{129}I is critical to assessing the performance of facilities where this waste will be stored or disposed.

The risk posed by radioiodine can be broadly categorized as being long-term and short-term. The long-term risks are those resulting from exposure to the long-lived isotope, ^{129}I, with a half-life of 16 million years. The short-term risks are those resulting from exposure to the short-lived isotope, ^{131}I, with a half-life of eight days. The risks associated with current groundwater contamination and nuclear waste disposal are related to ^{129}I. ^{131}I decays to the stable element xenon in a very short time, but its high specific activity makes it an immediate threat to those exposed. An example of the short-term risk from ^{131}I can be illustrated from the Chernobyl accident (Figure 1). The majority of the radiation emitted immediately after the Chernobyl accident was from ^{131}I. Studies show a link to thyroid cancer in exposed children that were less than five-years old at the time of the accident (e.g., Guiraud-Vitaux et al., 2008). This was attributed to the fact that more than 90% of the iodine in the human body is concentrated in the thyroid (Zaichick and Choporov, 1996). At Chernobyl, once the ^{131}I was taken up by children, it concentrated in their thyroids emitting beta particles (primarily 606 keV, 89% abundance) and gamma rays (primarily 364 keV, 81% abundance) that promoted thyroid cancer. Thus, ^{131}I is a problem associated with large scale accidents or failures at nuclear whereas ^{129}I is a problem related to environmental remediation and long-term stewardship of disposed nuclear waste. This report focuses on ^{129}I because it drives the long-term risk associated with groundwater contaminant plumes and nuclear waste disposal.
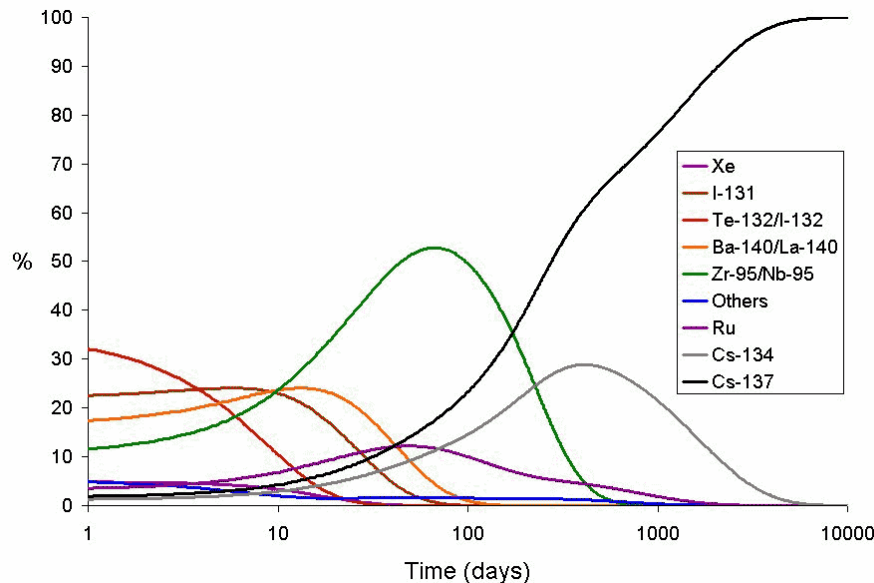
Figure 1. Relative activity emitted as a function of time after the Chernobyl accident. Note that ^{131}I accounted for most of the radioactivity during the first week (Gudiksen et al. (1989).

1.1. OBJECTIVES

The objectives of this report are to:

1) compile the background information necessary to understand behavior of ^{129}I in the environment,
2) discuss sustainable remediation approaches to ^{129}I contaminated groundwater, and
3) identify areas of research that will facilitate remediation of ^{129}I contaminated areas on DOE sites.

1.2. SUMMARY

- ^{131}I poses a very short-term risk (days to weeks) and ^{129}I is a very long-term risk (years to 1000s of years).
- ^{129}I has the lowest performance assessment derived inventory limit (based on mass of disposed Ci) in Savannah River Site and Hanford Site (and the former Yucca Mountain) disposal facilities.

- ^{129}I currently contaminating groundwater at the Hanford Site and the Savannah River Site is a potential threat to human health and the environment, hence a significant risk driver for DOE

- As U.S. and world-wide inventories of ^{129}I increase, understanding how to minimize its release to the environment and what to do if it is released becomes even more important

2. RADIOCHEMISTRY

2.1. RADIOIODINE SOURCES

2.1.1. Reactor Sources of Radioiodine

The principle mechanism for radioiodine production is neutron-induced fission. Neutron-induced fission is a nuclear reaction in which the nucleus of an atom splits into smaller parts, often producing free neutrons and energy. The reactions form a variety of fission products, including a suite of iodine isotopes.[2] Under normal reactor operation, radioiodine is contained within the irradiated fuel and/or targets used to produce specific isotopes. Only small quantities of radioiodine are released to regional environments of power and nuclear-materials-production nuclear reactors. Some nuclear accidents such as Chernobyl have released large quantities of radioiodine to the environment over relatively short time spans. Yet historically, it has been during irradiated nuclear fuel or target processing operations that large quantities of radioiodine were released to the environment over long periods of time. Reprocessing facilities are located in several countries and are used to chemically separate materials irradiated in power and production reactors. As a result of chemical separations process, radioiodine can be released to the environment through atmospheric and aqueous effluent. Most radioiodine in the DOE system was formed as a by-product of extraction of plutonium and other radionuclides from irradiated uranium targets and fuel reprocessing.

To provide an idea of the various iodine isotopes relative contribution to radiation over time, Kantelo et al. (1990) calculated the decay rate of iodine isotopes from a representative material irradiated at the Savannah River Site (SRS) (

Table 1). These calculations demonstrate that radioiodine activity very quickly decreases after reactor shutdown. Only two of the 19 radioiodine isotopes remain after 200 days, ^{129}I ($t_{1/2}$ = 1.6 x 10^7 years) and ^{131}I ($t_{1/2}$ = 8 days). Furthermore, by letting the irradiated material cool for 200 days, radioiodine activity decreases from 1,000,000,000 Ci to 2.5 Ci. At 300 days only 4.5 x 10^{-4} Ci of ^{131}I remain, while the original activity of ^{129}I remains. Hence, of all of the radioiodine isotopes produced, ^{129}I is generally the only one that will last long enough to be a long-term threat in groundwater.

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[2] In addition to fission products, each neutron-induced fission reaction in the fuel produces several neutrons, some of which induce additional fission and maintain a chain reaction. Some of the remaining neutrons interact with target materials in the reactor. One such interaction, neutron capture in a ^{238}U target, results in the production of ^{239}Pu.

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

Isotope	Half-Life	Curies Remaining at Various Times After Irradiation			
		0 sec	24 hrs	100 d	200 d
128	25m	1.5×10^4	-	-	-
129	1.6×10^7y	2.3×10^{-1}	2.3×10^{-1}	2.5×10^{-1}	2.5×10^{-1}
130m	9m	9.2×10^4	-	-	-
130	12h	1.4×10^5	3.5×10^4	-	-
131	8.0d	7.6×10^7	7.0×10^7	1.3×10^4	2.3×10^0
132	2.3h/3.3d**	1.1×10^6	8.9×10^7	-	-
133g	9s	3.8×10^6	-	-	-
133	21h	1.8×10^4	8.2×10^7	-	-
134m	4m	1.3×10^7	-	-	-
134	53m	2.0×10^8	1.3×10^8	-	-
135	6.6h	1.6×10^8	1.5×10^7	-	-
136m	47s	5.0×10^7	-	-	-
136	83s	7.9×10^7	-	-	-
137	24s	7.9×10^7	-	-	-
138	7s	4.1×10^7	-	-	-
139	2s	1.8×10^7	-	-	-
140	<1s	4.1×10^6	-	-	-
141	<1s	8.6×10^5	-	-	-
142	<1s	1.1×10^5	-	-	-
Totals		$\mathbf{1.0 \times 10^9}$	$\mathbf{2.6 \times 10^8}$	$\mathbf{1.3 \times 10^4}$	$\mathbf{2.5 \times 10^0}$

2.1.2. Natural Sources of Radioiodine

Radioiodine is also naturally produced in very small quantities, by the spontaneous fission of natural U (which contains 0.07% ^{235}U), cosmic ray spallation of trace levels of xenon (Xe) in the atmosphere, and by cosmic ray muons (high energy particles) striking tellurium-130 (Edwards 1962). These natural processes account for trace levels of radioiodine in the environment but no risk compared to anthropogenic sources. The ratio of stable [127]I to radioactive [129]I in the environment is more than 10,000,000 to 1. The global inventory of natural [129]I accumulated over the lifetime of the earth is estimated to be 10 Ci in the terrestrial environment and 30 Ci in oceans and the atmosphere (NCRP, 1983). Nuclear weapons testing, which began in 1945, has introduced approximately 10 Ci of [129]I into the atmosphere (NCRP, 1983).

2.2. RADIOCHEMISTRY OF RELEVANT IODINE ISOTOPES

As demonstrated in

Table 1, only ^{129}I and ^{131}I of the 19 radioiodine isotopes formed in reactors are of environmental concern 100 days after a release and only ^{129}I is of concern for long-term nuclear waste disposal. Table 2 shows the radiochemical properties of each of these isotopes.

Table 2. Radiochemical properties of ^{129}I and ^{131}I.

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

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

2.3. CONTAMINATED SITES AND GROUNDWATER SOURCES

As a product of uranium fission, ^{129}I occurs in the environment at several DOE facilities, but currently is only considered problematic at the Hanford Site and the Savannah River Site. Both of these sites have contaminant plumes that contain ^{129}I at concentrations well above the primary drinking water standard of 1 pCi/L. Studies have also shown the presence of ^{129}I in sediments or groundwater at other sites, but at lower concentrations than at Hanford or Savannah River Site. Hu et al. (2008) found maximum concentrations 2 pCi/L in groundwater from wells at nuclear test holes at the Nevada Test Site, but concentrations well below 1 pCi/L at satellite wells located outside the chimney-cavity of the nuclear tests. Hall (2005) reports very low concentrations of ^{129}I in groundwater from wells to the south of the Idaho National Laboratory (INL) boundary. He ties the origin of the ^{129}I in some of the wells to INL waste disposal based on spatial concentration variations and the concentrations of accompanying ^{36}Cl. The maximum concentration observed in groundwater at the West Valley Demonstration Project in 2007 was 5.6 pCi/L (WVDP, 2007). Using ^{129}I to stable iodine ratios, Rao and Fehn (1999) traced elevated ^{129}I in soil cores of western New York to atmospheric release of ^{129}I from the West Valley reprocessing plant. It is likely that other sites that processed spent fuels, uranium targets, or other sources of fissioned uranium may have small amounts of ^{129}I in their subsurface soils and groundwater.

2.3.1. Savannah River Site, Aiken, South Carolina

The history of radiodiodine production and release at the Savannah River Site is well documented in Kantelo et al. (1990). Five reactors operated to produce radionuclides essential to nuclear weapons. The radionuclides were extracted from irradiated materials at two locations – F-Area and H-Area. Between these is a landfill type burial ground for low-level radioactive solid waste known as the Old Radioactive Waste Burial Ground. The overall area, known as The General Separations Area, has multiple contaminant plumes in groundwater that contain ^{129}I. In both F-Area and H-Area, low-level radioactive liquid waste was discharged to seepage basins. Low mobility radionuclides are sequestered in the soils immediately beneath the basins, but more mobile radionuclides have migrated into the groundwater and discharge into Four Mile Branch, a small stream to the south that flows into the Savannah River. The F- and H-Area Seepage Basins received approximately 3 Ci of ^{129}I from 1955 to 1989. The seepage basins have since been closed and capped with a low permeability engineered cover built to RCRA specifications. The contaminant plumes are currently in active remediation.
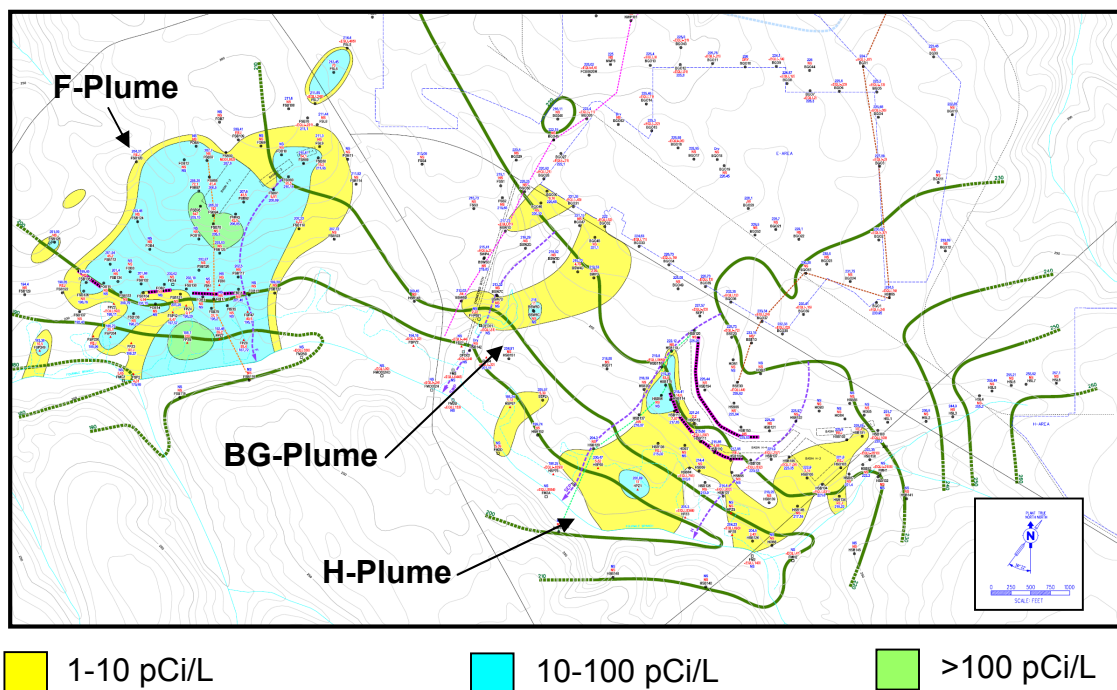
Figure 2: ^{129}I plume map of F, H, and Burial Ground (BG) plumes on the Savannah River Site; green lines are contours of water table potentiometric surface, blue dots with numbers are monitoring wells.

The F-Area Seepage Basins plume has the highest concentrations of ^{129}I, with numerous wells having concentrations 10s to 100s of times the drinking water standard. The highest concentration reported so far in 2009 is 1060 pCi/L in a well adjacent to the downgradient side of the largest basin. Concentrations of ^{129}I in this well have been rising over the past few

years, while concentrations of most other contaminants have been decreasing. This likely reflects release of sorbed ^{129}I from vadose zone sediments as pH has risen with time (Denham and Vangelas, 2008). The concentrations of ^{129}I in Four Mile Branch below F-Area also exceed the drinking water standard, but are typically <5 pCi/L. The high concentrations within the F-Area Seepage Basins plume make ^{129}I one of the primary risk drivers at this site. Field tests of an injectable amendment to treat ^{129}I in this plume are currently underway and the amendment is briefly discussed in Section 7.

The H-Area Seepage Basins plume has much lower concentrations of ^{129}I. The highest in the first half of 2009 was 79 pCi/L in a well adjacent to the largest basin. The bulk of the plume has concentrations that are <10 pCi/L. Likewise, the small plume emanating from the Old Radioactive Waste Burial Ground contains relatively low concentrations of ^{129}I. The highest concentration measured in this plume in 2009 is 11 pCi/L.

2.3.2. Hanford Site, Richland, Washington

The main onsite contributor of ^{129}I to groundwater is liquid discharges to cribs in the 200 Areas. Extensive plumes of ^{129}I at levels above the Drinking Water Standard are found in the 200 Areas (Figure 3). The major plume extends toward the southeast from the 200-East area. A smaller arm of the plume is moving toward the north between Gable Mountain and Gable Butte. There are some marked differences between the plumes at the Savannah River Site and those at Hanford. The Hanford Site plumes are much larger, covering >100 km^2 compared to the Savannah River Site plumes that covers <2 km^2. Conversely, the Hanford Sites plumes are much more dilute, rarely exceeding 5 pCi/L, whereas the Savannah River Site plumes have several wells that repeatedly record 50 to 100 pCi/L ^{129}I concentrations, and as noted in section 2.3.1, ^{129}I concentration >1000 pCi/L have been measured near the Seepage Basin and in the riparian zone associated in F-Area.

A great deal of attention has been directed to airborne emissions of ^{131}I, the short-lived isotope (Table 2), from the Hanford Site. In 1987, the Department of Energy began the Hanford Environmental Dose Reconstruction Project (HEDR) which analyzed some 19,000 pages of newly released data related to Hanford environmental releases and production (National Research Council 1995). The HEDR estimated how much radiation Hanford released and how much people were exposed to based on where they lived and what they ate and drank. For most of those exposed, the greatest part of their total dose came from drinking milk and eating food that was contaminated with radioactive materials from Hanford. Between 1944 and 1972, according to HEDR's estimates, about 2 million people were exposed either through the air or the Columbia River. ^{131}I accounted for >98% of the radiation dose they received (National Research Council 1995; Washington State Department of Health 2000). The Hanford Thyroid Disease Study reported that thyroid diseases, including thyroid cancer, were not more common among people in the Hanford vicinity (Davis et al. 2007). The study screened >3,000 people for thyroid diseases. This discussion is presented because it deals with radioiodine and there are important lessons learned from these purposeful and inadvertent releases. But it must be kept in mind that essentially all the ^{131}I that was the subject of the Hanford Study has completely decayed, and as such, no longer poses a health threat.
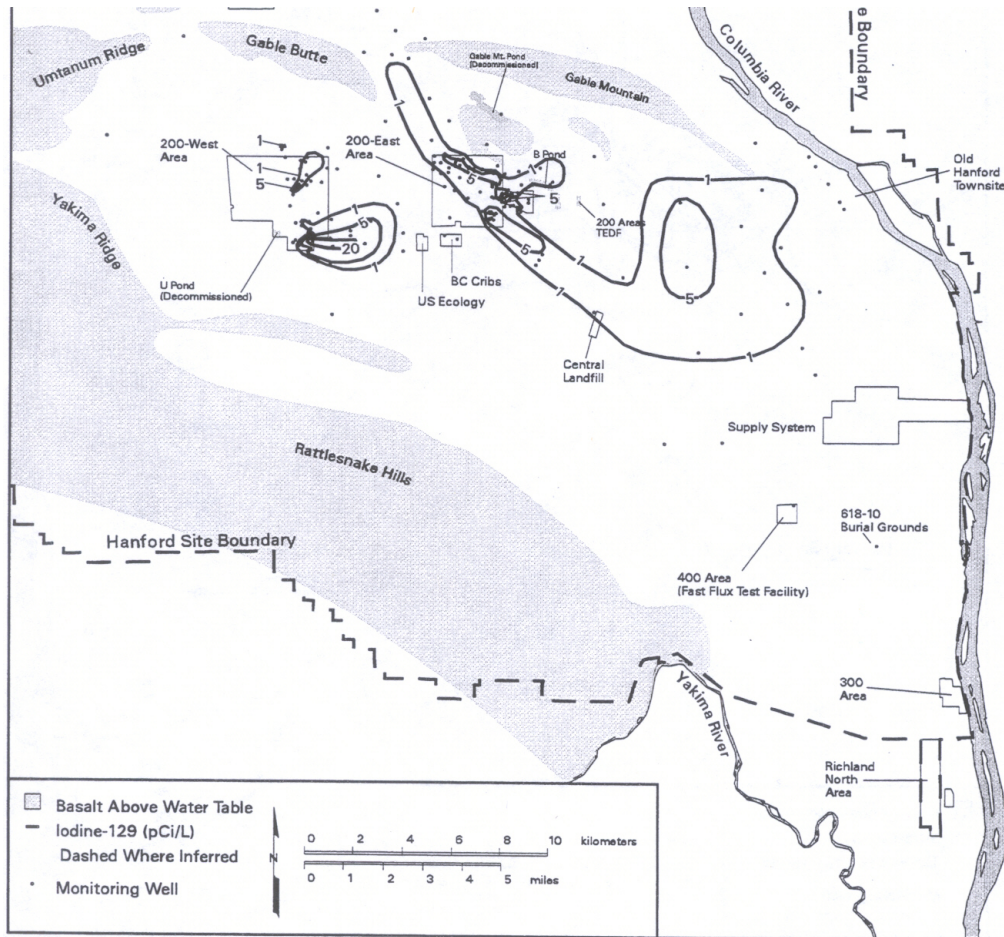
Figure 3. ^{129}I (pCi/L) plumes in the surface aquifer in the 200 Area on the Hanford Site, Washington State. The 200-East Area plume to the right is much larger, whereas the 200-West plume is smaller and contains some areas of higher concentrations.

2.4. SUMMARY

- Any site where products of uranium or plutonium fission were processed may have ^{129}I in the environment

- Within the DOE complex Idaho National Laboratory, Nevada Test Site, and the West Valley Demonstration Project have released ^{129}I to the environment, but only low concentrations have been detected

- The Hanford Site and the Savannah River Site both have major plumes containing ^{129}I at concentrations above the drinking water standard

3. RADIOIODINE EXPOSURE AND DOSE TO HUMANS

Iodine is an essential element for animals and has an important role in the endocrine system. Essentially all the iodine that enters the human body, either through the lungs or the gastrointestinal tract is assumed to be rapidly absorbed into body fluids (ICRP 1979; ICRP 1989). The adult thyroid gland, which weighs 14 g, contains >90% of all the body's iodine, i.e., it contains on average 12 mg of the body's 13 mg of iodine (ICRP 1975). Iodine in the thyroid undergoes a series of biochemical reactions to form hormones, which are important to metabolism in most body tissues, including the heart, skeletal muscles, liver, and kidney.

Iodine's biological half-life, that is the rate at which radioiodine is metabolized and eliminated from the body, is 12 days (Eckerman et al. 2002). The biological half-life is important, especially when it is compared to the physical half-life of the isotopes. For example ^{129}I, which has a physical half-life of 1.6×10^7 yr, would essentially not decay significantly during the time it was in a person that had received a dose from contaminated soil or groundwater. Thus, a single exposure of ^{129}I from the environment would not be sufficient to produce harm because it would not have sufficient time to decay and to release beta particle emissions (150 keV) to cause harm. Conversely, intake of ^{131}I, which has an 8-day half life, would undergo more than one half life in the time it was in the body, releasing beta emissions causing harm. For just this reason, ^{131}I poses most of the short term risk after nuclear incidences (Figure 1), whereas, risk from ^{129}I is only likely to be incurred through chronic long-term exposure.

Radioiodine can cause damage to the thyroid gland in the form of immediate physical damage (cell death from very high doses) or an increased incidence of cancer (BEIR 1990). Increased incidence of thyroid cancer from ionizing radiation have been observed with infants exposed to therapeutic X-rays, Japanese A-bomb survivors, and Marshall Islanders exposed to radioactive fallout from nuclear weapons tests. These studies showed that infants were the most vulnerable, especially during the first five years. Females were roughly three times more sensitive than males to radiogenic thyroid cancer.

A wealth of information regarding the health effects of radioiodine was gathered from the 1985 Chernobyl nuclear power accident. Data show that by 2006 (IAEA 2006), 20 years after the accident, the total number of reported cases of thyroid cancer had reached 5000 in the three most exposed countries: Belarus, Ukraine, and Russia. Interestingly, all of these cases occurred in people <18 years old at the time of exposure, and the fatality rate of those affected was much less than expected. To date (Ron, 2007), there have been a total of 15 deaths (0.3%) among this group. This mortality rate is low compared to the assumed fatality rate of 10% used by ICRP (1991) for estimating the fatal cancer thyroid death coefficient. Should the fatality rate not increase in subsequent years, it would mean that the existing fatal thyroid cancer coefficient (ICRP 1991) is a factor of more than 30 too high.

Another important phenomenon in iodine uptake in humans that greatly impacts the tendency for long lived (low-specific activity) radioiodine isotopes to promote thyroid cancer is that thyroids have a finite capacity to take up iodine leading to a situation in which iodine's relative uptake decreases as its intake increases (Figure 4). This phenomenon was first reported by Book (1977) on studies conducted with beagle dogs. He observed that the more [129]I dogs ingested, the <u>lower</u> the percentage of dose to the thyroid the dogs received. This occurred with [129]I, but not with the high specific activity isotope, [131]I (Figure 4). He did not offer a mechanistic biological explanation for his observations other than to say that he expected [129]I risk to be inherently limited resulting from physical (limited decay) and physiologic (limited of iodine uptake by thyroids) constraints.
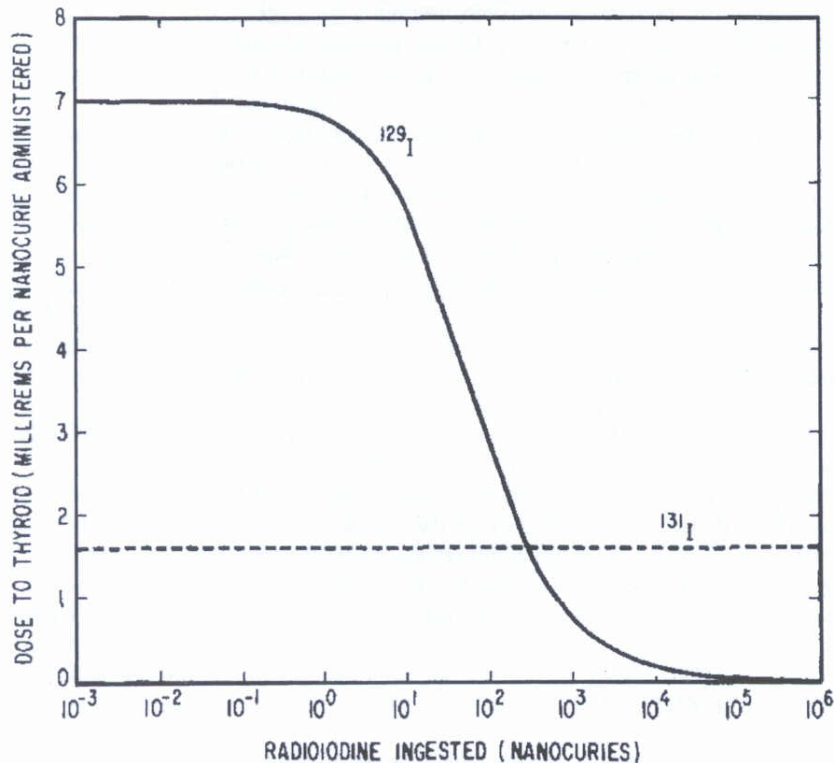
Figure 4. Calculated dose for humans as a function of the quantity of radioiodine ingested. Note that as one ingests between 10^{-3} to 10^{0} nCi [129]I that the maximum dose to the thyroid occurs. As the amount of [129]I ingested increases to 10^{0} and 10^{4} nCi the dose to the thyroid <u>decreases</u> sharply due to its low specific activity and from biologic mechanisms which serve to control the amount of intra- and extrathyroidal iodine. [131]I, which has a high specific activity, does not demonstrate a thyroid dose sensitivity to the amount of radioactivity ingestion (Book 1977).

One could put together a dosimetry argument demonstrating the unlikelihood of [129]I posing a serious health threat (Table 3). The Annual Limit of Intake (ALI) for [129]I, expressed in mass units, is 31 mg/yr. If the "standard man" ingests an average of 73 mg/yr of iodine, then 42% of the annual intake of iodine would have to be [129]I in order to reach the ALI level. The annual [129]I intake would have to be about triple, 31 mg/yr (5.5 µCi/yr [129]I), the total iodine

content of the body, 11 mg/yr (Table 3). Assuming all the iodine is in isotopic steady state with stable iodine in groundwater, 5 µg/L ^{127}I, it would require that the "standard man" drank water with an average ^{129}I concentration of 14.1 µg/L ^{129}I or 2.5 pCi/L.[3]

Table 3. Dosimetry Consideration for ^{129}I

Specific Activity = 1.7 x 10^{-4} Ci/g
Half-life = 1.57 x 10^7 yr
Annual Limit of Intake (ALI) = 2 x 10^5 Bq = 5.4 µCi (equivalent to 5 rem/yr) (ICRP 1979)

ALI = (5.4 x 10^{-6} Ci) x (5.74 x 10^3 g/Ci) = 0.031 g = 31 mg ^{129}I Annual Limit of Intake

Thyroid Content (I_2)	=	10 mg
Whole Body Content (I_2)	=	11 mg
Daily Intake	=	0.2 mg
Annual Intake	=	73 mg
Lifetime intake (70 yr)	=	5.1 g

Dose Conversion Factor (based on ICRP 1979)

(5.0 rem/5.4 x 10^{-6} Ci) = 9.3 x 10^5 rem/Ci
9.3 x 10^5 rem/Ci x 1.85 x 10^{-4} Ci/g = 172 rem/g

A more recent discovery has shown that the uptake of iodine by the thyroid decreased as the dietary intake increased (Zvonova 1989). Her study also showed that thyroid sizes measured in different geographic locations varied inversely with the quantity of iodine in the diet. For example, at an iodine intake of 200 µg/day, the iodine uptake by the thyroid would be about 30% and the thyroid mass would be about 20 g. An iodine intake of 400 µg/day resulted in a thyroid mass of only 10 g. The radiological dose from ^{129}I is due almost entirely to a low energy beta particle that has a very short range in tissue; thus, the dose is deposited only in the thyroid tissue. Since the dose is derived from the energy deposited in a particular mass of affected tissue, it is dependent upon the concentration of iodine in the thyroid and remains constant over a reasonable range of iodine intake.

Wilhite et al. (1998) used the data from Zvonova (1989) and concluded that at the relatively low levels of ^{129}I ingestion addressed in a performance assessment, isotopic dilution arguments as put forth by Cohen (1988) and Book (1977) do not limit the dose from ^{129}I.

These findings from Wilhite et al. (1998) and especially from Zvonova (1989) greatly weakens the simplified argument discussed above; namely, ^{129}I has a long half-life, low biological half-life, and the body can take up only a limited mass of iodine in the presence of an omnipresent background of ^{127}I. Yet, this argument is often made (Rogers and Associates

[3] 31mg/yr / 11 mg/yr = x ppb standard man / 5 ppb ^{127}I; x = 14.1 ppb = 2.47e-9 Ci/L =~2.5 pCi/L

Engineering Company 1987; Bhattacharyya and Janati 1987; IAEA 1987; Soldat 1976; Kocher 1981; Kocher 1991; Moeller 2005; Cohen 1988). At issue, is that this relatively new finding by Zvonova (1989) demonstrated that at elevated iodine environments, the thyroid shrinks and the rate of uptake decreases, compromising our ability to make linear extrapolations and assumptions regarding thyroid iodine uptake.

3.1. SUMMARY

The calculation of health risk from ^{129}I exposure at environmental levels would benefit from additional research that focuses on uptake and residence time in the body versus radiation exposure.

The observations and calculations presented that guide these conclusions are:

1. Stable iodine competes with radioiodine for a finite capacity within the thyroid. The "radiological hazard associated with ^{129}I appears inherently limited (Book 1977);" as was experimentally demonstrated, the more ^{129}I added to a biological system, the lower percentage dose to thyroid was measured.
2. Due to the long half-life of ^{129}I (16,000,000 yr), the short biological half-life (12 days), the finite capacity of the thyroid to sorb iodine, and the presence of much higher concentrations of stable iodine, has led many to believe that potential doses from ^{129}I are inherently limited and that ^{129}I should not be considered a problematic radionuclide in disposal or contamination settings. They argue that the ^{129}I would leave the body prior to it decaying. However, these facts do not take into consideration complicating, non-linear considerations demonstrating varying iodine uptake rates and thyroid size with concentration of iodine in the environment. Additionally, calculations conducted at appropriate environmental levels indicate that one of the key arguments (isotopic dilution) can not be used to reduce dose for ^{129}I.

4. BIOGEOCHEMISTRY OF IODINE

4.1. GENERAL IODINE CHEMISTRY

Iodine is a complicated element because it can exist in multiple physical states, as well as multiple oxidation states at environmentally relevant conditions. It readily reacts with organic compounds, further complicating its chemistry in organic-rich environments. Iodine is also an essential nutrient for plants and animals that concentrates in certain organs driving the regulatory drinking water limits for radioactive isotopes to very low concentrations. This together with its long half-life and relative mobility in the environment usually assures that ^{129}I is a risk driver at sites where abundant quantities were disposed.

Iodine can exist as a solid, liquid, or gas. The melting point of the solid is 113.6ºC, the boiling point of the liquid is 185ºC, and the critical temperature and pressure are 553ºC and 11753.7 kPa (Lauterbach and Ober, 1996). The solubility of elemental iodine in water at 25ºC is 340 mg/L with a vapor pressure of 4.1×10^{-4} atm. (Lauterbach and Ober, 1996). Parsly (1970) calculated the Henry's Law constant at 25ºC for elemental diiodine to be 3.0 moles/L·atm. Thermodynamic data from HSC Chemistry® indicates a value of 3.8 moles/L.atm, assuming ideal behavior for both the vapor and solution. Iodine hydrolyzes in water by four main reactions (Parsly, 1970):

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

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

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

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

Values for log K20ºC were calculated using HSC Chemistry® software version 3.0.

In addition, iodine can form numerous other species in which iodine has valence states -1, 0, +1, +5, and +7. The reactions for several species are shown in Table 4 with iodide (I^-) as the reactant species. Under conditions prevalent in groundwater and surface water only the -1, 0,

Table 4. Reactions and log K of selected aqueous species of iodine.

Reaction	log $K_{20ºC}$
$I^- + H^+ = HI$	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

and +5 valence states are common. Additional species may occur in natural waters because iodide forms aqueous complexes with various metals. For example, in most waters containing Hg(II) the aqueous complex HgI_2^o may compete with $HgCl_2^o$ as the dominant mercury species at mercury concentrations comparable to the iodide concentration. Consider the reaction:

$$HgCl_2^o + 2I^- = HgI_2^o + 2Cl^- \qquad logK_{20^oC} = 10.91 \qquad (5)$$

At molal chloride to iodide ratios less than 2.8×10^5 and mercury concentrations comparable to the iodide concentration, HgI_2^o would the stable Hg(II) complex. In many natural groundwaters the chloride to iodide ratio would favor the HgI_2^o, but not in seawater or many subsurface brines. Most other aqueous iodide complexes with metals require high iodide concentrations to account for a significant fraction of the metal species.

Iodide forms low solubility salts with several metals, notably Ag, Au, and Cu(I). Figure 5 shows the calculated aqueous concentration of the metal in equilibrium with metal salt and 10 µg/L I^-, assuming ideal behavior and no significant complexing by other constituents. The occurrence of natural iodide minerals containing Hg, Ag, and Cu, though rare, attests to the insolubility of these metal iodides. The solubility of metal iodates is typically much higher than iodides and thus metal iodates are unlikely to exert any control on iodate concentrations in most systems. The exception are arid alkaline environments such as the Chilean caliche deposits where iodate minerals are enriched enough to form a commercial source of iodine (Fuge and Johnson, 1986).
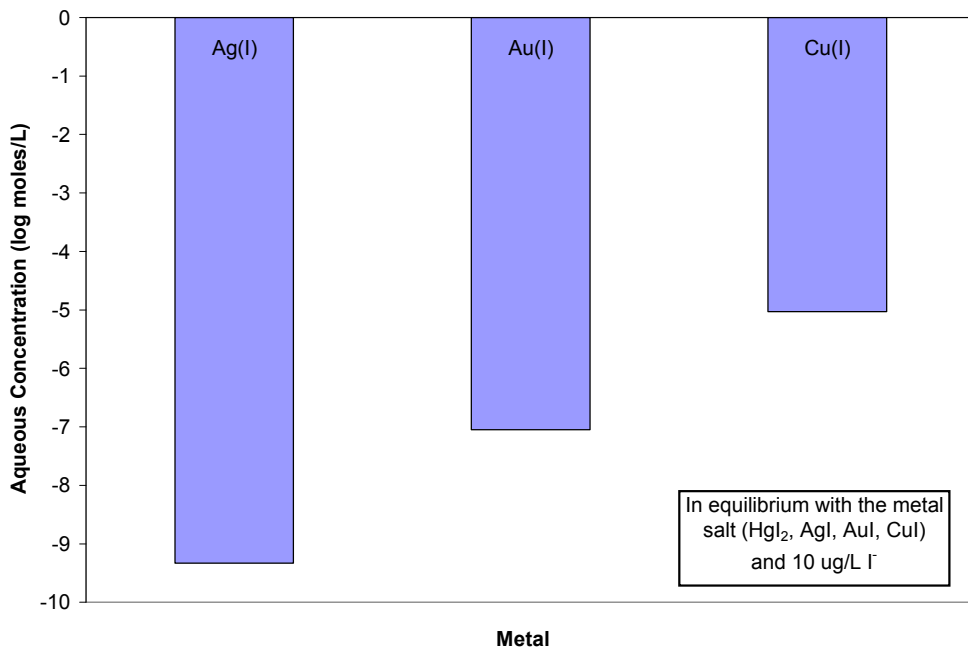
Figure 5. **Solubility of various metal iodides expressed as the aqueous metal concentration (log mole/L) at 10 ug/L iodide.**

Various forms of iodine react with organic molecules. Elemental iodine reacts in much the same way as chlorine and bromine, to form organo-iodine compounds. Most commonly these involve I^-, though specific properties of iodine allow for organic syntheses involving polyvalent iodine, usually I(III) and I(V). Zhdankin and Stang (2002) and Stang (2003) provide thorough reviews of the syntheses of polyvalent organo-iodine compounds. Skulski (2000) reviews 10 years of research at the Medical University of Warsaw, Poland into aromatic organo-iodine compounds. Another area of research into organic-iodine reactions has been the reactions that might occur with organic substances in nuclear reactors during an accident (e.g., Paquette et al., 1986; Malinauskas and Bell, 1987; Dickinson et al., 2001; Wren and Ball, 2001; and Taghipour and Evans, 2002). The focus of this research has been the effect of such reactions on release of radioactive iodine to the environment. Organic-iodine reactions pertinent to iodine mobility in natural waters and soils are discussed in a later section.

4.2. MOBILITY OF ^{129}I IN THE ENVIRONMENT

4.2.1. Aqueous Speciation

The chemistry of iodine under conditions associated with most ^{129}I environmental contamination is somewhat simplified because the only inorganic aqueous species that are common are I^-, I_2^o, and IO_3^-. Figure 6 shows the relation of these species in Eh-pH space. Iodate (IO_3^-) is stable at very oxidized conditions across the range of pH likely to be encountered in most contaminant plumes. Elemental iodine is stable at moderately oxidized and acidic conditions. Increased total iodine concentration expands the diiodine field as shown by the dotted line in Figure 6. Iodide (I^-) is the stable form over much of the range of conditions expected in contaminant plumes. The protonated forms HI and HIO_3 also exist in iodine solutions, but are only dominant at extreme conditions.

Figure 7 shows relative concentrations of the various inorganic aqueous species of iodine and how the speciation changes with changing conditions. At very high total iodine concentrations the species I_3^- can exist at acidic pH and moderate Eh as shown in Figure 8.
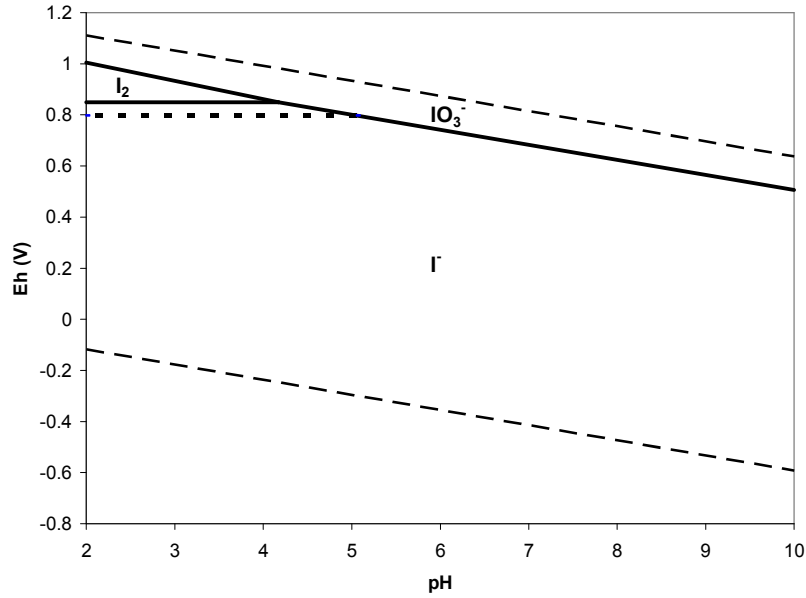
Figure 6. Eh-pH diagram of aqueous iodine speciation; solid line = total iodine concentration of 1µg/L, a typical groundwater concentration, dotted line = total iodine concentration of 58 µg/L, a typical seawater concentration (Fuge and Johnson, 1986); dashed lines are stability limits of water.
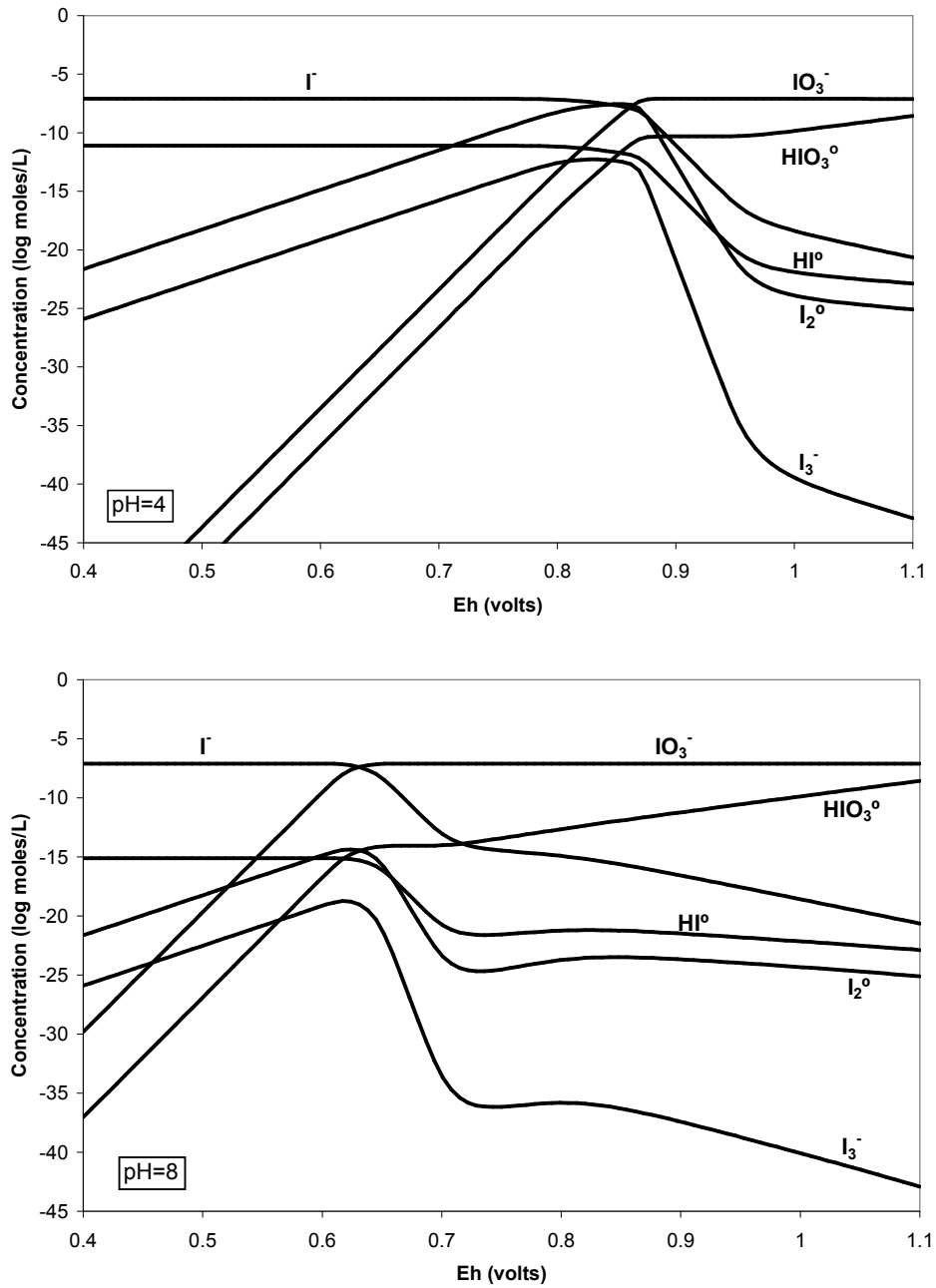
Figure 7: Aqueous inorganic speciation of iodine versus Eh at pH values of 4 (top) and 8 (bottom) at a total iodine concentration of 10 ug/L (diagrams calculated using The Geochemist's Workbench®, Bethke 2005).
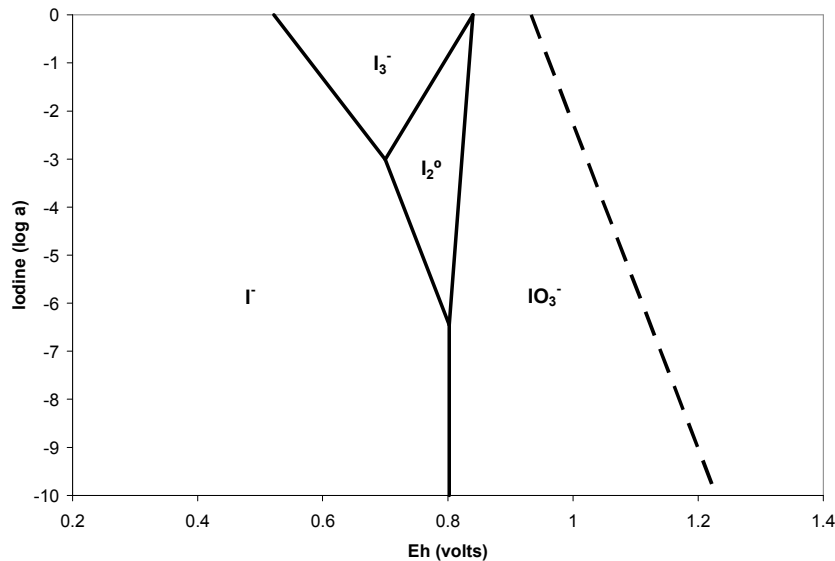
Figure 8. Iodine speciation in terms of species activity versus Eh at pH=5 (diagram calculated using The Geochemist's Workbench®).

4.2.2. Geochemical Processes in Soils[4]

Studies of [129]I in the environment are built on a base of knowledge about iodine behavior in the environment gained from studies of marine iodine. These relate to the importance of stable iodine as a nutrient to life-forms and the use of iodine as tracer of marine processes. Iodine chemistry in marine waters is governed by complex cycling between the atmosphere, photic zone waters, deep waters, and sediments (e.g. Luther et al., 1995). The complexity is evident in early studies of iodine speciation in seawater, for example in the energetic discussions on the presence and nature of oxidized iodine species in seawater (Sugawara and Terada, 1957; Shaw and Cooper, 1957; Sugawara and Terada, 1958; Johannesson, 1958; Shaw and Cooper, 1958). It is known that iodide is generally the dominant species in shallow photic zone waters, while iodate is generally dominant in deeper waters. The cycle summarized by Luther et al. (1995) includes:

- biologic reduction of iodate to account for shallow iodide
- re-oxidation of some of the iodide to intermediate species that can be volatilized to the atmosphere or react with organic matter
- release of iodide from decaying organic matter within sediments
- rentry of iodide released from decaying organic matter into deep waters to be re-oxidized to iodate or react with organic compounds in the sediments

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[4] In this report, the term "soil" refers to both surface soils and subsurface aquifer materials.

Similar types of reactions also influence the behavior of [129]I from its release at a waste site to its travel in groundwater to its surface exposure at seeplines or streams. A major difference is the more prominent role of [129]I interactions with minerals and organic matter.

The following sections discuss the geochemical and microbiological processes affecting [129]I behavior in the environment. Discussion of the geochemical processes differentiates between behavior of [129]I in organic-bearing soils and organic-poor soils. Organic-bearing soils include surface soils, wetland soils, and aquifer soils containing significant natural organic matter. However, most shallow contaminated aquifers are composed of organic-poor soils.

Organic-Bearing Soils

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

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

Comparisons between iodine sorption to organic-rich soils and organic-poor soils also demonstrate the importance of organic matter to sorption of iodine. In lysimeter studies of 4 soils with organic contents ranging from 0.2-6.8%, Sheppard and Thibault (1991) measured K_d values that were 1-2 orders of magnitude higher in the organic-rich soils relative to the organic-poor soils. Similar results were shown in comparative studies by Yoshida et al.

(1992), Bird and Schwartz (1996), Sheppard et al. (1996), and Yoshida et al. (1998). Kaplan (2003) compared iodide sorption in two soils that had similar grain-size, mineralogy, and pH values, but had very different organic carbon contents -- <200 versus 1395 mg/kg. Sorption was substantially higher in the organic-rich soil.

In many studies of shallow soils the observation has been made that sorption of iodine in oxic organic-rich sediments is greater than in anoxic organic-rich sediments. This was hinted at by Whitehead (1974) who found that drying organic-rich soils before measuring iodine Kd values substantially reduced the sorption. Sheppard and Hawkins (1995) explicity 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, 1996). The same relation was observed by Ashworth et al (2003) and Ashworth and Shaw (2006) in column studies where they noted much lower sorption in saturated anoxic portions of their columns than in unsaturated oxic portions. Likewise, the same observation has been made in the field by Maillant et al. (2007) who returned, after 15 years, to the site of an iodide injection into bog soils documented by Sheppard et al. (1989). They found that iodine Kd values were approximately 7 times higher in the surface bog soils than in the deeper anoxic bog soils. Release of soil-bound iodine has also been observed in two forest soils (9-56 fold increase) under flooded, anaerobic conditions (Yuita 1992). Iodate was the dominant (86% of water soluble I) form under non-flooded, oxidizing conditions, whereas iodide was the dominant (87% of water soluble I) form under flooded conditions. In one soil type, the soil solution concentration of organo-iodine increased 2.5 fold under flooded conditions. A very extensive sampling of iodine soil water from a forest, upland field, and rice paddy field in Japan revealed a strong negative relationship between soil Eh and soil water I concentrations (Yuita and Kihou 2005). In particular, soil water I concentrations begin to increase with decreasing Eh values below 200 mV. In summary, it appears that iodine binds to surface soils under oxic conditions and is released under strongly reducing conditions.

The activity of iodine in biota, the strong association with organic matter, the redox sensitivity and studies of marine iodine cycling have led to the hypothesis that microbial activity is involved in iodine sorption by organic matter in soils. Many researchers have tested this hypothesis by comparing iodine sorption onto sterilized and unsterilized soils (Behrens, 1982; Sheppard and Hawkins, 1995; Bird and Schwartz, 1996; Yoshida et al., 1998). These studies have confirmed that microbial activity is involved, but the nature of that influence is unresolved. Bors et al. (1991) showed that under specific conditions bacteria and fungi cells isolated from a soil did take up iodine, though they acknowledged that this did not resolve whether microbes are directly or indirectly involved in sorption of iodine in soils. Sheppard and Hawkins (1995) suggest that microbes exert an indirect effect on iodine sorption, perhaps just by their action of degrading organic matter under oxic conditions. Sheppard et al. (1996) reiterated this conclusion by showing that the organic content of 7 soils correlated positively with sorption, but enzymatic activity did not. Some of the iodide in their studies was irreversibly sorbed and they suggested that this iodide had converted to elemental iodine that reacted irreversibly with organic matter. Results reported by Yamaguchi et al. (2006) and Yamaguchi et al. (2009) using XANES to analyze iodine speciation also demonstrated that elemental iodine was ultimately the species that reacted

with organic matter. In anaerobic soils, iodate was reduced to elemental iodine that reacted with organic matter (Yamaguchi et al., 2006). In aerobic soils, iodine reaction with organic matter involved either reduction of iodate or oxidation of iodide (Yamaguchi et al., 2009). Yamaguchi et al. (2009) also concluded that microbes were not necessary for the reduction of iodate by humic substances. Maillant et al. (2007), studying the bog samples from the 15 year earlier iodide injection of Sheppard et al. (1989) found considerably more evidence of microbial behavior in the oxic surface layers than in the anoxic layers. They also observed iodine associated with polyphenols in the humified fraction of the soils. This is consistent with the findings of Warner et al. (2000) that observed that sorption rates of elemental iodine onto solid humic material were in the range of sorption rates onto the phenolic compounds. Thus, the exact role of soil microbes in sequestering iodine remains unclear, though it is generally agreed they play some role.

The role of humic substances in sorption of iodine also remains unclear. In soils used in iodide sorption studies by Bors et al. (1988) iodine was primarily sorbed to humic and fulvic acids. Fukui et al. (1996) also concluded that solid humic substances were important to iodine sorption because Kd values for pure humic substances were 10 times higher than for soils. Interestingly, they also observed that soluble humic acid and other soluble organic compounds had little influence on sorption of iodine. Bostock et al. (2003) and Maillant et al. (2007) demonstrated strong sorption of iodine to solid humic substances. Yet, Muramatsu et al. (1990b) and Yoshida et al. (1992) concluded that humic substances were not likely important in sorption to organic matter in the soils they studied.

Most researchers (e.g. Whitehead, 1973; Whitehead, 1974; Yoshida et al., 1992; Nishimaki et al., 1994; Yu et al., 1996; Fukui et al., 1996; Kaplan, 2003) have found that increased pH values are generally accompanied by decreased sorption of iodine. This is consistent with adsorption theory, that anions such as iodide and iodate, will adsorb less at pH values above the zero point of charge of the sorbent because the negatively charged surface tends to repel the negatively charged aqueous ions. Yet, Dai et al. (2004) found no correlation between iodate sorption and pH.

One common concern for many contaminants in organic-rich environments is increased mobility from aqueous complexing of the contaminant. Warwick et al. (1993) examined the mobility of fulvic and humic acid complexed iodine through columns of glacial sand. The fulvic acid complexed iodine was far more mobile through the column than the humic acid complexed iodine. Sheppard et al. (1995) observed that much of the iodine in pore fluids of a bog soil was associated with dissolved organic carbon. However, they found that the formation of this association was very slow. On the other hand, Fukui et al. (1996) found that soluble humic acid and other organic compounds had little effect on iodine sorption, and hence mobility. Sorption of soluble organo-iodide compounds is related to the insoluble organic content of the sample (Hu et al., 2005). Thus, experimental results are dependent on the soil used. Anthropogenic soluble organic compounds can complex dissolved iodine and decrease its sorption. Bors et al. (1988) observed this behavior with dibutyl-phosphate (DBP), nitrilotriacetic acid (NTA), and ethylenediaminetetraacetic acid (EDTA), with NTA showing the largest effect.

At many waste sites sorption in shallow soils is the dominant mechanism that attenuates migration of [129]I to groundwater, but volatilization may also occur. Volatilization in shallow soils potentially transfers [129]I from the waste site to the atmosphere. Volatilization can occur because elemental iodine, I_2, is volatile as are other potential species such as HOI or CH_3I. Methyl iodide (CH_3I) may be formed by microbial processes in soil. Whitehead (1981) found that iodine added to soils was lost in high percentages to volatilization after 30 days in a well ventilated room. However, soils that contained organic matter lost considerably less and the minerals montmorillonite, kaolinite , and ferric oxide also reduced volatilization. Conversely, simulations by Sheppard et al. (1994) based on measured degassing coefficients suggest that, under the right conditions degassing can reduce soil concentrations of [129]I significantly. Yet, measurements of volatilization of ^{125}I from cores of grassland and coniferous forest soils by Bostock et al. (2003) showed that this was not a major pathway for iodine movement in these soils. Nevertheless, Muramatsu et al. (2004) detected methyl iodide produced by microbial interactions in soils incubated with added iodine. They recommended that the volatilization pathway be considered in dose assessments. The findings of Connan et al. (2008) support this recommendation. They detected methyl iodide and a number of other volatile organic iodide compounds were in water to atmosphere fluxes from the Seine Estuary in France.

Volatile organic compounds have been assessed in 109 groundwater samples from five U.S. aquifers (Plummer et al. 2008). Approximately 46% of the samples containing methyl iodide had concentrations that would be expected from air-water equilibration, however 54% of the samples contained methyl iodide at concentrations in excess of that expected from atmospheric equilibration, some were 70x that value, and may have a biological source. Median methyl iodide concentrations ranged from 80-420 pg/L within the five aquifers.

Organic-Poor Soils

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

Sorption of iodine in subsurface aquifer materials occurs as adsorption to specific mineral surfaces. Quantification of this has been approached by measuring sorption in the bulk material and by measuring adsorption onto individual minerals common to aquifer materials. Measurements of iodine sorption onto bulk aquifer material, in general, show that sorption is weak, similar to organic poor surface soils (e.g., Lieser and Steinkopff, 1989; Alvarado-Quiroz et al., 2002; Schwer et al., 2005; Hu et al., 2008). In a compilation of iodine sorption studies on Hanford soils, Kaplan and Serne (1995) and Kaplan and Serne (2000) provided recommended K_d values for ^{129}I for use in performance assessment models. Kaplan and Serne (1995) recommended a range from 0 ml/g for high ionic strength, anoxic pore waters to 3 ml/g for low ionic strength oxic pore waters – all sediments were at neutral to high pH and contained low concentrations of organic matter. The relationship to ionic strength is consistent with the relation to salinity observed by Lieser and Steinkopff (1989). Similar low sorption of iodine on Savannah River Site aquifer material was suggested by compilations of studies in the literature by Kaplan and Millings (2006) and Kaplan (2006). Their recommended Kd values for performance assessment models were 0 ml/g for sandy sediments and 0.6 ml/g for clayey sediments.

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

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

Monomineralic Sorption Studies

Monomineralic studies of iodine sorption show similar results to bulk soil studies, but provide an additional level of detail. In general, iodate sorbs more strongly to individual minerals than iodide and the common soil minerals that most strongly bind iodate are ferric oxides and hydroxides (Neal and Truesdale, 1976; Couture and Seitz, 1983; Ticknor and Cho, 1990). Fuhrmann et al. (1998) observed an exception to the general iodide-iodate sorption relationship. Magnetite sorbed iodide more strongly than iodate. They also looked at redox changes in the sorbed iodate using XANES spectra. They observed that no reduction of iodate occurred when sorbed to the ferrous iron containing minerals biotite and magnetite, but reduction to elemental iodine did occur when iodate was sorbed to pyrite. Further reduction of the elemental iodine to iodide was not observed. Ticknor and Cho (1990) found that iodate sorption to hematite increased with increased total dissolved solids. Their experiments were done in a synthetic groundwater with relatively high concentrations of Na^+, Ca^{+2}, Cl^-, and SO_4^{-2} (2000, 2170, 6176, and 985 mg/L) indicating that the presence of one or more of these ions changed the surface chemistry of the hematite to favor iodate sorption. Musić et al. (1979) measured relatively strong sorption of iodate to freshly precipitated aluminum hydroxide, but noted that sorption decreased as the aluminum hydroxide aged.

Iodide also sorbs to common soil minerals. Musić et al. (1979) observed weak sorption of iodide to aluminum hydroxide. Sazarashi et al. (1994) measured Kd values of 2-3 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 organic matter. Substantial sorption of iodide to common minerals has been observed by some investigators. Kaplan et al. (2000) observed strong sorption of iodide to illite, which was inversely related to pH. Titanium oxides are a common minor component of soils and Mishra and Srinivasu (1992) found that 73% of iodide at a concentration of 10^{-7} molar sorbed to TiO_2 powder. Yet organo-clays show even stronger sorption of iodide (Bors et al., 1997).

4.2.3. Microbiological Processes Affecting [129]I Behavior

Though specific microbial mechanisms affecting iodine behavior in soils remain unclear, a significant amount of research has been done on the role of microbes in the marine iodine cycle. Additionally, several laboratory culture studies on iodine processing by various microbes have been done. These, together with the small number of soil studies, are presented here to highlight what is known about microbial influence on iodine behavior and the potential mechanisms that may control its transformation in organic-bearing soils.

Biological Reactions and the Global Iodine Cycle

Biological mechanisms are intrinsic to the global iodine cycle. Oceans are considered the primary source of iodine; accordingly, our understanding of biological transformations of iodine is derived largely from those processes that have been studied in marine environments. Based on thermodynamic considerations iodate/iodide levels in seawater are in disequilibrium, with iodide found at levels much higher than would be expected, especially

in certain surface waters, coastal and estuary regions, deep oxygenated water, and porewater of marine sediments where I^- concentration up to 40 $\mu g\ L^{-1}$ have been measured (Farrenkopf et al. 1997; Amachi 2008). The conversion of IO_3^- to I^- is thought to be catalyzed primarily via microbial activity, perhaps by the enzyme nitrate reductase or release of I^- from C-I or N-I bonds upon decomposition of organic matter (Tsunogai and Sase 1969; Farrenkopt et al. 1997; Wong et al. 2002; Waite and Truesdale 2003).

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

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

Accumulation and speciation of I in biological samples

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

Studies examining the accumulation of iodine by microorganisms are exceedingly sparse. A number of bacterial strains capable of iodide accumulation have been isolated from marine sediment (Amachi et al. 2005). All strains were classified within the *Flavobacteriaceae* family of the *Bacteroidetes* phylum. The maximum iodide content measured in cells was 30 $\mu g\ g^{-1}$ dry cells, and the maximum concentration factor based on the ratio of iodide in cells to that in the media was 5.5 x 10^3. By comparison, the brown algae, *Laminaria digitata*, has exhibited an iodide concentration factor of 1.5 x 10^5 (Küpper et al. 1998; Peter 2002).

Iodide uptake by bacterial cells was stimulated in the presence of glucose and O_2, and the process was saturable (0.073 µM affinity constant; 0.55 pmol min^{-1} mg dry cells^{-1} maximum velocity). Iodate was not accumulated. In a follow up study with one of these iodide-accumulating bacterial strains it was determined that glucose stimulated iodide uptake through the action of glucose oxidase, which generated extracellular H_2O_2 (Amachi et al. 2007). The authors proposed a model whereby extracellular H_2O_2, generated by glucose oxidase, is used to oxidize iodide to I_2 or HIO via an unidentified haloperoxidase. HIO is then transported across the cell membrane via a facilitated diffusion-type mechanism. Once inside the cell HIO would be reduced to iodide or form organo-iodine species. This scenario is strikingly similar to that observed in the brown algae, *L. digitata*, where iodide is oxidized to hypoiodous acid (HIO) by an extracellular haloperoxidase, which then enters the cell via facilitated diffusion (Küpper et al. 1998). Inside the cell, iodine is stored in the iodide form and it has been posited that it acts as an inorganic antioxidant, scavenging reactive oxygen species (Kupper et al. 2008). Very interestingly, data indicated that while inside *L. digitata* tissue, I$^-$ is surrounded by organic molecules such as phenols, carbohydrates, and proteins rather than an ordered hydration shell (Fig. 9). In the presence of H_2O_2 and peroxidase activity most of the available iodine is incorporated into aromatic organic molecules that may or may not undergo nucleophilic substitution with Cl$^-$, Br$^-$, or HO$^-$ to regenerate I$^-$.
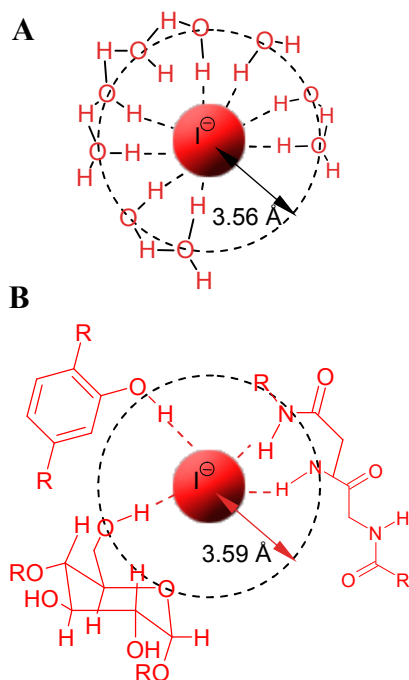
Figure 9: Cartoon of I$^-$ surrounded by A) aqueous hydration shell B) intracellular phenols, carbohydrates or amines (Kupper et al. 2008).

Biological formation of gaseous I

The generation of volatile organic I species has been well-established for marine macroalgae and to some extent for marine microalgae (Giese et al. 1999; O'Dowd et al. 2002; McFiggans et al. 2004); however, it has recently been suggested that marine bacteria may also play an important role in the annual production of CH$_3$I (Amachi et al. 2001; Amachi et al. 2004; Amachi 2008). Additionally, the role of terrestrial bacteria in global CH$_3$I fluxes has begun to be recognized. From early studies it was concluded that volatilization of iodine from surface soils was not a widespread phenomenon. Whitehead (1981) found that among 24 surface soils volatilization was negligible, except in an acid sandy soil where 57% of the iodine was volatilized. It was generally believed that the presence of organic matter inhibits volatilization in soils by binding available iodine.

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

Recently, a survey of 53 soil samples collected from rice paddies, forests, upland fields, and wetlands yielded detectable CH_3I production from spiked iodide (0.1 μM) in samples from each of these terrestrial environments (Amachi et al. 2003). Formation of other alkyl iodides was not observed. The addition of glucose or yeast extract could enhance CH_3I production, whereas the addition of antibiotics targeting prokaryotes (streptomycin and tetracycline) was strongly inhibitory (the fungal antibiotic, cyclohexamide had little effect). Very little methyl iodide was produced with autoclaved soils or under anaerobic conditions. These results suggest that soil bacteria (mainly, aerobic soil bacteria) may preferentially contribute to iodine volatilization from these soil environments. It is important to note that iodide methylation has been observed to occur primarily under aerobic or microaerobic conditions in other environments as well such as freshwater, seawater, brine waters, etc. (Stephenson and Motycka 1995; Amachi et al. 2001). The extrapolation of iodine methylation rates from laboratory studies with select soils to natural soil environments is, however, difficult because of the large variations in iodine levels among different soil types, the dependence of iodine availability on soil properties, and the concentration-dependent nature of methyl iodine formation (Amachi et al., 2001). Of particular interest, it has been suggested that biologically mediated iodine methylation could contribute to localized air concentrations of ^{129}I near nuclear production facilities or reprocessing plants, even after closure (Brauer and Strebin 1982; Muramatsu and Yoshida 1995).

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

Influence of redox conditions on alkyl iodine formation

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

Microbiological oxidation of Iodine

The initial description of iodide oxidation by a bacterial species was elicited by the death of fish in experimental aquaria, presumably due to iodine poisoning. The marine bacterium, *Pseudomonas iodooxidans* (γ-Proteobacteria), was isolated from tank water by observing colonies that produced a blue color on seawater-agar plates containing 4% glycerol, 0.12% starch, and 0.1% potassium iodide (Gozlan 1968). Iodine production could be detected in the presence of 8 mM but not 0.8 mM KI. The microorganism was highly resistant to iodine toxicity. Experimental evidence pointed towards the production of an extracellular haemoprotein peroxidase by *P. iodooxidans* that could oxidize iodide in the presence of H_2O_2 ($H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O$) (Gozlan 1973; Gozlan 1974). Importantly, the physiological status of the bacterial culture needed to be such that H_2O_2 was produced as a co-substrate for iodide oxidation.

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

In the most exhaustive study to date prospecting for iodide-oxidizing bacteria, strains were isolated from iodide-rich (63 μM to 1.2 mM) natural gas brine waters and seawater (Amachi et al. 2005). Iodide-oxidizing bacteria were not obtained from the 22 surface soil samples that were tested. Iodine-oxidizing bacteria were isolated directly from brine waters, but were only isolated from seawater after enrichment in the presence of 1 mM iodide (however, it was shown that KI does not influence the levels of iodide-oxidizing activity in the isolates). Why iodide-oxidizing bacteria can be enriched in the presence of high I concentrations (mM) is currently unknown. Amachi et al. (2005) suggest two possibilities. First, iodide oxidation generates energy using oxygen as an electron acceptor, a thermodynamically favorable

reaction ($2I^- + 2O_2 + 2H^+ \rightarrow I_2 + H_2O$ ($\Delta G^{0'}$ = -56 kJ/reaction). However, since the iodide oxidizing enzyme appears to be extracellular, this hypothesis is unlikely. Alternatively, IOB use oxidized iodine species to attack competing microbes giving them a selective advantage, especially in environments with high levels of I.

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

Biological Reduction of Iodine

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

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

Combined with a plethora of field observations concerning the distributions of iodide, iodate, and organic iodide, data from the studies described above and others have allowed oceanographers to begin to discern mechanisms that control iodine transformations within different compartments of the marine environment. For example, Farrenkopf and Luther (2002) contend that in the well-oxygenated surface layer of the Arabian Sea iodate uptake is dominated by phytoplankton incorporation, in the oxygen minimum zone, iodate uptake/turnover is dominated by bacterial reduction, and in the deep oxygenated waters reduction of iodate is not a quantifiable feature. The important point of these studies, as related to [129]I at a waste site, is that multiple biological and abiotic mechanisms contribute to

iodine transformations in the environment. These are likely to vary depending on the geochemical conditions – the presence and nature of organic matter, the redox potential, pH, and total iodine concentration.

Incorporation of Iodine into Organic Matter

As discussed in section 5.2.2.1, organic matter plays a primary role in the sorption of iodine to soils, and sorption is typically greater under aerobic, or oxic, conditions. Furthermore, a large number of studies have demonstrated a role for microbial activity in the sorption of iodine to soil (Johanson 2000). The majority of studies examining this phenomenon to date have simply demonstrated that soils or sediments treated with heat, chloroform, gamma irradiation, or prokaryotic antibiotics exhibit a considerable reduction in their iodine binding capacity (Johanson 2000; Muramatsu et al., 1990b, 1996, 2004; Amachi et al., 2003), whereas inoculation of sterilized soil with fresh soil or viable microorganisms can restore the iodine-organic matter binding potential (Muramatsu et al., 2004). Recently, Heumann et al. (2000) and Radlinger and Heumann (2000) took these experiments one step further by using ICP-MS to directly measure microbiological-dependent iodine incorporation into specific fractions of higher molecular weight organic matter. From the data, the authors concluded that the transformation of iodide into iodo-organic matter did not occur through direct fixation of iodide onto a specific organic fraction, but rather via a series of undefined, complex transfer mechanisms. It is important to note, that the microbial-dependent enhancement of iodine transformation into high molecular weight organic matter has thus far only been observed under aerobic conditions.

A growing body of literature has implicated microbial oxidases, perhydrolases, and particularly peroxidases in the halogenation of soil organic matter (Bastviken et al. 2007; Leri et al. 2007; Ortiz-Bernadez et al. 2007). Haloperoxidases, which can oxidize chloride, bromide, and/or iodide (not fluoride), have been identified in bacteria, fungi, plants, and algae (Asplund et al. 1991; Asplund 1995; van Pée and Unversucht 2003; Hofrichter and Ullrich 2006; Vaillancourt et al. 2006). Haloperoxidases are commonly classified according to the least favorable halogenation reaction that they can catalyze – chloroperoxidases use Cl^-, Br^- and I^-, bromoperoxidases utilize Br^- and I^-, and iodoperoxidases are limited to I^- as the halogen source. Among these enzymes, the heme- (ferriporhyrin) and vanadium-containing haloperoxidases and also perhydrolases exhibit non-specific substrate specificity, generating hypohalous acid via the direct H_2O_2-dependent oxidation of halides, and are thus capable of halogenating a wide variety of organic moieties. Among soil bacteria, these enzymes have been primarily identified in *Actinobacteria*, *Firmicutes*, and several groups of *Proteobacteria* (Passardi et al. 2007).

4.3. WASTE SITE-SCALE BEHAVIOR OF [129]I

Different processes will control [129]I behavior within different compartments of a waste site system. The compartments that are most likely to be pertinent to [129]I behavior are the disposal site itself, shallow organic-rich soils, the subsurface (arbitrarily chosen here as a

depth of >5 meters), the hyporheic zone, and surface water receiving groundwater discharge. In general, adsorption and/or microbially facilitated interaction with organic matter are the dominant attenuation processes for ^{129}I in these compartments. Precipitation is unlikely to occur naturally because the metals that form low solubility salts with iodide are present at such low concentrations. For compartments near the surface, potentially all but the subsurface, volatilization may reduce the mass of ^{129}I migrating to groundwater.
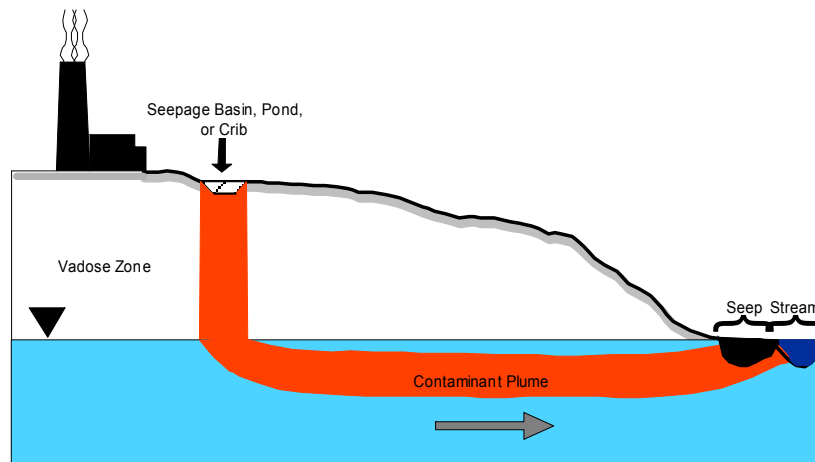
Figure 10: Diagram of a generic waste site.

Figure 10 is diagram of a generic waste site showing a plume originating from a basin or pond that migrates through the vadose zone, into the saturated zone and eventually crops out at a seepline/hyporheic zone associated with a stream. The surface topography is covered with soil that is often organic-rich at the surface, grading into an organic-poor shallow soil with depth. The surface soil is not saturated with water for long periods of time and is oxic. The bottoms of basins and ponds are often covered with organic-rich sediments, the organic matter derived from debris blown into the basins, algae growth, or the influxing waste. These sediments may be oxic or anoxic depending on the state of the basin. The subsurface materials of the vadose and unsaturated zones are beneath the basins. These are typically not organic-rich, but can be. A thick layer of organic-rich soil often occurs at the seepline/hyporheic zone where the plume crops out, because of the increased vegetation near the stream. Parts of this layer that are perpetually saturated with water are anoxic. Other parts may vary between oxic and anoxic as the water table rises and falls.

Assessment of ^{129}I transport and remediation must consider the waste site as a whole, because, as noted by Hu et al. (2005), ^{129}I behaves differently in the different compartments of a waste site. The nature of the waste release and the conditions of each compartment must be understood. Also of importance is the expected response of each compartment to the

influx of the contaminant plume, particularly the changes in pH and redox conditions. This should all be included in the conceptual site model.

In the generic waste site shown in Figure 10 migration of ^{129}I will be most attenuated by sorption in compartments with oxic organic-rich soils at the surface of the disposal site, if applicable, or at the seepline. The least attenuation will occur in the stream. Of the subsurface compartments, ^{129}I would be least attenuated in the organic-poor subsurface sediments or rocks of the vadose and saturated zones. Attenuation in the basin bottom sediments will depend on the amount of organic matter in the sediments and whether the basin bottom is oxic or anoxic. The same is true for the organic-rich seepline. The redox state of these compartments will likely depend on the variability of their water saturation. If the basin was used intermittently the bottom sediments may be oxic. If the bottom sediments were perpetually saturated, they may be anoxic. Though strong attenuation may occur at a basin bottom, surface soils, and the seepline, these are relatively small volume/thickness compartments at most waste sites. Typically, the organic-poor materials of the vadose and saturated zones are the largest compartment and ^{129}I can travel long distances in short times within this compartment because of relatively low attenuation by sorption. Hence, for a typical waste site like that in

At a waste configured like that in Figure 10 attenuation of ^{129}I may occur near the release point and near the exposure point, but for the travel path in between little attenuation would be expected. Of course, the mobility in all compartments depends on mineralogy, the chemistry of the plume, and hydrologic factors.

Variability of water saturation at the seepline may be seasonal, depending on the rise and fall of the water table. Thus, organic-rich soils at seeplines may alternately act as sinks for ^{129}I when they are oxic and sources of ^{129}I to pore water when they are anoxic. This suggests the possibility that seeplines may at times magnify the concentration of ^{129}I in pore water compared to the concentrations in upgradient groundwater. Figure 11 shows a generic scenario in which ^{129}I is migrating in groundwater to a stream. The water table is represented by the red dashed line. In the organic-rich soils of the stream floodplain there is a zone of oxic soils near the water table. The saturated portion of this zone receives ^{129}I from the advective flow of the contaminated groundwater. Unsaturated soils above the water table in this zone receive some ^{129}I from diffusion from the water table. The oxic organic-rich soils strongly bind the ^{129}I. When the water table (red dotted line) and stream level rise, a broad swath of the floodplain that was oxic becomes anoxic and formerly bound ^{129}I can be released to pore water. The pore water in this zone then contains the ^{129}I released from the soils plus that contained in the influxing groundwater. If the mass of ^{129}I released during the oxic to anoxic transition is large, the concentration in the groundwater discharging into the stream may be significantly higher than the concentration in upgradient groundwater. This may result in seasonal ^{129}I concentration variations at seeplines and within streams.
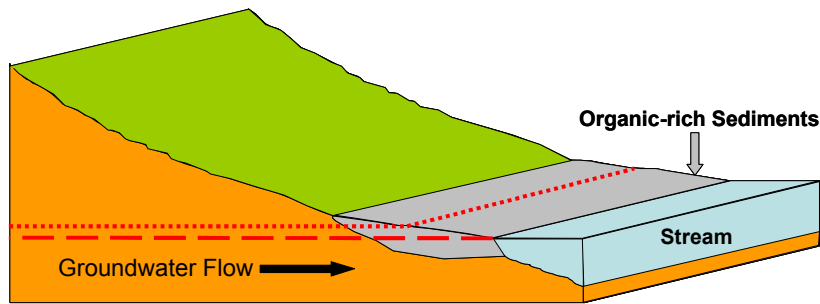
Figure 11: Generic diagram of contaminated groundwater flowing into a stream; red dashed line represents original water table, red dotted line represents elevated water table.

4.3.1. Summary

- Iodine behavior in the environment is complicated by its multiple physical states, multiple redox states, interactions with organic matter, and microbial transformations.

- Precipitation is not likely to be a natural attenuation mechanism for ^{129}I because iodide forms insoluble salts with only relatively scarce metal cations – Ag, Au, and Cu. Thus, adsorption and interaction with organic matter are the dominant attenuation mechanisms for ^{129}I in groundwater.

- In organic-bearing soils iodine sequestration is stronger under oxic conditions as compared to anoxic conditions.

- In organic-poor soils iodate is typically adsorbed more strongly than iodide and iodide adsorption is inversely related to pH.

- Microorganisms can catalyze I oxidation, reduction, accumulation, volatilization, and incorporation into organic matter. These biological processes are not well understood nor are their role in ^{129}I fate and transport, especially in the terrestrial environment (see Figure 12 for summary of known biological processes that interconvert I).

- Microbial-dependent enhancement of iodine transformation into high molecular weight organic matter has thus far only been observed under aerobic conditions and may be catalyzed by oxidases, perhydrolases, and/or peroxidases.

- The interplay between microorganisms and redox conditions will likely determine the mobility of dissolved ^{129}I in transition zones such as seeps, bogs, and basin bottoms where organic matter is present.
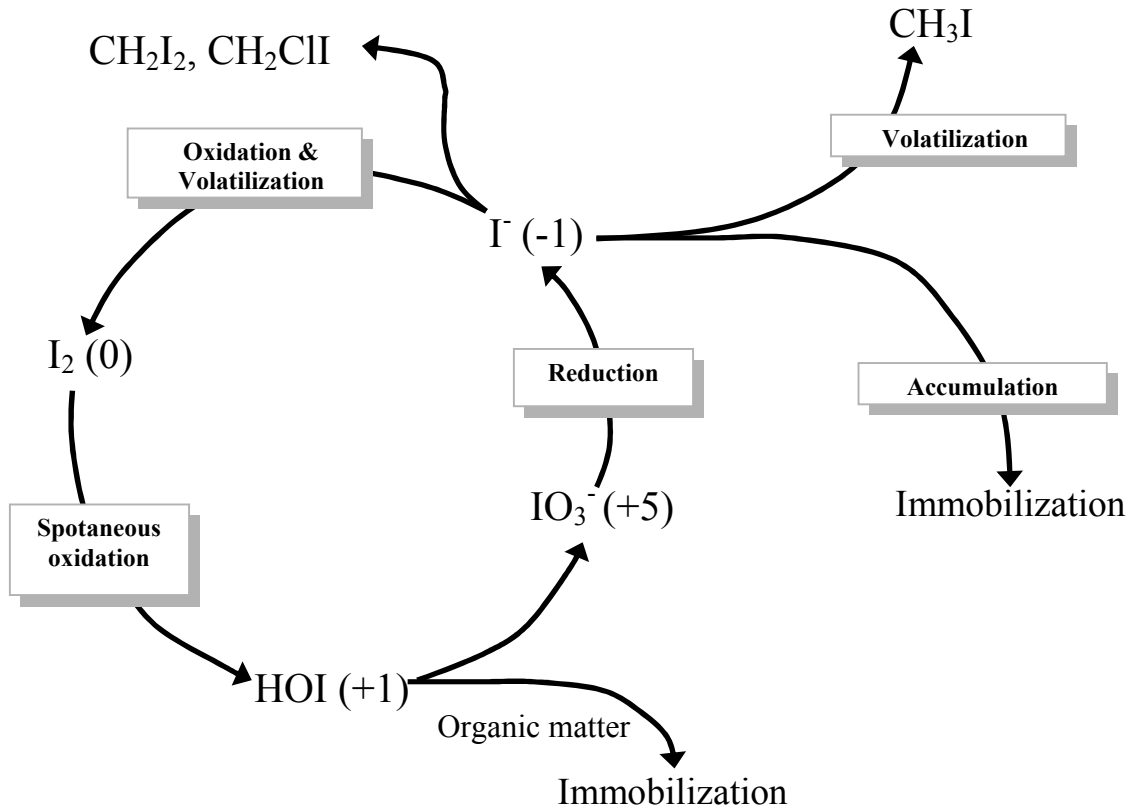
Figure 12: Biological transformations of iodine (Amachi et al. 2005).

5. ANALYTICAL DETECTION OF STABLE AND RADIOIODINE

5.1. RADIOLOGICAL METHODS

Careful measurements of ^{129}I concentrations are not easy to make by radiometric means because the nuclide emits only a low energy beta (maximum energy is 0.15 MeV) and gamma (0.035 MeV) rays. Gamma spectroscopy can non-destructively detect two of the most common radioisotopes, ^{129}I (39.6 keV) and ^{131}I (364 keV). However, they are generally characterized as low-energy gamma emitters, meaning they require a special arrangement for low-gamma energy detection. Due to the low counting efficiency of gamma detector (<2%), low γ-ray abundance (7.5%), and high background, a detection limit of 7 to 70 pCi has been obtained (Suarez et al. 1996). In addition, due to the low energy of X- γ-ray (29-40 keV) and normally big sample used (50 to 500 g), extensive self-absorption correction must be done to obtain accurate results.

A better counting efficiency of liquid scintillation counting for ^{129}I (60 to 95%) compared with γ-spectrometry (<5%) can be obtained because of the high beta energy of ^{129}I (154 (keV), though this depends on the quench level. However, a disadvantage of liquid scintillation counting is that the iodine must be separated from the sample matrix and other radionuclides. A detection limit of 4 pCi has been reported (Suarez et al. 1996). For liquid scintillation, it is also frequently necessary to include quenching curves to account for possible interferences that the sample matrix may have on counting.

Neutron activation analysis (NAA) is another radiometric method for the determination of ^{129}I. The method is based on neutron activation of ^{129}I to ^{130}I, a short-lived radionuclide, emitting high-energy γ-rays, 536 keV (99%), 668.5 keV (96%), and 739.5 keV (82%), which are easily and efficiently measured by γ-spectrometry. It is more sensitive than the other direct radiological analytical methods due to the high specific radioactivity of ^{130}I. However, there are some interfering nuclides, including those involving ^{235}U, ^{128}Te, and ^{133}Cs (Muramatsu et al. 1984). Because of the low concentrations of ^{129}I in most environmental samples, 10^{-8} to 10^{-2} ng/g, these interfering nuclides must be removed if they are present.

5.2. MASS SPECTROSCOPY METHODS

Mass spectrometric techniques, including accelerator mass spectrometry (AMS) and inductively coupled plasma mass spectrometry (ICP-MS), have been used for ^{129}I and ^{127}I determination. Prior to measurement by AMS, iodine needs to be separated from the sample and prepared as an AgI precipitate. AMS is extremely sensitive; for example a blank was reported to have a ^{129}I/^{127}I ratio of 1 x 10^{-13}, which corresponds to 4 x 10^{-19} Ci (or 10^{-9} Bq, 10^{-16} g or 10^5 atoms) of ^{129}I for 1 mg ^{127}I carrier, and the analytical uncertainty is lower than 10% for a ^{129}I/^{127}I ratio of 10^{-12} (Buraglio et al. 2000).

With ICP-MS, iodine separated from the samples is introduced to the instrument as solution or gaseous iodine (I_2). The iodine introduced to the plasma is decomposed into ions and the ions are separated by mass filters of either quadrupole type time-of-flight or combination of magnetic and electrostatic sector, and measured by ion detector. ICP-MS is much less sensitive than AMS, but requires less sample preparation. The use of ICP-MS for the detection of ^{129}I is low sensitivity (low ionization efficiency), because of isobaric and molecular ion interferences (^{129}Xe, $^{127}IH_2$, $^{89}Y^{40}Ar$, $^{115}In^{14}N$, $^{113}Cd^{16}O$), memory effects, low abundance sensitivity of ICP-MS (tailing from the ^{127}I peak, especially isobaric ^{129}Xe interference and tailing of ^{127}I (reviewed by Hou et al. 2009).

5.3. IODINE AQUEOUS-PHASE SPECIATION

Methods for speciation of ^{129}I in the environment should be the same as for stable iodine considering the natural sources and assuming isotopic equilibrium. There has been little research conducted regarding iodine speciation in terrestrial environments, especially under ambient conditions (Hou et al. 2009; Salbu 2007). This limitation hinders understanding of the fate and transport of iodine in the subsurface environment.

Ion chromatography has been used to distinguish I^-, IO_3^-, and organic-I (for example Kazuaki 1997) and is commonly used for the analysis of urine samples where total iodine concentrations are in the mg/L range. But this high range is unacceptable for most terrestrial environmental samples and all ^{129}I analyses. More recently, Schumann et al. (2005) introduced a promising ion chromatography technique for iodine speciation that separates I^- and IO_3^- during a 40-min elution time that has detection limits down to 20 µg L. The authors concluded that detailed quantitative determinations using calibrated iodine standards are still necessary for this technique.

Hou et al (2001) developed a chemical procedure for the separation of iodide and iodate from large seawater samples (up to 50 L). The method is based on different affinities of iodide, iodate, organo-iodine, and other anions to anion exchange columns. It involves several steps and ^{127}I and/or the ^{129}I is detected by ICP-MS or NAA. Because this technique concentrates the iodine, its detection limit is dependent on the sample size.

Schwehr and Santschi (2003) developed an aqueous iodine speciation technique that is rather straight forward and readily reproducible. Furthermore, they have conducted extensive testing of the technique (Schwehr and Santschi 2003; Schwehr et al. 2009). Iodide is determined directly by combining anion exchange chromatography and high performance liquid chromatography. Iodate and the total of organic iodine species are determined as iodide, with minimal sample preparation, compared to existing methods. Detection limit was ~1 nM (0.2 ppb) with less than 3% relative standard deviation for samples determined by standard additions to an iodide solution of 20 nM in 0.1 M NaCl. Again, because the technique concentrates the iodine on anion exchange resins, its detection limit is dependent on the sample size.

5.4. IODINE SOLID-PHASE SPECIATION

There have been two different approaches to speciating iodine associated to soils and sediments: direct spectroscopic methods and indirect extraction methods. The direct spectroscopic methods have been limited to the use of X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure spectra (EXAFS) (Shimamoto and Takahahi 2008; Fuhrmann et al. 1998; Kodama et al. 2006). These direct X-ray absorption spectroscopy techniques have not provided a great deal of information relevant to environmental samples because environmental samples tend to have iodine concentrations that are appreciably lower than this method's detection limits. The detection limit of XANES may be >10 µg/g ^{129}I (Hou et al. 2009). Consequently studies must be conducted at extremely high iodine concentrations, ppm to percent concentration levels. Shimamoto and Takahashi (2008) conducted XANES studies on soils amended with 55 µg/g I. They reported that most of the iodine in the soil was in an organic form. Fuhrmann et al. (1998) conducted XANES studies with mineral isolates and reported that pyrite reduced IO_3^- to I_2. This finding is very likely a result of using very high iodine concentrations and likely not a common process occurring in natural terrestrial environments for ^{129}I. They also observed that magnetite sorbed I^- from solution but not IO_3^- (this is contrary to popular belief that IO_3^- sorbs more strongly than I^- to mineral surfaces) and that biotite sorbed IO_3^- from solution, but not I^- from solution. XANES was also used by Kodama et al. (2006) to independently determine K_d values of iodate and iodide sorption onto a soil.

The second method of assessing the speciation of iodine on the solid phase is via sequential extraction or selective extraction. This technique involves adding extractants designed to remove iodine associated with a given phase (e.g., water soluble, carbonate, Fe-(oxy)hydroxide, organic matter, residual) or sorbed by a specific process (e.g., exchangeable). Sequential extractions have been carried out to investigate iodine speciation in sediments by Schmidtz and Autmann (1995), Hou et al. (2003), Stutz et al. (1999) and Yuita (1992). These are operationally defined parameters and as such do not carry mechanistic interpretations. In practice they suffer a number of pitfalls, although the application of sequential extractions to iodine is not nearly as problematic as it is with other ions that are more prone to complex, change oxidation, or precipitate, such as phosphate, or plutonium (Scheckel et al. 2003; Nirel and Morel 1989;Tessier and Campbell 1988). Hou et al. (2003) included a water solubile NH_4OAC exchange, carbonate (NH_4OAC (pH5), Fe-oxide (NH_2OH, HCl, pH2 80-100 °C), organic (NaOH 80-100 °C), and residue (remaining) fractionation scheme.

Not surprisingly, various extraction schemes were proposed and various solid phase fractions were found to sorb the most iodine. Schmitz and Aumann (1995) analyzed soils collected from a reprocessing plant in Germany and reported that 39 to 49% of the ^{129}I was associated with the water soluble fraction, where as only 4 to 15% was associated with the organic and 7 to 13% was associated with the residual fraction. However, a different distribution of stable iodine, ^{127}I was observed where only <4% occurred in the water soluble fraction. This difference between the two isotopes may be attributed to the different sources of the two isotopes and underscores an important point that the fate of iodine in the environment is controlled by more than just geochemical behavior. In the coastal and estuarine area of

Sellafield, most of the [129]I was associated with the oxides (53 to 66%) and organic (23-43%) fractions, whereas only <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).

5.5. SUMMARY

It is important that an analytical method for [129]I have the ability to measure [129]I at concentrations at or below the drinking water standard, which is 1 pCi/L. The γ-spectrometry and liquid scintillation counters are the least sensitive and have long counting times, but they are inexpensive and are quite accessible (Table 5). Direct γ-spectrometry measurement of a sample has a reported detection limit of 40 to 70 pCi, meaning it is not an especially good analytical technique for trying to detect 1 pCi/L [129]I. Detection limits improve by an order of magnitude if the [129]I is first preconcentrated as AgI and counted by γ-spectrometry or preconcentrated and counted by liquid scintillation counting (Table 5). The AgI/ γ-spectrometry method is routinely used in DOE regulatory laboratories to monitor [129]I plumes. Neutron activation analysis has the best detection limits of the methods in Table 5. ICP-MS can detect stable [129]I to 10 pCi/L. ICP-MS is sensitive enough to detect stable iodine at sub-ppb environmental levels. Only NAA and AMS are sensitive enough for direct analysis of environmental samples ($^{129}I/^{127}I$ ratio of $10^{-6} \sim 10^{-10}$). It should be kept in mind that the detection limit provided in Table 5 are examples of reported limits and vary between laboratories.

Table 5: Comparison of methods to measure [129]I (based on Hou et al. 2009).

Detection method	Sample preparation	Detection limit (pCi)	$^{129}I/^{127}I$	Reference
γ-spectrometry	Direct measurement	40-70 pCi	10^{-4} to 10^{-5}	Maro et al. 1999
γ-spectrometry	Separated iodine (AgI)	7 pCi	10^{-5} to 10^{-6}	Suarez et al. 1996
Liquid scintillation counting	Separated iodine	4 pCi	10^{-6} to 10^{-6}	Suarez et al. 1996
Neutron activation analysis	Separated MgI_2/I_2 absorbed on charcoal	4×10^{-4} pCi	10^{-10}	Hou et al. 1999
ICP-MS	Direct water measurement	10 pCi/L	10^{-5} to 10^{-6}	Brown et al. 2007

Perhaps the most exciting new developments are the emerging techniques that concentrate samples and provide us with information not only of the total concentration of iodine but also of its speciation (Hou et al. 2001; Schwehr and Santschi 2003). Through these techniques and hopefully ones less complicated, it may be possible to better understand the complex biogeochemical behavior of iodine in the subsurface environment.

6. POTENTIAL REMEDIATION STRATEGIES

6.1. ^{129}I REMEDIATION

Remediation of an indestructible inorganic contaminant in groundwater must exploit some chemical property of the contaminant to either remove it from groundwater or render it immobile. The chemistry of iodine makes both possible. The redox state of iodine is easily manipulated, in the iodide state it forms insoluble salts with some metals, and in the elemental state iodine is relatively volatile. ^{129}I in groundwater can be treated ex situ by pump-and-treat systems or in situ by emplacement of reactive amendments into a plume. Pump-and-treat systems can effectively remove ^{129}I from groundwater and concentrate it into a solid waste. However, disposal of the solid waste is a significant issue because the waste acceptance criteria for permitted waste disposal facilities are typically low for ^{129}I. Furthermore, ^{129}I rarely, if ever, occurs alone in a contaminant plume. Many of the contaminants usually associated with ^{129}I are not as amenable to treatment by pump-and-treat methods because they sorb more strongly to soils, subsurface sediments and rocks. Hence, in this document we focus on in situ treatments for ^{129}I.

A variety of materials have been shown to bind ^{129}I strongly, making them potential remediation reagents. Mattigod et al. (2003) published a comprehensive table of solid phases that have been tested as potential "getters" for ^{129}I. Getter is a term for a solid phase that strongly binds a target contaminant. In this case, Mattigod et al. (2003) were investigating getters that could be placed with stabilized waste in engineered subsurface disposal units to prevent release of ^{129}I to the environment. Their criteria for good getters for this purpose are from Viani (1999). Good getters:

- should have at least moderate adsorption/immobilization properties
- be stable for a long time in a post-closure environment
- should not adversely affect water chemistry
- should not be prohibitively expensive

Good in situ amendments to treat a contaminant should have all of these properties, as well as three important additional ones. A good in situ amendment:

- should be injectable into the target formation
- should be selective for the contaminant of interest
- should have a maximum volume of the reactive component, relative to inert materials

The reason for the first is obvious, though mobility can be a consideration. If injection of dissolved amendments displaces contaminated groundwater, then dissolved contaminants are only treated at the fringes of the injection. Sorbed contaminants may or may not be effectively treated before the dissolved amendment travels out of the treatment zone. The goal of injecting a particulate amendment is to have it be mobile enough to travel a short distance from the injection well, but not so mobile that it is never trapped by the formation.

The reason an in situ amendment must be relatively selective for the contaminant of interest is because the amendment can't be replaced infinitely with fresh or recycled amendment as is done in ex situ treatment systems. Thus, amendments that don't react with common ions in groundwater are effective for longer periods of time than those that do. Finally, the reason the reactive component volume must be maximized is that only a finite volume of particles can be injected into a treatment zone. Valuable pore space should be occupied by the minimum volume of inert material possible.

Most of the solid phases that have been tested for iodide immobilization are either clay minerals or phases containing copper, mercury, or silver. The clay minerals sorb ^{129}I by ion exchange, whereas phases containing copper, mercury, or silver immobilize ^{129}I by forming insoluble metal iodides.

The background concentration of stable natural iodine, ^{127}I, is of fundamental importance to in situ remediation of ^{129}I. ^{127}I interferes with ion exchange-based methods, competing with ^{129}I for exchange sites. This is important because in mass concentration units 1 pCi/L of ^{129}I is 0.006 µg/L and most groundwater contains near or greater than 1 µg/L ^{127}I. Thus, in most cases of ^{129}I contamination, ^{127}I concentrations are 1 to 2 orders of magnitude greater than ^{129}I concentrations.

For precipitation-based remediation methods, natural ^{127}I is a necessity. The goal of in situ precipitation methods for ^{129}I is to co-precipitate the anthropogenic ^{129}I with natural ^{127}I. The mass concentration of ^{129}I in contaminated groundwater is rarely high enough to force precipitation of ^{129}I directly. Thus, precipitation methods rely on the presence of 127I at much higher concentrations. The natural concentrations of ^{127}I in groundwater range from about 1 to 1300 µg/L (Fuge and Johnson, 1986), though the high end of this range occurs predominantly in mineral springs and subsurface brines. Groundwater at DOE sites is expected to have natural ^{127}I concentrations that are less than that of average seawater, 58 µg/L, reported by Fuge and Johnson (1986). For example, Table 6 shows maximum concentrations measured in groundwater at some DOE sites. Concentrations of ^{127}I >1 µg/L are high enough to allow precipitation with certain metal iodides. There is no isotopic fractionation between ^{127}I and ^{129}I during precipitation. Thus, if the natural ^{127}I concentration is reduced by 100 times during a precipitation treatment, the concentration of ^{129}I will be reduced by 100 times as well.

Table 6. Maximum natural ^{127}I concentrations reported at some DOE sites.

DOE Site	Natural ^{127}I (µg/L)	Reference
Savannah River	14	Millings et al. (2002)
Hanford	<5	Mattigod et al. (2003)
Idaho	16	Hall (2005)
Nevada Test Site	7	Kennealy et al. (1994)

The use of compounds consisting of or permeated by Hg, Cu, and Ag to remove ^{129}I from water follows the observation in nature of iodide minerals made up of these elements. The

use of these metals relies on their formation of insoluble salts with iodide. Cinnabar (HgS) is the primary reagent studied containing Hg (Sazarashi et al., 1994; Ikeda et al., 1994; Balsey et al., 1996; Kaplan et al., 2000; Mattigod et al., 2003). Manufactured materials containing mercury have also been studied for their ability to immobilize [129]I. These include zeolites (Chmielewská-Horváthová et al., 1995) and Hg-thiol Self-Assembled Monolayers and Mesoporous Silica [SAMMS] (Kaplan et al., 2000; Mattigod et al., 2003). Copper sulfides (Sazarashi et al., 1994; Balsey et al., 1996; Lefèvre et al., 2003; Mattigod et al., 2003), copper oxides (Haq et al., 1980; Lefèvre et al., 1999; Lefèvre et al., 2000), and copper metal (Haq et al., 1980) have all been tested for their ability to immobilize [129]I. The use of silver compounds to remove iodide from water has been standard practice in analytical chemistry for many decades (Murray and Avens, 1932). Silver, as silver nitrate, has also been used for decades to remove radioactive iodine vapors from offgas produced during nuclear processing (Kantelo et al., 1990). More recently, silver compounds have been tested as getters for [129]I in nuclear waste disposal and ex situ treatment of groundwater contaminated with [129]I. The forms of silver studied include activated charcoal impregnated with AgCl (Ho and Kraus, 1981; Karanfil et al., 2005), silver imbibed glass (Daniels and Srinivasan, 1982), silver substituted zeolites (Gradev, 1987; Chmielewská-Horváthová, E. and Lesný, J., 1995; Faghihian et al., 2002), activated carbon impregnated with metallic silver (Hoskins et al., 2002), Ag-thiol SAMMS (Kaplan et al., 2000; Mattigod et al., 2003), and silver oxide (Zhang et al., 2007). Currently a silver chloride amendment for in situ treatment of [129]I contamination is being developed and tested at the Savannah River National Laboratory.

Mercury, copper, and silver all have certain drawbacks when used in situ. The most obvious for mercury is that it is a highly regulated toxic metal. Even if it were demonstrated that the form of mercury used was not mobile, gaining regulatory and stakeholder acceptance for injecting it into the subsurface is unlikely. The effective forms of all of the metals are limited by their stability under various conditions.

Sazarashi et al. (1994) observed limited sorption of iodide on the clay minerals allophane, attapulgite, and montmorillonite, with allophane achieving the highest K_d value of 3.6 ml/g. Kaplan et al. (2000) measured higher sorption of iodide on illite with K_d values as high as 46 ml/g. Some clays can be altered to enhance their sorptive properties. For example, the ability of expandable clays to sorb iodide improves by several orders of magnitude when the inter-layer cations are replaced with organic quaternary alkylammonium ions (Bors, 1990; Bors, 1992; Bors et al., 1994; Bors et al., 1998). The sorption of iodide on these types of clays is reversible and appears to be the result of ion exchange (Bors et al., 1998). A primary concern with the in situ use of any organic material, including organo-clays, is their resistance to microbial degradation, and hence the longevity of their effectiveness in the subsurface.
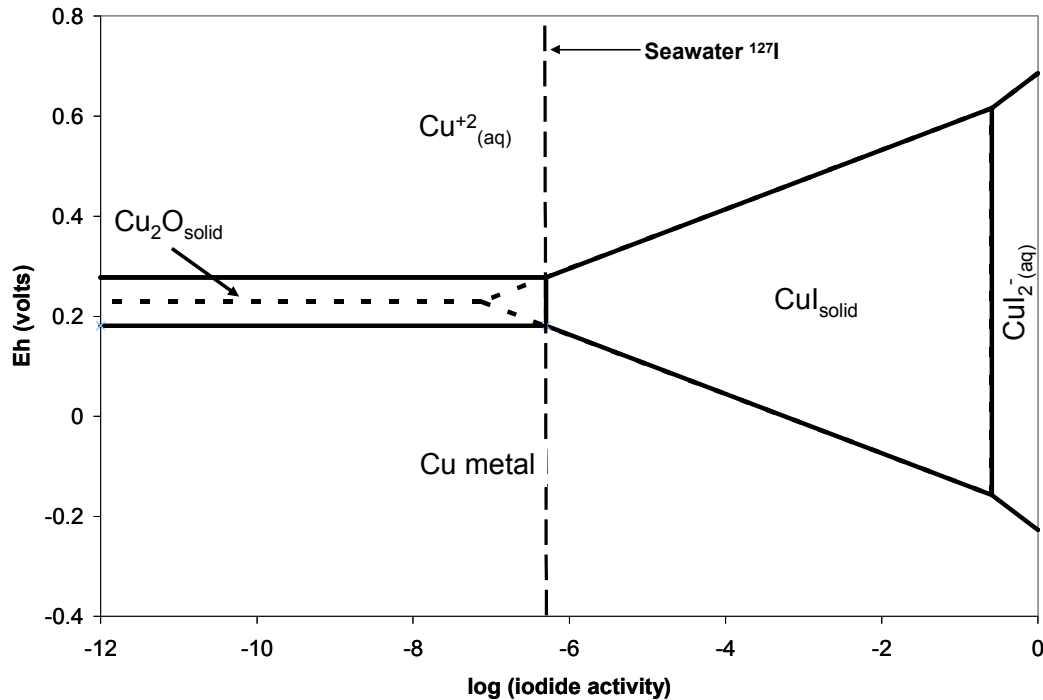
Figure 13. Eh (volts) vs. log of the iodide activity at [Cu]=13 mg/L, [Cl]=10 mg/L showing the stability field of CuI; solid line pH=5, dotted line pH=3; dashed vertical line shows the average ^{127}I concentration in seawater (Fuge and Johnson, 1986).

One way to assess use of Hg, Cu, and Ag as in situ reagents for ^{129}I immobilization is to consider the stability of the metal iodides at metal concentrations near their respective drinking water standards. A metal compound of solubility significantly higher than the drinking water standard for the metal is unlikely to gain widespread approval as an in situ amendment. In the following analysis it is assumed that the metal is present at 10 times the concentration of its drinking water standard and chloride, a common complexing ion for these metals, is present at 10 mg/L. For mercury the drinking water standard is 20 μg/L which is too low to cause precipitation of HgI. Hence, its toxicity aside, Hg is not an effective metal for immobilizing ^{129}I in situ. Copper does form an insoluble iodide under these conditions that will constrain the dissolved iodide concentration to 10 μg/L, but only at pH≤3 (Figure 13). At pH>3 Cu$_2$O becomes stable and as pH increases the iodide concentration in equilibrium with CuI increases. Furthermore, at low iodide concentrations CuI is only stable at more reducing conditions than are present in many water table aquifers. AgI is stable over a much wider range of iodide concentrations and redox conditions (Figure 14). Compounds containing silver are not good candidates for ^{129}I remediation if aquifer conditions are moderately reducing (Eh<0.3 volts), because AgI is not stable. Likewise, silver compounds are much less effective at removing ^{129}I from groundwater if chloride concentrations are high. This is because, at 25ºC, AgCl becomes more stable than AgI below a [I$^-$]/[Cl$^-$] molar ratio of approximately 4.5x10^{-7}. Hence, at [Cl$^-$]=1000 mg/L and [I$^-$] = 0.001 mg/L, AgCl is the stable solid phase rather than AgI.
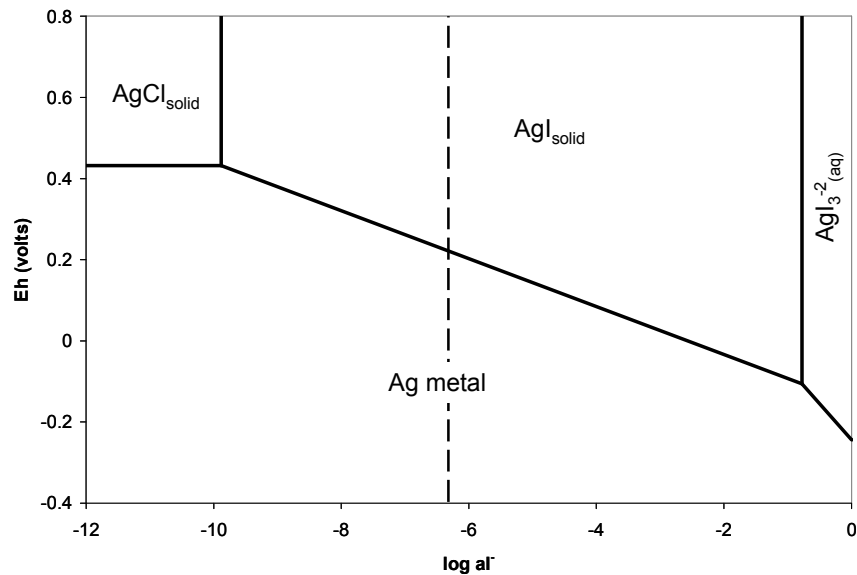
Figure 14. Eh (volts) vs. log of the iodide activity at [Ag]=1mg/L, [Cl]=10 mg/L; dashed line shows the average [127]I concentration in seawater (Fuge and Johnson, 1986).

Another property of iodine that can potentially be exploited for [129]I remediation is the volatility of elemental iodine (I_2). Conditions must be acidic and somewhat oxidizing for dissolved I_2 to be the dominant species of iodine. Hence, in acidic plumes in which iodide is the dominant iodine species, it may be possible to oxidize the iodide to dissolved I_2. With a Henry's Law constant of 3 moles/L-atm (Parsley, 1970; Sander, 1999), the I_2 should be easily transferred from the dissolved phase to the vapor phase by air sparging. Denham (2002) suggested this as a possible remedy for [129]I contamination in an acidic water table plume at the Savannah River Site. Subsequent preliminary laboratory experiments showed that sparging dissolved iodide-bearing water with an ozone-air mixture successfully removed iodine from the system (Denham and Looney, 2007). Exploiting the volatility of I_2 by oxidation of iodide while air sparging has the advantage of removing [129]I from the subsurface system, eliminating concerns over future mobility.

6.2. SUMMARY

- Any amendment to be used in situ for [129]I remediation should have the characteristics listed by Viani (1993) and reiterated by Mattigod (2003) and in addition should be injectable into the subsurface, selective for iodine in its dominant species, and have the maximum volume of reactant possible.

- Most promising "getters" involve reaction with Ag, Hg, or Cu. Ag has the characteristic to be the best in oxidizing conditions.

- In acidic plumes, it may be possible to oxidize iodide to elemental iodine and remove it completely from the system by air sparging.

7. TECHNICAL TARGET NEEDS

^{129}I has not received the same attention in basic and applied research that other contaminants associated with DOE plumes have. Other contaminants, such as uranium, plutonium, ^{90}Sr, and ^{99}Tc occur at more DOE facilities. Yet, at the Hanford Site and the Savannah River Site ^{129}I occurs in groundwater at concentrations significantly above the primary drinking water standard and there is no accepted method for treating it, other than pump-and-treat systems. Furthermore, ^{129}I is likely to continue to be a major risk driver for nuclear disposal facilities and decontamination and decommissioning (D&D) sites. Given these concerns and the inevitable increase in ^{129}I inventory resulting from nuclear electrical power generation in the United States and world-wide, more rigorous research into ^{129}I behavior in the environment and its remediation is warranted. Gaps in the knowledge of ^{129}I behavior and remediation are seen throughout this review of the state of science regarding ^{129}I. Listed below are lines of scientific inquiry that would significantly advance the goals of basic and applied research programs for accelerating ^{129}I environmental remediation and reducing uncertainty associated with disposal of ^{129}I waste.

7.1. APPLIED SCIENCE

- Evaluation of amendments or other treatment systems that can be applied in the subsurface to sequester ^{129}I from groundwater. They must be effective, cost effective, and acceptable to regulators. Because of the long half life of ^{129}I, 16 million years, a major requirement for the amendment to be considered effective is its longevity. Amendments that break down or release the sequestered ^{129}I in response to expected changes in geochemical parameters, such as seasonal redox changes, are not useful. In addition, an amendment must be compatible with remediation strategies for other contaminants. For example, silver-based amendments may not be compatible with bioreduction of other contaminants because silver is a biocide and the reducing conditions would convert Ag(I) to elemental silver. Ideally, a suite of amendments could be developed that would cover the situations and geochemical conditions pertinent to the existing ^{129}I plumes and potential future plumes. The amendments in this suite would also be potentially useful in nuclear waste disposal facilities as an ^{129}I sequestering agent.

- Field sampling methods that eliminate the necessity of collecting and shipping large samples of groundwater. Currently large samples of groundwater must be collected and processed in a laboratory to obtain enough ^{129}I to achieve detection limits near the drinking water standard, 1 pCi/L, by the most widely available radiochemical techniques, gamma spectrometry and liquid-scintillation counting. This represents a significant expense in monitoring for ^{129}I. Flow-through collectors of ^{129}I could be developed that would be easy to use in the field and eliminate much of the laboratory sample preparation. Such devices configured to hang in wells would be useful for long-term monitoring for ^{129}I.

- Develop and evaluate ways to manipulate areas with organic-rich soil to maximize ^{129}I sorption. The maximum sorption of ^{129}I is achieved in soils with elevated concentrations of organic matter, such as wetlands. In general, sorption is greater in these soils if they are oxic rather than anoxic. Thus, measures that minimize fluctuations between redox states of wetland soils or otherwise promote stronger sorption to the soils may minimize periodic releases of sorbed ^{129}I.

7.2. BASIC SCIENCE

- Develop analytical techniques that can identify the various ^{129}I species in the subsurface aqueous and solid phases at ambient concentrations and under ambient conditions. ^{129}I speciation in environmental samples has been shown to be concentration dependent (Schwehr et al. 2009) and the concentrations of interest are typically very low (5 μg/L background ^{127}I and 1 μg/L ^{129}I (0.006 μg/L ^{129}I)) and close to the detection limits of instruments that are readily available to most scientist, such as IC, gamma spectrometers and liquid scintillation counters. Development of analytical techniques for aqueous and solid phase speciation will lead to a better understanding of iodine biogeochemical behavior in the terrestrial environment. Presently, we have a reasonable understanding of where iodine is and how fast it moves from one place to another. Yet, its transitions between iodide, iodate, elemental iodine, and organic forms are poorly understood, in part, because analytical techniques that differentiate these species are difficult and not widely available. Perhaps most importantly, this information is often important to predicting ^{129}I behavior in changing geochemical conditions.

- Understand the nature of ^{129}I-organic interactions. Numerous studies have demonstrated the important role that natural organic matter plays in concentrating ^{129}I, yet the mechanisms and controlling factors by which this is accomplished are poorly understood. It is not clear what role microbes, redox processes, or the composition of the organic matter play. The ^{129}I-organic interaction is the only process that significantly attenuates ^{129}I in most systems. Further complicating matters, small organic moieties have been shown to complex contaminants and enhance, not attenuate, ^{129}I mobility. A thorough understanding of the processes controlling ^{129}I attenuation by natural organic matter may lead to a means of extending it to areas other than wetlands.

- Understand the biological processes that transform iodine species throughout different compartments of subsurface waste sites and the role that these processes have on ^{129}I flux. In particular, the extent that microorganisms influence ^{129}I volatilization and/or incorporation into organic matter is poorly understood in terrestrial environments. These processes likely play critical roles in ^{129}I fluxes from subsurface aquifers to the surface environment, where bioconcentration mechanisms could impact human health.

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