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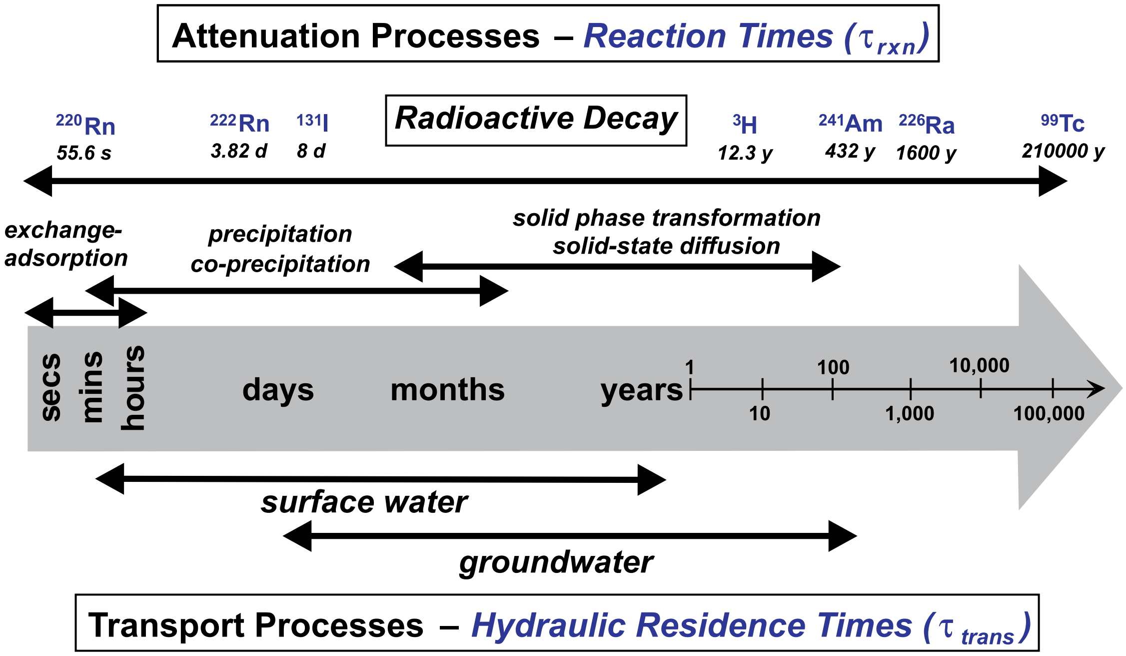
Monitored Natural Attenuation of Inorganic Contaminants in Ground Water

Volume 3

Assessment for Radionuclides Including Tritium, Radon, Strontium, Technetium, Uranium, Iodine, Radium, Thorium, Cesium, and Plutonium-Americium



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Notice

The U.S. Environmental Protection Agency through its Office of Research and Development managed portions of the technical work described here under EPA Contract No. 68-C-02-092 to Dynamac Corporation, Ada, Oklahoma (David Burden, Project Officer) through funds provided by the U.S. Environmental Protection Agency's Office of Air and Radiation and Office of Solid Waste and Emergency Response. It has been subjected to the Agency's peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

All research projects making conclusions or recommendations based on environmental data and funded by the U.S. Environmental Protection Agency are required to participate in the Agency Quality Assurance Program. This project did not involve the collection or use of environmental data and, as such, did not require a Quality Assurance Plan.

Foreword

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threatens human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients. Understanding site characterization to support the use of monitored natural attenuation (MNA) for remediating inorganic contaminants in ground water is a major priority of research and technology transfer for the U.S. Environmental Protection Agency's Office of Research and Development and the National Risk Management Research Laboratory. This document provides technical recommendations regarding the development of conceptual site models and site characterization approaches useful for evaluating the effectiveness of the natural attenuation component of ground-water remedial actions. This document addresses natural attenuation processes and data requirements specific to selected radionuclides.

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Executive Summary

The term "monitored natural attenuation," as used in this document and in the Office of Solid Waste and Emergency Response (OSWER) Directive 9200.4-17P, refers to "the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods." When properly employed, monitored natural attenuation (MNA) may provide an effective knowledge-based remedy where a thorough engineering analysis informs the understanding, monitoring, predicting, and documenting of the natural processes. In order to properly employ this remedy, the Environmental Protection Agency needs a strong scientific basis supported by appropriate research and site-specific monitoring implemented in accordance with the Agency's Quality System. The purpose of this series of documents, collectively titled "Monitored Natural Attenuation of Inorganic Contaminants in Ground Water," is to provide a technical resource for remedial site managers to define and assess the potential for use of site-specific natural processes to play a role in the design of an overall remedial approach to achieve cleanup objectives.

The current document represents the third volume of a set of three volumes that address the technical basis and requirements for assessing the potential applicability of MNA as part of a ground-water remedy for plumes with non-radionuclide and/or radionuclide inorganic contaminants. Volume 3, titled "Assessment for Radionuclides Including Tritium, Radon, Strontium, Technetium, Uranium, Iodine, Radium, Thorium, Cesium, and Plutonium-Americium," consists of individual chapters that describe 1) the natural processes that may result in the attenuation of the listed contaminants and 2) data requirements to be met during site characterization. Emphasis is placed on characterization of immobilization and/or radioactive decay processes that may control contaminant attenuation, as well as technical approaches to assess performance characteristics of the MNA remedy. A tiered analysis approach is presented to assist in organizing site characterization tasks in a manner designed to reduce uncertainty in remedy selection while distributing costs to address four primary issues:

1. Demonstration of dissolved plume stability via radioactive decay and/or active contaminant removal from ground water;
2. Determination of the rate and mechanism of attenuation by immobilization;
3. Determination of the long-term capacity for attenuation and stability of immobilized contaminants; and
4. Design of performance monitoring program, including defining triggers for assessing MNA failure, and establishing a contingency plan.

Where feasible, Agency-approved analytical protocols currently implemented for waste site characterization are identified, along with modifications that may be warranted to help insure the quality of site-specific data. In situations where Agency methods or protocols are unavailable, recommendations are made based on review of the existing technical literature. It is anticipated that future updates to these recommendations may be warranted with increased experience in the successful application of MNA as part of a ground-water remedy and the development of new analytical protocols.

This document is limited to evaluations performed in porous-media settings. Detailed discussion of performance monitoring system design in fractured rock, karst, and other such highly heterogeneous settings is beyond the scope of this document. Ground water and contaminants often move preferentially through discrete pathways (e.g., solution channels, fractures, and joints) in these settings. Existing techniques may be incapable of fully delineating the pathways along which contaminated ground water migrates. This greatly increases the uncertainty and costs of assessments of contaminant migration and fate and is another area of continuing research. As noted in OSWER Directive 9200.4-17P, "MNA will not generally be appropriate where site complexities preclude adequate monitoring." The directive provides additional discussion regarding the types of sites where the use of MNA may be appropriate. This document focuses on monitoring the saturated zone, but site characterization and monitoring for MNA or any other remedy typically would include monitoring of all significant pathways by which contaminants may move from source areas and contaminant plumes to impact receptors (e.g., surface water and indoor air).

Nothing in this document changes Agency policy regarding remedial selection criteria, remedial expectations, or the selection and implementation of MNA. This document does not supercede any guidance. It is intended for use as a technical reference in conjunction with other documents, including OSWER Directive 9200.4-17P, "Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites" (*http://www.epa.gov/swerust1/directiv/d9200417.pdf*).

Conceptual Background for Radionuclides

1.1 Background and Purpose

1.1.1 Document Organization

The purpose of this document is to provide a framework for assessing the potential application of monitored natural attenuation (MNA) as part of the remedy for inorganic contaminant plumes in ground water. It is organized as part of three volumes that provide: Volume 1 - a general overview of the framework and technical requirements for application of MNA to inorganic contaminant plumes (USEPA, 2007a); Volume 2 - contaminant-specific discussions addressing potential attenuation processes and site characterization requirements for non-radionuclides (USEPA, 2007b), and Volume 3 - contaminant-specific discussions addressing potential attenuation processes and site characterization requirements for radionuclides. Volume 1 is divided into three sections that address the regulatory and conceptual background for natural attenuation, the technical basis for natural attenuation of inorganic contaminants, and site characterization approaches to support assessment and application of MNA. The contaminant-specific chapters in Volumes 2 and 3 provide an overview of contaminant geochemistry, applicable natural attenuation processes, and specific site characterization requirements. Criteria for selecting specific contaminants for detailed overviews in this volume are described below.

The radionuclide contaminants selected for this document include: americium, cesium, iodine, plutonium, radium, radon, technetium, thorium, tritium, strontium, and uranium. The selection of these contaminants was based on two criteria. First, a selected element had to be one of high priority to the site remediation or risk assessment activities of the USEPA (USEPA, 1993a; USEPA, 2002a; USEPA, 2006a; USEPA, 2007c). Second, selection was based on chemical behavior considering chemical traits such as: toxicity, cations, anions, conservatively transported, non-conservatively transported, and redox sensitive elements (USEPA, 1999b; USEPA, 2004a). Using these characteristics of the contaminants, the general geochemical behavior of a wide range of radionuclide contaminants could be covered as well as the chemical classes that make up the Periodic Table. In addition, this selection accounts for many daughter and fission product contaminants that result from radioactive decay. This is important as the decay of radioisotopes can produce daughter products that may differ both physically and chemically from their parents. The selection of radionuclide contaminants for this document is representative of these characteristics.

1.1.2 Purpose of Document

This document is intended to provide a technical resource for determining whether MNA is likely to be an effective remedial approach for inorganic contaminants[1] in ground water. This document is intended to be used during the remedial investigation and feasibility study phases of a Superfund cleanup, or during the equivalent phases of a RCRA Corrective Action (facility investigation and corrective measures study, respectively). The decision to select MNA as the remedy (or part of the remedy) will be made in a Superfund Record of Decision (ROD) or a RCRA Statement of Basis (or RCRA permit).

The USEPA expects that users of this document will include USEPA and State cleanup programs and their contractors, especially those individuals responsible for evaluating alternative cleanup methods for a given site or facility. The overall policy for use of MNA in OSWER cleanup programs is described in the April 21, 1999 OSWER Directive titled, “Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action and Underground Storage Tank Sites” (Directive No. 9200.4-17P).

Both radiological and non-radiological inorganic contaminants are discussed in this document. There are two reasons for this. First, except for radioactive decay, the potential attenuation processes affecting inorganic contaminants are the same for both contaminant types. Second, several OSWER directives clarify the USEPA’s expectation that the decision-making approach and cleanup requirements used at CERCLA sites will be the same for sites with radiological and non-radiological inorganic contaminants, except where necessary to account for the technical differences between the two types of contaminants. Also, the 1999 OSWER Directive specified that the decision process for evaluating MNA as a potential remediation method should be the same for all OSWER cleanup programs.

This document is intended to provide an approach for evaluating MNA as a possible cleanup method for contaminated ground water. Although the focus of the document is on ground water, the unsaturated zone is discussed as a source of contaminants to ground water. Emphasis is placed on developing a more complete evaluation of the site through development of a conceptual site model[2] based on an understanding of the attenuation mechanisms, the geochemical conditions governing these mechanisms, the

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[1] *The term “inorganic contaminants” is used in this document as a generic term for metals and metalloids (such as arsenic); and also refers to radiologic as well as non-radiologic isotopes.*

[2] *A conceptual site model is a three-dimensional representation that conveys what is known or suspected about contamination sources, release mechanisms, and the transport and fate of those contaminants. The conceptual model provides the basis for assessing potential remedial technologies at the site. “Conceptual site model” is* ***not*** *synonymous with “computer model”; however, a computer model may be helpful for understanding and visualizing current site conditions or for predictive simulations of potential future conditions.*

capacity of the aquifer to sustain attenuation of the contaminant mass and prevent future contaminant migration, and indicators that can be used to monitor MNA performance.

This document focuses on technical issues and is not intended to address policy considerations or specific regulatory or statutory requirements. The USEPA expects that this document will be used in conjunction with the 1999 OSWER Directive (USEPA, 1999c). Users of this document should realize that different Federal and State remedial programs may have somewhat different remedial objectives. For example, the CERCLA and RCRA Corrective Action programs generally require that remedial actions: 1) prevent exposure to contaminated ground water, above acceptable risk levels; 2) minimize further migration of the plume; 3) minimize further migration of contaminants from source materials; and 4) restore ground-water conditions to cleanup levels appropriate for current or future beneficial uses, to the extent practicable. Achieving such objectives could often require that MNA be used in conjunction with other "active" remedial methods. For other cleanup programs, remedial objectives may be focused on preventing exposures above acceptable levels. Therefore, it is imperative that users of this document be aware of and understand the Federal and State statutory and regulatory requirements, as well as policy considerations that apply to a specific site for which this document will be used to evaluate MNA as a remedial option. As a general practice, individuals responsible for evaluating remedial alternatives should check with the overseeing regulatory agency to identify likely characterization and cleanup objectives for a particular site prior to investing significant resources.

Use of this document is generally inappropriate in complex fractured bedrock or karst aquifers. In these situations the direction of ground water flow cannot be predicted directly from the hydraulic gradient, and existing techniques may not be capable of identifying the pathway along which contaminated ground water moves through the subsurface. Understanding the contaminant flow field in the subsurface is essential for a technically justified evaluation of an MNA remedial option. MNA will not generally be appropriate where site complexities preclude adequate monitoring (USEPA, 1999c).

Because documentation of natural attenuation requires detailed site characterization, the data collected can be used to compare the relative effectiveness of other remedial options and natural attenuation. The technical information contained in this document can be used as a point of reference to evaluate whether MNA by itself, or in conjunction with other remedial technologies, is sufficient to achieve site-specific remedial objectives.

1.1.3 Policy Framework for Use of MNA

The term monitored natural attenuation (MNA) is used in this document when referring to a method of remediation. MNA is defined in the 1999 OSWER Directive as follows:

> ***"...the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods. The 'natural attenuation processes' that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These in-situ processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants. (USEPA, 1999c, page 3.)***

Even though several physical, chemical, and biological processes are included in the above definition, the1999 OSWER Directive goes on to state a preference for those processes that permanently degrade or destroy contaminants, and for use of MNA for stable or shrinking plumes, as noted below:

> ***"When relying on natural attenuation processes for site remediation, EPA prefers those processes that degrade or destroy contaminants. Also, EPA generally expects that MNA will only be appropriate for sites that have a low potential for contaminant migration." (USEPA, 1999c, page 3.)***
>
> ***"MNA should not be used where such an approach would result in either plume migration or impacts to environmental resources that would be unacceptable to the overseeing regulatory authority.*** **Therefore, sites where the contaminant plumes are no longer increasing in extent, or are shrinking, would be the most appropriate candidates for MNA remedies."** ***(USEPA, 1999c, page 18.)***

Control of contaminant sources is also an important aspect of EPA's policy. The actual policy language is given below:

> ***"Control of source materials is the most effective means of ensuring the timely attainment of remediation objectives.*** **EPA, therefore, expects that source control measures will be evaluated for all contaminated sites and that source control measures will be taken at most sites where practicable.** ***At many sites it will be appropriate to implement source control measures during the initial stages of site remediation ("phased remedial approach"), while collecting additional data to determine the most appropriate groundwater remedy." (USEPA, 1999c, page 22.)***

The 1999 OSWER Directive also provides a few general guidelines for use of MNA as a remedial approach for inorganic contaminants. The key policy concerns are that the specific mechanisms responsible for attenuation of inorganic contaminants should be known at a particular site, and the stability of the process should be evaluated and shown to be irreversible. The actual policy language is given below:

> ***MNA may, under certain conditions (e.g., through sorption or oxidation-reduction reactions), effectively reduce the dissolved concentrations and/or toxic forms of inorganic contaminants in groundwater and soil. Both metals and non-metals (including radionuclides) may be attenuated by sorption[3] reactions such as precipitation, adsorption on the surfaces of soil minerals, absorption into the matrix of soil minerals, or partitioning into organic matter. Oxidation-reduction (redox) reactions can transform the valence states of some inorganic contaminants to less soluble and thus less mobile forms (e.g., hexavalent uranium to tetravalent uranium) and/or to less toxic forms (e.g., hexavalent chromium to trivalent chromium). Sorption and redox reactions are the dominant mechanisms responsible for the reduction of mobility, toxicity, or bioavailability of inorganic contaminants. It is necessary to know what specific mechanism (type of sorption or redox reaction) is responsible for the attenuation of inorganics so that the stability of the mechanism can be evaluated. For example, precipitation reactions and absorption into a soil's solid structure (e.g., cesium into specific clay minerals) are generally stable, whereas surface adsorption (e.g., uranium on iron-oxide minerals) and organic partitioning (complexation reactions) are more reversible. Complexation of metals or radionuclides with carrier (chelating) agents (e.g., trivalent chromium with EDTA) may increase their concentrations in water and thus enhance their mobility. Changes in a contaminant's concentration, pH, redox potential, and chemical speciation may reduce a contaminant's stability at a site and release it into the environment. Determining the existence, and demonstrating the irreversibility, of these mechanisms is important to show that a MNA remedy is sufficiently protective.***
>
> ***In addition to sorption and redox reactions, radionuclides exhibit radioactive decay and, for some, a parent-daughter radioactive decay series. For example, the dominant attenuating mechanism of tritium (a radioactive isotopic form of hydrogen with a short half-life) is radioactive decay rather than sorption. Although tritium does not generate radioactive daughter products, those generated by some radionuclides (e.g., Am-241 and Np-237 from Pu-241) may be more toxic, have longer half-lives, and/or be more mobile than the parent in the decay series. Also, it is important that the near surface or surface soil pathways be carefully evaluated and eliminated as potential sources of external direct radiation exposure.[4]***
>
> ***Inorganic contaminants persist in the subsurface because, except for radioactive decay, they are not degraded by the other natural attenuation processes. Often, however, they may exist in forms that have low mobility, toxicity, or bioavailability such that they pose a relatively low level of risk. Therefore, natural attenuation of inorganic contaminants is most applicable to sites where immobilization or radioactive decay is demonstrated to be in effect and the process/mechanism is irreversible. (USEPA, 1999c, pages 8-9.)***

1.1.4 Applicable Regulatory Criteria

All remedial actions at CERCLA sites must be protective of human health and the environment and comply with applicable or relevant and appropriate requirements (ARARs) unless a waiver is justified. Cleanup levels for response actions under CERCLA are developed based on site-specific risk assessments, ARARs, and/or to-be-considered material (TBCs). The determination of whether a requirement is applicable, or relevant and appropriate, must be made on a site-specific basis (see 40 CFR §300.400(g)).

> ***"EPA expects to return usable ground waters to their beneficial uses whenever practicable" (see 40 CFR §300.430(a)(1)(iii)(F)). In general, drinking water standards provide relevant and appropriate cleanup levels for ground waters that are a current or potential source of drinking water. However, drinking water standards generally are not relevant and appropriate for ground waters that are not a current or potential source of drinking water (see 55 FR 8732, March 8, 1990). Drinking water standards include federal maximum contaminant levels (MCLs) and/or non-zero maximum contaminant level goals (MCLGs) established under the Safe Drinking Water Act (SDWA), or more stringent state drinking water standards. Other regulations may also be ARARs as provided in CERCLA §121(d)(2)(B).***

1.1.4.1 Radionuclide Standards

Current MCLs for radionuclides are set at 4 mrem/yr for the sum of the doses from beta particles and photon emitters, 15 pCi/L for gross alpha particle activity (including ^{226}Ra, but excluding uranium and radon), and 5 pCi/L combined for ^{226}Ra and ^{228}Ra. The current MCLs for beta emitters specify that MCLs are to be calculated based upon an

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[3] When a contaminant is associated with a solid phase, it is usually not known if the contaminant is precipitated as a three-dimensional molecular coating on the surface of the solid, adsorbed onto the surface of the solid, absorbed into the structure of the solid, or partitioned into organic matter. "Sorption" will be used in this Directive to describe, in a generic sense (i.e., without regard to the precise mechanism) the partitioning of aqueous phase constituents to a solid phase.

[4] External direct radiation exposure refers to the penetrating radiation (i.e., primarily gamma radiation and x-rays) that may be an important exposure pathway for certain radionuclides in near surface soils. Unlike chemicals, radionuclides can have deleterious effects on humans without being taken into or brought in contact with the body due to high-energy particles emitted from near surface soils. Even though the radionuclides that emit penetrating radiation may be immobilized due to sorption or redox reactions, the resulting contaminated near surface soil may not be a candidate for a MNA remedy as a result of this exposure risk.

annual dose equivalent of 4 mrem to the total body or any internal organ. It is further specified that the calculation is to be performed on the basis of a 2 liter per day drinking water intake using the 168 hours data listed in *"Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air or Water for Occupational Exposure,"* NBS Handbook 69 as amended August 1963, U.S. Department of Commerce (U.S. DOC, 1963). These calculations have been done for most beta emitters and published as part of the EPA guidance *"Use of Uranium Drinking Water Standards under 40 CFR 141 and 40 CFR 192 as Remediation Goals for Groundwater at CERCLA sites"* (OSWER No. 9283.1-14, November 6, 2001). This guidance also includes a list of radionuclides addressed by the gross alpha MCL. The MCL for uranium is 30 micrograms per liter (μg/L). Two isotopes of uranium are also addressed by ground-water standards under the Uranium Mill Tailings Radiation Control Act (UMTRCA). The concentration limit for the combined level of ^{234}U and ^{238}U is 30 pCi/L. Relevant standards for some of the radionuclides discussed in this document are shown in Table 1.1.

Table 1.1 Examples of mass concentration equivalents to activity-based standards for select radionuclides in ground water. Drinking water MCLs apply to total element concentration rather than specific radioactive isotopes except where indicated. Fact Sheets with summary information on the radionuclides in this list are available at http://www.epa.gov/superfund/health/contaminants/radiation/nuclides.htm.

Radionuclide Contaminant		Current MCL[a] or UMTRCA (pCi/L)	Mass Equiv to MCL, UMTRCA, or RBL (μg/L)
Americium	^{241}Am	15	0.0000044
Cesium	^{137}Cs	200	0.0000023
Tritium	^{3}H	20,000	0.0000021
Iodine	^{129}I	1	0.0057
Plutonium	^{238}Pu	15	0.00000088
	^{239}Pu	15	0.00024
	^{240}Pu	15	0.000066
	^{241}Pu	(27 RBL)[b]	0.00000026
	^{242}Pu	15	0.0038
	^{244}Pu	15	0.85
Radium	^{226}Ra	5[c]	0.0000051
	^{228}Ra	5[c]	0.000000018
Strontium	^{90}Sr	8	0.000000059
Technetium	^{99}Tc	900	0.053
Thorium	^{228}Th	15	0.000000018
	^{229}Th	15	0.000071
	^{230}Th	15	0.00074
	^{232}Th	15	140
Uranium	^{234}U	30[d]	30[d]
	^{238}U	30[d]	30[d]

[a] *Federal Register, Vol. 65, No. 236, December 2, 2000; MCL is 4 mrem/yr to the whole body or an organ, combined from all beta and photon emitters; MCL is 15 pCi/L, with the concentration level combined for all alpha emitters, except radon and uranium.*

[b] *Risk Based Limits calculated for 30-year exposure duration and 1 x 10^{-6} risk. These were calculated using equation 11 in Risk Assessment Guidance for Superfund (RAGS): Volume I: Human Health Evaluation Manual (Part B, Development of Risk-based Preliminary Remediation Goals), (page 37). The equations were adjusted to account for radioactive decay.*

[c] *MCL is 5 pCi/L combined for Ra-226 and Ra-228*

[d] *Federal Register, Vol. 42, No. 65, March 2, 2000, Rules and Regulations; MCL standard is 30 μg/L for uranium; UMTRCA ground-water standard is 30 pCi/Lcombined for U-234 and U-238.*

1.1.4.2 Use of Radionuclide Mass in Remediation

Typically units of decay rate instead of mass are used to quantify the concentration of radioactive material in contaminated environmental media because the carcinogenic risks of exposure to radioactively-contaminated materials are related more to the decay rate of the material than to its mass.[5] Generally, this convention is used due to the short half-lives of many of the radionuclides commonly encountered at contaminated sites. As examples for the decay-equivalent for a given radionuclide mass, one gram of ^{226}Ra has a decay rate (activity) of 3.7×10^{10} transformations (also referred to as disintegrations) per second, while one gram of ^{137}Cs has a decay rate of 3.2×10^{12} transformations per second. Except for long-lived nuclides with low specific activities such as ^{238}U, the energy emitted by the radioactive material during radioactive decay and absorbed by exposed biological tissue is the key driver of health effects from exposure to most radionuclides. In addition, radioactive materials may be detected and quantified by the type of radiation emitted and number of disintegrations (per unit time). For these reasons, the concentration of radioactive material in water is typically expressed in units of activity or decay rate, pCi/L.

Most of the radionuclide MCLs and UMTRCA ground-water standards are presented in the traditional units of pCi/L. Mass units, however, provide insight and information into treatment selection, treatment compatibility, and treatment efficiency, particularly for remedial actions involving mixed waste. For example, remediation goals expressed in mass are important for designing and evaluating treatment technologies such as soil separation, pump and treat, as well as subsurface barriers. In addition, transport models in which solid-liquid partitioning of the radionuclide is described are developed using mass-action reaction expressions. Radionuclide mass concentration is typically the required data input for these models. Typically units for expressing mass in environmental media for soil and water are mg/kg and mg/L, respectively. These mass units also can be expressed as parts per million (ppm) for soil and water, which is equivalent to mg/kg and mg/L. MCLs in pCi/L may be converted to their mass equivalent in mg/L, by the following equations:

$$\text{MCL(mg/L)} = 2.8 \times 10^{-15} * A * T_{1/2} * \text{MCL(pCi/L)}$$

where 2.8×10^{-15} for water is a conversion factor, A is the radionuclide atomic weight in g/mole, and $T_{1/2}$ is the radionuclide half-life in years. Most radionuclides of concern for site cleanups have half-lives ranging from a few years to 10,000 years. At MCL levels, the corresponding masses of most radionuclides represent extremely small values.

One important issue associated with using mass to characterize the quantities of radioactive material in the environment is that many elements, such as uranium, have several isotopes of the same element (See examples in Table 1.1.). For example, if one were to perform atomic absorption analysis of a water sample, and it revealed the presence of 1 mg/kg of uranium, there would be no way of knowing how much of the uranium in the sample is ^{238}U, ^{234}U, or ^{235}U, all of which are present in the environment naturally and due to anthropogenic activities. While the potential human health and ecological effects of uranium from its chemical toxicity are impacted by the total mass of the element, its potential for human health and ecological effects from its radioactivity will depend on the specific isotopes of uranium present, which could vary depending on whether one is dealing with naturally-occurring uranium or uranium that may have been enriched in ^{235}U as part of the uranium fuel cycle or part of weapons production. It is also important to note that the same mass of each uranium isotope has significantly different levels of radioactivity. A mass of 1 mg/kg of ^{238}U has an activity of 0.33 pCi/g, while the same mass of ^{235}U has 2.1 pCi/g and ^{234}U has 6,200 pCi/g.

Also, many radioactive elements are present in the environment along with their stable counterpart. One example is potassium, which occurs naturally in the environment, ranging from 0.1 to 1% in limestone to 3.5% in granite. In addition, a typical 70 kg adult contains 130 g of potassium. A very small fraction (0.01%) of this potassium is the naturally-occurring radioactive isotope ^{40}K. If one were to measure the amount of ^{40}K in soil and assume that ^{40}K made up all of the elemental potassium then the total mass of this element would be underestimated by 10,000 fold. Since the potential adverse effects of radioactive material are due to the energy released following radioactive decay, measurement of elemental mass present, e.g., total K by atomic emission spectroscopy, may not accurately represent the amount of radioactivity present and, therefore, its potential radiotoxicity. However, use of mass spectrometry for discrimination of the various isotopes of a given element may avoid this situation, since it would then be possible to convert isotopic mass concentration to activity using the decay half-life of a radioisotope.

Conversely, the measurement of the radioisotope activity will be a misrepresentation of the total mass of the given element, particularly for the majority of elements that have non-radioactive isotopes which may be present in much larger quantities on a mass basis. Accordingly, activity should not be used alone to determine or tailor the treatment required for remediation technologies, since technologies typically rely on chemical and/or physical processes that are sensitive to or driven by mass or concentration. For example, to design and implement a treatment technology for radioactive strontium (i.e., ^{90}Sr), it would be necessary to know the total mass of all stable (i.e., ^{84}Sr, ^{86}Sr, ^{87}Sr, ^{88}Sr) and radioactive isotopes of strontium in ground water. The same considerations would be necessary for other ground-water treatment technologies for dissolved concentrations of elements and their isotopic forms. For example in a pump and treat ground-water extraction system that utilizes ion exchange (chemical separation) or reverse osmosis (physical separation), chemical mass measurements would be used to determine the amount and type of reactant materials, exchange capacity and

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[5] *Discussions of radioactive decay phenomena and applicable units of measurement are provided in Appendix A.*

effectiveness (USEPA, 1996). Much the same can be said for immobilization or reduction technologies such as chemical solidification/stabilization treatability studies or treatments (USEPA, 2000b). Also, mass measurements are important in the determination of partition coefficients, K_d, values that are often employed in risk assessment modeling and remediation calculations. K_d values are expressed in mass units for the inorganic elements and isotopes (USEPA, 1999b; USEPA, 2004a). The values of K_d are assumed to be the same for all isotopic forms of the element.

In summary, given that risk or exposure is the basis for remedial actions, mass measurements are often required for determining, designing and selecting a remediation technology. This contrasts with the need for radiation specific isotopic measurements required in risk and exposure analysis. Users should note the different applications and perspectives with their corresponding measurement units of mass and activity.

1.2 Contaminant Risk Reduction Processes

As stated within the OSWER Directive on MNA (USEPA, 1999c), natural attenuation processes are those that ‘reduce mass, toxicity, mobility, volume or concentration of contaminants.’ For radionuclides, contaminant attenuation that results in mass loss or decreased mobility may occur either via radioactive decay or immobilization. In general, the development of a stable or shrinking contaminant plume will depend on the relative rate for the immobilization reaction(s) versus the rate of ground-water flow through the aquifer. This concept is illustrated in Figure 1.1 in which documented ranges for characteristic timescales of radioactive decay and several potential immobilization reactions are shown relative to commonly observed residence times for a parcel of water in ground water (and surface water) systems. Discussion of potential immobilization processes and the types of site characterization data to support identification of this attenuation process within a ground-water contaminant plume is provided in Volume 1, Section II of this series of documents (USEPA, 2007a). In general, immobilization may occur as a result of precipitation, co-precipitation, and/or adsorption reactions in which the contaminant chemically reacts with dissolved and/or solid components within the aquifer. For many of the radionuclide contaminants discussed in this volume, there are viable processes that may result in attenuation via immobilization within the subsurface. More specific discussion of immobilization mechanisms is provided in the individual contaminant chapters. However, several of the radionuclide contaminants discussed in this volume will remain mobile in ground water due to their inherent chemical properties. In these situations, radioactive decay may provide the only viable mechanism for mass loss of the contaminant.

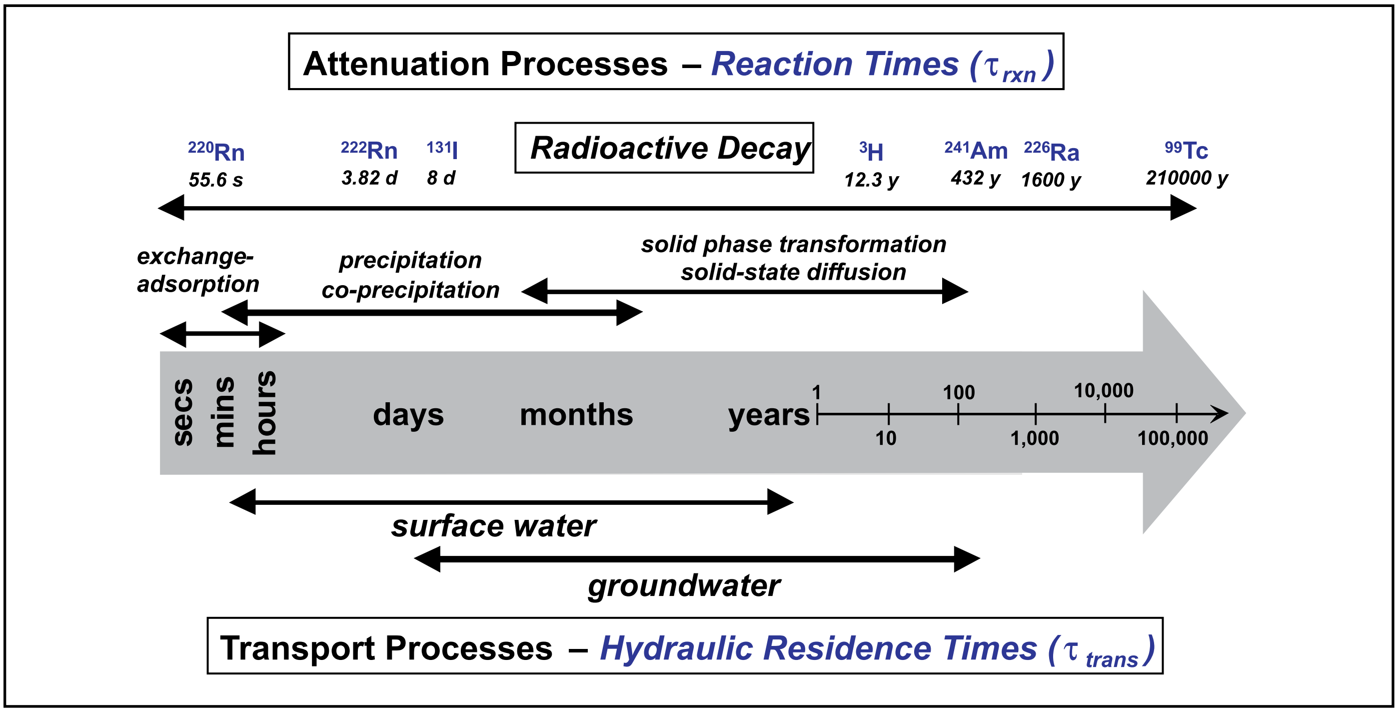


Figure 1.1 *Relative timescales of attenuation processes and fluid transport processes referenced to characteristic reaction times and hydraulic residence times. For radioactive decay, representative radionuclides with a range of decay half-lives (s = seconds, d = days, y = years) are shown. Representative time scales for several processes that result in contaminant immobilization are also shown.*

For radionuclides with relatively short decay half-lives, the development of a stable or shrinking ground-water plume may occur if the rate of decay is greater than the rate of ground-water transport. As illustrated in Figure 1.2 for radionuclides whose transport within the aquifer is not impeded due to chemical reaction, the ground-water plume may shrink, remain invariant (i.e., stable), or expand in size. Plume shrinkage may occur if radioactive decay is fast relative to the velocity of ground-water flow (e.g., ^{222}Rn (radon), 3.82 day half-life). Where the rates of decay and fluid transport are relatively similar, development of a stable plume may occur (e.g., ^{3}H (tritium), 12.3 year half-life). Finally, for long-lived radionuclides that may remain mobile (e.g., ^{99}Tc (technetium), 2.13x10^{5} year half-life), plume expansion is anticipated to occur. Estimated differences in the relative time scales to achieve cleanup levels for radionuclides addressed in this volume are illustrated in Figure 1.3. The trends shown in Figure 1.3 are based solely on the result of first-order radioactive decay (see Appendix) of a finite radionuclide activity ignoring the influence of ground-water transport on the distribution of contaminant mass/activity in space and time. There are several technical issues that also factor into this evaluation, including the relative magnitude (i.e., total activity of radionuclide) and rate of release of the radionuclide from the source term(s) that contribute to plume development (Figure 1.3c), as well as the chemical, radiological and/or toxicological characteristics of the decay product(s). For example, the complexity introduced by the in-growth of a radioactive daughter with different chemical properties would require simultaneous tracking of an overlapping plume that could behave very differently from that of the parent. However, the purpose of these illustrations is to draw attention to the large disparity in radioactive decay rate for the radionuclides that are encountered at contaminated sites. Further discussion of these issues is provided later in this document.

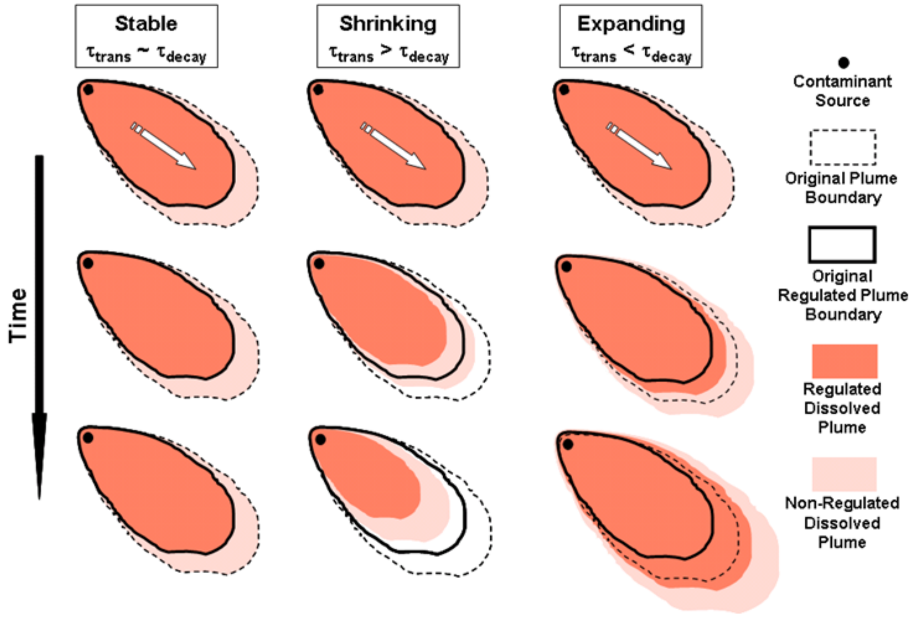


Figure 1.2 *Illustration of characteristic ground-water plumes that may develop for radionuclides whose transport is not impeded by chemical reaction: 1) stable plume – similar rates of fluid transport and decay, 2) shrinking plume – decay rate faster than fluid transport, and 3) expanding plume – decay rate slower than fluid transport. Regulated mobile plume refers to that portion of the plume where contaminant mass/activity exceeds Risk-based or ARAR criterion. The symbol "τ" refers to the characteristic time for transport* (τ_{trans}) *and radioactive decay* (τ_{decay}).

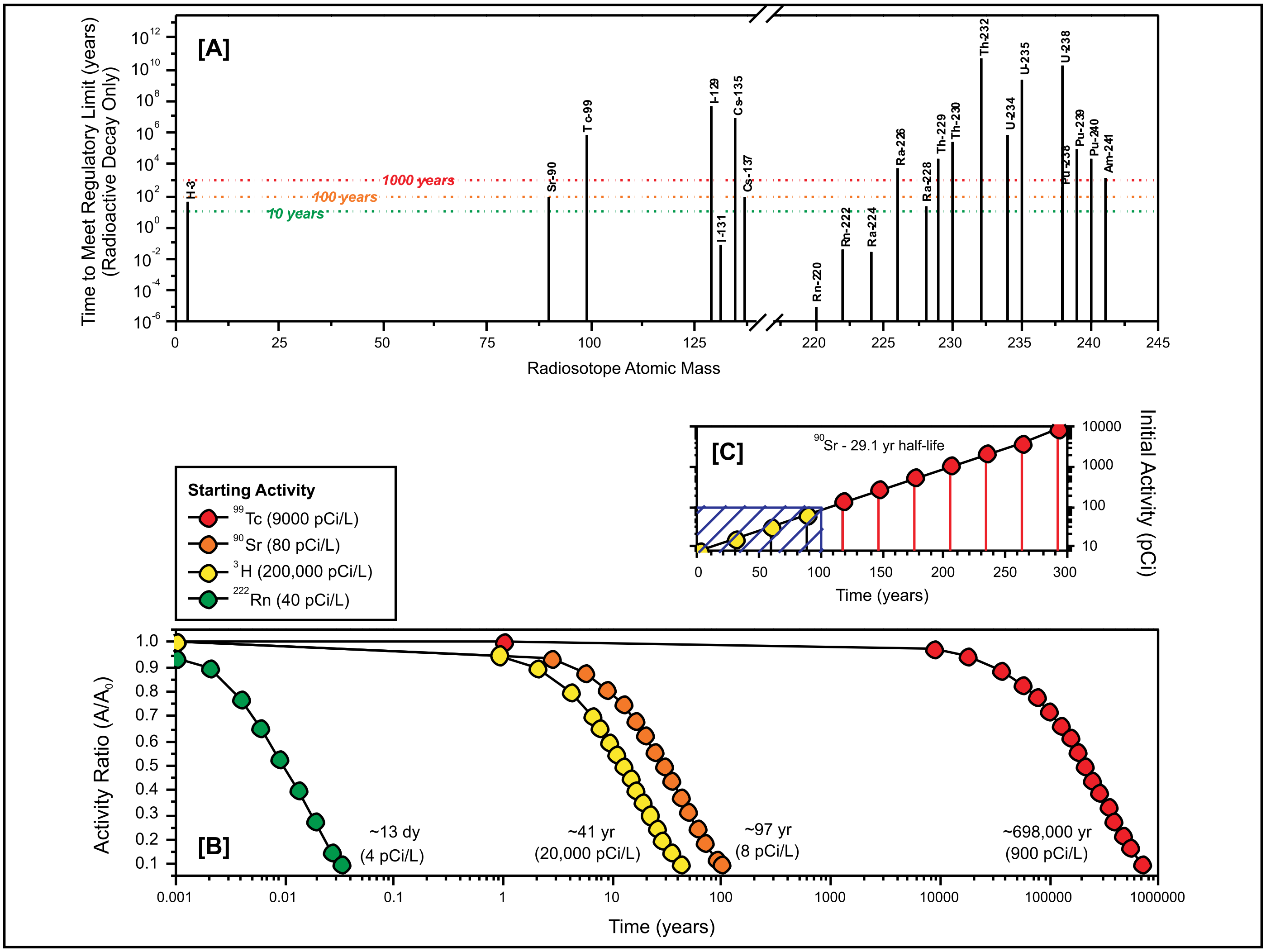
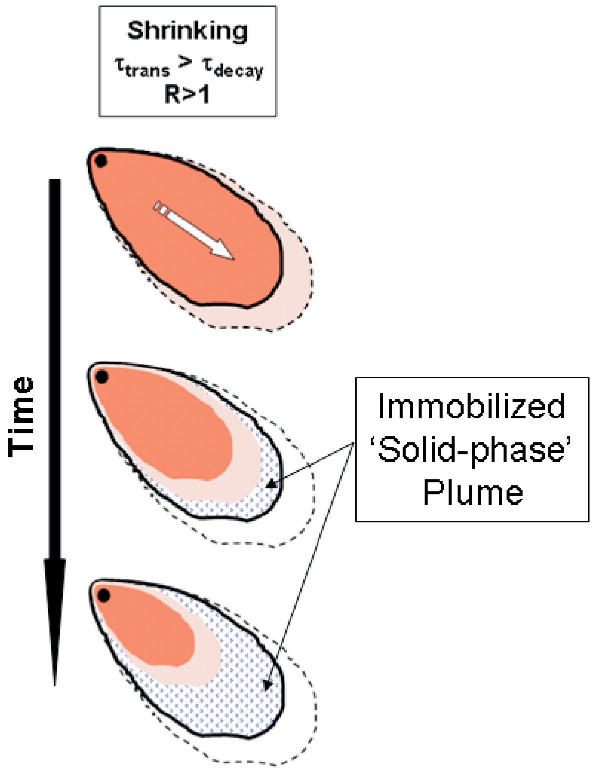


Figure 1.3 *Illustration of the importance of decay half-life and total activity on the viability of radioactive decay as an attenuation process for contaminant remediation. (A) Time to achieve ground-water cleanup standards following an order-of-magnitude activity reduction for radionuclides addressed in this volume. (B) Time series plots of decay-only activity reductions to achieve cleanup standard in ground water for an order-of-magnitude change in total activity for several radionuclides addressed in this volume. (C) Influence of total initial activity on the time to achieve representative cleanup standard (example is for ^{90}Sr in one liter of solution); blue hatched area shows region where a relevant mass equivalent cleanup standard may be achieved within 100 years.*

For several radionuclides discussed in this volume, reactions with dissolved or solid phase components within the aquifer lead to transfer of the contaminant from ground water onto aquifer solids. In this situation, characteristics of the contaminant plume may be governed by immobilization processes. In essence, there are two effective 'plumes' within the plume boundary: 1) the dissolved and mobile plume (including the mobile colloidal phase), and 2) the solid phase and immobile plume (Figure 1.4). As with non-radionuclides, the overall stability of the immobilized contaminant to resist re-mobilization becomes a critical factor for the viability of natural attenuation as a cleanup remedy. The stability of the immobilized radionuclide will be governed by the inherent chemical characteristics of the contaminant, the chemical characteristics of ground water, and the stability of aquifer solids to which the contaminant may be bound. Changes in ground-water chemistry over time may result in conditions that cause contaminant release or dissolution of host aquifer solids. Evaluation of this issue may be further complicated for radionuclides whose decay products possess inherent chemical properties that differ significantly from that of the parent radionuclide.



'Immobile' plume represents contaminant mass sorbed onto aquifer solids at any point in time

Future scenarios for evolution of 'immobile' plume:

- ***Declines in mass & spatial distribution due to radioactive decay***
- ***Remains invariant in mass & spatial distribution***
- ***Evolves to new state that serves as source for development of new dissolved plume caused by:***
  1) ***Radioactive decay produces more mobile daughter product(s)***
  2) ***Changes in ground-water chemistry cause re-mobilization***

Figure 1.4 *Depiction of plume development for a radionuclide that possesses decay rate slower than the rate of fluid transport* ($\tau_{trans} > \tau_{decay}$)*, but is subject to sorption processes that transfer it from ground water onto immobile aquifer solids* (*i.e., retardation factor,* $R > 1$)*. The dissolved plume shrinks leaving behind an immobile plume bound to aquifer solids.*

Evaluating the overall success of natural attenuation for remediation of radionuclides will require demonstrating that the rate and capacity for contaminant attenuation meets regulatory objectives (including time frame) and, in addition, that contaminant immobilization is sustainable to the extent that future health risks are reduced to acceptable limits. The latter requirement necessitates identifying the chemical speciation of the contaminant partitioned to the solid phase. This information is critical towards designing laboratory tests and reaction transport models used to assess and project potential for re-mobilization of the radionuclide. An overview explaining the types of immobilization mechanisms and the respective susceptibility to re-mobilization for each scenario is provided in Volume 1 of this series of documents (USEPA, 2007a) along with general procedures for assessing the susceptibility for contaminant re-mobilization. Specific discussions of radioactive decay phenomena, relevant immobilization processes and procedures for assessing the potential for re-mobilization are discussed within the individual contaminant chapters later in this volume.

1.3 Tiered Analysis Approach to Site Characterization

Site characterization to support evaluation and selection of MNA as part of a cleanup action for inorganic contaminant plumes in ground water will involve a detailed analysis of site characteristics controlling and sustaining attenuation. The level of detailed data that may be required to adequately characterize the capacity and stability of natural processes to sustain plume attenuation will likely necessitate significant resource outlays. Thus, it is recommended that site characterization be approached in a step-wise manner to facilitate collection of data necessary to progressively evaluate the existing and long-term effectiveness of natural attenuation processes within the aquifer. Implementation of a tiered analysis approach provides an effective way to screen sites for MNA that is cost effective because it prioritizes and limits the data that is needed for decision making at each screening step. Conceptually a tiered analysis approach seeks to progressively reduce uncertainty as site-specific data are collected. The decision-making approach presented in this document includes three decision tiers that require progressively greater information on which to assess the likely effectiveness of MNA as a remedy for inorganic contaminants in ground water. The fourth tier is included to emphasize the importance of determining appropriate parameters for long-term performance monitoring, once MNA has been selected as part of the remedy. Data collection and evaluation within the tiered analysis approach would be structured as follows:

I. Demonstration that the ground-water plume is not expanding and that sorption of the contaminant onto aquifer solids is occurring where immobilization is the predominant attenuation process;

II. Determination of the *mechanism and rate* of the attenuation process;

III. Determination of the *capacity* of the aquifer to attenuate the mass of contaminant within the plume and the *stability* of the immobilized contaminant to resist re-mobilization, and;

IV. Design performance monitoring program based on the mechanistic understanding developed for the attenuation process, and establish a contingency plan tailored to site-specific characteristics.

Elaboration on the objectives to be addressed and the types of site-specific data to be collected under each successive tier is provided below.

1.3.1 Tier I

The objective under Tier I analysis would be to eliminate sites where site characterization indicates that the ground-water plume is continuing to expand in aerial or vertical extent. For radionuclides in which radioactive decay is anticipated to provide the primary mode of attenuation, it is recommended that decay calculations (with or without incorporation of physical transport) be conducted to evaluate whether regulatory objectives can be met in an appropriate time frame given knowledge of source term characteristics (e.g., total activity and release rate) and/or radionuclide activities within the plume relative to points of compliance. For contaminants in which sorption onto aquifer solids is the most feasible attenuation process, an additional objective would be to demonstrate contaminant uptake onto aquifer solids. Analysis of ground-water plume behavior at this stage is predicated on adequate aerial and vertical delineation of the plume boundaries. Characterization of ground-water plume expansion could then be supported through analysis of current and historical data collected from monitoring wells installed along the path of ground-water flow. An increasing temporal trend in contaminant concentration in ground water at monitoring locations down gradient from a source area is indicative that attenuation is not occurring sufficient to prevent ground-water plume expansion.

An example illustrating the influence of total radionuclide activity on plume dynamics is shown Figure 1.5. Two scenarios are shown for a tritium plume that results from two different periods of release from a source area. In the left panel, the release of tritium into ground water at a fixed solution activity of 50,000 pCi/L occurred for a period of 12 months. For the hydrologic conditions specified in this scenario (Figure 1.5), insufficient attenuation would be projected based on radioactive decay alone. The activity of tritium in the plume centerline exceeds the MCL as the plume maximum passes the point of compliance. In contrast, if source control had been implemented such that release only occurred for a period of 1 month, it might be anticipated that radioactive decay may be sufficient to meet a cleanup objective such as an MCL for ground water. In this case, the maximum tritium activity is at or below the MCL as the plume maximum passes the point of compliance. This type of screening analysis is important to conduct early in the site characterization effort for radionuclides for which attenuation by immobilization is not significant. This illustration also points to the importance of understanding source characteristics both in terms of total contaminant mass/activity as well as rates of release.

Determination of contaminant sorption onto aquifer solids could be supported through the collection of aquifer cores coincident with the locations of ground-water data collection and analysis of contaminant concentrations on the retrieved aquifer solids. Illustration of the type of data trend anticipated for a site where sorption actively attenuates contaminant transport was provided in Volume 1 (USEPA, 2007a; Figure 1.2 in Section IC.1). Ultimately, sites that demonstrate ground-water plume expansion and a lack of contaminant sorption would be eliminated from further consideration of MNA as part of the cleanup remedy.

1.3.2 Tier II

The objective under Tier II analysis would be to eliminate sites where further analysis shows that attenuation rates are insufficient for attaining cleanup objectives established for the site within a timeframe that is reasonable compared to other remedial alternatives. (see USEPA, 1999c, pages 19-21, for a discussion of “reasonable timeframe for remediation”.) Data collection and analysis performed for Tier II would indicate whether MNA processes are capable of achieving remediation objectives, based on current geochemical conditions at the site. This data collection effort would also be designed to support identification of the specific mechanism(s) controlling contaminant attenuation.

An estimate of attenuation rates for long-lived radionuclides will typically involve calculation of the apparent transfer of mass from the aqueous to the solid phase, based on sampling of ground water and/or aquifer solids. It is recommended that these estimates be based as much as possible on field measurements rather than modeling predictions. A recommended approach is to identify hydrostratigraphic units for the site and develop a ground water flow model which can be used to estimate ground-water seepage velocities in each of these units (Further information on ground-water flow models was provided in Volume 1, Section I.D.). These seepage velocities can be combined with measured contaminant concentrations to estimate mass flux (mass per time per area) for each contaminant,

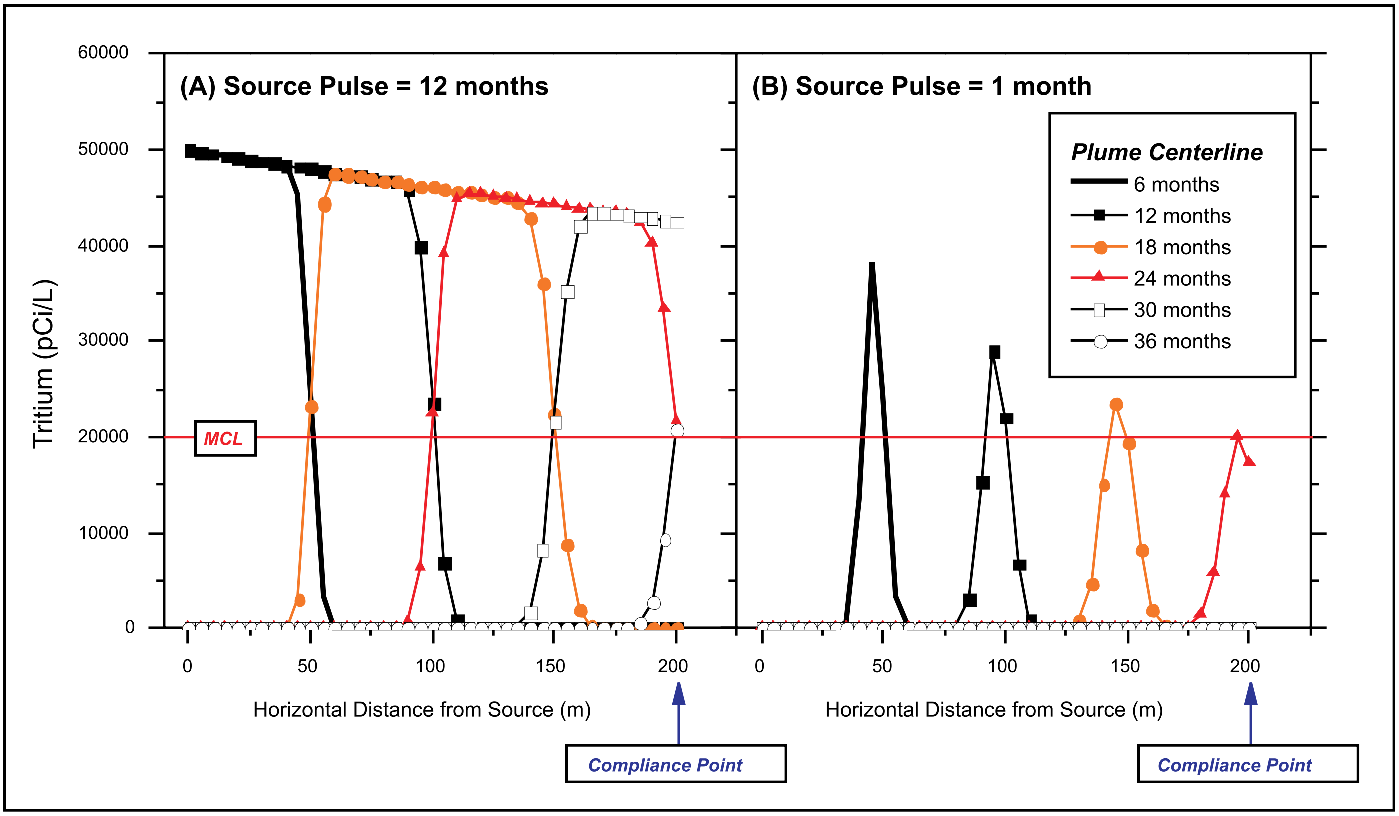


Figure 1.5 *One-dimensional, decay-transport model (Clement, 2001; Quezada et al., 2004; and Srinivasan and Clement, 2008 a & b) describing tritium transport in an homogeneous aquifer as a function of source characteristics: (A) 12-month release from source at 50,000 pCi/L and (B) 1-month release from source at 50,000 pCi/L. Assumptions: ground-water seepage velocity = 100 m/y, longitudinal dispersivity = 0.11 m, ^{3}H decay half-life = 12.35 y, insignificant influence from source term decay.*

in each hydrostratigraphic unit. The necessary data might include physical parameters such as hydraulic conductivities within the aquifer and hydraulic gradients. Changes in mass flux can then be used to estimate mass loss from the aqueous phase since the last sampling event, which is assumed to be the apparent attenuation rate. (Further information on estimating attenuation rates is provided in Volume 1, Section IIIA.5.)

Determination of attenuation mechanism will depend on collection of data to define ground-water chemistry, aquifer solids composition and mineralogy, and the chemical speciation of the contaminant in ground water and associated aquifer solids. This will entail a significant effort in the site-specific data collection effort, but provides the underpinning for further evaluation of the performance of MNA to be addressed in subsequent stages of the site characterization process. The goal of this characterization effort is to identify the aqueous and solid phase constituents within the aquifer that control contaminant attenuation. This data collection effort may include collection of field water quality data (e.g., pH, dissolved oxygen, alkalinity, ferrous iron, and dissolved sulfide), laboratory measurements of ground-water and aquifer solids chemical composition, microbial characteristics and/or mineralogy of the aquifer solids (as relevant to immobilization), and the chemical speciation of the contaminant in ground-water and/or the aquifer solids. Contaminant speciation refers to both oxidation state characterizations [e.g., U(VI) vs. U(IV)] as well as specific associations with chemical constituents in aquifer solids (e.g., precipitation of uranium oxide/silicate vs. adsorption of U(VI) to iron oxides). Evaluations of the subsurface microbiology may be necessary in situations where biotic processes play a direct or indirect role in governing contaminant attenuation. Indirect microbial influence on contaminant attenuation includes situations in which the predominant characteristics of the ground-water chemistry are controlled by microbial oxidation-reduction reactions. This situation may be more predominant in plumes in which readily degradable organic contaminants, such as hydrocarbons or chlorinated solvents, are also present. Ultimately, mechanistic knowledge of the attenuation process along with a detailed knowledge of the ground-water flow field provides the basis for subsequent evaluations to assess the long-term capacity of the aquifer to sustain contaminant attenuation.

1.3.3 *Tier III*

The objective under Tier III would be to eliminate sites where site data and analysis show that there is insufficient capacity in the aquifer to attenuate the contaminant mass to ground-water concentrations that meet regulatory objectives or that the stability of the immobilized contaminant is insufficient to prevent re-mobilization due to future changes in ground-water chemistry. Possible factors that could result in an insufficient capacity for attenuation include:

1. changes in ground-water chemistry result in slower rates of attenuation,
2. insufficient mass flux of aqueous constituents that participate in the attenuation reaction, and/or
3. insufficient mass of solid constituents in aquifer solids that participate in the attenuation reaction.

These factors pertain to situations where immobilization is the primary attenuation process. For immobilized contaminants, factors to consider relative to the long-term stability of the attenuated contaminant include changes in ground-water chemistry that could result in release of the contaminant from aquifer solids due to desorption from solid surfaces or dissolution of precipitates. For example, contaminant desorption could be caused by changes in ground-water pH, since the degree of adsorption is typically sensitive to this parameter. Alternatively, dissolution of a contaminant attenuated as a carbonate precipitate may result from decreases in ground-water pH and alkalinity.

Assessment of attenuation capacity will depend on knowledge of the flux of contaminants and associated reactants in ground-water, as well as the mass distribution of reactive aquifer solids along ground-water flow paths. In order to conduct this type of evaluation, adequate information is needed on the heterogeneity of the ground-water flow field, and the spatial and/or temporal variability in the distribution of aqueous and solids reactants within the plume. For situations where ground-water chemistry is governed by microbial processes, seasonal variations may exert an indirect influence on the effective capacity within the aquifer at any point in time. The general approach that can be taken is to estimate the attenuation capacity within the plume boundaries and compare this capacity with the estimated mass flux of aqueous phase contaminants emanating from source areas based on site-specific data. Exploring alternatives to minimize contaminant release from source areas may prove beneficial for sites that possess insufficient capacity to adequately attenuate the ground-water plume. Ultimately, this points to the critical importance of a detailed characterization of the system hydrology.

Assessment of the stability of an immobilized contaminant can be evaluated through a combination of laboratory testing and chemical reaction modeling within the context of existing and anticipated site conditions. Both analysis approaches can be developed based on the information gathered during Tier II efforts to characterize the specific attenuation process active within the ground-water plume. Through Tier II analysis, a specific attenuation reaction was defined that identified critical reaction parameters such as the identity of dissolved constituents that participated in the process. In addition, mechanistic understanding of the overall reaction provides the context for evaluating site conditions or dissolved constituents that may interfere with or reduce the efficiency of the attenuation reaction. For example, sites where the contaminant plume is reducing (e.g., sulfate-reducing conditions) while ambient ground-water is oxidizing may be susceptible to future influxes of dissolved oxygen. In this situation, the attenuation process may be due to precipitation of sulfides under sulfate-reducing conditions within the plume. Future exposure of these sulfides to oxygen may result in dissolution of the sulfide precipitate along with release of the contaminant back into ground water. Alternatively, sites where attenuation is predominated by contaminant adsorption onto existing aquifer solids may be sensitive to future influx of dissolved constituents due to land use changes that alter either the source or chemical composition of ground-water recharge. The sensitivity to contaminant re-mobilization can be assessed via laboratory tests employing aquifer solids collected from within the plume boundaries that can be exposed to solutions that mimic anticipated ground-water chemistries (e.g., ambient ground-water samples or synthetic solutions in which the concentrations of specific dissolved constituents can be systematically varied). A supplementary avenue to test contaminant stability could include use of chemical reaction models with adequate parameterization to replicate both the attenuation reaction as well as changes in water composition that may interfere with attenuation. The utility of this type of modeling analysis would be the ability to efficiently explore contaminant solubility under a range of hypothetical ground-water conditions in order to identify the ground-water parameters to which the attenuation reaction may be most sensitive. It is feasible to consider implementation of MNA as a component of the ground-water remedy if the analysis conducted through the previous Tiers indicates that the aquifer within the plume boundaries supports natural attenuation processes with sufficient efficiency, capacity, and stability. The technical knowledge obtained through identification of the specific attenuation mechanism and the sensitivity of the attenuation process to changes in ground-water chemistry can then be employed in designing a monitoring program that tracks continued performance of the MNA remedy.

1.3.4 *Tier IV*

The objective under Tier IV analysis is to develop a monitoring program to assess long-term performance of the MNA remedy and identify alternative remedies that could be implemented for situations where changes in site conditions could lead to remedy failure. Site data collected during characterization of the attenuation process will serve to focus identification of alternative remedies that best match site-specific conditions. The monitoring program will consist of establishing a network of wells: 1) that provide adequate aerial and vertical coverage to verify that the ground-water plume remains static or shrinks, and 2) that provide the ability to monitor ground-water chemistry throughout the zones where contaminant attenuation is occurring. It is recommended that the performance monitoring program include assessment of the consistency in ground-water flow behavior, so that adjustments to the monitoring network could be made to evaluate the influence of potential changes in the patterns of ground-water recharge to or predominant flow direction within the plume. In addition to monitoring ground-water parameters that track the attenuation reaction, periodic monitoring of parameters that track non-beneficial changes in ground-water conditions is also recommended. Monitoring the attenuation reaction will include continued verification of contaminant removal from ground water, but will also include tracking trends in other reactants that participate in the attenuation reaction (possible examples include pH, alkalinity, ferrous iron, and sulfate). For sites in which contaminant immobilization is the primary attenuation process, periodic collection of aquifer solids may be warranted to verify consistency in reaction mechanism. It is recommended that the selection of ground-water parameters to be monitored also include constituents that provide information on continued stability of the solid phase with which an immobilized contaminant is associated. Examples of this type of parameter might include ferrous iron or sulfate to track dissolution of iron oxides or sulfide precipitates, respectively. Non-contaminant performance parameters such as these will likely serve as "triggers" to alert site managers to potential remedy failure or performance losses, since the attenuation reaction will respond to these changed conditions. Since increases in mobile contaminant concentrations may be delayed relative to changes in site conditions, these monitoring parameters may improve the ability of site managers to evaluate and address the potential for ground-water plume expansion. In summary, the tiered analysis process provides a means to organize the data collection effort in a cost-effective manner that allows the ability to eliminate sites at intermediate stages of the site characterization effort.

A general synopsis of the objectives along with possible analysis approaches and/or data types to be collected under each tier is provided in Table 1.2. The types of data collected early in the site characterization process would typically be required for selection of appropriate engineered remedies, including characterization of the system hydrology, ground-water chemistry, contaminant distribution, and the aqueous speciation of the contaminant. These system characteristics can have direct influence on the selection of pump-and-treat or in-situ remedies best suited to achieve cleanup objectives for inorganic contaminants. This limits any loss on investment in site characterization for sites where selection of MNA as part of the ground-water remedy is ultimately determined not viable. The primary objective of progressing through the proposed tiered site analysis steps is to reduce uncertainty in the MNA remedy selection. The remaining discussion in this section of Volume 1 will elaborate on two issues that have been introduced above, specifically the use of models in site characterization and general factors to consider for implementation of a long-term performance monitoring program. These topics are addressed at this juncture to allow greater focus to discussions later in this volume pertaining specifically to attenuation processes (Volume 1, Section II) and the types of site characterization data needed for their identification (Volume 1, Section III). The following discussion provides perspective on the role of model applications in the site characterization process, the types of models that might be employed to help meet the objectives set forth under each tier, and potential limitations in the availability and adequacy of available model codes.

1.4 Incorporating Decay Phenomena into Descriptions of Subsurface Transport

The use of models to describe ground-water flow and contaminant transport for non-radionuclides was provided in Volume 1 of this document (Section I.D. in USEPA, 2007a; see also USEPA, 1996). In general, the types of models and supporting data needed as input data to describe contaminant transport of long-lived radionuclides will be similar to that needed for non-radionuclides in which chemical reactions control mass transfer within the aquifer. However, for short-lived radionuclides or for radionuclides in which the energy released during decay can impact reaction conditions, additional model constructs and/or input data may be needed. Models have been developed that can simultaneously describe contaminant transport for a parent radionuclide and daughter products that display variable degrees of sorption affinity for aquifer solids (e.g., van Genuchten, 1985; Srinivasan and Clement, 2008 a & b). This approach has application to short-lived radionuclides, since the influence of radioactive decay on the distribution of radionuclide activity/mass can be projected within the plume boundary (e.g., Figure 1.5). In these model applications, sorption to aquifer solids is typically represented by a linear sorption coefficient or "K_d" (see discussion below). This approach is most likely applicable to radionuclides and/or daughter products in which adsorption or ion exchange is the dominant mechanism for solid-liquid partitioning. However, it should be noted that these model applications may be limited both by the inadequacy of a linear sorption coefficient to describe contaminant partitioning (e.g., Bethke and Brady, 2000; Zhu, 2003) and the failure to account for contaminant precipitation reactions that may accompany changes in redox chemistry and/or major ion fluxes within the plume. Specific discussions on approaches to monitor and model contaminant solid-liquid partitioning are provided in the individual contaminant chapters later in this volume.

1.4.1 Variable Solid-Liquid Partitioning for Parent and Daughter Radionuclides

As described previously, radioactive decay processes result in the formation of a new radionuclide that may have significantly different chemical properties. Thus, while radioactive decay will result in mass-loss of the parent radionuclide, a more mobile daughter radionuclide may result. As an example, ^{226}Ra (typically associated with solids) decay to ^{222}Rn (a dissolved gas) presents a situation where the parent and daughter isotopes display very different reaction-transport characteristics in ground water. This may be an undesirable situation if the daughter radionuclide presents a similar

Table 1.2 Synopsis of site characterization objective to be addressed throughout the tiered analysis process and potential supporting data types and/or analysis approaches associated with each tier.

Tier	Objective	Potential Data Types and Analysis
I	Demonstrate active contaminant removal from ground water	• Ground-water flow direction (calculation of hydraulic gradients); aquifer hydrostratigraphy • Contaminant concentrations in ground water and aquifer solids • *Evaluation of potential for plume expansion based on estimation of activity/mass removal via radioactive decay compared to ground-water transport velocity in aquifer* • General ground-water chemistry
II	Determine mechanism and rate of attenuation	• Detailed characterization of system hydrology (spatial and temporal heterogeneity; flow model development) • Detailed characterization of ground-water chemistry • Subsurface mineralogy and/or microbiology • Contaminant speciation (ground water & aquifer solids) • Evaluate reaction mechanism (site data, laboratory testing, develop chemical reaction model)
III	Determine system capacity and stability of attenuation	• Determine contaminant & dissolved reactant fluxes (concentration data & water flux determinations) • Determine mass of available solid phase reactant(s) • Laboratory testing of immobilized contaminant stability (ambient ground water; synthetic solutions) • Perform model analyses to characterize aquifer capacity and to test immobilized contaminant stability (hand calculations, chemical reaction models, reaction-transport models)
IV	Design performance monitoring program and identify alternative remedy	• Select monitoring locations and frequency consistent with site heterogeneity • Select monitoring parameters to assess consistency in hydrology, attenuation efficiency, and attenuation mechanism • Select monitored conditions that "trigger" re-evaluation of adequacy of monitoring program (frequency, locations, data types) • Select alternative remedy best suited for site-specific conditions

or greater radiological or chemical risk. For example, the amount of radiation being released can actually rise over time as successive radioactive decay products undergo decay. Ultimately, the degree to which one needs to be concerned about this issue will depend on the number and total activity of radionuclide contaminants that are present in a particular plume. Given this information, one can make use of radioactive decay relationships to project increases in decay products and activity, or *in-growth*, with or without consideration of ground-water transport.

1.4.1.1 Daughter In-growth

Depending on the parent radionuclide of concern, there are four general scenarios that may be encountered in which unstable and/or stable nuclides may be produced: 1) unstable parent decays to a stable daughter (e.g., ^{137}Cs decay to stable ^{137}Ba), 2) unstable parent and unstable daughter have similar half-life (e.g., ^{227}Th decay to ^{223}Ra), 3) unstable parent has much longer half-life than unstable daughter (e.g., ^{226}Ra decay to ^{222}Rn), and 4) unstable parent has much shorter half-life than unstable daughter (e.g., ^{241}Am decay to ^{237}Np). The changes in parent and daughter activities/concentrations along with total activity in ground water are illustrated for these four scenarios in Figure 1.6. It can be seen that the production of daughter products can influence plume composition, potential radiological risks, and the dimensions of the plume if the daughter product displays a radiological or chemical risk and transport characteristics different from that of the parent radionuclide.

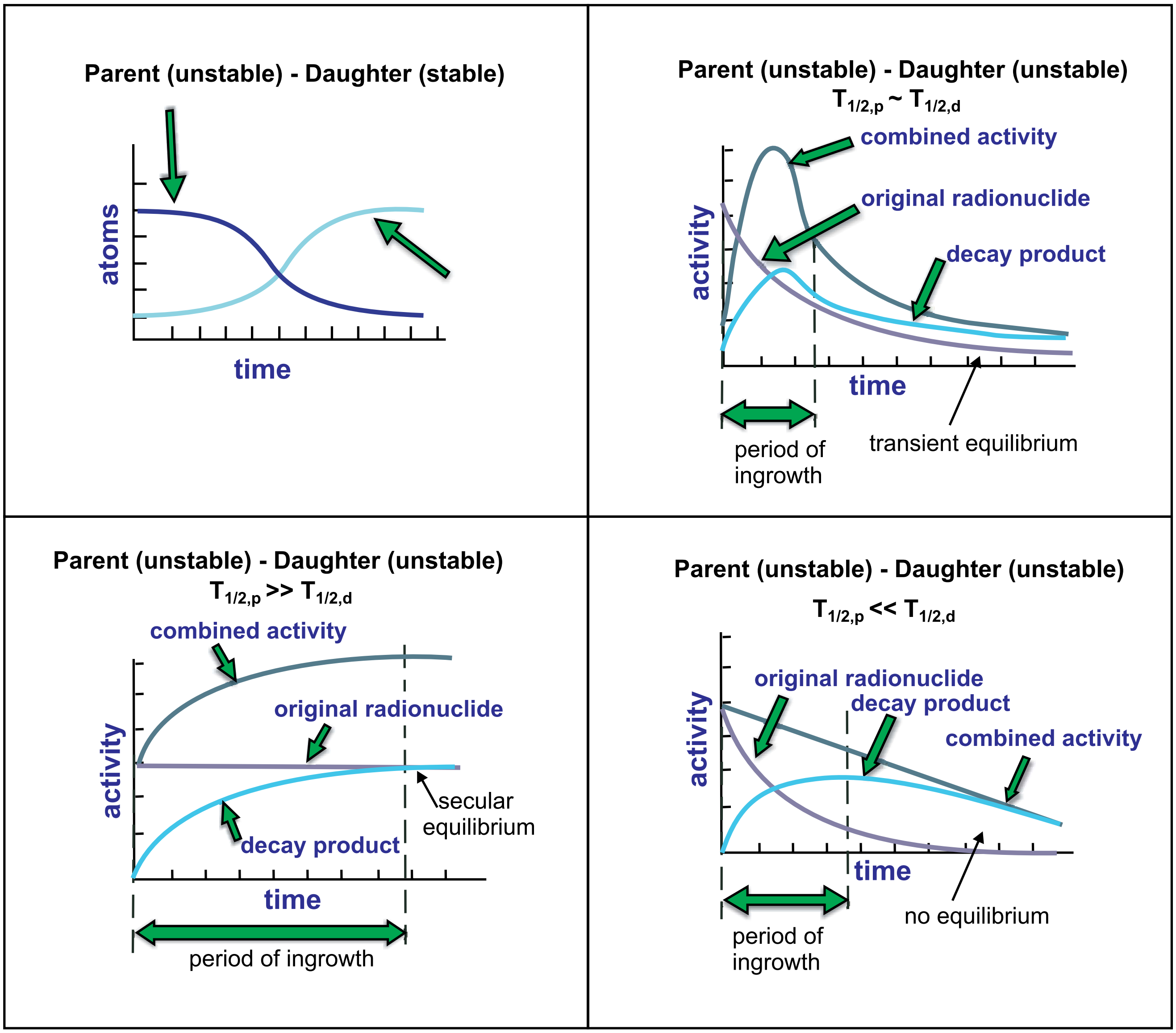


Figure 1.6 *Illustration of four decay in-growth scenarios that may be encountered for ground-water plumes contaminated with radionuclides. Illustrations were derived from the USEPA website - http://www.epa.gov/radiation/understand/equilibrium.html. $T_{1/2,p}$ = decay half-life of parent radionulide, $T_{1/2,d}$ = decay half-life of daughter radionuclide.*

1.4.1.2 Data Sources and Determination of Solid-Liquid Partitioning

As described in Section IIIB.3 in Volume 1 (USEPA, 2007a), there are several different approaches to describing solid-liquid partitioning in transport models. The simplest approach to modeling solid-liquid partitioning during ground-water flow is to use a linear sorption coefficient, or K_d, that represents contaminant uptake as a linear function of the total concentration in solution. The use and limitations of this approach are provided in various publications (e.g., USEPA, 1999a; Bethke and Brady, 2000; Davis and Curtis, 2003; Zhu, 2003). One significant limitation to use of the K_d approach is that the sorption coefficient is generally developed for (and only applicable to) a fixed set of ground-water chemical conditions. The chemical conditions in ground water affect the speciation of radionuclides in solution (e.g., complexation with dissolved carbonate), surface chemical properties of potential sorbents (e.g., charging behavior of oxyhydroxide minerals), and the types and tendency for chemical bond formation onto aquifer solids (e.g., pH dependence of cation sorption). Thus, even if a K_d was developed using well-preserved aquifer solids and sampled ground water from the site being characterized, chemical conditions may evolve within the plume to the extent that the developed K_d relationship may no longer provide a valid representation of radionuclide partitioning. From this perspective, use of a K_d obtained from literature reports or derived from site-specific tests should be done so following critical evaluation of the compatibility between test conditions and subsurface characteristics with the portion(s) of the contaminant plume for which contaminant attenuation is being assessed. Under many situations, selection of a K_d can single-handedly determine the results of contaminant attenuation calculations.

There are available compilations of sorption coefficients for the radionuclides addressed in this volume (USEPA, 1999 a & b; USEPA, 2004a). In these technical reviews, contaminant-specific partitioning coefficients were derived from published data sets for a wide range of soils. While these data may have limited applicability for a specific site, they do provide useful context for evaluating the relative mobility of various radionuclides that might be present in a ground-water plume. In contrast, there are more limited compilations describing radionuclide partitioning to various minerals in aquifer solids (e.g., iron oxyhydroxides, clay minerals such as montmorillonite) that are based on more detailed mechanistic descriptions of solid-liquid partitioning (e.g., surface complexation models; see Section IIB in Volume 1). However, the applicability of these models is usually limited to describe radionuclide transport in contaminant plumes due to the uncertainty in input parameters to describe mineral surface charging and/or the potential role of multiple mineral components participating in solid-liquid partitioning along transport pathways. Hybrid modeling approaches have been developed in which variable characteristics of sorbent phase(s) along transport pathways is addressed via collection of site-specific data, while allowing the ability to incorporate the influence of aqueous radionuclide speciation on the partitioning reaction (e.g., Davis and Curtis, 2003).

In situations where radionuclide precipitation reactions may control attenuation, verification of the accuracy and completeness of solubility reactions included in the thermochemical database is critical for model applications. There have been significant efforts over the past several years to review and update thermochemical databases available to describe radionuclide precipitation in ground-water systems. Examples of these efforts include those by the Nuclear Energy Agency (Guillaumont et al., 2003) and the Paul Scherrer Institute Laboratory for Waste Management (Thoenen et al., 2004) to critically evaluate existing published thermochemical data and provide the technical rationale for selection of specific constants based on the reliability of published methods and results in the technical literature. It is recommended that any modeling effort that incorporates descriptions of radionuclide precipitation as an attenuation mechanism make use of these technically reviewed databases.

Ultimately, the effort expended into the development of reactive-transport models will likely be governed by the type of attenuation processes anticipated to control radionuclide transport. It is recommended that the selection of appropriate modeling approaches be supported with the collection of site-specific data that verify the primary attenuation mechanisms for each radionuclide in a given ground-water plume (i.e., as set forth in recommendations for Tier II evaluation efforts).

1.4.1.3 Influence of Alpha-Recoil on Daughter Solid-Liquid Partitioning

In general, solid-liquid partitioning for radionuclides addressed in this volume will be governed by properties of the radionuclide and sorbent material, as well as the overall chemical conditions in ground water. As previously discussed, radioactive decay may result in daughter products that possess sorption characteristics significantly different than the parent nuclide. Radioactive decay of sorbed radionuclides may also alter properties of the solid to which they are partitioned. For some radionuclides, the energy released during radioactive decay is sufficient to either eject the daughter element from the solid structure (Kigoshi, 1971) or cause damage to the host solid (Fleischer, 1980). For the latter situation, the damage to the solid structure increases the susceptibility to dissolution (Eyal and Fleischer, 1985).

The potential influence of alpha-recoil is exemplified by the behavior of ^{238}U and ^{234}U solid-solution partitioning in ground-water systems in which ^{234}U becomes enriched in ground water (Ivanovich, 1994). For this decay chain, ^{238}U decay produces ^{234}Th along with emission of an alpha particle of sufficient energy to cause ejection of ^{234}Th into ground water. Subsequent serial decay of ^{234}Th (24.1 day half-life) to ^{234}Pa (6.7 hour half-life) and ultimately ^{234}U results in an elevated activity/concentration of ^{234}U relative to what would be anticipated based strictly on the solid-liquid partitioning for uranium and/or thorium. Additional examples of decay chains that may produce recoil effects include those for ^{228}Th, ^{229}Th, and ^{226}Ra (Sun and Semkow, 1998). Radionuclide transport models have been developed that incorporate the influence of alpha-recoil on the solid-liquid partitioning of parent and daughter radionuclides (Tricca et al., 2001; Maher et al., 2006). However, this phenomenon is not routinely recognized as a contributing factor in ground-water plumes at contaminated sites.

In general, the impact of this process is difficult to characterize in an aquifer and may play a minor role in contaminant plumes with concentrations that greatly exceed natural levels. However, given that mass-equivalent regulatory standards for many of the radionuclides addressed in this volume are quite low, the potential importance of alpha-recoil events should be qualitatively evaluated before ruling out the significance of this process. In other instances, consideration of alpha-recoil processes may be more relevant from the standpoint of explaining anomalous analytical results and/or selecting/tailoring an analytical method.

1.4.2 Colloid Generation and Transport

An overview of colloid generation and transport in ground water was provided in Section IIA.2 in Volume 1 (USEPA, 2007a). In that discussion, emphasis was placed on colloidal solids acting as carriers of inorganic contaminants within a ground-water plume. The types of colloids discussed included minerals and/or organic compounds native to the aquifer solids or formed from components in waste streams transported as part of the ground-water plume. It has been proposed that these colloid types be referred to as "pseudo-colloids" when describing radionuclide transport (Kim, 1991). The characteristics of carrier colloids and technical issues important for site characterization presented in Volume 1 also apply to radinonuclide transport in this volume. For the radionuclides addressed in this volume, an additional source of colloids may be derived from the radionuclide under certain chemical conditions. These mobile solids are referred to as *radiocolloids* or "real-colloids" (Kim, 1991), which can be derived from the polymerization and precipitation of the radionuclide to form solids with size dimensions on the order of nanometers. An example of this phenomenon is the formation of fine-grained thorium oxide solids possessing surface charge characteristics that maintain their mobility in porous media (e.g., Yun et al., 2006). A conceptual framework for understanding colloid stability and transport in ground water has been developed (Degueldre et al., 2000), and it is recommended that this be consulted as a point of reference for assessing the potential importance of this process at a given site.

Conflicting reports of the importance of colloidal transport for a given site exist in the literature (e.g., Savannah River Site – Kaplan et al., 1994 and Dai et al., 2002; Los Alamos National Laboratory – Penrose et al., 1990 and Marty et al., 1997). Review of these findings point to the critical need to 1) insure use and documentation of appropriate well design, construction, and screen development and/or re-development procedures, 2) employ sampling and analysis protocols that avoid the generation of analytical artifacts, and 3) develop a comprehensive knowledge of the potential sources of the contaminant along transport pathways throughout the plume (e.g., Dai et al., 2002; see Section 1.5.3 below). These observations suggest that colloidal transport is often invoked to explain apparent enhanced contaminant transport in place of direct observation of colloids along plausible transport pathways. In general, it appears that the common approach of identifying the presence of colloidal matter through comparison of filtered and unfiltered water samples will not be a reliable approach for confirming this transport mechanism for radionuclides. It is recommended that characterization of the chemical composition and structural identity of the purported colloids be determined in order to evaluate whether the identified solids are likely derived from the aquifer solids along transport pathways or if they are an artifact resulting from improper well development and/or sampling protocols. There is evidence that colloid mobilization may be short-lived within a given aquifer due to the high surface area and reactivity of colloidal materials (e.g., Miekeley et al., 1992). This is of particular importance for the development of contaminant transport models that may be used to project plume expansion or contraction. At present, the level of uncertainty relative to the capability to directly observe and model colloidal transport in ground water should be considered to be high. A brief review of sampling and analysis technologies for the collection and analysis of colloidal phases in ground water is provided below (Section 1.5.4) for sites where colloidal transport appears to play a critical role in contaminant transport.

1.5 Site Characterization

The objective of characterization efforts at a site where MNA is being considered as a component of the ground-water remedy is to evaluate the performance characteristics of existing conditions within the aquifer to achieve cleanup goals. Unlike engineered remedies where certain basic performance characteristics are generally understood, selection of MNA depends on developing detailed understanding of the active attenuation mechanisms within the plume and evaluating how changes in ground-water chemistry may impact the rate, capacity and long-term stability of contaminant attenuation. In order to develop a mechanistic understanding of the attenuation process(es) active within a plume, acquisition of characterization data describing hydrologic conditions, ground-water chemistry, contaminant speciation, and factors controlling solid-liquid partitioning is needed. Review of the types of required data, approaches to obtain these data, and the approaches to make use of these data to assess the feasibility of MNA selection was provided in Volume 1 of this document (USEPA, 2007a). Specifically, discussion within Volume 1 covered characterization of site hydrology (Section IIIA), characterization of ground-water chemistry including aqueous contaminant speciation (Section IIIB.1), and characterization of aquifer solids and the product(s) of contaminant immobilization reactions (Section IIIB.2). These characterization tasks also apply to the radionuclides discussed within this volume and specific recommendations are included in the individual contaminant chapters. The objective of this section is to highlight characteristics and analytical methodologies that are unique to contaminants subject to radioactive decay.

1.5.1 Overview of Methods for Radionuclide Measurement

As with stable elements, detection of radionuclides can be achieved using mass-based techniques (e.g., mass spectrometery) or the measurement of the interaction of various sources of electromagnetic radiation with the target radionuclide or chemical complexes it may form with other chemical constituents (e.g., absorption of radiation in the ultraviolet or visible spectrum). In general, the sensitivity of chemical methods based on absorption or emission of electromagnetic radiation is not sufficient to achieve detection levels comparable to mass-equivalent regulatory levels for many of the radionuclides of concern. Exceptions to this generalization are provided in the individual contaminant chapters included later in this volume, where applicable. Absorption- or emission-based chemical methods are also limited to measurement of total radionuclide abundance and are unable to differentiate between isotopes of a given element. However, the property of radioactive decay provides another approach to uniquely identify and quantify radionuclides. Radioactive decay results in the formation of a daughter element that may be unique to the decay event, and it also may result in the production of energetic particles (e.g., alpha particles) and/or radiation (e.g., gamma radiation) possessing energies that are also specific to the decay process (e.g., as reviewed in USEPA, 2006b). Thus, detection of these inherent products of the decay process can be used as an approach to uniquely identify and quantify the parent radionuclide. Since radioactive decay reactions follow known mechanisms with fixed reaction rates, it is generally feasible to measure the products of decay and calculate the activity/mass of the parent radionuclide that was necessary to produce the observed product activity/mass. As discussed in USEPA (2006b), these methods may be used for the purpose of detecting the presence of a particular radionuclide (i.e., screening methodologies) and the quantification of the activity- or mass-based concentration in the sampled medium.

There are some limitations to the use of radioactive decay as the basis for radionuclide detection. A notable example is the inability to distinguish ^{239}Pu and ^{240}Pu using alpha particle detection, since decay of both radionuclides produces alpha particles with energies that are unresolved employing available energy detection devices (e.g., Dai et al., 2002). The following discussion provides a brief overview of the more commonly used analytical methods with published standard approaches, as well as more recently developed mass-based methodologies that are seeing greater application for characterization of ground water with radionuclide contamination (e.g., Hou and Roos, 2008). It should be noted that many radionuclides of concern have low specific activities (e.g., ^{238}U or ^{235}U), and their measurement may be more appropriately addressed using mass-based methodologies (See Section 1.5.1.2 and individual radionuclide chapters for additional information.)

1.5.1.1 Radiometric Techniques

A recent compilation of radiometric methods used for site characterization to support environmental restoration efforts has been published by the USEPA (2007c). Section 6.0 of this compilation of standard analytical methods (SAM; Version 3.1; available at *http://www.epa.gov/nhsrc/pubs/reportSAM030107.pdf*) includes radiochemical methods that have a high likelihood of assuring analytical consistency. Criteria used to make this characterization included the historical use of the referenced methods and the availability of laboratory facilities across the nation with the capability and capacity to conduct sample analyses. The methods listed in this compilation include only radiometric methods based on the detection and quantification of gamma rays, alpha particles, or beta particles emitted during decay of the targeted radionuclide or a common daughter product, where the activity or mass of the radionuclide is derived using known characteristics of the decay process. The listed methods address analysis of both liquid and solid samples and sample preparation procedures needed based on requirements of the detection method. The methods can be used for determination of qualitative (i.e., radionuclide identification) and quantitative (i.e., radionuclide activity or mass) information for the sample matrix.

A broader list of radiochemical methods is provided in the Multi-Agency Radiological Laboratory Analytical Protocols (MARLAP) Manual available at *http://www.epa.gov/radiation/marlap/manual.html*. Analysis of liquid samples (or solids following dissolution) using the radiometric techniques described above requires significant sample processing 1) to isolate radionuclides of interest from potentially interfering matrix components, and 2) to present the sample in a configuration that optimizes counting statistics (e.g., to minimize absorption of alpha or beta particles prior to detection). A number of methods and techniques employed to separate and purify radionuclides contained in environmental samples are described in Chapter 14 (Separation Techniques) of the MARLAP Manual posted at the website listed above (USEPA, 2004b). Details on the analytical requirements, potential interferences and performance characteristics for the various radiometric techniques are provided in Chapter 15 of the MARLAP Manual (Quantification of Radionuclides; USEPA, 2004b). This document also provides discussion of the use of liquid scintillation methods in which decay of a radionuclide excites a compound ("fluor") that produces fluorescent radiation.

It is recommended that site managers also consult a concise compendium of methods for radionuclide detection and quantification in soils and water, entitled "Inventory of Radiological Methods" (USEPA, 2006b), which is available at *http://www.epa.gov/narel/IRM_Final.pdf*. In this document, a summary of nominal minimum detection limits for the various radionuclide detection methods is provided in Figure 2 (pg. 41) and a list of applicable methods for the radionuclides discussed in this volume is provided in Table 10 (pg. 42) of this publication (USEPA, 2006b).

Recent developments in the design of analytical systems that combine the steps of radionuclide isolation from the sample matrix in-line with various radiometric detection systems have facilitated the application of radiometric measurements in the field. Grate et al. (2008) provide a comprehensive review of the types of systems that have been developed along with their performance characteristics for detection and quantification of radionuclides in ground water. In situ sensors for long-term monitoring applications without use of consumable reagents have also been developed (e.g., Egorov et al., 2001) for the quantification of ^{99}Tc and ^{90}Sr in ground water. These analytical platforms will help address the need to collect spatial and temporal information on ground-water plume behavior. For contaminants in which desired detection limits can be achieved with short detector count times, these techniques provide the means to adjust sampling activities in the field.

1.5.1.2 Mass-based Techniques

For very long-lived radionuclides (those with half-lives over 10,000 years, e.g., $^{234/235/238}$U, $^{239/240/244}$Pu, ^{99}Tc, ^{129}I), mass-based techniques may be faster and more sensitive than nuclear-decay emission analyses. More recent environmental applications include the use of mass-based techniques for the analysis of nuclides with intermediate half lives, including ^{90}Sr, ^{226}Ra, and $^{135/137}$Cs. In addition, sample preparation for mass-based techniques can avoid some of the radionuclide separation and purification steps required for nuclear-decay emission analyses, providing added savings in time and labor, which is particularly true for alpha spectroscopy where sample self-adsorption concerns can lead to extensive labor intensive sample preparation. Becker (2003) and Lariviere et al. (2006) provide recent reviews of mass spectrometry applications for the determination of radionuclide concentrations in environmental samples. The sensitivity and mass-selectivity of these approaches, along with the ability to circumvent matrix and isobaric interferences, have significantly increased the utility of these methods. This can be further improved with the use of on-line techniques for the separation and enrichment of the targeted radionuclide from the sample matrix (e.g., Egorov et al., 2001; Miro and Hansen, 2006), similar to approaches used for radiometric measurements. These methods also provide the opportunity to simultaneously measure the concentrations of a range of stable isotopes that may provide information necessary to uniquely identify potential waste sources and/or ground-water transport pathways within the aquifer.

1.5.1.3 Radionuclide In-growth Corrections

As previously discussed, the activity and mass of a radionuclide continuously decreases in time due to radioactive decay (in the absence of production from decay of progenitors that may exist in contaminant source areas; see Section 1.5.3.2). For short-lived radionuclides, this may impact analytical results, since contaminant measurements are typically conducted after a period of time has elapsed since the time of sample collection. Since sample collection is conducted to provide a snapshot of plume conditions at a particular point in time, it is critical that analytical data for radionuclides be adjusted to account for decay losses during the interval between sample collection and analysis. Specifically, there is no method of preservation that can halt contaminant losses due to radioactive decay. These corrections apply both for situations where the target radionuclide is the parent isotope (i.e., decreasing activity with time) or a daughter isotope produced from decay of other radionuclides that may be present in the sample (i.e., increasing activity with time). An example of this latter phenomenon was illustrated by Dai et al. (2002) where a fraction of ^{240}Pu in ground-water samples was produced from decay of ^{244}Cm that was also present in the sample during storage. Without correction for production of ^{240}Pu during storage, the activities of this radionuclide would have been biased high, providing an inaccurate picture of the activity or concentration of ^{240}Pu at the time of sampling from within the plume. In this situation, ^{240}Pu accumulates in the sample with time due to its long half-life for radioactive decay. Due to the relatively low regulatory benchmarks for activity- and mass-based radionuclide concentrations in ground water, radionuclide in-growth corrections may be important for accurate descriptions of plume characteristics in time.

1.5.2 Chemical and Redox Speciation

Determination of the chemical speciation and redox state of a radionuclide in ground water is critical for assessing the factors controlling contaminant attenuation (or mobilization). As a point of reference, uranium is typically more mobile in its oxidized form [U(VI)], although the uranyl cation may adsorb onto mineral surfaces. Elevated alkalinity can suppress adsorption of the uranyl cation through formation of soluble carbonate complexes (Um et al., 2007). Confirmation of the speciation of uranium for this situation would be best achieved through confirmation of the predominant oxidation state of uranium in solution. For uranium, it would be possible to measure the relative proportion of U(VI) using kinetic phosphorimetry, since only the oxidized species is luminescent (Brina and Miller, 1992). Determination of the fraction of uranyl complexed with carbonate would then necessitate measurement of alkalinity (or inorganic carbon) with calculation of carbonate species using a chemical speciation model. Approaches to determine either redox state or solution speciation for specific radionuclides are provided in individual contaminant chapters later in this volume, where available. May et al. (2008) provide a recent review of methodologies that have been used to determine aqueous speciation of long-lived radionuclides in environmental samples, including evaluation of the analytical merits of the various methods for determining contaminant speciation.

1.5.3 Multiple Sources for Radionuclide of Concern

Characterization of radionuclide transport within a plume is commonly evaluated through the installation and sampling of multiple monitoring points within the aquifer. The transport behavior of a specific radionuclide is then inferred through measurement of the specific activity or mass concentration of the radionuclide in space and time relative to the measured velocity of ground-water flow through the aquifer. In many cases, evaluation of the physicochemical processes controlling transport of a specific radionuclide may be based on assumptions about the characteristics of fluid transport or the potential source(s) of the radionuclide. Since knowledge of source term characteristics is critical to assessing attenuation mechanisms and/or capacity within the aquifer, proper identification of the apparent up gradient source of the radionuclide at any location within an apparent plume is important to development of an accurate conceptualization of contaminant transport. Two issues that are important to consider relative to proper identification of the contaminant source include: 1) differentiating whether a single source term or multiple source terms contribute to the contaminant mass/activity throughout the plume, and 2) determination of whether the specific radionuclide was present in the initial source zone or whether it is a product of decay of more mobile parent radionuclides moving within the plume.

1.5.3.1 Isotopic Composition for Radionuclide Source Discrimination

Ground-water plumes may be derived from one or multiple sources at a site. In addition, large sites may have multiple source areas that contribute to multiple plumes that may or may not intersect at some location within the aquifer. Since determination of the capacity of the aquifer to attenuate the mass of contaminant within the plume is identified as a critical component of site characterization (Tier III in Section 1.3.3), information on the mass of contaminant being transported along ground-water flow paths within the aquifer needs to be determined. Radionuclide contaminants at a site may be derived from anthropogenic (i.e., historical disposal of process wastes) or natural sources. Comparison of the distribution of isotopes for a given radionuclide near suspected source areas and down gradient within a plume provides an approach to determine whether a single or multiple areas of contamination contribute to the mass of contaminant within the aquifer where MNA is being evaluated as a component of the ground-water remedy (e.g., Ketterer et al., 2004). This characterization approach can be supplemented with analysis of 1) unregulated radionuclides that may be characteristic of a particular waste stream and transported with the contaminant of concern (Brown et al., 2006; ruthenium as a tracer for different technetium sources) or 2) the distribution of stable isotopes for an element that is characteristic of the hydrologic source of ground water observed at a given location within a plume. As an example, studies examining the distribution of radionuclides and stable isotopes have been conducted at the Hanford Site in Richland, Washington to aid in differentiating contaminant sources for ground-water plumes at various locations throughout the site (Dresel et al., 2002; Christensen et al., 2004; Christensen et al., 2007). This information has been used to constrain interpretations of ground-water transport and projections of the mass of contaminants potentially being transported along critical transport pathways.

For radionuclide contaminants that may be derived from both anthropogenic and natural sources, determination of the contaminant isotopic distribution may provide one line of evidence for identifying the predominant contaminant source. For anthropogenic sources, knowledge of the manufacturing or utilization process may also be important for situations where characteristics of the raw materials may have varied over the lifetime of the process. For example, the manufacture of targets for production of plutonium may have made use of depleted or natural forms of uranium. Uranium also provides an example of a radionuclide that may have been present as a component of a waste stream disposed on site or derived from aquifer solids due to leaching reactions driven by movement of the plume through the aquifer. For example, isotopic ratios of ^{235}U:^{238}U or ^{236}U:^{238}U in ground water or aquifer solids within the plume may provide a signature for an anthropogenic source of this radionuclide (e.g., Marsden et al., 2001; Howe et al., 2002). This approach is applicable at sites where wastes may have been derived from operation of nuclear reactors or the processing of uranium fuels to support nuclear reactions. The unstable isotope ^{236}U does occur in nature (2.3415×10^7 yr half-life), but only at ultra-trace concentrations with a ^{236}U:^{238}U atom ratio of 10^{-14} (Zhao et al., 1997). The ratio of these isotopes is anticipated to be higher in wastes derived from reactor operations due to the production of elevated levels of ^{236}U during neutron irradiation of ^{235}U. In addition, the ratio of ^{235}U:^{238}U is anticipated to be higher in waste materials derived from use of ^{235}U due to enrichment of this radioisotope relative to ^{238}U in materials used in reactor operation (relative natural abundance of ^{238}U and ^{235}U is 99.275% and 0.720%, respectively). Conversely, the ratio of ^{235}U:^{238}U is anticipated to be lower in waste materials with depleted levels of ^{235}U due to extraction processes to produce a material enriched in ^{235}U for reaction operations (Meinrath et al., 2003). As illustrated by these possible scenarios, determination of isotopic ratios in environmental samples from a contaminated site provides a potentially important tool for determining contaminant sources and tracking contaminant transport within an aquifer.

1.5.3.2 Identification of Progenitors

Radionuclides in a contaminant plume may be present as a native component or as a daughter product from decay of *progenitor* radionuclides within a waste stream. Knowledge of process history for radionuclide production at a site and source term composition can help in the identification of possible progenitors. Since the progenitor and daughter radionuclides may have differing transport properties, this may complicate determination of the mechanism controlling transport of the daughter radionuclide (i.e., contaminant of concern) at different locations within the aquifer. Dai et al. (2002) provide a useful example where the presence of progenitors whose decay produces plutonium daughter products could potentially lead to misidentification of the controlling transport mechanism. In their field research, these authors identified that ^{244}Cm decay led to significant production of ^{240}Pu within a ground-water plume. The ^{244}Cm was present in a waste disposal area that was located along the path of an apparent single plume of plutonium within the aquifer. In previous research, Kaplan et al. (1994) had rationalized the apparently long transport distances for plutonium as being due mobile colloids. Through examination of the activities of plutonium isotopes and potential curium and/or americium progenitors documented in records of site activities and waste production, Dai et al. (2002) were able to demonstrate that ^{240}Pu observed at large distances from the source area was actually derived from in-growth from decay of ^{244}Cm that was more mobile in ground water.

Examples of possible progenitors that could lead to in-growth of ^{239}Pu or ^{240}Pu are illustrated in Table 1.3. The relative importance of progenitors for a given site will depend on the types of radionuclides in various waste sources, the total activity and half-life of the progenitors, and the relative mobility of the progenitors. As illustrated in Table 1.3, progenitors with half-lives that are significantly shorter than the daughter radionuclide of concern will be the ones that are most likely to cause significant contributions from in-growth. In addition, the mobility of the progenitor relative to the chemical conditions within the plume may also need to be evaluated as a part of the site characterization effort. The potential for contaminant in-growth during plume transport points to the importance of understanding the characteristics of potential waste sources relative to the types of radionuclides that might be present in addition to those that may be specifically targeted from a regulatory perspective.

Table 1.3 Illustration of potential decay paths from different progenitor sources leading to production of either ^{239}Pu or ^{240}Pu within a plume. Due to the relatively short half-life for the progenitor radioisotopes, appreciable activities of ^{240}Pu or ^{239}Pu may result if appreciable activities of the progenitors are present in the plume. Determination of possible decay paths to the target radionuclide was based on examination of the Chart of Nuclides (*http://www.nndc.bnl.gov/chart/*) maintained by the Brookhaven National Laboratory, National Nuclear Data Center relative to possible decay paths based on decay modes identified in the Appendix (EC = electron capture, β^- = electron emission, α = alpha decay). Decay half-life data were obtained using the WinChain program that provides electronic access to the ICRP38 Nuclear Decay Data Files (ICRP, 1983; Eckerman et al., 1994; m = minutes, h = hours, d = days, y = years). WinChain is a public domain software application available for download from Oak Ridge National Laboratory (*http://ordose.ornl.gov/downloads.html*).

Contaminant Radionuclide	Decay Progenitor	Decay Mode	Progenitor Decay Half-life
^{239}Pu	^{239}Np	β^-	2.355 d
	^{243}Cm	α	28.5 d
	^{243}Am (via ^{239}Np)	α (β^-)	7380 y
^{240}Pu	^{240}Np	β^-	65 m
	^{244}Cm	α	18.11 y
	^{244}Am (via ^{244}Cm)	β^- (α)	10.1 h

1.5.4 Procedures for Collection of Colloidal Radionuclide Forms

Determination of whether colloidal transport is a factor for radionuclide transport in ground water will be predicated on implementation of well installation, development, and sampling protocols that avoid potential artifacts leading to colloidal loss or production of colloidal material not present within the plume. As previously discussed in Volume 1 (USEPA, 2007a; Sections IIA.2.1 and IIIB.1.1), improper development of newly installed well screens and/or purging at high volumetric rates during sampling can also lead to the production of suspended solids that may mistakenly be identified as mobile colloids within the aquifer. Well installation procedures may be a source of suspended solids retrieved during well sampling. Two common types of solids include fine-grained materials used in drilling fluids (e.g., bentonite) and colloidal-sized aquifer solids either dislodged from the matrix or resulting from breakdown of larger-sized matrix particles due to physical forces from the drilling activity. Introduction of anthropogenic, fine-grained materials may be avoided through the use of drilling methods that do not require lubricants such as clay suspensions or through the use of water as the drilling fluid. Aggressive development of the well (e.g., surging and/or high pumping rates) can be used to remove these types of solids from within the well screen and the portion of the aquifer in contact with the screened interval. Another potential source of artifactual solids retrieved during sampling may be due to precipitated solids that accumulate on well-screen materials and are physically dislodged by the sampling activity (e.g., Houben, 2006). An example of this type of solid is the accumulation of iron oxides that result from the oxidation and precipitation of ferrous iron during natural or induced intrusions of dissolved oxygen within the screened interval of the aquifer. These types of solid accumulations may be susceptible to being dislodged at the beginning of well purging to establish stabilization for sampling. From this perspective, it is recommended that the well screen be redeveloped, when feasible, prior to initiating low-flow purging to establish stabilization of field parameters.

Another source for colloidal solids in the sampled water may derive from solid precipitation reactions occurring at the land surface during sample handling (e.g., Nilsson et al., 2008). As illustrated by Dai et al. (2002), Buesseler et al. (2003), and Hassellöv et al. (2007), formation of colloidal iron oxyhydroxides is a potential artifact when sampling from ground-water plumes under iron-reducing conditions. These authors have developed sampling procedures that prevent exposure to air, and, therefore, reduce the potential for rapid oxidation and precipitation of iron oxyhydroxides. Characterization of the chemical composition or mineralogy of recovered colloids provides one approach to assess the potential for artifacts. For example, the presence of fine-grained iron oxyhydroxides in ground water with elevated ferrous iron concentrations [>10 mg/L Fe(II)] is an indication that iron oxidation-precipitation reactions may be occurring during sample collection or processing. The use of procedures such as cross-flow filtration may also be necessitated to reliably isolate colloids from the ground-water sample with minimal introduction of artifacts (e.g., Dai et al., 2002; Hassellöv et al., 2007). As shown in the literature (e.g., Baumann et al., 2006; Baik et al., 2007), colloidal fractions that serve as carriers for radionuclide transport may reside in multiple size fractions that would typically pass a 0.45 μm membrane filter. Thus, use of a conventional filtration pore size such as 0.45 μm will not provide a reasonable means for differentiating between colloidal and truly dissolved contaminant forms in sampled ground water.

In general, colloidal sampling procedures have not progressed to the point of being a routine practice during ground-water sampling. Given that many of the regulatory limits for radionuclides equate to extremely low mass-based concentrations, there is a need to develop consensus approaches that reliably sample colloidal forms of contaminants from ground water. Ultimately, it is recommended that ground-water sampling for the purpose of evaluating the presence of mobile colloids be conducted using permanent monitoring points that have a clear record of well construction (including description of granular solid materials employed during drilling and screen placement within the formation), procedures used for screen development, and the data used to evaluate the adequacy of well development and sampling procedures.

1.5.5 Aquifer Solids

The objectives and methodologies presented in Sections IIIB and IIIC in Volume 1 (USEPA, 2007a) for solid phase characterization to support evaluation of MNA as a component of a ground-water remedy are directly applicable to radionuclides. In general, characterization of radionuclide speciation along with the determination of abiotic or biotic solid components that participate in contaminant immobilization represent the primary data requirements. Many of the radionuclides discussed in this volume can exist in multiple oxidation states in ground-water systems (e.g., uranium, plutonium, americium, technetium). Changes in oxidation state can dramatically alter transport characteristics of these radionuclides. An example of this phenomenon is the influence of reduction-oxidation reactions that transform uranium between U(VI) and U(IV) oxidation states. Different pathways for sorption or precipitation exist for U(VI) and U(IV), thus identification of the reaction mechanism controlling uranium immobilization will, in part, depend on knowledge of the oxidation state of uranium in aquifer solids. Knowledge of the controlling immobilization mechanism will subsequently govern the approach for assessing the capacity and stability of the attenuation process.

An additional consideration for characterization of radionuclide speciation in aquifer solids is the distribution of isotopes of the element. Methods are available for measuring isotope distributions in solid samples real-time in the field (ITRC, 2006) or in the laboratory using established procedures (USEPA, 2004b; USEPA, 2006b; USEPA, 2007d). For some of the radionuclides addressed in this document, there are no natural sources for aquifer solids (e.g., ^{240}Pu). However, several of the radionuclides addressed in this document will have natural sources due to the presence and decay of natural uranium (e.g., ^{234}U, ^{230}Th, ^{226}Ra, and ^{222}Rn from decay of ^{238}U) or other naturally occurring elements for which radioisotopic forms exist. In addition, stable isotopic forms exist for some radionuclides addressed in this document (e.g., strontium). The potential presence of multiple isotopes of a given element within the solid matrix points to the need to measure specific isotopes during analyses that depend on mass-specific detection. An example situation could be the application of extraction-based approaches to determine either total contaminant mass or chemical speciation within aquifer solids (e.g., USEPA, 2007a, Section IIIB.2; Filgueiras et al., 2002; Bacon and Davison, 2008). The distribution of isotopes within the aquifer solids can also be used to verify active immobilization reactions. It is anticipated that the distribution of long-lived isotopes in the solid matrix will reflect the isotopic distribution in ground water in portions of the plume where immobilization is actively occurring (Payne and Airey, 2006).

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Tritium

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Occurrence and Distribution

Tritium (^3H) is formed through natural and anthropogenic processes. Tritium is formed in the upper atmosphere through the interaction of fast neutrons with nitrogen (Jacobs, 1968; MacKenzie, 2000). Natural background levels have risen since weapons testing of nuclear devices from background levels of 1 to 10 tritium units to several hundred tritium units in the late 1960s (e.g., Egboka et al., 1983). [Tritium unit (TU) denotes the number of tritium atoms per 10^{18} atoms of hydrogen (Jacobs, 1968) and is calculated by the expression, TU = ^3H activity/(10^{18} * ^1H activity).] Levels of ^3H have since returned to near background levels as a result of the atmospheric detonation moratorium. Anthropogenic sources of ^3H derive from the production, use, and reprocessing of nuclear materials (Jacobs, 1968) or from land disposal of commercial products that incorporate ^3H as a functional component (Mutch and Mahony, 2008). Along with uranium, tritium is the most common radioactive contaminant found in ground water on U. S. Department of Energy (DOE) sites; identified on 12 of the 18 DOE facilities (DOE, 1992).

Geochemistry and Attenuation Processes

Radioactive Decay

Hydrogen has three isotopes: stable protium (^1H), stable deuterium (^2H), and radioactive tritium (^3H). The relative abundances of ^1H, ^2H, and ^3H in natural water are 99.984, 0.016, and 1×10^{-15} percent, respectively (Freeze and Cherry, 1979). Tritium has a half life for radioactive decay of 12.3 years, and disintegrates into stable ^3He by emission of a beta particle. Tritium oxidizes rapidly to form tritiated water, $^1HO^3H$, and its distribution in nature is controlled by the hydrologic cycle (Jacobs, 1968).

Adsorption

Tritium is generally considered not to sorb to aquifer solids and is typically assigned a partition coefficient, K_d, of 0 mL/g to describe its partitioning to geological solids (McKinley and Scholtis, 1993). All field studies indicate that tritium movement is indistinguishable from water movement (USEPA, 1999). Some non-zero K_d values for tritium were reported in the K_d compilation put together by Thibault et al. (1990). These non-zero K_d values were as great as 0.1 mL/g, but it is unclear what specific mechanism may have produced these observed non-zero values. Contemporary evaluations of ^3H transport in ground water assume conservative behavior for this constituent (e.g., Hu et al., 2008).

Site Characterization

Overview

Attenuation of ^3H might be achieved through radioactive decay (Table 2.1). Two factors that will dictate the adequacy of attenuation via radioactive decay include the rate of water transport and the total mass and release rate of ^3H into the subsurface plume. Evaluation of whether radioactive decay is sufficient to achieve cleanup goals will necessitate developing knowledge of the characteristics of ground-water flow throughout the plume, as well as the total activity/mass of ^3H within the plume and entering from uncontrolled source areas.

Table 2.1 Natural attenuation and mobilization pathways for tritium.

Attenuation Processes	*Mobilization Processes*	*Characterization Approach*
Radioactive decay	Not applicable	Determination of ground-water velocity along relevant transport pathways and contaminant mass release rate from source areas.

Aqueous Measurements

Relative to determination of the spatial distribution and temporal variations in ^3H concentration/activity within the plume, methods for the preservation and analysis of ^3H in ground water are reviewed in USEPA (2006; Section 3.2.1 and Section 4, Table 10, respectively). As a low energy beta-emitter, ^3H is most commonly analyzed using liquid scintillation radiometric methods. Possible interferences to this method include the presence of other radioisotopes emitting beta/alpha particles or gamma rays (e.g., ^{60}Co, ^{88}Y, ^{137}Cs), as well as other constituents that cause coloration of the water sample and potentially quench detection of fluorescence from the scintillation reaction. Warwick et al. (1999) have documented a simple distillation methodology to minimize analytical bias from these potential interferences. For sites with buried contaminant sources in the unsaturated zone, surface infiltration into the underlying saturated aquifer or periodic saturation from water table fluctuations may serve as a continuing source to a ^3H plume. Mapping out the locations and dimensions of these unsaturated zone sources may prove critical to reliable assessment of attenuation capacity within the aquifer. Field studies have shown that determination of $^3He/^4He$ ratios in soil gas from direct-push wells, via mass spectrometric detection in gas samples, may provide a useful technique to characterize contaminant source areas (Olsen et al., 2001; Peterson et al., 2002; Olsen et al., 2006). Since radioactive decay of ^{3}H produces ^{3}He, elevated ^{3}He/^{4}He ratios provide a potential signature of an elevated source of subsurface ^{3}H. While this analytical approach is currently not applied in a routine manner, it may provide critical information for assessment of attenuation potential. In addition, measurement of ^{3}H, ^{3}He, and ^{4}He has been used to track sources of water in the subsurface, including estimates of the age of ground water (e.g., Egboka et al., 1983; Poreda et al., 1988; Visser et al., 2007). For this purpose, it is important to assess whether isolated sources of dissolved gases, e.g., from volatile organic compounds, methane production, and/or N_2 production from denitrification, may influence the partitioning of ^{3}H, ^{3}He, and ^{4}He within ground-water samples collected from well screens positioned along the subsurface transport pathway being investigated (Visser et al., 2009). This information can supplement characterization of the hydrologic system influencing contaminant transport through the plume.

Long-term Stability and Capacity

Since immobilization is not an active mechanism for ^{3}H attenuation in ground water, assessment of long-term stability is not a factor. The long-term capacity for ^{3}H attenuation within a plume will be dictated by the relative rate of ground-water flow along relevant transport pathways compared to the rate for radioactive decay, given a known flux of ^{3}H entering the plume. Thus, a critical factor for assessing the overall capacity of the aquifer for attenuation will be evaluation of the mass flux of ^{3}H moving through the plume relative to the rate of water movement through the aquifer. Radioactive decay may be sufficient to prevent plume expansion, but this is not likely for sites with an uncontrolled source of ^{3}H entering the subsurface and/or characteristic times for ground-water transport that are significantly shorter than the half-life of radioactive decay. Relative to ^{3}H release from uncontrolled source areas, knowledge of the total contaminant mass as well as the rate and frequency of release into the saturated aquifer needs to be developed. As an example, Taffet et al. (1991) have shown that fluctuations in the water table elevation due to periodic infiltration or recharge events can result in periodic flushing of ^{3}H from typically unsaturated zones into the saturated aquifer. In order to make a reliable assessment of the mass/activity flux of ^{3}H into the plume, it will be important to understand the characteristics of the hydrogeologic system and the dynamics of water and contaminant transfer from contaminant source areas into the plume.

Tiered Analysis

Determination of the viability of ^{3}H remediation in ground water via monitored natural attenuation will depend upon proper assessment of contaminant loading to the aquifer relative to the velocity of ground-water travel along relevant transport pathways to the point(s) of compliance. The goal of site assessment is to demonstrate that radioactive decay is adequate to meet cleanup goals given current and projected hydrologic conditions for the site. The following tiered analysis structure for site characterization provides an approach to evaluate candidate sites and define the potential limitations of MNA as part of a remedy for ground-water cleanup.

Tier I. Site characterization under Tier I will involve demonstration that the ground-water plume is static or shrinking, has not reached compliance boundaries, and does not impact existing water supplies. It is also important at this stage of the site evaluation to determine source term characteristics such as the inventory of contaminant mass and the current and historical rate of release into the subsurface. Acquisition of this information in combination with identification of a stable plume provides justification for proceeding to Tier II characterization efforts.

Tier II. Under Tier II, the apparent rate of attenuation is determined. Estimates of a site attenuation rate(s) can be assessed via a well transect along the ground-water flow path. In addition, time-series data may be collected at one or more monitoring points within the plume (USEPA, 2007; Section IIIA.5). Since radioactive decay will be the dominant mechanism controlling ^{3}H attenuation, determination of the velocity of ground-water flow along relevant transport pathways will be critical to evaluating the potential cleanup time frame. This information will allow assessment of the relative timescales for contaminant attenuation and fluid transport and determination of whether remediation objectives can be met within the required regulatory time frame. Determination of the adequacy of radioactive decay to achieve cleanup goals will necessitate detailed analysis of system hydrology relative to flow pathway(s), flow velocity, and temporal variations in flow velocity and/or direction within the boundaries of the plume. This information, in combination with knowledge of contaminant source location(s), tritium mass, and release characteristics, can be employed to develop a decay-transport model to project ^{3}H activity/concentration distribution throughout the plume (e.g., see Figure 1.5). The demonstration of concurrence between conceptual and mathematical models describing tritium transport will entail development of site-specific parameterization of ground-water flow along relevant transport pathways.

Tier III. Under Tier III, it will be important to assess whether the capacity of the system is adequate to sustain ^{3}H attenuation (e.g., prevent plume expansion) relative to the mass of the contaminant being transported through the plume. Two principal factors that may influence capacity include changes in water transport and/or changes in ^{3}H mass/activity flux entering the plume. As identified by Taffet et al. (1991), source release characteristics may be influenced by the physical location of sources within the subsurface relative to the ground-water table. Fluctuations in infiltration through shallow, unsaturated zones and/or water table elevations within the aquifer due to variations in recharge may lead to periodic increases in ^{3}H release from contaminant source areas. Changes in land usage (including at recharge zones, wetlands, and over the contaminated site) and/or ground-water withdrawals from the aquifer may influence ground-water flow direction and velocity (USEPA, 2007; Section IIIA), which in turn directly influences ^{3}H travel time. It is recommended that additional tritium transport modeling be included to evaluate the impact of these various scenarios to be assured that these perturbations do not significantly diminish attenuation. If monitoring data and model projections support adequate capacity for ^{3}H attenuation within the plume, then the site characterization effort can progress to Tier IV.

Tier IV. Finally, under Tier IV a monitoring plan is established along with contingency plans in the event of MNA failure. It is recommended that the monitoring plan be designed to establish both continued plume stability and to identify changes in ground-water levels, flow velocity, or direction that might influence the efficiency of tritium removal via radioactive decay. In particular, sites at which residual tritium sources are left in unsaturated zones should include monitoring points to assess changes in the release of tritium to the saturated aquifer due to increased surface infiltration or rises in the ground-water table. Changes in system hydraulics may serve as monitoring triggers for potential MNA failure. In this instance, a contingency plan can be implemented that incorporates engineered strategies to arrest possible plume expansion beyond compliance boundaries. Possible strategies to prevent plume expansion include the installation of barriers to minimize tritium migration from source areas and/or ground-water extraction with surface treatment.

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Radon

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Occurrence and Distribution

Radon is a noble gas derived from the decay of uranium and thorium radioisotopes in geologic materials. Three common radioisotopic forms of this element include ^{222}Rn ("radon"), ^{220}Rn ("thoron"), and ^{219}Rn ("actinon"). Due to very short half-lives, ^{220}Rn ($t_{1/2}$ = 55.6 sec) and ^{219}Rn ($t_{1/2}$ = 3.96 sec) are not commonly detected in ground water. Radon (^{222}Rn) is produced from radioactive decay of ^{226}Ra and is part of the ^{238}U decay series. Radon in ground water may be derived from radioactive decay of mobile forms of ^{226}Ra or due to ejection from immobile aquifer solids as a result of alpha-recoil from ^{226}Ra (e.g., Hoehn et al., 1992; Skeppstrom and Olofsson, 2007). Radon is present in unimpacted ground-water systems due to the presence of naturally-occurring ^{238}U in rocks and soils (e.g., Hair and Baldwin, 1995; Veeger and Ruderman, 1998; Hughes et al., 2005; Campbell, 2006). Uranium concentrations in geological materials vary greatly (Fayek and Kyser, 1999; Wiegand, 2001) and have been shown by several researchers to have a strong correlation to ground-water radon concentrations (e.g., Vinson et al., 2009). For example, the relationship between granite bedrock and high radon levels has been observed (e.g., Sasser and Watson, 1978). Elevated radon concentrations occur near or within mines, especially uranium mines and/or uranium mill tailings (e.g., Landa and Gray, 1995; USEPA, 2008), and where radioactive waste is disposed in the subsurface. All categories of radioactive waste (high-level, low-level, and transuranic waste) contain concentrated levels of parent isotopes to ^{222}Rn (e.g., see Figure 3.1).

Geochemistry and Attenuation Processes

Radioactive Decay

Radon is a radioactive noble gas that is colorless and odorless. Radon has a half-life of 3.82 days and is formed through alpha decay of ^{226}Ra ($t_{1/2}$ = 1600 yr) in the ^{238}U decay series (Figure 3.1). During decay, ^{222}Rn emits a 5.0 MeV alpha particle. The decay products of ^{222}Rn have short half lives and variously emit alpha particles (e.g., 6.0 MeV, ^{218}Po; 7.6 MeV ^{214}Po), beta particles (e.g., 295 keV, ^{214}Pb; 352 keV, ^{214}Bi), and/or gamma radiation (e.g., 295 and 352 keV, ^{214}Pb; 609 keV, ^{214}Bi) before forming stable ^{206}Pb (Figure 3.2). As discussed later, emitted radiation from ^{222}Rn or its short-lived daughters provides for multiple approaches to quantify the concentration/activity of this radionuclide.

Aqueous Chemistry

Radon is classified as a noble gas in the periodic table of elements and is primarily transported as a dissolved gas in ground water (USEPA, 1999). Of the noble gases, radon has the highest reported solubility in water (Villalba et al., 2005). However, radon will tend to partition into air in soil pores in the variably saturated zone that is in contact with the ground-water table. Since ^{222}Rn is produced from the radioactive decay of ^{226}Ra, the mobility and/or accumulation of the parent isotope in the subsurface will, in part, influence the distribution of ^{222}Rn throughout an aquifer. As an example, spatial and temporal variability in radon concentrations in ground water have been linked to redox-controlled variations in the precipitation or dissolution of iron and/or manganese (hydr)oxide containing co-precipitated parent radium (Gainon et al., 2007; Dulaiova et al., 2008).

Radon in water has been demonstrated to preferentially partition into organic liquids (e.g., Lewis et al., 1987; Davis et al., 2003). Thus, the relative concentration of ^{222}Rn observed in ground-water samples may be influenced by the presence of water-soluble organic solutions or non-aqueous phase liquids (NAPLs) that may be present within a plume. As an example, depletions in soil-gas radon concentrations are used as a diagnostic indicator of the presence of subsurface NAPLs (e.g., Schubert et al., 2007; Garcia-Gonzalez et al., 2008). This variability in ^{222}Rn partitioning behavior may influence the dimensions of the plume, as well as the rate of radon transport through the aquifer.

Site Characterization

Overview

Attenuation of radon might be achieved through radioactive decay (Table 3.1). Two factors that will dictate the adequacy of attenuation via radioactive decay include the rate of water transport and the total mass and release rate of radon into the subsurface plume. For some sites, the volatile transfer of ^{222}Rn from shallow ground water into overlying unsaturated soil or directly into open or confined atmospheres may also reduce ground-water concentrations. However, reliance on this mass transfer process will necessitate determination of the potential consequence of this exposure pathway to human and/or ecosystem health. Unacceptable exposures to airborne radon via volatile loss from ground water may necessitate active control of ^{222}Rn mass transport through the aquifer. Evaluation of whether radioactive decay is sufficient to achieve cleanup goals will

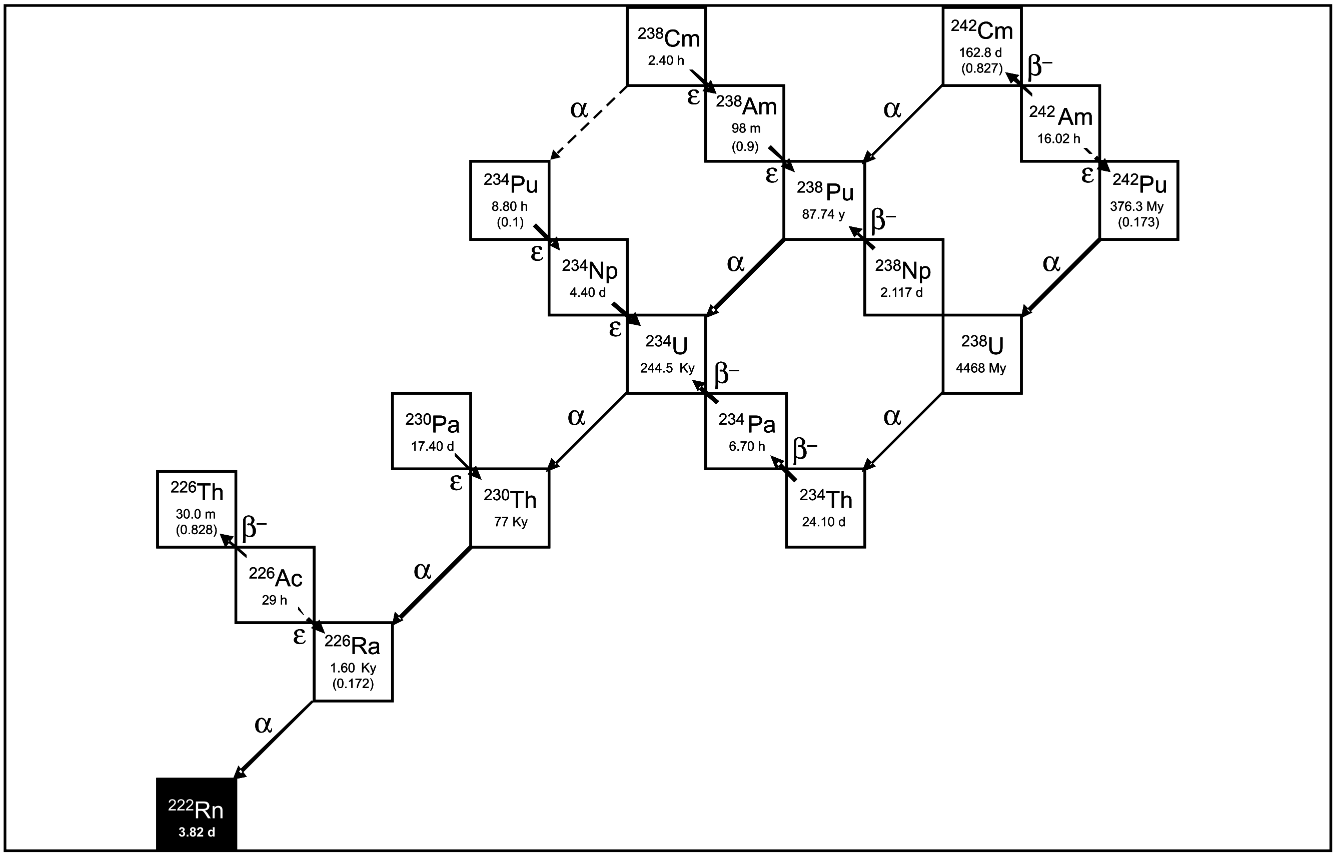

Figure 3.1 *Potential radioactive decay paths that lead to the production of ^{222}Rn based on data from ICRP (1983). Radioactive decay in these decay paths occurs via ejection of an alpha (α) or beta particle (β⁻), or electron capture (ε). The half-life is shown directly below the isotope that is subject to decay; My = megayears, Ky = kiloyears, y = years, d = days, m = minutes; numbers in parentheses indicate branching fraction.*

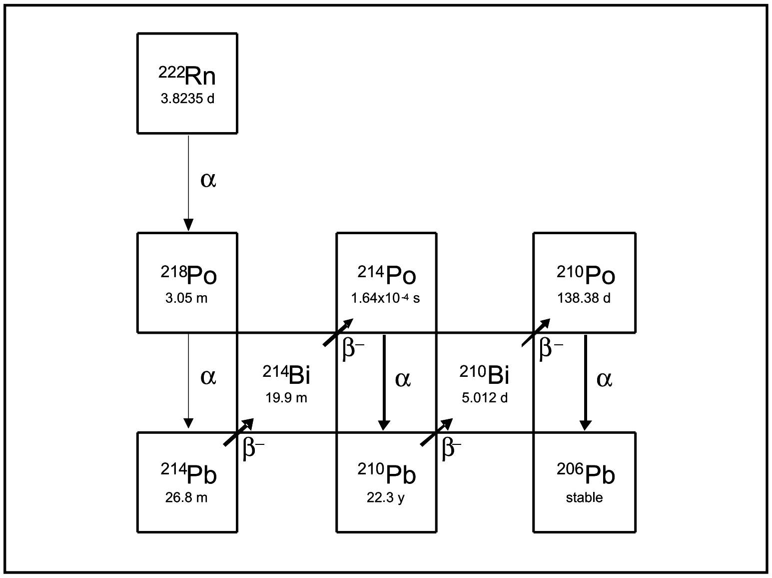

Figure 3.2 *Daughter radioisotopes resulting from the radioactive decay of ^{222}Rn based on data from ICRP (1983). Radioactive decay in this series occurs via ejection of an alpha (α) or beta particle (β⁻). The half-life is shown directly below the isotope that is subject to decay; y = years, d = days, m = minutes, s = seconds, stable = non-radioactive isotope.*

necessitate developing knowledge of the characteristics of ground-water flow throughout the plume, as well as the total activity/mass of radon within the plume and entering from uncontrolled source areas.

Table 3.1 Natural attenuation and mobilization pathways for radon.

Attenuation Processes	*Mobilization Processes*	*Characterization Approach*
Radioactive decay	Not applicable	Determination of ground-water velocity along relevant transport pathways and contaminant mass release rate from source areas.

Aqueous Measurements

Relative to determination of the spatial distribution and temporal variations in radon concentration/activity within the plume, common methods for the preservation and analysis of radon in ground water have been reviewed by Belloni et al. (1995). Three common analysis methods for direct and indirect determination of ^{222}Rn include 1) liquid scintillation counting, 2) degassification followed by Lucas cell counting, and 3) gamma counting. The most commonly employed method involves the partitioning of ^{222}Rn from the ground-water sample into either water soluble scintillators or organic scintillation liquids after radon extraction into an organic solvent, with counting of decay emissions from radon and/or its radioactive daughters (e.g., Freyer et al., 1997; Guiseppe et al., 2006; Leaney and Herczeg, 2006). For all of these methods, the accuracy of measured ^{222}Rn concentration/activity will depend on the use of ground-water sampling and processing methods that result in collection of a well sample that is representative of the aquifer, and that limit volatile loss of radon gas (e.g., Harris et al., 2006; Han et al., 2007; Talha et al., 2008).

Several studies have demonstrated measurement of radon in the field following isolation of ^{222}Rn from ground water into a gas phase, with detection achieved using a radon-in-air detector (e.g., Lee and Kim, 2006; Schubert et al., 2006; Kiliari and Pashalidis, 2008; Schmidt et al., 2008). The measurement is made using a radon-in-air detector and conversion of the measured partial pressure of ^{222}Rn in the gas phase to the corresponding amount of gas dissolved in the sampled ground water using Henry's Law. Important considerations for the reliability of this approach include accurate measurement or control of temperature and knowledge that the ground-water matrix can be reasonably represented as pure water. Schubert et al. (2008) have recently developed an approach by which ^{222}Rn is sampled directly into the gas phase via diffusion across a hydrophobic membrane. For low radon concentrations in surface water, Schubert et al. (2008) found that a porous membrane tubing length of at least 1-meter would be adequate for reliable ^{222}Rn quantification. This application indicates that passive, in-situ sampling of ^{222}Rn within the well screen may present an alternative to pumping ground water to the surface.

Partitioning of ^{222}Rn into non-aqueous phase liquids, which may be a component of the plume or intercepted by the ^{222}Rn plume at down gradient contaminant source areas, may interfere with analytical methodologies and/or confound interpretation of plume dimensions. The analytical methods employed for the detection of radon (directly or via daughter products) all involve transfer of the radionuclide from the sample matrix into either a solvent phase or gaseous matrix. The efficiency of the process to isolate radon will be influenced by the characteristics of the ground-water matrix. For sites where transported ^{222}Rn may encounter non-aqueous phase liquids, it is recommended that sample collection and analysis procedures be evaluated to ascertain if variations in ground-water matrix could influence the quality of analytical determinations of ^{222}Rn concentration/activity throughout the area of investigation.

Solid Phase Measurements

While partitioning of ^{222}Rn to aquifer solids is not known to occur (excluding free phase NAPLs trapped in the aquifer matrix), it may be necessary to assess the relative contributions of this radionuclide from the aquifer matrix versus dissolved ^{226}Ra or ^{222}Rn released from concentrated source areas, e.g., infiltration from uranium mill tailings. The concentration of ^{222}Rn supported by decay of naturally occurring ^{226}Ra within the aquifer may be ascertained by ground-water measurements in unimpacted portions of the aquifer with similar mineralogy and lithology as within the plume. In addition, aquifer solids may be collected from within the plume and allowed to equilibrate in a continuous flow configuration using sampled ground water in which dissolved ^{222}Rn has been allowed to decay away and dissolved ^{226}Ra has been chemically removed. Subsequent measurements of ^{222}Rn in the column outlet would reflect the quantity of ^{222}Rn supported by decay and release from ^{226}Ra associated with the aquifer solids, e.g., from natural and/or anthropogenic forms accumulated via historical attenuation of ^{238}U and/or ^{226}Ra transported from contaminant source areas. This level of characterization may be useful in ascertaining whether controls on the release of ^{222}Rn or ^{226}Ra from near-surface contaminant zones may be necessary to allow reliance on radioactive decay for attenuation of ^{222}Rn in the down gradient plume.

Long-term Stability and Capacity

Since immobilization is not an active mechanism for radon attenuation in ground water, assessment of long-term stability is not a factor. The long-term capacity for radon attenuation within a plume will be dictated by the relative rate of ground-water flow along relevant transport pathways compared to the rate for radioactive decay, given a known flux of radon entering the plume. Thus, a critical factor for assessing the overall capacity of the aquifer for attenuation will be evaluation of the mass flux of radon moving through the plume relative to the rate of water movement through the aquifer. Radioactive decay may be sufficient to prevent plume expansion, but this is not likely for sites with an uncontrolled source of radon entering the subsurface and/or characteristic times for ground-water transport that are significantly shorter than the half-life of radioactive decay for ^{222}Rn. Relative to radon release from uncontrolled source areas, knowledge of the total contaminant mass as well as the rate and frequency of release into the saturated aquifer needs to be developed. In addition, translocation of ^{226}Ra through the aquifer due to changes in chemistry may influence the dimensions and location of the observed ^{222}Rn plume. In order to make a reliable assessment of the mass/activity flux of radon into the plume, it will be important to understand the characteristics of the hydrogeologic system and the dynamics of water and contaminant transfer from contaminant source areas into the plume.

Tiered Analysis

Determination of the viability of radon remediation in ground water via monitored natural attenuation will depend upon proper assessment of contaminant loading to the aquifer relative to the velocity of ground-water travel along relevant transport pathways to the point(s) of compliance. The goal of site assessment is to demonstrate that radioactive decay is adequate to meet cleanup goals given current and projected hydrologic conditions for the site. The following tiered analysis structure for site characterization provides an approach to evaluate candidate sites and define the potential limitations of MNA as part of a remedy for ground-water cleanup.

Tier I. Site characterization under Tier I will involve demonstration that the ground-water plume is static or shrinking, has not reached compliance boundaries, and does not impact existing water supplies. It is also important at this stage of the site evaluation to determine source term characteristics such as the inventory of contaminant mass and the current and historical rate of release into the subsurface. Acquisition of this information in combination with identification of a stable plume provides justification for proceeding to Tier II characterization efforts.

Tier II. Under Tier II, the apparent rate of attenuation is determined. Estimates of a site attenuation rate(s) can be assessed via a well transect along the ground-water flow path. In addition, time-series data may be collected at one or more monitoring points within the plume (USEPA, 2007; Section IIIA.5). Since radioactive decay will be the dominant mechanism controlling radon attenuation, determination of the velocity of ground-water flow along relevant transport pathways will be critical to evaluating the potential cleanup time frame. This information will allow assessment of the relative timescales for contaminant attenuation and fluid transport and determination of whether remediation objectives can be met within the required regulatory time frame. Determination of the adequacy of radioactive decay to achieve cleanup goals will necessitate detailed analysis of system hydrology relative to flow pathway(s), flow velocity, and temporal variations in flow velocity and/or direction within the boundaries of the plume. This information, in combination with knowledge of contaminant source location(s), radon mass, and emanation characteristics from source zones, can be employed to develop a decay-transport model to project radon activity/concentration distribution throughout the plume. The demonstration of concurrence between conceptual and mathematical models describing radon transport will entail development of site-specific parameterization of ground-water flow along relevant transport pathways.

Tier III. Under Tier III, it will be important to assess whether the capacity of the system is adequate to sustain radon attenuation (e.g., prevent plume expansion) relative to the mass of the contaminant being transported through the plume. Two principal factors that may influence capacity include changes in water transport and/or changes in radon mass/activity flux entering the plume. Source release characteristics may be influenced by the physical location of sources within the subsurface relative to the ground-water table. Fluctuations in infiltration through shallow, unsaturated zones and/or water table elevations within the aquifer due to variations in recharge may lead to periodic increases in radon flux into ground water from contaminant source areas. Changes in land usage (including at recharge zones, wetlands, and over the contaminated site) and/or ground-water withdrawals from the aquifer may influence ground-water flow direction and velocity (USEPA, 2007; Section IIIA), which in turn directly influences radon travel time. It is recommended that additional radon transport modeling be included to evaluate the impact of these various scenarios to be assured that these perturbations do not significantly diminish attenuation. If monitoring data and model projections support adequate capacity for radon attenuation within the plume, then the site characterization effort can progress to Tier IV.

Tier IV. Finally, under Tier IV a monitoring plan is established along with contingency plans in the event of MNA failure. It is recommended that the monitoring plan be designed to establish both continued plume stability and to identify changes in ground-water levels, flow velocity, or direction that might influence the efficiency of radon removal via radioactive decay. In particular, sites at which residual, subsurface ^{226}Ra sources are left near the water table should include monitoring points to assess changes in the release of radon to the saturated aquifer due to increased surface infiltration or rises in the ground-water table. Changes in system hydraulics may serve as monitoring triggers for potential MNA failure. In this instance, a contingency plan can be implemented that incorporates engineered strategies to arrest possible plume expansion beyond compliance boundaries. Possible strategies to prevent plume expansion include the removal of ^{226}Ra from periodically saturated source areas and/or ground-water extraction with surface treatment.

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Strontium

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Occurrence and Distribution

^{90}Sr is produced in nuclear reactors as a product from fission of ^{235}U at a yield of about 6% (or 6 atoms of ^{90}Sr for every 100 fissions of ^{235}U). It is present in wastes and wastewaters associated with fuel handling and reprocessing. Otherwise, the primary inputs of ^{90}Sr to the environment are from nuclear bomb fallout, nuclear accidents (e.g., Chernobyl), and releases from nuclear power plant and nuclear propulsion emissions. Average ^{90}Sr activity in soils is 100 mCi/m^2 (USEPA, 1999). Non-radioactive (or stable) isotopes of Sr include ^{88}Sr (82.74% of total Sr), ^{86}Sr (9.75%), ^{87}Sr (6.96%), and ^{84}Sr (0.55%). ^{90}Sr is often a primary radioisotope of concern at low-level radioactive waste storage facilities because of its radiotoxicity, its relatively high mobility, and its general abundance in low-level wastes. Like stable isotopes of strontium, ^{90}Sr is always present in ground water in a divalent oxidation state [Sr(II)]. It forms weak aqueous complexes with carbonate, sulfate, and chloride and is typically present in natural waters as an uncomplexed cation. Because of similar charge and radius, strontium tends to mimic calcium in the environment. Consequently ^{90}Sr is often observed as an exchangeable cation on clay minerals, as a component of carbonate or sulfate minerals, and to a much lesser extent, sorbed weakly to iron (hydr)oxides and other minerals.

Geochemistry and Attenuation Processes

Radioactive Decay

Two radioactive isotopes of strontium that result from fission reactions during nuclear materials production are ^{89}Sr (50.5 day half-life; decays to stable ^{89}Y) and ^{90}Sr (28.8 year half-life). Of these radioisotopes, ^{90}Sr has been observed in ground water due to its longer half life, decaying to ^{90}Y and emitting a 546 keV maximum energy beta particle in the process. Subsequently, ^{90}Y decays with a half-life of 64 hours to stable ^{90}Zr (Figure 4.1). Several stable isotopes of strontium exist in nature (USEPA, 1999). The most prevalent stable isotope is ^{88}Sr, comprising about 82.6% of natural strontium. The other three stable isotopes and their relative abundance are ^{84}Sr (0.6%), ^{86}Sr (9.9%), and ^{87}Sr (7.0%). The majority of total dissolved strontium in ground water will typically consist of the stable isotopes. As an example, stable strontium concentrations in ground water for aquifers not impacted by radioactive wastes have been reported with ranges of 110-6120 μg/L (Jacobson and Wasserburg, 2005) and 14-43,500 μg/L (McIntosh and Walter, 2006). This compares to the mass-equivalent risk based concentration limit for ^{90}Sr of 0.000000059 μg/L (see Table 1.1).

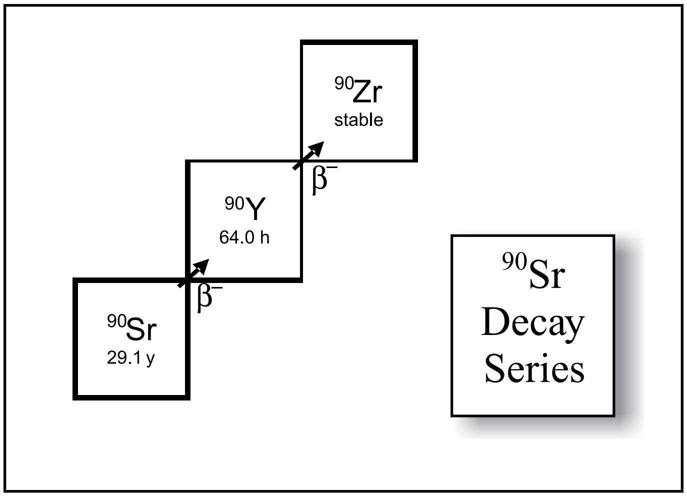

Figure 4.1 *Decay series for ^{90}Sr based on data from ICRP (1983). Radioactive decay in this series occurs via ejection of a beta particle (β⁻). The half-life is shown directly below the isotope that is subject to decay; y = years, h = hours, stable = non-radioactive isotope.*

Aqueous Speciation

Strontium predominantly occurs as an uncomplexed cation in solution (USEPA, 1999; Siegel and Bryan, 2003). There is some tendency for strontium to form carbonate complexes, but this is predicted to occur at relatively high pH (Figure 4.2; Felmy et al., 1998). Strontium can form complexes with organic constituents in solution, such as organic acids (acetate; Ragnarsdottir et al., 2001) or synthetic chelating agents (EDTA; Felmy and Mason, 2003). However, these complexes are not likely to play a major role in ground water, where more stable complexes of EDTA with other cations in solution would out-compete strontium complexation. As demonstrated by Pace et al. (2007), even strong chelating agents like EDTA appear to exert only a short-term influence on strontium aqueous speciation due to competition with other cations in solution that form more stable complexes with EDTA. There is indirect evidence that ^{90}Sr may bind to natural organic compounds such as fulvic acid (Zhao and Chen, 2006), but the overall influence of these compounds on the aqueous speciation of strontium will likely be limited to near-surface systems with high concentrations of dissolved organic carbon.

Solubility

Strontium may precipitate with dissolved carbonate or sulfate to form the minerals strontianite ($SrCO_3$) and celestite ($SrSO_4$), respectively. However, this is only anticipated for ground water with elevated concentrations of strontium and carbonate/sulfate. As shown in Figure 4.2a, precipitation of strontianite generally occurs under alkaline pH in ground water where natural stable strontium concentrations are elevated. In contrast, strontium may be coprecipitated during formation of carbonates of calcium or ferrous iron, e.g., under conditions of elevated alkalinity and/or ferrous iron that develop during microbial degradation of organic compounds (e.g., Roden et al., 2002; Fujita et al., 2004). As shown in Figure 4.2b, the precipitation of siderite ($FeCO_3$) or calcite ($CaCO_3$) would likely occur prior to the precipitation of strontianite from ground water. The degree that strontium may partition into these carbonates will be governed by competition with other divalent cations in solution that may be present at higher concentrations (Roden et al., 2002), although coprecipitation with calcite has been observed in natural systems (Ferris et al., 1995).

Adsorption

Because of the relatively high solubility of strontium-bearing minerals, adsorption tends to play a more important role in limiting strontium concentration in ground water. Cation exchange onto clay minerals is often the dominant adsorption reaction during transport through an aquifer (e.g., Cerling and Spalding, 1982; Serne and LeGore, 1996; USEPA, 1999; McKinley et al., 2007). Laboratory studies suggest that strontium may bind to the surface of oxide minerals (e.g., Carroll et al., 2008) and evaluation of biogenic iron (hydr)oxides collected from subsurface systems support the potential for this adsorption reaction under certain conditions (e.g., Ferris et al., 2000). Solid phase characterization data from some field studies of ^{90}Sr plumes suggest that strontium adsorption reactions may involve a combination of cation exchange onto clay minerals in combination with surface complexation reactions on oxyhydroxide minerals (e.g., Jackson and Inch, 1989).

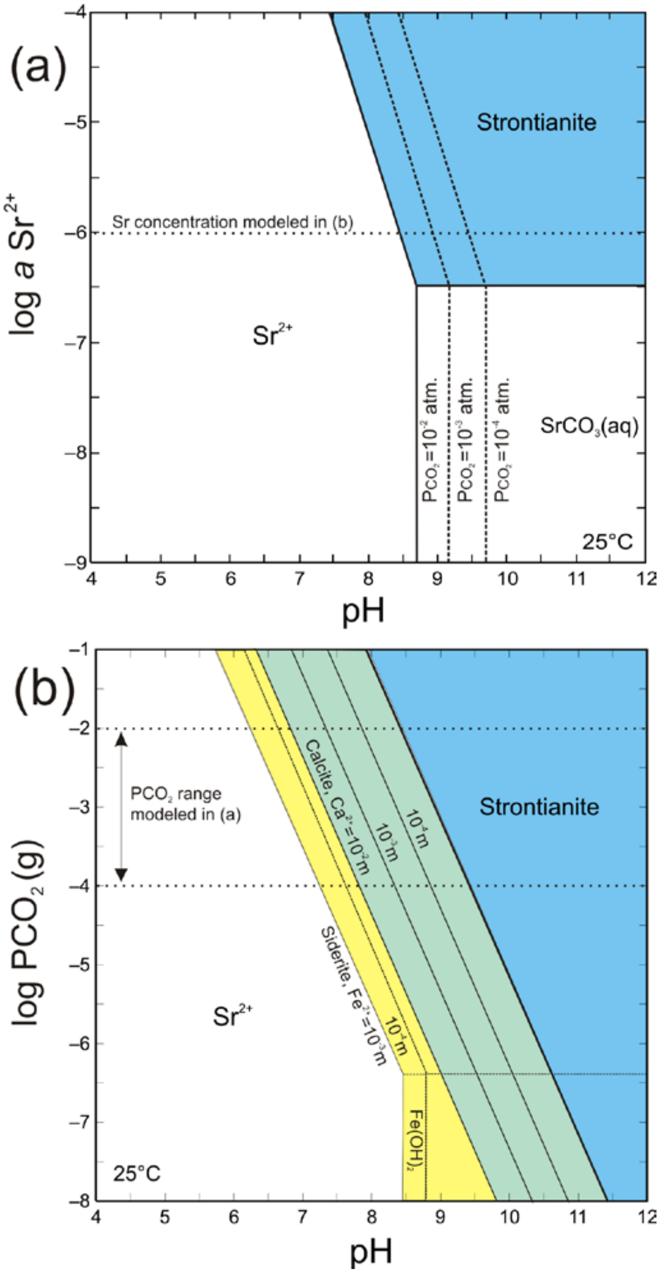

Figure 4.2 (*a*) *Solubility and speciation of strontium as a function of pH and PCO_2 (strontianite, $SrCO_3$).* (*b*) *Strontianite stability field ($Sr^{2+}=10^{-6}$m, 0.087 mg L^{-1}) in relation to stability fields for calcite ($CaCO_3$, variable Ca^{2+} concentration) and siderite ($FeCO_3$, variable Fe^{2+} concentration, FeO suppressed). Diagram constructed using the LLNL thermodynamic database (therm.com.V8.R6+) modified using the recommendations of Tournassat et al. (2008) for the solubility of strontianite.*

Site Characterization

Overview

Attenuation of ^{90}Sr might be achieved through radioactive decay with the influence of adsorption or coprecipitation reactions. In general, since strontium adsorption is dominated by highly reversible ion exchange reactions, it is anticipated that the primary function of this mechanism would be to limit the rate of mass transport to allow radioactive decay to remove sufficient contaminant mass. Co-precipitation reactions are likely to occur only under situations of high alkalinity production in concert with elevated concentrations of constituents such as calcium or ferrous iron. These processes would typically only be relevant to plumes with elevated microbial activity due to degradation of organic constituents also transported within the plume. A list of potential attenuation processes is provided in Table 4.1. Two factors that will dictate the adequacy of attenuation via radioactive decay and/or co-precipitation include the rate of water transport and the total mass and release rate of ^{90}Sr into the subsurface plume.

Table 4.1 Natural attenuation and mobilization pathways for strontium.

Attenuation Processes	*Mobilization Processes*	*Characterization Approach*
Radioactive decay	Not applicable	Determination of ground-water velocity along relevant transport pathways and contaminant mass release rate from source areas.
Adsorption onto aquifer minerals (clay minerals, iron oxyhydroxides)	Desorption due to decreasing pH or competition from major cations in ground water.	Evaluate total adsorption capacity of aquifer solids under representative ground-water chemistry; chemical extractions to assess concentrations of exchangeable ^{90}Sr in aquifer solids along relevant transport pathways.
Co-precipitation with Fe(II) carbonate or calcium carbonate	Dissolution due to decreasing pH or oxidation of Fe(II) carbonate	Evaluate formation of carbonate minerals along relevant transport pathways and determine ^{90}Sr association with this mineral fraction.

Aqueous Measurements

As a beta particle emitter (mean and end-point energy of 195.8 keV and 546.0 keV, respectively), ^{90}Sr can be quantified using radiometric analysis (USEPA, 2004; USEPA, 2006). However, the presence of other beta-emitting radionuclides in the sample can interfere with the determination of the activity/concentration of ^{90}Sr via detection of beta emissions due to overlap in their corresponding beta-emission spectra (Horwitz et al., 1991; Tinker et al., 1997). Examples of other beta-emitting radionuclides that may be present in the original sample include ^{90}Y (decay daughter; 232.5 keV mean, 643.2 keV end-point) or products from natural/anthropogenic uranium-thorium decay series (e.g., ^{214}Pb, 223 keV mean, 26.8 m half-life; ^{214}Bi, 642 keV mean, 19.9 m half-life). Procedures exist for the isolation of ^{90}Sr from liquid sample matrices (USEPA, 2004; USEPA, 2006), but in-growth of ^{90}Y following separation and the potential for incomplete isolation of Pb radioisotopes may need to be addressed (Beals et al., 2001). Sample storage to allow in-growth of ^{90}Y to secular equilibrium with ^{90}Sr (typically several weeks with detection of ^{90}Y) can address potential bias from ^{90}Y that may not initially be in secular equilibrium with ^{90}Sr (e.g., Fiskum et al., 2000). This storage time may also address the short-lived radioisotopes from the uranium-thorium decay series (e.g., ^{214}Pb and ^{214}Bi), but it may not necessarily address interference from ^{210}Pb (e.g., Goutelard et al., 2000). In the absence of interfering beta emitters, there are reported methods for on-line separation and simultaneous detection of ^{90}Sr and ^{90}Y via chromatographic techniques with simultaneous measurement of both radioisotopes (e.g., Egorov et al., 2006; Grate et al., 2008). Solid phase extraction resins may also be employed to isolate ^{90}Sr with immediate analysis of reacted resin (e.g. Fiskum et al., 2000; Beals et al., 2001), but the adsorption of non-targeted beta-emitting radionuclides needs to be initially evaluated for the various water chemistries that might be analyzed (e.g., Beals et al., 2001; Egorov et al., 2006). For solid phase extraction or other approaches to isolate ^{90}Sr from the water sample, a known trace mass of radioactive ^{85}Sr is commonly spiked into the sample matrix in order to assess chemical recovery of ^{90}Sr during sample processing.

Recent developments in the ICP-MS methodology allow detection of ^{90}Sr at levels comparable to reporting limits for radiometric techniques (Taylor et al., 2007; Hou and Roos, 2008). The improvement in detection limit has been achieved through the use of procedures for off-line and on-line concentration of ^{90}Sr in the analyzed sample (similar to methods employed for radiometric techniques) and through use of dynamic reaction cell configurations to control formation of molecular ions of similar mass that form in the plasma prior to introduction to the mass spectrometer. For example, Taylor et al. (2007) have demonstrated use of oxygen introduced into the plasma to convert ^{90}Zr (mass 90) to ^{90}ZrO^{+} molecular ions (mass 106), eliminating the positive bias to measured ^{90}Sr mass from ^{90}Zr that may be present in the sample. The presence of ^{90}Y does not significantly interfere with this approach given the low mass abundance of ^{90}Y at secular equilibrium (i.e., ^{90}Y/^{90}Sr mass ratio will be 0.025% at secular equilibrium). An additional benefit to using mass spectrometry is the ability to simultaneously monitor other stable and radioactive isotopes in the matrix. This analysis facilitates evaluation of the chemical conditions at locations where subsurface samples were retrieved, as well as make use of stable and/or radioactive isotope ratios as signatures of sources of water throughout the plume (e.g., Singleton et al., 2006; Christensen et al., 2007).

Solid Phase Measurements

Solid phase measurements that may provide information useful to assessing processes controlling ^{90}Sr retardation within the aquifer and the capacity along relevant transport pathways include the determination of ^{90}Sr partitioning to aquifer solids, the cation-exchange capacity of aquifer solids, and identification of aquifer solids mineralogy that may participate in adsorption and/or precipitation reactions. Evaluation of the mass distribution of ^{90}Sr between co-located ground water and aquifer solids throughout the plume provides an assessment of the extent that retardation reactions limit strontium migration. Bulk solid-phase partitioning can be conducted using total digestion or acid-extractable techniques (e.g., Friberg, 1997; Solecki, 2007) with appropriate measures to assess extraction efficiency and potential interference from other beta-emitters that may interfere with radiometric techniques (Chang et al., 2004; USEPA, 2004; USEPA, 2006). For these approaches, interference from matrix constituents, including other beta-emitters, could be significant due to release of these constituents as a result of dissolution of the solid matrix. As with aqueous measurements, these potential interferences need to be considered in the design of the analytical procedure. There are a range of aqueous reagent solutions that may be employed to measure the total cation exchange capacity of the aquifer solids, as well as the fraction of exchangeable ^{90}Sr (e.g., Cerling and Spalding, 1982; McKinley et al., 2007). An assumption of these procedures is that only exchangeable cations are released from the solid matrix. It is recommended that the potential for partial dissolution of the more labile mineral fraction in aquifer solids during extraction (e.g., Jackson and Inch, 1989) be assessed. This may be achieved through measurement of the major ion chemistry in the extract solution (e.g., iron, manganese, sulfate), which may serve as markers for the dissolution of oxides, sulfides or other components that may bind ^{90}Sr in a less labile form. Physical and chemical procedures, e.g., size fractionation or selective extraction of carbonate minerals, may also be employed to assist in identifying specific components with aquifer solids that dominate strontium solid-phase partitioning. Examples of procedures to identify the type and abundance of specific minerals along transport pathways are available in the literature (e.g., Cerling and Spalding, 1982; Jackson and Inch, 1983; McKinley et al., 2007). Additional information on analysis approaches and analytical techniques applied to solid phase characterization is provided in USEPA (2007; Section IIIB).

Long-term Stability and Capacity

The long-term stability of ^{90}Sr attenuated through adsorption or coprecipitation will depend upon the stability of the host mineral and the abundance of other ions which might displace adsorbed strontium. The most easily envisioned case of the first is that ^{90}Sr coprecipitated in carbonates might be remobilized if ambient pH were to decrease. Increases in divalent cation levels can be expected to work against ^{90}Sr immobilization for sites dominated by cation exchange reactions. Reductive dissolution of iron (hydr)oxides might cause remobilization of adsorbed ^{90}Sr. Review of the extent of plume development for a number of sites indicates that cation exchange within the saturated aquifer may have insufficient stability to prevent plume expansion (Brady et al., 2002). Thus, a critical factor for assessing the overall capacity of the aquifer for attenuation will be evaluation of the mass flux of ^{90}Sr moving through the plume relative to the rate of water movement through the aquifer. Radioactive decay may be sufficient to prevent plume expansion, but this is not likely for sites with an uncontrolled source of ^{90}Sr entering the subsurface and/or characteristic times for ground-water transport that are significantly shorter than the half-life of radioactive decay.

Tiered Analysis

Determination of the viability of ^{90}Sr remediation in ground water via monitored natural attenuation will depend upon proper assessment of contaminant loading to the aquifer relative to the velocity of ground-water travel and the prevailing geochemistry and mineralogy within the contaminant plume and the down gradient zone prior to the point(s) of compliance. The goal of site assessment is to demonstrate the process(es) controlling strontium sequestration onto aquifer solids and the long-term stability of solid phase strontium as a function of existing and anticipated ground-water chemistry. The following tiered analysis structure for site characterization provides an approach to evaluate candidate sites and define the potential limitations of MNA as part of a remedy for ground-water cleanup.

Tier I. Site characterization under Tier I will involve demonstration that the ground-water plume is static or shrinking, has not reached compliance boundaries, and does not impact existing water supplies. Once this is established through ground-water characterization, evidence is collected to demonstrate ^{90}Sr partitioning to aquifer solids within the plume. If immobilization processes are active throughout the plume, then there should be an observed increase in solid phase concentrations within regions of the plume with higher aqueous concentrations, e.g., near the source term. Evaluation of the mass/activity of ^{90}Sr distributed between ground water and aquifer solids throughout the plume is recommended to account for both existing and potentially mobile forms of ^{90}Sr. This field partitioning data may be supplemented by geochemical modeling that incorporates measured water chemistry (e.g., pH and major ion chemistry) throughout the plume to assess the potential for solubility control by precipitation of carbonate minerals. It is also important at this stage of the site evaluation to determine source term characteristics such as the inventory of contaminant mass and the current and historical rate of release into the subsurface. Acquisition of this information in combination with identification of a stable plume provides justification for proceeding to Tier II characterization efforts.

Tier II. Under Tier II, the apparent rate and mechanism(s) of attenuation are determined. Estimates of a site attenuation rate(s) can be assessed via a well transect along the ground-water flow path. In addition, time-series data may be collected at one or more monitoring points within the plume (USEPA, 2007; Section IIIA.5). This information will allow assessment of the relative timescales for contaminant attenuation and fluid transport and determination of whether remediation objectives can be met within the required regulatory time frame. As part of this analysis, it is critical to determine the relative contributions of radioactive decay and immobilization to the overall observed attenuation. Determination of the contribution of radioactive decay will necessitate detailed analysis of system hydrology relative to flow pathway(s), flow velocity, and temporal variations in flow velocity and/or direction within the boundaries of the plume. This information, in combination with knowledge of contaminant source release characteristics, can be employed to develop a decay-transport model to project ^{90}Sr activity/concentration distribution throughout the plume in the absence of adsorption/coprecipitation processes. For systems in which immobilization plays a role in observed attenuation, it will be necessary to identify whether adsorption onto existing aquifer minerals or coprecipitation with newly formed minerals predominates. This effort will require determination of the chemical speciation of solid phase ^{90}Sr and may be approached according to the following scheme:

1) Calculation of saturation state of ground water relative to precipitation of carbonate or (hydr)oxide minerals along relevant ^{90}Sr transport pathways;
2) Determination of aquifer mineralogy to determine the relative abundance of components with documented capacity for strontium adsorption (e.g., Jackson and Inch, 1983; 1989), with implementation of steps for aquifer solids collection, processing and analysis that avoid transformation of mineral species from reduced zones (e.g., oxidation of ferrous carbonate to ferric (hydr)oxide); and
3) Determination of ^{90}Sr-sediment associations via chemical extractions designed to target specific components within the aquifer sediment (e.g., Cerling and Spalding, 1982; McKinley et al., 2007).

This compilation of information will facilitate identification of the reaction(s) leading to ^{90}Sr attenuation. The demonstration of concurrence between conceptual and mathematical models describing strontium transport (both stabile and radioactive isotopes) will entail development of site-specific parameterization of the chemical processes controlling ^{90}Sr solid phase partitioning.

Tier III. Once the contributions from radioactive decay and adsorption/coprecipitation processes have been determined, the subsequent characterization effort under Tier III will involve determination of the stability of immobilized ^{90}Sr and the capacity of the aquifer to sustain continued uptake. It is recommended that the stability of immobilized ^{90}Sr be tested based on the anticipated evolution of ground-water chemistry concurrent with plume evolution. For example, changes in ground-water pH and/or cation composition can exert a significant influence on ^{90}Sr adsorption. Therefore, it is recommended that sediment leach tests be conducted to characterize the magnitude of ^{90}Sr re-mobilization as a function of pH for a ground-water chemistry representative of site conditions (including stable strontium isotopes present in ground water). It is recommended that the capacity for ^{90}Sr uptake onto aquifer solids be determined relative to the specific mechanism(s) identified in Tier II. For sites in which a continuing source of ^{90}Sr to the saturated aquifer exists, it is recommended that potential steps to minimize or eliminate this continued contaminant flux be evaluated and implemented where feasible. If site-specific tests demonstrate that the stability and capacity for ^{90}Sr immobilization, in combination with continued elimination of ^{90}Sr via radioactive decay, are sufficient to sustain attenuation, then the site characterization effort can progress to Tier IV.

Tier IV. Finally, under Tier IV a monitoring plan is established along with contingency plans in the event of MNA failure. It is recommended that the monitoring plan be designed to establish both continued plume stability and to identify changes in ground-water chemistry that may lead to re-mobilization of attenuated strontium (both ^{90}Sr and stable strontium isotopes). The specific chemical parameters to be monitored will include those identified under Tier III that may halt strontium partitioning to aquifer minerals and/or result in solubilization of precipitates into which strontium has been incorporated. Solution phase parameters that could alter either strontium coprecipitation or adsorption include changes in pH or concentrations of competing cations in ground water. As an example, increases in calcium concentrations in ground water could signal either 1) the potential for displacement of ^{90}Sr from cation exchange sites, or 2) the dissolution of calcium carbonate minerals in which strontium is coprecipitated. Changes in water chemistry may occur prior to observed changes in solution ^{90}Sr and, thus, serve as monitoring triggers for potential MNA failure. In this instance, a contingency plan can be implemented that incorporates engineered strategies to arrest possible plume expansion beyond compliance boundaries. Possible strategies to prevent plume expansion include ground-water extraction with surface treatment, installation of permeable reactive barriers to enhance uptake capacity perpendicular to the direction of plume advance, or enhancement of coprecipitation processes within the aquifer through the injection of soluble reactive components.

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Technetium

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Occurrence and Distribution

^{99}Tc is a fission product that is produced in nuclear power plants as a product from thermal neutron fission of ^{235}U (6.1% yield) and fission of ^{239}Pu (5.9% yield; IAEA, 2006). The metastable nuclear isomer of ^{99}Tc, ^{99m}Tc, has been used for many years in diagnostic nuclear medical imaging procedures due to emission of a 140 keV gamma ray during its decay to ^{99}Tc (Patton et al., 1966). ^{99m}Tc is a product of the decay of ^{99}Mo produced in nuclear fission reactions or it can be produced using a commercial medical cyclotron (e.g., Beaver and Hupf, 1971). There are no stable, naturally occurring isotopes of technetium. In nuclear reactor operations, ^{99}Tc is produced through several processes, and is often found in ion-exchange resins, filter sludges, evaporator bottoms, cartridge filters, trash, and decommissioning wastes. ^{99}Tc is present in a number of the high-level waste tanks at the Hanford Reservation and is a constituent of several ground-water plumes at this site (e.g., Hartman et al., 2006). Because it is long-lived and rapidly transported under oxidizing conditions, ^{99}Tc tends to dominate performance assessment calculations that are used to predict doses that might result from radionuclide releases from high and low-level waste facilities.

Geochemistry and Attenuation Processes

Radioactive Decay

^{99}Tc has a half-life of 213,000 years and decays to stable ^{99}Ru with the emission of a 293 keV maximum energy beta particle (ICRP, 1983; Eckerman et al., 1994; USEPA, 2002). The majority of technetium is generated as ^{99m}Tc from decay of the ^{99}Mo fission product. This metastable form (6.02 h half-life) decays to ^{99}Tc with the emission of a 140 keV gamma-ray. Based on a Maximum Contaminant Level (MCL) of 4 millirem per year for beta particle and photon radioactivity from man-made radionuclides in drinking water, one can estimate an equivalent activity-based MCL of 900 pCi/L for ^{99}Tc (mass equivalent concentration of 0.053 μg/L) assuming ^{99}Tc as the only beta- or photon-emitting radioisotope (USEPA, 2002).

Aqueous Speciation

^{99}Tc can exist in eight oxidation states ranging from Tc(-I) to Tc(VII). The two most common oxidation states are Tc(VII) and Tc(IV) under oxidizing and reducing conditions, respectively. Reviews of the aqueous geochemistry of technetium have been provided in USEPA (2004a), Siegel and Bryan (2003), and IAEA (2006). The pertechnetate anion (TcO_4^-) is the dominant chemical form of dissolved Tc(VII) in ground water. This anion has not been observed to form complexes of consequence in ground-water systems. There is evidence to support formation of soluble complexes with inorganic or organic ligands following reduction to Tc(IV). Formation of soluble Tc(IV) complexes with bicarbonate/carbonate is possible in ground water with elevated alkalinity (Wildung et al., 2000). Natural and synthetic chelating agents may also complex with Tc(IV), e.g., humic/fulvic acids and EDTA/NTA, respectively. Microcosm studies conducted by Maset et al. (2006) suggest that synthetic chelating agents would likely have minimal influence on the chemical speciation of Tc(IV) due to the presence of competing solid sorbents for aqueous Tc(IV) and/or major cation competition for complexation with EDTA/NTA. In contrast, there is evidence that natural dissolved organic compounds such as humic acid may form relatively stable complexes with reduced technetium (e.g., Maes et al., 2003; Gu and Ruan, 2007; Geraedts and Maes, 2008). These complexes may enhance Tc(IV) transport in organic-rich ground water under conditions unfavorable to sorption onto aquifer solids or where exposure to dissolved oxygen results in oxidation of complexed technetium (Gu and Ruan, 2007). In addition, these complexation reactions will be in competition with the tendency for Tc(IV) to form hydrous oxides with low solubility.

Solubility

The formation of precipitates incorporating Tc(VII) are not likely to form in ground water. In contrast, formation of hydrous oxides of Tc(IV) have been observed in soils and sediments influenced by microbial respiration of natural or anthropogenic sources of organic carbon (Istok et al., 2004; Abdelouas et al., 2005; Begg et al., 2008; Morris et al., 2008) or due to abiotic reduction in the presence of electron donors such as ferrous iron (Lloyd et al., 2000; Zachara et al., 2007; Peretyazhko et al., 2008). As a point of reference, the stability field for $TcO_2 \bullet 2H_2O$ is shown in Figure 5.1a when other Tc(IV) precipitate phases are suppressed from the speciation calculations. When all precipitate phases are allowed to form, a range of solids with varying technetium oxidation state are predicted to form (Figure 5.1b). However, many of the mixed- or lower-oxidation state solids for which solubility constants are published have not been observed to form in ground-water systems and it is recommended that their predicted presence based on model calculations be viewed as highly uncertain. The influence of different alkalinity levels in ground water on the stability of $TcO_2 \bullet 2H_2O$ is shown in Figure 5.2a. Based on these model projections, the formation of Tc(IV)-carbonate complexes could limit precipitation of this hydrous oxide in systems with alkaline pH and high carbonate alkalinity.

Available thermodynamic databases list solubility constants for technetium sulfides (e.g., Guillaumont et al., 2003; Rard, 2005), although recent critical reviews point to uncertainty in the reliability of these data (e.g., IAEA, 2006). Several experimental studies conducted in sulfidic systems indicate the potential formation of "Tc(IV)S_2-like" precipitates based on spectroscopic characterization of the reaction products (e.g., Wharton et al., 2000; Livens et al., 2004). These observations are consistent with formation of "Tc(IV)S_x" in high-level waste systems with a structural stoichiometry equivalent to Tc(IV)$_3$S(-II)$_2$(S(-I)$_2$)$_4$, nominally Tc_3S_{10} (Lukens et al., 2005). It should be noted that Lukens et al. (2005), based on structural analysis of technetium sulfide phases in these systems, call into question the formation of Tc(VII)$_2$$S_7$, which is commonly documented in available thermodynamic databases. These observations contrast with identification of Tc(VII) as the oxidation state in a Tc_2S_7 reference material (Wharton et al., 2000) and the recently observed formation of the phase in an experimental study (Liu et al., 2007). In addition, Liu et al. (2008) suggest that a Tc(IV)O_2-like phase may be the precipitate that forms upon interaction with Fe(II) sulfide. As shown in Figure 5.2b, thermodynamic calculations indicate that formation of technetium sulfide precipitates could compete with formation of the hydrous Tc(IV) oxide under sulfate-reducing conditions. In general, the ability to project what type of reaction controls precipitation of Tc(IV) with any certainty is limited for sulfate-reducing systems, although formation of $TcO_2 \bullet 2H_2O$ seems best supported.

Adsorption

Under oxidizing conditions, technetium is soluble and typically does not adsorb onto aquifer solids. The sorption K_d for ^{99}Tc is typically assumed to be zero (USEPA, 2004a). Values of $K_d > 0$ that have been reported in the literature have typically been associated with suboxic or anoxic ground-water systems where reduction of Tc(VII) to Tc(IV) is favored. There is evidence that Tc(IV) may adsorb to solid organic matter for systems undersaturated with respect to precipitation of hydrous Tc(IV) oxides or other reduced precipitate phases (Keith-Roach et al., 2003; Maes et al., 2003). Due to the difficulty of differentiating adsorption of Tc(IV) species versus precipitation or coprecipitation of Tc(IV)-bearing solids, it is generally understood that apparent retardation within an aquifer is due to the latter process.

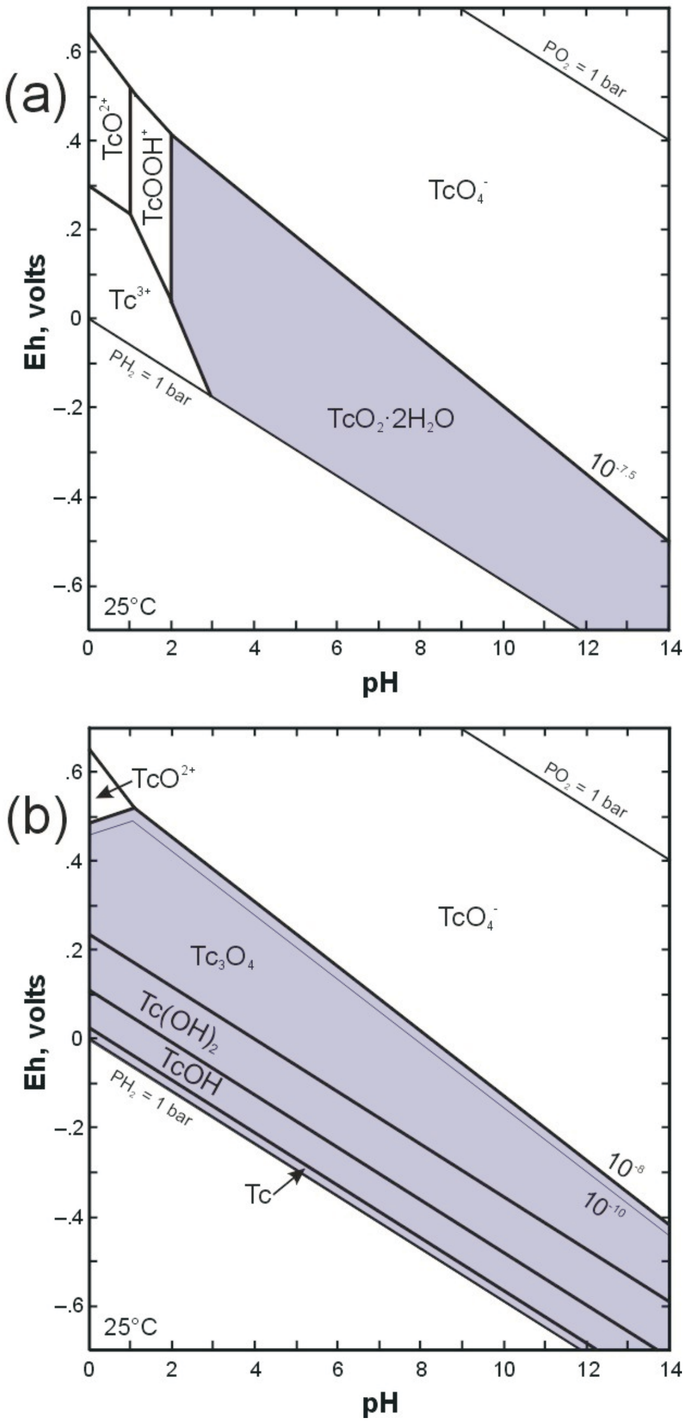

Figure 5.1 *Phase stability diagrams for technetium at 25°C. a) Eh-pH diagram for the system Tc-H_2O, Tc = $10^{-7.5}$ (53,903 pCi/L), showing metastable field for $TcO_2 \cdot 2H_2O$. b) Eh-pH diagram for the system Tc-H_2O, Tc = 10^{-10} to 10^{-8} (170-17,045 pCi/L), all phases unsuppressed (LLNL database).*

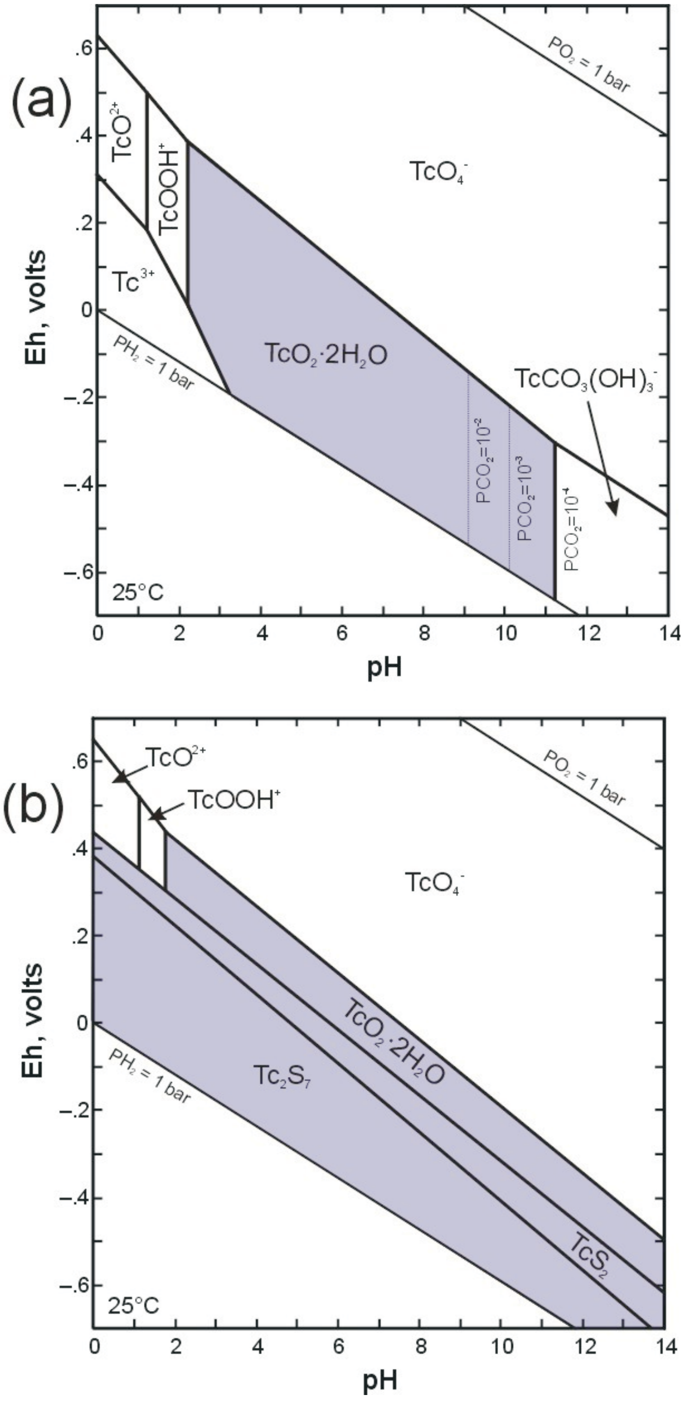

Figure 5.2 *Phase stability diagrams for technetium at 25°C. a) Eh-pH diagram for the system Tc-H_2O-CO_2, Tc = $10^{-7.5}$ (53,903 pCi/L), showing metastable field for $TcO_2 \cdot 2H_2O$. Tc(IV)-carbonate complex data from Hummel et al. (2002). b) Eh-pH diagram for the system Tc-H_2O-S; Tc = $10^{-7.5}$ and S = 10^{-3}.*

Site Characterization

Overview

Attenuation of ^{99}Tc might be achieved through precipitation or coprecipitation reactions under reducing conditions. Precipitation of sparingly soluble precipitates of Tc(IV) may form under reducing conditions, but this would likely only occur for relatively high concentrations of ^{99}Tc within the plume. For example, it is generally reported that ground water in which a hydrous Tc(IV) oxide controls aqueous technetium concentrations will have dissolved ^{99}Tc concentrations on the order of 10^{-8} mole/L (17,045 pCi/L; Hu et al., 2008). Coprecipitation with ferrous iron minerals under iron- and/or sulfate-reducing conditions may be a more likely pathway for immobilization. A list of potential attenuation processes is provided in Table 5.1.

Aqueous Measurements

Under oxidizing conditions, ^{99}Tc will be present as the soluble TcO_4^- anion, which is only slightly adsorbed to the solid phase. As a beta particle emitter ($E_{\beta max}$ = 294 keV), ^{99}Tc can be quantified using scintillation counting techniques (USEPA, 2004b; USEPA, 2006a). Interference from other beta-emitting radionuclides, e.g., ^{90}Sr ($E_{\beta max}$ = 546 keV), can be overcome through use of anion exchange resins to selectively retain the pertechnetate anion. Beals et al. (2000; 2001) and Fiskum et al. (2000) have demonstrated the use of solid phase extraction (SPE) resins in permeable disk configurations for rapid capture and analysis of ^{99}Tc in water samples. However, Beals et al. (2001) have noted the importance of re-measuring SPE disks at additional time intervals to confirm that initial measured counts are not due to interference for other short-lived beta-emitters that may also be retained on the resin. In addition, initial tests for extraction efficiency may need to be conducted to identify whether major anion concentrations interfere with pertechnetate uptake (e.g., elevated nitrate concentrations). There have also been recent efforts to develop field-deployable radiometric techniques to simplify and, in some cases, automate measurements of ^{99}Tc in ground water (Egorov et al., 2006; Hughes and DeVol, 2006; O'Hara et al., 2009). A common configuration for these radiometric systems is the physical mixing of an anion exchange resin and a solid scintillator to allow detection of the emitted radiation using a photomultiplier tube. A potential interfering radionuclide is ^{129}I, which is a beta emitter ($E_{\beta max}$ = 294 keV) that may be present in anionic form. However, O'Hara et al. (2009) has demonstrated that the lower sensitivity for ^{129}I detection will limit its interference potential in plumes where it is present in relatively lower concentrations than ^{99}Tc.

Mass spectrometric techniques can also be used to measure ^{99}Tc in ground water (e.g., Hou and Roos, 2008). Inductively coupled plasma-mass spectrometry (ICP-MS) methods have been developed. The main interference in determination of ^{99}Tc is mass overlap by atomic ions (^{99}Ru) or molecular ions ($^{98}MoH^+$) of mass 99, or peak tailing from ions with mass in the range of 98-100 atomic mass units. Several published studies illustrate use of ICP-MS for sensitive and accurate detection of ^{99}Tc in complex aqueous

Table 5.1 Natural attenuation and mobilization pathways for technetium.

Attenuation Processes	Mobilization Processes	Characterization Approach
Reduction of Tc(VII) and precipitation of Tc(IV) oxide/sulfide minerals	Oxidation of Tc(IV) to Tc(VI) with formation of pertechnetate anion	Evaluation of Tc concentration in ground water and in solid matrix. Evaluation of Tc solid-phase partitioning using sequential extraction methodologies coupled to methods to determine Tc oxidation state. Characterization of aqueous redox and chemical conditions in ground water with speciation model evaluation of potential Tc(IV) stability.
Reduction of Tc(VII) to Tc(IV) and coprecipitation with Fe(II)-bearing minerals	Oxidation of ferrous iron, sulfide, and/or Tc(IV)	Evaluation of Tc concentration in ground water and in solid matrix. Evaluation of Tc solid-phase partitioning using sequential extraction methodologies; examine correlation to extractable Fe, Ca, Mg and S. Batch and column testing to determine Tc uptake behavior and capacity of site-specific aquifer materials under variable geochemical conditions.

matrices (e.g., Richter et al., 1997; Eroglu et al., 1998; Kim et al., 2002). The potential for carryover of ^{99}Tc on system components between samples needs to be evaluated, but methods are available to eliminate this factor (e.g., Richter et al., 1997). Due to similarities in chemical behavior, rhenium (as perrhenate anion) can be used to monitor chemical recovery of pertechnetate during sample pre-concentration prior to detection (Mas et al., 2004).

Solid Phase Measurements

Solid phase measurements that may provide information useful to assessing processes controlling ^{99}Tc attenuation within the aquifer and the capacity along relevant transport pathways include the determination of ^{99}Tc partitioning to aquifer solids and identification of aquifer solids mineralogy that may participate in reduction or precipitation reactions. Evaluation of the mass distribution of ^{99}Tc between co-located ground water and aquifer solids throughout the plume provides an assessment of the extent that retardation reactions limit strontium migration. Bulk solid-phase partitioning can be conducted using total digestion or acid-extractable techniques with appropriate measures to assess extraction efficiency and potential interference from other beta-emitters that may interfere with radiometric techniques (USEPA, 2004b; USEPA, 2006a). Because the overall quantities of solid-phase ^{99}Tc are likely to be low, techniques for determination of total ^{99}Tc or the chemical fractionation of ^{99}Tc in aquifer solids is needed. Fusion methods that convert the solid matrix to a form easily dissolved in acid are recommended for total concentration measurements (Dixon et al., 1997; Zhao et al., 2008). The fusion methods incorporate reagents that minimize volatile losses of technetium.

The relative partitioning of ^{99}Tc with mineral components in the aquifer solids may be inferred from extractions designed to selectively dissolve reactive phases (e.g., carbonates, reducible oxides, or oxidizable sulfides). This approach has been used to assist interpretation of ^{99}Tc speciation in sediments (Keith-Roach et al., 2003). However, interpretation of sequential extraction data needs to be constrained by knowledge of the mineralogical composition of the aquifer solids, the types of major elements also extracted in any particular step, and the geochemical conditions under which the solids existed within the subsurface. Additional information on analysis approaches and analytical techniques applied to solid phase characterization is provided in USEPA (2007; Section IIIB). There are no methods that have been developed to identify the oxidation state of extracted ^{99}Tc at the concentrations likely to be encountered in aquifer solids. It should also be noted that dissolution of aquifer solids will likely release elements that interfere with radiometric or mass-spectrometric detection of ^{99}Tc at concentrations much higher than typically encountered in ground water. The performance of analytical procedures used to quantify released ^{99}Tc needs to be carefully evaluated in the context of the complex liquid matrices that will be encountered. The oxidation state and chemical binding environment of ^{99}Tc may also be assessed using X-ray absorption spectroscopy (see references in *Solubility* section). This technique can be used to identify the chemical speciation of technetium in aquifer solids collected and preserved in a manner to maintain in-situ characteristics.

Long-term Stability and Capacity

Two factors that will likely dictate the stability of attenuated ^{99}Tc and the capacity for the aquifer to sustain ^{99}Tc removal from ground water include the persistence of reducing conditions and the mass flux of ^{99}Tc transported along relevant flow paths. Identification of contaminant source areas, including waste form characteristics, may be necessary in order to understand contaminant loading relative to the source and flux of water moving through the plume. For example, it may be useful to examine isotopic signatures for other fission-product isotopes that provide unique markers for different contaminant sources (e.g., fission-produced stable ruthenium isotopes; Brown et al., 2006). Characterization of the total mass and rate of release of ^{99}Tc from uncontrolled source areas need to be understood relative to the apparent rates of pertechnetate reduction and sequestration in the plume. The apparent rate of attenuation at the leading edge of the plume can be assessed, by reference to a conservatively transported constituent (Hu et al., 2008), through time-series sampling at individual wells or by sampling from a well transect installed coincident with the direction of water flow. A situation where the flux of ^{99}Tc entering the plume exceeds the rate of attenuation at the leading edge of the plume will likely result in insufficient capacity to arrest plume expansion. The factors governing reducing conditions in the plume may also govern attenuation capacity, particularly in situations where the flux of degradable organic compounds or other electron donors through the plume may not be sustained. However, examination of the stability of reduced forms of technetium sequestered to subsurface solids suggests that solid phase Tc(IV) will remain stabile, even if more oxidizing conditions develop (e.g., McBeth et al., 2007; Begg et al., 2008).

Tiered Analysis

Determination of the viability of ^{99}Tc remediation in ground water via monitored natural attenuation will depend upon proper assessment of contaminant loading to the aquifer and prevailing geochemistry and mineralogy within the contaminant plume and the down gradient zone prior to the point(s) of compliance. Due to the long half-life for ^{99}Tc, radioactive decay will not provide a viable mechanism for plume attenuation. Therefore, the goal of site assessment will be to demonstrate the process(es) controlling ^{99}Tc sequestration onto aquifer solids and the long-term stability of solid phase ^{99}Tc as a function of existing and anticipated ground-water chemistry. The following tiered analysis structure for site characterization provides a technically defensible approach to evaluate candidate sites and define the potential limitations of MNA as part of a remedy for ground-water cleanup.

Tier I. Site characterization under Tier I will involve demonstration that the ground-water plume is static or shrinking, has not reached compliance boundaries, and does not impact existing water supplies. Once this is established through ground-water characterization, evidence is collected to demonstrate ^{99}Tc partitioning to aquifer solids within the plume. If natural attenuation processes are active throughout the plume, then there should be an observed increase in solid phase concentrations within regions of the plume with higher aqueous concentrations, e.g., near the source term. This field partitioning data may be supplemented by geochemical modeling that incorporates measured water chemistry (e.g., pH, Eh, and major ion chemistry) throughout the plume to assess the potential for solubility control by a ^{99}Tc precipitate such as a hydrous oxide phase. Identification of active sequestration to prevent ^{99}Tc migration in ground-water provides justification for proceeding to Tier II characterization efforts.

Tier II. Under Tier II, the apparent rate and mechanism(s) of attenuation are determined. Estimates of a site attenuation rate(s) can be assessed via a well transect along the ground-water flow path. In addition, time-series data may be collected at one or more monitoring points within the plume (USEPA, 2007; Section IIIA.5). This information will allow assessment of the relative timescales for contaminant immobilization and fluid transport and determination of whether remediation objectives can be met within the required regulatory time frame. In addition, the mechanism(s) for attenuation are to be identified under this stage of site characterization. This effort will require determination of the chemical speciation of solid phase ^{99}Tc and may be approached according to the following scheme:

1) Determination of solution and solid phase ^{99}Tc concentrations, along with the relative concentration of major ions/components in aquifer solids where attenuation is occurring;
2) Calculation of saturation state of ground water relative to measured aqueous chemistry;
3) Determination of aquifer mineralogy (Amonette, 2002) to determine the relative abundance of components that might support pertechnetate reduction (e.g., Fe(II) associated with aquifer solids) and/or coprecipitation; and
4) Determination of ^{99}Tc-sediment associations via chemical extractions designed to target specific components within the aquifer solids.

This compilation of information will facilitate identification of the reaction(s) leading to ^{99}Tc immobilization. It is recommended that identification of redox-sensitive components in aqueous and solid matrices be conducted using samples collected in a manner that preserves their in-situ speciation (USEPA, 2006b). The demonstration of concurrence between conceptual and mathematical models describing ^{99}Tc transport will entail development of site-specific parameterization of the chemical processes controlling ^{99}Tc solid phase partitioning.

Tier III. Once the partitioning mechanism(s) have been identified for the site, the subsequent characterization effort under Tier III will involve determination of the stability of immobilized ^{99}Tc and the capacity of the aquifer to sustain continued uptake. It is recommended that the stability of immobilized ^{99}Tc be tested based on the anticipated evolution of ground-water chemistry concurrent with decay of the plume. For example, changes in ground-water pH can exert a significant influence on the solubility of a hydrous Tc(IV) oxide. Therefore, it is recommended that sediment leach tests be conducted to characterize the magnitude of ^{99}Tc mobilization as a function of pH for a ground-water chemistry representative of site conditions. It is recommended that the capacity for ^{99}Tc uptake onto aquifer solids be determined relative to the specific mechanism(s) identified in Tier II. For example, if site characterization under Tier II indicated that microbial degradation of naturally occurring solid organic matter (SOM) resulted in reduction of Tc(VII) to insoluble Tc(IV), then the mass distribution of SOM within the aquifer needs to be determined. This site-specific capacity would then be compared to ^{99}Tc mass loading within the plume in order to assess the longevity of the natural attenuation process. If site-specific tests demonstrate the stability of immobilized ^{99}Tc and that there is sufficient capacity within the aquifer to sustain ^{99}Tc attenuation, then the site characterization effort can progress to Tier IV. For cases where contaminant stability is sufficient but aquifer capacity is insufficient for capture of the entire plume, then a determination of the benefits of contaminant source reduction is required.

Tier IV. Finally, under Tier IV a monitoring plan is established along with contingency plans in the event of MNA failure. It is recommended that the monitoring plan be designed to establish both continued plume stability and to identify changes in ground-water chemistry that may lead to re-mobilization of attenuated ^{99}Tc. The specific chemical parameters to be monitored will include those identified under Tier III that may halt ^{99}Tc partitioning and/or result in dissolution of either discrete ^{99}Tc precipitates or aquifer minerals that sequester ^{99}Tc from ground water. For example, solution phase parameters that could alter either ^{99}Tc precipitation include inorganic carbon (alkalinity), pH, and dissolved oxygen. In contrast, increases in the concentration of sulfate may indicate the dissolution of an important sorbent phase within the aquifer (e.g., oxidative dissolution of iron sulfide). Changes in these parameters may occur prior to observed changes in solution ^{99}Tc and, thus, serve as monitoring triggers for potential MNA failure. In this instance, a contingency plan can be implemented that incorporates alternative strategies to arrest possible plume expansion beyond compliance boundaries. Possible strategies to prevent plume expansion include pump and treat operations, installation of reactive barriers to enhance uptake capacity perpendicular to the direction of plume advance, or enhancement of attenuation processes within the aquifer through the injection of soluble reactive components that induce more reducing conditions.

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Uranium

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Occurrence and Distribution

Uranium is the heaviest naturally occurring element and all isotopes are radioactive. Although it occurs as an essential component in nearly 200 different minerals (Smith, 1984; Burns, 1999), the vast majority of naturally occurring uranium deposits are comprised of a few common minerals including oxides (uraninite and pitchblende), silicates (coffinite, soddyite, uranophane, and uranothorite), phosphates (autunite), and vanadates (carnotite). Uranium can be used to fuel nuclear power reactors either in its natural isotopic enrichment of 0.7% ^{235}U or at slight enrichments of between 3 – 5% ^{235}U. At much higher ^{235}U enrichments, uranium is also used in nuclear weapons. Civilian non-nuclear applications of (depleted) uranium include sailboat keels and counterweights in commercial aircraft. Depleted uranium is used extensively in military applications, notably in alloys for armor and armor-penetrating projectiles (Bleise et al., 2003). As a result of its widespread use, uranium is the most common radiological contaminant in soils and sediments (Riley et al., 1992) and is generally associated with uranium mining/refining sites, processing facilities for the commercial/civilian nuclear fuel cycle, production of nuclear materials for weapons, and artillery firing ranges and battlefields.

Typical groundwater concentrations of dissolved uranium are on the order of a few μg U/L, but range as high as 2000 μg U/L near natural uranium deposits in arid regions. In streams, levels of uranium are typically about 1 μg U/L, but values as high as 50 μg U/L are seen in granitic watersheds. The level of uranium in seawater is 3 μg U/L. In addition to the dissolved forms, colloidal forms of uranium are often present in water, and can be determined by decreases in concentration as a result of filtration (the filter pore size is often specified).

Some of the notable uranium contamination sites in the United States include Department of Energy (DOE) processing facilities located at Fernald, OH; Paducah, KY; Oak Ridge, TN; Savannah River Site, SC; Rocky Flats, CO; and Hanford, WA, as well as abandoned mines and former mill sites in the Colorado Plateau region of the southwest. In addition, the development of in-situ leach mining, which accounts for nearly all the uranium currently mined in the United States, has led to new sites of subsurface contamination in Texas, Wyoming, Nebraska, and New Mexico. Military firing ranges and research facilities contaminated with depleted uranium include the Aberdeen Proving Ground, MD; Jefferson Proving Ground, IN; Yakima Firing Center, WA; and Los Alamos and Sandia National Laboratories, NM. A summary of sites under the regulatory authority of either the USEPA or the Nuclear Regulatory Commission (NRC) was provided in USEPA (1993).

Geochemistry and Attenuation Processes

Radioactive Decay

Uranium transport in groundwater depends to a large extent on the oxidation state and radioactive decay phenomena for the predominant radioisotopes found in natural systems (USEPA, 1999). All of the isotopes of uranium are radioactive. Of the three naturally occurring isotopes, ^{238}U is the most abundant (99.275%; 4.468x10^{9} year half-life), followed by ^{235}U (0.720%; 7.038x10^{8} year half-life) and ^{234}U (0.005%; 2.445x10^{5} year half-life). The decay series for ^{238}U and ^{235}U are shown in Figure 6.1. Because ^{234}U is a decay product of ^{238}U, it generally occupies sites in minerals that have already been damaged by the release of an alpha particle during the ^{238}U decay process. This decay process, referred to as 'alpha recoil', may lead to ejection of the ^{238}U daughter (^{234}Th) directly into groundwater or indirectly increase the potential for ^{234}U leaching from aquifer solids damaged by the recoil process (Ivanovich, 1994; Tricca et al., 2001; Maher et al., 2006). The ^{234}U:^{238}U activity ratio in groundwater would increase proportionately, where ^{234}U is released during dissolution or from the rapid decay of ^{234}Th (and ^{234}Pa) following ejection from the solid surface.

The form of uranium waste materials will influence the relative distribution of uranium radioisotopes derived from sources of contamination. Preparation of uranium for use in reactors involves enrichment of the more fissile ^{235}U radioisotope to several percent, and for nuclear weapons enrichment to 90% or better is required. The residual material, or tails, derived from the enrichment process is referred to as "depleted uranium", which has a higher proportion of the ^{238}U radioisotope (Meinrath et al., 2003). Elevated levels of ^{236}U are produced by neutron activation of ^{235}U (Marsden et al., 2001; Boulyga and Becker, 2002); accordingly, this radioisotope may provide a "fingerprint" for the presence in the environment of uranium that has been irradiated in a nuclear reactor (Christensen et al., 2007) due to its relatively long half-life (2.3415 x 10^{7} years). Thus, excluding potential alpha recoil effects, differences in the relative abundance of uranium isotopes in groundwater will reflect source term characteristics. Possible progenitors that could introduce uranium isotopes via decay in-growth are shown in Table 6.1. Radioisotopes of neptunium, protactinium, and plutonium decay to produce uranium radioisotopes of importance. The decay half-lives for these progenitors range from minutes to many thousands of years. Knowledge of the presence of these radionuclides within the plume and sampled groundwater may be important for proper identification of the source of uranium radioisotopes as well as in-growth corrections that may be required to properly account for the mass/activity of the various uranium radioisotopes at the time of sample collection.

Table 6.1 Illustration of potential decay paths from different progenitor sources leading to production of uranium radioisotopes. Determination of possible decay paths to the target radionuclide was based on examination of the Chart of Nuclides (http://www.nndc.bnl.gov/chart/) maintained by the Brookhaven National Laboratory, National Nuclear Data Center (NNDC) relative to possible decay paths based on decay modes identified in the Appendix (EC = electron capture, β^- = electron emission, α = alpha decay). Decay half-life data were obtained using the WinChain program that provides electronic access to the ICRP38 Nuclear Decay Data Files (ICRP, 1983; Eckerman et al., 1994; m = minutes, h = hours, d = days, y = years). WinChain is a public domain software application available for download from Oak Ridge National Laboratory (http://ordose.ornl.gov/downloads.html).

Contaminant Radionuclide	Decay Progenitor	Decay Mode	Progenitor Decay Half-life
^{238}U	^{242}Pu	α	3.763 x 10^5 y
^{235}U	^{235}Np	EC	396.1 d
	^{239}Pu	α	24065 y
^{234}U	^{234}Np	EC	4.4 d
	^{234}Pa	β^-	6.70 h
	^{238}Pu	α	87.74 y
	^{238}Np → ^{238}Pu	$\beta^- \rightarrow \alpha$	2.117 d → 84.74 y
^{236}U	^{236}Np [1]	EC	153000 y
	^{240}Pu	α	6537 y

[1] *Decay data not available in WinChain; recommended values obtained from NuDat 2.4 database maintained at the NNDC (http://www.nndc.bnl.gov/nudat2/index.jsp).*

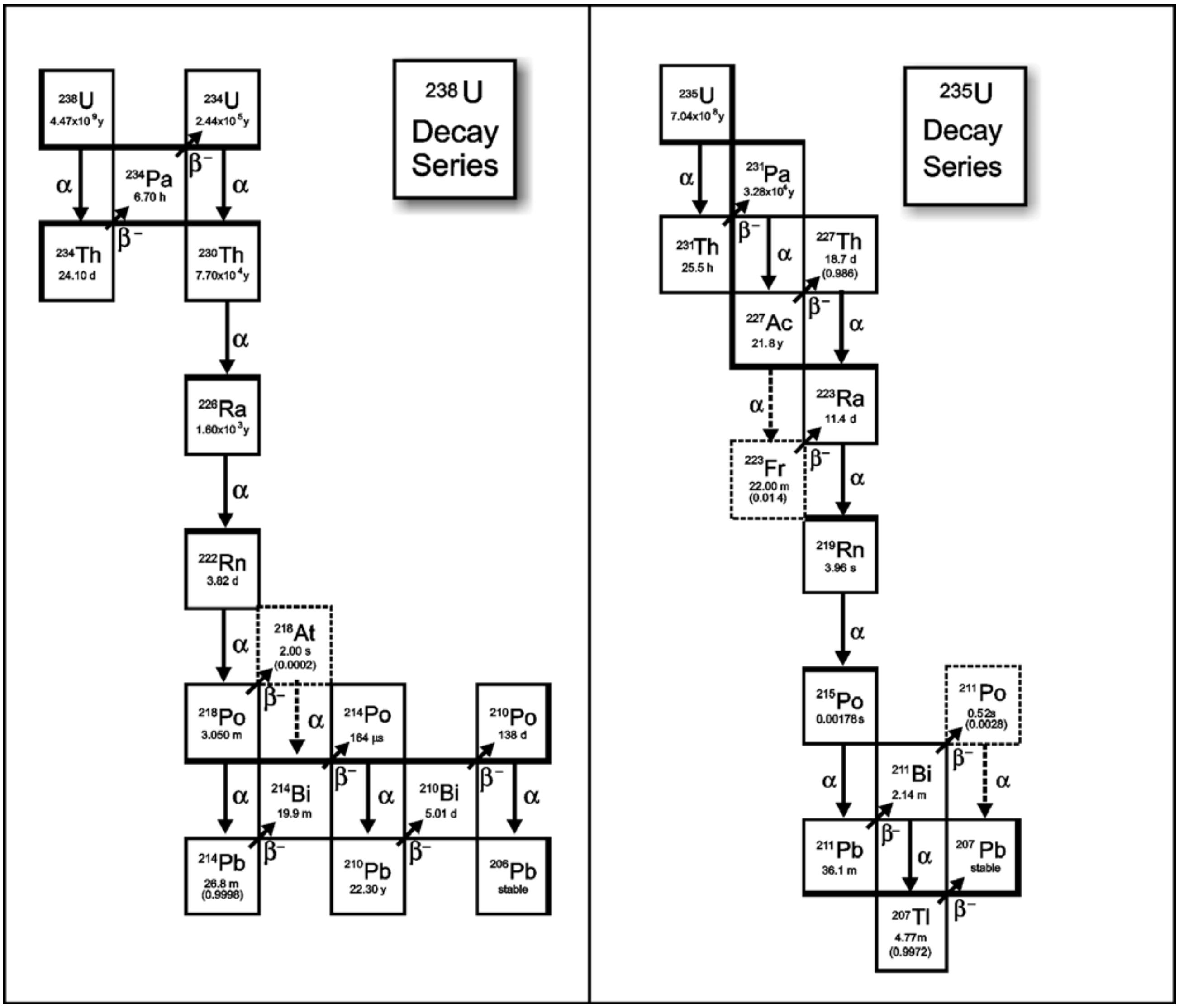

Figure 6.1 *Decay series for ^{238}U and ^{235}U based on data from ICRP (1983). Decay modes include those leading to ejection of an alpha particle (α) or a beta particle (β^-). The half-life is shown directly below the isotope that is subject to decay; y = years, d = days, h = hours, m = minutes, s = seconds, µs = microseconds. Numbers shown in parentheses below indicate the fractional abundance of the daughter isotope produced during branched decay of the parent isotope (e.g., decay of ^{218}Po follows two routes resulting in 98.98% production of ^{214}Pb and 0.02% production of ^{218}At).*

Aqueous Speciation

The environmental chemistry of uranium is largely dictated by its formal oxidation state (e.g., Fanghanel and Neck, 2002). Under ambient oxidizing conditions, the predominant uranium oxidation state is U(VI). Where oxygen is limited, U(IV) may dominate. The metallic form, U(0), does not occur naturally, and is readily oxidized to U(IV), and eventually U(VI), upon exposure to oxidizing conditions. A considerable body of literature discusses the mechanisms of "corrosion" of U(0) and U(IV) to U(VI) (e.g., Finch and Ewing, 1992; Finch and Murakami, 1999). Other oxidation states of uranium, e.g., U(V) and U(III), are rare and generally unstable to U(IV) and U(VI) under ambient conditions. In general, the solubility, and hence mobility, of uranium is greatest when it is in the U(VI) state. Complexation of U(VI) by inorganic anions such as carbonate, fluoride and phosphate may enhance the solubility and mobility of this species. When reducing conditions are present, U(IV) is generally immobile and found either as the insoluble oxide (uraninite) or the silicate (coffinite). A compilation of thermochemical data for uranium aqueous species and solid phases has been recently published by the Nuclear Energy Agency (Guillaumont et al., 2003). It is recommended that this and other sources (e.g., Hummel et al., 2002; Gorman-Lewis et al., 2008) be consulted prior to implementation of geochemical models to describe uranium fate and transport.

Under oxidizing conditions and environmental pH, U(VI) species dominate aqueous uranium concentrations. These highly soluble species are generally either hydroxy or carbonato complexes of the uranyl (UO_2^{2+}) cation (Figure 6.2), although elevated concentrations of potential inorganic or organic ligands near contaminant source zones may exert greater influence on U(VI) speciation (e.g., phosphate; Bonhoure et al., 2007). As shown in Figure 6.2, calcium (or other alkaline earth metals such as magnesium) and inorganic carbon in ground water tends to dominate the aqueous speciation of U(VI) under typical pH conditions (Dong et al., 2005; Dong and Brooks, 2006; Kelly et al., 2007; Dong and Brooks, 2008). The presence of these species at moderate ground-water concentrations has been verified, along with the reliability of the stability constants for calcium-carbonato complexes of U(VI) (Prat et al., 2009). As noted below, these speciation characteristics also influence the degree to which U(VI) will adsorb to aquifer solids. Under reducing conditions, U(IV) species, primarily the uranyl cation and its complexes, predominate, but, due to the very low solubility of U(IV) minerals, reach maximum concentrations on the order of 10 nM (2.4 µg U/L). For all practical purposes, therefore, only U(VI) aqueous species are at sufficient concentrations to be of environmental concern. Complexation with dissolved organic carbon may influence the aqueous chemistry of U(VI) in some ground-water systems, although field evidence suggests that this would be significant only in more acidic (pH<6) systems (e.g., Ranville et al., 2007).

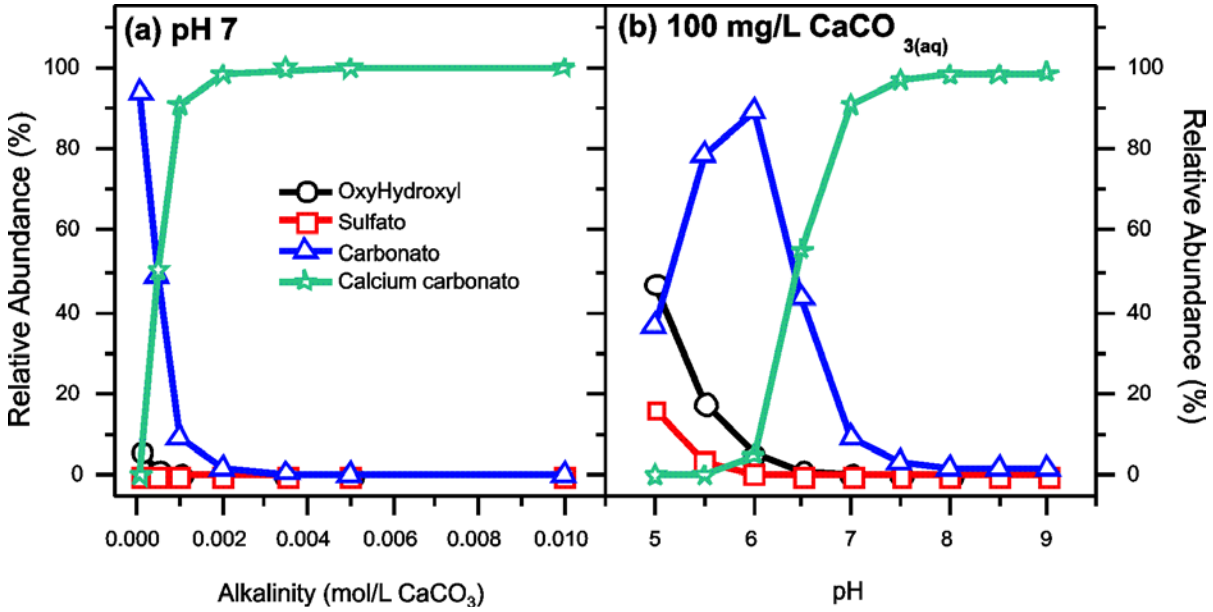

Figure 6.2 *Distribution of aqueous U(VI) species among oxyhydroxyl-, sulfate-, carbonate-, and calcium carbonate-complexes as a function of ground-water chemistry. (a) Dependence on alkalinity expressed as mol/L* $CaCO_{3(aq)}$ *; pH = 7, 0.005 mol/L NaCl, 0.001 mol/L* K_2SO_4 *, 0.001 mol/L* $MgNO_3$ *, 0.42 µmol/L U (100 µg U/L). (b) Dependence on pH; 0.001 mol/L* $CaCO_{3(aq)}$ *(100 mg/L* $CaCO_3$ *alkalinity), 0.005 mol/L NaCl, 0.001 mol/L* K_2SO_4*, 0.001 mol/L* $MgNO_3$*, 0.42 µmol/L U (100 µg U/L). Model predictions using Visual MINTEQ Version 2.53 (Based on MINTEQA2 described in Allison et al. (1991); available at* http://www.lwr.kth.se/English/OurSoftware/vminteq/*). Precipitation of Ca/Mg carbonates suppressed; slight oversaturation for pH > 8 and/or > 0.005 M* $CaCO_{3(aq)}$*.*

Solubility

Under ambient conditions, the thermodynamically stable uranium solid phases will be either U(VI) or U(IV) compounds. Thus, depleted U(0) will oxidize to U(IV) and, if sufficiently oxidizing conditions pertain, eventually to U(VI). The most stable U(VI) compounds are the phosphates and vanadates, but their formation is often limited by the relatively low concentrations of these two anions, and thus more soluble U(VI) oxides such as schoepite, which is bright yellow in color, are often seen, if any U(VI) solid phases are present. A significant fraction of the solid-phase U(VI) will be adsorbed to iron (hydr)oxide surfaces, the edges of clay minerals, and to organic matter, rather than precipitated as discrete U phases (discussed below). Maximum solubility of uranium is seen in oxidizing, phosphate-free, carbonate-rich solutions, and these are the principal reagents used for in-situ leach mining of uranium in the U.S. There are examples of uranium substitution into calcites from unimpacted (Sturchio et al., 1998; Kelly et al., 2003; Kelly et al., 2006) or contaminated environments (Wang et al., 2005a; Catalano et al., 2006), but this generally appears to occur only in locations where active precipitation of calcite or aragonite is occurring. The stability fields of U(VI) as a function of pH and various element combinations are shown in Figures 6.3 and 6.4. The pH-dependent solubility of U(VI) is shown in Figure 6.3 for systems containing carbonate and silica. In Figure 6.4, the role of phosphate in controlling U(VI) concentrations is illustrated. Precipitates of U(VI) have been observed to form near source areas where elevated uranium concentrations in ground water were likely to have existed. An example where the U(VI) silicate, sodium boltwoodite, formed near a uranium source area has been documented for the Hanford Site in Richland, WA (Catalano et al., 2004; McKinley et al., 2007). Examples of the types of uranium phosphate precipitates that have been identified include uranyl phosphate and uranium metaphosphate (Buck et al., 1996; Morris et al., 1996), barium meta-autinite (e.g., Jerden et al., 2003; Jerden and Sinha, 2003; Jerden and Sinha, 2006), and metatorbernite (Catalano et al., 2006; Arai et al., 2007).

Under reducing conditions, the stable U(IV) solid phases are uraninite and, if high dissolved silica pertains, coffinite. Organic complexes of U(IV) associated with humic material may also retain U(IV) in the solid phase. The solubility of the U(IV) phases is extremely low, and thus the presence of reducing conditions effectively halts the movement of uranium in soils and sediments, provided that colloidal-sized phases are not formed and transported. The most common uranium ore-forming process involves reductive precipitation of U(IV) phases as a result of microbiological activity to form a roll-front deposit (Langmuir, 1997). The stability fields for U(VI) and U(IV) as a function of pH and Eh for various water compositions are shown in Figure 6.5. The geochemical modeling results presented in Figures 6.3, 6.4, and 6.5 suggest that a wide variety of uranium-bearing precipitates are possible, especially in complex ground-water systems that invariably contain silica, carbonate/bicarbonate, calcium/magnesium, sodium, and sometimes phosphate. Furthermore, it may be difficult to predict associations of uranium in the solid phase based upon analysis of aqueous chemical data and solubility predictions from thermochemical data. In the absence of confirmatory solid phase characterization data, equilibrium model projections only indicate the possible formation of specific uranium-bearing precipitates.

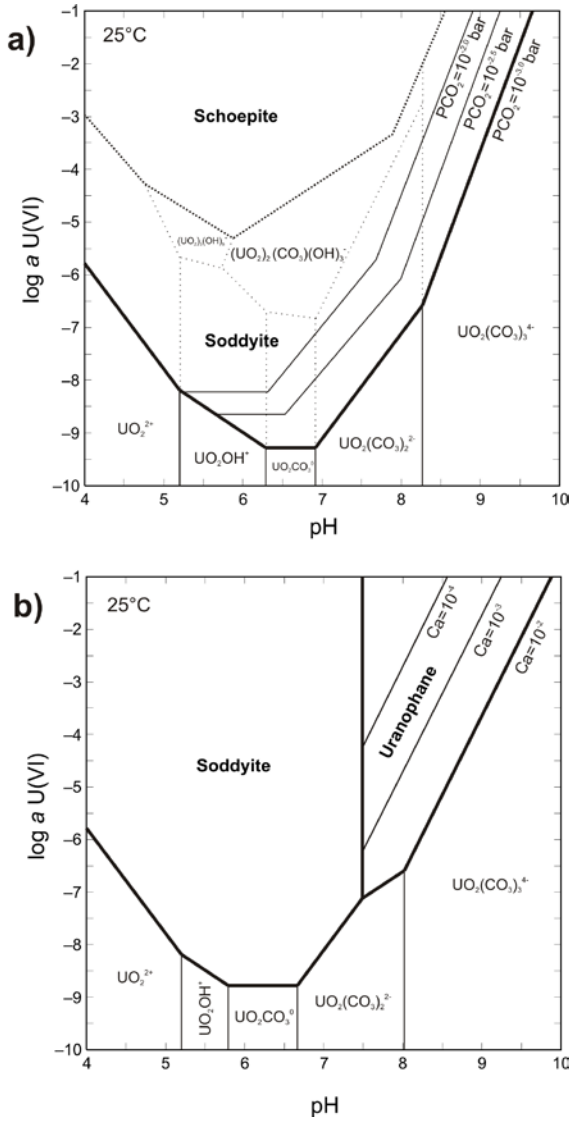

Figure 6.3 (*a*) *Solubility of U*(*VI*) *as a function of pH at various levels of* PCO_2 *and at* $aH_4SiO_4=10^{-4.0}$. *Bold lines show the pH-dependent solubility of soddyite* [$(UO_2)_2SiO_4{\cdot}2H_2O$] *at* $PCO_2=10^{-3.0}$ *bar. Note that the stability field of soddyite decreases with increasing* PCO_2. *Dashed lines show the metastable extensions of U*(*VI*) *aqueous species and the pH-dependent solubility of schoepite* [β-$UO_3{\cdot}2H_2O$] *at* $PCO_2=10^{-3}$ *bar.* (*b*) *Addition of Ca* (10^{-4} *to* 10^{-2}) *and Na* (10^{-3}). *Thermodynamic data for uranophane* ($Ca(H_3O)_2(UO_2)_2(SiO_4)_2{\cdot}3H_2O$) *are from Langmuir* (*1997; p. 552*). *Note that solubility studies by Pérez et al.* (*2000*) *suggest that uranophane may be less stable than depicted here.*

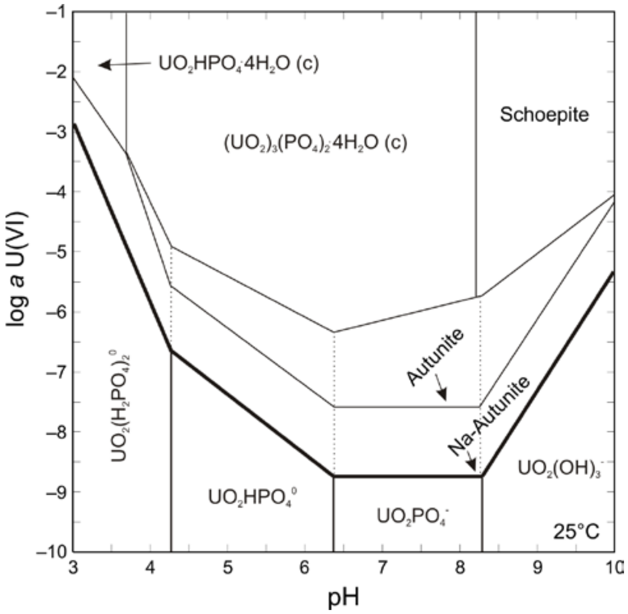

Figure 6.4 *Solubility of U(VI) as a function of pH and in the presence of phosphate ($10^{-3.5}$), sodium (10^{-3}), and calcium (10^{-3}). Na-Autunite ($Na_2(UO_2)_2(PO_4)_2$) is the least soluble solid across the pH range, followed by Autunite ($Ca(UO_2)_2(PO_4)_2$), $(UO_2)_3(PO_4)_2 \cdot 4H_2O$(c), Schoepite, and $UO_2HPO_4 \cdot 4H_2O$(c). Dashed lines show the metastable extensions of aqueous U(VI) species. Thermodynamic data for U-P complexes and solids are from Guillaumont et al. (2003).*

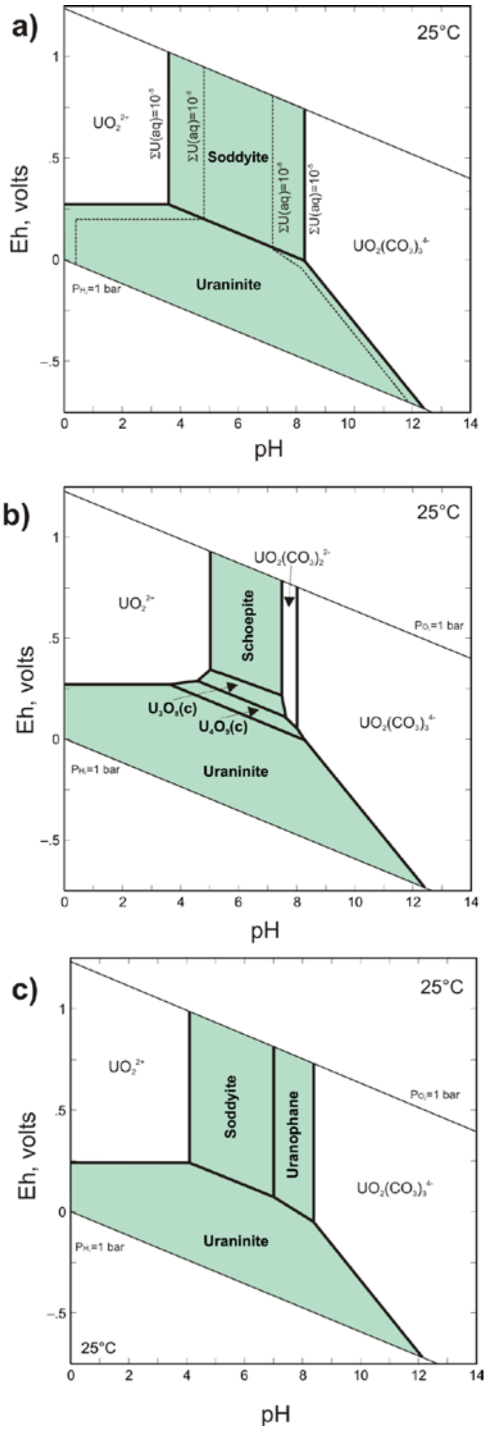

Figure 6.5 *Eh-pH diagrams for U at 25°C. (a) System U-O-H-Si-C, with $aH_4SiO_4 = 0^{-4.0}$ and $PCO_2 = 10^{-2.5}$ bar. (b) System U-O-H-C with $\Sigma U = 10^{-5}$ and $PCO_2 = 10^{-2.5}$ bar. (c) System U-O-H-C-Na-Ca with $\Sigma U = 10^{-5}$, $aH_4SiO_4 = 10^{-4.0}$, and $PCO_2 = 10^{-2.5}$ bar. Soddyite = $(UO_2)_2SiO_4 \cdot 2H_2O$; uraninite = UO_2; schoepite = β-$UO_3 \cdot 2H_2O$; uranophane = $Ca(H_3O)_2(UO_2)_2(SiO_4)_2 \cdot 3H_2O$.*

Adsorption

Adsorption of uranium typically involves inner-sphere complexation of uranyl (i.e., those containing UO_2^{2+}) species by oxygen ligands at the surfaces of iron oxyhydroxides, phosphates, and layered silicates. Uranyl species exhibit a high affinity for iron oxyhydroxide surfaces and for both basal and edge sites on layered aluminosilicates such as smectite and vermiculite. Adsorption of U(VI) to the aluminosilicate mineral, muscovite, has been observed in aquifer sediments at the Hanford Site in Richland, WA (Catalano et al., 2006; McKinley et al., 2007). Complexation of U(VI) by organic ligands in solid humic materials (primarily carboxylic-acid and phenolic groups) may also serve to remove uranium in shallow ground-water systems (Sowder et al., 2003).

A compilation of published K_d values for U(VI) sorption onto soils/sediments is documented in USEPA (1999). However, as recognized by the authors of this compilation, there are significant limitations to the application of published K_ds for site-specific applications where either the ground-water chemistry or the aquifer matrix differs significantly from the conditions under which a K_d was determined (Ochs et al., 2006). Davis and others (Davis and Curtis, 2003; Davis et al., 2004; Kohler et al., 2004) document an alternative approach whereby a site-specific K_d value is modeled through the use of a nonelectrostatic surface complexation model (NEM) developed as a function of site geochemistry for aquifer sediments. This approach incorporates the important influence of uranium solution speciation while avoiding the need to model the influence of individual mineral components (and their respective surface charging behavior). While this approach still requires site-specific data, it provides a means for projecting the influence of changes in ground-water chemistry on uranium sorption. The chemistry of ground water may be influenced by reaction with aquifer solids and/or external recharge/infiltration from atmospheric precipitation or surface water. As previously noted, alkalinity influences the aqueous speciation of U(VI), and it also influences the degree of sorption of U(VI) onto iron oxyhydroxides (e.g., Waite et al., 1994) and aquifer solids in which these minerals control uranium partitioning (e.g., Sato et al., 1997; Um et al., 2007). It has been demonstrated that changes in ground-water chemistry influence the transport of U(VI) through an aquifer (Dong et al., 2005; Yabusaki et al., 2008). Alternatively, transition from oxidizing to reducing conditions along the transport pathway may be accompanied by a shift from adsorption of U(VI) species to precipitation of U(IV)-bearing solids (Davis et al., 2006). Thus, it is recommended that reactive-transport models used to project subsurface uranium mobility directly incorporate the influence of major ion chemistry and redox conditions on the chemical speciation of uranium.

There is field evidence that adsorption of uranium to mineral surfaces within an aquifer may be an intermediate step to the formation of uranium-bearing precipitates. Murakami et al. (1997; 2005) have observed the association of nanoparticulate U(VI)-phosphate precipitates with iron oxyhydroxides in the weathering zone downgradient from a uranium ore deposit. The U(VI) mineral was identified as metatorbernite, which was present in ground water that was undersaturated with respect to precipitation of this mineral. Characterization of the textural associations between the nanocrystalline metatorbernite and iron oxyhydroxides present as fissure fillings, clay coatings, and nodules, along with compositional relationships between copper, phosphorous, and uranium (Sato et al., 1997) indicated that the formation of uranium precipitates was a secondary step following initial adsorption of these constituents onto iron oxyhydroxide mineral surfaces (Murakami et al., 2005). As summarized by Payne and Airey (2006), the observations in this subsurface system provide a point of reference for designing site characterization strategies and developing both conceptual and analytical models for interpreting and projecting uranium mobility in ground water.

Site Characterization

Overview

Uranium mobility in ground water is governed by the total concentration of uranium, the distribution of uranium species in water, and the nature of uranium partitioning in the solid phase. The development of conceptual site models for predicting the long-term fate of uranium at a contaminated site will require information on the concentration and chemical speciation of uranium in the aqueous phase and the solid phase. Table 6.2 illustrates possible attenuation and mobilization pathways for uranium in ground water. Details of the types of analytical measurements that may be conducted on sampled ground water and aquifer sediments to assist in identifying the attenuation mechanism(s) are discussed in the following paragraphs.

Aqueous Measurements

Overviews of radiometric techniques for determining the activity of uranium radioisotopes are provided in Tosheva et al. (2004) and USEPA (2006a). The sensitivity of these methods are generally good for uranium radioisotopes, but typically isolation of the analyte from the sample matrix is required prior to analysis. Becker (2003) and Lariviere et al. (2006) provide recent reviews of mass spectrometry applications for the determination of radionuclide concentrations in environmental samples. The sensitivity and mass-selectivity of these approaches, along with the ability to circumvent matrix and isobaric interferences, have significantly increased the utility of these methods. This can be further improved with the use of on-line techniques for the separation and enrichment of the targeted radionuclide from the sample matrix (e.g., Unsworth et al., 2001), similar to approaches used for radiometric measurements. Recent advances in automation of steps to isolate and concentrate the analyte prior to introduction to plasma-based mass spectrometers has increased the speed and utility of these multi-element analytical techniques.

Metilda et al. (2007) described development of an electrochemical sensor that facilitates selective extraction and detection of the uranyl anion [U(VI)] from natural water samples with a 5 μg/L detection limit. The sensor is constructed using an ion implanted polymer that can

Table 6.2 Natural attenuation and mobilization pathways for uranium.

Attenuation Processes	***Mobilization Processes***	***Characterization Approach***
Precipitation of uranium as U(IV) oxide or silicate phases in reduced systems	Increase in pH or alkalinity and/or transition to oxidizing conditions	Evaluation of U concentration in ground water and in solid matrix. Evaluation of U solid-phase partitioning using sequential extraction methodologies coupled to methods to determine U oxidation state. Characterization of aqueous redox and chemical conditions in ground water with speciation model evaluation of potential U(IV) stability.
Precipitation of uranium as U(VI) silicate or phosphate phases in oxic systems	Increase in alkalinity or dissolved organic carbon capable of forming solution complexes; decrease in silicate/phosphate concentration	Evaluation of U concentration in ground water and in solid matrix. Evaluation of U solid-phase partitioning using sequential extraction methodologies coupled to methods to determine U oxidation state; examine correlation to extractable phosphate and/or alkaline earth metals. Characterization of aqueous redox and chemical conditions in ground water with speciation model evaluation of potential U(VI) stability.
Adsorption or coprecipitation of U(VI) with iron oxyhydroxides, iron sulfides, and carbonates or adsorption onto clay mineral surfaces	Desorption due to high pH, high competing anion concentrations (e.g., carbonate), or high DOC concentrations. Reductive dissolution of iron hydroxides or oxidative dissolution of iron sulfides.	Evaluation of U concentration in ground water and in solid matrix. Evaluation of U solid-phase partitioning using sequential extraction methodologies; examine correlation to extractable Fe, Ca, Mg and S. Batch and column testing to determine U uptake behavior and capacity of site-specific aquifer materials under variable geochemical conditions.

be incorporated into optical detection configurations for screening or quantification of uranyl concentrations in aqueous solutions (James et al., 2008; Prasada Rao and Kala, 2008). The equipment needed for use of these sensors is suitable for use in field measurements. Recently, Liu et al. (2007) has demonstrated synthesis of a UO_2^{2+}-specific DNAzyme that can be incorporated into a simple sensor configuration for selective and sensitive quantification of uranyl. The authors demonstrated the performance of this analysis method for bicarbonate extracts of uranium-contaminated soils. Alternatively, detection of the uranyl dioxo-cation (UO_2^{2+}) can also be achieved in the laboratory using methods such as laser-induced kinetic phosphorimetry (Brina and Miller, 1992; Sowder et al., 1998; Elias et al., 2003), time-resolved laser-induced fluorescence spectroscopy (Wang et al., 2004; TRLIFS), or time-resolved emission spectroscopy (Billard et al., 2003). The latter two methods can be used to determine if multiple uranium species make up the mobile form of uranium. Greene et al. (2005) describe a method based on ultraviolet-visible detection of U(VI) following complexation with the organic chelating agent arsenazo III. Their adaptation of using solid phase extraction with C18 resin following buffering of the sample in pH 2 malonic acid resulted in elimination of interferences from commonly occurring ions and a detection limit of 40 nanogram/L. Thus, in addition to traditional methods that have been employed (e.g., USEPA, 2006a), there are a range of available methods for quantification of the uranyl ion in ground water at low concentrations, which will facilitate determination of the chemical speciation of mobile uranium when combined with analysis of the total uranium concentration.

Determination of the distribution of uranium radioisotopes may also be needed to determine the potential source or sources of uranium contributing to the ground-water plume. As outlined previously, contaminant sources of uranium from the production or processing of uranium for nuclear energy applications will lead to materials that are enriched or depleted in ^{235}U (or enriched in ^{236}U for reprocessed materials). Characterization of the ratios of uranium radioisotopes (^{234}U:^{238}U, ^{235}U:^{238}U, or ^{236}U:^{238}U) may be used to determine if the plume is derived from natural or anthropogenic sources (e.g., Zielinski et al., 1997). This information may be needed to determine the site-specific capacity for uranium immobilization under site-specific conditions. Also, as noted by Payne and Airey (2006), determination of the ratios of these radioisotopes in both ground water and aquifer solids can be used as a direct indicator of active attenuation, where activity ratios are anticipated to be similar for the two media where solid phase uranium concentration is dominated by the uranium mass from active attenuation within the aquifer. Both alpha spectrometry and plasma-based mass spectrometry can be used to obtain these data (e.g., Cizdziel et al., 2005; Zheng and Yamada, 2006; Stirling et al., 2007; Weyer et al., 2008).

Solid Phase Measurements

While it is evident that precipitation of uranium minerals may occur under reducing or oxidizing conditions, direct detection of these minerals via conventional methods such as X-ray diffraction will not be feasible in most cases due to low concentrations in aquifer solids. Use of microscopic techniques based on electron scattering/diffraction (Buck et al., 1996; Murakami et al., 1997; Jerden and Sinha, 2003; Murakami et al., 2005) or X-ray absorption (Arai et al., 2007) may be used for direct identification of uranium precipitates in aquifer solids. However, these techniques are generally labor-intensive and costly, and there are limitations to the ability to analyze a statistically representative mass or number of samples coincident with the dimensions of the contaminant plume. As demonstrated by Catalano and Brown (2004), accurate identification of individual solid species in heterogeneous mixtures using X-ray absorption spectroscopy will be limited by the similarities in the structures of uranium precipitates likely to form. For these reasons, use of liquid extractions, either for the determination of the total concentration of uranium in aquifer solids or the association of uranium with various components of the aquifer solids, provide the most tenable approach to ascertain the speciation or stability of attenuated uranium (Amonette et al., 1994). Extraction-based methods may be supplemented with characterization of select samples using electron microscopy, TRLIFS (Wang et al., 2005a; Wang et al., 2005b) or X-ray spectroscopy for confirmation of speciation assignments. As an example, use of X-ray absorption spectroscopy to determine the oxidation state of solid phase uranium (Yamamoto et al., 2008) may be valuable for confirming the attenuation mechanism.

Extraction of soils/sediments in combination with determination of specific radioisotope abundance in the liquid extracts has been used to identify potential sources of uranium contamination. Howe et al. (2002) used extraction solutions designed to target certain solid components in a series of sediment samples collected as a function of distance from a suspected contamination source to determine the influence of discharge from a nuclear fuel enrichment plant. Total uranium concentrations in sediments decreased with distance from the suspected source, and the $^{238}U/^{235}U$ ratio measured were significantly lower than those observed for a reference site with ^{238}U and ^{235}U at natural abundance ($^{238}U/^{235}U = 137.5$). Oliver et al. (2008) similarly used sequential extraction solutions in combination with determination of isotopic abundance of extracted ^{238}U and ^{235}U to assess the mobility of uranium derived from depleted uranium in soils at weapons test ranges. In both cases, it was possible to directly determine the contaminant signature from that of natural sources of uranium. The use of sequential extractions also provided indirect information on the partitioning mechanism for contaminant sources of uranium, as well as relative changes in the solid phase speciation along the transport pathway. This approach is limited by non-selective extraction of uranium associated with specific solid components (Schultz et al., 1999) or re-adsorption to un-extracted solid components (Schultz et al., 1998; Lucey et al., 2007).

Determination of extractable U(VI) using bicarbonate solutions has been evaluated by several research groups using kinetic phosphorimetry as the detection method. Elias et al. (2003) demonstrated that a 1 M $NaHCO_3$ solution (pH = 8.3) extracted freshly precipitated uranyl phosphate and uranyl hydroxide spiked into aquifer sediment samples when conducted under a nitrogen atmosphere. These authors also demonstrated that this solution did not extract U(IV) from reduced sediment samples under nitrogen, so this procedure could be used to monitor the U(VI) content of solid samples that may also contain U(IV)-bearing solids. Kohler et al. (2004) evaluated use of a mixed solution of 0.014 M $NaHCO_3$ and 0.0028 M Na_2CO_3 (pH = 9.45) to extract U(VI) from contaminated aquifer solids that had been dried in air. Additional evaluation of this procedure for contaminated sediment samples from this site indicated that the extraction must be conducted under nitrogen immediately after collection in order to avoid oxidation and extraction of U(IV) that may be present in reduced sediments (Davis et al., 2006). These authors again provided evidence that U(IV) solid species are not extracted by sodium bicarbonate solutions if the procedure is conducted under nitrogen prior to potential oxidation of U(IV) during sample storage or processing. While solutions of sodium bicarbonate appear to dissolve both adsorbed and precipitated forms of U(VI), this approach appears to provide a reliable measure of U(VI) content in the contaminated aquifer solids. The amount of U(IV) in the solids could then be determined following more aggressive extraction using nitric acid (such as in EPA SW-846 Method 3051) with detection of total extracted uranium.

Long-Term Stability and Capacity

The long-term stability of attenuated uranium will depend on the maintenance of either 1) ground-water chemistry that prevents solubilization of U(VI) precipitates (e.g., phosphates or silicates), 2) sufficiently low reduction potentials to prevent oxidation and consequent solubilization of U(IV) solids, or 3) stability of the sorbent mineral and sufficiently low concentrations of competing ions that could displace the sorbed uranyl ion. Once uranium has been precipitated or adsorbed, the sustainability of the geochemical driving force (e.g., phosphate/silicate, redox, pH, and/or available surface sites) is critical to whether natural attenuation will be a viable cleanup option. Thus, it is recommended that post-attenuation changes in water chemistry be carefully considered to ensure that re-mobilization of attenuated uranium does not occur. Of particular concern are situations in which uranium is attenuated under reducing conditions that are induced by characteristics of the contaminant plume, specifically if the natural conditions within the aquifer are more oxidizing. As reviewed by Suzuki and Suko (2006), uranium concentrations in ground water may decrease to acceptable levels as a result of uraninite precipitation under reducing conditions. However, numerous studies have shown that oxidation and dissolution of the newly formed uraninite occurs readily upon the onset of more oxidizing conditions (Wan et al., 2005; Moon et al., 2007; Wu et al., 2007; Komlos et al., 2008). Dissolved oxygen and nitrate are common oxidants in ground water that can cause remobilization of reduced uranium from aquifer solids.

Determination of capacity for attenuation will depend on knowledge of the specific mechanisms leading to uranium partitioning to aquifer solids and the flux of uranium being transmitted through the aquifer. Since uranium may be derived from both anthropogenic and natural sources, determination of the source of this contaminant is critical to assessment of available capacity for attenuation. For anthropogenic sources of contamination, it is important to understand the characteristics of uranium release into ground water. The Hanford 300 Area in Richland, Washington provides a clear example of how inadequate characterization of the spatial- and time-dependent release characteristics from uranium contaminant sources can lead to an inaccurate assessment of available capacity for attenuation within an aquifer (USEPA, 2008). The affective capacity for attenuation within the aquifer will also depend strongly on the characteristics and variability of ground-water chemistry and aquifer solids properties along transport pathways, as well as the impact of hydrologic dynamics on subsurface chemistry as a function of space and time.

Tiered Analysis

Determination of the viability of uranium remediation in ground water via monitored natural attenuation will depend upon proper assessment of contaminant loading to the aquifer and prevailing geochemistry and mineralogy within the contaminant plume and the down gradient zone prior to the point(s) of compliance. Due to the long half-lives for the uranium radioisotopes of most concern, radioactive decay will not provide a viable mechanism for plume attenuation. Therefore, the goal of site assessment will be to demonstrate the process(es) controlling uranium sequestration onto aquifer solids and the long-term stability of solid phase uranium as a function of existing and anticipated ground-water chemistry. A recent technical review highlights several technical aspects that need to be carefully evaluated at a site in order to insure that reliable projections of attenuation capacity and stability can be realized (USEPA, 2008). The following tiered analysis structure for site characterization provides a technically defensible approach to evaluate candidate sites and define the potential limitations of MNA as part of a remedy for ground-water cleanup.

Tier I. Site characterization under Tier I will involve demonstration that the ground-water plume is static or shrinking, has not reached compliance boundaries, and does not impact existing water supplies. Once this is established through ground-water characterization, evidence is collected to demonstrate uranium partitioning to aquifer solids within the plume. If natural attenuation processes are active throughout the plume, then there should be an observed increase in solid phase concentrations within regions of the plume with higher aqueous concentrations, e.g., near the source term. This field partitioning data may be supplemented by geochemical modeling that incorporates measured water chemistry (e.g., pH, Eh, and major ion chemistry) throughout the plume to assess the potential for solubility control by a uranium precipitate such as an oxide, silicate, or phosphate phase. Identification of active sequestration to prevent uranium migration in ground-water provides justification for proceeding to Tier II characterization efforts.

Tier II. Under Tier II, the apparent rate and mechanism(s) of attenuation are determined. Estimates of a site attenuation rate(s) can be assessed via a well transect along the ground-water flow path. In addition, time-series data may be collected at one or more monitoring points within the plume. This information will allow assessment of the relative timescales for contaminant immobilization and fluid transport and determination of whether remediation objectives can be met within the required regulatory time frame. In addition, the mechanism(s) for attenuation are to be identified under this stage of site characterization. This effort will require determination of the chemical speciation of aqueous and solid phase uranium and may be approached according to the following scheme:

1) Determination of solution speciation via direct analytical measurements to define dissolved uranium oxidation state and aqueous complexation (e.g., Sowder et al., 1998; Billard et al., 2003) in combination with speciation calculations based on characterized ground-water chemistry;
2) Determination of the oxidation state of solid phase uranium (e.g., Elias et al., 2003);
3) Calculation of saturation state of ground water relative to measured aqueous chemistry complimented by the possible isolation of discrete uranium mineral phases via density separations (or other schemes) in regions of the aquifer with highest solid phase concentrations;
4) Determination of aquifer mineralogy (Amonette, 2002) to determine the relative abundance of components with documented capacity for uranium sorption (e.g., Davis et al., 2004); and
5) Determination of uranium-sediment associations via chemical extractions designed to target specific components within the aquifer sediment (e.g., Schultz et al., 1998; Oliver et al., 2008).

This compilation of information will facilitate identification of the reaction(s) leading to uranium immobilization. It is recommended that identification of uranium chemical speciation in aqueous and solid matrices be conducted using samples collected in a manner that preserves the in-situ speciation of dissolved uranium and mineralogy (Davis et al., 2006; USEPA, 2006b) and prevents loss of uranium from aqueous samples (e.g., due to oxidation and precipitation of ferrous iron in anoxic ground water). The demonstration of concurrence between conceptual and mathematical models describing uranium transport will entail development of site-specific parameterization of the chemical processes controlling uranium solid phase partitioning.

Tier III. Once the partitioning mechanism(s) have been identified for the site, the subsequent characterization effort under Tier III will involve determination of the stability of immobilized uranium and the capacity of the aquifer to sustain continued uptake. It is recommended that the stability of immobilized uranium be tested based on the anticipated evolution of ground-water chemistry concurrent with decay of the plume. For example, changes in ground-water pH can exert a significant influence on uranium adsorption or precipitate solubility. Therefore, it is recommended that sediment leach tests be conducted to characterize the magnitude of uranium mobilization as a function of pH for a ground-water chemistry representative of site conditions. It is recommended that the capacity for uranium uptake onto aquifer solids be determined relative to the specific mechanism(s) identified in Tier II. For example, if site characterization under Tier II indicated that microbial degradation of naturally occurring solid organic matter (SOM) resulted in reduction of U(VI) to insoluble U(IV), then the mass distribution of SOM within the aquifer needs to be determined. This site-specific capacity would then be compared to uranium mass loading within the plume in order to assess the longevity of the natural attenuation process. Evaluation of uranium radioisotope distributions in samples of ground water and aquifer solids along transport pathways is recommended in order to confirm whether the source of uranium is from identified contaminant source areas or from natural sources that are not stable under plume chemical conditions. If site-specific tests demonstrate the stability of immobilized uranium and that there is sufficient capacity within the aquifer to sustain uranium attenuation, then the site characterization effort can progress to Tier IV. For cases where contaminant stability is sufficient but aquifer capacity is insufficient for capture of the entire plume, then a determination of the benefits of contaminant source reduction is required.

Tier IV. Finally, under Tier IV a monitoring plan is established along with contingency plans in the event of MNA failure. It is recommended that the monitoring plan be designed to establish both continued plume stability and to identify changes in ground-water chemistry that may lead to re-mobilization of attenuated uranium. The specific chemical parameters to be monitored will include those identified under Tier III that may halt uranium partitioning and/or result in dissolution of either discrete uranium precipitates or aquifer minerals that sequester uranium from ground water. For example, solution phase parameters that could alter either uranium precipitation or adsorption include inorganic carbon (alkalinity), major ion chemistry such as Ca/Mg, and/or pH. In contrast, the concentration of dissolved iron may indicate the dissolution of an important sorbent phase within the aquifer (e.g., reductive dissolution of iron oxides). Changes in these parameters may occur prior to observed changes in solution uranium and, thus, serve as monitoring triggers for potential MNA failure. In this instance, a contingency plan can be implemented that incorporates alternative strategies to arrest possible plume expansion beyond compliance boundaries. Possible strategies to prevent plume expansion include pump and treat operations, installation of reactive barriers to enhance uptake capacity perpendicular to the direction of plume advance, or enhancement of attenuation processes within the aquifer through the injection of soluble reactive components (e.g., injection of phosphate to drive precipitation of autinite-like phases; See Nimmons, 2007 and USEPA, 2007 for example technologies.).

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Iodine

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Occurrence and Distribution

Iodine occurs as a trace element in the Earth's crust (average abundance of 0.45 mg/kg), and the concentration of iodine in soil ranges from 0.5 to 40 mg/kg with higher values commonly associated with organic soils (Fuge and Johnson, 1986; Hou et al., 2009). There are 14 radioisotopes of iodine with half-lives greater than 10 minutes (Hou et al., 2009). The only stable isotope of iodine is ^{127}I and the most long-lived radioisotope is ^{129}I. The ^{129}I radioisotope is produced in nature by spontaneous fission of naturally-occurring uranium (spontaneous fission of ^{238}U and thermal-neutron induced fission of ^{235}U in the crust) or by the interaction of cosmic ray particles with xenon in the atmosphere (Schmidt et al., 1998; Hou, 2004), although the ^{129}I/^{127}I ratio from natural sources is substantially lower than that from human nuclear activity (Hou et al., 2009). Common anthropogenic sources of ^{129}I include the production and reprocessing of nuclear fuel, since ^{129}I is produced as a fission product with a fission yield of 0.9% from ^{235}U and 1.6% from ^{239}Pu (USEPA, 2004; Aldahan et al., 2007). Nuclear-fuel reprocessing facilities constitute the major source of ^{129}I released in the environment. For example, it has been estimated that two European facilities at La Hague in France and Sellafield in England released 2,300 kg of ^{129}I to the environment from the start of operations through 1998 (Hou et al., 2000; Frechou and Calmet, 2003). For an example within the United States, between 1955 and 1989, the Savannah River Site in South Carolina released 52 kg ^{129}I (Kantelo et al., 1993), a portion of which was released to the subsurface via seepage basins (Beals and Hayes, 1995; Denham et al., 2009). Release of ^{129}I into the subsurface has also been documented for the Idaho National Laboratory (e.g., Beasley et al., 1998; Cecil et al., 2003), and it is suggested that historical nuclear fuel reprocessing activities have served as a primary source of anthropogenic ^{129}I across North America (Rao and Fenn, 1999).

Geochemistry and Attenuation Processes

Radioactive Decay

Iodine has one stable isotope in nature, ^{127}I. Radioactive ^{129}I, with a half-life of 1.57x10^{7} years, is an important fission product with a fission yield of 0.9% from ^{235}U and 1.6% from ^{239}Pu. Fission of ^{235}U also leads to the production of ^{131}I. However, due to its short half-life of 8.04 days, ^{131}I releases do not typically generate ground-water plumes of significant extent.

Aqueous Speciation

In natural systems, iodine may exist in the -1, 0, +1, +5, and +7 oxidation states (e.g., Burger and Liebhafsky, 1973; Hou et al., 2009). Of these, the -1 (e.g., aqueous I$^-$ or "iodide") and +5 (e.g., aqueous IO_3^- or "iodate") oxidation states are the most abundant inorganic species in ground water. The stability range of I$^-$ encompasses almost the entire pH and Eh range typically encountered in ground water (Figure 7.1). Under acidic conditions (pH<4), $I_{2(aq)}$ (oxidation state 0; "iodine") can be produced from the oxidation of I$^-$ or the reduction of IO_3^-. Iodine partitions between a soluble species [$I_{2(aq)}$] and a dissolved gas [$I_{2(g)}$] with the volatile form being susceptible to transfer into air (Evans et al., 1993). Iodide can form complexes with metal ions, but these are generally the least stable of all the halide complexes, with a few notable exceptions. Iodide forms extremely strong complexes to some soft metals, including silver and mercury (Gammons and Yu, 1997; Pruszyński et al., 2006). Iodate can also form complexes with a range of metal ions in aqueous systems (e.g., Miyamoto et al., 2008). Iodine forms relatively strong chemical bonds with organic matter, where iodine covalently bonds with carbon in the molecular structure of natural organic matter compounds (Walters and Winchester 1971; Schlegel et al., 2006). Several terms are used in reference to organic iodine species, including "iodoorganic compounds", "iodinated organic compounds", and specific forms such as methyl iodide (e.g., Amachi et al., 2001; Schwehr et al., 2009). Aqueous I_2 and methyl iodide may be transported from ground-water systems as volatile species into the overlying vadose zone or shallow soils (Fuge and Johnson, 1986; Fuge, 1990). As discussed below, the formation of volatile iodine species may be mediated by abiotic or biotic reactions.

The redox speciation of iodine in ground water may be influenced by a combination of abiotic and biotic reactions. Abiotic reactions that have been documented to result in a change in the oxidation state of iodine include reaction with Fe- or Mn-bearing constituents, as well as natural organic matter compounds. For reaction with Fe species, reduction of IO_3^- to I$^-$ by ferrous iron or Fe(II)-bearing solid phases has been observed in controlled laboratory studies (Jia-Zhong and Whitfield, 1986; Councell et al., 1997; Hu et al., 2005; Glaus et al., 2008). These reactions may be influenced by the activity of iron-reducing bacteria stimulated within a plume with degradable organic co-contaminants. Natural organic matter (e.g., fulvic acid) and Mn(II) also have the capacity to reduce IO_3^- and/or $I_{2(aq)}$ to I$^-$ (e.g., Skogerboe and Wilson, 1981; Anschutz et al., 2000; Steinberg et al., 2008a). The reduction of IO_3^- by natural organic matter may ultimately lead to incorporation of iodine into the organic matter molecule via formation of hypoiodous acid (HIO) or $I_{2(aq)}$ as an intermediate (Steinberg et al., 2008a). In general, these reactions are viewed as an electrophilic substitution of hydrogen by iodine on a phenolic ring within the natural organic matter structure (Reiller et al., 2006). Iodine forms a covalent bond with the phenolic group, and this reaction may be preceded by the reduction of IO_3^- (e.g., Steinberg et al., 2008a). Iodide (I^-) may also be oxidized to IO_3^- during interaction with Mn(IV) oxides present in aquifer solids (Fox et al., 2009; Gallard et al., 2009). In the presence of natural organic matter, Mn(IV) oxide may catalyze formation of organoiodide compounds (Gallard et al., 2009; Schwehr et al., 2009).

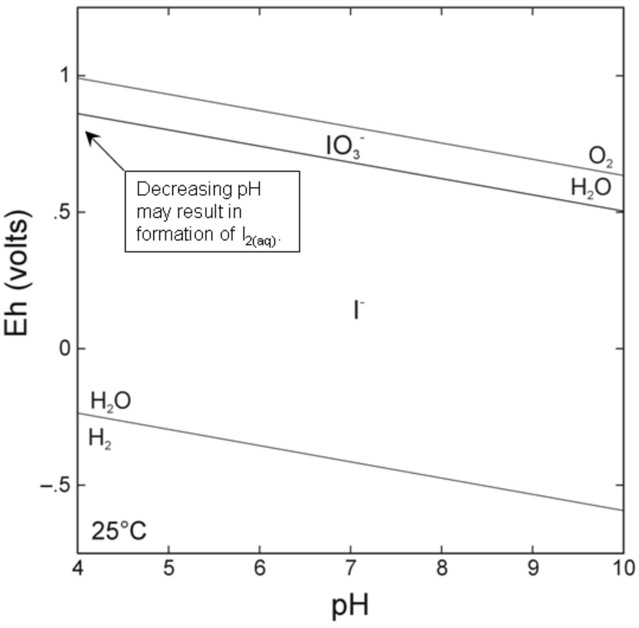

Figure 7.1. *Eh-pH diagram of dominant iodine aqueous species at 25°C (total I = 10^{-6} mol/L).*

Methylation and Volatilization

Sheppard et al. (2006) summarize available literature on the rate of volatile loss of iodine from soils. In general, review of available information for terrestrial systems indicates that the half-life for volatilization from soils is on the order of a decade or more. The potential for volatile losses will be mediated by characteristics of soils overlying the iodine plume, where soils containing higher content of organic carbon can act as a sorptive barrier for migration of volatile iodine species (Bostock et al., 2003). In this case, the effectiveness of the soil organic carbon for sorption of volatile iodine species may be limited by the form of volatile iodine, with $I_{2(aq)}$ being the most susceptible for sorption (see discussion above). Microbially-mediated production of volatile species of iodine appears to lead to formation of methyl iodide (CH_3I) as the primary volatile form (Amachi et al., 2001; Amachi et al., 2003; Muramatsu et al., 2004). While Muramatsa and Yoshida (1995) observed higher volatile losses of iodine under anoxic conditions where microbially-mediated production of methyl iodide appeared to dominate, the primary conduit for methyl iodide emissions was through plant shoots. Thus, it appears that direct volatile losses of iodine in shallow groundwater systems will be minimal, consistent with current recommendations discussed in Sheppard et al. (2006).

Adsorption

The adsorption of iodine onto various minerals that may be present in aquifer solids has been reviewed in USEPA (2004). For systems in which I^- and IO_3^- are the predominant species in groundwater, it is generally observed that IO_3^- adsorbs to a greater extent (Fukui et al., 1996; Hu et al., 2005; Kodama et al., 2006). The extent of ^{129}I adsorption will be limited by the presence of naturally occurring ^{127}I that may also be present in ground water and/or partitioned to aquifer solids (e.g., Tournassat et al., 2007). Another important factor for iodine adsorption is partitioning to natural organic matter (NOM) in aquifer solids. There are several studies that document the partitioning of iodine to organic carbon in aquifer solids via covalent bonding (Schlegel et al., 2006; Steinberg et al., 2008b), where $I_{2(aq)}$ appears to be a necessary intermediate. As discussed above, the intermediate $I_{2(aq)}$ species might be formed at low pH or via the abiotic/biotic reactions that lead to the oxidation of I^-, whereby iodine may be incorporated into organic species upon reaction with NOM (e.g., Warner et al., 2000; Reiller et al., 2006; Yamaguchi et al., 2006). As demonstrated by Gallard et al. (2009) and Schwehr et al. (2009), the relative distribution of iodine species resulting from the various redox reactions highlighted above will depend on the total iodine concentration as well as the relative abundance of reactants such as NOM and Mn(IV) oxides.

The hydrodynamics of the ground-water system may also exert control on the adsorption of iodine by influencing the total flux of oxidants or reductants that react with iodine during solid phase partitioning. This behavior is illustrated in the study by Ashworth and Shaw (2006a) where the dynamics of iodine solid-phase partitioning was monitored as a function of water content and redox potential. These dynamics are similar to what might be encountered at a fluctuating ground-water table at the "smear" zone that is commonly established at the interface between saturated and unsaturated aquifer solids. Ashworth et al. (2003; 2006b) have demonstrated this behavior in lysimeter experiments conducted in a manner to replicate the oxic-anoxic zonation that may develop at the water table in shallow ground-water systems. These studies have demonstrated accumulation of total iodine within the oxic-anoxic transition zone, which is consistent with observations of the vertical distribution of stable iodine in subsurface systems (e.g., Yuita and Kihou, 2005).

Site Characterization

Overview

Attenuation of ^{129}I might be achieved through sorption to aquifer solids. In general, two factors that appear to exert greatest influence on uptake of iodine onto aquifer solids are the predominance of the IO_3^- species and/or the presence of immobile NOM that can bind to iodine for systems where production of $I_{2(aq)}$ is active. These mechanisms will be influenced by the subsurface redox chemistry, which may be poised by available oxidants/reductants in ground water and aquifer solids or microbial processes that may be active throughout the plume. A list of potential attenuation processes is provided in Table 7.1.

For some sites, the volatile transfer of $I_{2(g)}$ or methylated species of ^{129}I from shallow ground water into overlying unsaturated soil or directly into open or confined atmospheres may also reduce ground-water concentrations. However, reliance on this mass transfer process will necessitate determination of the potential consequence of this exposure pathway to human and/or ecosystem health. Unacceptable exposures to airborne ^{129}I via volatile loss from ground water may necessitate active control of ^{129}I mass transport through the aquifer.

Table 7.1 Natural attenuation and mobilization pathways for iodine.

Attenuation Processes	Mobilization Processes	Characterization Approach
Adsorption of IO_3^- or I^- onto aquifer minerals (clay minerals, iron/manganese oxyhydroxides)	Desorption due to increasing pH or competition from major anions in ground water.	Evaluate total adsorption capacity of aquifer solids under representative ground-water chemistry; chemical extractions to assess concentrations and speciation of ^{129}I sorbed to aquifer solids along relevant transport pathways and determination of mobile iodine species in plume (^{127}I and ^{129}I).
Covalent bonding to immobile forms of NOM in aquifer solids	Degradation or mineralization of NOM resulting in release of complexed iodine; dissolution/ desorption of NOM into ground water	Determine concentration of aqueous and solid forms of NOM and bound ^{129}I along transport pathway(s).

Aqueous Measurements

Since ^{129}I decays by emitting β-particle with a maximum energy of 154.4 keV and γ-rays of 39.6 keV as well as X-rays (29–30 keV), it can be measured using γ-spectrometry and β-counting using liquid scintillation counting (Hou and Roos, 2008; Hou et al., 2009). The presence of other radionuclides with overlapping decay energy emissions (e.g., ^{137}Cs gamma peak at 32.1 keV) typically necessitates prior chemical separation of ^{129}I from the sample matrix. Alternatively, inductively coupled plasma-mass spectrometry (ICP-MS) may also be used for the quantification of ^{129}I via direct introduction of aqueous solutions or volatilization of iodine and introduction of the volatile species (Wuilloud and Altamirano, 2006; Brown et al., 2005; Wang and Jiang, 2008; Li et al., 2009). Recent developments in sample introduction schemes and techniques to minimize interference from formation of molecular ions within the plasma such as $^{127}I^{1}H^{1}H^{+}$ or interference from ions such as $^{129}Xe^{+}$ has improved the ability of ICP-MS for detection of ^{129}I at regulatory levels (Grinberg and Sturgeon, 2009). However, it should be noted that determination of ^{129}I by ICP-MS may ultimately be limited by the relative abundance of ^{127}I, with a reported lower limiting value of the $^{129}I/^{127}I$ mass concentration ratio of 10^{-7} in the analyzed sample (Li et al., 2009).

For the purpose of analyzing both total iodine and individual species of iodine in ground water, aqueous samples should not be acidified and are best stored in a gas-tight sample bottle with no head space. Acidification is to be avoided due to the potential pH-dependent species interconversions, e.g., reaction of I^- and IO_3^- to form I_2 (e.g., Cripps et al., 2003; Bhagat et al., 2008; Reid et al., 2008). It should also be noted that acidification of unfiltered ground-water samples may also be a source of high bias in measured dissolved iodine concentrations due to release from particulates in the sample (e.g., Buraglio et al., 2000). It is recommended that this situation be recognized and avoided in the monitoring system, since the resultant data may not be useful for evaluating mechanisms controlling contaminant transport. Tagami and Uchida (2005) investigated potential losses of total iodine from natural water samples for several storage conditions and holding times. In general, it has been observed that alkaline pH adjustment and storage below 5°C minimized analyte loss during storage (Tagami and Uchida, 2005; Wei et al., 2007). Losses of volatile species during sampling and handling could be minimized via direct sampling using in-situ diffusive membrane samplers deployed within the sampled water body or in-line during pumping from the ground-water well (e.g., Groszko and Moore, 1998).

Speciation of various iodine species in water samples can be conducted using chromatographic (Schwehr and Santschi, 2003; Yang et al., 2007; Wang and Jiang, 2008; Hou et al., 2009) or non-chromatographic (Bruchertseifer et al., 2003; Gonzalvez et al., 2009) methods of separation. For methods in which species separation and analysis is conducted in the laboratory following sample collection, confirmation of adequate preservation techniques is needed to demonstrate maintenance of in-situ chemical speciation of iodine. This can be accomplished by inclusion of field matrix spikes with additions of known iodine species at the point of sample collection. Field separation of I^- and IO_3^- species may be achieved through use of anion-exchange resins (e.g., Bruchertseifer et al., 2003; Cripps et al., 2003) with the potential to capture dissolved forms of potentially volatile species such as $I_{2(aq)}$ or CH_3I using solid-phase extraction (Bruchertseifer et al., 2003). Amachi et al. (2000) have proposed an alternative approach to isolate volatile inorganic and organic species of iodine from aqueous samples based on purge-and-trap in a container head space. As recommended in the review by Hou et al. (2009), the time between sampling and separation of iodine species should be minimized and is best conducted at the point of sample collection.

Solid Phase Measurements

Several methods have been documented for the analysis of total iodine in solid samples. These methods can be generally grouped as those that employ extraction of iodine from the solid matrix with alkali in liquid or solid form (Bing et al., 2004; Brown et al., 2005; Mani et al., 2007) or those that employ thermal extraction of iodine under an oxygen atmosphere (e.g., Izmer et al., 2003; Izmer et al., 2004; Chai et al., 2007, Englund et al., 2007; Balcone-Boissard et al., 2009). For the thermal extraction methods, extracted iodine is either trapped in an alkaline solution prior to analysis or delivered to the detection system in gas phase via direct coupling. Mani et al. (2007) describe use of a solution of tetra methyl ammonium hydroxide (TMAH) under relatively mild conditions for extraction of iodine from reference soils, sediments, and geochemical exploration samples. The values determined using extraction with TMAH compared well with published certified values for the reference soils. As has been demonstrated by Szidat et al. (2000a), it is important to assess the potential for sample contamination due to carryover throughout the analytical system. Assessment of carryover or losses of iodine species needs to include all processes of the entire analysis, including sampling, storage and sample preparation (Hou et al., 1998; Szidat et al., 2000b).

Distinguishing between stable (^{127}I) and contaminant forms of iodine (^{129}I) partitioned to aquifer solids may be necessary to properly identify the process(es) resulting in plume attenuation. Several published studies have made use of radiometric and mass-specific detection methods in order to identify the mass distribution of iodine isotopes, including evaluation of individual isotopes in reference soil/sediment materials. Values for ^{127}I concentration in Standard Reference Material 2709 (San Joaquin Soil) has been determined via several procedures involving either direct thermal volatilization of iodine from the solid matrix (e.g., Resano et al., 2005; 4.9 ± 0.3 mg/kg), thermal combustion and liquid trapping of ^{127}I (e.g., Marchetti et al., 1997; 4.67 ± 0.32 mg/kg), or decomposition of the soil via alkaline fusion followed by dissolution into a liquid matrix (Brown et al., 2005; 3.77-5.21 mg/kg). Marchetti et al. (1997) also report ^{127}I concentrations for Standard Reference Materials 2711 (Montana Soil; 2.67 ± 0.9 mg/kg) and 2704 (Buffalo River Sediment; 1.76 ± 0.07 mg/kg). Applications for the analysis of ^{129}I in solid materials have also been documented. For example, an updated measurement for the concentration of ^{129}I in the IAEA-375 reference soil material has been reported (Jiang et al., 2005). Schmidt et al. (1998) examined the influence of different approaches to extract and to assess recovery of ^{129}I and ^{127}I recovered from IAEA-375. Roberts and Caffee (2000) reported the results of an interlaboratory comparison study to assess the variability in ^{129}I concentrations determined for solid samples, which indicated that relative reporting errors could be high without adequate quality assurance measures. In addition, Izmer et al. (2004) have reported measurement of the ^{129}I/^{127}I ratio for Standard Reference Material 4357 (Ocean Sediment; 5.3x10^{-7} versus the certified 4.45x10^{-7}) using direct analysis of vapor by ICP-MS following extraction of iodine from the sediment by heating in an oxygen atmosphere. However, as discussed by Hou and Roos (2008), reliable determination of I^{129}/I^{127} ratios <10x^{-10} (i.e., a pre-nuclear age ratio) may require the use of accelerator mass spectrometry. Analysis of the ^{129}I/^{127}I ratio, in addition to the total ^{129}I concentration, provides a means to demonstrate ^{129}I plume attenuation onto subsurface solids along relevant ground-water flow paths.

Identification of the attenuation mechanism(s) that control iodine sorption within the plume may also necessitate determination of the chemical form of solid-phase iodine. While there are several approaches to chemically extract iodine from solid matrices for determination of total concentration, there are not established methods to extract iodine in a manner that preserves information on the nature of the chemical form of iodine originally in the solid matrix. Associations of iodine with specific solid components, e.g., iron oxyhydroxides or organic carbon, are often inferred based on apparent co-extraction of iodine with elements of the dissolved solid component (e.g., Fitoussi and Raisbeck, 2007; Hou et al., 2009 and references therein). As an example, Fitoussi and Raisbeck (2007) employed extraction of marine sediments with an alkaline TMAH solution in an effort to target ^{129}I associated with organic matter. However, further development of these types of extraction procedures is needed to verify the selectivity of the co-extraction process, since aggressive chemical solutions may also extract ^{129}I associated with other solid components. Alternatively, more recent studies have made use of X-ray absorption spectroscopy (XAS) to determine the in-situ oxidation state of solid-phase iodine and discern solid phase associations by reference to XAS spectra in model compounds (Kodama et al., 2006; Schlegel et al., 2006; Yamaguchi et al., 2006; Shimamoto and Takahashi, 2008). This technique provides the ability to differentiate between inorganic and organic forms of solid-phase iodine. While this analytical method is not routinely available, it does provide an approach to avoid potential analytical artifacts such as the oxidation/reduction of iodine that may occur during chemical extraction.

Long-term Stability and Capacity

The relative capacity for iodine sorption to aquifer solids, as well as the relative stability of sequestered ^{129}I, will likely depend on the effective period of contact between ground water and aquifer solids. As shown by Kaplan et al. (2000) and Um et al. (2004), systems in which there is a relatively short period of equilibration between ^{129}I and aquifer solids may be more susceptible to remobilization. As discussed above, the stability of adsorbed inorganic iodine species may also be influenced by changes in system redox, where the onset of reducing conditions tends to result in desorption of inorganic iodine as the I^- species. The formation of covalent bonds between iodine and immobile organic matter in aquifer solids is not a fast process, so this attenuation process may be limited for systems with higher ground-water flow velocities. The speciation of iodine in ground water and the sorption characteristics of aquifer solids will influence the relative importance of ground-water velocity on the degree of ^{129}I attenuation. Relative to the sorption characteristics of aquifer solids, Alvarado-Quiroz et al. (2002) have presented field data demonstrating changes in the apparent partitioning behavior of ^{129}I and ^{127}I along a ground-water flow path that transitions from surficial sands into a wetland area with elevated levels of sphagnum peat. The apparent in-situ partitioning constant for iodine measured along this flow path varied by 2-3 orders-of-magnitude, increasing with the change to a peaty texture in aquifer solids at the point of plume discharge within the wetland. As shown by Schwehr et al. (2005) for a coastal aquifer in California, attenuation of iodine may not be significant in situations where relatively high concentrations of competing anions exist (e.g., Cl^-) and the mobile form of ^{129}I is dominated by the iodide chemical species (I^-). The capacity for sorption of ^{129}I will also be limited by the concentration of stable iodine (^{127}I) within the plume. For example, in the F-Area plume on the Savannah River Site (Kantelo et al., 1993), background concentrations of stable iodine were 600 times greater than the ^{129}I concentrations (stable iodine = 270 μg/L and ^{129}I = 0.45 μg/L or 80 pCi/L).

Relative to iodine release from uncontrolled source areas, knowledge of the total contaminant mass as well as the rate and frequency of release into the saturated aquifer needs to be developed. In order to make a reliable assessment of the mass/activity flux of iodine into the plume, it will be important to understand the characteristics of the hydrogeologic system and the dynamics of water and contaminant transfer from contaminant source areas into the plume.

Tiered Analysis

Determination of the viability of ^{129}I remediation in ground water via monitored natural attenuation will depend upon proper assessment of contaminant loading to the aquifer relative to the sorption capacity of aquifer solids along relevant transport pathways to the point(s) of compliance. The goal of site assessment is to demonstrate that sorption is adequate to meet cleanup goals given current and projected hydrologic conditions for the site. The following tiered analysis structure for site characterization provides an approach to evaluate candidate sites and define the potential limitations of MNA as part of a remedy for ground-water cleanup.

Tier I. Site characterization under Tier I will involve demonstration that the ground-water plume is static or shrinking, has not reached compliance boundaries, and does not impact existing water supplies. Once this is established through ground-water characterization, evidence is collected to demonstrate ^{129}I partitioning to aquifer solids within the plume. If natural attenuation processes are active throughout the plume, then there should be an observed increase in solid phase concentrations concurrent with decreases in aqueous contaminant concentrations. This field partitioning data may be supplemented by geochemical modeling that incorporates measured water chemistry (e.g., pH, Eh, and major ion chemistry) throughout the plume to assess the predominant oxidation state of iodine within the plume. Identification of active sequestration to prevent ^{129}I migration in ground-water provides justification for proceeding to Tier II characterization efforts.

Tier II. Under Tier II, the apparent rate and mechanism(s) of attenuation are determined. Estimates of a site attenuation rate(s) can be assessed via a well transect along the ground-water flow path. In addition, time-series data may be collected at one or more monitoring points within the plume (USEPA, 2007; Section IIIA.5). This information will allow assessment of the relative timescales for contaminant immobilization and fluid transport and determination of whether remediation objectives can be met within the required regulatory time frame. In addition, the mechanism(s) for attenuation are to be identified under this stage of site characterization. This effort will require determination of the chemical speciation of solid phase ^{129}I and may be approached according to the following scheme:

1) Determination of solution and solid phase ^{129}I concentrations, along with the relative concentration of major ions/components in aquifer solids where attenuation is occurring, including analysis of trends in the distribution of ^{129}I with solid phase components that may be representative of potential sorbents;
2) Determination of aquifer mineralogy (Amonette, 2002) to determine the relative abundance of components that might support iodine sorption, e.g., iron oxyhydroxides and/or NOM; and
3) Determination of ^{129}I-solids associations via chemical extractions designed to target specific components within the aquifer solids.

This compilation of information will facilitate identification of the reaction(s) leading to ^{129}I immobilization. The demonstration of concurrence between conceptual and mathematical models describing ^{129}I transport will entail development of site-specific parameterization of the chemical processes controlling ^{129}I solid phase partitioning.

Tier III. Once the partitioning mechanism(s) have been identified for the site, the subsequent characterization effort under Tier III will involve determination of the stability of immobilized ^{129}I and the capacity of the aquifer to sustain continued uptake. It is recommended that the stability of immobilized ^{129}I be tested based on the anticipated evolution of ground-water chemistry concurrent with decay of the plume. For example, changes in the concentrations of dissolved halogen anions such as chloride or bromide can result in desorption of iodine from aquifer solids. Therefore, it is recommended that sediment leach tests be conducted to characterize the magnitude of ^{129}I mobilization as a function of halogen anion concentrations for a ground-water chemistry representative of site conditions (e.g., Kaplan et al., 2000). It is recommended that the capacity for ^{129}I uptake onto aquifer solids be determined relative to the specific mechanism(s) identified in Tier II. For example, if sight characterization under Tier II indicated that immobile NOM was the primary sorbent leading to ^{129}I attenuation, then the mass distribution of NOM within the aquifer needs to be determined (e.g., Alvarado-Quiroz et al., 2002). This site-specific capacity would then be compared to ^{129}I mass loading within the plume in order to assess the longevity of the natural attenuation process. The flux or mass loading of ^{129}I through the aquifer source release characteristics may be influenced by the physical location of sources within the subsurface relative to the ground-water table. Fluctuations in infiltration through shallow, unsaturated zones and/or water table elevations within the aquifer due to variations in recharge may lead to periodic increases in ^{129}I flux into ground water from contaminant source areas. It is recommended that additional iodine transport modeling be included to evaluate the impact of these various scenarios to be assured that these perturbations do not significantly diminish attenuation. If site-specific tests demonstrate the stability of immobilized ^{129}I and that there is sufficient capacity within the aquifer to sustain ^{129}I attenuation, then the site characterization effort can progress to Tier IV. For cases where contaminant stability is sufficient but aquifer capacity is insufficient for capture of the entire plume, then a determination of the benefits of contaminant source reduction is recommended.

Tier IV. Finally, under Tier IV a monitoring plan is established along with contingency plans in the event of MNA failure. It is recommended that the monitoring plan be designed to establish both continued plume stability and to identify changes in ground-water chemistry that may lead to re-mobilization of attenuated ^{129}I. The specific chemical parameters to be monitored will include those identified under Tier III that may halt ^{129}I partitioning and/or result in dissolution of aquifer minerals that sequester ^{99}Tc from ground water. For example, a solution phase condition that could result in ^{129}I desorption includes development of reducing conditions within a previously oxic zone where IO_3^- was the predominant attenuated species. In contrast, increases in the concentration of dissolved ferrous iron may indicate the dissolution of an important sorbent phase within the aquifer (e.g., reductive dissolution of iron oxyhydroxides). For sites at which residual, subsurface ^{129}I sources are left near the water table, it is recommended that the site monitoring program include locations to assess changes in the release of ^{129}I to the saturated aquifer due to increased surface infiltration or rises in the ground-water table. Changes in these chemical and hydrologic parameters may occur prior to observed changes in solution ^{129}I, and thus serve as monitoring triggers for potential MNA failure. In this instance, a contingency plan can be implemented that incorporates alternative strategies to arrest possible plume expansion beyond compliance boundaries. Possible strategies to prevent plume expansion include pump and treat operations, installation of reactive barriers to enhance uptake capacity perpendicular to the direction of plume advance, or enhancement of attenuation processes within the aquifer through the injection of soluble reactive components that induce more oxidizing conditions.

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Radium

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Occurrence and Distribution

Radium in ground water may be derived from both natural and anthropogenic sources. Four radioisotopes of radium, ^{228}Ra, ^{224}Ra, ^{226}Ra and ^{223}Ra, are derived as decay products from naturally-occurring ^{232}Th, ^{235}U or ^{238}U radioisotopes in soils and rocks. As such, occurrence and distribution of radium in the natural environmental is largely controlled by the distribution of thorium and uranium. Bowen (1979) reported radium concentrations in rocks to range from 0.6 x 10^{-6} to 1.1 x 10^{-6} mg/kg and in sediments to be ~0.8 x 10^{-6} mg/kg. Radium concentrations in igneous rocks increase by 100 times along the geological sequence: ultrabasic (0.009 x 10^{-6} mg/kg), basic igneous (0.6 x 10^{-6} mg/kg), intermediate igneous (0.917 x 10^{-6} mg/kg), and granitic igneous (1.40 x 10^{-6} mg/kg) (Ames and Rai, 1978). The radium content of granitic igneous, sandstones, shales and limestones are all about the same, ~1 x 10^{-6} mg/kg.

There have been several reports relating geological land forms and land utilizations to total radium concentrations in drinking water (Rama and Moore, 1984; Longtin, 1988; Michel and Cothern, 1986; Michel, 1990; dePaul and Szabo, 2007; Vinson et al., 2009). Geological formations containing elevated uranium or thorium concentrations have been shown to contain elevated dissolved radium concentrations in their porewaters (Michel, 1990). Ground water impacted by agriculture has also been shown to have elevated radium concentration (Sidle et al., 2001). Waste solids and products of phosphate fertilizer production may contain elevated levels of uranium, and, subsequently, serve as a source of radioisotopes of radium that could leach into ground water (Rutherford et al., 1995; Rutherford et al., 1996; Kim et al., 2006). Finally, extensive surveys of ground water wells have shown that land uses that result in the acidification of ground water, to pH levels less than 5, were correlated to elevated radium concentrations (Michel and Cothern, 1986; Szabo and dePaul, 1998).

Anthropogenic sources of radium include phosphate mining areas (uranium exists as impurities in rock phosphates at concentrations of 100 to 150 mg/kg; Altschuler, 1973), uranium mining areas (Landa and Gray, 1995), areas impacted by oil-field brines (Pardue and Guo, 1998; Zielinski and Budhan, 2007; Bou-Rabee et al., 2009), and facilities where nuclear materials have been manufactured or processed (Siegel and Bryan, 2003). Other potential localized sources of radium include ground-water well drilling fluids whose composition includes natural barite with varying levels of coprecipitated radium (Clark et al., 2004), as well as luminescent devices that historically made use of radium as a material component (Baker and Toque, 2005).

Geochemistry and Attenuation Processes

Radioactive Decay

According to documentation in Tuli (2005), there are 37 radioisotopes of radium, four of which occur naturally as a part of the decay series for ^{238}U, ^{235}U, and ^{232}Th. Following are the four natural radioisotopes of radium, along with their respective half-life and natural decay progenitor (see also Uranium and Thorium chapters):

- ^{223}Ra has a half life of 11.434 days and is part of the ^{235}U decay series,
- ^{224}Ra has a half life of 3.66 days and is part of the ^{232}Th decay series,
- ^{226}Ra has a half life of 1600 years and is part of the ^{238}U decay series, and
- ^{228}Ra has a half life of 5.75 years and is part of the ^{232}Th decay series.

Since ^{232}Th is produced in the ^{236}U decay series, the relative abundance of ^{224}Ra and ^{228}Ra may be increased, relative to typical natural abundance, for sites where enriched uranium sources contribute to the ground-water plume. Likewise, elevated levels of ^{223}Ra may also be observed for sites where ^{235}U from uranium enrichment and processing activities are a source for contaminant plume development. These decay series are illustrated in Figure 8.1. Due to its relatively longer half life and production within the ^{238}U decay series, ^{226}Ra is typically the most abundant radioisotope in natural systems. The decay of the four naturally-occurring radioisotopes of radium produces radioisotopes of radon as follows: 1) ^{228}Ra decay produces ^{220}Rn (or “thoron”) via ^{224}Ra (see Figure 8.1), 2) ^{226}Ra decay produces ^{222}Rn (or “radon”; see Figure 8.2), and 3) ^{223}Ra decay produces ^{219}Rn (or “actinon”; see Figure 8.1). The energy of alpha particles produced during thorium decay is sufficient to eject the radium radioisotopes from the surface of solid matrices (Cowart and Burnett, 1994). As discussed by Vinson et al. (2009), alpha recoil is a likely physical mechanism that enhances the mobility of radium. This process will compete with chemical processes, such as adsorption and coprecipitation, which serve to limit radium mobility (discussed below).

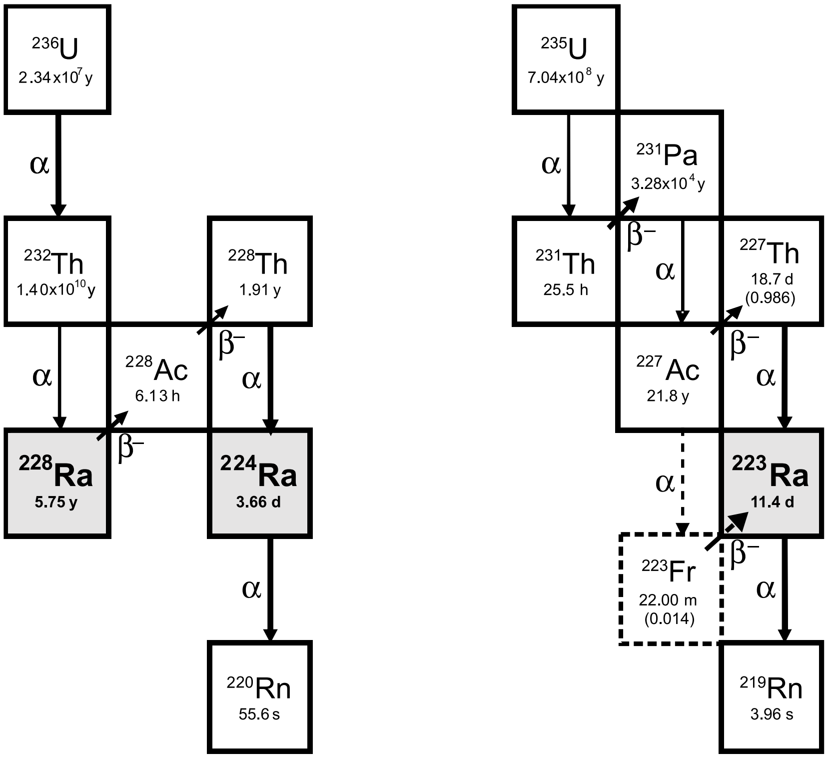

Figure 8.1 *Production of ^{228}Ra, ^{224}Ra, and ^{223}Ra (and the radon daughters of ^{224}Ra and ^{223}Ra) from the decay of ^{236}U and ^{235}U that may be present in ground water at levels greater than natural abundance due to uranium enrichment activities. Decay modes include those leading to ejection of an alpha particle (α) or a beta particle (β-). The half-life is shown directly below the isotope that is subject to decay; y = years, d = days, h = hours, m = minutes, s = seconds. Numbers shown in parentheses below indicate the fractional abundance of the daughter isotope produced during branched decay of the parent isotope (e.g., decay of ^{227}Ac follows two routes resulting in 98.6% production of ^{227}Th and 0.014% production of ^{223}Fr). Decay half-life data were obtained using the WinChain program that provides electronic access to the ICRP38 Nuclear Decay Data Files (ICRP, 1983; Eckerman et al., 1994; m = minutes, h = hours, d = days, y = years). WinChain is a public domain software application available for download from Oak Ridge National Laboratory (http://ordose.ornl.gov/downloads.html).*

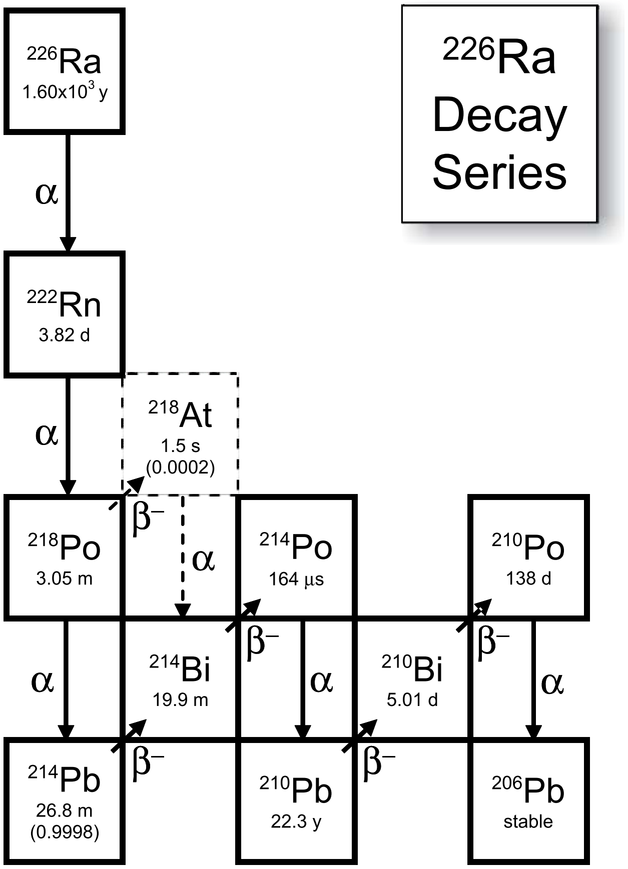

Figure 8.2 *Decay series for ^{226}Ra based on data from ICRP (1983). Decay modes include those leading to ejection of an alpha particle (α) or a beta particle (β-). The half-life is shown directly below the isotope that is subject to decay; y = years, d = days, m = minutes, s = seconds, µs = microseconds. Numbers shown in parentheses below indicate the fractional abundance of the daughter isotope produced during branched decay of the parent isotope (e.g., decay of ^{218}Po follows two routes resulting in 98.98% production of ^{214}Pb and 0.02% production of ^{218}At). Decay half-life data were obtained using the WinChain program that provides electronic access to the ICRP38 Nuclear Decay Data Files (ICRP, 1983; Eckerman et al., 1994; m = minutes, h = hours, d = days, y = years). WinChain is a public domain software application available for download from Oak Ridge National Laboratory (http://ordose.ornl.gov/downloads.html).*

Aqueous Speciation

Radium is an alkaline-earth element. These elements follow a number of trends that help predict their chemical behavior in the aqueous and solid phases in the subsurface environment. All alkaline-earth elements have +2 oxidation states and their hydrated ionic radii increase in the order $Ra^{2+} < Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+}$ (Huheey, 1983). The thermodynamic data of aqueous and solid speciation of radium was reviewed by Langmuir and Riese (1985). Ra^{2+} has little tendency to form aqueous complexes and of the alkaline-earth metals, Ra^{2+} shows the least tendency for complex formation (Langmuir and Riese, 1985). Furthermore, it may be assumed that Ra^{2+} does not hydrolyze (Baes and Mesmer, 1976). Throughout the pH range of 3 to 10, the uncomplexed ion Ra^{2+} is expected to be the dominant aqueous species for dissolved radium (Pardue and Guo, 1998; Sturchio et al., 2001; USEPA 2004). As illustrated by the analyses presented in evaluations of radium aqueous chemistry by Paige et al. (1998) and Sturchio et al. (2001), the existence of aqueous complexes of radium, such as $RaSO_{4(aq)}$, would likely only be significant under extreme conditions such as may be present in sulfuric acid leach solutions within contaminant source areas. Transport of radium downgradient into more dilute ground-water conditions would result in the conversion to Ra^{2+} as the predominant aqueous species.

Solubility

Most radium compounds, including $Ra(NO_3)_2$, $RaCl_2$, and $Ra(IO_3)_2$, are very soluble. Precipitates of radium that are sparingly soluble include $RaCO_3$ and $RaSO_4$ (Langmuir and Melchior, 1985; Baker and Toque, 2005). In ground water containing moderate to high sulfate concentrations, radium can precipitate as $RaSO_4$ or coprecipitate with barium as $(Ba,Ra)SO_4$ (Langmuir and Melchior, 1985; Pardue and Guo, 1998), and, to a lesser extent, radium may coprecipitate with calcium in gypsum (Beddow et al., 2006; Yoshida et al., 2009). Likewise, radium may be coprecipitated with calcium during calcite precipitation in ground-water systems with elevated alkalinity (Yoshida et al., 2008). Coprecipitation is expected to be more common because ground-water concentrations of radium are typically too low to support pure phase precipitation of $RaSO_4$. As a point of reference, stability fields for potential sulfate or carbonate precipitates of calcium or barium that may coprecipitate radium are shown in Figure 8.3. In these plots, the shaded regions show where these precipitate phases would form and remain stable. In general, carbonates would dominate at pH>7 in ground-water systems with elevated alkalinity. In addition, these diagrams illustrate that barium sulfate (barite) is much less soluble than calcium sulfate (gypsum). These projections appear to be consistent with observations made for some ground-water and sediment systems (Pardue and Guo, 1998; Martin and Akber, 1999; Grundl and Cape, 2006).

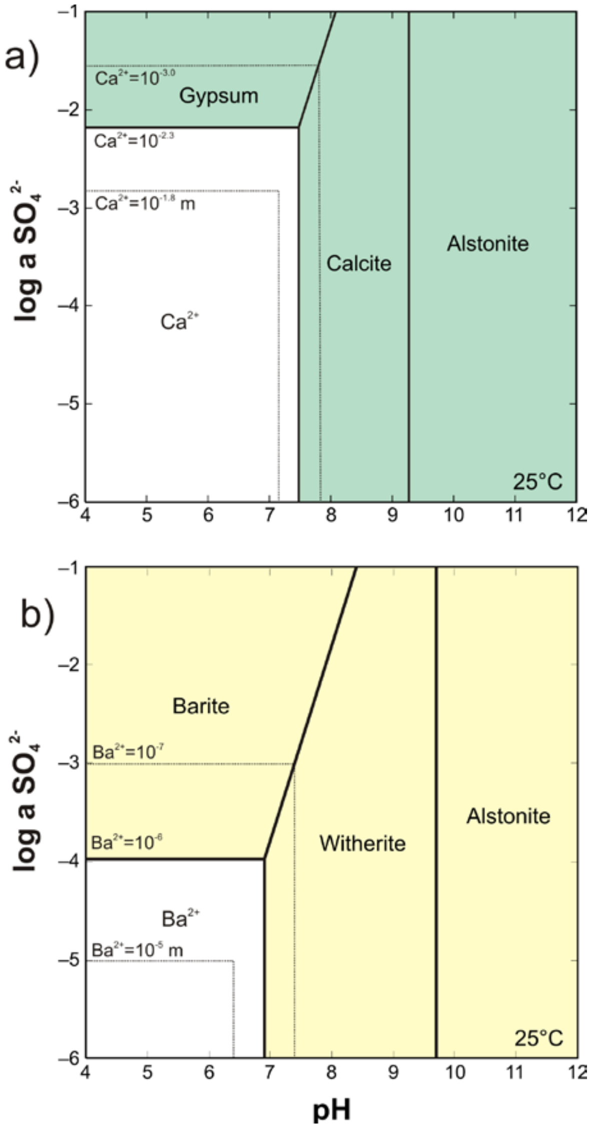

Figure 8.3 *pH – log aSO_4^{2-} diagrams showing stability fields for minerals in the Ba-Ca-Ra-SO_4-CO_2-H_2O system. Solubility data for Ra carbonate were taken from Langmuir and Riese (1985). Gypsum=$CaSO_4{\cdot}2H_2O$; Calcite=$CaCO_3$; Alstonite=$BaCa(CO_3)_2$; Barite=$BaSO_4$; Witherite=$BaCO_3$. a) $PCO_2=10^{-3}$ bars and variable Ca^{2+} from 10^{-3} m to $10^{-1.8}$ m. b) $PCO_2=10^{-3}$ bars and variable Ba^{2+} from 10^{-7} m to 10^{-5} m. At the MCL for Ra (2.2e-13 m), the Ra carbonate and Ra sulfate end-members are highly undersaturated at $PCO_2=10^{-3}$ bars and log a SO_4^{2-} from -6 to -1; however, Ra could be sequestered by Ba and Ca sulfates and carbonates.*

Adsorption

Recent overviews of radium adsorption processes in subsurface systems have been provided in USEPA (2004) and IAEA (2006). In general, it is assumed that ion exchange reactions would control radium adsorption based on patterns of uptake onto clay minerals (Tachi et al., 2001) and the apparent reversibility of the adsorption process (Ames et al., 1983; Centeno et al., 2004). For systems in which ion exchange reactions dominate radium partitioning to aquifer solids, the presence of competing cations in ground water will limit the extent of radium uptake (Berry et al., 1994). However, patterns in ground-water chemistry for some field studies (Herczeg et al., 1988), as well as direct observations in radium distributions in ground-water and associated aquifer solids (Gonneea et al., 2008), indicate that adsorption to iron/manganese oxides can also play a significant role in radium attenuation. In most instances, it is reported that radium adsorption onto iron/manganese oxides increases with pH, which is commonly observed for cations that form inner-sphere surface complexes on these solids. Based on use of manganese oxides in the pre-concentration of radium from water samples, it is suggested that these minerals exert some degree of selectivity for radium adsorption (Moore and Reid, 1973; see also discussion under *Aqueous Measurements*). At present, there is insufficient information to conclude that radium will show a preference for adsorption onto manganese oxides over iron oxides.

Hidaka et al. (2007) have observed excess accumulation of ^{226}Ra in the clay mineral, illite, within sandstone formations near the Oklo uranium deposit. Comparison of the relative distributions of stable and radioactive isotopes of radium, barium, lead, and uranium for illite and other aquifer minerals (calcite and quartz) indicated that radium was selectively taken up by illite, potentially as a result of ion exchange within interlayer sites of this clay mineral. The close correspondence between elevated concentrations of both radium and barium with illite suggests that the ultimate fate of adsorbed radium may have been coprecipitation of barite. However, no information was presented on either the concentrations of sulfur or sulfate with illite from these aquifer solids, which would be needed to provide evidence for coprecipitation in barite as the long-term immobilization process. Alternatively, both radium and barium may have been selectively retained on ion exchange sites that resisted desorption over time in this aquifer system.

Site Characterization

Attenuation of radium might be achieved through coprecipitation or adsorption dependent on the prevailing ground-water chemistry within the plume and the relative abundance and stability of immobile sorbent phases associated with aquifer solids. While radioactive decay may be a viable process for the short-lived radioisotopes, i.e., ^{223}Ra, ^{224}Ra, and ^{228}Ra, this will likely not serve as a viable attenuation process for plumes dominated by the longer-lived ^{226}Ra. Co-precipitation reactions are likely to occur only under situations where elevated sulfate concentrations drive precipitation of minerals such as barite or gypsum. Adsorption onto iron/manganese oxides and clay minerals will likely be the dominant attenuation process for aquifers undersaturated with respect to precipitation of sulfate/carbonate minerals. A list of potential attenuation processes is provided in Table 8.1. Two factors that will dictate the adequacy of attenuation via coprecipitation or adsorption include the rate of water transport and the total mass and release rate of radium into the subsurface plume. Details of the types of analytical measurements that may be conducted on sampled ground water and aquifer sediments to assist in identifying the attenuation mechanism(s) are discussed in the following paragraphs.

Table 8.1 Natural attenuation and mobilization pathways for radium.

Attenuation Processes	Mobilization Processes	Characterization Approach
Coprecipitation with sulfate minerals such as barite or gypsum	Dissolution due to decreasing ground-water sulfate concentrations and/or microbially driven sulfate reduction	Evaluate formation of sulfate minerals along relevant transport pathways and determine radium association with this mineral fraction.
Adsorption or ion exchange onto aquifer minerals (clay minerals, iron/manganese oxyhydroxides)	Desorption due to decreasing pH or competition from major cations in ground water; reductive dissolution of iron/manganese oxyhydroxides.	Evaluate total adsorption capacity of aquifer solids under representative ground-water chemistry; chemical extractions to assess concentrations of exchangeable radium fractions in aquifer solids along relevant transport pathways.

Aqueous Measurements

Due to its longer half-life, ^{226}Ra is the primary radioisotope encountered in ground-water plumes developed from the disposal of radium-bearing wastes with distributions of uranium and thorium parent radioisotopes similar to those found in natural systems. However, analysis of ^{228}Ra, ^{223}Ra, and/or ^{224}Ra may be warranted for situations in which delineation of the source(s) of ground-water radium contamination is needed (e.g., contaminant source zones that may have elevated levels of ^{235}U or ^{236}U parents; Martin and Akber, 1999). Measurement of the distribution of radium radioisotopes has been used as a marker for radium-enriched ground-water discharge zones into surface water (e.g., Lauria and Godoy, 2002). As shown above, decay of radium radioisotopes involves emission of an alpha particle (predominant energies: ^{226}Ra, 4.60 and 4.78 MeV; ^{223}Ra, 5.54, 5.61, 5.72, and 5.75 MeV; ^{224}Ra, 5.45 and 5.69 MeV) or beta particle emission (^{228}Ra, 12-40 keV), and, thus, can be measured using radiometric techniques (USEPA, 2006; Hou and Roos, 2008). Analysis of radium in environmental samples generally is targeted towards detection of ^{226}Ra and ^{228}Ra due to relative abundance. For both of these radioisotopes, it is common to determine activity indirectly via quantification of their first progeny, ^{222}Rn for ^{226}Ra and ^{228}Ac for ^{228}Ra (USEPA, 2006). This approach typically entails chemical separation of the parent/daughter radioisotope from the sample matrix to avoid interference from other radioisotopes that may be present (e.g., ^{230}Th, ^{234}U, ^{90}Sr) followed by a period of daughter in-growth to establish secular equilibrium between the parent and its daughter (USEPA, 2006; Hou and Roos, 2008). Due to similarity in chemical properties, ^{133}Ba is typically employed as a tracer for determining chemical recovery during separation of radium isotopes from the sample matrix. In general, these radiometric techniques provide typical detection limits of 1 pCi/L for both ^{226}Ra ($1\text{x}10^{-9}$ mg/L) and ^{228}Ra ($3.7\text{x}10^{-12}$ mg/L) (USEPA, 2006). If analysis of the short-lived radioisotopes ^{223}Ra and ^{224}Ra is planned, then the isolation and quantification should be conducted as soon as possible after sample collection. Otherwise, loss of parent and daughter radioisotopes due to decay during sample holding may result in activities below analytical detection.

Radium radioisotopes may be separated from the ground-water matrix via chemical extraction, coprecipitation with lead/barium sulfate (Bandong et al., 2005) or manganese dioxide, or through use of ion exchange or chelating resins (Rihs and Condomines, 2002; Lariviere et al., 2005; Aguado et al., 2008). Chemical extraction is commonly employed in combination with detection using liquid scintillation due to the availability of liquid scintillants that are efficient for radium extraction (e.g., Aupiais, 2005). Separation via coprecipitation with or adsorption onto manganese dioxide is frequently used to concentrate radium from water samples prior to a wide range of detection methods (Eikenberg et al., 2001; Dulaiova and Burnett, 2004; Ghaleb et al., 2004; Nour et al., 2004; Zoriy et al., 2005; Karamanis et al., 2006; Peterson et al., 2009), and there have been detailed studies to evaluate the various analytical parameters that influence the efficiency of radium extraction from water samples using this separation method (Eikenberg et al., 2001; Dimova et al., 2008; Garcia-Solsona et al., 2008; Moore, 2008). Pre-concentration of radium onto manganese dioxide has also been employed in field measurement methods that provide indirect quantification of radium radioisotopes based on detection of progeny such as radon (Kim et al., 2001; Dimova et al., 2007).

For the longer-lived ^{226}Ra, mass-based detection techniques, using ICP-MS as the analytical platform, have become increasingly reliable and sensitive. Hou and Roos (2008) have reviewed issues of potential analytical interference from the sample matrix, many of which can be largely controlled with the advent of improved sample introduction systems and collision-cell technologies for the interface between the plasma and the mass spectrometer (Lariviere et al., 2006). As with radiometric techniques, separation of ^{226}Ra from the matrix improves analytical detection and interference from the sample matrix (Lariviere et al., 2003). Recent developments have made it possible to incorporate and automate the separation procedure in-line with the ICP-MS system (Lariviere et al., 2003; Benkhedda et al., 2005), thus achieving improvements in sample throughput. In general, the sensitivity of mass-based detection is currently insufficient for this technique to compete with the radiometric techniques described above for ground water where detection of low concentrations may be needed.

> ***[It should be noted that use of drilling fluids containing barite should be avoided during ground-water well installation due to the potential bias resulting from dissolution of naturally-occurring radium associated with barite in residual drilling fluids that can be difficult to remove from the screened interval. Due to the half-lives of the various radium radioisotopes, ^{226}Ra would be the most likely source of contamination from barite in drilling fluid.]***

Solid Phase Measurements

Solid phase measurements that may provide information useful to assessing processes controlling radium retardation within the aquifer and the capacity along relevant transport pathways include the determination of partitioning of radium radioisotopes to aquifer solids, the cation-exchange capacity of aquifer solids, and identification of aquifer solids mineralogy that may participate in adsorption and/or coprecipitation reactions. Evaluation of the mass distribution of radium radioisotopes between co-located ground water and aquifer solids throughout the plume provides an assessment of the extent that retardation reactions limit radium migration. Different approaches have been applied to the determination of the solid-phase speciation of radium in aquifer solids. One approach involves looking for correlations between radium and other elements within aquifer solids as a function of grain size or density fractions using either non-destructive (i.e., X-ray fluorescence for stable elements and alpha/gamma spectrometry for radioisotopes of radium) or destructive techniques based on decomposition of the solid sample with strong acids or alkaline fusion. Iwaoka et al. (2009) describe approaches for analyzing ore materials using acid or alkaline fusion decomposition methods prior to mass-based determination of stable element concentrations and gamma spectrometry to determine total ^{226}Ra and/or ^{228}Ra concentrations via detection of ^{214}Bi and ^{228}Ac progeny, respectively. For decomposition methods that solubilize radium into a liquid matrix, methods discussed under the section on *Aqueous Measurements* for sample preparation and analysis may be applicable. Ghaleb et al. (2004) and Lariviere et al. (2007) discuss approaches to pre-condition extract samples prior to analysis in order to remove high concentrations of matrix elements and/or radionuclides that might interfere with analytical quantification of radium. As described by Saint-Fort et al. (2007), it may be possible to use field-screening detection methods, based on measurements of total radiation with field meters, for the purpose of targeting samples for more detailed laboratory characterization.

Since radium attenuation will likely involve partitioning to existing or newly formed solid phases within the aquifer, chemical extraction procedures are commonly employed to target specific phases. For systems in which ion-exchange onto clay minerals is suspected, aquifer solids may be extracted using a concentrated salt solution with a cation that would displace radium from the exchange sites. An assumption of these procedures is that only exchangeable cations are released from the solid matrix. It is recommended that the potential for partial dissolution of the more labile mineral fraction in aquifer solids during extraction be assessed (e.g., Jackson and Inch, 1989). This may be achieved through measurement of the major ion chemistry in the extract solution (e.g., iron, manganese, sulfate), which may serve as markers for the dissolution of oxyhydroxides, sulfates or other components that may bind radium in a less labile form. Solutions containing a strong chemical reducing agent are commonly employed to target iron/manganese oxides to which radium (or barium) may be adsorbed or coprecipitated (Aguado et al., 2004; Charette et al., 2005). Benes et al. (1981) and Rutten et al. (2002) describe procedures for selective dissolution of barite using solutions of EDTA in ammonium hydroxide or an ammonium chloride solution at pH 7, respectively. For aquifer solids in which it is feasible to selectively dissolve radium-bearing barite, it may be possible to measure the ratio of extracted ^{228}Ra and ^{226}Ra relative to the concentration of these radioisotopes in co-located ground water, to determine whether solid-phase radium is a background component of the aquifer solids (i.e., ^{226}Ra predominates) or a newly-formed component (i.e., ^{228}Ra and ^{226}Ra reflect ground-water composition) derived from attenuation of radium within the ground-water plume (e.g., Zielinski et al., 2001). Alternatively, radium association with barite or other relatively insoluble phases may be assessed by selective extraction of other potential sorbent mineral phases prior to examination of radium associated with residual solids. Several studies have shown that radium coprecipitated with barite or strongly bound to clay minerals may not be extracted by solutions designed to target radium partitioned to readily accessible ion exchange sites, weak acid extractable phases (e.g., calcite), and/or reducible iron/manganese oxides (Pardue and Guo, 1998; Hidaka et al., 2007; Leopold et al., 2007).

Determination of the host mineral phase(es) dissolved for each extraction step is recommended, along with the use of surrogate radium-bearing phases spiked into the sediment to confirm accuracy of the procedure (e.g., Rudd et al., 1988). The choice of appropriate radium surrogate phase(s) would be governed by site-specific geochemical conditions or characterization of the mineralogy of the aquifer sediment. Based on information for likely endpoints for solid-phase partitioning, radium-bearing surrogate phases may include radium-bearing barite (natural or synthesized), radium-bearing gypsum or calcite, radium adsorbed to or coprecipitated with iron/manganese oxides, or radium-exchanged clay minerals. Spiking aquifer solids with these surrogate phases provides the basis for assessing the actual selectivity of the various extraction solutions used to target specific solid components. Physical and chemical procedures, e.g., size fractionation, may also be employed to assist in identifying specific components within aquifer solids that dominate radium solid-phase partitioning. Examples of procedures to identify the type and abundance of specific minerals along transport pathways are available in the literature (e.g., Amonette, 2002). Additional information on analysis approaches and analytical techniques applied to solid phase characterization is provided in USEPA (2007; Section IIIB).

Long-Term Stability and Capacity

The long-term stability of radium attenuated through coprecipitation or adsorption will depend upon the stability of the host mineral and the abundance of other ions which might displace adsorbed radium. The most easily envisioned case of the first is that radium coprecipitated in sulfate minerals might be remobilized if sulfate-reducing conditions develop (e.g., Pardue and Guo, 1998; Landa, 2003; Martin et al., 2003) due to a decreased influx of oxygen as terminal electron acceptor and/or an increased influx of readily degradable organic compounds in excess of the capacity of other terminal electron acceptors [e.g., solid phase Fe(III) or Mn(IV)] consumed as a result of stimulated microbial activity. Dissolution of host sulfate precipitates may also result from a decrease in ground-water sulfate concentration (e.g., Pulhani et al., 2007). In addition, reductive dissolution of manganese and/or iron oxyhydroxides might cause remobilization of adsorbed radium (e.g., Herczeg et al., 1988; Landa, 2003). Increases in divalent cation levels can also be expected to work against radium immobilization for sites dominated by cation exchange reactions (e.g., Martin and Akber, 1999; Sturchio et al., 2001). Review of the extent of plume development for a number of sites indicates that cation exchange within the saturated aquifer may have insufficient stability to prevent plume expansion (Brady et al., 2002). Thus, a critical factor for assessing the overall capacity of the aquifer for attenuation will be evaluation of the mass flux of dissolved radium moving through the plume relative to the rate of water movement through the aquifer.

Translocation of ^{226}Ra through the aquifer due to changes in chemistry may also influence the dimensions and location of a co-occurring ^{222}Rn plume. This may pose a concern at sites with shallow ground-water systems where exposure to radon in indoor air and/or exposure of ecological/human receptors in surface water following ground-water discharge may present potential contaminant exposure pathways. In order to make a reliable assessment of the mass/activity flux of radon throughout the plume, it will be important to understand the characteristics of the hydrogeologic system and the dynamics of water and radium transfer throughout the plume (see Radon chapter).

Tiered Analysis

Determination of the viability of radium remediation in ground water via monitored natural attenuation will depend upon proper assessment of contaminant loading to the aquifer relative to the velocity of ground-water travel and the prevailing geochemistry and mineralogy within the contaminant plume and the down gradient zone prior to the point(s) of compliance. The goal of site assessment is to demonstrate the process(es) controlling ^{226}Ra sequestration onto aquifer solids and the long-term stability of solid phase radium as a function of existing and anticipated ground-water chemistry. If short-lived ^{223}Ra, ^{224}Ra, and/or ^{228}Ra are a component of the plume, then radioactive decay may serve as a primary attenuation mechanism for these radioisotopes. The following tiered analysis structure for site characterization provides an approach to evaluate candidate sites and define the potential limitations of MNA as part of a remedy for ground-water cleanup.

Tier I. Site characterization under Tier I will involve demonstration that the ground-water plume is static or shrinking, has not reached compliance boundaries, and does not impact existing water supplies. Once this is established through ground-water characterization, evidence is collected to demonstrate radium partitioning to aquifer solids within the plume. If immobilization processes are active throughout the plume, then there should be an observed increase in solid phase concentrations within regions of the plume with higher aqueous concentrations, e.g., near the source term. Evaluation of the mass/activity of radium distributed between ground water and aquifer solids throughout the plume is recommended to account for both existing and potentially mobile forms of radium. This field partitioning data may be supplemented by geochemical modeling that incorporates measured water chemistry (e.g., pH and concentrations of barium, calcium, and sulfate) throughout the plume to assess the potential for solubility control by coprecipitation with sulfate minerals. It is also important at this stage of the site evaluation to determine source term characteristics such as the inventory of contaminant mass and the current and historical rate of release into the subsurface. Acquisition of this information in combination with identification of a stable plume provides justification for proceeding to Tier II characterization efforts.

Tier II. Under Tier II, the apparent rate and mechanism(s) of attenuation are determined. Estimates of a site attenuation rate(s) can be assessed via a well transect along the ground-water flow path. In addition, time-series data may be collected at one or more monitoring points within the plume (USEPA, 2007; Section IIIA.5). This information will allow assessment of the relative timescales for contaminant attenuation and fluid transport and determination of whether remediation objectives can be met within the required regulatory time frame. As part of this analysis, it is critical to determine the relative contributions of radioactive decay (for short-lived ^{223}Ra, ^{224}Ra, and/or ^{228}Ra) and immobilization to the overall observed attenuation. Determination of the contribution of radioactive decay will necessitate detailed analysis of system hydrology relative to flow pathway(s), flow velocity, and temporal variations in flow velocity and/or direction within the boundaries of the plume. This information, in combination with knowledge of contaminant source release characteristics, can be employed to develop a decay-transport model to project radionuclide activity/concentration distribution throughout the plume in the absence of adsorption/coprecipitation processes. For systems in which immobilization plays a role in observed attenuation, it will be necessary to identify whether adsorption onto existing aquifer minerals or coprecipitation with newly formed minerals predominates. This effort will require determination of the chemical speciation of solid phase ^{226}Ra and may be approached according to the following scheme:

1. Calculation of saturation state of ground water relative to precipitation of sulfate minerals along relevant radium transport pathways;
2. Determination of aquifer mineralogy to determine the relative abundance of components with documented capacity for radium adsorption with implementation of steps for aquifer solids collection, processing and analysis that avoid transformation of mineral species from reduced zones (e.g., oxidation of ferrous carbonate to ferric (hydr)oxide); and
3. Determination of solid phase radium associations via chemical extractions designed to target specific components within the aquifer solids.

This compilation of information will facilitate identification of the reaction(s) leading to radium attenuation. The demonstration of concurrence between conceptual and mathematical models describing radium transport will entail development of site-specific parameterization of the chemical processes controlling radium solid phase partitioning.

Tier III. Once the contributions from radioactive decay and adsorption/coprecipitation processes have been determined, the subsequent characterization effort under Tier III will involve determination of the stability of immobilized radium and the capacity of the aquifer to sustain continued uptake. It is recommended that the stability of immobilized radium be tested based on the anticipated evolution of ground-water chemistry concurrent with plume evolution. For example, changes in ground-water pH and/or cation composition can exert a significant influence on radium adsorption. Therefore, it is recommended that sediment leach tests be conducted to characterize the magnitude of radium re-mobilization as a function of pH for a ground-water chemistry representative of site conditions. It is recommended that the capacity for radium uptake onto aquifer solids be determined relative to the specific mechanism(s) identified in Tier II. For sites in which a continuing source of radium to the saturated aquifer exists, it is recommended that potential steps to minimize or eliminate this continued contaminant flux be evaluated and implemented where feasible. If site-specific tests demonstrate that the stability and capacity for radium immobilization are sufficient to sustain attenuation, then the site characterization effort can progress to Tier IV.

Tier IV. Finally, under Tier IV a monitoring plan is established along with contingency plans in the event of MNA failure. It is recommended that the monitoring plan be designed to establish both continued plume stability and to identify changes in ground-water chemistry that may lead to re-mobilization of attenuated radium. The specific chemical parameters to be monitored will include those identified under Tier III that may halt radium partitioning to aquifer minerals and/or result in solubilization of precipitates into which radium has been incorporated. Solution phase parameters that could alter either radium coprecipitation or adsorption include changes in pH and sulfate concentrations and/or increased concentrations of competing cations in ground water. As an example, increases in barium concentrations in ground water could signal either 1) the potential for displacement of radium from cation exchange sites, or 2) the dissolution of barium sulfate minerals in which radium is coprecipitated. Likewise, increases in Fe(II), Mn(II), and/or dissolved sulfide concentrations may signal the onset of reducing conditions that are dissolving aquifer solid phases to which radium is partitioned (e.g., sulfate precipitates or iron/manganese oxides). Changes in water chemistry may occur prior to observed changes in solution radium activity/concentration and, thus, serve as monitoring triggers for potential MNA failure. In this instance, a contingency plan can be implemented that incorporates engineered strategies to arrest possible plume expansion beyond compliance boundaries. Possible strategies to prevent plume expansion include ground-water extraction with surface treatment, installation of permeable reactive barriers to enhance uptake capacity perpendicular to the direction of plume advance, or enhancement of coprecipitation processes within the aquifer through the injection of soluble reactive components.

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Thorium

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Occurrence and Distribution

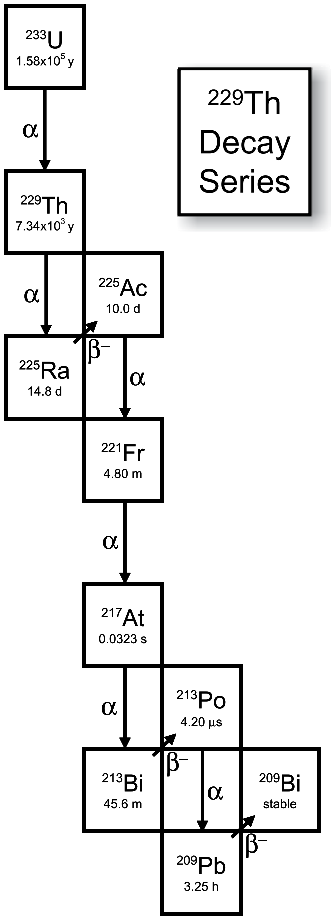
Thorium rock content varies greatly depending on the rock's origin (Adam and Richardson, 1960; Deer et al., 1967; Ames and Rai, 1978). Thorium concentrations in sedimentary rocks range from 1.1 mg/kg in limestone to 49 mg/kg in bauxite. It concentrates in sedimentary rocks primarily by selective adsorption on clays and coprecipitation in heavy resistate minerals, such as monazite [$(Ce,La,Th)PO_4$] or zircon ($ZrSiO_4$). Concentrations of thorium in metamorphic rocks are especially variable, ranging from 0.03 mg/kg in marble to 13.1 mg/kg in gneiss. Thorium concentrations in igneous rocks increase along the petrologic series from basalts (0.5 to 2 mg/kg) to granites (10 to 20 mg/kg). Finally, thorium concentrations in unimpacted sediments vary from 3.8 to 12.4 mg/kg (Govindaraju, 1994). Most thorium-containing minerals are sparingly soluble and resistant to erosion (Frondel, 1958). Thorium is an essential structural constituent in few minerals. Instead thorium usually occurs in variable concentrations in solid solution in rare-earth, zirconium, and uranium minerals. Thorium exists in commercial concentrations (percent levels) in detrital sands containing monazite and zircon (e.g., Baxter, 1996; Powell et al., 2007). Since long-lived thorium radioisotopes derive from decay of naturally-occurring radioisotopes of uranium, elevated subsurface concentrations of thorium may be encountered at sites where uranium mining, uranium ore milling, or uranium nuclear fuel production and nuclear fuel reprocessing has taken place (Carvalho and Oliveira, 2007; USEPA, 2008).

Thorium content in natural streams is very low, rarely exceeding 1 μg/L or 0.1 pCi/L ^{232}Th (Hem, 1985), and it is even lower in oceans, averaging ~5.3×10^{-5} μg/L (Huh and Bacon, 1985). As will be discussed below, these concentrations are low because thorium partitions strongly to essentially all mineral surfaces and it readily forms sparingly soluble precipitates, such as thorianite (or hydrous thorium oxide), ThO_2, in many ground-water systems (Langmuir and Herman, 1980). However, some naturally high thorium concentrations in ground water exist. Thorium concentrations in excess of 2000 μg/L were reported in acidic ground waters beneath uranium tailings sites (Langmuir and Herman, 1980). In another example, natural aqueous thorium concentrations of >22 μg/L were detected in Soap Lake in eastern Washington (LaFlamme and Murray, 1987).

Geochemistry and Attenuation Processes

Radioactive Decay

There are 26 radioisotopes of thorium, 14 of which have half-lives less than one second. Thorium isotopes that may be of concern for waste disposal operations include ^{227}Th ($t_{1/2}$ = 18.718 days), ^{228}Th ($t_{1/2}$ = 1.9131 years), ^{229}Th ($t_{1/2}$ =7340 years; Figure 9.1), ^{230}Th ($t_{1/2}$ = 77,000 years; Figure 9.2), ^{231}Th ($t_{1/2}$ = 25.52 hours), ^{232}Th ($t_{1/2} = 1.405 \times 10^{10}$ years), and ^{234}Th ($t_{1/2}$ = 24.1 days). The ^{229}Th radioisotope is produced from decay of man-made ^{233}U, which is proposed for use to produce the ^{213}Bi radioisotope for medical therapy applications (e.g., Apostolidis et al., 2005). However, while there is a limited inventory of ^{233}U ($t_{1/2} = 1.585 \times 10^5$ years) at some DOE sites, the amount of ^{229}Th is not considered to be a significant issue for ground water. Two thorium radioisotopes, ^{234}Th and ^{230}Th, occur naturally as decay products within the ^{238}U decay series. The ^{231}Th and ^{227}Th radioisotopes are produced within the ^{235}U decay series, and ^{228}Th is a decay product within the ^{232}Th decay series (Figure 9.3). Of the three longest-lived thorium radioisotopes, ^{232}Th is the most abundant in nature (>99%), and it may also be derived from decay of ^{236}U ($t_{1/2} = 2.341 \times 10^7$ years) at sites where spent nuclear fuel was disposed or reprocessed. As can be seen in Figures 9.1-9.3, radioisotopes of radium and radon are produced in the decay series for ^{229}Th, ^{230}Th, and ^{232}Th.



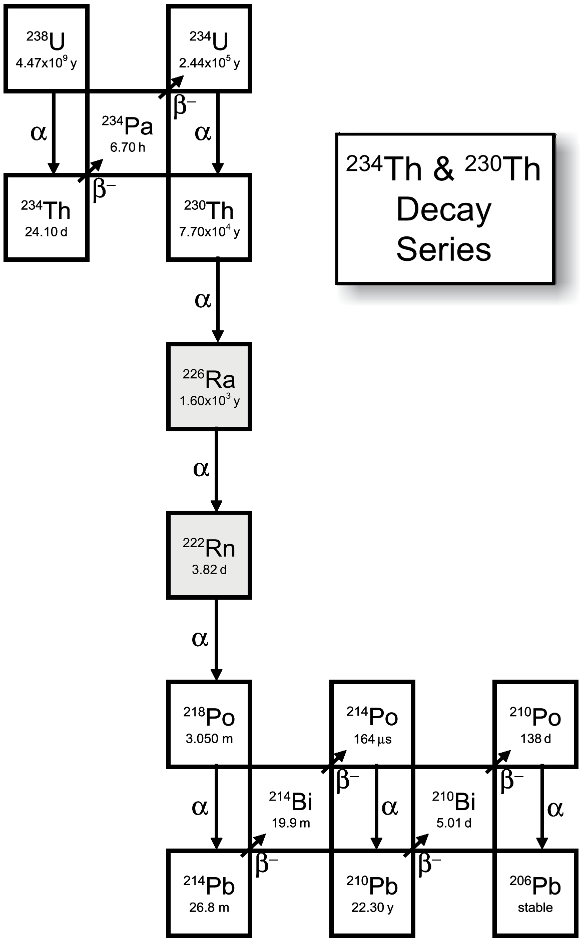


Figure 9.1 *Decay series for ^{229}Th including parent ^{233}U. The half-life is shown directly below the isotope that is subject to decay; y = years, d = days, h = hours, m = minutes, s = seconds, µs = microseconds, stable = non-radioactive isotope. Decay half-life data were obtained using the WinChain program that provides electronic access to the ICRP38 Nuclear Decay Data Files (ICRP, 1983; Eckerman et al., 1994). WinChain is a public domain software application available for download from Oak Ridge National Laboratory (http://ordose.ornl.gov/downloads.html).*

Figure 9.2 *Decay series for ^{234}Th and ^{230}Th including parents ^{238}U and ^{234}U. Production of ^{226}Ra and "radon" (^{222}Rn) within this decay series is highlighted. The half-life is shown directly below the isotope that is subject to decay; y = years, d = days, h = hours, m = minutes, µs = microseconds, stable = non-radioactive isotope. Decay half-life data were obtained using the WinChain program that provides electronic access to the ICRP38 Nuclear Decay Data Files (ICRP, 1983; Eckerman et al., 1994). WinChain is a public domain software application available for download from Oak Ridge National Laboratory (http://ordose.ornl.gov/downloads.html).*

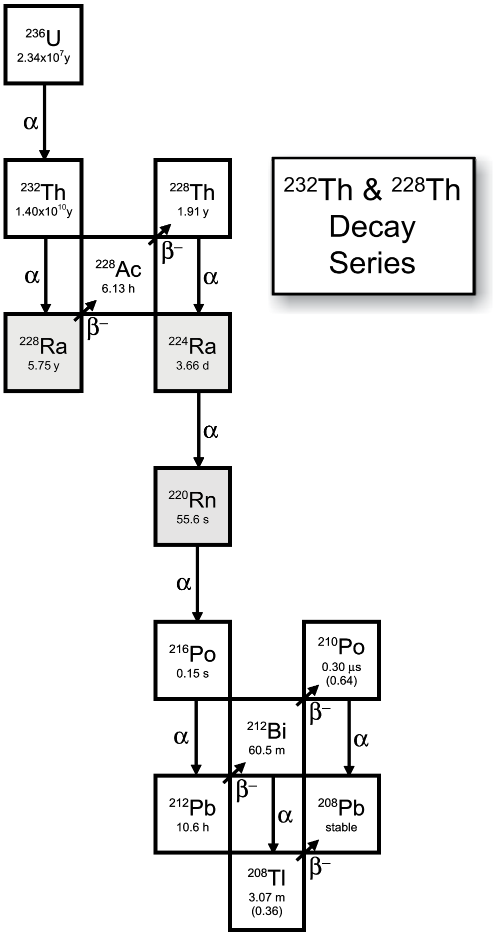


Figure 9.3 *Decay series for ^{232}Th including parent ^{236}U and progeny ^{228}Th. Production of ^{228}Ra, ^{224}Ra, and "thoron" (^{220}Rn) within this decay series is highlighted. The half-life is shown directly below the isotope that is subject to decay; y = years, d = days, h = hours, m = minutes, s = seconds, µs = microseconds, stable = non-radioactive isotope. Decay half-life data were obtained using the WinChain program that provides electronic access to the ICRP38 Nuclear Decay Data Files (ICRP, 1983; Eckerman et al., 1994). WinChain is a public domain software application available for download from Oak Ridge National Laboratory (http://ordose.ornl.gov/downloads.html).*

Aqueous Speciation

Although other oxidation states of thorium can exist under extreme laboratory settings, only Th(IV) is found in nature. The atomic radius of Th^{+4} is 9.9 nm, and because of its very small size and high charge it has an exceptionally high effective charge that undergoes extensive interaction with water and many anions. The available thermodynamic data for thorium aqueous species and solids have been compiled and critically reviewed (Hala and Miyamoto, 2007; Rand et al., 2008). Thorium exists as a complex, *i.e.*, a species other than Th^{4+}, in solutions of pH >3.5 (Figure 9.4a). Above pH 3.5, thorium readily undergoes hydrolysis to form a number of species, of which Th(OH)$_2^{2+}$, Th(OH)$_3^{+}$, and Th(OH)$_4^0$(*aq*) are the most predominant (Neck and Kim, 2001). Polynuclear complexes, in which more than one Th(IV) atom is incorporated within the structure of the aqueous complex, may also form at higher thorium concentrations (Rothe et al., 2002; Tsushima, 2008; Walther et al., 2009). It is this tendency to form polymeric species that is cited as a potential form of colloidal species that may be transported (see *Solubility*).

A ranking of inorganic anions in order of their increasing tendency to form complexes with thorium are: nitrite < chloride < phosphate < sulfate < fluoride (Langmuir and Herman, 1980). There is also evidence that the presence of synthetic chelating agents, such as citrate, EDTA or NTA in liquid waste streams, may also influence the speciation of thorium near contaminant source zones (Felmy et al., 2006; Cartwright et al., 2007). Under relatively acidic conditions in ground water with high sulfate concentrations, Th(IV) complexation with sulfate may dominate its aqueous speciation (Figure 9.4b; Felmy and Rai, 1992; Rand et al., 2008). Historical observations of elevated thorium concentrations in waters with elevated alkalinity have been attributed, in part, to the formation of aqueous complexes with carbonate (e.g., Anderson et al., 1982; LaFamme and Murray, 1987). Aqueous carbonate has been reported to form strong complexes with thorium to form ternary species with the general species formula Th(OH)$_y$(CO$_3$)$_z^{4\text{-}y\text{-}2z}$ (Osthols et al., 1994; Altmaier et al., 2005; Altmaier et al., 2006; Rand et al., 2008). The potential influence of dissolved carbonate on the aqueous speciation of Th(IV) is illustrated in Figure 9.5 for a system with elevated sulfate. For these equilibrium calculations, the partial pressure of CO$_2$ was varied from 0.0001 to 0.01 atmosphere, which results in an increase in the stability field of the ternary aqueous species, Th(OH)$_2$(CO$_3$)$^{2-}$, and a concomitant shrinkage in the stability fields for both solid phase ThO$_2$(am) and aqueous Th(OH)$_4$. It is anticipated that the formation of aqueous carbonate complexes may decrease thorium adsorption onto aquifer minerals for systems with elevated alkalinity (see *Solubility*).

Based on laboratory studies, complexation of thorium by natural forms of dissolved organic carbon (DOC) such as humic/fulvic acids may be expected to occur (Nash and Choppin, 1980; Reiller et al., 2008; Benes, 2009). In general, it has been proposed that formation of complexes with dissolved natural organic matter could dominate thorium speciation in ground water with elevated concentrations of DOC (e.g., Langmuir and Herman, 1980), although there are very few published data for subsurface systems to support this notion. Gaffney et al. (1992) provided direct analysis data for pore water sampled from a shallow wetland system that demonstrate thorium association with DOC for filtered samples. Also, Dia et al. (2000) present ground-water data for an aquifer flow path along a hill slope terminating in a wetland-riverine area that support a positive relationship between DOC and thorium (filtered, <0.2 μm). Characterization of the size distribution of DOC and thorium concentrations following further size-fractionation of <0.2 μm-filtered ground water below a wetland system suggests a potential strong association between thorium and colloidal forms of natural organic matter (Pourret et al., 2007). However, as demonstrated by Hassellov et al. (2007), conclusions about the apparent colloidal nature of particle-reactive contaminants such as thorium should be viewed with caution when strict controls are not taken at the point of sampling to prevent intrusion of oxygen in suboxic or anoxic ground-water samples. For example, precipitation of ferrous iron at concentrations as low as 3 mg/L potentially confound these interpretations, since both thorium and DOC will tend to partition to these colloidal solids that form during sample holding of un-acidified samples prior to commonly employed fractionation procedures. Thus, while existing chemical data support the potential for thorium to migrate with dissolved or colloidal forms of DOC, there is inadequate field data to support that this process can result in facilitated transport of thorium over large distances in an aquifer.

Solubility

Dissolution, precipitation, and coprecipitation are important processes controlling aqueous thorium concentrations. Current reviews of thermodynamic data describing the solubility of pure precipitates of thorium are available in Hala and Miyamoto (2007) and Rand et al. (2008). The main thorium-containing minerals are resistant to chemical weathering and do not dissolve readily at low temperatures in surface and ground waters. Hydrous thorium oxide, ThO_2, has been shown to precipitate in laboratory experiments conducted at low temperatures (Ryan and Rai, 1987). If this solid forms in nature, it is likely that it would become increasingly more crystalline and increasingly less soluble (Fanghanel and Neck, 2002). As noted above, thorium tends to form polymeric hydrolysis species, and this process has been observed to cause elevated apparent soluble thorium concentrations in pure aqueous suspensions of hydrous thorium oxide (Fanghanel and Neck, 2002). It has been proposed that these colloidal thorium species could influence concentrations in ground-water, although there are no field observations to verify the importance of this process. Osthols et al. (1994) determined that the solubility of ThO_2 increases greatly in the presence of dissolved carbonate. As can be seen in Figure 9.5, the range of pH at which aqueous concentrations of Th(IV) are controlled by ThO_2 solubility shrinks significantly with increasing dissolved carbonate concentrations (i.e., $10^{-4} \leq PCO_2 \leq 10^{-2}$).

Adsorption

The partitioning of thorium to a range of soils and aquifer solids has been presented in USEPA (1999). In general, this review supports the observation of the tendency for thorium to partition to aquifer solids. Under near-neutral pH conditions, thorium will primarily exist as a neutral dissolved species (see Figure 9.4) and has been observed to adsorb onto oxide and silicate minerals over a wide pH range with significant adsorption observed even under acidic conditions (e.g., Reiller et al., 2002; Bradbury and Baeyens, 2009). Several studies have demonstrated that thorium adsorption to mineral surfaces involves the formation of chemical bonds with surface functional groups (Dahn et al., 2002; Seco et al., 2009), and these reactions can be described using surface complexation models (e.g., Degueldre and Kline, 2007; Bradbury and Baeyens, 2009). Laboratory studies examining thorium partitioning to a wide range of mineral components reveal that thorium adsorption occurs on all types that might be encountered in aquifers (e.g., Guo et al., 2002; Geibert and Usbeck, 2004; Santschi et al., 2006). The adsorption of thorium to mineral surfaces may be inhibited (or desorption increased) with increasing concentrations of carbonate or dissolved organic matter in ground water (e.g., Laflamme and Murray, 1987; Reiller et al., 2002). As shown by Reiller et al. (2002), the influence of dissolved organic matter such as humic/fulvic compounds will likely depend on the relative concentration of dissolved organic matter and available adsorption sites on aquifer solids, with adsorption inhibition (or desorption) becoming a factor when dissolved organic matter concentrations exceed adsorption site concentrations. These authors also demonstrated that thorium adsorption may increase under conditions where humic/fulvic compounds partition to the mineral surface. Thus, it is anticipated that thorium will also partition to immobile forms of natural organic matter that may be present in aquifer solids for shallow ground-water systems.

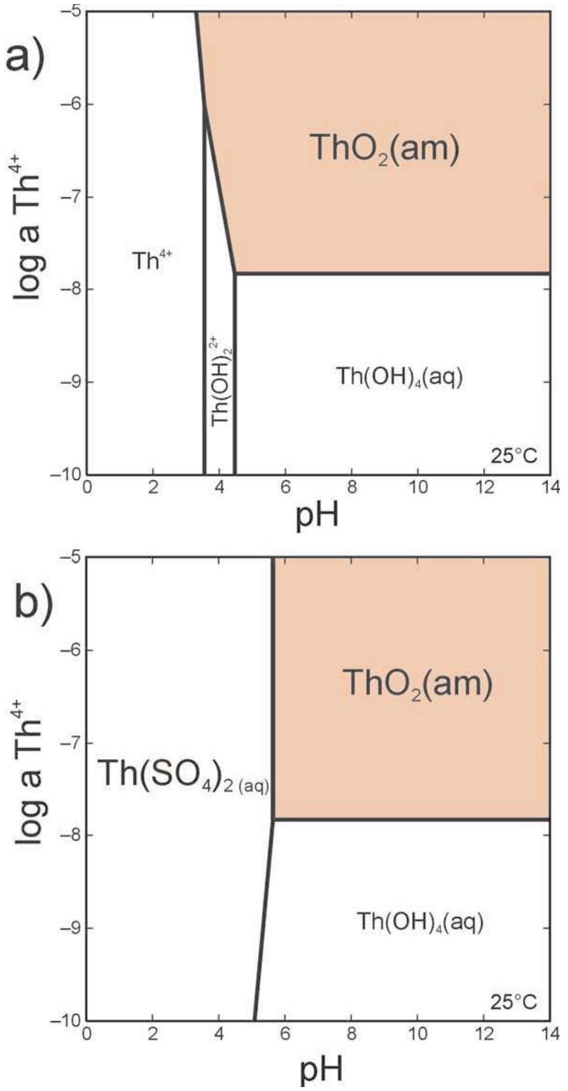


Figure 9.4 *Solubility of ThO$_2$(am) in (a) pure water and (b) 1 mM SO$_4^{2-}$. Diagrams constructed at 25°C using the LLNL thermodynamic database (therm.com.v8.R6+) modified using data reported in Altmaier et al. (2006) for the solubility of ThO$_2$(am) and Rand et al. (2008) for the solubility of Th(SO$_4$)$_2$·9H$_2$O.*

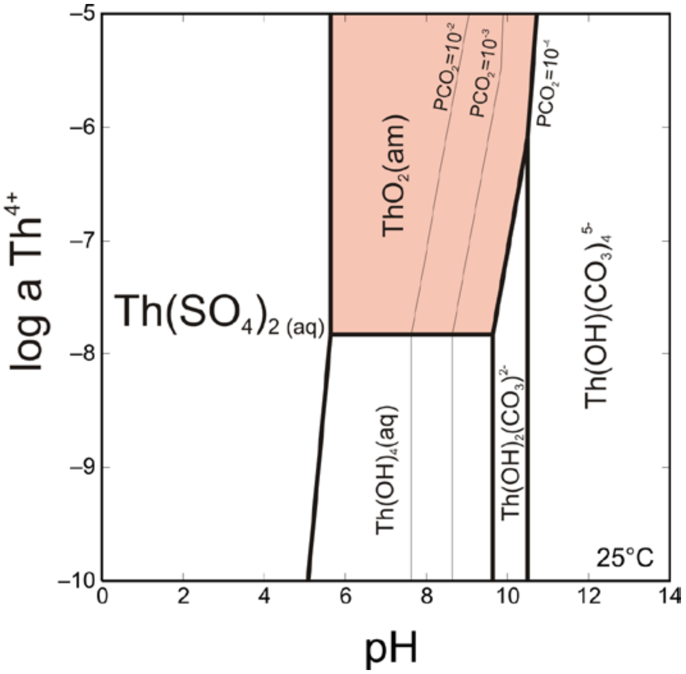


Figure 9.5. *Solubility of ThO$_2$(am) over variable log PCO$_2$ values (-4 to -2) and 1 mM SO$_4^{2-}$. Diagram constructed at 25°C using the LLNL thermodynamic database (therm.com.v8.R6+) modified using data reported in Altmaier et al. (2006) for Th-OH-CO$_3$ complexes and ThO$_2$(am) solubility, and Rand et al. (2008) for the solubility of Th(SO$_4$)$_2$·9H$_2$O. The light gray lines show the increase of the stability field for the aqueous species, Th(OH)$_2$(CO$_3$)$^{2-}$ with increasing PCO$_2$.*

Site Characterization

Attenuation of radium might be achieved through coprecipitation or adsorption dependent on the prevailing ground-water chemistry within the plume and the relative abundance and stability of immobile sorbent phases associated with aquifer solids. While radioactive decay may be a viable process for the short-lived radioisotopes, i.e., ^{228}Th or ^{234}Th, this will likely not serve as a viable attenuation process for plumes dominated by the longer-lived ^{232}Th. Due to the low solubility of hydrous thorium oxide, precipitation of this phase may occur near contaminant source areas where elevated dissolved thorium concentrations may exist. Adsorption onto clay minerals, iron/manganese oxides, and/or immobile forms of natural organic matter will likely be the dominant attenuation process for aquifers undersaturated with respect to precipitation of thorium. A list of potential attenuation processes is provided in Table 9.1. Two factors that will dictate the adequacy of attenuation via precipitation or adsorption include the rate of water transport and the total mass and release rate of thorium into the subsurface plume. Details of the types of analytical measurements that may be conducted on sampled ground water and aquifer sediments to assist in identifying the attenuation mechanism(s) are discussed in the following paragraphs.

Table 9.1 Natural attenuation and mobilization pathways for thorium.

Attenuation Processes	Mobilization Processes	Characterization Approach
Radioactive decay for short-lived radioisotopes (e.g., ^{228}Th, ^{234}Th)	Not applicable	Determination of ground-water velocity along relevant transport pathways and contaminant mass release rate from source areas.
Precipitation	Dissolution due to changes in ground-water chemistry	Evaluate formation of hydrous thorium oxide along relevant transport pathways based on calculated chemical saturation state of ground water.
Adsorption onto aquifer minerals (clay minerals, iron/manganese oxyhydroxides; immobile forms of natural organic matter)	Desorption due to decreasing pH, increases in alkalinity or complexation by organic ligands in ground water; reductive dissolution of iron/manganese oxyhydroxides.	Evaluate total adsorption capacity of aquifer solids under representative ground-water chemistry; chemical extractions to assess concentrations of thorium partitioned to sorbent phases in aquifer solids along relevant transport pathways.

Aqueous Measurements

Available methods for the determination of thorium radionuclides in ground water are reviewed in USEPA (2006a) and Hou and Roos (2008). In general, short-lived radioisotopes (^{228}Th, ^{234}Th) are best determined by radiometric methods, while long-lived radioisotopes (^{229}Th, ^{232}Th) can also be measured using mass spectrometric methods. Alpha spectrometry is the most common method used for detection of ^{228}Th, ^{230}Th, and ^{232}Th with some form of separation (e.g., extraction chromatography) of the thorium radioisotope from the ground-water matrix conducted prior to analysis (e.g., Grate et al., 1999; Tsaia et al., 2008). The use of mass spectrometry for analysis of longer-lived thorium radioisotopes is discussed by Lariviere et al. (2006) and Rozmaric et al. (2009). As with radiometric techniques, separation of the thorium radioisotope from the water matrix improves analysis by concentrating thorium for improved sensitivity and isolating thorium radioisotopes from potentially interfering constituents such as major ions and/or other actinides.

Solid Phase Measurements

The types of solid phase measurements that may be needed to assess thorium attenuation via immobilization and to differentiate natural versus contamination sources within the plume include determinations of total thorium concentrations, activity/concentration of specific thorium radioisotopes, as well as the partitioning of thorium to specific solid phase components along relevant transport pathways. For complete dissolution of the solid matrix, use of concentrated acid mixtures and/or alkaline fusion to break down resistant silicate components is typically required (Le Fevre and Pin, 2002; Selvig et al., 2005; Godoy et al., 2006; Galindo et al., 2007; Jia et al., 2008). As noted by Blanco et al. (2005) and Shimada-Fujiwara et al. (2009), use of hydrofluoric acid may lead to loss of thorium via precipitation of insoluble thorium fluoride during procedures that employ this strong acid (e.g., SW-846 Method 3052) if steps are not taken to prevent its formation. As with measurements for ground-water samples, isolation of the dissolved thorium radioisotopes from the sample matrix is commonly employed to improve the accuracy of radioisotope determinations. As demonstrated by Ketterer et al. (2000a; 2000b), analysis of the ratio of thorium radioisotopes in solid samples may assist in differentiating potential sources of elevated thorium concentrations in aquifer solids. Thorium contamination derived from the processing of uranium-bearing materials would likely have distributions of thorium radioisotopes that differ significantly from that observed in natural or background settings at a site. For example, depleted uranium wastes with ^{225}U:^{235}U ratios much lower than observed in aquifer solids from background locations may also have ^{230}Th:^{232}Th ratios higher than observed in background locations due to ^{230}Th derived from the ^{238}U decay series. Sims et al. (2008) recently reported on the results of an inter-laboratory comparison for the determination of ^{230}Th:^{232}Th ratios in a wide range of solid reference materials, demonstrating the potential applicability of this forensic tool for site investigations.

Sequential extraction procedures may be employed to help identify the reactive solid component(s) controlling thorium adsorption within the contaminant plume. Determination of the host mineral phase(es) dissolved for each extraction step is recommended, along with the use of surrogate thorium-bearing phases spiked into the sediment to confirm accuracy of the procedure (e.g., Rudd et al., 1988). The choice of appropriate thorium surrogate phase(s) would be governed by site-specific geochemical conditions or characterization of the mineralogy of the aquifer sediment. Based on information for likely endpoints for solid-phase partitioning, thorium adsorbed to existing/newly formed iron/manganese oxides or clay minerals may provide reasonable surrogates. Spiking aquifer solids with these surrogate phases provides the basis for assessing the actual selectivity of the various extraction solutions used to target specific solid components. Physical and chemical procedures, e.g., size fractionation, may also be employed to assist in identifying specific components within aquifer solids that dominate thorium solid-phase partitioning. Examples of procedures to identify the type and abundance of specific minerals along transport pathways are available in the literature (e.g., Amonette, 2002). Additional information on analysis approaches and analytical techniques applied to solid phase characterization is provided in USEPA (2007; Section IIIB).

Long-term Stability and Capacity

Limitations for the attenuation of thorium via adsorption onto aquifer solids are not anticipated due to the relative abundance of reactive surface area for uptake. However, this behavior is predicated on the absence of dissolved/mobile constituents that may compete for binding with thorium. As discussed previously, formation of soluble complexes with carbonate or dissolved organic carbon can increase the mobility of thorium. Examples where the concentrations of these constituents might be anticipated include 1) contaminant plumes in which recalcitrant and/or degradable organic contaminants are also present and 2) shallow ground-water systems in which a downward flux of natural sources of dissolved organic carbon from overlying soils (e.g., humic or fulvic components) is supported by surface infiltration from surface sources of water and/or fluctuations of the shallow ground-water table. Recalcitrant organic contaminants, such as synthetic chelating agents that may have been used in process solutions, may facilitate thorium migration via formation of mobile complexes in ground water. Degradation of organic contaminants within a plume will lead to the production of excess alkalinity relative to the natural ground-water conditions, which could impede adsorption or precipitation of thorium via complexation with dissolved carbonate. Also, the spread of reducing conditions that may accompany down gradient transport of organic contaminants could lead to reductive-dissolution of iron/manganese oxyhydroxides and re-mobilization of adsorbed or coprecipitated thorium.

Due to the tendency for thorium to bind with natural organic matter, periodic influxes of these components from overlying soils may lead to expansion of the thorium plume in shallow ground-water systems (e.g., Marley et al., 1993). However, results from monitoring of colloid concentrations within landfill leachate and down gradient monitoring locations of an impacted aquifer indicate that the distance of colloid-facilitated transport may be limited (Baumann et al., 2006). For shallow ground-water plumes, the spatial distribution of monitoring locations will thus be an important factor in assessing the impact of natural organic matter migration on thorium transport. As an example, McCarthy et al. (1998a; 1998b) have described field investigations for a historical shallow, unlined disposal site for radioactive waste in which episodic radionuclide leaching from subsurface waste residuals has occurred due to interactions with surface water infiltration and/or water table fluctuations that mobilize natural organic matter from overlying soils. Contaminant migration occurred along preferential flow paths through a fractured bedrock system, discharging via down gradient seeps approximately 80 meters from the shallow disposal area. For sites with similar disposal scenarios, the physical characteristics of the disposal system and the shallow hydrologic system (water flow and chemistry) are critical factors to evaluate relative to the sustainability of natural attenuation processes.

Tiered Analysis

Determination of the viability of monitored natural attenuation for remediation of long-lived thorium radioisotopes in ground water will depend upon proper assessment of contaminant loading to the aquifer relative to the velocity of ground-water travel and the prevailing geochemistry and mineralogy within the contaminant plume and the down gradient zone prior to the point(s) of compliance. The goal of site assessment is to demonstrate the process(es) controlling thorium sequestration onto aquifer solids and the long-term stability of solid phase thorium as a function of existing and anticipated ground-water chemistry. The following tiered analysis structure for site characterization provides an approach to evaluate candidate sites and define the potential limitations of MNA as part of a remedy for ground-water cleanup.

Tier I. Site characterization under Tier I will involve demonstration that the ground-water plume is static or shrinking, has not reached compliance boundaries, and does not impact existing water supplies. Once this is established through ground-water characterization, evidence is collected to demonstrate thorium partitioning to aquifer solids within the plume. If immobilization processes are active throughout the plume, then there should be an observed increase in solid phase concentrations within regions of the plume with higher aqueous concentrations, e.g., near the source term. Evaluation of the mass/activity of thorium distributed between ground water and aquifer solids throughout the plume is recommended to account for both existing and potentially mobile forms of thorium. This field partitioning data may be supplemented by geochemical modeling that incorporates measured water chemistry (e.g., pH and major ion chemistry) throughout the plume to assess the potential for aqueous thorium species that may limit precipitation or adsorption of thorium along relevant transport pathways (e.g., complexation with carbonate or dissolved organic matter). It is also important at this stage of the site evaluation to determine source term characteristics such as the inventory of contaminant mass and the current and historical rate of release into the subsurface. Determination of the distribution of thorium radioisotopes in ground water and aquifer solids both upgradient and within the plume is recommended to assist in differentiating between natural and anthropogenic source contributions. For example, the presence of ^{229}Th and/or ^{228}Th (due to its short half-life) would indicate a source of thorium other than natural levels derived from the aquifer. These assessments could be supplemented by examination of radionuclide production/process history and projected inventories for the site. Acquisition of this information in combination with identification of a stable plume provides justification for proceeding to Tier II characterization efforts.

Tier II. Under Tier II, the apparent rate and mechanism(s) of attenuation are determined. Estimates of a site attenuation rate(s) can be assessed via a well transect along the ground-water flow path. In addition, time-series data may be collected at one or more monitoring points within the plume (USEPA, 2007; Section IIIA.5). This information will allow assessment of the relative timescales for contaminant attenuation and fluid transport and determination of whether remediation objectives can be met within the required regulatory time frame. If concentrations of short-lived thorium radioisotopes (e.g., ^{228}Th, ^{234}Th) are elevated within a plume, it may be important to determine the relative contributions of radioactive decay and immobilization to the overall observed attenuation. Determination of the contribution of radioactive decay will necessitate detailed analysis of system hydrology relative to flow pathway(s), flow velocity, and temporal variations in flow velocity and/or direction within the boundaries of the plume. This information, in combination with knowledge of contaminant source release characteristics, can be employed to develop a decay-transport model to project the activity/concentration distribution of thorium radioisotopes throughout the plume in the absence of adsorption or precipitation processes. For systems in which immobilization plays a role in observed attenuation, it will be necessary to identify whether adsorption onto existing aquifer minerals or newly formed minerals predominates. Measurements of changes in ground-water chemistry along a transport pathway, e.g., decreasing ferrous iron concentrations coupled to increasing dissolved oxygen concentrations, may be used to infer formation of newly formed minerals. Confirmation of thorium adsorption onto existing or newly formed aquifer minerals will necessitate determination of the chemical speciation of solid phase thorium and may be approached according to the following scheme:

1. Calculation of saturation state of ground water relative to precipitation of hydrous thorium oxide and potential newly formed aquifer minerals (e.g., carbonates, Fe/Mn (hydr)oxides) along relevant thorium transport pathways;
2. Determination of aquifer mineralogy to determine the relative abundance of components with documented capacity for thorium adsorption , with implementation of steps for aquifer solids collection, processing and analysis that avoid transformation of mineral species from reduced zones (e.g., oxidation of ferrous carbonate/sulfide to ferric (hydr) oxide; USEPA, 2006b); and
3. Determination of thorium-sediment associations via chemical extractions designed to target specific components within the aquifer sediment.

This compilation of information will facilitate identification of the reaction(s) leading to thorium attenuation. The demonstration of concurrence between conceptual and mathematical models describing thorium transport will entail development of site-specific parameterization of the chemical processes controlling thorium solid phase partitioning.

Tier III. Once the contributions from radioactive decay and adsorption/precipitation processes have been determined, the subsequent characterization effort under Tier III will involve determination of the stability of immobilized thorium and the capacity of the aquifer to sustain continued uptake. It is recommended that the stability of immobilized thorium be tested based on the anticipated evolution of ground-water chemistry concurrent with plume evolution. For example, changes in ground-water pH and/or alkalinity can exert a significant influence on thorium adsorption. Therefore, it is recommended that leach tests with aquifer solids be conducted to characterize the magnitude of thorium re-mobilization as a function of pH for a ground-water chemistry representative of site conditions. It is recommended that the capacity for thorium uptake onto aquifer solids be determined relative to the specific mechanism(s) identified in Tier II. For sites in which a continuing source of thorium to the saturated aquifer exists, it is recommended that potential steps to minimize or eliminate this continued contaminant flux be evaluated and implemented where feasible. If site-specific tests demonstrate that the stability and capacity for thorium immobilization, in combination with continued elimination of short-lived thorium radioisotopes via radioactive decay, are sufficient to sustain attenuation, then the site characterization effort can progress to Tier IV.

Tier IV. Finally, under Tier IV a monitoring plan is established along with contingency plans in the event of MNA failure. It is recommended that the monitoring plan be designed to establish both continued plume stability and to identify changes in ground-water chemistry that may lead to re-mobilization of attenuated thorium. The specific chemical parameters to be monitored will include those identified under Tier III that may halt thorium partitioning to aquifer minerals and/or result in solubilization of thorium precipitates. Solution phase parameters that could alter the extent of thorium adsorption include decreases in pH, increases in alkalinity, and/or increases in the concentration of DOC in ground water. Changes in water chemistry may occur prior to observed changes in dissolved thorium and, thus, serve as monitoring triggers for potential MNA failure. Sites at which residual anthropogenic contaminant sources are left in unsaturated zones should include monitoring points to assess changes in the release of thorium to the saturated aquifer due to increased surface infiltration or rises in the ground-water table. Changes in system hydraulics may serve as monitoring triggers for potential MNA failure. In this instance, a contingency plan can be implemented that incorporates engineered strategies to arrest possible plume expansion beyond compliance boundaries. Possible strategies to prevent plume expansion include ground-water extraction with surface treatment, installation of permeable reactive barriers to enhance uptake capacity perpendicular to the direction of plume advance, or enhancement of adsorption capacity within the aquifer through the injection of soluble reactive components that precipitate within the formation.

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Cesium

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Occurrence and Distribution

As a major fission product, the introduction of radioisotopes of cesium to the environment is primarily a result of fallout from nuclear weapons testing (e.g., Robison et al., 2003), accidental releases from power and nuclear materials production reactors (e.g., Korobova et al., 2008), and releases from radioactive materials processing/storage facilities. To a much lesser degree, ^{137}Cs can be introduced into the environment or pose a risk to humans as a result of its use in a number of industrial devices, such as moisture-density gauges, widely used in the construction industry, leveling gauges, used in industries to detect liquid flow in pipes and tanks, thickness gauges, for measuring thickness of sheet metal, paper, film and many other products, as well as well-logging devices used in the drilling industry to help characterize rock strata. Hospitals and associated research laboratories are another potential source of ^{137}Cs to the environment, due to the use of this radioisotope in medical therapies to treat cancer. Stable cesium (^{133}Cs) is also present in the environment at concentrations significantly higher than typically encountered for its radioactive isotopes (e.g., Kreamer et al., 1996; Stetzenbach et al., 1999; Millings et al., 2003). The largest source of ^{133}Cs is in the form of the mineral pollucite ($CsAlSi_2O_6$; Teertstra and Cerny, 1995), which is recovered during mining for commercial uses of stable cesium (Butterman et al., 2005).

Geochemistry and Attenuation Processes

Radioactive Decay

Four isotopes of cesium are produced from thermal neutron fission of ^{235}U, including ^{133}Cs (stable), ^{134}Cs ($t_{1/2}$ = 2.07 years), ^{135}Cs ($t_{1/2}$ = 2.3x10^6 years), and ^{137}Cs ($t_{1/2}$ = 30.0 years) (Isnard et al., 2009). The stable isotope, ^{133}Cs, predominates in natural systems that have not been impacted by releases of fission products generated from controlled/uncontrolled nuclear reactions and from the production or processing of nuclear fuels. The radioisotope, ^{134}Cs, is produced from neutron capture by fission-produced ^{133}Cs, but only at low yield (Chung et al., 1992). The amount of ^{135}Cs produced during fission is governed by the extent that its parent, ^{135}Xe, is converted to ^{136}Xe during neutron irradiation (Hou and Roos, 2008). However, due to its long half-life, ^{135}Cs may persist at impacted sites even if initially present at substantially lower levels than ^{137}Cs (Pibida et al., 2004). The decay of ^{137}Cs to stable ^{137}Ba occurs via both a direct pathway (5%) and an indirect pathway via metastable ^{137m}Ba (95%). In general, ^{137}Cs is of greatest concern from a radiation exposure perspective, since decay of the ^{137m}Ba ($t_{1/2}$ = 2.552 min) intermediate results in the emission of a 662 keV gamma ray. Some general aspects of the decay reactions are illustrated in Figure 10.1.

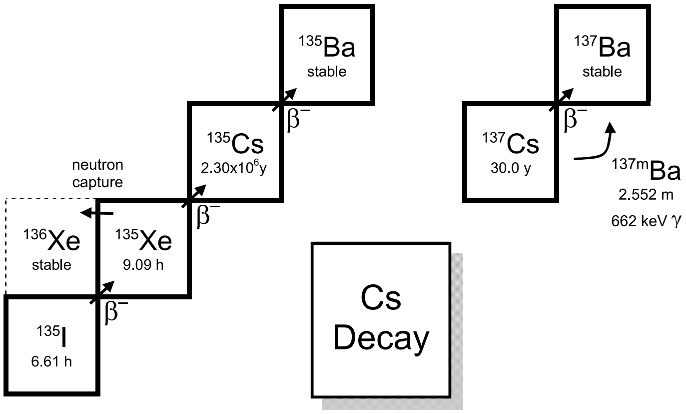

Figure 10.1 *Decay reactions involving ^{135}Cs and ^{137}Cs. Radioactive decay for ^{137}Cs occurs via both a metastable intermediate (^{137m}Ba) and directly to ^{137}Ba via ejection of a beta particle (β^-). The decay of ^{137m}Ba to ^{137}Ba involves emission of a 662 keV gamma (γ) ray. The half-life is shown directly below the isotope that is subject to decay; y = years, h = hours, m = minutes, stable = non-radioactive isotope. Decay half-life data were obtained using the WinChain program that provides electronic access to the ICRP38 Nuclear Decay Data Files (ICRP, 1983; Eckerman et al., 1994). WinChain is a public domain software application available for download from Oak Ridge National Laboratory (http://ordose.ornl.gov/downloads.html).*

Aqueous Speciation

Cesium is a highly water soluble alkali metal, and, as with other alkali metals, it exists as a monovalent cation that forms few precipitation products. Additionally, cesium exists in the monovalent oxidation state throughout the range of redox conditions normally found in nature (USEPA, 1999). Since cesium does not form insoluble precipitates in low-temperature subsurface systems, adsorption onto aquifer solids is the dominant process controlling its solid phase partitioning in ground water.

Adsorption

The primary process for cesium adsorption onto aquifer solids is via ion exchange onto minerals with layered structures and high cation exchange capacity, including 2:1 layer-silicate minerals and layered manganese oxides (USEPA, 1999; Siegel and Bryan, 2003; Lopano et al., 2009). While solid components such as natural organic matter or variable charge oxide minerals may possess negatively-charged surface sites for cation exchange, cesium exchange with these phases is generally observed to be readily reversible (Valcke and Cremers, 1994). Cesium is a large cation with a tendency to easily lose water molecules that coordinate with this ion in groundwater. When cesium ions migrate into the interlayer spaces within expandable 2:1 layer-silicates and lose these waters of hydration, the clay interlayers can collapse and limit the exchangeability of adsorbed cesium. Models that successfully predict cesium adsorption data onto soils typically distribute the total density of adsorption sites between fractions with low and high selectivity/affinity for cesium (e.g., Bradbury and Baeyans, 2000; Zachara et al., 2002). Generally, the portion of the aquifer solids that show greatest selectivity for cesium adsorption is referred to as the micaceous fraction.

Specific sorption of cesium to micaceous fractions of soils is strong with the greatest sorption occurring along the weathered edges of micas (Tamura, 1963; Sawhney, 1970; Francis and Brinkley, 1976). Micaceous minerals (biotite, muscovite) are 2:1 layer-silicates containing permanent negative-charge due to isomorphic substitution in the crystal structure. The resulting negative charge is balanced primarily by potassium within the interlayer space. Vermiculites and smectites are similar in structure, but have a lower proportion of edge sites versus the true micas (Sawhney, 1970). Literature on the sorption of cesium in soils of varying mineralogy is abundant (Coleman et al., 1963; Tamura, 1963; Sawhney and Frink, 1964; Sawhney, 1965; Sawhney, 1966a; Sawhney, 1966b; Sawhney,1972). Micaceous clays can be transformed into illites, vermiculites, smectites, or kaolinites depending on the amount they have been physically, chemically, and biologically weathered. Generally, as the degree or intensity of weathering increases, mineral abundance changes in the order of: mica < illite < vermiculite < smectite < kaolinite, indicating that less weathered soils would generally show greater capacity for selective adsorption of cesium. Studies of clay minerals isolated from contaminated soils have confirmed that micaceous clay minerals selectively concentrate cesium (e.g., McKinley et al., 2001; Cha et al., 2006).

Site Characterization

Overview

Attenuation of ^{137}Cs might be achieved through radioactive decay with the influence of adsorption or ion exchange reactions. In general, since cesium adsorption is dominated by partially reversible ion exchange reactions, it is anticipated that the primary function of this mechanism would be to limit the rate of mass transport to allow radioactive decay to remove sufficient contaminant mass. A list of potential attenuation processes is provided in Table 10.1. Two factors that will dictate the adequacy of attenuation via radioactive decay include the rate of water transport and the total mass and release rate of ^{137}Cs into the subsurface plume.

Table 10.1 Natural attenuation and mobilization pathways for cesium.

Attenuation Processes	Mobilization Processes	Characterization Approach
Radioactive decay	Not applicable	Determination of ground-water velocity along relevant transport pathways and contaminant mass release rate from source areas.
Adsorption or ion exchange onto aquifer minerals (clay minerals, layered manganese oxides)	Desorption due to decreasing pH or competition from major cations in ground water; reductive dissolution of manganese oxides.	Evaluate total adsorption capacity of aquifer solids under representative ground-water chemistry; chemical extractions to assess concentrations of exchangeable ^{137}Cs in aquifer solids along relevant transport pathways.

Aqueous Measurements

Decay of ^{137}Cs results in emission of β-particles with maximum energies of 514 keV (94.4%) and 1175 keV (5.4%), and it is accompanied by high-abundance (85.1%) γ-ray emission with energy of 661.7 keV (USEPA, 2006; Hou and Roos, 2008). Due to the abundance and low self-absorption of the γ-ray emission, gamma spectrometry is the common radiometric analysis technique applied for quantification of ^{137}Cs in environmental samples. While mass spectrometry can be used for analysis of ^{137}Cs, the sensitivity of this approach is inferior to gamma spectrometry. In contrast, mass spectrometry can be used for quantification of stable ^{133}Cs and long-lived ^{135}Cs. Interference from matrix ions with similar mass (e.g., stable ^{135}Ba) can be minimized using off-line ion exchange (Epov et al., 2004) or in-line chromatographic separation procedures (Evans et al., 2007; Liezers et al., 2009), although quantification of ^{135}Cs still may suffer from polyatomic interferences for inductively coupled plasma-mass spectrometry (e.g., Epov et al., 2003).

Solid Phase Measurements

Solid phase measurements that may provide information useful to assessing processes controlling ^{137}Cs retardation within the aquifer and the capacity along relevant transport pathways include the determination of ^{137}Cs partitioning to aquifer solids, the cation exchange capacity (CEC) of aquifer solids, and identification of aquifer solids mineralogy that may participate in adsorption reactions. Evaluation of the mass distribution of ^{137}Cs between co-located ground water and aquifer solids throughout the plume provides an assessment of the extent that retardation reactions limit cesium migration. Bulk solid-phase partitioning can be conducted using total digestion/alkaline decomposition or acid-extractable techniques (e.g., Taylor et al., 2007; Michel et al., 2008) with appropriate measures to assess extraction efficiency (Chang et al., 2004). There are a range of aqueous reagent solutions that may be employed to measure the total CEC of the aquifer solids, as well as the fraction of exchangeable ^{137}Cs (e.g., Cerling and Spalding, 1982; Zachara et al., 2002; de Koning et al., 2007). However, since the measured capacity is dependent on both the concentration of competing cations and the influence of ground-water chemistry on the physicochemical characteristics of the exchanging solid phase, a portion of the tests to determine CEC of aquifer solids should include water chemistries representative of conditions within the plume. In addition, tests to assess uptake of ^{137}Cs should incorporate concentrations of ^{133}Cs that are representative of site ground water.

An assumption to tests for determination of CEC is that only exchangeable cations are released from the solid matrix. It is recommended that the potential for partial dissolution of the more labile mineral fraction in aquifer solids during extraction (e.g., Jackson and Inch, 1989) be assessed, particularly for tests where the extracting solution chemistry is significantly different from the ground-water chemistry at locations where aquifer solids are sampled. This may be achieved through measurement of the major ion chemistry in the extract solution (e.g., iron, manganese, sulfate, dissolved organic carbon), which may serve as markers for the dissolution/leaching of minerals or organic matter that may bind ^{137}Cs in a less labile form. Work reported by Bunzl et al. (1999) indicates that sample drying and storage should not significantly impact the extractability of cesium in soils. Physical and chemical procedures, e.g., size fractionation, may also be employed to assist in identifying specific components within aquifer solids that dominate cesium solid-phase partitioning. It should be noted that cesium partitioning to aquifer solids is not confined primarily to the clay-sized fraction (<2 μm particle size), so solid-phase partitioning measurements should include analysis of the whole aquifer solids sample in addition to any size fractions that may be isolated from the original sample (Zachara et al., 2002; Dion et al., 2005; Cha et al., 2006). Examples of procedures to identify the type and abundance of specific minerals along transport pathways are available in the literature (e.g., Cerling and Spalding, 1982; Jackson and Inch, 1983; McKinley et al., 2001). Additional information on analysis approaches and analytical techniques applied to solid phase characterization is provided in USEPA (2007; Section IIIB).

The activity/concentration of ^{137}Cs in shallow aquifers may be supported, in part, by contributions from historical atmospheric fallout from nuclear weapon testing and infiltration into the subsurface (e.g., Ciszewski et al., 2008). In general, these contributions are limited to shallow soils, but the potential contribution from this source should be recognized relative to the selection and analysis of aquifer solids for determination of background concentrations/activities and/or contaminant distribution relative to source areas. In some cases, evaluation of the activity ratio of ^{137}Cs and $^{239+240}$Pu may be used to help differentiate potential sources of ^{137}Cs in aquifer solids (e.g., Hodge et al., 1996; Kirchner et al., 2002; Turner et al., 2003). This approach to contaminant source delineation would require some knowledge of the ratio of these radioisotopes in potential sources based on site process history/inventories and/or measurements of samples collected from source areas.

Long-term Stability and Capacity

The long-term stability of ^{137}Cs attenuated through adsorption (ion exchange) will depend upon the stability of the host mineral and the abundance of other ions which might displace adsorbed cesium. Increases in monovalent cation levels can be expected to work against ^{137}Cs immobilization for sites dominated by cation exchange reactions. While strong binding onto micaceous clay minerals is evident from laboratory and field studies, there is sufficient evidence to support that the variability of ground-water chemistry and aquifer solids properties anticipated at different sites precludes reliance on immobilization as the attenuation endpoint (Comans et al., 1989; Smith and Comans, 1996; de Koning and Comans, 2004; Pinder III et al., 2005). Review of the extent of plume development for a number of sites indicates that cation exchange within the saturated aquifer may have insufficient stability to prevent plume expansion (Brady et al., 2002). Thus, a critical factor for assessing the overall capacity of the aquifer for attenuation will be evaluation of the mass flux of ^{137}Cs moving through the plume relative to the rate of water movement through the aquifer. Field studies have indicated that ^{137}Cs in contaminated soils can migrate down into shallow ground water as a result of infiltration of surface water sources (Pinder III et al., 2005; Paller et al., 2008). Thus, in order to make a reliable assessment of the mass/activity flux of ^{137}Cs into the plume, it will be important to understand the characteristics of the hydrogeologic system and the dynamics of water and contaminant transfer from contaminant source areas into the plume. Radioactive decay may be sufficient to prevent plume expansion, but this is not likely for sites with an uncontrolled source of ^{137}Cs entering the subsurface and/or characteristic times for ground-water transport that are significantly shorter than the half-life of radioactive decay.

Tiered Analysis

Determination of the viability of ^{137}Cs remediation in ground water via monitored natural attenuation will depend upon proper assessment of contaminant loading to the aquifer relative to the velocity of ground-water travel and the prevailing geochemistry and mineralogy within the contaminant plume and the down gradient zone prior to the point(s) of compliance. The goal of site assessment is to demonstrate that retardation of ^{137}Cs migration within the plume is adequate to allow radioactive decay to reduce

^{137}Cs mass/activity to below required cleanup levels. The following tiered analysis structure for site characterization provides an approach to evaluate candidate sites and define the potential limitations of MNA as part of a remedy for ground-water cleanup.

Tier I. Site characterization under Tier I will involve demonstration that the ground-water plume is static or shrinking, has not reached compliance boundaries, and does not impact existing water supplies. Once this is established through ground-water characterization, evidence is collected to demonstrate ^{137}Cs partitioning to aquifer solids within the plume. If ion exchange processes are active throughout the plume, then there should be an observed increase in solid phase concentrations within regions of the plume with higher aqueous concentrations, e.g., near the source term. Evaluation of the mass/activity of ^{137}Cs distributed between ground water and aquifer solids throughout the plume is recommended to account for both existing and potentially mobile forms of ^{137}Cs. It is also important at this stage of the site evaluation to determine source term characteristics such as the inventory of contaminant mass and the current and historical rate of release into the subsurface. Acquisition of this information in combination with identification of a stable plume provides justification for proceeding to Tier II characterization efforts.

Tier II. Under Tier II, the apparent rate and mechanism(s) of attenuation are determined. Estimates of a site attenuation rate(s) can be assessed via a well transect along the ground-water flow path. In addition, time-series data may be collected at one or more monitoring points within the plume (USEPA, 2007; Section IIIA.5). This information will allow assessment of the relative timescales for contaminant attenuation and fluid transport and determination of whether remediation objectives can be met within the required regulatory time frame. As part of this analysis, it is critical to determine the relative contributions of radioactive decay and immobilization to the overall observed attenuation. Determination of the contribution of radioactive decay will necessitate detailed analysis of system hydrology relative to flow pathway(s), flow velocity, and temporal variations in flow velocity and/or direction within the boundaries of the plume. This information, in combination with knowledge of contaminant source release characteristics, can be employed to develop a decay-transport model to project ^{137}Cs activity/concentration distribution throughout the plume in the absence of adsorption. Assessment of the impact of adsorption on the rate of ^{137}Cs migration will necessitate determination of the extent of solid phase partitioning along transport pathways within the plume according to the following scheme:

1. Determination of aquifer mineralogy to determine the relative abundance of components with documented capacity for cesium adsorption (e.g., Jackson and Inch, 1983; Jackson and Inch, 1989; McKinley et al., 2001; Amonette, 2002), and
2. Determination of ^{137}Cs -sediment associations via chemical extractions designed to target specific components within the aquifer sediment (e.g., Cerling and Spalding, 1982; McKinley et al., 2001; Zachara et al., 2002).

This compilation of information will facilitate identification of the reaction(s) leading to ^{137}Cs attenuation. The demonstration of concurrence between conceptual and mathematical models describing cesium transport (including ^{133}Cs) will entail development of site-specific parameterization of the chemical processes controlling cesium solid-phase partitioning.

Tier III. Once the contributions from radioactive decay and adsorption (ion exchange) processes has been determined, the subsequent characterization effort under Tier III will involve determination of the stability of immobilized ^{137}Cs and the capacity of the aquifer to sustain retardation of ^{137}Cs transport. It is recommended that the stability of immobilized ^{137}Cs be tested based on the anticipated evolution of ground-water chemistry concurrent with plume evolution. For example, changes in ground-water pH and/or cation composition can exert a significant influence on ^{137}Cs adsorption. Therefore, it is recommended that sediment leach tests be conducted to characterize the magnitude of ^{137}Cs re-mobilization as a function of pH for a ground-water chemistry representative of site conditions (including ^{133}Cs in site ground water). It is recommended that the capacity for ^{137}Cs uptake onto aquifer solids be determined relative to the specific mechanism(s) identified in Tier II. For sites in which a continuing source of ^{137}Cs to the saturated aquifer exists, it is recommended that potential steps to minimize or eliminate this continued contaminant flux be evaluated and implemented where feasible. If site-specific tests demonstrate that the stability and capacity for ^{137}Cs adsorption, in combination with continued elimination of ^{137}Cs via radioactive decay, are sufficient to sustain plume attenuation, then the site characterization effort can progress to Tier IV.

Tier IV. Finally, under Tier IV a monitoring plan is established along with contingency plans in the event of MNA failure. It is recommended that the monitoring plan be designed to establish both continued plume stability and to identify changes in ground-water chemistry that may lead to re-mobilization of attenuated cesium (both ^{137}Cs and stable ^{133}Cs). The specific chemical parameters to be monitored will include those identified under Tier III that may halt cesium partitioning to aquifer minerals. Solution phase parameters that could alter cesium adsorption include changes in pH or increases in the concentrations of competing cations in ground water. As an example, increases in potassium (K^+) or ammonium (NH_4^+) concentrations in ground water could signal the potential for displacement of ^{137}Cs from cation exchange sites. Changes in water chemistry may occur prior to observed changes in solution ^{137}Cs and, thus, serve as monitoring triggers for potential MNA failure. In this instance, a contingency plan can be implemented that incorporates engineered strategies to arrest possible plume expansion beyond compliance boundaries. Possible strategies to prevent plume expansion include ground-water extraction with surface treatment or installation of permeable reactive barriers to enhance uptake capacity perpendicular to the direction of plume advance. For sites in which residual subsurface contamination is left in place, it is also recommended that the monitoring plan be designed to identify changes in ground-water levels, flow velocity, or direction that might influence the efficiency of ^{137}Cs removal via radioactive decay. In particular, sites at which residual ^{137}Cs sources are left in unsaturated zones should include monitoring points to assess changes in the release of ^{137}Cs to the saturated aquifer due to increased surface infiltration or rises in the ground-water table. Changes in system hydraulics may serve as monitoring triggers for potential MNA failure.

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Plutonium and Americium

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Occurrence and Distribution

Elevated concentrations of the radioisotopes of plutonium and americium in ground water are generally attributed to man-made sources such as the production and processing of nuclear materials for power generation or weapons production and testing. Trace amounts of ^{239}Pu exist in nature, primarily in uranium ore deposits, as a result of neutron capture by ^{238}U (Curtis et al., 1999; Wilcken et al., 2008). Low levels of plutonium radioisotopes are distributed throughout surface soils due to historical atmospheric testing of nuclear weapons, and the radioisotopes ^{240}Pu, ^{241}Pu, and ^{242}Pu are considered to be derived solely from anthropogenic sources (Ketterer and Szechenyi, 2008). Releases of plutonium and americium radioisotopes from shallow, subsurface disposal systems (Carlton, 1997; Groenewold et al., 2005; Cantrell, 2009) and/or accidental releases from processing or storage facilities for nuclear materials (e.g., Lee and Clark, 2005) account for the majority of elevated concentrations observed in the subsurface at federal or commercial sites across the United States (Hu et al., 2010). The primary source of ^{241}Am in the environment is derived from the production and disposal/release of plutonium. As discussed below, these radionuclides are typically encountered together due to parent-daughter relationships in relevant decay chains.

Geochemistry and Attenuation Processes

Radioactive Decay

There are fifteen radioisotopes of plutonium; the three most common ones are ^{239}Pu (~94%), ^{240}Pu (~6%), ^{241}Pu (0.4%). The decay half-life of ^{239}Pu is 24,100 years, and it decays to ^{235}U with the emission of an alpha particle (Figure 11.1). The decay half-life of ^{240}Pu is 6540 years, producing ^{236}U via alpha decay (Figure 11.2). The ^{241}Pu radioisotope ($t_{1/2} = 14.4$ years) decays to ^{241}Am ($t_{1/2} = 432$ years) via emission of a beta particle (Figure 11.3). The ^{241}Am radioisotope subsequently decays to ^{237}Np ($t_{1/2} = 2.14$ million years) with the emission of an alpha particle. Possible progenitors that could introduce uranium isotopes via decay in-growth are shown in Table 11.1. Transuranic radioisotopes such as americium, curium, and neptunium decay to produce plutonium and/or americium radioisotopes of importance (e.g., Carlton, 1997; Dai et al., 2002). The decay half-lives for these progenitors range from minutes to many thousands of years. Knowledge of the presence of these radionuclides within the plume and sampled ground water may be important for proper identification of the source of plutonium/americium radioisotopes as well as in-growth corrections that may be required to properly account for the mass/activity of these radioisotopes at the time of sample collection.

Table 11.1 Illustration of potential decay paths from different progenitor sources leading to production of americium and plutonium radioisotopes. Determination of possible decay paths to the target radionuclide was based on examination of the Chart of Nuclides (http://www.nndc.bnl.gov/chart/) maintained by the Brookhaven National Laboratory, National Nuclear Data Center (NNDC) relative to possible decay paths based on decay modes identified in the Appendix (EC = electron capture, β^- = electron emission, α = alpha decay). Decay half-life data were obtained using the WinChain program that provides electronic access to the ICRP38 Nuclear Decay Data Files (ICRP, 1983; Eckerman et al., 1994; m = minutes, h = hours, d = days, y = years). WinChain is a public domain software application available for download from Oak Ridge National Laboratory (http://ordose.ornl.gov/downloads.html).

Contaminant Radionuclide	Decay Progenitor	Decay Mode	Progenitor Decay Half-life
^{241}Am	^{241}Cm	EC	32.8 d
	^{241}Pu	β^-	14.4 y
^{239}Pu	^{239}Np	β^-	2.355 d
	^{243}Cm	α	28.5 y
	^{243}Am (via ^{239}Np)	α (β^-)	7380 y (2.355 d)
^{240}Pu	^{240}Am	EC	50.8 h
	^{240}Np	β^-	65 m
	^{244}Cm	α	18.11 y
^{241}Pu	^{245}Cm	α	8500 y

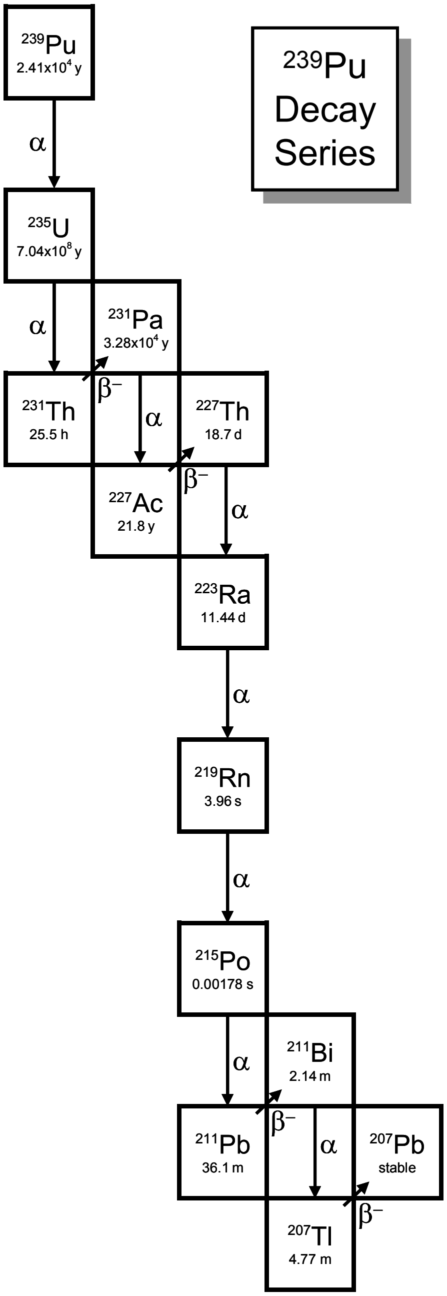

Figure 11.1 *Decay series for ^{239}Pu. The half-life is shown directly below the isotope that is subject to decay; y = years, d = days, h = hours, m = minutes, s = seconds, stable = non-radioactive isotope. Decay half-life data were obtained using the WinChain program that provides electronic access to the ICRP38 Nuclear Decay Data Files (ICRP, 1983; Eckerman et al., 1994). WinChain is a public domain software application available for download from Oak Ridge National Laboratory (http://ordose.ornl.gov/downloads.html).*

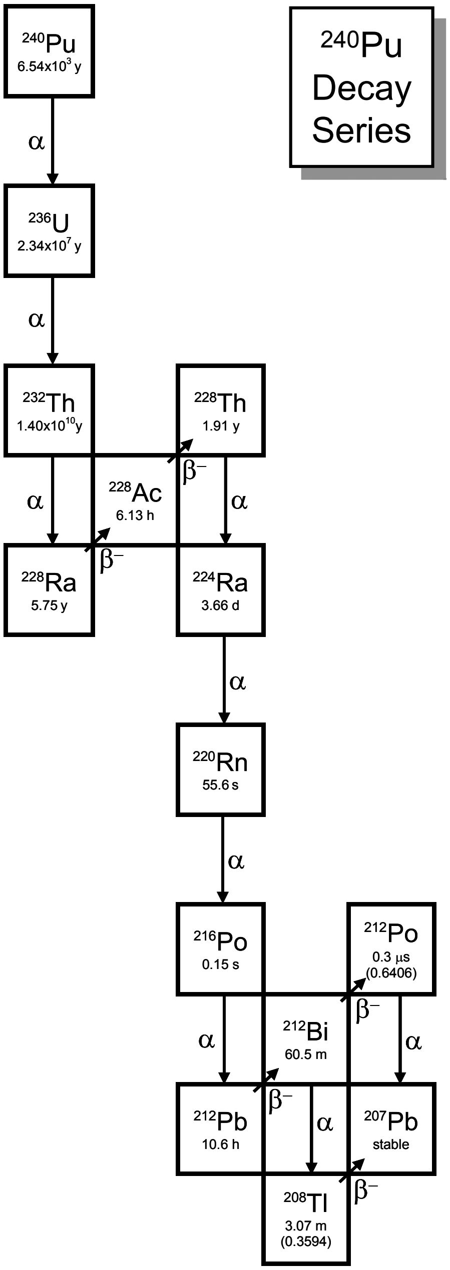

Figure 11.2 *Decay series for ^{240}Pu. The half-life is shown directly below the isotope that is subject to decay; y = years, h = hours, d = days, m = minutes, s = seconds, µs = microseconds, stable = non-radioactive isotope. Decay half-life data were obtained using the WinChain program that provides electronic access to the ICRP38 Nuclear Decay Data Files (ICRP, 1983; Eckerman et al., 1994). WinChain is a public domain software application available for download from Oak Ridge National Laboratory (http://ordose.ornl.gov/downloads.html).*

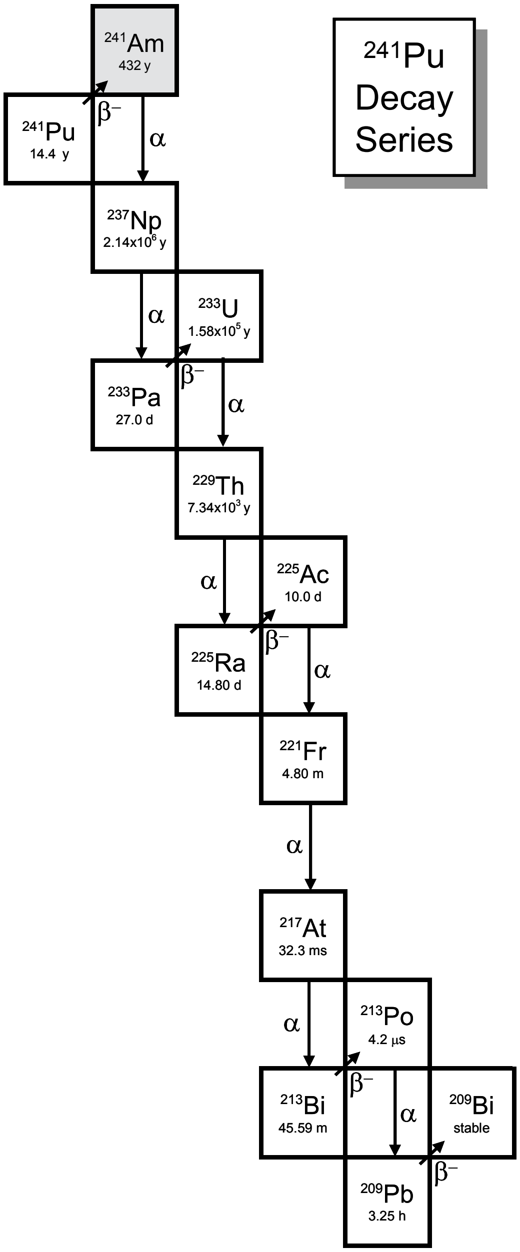

Figure 11.3 *Decay series for ^{241}Pu, including daughter ^{241}Am. The half-life is shown directly below the isotope that is subject to decay; y = years, h = hours, m = minutes, ms = milliseconds, µs = microseconds, stable = non-radioactive isotope. Decay half-life data were obtained using the WinChain program that provides electronic access to the ICRP38 Nuclear Decay Data Files (ICRP, 1983; Eckerman et al., 1994). WinChain is a public domain software application available for download from Oak Ridge National Laboratory (http://ordose.ornl.gov/downloads.html).*

Aqueous Speciation

Plutonium has four possible oxidation states (i.e., +3, +4, +5, and +6) under typical subsurface conditions and can exist in any of these in aqueous solutions. In general, Pu(IV) species are considered to be most common, but all oxidations may play a role in controlling plutonium speciation and migration (e.g., Clark et al., 1995). Comprehensive reviews on the chemical thermodynamics of plutonium include those by Lemire et al. (2001) and Guillamont et al. (2003), which address the various aqueous species likely to be encountered under typical ground-water conditions. Examples of plutonium species for these four oxidation states are illustrated in Figure 11.4, including Pu(III)$^{3+}$, Pu(IV)O$_2$, Pu(V)O$_2^{+}$, and Pu(VI)O$_2$(CO$_3$)$_2^{2-}$. The distribution of plutonium species between reduced [Pu(III), Pu(IV)] and oxidized [Pu(V), Pu(VI)] forms is considered to exert the greatest influence on the mobility of this radionuclide in ground water (e.g., Dai et al., 2002; Kaplan et al., 2004). Plutonium may form soluble complexes with a range of anions common to ground water, and these reactions can play a role in the predominant plutonium oxidation state (Choppin et al., 1997). Tetravalent plutonium [Pu(IV)] forms hydrolysis and/or polymeric species in water to a greater extent than the other oxidation states (Baes and Mesmer, 1976), although these reactions may contribute to Pu(VI) speciation at elevated concentrations encountered near source zones (e.g., Reilly and Neu, 2006). Plutonium in its Pu(VI), Pu(V), and Pu(IV) oxidation states may also form dissolved complexes with carbonate (Clark et al., 1995; Clark et al., 1998; Topin et al., 2009). Formation of solution complexes with synthetic organic chelation agents present in co-contaminants may also occur, which has motivated the review of available thermochemical data for the purpose of calculating potential impacts on plutonium chemical speciation (Hummel et al., 2005). While the formation solution complexes with synthetic ligands (e.g., EDTA) is supported within the technical literature (Meyer et al., 2007; Hummel et al., 2007), the relative impact of these species on plutonium transport will be limited by competition reactions with dissolved and solid constituents along relevant flow paths within the aquifer. As demonstrated by Rai et al. (2008), the chemical speciation of strong complexants such as EDTA may be dominated by reactions with aquifer constituents that are present at much higher concentrations than plutonium. For shallow ground-water systems with elevated concentrations of natural dissolved organic carbon, plutonium may form soluble complexes with dissolved humic/fulvic compounds (e.g., Marquardt et al., 2004; Reiller, 2005; Dardenne et al., 2009; Szabo et al., 2010).

The chemistry of americium is less complex than that of plutonium, since americium exists primarily in the trivalent state under natural conditions (Clark et al., 1995). The aqueous chemistry of Am(III) has been reviewed in Silva et al. (1995) and updated in Guillamont et al. (2003). As with plutonium, formation of complexes with dissolved carbonate can be important in ground water with elevated alkalinity (e.g., Clark et al., 1995; Vercouter et al., 2005). As shown in Figure 11.5, carbonate complexes can dominate americium speciation in solution. Americium may also form complexes with humic/fulvic compounds (e.g., Kim et al., 1993). It has been demonstrated that formation of soluble complexes with humic/fulvic compounds can potentially facilitate transport of Am(III) in shallow ground water where surface recharge events can result in increased organic carbon concentrations and aquifer flow velocities (e.g., Marley et al., 1993; Artinger et al., 1998; McCarthy et al., 1998).

Solubility

Both Am(III) and Pu(IV) form hydrous oxide phases with low solubility (Silva et al., 1995; Guillamont et al., 2003; Hala and Miyamoto, 2007), and these precipitates might control aqueous concentration of Am(III) or Pu(IV) near source zones where elevated concentrations of these radionuclides might be encountered. As shown in Figure 11.4, precipitation of Pu(IV) phases is projected to dominate over the other plutonium oxidation states under most ground-water conditions. However, this also points to the importance of ground-water redox on the precipitation and stability of Pu(IV) hydrous oxides. Reduction of Pu(IV) in the presence of reducing agents such as ferrous iron could potentially increase overall plutonium solubility (e.g., Rai et al., 2002). Likewise, oxidation of Pu(IV) could also increase plutonium solubility. Laboratory solubility studies using systems where redox and oxygen concentrations have been controlled indicate that hydrous Pu(IV)O_2 can be partially oxidized, with soluble plutonium being controlled by Pu(V) species (Neck et al., 2007). There is recent evidence that, in the presence of phosphate, Pu(VI) may behave analogous to U(VI) and form Pu(VI)-phosphates (Rai et al., 2005). However, there is currently insufficient knowledge on the likely formation of this type of precipitate to assess the impact of phosphate in ground water on aqueous plutonium concentrations in oxidizing systems. As shown in Figure 11.5, formation of americium hydroxycarbonate may dominate over hydrous oxides in ground water with near-neutral pH and elevated alkalinity. This is supported by laboratory thermochemical studies that predict hydroxycarbonates as the more stable phase for actinium(III) and lanthanum(III) metals (Merli et al., 1997). In addition, it has been shown that Am(III) readily substitutes for Ca(II) in the calcite structure (Curti, 1999; Stumpf et al., 2006). Thus, precipitation of carbonates may also exert control on americium solubility in ground water with elevated alkalinity. In general, formation of solution complexes with synthetic or natural organic ligands is anticipated to interfere with precipitation of the various precipitate phases discussed above for plutonium and americium.

Adsorption

The adsorption of plutonium and americium is anticipated to be the predominant mechanism controlling solid partitioning in ground-water systems. A general overview of adsorption processes for plutonium and americium onto aquifer solids is provided in USEPA (1999) and USEPA (2004), respectively. Bradbury and Baeyans (2009) and Degueldre and Bolek (2009) have demonstrated that americium and plutonium adsorption onto common aquifer minerals can be modeled using surface complexation reactions that account for the influence of pH and competing aqueous speciation reactions. For americium, formation of soluble complexes is the predominant factor limiting adsorption to aquifer solids. However, this influence may be transient depending on aquifer conditions. For example, while complexation with soluble humic/fulvic compounds have been observed to suppress americium adsorption in model systems (e.g., Pathak and Choppin, 2007), long-term column studies have shown that this effect may be limited by competitive adsorption reactions along the transport pathway (Artinger et al., 2002). Formation of soluble complexes may also limit plutonium adsorption. For example, Sanchez et al. (1985) demonstrated that formation of soluble carbonate complexes can suppress adsorption of Pu(IV) and Pu(V) hydrous iron oxides. However, as shown via detailed field characterization, it appears that controls on the plutonium oxidation state will exert the greatest influence on plutonium migration (Dai et al., 2002; Buesseler et al., 2009). For systems in which more oxidized (and mobile) plutonium species have been introduced into the subsurface, interaction with natural reducing compounds may increase plutonium adsorption along the flow path through reduction to Pu(IV) (e.g., Powell et al., 2005; Buerger et al., 2007; Roberts et al., 2008).

Site Characterization

Overview

Plutonium and americium mobility in ground water is governed by their total dissolved concentration, the distribution of plutonium/americium species in water, and the nature of plutonium/americium partitioning to aquifer solids. The development of a conceptual site model for predicting the long-term fate of plutonium/americium at a contaminated site will require information on the concentration and chemical speciation of plutonium/americium in the aqueous phase and the solid phase. Table 11.2 illustrates possible attenuation and mobilization pathways for plutonium and americium in ground water. Details of the types of analytical measurements that may be conducted on sampled ground water and aquifer sediments to assist in identifying the attenuation mechanism(s) are discussed in the following paragraphs.

Aqueous Measurements

Overviews of radiometric techniques for determining the activity of plutonium and americium radioisotopes is provided in USEPA (2006). More recent reviews of the use of radiometric and mass spectrometric methods for the quantification of americium and plutonium radioisotopes is provided in Hou and Roos (2008), Qiao et al. (2009), and Vajda and Kim (2010a; 2010b). Of the radioisotopes of plutonium and americium discussed in this chapter, all are alpha-emitters except for ^{241}Pu (beta-emitter). Liquid scintillation counting can be used to measure ^{241}Pu directly or indirect detection of its daughter, ^{241}Am, can be employed using alpha spectrometry. The energies of alpha particles released from ^{239}Pu and ^{240}Pu are too similar to be resolved using alpha spectrometry (5.147 MeV and 5.170 MeV, respectively), so the activity of these isotopes is usually

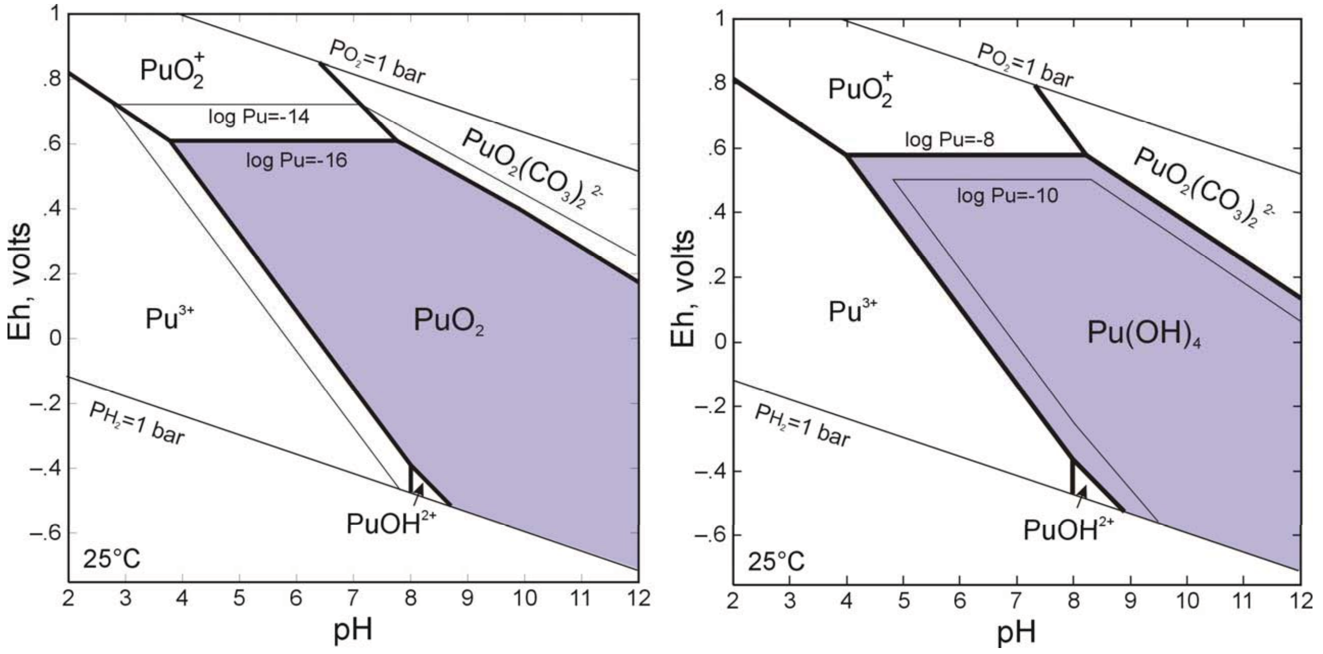

Figure 11.4 *Eh-pH stability diagram for Pu at 25 °C and $PCO_2 = 10^{-2.5}$ atm. Diagrams are for solubility control by PuO_2 and $Pu(OH)_4$ (see text). Examples of the four oxidation states of plutonium include $Pu(III)^{3+}$, $Pu(IV)O_2$, $Pu(V)O_2^+$, and $Pu(VI)O_2(CO_3)_2^{2-}$.*

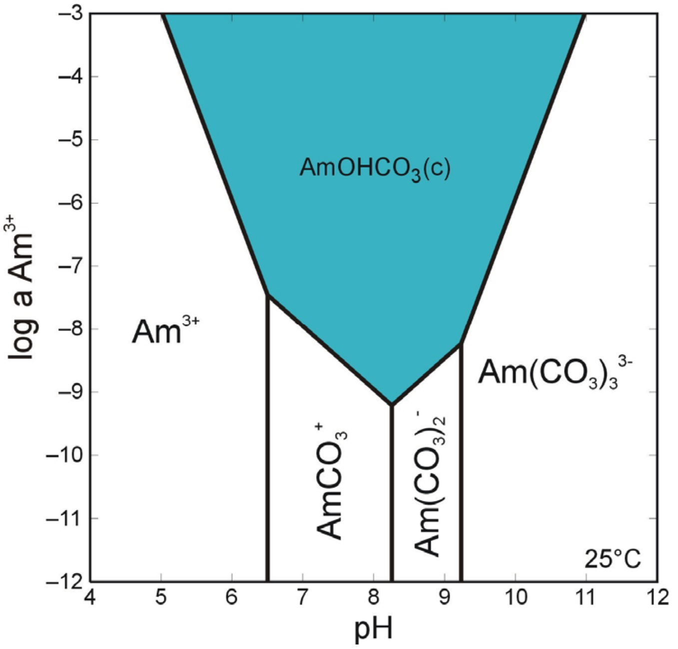

Figure 11.5 *Solubility diagram for Am(III) at $PCO_2 = 10^{-2.5}$ atm and $PO_2 = 0.2$ atm.*

Table 11.2 Natural attenuation and mobilization pathways for plutonium and americium.

Attenuation Processes	Mobilizaton Processes	Characterization Approach
Plutonium		
Radioactive decay of ^{241}Pu	Not applicable	Determination of ground-water velocity along relevant transport pathways and contaminant mass release rate from source areas.
Reduction of Pu(VI) or Pu(V) and precipitation of Pu(IV) hydrous oxide minerals	Dissolution due to decreased pH, increased alkalinity, or oxidation of Pu(IV) to more mobile species of Pu(VI)/ Pu(V) or further reduction of Pu(IV) to Pu(III).	Evaluation of Pu concentration and oxidation state in ground water and in solid matrix. Evaluation of Pu solid-phase partitioning using extraction methodologies coupled to methods to determine Pu oxidation state. Characterization of aqueous redox and chemical conditions in ground water with speciation model evaluation of potential Pu(IV) stability.
Adsorption or coprecipitation of Pu with iron/manganese oxyhydroxides, iron sulfides, and carbonates or adsorption onto clay mineral surfaces	Desorption due to decreased pH, increased alkalinity, or high DOC concentrations. Reductive dissolution of iron/ manganese oxyhydroxides or oxidative dissolution of iron sulfides. Oxidation of adsorbed Pu(IV) to Pu(V)/ Pu(VI).	Evaluation of Pu concentration and oxidation state in ground water and aquifer solids. Evaluation of Pu solid-phase partitioning using extraction methodologies; examine correlation to extractable Fe/Mn, Ca, Mg and S. Batch and column testing to determine Pu uptake behavior and capacity of site-specific aquifer materials under variable geochemical conditions.
Americium		
Adsorption or coprecipitation of Am(III) with iron/manganese oxyhydroxides, iron sulfides, and carbonates or adsorption onto clay mineral surfaces	Desorption due to decreased pH or high DOC concentrations (e.g., humic/fulvic compounds). Reductive dissolution of iron/ manganese oxyhydroxides or oxidative dissolution of iron sulfides.	Evaluation of Am concentration in ground water and in solid matrix. Evaluation of Am solid-phase partitioning using extraction methodologies; examine correlation to extractable Fe/Mn, Ca, Mg and S. Batch and column testing to determine Am uptake behavior and capacity of site-specific aquifer materials under variable geochemical conditions.

reported as the sum of their combined contribution to the spectral peak, i.e., $^{239+240}$Pu. The sensitivity of these methods is generally good for these radioisotopes, but typically isolation of the analyte from the sample matrix and interfering radionuclides is required prior to analysis. As noted by Singhal et al. (2008), high concentrations of natural organic matter may significantly decrease the efficiency of target radionuclide isolation. These authors observed that oxidative destruction of dissolved organic carbon prior to the separation procedure improved recovery. The yield of isolation procedures is typically assessed by introducing a different isotope of the radionuclide that is not anticipated to be present or detected in the original sample (e.g., Pike et al., 2009).

Determination of the ratios of plutonium isotopes may be useful in determining potential contaminant sources (e.g., atmosphere fall-out versus site-specific wastes). While radiometric methods can be employed for this purpose, the inability to separately determine the activities of ^{239}Pu and ^{240}Pu limits their applicability. Use of mass spectrometric techniques, including inductively coupled plasma mass spectrometry (ICP-MS), provides the means to directly quantify the individual plutonium radioisotopes that can be used as a signature to differentiate contributions from different contaminant sources. Reviews of the applicability and limitations of ICP-MS for quantification of plutonium radioisotopes can be found in Zoriy et al. (2005), Lariviere et al. (2006), Hou and Roos (2008), and Ketterer and

Szechenyi (2008). Examples where plutonium radioisotope ratios were employed to differentiate contaminant sources at contaminated sites include Marty et al. (1997; Los Alamos), Dai et al. (2002; Savannah River Site), and Dai et al. (2005; Hanford Site). These comparisons are based on historical or site-specific records of waste characteristics from the production and processing of nuclear materials, where radioisotope ratios such as ^{240}Pu/^{239}Pu can be attributed to distinct sources (e.g., ^{240}Pu/^{239}Pu = 0.18 for atmospheric fallout, 0.01-0.07 for weapon production, or 0.40 for Chernobyl fallout; Warneke et al., 2003). Most of these studies are based on field sampling campaigns in which mass spectrometric methods were incorporated up-front in the field sampling and laboratory analysis plans. Michel et al. (2007) demonstrated that one can acid-extract sample planchets prepared for alpha-spectrometry for the purpose of determining individual ^{239}Pu and ^{240}Pu activities by ICP-MS. Thus, archived planchet deposits from radiometric analyses for a given site may be used to supplement knowledge of plume characteristics and contaminant source apportionment.

Determination of the oxidation state(s) of plutonium in sampled ground water can provide useful information on the mechanisms controlling transport (e.g., Dai et al., 2002; Buesseler et al., 2009). Radiochemical methods have been developed for separating plutonium into its more reduced [Pu(III) and Pu(IV)] and more oxidized [Pu(V) and Pu(VI)] states (Lovett and Nelson, 1981). The accuracy of these methods is assessed by spiking samples with tracer radioisotopes with known oxidation state (e.g., ^{244}Pu(III/IV) in NIST SRM-996 Spike Assay and Isotopic Standard and ^{242}Pu(V/VI) in SRM-4334C). Description and application of methods to measure the distribution of plutonium oxidation states in aqueous samples is provided in several studies in which species detection is achieved either off-line or in-line with the detection system (e.g., Grate and Egorov, 1998; Kuczewski et al., 2003; Powell et al., 2005; Fajardo et al., 2008). The separation of plutonium species with different oxidation states is possible due to their inherent differences in chemical reactivity. In principal, detection of the separated species can be achieved with either radiometric or mass spectrometric methods. One advantage of using mass spectrometry is the ability of directly determining the distribution of plutonium radioisotopes across the range of oxidation-state species within the sample. This approach has proven useful in differentiating the sources of plutonium contamination sources in ground water at large and/or complex waste sites (e.g., Buesseler et al., 2009).

Solid Phase Measurements

Analysis of plutonium association with aquifer solids may be necessary in order to confirm active attenuation of contaminants from the ground-water plume and to identify the reaction process(es) controlling plutonium immobilization. Determination of the form in which plutonium and americium is being immobilized underpins projections of the capacity for continued attenuation of contaminant mass within the plume and the long-term stability of immobilized radionuclides with long decay half-lives. Methods for the extraction of plutonium/americium from solids are well-documented (e.g., Croudace et al., 1998; Epov et al., 2007; Varga et al., 2007; Michel et al., 2008; Payne et al., 2008; Choiniere et al., 2009; Eikenberg et al., 2009). Since these methods also extract other actinides or fission products, as well as matrix elements, isolation of the plutonium/americium radioisotopes is a critical step to insure measurement accuracy. For determination of total solid-phase plutonium, it may also be necessary to assess the distribution of radioisotopes to confirm that the extracted radioisotopes are representative of those being attenuated from the plume.

Sequential extractions using solutions designed to attack specific solid phase components have been used in an attempt to better define the chemical speciation of plutonium and americium in solid samples (e.g., Schultz et al., 1998). This work has demonstrated the difficulty of uniquely identifying solid phase speciation for plutonium, due to its tendency to re-adsorb to un-extracted solid components prior to solid-liquid separation. Schultz et al. (2000) and Lucey et al. (2007) discuss results on studies designed to minimize plutonium re-adsorption through addition of a complexing ligand in the extractant solutions. This work demonstrates significant improvement in eliminating this analytical artifact, but these results also show that some selectivity of an extractant to target a specific solid-phase association may be lost. In addition, Lucey et al. (2007) demonstrate the need to take precautions to preserve redox characteristics of solid samples retrieved from reduced systems, which dictates application of extractions in an oxygen-free analytical system (e.g., anaerobic glove box or closed fluid handling systems). Evaluations have not been conducted to determine whether these extraction procedures may influence the in-situ oxidation state of solid-phase plutonium prior to extraction, so reliance on spectroscopic methods to identify in-situ plutonium oxidation state and/or chemical associations is currently warranted (e.g., Duff et al., 2001; Kaplan et al., 2007).

Long-term Stability and Capacity

The long-term stability of immobilized plutonium will depend on the maintenance of either 1) sufficiently low reduction potentials to prevent oxidation and consequent solubilization of Pu(IV) solids or 2) stability of the sorbent mineral and sufficiently low concentrations of competing ions that could displace adsorbed plutonium. Once plutonium has been precipitated or adsorbed, the sustainability of the geochemical driving force (e.g., redox, pH, and/or available surface sites) is critical to whether natural attenuation will be a viable cleanup option. The long-term stability of immobilized americium will depend on the maintenance of either 1) near-neutral pH and/or sufficiently high alkalinity or 2) stability of the sorbent mineral and sufficiently low concentrations of competing ions that could displace adsorbed americium. Thus, it is recommended that post-attenuation changes in water chemistry be carefully considered to ensure that re-mobilization of attenuated plutonium/americium does not occur. For plutonium, a particular concern are situations in which plutonium is attenuated under reducing conditions that are induced by characteristics of the contaminant plume, specifically if the natural conditions within the aquifer are more oxidizing. As shown by Dai et al. (2002) and Buesseler et al. (2009), the more oxidized forms of plutonium tend to be the most mobile.

Determination of capacity for attenuation will depend on knowledge of the specific mechanisms leading to plutonium/americium partitioning to aquifer solids and the flux of these contaminants being transmitted through the aquifer. Site conditions under which attenuation capacity may be limited include those in which periodic surface recharge events flush these contaminants from un-lined, shallow disposal units where leachate collection systems do not exist. Factors that tend to interfere with contaminant immobilization under these settings include ground-water flow rates that limit the time of contact with aquifer solids and the introduction of soil-derived organic carbon that complexes plutonium/americium. The affective capacity for attenuation within the aquifer will also depend strongly on the characteristics and variability of ground-water chemistry and aquifer solids properties along transport pathways, as well as the impact of hydrologic dynamics on subsurface chemistry as a function of space and time.

Tiered Analysis

Determination of the viability of plutonium and americium remediation in ground water via monitored natural attenuation will depend upon proper assessment of contaminant loading to the aquifer and prevailing geochemistry and mineralogy within the contaminant plume and the down gradient zone prior to the point(s) of compliance. While radioactive decay will contribute to attenuation of ^{241}Pu and ^{241}Am, decay will not provide a viable mechanism for plume attenuation for the longer-lived ^{239}Pu and ^{240}Pu. Therefore, the goal of site assessment will be to demonstrate the process(es) controlling contaminant sequestration onto aquifer solids and the long-term stability of solid phase plutonium and/or americium as a function of existing and anticipated ground-water chemistry. The following tiered analysis structure for site characterization provides a technically defensible approach to evaluate candidate sites and define the potential limitations of MNA as part of a remedy for ground-water cleanup.

Tier I. Site characterization under Tier I will involve demonstration that the ground-water plume is static or shrinking, has not reached compliance boundaries, and does not impact existing water supplies. Once this is established through ground-water characterization, evidence is collected to demonstrate plutonium/americium partitioning to aquifer solids within the plume. If natural attenuation processes are active throughout the plume, then there should be an observed increase in solid phase concentrations within regions of the plume with higher aqueous concentrations, e.g., near the source term. This field partitioning data may be supplemented by geochemical modeling that incorporates measured water chemistry (e.g., pH, Eh, and major ion chemistry) throughout the plume to assess the potential for solubility control by a Pu(IV) or Am(III) precipitate such as a hydrous oxide phase. Identification of active sequestration to prevent plutonium/americium migration in ground-water provides justification for proceeding to Tier II characterization efforts.

Tier II. Under Tier II, the apparent rate and mechanism(s) of attenuation are determined. Estimates of a site attenuation rate(s) can be assessed via a well transect along the ground-water flow path. In addition, time-series data may be collected at one or more monitoring points within the plume (USEPA, 2007; Section IIIA.5). This information will allow assessment of the relative timescales for contaminant immobilization and fluid transport and determination of whether remediation objectives can be met within the required regulatory time frame. In addition, the mechanism(s) for attenuation are to be identified under this stage of site characterization. This effort will require determination of the chemical speciation of solid phase plutonium/americium and may be approached according to the following scheme:

1.) Determination of solution and solid phase plutonium/americium concentrations, along with the relative concentration of major ions/components in aquifer solids where attenuation is occurring;
2.) Calculation of saturation state of ground water relative to measured aqueous chemistry for potential Pu(IV) or Am(III) precipitates; and
3.) Determination of aquifer mineralogy (Amonette, 2002) to determine the relative abundance of components that might support adsorption and/or coprecipitation of plutonium/americium.

This compilation of information will facilitate identification of the reaction(s) leading to plutonium/americium immobilization. It is recommended that identification of redox-sensitive components in aqueous and solid matrices be conducted using samples collected in a manner that preserves their in-situ speciation (USEPA, 2006b). The demonstration of concurrence between conceptual and mathematical models describing plutonium/americium transport will entail development of site-specific parameterization of the chemical processes controlling plutonium/americium solid phase partitioning.

Tier III. Once the partitioning mechanism(s) have been identified for the site, the subsequent characterization effort under Tier III will involve determination of the stability of immobilized plutonium/americium and the capacity of the aquifer to sustain continued uptake. It is recommended that the stability of immobilized plutonium/americium be tested based on the anticipated evolution of ground-water chemistry concurrent with decay of the plume. For example, changes in ground-water pH and/or alkalinity can exert a significant influence on the adsorption of plutonium/americium onto aquifer solids. Therefore, it is recommended that sediment leach tests be conducted to characterize the magnitude of plutonium/americium mobilization as a function of pH and alkalinity for a ground-water chemistry representative of site conditions. It is recommended that the capacity for plutonium/americium uptake onto aquifer solids be determined relative to the specific mechanism(s) identified in Tier II. For example, if site characterization under Tier II indicated that plutonium/americium adsorption onto hydrous iron/manganese oxides was the predominant attenuation process, then the mass distribution of these mineral components along relevant ground-water flow paths needs to be determined. This site-specific capacity would then be compared to plutonium/americium mass loading within the plume in order to assess the longevity of the natural attenuation process. If site-specific tests demonstrate adequate stability of immobilized plutonium/americium and sufficient capacity within the aquifer to sustain plutonium/americium attenuation, then the site characterization effort can progress to Tier IV. For cases where contaminant stability is sufficient but aquifer capacity is insufficient for capture of the entire plume, then a determination of the benefits of contaminant source reduction is required.

Tier IV. Finally, under Tier IV a monitoring plan is established along with contingency plans in the event of MNA failure. It is recommended that the monitoring plan be designed to establish both continued plume stability and to identify changes in ground-water chemistry that may lead to re-mobilization of attenuated plutonium/americium. The specific chemical parameters to be monitored will include those identified under Tier III that may halt plutonium/americium partitioning and/or result in dissolution of either discrete plutonium/americium precipitates or aquifer minerals that sequester plutonium/americium from ground water. For example, solution phase parameters that could alter either plutonium/americium precipitation include inorganic carbon (alkalinity), pH, and dissolved organic carbon concentration. Changes in these parameters may occur prior to observed changes in solution plutonium/americium and, thus, serve as monitoring triggers for potential MNA failure. In addition, sites at which residual plutonium/americium sources are left in unsaturated zones should include monitoring points to assess changes in the release of these contaminants to the saturated aquifer due to increased surface infiltration or rises in the ground-water table. Changes in system hydraulics may serve as monitoring triggers for potential MNA failure. In this instance, a contingency plan can be implemented that incorporates alternative strategies to arrest possible plume expansion beyond compliance boundaries. Possible strategies to prevent plume expansion include pump and treat operations, isolation or stabilization of near-surface contaminant source zones, or installation of reactive barriers to enhance uptake capacity perpendicular to the direction of plume advance.

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Appendix A - Radioactive Decay Processes

Basic concepts describing radionuclides and radioactive decay can be obtained from several sources (USEPA, 2000; Siegel and Bryan, 2003). The term *radionuclide* used throughout this document refers to an unstable atom that releases energy and/or particles during conversion to a new atom. An atom is composed of neutrons, protons, and electrons, where electrons orbit around a nucleus composed of neutrons and protons. Atoms with the same number of protons, but different numbers of neutrons are referred to as *isotopes*. For example, the element radium has six isotopes; radium-223, radium-224, radium-225, radium-226, radium-227 and radium-228. While each of the radium isotopes contains 88 protons in their nucleus, the number of neutrons for each isotope is different. The variation in the number of neutrons does not change the element or its chemical properties, but it can affect the stability of the element. This instability can result in radioactive decay, leading to use of the term *radioisotopes* for unstable isotopes. For consistency in this document, the term radionuclide will be used when referring to radioisotopes.

Radionuclide X possesses an atomic number Z and mass number A, and is represented as ${}^{A}_{Z}X$ or ${}^{A}X$ where A = Z + N and is the sum of the numbers of protons (Z) and neutrons (N) in the nucleus (e.g., radium-223 is alternatively represented by ${}^{223}Ra$). Radioactivity is the property of spontaneous emission of particles or electromagnetic radiation from an unstable nuclide. The principal modes of radioactive decay include transformation via emission of alpha, beta, and positron (positively charged beta particle) particles, and via orbital electron capture. Following decay, if the daughter nucleus is left in an excited state, the excess energy may be shed through the emission of a gamma ray or, alternatively, through the ejection of an inner shell orbital electron -- a process termed internal conversion. The three primary types of radiation emitted during or following radioactive decay are: alpha (α) and beta (β) particles and gamma (γ) rays. Examples of radioactive decay characteristics for radionuclides addressed within this volume are shown in Table 1.2.

Specific activity, the rate of radioactive decay per unit mass, is fixed for any specific radionuclide regardless of its chemical or physical state. However, the rate differs greatly for different radionuclides. The decay rate is typically expressed in terms of a half-life, which is the time required for the radioactivity of a radionuclide to decay to one-half of its original value. Half-lives for the different radionuclides vary from fractions of a second to billions of years. Although chemical transformations are typically sensitive to temperature, pressure, physical states, and other factors, radioactive decay transformations are not.

Modes of Radioactive Decay

Radioactive decay occurs because the balance of neutrons and protons in the nucleus of the nuclide is unstable. The nuclide tries to reach a more stable configuration by emitting particles and/or electromagnetic radiation (γ-rays). Nuclides emitting α particles (${}^{4}_{2}He$) decrease in A by four units and in Z by two units:

$${}^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He}$$

α-particles are usually emitted with between 3 and 9 MeV of kinetic energy, but, since they are relatively massive and doubly charged, they do not penetrate very far into matter. A thick sheet of paper is sufficient to completely stop α particles.

Beta (β) decay processes include electron emission (β^-), positron emission (β^+) and electron capture (EC). The first of these reactions, known as negatron decay or, simply, as negative β-decay, can be represented as $n \rightarrow p^+ + e^-$, where n = neutron, p^+ = proton, and e^- = electron. A specific example of this decay process is the decay of ${}^{137}Cs$:

$${}^{137}_{55}\mathrm{Cs} \rightarrow {}^{137}_{56}\mathrm{Ba} + e^-$$

(electron emission or beta-minus decay)

The emitted electron is called the β particle. The result is an increase in Z by one unit with no change in A. Unlike the discrete energies of α decay, there is a broad, continuous distribution of energies, extending from almost zero to some maximum value from β decay. If negative β-particle emission occurs for nuclei possessing a high (and unstable) N/Z value, then a reverse process might be expected to occur - specifically decay should convert a proton to a neutron. As in negatron decay, this process may be repeated in several consecutive steps before a stable N/Z value is obtained. Conversion of a proton to a neutron can occur in two different ways - either by emission of a positron (positive beta decay, where the reaction is $p^+ \rightarrow n + e^+$; e^+ = positron) or by absorption of an electron, usually from the K or L shells of the atom (electron capture, where the reaction is $p^+ + e^- \rightarrow n$). Examples of these two decay processes include:

$${}^{11}_{6}\mathrm{C} \rightarrow {}^{11}_{5}\mathrm{B} + e^+ \ (\text{positron emission or beta-plus decay})$$ and

$${}^{240}_{95}\mathrm{Am} + e^- \rightarrow {}^{240}_{94}\mathrm{Pu} \ (\text{electron capture})$$

Fission decay can be either spontaneous or neutron-induced. Spontaneous fission is a naturally occurring process in which a nucleus breaks into two fragments, along with the emission of 2-3 neutrons. An example of a spontaneous fission decay process is:

$$^{252}_{98}Cf \rightarrow ^{98}_{38}Sr + ^{152}_{60}Nd + 2 \text{ neutrons}$$

The neutron-induced fission process is initiated by capturing a neutron, as in:

$$^{235}_{92}U + {}^{1}n \rightarrow ^{140}_{56}Ba + ^{94}_{36}Kr + 2 \text{ neutrons}$$

The nuclides formed in a fission process are called fission products. Each fissionable nuclide can produce a wide range of fission products, many of which are not radioactive. In a group of identical radionuclides, several decay modes may be observed. The competition is expressed by the *branching ratios* which correspond to the relative probability of occurrence of a decay mode. In general, the branching ratio for a particular decay mode is defined as the ratio of the number of atoms decaying by that decay mode to the number decay in total. As an example, plutonium-241 (^{241}Pu) decays to americium-241 (^{241}Am) and uranium-237 (^{237}U) via beta emission and alpha emission, respectively. However, the probability for decay to ^{241}Am is much higher and thus dominates the distribution of decay products (i.e., the fraction of ^{237}U produced during ^{241}Pu decay is approximately 2.45x10^{-5}; Appendix A in USEPA, 1993b, EPA/402/R93/081). Discussion of the significance of branching to decay for radionuclides addressed in this volume is provided in the individual contaminant chapters.

Modes of Nuclear De-excitation (Following Decay)

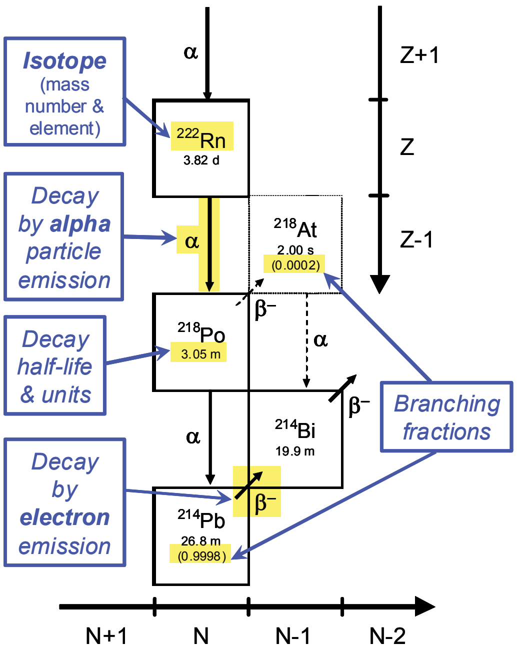
Often, the daughter nucleus resulting from radioactive decay is left in an excited state. The nucleus can shed this excess energy, or de-excite, via two processes: gamma ray emission and internal conversion (IC). The first process, gamma emission, involves the removal of excess energy with the emission of a gamma ray. Gamma rays are electromagnetic radiation similar to X rays, ultraviolet and visible light, and radio waves. Emitted γ-rays decrease the mass of the nucleus by an amount corresponding to the energy carried away by the γ-rays. For example, in α decay of ^{238}U, 77% of the α particles have 4.18 MeV and 23% have 4.13 MeV of energy. Decay by emission of 4.13 MeV α particles leaves the nucleus with 0.05 MeV greater energy than do 4.18-MeV α emissions. This 0.05 MeV difference is accounted for through emission of a γ ray of that energy. Emission of γ-rays occurs immediately ($\leq 10^{-12}$ s) following α- or β-decay, but in some cases the nucleus may remain in the higher energy state for a measurable length of time (milliseconds or greater). The excited state of the nucleus and its daughter state are referred to as a nuclear *isomer*. Gamma rays are emitted with a discrete energy, like α-particles, rather than with a continuous spectrum of energies as negatron and positron decay particles are in β-decay. Since they have no mass or charge, γ-rays do not interact readily with matter and therefore exhibit greater penetration in air and matter than charged particles. The second process, internal conversion, involves energy transfer from the nucleus to an inner electron shell, resulting in the ejection of a high-energy electron. As with decay by orbital electron capture, the inner shell electron vacancy is quickly filled by an outer shell electron and also results in emission of an X-ray.

It should be noted that a number of radionuclides decay without leaving an excited daughter nucleus, and therefore do not result in gamma emission or internal conversion. These isotopes are known as pure emitters. Several beta emitters, including ^{3}H, ^{14}C, ^{32}P, ^{90}Sr, and ^{90}Y, decay without gamma emission. The absence or presence of gamma emission is an important consideration for radiation detection and measurement and for radiation protection.

Decay Chains

Most naturally occurring radioactive materials and many fission products undergo radioactive decay through a series of transformations rather than in a single step. Until the last step, these radionuclides emit energy or a particle(s) with each transformation and become another radionuclide. Man-made elements, which are all heavier than uranium and unstable, undergo decay in this way. This *decay chain*, or decay series, ends in a stable nuclide. For example, the decay chain for uranium-238 (^{238}U) is illustrated in Figure A.1. Uranium-238 has the longest half-life, 4.5 billion years, and polonium-214 the shortest, 164 microseconds. The last radionuclide in the chain, polonium-210 (^{210}Po) transforms to the stable nuclide, lead-206 (^{206}Pb). The following labeling scheme is used in Figure A.1 and throughout this document to illustrate radioactive decay processes:

Stable isotopes exist for some of the elements addressed in this volume (e.g., strontium; ^{84}Sr, ^{86}Sr, ^{87}Sr, ^{88}Sr). As the name implies, stable isotopes do not undergo radioactive decay. It is important to note that a stable isotope for a given element may not be derived from decay of an unstable isotope of the same element. As an example, the chapter on strontium, included in this volume, focuses on discussion of ^{90}Sr as a radionuclide commonly encountered in groundwater plumes at sites with radioactive wastes (USEPA, 1993a). Radioactive decay of ^{90}Sr leads to the production of ^{90}Y (beta decay), which subsequently decays to stable ^{90}Zr. Thus, stable isotopic versions of strontium present within a plume may be derived from a source other than that releasing ^{90}Sr into the subsurface. Stable isotopes of strontium that may be present within a plume are likely derived from natural sources within the aquifer (e.g., due to weathering of mineral components within aquifer solids). From a site characterization perspective, it is important to understand that unstable and stable isotopes for a given element may occur within a plume, since this may govern the types of contaminant detection methods that are employed to define transport of the radionuclide targeted for remediation.



- x-axis corresponds with change in number of neutrons (decreasing to the right)
- y-axis corresponds with change in atomic number (decreasing down)
- arrows point in "direction" of decay process
- solid lines correspond to the predominant decay reaction
- dashed lines correspond to a branching decay reaction of secondary importance

There are several sources for tabulated data characterizing decay of radionuclides. The source used by the USEPA in risk calculations is derived from the ICRP38 Nuclear Decay Data Files (e.g., Appendix A in USEPA, 1993b, EPA/402/R93/081). Another source of decay data is the Evaluated Nuclear Structure Data File (ENSDF; *http://www.nndc.bnl.gov/ensdf/*), which contains evaluated nuclear structure and decay information for over 2900 nuclides. Technical evaluations of these data are published in Nuclear Data Sheets (*http://www.nndc.bnl.gov/nds/*), which is a journal primarily devoted to the publication of evaluated nuclear structure and decay data.

Units and Specific Activity

The Curie (Ci) has been used as a radioactive decay unit for many years and is still being used widely in the United States, but the unit used under the International System of Units (SI), Becquerel (Bq), has practically replaced the Curie unit and is the only unit accepted by most scientific publishers. The two are related as follows:

$$1 \text{ Becquerel (Bq)} = 1 \text{ disintegration s}^{-1}$$

$$1 \text{ Curie (Ci)} = 3.7 \times 10^{10} \text{ s}^{-1} \text{ (Bq) or}$$
$$1 \text{ Bq} = 27 \text{ pCi } (\text{p} = 10^{-12})$$

The specific radioactivity describes the relationship between radioactivity and mass and is the decay rate (counts per unit of time) per unit mass of a substance. It is necessary to make clear whether the mass refers to a pure radionuclide or to a mixture – the SI unit is Bq kg^{-1}. For practical purposes specific radioactivity is also defined in dpm g^{-1} or dpm mole^{-1}. Activity concentration (or "radioactive concentration") is given in Bq m^{-3} or Bq l^{-1}. For example, the total atoms in 1 g of ^{32}P ($t_{1/2}$ = 14.3 days) is:

$$1 \text{ g} = 1/32 \text{ moles of } ^{32}\text{P}$$
$$= (6.023 \text{ x } 10^{23})/32 \text{ atoms of } ^{32}\text{P}.$$

From the decay equation:

$$dN/dt = -\lambda N$$

where N is the number of radioactive atoms, t is time (s) and λ is the decay constant ($0.693/t_{1/2}$). The activity can be obtained from:

$$dN/dt = (-)\frac{0.693 \times 6.022 \times 10^{23}}{32 \times 14.3 \times 24 \times 60 \times 60} \text{ disintegrations s}^{-1}$$

$$= (-)1.055 \times 10^{16} \text{ disintegrations s}^{-1}$$

where the minus sign indicates that the total number of atoms in the sample, N is decreasing over time. Therefore, 1 g of pure ^{32}P has the activity of 1.055×10^{16} Bq (or 2.853×10^{5} Ci).

With a half-life of 1599±4 y, the specific activity per gram of ^{226}Ra is 0.988 Ci or 3.7×10^{10} Bq or 2.9×10^{12} dpm. The specific activities of some of the longer-lived naturally occurring radioactive species are: ^{40}K, 31.3 kBq kg^{-1}; ^{232}Th, 4.05 MBq kg^{-1}; and ^{238}U, 12.4 MBq kg^{-1}.

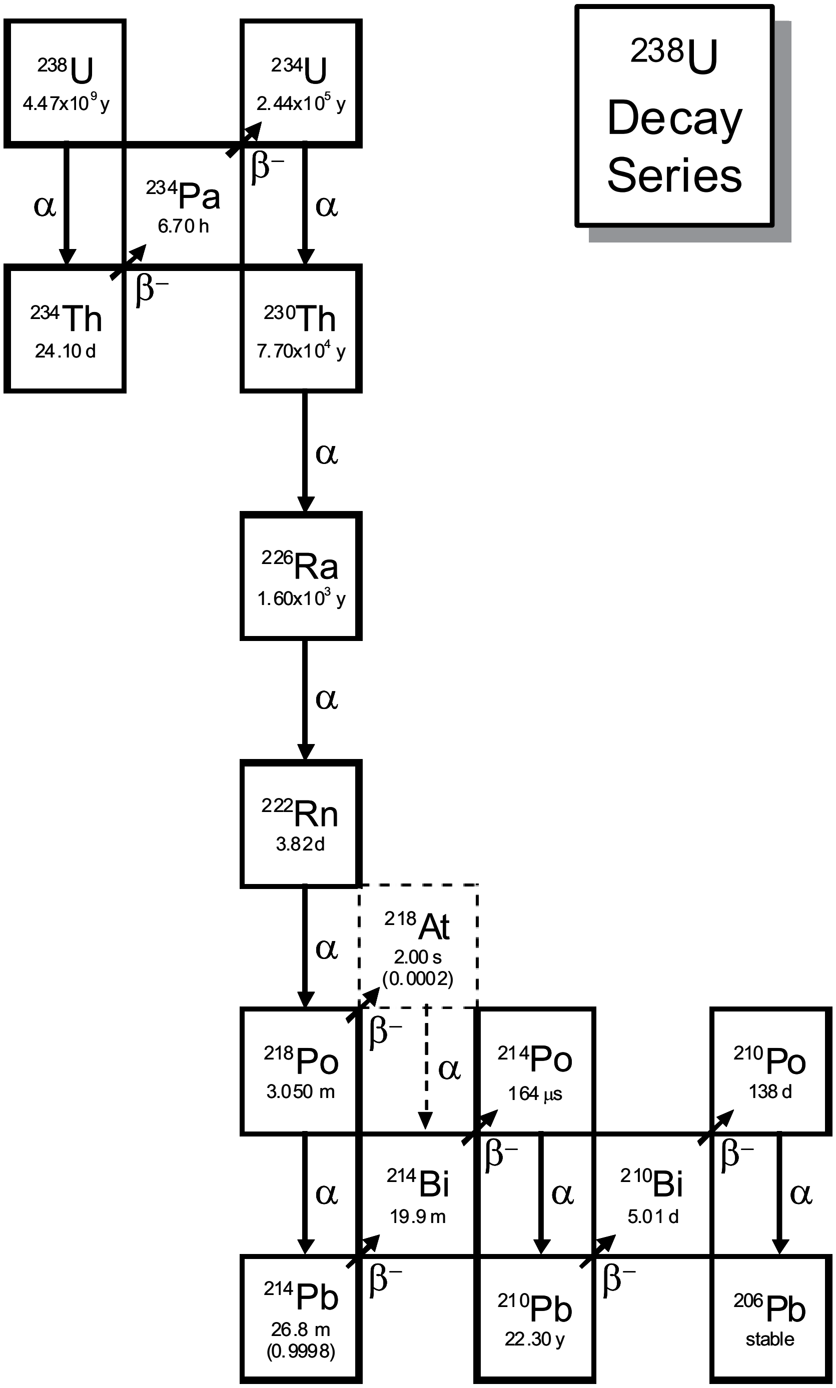


Figure A.1 *Decay chain for ^{238}U showing intermediate nuclides formed during series transformation to stable ^{206}Pb. Half-lives for radioactive decay were obtained using the WinChain program that provides electronic access to the ICRP38 Nuclear Decay Data Files (ICRP, 1983; Eckerman et al., 1994); µs = microseconds, s = seconds, m = minutes, d = days, y = years. Decay types are shown as α for alpha particle emission and β^- for electron emission. Decay branching is shown for ^{218}Po with the branching fraction for both daughter products (^{214}Pb and ^{218}At) shown in parentheses (α decay dominates).*

In general, the longer-lived radionuclides decay slowly and are more persistent in the environment. However, their specific activity is relatively low. Shorter-lived radionuclides decay more quickly to stable forms, and their specific activity is generally much higher than those of longer-lived radionuclides. The daughter products of a number of decaying radionuclides are themselves radionuclides, which can also provide significant doses of radiation. For example, ^{90}Sr decays to ^{90}Y which subsequently decays to stable ^{90}Zr. The contribution from ^{90}Y is approximately 8% of that from ^{90}Sr based on drinking water contaminated with ^{90}Sr and ^{90}Y in equilibrium.

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