

# **CNWRA** A center of excellence in earth sciences and engineering™

Geosciences and Engineering Division  
6220 Culebra Road • San Antonio, Texas, U.S.A. 78238-5166  
(210) 522-5160 • Fax (210) 522-5155

November 1, 2007  
Contract No. NRC-02-07-006  
Account No. 20.14003.01.007  
NMSS06n—PROJ0734, PROJ0735

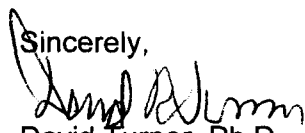
ATTN: Document Control Desk  
U.S. Nuclear Regulatory Commission  
Mr. Michael Fuller  
Division of Waste Management and Environmental Protection  
Two White Flint North  
11555 Rockville Pike  
Washington, DC 20852

Subject: Final Version of the Recommended Site-Specific Sorption Coefficients for Reviewing  
Non-High-Level Waste Determinations at the Savannah River Site and Idaho National  
Laboratory (Intermediate Milestone 06004.01.007.255)

Dear Mr. Fuller:

This letter transmits the final version of the subject deliverable, which is identified in the Task 7 portion of the Operations Plan for Technical Assistance in Evaluating Non-High-Level Waste Determinations for the U.S. Department of Energy in South Carolina and Idaho. Revision 1 of this deliverable was transmitted on October 25, 2007, in response to U.S. Nuclear Regulatory Commission (NRC) comments. This final version is being transmitted pursuant to your email dated November 1, 2007, to close the ticket. As per NRC guidance, we have removed the draft headers and footers.

If you have any questions about this report, please do not hesitate to contact me (210.522.2139) or Mr. James Prikryl (210.522.5667).

Sincerely,  
  
David Turner, Ph.D.  
Assistant Director  
Non-Repository Programs

ECP/DRT/lis  
Enclosure

cc:  
D. DeMarco  
S. Kim  
B. Meehan  
C. Barr  
A. Turner Gray  
S. Flanders  
A. Bradford  
A. Kock  
H. Artt  
W. Patrick  
B. Sagar  
J. Prikryl  
D. Pickett  
Record Copy B—IQS  
Letter Only:  
CNWRA Directors  
CNWRA Managers  
L. Gutierrez



Washington Office • Twinbrook Metro Plaza #210  
12300 Twinbrook Parkway • Rockville, Maryland 20852-1606

**RECOMMENDED SITE-SPECIFIC SORPTION  
COEFFICIENTS FOR REVIEWING NON-HIGH-LEVEL  
WASTE DETERMINATIONS AT  
THE SAVANNAH RIVER SITE AND  
IDAHO NATIONAL LABORATORY**

*Prepared for*

**U.S. Nuclear Regulatory Commission  
Contract NRC-02-07-006**

*Prepared by*

**James D. Prikryl  
David A. Pickett  
Center for Nuclear Waste Regulatory Analyses  
San Antonio, Texas**

**October 2007**

# CONTENTS

Section	Page
FIGURES .....	iv
TABLES .....	vi
EXECUTIVE SUMMARY .....	viii
ACKNOWLEDGMENTS .....	ix
ABBREVIATIONS/ACRONYMS .....	x
 1 INTRODUCTION .....	 1-1
1.1 Purpose .....	1-1
1.2 Use of Sorption Coefficients in Performance Assessment .....	1-2
1.3 Approach to Data Review .....	1-2
1.4 $K_d$ Measurements .....	1-3
1.5 Factors Affecting Sorption and Transport .....	1-5
 2 SAVANNAH RIVER SITE .....	 2-1
2.1 Waste Management Background .....	2-1
2.2 Description of the General Separations Area .....	2-1
2.3 Designation of Risk-Significant Radionuclides .....	2-7
2.4 Sorption Coefficients .....	2-8
2.4.1 Carbon .....	2-12
2.4.2 Nickel .....	2-13
2.4.3 Selenium .....	2-19
2.4.4 Strontium .....	2-23
2.4.5 Niobium .....	2-27
2.4.6 Technetium .....	2-29
2.4.7 Tin .....	2-34
2.4.8 Iodine .....	2-38
2.4.9 Cesium .....	2-41
2.4.10 Lead .....	2-44
2.4.11 Uranium .....	2-49
2.4.12 Neptunium .....	2-53
2.4.13 Plutonium .....	2-57
2.4.14 Americium .....	2-65
2.4.15 Curium .....	2-68
 3 IDAHO NATIONAL LABORATORY .....	 3-1
3.1 Waste Management Background .....	3-1
3.2 Description of Idaho Nuclear Technology and Engineering Center Tank Farm Facility .....	3-1
3.3 Designation of Risk-Significant Radionuclides .....	3-8
3.4 Sorption Coefficients .....	3-8
3.4.1 Carbon .....	3-9
3.4.2 Strontium .....	3-13
3.4.3 Technetium .....	3-18
3.4.4 Iodine .....	3-21
3.4.5 Cesium .....	3-25

## CONTENTS (continued)

Section		Page
	3.4.6 Lead .....	3-29
	3.4.7 Uranium .....	3-32
	3.4.8 Neptunium .....	3-37
	3.4.9 Plutonium .....	3-41
	3.4.10 Americium .....	3-48
	3.4.11 Curium .....	3-50
4	SUMMARY AND CONCLUSIONS .....	4-1
5	REFERENCES .....	5-1

## FIGURES

Figure	Page
2-1 Hydrostratigraphic Units at the GSA (Modified From Buice, et al., 2005) . . . . .	2-2
2-2 Measured and Estimate Site-Specific and Generic Carbon $K_d$ Ranges and Values and Recommended Carbon $K_d$ Values for Aquifer Units . . . . .	2-14
2-3 Measured and Estimated Site-Specific and Generic Nickel $K_d$ Ranges and Values and Recommended Nickel $K_d$ Values for Aquifer Units . . . . .	2-20
2-4 Measured and Estimated Site-Specific and Generic Selenium $K_d$ Ranges and Values and Recommended Selenium $K_d$ Values for Aquifer Units . . . . .	2-24
2-5 Measured and Estimated Site-Specific and Generic Strontium $K_d$ Ranges and Values and Recommended Strontium $K_d$ Values for Aquifer Units . . . . .	2-28
2-6 Measured and Estimated Site-Specific and Generic Niobium $K_d$ Ranges and Values and Recommended Niobium $K_d$ Values for Aquifer Units . . . . .	2-31
2-7 Measured and Estimated Site-Specific and Generic Technetium $K_d$ Ranges and Values and Recommended Technetium $K_d$ Values for Aquifer Units . . . . .	2-35
2-8 Measured and Estimated Site-Specific and Generic Tin $K_d$ Ranges and Values and Recommended Tin $K_d$ Values for Aquifer Units . . . . .	2-37
2-9 Measured and Estimated Site-Specific and Generic Iodine $K_d$ Ranges and Values and Recommended Iodine $K_d$ Values for Aquifer Units . . . . .	2-43
2-10 Measured and Estimated Site-Specific and Generic Cesium $K_d$ Ranges and Values and Recommended Cesium $K_d$ Values for Aquifer Units . . . . .	2-47
2-11 Measured and Estimated Site-Specific and Generic Lead $K_d$ Ranges and Values and Recommended Lead $K_d$ Values for Aquifer Units . . . . .	2-51
2-12 Uranium $K_d$ Values as a Function of pH From Serkiz and Johnson (1994) . . . . .	2-52
2-13 Measured and Estimated Site-Specific and Generic Uranium $K_d$ Ranges and Values and Recommended Uranium $K_d$ Values for Aquifer Units . . . . .	2-56
2-14 Measured and Estimated Site-Specific and Generic Neptunium $K_d$ Ranges and Values and Recommended Neptunium $K_d$ Values for Aquifer Units . . . . .	2-59
2-15 Measured and Estimated Site-Specific and Generic Plutonium $K_d$ Ranges and Values and Recommended Plutonium $K_d$ Values for Aquifer Units . . . . .	2-66
2-16 Measured and Estimated Site-Specific and Generic Americium $K_d$ Ranges and Values and Recommended Americium $K_d$ Values for Aquifer Units . . . . .	2-70
2-17 Measured and Estimated Site-Specific and Generic Curium $K_d$ Ranges and Values and Recommended Curium $K_d$ Values for Aquifer Units . . . . .	2-73
3-1 Schematic of the Subsurface at INTEC (Not to Scale, Taken From DOE, 2006c) . . .	3-4
3-2 Measured and Estimated Site-Specific Carbon $K_d$ Ranges and Values and Recommended Carbon $K_d$ Values for Alluvium, Interbed Sediments, and Basalt . .	3-14
3-3 Measured and Estimated Site-Specific Strontium $K_d$ Ranges and Values and Recommended Strontium $K_d$ Values for Alluvium, Interbed Sediments . . . . .	3-19
3-4 Measured and Estimated Site-Specific and Analogous Technetium $K_d$ Ranges and Values and Recommended Technetium $K_d$ Values for Alluvium . . . . .	3-23
3-5 Measured and Estimated Site-Specific and Analogous Iodine $K_d$ Ranges and Values and Recommended Iodine $K_d$ Values for Alluvium . . . . .	3-26
3-6 Measured and Estimated Site-Specific and Analogous Cesium $K_d$ Ranges and Values and Recommended Cesium $K_d$ Values for Alluvium . . . . .	3-30

## FIGURES (continued)

Figure	Page
3-7 Measured and Estimated Site-Specific and Analogous Lead $K_d$ Ranges and Values and Recommended Lead $K_d$ Values for Alluvium . . . . .	3-33
3-8 Measured and Estimated Site-Specific and Analogous Uranium $K_d$ Ranges and Values and Recommended Uranium $K_d$ Values for Alluvium . . . . .	3-38
3-9 Measured and Estimated Site-Specific and Analogous Neptunium $K_d$ Ranges and Values and Recommended Neptunium $K_d$ Values for Alluvium . . . . .	3-42
3-10 Measured and Estimated Site-Specific and Analogous Plutonium $K_d$ Ranges and Values and Recommended Plutonium $K_d$ Values for Alluvium . . . . .	3-47
3-11 Measured and Estimated Site-Specific and Analogous Americium $K_d$ Ranges and Values and Recommended Americium $K_d$ Values for Alluvium . . . . .	3-51
3-12 Estimated Site-Specific Curium $K_d$ Ranges and Values and Recommended Curium $K_d$ Values for Alluvium, Interbed Sediments, and Basalt at INL . . . . .	3-53

## TABLES

Table	Page
1-1	Example Effects of Environmental Factors on $K_d$ ..... 1-5
2-1	Chemistry of Water in Shallow Aquifer and Confining Units in the Central and Southern Part of the Savannah River Site ..... 2-6
2-2	Mineralogical and Hydrogeochemical Characteristics of Hydrostratigraphic Units at the Savannah River Site ..... 2-9
2-3	Measured, Estimated, and Recommended $K_d$ Values for Carbon in Aquifer Sediments and Clay Confining Units at the Savannah River Site ..... 2-13
2-4	Measured, Estimated, and Recommended $K_d$ Values for Nickel in Aquifer Sediments and Clay Confining Units at the Savannah River Site ..... 2-17
2-5	Measured, Estimated, and Recommended $K_d$ Values for Selenium in Aquifer Sediments and Clay Confining Units at the Savannah River Site ..... 2-22
2-6	Measured, Estimated, and Recommended $K_d$ Values for Strontium in Aquifer Sediments and Clay Confining Units at the Savannah River Site ..... 2-26
2-7	Recommended $K_d$ Values for Niobium in Aquifer Sediments and Clay Confining Units at the Savannah River Site ..... 2-30
2-8	Measured, Estimated, and Recommended Technetium $K_d$ Values for Aquifer Sediments and Clay Confining Units at the Savannah River Site ..... 2-33
2-9	Estimated and Recommended Tin $K_d$ Values for Aquifer Sediments and Clay Confining Units at the Savannah River Site ..... 2-36
2-10	Measured, Estimated, and Recommended Iodine $K_d$ Values for Aquifer Sediments and Clay Confining Units at the Savannah River Site ..... 2-40
2-11	Measured, Estimated, and Recommended Cesium $K_d$ Values for Aquifer Sediments and Clay Confining Units at the Savannah River Site ..... 2-45
2-12	Measured, Estimated, and Recommended Lead $K_d$ Values for Aquifer Sediments and Clay Confining Units at the Savannah River Site ..... 2-48
2-13	Measured, Estimated, and Recommended Uranium $K_d$ Values for Aquifer Sediments and Clay Confining Units at the Savannah River Site ..... 2-54
2-14	Measured, Estimated, and Recommended Neptunium $K_d$ Values for Aquifer Sediments and Clay Confining Units at the Savannah River Site ..... 2-58
2-15a	Characteristics of Sediments in Plutonium Batch Sorption Experiments ..... 2-61
2-15b	Range of Plutonium $K_d$ Values Measured With Respect to Sediment Type, Plutonium Oxidation State, and Reaction Time ..... 2-61
2-15c	Range of Plutonium $K_d$ Values Measured in Sediments Over the pH Range of Groundwater Expected at the Savannah River Site (pH 5.2 to 7.7) ..... 2-62
2-15d	Measured, Estimated, and Recommended Plutonium $K_d$ Values for Aquifer Sediments and Clay Confining Units at the Savannah River Site ..... 2-64
2-16	Measured, Estimated, and Recommended Americium $K_d$ Values for Aquifer Sediments and Clay Confining Units at the Savannah River Site ..... 2-68
2-17	Estimated and Recommended Curium $K_d$ Values for Aquifer Sediments and Clay Confining Units at the Savannah River Site ..... 2-71
3-1	Typical Chemical Composition of Idaho National Laboratory Basalt. Oxide Contents In wt% and Strontium and Barium Contents In mg/L ..... 3-5
3-2	Composition of Eastern Snake River Plain Aquifer Groundwater ..... 3-5

## TABLES (continued)

Table	Page
3-3 Composition of Perched Water and Aquifer Water Collected At the Idaho National Laboratory .....	3-6
3-4 Mineralogic and Hydrogeochemical Characteristics of Units At the Idaho National Laboratory .....	3-10
3-5 Measured and Recommended $K_d$ Values for Carbon in Alluvium, Interbed Sediments, and Basalt at the Idaho National Laboratory .....	3-12
3-6 Measured and Recommended $K_d$ Values for Strontium in Alluvium, Interbed Sediments, and Basalt at the Idaho National Laboratory .....	3-17
3-7 Measured and Recommended Technetium $K_d$ Values for Alluvium, Interbed Sediments, and Basalt at the Idaho National Laboratory .....	3-21
3-8 Recommended Iodine $K_d$ values for Alluvium, Interbed Sediments, and Basalt at the Idaho National Laboratory .....	3-24
3-9 Measured and Recommended Cesium $K_d$ Values for Alluvium, Interbed Sediments, and Basalt at the Idaho National Laboratory .....	3-28
3-10 Recommended Lead $K_d$ Values for Alluvium, Interbed Sediments, and Basalt at the Idaho National Laboratory .....	3-32
3-11 Measured and Recommended Uranium $K_d$ Values for Alluvium, Interbed Sediments, and Basalt at the Idaho National Laboratory .....	3-36
3-12 Measured and Recommended Neptunium $K_d$ Values for Alluvium, Interbed Sediments, and Basalt at the Idaho National Laboratory .....	3-40
3-13 Measured and Recommended Plutonium $K_d$ Values for Alluvium, Interbed Sediments, and Basalt at the Idaho National Laboratory .....	3-45
3-14 Measured and Recommended Americium $K_d$ Values for Alluvium, Interbed Sediments, and Basalt at the Idaho National Laboratory .....	3-50
3-15 Recommended Curium $K_d$ Values for Alluvium, Interbed Sediments, and Basalt at the Idaho National Laboratory .....	3-52
4-1 Summary of Recommended $K_d$ Values (mL/g) for Risk-Significant Radionuclides in Hydrostratigraphic Units at the Savannah River Site .....	4-2
4-2 Summary of Recommended $K_d$ Values (mL/g) for Risk-Significant Radionuclides in Hydrostratigraphic Units at the Idaho National Laboratory .....	4-3



## EXECUTIVE SUMMARY

To satisfy non-high-level radioactive waste determinations for facilities at the Savannah River Site (SRS) and the Idaho National Laboratory (INL) under Section 3116 of the Ronald W. Reagan National Defense Authorization Act, the U.S. Department of Energy (DOE) commonly performs a deterministic performance assessment that includes evaluating potential radionuclide exposure via groundwater transport. In its consultative role in the waste determination process, the U.S. Nuclear Regulatory Commission reviews the performance assessments, including deterministic radionuclide geosphere transport simulations that use sorption coefficients, or  $K_d$ s. To aid in these reviews, this report documents a sorption coefficient database tailored to site-specific subsurface conditions for risk-significant radioelements at SRS (carbon, nickel, selenium, strontium, niobium, technetium, tin, iodine, cesium, lead, uranium, neptunium, plutonium, americium, and curium) and INL (carbon, strontium, technetium, iodine, cesium, lead, uranium, neptunium, plutonium, americium, and curium) and recommends  $K_d$  values appropriate for the respective hydrogeochemical environments. The recommended  $K_d$  values are based on the sorption behavior of each radioelement, available data on site hydrogeochemical and mineralogical conditions, and reported site-specific  $K_d$  values. When site-specific data were not available for a particular radioelement,  $K_d$  data on analogous systems and generic data from the open literature were evaluated to provide a technical basis for the  $K_d$  recommendation. The recommended values tended toward the lower, more conservative end of data ranges because of the uncertainties not only in the appropriate choice of sorption coefficients, but also in the simplified  $K_d$ -based groundwater transport model itself. The selection of low values is intended to ensure that groundwater pathway models will be unlikely to underestimate potential dose. Values were assigned a low or high level of uncertainty based on the availability of site-specific information. These recommendations should be used with care in light of new information that becomes available on site-specific sorption coefficients or hydrogeochemical conditions. This report is not to be construed as providing the technical basis for parameters DOE uses in its performance assessments. The results of this data review can be used, in a risk-informed manner, to identify potential areas of focused laboratory studies.

## ACKNOWLEDGMENTS

This report was prepared to document work performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA) for the U.S. Nuclear Regulatory Commission (NRC) under Contract No. NRC-02-02-012. The activities reported here were performed on behalf of the NRC Office of Federal and State Materials and Environmental Management Programs, Division of Waste Management and Environmental Protection. This report is an independent product of CNWRA and does not necessarily reflect the view or regulatory position of NRC.

The authors would like to thank H. Arlt, C. Barr, C. Ridge, and K. Pinkston (NRC) for constructive comments and suggestions on earlier drafts. Thanks to M. Juckett and D. Turner for their thoughtful reviews and Lee Selvey and Lauren Mulverhill for word processing and technical editing support.

## QUALITY OF DATA, ANALYSES, AND CODE DEVELOPMENT

**DATA:** No original data were generated from the analyses presented in this report. Sources of data cited in this report should be consulted for determining the level of quality of those data.

**ANALYSES AND CODE:** No codes were used in the analyses contained in this report.

## **ABBREVIATIONS/ACRONYMS**

CEC	cation exchange capacity
COC	contaminant of concern
DEXOU	D-Area expanded operable unit
DO	dissolved oxygen
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
GSA	General Separations Area
NRC	U.S. Nuclear Regulatory Commission
INL	Idaho National Laboratory
INTEC	Idaho Nuclear Technology and Engineering Center
SDA	Subsurface Disposal Area
SRPA	Snake River Plain Aquifer
SRS	Savannah River Site
TDS	total dissolved solid

# 1 INTRODUCTION

One of the requirements for satisfying non-high-level waste determinations for planned and existing facilities at the Savannah River Site (SRS) and Idaho National Laboratory (INL) under Section 3116 of the Ronald W. Reagan National Defense Authorization Act for Fiscal Year 2005 is that the U.S. Department of Energy (DOE) dispose of radioactive waste resulting from reprocessing in accordance with the performance objectives set out in 10 CFR Part 61, Subpart C. In satisfying one of these objectives—Protection of the General Population from Releases of Radioactivity (10 CFR 61.41)—DOE commonly performs a performance assessment that includes evaluating potential exposure via a groundwater pathway. Such calculations typically include groundwater transport calculations that involve the use of sorption coefficients ( $K_d$ ) that assume equilibrium partitioning of a dissolved contaminant radionuclide between the groundwater solution and the host matrix. While the assumptions underlying the use of constant  $K_d$ s for given hydrostratigraphic units (e.g., invariable chemical conditions, relatively rapid sorption and desorption kinetics, linear concentration dependence) are not always satisfied, using  $K_d$ s to model the transport of dilute solutions of radionuclides in a homogeneous hydrochemical and geochemical environment can provide useful results. In performance assessments supporting waste determinations, DOE uses both site-specific and generic values in radionuclide transport models. This evaluation of site-specific data is not intended as an exhaustive treatise on sorption and contaminant transport. More detailed discussions of sorption mechanisms may be obtained from sources such as Hochella and White (1990). In addition, this review does not explicitly address in detail the effects of flow on sorption; hydraulic and physical properties of the transport medium are discussed only to the extent necessary for selecting appropriate  $K_d$  values.

## 1.1 Purpose

In its consultative role in the Section 3116 waste determination process, the U.S. Nuclear Regulatory Commission (NRC) reviews any relevant performance assessments and provides comments as appropriate. These reviews include evaluating whether sorption coefficients DOE uses for radionuclide transport in the geosphere reasonably reflect expected local conditions. In other words, NRC staff is interested in whether site-specific data were used, whether hydrochemical conditions along the groundwater pathway were considered in choosing  $K_d$ s, and whether any uses of non-site-specific data were warranted and appropriate. For NRC staff reviewing DOE non-high-level waste determinations, the purposes of this report are (i) to document the sorption coefficient database tailored to site-specific subsurface conditions for risk-significant radionuclides and relevant decay chain members; (ii) to recommend sorption coefficient values, or ranges of values, for radionuclide species appropriate for those specific hydrochemical and geochemical environments found at SRS and INL; and (iii) to suggest appropriate ways to evaluate DOE values in light of the compiled information.

While this report does recommend appropriate sorption coefficients for transport based on careful analysis, these values should not be accepted without acknowledging any new data, considerations, or other information provided in DOE reports. For example, new understanding may emerge about the long-term evolution of SRS groundwater hydrochemistry. The inclusion of a recommended value in this report does not constitute a technical basis for DOE use of the value. Likewise, a recommendation in this report does not preclude the acceptability of different values DOE uses. DOE will always be expected to provide the technical basis, independent of

this report, for parameters employed in its models. Recommendations in this report tend to bound the lower range of measurements. If independent NRC staff analyses of  $K_d$ s were to be conducted, uncertainties reflected in the data reported here should be considered.

## **1.2 Use of Sorption Coefficients in Performance Assessment**

The sorption coefficient commonly has units of mL/g<sup>1</sup> or L/kg and represents the ratio of the amount of contaminant on the solid per unit mass to the amount of the contaminant in the fluid per unit volume. The effects of sorption are to slow transport relative to unretarded species and accentuate the attenuating effects of dispersion. Therefore, highly sorbing radionuclides (i.e., those with high  $K_d$  values) initially tend to be less important contributors to groundwater dose in the absence of colloidal effects. In relatively straightforward radionuclide transport models such as those DOE uses in non-high-level waste determinations, this ratio is typically assumed to be constant for a given stratum along the hydrologic transport pathway. Unit-specific values are intended to reflect the dependence of  $K_d$ s on mineralogical and surface area properties of the rocks in that unit. Sorption coefficients also depend on hydrogeochemical factors and, as such, should reflect the chemical characteristics of the transporting water. Dependence of  $K_d$ s on such factors as pH and oxidation-reduction potential is well known and is related to the effects of these factors on aqueous speciation. For example, actinides such as neptunium and uranium show strong pH variation in  $K_d$ , with sharply defined peaks at moderate pH values. Aqueous complexation with organic and inorganic species (e.g., carbonate and sulfate) also affects surface-solution partitioning. The presence of colloids in groundwater can lead to higher mobility of strongly sorbing radioelements such as plutonium—an effect that is not captured in typical  $K_d$  approaches. The nature of the host rock may also affect transport in ways unaccounted for in simple porous-medium models (e.g., fractures may provide fast transport pathways).

Because these lithologic and hydrogeochemical factors are not always well constrained for a given transport model, it is often necessary to make conservative selections of  $K_d$  values that are at the low end of reasonable ranges. In this way, the model is less likely to overpredict the favorable effects of sorption. Such an approach is useful in the case of spatial and temporal variation. For example, the General Separations Area at SRS (see Chapter 2) was subject to extensive acid groundwater contamination during the 20<sup>th</sup> century, imparting a range of groundwater pH from 3.4 to 7.1, with estimated “background” values of 4.8 to 6.8 (Kaplan, et al., 1994; Kaplan, 2004; Dai, et al., 2002; Serkiz and Johnson, 1994; Vyas, et al., 2001). Because actinide sorption coefficients can vary over one or two orders of magnitude over this pH range, it is clear that potential variation in pH must be considered in assigning model parameters.

## **1.3 Approach to Data Review**

In this review, the correspondence between field conditions (i.e., subsurface mineralogy and aqueous chemistry) and the data used to estimate  $K_d$  values for each radionuclide contaminant of concern (COC) at SRS and INL were considered. In many cases, site-specific  $K_d$  data for the COCs at SRS and INL are available. When site-specific  $K_d$  data were not available, data from the open literature on comparable systems to SRS and INL were consulted and analyzed. The

---

<sup>1</sup>The most widely accepted unit for  $K_d$  is mL/g and there are no comparable English units that are generally accepted.

result of this data review is a recommended  $K_d$  value for each COC at SRS and INL. The approach used here is to recommend a single, deterministic value; ranges of values presented are not intended explicitly to be applied directly as probability distributions for probabilistic models. The following general procedure was used in the  $K_d$  analysis:

- (1) The mineralogical and hydrogeochemical characteristics of subsurface units along transport pathways at SRS and INL are described (e.g., sandy aquifer sediments and clay-rich confining units at SRS and alluvium, interbed sediments, and basalt at INL).
- (2) The radionuclide contaminants of concern at SRS and INL are designated (see Sections 2.3 and 3.3).
- (3) For each COC at SRS and INL
  - The general chemistry and important sorptive aspects of the contaminant are briefly described.
  - Site-specific measurements of  $K_d$  values and/or measurements of  $K_d$  values under analogous conditions to SRS or INL are summarized.
  - Literature-based reference  $K_d$  estimates and recommendations prepared for use in previous transport assessments at SRS and INL, which take into account site hydrogeochemical conditions, are mentioned (e.g., Kaplan, 2006 for SRS and Cooper, et al., 2006 for INL).
  - $K_d$  values from compendia of sediment and rock types comparable to subsurface geologic units at SRS and INL are mentioned (e.g., Sheppard and Thibault, 1990; Looney, et al., 1987).
  - Based on the above data review, a recommended  $K_d$  value is presented.

Recommended  $K_d$  values in this review are based on knowledge of the hydrogeochemistry of each COC, available data on site chemical conditions, and reported  $K_d$  values from site-specific experiments or experiments conducted under the most analogous conditions. The most analogous conditions are chosen on the basis of sediment lithology and mineralogy and site hydrogeochemistry, with greatest weight being given to results from experiments that closely emulate field conditions. The following sections provide some background information on how (i) measurement methods can affect the interpretation of reported  $K_d$  values and (ii) specific environmental factors affect contaminant subsurface transport.

## 1.4 $K_d$ Measurements

Although detailed evaluation of all methods used for measuring  $K_d$ s relevant for SRS and INL is beyond the scope of this report, it is useful to understand these methods when evaluating radionuclide transport models. A reported  $K_d$  is partly a function of the method used to determine it—batch, column, or *in-situ* measurements—and of intramethod variations, such as solid–solution ratio in batch experiments, flow rates in column experiments, and particle-size fractions measured for *in-situ* measurements. Batch or column tests are the two most commonly used methods for measuring equilibrium  $K_d$ s. Each method may use either

single-mineral samples, mineral composites, or actual sediment or rock samples. While single-mineral analyses provide important data on processes, actual samples and mineral composites are preferred when site-specific empirical  $K_d$ s are needed for model application. These latter methods will more accurately capture all mineral effects, as well as any water–rock interactions affecting system chemistry. Some sorption experiments use synthetic, rather than sampled, groundwaters. The synthetic waters reflect major cation and anion chemistry and pH but may not account for characteristics such as the presence of organic substances. Nevertheless, the use of synthetic groundwaters may allow experimenters better chemical control by avoiding chemical sampling effects such as degassing.

The batch method, which involves placing a solid and solution containing the contaminant of interest into a vessel and mixing the sample for a prescribed time, has the advantage of being relatively fast and simple. Batch testing is generally the method of choice for strongly sorbing contaminants due to the extremely long time requirements of column tests for such contaminants. Batch tests have the disadvantage of being conducted under conditions far removed from those observed in the field. Specifically, they are carried out under static conditions (no advective flow), at solid–liquid ratios much lower than present in the field, and only under saturated conditions.

The column method consists of packing a glass or plastic column with a sediment or crushed rock sample. Solutions containing the contaminant are pumped through the column, and the effluents are collected and analyzed. Breakthrough occurs when the effluent concentration rises substantially. Column tests have the advantage of being conducted under conditions that more closely approximate those in the field. Specifically, columns may be packed to have bulk densities and porosities similar to those observed in the field, column tests are conducted under advective and dispersive flow conditions similar to those in the field, and column tests may be conducted under a variety of different moisture conditions. When available, reported  $K_d$  values from column transport experiments will generally be given greater credence in  $K_d$  recommendations than  $K_d$  values from batch equilibrium experiments. Nevertheless, some limitations of column experiments must be acknowledged when evaluating their results. For example, column experiments using crushed basalt may present excessive surface area compared to field conditions or may reflect sorption on fresh surfaces rather than the weathered or coated surfaces present in an aquifer. A column test may yield lower  $K_d$  values than an analogous batch test if, for example, sorption kinetics are overcome by high column flow velocities. Other considerations include column aspect ratios and column diameter relative to grain size (e.g., Relyea, 1982).

*In-situ* field measurements of  $K_d$  are sometimes determined by measuring the ratio of the concentration of the contaminant of interest in sampled sediment or rock to the concentration in sampled groundwater or porewater. These field measurements may more accurately indicate contaminant partitioning because the  $K_d$  is derived under actual field conditions. However, Payne, et al. (2001) reported that *in-situ* uranium  $K_d$ s varied over a wide range of about two orders of magnitude at the Koongarra uranium deposit in Northern Australia. Variations in  $K_d$ s were attributed to the heterogeneity of the field site, which reflects the complexity of most geologic systems.

Several experimental methods have been used to determine the concentration of metal contaminants in field samples. The total digestion method involves complete dissolution of all solid phase components in the sample. Measurements of this sort may often lead to

overestimates of  $K_d$  values if the contaminant concentration on the solid includes mass that is not exchangeable with the aqueous phase. A more commonly used procedure is the hot nitric acid procedure outlined in SW-846 Method 3050b (EPA, 1986). This method is intended to release exchangeable ions specifically adsorbed to clays, oxides, and organic matter, but would not release metals associated with insoluble minerals. More information may be gained from sequential extraction methods, which have been developed to selectively remove metals associated with the solid. These procedures are useful in categorizing the metals into several operationally defined geochemical fractions, such as exchangeable, specifically adsorbed, and metals associated with carbonates, organic matter, and/or iron and manganese oxides. Disadvantages of sequential extraction methods are that the extractant may remove metals associated with other fractions. Also, readsorption of extracted metals to the remaining solid phase may lead to artificially low concentrations of the metal being associated with that fraction.

## 1.5 Factors Affecting Sorption and Transport

In the subsurface, contaminants have the potential to be found (i) dissolved in the groundwater, (ii) occupying ion exchange sites on mineral constituents, (iii) adsorbed on mineral constituents, (iv) associated with insoluble organic matter, and (v) precipitated as pure or mixed solids. Sorption, defined as the accumulation of ions at the interface between a solid phase and an aqueous phase (and including both ion exchange and adsorption), is affected both by the nature of the solid substrate and the chemical form of the contaminant and solvent (Table 1-1). Some minerals, such as clays and iron oxyhydroxides, contribute to higher  $K_d$ s due to surface chemical characteristics and high effective surface areas. Quartz, the main constituent of sandstone, tends to be less sorptive. Cation sorption has been correlated with such properties as pH and oxidation-reduction potential and the content of clays, organic matter, iron and

<b>Table 1-1. Example Effects of Environmental Factors on <math>K_d</math></b>	
<b>Factor (Increasing)</b>	<b>General Effect on <math>K_d</math></b>
Clay content	Increase
Iron and manganese oxide content	Increase
Quartz content	Decrease
Grain size	Decrease
Specific surface area	Increase
pH	Increase (cation) Decrease (anion)
Aqueous carbonate	Decrease (actinides) at high pH
Oxidation-reduction potential or Eh	Decrease (uranium) Decrease (plutonium) Decrease (technetium)
Cation exchange capacity	Increase



Total dissolved solids	Decrease
------------------------	----------

manganese oxides, and calcium carbonate. Anion sorption has been correlated with iron and manganese oxide content, pH, and oxidation-reduction potential.

The pH is a very important parameter, directly influencing sorption/desorption, aqueous complex formation, and oxidation-reduction reactions. Many sorption sites of mineral constituents are pH dependent (i.e., iron and manganese oxides, organic matter, carbonates, and edge sites of clay minerals). As pH decreases, the number of negative surface sites for cation sorption diminishes while the number of sites for anion sorption increases. As the pH becomes more acidic, cations face competition from  $H^+$  for available charged sites. In general, although dependent on the aqueous speciation of a given contaminant, maximum retention of cationic metals occurs at  $pH > 7$ , and maximum retention of anionic metals occurs at  $pH < 7$ . However, cationic metal retention can decrease with increasing pH due to the formation of negatively charged metal ligand complexes. For example, the sorption behavior of actinides (e.g., uranium and plutonium), which is characterized by rapidly increasing sorption at pH values between 5 and 7, decreases at pH values greater than 7 to 9 in response to the formation of negatively charged mixed carbonate/hydroxyl and carbonate species.

Radionuclides exist in solution as either free (uncomplexed) metal ions or in various soluble complexes with inorganic or organic ligands. Common inorganic ligands are  $SO_4^{2-}$ ,  $Cl^-$ ,  $OH^-$ ,  $NO_3^-$ , and  $CO_3^{2-}$ . The formation of stable complexes in solution can significantly affect the transport of contaminants relative to the free metal ion. Due to complexation, the resulting species may be positively or negatively charged or be electrically neutral. Therefore, depending on the surface charge of available sites, the metal complex may be weakly sorbed or strongly sorbed relative to the free ion. Because ions compete for available surface sites, a high total dissolved solids content would tend to decrease sorption of any single contaminant.

Contaminant oxidation state strongly influences sorption behavior. For example, U(VI), or uranium in the 6+ oxidation state, is considerably more mobile than U(IV). The near-surface oxidizing conditions important to transport at INL and SRS, therefore, will favor uranium mobility in comparison with more reducing conditions found, for example, in deep, static aquifers.

The sorption effects of these hydrogeochemical and mineralogic effects can be simulated through the use of mechanistic surface complexation models. Kaplan (2006) discussed the use of such models for contaminant transport studies at SRS, but concluded that data support was insufficient for their general use in performance assessments at SRS. Surface complexation models have also not been widely applied at INL.

There is both laboratory and field evidence that fractions of some actinides (e.g., plutonium, americium, curium, and uranium) can migrate at rates that are greater than predicted by equilibrium  $K_d$  measurements. For example, Newman, et al. (1996) and Fjeld, et al. (2001) observed high mobility fractions of plutonium and americium in column tests conducted on basalt and sedimentary interbeds from INL. The enhanced-mobility fraction responsible for the early elution of plutonium and americium in the column tests raises questions about the mechanisms responsible for transport of plutonium and americium—specifically, the potential role of colloids. Dai, et al. (2002) found that a small fraction of total mobile plutonium in SRS sediments is associated with colloids, and Kaplan, et al. (1994) found that appreciable fractions of plutonium, thorium, and uranium in an acidic plume have been traveling through an aquifer

underlying SRS in association with mobile colloids at rates appreciably greater than anticipated. If these enhanced-mobility fractions are substantial and are being transported as colloids, their effects need to be considered in applying sorption-based transport models.

Aside from mineralogic constituents, hydrogeologic characteristics of the host rock also affect solute transport. For example, lower grain size and lower porosity may promote sorption by increasing the available specific surface area. Low permeability may lead to slower flow rates that could make sorption more effective because any kinetic barriers are more easily surmounted. Abundant fractures may provide fast water pathways that diminish water–rock interaction; in addition, fracture surfaces may provide contrasting mineralogic sorption environments versus the matrix. In the case of INL, for example, basalt fracture iron oxide coatings may be a significant factor for contaminant  $K_d$ s.

## 2 SAVANNAH RIVER SITE

### 2.1 Waste Management Background

Two types of radioactive waste disposal facilities governed by the Ronald W. Reagan National Defense Authorization Act for Fiscal Year 2005 consultative process are located at the Savannah River Site (SRS): grouted tanks and salt waste vaults. In the F and H-Areas of the General Separations Area (GSA), the U.S. Department of Energy (DOE) plans to close liquid radioactive waste tanks in place by removing waste to the maximum extent practical, filling the emptied tanks with grout (intended to immobilize any residual radionuclides), and constructing an engineered cap (e.g., DOE, 2005). In Z-Area of the GSA, DOE plans to dispose of a cementitious wasteform ("saltstone") containing the low-activity stream resulting from treatment of tank salt wastes (DOE, 2006a). For both disposal scenarios, waste determinations are supported by a performance assessment that includes modeled groundwater radionuclide transport. Because these facilities are all located on the same upland area in the GSA within a 5-km [3-mi] distance, they have the same environment with respect to hydrologic transport.

As mentioned in Section 1.2, the hydrochemistry of groundwater in the GSA bears the imprints of acid contamination, which is currently being actively remediated. These efforts are expected to lead to soil and groundwater cleanup and source isolation within the next few decades (e.g., Westinghouse Savannah River Company, 2002). By the time potential radionuclide releases would occur from closed tanks and the salt waste facility, it is expected that groundwater pH levels will have returned to natural background values.

### 2.2 Description of the General Separations Area

The GSA is an approximately 24-km<sup>2</sup> [9.3-mi<sup>2</sup>] area located in the central part of SRS. This area contains a number of radioactively contaminated facilities including a low-level radioactive waste disposal area, two large nuclear materials separation facilities, the Defense Waste Processing Facility, the Saltstone Disposal Facility, the Saltstone Processing Facility, the H-Tank Farm, and the F-Tank Farm. These facilities are located approximately 10 km [6.2 mi] from the nearest SRS site boundary on well-drained topographic highs bounded by three small black water streams called Upper Three Runs Creek, Fourmile Branch, and McQueen Branch.

SRS is underlain by Tertiary age unconsolidated and semiconsolidated sediments of the Floridan Aquifer System. The hydrostratigraphy of SRS consists of three vertically stacked aquifer zones and two confining zones that will be potentially impacted by release of contaminants from facilities within the GSA. The hydrostratigraphy of SRS has been the subject of several different classifications. This report incorporates the hydrostratigraphic nomenclature currently established for SRS vicinity by Aadland, et al. (1995). From top to bottom, the hydrostratigraphic units present beneath the GSA are: the Upper Three Runs aquifer, the Gordon confining unit, and the Gordon aquifer (Figure 2-1). The Upper Three Runs aquifer is locally divided into informal lower and upper aquifer zones separated by the tan clay confining zone.

The Upper Three Runs aquifer includes all sediments from the ground surface to the top of the Gordon confining unit. The upper aquifer zone (commonly referred to as the Water Table aquifer) consists of all sediments from the ground to the top of the tan clay confining zone and

HYDROSTRATIGRAPHIC UNIT		THICKNESS RANGE (FEET)
Upper Three Runs Aquifer	Upper Zone (Water Table Aquifer)	0-110
	Tan Clay	0-33
	Lower Zone (Barnwell McBean Aquifer)	39-81
Gordon Confining Unit (Green Clay)		2-30
Gordon Aquifer Unit		52-107
Crouch Branch Confining Unit		>100

**Figure 2-1. Hydrostratigraphic Units at the GSA (Modified From Buice, et al., 2005)**

includes the Upland unit, Tobacco Road Sand, and part of the Dry Branch Formation (Aadland, et al., 1995). This zone is characterized by sand and clayey sand with minor intercalated clay layers. The sediment within the Upland unit is commonly very dense and clayey and contains some gravelly sand. The term "Upland unit" is an informal name used to describe sediments at higher elevations located in the Upper Coastal Plain in southwestern South Carolina. The tan clay confining zone includes sediment of the Dry Branch Formation. The zone contains light-yellowish tan to orange clay and sandy clay interbedded with clayey sand and sand. The tan clay is dispersed vertically and horizontally and is not continuous over long distances (Aadland, et al., 1991). The lower aquifer zone (commonly referred to as the Barnwell McBean aquifer) consists dominantly of fine-grained, well-sorted sand and clayey sand of the Tinker/Santee Formation and parts of the Dry Branch Formation. The bulk of carbonate sediment present beneath the GSA is included in the lower aquifer zone. Descriptions of drill core indicate that the carbonate sediment in the SRS vicinity has a dominant siliciclastic component and consists of calcareous sand, micritic sand, shelly sand, and some sandy calcarenite and shelly limestone.

Strom and Kaback (1992) determined the mineralogical composition of 28 samples from the Upper Three Runs aquifer collected from wells within SRS by x-ray diffraction. The samples consisted of quartz with 2- to 40-wt% detrital clay. An examination of the mineralogical data reported by Strom and Kaback (1992) indicates that smectite and kaolinite are the dominant clay minerals in the upper zone of the Upper Three Runs aquifer and the tan clay confining unit and that smectite is the dominant clay mineral in the lower zone of the Upper Three Runs aquifer. Minor to trace amounts of illite, chlorite, pyrite, plagioclase, and K-feldspar were present in both aquifer zones and the tan clay confining unit. Calcite was detected in minor to trace amounts in the lower zone of the Upper Three Runs aquifer.

Several researchers have described the lithological and mineralogical properties of sediments from the Upper Three Runs aquifer used in radionuclide partitioning studies at SRS. Serkiz and Johnson (1994) analyzed sediment samples taken at depths ranging from 4 to 28 m [13 to 93 ft] from the upper zone of the Upper Three Runs aquifer downgradient of the F- and H-Area seepage basins within the GSA. Sand, silt, and clay contents of the sediments were 57 to 99 wt%, 0 to 12 wt%, and 0.5 to 42 wt%, respectively. The cation exchange capacity (CEC) of the sediment varied from <0.1 to 2.9 meq/100 g. The CECs were noted to be relatively low due to the high percentage of sand in the sediments. No correlation between clay fraction of the soil and CEC was observed.

Kaplan (2003) described the characteristics of an upland sample collected at a depth of 2 m [6 ft] near the E-Area low-level waste facility and a wetland sample collected from the surface of a wetland area along the Savannah River. The particle size distribution of the two samples was similar (79- to 80-wt% sand, 14- to 15-wt% silt, and 5- to 6-wt% clay). Smectite and kaolinite were the dominant clays in the upland sample, and smectite was the dominant clay in the wetland sample. The CECs of the samples were 4.75 and 3.99 meq/100g for the wetland and upland sample, respectively. Although organic carbon contents were low in both samples, the wetland sample had an appreciably greater organic carbon concentration {1,395 mg/kg [1,395 ppm]} than the upland sample {<200 mg/kg [<200 ppm]}. The very low organic carbon concentration in the upland sample indicates that little organic matter is leached into the underlying sediments.

Hu, et al. (2005) described the characteristics of a surface soil, a subsoil {composite of sediments collected at a depth of 12 m [39 ft]}, and an aquifer sediment collected from the upper zone of the Upper Three Runs aquifer. Sand, silt, and clay weight percentages were 87.6, 2.9, and 9.5 for the surface soil; 76.7, 3.5, and 19.8 for the subsoil; and 97.2, 0.9, and 1.9 for the aquifer sediment. Smectite and kaolinite were the dominant clays in all the samples, and goethite (an iron oxyhydroxide) was noted to be present in the subsoil and aquifer sediment. Extractable iron contents (a measure of iron-oxide mineral coatings) were 2.82 g/kg [2,820 ppm] for the surface soil, 16.2 g/kg [16,200 ppm] for the subsoil, and 7.3 g/kg [7,300 ppm] for the aquifer soil. The CECs of the samples were 1.3, 1.8, and 0.064 meq/100 g for the surface soil, subsoil, and aquifer sediment, respectively. The surface soil contained 2.3-wt% organic matter, whereas the subsoil and aquifer soil contained 0.07-wt% and 0.01-wt% organic matter, respectively. Low organic matter contents in the subsoil and aquifer soil again indicates that little organic matter is leached into the underlying sediments.

Barnett, et al. (2000) described the chemical and mineralogical properties of a sediment sample acquired at a depth of 45 m [150 ft] from the lower zone of the Upper Three Runs aquifer (McBean Formation) near the old burial grounds within the GSA. The sample consisted of

69-wt% sand, 7-wt% silt, and 24-wt% clay and was dominated by sand-sized quartz coated with iron oxides. Smectite was the dominant clay mineral and also contained iron-oxide coatings. The sediment contained 0.12 g/kg [120 ppm] organic matter, 0.06 g/kg [60 ppm] manganese, and 25.7 g/kg [25,700 ppm] iron.

The Gordon confining unit includes sediments of the Warley Hill Formation and is commonly referred to as the “green clay.” The unit comprises layers of interbedded silty and clayey sand, sandy clay, and clay that thicken and thin and pinch out abruptly. The clay is stiff and hard and is often fissile. Glauconite is a common constituent and imparts a distinctive greenish color to the sediment, hence the informal name “green clay.” Zones of silica-cemented sand and clay are noted in some cores taken from SRS (Aadland, et al., 1995). In the vicinity of the GSA, the Gordon confining unit includes some calcareous sediment and limestone, primarily calcareous sand and clayey sand with subordinate calcareous and micritic clay, sandy micrite, and limestone.

X-ray diffraction analyses of four muddy-sand samples, collected from the Gordon confining unit from wells within SRS, were reported to consist mostly of quartz with 18- to 42-wt% clay minerals (Strom and Kaback, 1992). Smectite was the dominant clay mineral, with minor to trace amounts of illite and kaolinite. Textural analyses made on 10 sandy mud and muddy sand samples from the Gordon confining unit averaged 47.3-wt% mud, 52.2-wt% sand, and 0.5-wt% gravel (Bledsoe, et al., 1990).

The Gordon aquifer constitutes the basal unit of the Floridan Aquifer System. Beneath the GSA, the Gordon aquifer is made up of the loose sand and clayey sand of the Congaree and Fourmile Formations (Aadland, et al., 1991; 1995). The sand within the Gordon aquifer is yellowish to grayish orange in color and is sub to well rounded, moderately to poorly sorted, and medium to coarse grained. Pebbly layers and zones of iron and silica cement are common. Clay beds and stringers are present, but they are too thin and discontinuous to be more than local confining beds. Small amounts of calcareous sediment occur sporadically within the unit.

Petrographic analyses of 42 thin sections show that sand-rich sediments from the Gordon aquifer unit consist of 98.4-wt% framework quartz, 0.3-wt% feldspar, 0.5-wt% heavy minerals, 0.4-wt% opaque minerals, 0.4-wt% muscovite, and 0.1-wt% glauconite (Robertson and Thayer, 1990). Strom and Kaback (1992) did semiquantitative x-ray diffraction analyses of 18 Gordon aquifer clay-bearing samples collected within SRS. Their results showed that the sand consists mostly of quartz with 5- to 18-wt% clay. Smectite and kaolinite were reported to be the dominant clay minerals, with minor or trace amounts of illite. Authigenic minerals included clinoptilolite, cristobalite, and chalcedony. X-ray diffraction analyses of 4 sandy mud samples from intra-aquifer confining layers were reported to consist of quartz and 51- to 64-wt% clay minerals, chiefly kaolinite with minor illite and smectite.

Groundwater beneath the GSA flows toward streams and swamps and into the Savannah River at rates ranging from inches to a few hundred feet per year. The depth at which nearby streams cut into sediments, the lithology of the sediments, and the orientation of the sediment formations control the horizontal and vertical movement of the groundwater. The valleys of smaller perennial streams, such as Fourmile Branch and McQueen Branch, allow discharge from the shallow saturated geologic formations (e.g., the Upper Three Runs aquifer). The valleys of major streams, such as Upper Three Runs Creek, drain formations of greater depth (e.g., the

Gordon aquifer). Because of these discharges, flow is not expected to penetrate into stratigraphic units beneath the Gordon aquifer within and in the vicinity of the GSA.

Strom and Kaback (1992) investigated the chemistry of water in aquifers at SRS. Along the northern boundary of SRS, groundwaters in the Upper Three Runs and Gordon aquifers are very low in total dissolved solids {< 20 mg/L [ $<20$  ppm]} and contain high concentrations of dissolved oxygen {6 to 11 mg/L [6 to 11 ppm]}. Waters in this area are relatively acidic (pH 5 to 6), and there are no predominant cations or anions in the water. In this portion of SRS, the confining units that separate shallow aquifers are only of local extent, and the hydraulic gradient is downward from the Tertiary formations into the underlying Cretaceous formations.

South of Upper Three Runs Creek in the central and southern portions of SRS, which includes the GSA, shallow confining units are more laterally extensive, and waters within the Upper Three Runs and Gordon aquifers are geochemically distinctive. The chemical characteristics of waters in the shallow aquifers and confining units in this part of SRS are listed in Table 2-1. Groundwater in this area has total dissolved solids ranging from 5 to 150 mg/L [5 to 150 ppm]. Calcium and bicarbonate are the predominant ions, due largely to chemical reactions between groundwater and calcite-bearing units that are scattered sporadically through the Tertiary section. Waters in this area are slightly acidic to neutral (pH 5.2 to 7.7). Dissolved oxygen concentrations are variable {0.02 to 10 mg/L [0.02 to 10 ppm]} suggesting some interaction with organic matter.

Aqueous wastes from a nuclear materials processing facility on the GSA were released over a 33-year period to unlined seepage basins. Three basins covering approximately 2.8 ha [7 acres] were built in the F Area, and 4 basins covering 6.5 ha [16 acres] were constructed in the H Area. The seepage basins were designed to allow the effluent to percolate into the surrounding environment, where soil sorption processes were expected to retard the movement of the waste constituents. The wastes contained high concentrations of strong acids, sodium, tritium, and trace amounts of numerous radionuclides and metals (Kaplan, et al., 1994). Due to these releases, soils and groundwater beneath the GSA have widely varying groundwater chemistries and contaminant concentrations.

Several researchers have described the aqueous chemistry of acid-contaminated groundwater in the Upper Three Runs aquifer beneath the GSA (Serkiz and Johnson, 1994; Kaplan, et al., 1994; Dai, et al., 2002). These waters have acidic pHs (3.0 to 4.2); low inorganic and organic carbon contents; and high nitrate, tritium, and dissolved oxygen contents. Waters have elevated concentrations of cations such as  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{Si}^{4+}$ , consistent with acid leaching of aquifer matrix materials such as clays (e.g., kaolinite) and surface mineral coatings (e.g., iron oxyhydroxides). Contaminated waters are also enriched in radionuclides such as Pu-239, Am-241, Cm-243, Cm-244, and U-238 (Kaplan, et al., 1994) and in metals such as lead, zinc, cadmium, and copper (Dai, et al., 2002).

The chemistry of groundwater and mineralogic composition of sediments beneath the GSA will affect contaminant transport. Due to the release of acidic aqueous wastes, groundwater beneath the GSA currently has widely varying chemistry. However, in the future it is anticipated that acid-contaminated waters beneath the GSA will return to normal chemical conditions due to natural flushing of the aquifer and clay confining units by infiltrating rainwater. In addition, efforts are underway to remediate acid-contaminated areas beneath the GSA to speed the return to normal chemical conditions. These efforts are expected to lead to soil and

<b>Table 2-1. Chemistry of Water in Shallow Aquifer and Confining Units in the Central and Southern Part of the Savannah River Site*</b>				
	<b>Upper Three Runs Aquifer (Upper Zone) and Tan Clay</b>	<b>Upper Three Runs Aquifer (Lower Zone)</b>	<b>Gordon Confining Unit</b>	<b>Gordon Aquifer</b>
pH	5.2– 6.3	6.0–7.7	5.8–6.8	5.7–7.6
Specific Conductance (μS)	22–81	6.8–192	39–102	66–216
Total Dissolved Solids (mg/L)	5–53	45–102	19–55	28–150
Oxidation-Reduction Potential (V)	0.09–0.30	(–0.05)–0.13	0.07–0.23	(–0.09)–0.12
Eh (mV)	291–497	150–325	266–427	113–316
Dissolved Oxygen (mg/L)	7.33–9.6	0.41–9.82	5.35–9.98	0.02–4.33
Ca <sup>2+</sup> (mg/L)	1.2–12	7.2–38	4.4–17	9–45
Mg <sup>2+</sup> (mg/L)	0.38–0.74	0.24–0.79	0.32–0.47	0.48–1.1
Na <sup>+</sup> (mg/L)	0.66–3.3	1.2–2.8	0.9–1.5	0.87–1.9
K <sup>+</sup> (mg/L)	0.3–2.2	0.43–2.9	0.52–1.6	0.35–4.3
HCO <sub>3</sub> <sup>–</sup> (mg/L)	1.2–30	20–101	12–47	27–114
SO <sub>4</sub> <sup>2–</sup> (mg/L)	0.36–1.77	0.73–3.8	0.68–2.74	0.63–13.8
Cl <sup>–</sup> (mg/L)	1.50–7.58	1.95–2.88	2.16–3.31	2.40–2.74
F <sup>–</sup> (mg/L)	<0.05–0.07	<0.05–0.34	<0.05–0.10	<0.05–0.11
*Strom and Kaback provide no chemistry data for the tan clay confining unit. Based on mineralogic similarities (e.g., the lack of calcite), the tan clay is expected to have chemical properties similar to the upper zone of the Upper Three Runs Aquifer. Strom, R.N. and D.S. Kaback. “SRP Baseline Hydrogeologic Investigation: Aquifer Characterization, Groundwater Geochemistry of the Savannah River Site and Vicinity.” WSRC–RP–92–450. Aiken, South Carolina: Westinghouse Savannah River Company. 1992.				

groundwater cleanup, and source isolation within the next few decades (e.g., Westinghouse Savannah River Company, 2002). Due to natural flushing and remediation, groundwater in the hydrostratigraphic units beneath GSA is expected to have the following chemical characteristics that will affect contaminant transport:

- Slightly acidic to neutral pH (pH of 5.2 to 7.7; Table 2-1)
- Variable total dissolved solids (TDS)
- Cation concentrations dominated by Ca<sup>2+</sup> and anion concentrations dominated by HCO<sub>3</sub><sup>–</sup>
- Variable dissolved O<sub>2</sub> concentrations due to interaction with organic matter



Natural organic matter is present in surface sediments and may be present in the less hydraulically conductive clay-rich confining units at GSA, potentially resulting in reducing conditions in some isolated, relatively immobile groundwater.

Mineralogic characteristics will affect the partitioning of contaminants between groundwater and solid materials in hydrostratigraphic units beneath GSA, including

- Compositions dominated by quartz grains and clays that are commonly coated with iron oxides and iron-oxyhydroxides
- Clay mineral contents accounting for 1 to 25 wt% of sediments composing aquifer units and up to 65 wt% of sediments composing confining units
- The presence of calcareous sediments in deeper hydrostratigraphic units (i.e., in the lower zone of the Upper Three Runs aquifer, Gordon confining unit, and Gordon aquifer)

Iron oxides and iron oxyhydroxides can strongly adsorb actinides, such as uranium, under certain chemical conditions. For example, uranium sorbs strongly to ferrihydrite over the pH range of 5 to 8 (Waite, et al., 1994). Clay minerals provide sites for sorption and ion exchange with contaminant-bearing water. For example, cesium adsorbs primarily via ion exchange with clay minerals. Smectite and kaolinite have been reported to be the most abundant clay minerals in sediments at SRS (Strom and Kaback, 1992). Smectite has the largest cation exchange capacities of the clay minerals present at SRS.

Reaction of groundwater and calcareous sediments can increase calcium and bicarbonate concentrations, thereby increasing groundwater pH and ionic strength. The sorption of many of the contaminants at SRS is sensitive to pH. For example, sorption of strontium and cesium, which exist as cationic species in natural waters, increases with increasing pH, while sorption of selenium, technetium, and iodine, which exist as anionic species in natural waters, decreases with increasing pH. On the other hand, the sorption behavior of actinides, such as uranium and plutonium, is characterized by rapidly increasing sorption at pH values between 5 and 7 and then decreasing sorption at pH values greater than 7 to 9 in response to the formation of mixed carbonate/hydroxyl and carbonate species. In addition, the increased concentration of calcium in groundwater resulting from dissolution of calcite-bearing sediments can reduce the sorption of contaminants such as strontium and lead due to competition for adsorption sites.

## **2.3 Designation of Risk-Significant Radionuclides**

The COCs chosen for analysis in this report are based both on previous model results and on more general considerations of hydrochemical behavior and dose effects. For example, a radionuclide with a high-dose-conversion factor could be important if its sorption coefficient is not as high as supposed. In addition, inclusion on the DOE list of highly radioactive radionuclides was considered. DOE analyses (Rosenberger, et al., 2005; Buice, et al., 2005) have indicated that isotopes of selenium, technetium, iodine, and neptunium are potentially important in groundwater pathway dose calculations for salt waste and grouted tank facilities. Uranium is important in waste inventories and is relatively mobile in many environments. Other actinides—plutonium, americium, and curium—are included due to potentially important dose effects if sorption coefficients are overestimated. Isotopes of strontium and cesium, though relatively short lived, have high inventories and could be important if groundwater travel

pathways are short. Carbon and lead provide significant doses in some preliminary unpublished U.S. Nuclear Regulatory Commission analyses, and radioisotopes of tin, niobium, and nickel may have elevated inventories in some wasteforms.

## 2.4 Sorption Coefficients

The hydrostratigraphic units that will be affected by release of contaminants from waste storage facilities at the GSA (e.g., the Saltstone Disposal Facility) are the upper and lower aquifer zones and the tan clay confining zone of the Upper Three Runs aquifer, the Gordon confining unit, and the Gordon aquifer. With the exception of surficial soils and sediments of the upper zone of the Upper Three Runs aquifer, little or no site-specific sorption data exists for the hydrostratigraphic units beneath the GSA. As a result, previous SRS contaminant transport models have classified aquifer units as sandy-textured sediment or soil and, for each COC, a single or uniform  $K_d$  has been assigned to all aquifer units (Cook, et al., 2005, 2000; Buice, et al., 2005; Kaplan, 2005; Rosenberger, et al., 2005). Similarly, confining units (i.e., the tan clay and Gordon confining unit) beneath the GSA have been classified as clay sediments and assigned a single or uniform  $K_d$  for each COC.

In this review, site-specific  $K_d$  measurements and literature-recommended  $K_d$  values for the COCs are analyzed and reviewed to derive a recommended  $K_d$  value for each hydrostratigraphic unit beneath SRS. In many instances where site-specific  $K_d$  measurements are lacking for hydrostratigraphic units, the mineralogic and hydrogeochemical characteristics of the units are evaluated to derive a  $K_d$  recommendation. The mineralogical and expected hydrogeochemical characteristics of each hydrostratigraphic unit are summarized in Table 2-2. Examination of the listed mineralogical and chemical properties in Table 2-2 indicates that the mineralogical and chemical properties of the aquifer units and the confining units are quite similar. The most notable difference is the presence of calcareous (calcite-bearing) sediments in the deeper hydrostratigraphic units (i.e., the lower zone of the Upper Three Runs aquifer, the Gordon confining unit, and the Gordon aquifer) and the related higher minimum pH of these units.

Sheppard and Thibault (1990) (see also Thibault, et al., 1990) provided a compilation of soil solid/liquid  $K_d$  values for use in environmental assessments for nuclear waste disposal. This compilation was originally prepared for assessing the concept of disposing Canadian spent fuel deep in Precambrian Shield plutonic rock. Due to the absence or lack of site-specific  $K_d$  measurements on soils and sediments for many of the COCs at SRS,  $K_d$  values from the compilation of Sheppard and Thibault (1990) have been treated as an independent source and used in performance assessments and special analyses at SRS (Cook, et al., 2005, 2000; Buice, et al., 2005; Kaplan, 2005; Rosenberger, et al., 2005).

The compilation of Sheppard and Thibault (1990) listed  $K_d$  values for 48 different elements in 4 different mineral soil types (sand, loam, clay, and organic). Values were compiled from measurements reported in the peer-reviewed literature. If no data existed in the literature for a given element, then the soil-to-plant concentration ratio was used to indicate the element's bioavailability and to predict a  $K_d$  value (Baes, et al., 1984). The soil-to-plant concentration ratio is a measure of the root uptake of a radionuclide incorporated into the surface horizon of soil and represents the ratio of radionuclide concentration in plant and soil at harvestable maturity. Based on a strong negative correlation between the soil-to-plant concentration ratio and  $K_d$ , Thibault, et al. (1990) used observed and predicted  $K_d$  values from regression analyses to

**Table 2-2. Mineralogical and Hydrogeochemical Characteristics of Hydrostratigraphic Units at the Savannah River Site**

<b>Unit</b>	<b>Lithology*</b>	<b>Mineralogy†</b>	<b>pH Range‡</b>	<b>Other Hydrogeochemical Aspects‡</b>
Upper Three Runs Aquifer: Upper Zone	Sand and clayey sand; minor intercalated clay layers	Major constituents: quartz, smectite, kaolinite Minor constituents: plagioclase, K-feldspar, illite, pyrite, chlorite, iron oxyhydroxides	5.2–6.8	Variable dissolved O <sub>2</sub> Ions dominated by Ca <sup>2+</sup> , HCO <sub>3</sub> <sup>-</sup> total dissolved solids: <50 mg/L [ $<50$ ppm]
Tan Clay Confining Unit	Clay and sandy clay interbedded with clayey sand and sand	Major constituents: quartz, smectite, kaolinite Minor constituents: plagioclase, K-feldspar, illite, pyrite, chlorite, iron oxyhydroxides	5.2–6.8	Variable dissolved O <sub>2</sub> Ions dominated by Ca <sup>2+</sup> , HCO <sub>3</sub> <sup>-</sup> total dissolved solids: <50 mg/L [ $<50$ ppm]
Upper Three Runs Aquifer: Lower Zone	Sand and clayey sand; interspersed calcareous sand, micritic sand, and shelly sand	Major constituents: quartz, smectite Minor constituents: kaolinite, plagioclase, K-feldspar, illite, pyrite, chlorite, iron oxyhydroxides, calcite	6.0–7.7	Variable dissolved O <sub>2</sub> Ions dominated by Ca <sup>2+</sup> , HCO <sub>3</sub> <sup>-</sup> total dissolved solids: 50 to 150 mg/L [50 to 150 ppm]
Gordon Confining Unit	Interbedded silty and clayey sand, sandy clay and clay; some calcareous sediment and limestone	Major constituents: quartz, smectite, glauconite Minor constituents: kaolinite, illite, iron oxyhydroxides, calcite	5.8–6.8	Variable dissolved O <sub>2</sub> Ions dominated by Ca <sup>2+</sup> , HCO <sub>3</sub> <sup>-</sup> total dissolved solids: <50 mg/L [ $<50$ ppm]

**Table 2-2. Mineralogical and Hydrogeochemical Characteristics of Hydrostratigraphic Units at the Savannah River Site (continued)**

Unit	Lithology*	Mineralogy†	pH Range‡	Other Hydrogeochemical Aspects‡
Gordon Aquifer	Loose sand and clayey sand; zones of iron and silica cement; small amounts of calcareous sediment	Major constituents: quartz, smectite, kaolinite Minor constituents: illite, feldspar, muscovite, pyrite, glauconite, clinoptilolite, cristobalite, chalcedony, iron oxyhydroxides, calcite	5.7–7.6	Variable dissolved O <sub>2</sub> ions dominated by Ca <sup>2+</sup> , HCO <sub>3</sub> <sup>-</sup> total dissolved solids: 50 to 150 mg/L [50 to 150 ppm]
<p>*Lithologic characterization based on data from Aadland, R.K., J.A. Gellici, and P.A. Thayer. "Hydrogeologic Framework of West-Central South Carolina." Report 5. PIT-MISC-0112. State of South Carolina Department of Natural Resources, Water Resources Division. 1995.</p> <p>†Mineralogic characterization based on data from Strom, R.N. and D.S. Kaback. "SRP Baseline Hydrogeologic Investigation: Aquifer Characterization, Groundwater Geochemistry of the Savannah River Site and Vicinity." WSRC-RP-92-450. Aiken, South Carolina: Westinghouse Savannah River Company. 1992; Kaplan, D.I. "Influence of Surface Charge of an Fe-Oxide and an Organic Matter Dominated Soil on Iodide and Per technetate Sorption." <i>Radiochimica Acta</i>. Vol. 91, No. 3. pp. 173–178. 2003; Hu, Q., Z. Pihong, J.E. Moran, and J.C. Seaman. "Sorption and Transport of Iodine Species in Sediments from Savannah River and Hanford Sites." <i>Journal of Contaminant Hydrology</i>. Vol. 78. pp. 185–205. 2005; and Barnett, M.O., P.M. Jardine, S.C. Brooks, and H.M. Selim. "Adsorption and Transport of Uranium(VI) in Subsurface Media." <i>Soil Science Society American Journal</i>. Vol. 64. pp. 908–917. 2000.</p> <p>‡Chemical characterization based on data from Strom, R.N. and D.S. Kaback. "SRP Baseline Hydrogeologic Investigation: Aquifer Characterization, Groundwater Geochemistry of the Savannah River Site and Vicinity." WSRC-RP-92-450. Aiken, South Carolina: Westinghouse Savannah River Company. 1992. The pH range does not include lower values resulting from acid contamination.</p>				

develop a model to estimate the  $K_d$  of a given radionuclide for each soil type from a measured soil-to-plant concentration ratio.

In the compilation of Sheppard and Thibault (1990), the soils that contained at least 70-wt% sand-sized particles were classified as sand soils, and those containing at least 35-wt% clay-sized particles were classified as clay soils. Loam soils had an even distribution of sand-, clay-, and silt-sized particles or consisted of up to 80-wt% silt-sized particles. Organic soils contained >30-wt% organic matter. Based on particle size analyses, aquifer sediments beneath the GSA are most comparable to sand soils, and clay confining units are most comparable to clay soils defined by Sheppard and Thibault (1990). The range and “default”  $K_d$  values for sand and clay reported by Sheppard and Thibault (1990) for each COC in this review are graphically illustrated in Figures 2-2 through 2-11 and Figures 2-13 through 2-17. “Default”  $K_d$ s for a given COC were the geometric mean of all reported  $K_d$  observations or were predicted using soil-to-plant concentration ratios for COCs with no observations (Sheppard and Thibault, 1990).

To aid in environmental assessments of waste sites at the Savannah River Plant, Looney, et al. (1987) estimated  $K_d$  ranges and “reference” soil  $K_d$  values for 31 elements. The estimated  $K_d$  ranges presented by Looney, et al. (1987) were based on the literature and represent, as available, onsite measurements, values for silty soils, and values for all soils. Literature sources used to estimate the  $K_d$  ranges included Sheppard, et al. (1984); Baes and Sharp (1983); Hoeffner (1985); Ames and Rai (1978); Callahan, et al. (1979); and U.S. Environmental Protection Agency (EPA) (1985). The “reference”  $K_d$  values specified by Looney, et al. (1987) for SRS soils were predicted based on the general solution and solid surface properties and reactions expected in the subsurface at SRS.

A compilation of estimated  $K_d$  values for contaminants at the SRS tabulated by Kaplan (2006) has been useful in this data review. Kaplan (2006) estimated “best” and “reasonably conservative”  $K_d$  values for 40 elements in sandy subsurface sediment and clayey subsurface sediment for use in SRS-related performance assessment calculations related to SRS. The “best” estimates provide guidance on the most likely  $K_d$  value for a given contaminant and are based on site-specific measurements and literature experimental data. When site-specific and literature data were not available, chemical analogs were used in the “best” estimates of  $K_d$  values. The “reasonably conservative” values represent lower bounding values that consider the range of physical, chemical, and mineralogical conditions that often lead to enhanced radionuclide migration. Ideally, the “reasonably conservative” value was based on the lower limit of multiple  $K_d$  measurements. In the absence of sufficient data, the “reasonably conservative” value was based on an assumed range of values, using the “best” value as a central point in the range. The sandy subsurface sediment was conceptualized as a sediment containing a clay and silt content less than 25 wt%, and the clayey subsurface sediment was conceptualized as a sediment containing a clay and silt content of 25 to 45 wt%. Based on these particle size characteristics, aquifer units beneath the GSA are most comparable to the sandy subsurface sediments, and clay confining units are most comparable to the clayey subsurface sediments.

When little or no site-specific or analogous  $K_d$  data could be found for a COC at SRS, the default soil and clay  $K_d$  values specified by Sheppard and Thibault (1990), the soil reference  $K_d$  values estimated for SRS by Looney, et al. (1987), and the “reasonably conservative” and “best”  $K_d$  values estimated for sandy and clayey subsurface sediment at SRS by Kaplan (2006) were in

some cases directly incorporated into the  $K_d$  recommendations in this review. In other cases, these values are presented to help determine whether the recommended  $K_d$  values for SRS are reasonable.

### 2.4.1 Carbon

The C-14 present in SRS waste streams originates from nuclear fuel processing and is predominantly inorganic in nature. In the GSA environment, inorganic carbon transport occurs via both slow aqueous transport as  $\text{HCO}_3^-$  ion and rapid transport of  $\text{CO}_2$  gas. Carbon-14 transport is likely to be affected by reactions other than sorption, but an empirical  $K_d$  approach may be sufficient for understanding potential transport.

McIntyre (1988) performed batch experiments using carbon, Savannah River Plant soil, and Savannah River Plant burial ground groundwater. The Savannah River Plant soil composition was 72-wt% sand, 5-wt% silt, and 23-wt% clay with a moisture content of near 16 percent. The groundwater used in the experiments had a pH of 6.0. After 7 hours of equilibration, carbon  $K_d$  values ranged from 1.6 to 2.3 mL/g (average of 2.0 mL/g). After 72 hours of equilibration, carbon  $K_d$  values ranged from 46.9 to 63.2 mL/g (average of 55 mL/g).

Sheppard and Thibault (1990) estimated a carbon default  $K_d$  for sand of 5.0 mL/g (three observations ranging from 1.7 to 7.1 mL/g) and a carbon default  $K_d$  for clay of 1.0 mL/g (based on a soil-to-plant concentration ratio). Looney, et al. (1987) estimated a reference SRS soil  $K_d$  of 0.01 mL/g for carbon. Kaplan (2006) estimated “best” and “reasonably conservative”  $K_d$  values of 0 mL/g for carbon in both sandy subsurface sediment and clayey subsurface sediment at SRS. The estimation of Kaplan (2006) was based on the judgment that carbon is expected to exist as  $\text{HCO}_3^-$  in the aqueous phase, and therefore, little sorption is expected.

Measured, estimated, and recommended carbon  $K_d$  values are summarized in Table 2-3. Site-specific carbon  $K_d$  values from the batch experiments of McIntyre (1988) using Savannah River Plant soil (upper zone of Upper Three Runs aquifer) ranged from 1.6 to 2.3 mL/g after 7 hours of equilibration. This  $K_d$  range is bracketed by the carbon  $K_d$  value estimated by Kaplan (2006) (0 mL/g) for sandy subsurface sediment at SRS, the SRS reference soil carbon  $K_d$  value estimated by Looney, et al. (1987) (0.01 mL/g), and the carbon  $K_d$  value estimated for sand by Sheppard and Thibault (1990) (5 mL/g). A carbon  $K_d$  value of 2 mL/g, which is the average of the measured carbon  $K_d$  values in the 7-hour batch test of McIntyre (1988), is recommended for the upper zone of the Upper Three Runs aquifer. The mineral composition of the aquifer units is not significantly different and should not greatly affect carbon sorption. Due to the presence of calcareous sediments, groundwater in the lower zone of the Upper Three Runs aquifer and the Gordon aquifer have higher bicarbonate contents than the upper zone of the Upper Three Runs aquifer. These higher bicarbonate contents could potentially enhance the mobility of carbon as  $\text{HCO}_3^-$ . Therefore, a carbon  $K_d$  value of 1 mL/g is recommended for the lower zone of the Upper Three Runs Aquifer and the Gordon Aquifer.

No site-specific data are available for carbon partitioning to the clay confining units at SRS. Based on the carbon  $K_d$  value of 1 mL/g estimated by Sheppard and Thibault (1990) for clay and the carbon  $K_d$  value of 0 mL/g estimated by Kaplan (2006) for SRS clayey subsurface

**Table 2-3. Measured, Estimated, and Recommended  $K_d$  Values for Carbon in Aquifer Sediments and Clay Confining Units at the Savannah River Site**

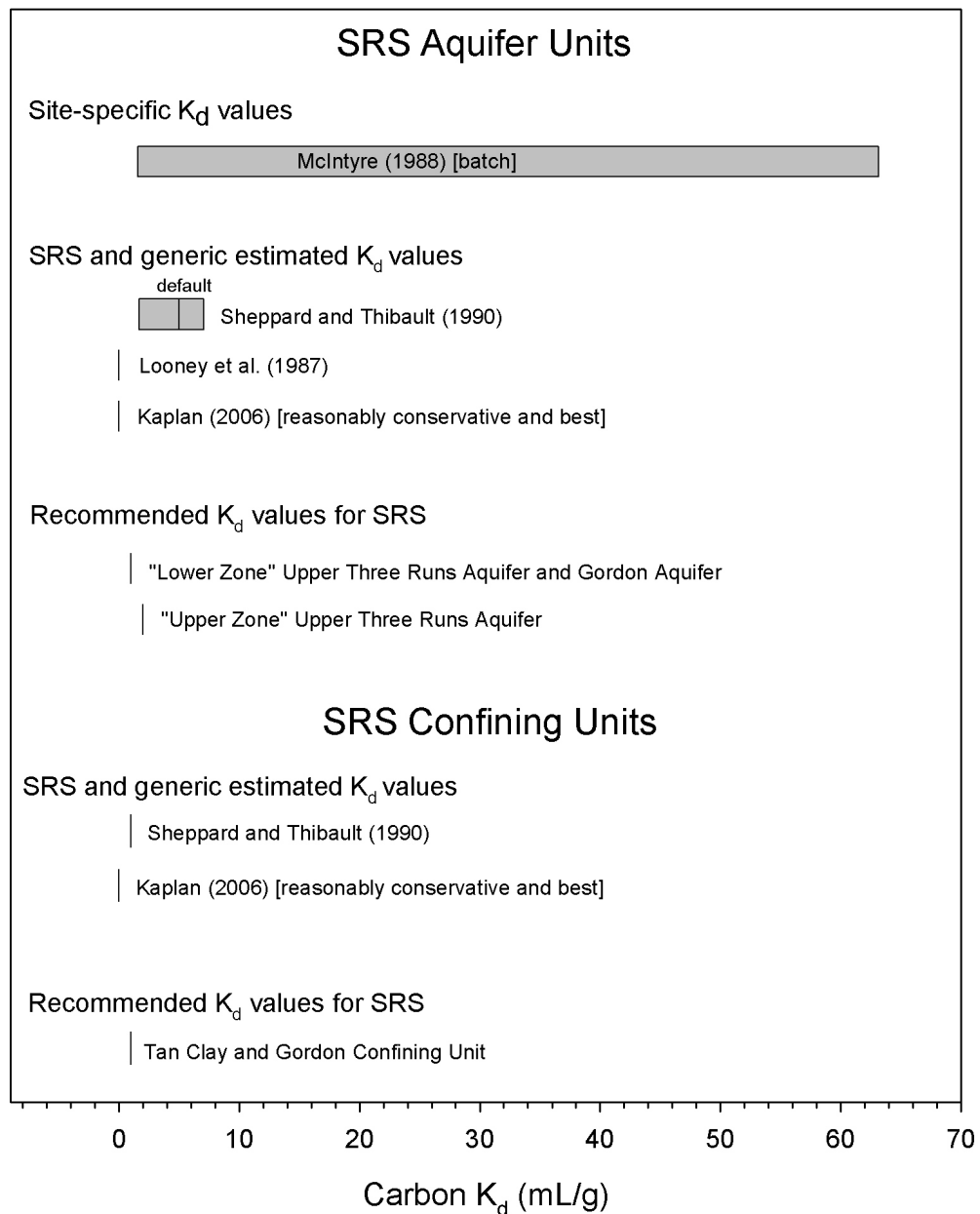
	Measured Carbon $K_d$ (mL/g)	Test Method	Savannah River Site-Specific “Reasonably Conservative”/ “Best” Estimated Carbon $K_d$ (mL/g)*	Generic Estimated Carbon $K_d$ (mL/g)†	Recommended Carbon $K_d$ (mL/g)
Upper Three Runs Aquifer: Upper	1.6–63.2‡	Batch	0/0	5	2
Tan Clay Confining Unit	—		0/0	1	1
Upper Three Runs Aquifer: Lower	—		0/0	5	1
Gordon Confining Unit	—		0/0	1	1
Gordon Aquifer	—		0/0	5	1
<p>*Kaplan, D.I. “Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site (U).” WSRC–TR–2006–00004. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company. 2006.</p> <p>†Sheppard, M.I. and D.H. Thibault. “Default Soil Solid/Liquid Partition Coefficients, <math>K_d</math>s, for Four Major Soil Types: A Compendium.” <i>Health Physics</i>. Vol. 59, No. 4. pp. 471–482. 1990.</p> <p>‡McIntyre, P.F. “Sorption Properties of Carbon-14 on Savannah River Plant Soil.” DPST–88–900. Aiken, South Carolina: E.I. du Pont de Nemours and Company, Savannah River Plant. 1998.</p>					

sediment and considering the carbon  $K_d$  values of 1 and 2 mL/g recommended for aquifer units at SRS, a carbon  $K_d$  value of 1 mL/g is recommended for confining units at SRS.

The position of the carbon  $K_d$  values recommended in this review with respect to measured and estimated site-specific and generic carbon  $K_d$  ranges and values is graphically displayed in Figure 2-2. This figure illustrates the uncertainty associated with the carbon  $K_d$  values recommended for SRS aquifer units and clay confining units. The recommended carbon  $K_d$  values are associated with high uncertainty due to limited site-specific sorption data. The recommended carbon  $K_d$  values of 1 and 2 mL/g for SRS aquifer units are based solely on site-specific carbon sorption data reported by McIntyre (1988). The recommended carbon  $K_d$  value of 1 mL/g for SRS confining units is based on a carbon soil-to-plant concentration ratio reported by Sheppard and Thibault (1990) for clay and expert judgment (Kaplan, 2006).

## 2.4.2 Nickel

The most common oxidation state of nickel is +2, although 0, +1, +3, and +4 nickel complexes are observed. Available nickel sorption studies indicate that sorption of nickel is strongly pH dependent and increases with increasing pH (Christensen, et al., 1996). Several studies on



**Figure 2-2. Measured and Estimated Site-Specific and Generic Carbon  $K_d$  Ranges and Values and Recommended Carbon  $K_d$  Values for Aquifer Units and Confining Units at SRS (Table 2-3). Recommended Carbon  $K_d$  Values Are Associated With High Uncertainty Due to Limited Site-Specific Sorption Data.**



sorption of heavy metals onto soils indicate that nickel is among the most mobile of heavy metals (Kabata-Pendias and Pendias, 1984; Alloway, 1995).

Crapse, et al. (2004) performed sequential extractions to estimate nickel  $K_d$  values on two major soil types at the D-Area of SRS: upland subsurface soils associated with a low pH/high sulfate/metals plume downgradient of the D-Area Coal Pile Runoff Basin at the D-Area expanded operable unit (DEXOU) and surface ash material discharged to the wetland from the D-Area Ash Basin. The upland subsurface soils were collected from the lower zone of the Upper Three Runs aquifer, and the wetland samples were collected from the upper zone of the Upper Three Runs aquifer. The upland subsurface soils consisted of ash-impacted and nonash-impacted samples. Ash impacted upland soils had higher pHs and higher  $K_d$ s than nonash-impacted upland soils. Estimated nickel  $K_d$  values for ash-impacted upland subsurface soils ranged from 3,100 to 28,000 mL/g over the pH range of 7.5 to 7.9. Estimated nickel  $K_d$  values for nonash-impacted soils ranged from 0.19 to >347 mL/g over the pH range of 3.2 to 6.3. Estimated  $K_d$  values for the wetland soil ranged from 284 to 6,500 mL/g over the pH range of 4.5 to 6.1. In both soils, nickel  $K_d$  values increased with increasing pH. The increase in nickel  $K_d$  was attributed in part to the increased cation exchange capacity and increased iron-oxyhydroxide concentrations in the sediments expected with increased pH. Over the pH range expected in the subsurface at the SRS (5.2 to 7.7), nickel  $K_d$  values in the nonash-impacted upland soil ranged from 81 to >347 mL/g, and nickel  $K_d$  values in the wetland soil ranged from 284 to 6,500 mL/g.

Kaplan and Serkiz (2004) conducted batch experiments to measure nickel  $K_d$  values on a clayey sediment and a sandy sediment collected from the E-Area at SRS as a function of pH and dissolved oxygen (DO) content. The sediments were collected from the upper zone of the Upper Three Runs aquifer and represented end members with respect to contaminant sorption properties expected in the E-Area subsurface. Average nickel  $K_d$  values were reported at DO concentrations ranging from 0 to 300 mg/L [0 to 300 ppm] for pHs of 3.9, 5.3, and 6.7. Table 2-1 indicates that DO concentrations ranging from 0 to 10 mg/L [0 to 10 ppm] are characteristic of sandy aquifer and clay confining units beneath the GSA. At pH 3.9 and DO concentrations of 0 and 10 mg/L [0 to 10 ppm], Kaplan and Serkiz (2004) reported average nickel  $K_d$  values of 2.3 and 1.8 mL/g for clayey sediment and average nickel  $K_d$  values of 0.6 and 1.3 mL/g for sandy sediment. At pH 5.3 and DO concentrations of 0 and 10 mg/L [0 to 10 ppm], Kaplan and Serkiz (2004) reported average nickel  $K_d$  values of 29.5 and 65.3 mL/g for clayey sediment and average nickel  $K_d$  values of 6.8 and 7.7 mL/g for sandy sediment. At pH 6.7 and DO concentrations of 0 and 10 mg/L, Kaplan and Serkiz (2004) reported average nickel  $K_d$  values of 287 and 521 mL/g for clayey sediment and average nickel  $K_d$  values of 150 and 279 mL/g for sandy sediment.

Powell, et al. (2001) reported *in-situ* nickel  $K_d$  values for seven “matched” pore water and soil pairs collected at the D-Area expanded operable unit (DEXOU) located in the southwestern part of the SRS. The soils were collected from the upper zone of the Upper Three Runs aquifer at depths of 0.3 to 10 m [1 to 34 ft]. Field measurements of pH were in the range of 4.59 to 6.57 for all the soil collection locations. The nickel  $K_d$  values were estimated using EPA Method 3050b (EPA, 1986) and ranged from 0.63 to >310 mL/g. Over the pH range expected in the subsurface at SRS (5.2 to 7.7), Powell, et al. (2001) reported nickel  $K_d$  values ranging from 27 to >310 mL/g. EPA Method 3050b is a hot nitric extraction that likely overestimates the metals actually available for transport. Therefore, the nickel  $K_d$  values measured by Powell,

et al. (2001) (0.63 to >310 mL/g) likely underestimated actual nickel  $K_d$  values on soils at DEXOU.

Kaplan and Serkiz (2000) performed desorption measurements to measure nickel  $K_d$  values on shallow contaminated sediments from the TNX Outfall Operable Unit at the SRS. The desorption  $K_d$  values were based on extractable portions that comprised the exchangeable, organic-bound, amorphous Fe-oxide bound, and water extractable fractions. Basing the  $K_d$  estimates on these extractable fractions instead of the more easily determined total concentrations in the sediment, more conservative and technically defensible  $K_d$  values were measured. The contaminated sediments were collected at depths of 0 to 0.6 m [0 to 2 ft] by hand auger and were composed dominantly of sand and silt (i.e., sand and silt contents ranging from 80 to 94 wt%). The pH of the sediments ranged from 4.00 to 4.53. Measured nickel  $K_d$  values ranged from 257 to 404 mL/g.

Examination of  $K_d$  values listed in the compendium of default soil solid/liquid  $K_d$  values of Thibault, et al. (1990) indicates three clayey sand  $K_d$  values listed for soils from South Carolina. These values are from a study by Neiheisal (1983) and are 115, 116, and 120 mL/g. The composition and pH of solutions used in the Neiheisal (1983) study were not listed in the compendium of Thibault, et al. (1990).

Several researchers have measured nickel  $K_d$  values in sediments and soils from localities other than SRS. These studies are described next.

Christensen, et al. (1996) performed batch equilibrium experiments to measure nickel  $K_d$  values as a function of pH for sandy aquifer materials obtained at 12 locations in Denmark. Sorption experiments consisted of 10 g [0.02 lb] of aquifer material and 50 mL [1.7 oz] of  $10^{-3}$  M  $\text{CaCl}_2$  solution equilibrated for 48 hours. Aquifer materials consisted of >95-wt% sand-sized particles. Measured nickel  $K_d$  values ranged from 3 to 7,250 mL/g over the pH range of 4.9 to 8.87 and increased strongly with increasing pH.

Reddy and Dunn (1986) conducted batch equilibrium experiments to measure nickel  $K_d$  values on three soils as a function of nickel concentration in solution. Measured  $K_d$  values for nickel ranged from 152 to 388 mL/g. The Mecklenburg clay, with the highest CEC, gave the highest  $K_d$  values. Measured nickel  $K_d$  values increased as the concentration of nickel increased in test solutions.

Veeresh, et al. (2003) performed batch equilibrium experiments to measure nickel  $K_d$  values on three soils from different climatic regions of India. A 0.005 M  $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  solution was used in the batch experiments. Soils had varying particle size characteristics and pHs: a silty sand soil (85-wt% sand and silt, 15-wt% clay) with a pH of 5.2, a clay-rich silty sand soil (72-wt% sand and silt, 28-wt% clay) with a pH of 7.1, and a clay-rich soil (63-wt% clay, 27-wt% sand and silt) with a pH of 8.6.  $K_d$  values determined from sorption isotherms were 9 mL/g for the silty sand soil, 24 mL/g for the clay-rich silty sand soil, and 329 mL/g for the clay-rich soil.

Sheppard and Thibault (1990) estimated a nickel default  $K_d$  for sand of 400 mL/g (11 observations ranging from 60 to 3,600 mL/g) and a nickel default  $K_d$  for clay of 650 mL/g (10 observations ranging from 305 to 2,467). Looney, et al. (1987) estimated a reference SRS soil  $K_d$  of 100 mL/g for nickel from an estimated range of 10 to 1,000 mL/g. Kaplan (2006) estimated “reasonably conservative” and “best” nickel  $K_d$  values of 5 and 7 mL/g for sandy

subsurface sediment and “reasonably conservative” and “best” nickel  $K_d$  values of 21 and 30 mL/g for clayey subsurface sediment at SRS. The estimated nickel  $K_d$  values estimated by Kaplan (2006) were based on the nickel sorption data of Kaplan and Serkiz (2004) measured at a pH of 5.3.

Measured, estimated, and recommended nickel  $K_d$  values are summarized in Table 2-4. At pHs expected in the subsurface for SRS (5.2 to 7.7), site-specific  $K_d$  values ranging from 81 to 6,500 mL/g (Crapse, et al., 2004), 6.8 to 279 mL/g (Kaplan and Serkiz, 2004), and 27 to >310 mL/g (Powell, et al., 2001) were reported for sandy soils and sediments collected from the Upper Three Runs aquifer.

<b>Table 2-4. Measured, Estimated, and Recommended <math>K_d</math> Values for Nickel in Aquifer Sediments and Clay Confining Units at the Savannah River Site</b>					
	<b>Measured Nickel <math>K_d</math> (mL/g)</b>	<b>Test Method</b>	<b>Savannah River Site-Specific “Reasonably Conservative”/ “Best” Estimated Nickel <math>K_d</math> (mL/g)*</b>	<b>Generic Estimated Nickel <math>K_d</math> (mL/g)†</b>	<b>Recommended Nickel <math>K_d</math> (mL/g)</b>
Upper Three Runs Aquifer: Upper	284-6,500‡ 0.6-521§ 0.63->310¶ 257-404#	<i>In situ</i> Batch <i>In situ</i> <i>In situ</i>	5/7	400	10
Tan Clay Confining Unit			21/30	650	21
Upper Three Runs Aquifer: Lower	0.19-28,000‡	<i>In situ</i>	5/7	400	80
Gordon Confining Unit			21/30	650	150
Gordon Aquifer			5/7	400	80
<p>*Kaplan, D.I. “Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site (U).” WSRC-TR-2006-00004. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company. 2006.</p> <p>†Sheppard, M.I. and D.H. Thibault. “Default Soil Solid/Liquid Partition Coefficients, <math>K_d</math>s, for Four Major Soil Types: A Compendium.” <i>Health Physics</i>. Vol. 59, No. 4. pp. 471-482. 1990.</p> <p>‡Crapse, K.P., S.M. Serkiz, A. Pishko, P.C. McKinsey, R.L. Brigmon, E.P. Shine, C. Fliermans, and A.S. Knox. “Monitored Natural Attenuation of Inorganic Contaminants Treatability Study Final Report.” WSRC-TR-2004-00124. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company, Savannah River Site. 2004.</p> <p>§Kaplan, D.I. and S.M. Serkiz. “Influence of Dissolved Organic Carbon and pH on Contaminant Sorption to Sediment.” WSRC-RP-2004-00593. Aiken, South Carolina: Westinghouse Savannah River Company. 2004.</p> <p>¶Powell, K.R., S. Serkiz, and D.I. Kaplan. “Evaluation of the D-Area Expanded Operable Unit for Monitored Natural Attenuation of Inorganic Constituents of Concern: Interim Report.” WSRC-TR-2001-00574. Aiken, South Carolina: Westinghouse Savannah River Company. 2001.</p> <p>#Kaplan, D.I. and S.M. Serkiz. “<i>In-Situ</i> <math>K_d</math> Values and Geochemical Behavior for Inorganic and Organic Constituents of Concern at the TNX Outfall Delta.” WSRC-TR-99-00488. Aiken, South Carolina: Westinghouse Savannah River Company. 2000.</p>					

The nickel  $K_d$  values reported by Neiheisal (1983) for soils from South Carolina (115 to 120 mL/g) and the reference SRS soil nickel  $K_d$  value of 100 mL/g estimated by Looney, et al. (1987) are within the ranges of SRS for these site-specific nickel  $K_d$  values. With the exception of nickel  $K_d$  values for wetland soil at the DEXOU reported by Crapse, et al. (2004) (284 to 6,500 mL/g), the default nickel  $K_d$  value of 400 mL/g recommended by Sheppard and Thibault (1991) lies outside or at the high end of SRS site-specific nickel  $K_d$  values reported by Kaplan and Serkiz (2000, 2004) and Powell, et al. (2001). The “reasonably conservative” and “best” nickel  $K_d$  values of 5 and 7 mL/g estimated by Kaplan (2006) for sandy subsurface sediment at SRS were based on the  $K_d$  range of 6.8 to 7.7 mL/g measured on sandy sediment at the E-Area at pH 5.3 by Kaplan and Serkiz (2004). Based on the previous observations and considering that pH in the upper zone of the Upper Three Runs aquifer may be as low as 5.2 (Table 2-2), a nickel  $K_d$  value of 10 mL/g is recommended for the upper zone of the Upper Three Runs aquifer. This value lies between the nickel  $K_d$  values reported by Kaplan and Serkiz (2004) at a pH of 5.3 (6.8 to 7.7 mL/g) and those reported by Powell, et al. (2001) at pHs expected at the SRS (27 to >310) for sandy sediments from the upper zone of the Upper Three Runs aquifer. Because nickel  $K_d$  values are highly sensitive to pH (i.e., nickel  $K_d$  increases significantly with increasing pH) and pH is higher in deeper aquifer units at SRS (Table 2-2), a nickel  $K_d$  value of 80 mL/g is recommended for the lower zone of the Upper Three Runs aquifer and the Gordon aquifer. This value is at the low end of the nickel  $K_d$  range of 81 to >347 mL/g reported for sediments from the lower zone of the Upper Three Runs aquifer by Crapse, et al. (2004) at pHs expected in the subsurface at SRS.

Kaplan and Serkiz (2004) reported nickel  $K_d$  values ranging from 29.5 to 65.3 at a pH of 5.3 and from 287 to 521 mL/g at a pH of 6.7 on clayey sediment from the E-Area of SRS. Veeresh, et al. (2003) reported a nickel  $K_d$  value of 329 mL/g for a clay-rich soil from India. Reddy and Dunn (1986) reported nickel  $K_d$  values on soils ranging from 152 to 388 mL/g and observed that soils with the highest cation exchange capacities gave the highest  $K_d$  values. Sheppard and Thibault (1990) recommend a nickel default  $K_d$  value of 650 mL/g for clay. The “reasonably conservative” and “best” nickel  $K_d$  values of 21 and 30 mL/g estimated by Kaplan (2006) for clayey sediments at SRS are based on the nickel  $K_d$  range of 29.5 to 65.3 at a pH of 5.3 reported by Kaplan and Serkiz (2004) for clayey sediment from the E-Area. Based on the previous observations and considering that pH in the tan clay confining unit may be as low as 5.2 (Table 2-2), the “reasonably conservative” nickel  $K_d$  value of 21 mL/g estimated by Kaplan (2006) for SRS sandy subsurface sediments is recommended for the tan clay. Because nickel  $K_d$  values are highly sensitive to pH (i.e., nickel  $K_d$  increases significantly with increasing pH) and pH is higher in the Gordon confining unit (Table 2.2), a nickel  $K_d$  value of 150 mL/g is recommended for the Gordon confining unit. This value lies at the approximate midpoint between the nickel  $K_d$  ranges reported by Kaplan and Serkiz (2004) on clayey subsurface sediments at SRS at pHs of 5.3 (29.5 to 65.3 mL/g) and 6.7 (287 to 521 mL/g). The position of the nickel  $K_d$  values recommended in this review with respect to measured and estimated site-specific and generic nickel  $K_d$  ranges and values is graphically displayed in Figure 2-3. This figure illustrates the uncertainty associated with the nickel  $K_d$  values recommended for SRS aquifer units and clay confining units. Due to available site-specific nickel sorption data (Crapse, et al., 2004; Kaplan and Serkiz, 2000, 2004; Powell, et al., 2001), the recommended nickel  $K_d$  values are associated with low uncertainty.

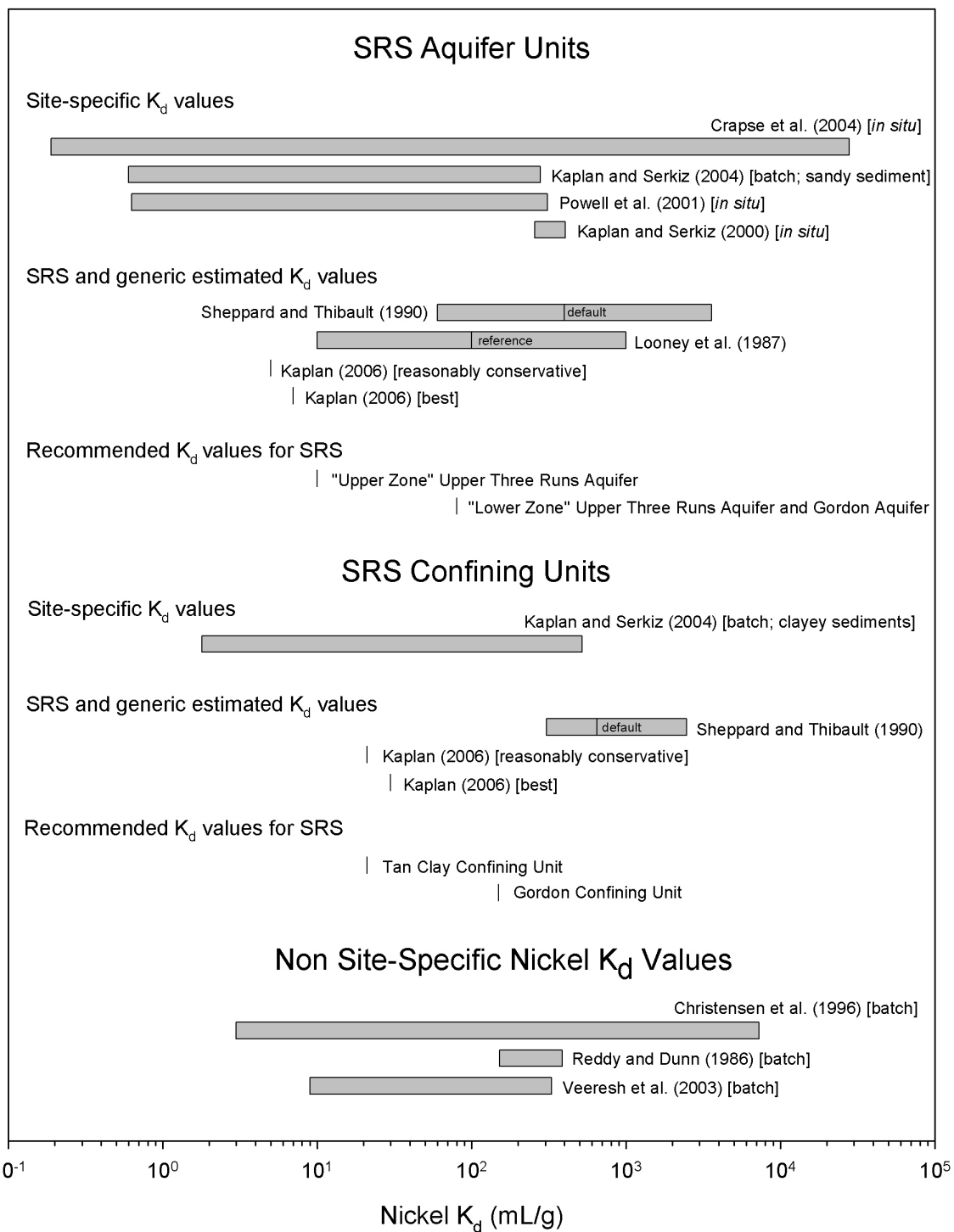
### 2.4.3 Selenium

Se-79 can exist in the -2, 0, +2, +4, and +6 valence states. Selenium in the +6 or selenate state ( $\text{SeO}_4^{2-}$ ) is stable under alkaline and oxidizing conditions. Selenium in the +4 state occurs naturally as selenite ( $\text{SeO}_3^{2-}$ ). Selenite tends to oxidize to the +6 state in alkaline oxidizing solutions, but not in an acid medium. Selenite binds tightly to iron and aluminum oxides. Thus, selenite is quite insoluble in soils and generally not present in waters in any appreciable amount.

Kaplan and Serkiz (2006) conducted batch experiments to measure selenium  $K_d$  values on a clayey sediment and a sandy sediment collected from the E-Area at SRS as a function of pH and DO content. The sediments were collected from the upper zone of the Upper Three Runs aquifer and represented end members with respect to contaminant sorption properties expected in the E-Area subsurface. Average selenium  $K_d$  values were reported at DO concentrations ranging from 0 to 300 mg/L [0 to 300 ppm] for pHs of 3.9, 5.3, and 6.7. Table 2-1 indicates that DO concentrations ranging from 0 to 10 mg/L [0 to 10 ppm] are characteristic of sandy aquifer and clay confining units beneath the GSA. At pH 3.9 and a DO concentration of 0 mg/L, Kaplan and Serkiz (2006) reported an average selenium  $K_d$  value of 1,041 mL/g for clayey sediment and an average selenium  $K_d$  value of 1,041 mL/g for sandy sediment. At pH 5.3 and a DO concentration of 0 mg/L [0 ppm], Kaplan and Serkiz (2006) reported an average selenium  $K_d$  value of 1,041 mL/g for clayey sediment and an average selenium  $K_d$  value of 1,311 mL/g for sandy sediment. At pH 6.7 and a DO concentrations of 0 mg/L [0 ppm], Kaplan and Serkiz (2006) reported an average selenium  $K_d$  value of 1,041 mL/g for clayey sediment and an average selenium  $K_d$  value of 601 mL/g for sandy sediment. Kaplan and Serkiz (2006) noted that the sandy sediment, but not the clayey sediment, showed the characteristic decrease in  $K_d$  values as pH increased. Also troubling was that the sandy sediment had similar and larger  $K_d$  values than the clayey sediment at pHs of 3.9 and 5.3, respectively.

Powell, et al. (2001) reported *in-situ* selenium  $K_d$  values for seven “matched” pore water and soil pairs collected at DEXOU located in the southwestern part of SRS. The soils were collected from the upper zone of the Upper Three Runs aquifer at depths of 0.3 to 10 m [1 to 34 ft]. Field measurements of pH were found to be in the range of 4.59 to 6.57 for all the soil collection locations. The selenium  $K_d$  values were estimated using EPA Method 3050b and ranged from 0.7 to 270 mL/g. Over the pH range expected in the subsurface at the SRS (5.2 to 7.7), Powell, et al. (2001) reported selenium  $K_d$  values that also ranged from 0.7 to 270 mL/g. EPA Method 3050b (EPA, 1986) is a hot nitric extraction that likely overestimates the metals actually available for transport. Therefore, the selenium  $K_d$  values measured by Powell, et al. (2001) (0.7 to 270 mL/g) likely underestimated actual selenium  $K_d$  values on soils at the DEXOU.

Kaplan and Serkiz (2000) performed desorption measurements to measure selenium  $K_d$  values on shallow contaminated sediments from the TNX Outfall Operable Unit at SRS. The desorption  $K_d$  values were based on extractable portions that comprised the exchangeable, organic-bound,



**Figure 2-3. Measured and Estimated Site-Specific and Generic Nickel  $K_d$  Ranges and Values and Recommended Nickel  $K_d$  Values for Aquifer Units and Confining Units at SRS (Table 2-4). Recommended Nickel  $K_d$  Values Are Associated With Low Uncertainty Due to Available Site-Specific Sorption Data.**

amorphous Fe-oxide bound, and water extractable fractions. Basing the  $K_d$  estimates on these extractable fractions instead of the more easily determined total concentrations in the sediment, more conservative and technically defensible  $K_d$  values were measured. The contaminated sediments were collected at depths of 0 to 0.6 m [0 to 2 ft] by hand auger and were composed dominantly of sand and silt (i.e., sand and silt contents ranging from 80 to 94 wt%). The pH of the sediments ranged from 4.00 to 5.78. Measured selenium  $K_d$  values ranged from 219 to 267 mL/g. Over the pH range expected in the subsurface at SRS (5.2 to 7.7), Kaplan and Serkiz (2000) reported selenium  $K_d$  values of 254 and 248 mL/g for sediments with pHs of 5.26 and 5.78, respectively.

Kaplan (2004) estimated  $K_d$  values for selenium in sandy soil and clay for use in a special analysis of the Slit and Engineered Trenches Special Analysis and the Intermediate Level Vault Special Analysis at SRS. The values estimated by Kaplan (2004) were extracted from the compendium of soil solid/liquid partition coefficients for four major soil types (Thibault, et al., 1990). Selenium  $K_d$  values for sand soil types between pH 5.3 and 6.3 were reported as 70, 70, and 36 mL/g, and generally increased as pH decreased, which is expected for anionic radionuclides such as  $\text{SeO}_4^{2-}$  and  $\text{SeO}_3^{2-}$ . According to Kaplan (2004), selenium  $K_d$  values for clay sediments between pH 5.0 and 6.0 were reported as 76, 140, 80, 246, and 170 mL/g. Based on this tabulation, Kaplan (2004) estimated a selenium  $K_d$  value of 36 mL/g for soils and a selenium  $K_d$  value of 76 mL/g for clay for use in transport modeling.

Sheppard and Thibault (1990) specified a selenium default  $K_d$  for sand of 55 mL/g (three observations ranging from 36 to 70 mL/g) and a selenium default  $K_d$  for clay of 115 mL/g (14 observations ranging from 36 to 246 mL/g). Looney, et al. (1987) recommended a reference SRS soil  $K_d$  of 2.5 mL/g for selenium from an estimated range of 1 to 100 mL/g. Kaplan (2006) estimated “reasonably conservative” and “best” selenium  $K_d$  values of 800 and 1,000 mL/g for sandy subsurface sediment and “reasonably conservative” and “best” selenium  $K_d$  values of 800 and 1,000 mL/g for clayey subsurface sediment at SRS. The estimations of Kaplan (2006) were based on the selenium sorption data of Kaplan and Serkiz (2006) described previously.

Measured, estimated, and recommended selenium  $K_d$  values are summarized in Table 2-5. Kaplan and Serkiz (2006) reported selenium  $K_d$  values ranging from 601 to 1,311 mL/g on sandy sediment from the E-Area of SRS over the pH range of 3.9 to 6.7. This same selenium  $K_d$  range was observed at pHs expected in the subsurface at SRS (pH 5.2 to 7.7). Powell, et al. (2001) reported selenium  $K_d$  values ranging from 0.7 to 270 mL/g for sediments collected from the upper zone of the Upper Three Runs aquifer at the DEXOU over the pH range of 4.59 to 6.57. Over the pH range expected in the subsurface at the SRS (5.2 to 7.7), Powell, et al. (2001) reported selenium  $K_d$  values that also ranged from 0.7 to 270 mL/g. The selenium  $K_d$  values reported by Powell, et al. (2001) were determined using EPA Method 3050b, which is an extraction method that likely underestimates actual  $K_d$  values. Kaplan and Serkiz (2000) reported selenium  $K_d$  values ranging from 219 to 267 mL/g on shallow contaminated soils from the TNX Outfall Operable Unit at the SRS over the pH range of 4.0 to 5.78. Over the pH range expected in the subsurface at SRS (5.2 to 7.7), Kaplan and Serkiz (2000) reported selenium  $K_d$  values of 254 and 248 mL/g for sediments with pHs of 5.26 and 5.78, respectively. Over the pH range of 5.3 to 6.3, Kaplan (2004) estimated a selenium  $K_d$  value of 36 mL/g for aquifer units (i.e., soils) at SRS based on an analysis of  $K_d$  data for selenium in the compilation of soil/liquid partition coefficients of Thibault, et al. (1990). The compilation of Sheppard and Thibault (1990) specified a selenium  $K_d$  of 55 mL/g for sand soils. Looney, et al. (1987) estimated a much lower

**Table 2-5. Measured, Estimated, and Recommended  $K_d$  Values for Selenium in Aquifer Sediments and Clay Confining Units at the Savannah River Site**

	Measured Selenium $K_d$ (mL/g)	Test Method	Savannah River Site-Specific "Reasonably Conservative"/ "Best" Estimated Selenium $K_d$ (mL/g)*	Generic Estimated Selenium $K_d$ (mL/g)†	Recommended Selenium $K_d$ (mL/g)
Upper Three Runs Aquifer: Upper	601–1,311‡ 0.7–>270§ 219–267¶	Batch <i>In situ</i> <i>In situ</i>	800/1,000	55	425
Tan Clay Confining Unit	—	—	800/1,000	115	800
Upper Three Runs Aquifer: Lower	—	—	800/1,000	55	425
Gordon Confining Unit	—	—	800/1,000	115	800
Gordon Aquifer	—	—	800/1,000	55	425

\*Kaplan, D.I. "Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site (U)." WSRC–TR–2006–00004. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company. 2006.

†Sheppard, M.I. and D.H. Thibault. "Default Soil Solid/Liquid Partition Coefficients,  $K_d$ s, for Four Major Soil Types: A Compendium." *Health Physics*. Vol. 59, No. 4. pp. 471–482. 1990.

‡Kaplan, D.I. and S.M. Serkiz. "Influence of Dissolved Organic Carbon and pH on Anion Sorption to Sediment." WSRC–RP–2006–00005. Aiken, South Carolina: Westinghouse Savannah River Company. 2006.

§Powell, K.R., S. Serkiz, and D.I. Kaplan. "Evaluation of the D-Area Expanded Operable Unit for Monitored Natural Attenuation of Inorganic Constituents of Concern: Interim Report." WSRC–TR–2001–00574. Aiken, South Carolina: Westinghouse Savannah River Company. 2001.

¶Kaplan, D.I. and S.M. Serkiz. "*In-Situ*  $K_d$  Values and Geochemical Behavior for Inorganic and Organic Constituents of Concern at the TNX Outfall Delta." WSRC–TR–99–00488. Aiken, South Carolina: Westinghouse Savannah River Company. 2000.

selenium  $K_d$  value of 2.5 mL/g for SRS soil. Based on the selenium sorption data of Kaplan and Serkiz (2006), Kaplan (2006) estimated a "reasonably conservative" selenium  $K_d$  of 800 mL/g for sandy sediments at SRS. Based on the previous observations, a selenium  $K_d$  value of 425 mL/g is recommended for aquifer units at SRS. This value lies between the measured selenium  $K_d$  value of 248 mL/g reported by Kaplan and Serkiz (2000) at a pH of 5.78 and the



measured selenium  $K_d$  value of 601 mL/g reported by Kaplan and Serkiz (2006) for sandy subsurface sediment at SRS at a pH of 6.7.

Kaplan and Serkiz (2006) reported a selenium  $K_d$  value of 1,041 mL/g on clayey sediment from the E Area of SRS over the pH range of 3.9 to 6.7. Over the pH range of 5.0 to 6.0, Kaplan (2004) estimated a selenium  $K_d$  value of 76 mL/g for clay units at SRS. This recommendation was based on an analysis of  $K_d$  data for selenium in the compilation of soil/liquid partition coefficients of Thibault, et al. (1990). The compilation of Sheppard and Thibault (1990) (also Thibault, et al., 1990) recommended a selenium  $K_d$  of 115 mL/g for clay soils. Based on the site-specific selenium sorption data of Kaplan and Serkiz (2006), Kaplan (2006) estimated a “reasonably conservative” selenium  $K_d$  of 800 mL/g for clayey sediments at SRS, and this value is recommended for clay confining units at SRS.

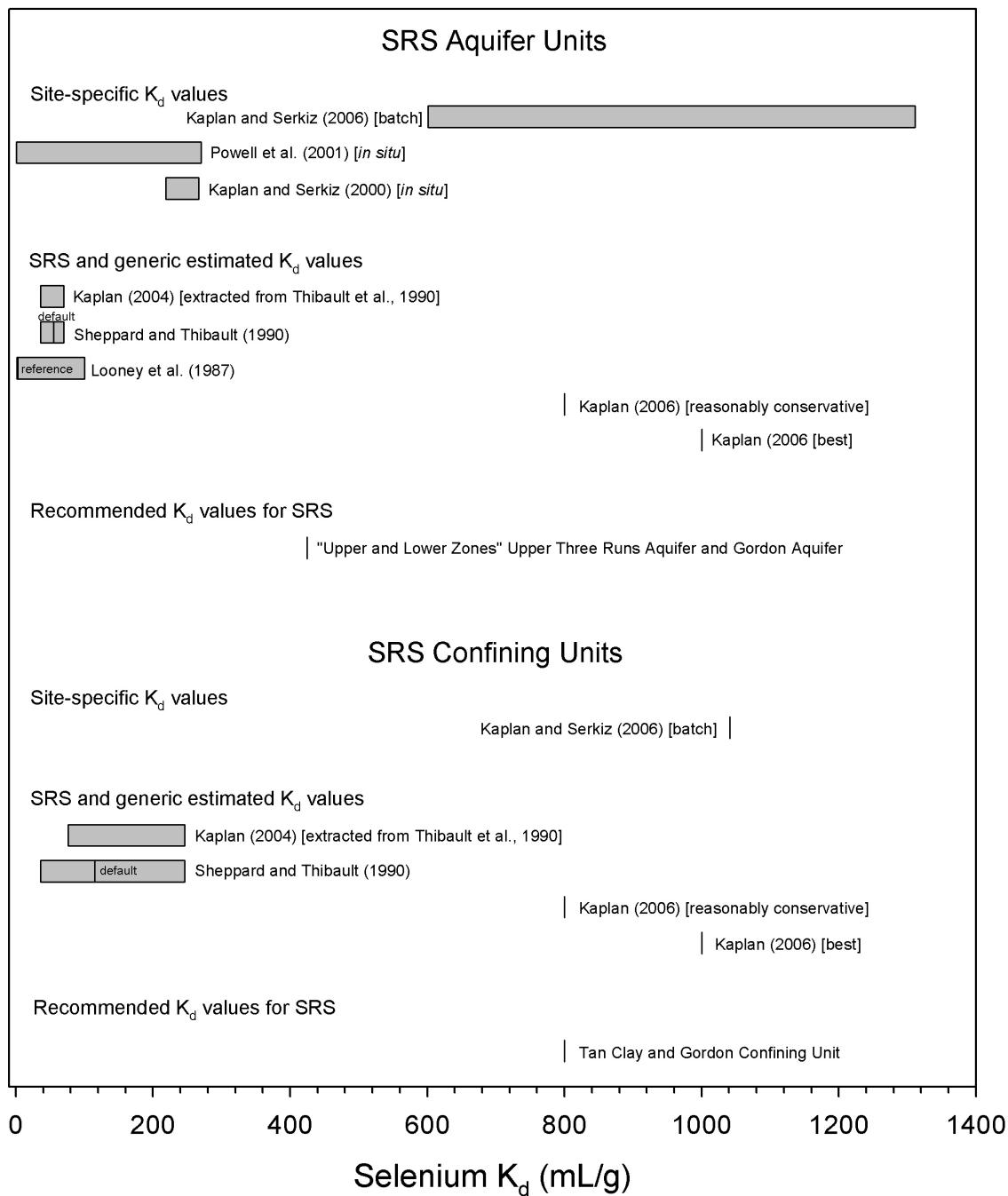
The position of the selenium  $K_d$  values recommended in this review with respect to measured and estimated site-specific and generic selenium  $K_d$  ranges and values is graphically displayed in Figure 2-4. This figure illustrates the uncertainty associated with the selenium  $K_d$  values recommended for SRS aquifer units and clay confining units. Due to the wide range in measured site-specific selenium  $K_d$  values, the recommended selenium  $K_d$  values are associated with high uncertainty. For example, Kaplan and Serkiz (2006) reported selenium  $K_d$  values ranging from 601 to 1,311 mL/g over the pH range of 3.9 to 7.6 for sandy sediment from the E-Area, whereas Powell, et al. (2001) reported selenium  $K_d$  values ranging from 219 to 267 mL/g over the pH range of 4.0 to 5.78 for soil samples from the D-Area.

#### **2.4.4 Strontium**

Sr-90 exists primarily as the uncomplexed  $\text{Sr}^{2+}$  ion over the pH range of natural waters (pH 3 to 10).  $\text{Sr}^{2+}$  adsorbs to both clay and carbonate minerals. For clays, the extent to which strontium partitions from the aqueous phase to the solid phase is expected to be controlled primarily by the CEC of the solid phase. Other factors affecting strontium  $K_d$  values are pH and ionic strength. Strontium  $K_d$  values have been reported to increase with increasing pH (Prout, 1958; Rhodes, 1957). This trend is likely the result of hydrogen ions competing with  $\text{Sr}^{2+}$  for exchange sites. Elevated concentrations of major cations (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) can greatly reduce strontium  $K_d$  values (Bunde, et al., 1998, 1997). Strontium  $K_d$  values may decrease from 100 to 200 mL/g in low ionic strength solutions to less than 5 mL/g in high ionic strength solutions (Routson, et al., 1980). There is little tendency for strontium to form complexes with inorganic or organic ligands (Faure and Powell, 1972; Stevenson and Fitch, 1986).

Hoeffner (1985) summarized strontium sorption studies conducted to determine the performance of the low-level waste burial ground at SRS. The majority of studies used a Savannah River Plant soil taken from depths 2.5–3.0 m [8–10 ft] below grade and a low ionic strength groundwater representative of the burial ground (pH 5.0). Hoeffner (1985) reported an expected range of strontium  $K_d$  values from 1.5 to 3,000 mL/g over a pH range of 3.4 to 7.3, and for a groundwater of typical composition at the SRS burial ground (pH 4.7), a  $K_d$  value of 7.5 mL/g is expected.

Ryan (1982) performed batch strontium sorption experiments using SRS burial ground core samples and groundwater. The measured strontium  $K_d$  values from the experiments ranged from 1.1 to 10.9 mL/g.



**Figure 2-4. Measured and Estimated Site-Specific and Generic Selenium  $K_d$  Ranges and Values and Recommended Selenium  $K_d$  Values for Aquifer Units and Confining Units at SRS (Table 2-5). Recommended Values Are Associated With High Uncertainty Due to the Wide Range in Measured Site-Specific Selenium  $K_d$  Values.**

McConnell, et al. (1995) reported strontium  $K_d$  values ranging from 20 to 40 mL/g for SRS soil used in lysimeter tests to obtain information on the performance of radioactive wasteforms and DO. The sediments were collected from the upper zone of the Upper Three Runs aquifer. These values were obtained using a batch method. The pH and composition of the solution used in the batch test was not reported.

Kaplan and Serkiz (2004) conducted batch experiments to measure strontium  $K_d$  values on a clayey sediment and a sandy sediment collected from the E-Area at SRS as a function of pH and DO content. The sediments were collected from the upper zone of the Upper Three Runs aquifer and represented end members with respect to contaminant sorption properties expected in the E-Area subsurface. Average strontium  $K_d$  values were reported at DO concentrations ranging from 0 to 300 mg/L [0 to 300 ppm] for pHs of 5.3 and 6.7. Table 2-1 indicates that DO concentrations ranging from 0 to 10 mg/L [0 to 10 ppm] are characteristic of sandy aquifer and clay confining units beneath the GSA. At pH 5.3 and DO concentrations of 0 to 10 mg/L [0 to 10 ppm], Kaplan and Serkiz (2004) reported average strontium  $K_d$  values of 16.6 and 42.6 mL/g for clayey sediment and average strontium  $K_d$  values of 4.5 and 5.5 mL/g for sandy sediment. At pH 6.7 and DO concentrations of 0 to 10 mg/L [0 to 10 ppm], Kaplan and Serkiz (2004) reported average strontium  $K_d$  values of 97.4 and 67.7 mL/g for clayey sediment and average strontium  $K_d$  values of 46.9 and 60.4 mL/g for sandy sediment.

Kaplan and Serkiz (2000) performed desorption measurements to measure strontium  $K_d$  values on shallow contaminated sediments from the TNX Outfall Operable Unit at SRS. The desorption  $K_d$  values were based on extractable portions that comprised the exchangeable, organic-bound, amorphous Fe-oxide bound, and water extractable fractions. Basing the  $K_d$  estimates on these extractable fractions instead of the more easily determined total concentrations in the sediment, more conservative and technically defensible  $K_d$  values were measured. The contaminated sediments were collected at depths of 0 to 0.6 m [0 to 2 ft] by hand auger and were composed dominantly of sand and silt (i.e., sand and silt contents ranging from 80 to 94 wt%). The pH of the sediments ranged from 4.00 to 5.78. Measured strontium  $K_d$  values ranged from 1,676 to 5,518 mL/g. Over the pH range expected in the subsurface at the SRS (5.2 to 7.7), Kaplan and Serkiz (2000) reported strontium  $K_d$  values of 1,676 and 1,886 mL/g for sediments with pHs of 5.26 and 5.78, respectively.

Sheppard and Thibault (1990) recommended a strontium default  $K_d$  for sand of 15 mL/g (81 observations ranging from 0.05 to 190 mL/g) and a strontium default  $K_d$  for clay of 110 mL/g (24 observations ranging from 3.6 to 32,000 mL/g). Looney, et al. (1987) specified a reference SRS soil  $K_d$  of 8.0 mL/g for strontium from an estimated range of 1 to 1,000 mL/g. Kaplan (2006) estimated “reasonably conservative” and “best” strontium  $K_d$  values of 4 and 5 mL/g for sandy subsurface sediment and “reasonably conservative” and “best” strontium  $K_d$  values of 12 and 17 mL/g for clayey subsurface sediment at SRS. The estimations of Kaplan (2006) were based on the strontium sorption data of Kaplan and Serkiz (2004) measured at a pH of 5.3.

Measured, estimated, and recommended strontium  $K_d$  values are summarized in Table 2-6. Over the pH range of 3.4 to 7.3, Hoeffner (1985) reported an expected range of strontium  $K_d$  values from 1.5 to 3,000 mL/g. These values are based on a summary of strontium sorption studies of shallow sediments at the SRS burial ground. For a groundwater of typical composition at the SRS burial ground (pH 4.7), Hoeffner (1985) reports an expected strontium  $K_d$  value of 7.5 mL/g. This expected value is in agreement with strontium  $K_d$  values measured by Ryan (1982) using shallow soil samples and groundwater from the SRS burial ground (1.1 to

**Table 2-6. Measured, Estimated, and Recommended  $K_d$  Values for Strontium in Aquifer Sediments and Clay Confining Units at the Savannah River Site**

	Measured Strontium $K_d$ (mL/g)	Test Method	Savannah River Site-Specific "Reasonably Conservative"/ "Best" Estimated Strontium $K_d$ (mL/g)*	Generic Estimated Strontium $K_d$ (mL/g)†	Recommended Strontium $K_d$ (mL/g)
Upper Three Runs Aquifer: Upper	1.5–3,000‡ 1.1–10.9§ 20–40¶ 4.5–97.4# 1,676–5,518**	Batch Batch Batch Batch <i>In situ</i>	4/5	15	5
Tan Clay Confining Unit			12/17	110	12
Upper Three Runs Aquifer: Lower			4/5	15	25
Gordon Confining Unit			12/17	110	50
Gordon Aquifer			4/5	15	25

\*Kaplan, D.I. "Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site (U)." WSRC-TR-2006-00004. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company. 2006.

†Sheppard, M.I. and D.H. Thibault. "Default Soil Solid/Liquid Partition Coefficients,  $K_d$ s, for Four Major Soil Types: A Compendium." *Health Physics*. Vol. 59, No. 4. pp. 471–482. 1990.

‡Hoeffner, S.L. "Radionuclide Sorption on Savannah River Plant Burial Ground Soil—A Summary and Interpretation of Laboratory Data." DP-1702. Aiken, South Carolina: E.I. du Pont de Nemours and Company, Savannah River Laboratory. 1985.

§Ryan, J.P. "Batch and Column Strontium Distribution Coefficients with Water-Saturated Soil Strata from the Savannah River Plant Burial Ground." Environmental Migration of Long-Lived Radionuclides. International Symposium Proceedings, Knoxville, Tennessee. Vienna, Austria: International Atomic Energy Agency. 1982.

¶McConnell, Jr., J.W., R.D. Rogers, J.D. Jastrow, W.E. Sanford, S.R. Cline, T.M. Sullivan, and M. Fuhrmann. "Results after Ten Years of Field Testing Low-level Radioactive Waste Forms Using Lysimeters."

ANL/ER/CP 95275. Idaho Falls, Idaho: Idaho National Engineering Laboratory. 1995.

#Kaplan, D.I. and S.M. Serkiz. "Influence of Dissolved Organic Carbon and pH on Contaminant Sorption to Sediment." WSRC-RP-2004-00593. Aiken, South Carolina: Westinghouse Savannah River Company. 2004.

\*\*Kaplan, D.I. and S.M. Serkiz. "*In-Situ*  $K_d$  Values and Geochemical Behavior for Inorganic and Organic Constituents of Concern at the TNX Outfall Delta." WSRC-TR-99-00488. Aiken, South Carolina: Westinghouse Savannah River Company. 2000.

10.9 mL/g). The strontium  $K_d$  values measured by McConnell, et al. (1995) on SRS soil (20 to 40 mL/g) are slightly higher than those measured by Ryan (1982). The pH of the solution used by McConnell, et al. (1995) was not reported but may have had a higher pH than the burial ground groundwater used in the Ryan (1982) study. Kaplan and Serkiz (2004) reported strontium  $K_d$  values on sandy sediment from the E-Area of SRS that ranged from 4.5 to

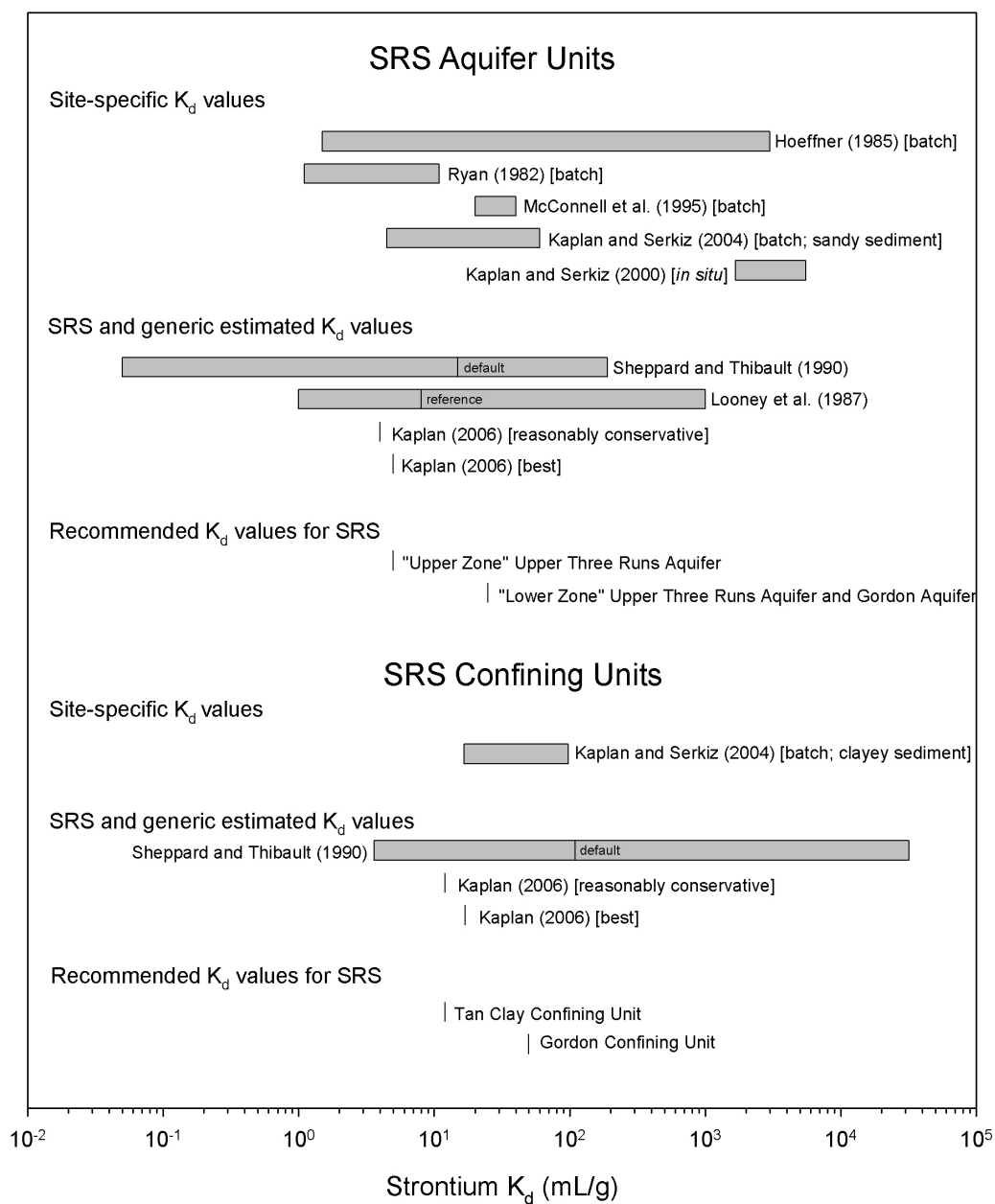
5.5 mL/g at a pH of 5.3 and from 46.9 to 60.4 mL/g at a pH of 6.7. Kaplan and Serkiz (2000) reported strontium  $K_d$  values of 1,676 and 1,886 mL/g on contaminated sediments from the SRS with pHs of 5.26 and 5.78, respectively. With the exception of the strontium  $K_d$  values reported by Kaplan and Serkiz (2000), the reported site-specific strontium  $K_d$  values correspond well to the recommended strontium  $K_d$  value for sand of Sheppard and Thibault (1990) (15 mL/g) and to the strontium  $K_d$  value of 8 mL/g estimated by Looney, et al. (1987) for SRS soil. The “reasonably conservative” and “best” strontium  $K_d$  values of 4 and 5 mL/g estimated by Kaplan (2006) for sandy subsurface sediment at SRS were based on the  $K_d$  range of 4.5 to 5.5 mL/g measured on sandy sediment at the E-Area at pH 5.3 by Kaplan and Serkiz (2004). Based on the above observations, a strontium  $K_d$  value of 5 mL/g is recommended for the upper zone of the Upper Three Runs aquifer at SRS. This value is the median of the strontium  $K_d$  values measured by Kaplan and Serkiz (2004) on sandy subsurface sediments at SRS at a pH of 5.3 (4.5 to 5.5 mL/g), which corresponds to the low end of the pH range expected at SRS (pH of 5.2 to 6.0). The lower zone of the Upper Three Runs aquifer and the Gordon aquifer have reported pH values above 6.0 and 5.7, respectively. Because strontium  $K_d$  values are sensitive to pH (i.e., strontium  $K_d$  increases with increasing pH), a strontium  $K_d$  value of 25 mL/g is recommended for the lower zone of the Upper Three Runs aquifer and the Gordon aquifer. This value lies at the approximate midpoint between the strontium  $K_d$  ranges reported by Kaplan and Serkiz (2004) on sandy subsurface sediments at SRS at pHs of 5.3 (4.5 to 5.5 mL/g) and 6.7 (46.9 to 60.4 mL/g).

Kaplan and Serkiz (2004) reported strontium  $K_d$  values on clayey sediment from the E-Area of SRS that ranged from 16.6 to 42.6 mL/g at a pH of 5.3 and from 67.7 to 97.6 mL/g at a pH of 6.7. These measured values are lower than the default strontium  $K_d$  value of 110 mL/g estimated by Sheppard and Thibault (1990) for clay. Based on the strontium  $K_d$  values reported by Kaplan and Serkiz (2004) at a pH of 5.3, Kaplan (2006) estimated a “reasonably conservative” strontium  $K_d$  value of 12 for clayey sediments at SRS. Based on the above observations and considering that pH in the tan clay confining unit may be as low as 5.2 (Table 2-2), the “reasonably conservative” strontium  $K_d$  value of 12 mL/g estimated by Kaplan (2006) for SRS sandy subsurface sediments is recommended for the tan clay. Because strontium  $K_d$  values are sensitive to pH (i.e., strontium  $K_d$  increases with increasing pH) and pH is higher in the Gordon confining unit (Table 2-2) (pH 5.8 to 6.8), a strontium  $K_d$  value of 50 mL/g is recommended for the Gordon confining unit. This value lies at the approximate midpoint between the strontium  $K_d$  ranges reported by Kaplan and Serkiz (2004) on clayey subsurface sediments at SRS at pHs of 5.3 (16.6 to 42.6 mL/g) and 6.7 (67.7 to 97.6 mL/g).

The position of the strontium  $K_d$  values recommended in this review with respect to measured and estimated site-specific and generic strontium  $K_d$  ranges and values is graphically displayed in Figure 2-5. This figure illustrates the uncertainty associated with the strontium  $K_d$  values recommended for SRS aquifer units and clay confining units. Due to available site-specific strontium sorption data (Hoeffner, 1985; Kaplan and Serkiz, 2004, 2000), the recommended strontium  $K_d$  values are associated with low uncertainty.

#### **2.4.5 Niobium**

Niobium is present in nuclear waste as a result of the activation of zirconium pellets associated with nuclear fuel. Radioactive niobium is a metal that is present in radioactive wastes as Nb-95 (half-life of 35 days), Nb-93 (half-life of 13.6 years), and Nb-94 (half-life of 20,300 years). Knowledge of the behavior of niobium in the environment is limited. Niobium in soils is reported



**Figure 2-5. Measured and Estimated Site-Specific and Generic Strontium  $K_d$  Ranges and Values and Recommended Strontium  $K_d$  Values for Aquifer Units and Confining Units at SRS (Table 2-6). Recommended Strontium  $K_d$  Values Are Associated With Low Uncertainty Due to Available Site-Specific Sorption Data.**

to be rather immobile (Rhodes, 1957), being present as insoluble Nb(V) oxides and hydroxides.  $\text{Nb}(\text{OH})_5$  is expected to be the predominant form according to its hydrolysis properties in the pH and Eh ranges found in most soils (Baes and Mesmer, 1976). No site-specific sorption data for niobium on subsurface units at SRS were found in the literature. Rhodes (1957) performed a batch equilibrium experiment to measure niobium  $K_d$  values on a calcareous sandy soil. Rhodes (1957) reported a  $K_d$  value of  $>1,980$  mL/g for combined zirconium and niobium. The extent to which this value is valid for niobium only was not specified due to analytical difficulties.

Echevarria, et al. (2005) performed batch experiments to study niobium sorption on three soils from northeastern France. Soils consisted of one Luvisol (a sand-rich soil) and two Cambisols (clay-rich soils). Batch experiments consisted of soil-liquid ratios of 1 to 10 using deionized water. Measured niobium  $K_d$  values after 3 days were 1,978 mL/g for the Luvisol and 3,228 and 2,512 mL/g for the Cambisols. These values continued to increase after 3 days. Extrapolation of isotherm data suggested that after 30 days, niobium  $K_d$  values would have reached 4,524 mL/g for the Luvisol and 8,370 and 4,729 mL/g for the Cambisols.

Based on soil-to-plant concentration ratios, Sheppard and Thibault (1990) estimated a niobium default  $K_d$  for sand of 160 mL/g and a niobium default  $K_d$  for clay of 900 mL/g. A reference soil  $K_d$  for niobium at SRS was not included in the compilation of Looney, et al. (1987). Kaplan (2006) estimated “best” and “reasonably conservative”  $K_d$  values of 0 mL/g for niobium in both sandy subsurface sediment and clayey subsurface sediment at SRS. The niobium  $K_d$  values estimated by Kaplan (2006) were not based on site-specific data for niobium sorption on SRS sediments.

Recommended and estimated niobium  $K_d$  values are summarized in Table 2-7. Sheppard and Thibault (1990) recommended a niobium default  $K_d$  for sand of 160 mL/g. This recommended value is much lower than the measured niobium  $K_d$  value of a sand-rich soil from northeastern France (1,978 mL/g after 3 days of equilibrium) (Echevarria, et al., 2005). A niobium  $K_d$  value of 160 mL/g is, therefore, considered reasonably conservative and is recommended for aquifer units at SRS.

Sheppard and Thibault (1990) recommended a niobium default  $K_d$  for clay of 900 mL/g; this value is much lower than the measured niobium  $K_d$  values of two clay-rich soils from northeastern France (3,228 and 2,512 mL/g after 3 days of equilibrium) (Echevarria, et al., 2005). The niobium  $K_d$  value of 900 mL/g recommended by Sheppard and Thibault (1990) is, therefore, considered reasonably conservative and is recommended for clay confining units at SRS.

The position of the niobium  $K_d$  values recommended in this review with respect to estimated site-specific and generic niobium  $K_d$  ranges and values is graphically displayed in Figure 2-6. This figure illustrates the uncertainty associated with the niobium  $K_d$  values recommended for SRS aquifer units and clay confining units. The recommended niobium  $K_d$  values are associated with high uncertainty due to the lack of site-specific sorption data.

#### **2.4.6 Technetium**

Tc-99 occurs in the oxidized (+7) state, predominantly as pertechnetate ( $\text{TcO}_4^-$ ), over the complete pH range of natural waters, generally sorbs poorly to sediments, and is typically highly mobile (e.g., Denys, et al. 2003; Kaplan, 2003; Mashkin and Shikov 2000). The sorption

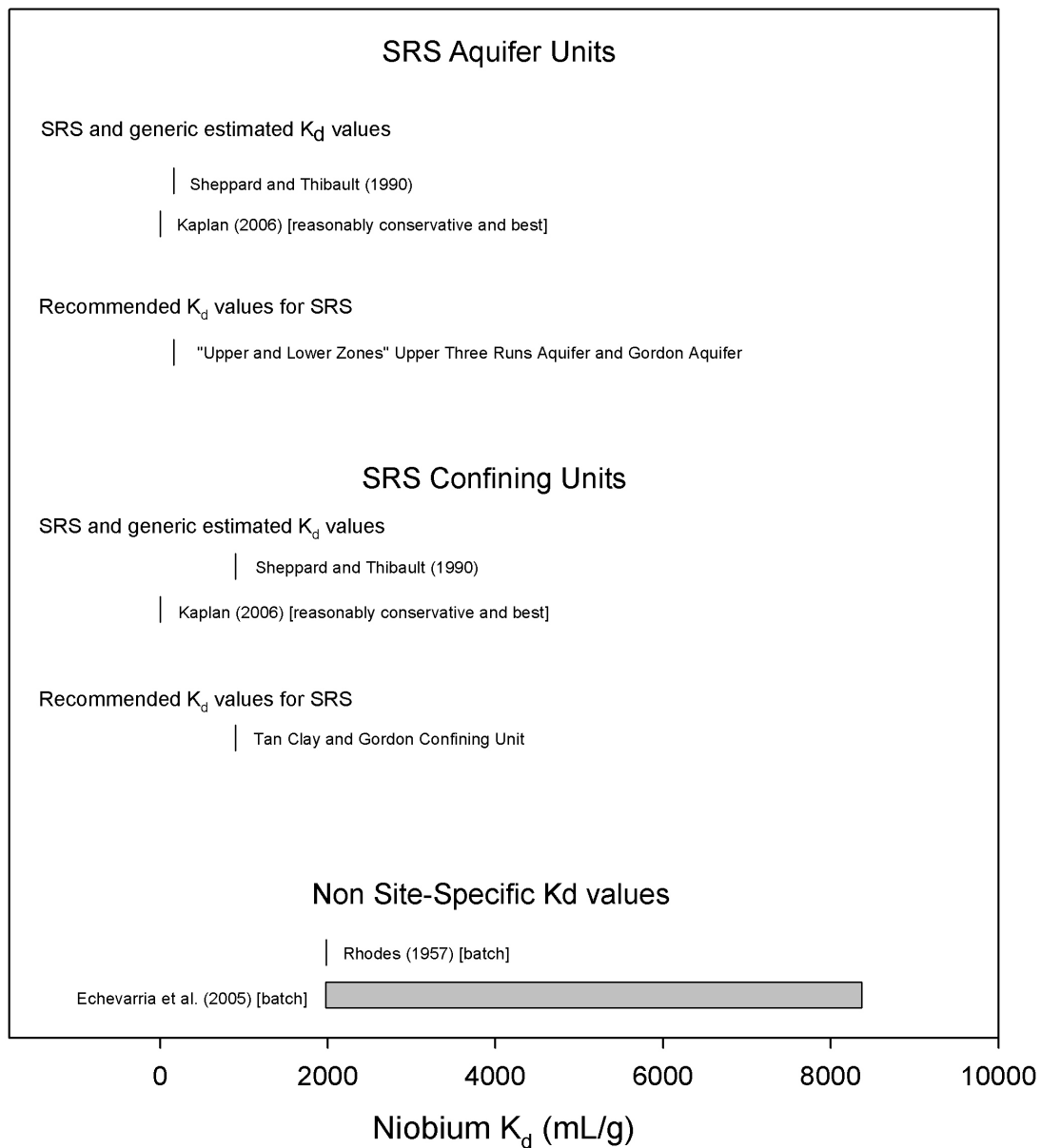
<b>Table 2-7. Recommended <math>K_d</math> Values for Niobium in Aquifer Sediments and Clay Confining Units at the Savannah River Site</b>				
	<b>Measured Niobium <math>K_d</math> (mL/g)</b>	<b>Savannah River Site-Specific “Reasonably Conservative”/ “Best” Estimated Niobium <math>K_d</math> (mL/g)*</b>	<b>Generic Estimated Niobium <math>K_d</math> (mL/g)†</b>	<b>Recommended Niobium <math>K_d</math> (mL/g)</b>
Upper Three Runs Aquifer: Upper	—	0/0	160	160
Tan Clay Confining Unit	—	0/0	900	900
Upper Three Runs Aquifer: Lower	—	0/0	160	160
Gordon Confining Unit	—	0/0	900	900
Gordon Aquifer	—	0/0	160	160
<p>*Kaplan, D.I. “Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site (U).” WSRC–TR–2006–00004. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company. 2006.</p> <p>†Sheppard, M.I. and D.H. Thibault. “Default Soil Solid/Liquid Partition Coefficients, <math>K_d</math>s, for Four Major Soil Types: A Compendium.” <i>Health Physics</i>. Vol. 59, No. 4. pp. 471–482. 1990.</p>				

behavior of technetium is highly redox sensitive. Experimental data indicate that technetium mobility increases with increasing pH (Denys, et al., 2003) and decreases under organic-rich, reducing conditions (Mashkin and Shidov, 2000). The pH effect may arise from pH-dependent changes in surface charge, or may reflect the role of organic matter, which both provide anion sorption sites for  $\text{TcO}_4^-$  and reduce pH (Kaplan, 2003).

Hoeffner (1985) summarized radionuclide sorption studies conducted to determine the performance of the low-level waste burial ground at the Savannah River Plant. A technetium  $K_d$  value of 0.16 mL/g is reported for a batch experiment using a Savannah River Plant soil and a low ionic strength groundwater representative of the SRS burial ground (pH 5.0). Hoeffner (1985) also reported the results of a technetium sorption study on soils with varying clay contents. Measured technetium  $K_d$  values for sand-rich soils (clay contents of 10 to 11 wt%) ranged from 0.1 to 0.23 mL/g, while technetium  $K_d$  values for clay-rich soils (clay contents of 30 to 45 wt%) ranged from 0.33 to 1.32 mL/g.

Kaplan (2003) measured  $K_d$  values for technetium as a function of pH on two sediments from SRS. Over the pH range of 2 to 9, technetium  $K_d$  values ranged from  $-0.1$  to  $0.1$  mL/g for a silty-sand upland SRS sediment (0.3 wt%  $\text{Fe}_2\text{O}_3$ , <0.02 wt% organic carbon). Over the pH





**Figure 2-6. Measured and Estimated Site-Specific and Generic Niobium  $K_d$  Ranges and Values and Recommended Niobium  $K_d$  Values for Aquifer Units and Confining Units at SRS (Table 2-7). Recommended Niobium  $K_d$  Values Are Associated With High Uncertainty Due to the Lack of Site-Specific Sorption Data.**

range of 3 to 7, technetium  $K_d$  values ranged from 0 to 0.3 mL/g for a silty-sand wetland SRS sediment (0.01 wt%  $\text{Fe}_2\text{O}_3$ , 0.14 wt% organic carbon). For both sediments,  $K_d$  tended to decrease with increasing pH, as expected for an anionic species. Kaplan suggested that the negative  $K_d$  values measured for technetium were due to anion exclusion effects.

Routson, et al. (1977) used batch equilibrium experiments to measure  $K_d$  values for technetium on soil from South Carolina as a function of the concentration of dissolved sodium bicarbonate. The location where the soil sample was taken was not revealed, but it could have been collected from SRS. The soil contained <0.2 mg/g [200 ppm]  $\text{CaCO}_3$ , 3.6-wt% silt, 37.2-wt% clay, and had a CEC of 2.5 meq/100 g and a pH of 5.1. The measurements indicated that technetium did not sorb to the soil sample. The measured  $K_d$  values for technetium were 0.02, -0.05, -0.033, and 0.010 mL/g for 0.002, 0.008, 0.020, and 0.200 M  $\text{NaHCO}_3$  solutions, respectively.

Sheppard and Thibault (1990) estimated a technetium default  $K_d$  for sand of 0.1 mL/g (19 observations ranging from 0.01 to 16 mL/g) and a technetium default  $K_d$  for clay of 1.0 mL/g (4 observations ranging from 1.16 to 1.32 mL/g). Looney, et al. (1987) estimated a reference SRS soil  $K_d$  of 0.001 mL/g for technetium from a specified range of 0.001 to 100 mL/g. Kaplan (2006) estimated “reasonably conservative” and “best” technetium  $K_d$  values of 0.05 and 0.1 mL/g for sandy subsurface sediment and “reasonably conservative” and “best” technetium  $K_d$  values of 0.1 and 0.2 mL/g for clayey subsurface sediment at SRS. The technetium  $K_d$  values estimated by Kaplan (2006) were based on the technetium sorption data of Hoeffner (1985) and Kaplan (2003) described previously.

Measured, estimated, and recommended technetium  $K_d$  values are summarized in Table 2-8. Hoeffner (1985) reports a technetium  $K_d$  value of 0.16 mL/g for a shallow soil collected from the SRS burial ground and technetium  $K_d$  values ranging from 0.1 to 0.23 mL/g for shallow sand-rich soils from SRS. Kaplan (2003) measured technetium  $K_d$  values for an upland soil and wetland soil at SRS over pH ranges of 2 to 9 and 3 to 7, respectively. For the upland soil, technetium  $K_d$  values ranged from -0.1 to 0.1, and for the wetland soil, technetium  $K_d$  values ranged from 0 to 0.3. These values are in agreement with the technetium  $K_d$  values reported by Hoeffner (1985). Routson, et al. (1977) reported measured technetium  $K_d$  values ranging from -0.05 to 0.02 for soils from South Carolina. The technetium  $K_d$  value for sand estimated by Sheppard and Thibault (1990) (0.1 mL/g) and the reference technetium  $K_d$  value for SRS soil estimated by Looney, et al. (1987) (0.001 mL/g) are within the technetium  $K_d$  values measured at SRS (Hoeffner, 1985; Kaplan, 2003). Based on the technetium  $K_d$  values reported by Hoeffner (1985) and Kaplan (2003), Kaplan (2006) estimated a “reasonably conservative” technetium  $K_d$  value of 0.05 mL/g for sandy subsurface sediments at SRS. An examination of the technetium sorption data of Kaplan (2003) indicates that over the pH range expected at SRS (5.2 to 7.7), technetium  $K_d$  values in the upland and wetland sediments were at or below 0. The mineral composition of the aquifer units at SRS is not significantly different and, thus, these units would be expected to exhibit similar technetium sorption. Based on the above analysis, a technetium  $K_d$  value of 0 is recommended for aquifer units at SRS.

Hoeffner (1985) reported technetium  $K_d$  values ranging from 0.33 to 1.32 mL/g for clay-rich soils from SRS. The hydrostratigraphic unit from which these soils were collected was not specified. However, the reported clay contents of these soils (30 to 45 wt%) are comparable to clay contents found in the tan clay and Gordon confining units. Therefore, it is assumed that these technetium  $K_d$  values are, at least, analogous to values for the tan clay and the Gordon

**Table 2-8. Measured, Estimated, and Recommended Technetium  $K_d$  Values for Aquifer Sediments and Clay Confining Units at the Savannah River Site**

	Measured Technetium $K_d$ (mL/g)	Test Method	Savannah River Site-Specific “Reasonably Conservative”/ “Best” Estimated Technetium $K_d$ (mL/g)*	Generic Estimated Technetium $K_d$ (mL/g)†	Recommended Technetium $K_d$ (mL/g)
Upper Three Runs Aquifer: Upper	0.1–0.23‡ –0.1–0.3§ –0.05–0.02¶	Batch Batch Batch	0.05/0.1	0.1	0
Tan Clay Confining Unit	0.33–1.32‡	Batch	0.1/0.2	1	0.3
Upper Three Runs Aquifer: Lower	—		0.05/0.1	0.1	0
Gordon Confining Unit	—		0.1/0.2	1	0.3
Gordon Aquifer	—		0.05/0.1	0.1	0

\*Kaplan, D.I. “Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site (U).” WSRC–TR–2006–00004. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company. 2006.

†Sheppard, M.I. and D.H. Thibault. “Default Soil Solid/Liquid Partition Coefficients,  $K_d$ s, for Four Major Soil Types: A Compendium.” *Health Physics*. Vol. 59, No. 4. pp. 471–482. 1990.

‡Hoeffner, S.L. “Radionuclide Sorption on Savannah River Plant Burial Ground Soil—A Summary and Interpretation of Laboratory Data.” DP–1702. Aiken, South Carolina: E.I. du Pont de Nemours and Company, Savannah River Laboratory. 1985.

§Kaplan, D.I. “Influence of Surface Charge of an Fe-Oxide and an Organic Matter Dominated Soil on Iodide and Pertechnetate Sorption.” *Radiochimica Acta*. Vol. 91, No. 3. pp. 173–178. 2003.

¶Routson, R.C., G. Jansen, and A.V. Robinson. “ $^{241}\text{Am}$ ,  $^{237}\text{Np}$ , and  $^{99}\text{Tc}$  Sorption on Two United States Subsoils From Differing Weathering Intensity Areas.” *Health Physics*. Vol. 33. pp. 311–317. 1977.

confining units. The technetium  $K_d$  value for clay estimated by Sheppard and Thibault (1990) (1.0 mL/g) is within the range of values for the clay-rich soils reported by Hoeffner (1985). Based on the technetium  $K_d$  values reported by Hoeffner (1985) and Kaplan (2003), Kaplan (2006) estimated “reasonably conservative” and “best” technetium  $K_d$  values of 0.1 and 0.2 mL/g, respectively, for clayey subsurface sediments at SRS. However, the technetium  $K_d$  values of –0.1 to 0.3 mL/g reported by Kaplan (2003) were measured on silty-sand sediments. Therefore, a technetium  $K_d$  value of 0.3 mL/g is recommended for clay confining units at SRS.

This value is at the low end of the range of technetium  $K_d$  values reported by Hoeffner (1985) (0.33 to 1.32 mL/g) for clay-rich soils and at the high end of the range of technetium  $K_d$  values reported by Kaplan (2003) (–0.1 to 0.3 mL/g) for silty-sand sediments.

The position of the technetium  $K_d$  values recommended in this review with respect to measured and estimated site-specific and generic technetium  $K_d$  ranges and values is graphically displayed in Figure 2-7. This figure illustrates the uncertainty associated with the technetium  $K_d$  values recommended for SRS aquifer units and clay confining units. Due to available site-specific technetium sorption data (Hoeffner, 1985; Kaplan, 2003), the recommended technetium  $K_d$  values are associated with low uncertainty.

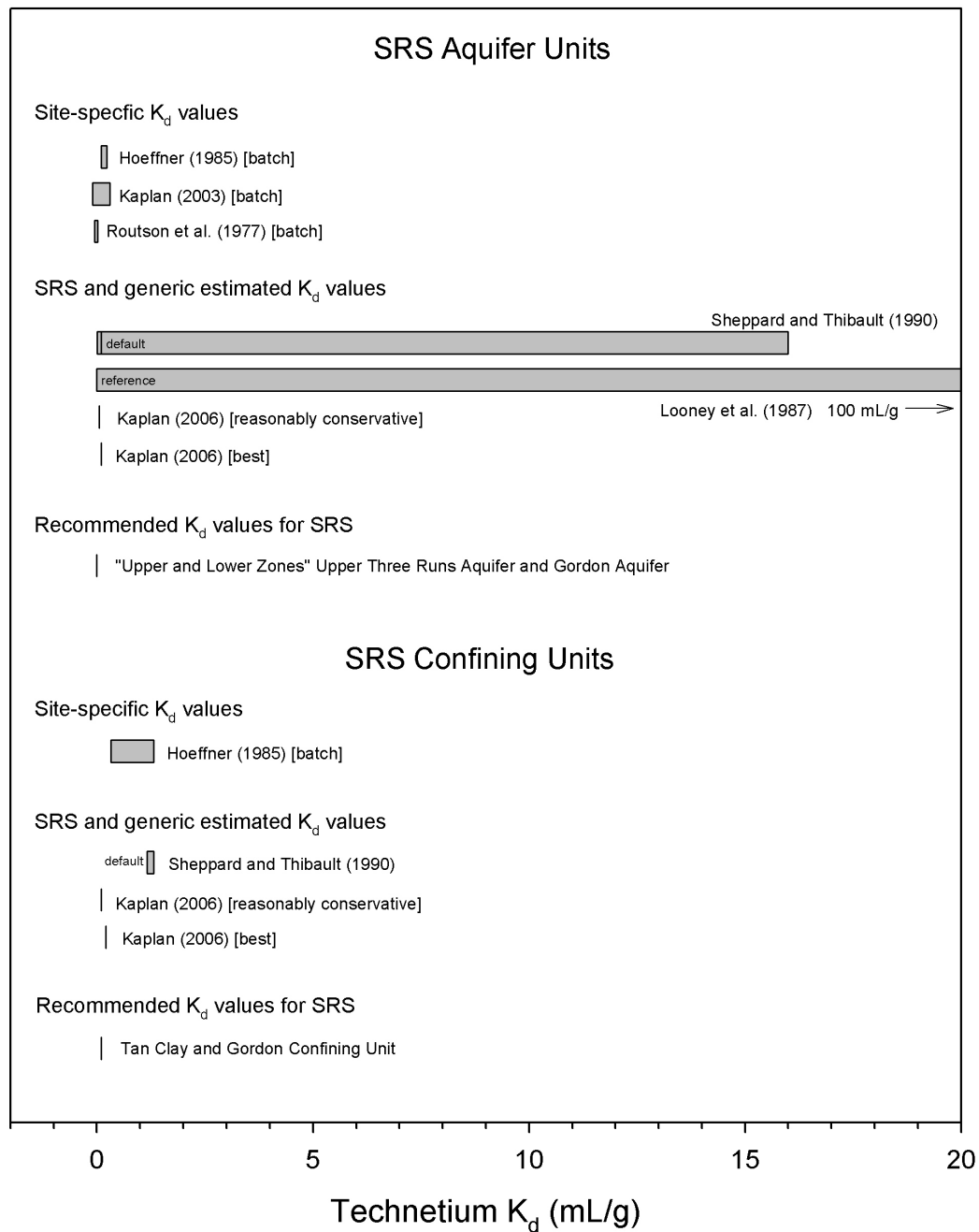
#### **2.4.7 Tin**

The sorptive properties of Sn-121 are poorly known. Sn(IV) is expected to be the predominant tin species in natural waters. Limited evidence seems to indicate that  $\text{Sn}(\text{OH})_4^0$  is a major dissolved species controlling the solubility of  $\text{SnO}_2(\text{s})$  in the pH range 2 to 10 (Kedziorek, et al., 2007).

No site-specific tin sorption data are available for SRS. Kedziorek, et al. (2007) performed batch experiments in the pH range of 2 to 12 to study the solubility of Sn(IV) and its adsorption by solids under consideration for radioactive waste storage (MX-80 bentonite and Callovo-Oxfordian argillite from the Bure site in Eastern France). Measured tin  $K_d$  values ranged from 725 to 12,000 mL/g. Kedziorek, et al. (2007) indicated that tin sorption was independent of pH and was most likely controlled by clay minerals.

Sheppard and Thibault (1990) specified a tin default  $K_d$  for sand of 130 mL/g and for clay of 670 mL/g; both values were based on a soil-to-plant concentration ratio. Looney, et al. (1987) estimated a reference SRS soil  $K_d$  of 100 mL/g for tin. Kaplan (2006) estimated “reasonably conservative” and “best” tin  $K_d$  values of 500 and 2,000 mL/g for sandy subsurface sediment and “reasonably conservative” and “best” tin  $K_d$  values of 2,500 and 5,000 mL/g for clayey subsurface sediment at SRS. The tin  $K_d$  values estimated by Kaplan (2006) were based partly on reported lead  $K_d$  values measured on SRS burial ground sediment by Bibler and Marson (1992). Although lead is a divalent metal and tin exists dominantly in the tetravalent state  $[\text{Sn}(\text{IV})]$ , they were considered to be chemically analogous and to have a similar sorptive behavior by Kaplan (2006). Other than being in Group IVA of the periodic chart, Kaplan (2006) gave no other technical basis for the similar chemical behavior of tin and lead. Bibler and Marson (1992) reported lead  $K_d$  values ranging from 63 to >2 million mL/g. However, it is likely that these experiments were conducted at concentrations above the solubility limit of lead {e.g., initial  $\text{Pb}^{2+}$  of 5 mg/L [5 ppm]} and therefore reflect precipitation more than adsorption.

Recommended and estimated tin  $K_d$  values are summarized in Table 2-9. The tin  $K_d$  value for sand estimated by Sheppard and Thibault (1990) (130 mL/g) is in good agreement with the tin  $K_d$  value for SRS soil specified by Looney, et al. (1987) (100 mL/g). The tin  $K_d$  value for sand estimated by Sheppard and Thibault (1990) was based on a soil-to-plant concentration ratio, and the tin  $K_d$  value for soil estimated by Looney, et al. (1987) was based on nonsite-specific literature data. Based on reported lead  $K_d$  values measured on SRS burial ground sediment by Bibler and Marson (1992), Kaplan (2006) estimated a “reasonably conservative” tin  $K_d$  value of 500 mL/g for sandy subsurface sediments at SRS. Lead and tin were considered chemically analogous and to have a similar sorptive behavior. Lacking site-specific tin sorption data, the

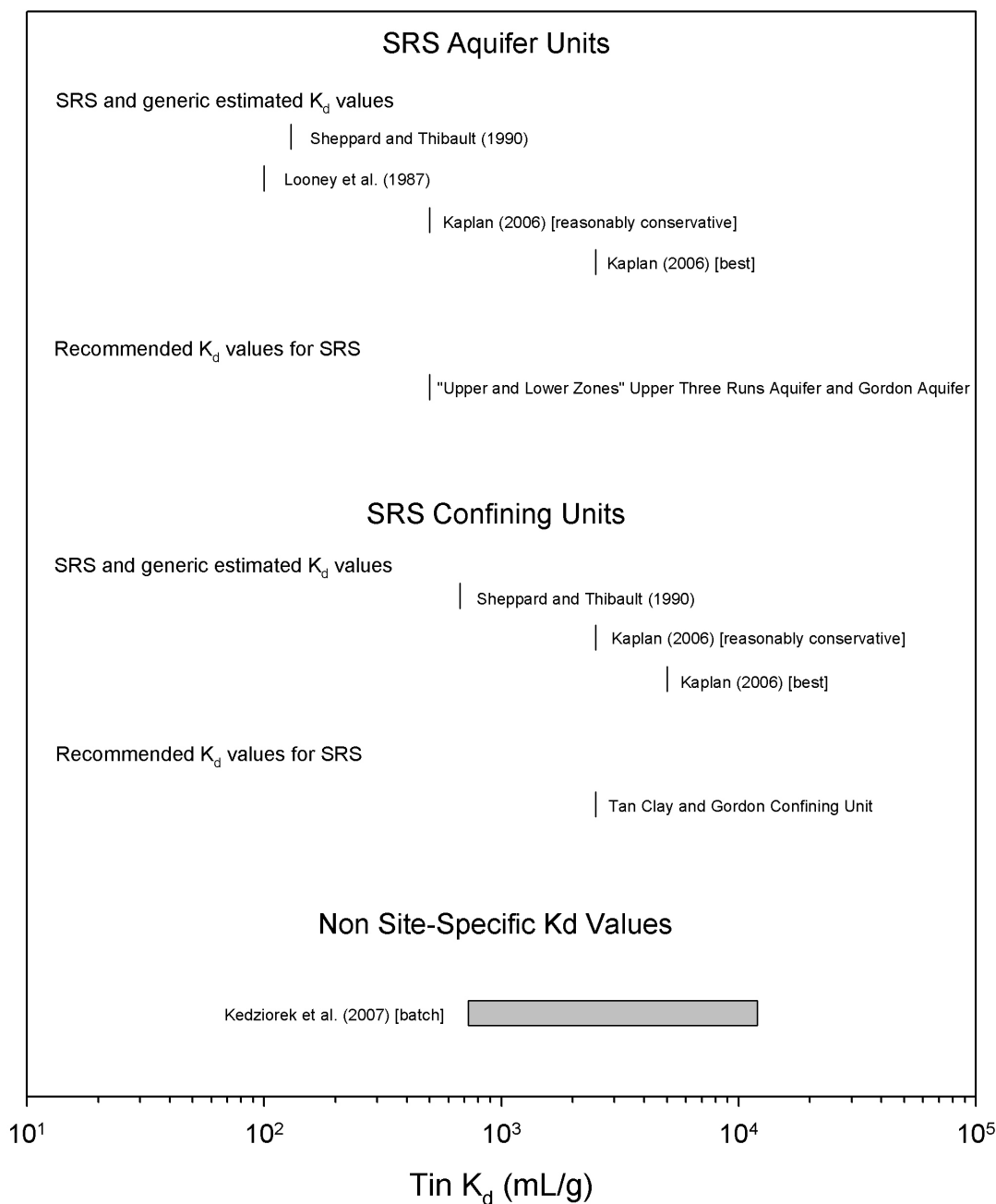


**Figure 2-7. Measured and Estimated Site-Specific and Generic Technetium  $K_d$  Ranges and Values and Recommended Technetium  $K_d$  Values for Aquifer Units and Confining Units at SRS (Table 2-8). Recommended Technetium  $K_d$  Values Are Associated With Low Uncertainty Due to Available Site-Specific Sorption Data.**

<b>Table 2-9. Estimated and Recommended Tin <math>K_d</math> Values for Aquifer Sediments and Clay Confining Units at the Savannah River Site</b>				
	<b>Measured Tin <math>K_d</math> (mL/g)</b>	<b>Savannah River Site-Specific “Reasonably Conservative”/ “Best” Estimated Tin <math>K_d</math> (mL/g)*</b>	<b>Generic Estimated Tin <math>K_d</math> (mL/g)†</b>	<b>Recommended Tin <math>K_d</math> (mL/g)</b>
Upper Three Runs Aquifer: Upper	—	500/2,000	130	500
Tan Clay Confining Unit	—	2,500/5,000	670	2,500
Upper Three Runs Aquifer: Lower	—	500/2,000	130	500
Gordon Confining Unit	—	2,500/5,000	670	2,500
Gordon Aquifer	—	500/2,000	130	500
<p>*Kaplan, D.I. “Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site (U).” WSRC–TR–2006–00004. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company. 2006.</p> <p>†Sheppard, M.I. and D.H. Thibault. “Default Soil Solid/Liquid Partition Coefficients, <math>K_d</math>s, for Four Major Soil Types: A Compendium.” <i>Health Physics</i>. Vol. 59, No. 4. pp. 471–482. 1990.</p>				

“reasonably conservative” tin  $K_d$  value of 500 mL/g estimated by Kaplan (2006) is recommended for aquifer units at SRS. Sheppard and Thibault (1990) estimated a tin  $K_d$  value for clay of 670 mL/g based on a soil-to-plant concentration ratio. Based on reported lead  $K_d$  values measured on SRS burial ground sediment by Bibler and Marson (1992), Kaplan (2006) estimated a “reasonably conservative” tin  $K_d$  value of 2,500 mL/g for clayey subsurface sediments at SRS. The conservative tin  $K_d$  value of 2,500 mL/g estimated by Kaplan (2006) is near the low end of the tin  $K_d$  range measured on clay-rich materials by Kedziorek, et al. (2007) (725 to 12,000 mL/g). Therefore, the “reasonably conservative” tin  $K_d$  value of 2,500 mL/g estimated by Kaplan (2006) is recommended for clay confining units at SRS.

The position of the tin  $K_d$  values recommended in this review with respect to estimated site-specific and generic tin  $K_d$  ranges and values is graphically displayed in Figure 2-8. This figure illustrates the uncertainty associated with the tin  $K_d$  values recommended for SRS aquifer units and clay confining units. The recommended tin  $K_d$  values are associated with high uncertainty due to the lack of site-specific sorption data.



**Figure 2-8. Measured and Estimated Site-Specific and Generic Tin  $K_d$  Ranges and Values and Recommended Tin  $K_d$  Values for Aquifer Units and Confining Units at SRS (Table 2-9). Recommended Tin  $K_d$  Values Are Associated With High Uncertainty Due to the Lack of Site-Specific Sorption Data.**

### 2.4.8 Iodine

I-129 generally occurs as iodate ( $\text{IO}_3^-$ ), iodide ( $\text{I}^-$ ), or organic iodine in natural environments. Sorption of iodine species appears to be controlled in part by soil organic matter and in part by iron and aluminum oxides, with adsorption of iodine becoming increasingly important under more acid conditions. Although the extent of sorption is typically low, especially in systems containing little or no organic matter,  $\text{I}^-$  and  $\text{IO}_3^-$  are sorbed to a measurable extent by soils and some oxide minerals at near-neutral and alkaline pH conditions. The adsorption behavior of  $\text{IO}_3^-$  also appears to be appreciably different from that of  $\text{I}^-$ , because  $\text{IO}_3^-$  sorbs much more strongly than  $\text{I}^-$  to soil and mineral surfaces (Ticknor and Cho, 1990). Mechanisms causing this sorption behavior of iodine at near-neutral and alkaline pH conditions are not completely understood. Some have proposed that this observed adsorption behavior in soils may be the result of the oxidation of  $\text{I}^-$  and/or reduction of  $\text{IO}_3^-$  to the more reactive molecular  $\text{I}_2^0(\text{aq})$  and/or its hydrolysis products (Ticknor and Cho, 1990).

Hoeffner (1985) summarized iodine sorption studies conducted to determine the performance of the low-level waste burial ground at SRS. Hoeffner (1985) describes a batch equilibrium study to measure  $\text{I}^- K_d$  values as a function of  $\text{I}^-$  concentration using a Savannah River Plant soil taken from depths 2.5–3.0 m [8–10 ft] below grade and a low ionic strength groundwater representative of the burial ground (pH 5.0).  $K_d$  values ranged from 10 mL/g at 5 ppb  $\text{I}^-$  to 3.6 mL/g at 500 ppb  $\text{I}^-$ . Differences in pH were also noted to influence  $\text{I}^-$  sorption. Hoeffner (1985) reported an expected range of I-129  $K_d$  values from 3 to 10 mL/g over a pH range of 3.4 to 7.3, and an expected  $K_d$  of 5 mL/g with a groundwater of typical composition at the SRS burial ground (pH 4.7).

Kaplan (2003) measured  $K_d$  values for  $\text{I}^-$  as a function of pH on two sediments from SRS using batch techniques (14-day equilibrium). Over the pH range of 3.5 to 7,  $\text{I}^- K_d$  values ranged from 0.6 to 0.7 mL/g for a silty-sand upland SRS sediment (0.3 wt%  $\text{Fe}_2\text{O}_3$ , <0.02 wt% organic carbon) and from 1 to 2 mL/g for a silty-sand wetland SRS sediment (0.01 wt%  $\text{Fe}_2\text{O}_3$ , 0.14 wt% organic carbon). The  $K_d$  values were consistently greater for the wetland sediment and were attributed to its greater organic matter content. The measured  $\text{I}^- K_d$  values also generally decreased with increasing pH, as would be expected for dissolved anionic contaminants.

Hu, et al. (2005) conducted column studies of  $\text{I}^-$  and iodate ( $\text{IO}_3^-$ ) sorption and transport on three uncontaminated sediments from SRS. The sediments were collected at different depths (surface soil, subsoil, and aquifer soil), providing an opportunity to examine the influence of organic matter, clay mineralogy, soil pH, and texture on the transport behavior of iodine species. For SRS surface soil {pH 4.9, 2.3-wt% organic matter, 9.5-wt% clay, 2.8 g/kg iron [2,800 ppm], 1.3 g/kg Al [1,300 ppm]}, retardation factors ranged from 0.93 to 0.99 for  $\text{I}^-$  and 2.29 to 2.92 for  $\text{IO}_3^-$ . For the SRS subsoil {pH 5.36; 0.072-percent organic matter, 19.8-wt% clay, 16.2 g/kg [16,200 ppm] iron, 2.9 g/kg [2,900 ppm] Al}, retardation factors for  $\text{I}^-$  ranged from 5.5 to 6.3, and no breakthrough for  $\text{IO}_3^-$  was observed. For aquifer soil {pH 5.42, 0.013-percent organic matter, 1.9-wt% clay, 7.3 g/kg [7,300 ppm] iron, 0.42 g/kg [420 ppm] Al}, retardation factors ranged from 1.00 to 1.35 for  $\text{I}^-$  and 7.92 to 16.2 for  $\text{IO}_3^-$ . Results indicate very limited sorption of  $\text{I}^-$  during transport in surface soil and aquifer soil. Retardation factors ranged from



0.93 to 1.35, which equate to  $K_d$  values of approximately (-0.015) to 0.09 mL/g.<sup>2</sup> However, there was significant retardation of  $I^-$  in the subsoil sample; the retardation factors of 5.5 to 6.3 equate to  $K_d$  values of approximately 1 to 1.4 mL/g. The subsoil sample contained appreciable amounts of iron and aluminum oxide minerals, which possess positively charged surfaces and contribute to anion adsorption. Iodate is expected to exhibit more retarded transport than  $I^-$  because it interacts more strongly with clays and organic matter. This behavior was confirmed in this study;  $IO_3^-$  consistently showed greater sorption than  $I^-$ . Measured retardation factors for  $IO_3^-$  in surface and aquifer soils ranged from 2.29 to 16.2, which equate to  $K_d$  values of approximately 0.3 to 4.0 mL/g.

Kaplan and Serkiz (2006) conducted batch experiments to measure iodine  $K_d$  values, as  $I^-$ , on a clayey sediment and a sandy sediment collected from the E-Area at SRS as a function of pH and DO. The sediments were collected from the upper zone of the Upper Three Runs aquifer and represented end members with respect to contaminant sorption properties expected in the E-Area subsurface. Iodine  $K_d$  values were reported at DO concentrations ranging from 0 to 300 mg/L [0 to 300 ppm] for pHs of 3.9, 5.3, and 6.7. Table 2-1 indicates that DO concentrations ranging from 0 to 10 mg/L are characteristic of sandy aquifer and clay confining units beneath GSA. At pH 3.9 and a DO concentration of 0 mg/L [0 ppm], Kaplan and Serkiz (2006) reported an iodine  $K_d$  value of  $-0.2 \pm 0.2$  mL/g ( $\pm$  95-percent confidence interval) for clayey sediment and an iodine  $K_d$  value of 0 mL/g for sandy sediment. At pH 5.3 and a DO concentration of 0 mg/L [0 ppm], Kaplan and Serkiz (2006) reported an iodine  $K_d$  value of  $0.1 \pm 0.4$  mL/g for clayey sediment and an iodine  $K_d$  value of 0 mL/g for sandy sediment. At pH 6.7 and a DO concentration of 0 mg/L [0 ppm], Kaplan and Serkiz (2006) reported an iodine  $K_d$  value of  $0.2 \pm 0.1$  mL/g for clayey sediment and an iodine  $K_d$  value of 0 mL/g for sandy sediment.

Sheppard and Thibault (1990) specified an iodine default  $K_d$  for sand of 1.0 mL/g (22 observations ranging from 0.04 to 81 mL/g) and an iodine default  $K_d$  for clay of 1.0 mL/g (8 observations ranging from 0.2 to 29). Looney, et al. (1987) estimated a reference SRS soil  $K_d$  of 0.2 mL/g for iodine from an estimated range of 0.001 to 100 mL/g. Kaplan (2006) estimated “reasonably conservative” and “best” iodine  $K_d$  values of 0 mL/g for sandy subsurface sediment and “reasonably conservative” and “best” iodine  $K_d$  values of 0.3 and 0.6 mL/g for clayey subsurface sediment at SRS. The iodine  $K_d$  values estimated by Kaplan (2006) were based on the iodine sorption data of Hoeffner (1985), Kaplan (2003), and Kaplan and Serkiz (2006) described previously.

Measured, estimated, and recommended iodine  $K_d$  values are summarized in Table 2-10. Hoeffner (1985) reported a measured range of iodine  $K_d$  values for SRS soils of 3 to 10 mL/g over a pH range of 3.4 to 7.3 and an expected iodine  $K_d$  of 5 mL/g with a groundwater of typical composition at the SRS burial ground (pH 4.7). These values are higher than iodine  $K_d$  values measured by Kaplan (2003) on silty-sand upland and wetland sediments from SRS. Over the pH range of 3.5 to 7, Kaplan (2003) reported an iodine  $K_d$  range of 0.6 to 0.7 mL/g for the upland soil and an iodine  $K_d$  range of 1 to 2 mL/g for the wetland soil. Hu, et al. (2005) performed column experiments to measure  $I^-$  and  $IO_3^-$  retardation factors in a surface soil, a

---

<sup>2</sup>Retardation factor ( $R_f$  converted to  $K_d$  based on following equation:  $K_d = \frac{(R_f - 1)}{\rho_b} \theta$  ,

where  $\theta$  is porosity and  $\rho_b$  is bulk density.

**Table 2-10. Measured, Estimated, and Recommended Iodine  $K_d$  Values for Aquifer Sediments and Clay Confining Units at the Savannah River Site**

	Measured Iodine $K_d$ (mL/g)	Test Method	Savannah River Site-Specific “Reasonably Conservative”/ “Best” Estimated Iodine $K_d$ (mL/g)*	Generic Estimated Iodine $K_d$ (mL/g)†	Recommended Iodine $K_d$ (mL/g)
Upper Three Runs Aquifer: Upper	3–10‡ 0.6–2§ –0.015–4¶ –0.4–0.5#	Batch Batch Column Batch	0/0	1.0	0
Tan Clay Confining Unit			0.3/0.6	1.0	0.2
Upper Three Runs Aquifer: Lower			0/0	1.0	0
Gordon Confining Unit			0.3/0.6	1.0	0.2
Gordon Aquifer			0/0	1.0	0

\*Kaplan, D.I. “Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site (U).” WSRC–TR–2006–00004. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company. 2006.

†Sheppard, M.I. and D.H. Thibault. “Default Soil Solid/Liquid Partition Coefficients,  $K_d$ s, for Four Major Soil Types: A Compendium.” *Health Physics*. Vol. 59, No. 4. pp. 471–482. 1990.

‡Hoeffner, S.L. “Radionuclide Sorption on Savannah River Plant Burial Ground Soil—A Summary and Interpretation of Laboratory Data.” DP–1702. Aiken, South Carolina: E.I. du Pont de Nemours and Company, Savannah River Laboratory. 1985.

§Kaplan, D.I. “Influence of Surface Charge of an Fe-Oxide and an Organic Matter Dominated Soil on Iodide and Pertechnetate Sorption.” *Radiochimica Acta*. Vol. 91, No. 3. pp. 173–178. 2003.

¶Hu, Q., Z. Pihong, J.E. Moran, and J.C. Seaman. “Sorption and Transport of Iodine Species in Sediments from Savannah River and Hanford Sites.” *Journal of Contaminant Hydrology*. Vol. 78. pp. 185–205. 2005.

#Kaplan, D.I. and S.M. Serkiz. “Influence of Dissolved Organic Carbon and pH on Anion Sorption to Sediment.” WSRC–RP–2006–00005. Aiken, South Carolina: Westinghouse Savannah River Company. 2006.

subsoil, and an aquifer soil from SRS. For  $I^-$ , retardation factors measured for the 3 soils ranged from 0.93 to 6.3, which equate to iodine  $K_d$  values ranging from –0.015 to 1.4 mL/g. For  $IO_3^-$ , retardation factors measured on the three soils ranged from 2.29 to 16.2, which equate to  $K_d$  values of 0.3 to 4.0 mL/g. The range of iodine  $K_d$  values measured by Hu, et al. (2005) (–0.015 to 4.0 mL/g) are consistent with the measured iodine  $K_d$  values of Kaplan (2003). The estimated iodine  $K_d$  value for sand of Sheppard and Thibault (1990) (1.0 mL/g) and the reference iodine  $K_d$  value of 0.2 mL/g specified by Looney, et al. (1987) for SRS soil are within the range of iodine  $K_d$  values measured on SRS sediments by Kaplan (2003) and Hu, et al. (2005). Kaplan and Serkiz (2006) reported iodine  $K_d$  values of 0 mL/g on sandy subsurface sediments from SRS over the pH range of 3.9 to 6.7. Based on the iodine  $K_d$  values reported by

Hoeffner (1985), Kaplan (2003), and Kaplan and Serkiz (2006), Kaplan (2006) estimated a “reasonably conservative” iodine  $K_d$  value of 0 mL/g for sandy sediments at SRS. The mineral compositions of the aquifer units at SRS are not significantly different and, thus, these units should exhibit similar iodine sorption. Based on the range of reported site-specific iodine  $K_d$  values summarized previously and considering the “reasonably conservative” iodine  $K_d$  estimated by Kaplan (2006) for SRS sandy sediments, an iodine  $K_d$  value of 0 mL/g is recommended for aquifer units at SRS.

Kaplan and Serkiz (2006) reported iodine  $K_d$  values of  $0.1 \pm 0.4$  mL/g and  $0.2 \pm 0.1$  mL/g on clayey subsurface sediments from SRS at pHs of 5.3 and 6.7, respectively. Based on the iodine  $K_d$  values reported by Hoeffner (1985), Kaplan (2003), and Kaplan and Serkiz (2006), Kaplan (2006) estimated a “reasonably conservative” iodine  $K_d$  value of 0.3 mL/g for clayey subsurface sediments at SRS. Sheppard and Thibault (1990) recommended a default iodine  $K_d$  value of 1.0 for clay. Based on the iodine  $K_d$  values reported by Kaplan and Serkiz (2006) at pHs of 5.3 and 6.7 and considering the “reasonably conservative” iodine  $K_d$  estimated by Kaplan (2006) for SRS clayey sediments, an iodine  $K_d$  value of 0.2 mL/g is recommended for clay confining units at SRS.

The position of the iodine  $K_d$  values recommended in this review with respect to measured and estimated site-specific and generic iodine  $K_d$  ranges and values is graphically displayed in Figure 2-9. This figure illustrates the uncertainty associated with the iodine  $K_d$  values recommended for SRS aquifer units and clay confining units. Due to available site-specific iodine sorption data (Kaplan, 2003; Hu et al., 2005; Kaplan and Serkiz, 2006), the recommended iodine  $K_d$  values are associated with low uncertainty.

#### **2.4.9 Cesium**

Cs-137 exists in the environment in the +1 oxidation state. Cesium forms few stable complexes and is likely to exist in groundwater as the uncomplexed  $\text{Cs}^+$  ion.  $\text{Cs}^+$  primarily adsorbs via ion exchange reactions with sedimentary clay minerals. In general, most soils sorb cesium rather strongly (Ames and Rai, 1978). The extent to which adsorption will occur will depend on the concentration of clays in the soil and the concentration of major cations, such as  $\text{K}^+$ , that can effectively compete with  $\text{Cs}^+$  for adsorption sites. Cesium may also adsorb to iron oxides (Schwertmann and Taylor, 1989). Sorption of  $\text{Cs}^+$  is pH dependent and increases with increasing pH. Prout (1958) reported that cesium adsorption to iron-oxide-dominated soils from South Carolina decreased dramatically when the pH was less than 6.

Hoeffner (1985) summarized cesium sorption studies conducted to determine the performance of the low-level waste burial ground at SRS. The majority of studies used a Savannah River Plant soil taken from depths 2.5–3.0 m [8–10 ft] below grade and a low ionic strength groundwater representative of the burial ground (pH 5.0). Hoeffner (1985) found that cesium sorption was very dependent on pH and solution concentration. Hoeffner (1985) reported an expected range of cesium  $K_d$  values from 330 to 1800 mL/g over a pH range of 3.4 to 7.3 and an expected  $K_d$  value of 500 for a groundwater of typical composition at SRS burial ground (pH 4.7).

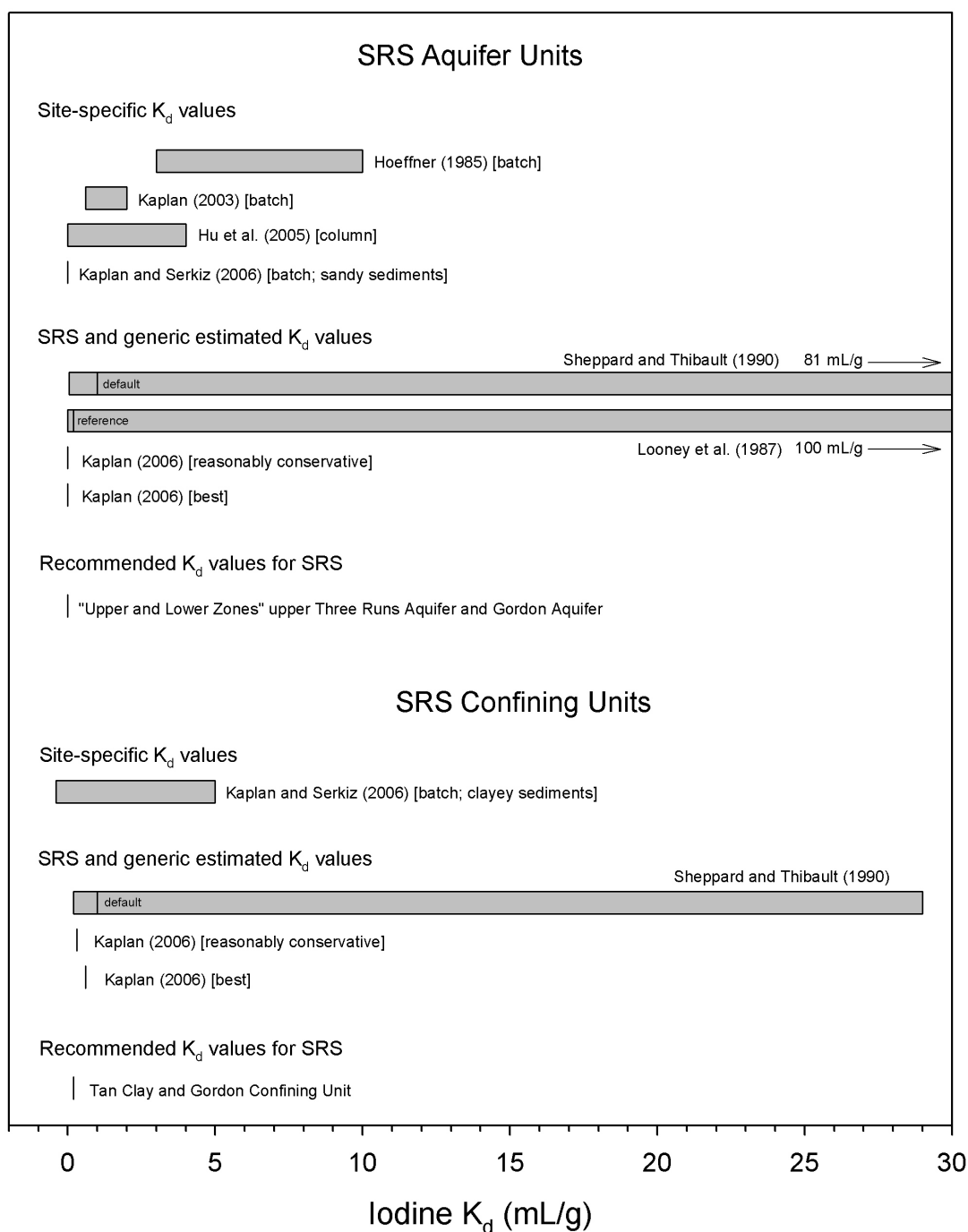
McConnell, et al. (1995) reported a cesium  $K_d$  value of 37 mL/g for SRS soil used in lysimeter tests to obtain information on the performance of radioactive wastefoms. This value was

obtained using a batch method. The composition and pH of the solution used in the batch test was not reported.

Elprince, et al. (1977) performed batch sorption experiments on surficial sediments collected from five streams (Upper Three Runs, Four Mile Creek, Pen Branch, Steel Creek, and Lower Three Runs), Par Pond, and the Savannah River at SRS. The Par Pond, Steel Creek, and Upper Three Runs sediments had a high percentage of quartz (54–66 wt%) and a lower CEC than the Pen Branch, Lower Three Runs, Four Mile Creek, and Savannah River sediments (<29- through 40-wt% quartz). The solution used in the batch experiments was a low ionic strength sodium solution (0.005 M sodium); the pH of the solution was not reported. Cesium  $K_d$  values for samples with the low CEC (Par Pond, Steel Creek, and Upper Three Runs) ranged from 18.3 to 40.1 mL/g. Cesium  $K_d$  values for sediments with a high CEC (Pen Branch, Lower Three Runs, Four Mile Creek, and Savannah River) ranged from 83.6 to 130 mL/g. The low CEC samples with high percentages of quartz were assumed to be sand-rich soils, and the samples with high CEC and low percentages of quartz were assumed to be clay-rich or clay soils.

Sheppard and Thibault (1990) estimated a cesium default  $K_d$  for sand of 280 mL/g (81 observations ranging from 0.2 to 10,000 mL/g) and a cesium default  $K_d$  for clay of 1,900 mL/g (28 observations ranging from 37 to 31,500). Looney, et al. (1987) estimated a reference SRS soil  $K_d$  of 500 mL/g for cesium from an expected range of 10 to 100,000 mL/g. Kaplan (2006) estimated “reasonably conservative” and “best” cesium  $K_d$  values of 15 and 50 mL/g for sandy subsurface sediment and “reasonably conservative” and “best” cesium  $K_d$  values of 180 and 250 mL/g for clayey subsurface sediment at the SRS. The cesium  $K_d$  values estimated by Kaplan (2006) were based on cesium sorption data of Hoeffner (1985), Bibler and Marson (1992), Johnson (1995), and Goto (2001). As reported in Kaplan (2006), Bibler and Marson (1992) performed batch sorption experiments to measure cesium  $K_d$  values on four soils collected from the E-Area at SRS. Reported cesium  $K_d$  values ranged from 7 to 37 mL/g on these soils. Kaplan (2006) reported that Johnson (1995) performed field tests (squeezed pore water out of aquifer sediment) using subsurface F-Area sediments and measured cesium  $K_d$  values ranging from 5 to 95 mL/g over the pH range of 4.2 to 6.4. The measured cesium  $K_d$  values were very pH dependent and increased with increasing pH. At pH 5.5, Johnson (1995) measured cesium  $K_d$  values ranging from 20 to 35 mL/g. Kaplan (2006) reported that Goto (2001) conducted cesium sorption experiments with 5 SRS sediments of varying clay content. Measured cesium  $K_d$  values ranged from  $21 \pm 7$  to  $225 \pm 51$  mL/g ( $\pm$  95-percent confidence interval) and varied directly with clay content. Sediments with clay content >10 wt% had cesium  $K_d$  values >139 mL/g, and those with clay content <10 wt% had cesium  $K_d$  values ranging from 15 to 73 mL/g.

Measured, estimated, and recommended cesium  $K_d$  values are summarized in Table 2-11. Hoeffner (1985) reported a range of cesium  $K_d$  values for SRS soils ranging from 330 to 1,800 mL/g over a pH range of 3.4 to 7.3 and an expected cesium  $K_d$  of 500 mL/g for a groundwater of typical composition at the SRS burial ground (pH 4.7). McConnell, et al. (1995) reported a measured cesium  $K_d$  value of 37 mL/g for an SRS soil; however, the pH and composition of the water used in the batch sorption experiments were not reported. Elprince, et al. (1977) report measured cesium  $K_d$  values ranging from 18.3 to 40.1 for sand-rich, low CEC surficial sediments from SRS and cesium  $K_d$  values ranging from 83.6 to 130 mL/g for



**Figure 2-9. Measured and Estimated Site-Specific and Generic Iodine  $K_d$  Ranges and Values and Recommended Iodine  $K_d$  Values for Aquifer Units and Confining Units at SRS (Table 2-10). Recommended Iodine  $K_d$  Values Are Associated With Low Uncertainty Due to Available Site-Specific Sorption Data.**

clay-rich, high CEC surficial sediments from SRS. Kaplan (2006) estimated a “reasonably conservative” cesium  $K_d$  of 15 mL/g for sandy subsurface sediments at SRS. This “reasonably conservative”  $K_d$  value was based on site-specific cesium  $K_d$  measurements reported by Bibler and Marson (1992) (7 to 37 mL/g), Johnson (1995) (5 to 95 mL/g), and Goto (2001) (15 to 73 mL/g; sediments with clay content <10 wt%). These values are consistent with the measured site-specific cesium  $K_d$  values reported by Elprince, et al. (1977) for sand-rich surficial sediments (18.3 to 40.1 mL/g), but lower than the range of cesium  $K_d$  values for SRS soils reported by Hoeffner (1985) (330 to 1,800 mL/g). The default cesium  $K_d$  value for sand of 280 mL/g from the compilation of Sheppard and Thibault (1990) and the reference soil cesium  $K_d$  of 500 mL/g estimated by Looney, et al. (1987) are greater than the site specific cesium  $K_d$  values measured by Elprince, et al. (1977), Bibler and Marson (1992), Johnson (1995), and Goto (2001). Based on the measured cesium  $K_d$  values of Elprince, et al. (1997), Bibler and Marson (1992), Johnson (1995), and Goto (2001) and considering the “reasonably conservative” cesium  $K_d$  of 15 mL/g estimated by Kaplan (2006) for sandy subsurface sediments at SRS, a cesium  $K_d$  value of 15 mL/g is recommended for the upper zone of the Upper Three Runs aquifer. The lower zone of the Upper Three Runs aquifer and the Gordon aquifer have reported pH values mainly above 6.0 and 5.7, respectively. Because cesium sorption increases with increasing pH, a cesium  $K_d$  value of 50 mL/g is recommended for these aquifer units. This recommended value lies between cesium  $K_d$  values of 20 to 35 mL/g measured by Johnson (1995) at a pH of 5.5 and the maximum cesium  $K_d$  value of 95 mL/g measured by Johnson (1995) over the pH range of 4.2 to 6.4.

Elprince, et al. (1977) reported measured cesium  $K_d$  values ranging from 83.6 to 130 mL/g for clay-rich, high CEC surficial sediments from SRS. Kaplan (2006) estimated a “reasonably conservative” cesium  $K_d$  of 180 mL/g for clayey subsurface sediments at SRS. This “reasonably conservative”  $K_d$  value was based on site-specific cesium  $K_d$  measurements reported by Goto (2001) (cesium  $K_d$  >139 mL/g for sediments with clay content >10 wt%). The site-specific cesium  $K_d$  values reported by Elprince, et al. (1977) and Goto (2001) are much lower than the cesium  $K_d$  value of 1,900 mL/g recommended by Sheppard and Thibault (1990) for clay. Based on the measured cesium  $K_d$  values of Elprince, et al. (1997) and Goto (2001) and considering the “reasonably conservative” cesium  $K_d$  of 180 mL/g estimated by Kaplan (2006) for clayey subsurface sediments at SRS, a cesium  $K_d$  value of 150 mL/g is recommended for the clay confining units at SRS.

The position of the cesium  $K_d$  values recommended in this review with respect to measured and estimated site-specific and generic cesium  $K_d$  ranges and values is graphically displayed in Figure 2-10. This figure illustrates the uncertainty associated with the cesium  $K_d$  values recommended for SRS aquifer units and clay confining units. Due to available site-specific cesium sorption data (Elprince, et al., 1977; Bibler and Marson, 1992; Johnson, 1995; Goto, 2001), the recommended cesium  $K_d$  values are associated with low uncertainty.

#### **2.4.10 Lead**

Pb-210 has 3 known oxidation states, 0, +2, and +4, and the most common redox state found in the environment is the divalent form. Dissolved lead in natural systems may exist in free ionic form ( $Pb^{2+}$ ) and also as hydrolytic and complex species. At pH values exceeding 7, aqueous lead exists mainly as carbonate complexes [ $Pb(CO_3)_0(aq)$  and  $Pb(CO_3)_2^{2-}$ ]. Studies have shown

**Table 2-11. Measured, Estimated, and Recommended Cesium  $K_d$  Values for Aquifer Sediments and Clay Confining Units at the Savannah River Site**

	Measured Cesium $K_d$ (mL/g)	Test Method	Savannah River Site-Specific “Reasonably Conservative”/ “Best” Estimated Cesium $K_d$ (mL/g)*	Generic Estimated Cesium $K_d$ (mL/g)†	Recommended Cesium $K_d$ (mL/g)
Upper Three Runs Aquifer: Upper	330–1,800‡ 37§ 18.3–130¶ 7–37# 5–95** 15–377††	Batch Batch Batch Batch <i>In situ</i> Batch	15/50	280	15
Tan Clay Confining Unit	—	—	180/250	1,900	150
Upper Three Runs Aquifer: Lower	—	—	15/50	280	50
Gordon Confining Unit	—	—	180/250	1,900	150
Gordon Aquifer	—	—	15/50	280	50

\*Kaplan, D.I. “Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site (U).” WSRC–TR–2006–00004. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company. 2006.

†Sheppard, M.I. and D.H. Thibault. “Default Soil Solid/Liquid Partition Coefficients,  $K_d$ s, for Four Major Soil Types: A Compendium.” *Health Physics*. Vol. 59, No. 4. pp. 471–482. 1990.

‡Hoeffner, S.L. “Radionuclide Sorption on Savannah River Plant Burial Ground Soil—A Summary and Interpretation of Laboratory Data.” DP–1702. Aiken, South Carolina: E.I. du Pont de Nemours and Company, Savannah River Laboratory. 1985.

§McConnell, Jr., J.W., R.D. Rogers, J.D. Jastrow, W.E. Sanford, S.R. Cline, T.M. Sullivan, and M. Fuhrmann. “Results After Ten Years of Field Testing Low-level Radioactive Waste Forms Using Lysimeters.” ANL/ER/CP 95275. Idaho Falls, Idaho: Idaho National Engineering Laboratory. 1995.

¶Elprince, A.M., C.I. Rich, and D.C. Martens. “Effect of Temperature and Hydroxy Aluminum Interlayers on the Adsorption of Trace Radioactive Cesium by Sediments near Water-Cooled Nuclear Reactors.” *Water Resources Research*. Vol. 13, No. 2. pp. 375–380. 1977.

#Bibler, J.P. and D.B. Marson. “Behavior of Mercury, Lead, Cesium, and Uranyl Ions on Four SRS Soils.” WSRC–RP–92–326. Aiken, South Carolina: Westinghouse Savannah River Company. 1992.

\*\*Johnson, W.H. “Sorption Models for U, Cs, and Cd on Upper Atlantic Coastal Plain Soils.” A Thesis Presented to the Academic Faculty at Georgia Institute of Technology, Atlanta, Georgia. 1995.

††Goto, M. “Development of a Quantitative Model for Binding Cesium to SRS soils.” Masters’ Degree Thesis. Georgia Institute of Technology, Atlanta, Georgia. 2001.

that, in neutral to high pH conditions,  $\text{Pb}^{2+}$  can preferentially exchange for  $\text{Ca}^{2+}$  and  $\text{K}^+$  (Zimdahl and Hassett, 1977; Bittel and Miller, 1974). Under acidic pH conditions, hydrogen ions and aluminum ions will displace lead from mineral exchange sites. Lead is known to adsorb onto soil constituent surfaces such as clays, oxides, hydroxides, oxyhydroxides, and organic matter. Lead adsorption studies on bulk soils indicate that the adsorption is strongly correlated with pH and the CEC values of soils (Bittel and Miller, 1974; Griffin and Shimp, 1976; Haji-Djafari, et al., 1981; Scrudato and Estes, 1975; Zimdahl and Hassett, 1977). Properties that affect CEC of soils, such as organic matter content, clay content, and surface area, have a greater effect on lead adsorption than soil pH.

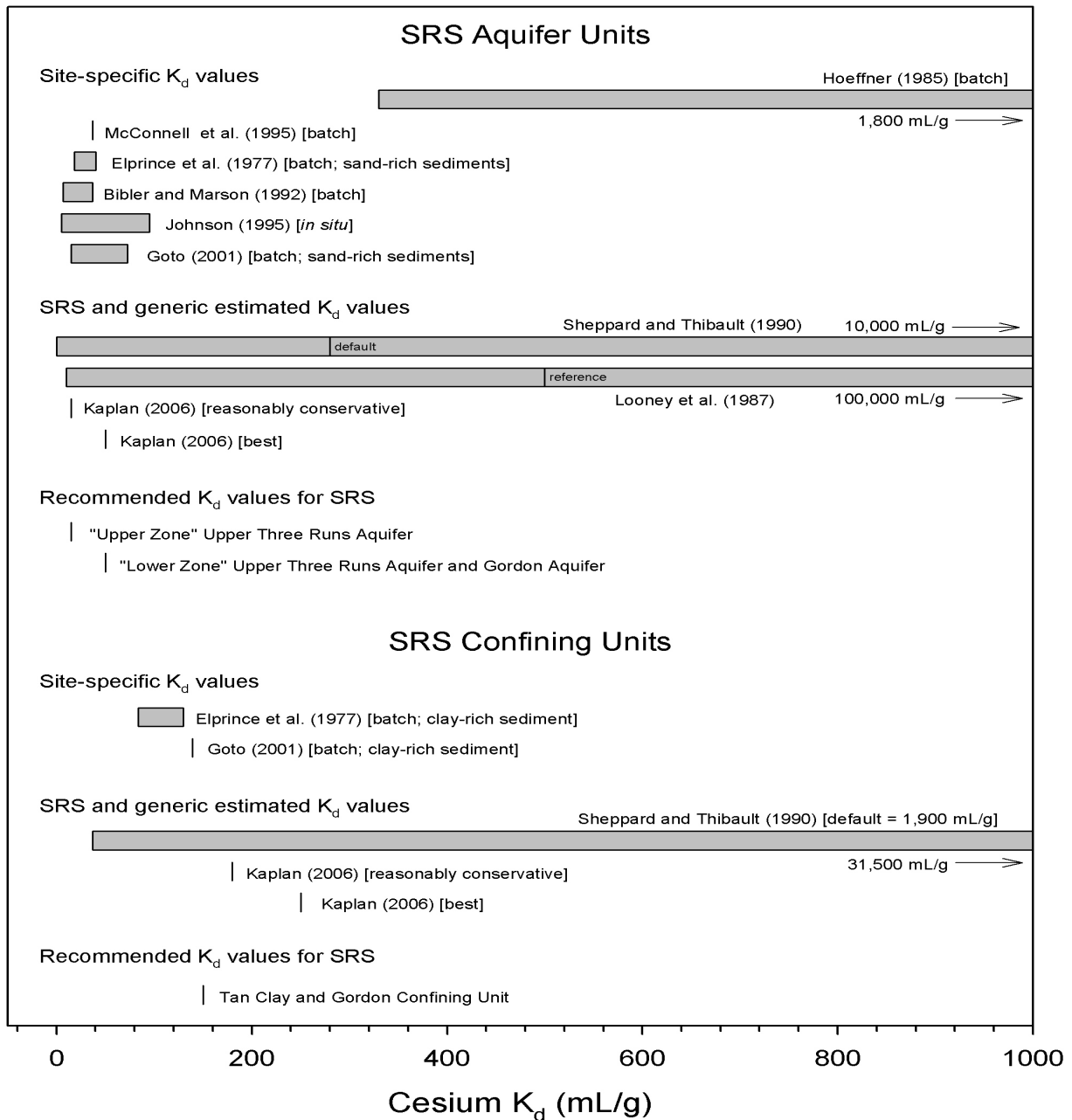
Bibler and Marson (1992) performed batch sorption experiments to measure lead  $K_d$  values on four Savannah River soils collected from the E-Area. Bibler and Marson (1992) reported lead  $K_d$  values ranging from 63 to >2,000,000 mL/g. However, it is likely that these experiments were conducted at concentrations above the solubility limit of lead (e.g., initial  $\text{Pb}^{2+}$  of 5 mg/L), and therefore reflect precipitation more than adsorption.

Kaplan and Serkiz (2000) performed desorption measurements to measure lead  $K_d$  values on shallow contaminated sediments from the TNX Outfall Operable Unit at SRS. The desorption  $K_d$  values were based on extractable portions that were comprised of the exchangeable, organic-bound, amorphous Fe-oxide bound, and water extractable fractions. Basing the  $K_d$  estimates on these extractable fractions instead of the more easily determined total concentrations in the sediment, more conservative and technically defensible  $K_d$  values were measured. The contaminated sediments were collected at depths of 0 to 0.6 m [0 to 2 ft] by hand auger and were composed dominantly of sand and silt (i.e., sand and silt contents ranging from 80 to 94 wt%). The sediment pH of the sediments ranged from 4.00 to 5.78. Measured lead  $K_d$  values ranged from >11,460 to >38,751 mL/g. Over the pH range expected in the subsurface at SRS (5.2 to 7.7), Kaplan and Serkiz (2000) reported lead  $K_d$  values of >34,511 and >11,460 mL/g for sediments with pHs of 5.26 and 5.78, respectively.

Haji-Djafari, et al. (1981) measured lead  $K_d$  values on sandy sediments from the Split Rock Formation in central Wyoming as a function of pH. The  $K_d$  values reported in this study are listed in EPA (1999). Lead  $K_d$  values for pHs of 2.0, 4.5, 5.75, and 7.0 were 20, 100, 1,500, and 4,000 mL/g, respectively. As expected, lead adsorption increased with increasing pH. Gerriste, et al. (1982) examined lead adsorption onto generic soils as a function of pH. Results indicated that lead adsorption increased with increasing soil pH (from 4 to 8). A summary of  $K_d$  values reported by Gerriste, et al. (1982) are also listed in EPA (1999). Lead  $K_d$  values for pHs of 4.5, 5.0, 7.5, and 8.0 were 280; 1,295; 3,000; and 4,000 mL/g, respectively.

Sheppard and Thibault (1990) estimated a lead default  $K_d$  for sand of 270 mL/g (3 observations ranging from 19 to 405 mL/g) and a lead default  $K_d$  for clay of 550 mL/g (based on a soil-to-plant concentration ratio). Looney, et al. (1987) estimated a reference SRS soil  $K_d$  of 100 mL/g for lead from an expected range of 1 to 10,000 mL/g. Kaplan (2006) estimated “reasonably conservative” and “best” lead  $K_d$  values of 500 and 2,000 mL/g for sandy subsurface sediment and “reasonably conservative” and “best” lead  $K_d$  values of 2,500 and 5,000 mL/g for clayey subsurface sediment at the SRS. The Kaplan (2006) estimations were based in part on the measured lead  $K_d$  values reported by Bibler and Marson (1992).





**Figure 2-10. Measured and Estimated Site-Specific and Generic Cesium  $K_d$  Ranges and Values and Recommended Cesium  $K_d$  Values for Aquifer Units and Confining Units at SRS (Table 2-11). Recommended Cesium  $K_d$  Values Are Associated With Low Uncertainty Due to Available Site-Specific Sorption Data.**

Measured, estimated, and recommended lead  $K_d$  values are summarized in Table 2-12. Kaplan and Serkiz (2000) reported lead  $K_d$  values of >34,511 and >11,460 mL/g for contaminated sediments collected at the SRS with pHs of 5.26 and 5.78, respectively. Haji-Djafari, et al. (1981) reported measured lead  $K_d$  values on sandy sediments ranging from 20 to 4,000 mL/g over the pH range of 2.0 to 7.0. At pHs of 5.75 and 7.0, lead  $K_d$  values were 1,500 and 4,000 mL/g, respectively. Gerriste, et al. (1982) reported measured lead  $K_d$  values on generic soils ranging from 280 to 4,000 mL/g over the pH range of 4.5 to 8.0. At a pH of 5.0 and 7.5, lead  $K_d$  values of 1,295 and 3,000 mL/g were reported. The default lead  $K_d$  value for sand of 270 mL/g from the compilation of Sheppard and Thibault (1990) and the reference SRS soil lead  $K_d$  of 100 mL/g estimated by Looney, et al. (1987) are much lower than the lead  $K_d$  values reported by Haji-Djafari, et al. (1981) at pHs of 5.75 and 7.0 (1,500 and 4,000 mL/g, respectively) and by Gerriste, et al. (1982) at pHs of 5.0 and 7.5 (1,295 and 3,000 mL/g, respectively). The “reasonably conservative” lead  $K_d$  value of 500 mL/g estimated by Kaplan (2006) for sandy subsurface sediment at SRS is also lower than the lead  $K_d$  values reported by Haji-Djafari, et al. (1981) at pHs of 5.75 and 7.0 and by Gerriste, et al. (1982) at pHs of 5.0 and

**Table 2-12. Measured, Estimated, and Recommended Lead  $K_d$  Values for Aquifer Sediments and Clay Confining Units at the Savannah River Site**

	Measured Lead $K_d$ (mL/g)	Test Method	Savannah River Site-Specific “Reasonably Conservative”/ “Best” Estimated Lead $K_d$ (mL/g)*	Generic Estimated Lead $K_d$ (mL/g)†	Recommended Lead $K_d$ (mL/g)
Upper Three Runs Aquifer: Upper	63–2.0 × 10 <sup>6</sup> ‡ >11,460– >38,751§	Batch <i>In situ</i>	500/2,000	270	500
Tan Clay Confining Unit	—		2,500/5,000	550	2,500
Upper Three Runs Aquifer: Lower	—		500/2,500	270	1,500
Gordon Confining Unit	—		2,500/5,000	550	2,500
Gordon Aquifer	—		500/2,500	270	1,500

\*Kaplan, D.I. “Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site (U).” WSRC–TR–2006–00004. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company. 2006.

†Sheppard, M.I. and D.H. Thibault. “Default Soil Solid/Liquid Partition Coefficients,  $K_d$ s, for Four Major Soil Types: A Compendium.” *Health Physics*. Vol. 59, No. 4. pp. 471–482. 1990.

‡Bibler, J.P. and D.B. Marson. “Behavior of Mercury, Lead, Cesium, and Uranyl Ions on Four SRS Soils.” WSRC–RP–92–326. Aiken, South Carolina: Westinghouse Savannah River Company. 1992.

§Kaplan, D.I. and S.M. Serkiz. “*In Situ*  $K_d$  Values and Geochemical Behavior for Inorganic and Organic Constituents of Concern at the TNX Outfall Delta.” WSRC–TR–99–00488. Aiken, South Carolina: Westinghouse Savannah River Company. 2000.

7.5 and is significantly lower than site-specific lead  $K_d$  values reported by Kaplan and Serkiz (2000) at pHs of 5.26 and 5.78 (>34,511 and >11,460, respectively). Based on these observations, the “reasonably conservative” lead  $K_d$  value of 500 mL/g recommended for SRS sandy subsurface sediments by Kaplan (2006) is recommended for the upper zone of the Upper Three Runs aquifer. The lower zone of the Upper Three Runs aquifer and the Gordon aquifer have reported pH values above 6.0 and 5.7, respectively. Because lead  $K_d$  values are highly sensitive to pH (i.e., lead  $K_d$  increases significantly with increasing pH), a lead  $K_d$  value of 1,500 mL/g is recommended for the lower zone of the Upper Three Runs aquifer and the Gordon aquifer. This value was approximated for a pH of 6.0 based on the lead  $K_d$  values of 1,500 and 4,000 mL/g reported by Haji-Djafari, et al. (1981) at pHs of 5.75 and 7.0 and the lead  $K_d$  values of 1,295 and 3,000 mL/g reported by Gerriste, et al. (1982) at pHs of 5.0 and 7.5.

Sheppard and Thibault (1990) recommend a default lead  $K_d$  value of 550 mL/g for clay based on a soil-to-plant concentration ratio. Kaplan (2006) estimated a “reasonably conservative” lead  $K_d$  value of 2,500 mL/g for clayey subsurface sediment at the SRS based in part on measured lead  $K_d$  values reported by Bibler and Marson (1992). Lacking additional site specific or generic lead sorption data on clay sediments, the “reasonably conservative” lead  $K_d$  value of 2,500 mL/g estimated by Kaplan (2006) is recommended for clay confining units at SRS.

The position of the lead  $K_d$  values recommended in this review with respect to measured and estimated site-specific and generic lead  $K_d$  ranges and values is graphically displayed in Figure 2-11. This figure illustrates the uncertainty associated with the lead  $K_d$  values recommended for SRS aquifer units and clay confining units. The recommended lead  $K_d$  values are associated with high uncertainty due to wide variation in measured site-specific sorption data. For example, Bibler and Marson (1992) reported lead  $K_d$  values ranging from 2 to 2 million mL/g on soils from the E-Area and Kaplan and Serkiz (2000) measured lead  $K_d$  values ranging from >11,460 to >38,751 on contaminated SRS sediments over the pH range of 4.0 to 5.78.

## 2.4.11 Uranium

In natural environments, the most important oxidation states of uranium are +4 and +6. U(VI) species dominate in oxidizing environments; the dominant species are  $\text{UO}_2^{2+}$  at pH values less than 5 and mixed carbonate/hydroxyl and carbonate species at pH values between 5 and 9 (Langmuir, 1997). In low ionic strength solutions with low U(VI) concentrations,  $\text{UO}_2^{2+}$  concentrations will likely be controlled by cation exchange and adsorption processes. The uranyl ion and its complexes adsorb onto clays (Ames, et al. 1982), organics (Read, et al. 1993; Shanbhag and Choppin, 1981), and oxides (Hsi and Langmuir, 1985; Waite, et al. 1994). As ionic strength increases, other ions, notably  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$ , displace the uranyl ion from soil exchange sites, forcing it into solution. U(VI) retention by soils and rocks in alkaline conditions is poor because of the predominance of neutral and negatively charged species. An increase in  $\text{pCO}_2$  in soil solutions reduces U(VI) adsorption by promoting the formation of poorly sorbing carbonate complexes (Pabalan, et al., 1998). U(IV) species dominate in reducing environments. U(IV) tends to hydrolyze and form strong hydrolytic complexes. U(IV) also forms strong complexes with naturally occurring organic materials.

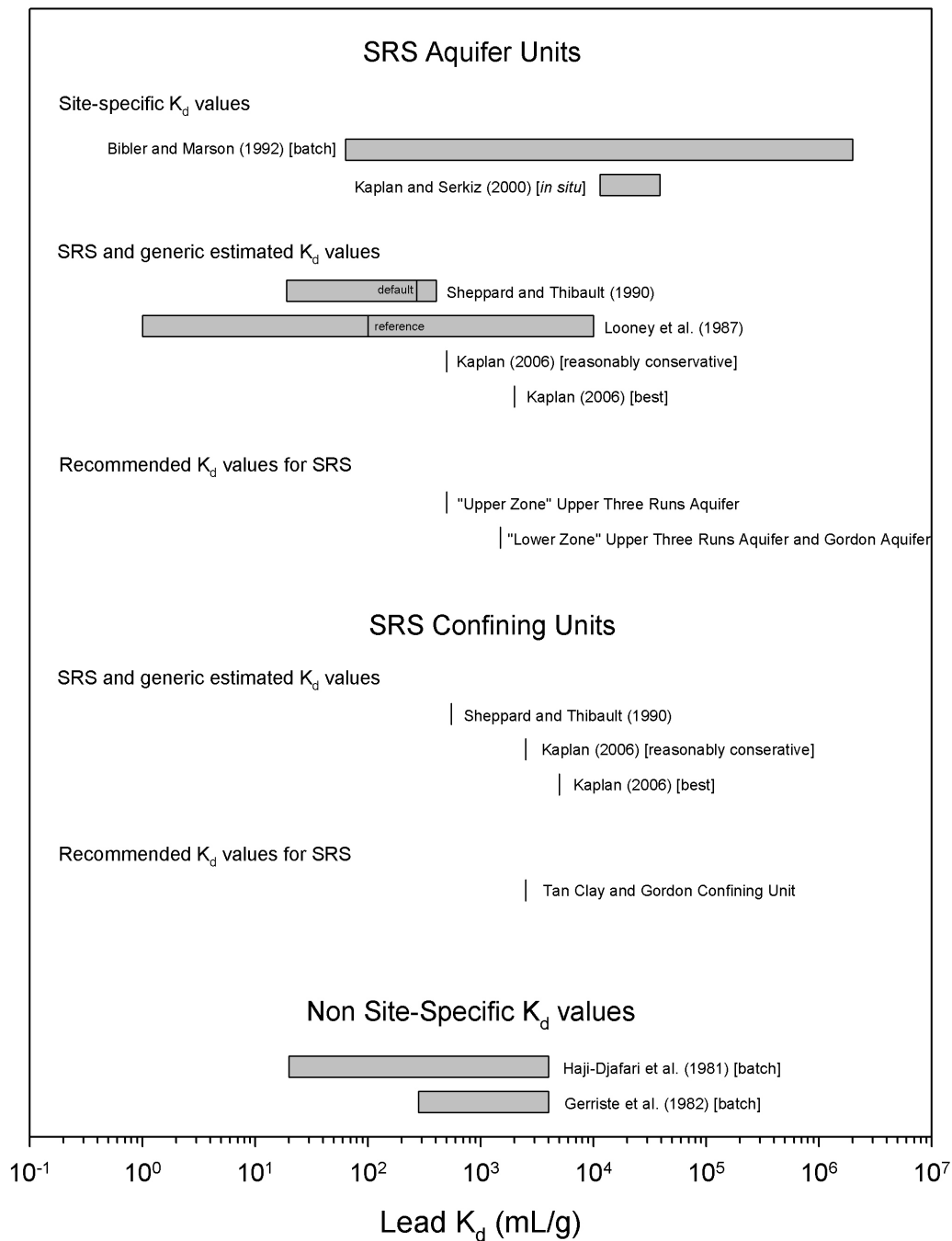
Serkiz and Johnson (1994) investigated the partitioning of uranium on soil in contaminated groundwater downgradient of the F and H Areas Seepage Basins at SRS. Their study tabulated an extensive set of field-derived  $K_d$  values for U-238 and U-235 for 48 soil/porewater samples.

The soil/porewater samples were collected over a range of geochemical conditions (e.g., pH and contaminant concentration). The  $K_d$  values determined by Serkiz and Johnson (1994) are plotted as a function of pH in Figure 2-12. The uranium  $K_d$  values vary from 1.2 to 34,000 mL/g over a pH range of 3 to 6.8. The  $K_d$  values indicate that uranium sorption increases with increasing pH over the range 3 to 5.2. The adsorption of uranium is at a maximum at approximately pH 5.2 and then decreases with increasing pH over the pH range of 5.2 to 6.8. Serkiz and Johnson found that the field-derived  $K_d$  values for U-238 and U-235 were not well correlated with the weight percentage of clay-sized particles or CEC of the soil samples, and they proposed that the uranium was not binding to clays by a cation exchange reaction, but rather to a mineral surface coating with a variable surface charge due to varying porewater pH.

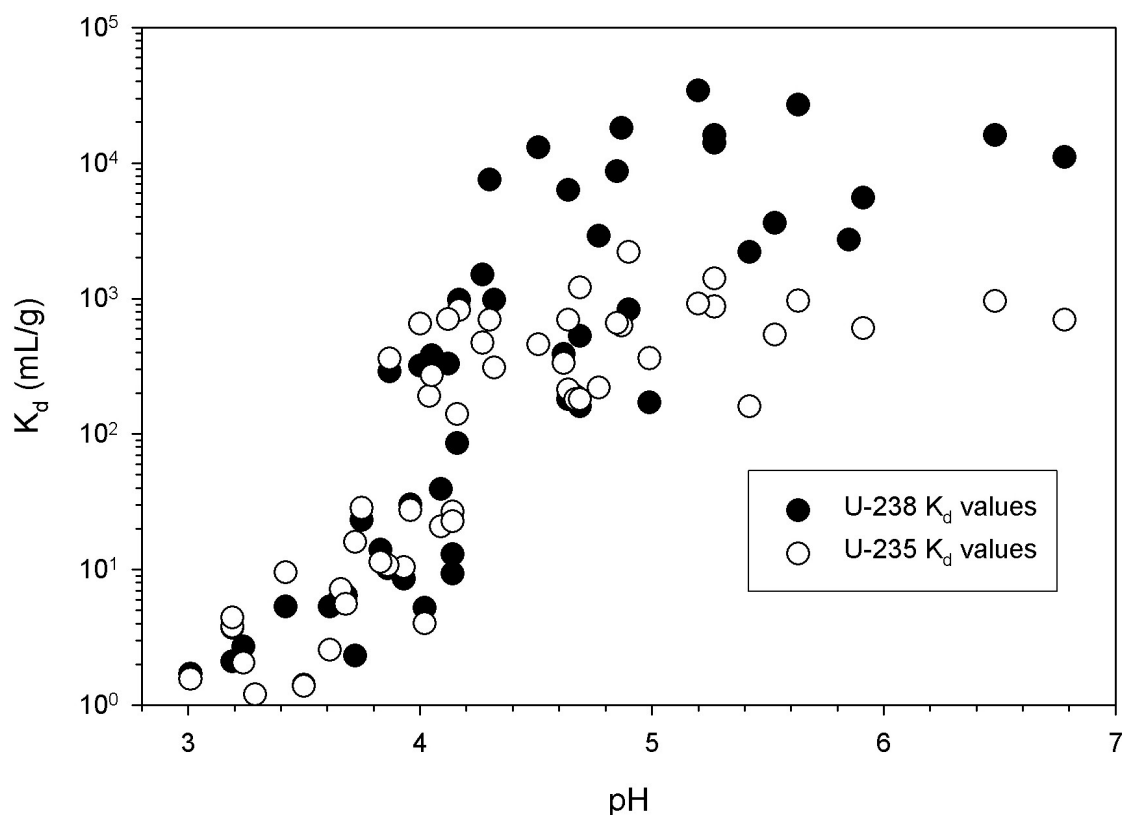
Johnson (1995) conducted field and laboratory studies to determine the processes controlling uranium sorption to SRS sediments. A portion of this work involved determining  $K_d$  values on paired sediment-pore water samples collected within a contaminated plume from the F Area at SRS. Sequential extractions were used to determine uranium concentrations in sediment and pore water uranium concentrations in a saturated past extract. Johnson (1995) reported uranium  $K_d$  values of 87 mL/g at pH 4.7, 100 mL/g at pH 4.75, 37 mL/g at pH 5.05, and 93 mL/g at pH 5.12. Johnson (1995) attributed the lack of a trend in the uranium  $K_d$  values with pH to mineralogical variations in the sampled sediments. Johnson (1995) also performed batch sorption tests using a sandy subsurface F-Area sediment to measure uranium  $K_d$  values as a function of pH. At pHs of 4.82, 4.87, 5.01, and 5.04, Johnson (1995) reported uranium  $K_d$  values of 116, 153, 198, and 238 mL/g, respectively.

Kaplan and Serkiz (2000) performed desorption measurements to measure uranium  $K_d$  values on shallow contaminated sediments from the TNX Outfall Operable Unit at SRS. The desorption  $K_d$  values were based on extractable portions that comprise the exchangeable, organic-bound, amorphous Fe-oxide bound, and water extractable fractions. Basing the  $K_d$  estimates on these extractable fractions instead of the more easily determined total concentrations in the sediment, more conservative and technically defensible  $K_d$  values were measured. The contaminated sediments were collected at depths of 0 to 0.6 m [0 to 2 ft] by hand auger and were composed dominantly of sand and silt (i.e., sand and silt contents ranging from 80 to 94 wt%). The sediment pH of the sediments ranged from 4.00 to 5.78. Measured uranium  $K_d$  values ranged from 170 to 6,493 mL/g. Over the pH range expected in the subsurface at the SRS (5.2 to 7.7), Kaplan and Serkiz (2000) reported uranium  $K_d$  values of 170 and 2,110 mL/g for sediments with pHs of 5.26 and 5.78, respectively.

Barnett, et al. (2000) conducted batch tests to study uranium sorption onto a sediment sample from SRS. The sediment sample was acquired from a depth of 45 m [148 ft] in the McBean Formation (lower zone of the Upper Three Runs aquifer) near the burial ground site. The sediment consisted of 69-wt% sand, 7-wt% silt, and 24-wt% clay. Sand-sized particles were noted to be coated with iron oxides. The sediment had 25.7 g/kg [25,700 ppm] iron, 0.12 g/kg [120 ppm] organic matter, and a pH of 4.1. A 0.01 M NaNO<sub>3</sub> solution that was adjusted to the pH of the solid phase (4.1) was used in adsorption isotherm measurements. Barnett, et al. (2000) reported a  $K_d$  value of  $230 \pm 7$  mL/g ( $\pm$  95-percent confidence interval) for the SRS sediment.



**Figure 2-11. Measured and Estimated Site-Specific and Generic Lead  $K_d$  Ranges and Values and Recommended Lead  $K_d$  Values for Aquifer Units and Confining Units at SRS (Table 2-112). Recommended Lead  $K_d$  Values Are Associated With High Uncertainty Due to Wide Variation in Measured Site-Specific Sorption Data.**



**Figure 2-12. Uranium  $K_d$  Values as a Function of pH From Serkiz and Johnson (1994)**

Sheppard and Thibault (1990) estimated a uranium default  $K_d$  for sand of 35 mL/g (24 observations ranging from 0.03 to 2,200 mL/g) and a uranium default  $K_d$  for clay of 1,600 (7 observations ranging from 46 to 395,100). Looney, et al. (1987) specified a reference SRS soil  $K_d$  of 40 mL/g for uranium from an estimated range of 0.1 to 1,000,000 mL/g. Kaplan (2006) estimated “reasonably conservative” and “best” uranium  $K_d$  values of 100 and 200 mL/g for sandy subsurface sediment and “reasonably conservative” and “best” uranium  $K_d$  values of 150 and 300 mL/g for clayey subsurface sediment at SRS. The uranium  $K_d$  values estimated by Kaplan (2006) were based on the uranium sorption data of Serkiz and Johnson (1994) and Johnson (1995) described previously.

Measured, estimated, and recommended uranium  $K_d$  values are summarized in Table 2-13. Serkiz and Johnson (1994) reported  $K_d$  values for U-238 and U-235 in soil/porewater samples collected from the upper zone of the Upper Three Runs aquifer that ranged from 1.2 to 34,000 mL/g over the pH range of 3 to 6.8 (Figure 2-4). Over the pH range expected in aquifer units beneath SRS (5.2 to 7.7), uranium  $K_d$  values range from about 100 to 34,000 mL/g. Johnson (1995) reported uranium  $K_d$  values in sediment/porewater samples collected from the upper zone of the Upper Three Runs aquifer that ranged from 37 to 100 mL/g over the pH range of 4.7 to 5.12. Johnson (1995) also reported uranium  $K_d$  values measured by batch methods using sandy subsurface F-Area sediment that ranged from 116 to 238 mL/g over the pH range of 4.82 to 5.04. Kaplan and Serkiz (2000) reported uranium  $K_d$  values of 170 and 2,110 mL/g

for contaminated sediments at the SRS with pHs of 5.26 and 5.78, respectively. Barnett, et al. (2000) reported a uranium  $K_d$  value of  $230 \pm 7$  mL/g for a sediment sample acquired from the lower zone of the Upper Three Runs aquifer near the burial ground site. This uranium  $K_d$  value was determined in a solution at low pH (i.e., pH 4.1). Clays in the lower zone of the Upper Three Runs aquifer are dominated by smectite, which has a high CEC capacity, and this may account for the higher minimum uranium  $K_d$  value observed for this single sediment sample from this unit when compared to measured uranium  $K_d$  values reported by Serkiz and Johnson (1994) for the upper zone of the Upper Three Runs aquifer at a similar pH of 4.1. Based on the measured uranium  $K_d$  values reported by Serkiz and Johnson (1994) and Johnson (1995), Kaplan (2006) estimated a “reasonably conservative” uranium  $K_d$  of 100 mL/g for sandy subsurface sediments at SRS. When compared to the uranium sorption data of Serkiz and Johnson (1994) (Figure 2-12), the estimated default uranium  $K_d$  value of 35 mL/g of Sheppard and Thibault (1990) for sand and the estimated uranium  $K_d$  value of 40 mL/g of Looney, et al. (1987) for soil at SRS correspond to measured uranium  $K_d$  values in low pH groundwater (e.g., pH < 4.3). Groundwater in the upper zone of the Upper Three Runs aquifer has an expected minimum pH of 5.2. Based on the uranium sorption data of Serkiz and Johnson (1994) and Johnson (1995), a uranium  $K_d$  value of 100 mL/g is recommended for the upper zone of the Upper Three Runs aquifer. Groundwater in the lower zone of the Upper Three Runs aquifer and the Gordon aquifer have expected pHs of 5.7 to 7.7. Uranium  $K_d$  values tend to reach a maximum at a pH of about 6.5 and then decrease with increasing pH (Pabalan, et al., 1998). Due to the absence of measured site-specific uranium  $K_d$  values at pHs above 6.8, the same value of 100 mL/g is recommended for the lower zone of the Upper Three Runs aquifer and the Gordon aquifer at SRS.

No site-specific uranium sorption data were found for clay confining units at SRS. Sheppard and Thibault (1990) recommended a default uranium  $K_d$  of 1,600 mL/g for clay. Based on the measured uranium  $K_d$  values reported by Serkiz and Johnson (1994), Johnson (1995), and Kaplan (2006) estimated a “reasonably conservative” uranium  $K_d$  of 150 mL/g for clayey subsurface sediments at SRS and this value is recommended for the tan clay unit at SRS. Groundwater in the tan clay confining unit has an expected minimum pH of 5.2, whereas groundwater in the Gordon confining unit has an expected pH range of 5.8 to 6.8 (Table 2-2). Because uranium  $K_d$  values tend to reach a maximum at a pH of about 6.5, a higher uranium  $K_d$  value of 300 mL/g is recommended for the Gordon confining unit. This value corresponds to the “best” uranium  $K_d$  value estimated by Kaplan (2006) for clayey subsurface sediments at SRS.

The position of the uranium  $K_d$  values recommended in this review with respect to measured and estimated site-specific and generic uranium  $K_d$  ranges and values is graphically displayed in Figure 2-13. This figure illustrates the uncertainty associated with the uranium  $K_d$  values recommended for SRS aquifer units and clay confining units. Due to available site-specific uranium sorption data (Serkiz and Johnson, 1994; Johnson (1995); Kaplan and Serkiz, 2000), the recommended uranium  $K_d$  values are associated with low uncertainty.

#### **2.4.12 Neptunium**

Np-237 may exist in several valence states; Np(VI), Np(V), and Np(IV) being the most important in natural waters. Over the pH range of most natural waters, Np(V) is present primarily as the cation  $\text{NpO}_2^+$ . Np(V) aqueous species sorb to some extent to iron oxides and clays, but do not sorb to a major degree on most common minerals. Therefore, dissolved Np(V) is considered to

**Table 2-13. Measured, Estimated, and Recommended Uranium  $K_d$  Values for Aquifer Sediments and Clay Confining Units at the Savannah River Site**

	Measured Uranium $K_d$ (mL/g)	Test Method	Savannah River Site-Specific "Reasonably Conservative"/ "Best" Estimated Uranium $K_d$ (mL/g)*	Generic Estimated Uranium $K_d$ (mL/g)†	Recommended Uranium $K_d$ (mL/g)
Upper Three Runs Aquifer: Upper	1.2–34,000‡ 170–6,493§ 37–100¶ 116–238¶	<i>In situ</i> <i>In situ</i> <i>In situ</i> Batch	100/200	35	100
Tan Clay Confining Unit	—	—	150/300	1,600	150
Upper Three Runs Aquifer: Lower	223–237#	Batch	100/200	35	100
Gordon Confining Unit	—	—	150/300	1,600	300
Gordon Aquifer	—	—	100/200	35	100

\*Kaplan, D.I. "Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site (U)." WSRC-TR-2006-00004. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company. 2006.

†Sheppard, M.I. and D.H. Thibault. "Default Soil Solid/Liquid Partition Coefficients,  $K_d$ s, for Four Major Soil Types: A Compendium." *Health Physics*. Vol. 59, No. 4. pp. 471–482. 1990.

‡Serkiz, S.M. and W.H. Johnson. "Uranium Geochemistry in Soil and Groundwater at the F and H Seepage Basins (U)." EPD-SGS-94-307. Aiken, South Carolina: Westinghouse Savannah River Company. 1994.

§Kaplan, D.I. and S.M. Serkiz. "*In-Situ*  $K_d$  Values and Geochemical Behavior for Inorganic and Organic Constituents of Concern at the TNX Outfall Delta." WSRC-TR-99-00488. Aiken, South Carolina: Westinghouse Savannah River Company. 2000.

¶Johnson, W.H. "Sorption Models for U, Cs, and Cd on Upper Atlantic Coastal Plain Soils." A Thesis Presented to the Academic Faculty at Georgia Institute of Technology, Atlanta, Georgia. 1995.

#Barnett, M.O., P.M. Jardine, S.C. Brooks, and H.M. Selim. "Adsorption and Transport of Uranium(VI) in Subsurface Media." *Soil Science Society American Journal*. Vol. 64. pp. 908–917. 2000.

be relatively mobile in soil systems. Because  $\text{NpO}_2^+$  does not compete favorably with dissolved  $\text{Ca}^{2+}$  and other divalent ions for adsorption sites on soils, the  $K_d$  values for Np(V) are relatively low (Kaplan and Serne, 2000). The adsorption of Np(V) is strongly dependent on pH. Typically, the sorption of Np(V) on iron oxides is negligible at pH values less than 5 and increases rapidly at pH values between 5 and 7. On silicates, the sorption of Np(V) is negligible at pH values less than 6 and increases rapidly at pH values between 6 and 8. This pH dependency is expected for ions present in solution primarily as cations. In carbonate-containing solutions, the adsorption of Np(V) on iron oxides and silicates has been observed to decrease at pH values



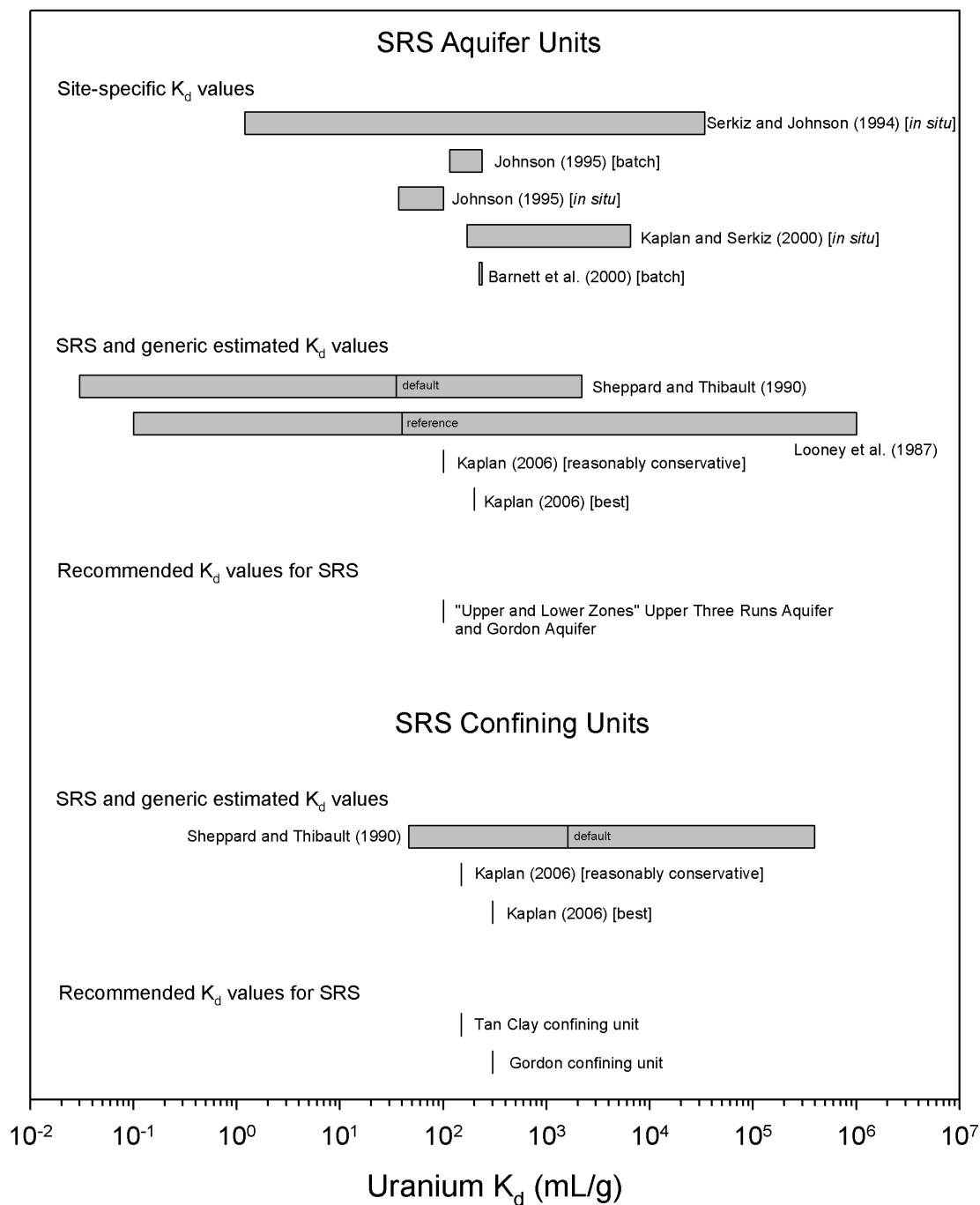
greater than 7 to 9 and 8 to 9, respectively. in response to formation of aqueous Np(V) carbonate complexes. Aqueous organic complexes can enhance Np(V) solubility, but sedimentary organic matter is not known to notably affect Np(V) sorption.

Routson, et al. (1977) used batch equilibrium experiments to measure  $K_d$  values for Np-237 on a South Carolina soil as a function of the concentrations of dissolved calcium and sodium. The location of the soil sample was not revealed, but it could have been collected from SRS. The soil consisted of 3.6-wt% silt and 37.2-wt% clay and had a moderate exchange capacity (2.5 meq/100 g) and a pH of 5.1. The  $K_d$  values were measured in 0.002 and 0.2 M  $\text{Ca}(\text{NO}_3)_2$  solutions and 0.015, 0.03, 0.30, 0.75, and 3.0 M  $\text{NaNO}_3$  solutions. Measured  $K_d$  values for the 0.002 and 0.2 M  $\text{Ca}(\text{NO}_3)_2$  solutions were 0.25 and 0.16 mL/g, respectively. Measured  $K_d$  values for the  $\text{NaNO}_3$  solutions ranged from 0.43 to 0.66 mL/g and decreased with increasing concentration of dissolved sodium.

Nishita, et al. (1981) studied the extractability of Np(V) for several types of soils as a function of pH. For sandy soils with organic matter contents ranging from 2.4 to 5.7 percent, moderate exchange capacities (15 to 20 meq/100 g) and final solution pHs in the range of groundwater pHs expected at SRS (pH 4.1 to 6.8), Nishita, et al. (1981) reported neptunium  $K_d$  values ranging from 3 to 95 mL/g.

Sheppard and Thibault (1990) estimated a neptunium default  $K_d$  for sand of 5 mL/g (16 observations ranging from 0.5 to 390 mL/g) and a neptunium default  $K_d$  for clay of 55 mL/g (4 observations ranging from 0.4 to 2,575). Looney, et al., (1987) specified a reference SRS soil  $K_d$  value of 10 mL/g for neptunium from an estimated range of 0.1 to 1,000 mL/g. Kaplan (2006) estimated “reasonably conservative” and “best” neptunium  $K_d$  values of 0.2 and 0.6 mL/g for sandy subsurface sediment and “reasonably conservative” and “best” neptunium  $K_d$  values of 25 and 35 mL/g for clayey subsurface sediment at the SRS. The neptunium  $K_d$  values estimated by Kaplan (2006) were based on a neptunium sorption study using SRS sediments conducted by Sheppard, et al. (1979). As reported by Kaplan (2006), Sheppard, et al. (1979) measured neptunium  $K_d$  values of 0.25 and 0.16 mL/g for a sediment with a pH of 5.1 and a clay content of 0.5 wt%. Kaplan (2006) indicated that the pH and clay content of the sediment was lower than assumed for typical sandy and clayey sediments used in the  $K_d$  estimations at SRS and, therefore, higher neptunium  $K_d$  values were reported.

Measured, estimated, and recommended neptunium  $K_d$  values are summarized in Table 2-14. Routson, et al. (1977) reported measured neptunium  $K_d$  values ranging from 0.16 to 0.66 mL/g on a South Carolina soil having a pH of 5.1. Nishita, et al. (1981) reported neptunium  $K_d$  values ranging from 3 to 95 mL/g for generic sandy soils over the pH range of 4.1 to 6.8. The estimated neptunium  $K_d$  value of 5 mL/g of Sheppard and Thibault (1990) for sand and the specified reference neptunium  $K_d$  values of 10 mL/g of Looney, et al. (1987) for SRS soil are at the low end of the neptunium  $K_d$  range reported by Nishita, et al. (1981). Based on limited site-specific neptunium  $K_d$  measurements of Sheppard, et al. (1979), Kaplan (2006) estimated a “reasonably conservative” neptunium  $K_d$  value of 0.2 mL/g for sandy subsurface sediments at SRS. This value is in agreement with the measured neptunium  $K_d$  values reported by Routson, et al. (1977) on a South Carolina soil with a pH of 5.1. Like uranium, sorption of neptunium is strongly dependent on pH. Groundwater in the upper zone of the Upper Three Runs aquifer has an expected minimum pH of 5.2. Based on these observations, the “reasonably conservative” neptunium  $K_d$  value of 0.2 mL/g estimated by Kaplan (2006) is recommended for the upper zone of the Upper Three Runs aquifer. Groundwater in the lower zone of the Upper



**Figure 2-13. Measured and Estimated Site-Specific and Generic Uranium  $K_d$  Ranges and Values and Recommended Uranium  $K_d$  Values for Aquifer Units and Confining Units at SRS (Table 2-13). Recommended Uranium  $K_d$  Values Are Associated With Low Uncertainty Due to Available Site-Specific Sorption Data.**

Three Runs aquifer and the Gordon aquifer have expected pH ranges of 6.0 to 7.7 and 5.7 to 7.6, respectively. Neptunium sorption on silicates increases with increasing pH with maximum sorption occurring at a pH of about 8.0 (Bertetti, et al., 1998). Therefore, the “best” neptunium  $K_d$  value of 0.6 mL/g estimated by Kaplan (2006) is recommended for the lower zone of the Upper Three Runs aquifer and the Gordon aquifer at SRS.

No site-specific neptunium sorption data for clay confining units at SRS were found in the literature. Sheppard and Thibault (1990) estimated a default neptunium  $K_d$  value of 55 mL/g for clay. Kaplan (2006) estimated a “reasonably conservative” neptunium  $K_d$  value of 25 mL/g for clayey subsurface sediments at SRS. This “reasonably conservative” value is recommended for clay confining units at SRS.

The position of the neptunium  $K_d$  values recommended in this review with respect to measured and estimated site-specific and generic neptunium  $K_d$  ranges and values is graphically displayed in Figure 2-14. This figure illustrates the uncertainty associated with the neptunium  $K_d$  values recommended for SRS aquifer units and clay confining units. The recommended neptunium  $K_d$  values are associated with high uncertainty due to limited site-specific sorption data. For example, the recommended neptunium  $K_d$  value of 0.2 mL/g for the upper zone of the Upper Three Runs Aquifer based on reported neptunium  $K_d$  values measured by Routson, et al. (1977) on South Carolina soils and two neptunium  $K_d$  values measured by Sheppard, et al. (1979) on SRS sediments. No site-specific neptunium sorption data exists for SRS confining units.

#### **2.4.13 Plutonium**

In the range of pH and conditions typically encountered in natural waters, Pu-239 can exist in all 4 oxidation states, namely +3, +4, +5, and +6. Under oxidizing conditions, Pu(IV), Pu(V), and Pu(VI) are common, whereas under reducing conditions, Pu(III) and Pu(IV) exist. Plutonium is known to adsorb onto soil components such as clays, oxides, hydroxides, oxyhydroxides, aluminosilicates, and organic matter. Depending on the properties of the substrates, pH, and the composition of solutions, plutonium would adsorb with affinities varying from low ( $K_d = 10$  mL/g) to extremely high ( $K_d = 300,000$  mL/g) (Baes and Sharp, 1983; Thibault, et al., 1990). Under conditions of low pH and high concentrations of dissolved organic carbon, it appears that plutonium-organic complexes may control adsorption and mobility of plutonium. At neutral to alkaline pH (>7), dissolved plutonium forms very strong hydroxy-carbonate mixed ligand complexes, resulting in desorption and increased mobility in the environment. Studies have shown the potential importance of colloid-facilitated transport of plutonium in soil systems (Penrose, et al., 1990). Dai, et al. (2002) and Kaplan, et al. (1994) have found that small fractions of total mobile plutonium in SRS sediments are associated with colloids.

A number of studies indicate that iron hydroxides adsorb and reduce Pu(V) and Pu(VI) to a tetravalent state at the solid surface. Fjeld, et al. (2003) have described a conceptual model where plutonium transport through sediment columns is controlled by the net rate of reduction of adsorbed Pu(V) to adsorbed Pu(IV). Field studies have supported this model in SRS vadose zone sediments (Kaplan, et al., 2004). In this model, oxidized plutonium can mobilize as Pu(V), and the Pu(V) can readsorb onto iron-bearing minerals and be slowly reduced to Pu(IV). In this way, kinetic control of plutonium transport can allow a small fraction to move while the bulk of

**Table 2-14. Measured, Estimated, and Recommended Neptunium  $K_d$  Values for Aquifer Sediments and Clay Confining Units at the Savannah River Site**

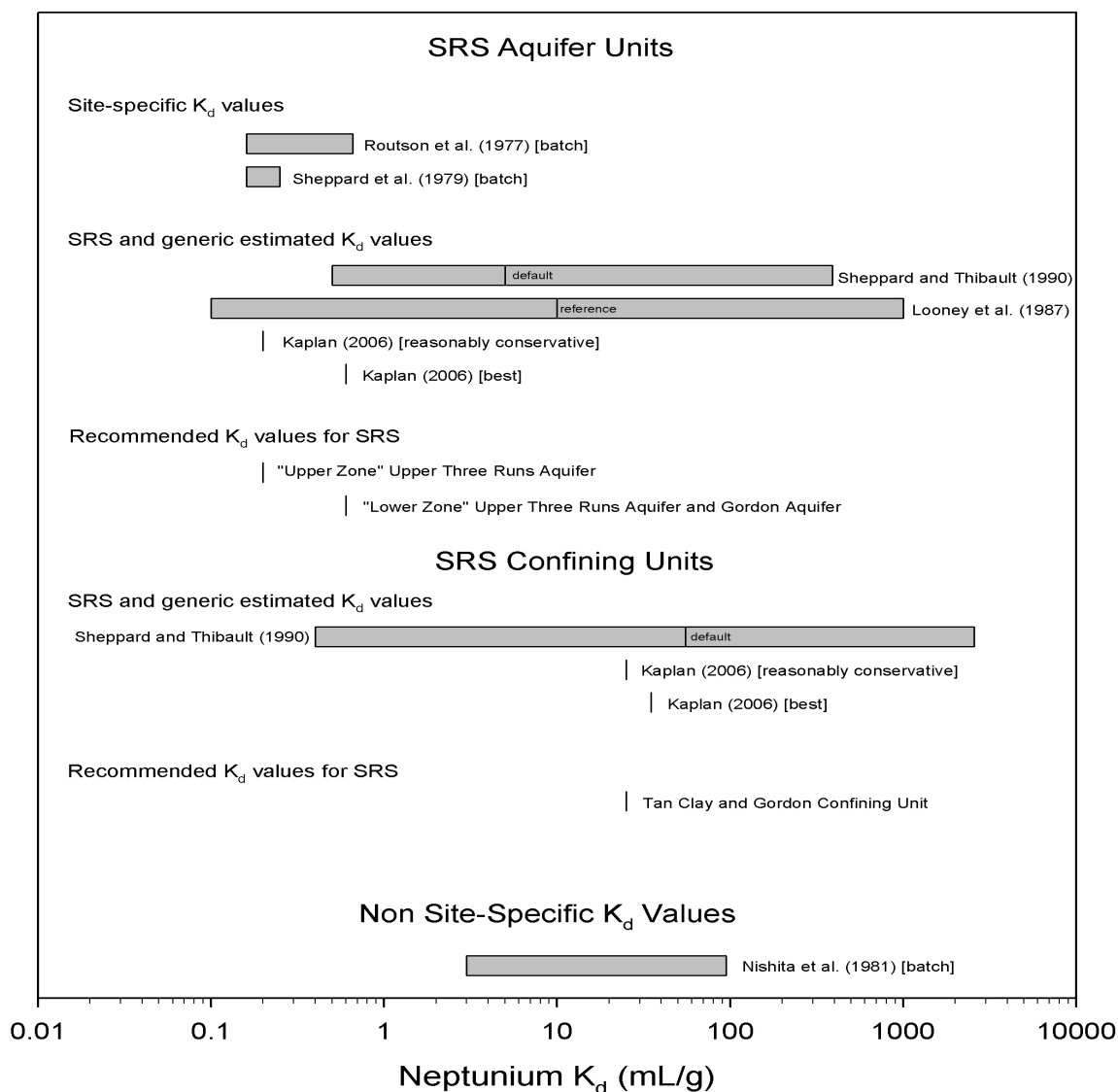
	Measured Neptunium $K_d$ (mL/g)	Test Method	Savannah River Site-Specific "Reasonably Conservative"/ "Best" Estimated Neptunium $K_d$ (mL/g)*	Generic Estimated Neptunium $K_d$ (mL/g)†	Recommended Neptunium $K_d$ (mL/g)
Upper Three Runs Aquifer: Upper	0.16–0.66‡ 0.16–0.25§	Batch Batch	0.2/0.6	5	0.2
Tan Clay Confining Unit	—		25/35	55	25
Upper Three Runs Aquifer: Lower	—		0.2/0.6	5	0.6
Gordon Confining Unit	—		25/35	55	25
Gordon Aquifer	—		0.2/0.6	5	0.6

\*Kaplan, D.I. "Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site (U)." WSRC-TR-2006-00004. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company. 2006.

†Sheppard, M.I. and D.H. Thibault. "Default Soil Solid/Liquid Partition Coefficients,  $K_d$ s, for Four Major Soil Types: A Compendium." *Health Physics*. Vol. 59, No. 4. pp. 471–482. 1990.

‡Routson, R.C., G. Jansen, and A.V. Robinson. "<sup>241</sup>Am, <sup>237</sup>Np, and <sup>99</sup>Tc Sorption on Two United States Subsoils from Differing Weathering Intensity Areas." *Health Physics*. Vol. 33. pp. 311–317. 1977.

§Sheppard, J.C., M.J. Campbell, J.A. Kittrick, and T.L. Hardt. "Retention of Neptunium, Americium, and Curium by Diffusible Soil Particles." *Environmental Science and Technology*. Vol. 13. pp. 680–684. 1979.



**Figure 2-14. Measured and Estimated Site-Specific and Generic Neptunium  $K_d$  Ranges and Values and Recommended Neptunium  $K_d$  Values for Aquifer Units and Confining Units at SRS (Table 2-14). Recommended Neptunium  $K_d$  Values Are Associated With High Uncertainty Due to Limited Site-Specific Sorption Data.**

plutonium is largely immobile. This type of nonequilibrium behavior is difficult to capture with a  $K_d$  approach, but  $K_d$  can be used if the system is assumed to have reached steady state with respect to plutonium redox kinetics.

Prout (1958) studied adsorption of plutonium +3, +4, and +6 redox states on a Savannah River Plant soil as a function of pH. The calculated  $K_d$  ranges were from  $<10$  to  $>10,000$  mL/g for Pu(III);  $\sim 100$  to  $\sim 10,000$  mL/g for Pu(IV); and  $<10$  to  $\sim 3,000$  mL/g for Pu(VI). The large range in values is due to the broad pH range studied. Maximum  $K_d$  values were observed between pH values of about 6.5 to 8.5. Because the initial concentrations of plutonium used in these experiments were about  $10^{-6}$  M, precipitation reactions may have accounted for some of the observed removal of plutonium from solution.

Hoeffner (1985) summarized plutonium sorption studies conducted to determine the performance of the low-level waste burial ground at SRS. The majority of studies used a Savannah River Plant soil taken from depths 2.5–3.0 m [8–10 ft] below grade and a low ionic strength groundwater representative of the burial ground (pH 5.0). Hoeffner (1985) reported expected ranges of Pu(III), Pu(IV), and Pu(VI)  $K_d$  values. Over a pH range of 3.4 to 7.3 and for a groundwater of typical composition at SRS (pH 4.7) (i) Pu(III)  $K_d$  values are expected to range from 800 to  $>10,000$  mL/g and a  $K_d$  value of 8,000 mL/g is expected; (ii) Pu(IV)  $K_d$  values are expected to range from 120 to 7,100 mL/g; and a  $K_d$  of 150 mL/g is expected; and (iii) Pu(VI)  $K_d$  values are expected to range from 7 to 250 mL/g, and a  $K_d$  value of 9 mL/g is expected.

Powell, et al. (2002) performed Pu(V) and Pu(IV) batch tests on sediments collected from SRS as a function of pH and contact time. Sediments were selected to represent end members with respect to sediment properties existing on SRS that were likely to influence plutonium sorption. Characteristics of the sediments are listed in Table 2-15a. Powell, et al. (2002) did not specify the location, depth, or hydrostratigraphic unit from which the sediments were collected. However, based on particle size characteristics, the sandy subsurface and surface sediments are most comparable to aquifer units beneath the GSA, and the clayey subsurface and surface sediments are most comparable to confining units beneath the GSA. All experiments were performed using 0.02 M NaClO<sub>4</sub> solutions. For each sediment,  $K_d$  values for Pu(IV) were determined after 24 hours of reaction, and  $K_d$  values for Pu(V) were determined after 24 hours and 33 days of reaction. The range of plutonium  $K_d$  values measured for all the sediments are listed in Table 2-15b.

Results of the plutonium sorption experiments of Powell, et al. (2002) indicated a general trend of increasing Pu(IV) sorption with increasing pH for all the sediments. Maximum sorption for each sediment was observed at higher pHs (pH  $>6.0$ ). The  $K_d$  values for Pu(V) shifted with time (i.e., from 24 hours to 33 days) to resemble those of Pu(IV) for all the sediments studied, suggesting reduction of Pu(V) to Pu(IV). Stronger sorption to the surface clayey sediment was attributed to the greater surface area and organic matter concentration of this sediment. The plutonium sorption data of Powell, et al. (2002) were analyzed with respect to the pH range of groundwater expected at SRS (pH 5.2 to 7.7). The range of plutonium  $K_d$  values measured for all the sediments at this pH range is listed in Table 2-15c. Examination of the data indicates that the Pu(IV)  $K_d$  values at 24 hours resemble the Pu(V)  $K_d$  values at 33 days except for the surface clayey sediment. For the surface clayey sediment, Pu(V)  $K_d$  values are much greater at 33 days than Pu(IV)  $K_d$  values at 24 hours. Stronger sorption to the surface clayey sediment can again be attributed to the greater surface area and organic matter concentration of this sediment.

<b>Table 2-15a. Characteristics of Sediments in Plutonium Batch Sorption Experiments*</b>				
<b>Sediment</b>	<b>Sand/Silt/Clay (wt%)</b>	<b>Surface Area (m<sup>2</sup>/g)</b>	<b>pH</b>	<b>Organic matter (wt%)</b>
Subsurface Sandy	97/2/1	1.27	5.10	<0.01
Subsurface Clayey	58/30/12	15.31	4.55	Not applicable
Surface Sandy	93/6/1	1.37	4.70	<0.01
Surface Clayey	67/25/8	9.24	5.83	3.2
*Used by Powell, B.A., R.A. Fjeld, J.T. Coates, D.I. Kaplan, and S.M. Serkiz. "Plutonium Oxidation State Geochemistry in the SRS Subsurface Environment (U)." WSRC-TR-2003-00035. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company, Savannah River Site. 2002.				

<b>Table 2-15b. Range of Plutonium K<sub>d</sub> Values Measured With Respect to Sediment Type, Plutonium Oxidation State, and Reaction Time. The pH Range Over Which Measurements Were Collected for Each Sediment Type and Oxidation State Is Also Shown.*</b>			
<b>Sediment</b>	<b>Plutonium Oxidation State</b>	<b>pH Range</b>	<b>Plutonium K<sub>d</sub> Range (mL/g)</b>
Subsurface Sandy	Pu(IV) at 24 hours	1.91–9.28	8–9,300
Subsurface Sandy	Pu(V) at 24 hours	1.81–6.83	6–1,100
Subsurface Sandy	Pu(V) at 33 days	1.91–5.62	3–4,900
Subsurface Clayey	Pu(IV) at 24 hours	1.71–7.91	90–50,000
Subsurface Clayey	Pu(V) at 24 hours	1.67–8.95	4–660
Subsurface Clayey	Pu(V) at 33 days	1.63–8.89	60–10,000
Surface Sandy	Pu(IV) at 24 hours	2.05–10.47	100–1,100
Surface Sandy	Pu(V) at 24 hours	1.90–8.26	7–110
Surface Sandy	Pu(V) at 33 days	1.91–7.86	150–20,000
Surface Clayey	Pu(IV) at 24 hours	1.78–9.95	500–4,600
Surface Clayey	Pu(V) at 24 hours	1.68–9.69	300–2,600
Surface Clayey	Pu(V) at 33 days	1.68–9.15	500–33,000
*Measured in Powell, B.A., R.A. Fjeld, J.T. Coates, D.I. Kaplan, and S.M. Serkiz. "Plutonium Oxidation State Geochemistry in the SRS Subsurface Environment (U)." WSRC-TR-2003-00035. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company, Savannah River Site. 2002.			

Sheppard and Thibault (1990) estimated a plutonium default  $K_d$  for sand of 550 mL/g (39 observations ranging from 27 to 3,600 mL/g) and a plutonium default  $K_d$  for clay of 5,100 mL/g (18 observations ranging from 316 to 190,000). Looney, et al. (1987) estimated a reference SRS soil  $K_d$  value of 100 mL/g for plutonium from an estimated range of 10 to 100,000 mL/g. Kaplan (2006) estimated “reasonably conservative” and “best” plutonium  $K_d$  values of 180 and 270 mL/g for sandy subsurface sediment and “reasonably conservative” and “best” plutonium  $K_d$  values of 2,950 and 5,900 mL/g for clayey subsurface sediment at the SRS. The plutonium  $K_d$  values estimated by Kaplan (2006) were based on the plutonium sorption data of Powell, et al. (2002).

Measured, estimated, and recommended plutonium  $K_d$  values are summarized in Table 2-15d. Hoeffner (1985) reported expected plutonium  $K_d$  ranges for Pu(III) (800 to >10,000 mL/g), Pu(IV) (120 to 7,100 mL/g), and Pu(VI) (7 to 250 mL/g) for SRS soil over a pH range of 3.4 to 7.3. For a groundwater of typical composition at the SRS burial ground (4.7), Hoeffner (1985) reports expected plutonium  $K_d$  value of 8,000 mL/g for Pu(III), 150 mL/g for Pu(IV), and 9 mL/g for

**Table 2-15c. Range of Plutonium  $K_d$  Values Measured in Sediments Over the pH Range of Groundwater Expected at the Savannah River Site (pH 5.2 to 7.7)\***

<b>Sediment</b>	<b>Plutonium Oxidation State</b>	<b>pH Range</b>	<b>Plutonium <math>K_d</math> Range (mL/g)</b>
Subsurface Sandy	Pu(IV) at 24 hrs	5.85–7.70	390–2,800
Subsurface Sandy	Pu(V) at 24 hrs	5.30–6.83	9–1,100
Subsurface Sandy	Pu(V) at 33 days	5.10–5.62	600–4,900
Subsurface Clayey	Pu(IV) at 24 hrs	4.81–6.68	2,100–18,000
Subsurface Clayey	Pu(V) at 24 hrs	5.30–6.02	50–440
Subsurface Clayey	Pu(V) at 33 days	4.95–5.68	4,700–10,000
Surface Sandy	Pu(IV) at 24 hrs	6.73	130
Surface Sandy	Pu(V) at 24 hrs	5.26–6.98	20–110
Surface Sandy	Pu(V) at 33 days	5.26–6.98	270–2,900
Surface Clayey	Pu(IV) at 24 hrs	6.09–6.83	1,000–4,600
Surface Clayey	Pu(V) at 24 hrs	5.10–6.89	1,300–2,600
Surface Clayey	Pu(V) at 33 days	4.67–6.81	8,200–33,000

\*Measured in Powell, B.A., R.A. Fjeld, J.T. Coates, D.I. Kaplan, and S.M. Serkiz. “Plutonium Oxidation State Geochemistry in the SRS Subsurface Environment (U).” WSRC–TR–2003–00035. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company, Savannah River Site. 2002.



Pu(VI). Powell, et al. (2002) reported measured plutonium  $K_d$  values for four different soil types from SRS as a function of pH and contact time. Over the pH range expected at SRS (5.2 to 7.7), the plutonium  $K_d$  range for Pu(IV) at 24 hours ranged from 130 to 18,000 mL/g, the plutonium  $K_d$  range for Pu(V) at 24 hours ranged from 9 to 2,600 mL/g, and the plutonium  $K_d$  range for Pu(V) at 33 days ranged from 270 to 33,000 mL/g. Except for the surface clayey sediment, the  $K_d$  range for Pu(IV) at 24 hours resembled the  $K_d$  range for Pu(V) at 33 days. The expected plutonium  $K_d$  value reported by Hoeffner (1985) for Pu(IV) (150 mL/g) is at the low end of the range of plutonium  $K_d$  values measured by Powell, et al. (2002) for Pu(IV) at 24 hours (130 to 18,000 mL/g) and for Pu(V) at 33 days (270 to 33,000 mL/g). The default plutonium  $K_d$  value of 550 mL/g estimated by Sheppard and Thibault (1990) for sand and the reference plutonium  $K_d$  value of 100 mL/g specified by Looney, et al. (1987) for soil at SRS lie at the low end of the Pu(IV)  $K_d$  range reported by Hoeffner (1985) (120 to 7,100 mL/g) and at the low end of the range of plutonium  $K_d$  values measured by Powell, et al. (2002) for Pu(IV) at 24 hours (130 to 18,000 mL/g) and for Pu(V) at 33 days (270 to 33,000 mL/g). Based on these observations and considering the apparently rapid rate of surface reduction of sorbed Pu(V), a plutonium  $K_d$  value of 250 mL/g is recommended for all the aquifer units at SRS. This value is below the lowest observed Pu(IV) and longer term Pu(V)  $K_d$ s observed by Powell, et al. (2002) for subsurface sandy sediments in the pH range of interest (Table 2-15c). This value is also in agreement with the “reasonably conservative” (180 mL/g) and “best” (270 mL/g) plutonium  $K_d$  values estimated by Kaplan (2006), which are based on the plutonium sorption data of Powell, et al. (2002).

Sheppard and Thibault (1990) estimated a default plutonium  $K_d$  of 5,100 mL/g for clay. Powell, et al. (2002) reports measured Pu(IV) and Pu(V)  $K_d$  ranges on a subsurface clayey and a surface clayey sediment collected at SRS. Although these sediments were collected in the upper zone of the Upper Three Runs aquifer, their mineralogic compositions and high surface areas may be comparable to clay confining units at SRS (see Table 2-15a). Over the pH range expected at SRS (5.2 to 7.7), the plutonium  $K_d$  range for Pu(IV) in these clayey sediments was 1,000 to 18,000 mL/g at 24 hours. The plutonium  $K_d$  range for Pu(V) in the clayey sediments was 4,700 to 33,000 mL/g at 33 days. Based on the Pu(IV)  $K_d$  range at 24 hours and the Pu(V)  $K_d$  range at 33 days and considering the apparently rapid rate of surface reduction of sorbed Pu(V), a plutonium  $K_d$  of 2,500 mL/g is recommended for clay confining units at SRS. This value is in agreement with the “reasonably conservative” plutonium  $K_d$  value of 2,950 mL/g estimated by Kaplan (2006), which is also based on the plutonium sorption data of Powell, et al. (2002).

In the performance assessment for the salt waste facility (Cook, et al., 2005), DOE employed a plutonium sorption model that considered two composite oxidation state species with different sorption properties—Pu(III/IV) and Pu(V/VI)—and calculated species abundance based on kinetic oxidation-reduction rates (Kaplan, 2004). If such an approach were employed, it would be appropriate to use the lowest Powell, et al. (2002) 24-hour sorption coefficients for Pu(IV) and Pu(V) for the pH range of interest for the two composite species (Table 2-15c). Kaplan (2004) summarized the Powell, et al. (2002) data; if Kaplan’s values for appropriately bounding pH (5.25) were lower than those suggested by Table 2-15c, the lower value was selected. Thus, for the plutonium oxidation state model, the following  $K_d$  values are recommended:

- Pu(III/IV) in aquifers (subsurface sandy) = 350 mL/g (Kaplan, 2004, at pH 5.25)  
Pu(V/VI) in aquifers (subsurface sandy) = 9 mL/g (Table 2-15c)

**Table 2-15d. Measured, Estimated, and Recommended Plutonium K<sub>d</sub> Values for Aquifer Sediments and Clay Confining Units at the Savannah River Site**

	Measured Plutonium K <sub>d</sub> (mL/g)	Test Method	Savannah River Site-Specific “Reasonably Conservative”/ “Best” Estimated Plutonium K <sub>d</sub> (mL/g)*	Generic Estimated Plutonium K <sub>d</sub> (mL/g)†	Recommended Plutonium K <sub>d</sub> (mL/g)
Upper Three Runs Aquifer: Upper					
Pu(III)	10–10,000‡ 800–10,000§	Batch Batch			
Pu(IV)	100–10,000‡ 120–7,100§ 8–50,000¶	Batch Batch Batch			
Pu(V)	3–33,000¶	Batch			
Pu(VI)	10–3,000‡ 7–250§	Batch Batch	180/270	550	250
Pu(total)					
Tan Clay Confining Unit	—		2,950/5,900	5,100	2,500
Upper Three Runs Aquifer: Lower	—		180/270	550	250
Gordon Confining Unit	—		2,950/5,900	5,100	2,500
Gordon Aquifer	—		180/270	550	250

\*Kaplan, D.I. “Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site (U).” WSRC–TR–2006–00004. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company. 2006.

†Sheppard, M.I. and D.H. Thibault. “Default Soil Solid/Liquid Partition Coefficients, K<sub>d</sub>s, for Four Major Soil Types: A Compendium.” *Health Physics*. Vol. 59, No. 4. pp. 471–482. 1990.

‡Prout, W.E. “Adsorption of Radioactive Wastes by Savannah River Plant Soil.” *Soil Science*. Vol. 84. pp. 13–17. 1958.

§Hoeffner, S.L. “Radionuclide Sorption on Savannah River Plant Burial Ground Soil—A Summary and Interpretation of Laboratory Data.” DP–1702. Aiken, South Carolina: E.I. du Pont de Nemours and Company, Savannah River Laboratory. 1985.

¶Powell, B.A., R.A. Fjeld, J.T. Coates, D.I. Kaplan, and S.M. Serkiz. “Plutonium Oxidation State Geochemistry in the SRS Subsurface Environment (U).” WSRC–TR–2003–00035. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company, Savannah River Site. 2002.

- Pu(III/IV) in confining units (subsurface clayey) = 2,100 mL/g (Table 2-15c)  
Pu(V/VI) in confining units (subsurface clayey) = 50 mL/g (Table 2-15c)

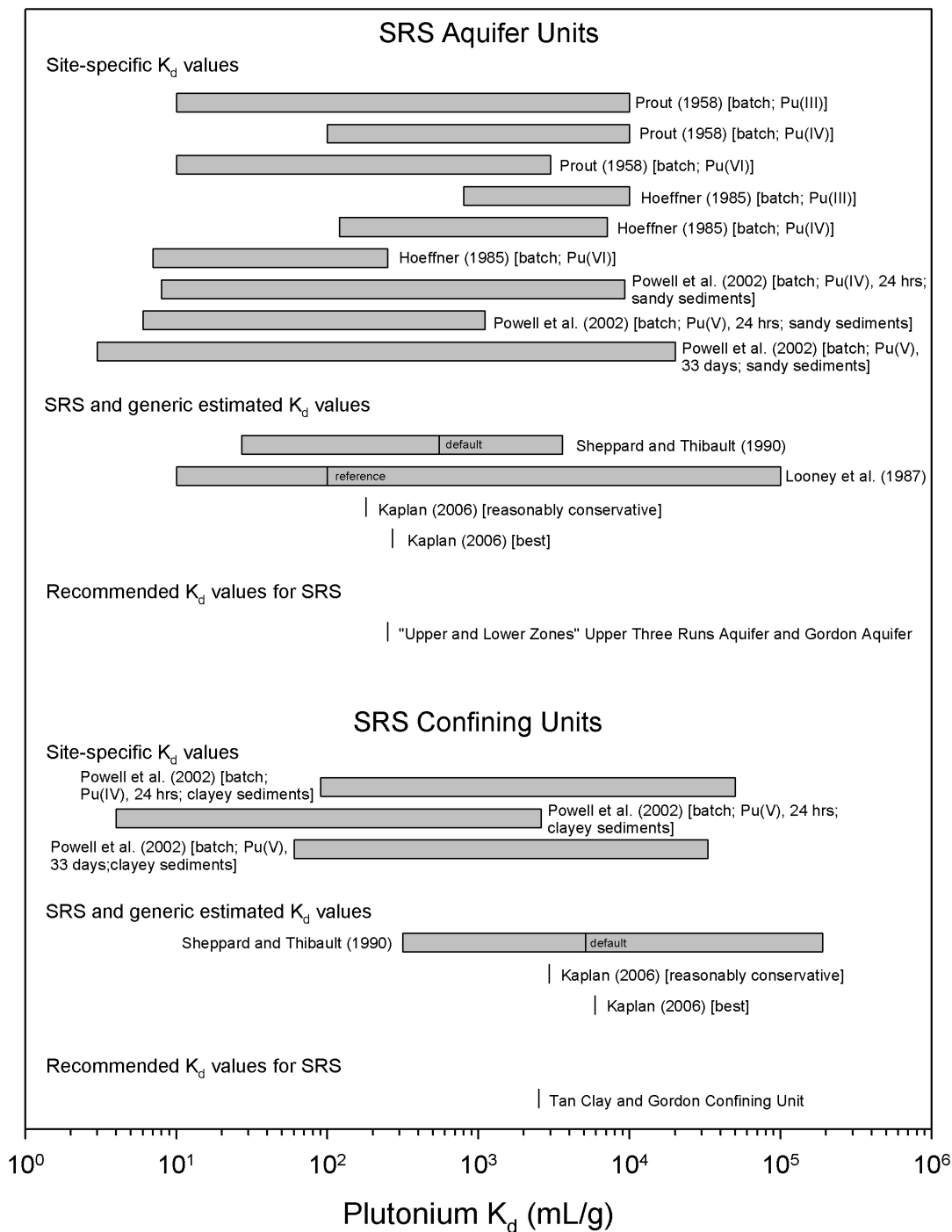
The position of the plutonium  $K_d$  values recommended in this review with respect to measured and estimated site-specific and generic plutonium  $K_d$  ranges and values is graphically displayed in Figure 2-15. This figure illustrates the uncertainty associated with the plutonium  $K_d$  values recommended for SRS aquifer units and clay confining units. Due to available site-specific plutonium sorption data (Hoeffner, 1985; Powell, et al., 2002), the recommended plutonium  $K_d$  values are associated with low uncertainty.

#### 2.4.14 Americium

Am-241 can exist in the +3, +4, +5, and +6 valence states, but americium predominantly occurs as Am(III) in natural environments. Sorption studies indicate that Am(III) readily sorbs to minerals, crushed rock, and soil materials and, along with plutonium, is considered one of the most immobile actinide elements in the environment (Lu, et al., 1998; Ticknor, et al., 1996). Based on studies of Am(III) on single mineral phases and crushed rock, the adsorption of Am(III) is strongly pH dependent and increases with increasing pH with peak adsorption occurring between pH values of 5 and 6. This observed pH dependence is expected, because the dominant aqueous species of americium in the pH range of natural waters are primarily  $\text{Am}^{3+}$  and cationic carbonate complexes at acidic and basic pH values, respectively. High levels of soil organic matter can enhance americium mobility (Artinger, et al., 1998; Schuessler, et al., 2000; Ticknor, et al., 1996). In soil environments, clay minerals are expected to control americium sorption, and  $K_d$  values are expected to correlate with CEC. Studies have shown the potential importance of colloid-facilitated transport of americium in soil systems (Penrose, et al., 1990). Kaplan, et al. (1994) found that small fractions of total mobile americium in SRS sediments are associated with colloids.

Routson, et al., (1977) used batch equilibrium experiments to determine  $K_d$  values for Am-241 on a subsoil sample from South Carolina as a function of solution concentration of calcium ( $\text{Ca}^{2+}$ ) and of sodium ( $\text{Na}^+$ ). The exact location of the South Carolina soil used in this study was not revealed, but it could have been collected at SRS. The soil had a moderate exchange capacity (2.5 meq/100 g), a pH of 5.1, and consisted of 3.6-wt% silt and 37.2-wt% clay. The americium  $K_d$  values were determined in 0.002, 0.02, 0.05, 0.1, and 0.2 M  $\text{Ca}(\text{NO}_3)_2$  solutions and 0.015, 0.03, 0.3, 0.75, and 3.0 M  $\text{NaNO}_3$  solutions. The pH values for selected samples of the americium solutions in the calcium and sodium systems were 7.1 and 6.1. For the solution concentrations used in the experiments, the  $K_d$  values for americium ranged from 1.0 to 67 mL/g as a function of dissolved calcium and 1.6 to 280 mL/g as a function of dissolved sodium.  $K_d$  values decreased in all cases with increasing solution concentrations of calcium and sodium.

Sheppard and Thibault (1990) suggested an americium default  $K_d$  for sand of 1,900 mL/g (29 observations ranging from 8.2 to 300,000 mL/g) and an americium default  $K_d$  for clay of 8,400 mL/g (11 observations ranging from 25 to 400,000). Looney, et al. (1987) estimated a reference SRS soil  $K_d$  value of 100 mL/g for americium from an estimated range of 1 to 100,000 mL/g. Kaplan (2006) estimated “reasonably conservative” and “best” americium  $K_d$  values of 550 and 1,100 mL/g for sandy subsurface sediment and “reasonably conservative” and “best” americium  $K_d$  values of 4,250 and 8,500 mL/g for clayey subsurface sediment at the SRS. The Kaplan (2006) estimations are based on reported cerium  $K_d$  values measured on



**Figure 2-15. Measured and Estimated Site-Specific and Generic Plutonium  $K_d$  Ranges and Values and Recommended Plutonium  $K_d$  Values for Aquifer Units and Confining Units at SRS (Table 2-15d). Recommended Plutonium  $K_d$  Values Are Associated With Low Uncertainty Due to Available Site-Specific Sorption Data.**

SRS sandy and clayey sediments by Kaplan and Serkiz (2004). Kaplan (2006) used cerium as a chemical analog for americium; both cerium and americium are trivalent cations. At a pH of 5.3, Kaplan and Serkiz (2004) reported a cerium  $K_d$  of 1,220 mL/g for SRS sandy sediment and a cerium  $K_d$  of 8,697 mL/g for SRS clayey sediment. Kaplan and Serkiz (2004) also measured europium  $K_d$  values on the SRS sandy and clayey sediments. Both europium and cerium are trivalent cations and had similar  $K_d$  values for the given SRS sediments. At a pH of 5.3, Kaplan and Serkiz (2004) reported a europium  $K_d$  of 1,168 mL/g for SRS sandy sediment and a europium  $K_d$  of 9,020 mL/g for the SRS clayey sediment.

Measured, estimated, and recommended americium  $K_d$  values are summarized in Table 2-16. Routson, et al. (1977) reported measured americium  $K_d$  values ranging from 1.0 to 280 for a soil from South Carolina as a function of  $\text{Ca}^{2+}$  and  $\text{Na}^+$  solution concentration. The pH values of selected samples of solutions used in the americium sorption experiments were 6.1 and 7.1. Routson, et al. (1977) reported that measured americium  $K_d$  values increased with decreasing calcium and sodium concentration. At the low concentrations of  $\text{Ca}^{2+}$  and  $\text{Na}^+$  expected in groundwater at SRS, americium  $K_d$  values in sediments at SRS would most likely correspond to the high end of the americium  $K_d$  range reported by Routson, et al. (1977). The default americium  $K_d$  of 1,900 mL/g for sand estimated by Sheppard and Thibault (1990) is much greater than the reported americium  $K_d$  values of Routson, et al. (1977). The reference americium  $K_d$  value of 100 mL/g estimated by Looney, et al. (1987) for soil at SRS is within the range of measured americium  $K_d$  values reported by Routson, et al. (1977). Kaplan (2006) estimated a “reasonably conservative” americium  $K_d$  value of 550 mL/g for sandy subsurface sediments at SRS based on measured cerium  $K_d$  values reported by Kaplan and Serkiz (2004). The “reasonably conservative” americium  $K_d$  value of Kaplan (2006) is slightly higher than the americium  $K_d$  values reported by Routson, et al. (1977). The mineral compositions of the aquifer units at SRS are not significantly different and, thus, should not affect americium sorption. Sorption of americium is strongly pH dependent with maximum sorption occurring at pHs between 5 and 6. These pHs correspond to the minimum pHs of all the aquifer units at SRS. As indicated above, due to the low  $\text{Ca}^{2+}$  and  $\text{Na}^+$  content of the groundwater at SRS, americium  $K_d$  values for sediments at SRS would most likely correspond to the high end of the americium  $K_d$  range reported by Routson, et al. (1977). Therefore, an americium  $K_d$  value of 250 is recommended for the upper zone of the Upper Three Runs aquifer at SRS. Groundwater in the lower zone of the Upper Three Runs aquifer and the Gordon aquifer have minimum expected pHs of 6.0 and 5.7, respectively, but in the absence of a more quantitative pH dependence, the same 250 mL/g value is recommended for the lower zone of the Upper Three Runs aquifer and the Gordon aquifer at SRS. The use of the high Sheppard and Thibault (1990) value of 1,900 mL/g would be qualitatively inconsistent with observations of some degree of dissolved americium mobility in the F Area (Kaplan, et al., 1994).

Sheppard and Thibault (1990) estimated a default americium  $K_d$  of 8,400 mL/g for clay. Kaplan (2006) estimated a “reasonably conservative” americium  $K_d$  value of 4,250 mL/g for clayey subsurface sediments at SRS based on measured cerium  $K_d$  values reported by Kaplan and Serkiz (2004). Both cerium and americium are trivalent cations and Kaplan (2006) used cerium as a chemical analog for americium. Lacking site-specific americium sorption data for clay sediments, the “reasonably conservative” americium  $K_d$  value of 4,250 mL/g estimated by Kaplan (2006) is recommended for clay confining units at SRS.

**Table 2-16. Measured, Estimated, and Recommended Americium  $K_d$  Values for Aquifer Sediments and Clay Confining Units at the Savannah River Site**

	Measured Americium $K_d$ (mL/g)	Test Method	Savannah River Site-Specific "Reasonably Conservative"/ "Best" Estimated Americium $K_d$ (mL/g)*	Generic Estimated Americium $K_d$ (mL/g)†	Recommended Americium $K_d$ (mL/g)
Upper Three Runs Aquifer: Upper	1–280‡	Batch	550/1,100	1,900	250
Tan Clay Confining Unit	—		4,250/8,500	8,400	4,250
Upper Three Runs Aquifer: Lower	—		550/1,100	1,900	250
Gordon Confining Unit	—		4,250/8,500	8,400	4,250
Gordon Aquifer	—		550/1,100	1,900	250

\*Kaplan, D.I. "Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site (U)." WSRC-TR-2006-00004. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company. 2006.

†Sheppard, M.I. and D.H. Thibault. "Default Soil Solid/Liquid Partition Coefficients,  $K_d$ s, for Four Major Soil Types: A Compendium." *Health Physics*. Vol. 59, No. 4. pp. 471–482. 1990.

‡Routson, R.C., G. Jansen, and A.V. Robinson. "<sup>241</sup>Am, <sup>237</sup>Np, and <sup>99</sup>Tc Sorption on Two United States Subsoils from Differing Weathering Intensity Areas." *Health Physics*. Vol. 33. pp. 311–317. 1977.

The position of the americium  $K_d$  values recommended in this review with respect to measured and estimated site-specific and generic americium  $K_d$  ranges and values is graphically displayed in Figure 2-16. This figure illustrates the uncertainty associated with the americium  $K_d$  values recommended for SRS aquifer units and clay confining units. The recommended americium  $K_d$  values are associated with high uncertainty due to the lack of site-specific sorption data.

#### 2.4.15 Curium

Cm-243 is a transuranic (actinide) element, and exists in the +3 oxidation state in natural waters. Curium is quite similar geochemically to americium (Guillaumont, et al., 2003). The dominant aqueous species of curium in the pH range of natural waters are primarily cations such as  $\text{Cm}^{3+}$  and Cm(III) carbonate complexes at acidic and basic pH values, respectively. Available curium sorption studies indicate that sorption of curium is strongly pH dependent and increases with increasing pH with maximum adsorption occurring between pH values of 5 and 6. Compared to other actinides, curium is considered to be immobile in soil environments, and exhibits high  $K_d$  values. However, the tendency of curium, like americium, to strongly adsorb to

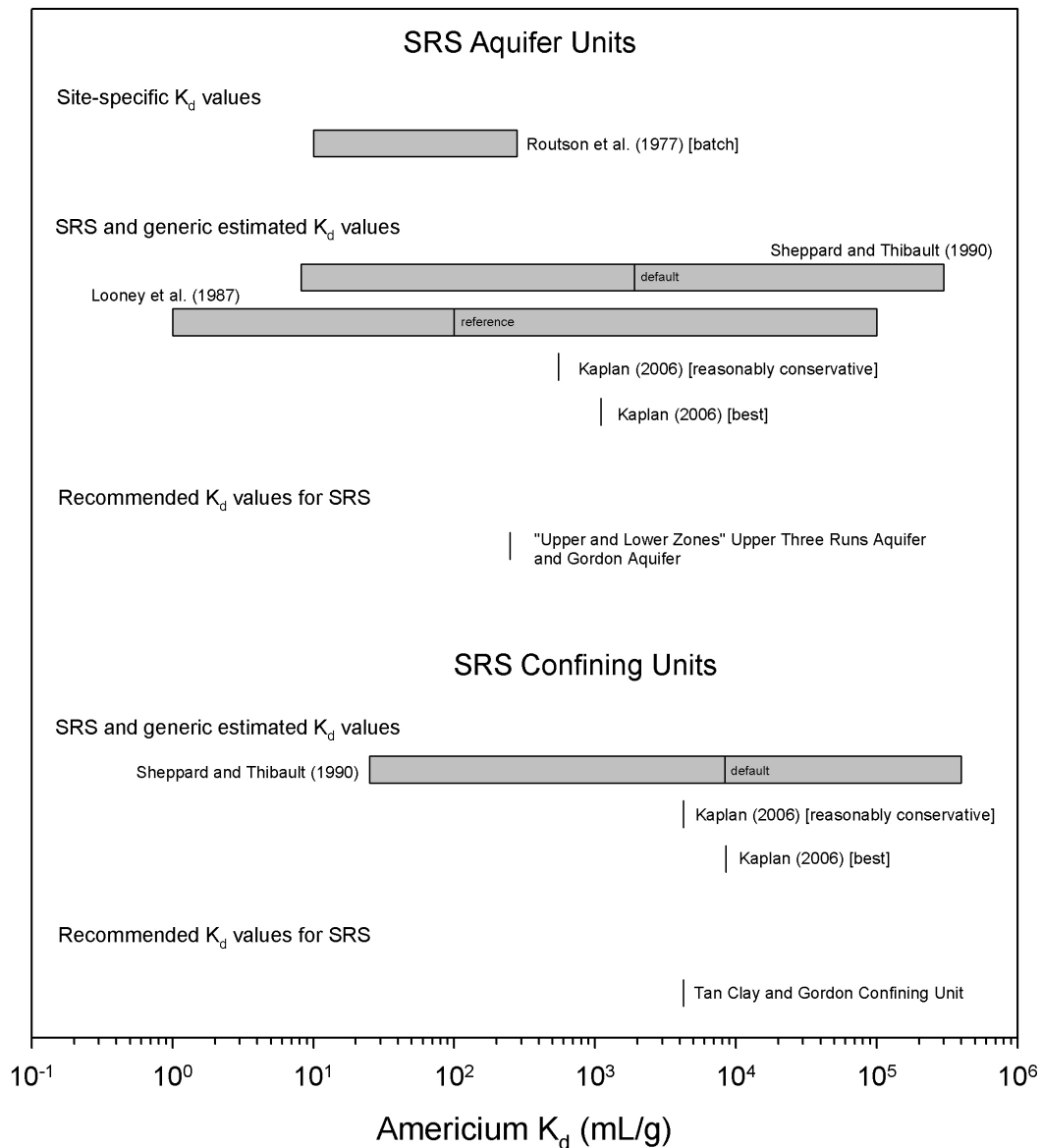
soil particles indicates that there is potential for colloid-facilitated transport of curium. Kaplan, et al. (1994) found that small fractions of total mobile curium in SRS sediments are associated with colloids.

Using cerium (a trivalent cation) as an analog to curium, Kaplan and Serkiz (2000) estimated curium  $K_d$  values ranging from 255 to 4,074 mL/g on contaminated sediments at SRS. Kaplan and Serkiz (2000) performed desorption measurements to measure cerium  $K_d$  values on shallow contaminated sediments from the TNX Outfall Operable Unit at SRS. The desorption  $K_d$  values were based on extractable portions that comprise the exchangeable, organic-bound, amorphous Fe-oxide bound, and water extractable fractions. Basing the  $K_d$  estimates on these extractable fractions instead of the more easily determined total concentrations in the sediment, more conservative and technically defensible  $K_d$  values were measured. The contaminated sediments were collected at depths of 0 to 0.6 m [0 to 2 ft] by hand auger and were composed dominantly of sand and silt (i.e., sand and silt contents ranging from 80 to 94 wt%). The sediment pH of the sediments ranged from 4.00 to 5.78. Measured cerium  $K_d$  values ranged from 255 to 4,074 mL/g.

Nishita, et al. (1981) studied the extractability of Cm-244 for several types of soils as a function of pH. For sandy soils with organic matter contents ranging from 2.4 to 5.7 wt%, moderate CEC (15 to 20 meq/100 g) and final solution pHs ranging from 4.39 to 6.17, Nishita, et al. (1981) reported curium  $K_d$  values ranging from 186 to 23,350 mL/g.

Sheppard and Thibault (1990) suggested a curium default  $K_d$  for sand of 4,000 mL/g (2 observations ranging from 780 to 22,970 mL/g) and a curium default  $K_d$  for clay of 6,000 (based on a soil-to-plant concentration ratio). Looney, et al., (1987) estimated a reference SRS soil  $K_d$  value of 3,160 mL/g for curium from an estimated range of 100 to 100,000 mL/g. Kaplan (2006) estimated “reasonably conservative” and “best” curium  $K_d$  values of 550 and 1,100 mL/g for sandy subsurface sediment and “reasonably conservative” and “best” curium  $K_d$  values of 4,250 and 8,500 mL/g for clayey subsurface sediment at the SRS. The Kaplan (2006) estimations were based on reported cerium  $K_d$  values measured on SRS sandy and clayey sediments by Kaplan and Serkiz (2004). Due to similarities in aqueous chemistry, the sorptive characteristics of curium on sandy and clayey sediments at SRS are expected to be very similar to those of cerium. At a pH of 5.3, Kaplan and Serkiz (2004) reported a cerium  $K_d$  of 1,220 mL/g for SRS sandy sediment and a cerium  $K_d$  of 8,697 mL/g for SRS clayey sediment. Kaplan and Serkiz also measured europium  $K_d$  values on the SRS sandy and clayey sediments. Both europium and cerium are trivalent cations and had similar  $K_d$  values for the given SRS sediments. At a pH of 5.3, Kaplan and Serkiz (2004) reported a europium  $K_d$  of 1,168 mL/g for SRS sandy sediment and a europium  $K_d$  of 9,020 mL/g for the SRS clayey sediment.

Recommended and estimated curium  $K_d$  values are summarized in Table 2-17. Using cerium (a trivalent cation) as an analog to curium, Kaplan and Serkiz (2000) estimated curium  $K_d$  values ranging from 255 to 4,074 mL/g on contaminated sediments at SRS. Likewise, Kaplan (2006) estimated a “reasonably conservative” curium  $K_d$  value of 550 mL/g for sandy subsurface sediments at SRS based on measured cerium  $K_d$  values reported by Kaplan and Serkiz (2004). Nishita, et al. (1981) reported curium  $K_d$  values ranging from 186 to 23,350 mL/g for generic soils over the pH range of 4.39 to 6.17. The default curium  $K_d$  value of 4,000 mL/g estimated by Sheppard and Thibault (1990) for sand and the reference curium  $K_d$  of 3,160 mL/g specified



**Figure 2-16. Measured and Estimated Site-Specific and Generic Americium  $K_d$  Ranges and Values and Recommended Americium  $K_d$  Values for Aquifer Units and Confining Units at SRS (Table 2-16). Recommended Americium  $K_d$  Values Are Associated With High Uncertainty Due to the Lack of Site-Specific Sorption Data.**



by Looney, et al. (1987) for soil at SRS are within the curium  $K_d$  range reported by Nishita, et al. (1981). However, these values are at the high end of the curium  $K_d$  ranges estimated by Kaplan and Serkiz (2000) for SRS contaminated soils (255 to 4,074 mL/g) and are greater than the “reasonably conservative” curium  $K_d$  value of 550 mL/g estimated by Kaplan (2006). Based on the estimated curium  $K_d$  values of Kaplan and Serkiz (255 to 4,074 mL/g) and considering the “reasonably conservative” curium  $K_d$  value of 550 mL/g estimated by Kaplan (2006), a curium  $K_d$  value of 300 mL/g is recommended for aquifer units at SRS. The use of the high Sheppard and Thibault (1990) value of 4,000 mL/g for the aquifer units would be qualitatively inconsistent with observations of some degree of dissolved curium mobility in the F Area (Kaplan, et al., 1994).

Sheppard and Thibault (1990) estimated a default curium  $K_d$  of 6,000 mL/g for clay. Kaplan (2006) estimated a “reasonably conservative” curium  $K_d$  value of 4,250 mL/g for clayey subsurface sediments at SRS based on measured cerium  $K_d$  values reported by Kaplan and Serkiz (2004). Both cerium and curium are trivalent cations and Kaplan (2006) used cerium as a chemical analog for curium. Lacking site-specific curium sorption data for clay sediments, the “reasonably conservative” curium  $K_d$  value of 4,250 mL/g estimated by Kaplan (2006) is recommended for clay confining units at SRS.

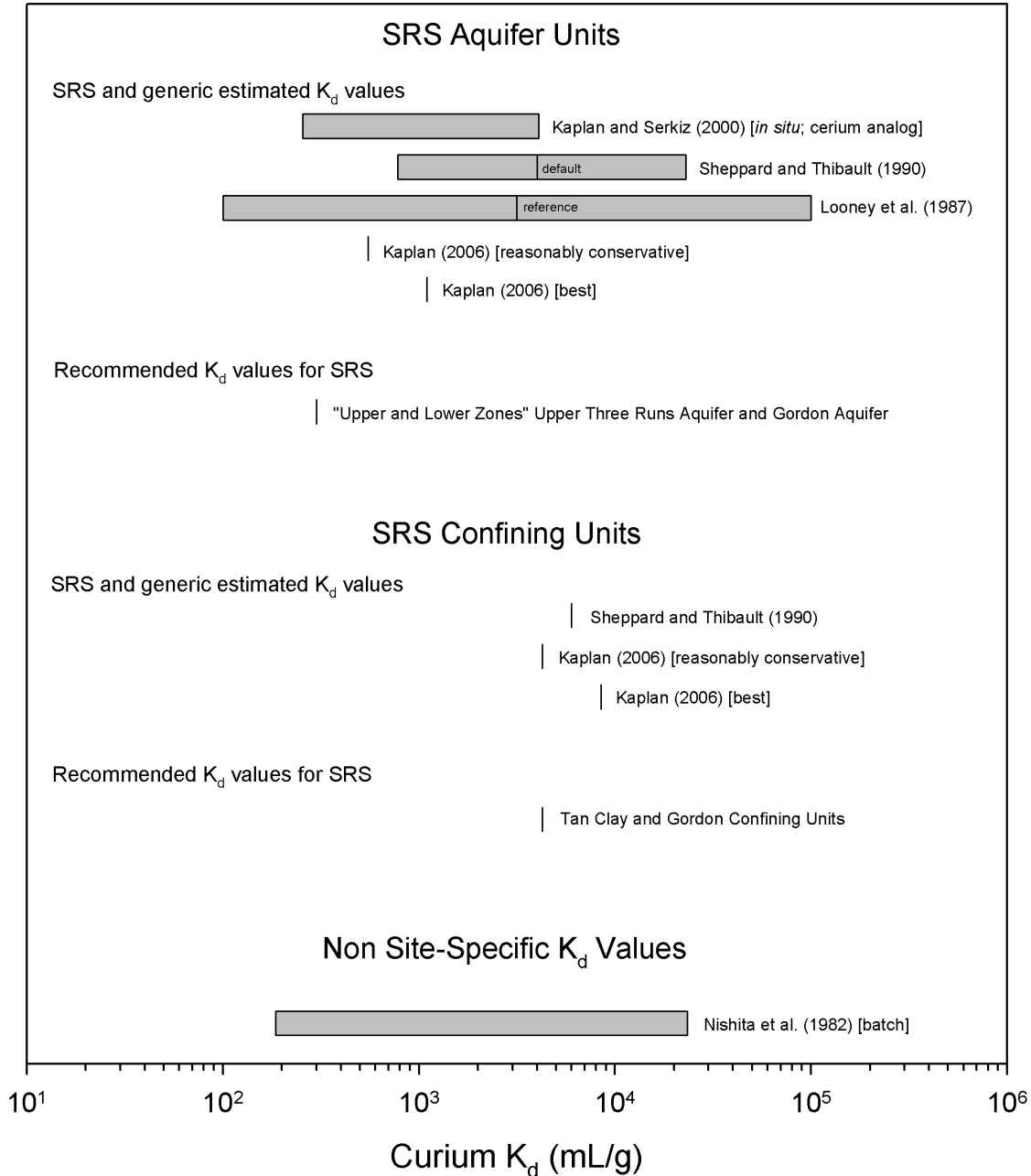
**Table 2-17. Estimated and Recommended Curium  $K_d$  Values for Aquifer Sediments and Clay Confining Units at the Savannah River Site**

	<b>Measured Curium <math>K_d</math> (mL/g)</b>	<b>Savannah River Site-Specific “Reasonably Conservative”/ “Best” Estimated Curium <math>K_d</math> (mL/g)</b>	<b>Generic Estimated Curium <math>K_d</math> (mL/g)†</b>	<b>Recommen ded Curium <math>K_d</math> (mL/g)</b>
Upper Three Runs Aquifer: Upper	—	550/1,100	4,000	300
Tan Clay Confining Unit	—	4,250/8,500	6,000	4,250
Upper Three Runs Aquifer: Lower	—	550/1,100	4,000	300
Gordon Confining Unit	—	4,250/8,500	6,000	4,250
Gordon Aquifer	—	550/1,100	4,000	300

\*Kaplan, D.I. “Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site (U).” WSRC-TR-2006-00004. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company. 2006.

†Sheppard, M.I. and D.H. Thibault. “Default Soil Solid/Liquid Partition Coefficients,  $K_d$ s, for Four Major Soil Types: A Compendium.” *Health Physics*. Vol. 59, No. 4. pp. 471–482. 1990.

The position of the curium  $K_d$  values recommended in this review with respect to measured and estimated site-specific and generic curium  $K_d$  ranges and values is graphically displayed in Figure 2-17. This figure illustrates the uncertainty associated with the curium  $K_d$  values recommended for SRS aquifer units and clay confining units. The recommended curium  $K_d$  values are associated with high uncertainty due to the lack of site-specific sorption data.



**Figure 2-17. Measured and Estimated Site-Specific and Generic Curium  $K_d$  Ranges and Values and Recommended Curium  $K_d$  Values for Aquifer Units and Confining Units at SRS (Table 2-17). Recommended Curium  $K_d$  Values Are Associated With High Uncertainty Due to the Lack of Site-Specific Sorption Data.**

## **3 IDAHO NATIONAL LABORATORY**

### **3.1 Waste Management Background**

At Idaho National Laboratory (INL), the U.S. Department of Energy (DOE) has used tanks at the Idaho Nuclear Technology and Engineering Center (INTEC) Tank Farm Facility to store a variety of radioactive liquid wastes. DOE has cleaned the tanks to remove the bulk of the waste and now plans to close the facility by stabilizing any residual radioactive materials in the tanks by filling them, in place, with grout (DOE, 2006b). In addition to the residual wastes at the bottom of the tanks, in two of the tanks, radionuclides have contaminated the sand pad underlying the tank as a result of inadvertent back-siphoning of first-cycle extraction fluid from reprocessing from the large tanks into the concrete vaults. As part of the demonstration of compliance with performance objectives, the DOE has modeled groundwater transport from the tank heels and sandpads into the Tank Farm Facility subsurface.

As at Savannah River, the INTEC subsurface has been locally contaminated by previous disposal activities and spills. There are two sources of contamination in the subsurface at INTEC: (i) contamination from a former injection well that released low activity waste water directly into the aquifer south of the Tank Farm Facility and (ii) contamination from piping leaks. The subsurface at the Tank Farm Facility was significantly contaminated as a result of a 1972 leak of 70,400 L [18,600 gal] of sodium-bearing waste, which entered the vadose zone during an unsuccessful attempt at transferring the waste between tanks. Approximately  $5.9 \times 10^8$  MBq [ $1.59 \times 10^4$  Ci] of strontium-90 and  $1.1 \times 10^5$  MBq [3 Ci] of technetium-99 were released during the event (DOE–Idaho, 2006a). Maximum concentrations measured in shallow perched water underneath the Tank Farm Facility are 200,000 pCi/L for strontium-90, while maximum measured concentrations in the saturated zone are 3,000 pCi/L for technetium-99 (DOE–Idaho, 2006a,b). Other COCs detected in the subsurface as a result of the release of radioactivity into the environment from the 1972 event and from the injection well located south of the Tank Farm Facility include tritium, neptunium-237, plutonium-239, plutonium-240, and uranium-234.

### **3.2 Description of Idaho Nuclear Technology and Engineering Center Tank Farm Facility**

The INTEC is a large industrial complex located in the south-central portion of INL. INL is an approximately 2,305-km<sup>2</sup> [890-mi<sup>2</sup>] reservation in southeastern Idaho owned by the U.S. government. The INTEC facility is located approximately 29 km [18 mi] from the closest eastern boundary, approximately 23 km [14 mi] from the closest western boundary, approximately 16 km [10 mi] from the closest southern boundary, and approximately 29 km [18 mi] from the closest northern boundary. INL and INTEC are located in a broad, relatively flat plain in the Pioneer Basin—a closed drainage basin. INTEC is approximately 460 m [1,500 ft] from the Big Lost River channel. The Big Lost River is an intermittent stream that sinks into the permeable vadose zone and the Snake River Plain Aquifer (SRPA) below. The Big Lost River enters INL in the southern portion of its western boundary, and in the wettest years, flows east and north where it ends in the Big Lost River playas and sinks located approximately 15 km [9 mi] north of INTEC.

The historical mission of INTEC, formerly known as the Idaho Chemical Processing Plant, was to recover fissile uranium by reprocessing spent nuclear fuel. The resulting liquid waste

generated from this process was acidic and radioactive. The liquid contained fission products, activation products, transuranic radionuclides, and various metals. The liquid waste was temporarily stored in the underground Tank Farm Facility at INTEC until the liquid radioactive waste was converted to a solid granular form. The Tank Farm Facility, located within the northern portion of INTEC, comprises eleven 1,000-m<sup>3</sup> [300,000-gal] stainless steel tanks in unlined concrete vaults of various construction, four inactive 100-m<sup>3</sup> [30,000-gal] stainless steel tanks, interconnecting waste transfer lines, and associated support instrumentation and valves.

INTEC is underlain by an alluvial veneer of Pleistocene-to-Holocene Big Lost River flood plain deposits and a sequence of Quaternary volcanic rocks and sedimentary interbeds (Whitehead, 1992). The Tank Farm Facility is embedded in 13 m [43 ft] of alluvial silt, sand, and gravel that lie above an alternating sequence of basalt lava flows and interbedded sediments (Figure 3-1). Stratigraphic sections derived from well characterization activities at or near INTEC indicate that basalt flows and sedimentary interbeds comprise horizontal to slightly inclined layers. More than 30 geologic units compose the vadose zone and the upper portion of the SRPA, including 19 basalt flow groups, 11 sedimentary interbeds, and surficial alluvium.

Alluvium and interbed sediments at INL include particles from clay to gravel sized. The alluvium typically is a few meters thick and has undergone little artificial disturbance over much of INL. Sedimentary interbeds may be as thick as 20 m [60 ft]. Sedimentary interbeds accumulated above basalt flows for hundreds to hundreds of thousands of years during periods of volcanic quiescence. Much of the alluvium and interbed sediment at INL was deposited by meltwater discharge and periodic floods along the ancestral channel and flood plain of the Big Lost River during past glacial declines (Rathburn, 1993). Another major part of the alluvium and sedimentary interbeds is loess and aeolian material derived from fine alluvial deposits having grain sizes ranging from fine silt to very fine sand. Clay- and sand-sized sediment was also transported by water and wind into the fractures of the underlying basalt flows. Besides silt, sand, and gravel, sedimentary interbeds may contain small clay lenses, scoria, and basalt rubble (Nimmo, et al., 2004).

During periods of volcanic quiescence, sediment accumulated in the topographic depressions of underlying basalt flows to form the sedimentary interbeds. Mineralogically, the interbed sediments closely resemble the alluvium. However, the interbed sediments have a greater density, more uniform structure, and are less aggregated than the alluvium (Nimmo, et al., 2004). Some interbed sediments are highly stratified and have internal layers and lenses that differ substantially in texture, structure, and geochemical composition due to varying depositional conditions or baking by a flow of fresh lava.

As determined by sieve analysis, optical scattering, and other methods, grain sizes of alluvium and interbed sediments range from clay to pebble sized (Bartholomay, et al., 1989; Perkins and Nimmo, 2000; Perkins, 2003; Winfield, 2003). Most alluvium and interbed sediment falls within the silt loam textural class, containing about 0 to 27-wt% clay, 55- to 80-wt% silt, and 10- to 35-wt% sand. Significant lithologic variations occur within surficial sediment and sedimentary interbeds as a result of changes in the depositional environment through time (Rightmire and Lewis, 1987). Weakly developed to well-developed paleosols containing carbonized zones and abundant clay cutans occur in both the alluvium and sedimentary interbeds (Forman, et al., 1993). Carbonized zones represent vegetation that was inundated and baked by lava flows during the geologic past. Besides paleosols, sedimentary structures in the alluvium and interbed sediments that could influence the movement of contaminants include cracks formed

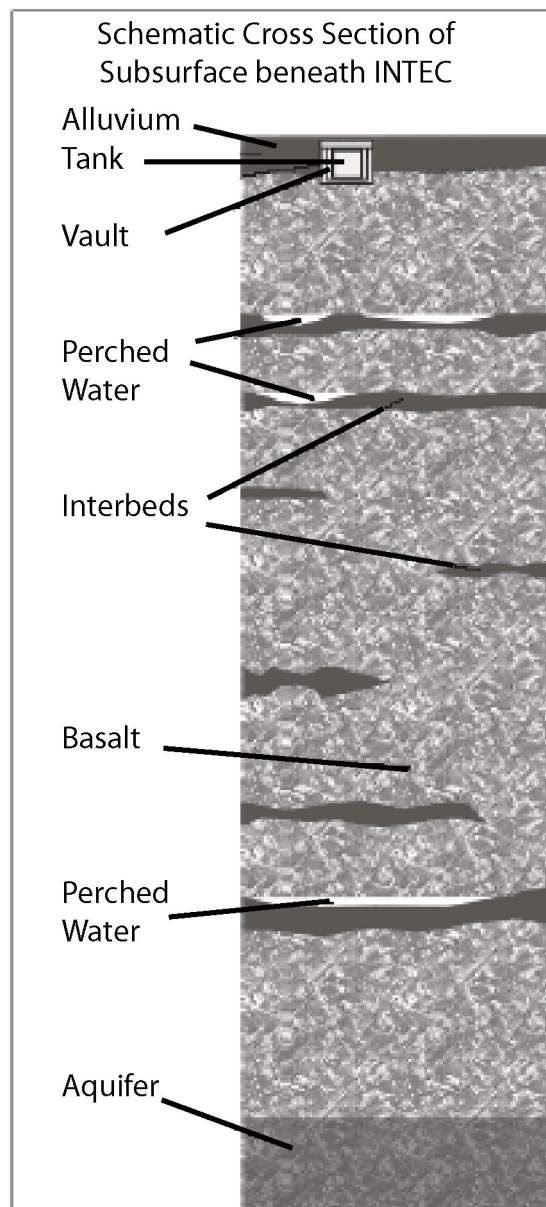
by hydrocompaction and dessication, freeze–thaw features, burrow and rootlet holes, caliche development, horizontal laminations, ripple cross-stratification, planar cross-stratification, lenticular bedding, flaser bedding, rip-up clasts, load casts, and varves (Rightmire and Lewis, 1987).

Analyses of bulk mineralogy of INL alluvium and interbed sediments show the presence of quartz, plagioclase feldspar, K-feldspar, pyroxene, olivine, calcite, dolomite, and clay minerals (Bartholomay, 1990; Bartholomay, et al., 1989). In general, quartz and plagioclase feldspar are the most abundant minerals in the sediment in the south and western portions of INL, which includes INTEC, while calcite and quartz are the most abundant minerals to the north (Bartholomay, 1990). Clay minerals are also present in most of the sediment samples from INL. Analyses of the clay minerals sampled throughout INL indicate that illite predominates (ranging from 10 to 100 percent) and that lesser amounts of smectite, mixed-layer illite/smectite, kaolinite, and possible chlorite are present (Bartholomay, et al., 1989; Reed and Bartholomay, 1994). Abundance of clay minerals in interbed samples from the Subsurface Disposal Area (SDA), located approximately 12 km [7.5 mi] southwest of INTEC, ranges from 0 to 60 percent and averages about 20 percent (Bartholomay, 1990). Mineralogical analyses indicated that most of the carbonate in INL sediments is in the form of calcite (Bartholomay, et al., 1989). Calcite contents in samples from the SDA range from zero, for most of the samples, to 54 percent. Rightmire and Lewis (1987) reported trace amounts of iron oxyhydroxides, hematite, siderite, and dolomite in some INL sediment samples.

Basalt flows are mostly thin {3 to 9 m [10 to 30 ft]}, tube-fed pahoehoe flows (Anderson, et al., 1999). Outcrop exposures indicate that individual basalt flows generally form long, sinuous lobes having median length/width ratios of about 3:1 (Welhan, et al., 1997). Some flows are as long as several kilometers (Kuntz, et al., 1994). Many of the flows have closely spaced fractures up to a few meters wide and tens of meters long. These may be opened or filled with rubble, sediment, or younger lava. In some places, basalt flows are cut by vertical fissures, dikes, and tension cracks (Anderson, et al., 1999).

Basalt flows and other volcanic deposits combine into basalt flow groups that range from 3 to 20 m [10 to 60 ft] thick and are internally interbedded with discontinuous scoria and thin layers of sediment (Nimmo, et al., 2004). Each basalt flow group is a complex assemblage of overlapping flows and deposits related to a single eruption. A basalt flow group comprises several, perhaps hundreds, of distinct basalt flows that occurred in a time interval brief enough that little or no sediment accumulated between them.

Most basalt flows at INL have the chemical characteristics of both tholeiitic and alkali olivine basalts. Typical basalt samples consist mainly of plagioclase feldspar, pyroxene, and olivine and contain lesser amounts of ilmenite, magnetite, hematite, and accessory apatite (Kuntz, et al., 1980; Rightmire and Lewis, 1987; Knobel, et al., 1997). The typical chemical composition of basalt samples at INL is shown in Table 3-1. The basalts are rich in iron and calcium and poor in sodium and potassium.



**Figure 3-1. Schematic of the Subsurface at INTEC (Not to Scale,  
Taken From DOE-Idaho, 2006c)**

<b>Table 3-1. Typical Chemical Composition of Idaho National Laboratory Basalt.* Oxide Contents in wt% and Strontium and Barium Contents in mg/L.</b>										
<b>SiO<sub>2</sub></b>	<b>TiO<sub>2</sub></b>	<b>Al<sub>2</sub>O<sub>3</sub></b>	<b>Fe<sub>2</sub>O<sub>3</sub></b>	<b>MnO</b>	<b>MgO</b>	<b>CaO</b>	<b>Na<sub>2</sub>O</b>	<b>K<sub>2</sub>O</b>	<b>Strontium</b>	<b>Barium</b>
45–48	1.3–3.8	12–15	12–17	0.17–0.23	5–10	9–11	2.1–2.7	0.3–0.9	230–352	193–507
*Colello, J.J., J.J. Rosentreter, R.C. Bartholomay, and M.J. Liszewski. "Strontium Distribution Coefficients of Basalt Core Samples from the Idaho National Engineering and Environmental Laboratory, Idaho." U.S. Geological Survey Water Resource Investigations Report 98-4256. 1998.										

Fractures and vesicles within basalts commonly are coated with fine-grained sediment infill and sometimes with secondary minerals consisting of calcite, clays, zeolites, silica, iron oxides, and iron oxyhydroxides (Rightmire and Lewis, 1987; Morse and McCurry, 1997). Fractures within and contacts between individual basalt flows provide a complex network of potential vertical and horizontal pathways for the movement of water and wastes within the vadose zone and the aquifer.

The vadose zone is about 150 m [450 ft] thick near the INTEC and overlies the SRPA (Martian, et al., 2006). The SRPA is one of the largest and most productive aquifers in the United States, receiving natural recharge at and near the INTEC from precipitation and Big Lost River underflow (Bennett, 1990). Several perched water zones underlie the INTEC facility. Occurrences of perched water at the INTEC correspond to flow barriers created by low permeability portions of sedimentary interbeds. The perching of water in the vadose zone is brought about primarily by operational processes and landscape watering and secondarily by ephemeral Big Lost River seepage that releases water into the subsurface.

Analyses of water samples from eight SRPA wells at INL indicate that the waters are a calcium magnesium bicarbonate type (Knobel, et al., 1997, 1992), which is typical of most water in the SRPA. The composition of major cations and anions in the SRPA based on Wood and Low's (1986) characterization is listed in Table 3-2. These data indicate that groundwater from the SRPA is typically alkaline with significant bicarbonate concentration.

Water chemistry data for perched groundwater at INL can vary depending on the location of the wells and the timing of sample collection. Some samples collected from the SDA contain waste constituents leached from radiochemical and organic wastes (Bartholomay and Tucker, 2000).

Water chemistry data from perched groundwater samples from INL generally show chemical characteristics similar to SRPA water (Barracough, et al., 1976; Rightmire and Lewis, 1987;

<b>Table 3-2. Composition of Eastern Snake River Plain Aquifer Groundwater*</b>			
<b>Component</b>	<b>Mean (mg/L)</b>	<b>Maximum (mg/L)</b>	<b>Minimum (mg/L)</b>
Ca <sup>2+</sup>	51	120	5
K <sup>+</sup>	4	12	0
Mg <sup>2+</sup>	18	54	0.2
Na <sup>+</sup>	26	140	4



<b>Table 3-2. Composition of Eastern Snake River Plain Aquifer Groundwater* (continued)</b>			
<b>Component</b>	<b>Mean (mg/L)</b>	<b>Maximum (mg/L)</b>	<b>Minimum (mg/L)</b>
Cl <sup>-</sup>	28	230	1.8
SO <sub>4</sub> <sup>2-</sup>	41	218	1.8
HCO <sub>3</sub> <sup>-</sup>	220	510	52
F <sup>-</sup>	0.6	11	0.03
SiO <sub>2</sub>	50	138	5.8
pH	7.8	9.1	7.0
Ionic strength (mol/L)	0.008	0.02	0.004
*Wood, W.W. and W.H. Low. "Aqueous Geochemistry and Diagenesis in the Eastern Snake River Plain Aquifer System, Idaho." <i>Geological Society of America Bulletin</i> 97. 1986.			

Knobel, et al., 1992; Bartholomay, 1998; Del Debbio and Thomas, 1989). The chemical composition of a perched water sample from the vadose zone taken at a depth of 38 m [125 ft] south of the Test Reactor Area near the Big Lost River and aquifer water taken at a depth of 140 m [460 ft] west of the Test Reactor Area are listed in Table 3-3 (Del Debbio and Thomas, 1989). The data indicate that both groundwaters are buffered by a carbonate/bicarbonate system and have an average pH of 8. Oxygen analyses indicate that the groundwaters are saturated with oxygen thus creating oxidizing conditions.

Several chemical properties of water will affect the mobility of contaminants at INL including pH, alkalinity, dissolved organic carbon, system oxidation state, and the concentration of aqueous complexing agents. Water from perched zones at INL and from the SRPA have the following characteristics that can significantly affect contaminant transport:

- pH that ranges from 7.2 to 8.4 (Nimmo, et al., 2004)
- Cation concentrations dominated by Ca<sup>2+</sup> and anion concentrations dominated by HCO<sub>3</sub><sup>-</sup>
- Dissolved O<sub>2</sub> concentrations that are nearly saturated to slightly supersaturated with respect to air

<b>Table 3-3. Composition of Perched Water and Aquifer Water Collected At the Idaho National Laboratory*</b>		
<b>Component</b>	<b>Perched Water (mg/L)</b>	<b>Aquifer Water (mg/L)</b>
Ca <sup>2+</sup>	44	48
Mg <sup>2+</sup>	14	18
SiO <sub>2</sub>	18	26

<b>Table 3-3. Composition of Perched Water and Aquifer Water Collected At the Idaho National Laboratory* (continued)</b>		
<b>Component</b>	<b>Perched Water (mg/L)</b>	<b>Aquifer Water (mg/L)</b>
Iron (total)	<0.02	<0.02
Na <sup>+</sup>	8.2	8.5
K <sup>+</sup>	1.6	2.1
Cl <sup>-</sup>	7.4	12
SO <sub>4</sub> <sup>2-</sup>	22	24
HCO <sub>3</sub> <sup>-</sup>	207	206
O <sub>2</sub>	7.4	7.6
pH	8.1	8.0
Eh	750 mV	750 mV
*Del Debbio, J.A. and T.R. Thomas. "Transport Properties of Radionuclides and Hazardous Chemical Species in Soils at the Idaho Chemical Processing Plant." WINCO-1068. Idaho Falls, Idaho: Westinghouse Idaho Nuclear Company, Inc. 1989.		

- Dissolved organic carbon concentrations that are generally smaller than 1 mg/L [1 ppm] (Knobel, et al., 1992) or about 1 mg/L [1 ppm] (Busenberg, et al., 2000)
- Saturation indices that indicate the water is typically nearly saturated with respect to calcite (Nimmo, et al., 2004)

Most groundwaters at the INL site have dissolved O<sub>2</sub>, which restricts the extent to which redox conditions can vary at least in mobile contaminated water at the site. Natural organic matter can be present in some of the less hydraulically conductive materials at INL, thereby potentially resulting in reducing conditions in some isolated, relatively immobile waters at the site. Lower redox potentials have been observed at a few locations beneath the INTEC, where the perched water appears to have been affected by past releases of fuel hydrocarbons (Golder Associates, Inc., 1991).

Mineralogical characteristics will also affect the mobility of contaminants at INL. The mineralogic properties that are important to the partitioning of contaminants between groundwater and the sediment and basalt units beneath INL include

- The presence of calcite in both basalt fractures and in sedimentary interbeds
- Iron oxyhydroxides, which can strongly adsorb actinides under certain conditions, are commonly observed on fracture surfaces in basalt and in the interbed sediments
- Clay minerals, most commonly identified as illite, which account for an average of 20 wt% of the interbed sediments (Bartholomay, 1990)

The clay minerals that are present in the system provide sites for sorption or ion exchange with contaminant-bearing water. Both smectite and mixed-layer smectite clays were observed in some interbed samples; these clays have the largest cation exchange capacities (CEC) of the clay minerals present. For example, samples from the SDA with low CECs contained illite, while high CEC samples contained from 9- to 33-wt% expandable layer clays, mixed layer clays, and smectite (Rightmire and Lewis, 1987).

The previously noted chemical and mineralogic characteristics define the environment that will control contaminant mobility at INL. For example, the presence of O<sub>2</sub> and dissolved organic carbon affects the oxidation-reduction characteristics of the system and hence the affinity of the chemical species for the aqueous or solid phase. Oxygen in the vadose zone may be depleted by reaction with organic materials released from waste tanks, creating localized reducing conditions that may affect contaminant mobility. However, due to the mineralogic characteristics of the basalt and interbed sediments at INL, the buffering capacity of the vadose zone and aquifer system beneath INL is great, and reducing conditions potentially caused by waste releases are not expected to persist as water moves vertically through the system.

### **3.3 Designation of Risk-Significant Radionuclides**

The COCs chosen for analysis in this report are based both on previous model results and on more general considerations of hydrochemical behavior and dose effects. In addition, inclusion on the DOE list of highly radioactive radionuclides was considered (DOE, 2006b). DOE performance assessment results suggested that isotopes of strontium, technetium, and iodine may be most important to groundwater dose (DOE–Idaho, 2003). In the models, the transported strontium arose chiefly from the sandpad inventories, because tank-derived strontium would have mostly decayed by the time tanks failed. Uranium and neptunium are significant in waste inventories and are relatively mobile in the subsurface environment at the site. Other actinides—plutonium, americium, and curium—are included due to potentially important dose effects if sorption coefficients are overestimated. DOE included potentially mobile carbon and cesium radioisotopes in their list of highly radioactive radionuclides; lead is also significant in inventories and potentially mobile in the subsurface.

### **3.4 Sorption Coefficients**

The hydrostratigraphic units that will be affected by release of contaminants from storage facilities at INTEC are alluvium, sedimentary interbeds, and basalt. For many of the COCs in this review, site-specific  $K_d$  data for subsurface media at the INTEC or for subsurface media at INL facilities in the vicinity of INTEC (e.g., the Surface Disposal Area and Test Reactor Area) are available. In this review, site-specific  $K_d$  measurements and literature-recommended  $K_d$  values for the COCs at INL are analyzed and reviewed to derive a recommended  $K_d$  value for alluvium, sedimentary interbeds, and basalt beneath INL. In some instances where site-specific  $K_d$  measurements are lacking for hydrostratigraphic units, the mineralogic and hydrogeochemical characteristics of the units (summarized in Table 3-4) are used in the  $K_d$  recommendation. Table 3-4 indicates that the lithologic, mineralogic, and chemical composition of the alluvium and sedimentary interbed units are not significantly different. Therefore, when site-specific  $K_d$  data are available for a COC for one of these units but not the other, the  $K_d$  recommendation based on the site-specific  $K_d$  data is applied to both units.

Many researchers have measured  $K_d$  values in sediments and basalt from the Hanford site in southeastern Washington for the COCs in this review. The hydrogeochemical environment at the Hanford site is analogous to INL in many aspects (i.e., alkaline pH, high carbonate concentrations, oxidizing conditions, and similar though not identical sediment and basalt mineral compositions). When available, reported  $K_d$  values from Hanford for the COCs in this review are presented to help determine whether the recommended  $K_d$  values for INL are reasonable.

To aid in transport model simulations at INTEC, Cooper, et al. (2006) estimated  $K_d$  ranges and recommended  $K_d$  values for a number of radionuclides in alluvium, interbed sediments, and basalt. For many of the designated radionuclides in this review, these estimated  $K_d$  ranges and recommended  $K_d$  values were useful in determining whether the  $K_d$  values recommended for the INL in this review are reasonable. In the  $K_d$  estimates of Cooper, et al. (2006), site-specific INTEC data from INTEC was given the highest priority in the  $K_d$  recommendations. When site-specific INTEC data was not available, INL-SDA data were judged to be most representative. Sediments from the SDA have been studied more thoroughly than INTEC sediments, originate from the same geologic source, and possess similar geochemical properties. The main difference between these two subsurface regions is in the grain size distribution, CEC, and reactive surface area of the respective sediments. Based on reported data from Bartholomay, et al. (1989),  $K_d$  estimates based on SDA data were scaled according to typical CEC of the respective sediments (INTEC/SDA = 1:5). When SDA data were not available, data from the open literature on comparable sediments were employed, using INTEC and SDA geochemistry as a guide. The results of the Cooper, et al. (2006) analyses were three  $K_d$  values for each contaminant in each subsurface unit (alluvium, interbed sediments, and basalt): a minimum estimated  $K_d$  value, a maximum estimated  $K_d$  value, and a recommended  $K_d$  value. For each of the COCs in this review analyzed by Cooper, et al. (2006), the estimated range (i.e., the minimum and maximum estimated  $K_d$  value) and recommended  $K_d$  are graphically illustrated in Figures 3-2 through 3-12 for alluvium, interbed sediments, and basalt.

### **3.4.1 Carbon**

The C-14 present in INL waste streams originates from nuclear fuel processing and is predominantly inorganic in nature. Inorganic carbon transport occurs via both slow aqueous transport as  $\text{HCO}_3^-$  ion and rapid transport of  $\text{CO}_2$  gas. Carbon transport is likely to be affected by reactions other than sorption, but an empirical  $K_d$  approach may be sufficient for understanding potential transport.

Plummer, et al. (2004) conducted an unsaturated column study to determine carbon transport in INL surficial sediments collected from playas adjacent to the SDA. The water used in the column experiments was a synthetic vadose zone water (pH 7.8) formulated to approximate the composition of natural infiltrating water at the SDA. Results indicated that approximately 70 percent of total carbon was released from the surface of the column as  $\text{CO}_2$  gas, 4 percent exited as the aqueous phase, 2 percent was lost to sampling, and 24 percent remained in the column (1 percent in soil gas, 3 percent in soil water, and 20 percent adsorbed). After fitting the carbon data to a multiphase transport equation that accounted for minor variations in pH, carbon  $K_d$  values of  $0.5 \pm 0.1$  mL/g were calculated for the first 3 months following carbon injection and ranged from 0.8 to 2.4 mL/g after 1 year of transport.

**Table 3-4. Mineralogic and Hydrogeochemical Characteristics of Units at the Idaho National Laboratory**

<b>Unit</b>	<b>Lithology*</b>	<b>Mineralogy†</b>	<b>pH Range‡</b>	<b>Other Hydrochemical Aspects‡</b>
Alluvium	Silt loam (0–27-percent clay, 55–80-percent silt, 10–35-percent sand)	Major constituents: quartz, plagioclase, illite. Minor constituents: K-feldspar, pyroxene, olivine, calcite, dolomite, iron oxyhydroxides, smectite, mixed layer illite/smectite, kaolinite, chlorite, hematite, siderite	7.2–8.4	High dissolved O <sub>2</sub> Cations dominated by Ca <sup>2+</sup> Anions dominated by HCO <sub>3</sub> <sup>-</sup> Low dissolved organic carbon Water near calcite saturation
Sedimentary Interbeds	Silt loam (0–27-percent clay, 55–80-percent silt, 10–35-percent sand); some small clay lenses, scoria, and basalt rubble	Major constituents: quartz, plagioclase, illite. Minor constituents: K-feldspar, pyroxene, olivine, calcite, dolomite, iron-oxyhydroxides, smectite, mixed layer illite/smectite, kaolinite, chlorite, hematite, siderite	7.2–8.4	High dissolved O <sub>2</sub> Cations dominated by Ca <sup>2+</sup> Anions dominated by HCO <sub>3</sub> <sup>-</sup> Low dissolved organic carbon Water near calcite saturation

**Table 3-4. Mineralogic and Hydrogeochemical Characteristics of Units At the Idaho National Laboratory (continued)**

Unit	Lithology*	Mineralogy†	pH Range‡	Other Hydrochemical Aspects‡
Basalt	Tube fed pahoehoe flows; closely spaced fractures often filled with rubble, sediments, or younger lava	Major constituents: plagioclase, pyroxene, olivine. Minor constituents: ilmenite, magnetite, hematite, apatite. Fractures and vesicles commonly coated with calcite, clays, zeolites, silica, iron oxides, and iron oxyhydroxides	7.2– 8.4	High dissolved O <sub>2</sub> Cations dominated by Ca <sup>2+</sup> Anions dominated by HCO <sub>3</sub> <sup>-</sup> Low dissolved organic carbon Water near calcite saturation

\*Lithologic characterization based on data from Bartholomay, R.C., L.L. Knobel, and L.C. Davis. "Mineralogy and Grain Size of Surficial Sediment from the Big Lost River Drainage and Vicinity, with Chemical and Physical Characteristics of Geologic Materials from Selected Sites at the Idaho National Engineering Laboratory, Idaho." U.S. Geological Survey Open-File Report 89-384. 1989; Nimmo, J.R., J.P. Rousseau, K.S. Perkins, K.G. Stollenwerk, P.D. Glynn, R.C. Bartholomay, and L.L. Knobel. "Hydraulic and Geochemical Framework of the Idaho National Engineering and Environmental Laboratory Vadose Zone." *Vadose Zone Journal*. Vol. 3. pp. 6–34. 2004; and Anderson, S.R., M.A. Kuntz, and L.C. Davis. "Geologic Controls of Hydraulic Conductivity in the Snake River Plain Aquifer at and Near the Idaho National Engineering and Environmental Laboratory, Idaho." U.S. Geological Survey Water Resources Investigations Report 99-4033. 1999.

†Mineralogic characterization based on data from Bartholomay, R.C., L.L. Knobel, and L.C. Davis. "Mineralogy and Grain Size of Surficial Sediment from the Big Lost River Drainage and Vicinity, with Chemical and Physical Characteristics of Geologic Materials from Selected Sites at the Idaho National Engineering Laboratory, Idaho." U.S. Geological Survey Open-File Report 89-384. 1989; Bartholomay, R.C. "Mineralogical Correlation of Surficial Sediment from Area Drainages With Selected Sedimentary Interbeds at the Idaho National Engineering Laboratory, Idaho." U.S. Geological Survey Water Resources Investigations Report 90-4147. 1990; Rightmire, C.T. and B.D. Lewis. "Hydrogeology and Geochemistry of the Unsaturated Zone, Radioactive Waste Management Complex, Idaho National Engineering Laboratory, Idaho." U.S. Geological Survey Water Resources Investigations Report 87-4198. 1987; Kuntz, M.A., G.B. Dalrymple, D.E. Champion, and D.J. Doherty. "Petrography, Age, and Paleomagnetism of Volcanic Rocks at the Radioactive Waste Management Complex, Idaho National Engineering Laboratory, Idaho." U.S. Geological Survey Open-File Report 80-388. 1980; and Knobel, L.L., R.C. Bartholomay, and B.R. Orr. "Preliminary Delineation of Natural Geochemical Reactions, Snake River Plain Aquifer System, Idaho National Engineering Laboratory and Vicinity, Idaho." U.S. Geological Survey Water Resources Investigations Report 97-4093. DOE/ID-22139. 1997.

‡Chemical characterization based on data from Nimmo, J.R., J.P. Rousseau, K.S. Perkins, K.G. Stollenwerk, P.D. Glynn, R.C. Bartholomay, and L.L. Knobel. "Hydraulic and Geochemical Framework of the Idaho National Engineering and Environmental Laboratory Vadose Zone." *Vadose Zone Journal*. Vol. 3. pp. 6–34. 2004; Wood, W.W. and W.H. Low. "Aqueous Geochemistry and Diagenesis in the Eastern Snake River Plain Aquifer System, Idaho." *Geological Society of America Bulletin* 97. 1986; Del Debbio, J.A. and T.R. Thomas. "Transport Properties of Radionuclides and Hazardous Chemical Species in Soils at the Idaho Chemical Processing Plant." WINCO-1068. Idaho Falls, Idaho: Westinghouse Idaho Nuclear Company, Inc. 1989; Knobel, L.L., B.R. Orr, and L.D. Cecil. "Summary of Background Concentrations of Selected Radiochemical and Chemical Constituents in Groundwater from the Snake River Plain Aquifer, Idaho—Estimated from an Analysis of Previously Published Data." *Journal of Idaho Academy of Sciences*. Vol. 28. pp. 48–61. 1992; and Busenberg, E., L.N. Plummer, M.W. Doughten, P.K. Widman, and R.C. Bartholomay. "Chemical and Isotopic Composition and Gas Concentrations of Ground Water and Surface Water from Selected Sites at and near the Idaho National Engineering and Environmental Laboratory, Idaho, 1994–97." U.S. Geological Survey Open-File Report 00-81. 2000.

Based on the Plummer, et al. (2004) study, Cooper, et al. (2006) estimated that the  $K_d$  for carbon in alluvium and interbed sediments could range from 0.5 to 2.4 mL/g and recommended a carbon  $K_d$  value of 1.6 mL/g for alluvium and interbed sediments at INTEC. Cooper, et al. (2006) found no data for carbon partitioning in basalt at INL and recommended a  $K_d$  of 0 mL/g.

Measured and recommended carbon  $K_d$  values are summarized in Table 3-5. Site-specific carbon  $K_d$  values from the column experiment of Plummer, et al. (2004) using INL alluvium ranged from 0.5 to 2.4 mL/g. Cooper, et al. (2006) recommended a carbon  $K_d$  value of 1.6 mL/g for alluvium and interbed sediments at INTEC, which is the median of the range of carbon  $K_d$  values reported for the 1-year transport experiment of Plummer, et al. (2004). In this review, a carbon  $K_d$  value of 1 mL/g is recommended for INL alluvium and interbed sediments. This recommendation is estimated from the minimum of the range of values reported by Plummer, et al. (2004) for the 1-year transport experiment (0.8 mL/g). No site-specific or literature-derived data are available for carbon partitioning to basalt, and a value of 0 mL/g is recommended. For basalt, there is no clear basis for using carbon  $K_d$  values reported for sediments or soils (e.g., Thibault, et al., 1990).

The position of the carbon  $K_d$  values recommended in this review with respect to measured and estimated site-specific carbon  $K_d$  ranges and values is graphically displayed in Figure 3-2. This figure illustrates the uncertainty associated with the carbon  $K_d$  values recommended for alluvium, interbed sediments, and basalt at INL. The recommended carbon  $K_d$  values are associated with high uncertainty due to limited site-specific sorption data. The recommended carbon  $K_d$  value of 1 mL/g for INL alluvium and interbed sediments is based solely on site-specific carbon sorption data reported by Plummer, et al. (2004). No site-specific carbon sorption data exists for INL basalt.

<b>Table 3-5. Measured and Recommended <math>K_d</math> Values for Carbon in Alluvium, Interbed Sediments, and Basalt at the Idaho National Laboratory</b>				
	<b>Measured Carbon <math>K_d</math> (mL/g)</b>	<b>Test Method</b>	<b>Idaho Nuclear Technology and Engineering Center-Specific Recommended Carbon <math>K_d</math> (mL/g)*</b>	<b>Recommended Carbon <math>K_d</math> (mL/g)</b>
Alluvium	0.5–2.4†	Column	1.6	1
Sedimentary Interbeds	—	—	1.6	1
Basalt	—	—	0	0
<p>*Cooper, D.C., G.D. Redden, and L.C. Hull. DOE/NE-ID-11227, "Operable Unit 3-14 Tank Farm Soil and Groundwater Remedial Investigation/Baseline Risk Assessment—Appendix D: Estimation of <math>K_d</math> Values for INTEC Groundwater Model." Idaho Falls, Idaho: DOE-Idaho. 2006.</p> <p>† Plummer, M.A., L.C., Hull, and D.T. Fox. "Transport of Carbon-14 in a Large Unsaturated Soil Column." <i>Vadose Zone Journal</i>. Vol. 3. pp.109–121. 2004.</p>				

### 3.4.2 Strontium

Sr-90 exists primarily as the uncomplexed  $\text{Sr}^{2+}$  ion over the pH range of natural waters (pH 3 to 10).  $\text{Sr}^{2+}$  adsorbs to both clay minerals and carbonate minerals. The extent to which strontium partitions from the aqueous phase to the solid phase is expected to be controlled primarily by the CEC of the solid phase. Other factors affecting strontium  $K_d$  values are pH and ionic strength. Strontium  $K_d$  values have been reported to increase with increasing pH (Prout, 1958; Rhodes, 1957). This trend is likely the result of hydrogen ions competing with  $\text{Sr}^{2+}$  for exchange sites. Elevated concentrations of major cations (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) can greatly reduce strontium  $K_d$  values (Bunde, et al., 1998, 1997). Strontium  $K_d$  values may decrease from 100 to 200 mL/g in low ionic strength solutions to less than 5 mL/g in high ionic strength solutions (Routson, et al., 1980). There is little tendency for strontium to form complexes with inorganic or organic ligands (Faure and Powell, 1972; Stevenson and Fitch, 1986).

A number of researchers have investigated strontium sorption onto INL alluvium, interbed sediments, and basalt. In general, these studies indicate that strontium sorption is strongly affected by variability in both solution composition and mineral content.

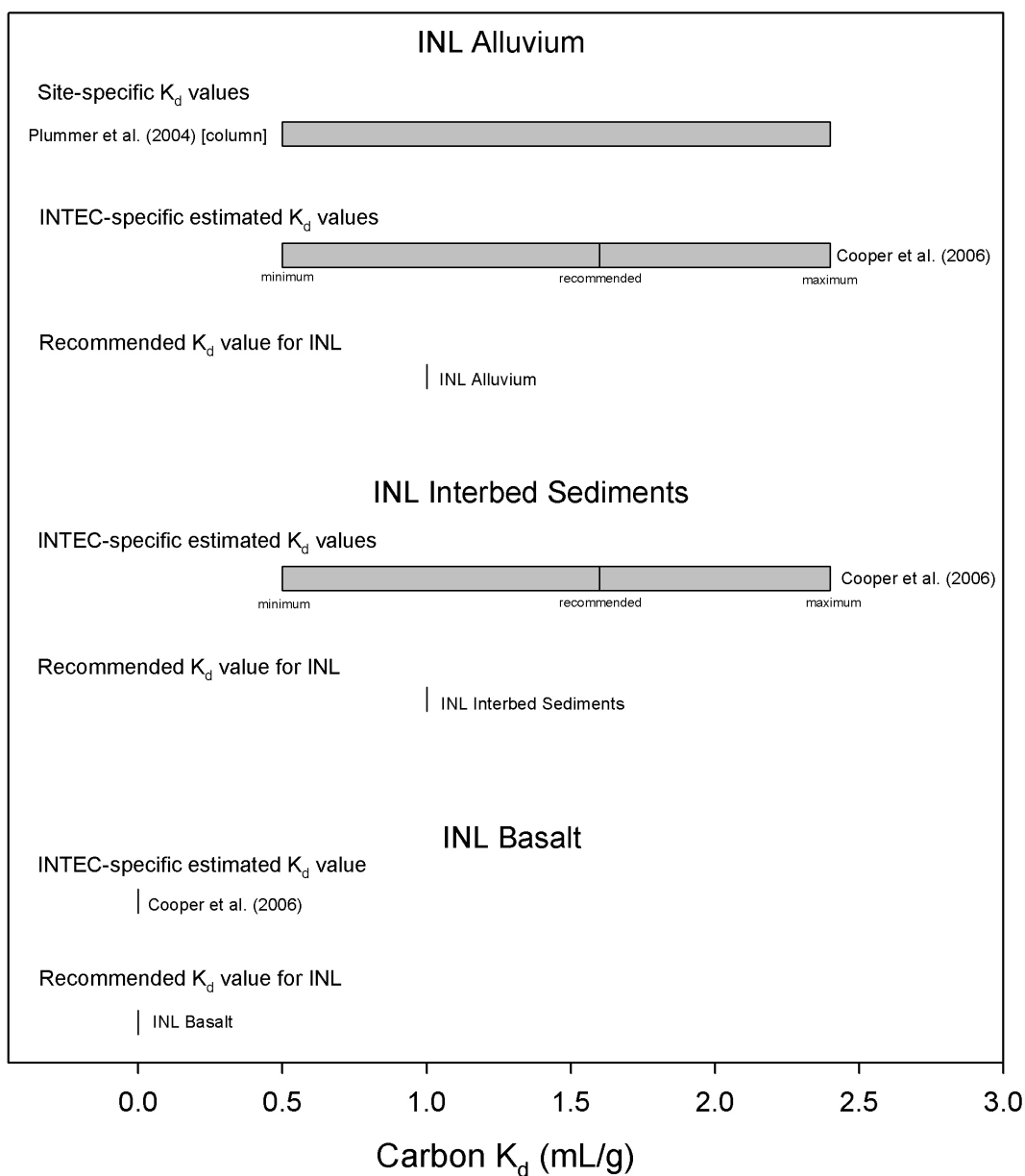
Liszewski, et al. (1997) measured strontium  $K_d$ s for 20 surficial sediment samples collected at INL. Batch experimental techniques were used to determine  $K_d$ s using a synthesized aqueous solution representative of wastewater in INL waste disposal ponds (pH  $8.0 \pm 0.1$ ). Strontium  $K_d$  values of the 20 surficial sediments ranged from 36 to 275 mL/g, indicating significant variability in the strontium sorptive capacities. Liszewski, et al. (1997) attributed the strontium  $K_d$  variability to physical and chemical properties of the sediments and compositional changes in the equilibrated solutions after mixing with the sediments. In similar batch experiments conducted on interbed sediments from INL, Liszewski, et al. (1998) report strontium  $K_d$  values that ranged from 66 to 266 mL/g using low ionic strength solutions.

Hemming, et al. (1997) conducted batch experiments using INL surficial sediments to examine the effect of different experimental techniques on experimentally derived strontium  $K_d$  values at a fixed pH of 8.0. Strontium  $K_d$  values ranged from 11 to 23 mL/g among the three experimental variables examined: method of sample agitation (rotating mixer and shaker table), solid/liquid ratio (1:2 and 1:20), and method of sediment preparation (crushed and noncrushed).

Del Debbio and Thomas (1989) measured strontium  $K_d$  values on alluvium, interbed sediments, and basalt collected at INL. Batch experiments were performed on the materials at a 1:20 solid/liquid ratio using a low ionic strength groundwater (pH 8.0) collected from an onsite well. Measured strontium  $K_d$  values ranged from 35 to 52 mL/g for the alluvium, 110 to 186 mL/g for the interbed sediments, and 1.1 to 2.7 mL/g for the basalt.

Schmalz (1972) performed batch experiments to measure strontium  $K_d$  values using alluvium from INL and a low ionic strength pond water with a pH of 9.2 collected from the Test Reactor Area. The pond water was spiked with varying concentrations of strontium. Strontium  $K_d$  values measured on four soil samples varied over a narrow range (23 to 26 mL/g).





**Figure 3-2. Measured and Estimated Site-Specific Carbon  $K_d$  Ranges and Values and Recommended Carbon  $K_d$  Values for Alluvium, Interbed Sediments, and Basalt at INL (Table 3-5). Recommended Carbon  $K_d$  Values Are Associated With High Uncertainty Due to Limited Site-Specific Sorption Data.**

Hawkins and Short (1965) performed batch tests to measure strontium  $K_d$  values on alluvial soil from INL as a function of solution chemistry. A solution for use in these tests was synthesized to simulate INL groundwater. The chemistry of this solution was then varied with respect to  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{NH}_4^+$ .  $K_d$  values measured for strontium ranged from 8.3 to 16.6 mL/g. Based on these tests, equations were developed to predict the sorption of strontium at varying solution chemistries.

Newman, et al. (1996) summarized results from short-term (400-hour) batch experiments and column tests measuring strontium  $K_d$  for basalt and interbed sediments. The batch and column tests were conducted using a synthetic groundwater formulated to approximate the composition observed in SRPA field samples (ionic strength = 0.0048 M; pH 8.0) (Wood and Low, 1986). For batch tests, strontium  $K_d$  values ranged from 9 to 13 mL/g for basalt and from 42 to 63 mL/g for interbed sediments. For column tests, strontium  $K_d$  values ranged from 6.3 to 6.5 mL/g for basalt and >47 mL/g for interbed sediments.

Fjeld, et al. (2001) performed laboratory column tests to characterize the mobility of strontium in a basalt sample and a composite of sedimentary interbed from INL. The solution used in the tests was a low ionic strength (0.004 M) synthetic groundwater (pH 8.0) formulated to approximate the major ion concentration of SRPA groundwater samples (Wood and Low, 1986). Strontium retardation factors ranged from 25 to 33 for basalt and >200 for interbed sediments. Based on the reported porosities and bulk densities of the basalt and interbed columns, these retardation factors equate to  $K_d$  values of 6.8 to 9.7 mL/g<sup>1</sup> for basalt and >47 mL/g for interbed sediments.

Colello, et al. (1998) measured strontium  $K_d$  values for 24 crushed basalt core samples collected at INL. Batch experiments were used to measure the  $K_d$  values using an aqueous solution representative of wastewater in waste disposal ponds (pH 8.0). Calculated strontium  $K_d$  values of the crushed basalt core samples ranged from 3.6 to 29.4 mL/g. The results indicated a narrow range of variability in the strontium sorptive capacities of basalt relative to those of sedimentary materials at INL. No correlation was observed between strontium  $K_d$  and any physical properties of the basalt.

Porro, et al. (2000) performed column and batch adsorption tests to determine strontium  $K_d$  values in crushed basalt from INL. All column and batch tests were conducted using a synthetic groundwater formulated to approximate the composition observed in SRPA samples. The synthetic groundwater had a low ionic strength (0.0048 M) and a pH of 8.0. Column tests were conducted at saturated and unsaturated moisture contents. Measured strontium  $K_d$  values for the column tests ranged from 2.37 to 4.26 mL/g and were not significantly affected by moisture content. Batch tests were conducted at several solid/liquid ratios (0.25 to 2.33). Measured strontium  $K_d$  values for the batch tests ranged from 0.58 mL/g at the highest solid/liquid ratio to 2.56 mL/g at the lowest solid/liquid ratio. Column tests conducted at various moisture contents from saturation to 20 percent consistently resulted in essentially the same  $K_d$  value and, therefore, were considered to be more robust than the batch tests.

---

<sup>1</sup>Retardation factor ( $R_f$  converted to  $K_d$  based on following equation:  $K_d = \frac{(R_f - 1)}{\rho_b} \theta$ , where  $\theta$  is porosity and  $\rho_b$  is bulk density.

Cooper, et al. (2006) estimated a strontium  $K_d$  range of 8 to 20 mL/g for INTEC alluvium and recommended a strontium  $K_d$  value of 12 mL/g for INTEC alluvium. For sedimentary interbeds, Cooper, et al. (2006) estimated a range of strontium  $K_d$  values from 25 to 84 mL/g with a recommended strontium  $K_d$  value of 50 mL/g. The estimated  $K_d$  values for alluvium and sedimentary interbeds were determined using equations developed by Hawkins and Short (1965) to predict the sorption of strontium at varying solution chemistries. The  $K_d$  values were calculated using the PHREEQC geochemical code and water analyses for perched zone wells at the INTEC compiled by Roddy (2005). For basalt, Cooper, et al. (2006) estimated a strontium  $K_d$  range of 0 to 15 mL/g and recommended a strontium  $K_d$  value of 0.5 mL/g. Cooper, et al. (2006) indicate that the strontium  $K_d$  estimates and recommendations for basalt were taken from Colello, et al. (1998), with the recommended strontium  $K_d$  value equal to the minimum strontium  $K_d$  value observed for basalt. However, Colello, et al. (1998) reported measured strontium  $K_d$  values ranging from 3.6 to 29.4 mL/g for basalt, which is not in agreement with the minimum and maximum estimated strontium  $K_d$  values for basalt reported by Cooper, et al. (2006).

Measured and recommended strontium  $K_d$  values are summarized in Table 3-6. For alluvium, site-specific strontium  $K_d$  values for the 5 listed batch experiments range from a minimum of 8.3 mL/g (Hawkins and Short, 1965) to a maximum of 275 mL/g (Liszewski, et al., 1997). Review of the laboratory procedures used by Liszewski, et al. (1997) to measure strontium  $K_d$  values on alluvium indicates that they may be biased toward higher values because of the water used in the measurements (i.e., synthesized aqueous solution representative of wastewater from disposal ponds). Therefore, the measured values of Liszewski, et al. (1997) may not be representative of natural geochemical conditions in the alluvium. Removing the Liszewski, et al. (1997) strontium  $K_d$  values from the analysis results in a maximum measured  $K_d$  value of 52 mL/g for the alluvium (Del Debbio and Thomas, 1989). A reasonably conservative strontium  $K_d$  value of 12 mL/g is recommended for INL alluvium based on the minimum measured  $K_d$  value of 8.3 mL/g (Hawkins and Short, 1965) and the maximum measured  $K_d$  value of 52 mL/g (Del Debbio and Thomas, 1989). This recommended strontium  $K_d$  value is in agreement with the strontium  $K_d$  value of 12 mL/g recommended by Cooper, et al. (2006) for INTEC alluvium.

For interbed sediments, site-specific strontium  $K_d$  values for the three listed batch experiments range from a minimum of 42 mL/g (Newman, et al., 1996) to a maximum of 266 mL/g (Liszewski, et al., 1997). The  $K_d$  value for 2 listed column experiments is >47 mL/g (Newman, et al., 1996; Fjeld, et al., 2001). Again the measured strontium  $K_d$  values of Liszewski, et al. (1997) may be biased high and not representative of natural chemical conditions in the interbed sediments because of the water used in the experiments (i.e., synthesized aqueous solution representative of wastewater from disposal ponds). Removing the Liszewski, et al. (1997) strontium  $K_d$  values from the analysis results in a maximum  $K_d$  value of 186 mL/g for the interbed sediments (Del Debbio and Thomas, 1989). Based on the strontium  $K_d$  values reported for the two column experiments (>47 mL/g), which are within the range of strontium  $K_d$  values reported for the batch experiments (42 to 186 mL/g), a  $K_d$  value of 50 mL/g appears to be appropriate for interbed sediments at INL. A strontium  $K_d$  value of 50 mL/g is in agreement with the strontium  $K_d$  value of 50 recommended by Cooper, et al. (2006) for INTEC interbed sediments. However, sensitivity studies conducted on models simulating past contaminant transport at the site (Rodriguez, et al., 1997, Appendix F) concluded that a strontium  $K_d$  of 12–24 mL/g matched observations well for both the unsaturated and saturated zones. On this basis, a conservative  $K_d$  of 12 mL/g is recommended for strontium in the interbed sediments.

**Table 3-6. Measured and Recommended  $K_d$  Values for Strontium in Alluvium, Interbed Sediments, and Basalt at the Idaho National Laboratory**

	<b>Measured Strontium <math>K_d</math> (mL/g)</b>	<b>Test Method</b>	<b>Idaho Nuclear Technology and Engineering Center-Specific Recommended Strontium <math>K_d</math> (mL/g)*</b>	<b>Recommended Strontium <math>K_d</math> (mL/g)</b>
Alluvium	36–275† 11–23‡ 35–52§ 23–26¶ 8.3–16.6#	Batch Batch Batch Batch Batch	12	12
Sedimentary Interbeds	66–266** 110–186§ 42–63†† >47†† >47‡ ‡	Batch Batch Batch Column Column	50	12
Basalt	1.1–2.7§ 9.0– 3†† 6.3–6.5†† 3.6–29.4§§ 0.58–2.56¶¶ 2.37–4.26¶¶	Batch Batch Column Batch Batch Column	0.5	2

\*Cooper, D.C., G.D. Redden, and L.C. Hull. DOE/NE-ID-11227, "Operable Unit 3-14 Tank Farm Soil and Groundwater Remedial Investigation/Baseline Risk Assessment—Appendix D: Estimation of  $K_d$  Values for INTEC Groundwater Model." Idaho Falls, Idaho: DOE-Idaho. 2006.

†Liszewski, M.J., J.J. Rosentreter, and K.E. Miller. "Strontium Distribution Coefficients of Surficial Sediment Samples from the Idaho National Engineering Laboratory, Idaho." U.S. Geological Survey Water Resource Investigations Report 97-4044. 1997.

‡Hemming, C.H., R.L. Bunde, M.J. Liszewski, J.J. Rosentreter, and J. Welhan. "Effect of Experimental Technique on the Determination of Strontium Distribution Coefficients of a Surficial Sediment from the Idaho National Engineering Laboratory, Idaho." *Water Research*. Vol. 31, Issue 7. pp. 1,629–1,636. 1997.

§Del Debbio, J.A. and T.R. Thomas. "Transport Properties of Radionuclides and Hazardous Chemical Species in Soils at the Idaho Chemical Processing Plant." WINCO-1068. Idaho Falls, Idaho: Westinghouse Idaho Nuclear Company, Inc. 1989.

¶Schmalz, B.L. "Radionuclide Distribution in Soil Mantle of the Lithosphere as a Consequence of Waste Disposal at the National Reactor Testing Station." IDO-10049. Idaho Falls, Idaho: United States Atomic Energy Commission, Idaho Operations Office. 1972.

\*\*Liszewski, M.J., J.J. Rosentreter, K.E. Miller, and R.C. Bartholomay. "Strontium Distribution Coefficients of Surficial and Sedimentary Interbed Sediment Samples From the Idaho National Engineering Laboratory, Idaho." U.S. Geological Survey Water Resource Investigations Report 98-4037. 1989.

#Hawkins, D.B. and H.L. Short. "Equations for the Sorption of Cesium and Strontium on Soil and Clinoptilolite." IDO-12046. Idaho Falls, Idaho: Atomic Energy Commission, Idaho Operations Office. 1965.

††Newman, M.E., I. Porro, R. Scott, R.M. Dunnivant, R.W. Goff, M.D. Blevins, S.M. Ince, J.D. Leyba, T.A. DeVol, A.W. Elzerman, and R.A. Fjeld. "Evaluation of the Mobility of Am, Cs, Co, Pu, Sr, and U Through INEL Basalt and Interbed Materials: Summary Report of the INEL/Clemson University Laboratory Studies." ER-WAG7-82, INEL-95/282. Idaho Falls, Idaho: Idaho National Engineering Laboratory. 1996.

‡‡Fjeld, R.A., T.A. DeVol, R.W. Goff, M.D. Blevins, D.D. Brown, S.M. Ince, A.W. Elzerman, and M.E. Newman. "Characterization of the Mobilities of Selected Actinides and Fission/activation Products in Laboratory Columns Containing Subsurface Material from the Snake River Plain." *Nuclear Technology*. Vol. 135. pp. 92–108. 2001.

§§Colello, J.J., J.J. Rosentreter, R.C. Bartholomay, and M.J. Liszewski. "Strontium Distribution Coefficients of Basalt Core Samples from the Idaho National Engineering and Environmental Laboratory, Idaho." U.S. Geological Survey Water Resource Investigations Report 98-4256. 1998.

¶¶Porro, I., M.E. Newman, and F.M. Dunnivant. "Comparison of Batch and Column Methods for Determining Strontium Distribution Coefficients for Unsaturated Transport in Basalt." *Environmental Science and Technology*. Vol. 34. pp. 1,679–1,686. 2000.

For basalt, site-specific strontium  $K_d$  values for 4 listed batch experiments range from a minimum of 0.58 mL/g (Porro, et al., 2000) to a maximum of 29.4 mL/g (Colello, et al., 1998). Site-specific strontium  $K_d$  values for three listed column experiments range from a minimum of 2.37 mL/g (Porro, et al., 2000) to a maximum of 9.7 mL/g (Fjeld, et al., 2001). Review of the laboratory procedures used by Colello, et al. (1998) to measure strontium  $K_d$  values on basalt indicates that they may be biased toward higher values because of the water used in the measurements (i.e., synthesized aqueous solution representative of wastewater from disposal ponds). Therefore, the measured values of Colello, et al. (1998) may not be representative of natural chemical conditions in the basalt. Removing the Colello, et al. (1998) strontium  $K_d$  values from consideration results in a maximum measured  $K_d$  value of 13 mL/g for the basalt (Newman, et al., 1996). Based on the range of strontium  $K_d$  values reported for the column experiments (2.37 to 9.7 mL/g), which are within the range of strontium  $K_d$  values reported for the batch experiments (0.58 to 13 mL/g), a  $K_d$  value of 2 mL/g is recommended for basalt at INL.

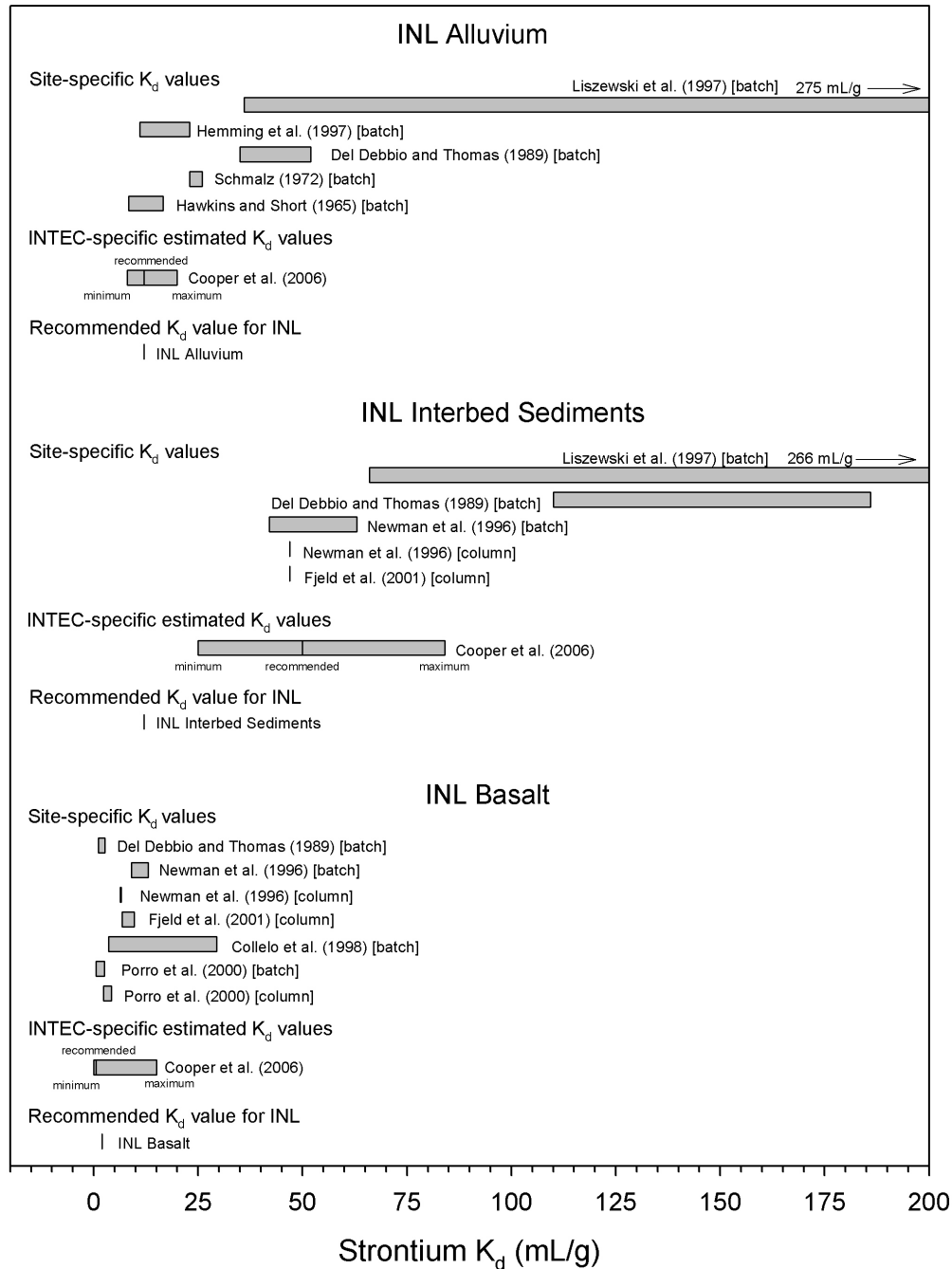
The position of the strontium  $K_d$  values recommended in this review with respect to measured and estimated site-specific strontium  $K_d$  ranges and values is graphically displayed in Figure 3-3. This figure illustrates the uncertainty associated with the strontium  $K_d$  values recommended for alluvium, interbed sediments, and basalt at INL. Due to available site-specific strontium sorption data (Figure 3-3), the recommended strontium  $K_d$  values are associated with low uncertainty.

### 3.4.3 Technetium

Tc-99 predominantly occurs in oxidized (+7) state, as pertechnetate ( $\text{TcO}_4^-$ ) over the complete pH range of natural waters, generally sorbs poorly to sediments, and is typically highly mobile (e.g., Denys, et al., 2003; Kaplan, 2003; Mashkin and Shikov, 2000). The sorption behavior of technetium is highly redox sensitive. Experimental data indicate that technetium mobility increases with increasing pH (Denys, et al., 2003) and decreases under organic-rich, reducing conditions (Mashkin and Shikov, 2000). The pH effect may arise from pH-dependent changes in surface charge or may reflect the role of organic matter; both provide anion sorption sites for  $\text{TcO}_4^-$  and reduce pH (Kaplan, 2003).

Del Debbio and Thomas (1989) performed column experiments to determine technetium sorption onto alluvium, interbed sediments, and basalt at INL. The experiments used a low ionic strength groundwater (pH 8.0) collected from an onsite well. Measured retardation factors were  $<1.0$  on alluvium and interbed sediments, indicating no retention of technetium. The measured retardation factor for one basalt column experiment was 1.1, which equates to a technetium  $K_d$  of 0.016 mL/g using the reported bulk density and porosity of the basalt column.

Cooper, et al. (2006) used the technetium sorption data reported by Del Debbio and Thomas (1989) to recommend a technetium  $K_d$  value of 0 mL/g for alluvium and interbed sediments at INTEC. Cooper, et al. (2006) examined technetium behavior in other systems to establish a range of minimum and maximum technetium  $K_d$  estimates at INTEC. For example, Kaplan (2003) reported technetium  $K_d$  values that ranged from  $-0.1$  to  $0.1$  mL/g for a silty-sand upland Savannah River Site (SRS) sediment (0.3 wt%  $\text{Fe}_2\text{O}_3$ ,  $<0.02$  wt% organic carbon) and from 0 to 0.3 mL/g for a silty-sand wetland SRS sediment (0.01 wt%  $\text{Fe}_2\text{O}_3$ , 0.14 wt% organic carbon). Sheppard and Thibault (1991) conducted a 4-year lysimeter study of technetium transport in



**Figure 3-3. Measured and Estimated Site-Specific Strontium  $K_d$  Ranges and Values and Recommended Strontium  $K_d$  Values for Alluvium, Interbed Sediments, and Basalt at INL (Table 3-6). Recommended Strontium  $K_d$  Values Are Associated With Low Uncertainty Due to Available Site-Specific Sorption Data.**

surficial soils and reported technetium  $K_d$  values ranging from 0.1 to 1.4 mL/g for sediments with 0.2 to 0.3 wt% organic carbon. Cooper, et al. (2006) indicated that the SRS upland sediment was most similar to INTEC sediment interbeds, while the SRS wetland sediment and lysimeter studies were most comparable to INTEC alluvium. Therefore, Cooper, et al. (2006) estimated a technetium  $K_d$  range of -0.1 to 1.4 mL/g for alluvium and a technetium  $K_d$  range of -0.1 to 0.1 mL/g for interbed sediments. Noting the lack of direct measurements, Cooper, et al. (2006) estimated a minimum and recommended technetium  $K_d$  for INTEC basalt of 0 mL/g.

Several studies have measured technetium  $K_d$  values in sediments from the Hanford site. The sediments and hydrogeochemical environment at the Hanford site are analogous to INL (i.e., alkaline pH, high carbonate concentrations, oxidizing conditions, and similar though not identical sediment mineral compositions). These studies are summarized next.

Kaplan, et al. (1998a,b) used batch equilibrium techniques to measure  $K_d$  values for technetium under oxic conditions on sediment samples from the Hanford site. The groundwater selected for the sorption studies was an uncontaminated groundwater for the Hanford site with a low ionic strength and pH of 8.4. The mean  $K_d$  values of three replicates measured for technetium on each Hanford sediment sample ranged from -0.04 to 0.01 mL/g. The measurements indicated essentially no sorption of technetium on Hanford sediments. Kaplan, et al. (1998b) suggested that the negative  $K_d$  values measured for technetium were due to anion exclusion effects.

Kaplan and Serne (1998) and Kaplan, et al. (1996) used batch techniques to measure the technetium  $K_d$  values, as  $\text{TcO}_4^-$ , on three sediments for the Hanford site. The measurements were conducted with a groundwater sample (pH 8.3) taken from a well located in an uncontaminated area of the Hanford site. The  $K_d$  values at 266 days of contact time were very low for all sediments and ranged from -0.18 to 0.11 mL/g.

Serne, et al. (1993) measured  $K_d$  values for  $\text{TcO}_4^-$  on three samples of sediment (two loamy sands and one sand) from the Hanford Formation. Batch equilibrium tests under oxidizing conditions were conducted using an uncontaminated groundwater (pH 8.14) sample from the Hanford site. Under the conditions studied, no significant sorption of technetium was measured; technetium  $K_d$  values ranged from 0.1 to 0.2 mL/g.

Measured and recommended technetium  $K_d$  values are summarized in Table 3-7. Site-specific technetium  $K_d$  values for alluvium and sedimentary interbeds from the column experiments of Del Debbio and Thomas (1989) indicate essentially no sorption of technetium. These results are in agreement with batch experiments of technetium sorption on sediments at the Hanford site, which showed technetium  $K_d$  values ranging from -0.04 to 0.2 mL/g (Kaplan, et al., 1998a,b, 1996; Kaplan and Serne, 1998; Serne, et al., 1993). Based on the column experiments of Del Debbio and Thomas (1989), a technetium  $K_d$  value of 0 mL/g is recommended for INL alluvium and interbed sediments. This value is in agreement with the technetium  $K_d$  value recommended by Cooper, et al. (2006) for INTEC alluvium and interbed sediments, which was also based on the column experiments of Del Debbio and Thomas (1989). A site-specific technetium  $K_d$  value of 0.016 mL/g was reported for basalt from the column experiments of Del Debbio and Thomas (1989). Lacking no other site-specific measurements, a technetium  $K_d$  value of 0 mL/g is recommended for basalt at INL.

<b>Table 3-7. Measured and Recommended Technetium <math>K_d</math> Values for Alluvium, Interbed Sediments, and Basalt at the Idaho National Laboratory</b>				
	<b>Measured Technetium <math>K_d</math> (mL/g)</b>	<b>Test Method</b>	<b>Idaho Nuclear Technology and Engineering Center-Specific Recommended Technetium <math>K_d</math> (mL/g)*</b>	<b>Recommended Technetium <math>K_d</math> (mL/g)</b>
Alluvium	0†	Column	0	0
Sedimentary Interbeds	0†	Column	0	0
Basalt	0.016†	Column	0	0
<p>*Cooper, D.C., G.D. Redden, and L.C. Hull. DOE/NE-ID-11227, "Operable Unit 3-14 Tank Farm Soil and Groundwater Remedial Investigation/Baseline Risk Assessment—Appendix D: Estimation of <math>K_d</math> Values for INTEC Groundwater Model." Idaho Falls, Idaho: DOE-Idaho. 2006.</p> <p>†Del Debbio, J.A. and T.R. Thomas. "Transport Properties of Radionuclides and Hazardous Chemical Species in Soils at the Idaho Chemical Processing Plant." WINCO-1068. Idaho Falls, Idaho: Westinghouse Idaho Nuclear Company, Inc. 1989.</p>				

The position of the technetium  $K_d$  values recommended in this review with respect to measured and estimated site-specific and analogous technetium  $K_d$  ranges and values is graphically displayed in Figure 3-4. This figure illustrates the uncertainty associated with the technetium  $K_d$  values recommended for alluvium, interbed sediments, and basalt at INL. Due to available site-specific sorption data (Del Debbio and Thomas, 1989) and analogous technetium sorption data from the Hanford site (Kaplan, et al., 1998a,b; Kaplan and Serne, 1998; Serne, et al., 1993), the recommended technetium  $K_d$  values are associated with low uncertainty.

### 3.4.4 Iodine

I-129 generally occurs as iodate ( $\text{IO}_3^-$ ), iodide ( $\text{I}^-$ ), or organic iodine in natural environments. Sorption of iodine species appears to be controlled in part by soil organic matter and in part by iron and aluminum oxides, with adsorption of iodine becoming increasingly important under more acid conditions. Although the extent of sorption is typically low, especially in systems containing little or no organic matter,  $\text{I}^-$  and  $\text{IO}_3^-$  are sorbed to a measurable extent by soils and some oxide minerals at near-neutral and alkaline pH conditions. The adsorption behavior of  $\text{IO}_3^-$  also appears to be appreciably different from that of  $\text{I}^-$ , in that  $\text{IO}_3^-$  sorbs much more strongly than  $\text{I}^-$  to soil and mineral surfaces (Ticknor and Cho, 1990). Mechanisms causing this sorption behavior at near-neutral and alkaline pH conditions are not completely understood. Some have proposed that this observed adsorption behavior in soils may be the result of the oxidation of  $\text{I}^-$  and/or reduction of  $\text{IO}_3^-$  to the more reactive molecular  $\text{I}_2^0(\text{aq})$  and/or its hydrolysis products (Ticknor and Cho, 1990).



No site-specific measurement of iodine  $K_d$  values for alluvium, interbed sediment, or basalt at INL were found in the literature. Based on transport model calibration (i.e., visual fitting of a model predicted plume and an I-129 plume interpreted from measured data), Arnett, et al. (1990) estimated a retardation factor of 2 for I-129 at INL.

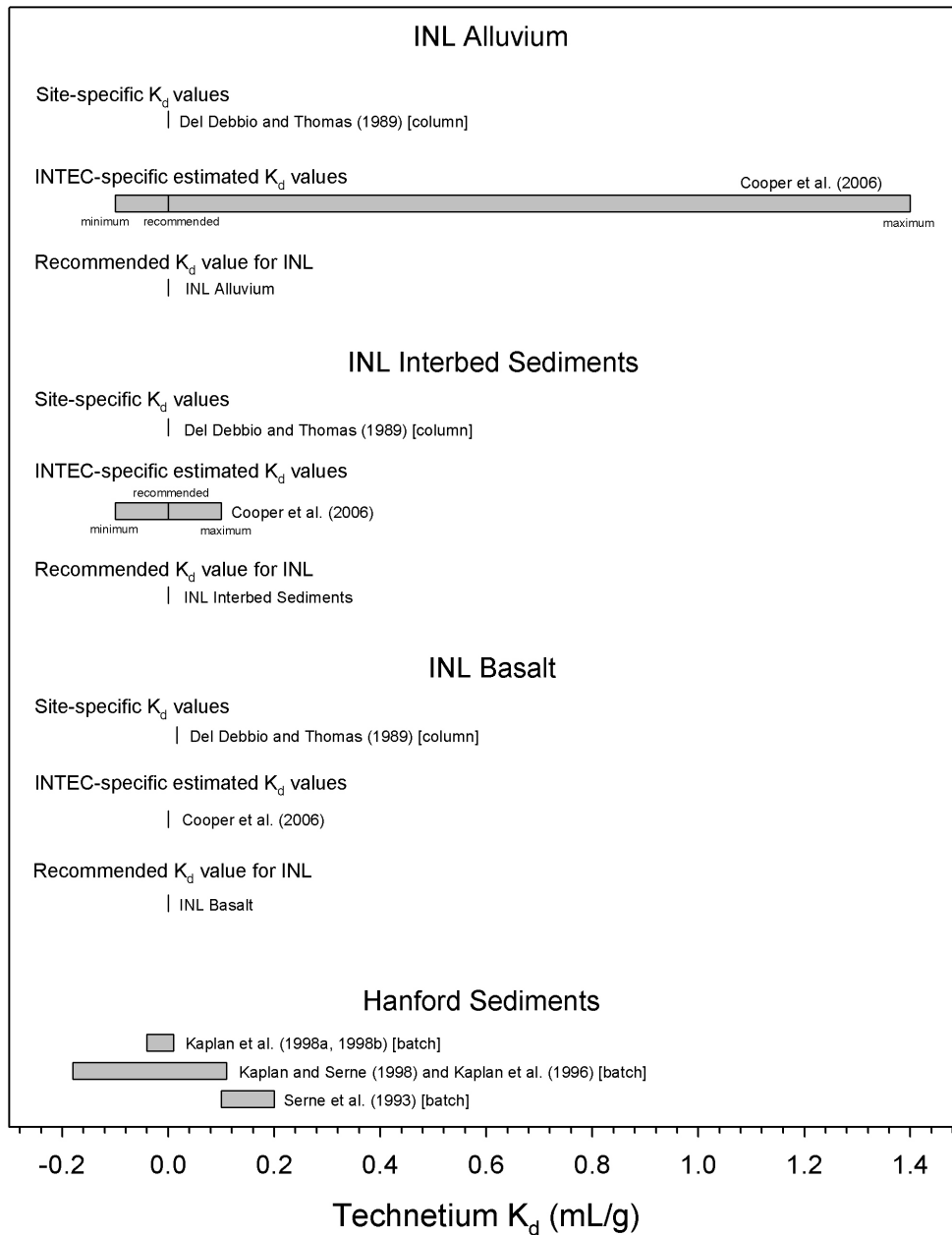
Cooper, et al. (2006) analyzed comparable systems and estimated iodine  $K_d$  values ranging from 0.04 to 8.7 mL/g with a recommended iodine  $K_d$  value of 1.5 mL/g for INTEC alluvium. For sedimentary interbeds, Cooper, et al. (2006) estimated iodine  $K_d$  values ranging from 0.04 to 3 mL/g with a recommended iodine  $K_d$  value of 0.7 mL/g. The estimated iodine  $K_d$  ranges for alluvium and interbed sediments are based on measured iodine  $K_d$  values from a field lysimeter experiment conducted by Sheppard and Thibault (1991). In soil horizons most comparable to INTEC alluvium (0.2 to 0.3 wt% organic carbon), iodine  $K_d$  values ranged from 0.1 to 8.7 mL/g at 1 year of transport and ranged from 0.04 to 0.06 mL/g at 4 years of transport. The recommended iodine  $K_d$  values for alluvium and interbed sediments are based on batch experiments conducted by Kaplan (2003) on two SRS sediments that are comparable to INTEC sediments. An upland sediment roughly corresponding to INTEC interbed sediments displayed an iodine  $K_d$  of  $0.7 \pm 0.1$  mL/g. A wetland sediment roughly corresponding to INTEC alluvium (higher organic carbon) displayed an iodine  $K_d$  of  $1.5 \pm 0.5$  mL/g. Noting the lack of direct measurements, Cooper, et al. (2006) estimated a minimum and recommended iodine  $K_d$  for INTEC basalt of 0 mL/g.

Several studies have measured iodine  $K_d$  values in sediments from the Hanford site. Kaplan, et al. (2000, 1996) performed batch experiments to measure the  $K_d$  values for iodine, as  $I^-$ , on three surficial sediment samples from the Hanford site. The measurements were conducted with a groundwater sample (pH 8.46) taken from a well located in an uncontaminated area of the Hanford site. The average measured  $K_d$  values at 330 days were 9.83, 6.83, and 4.72 mL/g for a very coarse sand, sand, and silty loam sediments, respectively. Kaplan, et al. (2000, 1996) noted that  $K_d$  values increased as a function of time; for example,  $K_d$  values increased from 0.19 to 9.83 over 330 days of contact time for the very coarse sand.

Kaplan, et al. (1998a) used batch equilibrium tests to measure the  $K_d$  values for  $I^-$  under oxic conditions on 20 sediment samples taken from a borehole in the Hanford formation at the Hanford site. The solution used in the tests was an uncontaminated groundwater with a low ionic strength and a pH of 8.4. Measured  $K_d$  values ranged from -0.03 to 0.23 mL/g and indicated essentially no sorption of  $I^-$  on the Hanford sediments under these conditions.

Serne, et al. (1993) conducted batch equilibrium tests to measure the  $K_d$  values for  $I^-$  on three surficial sediments: two loamy sands and one sand. The measurements were conducted using an uncontaminated groundwater (pH 8.14) sample from the Hanford site. After 35 days of contact time, the  $K_d$  values measured for  $I^-$  were 1.5 mL/g and 2.6 mL/g for the two loamy sand samples and 1.2 mL/g for the sand sample.

Hu, et al. (2005) conducted column studies of  $I^-$  and iodate ( $IO_3^-$ ) sorption and transport on a sediment sample from the Hanford site. The sediment consisted of a composite of core samples taken at 9 to 12 m [30 to 80 ft] below surface. For  $I^-$ , retardation factors ranged from 1.05 to 1.33, which equate to  $K_d$  values of approximately 0.01 to 0.1 mL/g. For  $IO_3^-$ , retardation factors ranged from 1.41 to 1.93, which equate to  $K_d$  values of approximately 0.1 to 0.25 mL/g.



**Figure 3-4. Measured and Estimated Site-Specific and Analogous Technetium  $K_d$  Ranges and Values and Recommended Technetium  $K_d$  Values for Alluvium, Interbed Sediments, and Basalt at INL (Table 3-7). Recommended Technetium  $K_d$  Values Are Associated With Low Uncertainty Due to Available Site-Specific and Analogous Sorption Data.**

<b>Table 3-8. Recommended iodine <math>K_d</math> Values for Alluvium, Interbed Sediments, and Basalt at the Idaho National Laboratory</b>				
	<b>Measured iodine <math>K_d</math> (mL/g)</b>	<b>Test Method</b>	<b>Idaho Nuclear Technology and Engineering Center-Specific Recommended iodine <math>K_d</math> (mL/g)*</b>	<b>Recommended iodine <math>K_d</math> (mL/g)</b>
Alluvium	—	—	1.5	0.1
Sedimentary Interbeds	—	—	0.7	0.1
Basalt	—	—	0	0
*Cooper, D.C., G.D. Redden, and L.C. Hull. DOE/NE-ID-11227, "Operable Unit 3-14 Tank Farm Soil and Groundwater Remedial Investigation/Baseline Risk Assessment—Appendix D: Estimation of $K_d$ Values for INTEC Groundwater Model." Idaho Falls, Idaho: DOE-Idaho. 2006.				

Recommended iodine  $K_d$  values are summarized in Table 3-8. Based on an analysis of comparable systems, Cooper, et al. (2006) estimated that iodine  $K_d$  values for alluvium at INL should range from 0.04 to 8.7 mL/g and recommended an iodine  $K_d$  value of 1.5 mL/g. For interbed sediments, Cooper, et al. (2006) estimated iodine  $K_d$  values ranging from 0.04 to 3 mL/g and recommended an iodine  $K_d$  value of 0.7 mL/g. The range of iodine  $K_d$  values estimated by Cooper, et al. (2006) is within the range of iodine  $K_d$  values measured in batch experiments of sediments from the Hanford site (–0.03 to 9.84 mL/g) (Kaplan, et al., 2000, 1998a, 1996; Serne, et al., 1993), but is greater than the range of iodine  $K_d$  values measured in a column experiment using Hanford sediments (0.01 to 0.25 mL/g) (Hu, et al., 2005).

There is clear evidence that iodine is unlikely to travel unretarded in the INL subsurface. However, lacking any site-specific data, it is reasonable to employ a conservative  $K_d$  that represents the low end of values from subsurface samples from the analogous Hanford site

(Kaplan, et al., 1998a; Hu, et al., 2005). Therefore, an iodine  $K_d$  value of 0.1 mL/g is recommended for alluvium and sedimentary interbeds at INL. Lacking any direct or analogous measurements, the iodine  $K_d$  of 0 mL/g recommended by Cooper, et al. (2006) for INTEC basalt is recommended for basalt at INL.

The position of the iodine  $K_d$  values recommended in this review with respect to measured and estimated site-specific and analogous iodine  $K_d$  ranges and values is graphically displayed in Figure 3-5. This figure illustrates the uncertainty associated with the iodine  $K_d$  values recommended for alluvium, interbed sediments, and basalt at INL. Although analogous iodine sorption data is available for sediments from the Hanford site (Kaplan, et al., 2000, 1998a, 1996; Serne, et al., 1993; Hu, et al., 2005), the recommended iodine  $K_d$  values are associated with high uncertainty due to the lack of site-specific iodine sorption data.

### 3.4.5 Cesium

Cs-137 exists in the environment in the +1 oxidation state. Cesium forms few stable complexes and is likely to exist in groundwater as the uncomplexed  $\text{Cs}^+$  ion.  $\text{Cs}^+$  primarily adsorbs via ion exchange reactions with sedimentary clay minerals. In general, most soils sorb cesium rather strongly (Ames and Rai, 1978). The extent to which adsorption will occur will depend on the concentration of clays in the soil and the concentration of major cations, such as  $\text{K}^+$ , that can effectively compete with  $\text{Cs}^+$  for adsorption sites. Cesium may also adsorb to iron oxides (Schwertmann and Taylor, 1989).

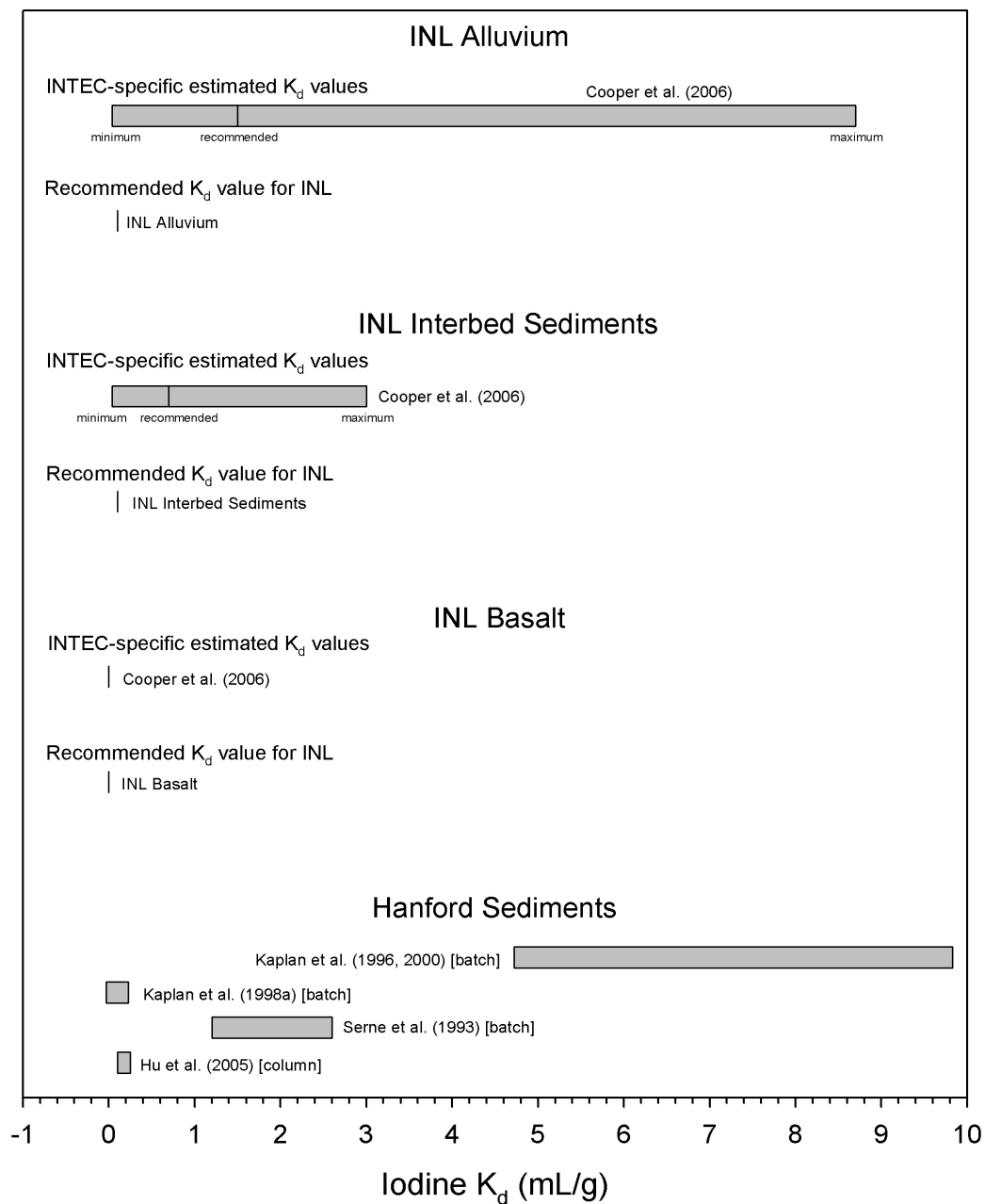
Schmalz (1972) performed batch experiments to measure cesium  $K_d$  values using alluvium from INL and a low ionic strength pond water with a pH of 9.2 collected from the Test Reactor Area. The pond water was spiked with varying concentrations of cesium. Cesium  $K_d$  values measured on 4 soil samples ranged from 589 to 1,253 mL/g.

Hawkins and Short (1965) performed batch tests to measure cesium  $K_d$  values on alluvial soil from INL as a function of solution chemistry. A solution for use in these tests was synthesized to simulate INL groundwater. The chemistry of this solution was then varied with respect to  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cs}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{NH}_4^+$ .  $K_d$  values measured for cesium ranged from 75 to 225 mL/g. Based on these tests, equations were developed to predict the sorption of cesium at varying solution chemistries.

Newman, et al. (1996) summarized results from short-term (400-hour) batch experiments and column tests measuring cesium  $K_d$  values for basalt and interbed sediments. The batch and column tests were conducted using a synthetic groundwater formulated to approximate the composition observed in SRPA field samples (ionic strength = 0.0048 M; pH 8.0) (Wood and Low, 1986). For batch tests, cesium  $K_d$  values ranged from 39 to 43 mL/g for basalt and from 2,230 to 3,260 mL/g for interbed sediments. For column tests, cesium  $K_d$  values ranged from 39 to 44 mL/g for basalt and >49 mL/g for interbed sediments. The cesium  $K_d$  value of >49 mL/g for interbed sediments represents a retardation factor of >200, which corresponds to the maximum number of pore volumes eluted during the column tests.

Fjeld, et al. (2001) performed laboratory column tests to characterize the mobility of cesium in a basalt sample and a composite of sedimentary interbed from INL. The solution used in the tests was a low ionic strength (0.004 M) synthetic groundwater (pH 8.0) formulated to approximate the major ion concentration of SRPA groundwater samples (Wood and Low, 1986). Cesium retardation factors ranged from 70 to 88 for basalt and >200 and >800 for interbed sediments. Based on the reported porosities and bulk densities of the basalt and interbed columns, these retardation factors equate to  $K_d$  values of 21 to 24.7 mL/g for basalt and >49 and >194 mL/g for interbed sediments.

Cooper, et al. (2006) estimated a cesium  $K_d$  range of 10 to 160 mL/g for alluvium and interbed sediments at INTEC and recommended a cesium  $K_d$  value of 50 mL/g for alluvium and interbed sediments. The estimated cesium  $K_d$  range for the alluvium and interbed sediments was calculated using the equation of Hawkins and Short (1965) and minimum and maximum values for measured geochemical parameters in INTEC alluvium and interbed sediments (see Cooper, et al., 2006, Table D-2-2). The recommended cesium  $K_d$  values of 50 mL/g for alluvium and



**Figure 3-5. Measured and Estimated Site-Specific and Analogous Iodine  $K_d$  Ranges and Values and Recommended Iodine  $K_d$  Values for Alluvium, Interbed Sediments, and Basalt at INL (Table 3-8). Recommended Iodine  $K_d$  Values Are Associated With High Uncertainty Due to the Lack of Site-Specific Sorption Data.**

interbed sediments were based on the study of Fjeld, et al. (2001). For basalt, Cooper, et al. (2006) estimated a cesium  $K_d$  range of 0 to 44 mL/g with a recommended cesium  $K_d$  value of 25 mL/g. The recommended cesium  $K_d$  value for basalt was based on the study of Fjeld, et al. (2001).

Researchers have measured cesium  $K_d$  values for sediments and basalt from the Hanford site. Serne, et al. (1993) conducted batch equilibrium tests to measure the  $K_d$  values for cesium on three surficial sediments: two loamy sands and one sand. The measurements were conducted using an uncontaminated groundwater (pH 8.14) sample from the Hanford site. The  $K_d$  values measured for cesium were 620 mL/g and 7,610 mL/g for the two loamy sand samples and 2,190 mL/g for the sand sample.

Ames, et al. (1982) conducted batch equilibrium tests to measure cesium sorption onto Umtanum, Flow E, and Pomona basalts from the Hanford site as a function of groundwater and aqueous cesium concentration. The pH of solutions used in the experiments ranged from 8.2 to 8.7; aqueous cesium contents ranged from approximately  $2.5 \times 10^2 \mu\text{M}$  to approximately  $2 \times 10^{-6} \mu\text{M}$ . For Umtanum basalt, cesium  $K_d$  values ranged from 27 to 1,084 mL/g using a 0.002 M solution and from 28 to 1,025 mL/g using a 0.013 M solution. For Flow E basalt, cesium  $K_d$  values ranged from 18 to 487 mL/g using a 0.002 M solution and from 20 to 617 mL/g using a 0.013 M solution. For Pomona Basalt, cesium  $K_d$  values ranged from 48 to 1,281 mL/g using a 0.002 M solution and from 56 to 902 mL/g using a 0.013 M solution. In all the tests cesium  $K_d$  values decreased with increasing cesium content; however, solution concentration had little effect on  $K_d$  values.

Measured and recommended cesium  $K_d$  values are summarized in Table 3-9. Site-specific cesium  $K_d$  values for alluvium from batch experiments range from a minimum of 75 mL/g (Hawkins and Short, 1965) to a maximum of 1,253 mg/L (Schmalz, 1972). These values are near the lower end of the range of cesium  $K_d$  values measured on surficial sediments from the Hanford site by batch methods (620 to 7,610 mL/g) (Serne, et al., 1993). Review of the laboratory procedures used by Schmalz (1972) to measure cesium  $K_d$  values on alluvium indicates that they may be biased high because of the water used in the measurements (i.e., low ionic strength pond water with a pH of 9.2). Therefore, the measured values of Schmalz (1972) may not be representative of natural chemical conditions in the alluvium. Removing the Schmalz (1972) strontium  $K_d$  values from the analysis results in a maximum measured  $K_d$  value of 225 mL/g for the alluvium (Hawkins and Short, 1965). Based on the range of cesium  $K_d$  values measured by Hawkins and Short (1965) on alluvial soil from INL (75 to 225 mL/g), a cesium  $K_d$  value of 75 mL/g is recommended for alluvium. This value is slightly higher than the cesium  $K_d$  value of 50 mL/g recommended by Cooper, et al. (2006). However, the cesium  $K_d$  value recommended by Cooper, et al. (2006) is based on column experiments conducted by Fjeld, et al. (2001) using interbed sediments rather than alluvium. In addition, cesium breakthrough was not achieved in the column experiments of Fjeld, et al. (2001) and the cesium  $K_d$  value of 50 mL/g cited by Cooper, et al. (2006) is considered to provide only an approximate lower boundary for cesium retention.

<b>Table 3-9. Measured and Recommended Cesium <math>K_d</math> Values for Alluvium, Interbed Sediments, and Basalt at the Idaho National Laboratory</b>				
	<b>Measured Cesium <math>K_d</math> (mL/g)</b>	<b>Test Method</b>	<b>Idaho Nuclear Technology and Engineering Center-Specific Recommended Cesium <math>K_d</math> (mL/g)*</b>	<b>Recommended Cesium <math>K_d</math> (mL/g)</b>
Alluvium	589–1,253† 75–225‡	Batch Batch	50	75
Sedimentary Interbeds	2,230–3,260§ >49§ >194¶	Batch Column Column	50	200
Basalt	39–43§ 39–44§ 21–24.7¶	Batch Column Column	25	25
<p>*Cooper, D.C., G.D. Redden, and L.C. Hull. DOE/NE-ID-11227, "Operable Unit 3-14 Tank Farm Soil and Groundwater Remedial Investigation/Baseline Risk Assessment—Appendix D: Estimation of <math>K_d</math> Values for INTEC Groundwater Model." Idaho Falls, Idaho: DOE-Idaho. 2006.</p> <p>†Schmalz, B.L. "Radionuclide Distribution in Soil Mantle of the Lithosphere as a Consequence of Waste Disposal at the National Reactor Testing Station." IDO-10049. Idaho Falls, Idaho: United States Atomic Energy Commission, Idaho Operations Office. 1972.</p> <p>‡Hawkins, D.B. and H.L. Short. "Equations for the Sorption of Cesium and Strontium on Soil and Clinoptilolite." IDO-12046. Idaho Falls, Idaho: Atomic Energy Commission, Idaho Operations Office. 1965.</p> <p>§Newman, M.E., I. Porro, R. Scott, R.M. Dunnivant, R.W. Goff, M.D. Blevins, S.M. Ince, J.D. Leyba, T.A. DeVol, A.W. Elzerman, and R.A. Fjeld. "Evaluation of the Mobility of Am, Cs, Co, Pu, Sr, and U Through INEL Basalt and Interbed Materials: Summary Report of the INEL/Clemson University Laboratory Studies." ER-WAG7-82, INEL-95/282. Idaho Falls, Idaho: Idaho National Engineering Laboratory. 1996.</p> <p>¶Fjeld, R.A., T.A. DeVol, R.W. Goff, M.D. Blevins, D.D. Brown, S.M. Ince, A.W. Elzerman, and M.E. Newman. "Characterization of the Mobilities of Selected Actinides and Fission/activation Products in Laboratory Columns Containing Subsurface Material from the Snake River Plain." <i>Nuclear Technology</i>. Vol. 135. pp. 92–108. 2001.</p>				

For sedimentary interbed materials, site-specific cesium  $K_d$  values from a batch sorption experiment ranged from 2,230 to 3,260 mL/g (Newman, et al., 1996). Site-specific cesium  $K_d$  values from 2 column experiments using sedimentary interbed materials were >49 and >194 mL/g (Newman, et al., 1996; Fjeld, et al., 2001). In the column experiments, cesium breakthrough was not observed in the interbed sediments. The reported cesium  $K_d$  estimate of Fjeld, et al. (2001) (>194 mL/g) is based on gamma-spectroscopic analyses of intact cores and is considered to provide an approximate lower boundary for cesium retention. Based on the column experiment of Fjeld, et al. (2001), a cesium  $K_d$  value of 200 mL/g is recommended for interbed sediments at INL. This value is higher than the cesium  $K_d$  value of 50 mL/g recommended by Cooper, et al. (2006), which was also based on the column experiments of Fjeld, et al. (2001). However, Cooper, et al. (2006) did not cite the reported cesium  $K_d$  estimate of >194 mL/g based on gamma-spectroscopic analyses of intact cores from the Fjeld, et al. (2001) study, which is considered to provide a more accurate approximate lower boundary for cesium retention.

Site-specific cesium  $K_d$  values from a batch sorption experiment using crushed basalt from INL ranged from 39 to 43 mL/g (Newman, et al., 1996). These values are in agreement with

site-specific cesium  $K_d$  values from two column experiments using crushed basalt from INL. One basalt column experiment reported cesium  $K_d$  values ranging from 39 to 44 mL/g (Newman, et al., 1996), and the other column experiment reported cesium  $K_d$  values ranging from 21 to 24.7 mL/g (Fjeld, et al., 2001). These values correspond to the low end of the range of cesium  $K_d$  values reported from batch experiments on basalts from the Hanford site (18 to 1,281 mL/g) (Ames, et al., 1982). Based on the range of cesium  $K_d$  values measured in the column experiments of Newman, et al. (1996) and Fjeld, et al. (2001) (21 to 44 mL/g), a cesium  $K_d$  value of 25 mL/g is recommended for basalt at INL. This value is in agreement with the cesium  $K_d$  value of 25 mL/g recommended by Cooper, et al. (2006), which was based on the column experiments of Fjeld, et al. (2001).

The position of the cesium  $K_d$  values recommended in this review with respect to measured and estimated site-specific and analogous cesium  $K_d$  ranges and values is graphically displayed in Figure 3-6. This figure illustrates the uncertainty associated with the cesium  $K_d$  values recommended for alluvium, interbed sediments, and basalt at INL. Due to available site-specific sorption data (Hawkins and Short, 1965; Newman, et al., 1996; Fjeld, et al., 2001), the recommended cesium  $K_d$  values are associated with low uncertainty.

### 3.4.6 Lead

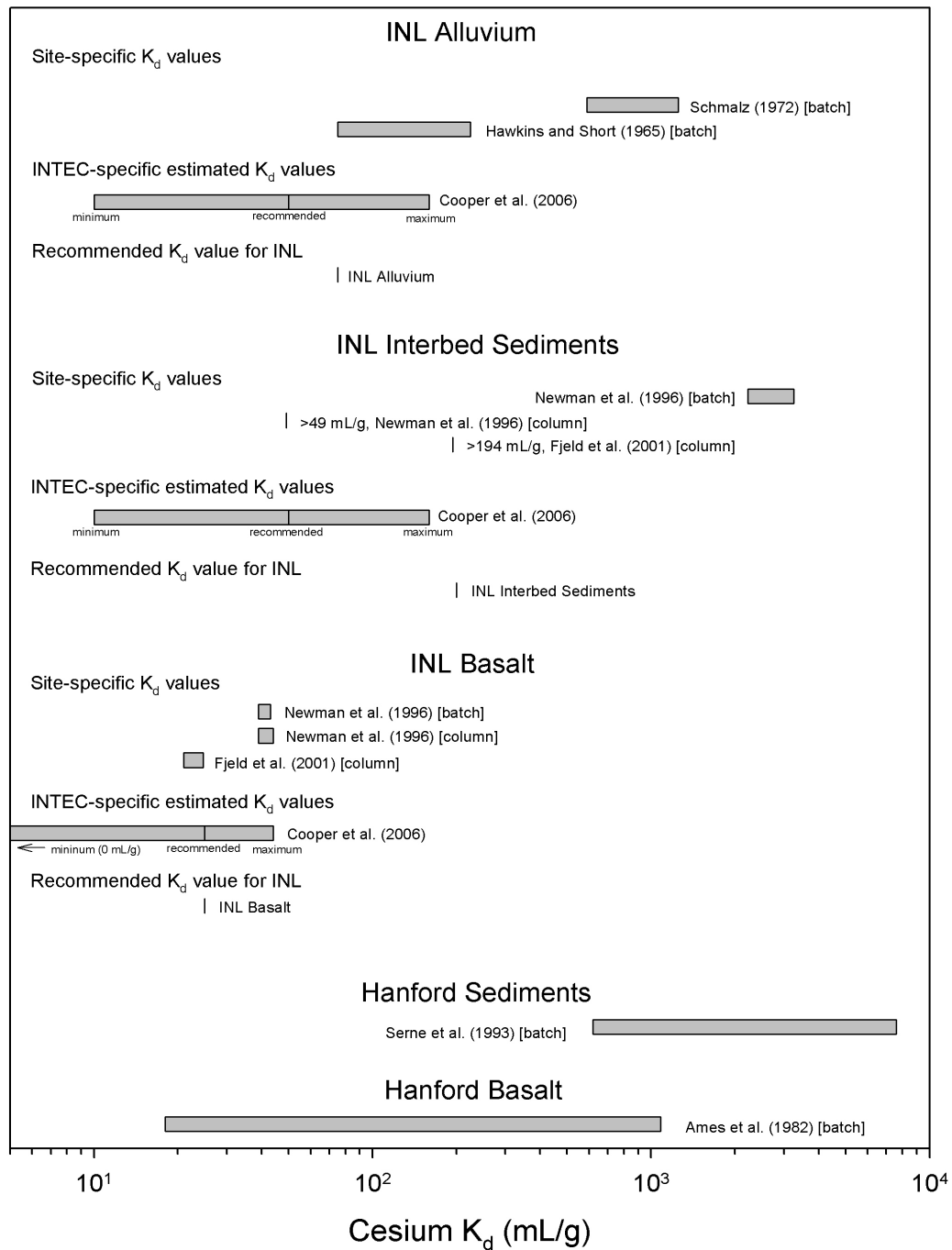
Pb-210 has 3 known oxidation states—0, +2, and +4—and the most common redox state found in the environment is the divalent form. Dissolved lead in natural systems may exist in free ionic form ( $Pb^{2+}$ ) and also as hydrolytic and complex species. At pH values exceeding 7, aqueous lead exists mainly as carbonate complexes  $\{Pb[(CO_3)^0(aq)]$  and  $Pb(CO_3)_2^{2-}\}$ . Studies have shown that, in neutral to high pH conditions,  $Pb^{2+}$  can preferentially exchange for  $Ca^{2+}$  and  $K^+$  (Zimdahl and Hassett, 1977; Bittel and Miller, 1974). Under acidic pH conditions, hydrogen ions and aluminum ions will displace lead from mineral exchange sites. Lead is known to adsorb onto soil constituent surfaces such as clays, oxides, hydroxides, oxyhydroxides, and organic matter. Lead adsorption studies on bulk soils indicate that the adsorption is strongly correlated with pH and the CEC values of soils (Bittel and Miller, 1974; Griffin and Shimp, 1976; Haji-Djafari, et al., 1981; Scudato and Estes, 1975; Zimdahl and Hassett, 1977). Properties that affect CEC of soils, such as organic matter content, clay content, and surface area, have a greater effect on lead adsorption than soil pH.

No site-specific data on lead sorption on geologic media at INL were found in the literature. Rodriguez, et al. (1997) analyzed systems comparable to the INL and estimated that lead  $K_d$  values for sediments and basalt at INL should range from 30 to 1,000 mL/g and 5 to 50 mL/g, respectively. Based on these ranges, Rodriguez, et al. (1997) recommended a lead  $K_d$  value of 270 mL/g for INL sediments and a lead  $K_d$  value of 10 mL/g for INL basalt.

Gerriste, et al. (1982) examined lead adsorption onto generic soils as a function of pH. Results indicated that lead adsorption increased with increasing soil pH (from 4 to 8). A summary of  $K_d$  values reported by Gerriste, et al. (1982) is listed in EPA (1999). Lead  $K_d$  values for pHs of 4.5, 5.0, 7.5, and 8.0 were 280; 1,295; 3,000; and 4,000 mL/g; respectively.

Rhoads, et al. (1992) investigated lead adsorption by a subsurface soil from the Hanford site. Adsorption data from these experiments showed that  $K_d$  values increased with decreasing lead





**Figure 3-6. Measured and Estimated Site-Specific and Analogous Cesium  $K_d$  Ranges and Values and Recommended Cesium  $K_d$  Values for Alluvium, Interbed Sediments, and Basalt at INL (Table 3-9). Recommended Cesium  $K_d$  Values Are Associated With Low Uncertainty Due to Available Site-Specific Sorption Data.**

concentrations in solution {from 0.2 to 0.0001 mg/L [0.2 to 0.0001 ppm]}. At a fixed pH of 8.35, the authors found that  $K_d$  values, which ranged from 13,000 to 79,000 mL/g, were log-linearly correlated with equilibrium concentrations of lead in solution.

Based on the data sets reported by Gerriste, et al. (1982) and Rhoads, et al. (1992), a lookup table was developed to estimate the range of lead  $K_d$  values as a function of soil pH and equilibrium lead concentration (EPA, 1999). Gerriste, et al. (1982) measured adsorption data for 2 well-characterized soils using a range of lead concentrations {0.001 to 0.1 mg/L [0.001 to 0.1 ppm]}, which precluded the possibility of precipitation reactions. Similarly, the adsorption data reported by Rhoads, et al. (1992) encompassed a range of lead concentrations from 0.0001 to 0.2 mg/L [0.0001 to 0.2 ppm] at a fixed pH value. Both of these data sets were used for estimating the range of  $K_d$  values for the range of pH and aqueous lead concentration values associated with soils. For the range of pH values expected at INL (pH 6.4–8.7), equilibrium lead concentrations from 0.1 to 0.9  $\mu\text{g/L}$  [0.1 to 0.9 ppb], 1.0 to 9.9  $\mu\text{g/L}$  [1.0 to 9.9 ppb], 10 to 99.9  $\mu\text{g/L}$  [10 to 99.9 ppb], and 100 to 200  $\mu\text{g/L}$  [100 to 200 ppb] were estimated to have lead  $K_d$  values ranging from 4,360 to 23,270 mL/g; 1,950 to 10,760 mL/g; 900 to 4,970 mL/g; and 710 to 2,300 mL/g; respectively.

Veeresh, et al. (2003) performed batch equilibrium experiments to measure lead  $K_d$  values on three soils. A 0.005 M  $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  solution was used in the batch experiments. Soils had varying particle size characteristics: a silty sand soil (85-wt% sand and silt, 15-wt% clay) at pH 5.1, a clay-rich silty sand soil (72-wt% sand and silt, 28-wt% clay) at pH 7.1, and a clay-rich soil (63-wt% clay, 27-wt% sand and silt) at pH 8.6.  $K_d$  values determined from sorption isotherms were 87 mL/g for the silty sand soil, 726 mL/g for the clay-rich silty sand soil, and 7,083 mL/g for the clay-rich soil.

Recommended lead  $K_d$  values are summarized in Table 3-10. No site-specific  $K_d$  data are available for lead adsorption on INL subsurface media. Based on an analysis of comparable systems, Rodriguez, et al. (1997) determined that lead  $K_d$  values in sediments at INL could range from 30 to 1,000 mL/g and recommended a lead  $K_d$  value of 270 mL/g. Measured lead  $K_d$  values from batch sorption studies at alkaline pH on generic soils (3,000 to 4,000 mL/g) (Gerriste, et al., 1982) and sediments from the Hanford site (13,000 to 79,000 mL/g) (Rhoads, et al., 1992) have much higher values than estimated by Rodriguez, et al. (1997). From the batch sorption experiments of Veeresh, et al. (2003), the silty sand soil and clay-rich silty sand soil noted previously are most comparable to sediments at INL, and the low ionic strength, calcium-rich solution used in the experiments is comparable to groundwater at INL. Measured  $K_d$  values for the silty sand soil and the clay-rich silty sand soil were 87 mL/g and 726 mL/g, respectively; however, the 87 mL/g value was from a pH 5.1 experiment. Considering the strong pH dependence of the lead  $K_d$  (e.g., Gerriste, et al., 1982), this especially low result can be discounted for the INL subsurface environment. The lowest value from the EPA (1999) lookup table for INL conditions was 710 mL/g. Based on these observations, the lead  $K_d$  value of 270 mL/g recommended by Rodriguez, et al. (1997) for sediments at INL is conservative and is recommended in this review for alluvium and sedimentary interbeds. Based on an analysis of comparable systems, Rodriguez, et al. (1997) estimated that lead  $K_d$  values in basalt at INL could range from 5 to 50 mL/g and recommended a lead  $K_d$  value of 10 mL/g. Lacking direct sorption data for lead, a lead  $K_d$  value of 10 mL/g is recommended for basalt.

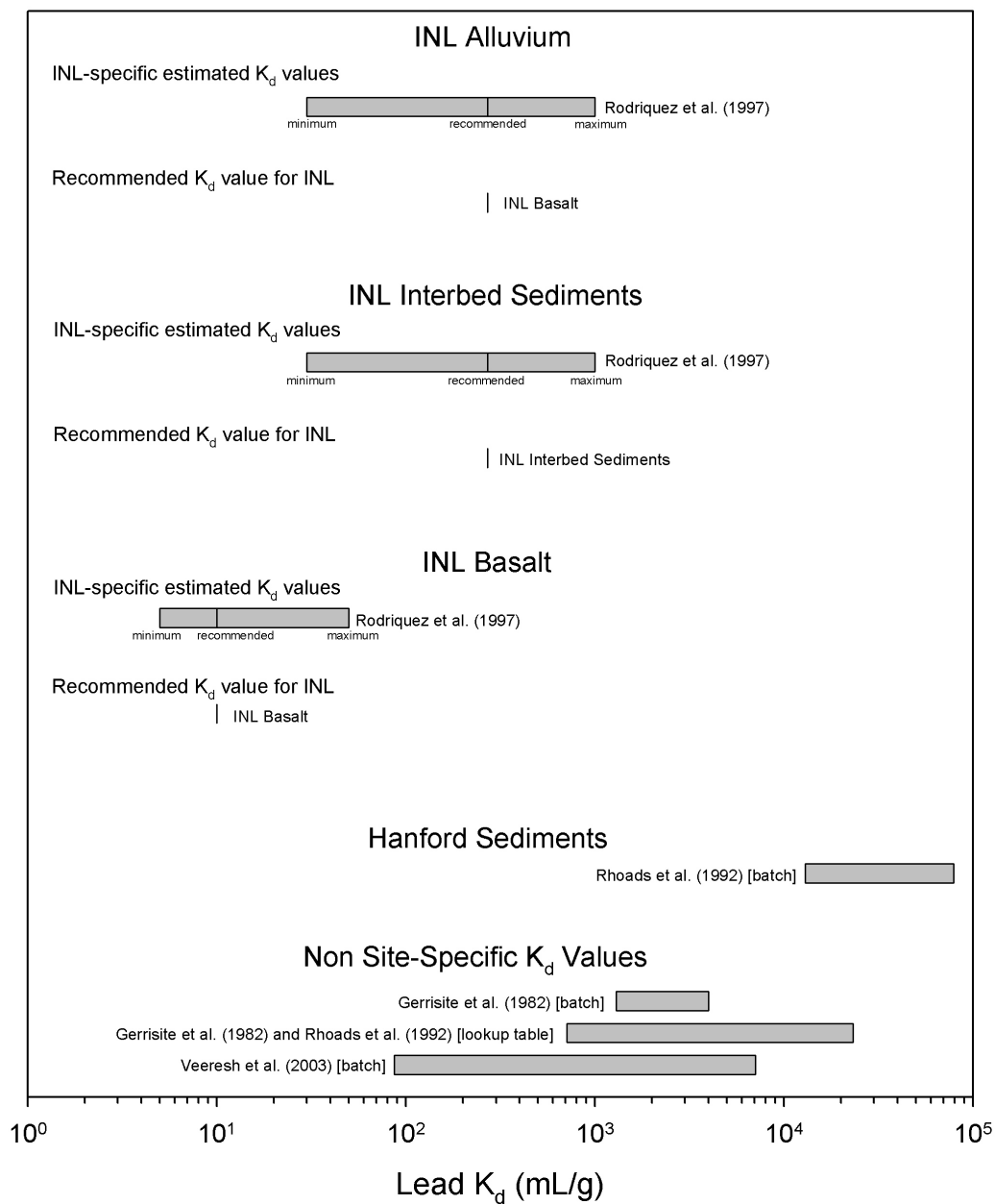
<b>Table 3-10. Recommended Lead <math>K_d</math> Values for Alluvium, Interbed Sediments, and Basalt at the Idaho National Laboratory</b>				
	<b>Measured Lead <math>K_d</math> (mL/g)</b>	<b>Test Method</b>	<b>Idaho National Laboratory-Specific Recommended Lead <math>K_d</math> (mL/g)*</b>	<b>Recommended Lead <math>K_d</math> (mL/g)</b>
Alluvium	—	—	270	270
Sedimentary Interbeds	—	—	270	270
Basalt	—	—	10	10
*Rodriguez, R.R., A.L. Schafer, J. McCarthy, P. Martian, D.E. Burns, D.E. Raunig, N.A. Burch, and R.L. VanHorn. DOE/ID-10534, "Comprehensive RI/FS for the Idaho Chemical Processing Plant OU 3-13 at the INEEL—Part A, RI/BRA Report (Final)." Idaho Falls, Idaho: Idaho National Engineering Laboratory, DOE-Idaho. 1997.				

The position of the lead  $K_d$  values recommended in this review with respect to measured and estimated site-specific and analogous lead  $K_d$  ranges and values is graphically displayed in Figure 3-7. This figure illustrates the uncertainty associated with the lead  $K_d$  values recommended for alluvium, interbed sediments, and basalt at INL. The recommended lead  $K_d$  values are associated with high uncertainty due to the lack of site-specific lead sorption data.

### 3.4.7 Uranium

In natural environments, the most important oxidation states of uranium are +4 and +6. U(VI) species dominate in oxidizing environments; the dominant species are  $UO_2^{2+}$  at pH values less than 5 and mixed carbonate/hydroxyl and carbonate species at pH values between 5 and 9 (Langmuir, 1997). In low ionic strength solutions with low U(VI) concentrations,  $UO_2^{2+}$  concentrations will likely be controlled by cation exchange and adsorption processes. The uranyl ion and its complexes adsorb onto clays (Ames, et al. 1982), organics (Read, et al. 1993; Shanbhag and Choppin, 1981), and oxides (Hsi and Langmuir, 1985; Waite, et al., 1994). As ionic strength increases, other ions, notably  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $K^+$ , displace the uranyl ion from soil exchange sites, forcing it into solution. U(VI) retention by soils and rocks in alkaline conditions is poor because of the predominance of neutral and negatively charged species. An increase in  $pCO_2$  in soil solutions reduces U(VI) adsorption by promoting the formation of poorly sorbing carbonate complexes (Pabalan, et al., 1998). U(IV) species dominate in reducing environments. U(IV) tends to hydrolyze and form strong hydrolytic complexes. U(IV) also forms strong complexes with naturally occurring organic materials.

Several researchers have conducted sorption studies of uranium onto INL sediments and basalts. These studies are described next.



**Figure 3-7. Measured and Estimated Site-Specific and Analogous Lead  $K_d$  Ranges and Values and Recommended Lead  $K_d$  Values for Alluvium, Interbed Sediments, and Basalt at INL (Table 3-10). Recommended Lead  $K_d$  Values Are Associated With High Uncertainty Due to the Lack of Site-Specific Sorption Data.**

Leecaster and Hull (2004) conducted batch experiments to measure uranium  $K_d$  values on 36 SDA interbed sediment samples in a synthetic groundwater. The simulated groundwater had a low ionic strength, a pH of  $8.0 \pm 0.2$ , and contained important cations and anions present in vadose zone waters at the SDA. Batch tests were carried out for time periods of 48 to 56 days. Measured uranium  $K_d$  values ranged from 0.6 to 48 mL/g with a median of 17.9 mL/g. When compared to sediment properties, uranium  $K_d$  values correlated most strongly to CEC, suggesting that surface reactions with clay minerals control uranium sorption chemistry in the INL subsurface.

Grossman, et al. (2001) conducted batch sorption experiments to characterize the sorption behavior of uranium at INL. Batch experiments were conducted with depth-discrete core samples of sedimentary interbed from beneath the Radioactive Waste Management Complex. The solution used for the batch experiments was a low ionic strength synthetic groundwater (pH 8.0) based on Wood and Low's (1986) characterization of the SRPA. Partitioning data were collected for between 48 and 56 days. Measured uranium  $K_d$  values ranged from 23 to 74 mL/g.

Newman, et al. (1996) summarized results from short-term (400-hour) batch experiments and column tests measuring uranium  $K_d$  values for basalt and interbed sediments. The batch and column tests were conducted using a synthetic groundwater formulated to approximate the composition observed in SRPA field samples (ionic strength = 0.0048 M; pH 8.0) (Wood and Low, 1986). For batch tests, uranium  $K_d$  values ranged from 4 to 6 mL/g for basalt and from 3 to 6 mL/g for interbed sediments. For column tests, uranium  $K_d$  values ranged from 0.2 to 0.3 mL/g for basalt and 7.34 to 11.43 mL/g interbed sediments.

Fjeld, et al. (2001) performed laboratory column tests to characterize the mobility of uranium in a basalt sample and a composite of sedimentary interbed from INL. The solution used in the tests was a low ionic strength (0.004 M) synthetic groundwater (pH 8.0) formulated to approximate the major ion concentration of SRPA groundwater samples (Wood and Low, 1986). Uranium retardation factors ranged from 5.1 to 6.1 for basalt and 30 to 31 for interbed sediments. Based on the reported porosities and bulk densities of the basalt and interbed columns, these retention factors equate to  $K_d$  values of 1.30 to 1.42 mL/g for basalt and 7.38 to 8.18 mL/g for interbed sediments.

An unpublished study of uranium transport through unsaturated sediments in a near field-scale column reactor packed with SDA surficial sediments (Cooper, et al., 2006) indicated that uranium  $K_d$  values can range from 4 to 50 mL/g.

Cooper, et al. (2006) estimated that uranium  $K_d$  values for alluvium and interbed sediments at INTEC should range from 0.12 to 12 mL/g and recommended a uranium  $K_d$  value of 1.6 mL/g for the alluvium and interbed sediments. The minimum and maximum uranium  $K_d$  values estimated by Cooper, et al. (2006) represented the range of values from batch and column experiments conducted on SDA sediments by Leecaster and Hull (2004), Grossman, et al. (2001), and Fjeld, et al. (2001), as scaled to CEC (INTEC/SDA = 1:5). The recommended uranium  $K_d$  value for alluvium and interbed sediments was based on the column experiments of Fjeld, et al. (2001), as scaled to CEC. Based on the column experiments of Fjeld, et al. (2001), Cooper, et al. (2006) estimated a uranium  $K_d$  range of 0 to 1.4 mL/g for INTEC basalt and recommended a uranium  $K_d$  value of 0 mL/g.

Researchers have measured uranium  $K_d$ s in basalt and surficial sediments from the Hanford site. These measurements are described next.

Kaplan and Serne (1995) and Lindenmeier, et al. (1995) performed unsaturated column tests to measure uranium sorption onto a loamy sand sediment taken from the Hanford site. The solution used in the experiments was a low ionic strength, low organic content, uncontaminated groundwater (pH 8.3) from the site. Kaplan and Serne (1995) reported measured  $K_d$  values ranging from 0.08 to 2.81 mL/g, and Lindenmeier, et al. (1995) reported  $K_d$  values ranging from 0.2 to 2.7 mL/g. In both studies, uranium  $K_d$  values typically increased with increasing degree of column saturation.

Kaplan, et al. (1998c) conducted batch tests to measure uranium sorption onto a silty loam and coarse sand taken from trenches at the Hanford site. The solution used in the tests was an uncontaminated groundwater from the Hanford site (pH 8.3). Measured  $K_d$  values ranged from 1.07 to 2.44 mL/g for the silty loam and from 0.14 to 0.2 mL/g for the coarse sand.

Kaplan, et al. (1996) performed batch and unsaturated column tests to measure uranium sorption onto surficial sediments from the Hanford site using an uncontaminated groundwater (pH 8.46). Measured  $K_d$  values ranged from 0.9 to 3.5 mL/g for the batch tests and 0.1 to 0.64 mL/g for the unsaturated column tests.

Ames, et al. (1982) conducted batch equilibrium tests to measure uranium sorption onto Umtanum, Flow E, and Pomona basalts from the Hanford site under oxidizing conditions using two synthetic groundwater solutions. The compositions of the solutions were based on those of groundwater samples taken at depth from the Columbia River basalt formations. Four initial concentrations of uranium were used for the measurements ( $1.0 \times 10^{-4}$ ,  $1.0 \times 10^{-5}$ ,  $1.0 \times 10^{-6}$ , and  $1.0 \times 10^{-7}$  M uranium). The pH values of the final solutions ranged from 7.65 to 8.48. Measured uranium  $K_d$  values for the basalts ranged from 0.19 to 20 mL/g and decreased with increasing uranium content.

In a similar study, Salter, et al. (1981) conducted batch experiments to measure uranium sorption onto Columbia River basalts (Umtanum, Flow E, and Pomona basalts). Measurements were conducted with two synthetic groundwater solutions having compositions representative of the groundwater present in basalt formations at the Hanford site.  $K_d$  values were determined for initial concentrations of  $1.0 \times 10^{-4}$ ,  $1.0 \times 10^{-5}$ ,  $1.0 \times 10^{-6}$ ,  $1.0 \times 10^{-7}$ , and  $2.15 \times 10^{-8}$  M uranium. Measured uranium  $K_d$  values for the basalts ranged from 0.2 to 56 mL/g, and as expected, decreased with increasing uranium content.

Measured and recommended uranium  $K_d$  values are summarized in Table 3-11. Measured uranium  $K_d$  values from column experiments conducted on INL alluvium range from 4 to 50 mL/g (Cooper, et al., 2006). Cooper, et al. (2006) also estimated a uranium  $K_d$  range of 0.12 to 12 mL/g for INTEC alluvium and recommended a uranium  $K_d$  value of 1.6 mL/g. The estimated uranium  $K_d$  range and recommended uranium  $K_d$  for alluvium reported by Cooper, et al. (2006) represent the range of uranium  $K_d$  values from batch and column experiments conducted on SDA sediments by Leecaster and Hull (2004), Grossman, et al. (2001), and Fjeld, et al. (2001), scaled to CEC (INTEC/SDA = 1:5). Measured uranium  $K_d$  values from batch and column experiments conducted on surficial sediments from Hanford have  $K_d$  values at the low end of the uranium  $K_d$  range estimated by Cooper, et al. (2006). Measured uranium  $K_d$  values from batch experiments range from 0.9 to 3.5 mL/g (Kaplan, et al., 1998c, 1996). Measured

<b>Table 3-11. Measured and Recommended Uranium <math>K_d</math> Values for Alluvium, Interbed Sediments, and Basalt at the Idaho National Laboratory</b>				
	<b>Measured Uranium <math>K_d</math> (mL/g)</b>	<b>Test Method</b>	<b>Idaho Nuclear Technology and Engineering Center-Specific Recommended Uranium <math>K_d</math> (mL/g)*</b>	<b>Recommended Uranium <math>K_d</math> (mL/g)</b>
Alluvium	4–50†	Column	1.6	1.6
Sedimentary Interbeds	0.6–48‡ 23–74§ 3–6¶ 7.43–11.43¶ 7.38–8.18#	Batch Batch Batch Column Column	1.6	1.6
Basalt	4–6¶ 0.2–0.3¶ 1.3–1.42#	Batch Column Column	0	0.2
<p>*Cooper, D.C., G.D. Redden, and L.C. Hull. DOE/NE-ID-11227, “Operable Unit 3-14 Tank Farm Soil and Groundwater Remedial Investigation/Baseline Risk Assessment—Appendix D: Estimation of <math>K_d</math> Values for INTEC Groundwater Model.” Idaho Falls, Idaho: DOE-Idaho. 2006.</p> <p>†Cooper, D.C., G.D. Redden, and L.C. Hull. DOE/NE-ID-11227, “Operable Unit 3-14 Tank Farm Soil and Groundwater Remedial Investigation/Baseline Risk Assessment—Appendix D: Estimation of <math>K_d</math> Values for INTEC Groundwater Model.” Idaho Falls, Idaho: DOE-Idaho. 2006.</p> <p>‡Leecaster, M.K. and L.C. Hull. “Spatial Distribution of Neptunium and Uranium Partition Coefficients (<math>K_d</math>) for Interbed Sediments at a Radioactive Waste Subsurface Disposal Area.” ICP/EXT-03-00088. Rev. 0. Idaho Falls, Idaho: Idaho National Engineering and Environmental Laboratory. 2004.</p> <p>§Grossman, C.J., R.A. Fjeld, J.T. Coates, and A.W. Elzerman. “The Sorption of Selected Radionuclides in Sedimentary Interbed Soils from the Snake River Plain.” INEEL/EXT-01-01106. Rev. 0. Idaho Falls, Idaho: Idaho National Engineering and Environmental Laboratory. 2001.</p> <p>¶Newman, M.E., I. Porro, R. Scott, R.M. Dunnivant, R.W. Goff, M.D. Blevins, S.M. Ince, J.D. Leyba, T.A. DeVol, A.W. Elzerman, and R.A. Fjeld. “Evaluation of the Mobility of Am, Cs, Co, Pu, Sr, and U Through INEL Basalt and Interbed Materials: Summary Report of the INEL/Clemson University Laboratory Studies.” ER-WAG7-82, INEL-95/282. Idaho Falls, Idaho: Idaho National Engineering Laboratory. 1996.</p> <p>#Fjeld, R.A., T.A. DeVol, R.W. Goff, M.D. Blevins, D.D. Brown, S.M. Ince, A.W. Elzerman, and M.E. Newman. “Characterization of the Mobilities of Selected Actinides and Fission/activation Products in Laboratory Columns Containing Subsurface Material from the Snake River Plain.” <i>Nuclear Technology</i>. Vol. 135. pp. 92–108. 2001.</p>				

uranium  $K_d$  values from column experiments range from 0.08 to 2.81 mL/g (Kaplan and Serne, 1995; Lindenmeier, et al., 1995). The uranium  $K_d$  value of 1.6 mL/g recommended by Cooper, et al. (2006) is within the range of reported uranium  $K_d$  values measured on surficial sediments from Hanford (0.08 to 3.5 mL/g). Based on the recommendation of Cooper, et al. (2006), a uranium  $K_d$  value of 1.6 mL/g is recommended for alluvium at INL.

Measured uranium  $K_d$  values from batch experiments conducted on INL sedimentary interbed materials range from 0.6 to 74 mL/g (Leecaster and Hull, 2004; Grossman, et al., 2001; Newman, et al., 1996). Measured uranium  $K_d$  values from column experiments conducted on INL interbed sediments vary over a much narrower range (7.38 to 11.43 mL/g) (Newman, et al., 1996; Fjeld, et al., 2001). Cooper, et al. (2006) scaled the uranium  $K_d$  values reported by

Leecaster and Hull (2004), Grossman, et al. (2001), and Fjeld, et al. (2001) with respect to observed differences in the CEC of INTEC and SDA interbed sediments (INTEC/SDA = 1:5). Based on this scaling, Cooper, et al. (2006), estimated a uranium  $K_d$  range of 0.12 to 12 mL/g for interbed sediments at INTEC and recommended a uranium  $K_d$  value of 1.6 mL/g. Based on the recommendation of Cooper, et al. (2006), a uranium  $K_d$  value of 1.6 mL/g is recommended for interbed sediments at INL.

Measured uranium  $K_d$  values from a batch experiment conducted on INL basalt range from 4 to 6 mL/g (Newman, et al., 1996). Measured uranium  $K_d$  values from column experiments conducted on INL basalt range from 0.2 to 1.42 mL/g (Newman, et al., 1996; Fjeld, et al., 2001). These values are comparable to the low end of uranium  $K_d$  values measured from batch experiments using basalt from the Hanford site (0.19 to 56 mL/g) (Ames, et al., 1982; Salter, et al., 1981). Based on the column experiments of Newman, et al. (1996) and Fjeld, et al. (2001), a uranium  $K_d$  value of 0.2 mL/g is recommended for basalt. This value is greater than the uranium  $K_d$  value of 0 mL/g recommended by Cooper, et al. (2006), which was based solely on the column experiments of Fjeld, et al. (2001).

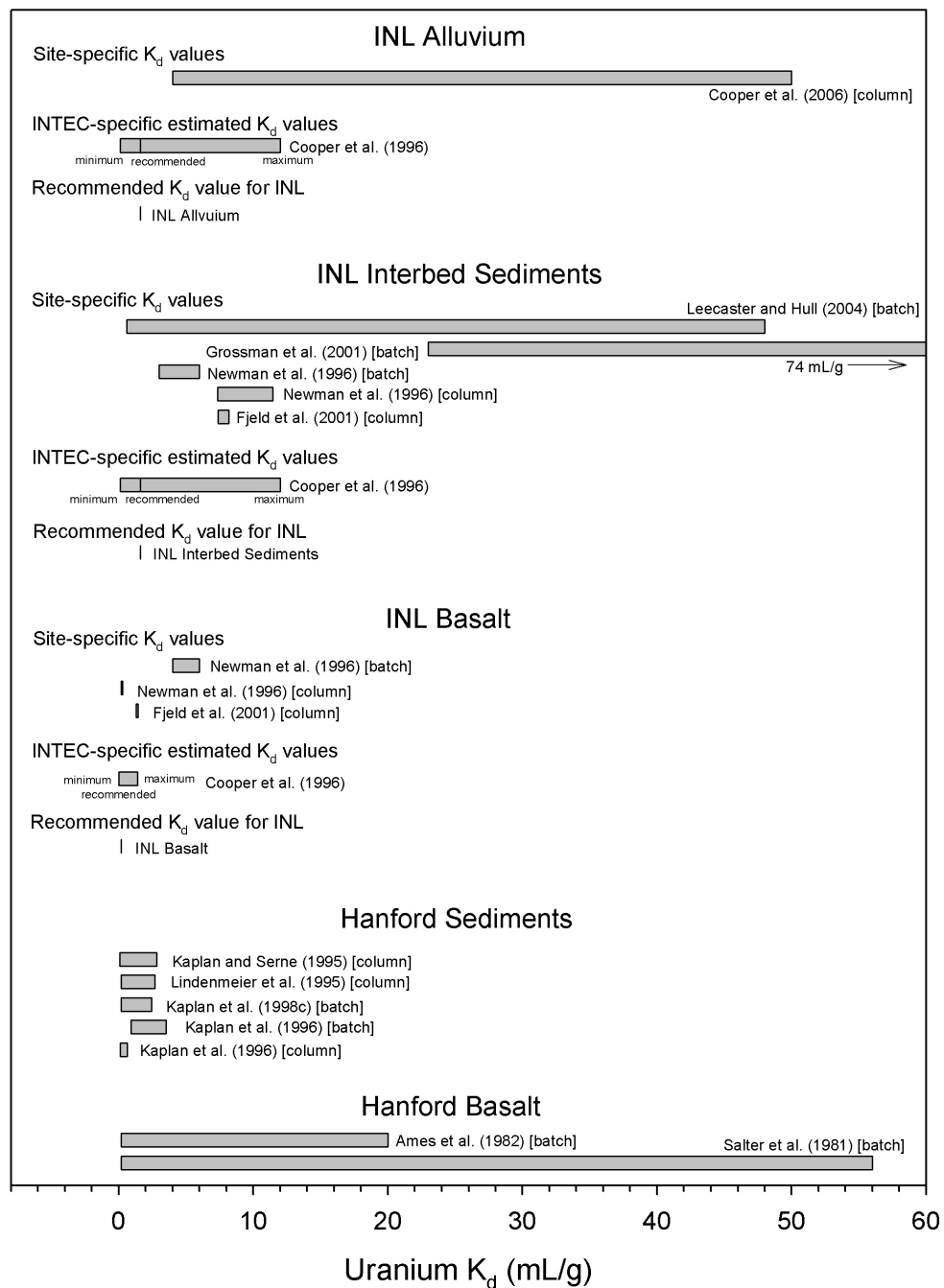
The position of the uranium  $K_d$  values recommended in this review with respect to measured and estimated site-specific and analogous uranium  $K_d$  ranges and values is graphically displayed in Figure 3-8. This figure illustrates the uncertainty associated with the uranium  $K_d$  values recommended for alluvium, interbed sediments, and basalt at INL. Due to available site-specific uranium sorption data (e.g., Leecaster and Hull, 2004; Newman, et al., 1996; Fjeld, et al., 2001) and analogous uranium sorption data from the Hanford site (e.g., Kaplan and Serne, 1995; Kaplan, et al., 1998c, 1996), the recommended uranium  $K_d$  values are associated with low uncertainty.

### **3.4.8 Neptunium**

Np-237 may exist in several valence states. Np(VI), Np(V), and Np(IV) are the most important valence states in natural waters. Over the pH range of most natural waters, Np(V) is dominant and present primarily as the cation  $\text{NpO}_2^+$ . Np(V) aqueous species sorb to some extent to iron oxides and clays, but do not sorb to a major degree on most common minerals. Therefore, dissolved Np(V) is considered to be relatively mobile in soil systems. Because  $\text{NpO}_2^+$  does not compete favorably with dissolved  $\text{Ca}^{2+}$  and other divalent ions for adsorption sites on soils, the  $K_d$  values for Np(V) are relatively low (Kaplan and Serne, 2000). The adsorption of Np(V) is strongly dependent on pH. Typically, the sorption of Np(V) on iron oxides is negligible at pH values less than 5 and increases rapidly at pH values between 5 and 7. On silicates, the sorption of Np(V) is negligible at pH values less than 6 and increases rapidly at pH values between 6 and 8. This pH dependency is expected for ions present in solution primarily as cations. In carbonate-containing solutions, the adsorption of Np(V) on iron oxides and silicates has been observed to decrease at pH values greater than 7 to 9 and 8 to 9, respectively, in response to formation of aqueous Np(VI) carbonate complexes. Aqueous organic complexes can enhance Np(V) solubility, but sedimentary organic matter is not known to notably affect Np(V) sorption.

Mincher, et al. (2003) conducted batch experiments to investigate neptunium sorption onto SDA soils collected at depths of 0.5 to 6 m [1.6 to 20 ft] at INL. A simulated low ionic strength simulated groundwater (pH 7.55) was used in the batch experiments. At 3-hour contact times, neptunium  $K_d$  values of  $49 \pm 12$  mL/g were reported.





**Figure 3-8. Measured and Estimated Site-Specific and Analogous Uranium  $K_d$  Ranges and Values and Recommended Uranium  $K_d$  Values for Alluvium, Interbed Sediments, and Basalt at INL (Table 3-11). Recommended Uranium  $K_d$  Values Are Associated With Low Uncertainty Due to Available Site-Specific Sorption Data.**

Leecaster and Hull (2004) conducted batch experiments to measure neptunium  $K_d$  values on 36 SDA interbed sediment samples in a synthetic groundwater. The simulated groundwater had a low ionic strength, a pH of  $8.0 \pm 0.2$ , and contained important cations and anions present in vadose zone waters at the SDA. Batch tests were carried out for time periods of 48 to 56 days. Measured neptunium  $K_d$  values ranged from 0.1 to 251 mL/g with a median of 35 mL/g. When compared to sediment properties, neptunium  $K_d$  values correlated most strongly to CEC, suggesting that surface reactions with clay minerals control neptunium sorption chemistry in the INL subsurface.

Grossman, et al. (2001) conducted batch sorption experiments to characterize the sorption behavior of neptunium at INL. Batch experiments were conducted with depth-discrete core samples of sedimentary interbed from beneath the Radioactive Waste Management Complex. The solution used for the batch experiments was a low ionic strength synthetic groundwater (pH 8.0) based on the Wood and Low (1986) SRPA characterization. Partitioning data were collected for 56 days. Measured neptunium  $K_d$  values ranged from 38 to 280 mL/g.

Dicke (1997) analyzed comparable systems and estimated that neptunium  $K_d$  values for sediments and basalt at INL should range from 1 to 80 mL/g and 1.3 to 51 mL/g, respectively. Based on these ranges, Dicke (1997) recommended a neptunium  $K_d$  value of 8 mL/g for both INL sediments and INL basalt.

Cooper, et al. (2006) estimated that neptunium  $K_d$  values for alluvium and interbed sediments at INTEC should range from 0.1 to 60 mL/g and recommended a neptunium  $K_d$  value of 2 mL/g for the alluvium and interbed sediments. The minimum and maximum neptunium  $K_d$  values estimated by Cooper, et al. (2006) represented the range of values from batch experiments conducted on SDA sediments by Mincher, et al. (2003), Leecaster and Hull (2004), and Grossman, et al. (2001), as scaled to CEC (INTEC/SDA = 1:5). The recommended neptunium  $K_d$  value of 2 mL/g was based on field lysimeter experiments conducted on a sandy sediment roughly comparable to INTEC alluvium and interbed sediments (Sheppard and Thibault, 1991). In these experiments, Sheppard and Thibault (1991) reported neptunium  $K_d$  values ranging from 0.5 to 1.6 mL/g at 1-year aging and 0.6 to 5 mL/g at 4-year aging with a median value of 2 mL/g. Lacking site-specific  $K_d$  data for basalt, Cooper, et al. (2006) assumed that the neptunium  $K_d$  value of 8 mL/g recommended by Dicke (1997) for basalt provided a reasonable maximum value and recommended a neptunium  $K_d$  value of 0 mL/g for basalt.

Researchers have measured neptunium  $K_d$  values in surficial sediments from the Hanford site. Serne, et al. (1993) measured  $K_d$  values for Np(V) in groundwater contacting surficial sediments from the Hanford site. The pH of the Hanford groundwater was 8.3. The sediment used in the experiment contained 87-wt% sand, 7-wt% silt, and 6-wt% clay. The  $K_d$  values measured at 5 and 44 days were  $13.5 \pm 3$  and  $29.1 \pm 3.6$  mL/g, respectively.

Kaplan, et al. (1996) conducted batch experiments to measure the  $K_d$  values for Np(V) on three surficial sediment samples from Hanford. The measurements were conducted with a groundwater (pH 8.46) taken from an uncontaminated well on the Hanford site. Sediments included a sand, silty loam, and very coarse sand. Kaplan, et al. (1996) observed that the  $K_d$  values increased as a function of time.  $K_d$  values measured at 7 days were 2.17 mL/g for the sand, 2.67 mL/g for the silty loam, and 14.17 mL/g for the coarse sand.  $K_d$  values measured at 77 days were 3.62 mL/g for the sand, 13.48 mL/g for the silty loam, and 19.86 mL/g for the coarse sand.

Measured and recommended neptunium  $K_d$  values are summarized in Table 3-12. Mincher, et al. (2003) measured site-specific neptunium  $K_d$  values ranging from 37 to 61 mL/g for alluvium at INL. Measured neptunium  $K_d$  values for surficial sediments from Hanford determined using batch methods ranged from 2.17 to 29.1 mL/g (Kaplan, et al., 1996; Serne, et al., 1993). Based on field lysimeter experiments conducted by Sheppard and Thibault (1991) on a sandy sediment roughly comparable to INTEC alluvium, Cooper, et al. (2006) recommended a neptunium  $K_d$  of 2 mL/g for INTEC alluvium. The value is comparable to the low end of the range of neptunium  $K_d$  values measured on surficial sediments at Hanford (2.17 to 29.1 mL/g). Based on the neptunium  $K_d$  recommendation of Cooper, et al. (2006), a neptunium  $K_d$  value of 2 mL/g is recommended for alluvium at INL.

Measured neptunium  $K_d$  values for sedimentary interbed materials from batch experiments range from a minimum of 0.1 mL/g (Leecaster and Hull, 2004) to a maximum of 280 mg/L (Grossman, et al., 2001). Based on an analysis of comparable systems, Dicke (1997) estimated a neptunium  $K_d$  range of 1 to 80 mL/g for INL sediments and recommended a neptunium  $K_d$  of 8 mL/g. Based on field lysimeter experiments conducted by Sheppard and Thibault (1991) on a sandy sediment roughly comparable to INTEC interbed sediments, Cooper, et al. (2006) recommended a neptunium  $K_d$  of 2 mL/g for INTEC interbeds. Based on these observations, a neptunium  $K_d$  value of 5 mL/g is recommended for sedimentary interbed materials at INL. This value is the midpoint between the neptunium  $K_d$  of 8 mL/g recommended by Dicke (1997) for

**Table 3-12. Measured and Recommended Neptunium  $K_d$  Values for Alluvium, Interbed Sediments, and Basalt at the Idaho National Laboratory**

	Measured Neptunium $K_d$ (mL/g)	Test Method	Idaho Nuclear Technology and Engineering Center-Specific Recommended Neptunium $K_d$ (mL/g)*	Recommended Neptunium $K_d$ (mL/g)
Alluvium	37–61†	Batch	2	2
Sedimentary Interbeds	0.1–251‡ 38–280§	Batch Batch	2	5
Basalt	—	—	0	0.2

\*Cooper, D.C., G.D. Redden, and L.C. Hull. DOE/NE-ID-11227, "Operable Unit 3-14 Tank Farm Soil and Groundwater Remedial Investigation/Baseline Risk Assessment—Appendix D: Estimation of  $K_d$  Values for INTEC Groundwater Model." Idaho Falls, Idaho: DOE-Idaho. 2006.

†Mincher, B.J., R.V. Fox, D.C. Cooper, and G.S. Groenewold. "Neptunium and Plutonium Sorption to Snake River Plain, Idaho Soil." *Radiochimica Acta*. Vol. 91. pp. 397–401. 2003.

‡Leecaster, M.K. and L.C. Hull. "Spatial Distribution of Neptunium and Uranium Partition Coefficients ( $K_d$ ) for Interbed Sediments at a Radioactive Waste Subsurface Disposal Area." ICP/EXT-03-00088. Rev. 0. Idaho Falls, Idaho: Idaho National Engineering and Environmental Laboratory. 2004.

§Grossman, C.J., R.A. Fjeld, J.T. Coates, and A.W. Elzerman. "The Sorption of Selected Radionuclides in Sedimentary Interbed Soils from the Snake River Plain." INEEL/EXT-01-01106. Rev. 0. Idaho Falls, Idaho: Idaho National Engineering and Environmental Laboratory. 2001.

INL sediments and the neptunium  $K_d$  of 2 mL/g recommended by Cooper, et al. (2006) for INTEC interbed sediments.

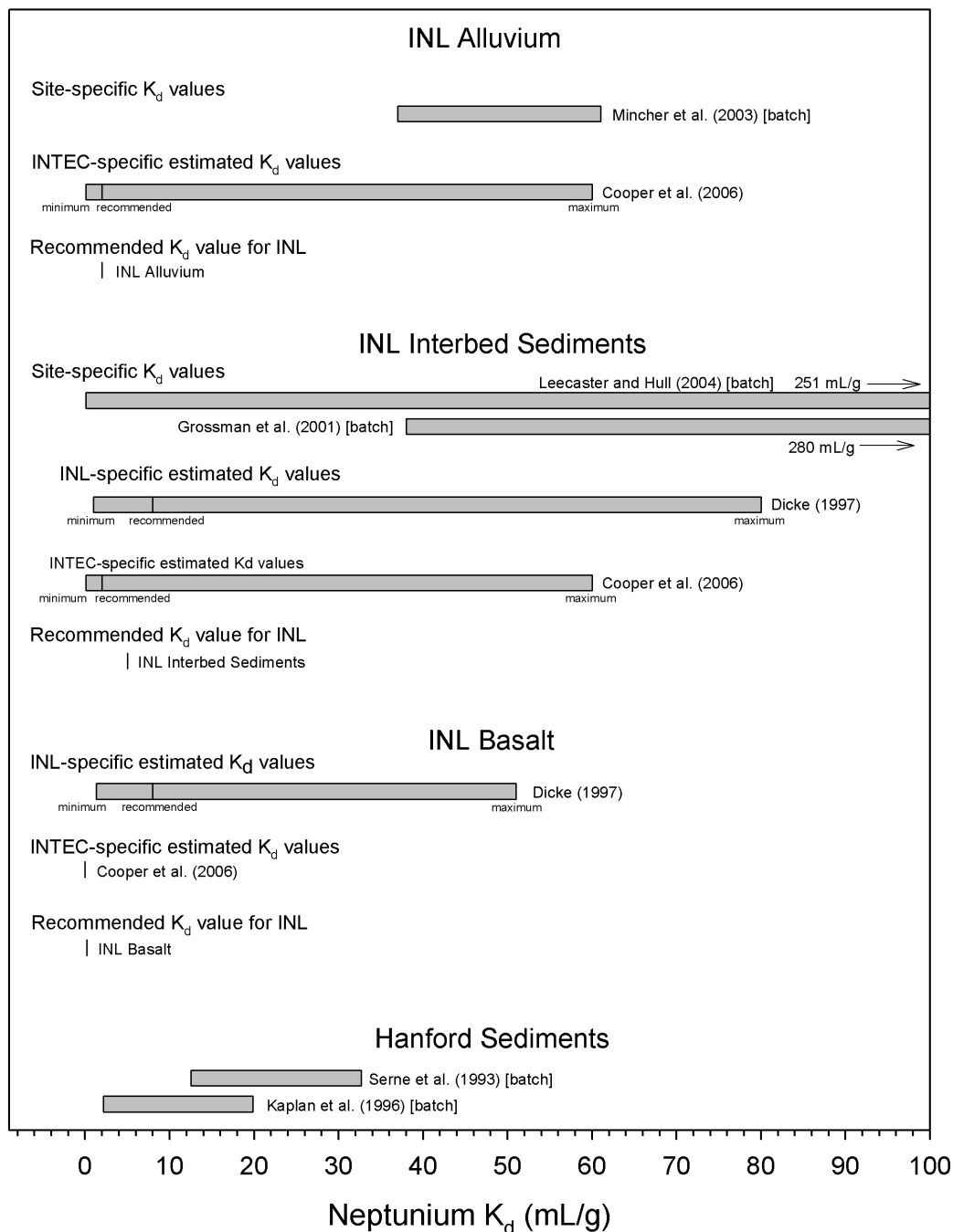
No site-specific neptunium sorption data are available for basalt from INL. Dicke (1997) estimated a neptunium  $K_d$  range of 1.3 to 51 for INL basalt based on analyses of comparable systems and recommended a neptunium  $K_d$  of 8 mL/g. Cooper, et al. (2006) recommended a neptunium  $K_d$  value of 0 mL/g for INTEC basalt. Beasley, et al. (1998) observed migration of contaminant radionuclides in the SRPA fractured basalt aquifer and calculated relative concentrations of radionuclides along the transport pathway. Based on limited U-236 and Np-237 results, and consistent with an earlier basalt aquifer modeling study, Beasley, et al. (1998) concluded that neptunium and uranium were retarded similarly. Therefore, we recommend the basalt  $K_d$  for neptunium be the same as for uranium—0.2 mL/g.

The position of the neptunium  $K_d$  values recommended in this review with respect to measured and estimated site-specific and analogous neptunium  $K_d$  ranges and values is graphically displayed in Figure 3-9. This figure illustrates the uncertainty associated with the neptunium  $K_d$  values recommended for alluvium, interbed sediments, and basalt at INL. Due to available site-specific neptunium sorption data (e.g., Leecaster and Hull, 2004; Grossman, et al., 2001) and analogous neptunium sorption data from the Hanford site (Serne, et al., 1993; Kaplan, et al., 1996), the recommended neptunium  $K_d$  values are associated with low uncertainty.

### **3.4.9 Plutonium**

In the range of pH and conditions typically encountered in natural waters, Pu-239 can exist in all 4 oxidation states, namely +3, +4, +5, and +6. Under oxidizing conditions, Pu(IV), Pu(V), and Pu(VI) are common, whereas under reducing conditions, Pu(III) and Pu(IV) exist. Plutonium is known to adsorb onto soil components such as clays, oxides, hydroxides, oxyhydroxides, aluminosilicates, and organic matter. Depending on the properties of the substrates, pH, and the composition of solutions, plutonium would adsorb with affinities varying from low ( $K_d = 10$  mL/g) to extremely high ( $K_d = 300,000$  mL/g) (Baes and Sharp, 1983; Thibault, et al., 1990). Under conditions of low pH and high concentrations of dissolved organic carbon, it appears that plutonium–organic complexes may control adsorption and mobility of plutonium. At neutral to alkaline pH (>7), dissolved plutonium forms very strong hydroxy–carbonate mixed ligand complexes, resulting in desorption and increased mobility in the environment. Studies have shown the potential importance of colloid-facilitated transport of plutonium in soil systems. Laboratory studies by Penrose, et al. (1990) predicted that the movement of plutonium would be limited to less than a few meters through a shallow aquifer within the site of the Los Alamos National Laboratory. However, plutonium was detected in monitoring wells as far as 3,390 m [11,120 ft] downgradient from the point source. Almost all of the plutonium in the groundwater at the 3,390-m [11,120-ft] well was associated with colloids.

A number of studies indicate that iron hydroxides adsorb and reduce Pu(V) and Pu(VI) to its tetravalent state at the solid surface. Fjeld, et al. (2003) have described a conceptual model for plutonium transport through sediment columns where plutonium transport is controlled by the net rate of reduction of adsorbed Pu(V) to adsorbed Pu(IV). In this model, oxidized plutonium can mobilize as Pu(V), and the Pu(V) can readsorb onto iron bearing minerals and be slowly reduced to Pu(IV). In this way, kinetic control of plutonium transport can allow a small fraction to move while the bulk of plutonium is largely immobile. This type of nonequilibrium behavior is



**Figure 3-9. Measured and Estimated Site-Specific and Analogous Neptunium  $K_d$  Ranges and Values and Recommended Neptunium  $K_d$  Values for Alluvium, Interbed Sediments, and Basalt at INL (Table 3-12). Recommended Neptunium  $K_d$  Values Are Associated With Low Uncertainty Due to Available Site-Specific and Analogous Sorption Data.**

difficult to capture with a  $K_d$  approach, but  $K_d$  can be used if the system is assumed to have reached steady state with respect to plutonium redox kinetics.

Mincher, et al. (2003) conducted batch experiments to investigate plutonium sorption onto SDA soils collected at depths of 0.5 to 6 m [1.6 to 20 ft] at INL. A low ionic strength simulated groundwater (pH 7.55) was used in the batch experiments. At 3-hour contact times, plutonium  $K_d$  values of  $54 \pm 26$  mL/g were reported.

Newman, et al. (1996) summarized results from short-term (400-hour) batch experiments measuring plutonium  $K_d$  values for basalt, interbed sediments, and surficial soils and column tests measuring plutonium  $K_d$  values for basalt and interbed sediments. The batch and column tests were conducted using a synthetic groundwater formulated to approximate the composition observed in SRPA field samples (ionic strength = 0.0048 M; pH 8.0) (Wood and Low, 1986). A series of batch tests was also conducted on basalt, interbed sediments, and surficial soils in the presence of EDTA, a strong chelating agent that forms negative or neutral complexes with metals. For batch tests, Pu(V)  $K_d$  values ranged from 70 to 130 mL/g for basalt; 5,100 to 7,900 mL/g for interbed sediments; and 7,800 to 22,000 mL/g for surficial soils. Pu(VI)  $K_d$  values for the batch tests ranged from 12 to 24 mL/g for basalt; 110 to 690 mL/g for interbed sediments; and 1,800 to 4,900 mL/g for surficial soils. Plutonium  $K_d$  values in the presence of EDTA for the batch tests ranged from 0.04 to 0.05 mL/g for basalt, 4 to 5 mL/g for interbed sediments, and 40 to 490 mL/g for surficial soils. However, organic complexants such as EDTA are not expected to be important for subsurface plutonium transport at INL. For column tests, total plutonium mobility was characterized by high and low mobility fractions. For basalt, the high mobility fraction (10 to 55 percent) had an estimated  $K_d$  value of 0.17 mL/g and a remaining low mobility fraction with an estimated  $K_d$  of  $>60$  mL/g. For interbed sediments, the high mobility fraction (~1 percent) was too small to determine a  $K_d$  value, and the remaining low mobility fraction had an estimated  $K_d$  of  $>47$  mL/g.

Fjeld, et al. (2001) performed laboratory column tests to characterize the mobility of plutonium in a basalt sample and a composite of sedimentary interbed from INL. The solution used in the tests was a low ionic strength (0.004 M) synthetic groundwater (pH 8.0) formulated to approximate the major ion concentration of SRPA groundwater samples (Wood and Low, 1986). Plutonium mobility was characterized by two fractions in both basalt and interbed sediments. For basalt, a high mobility fraction (17 to 29 percent) had retardation factors ranging from 1.2 to 5.0, and a remaining low mobility fraction had a retardation factor  $>200$ . For interbed sediments, a high mobility fraction (1.1 to 2.4 percent) had retardation factors of ~3, and a remaining low mobility fraction had a retardation factor  $>200$ . Based on reported porosities and bulk densities of packed columns, retardation factors for basalt equate to  $K_d$  values ranging from 0.05 to 1.14 mL/g for the high mobility fraction and  $>60$  mL/g for the low mobility fraction and for interbed sediments a  $K_d$  value of ~0.46 mL/g for the high mobility fraction and  $>47$  mL/g for the low mobility fraction.

Dicke (1997) analyzed comparable systems and estimated a plutonium  $K_d$  range of 5,100 to 22,000 mL/g for sediments at INL and a plutonium  $K_d$  range of 70 to 130 mL/g for basalt. Dicke (1997) recommended a plutonium  $K_d$  value of 5,100 mL/g for sediments, and a value of

100 mL/g for basalt. Navratil<sup>2</sup> reviewed historical studies of plutonium sorption on SDA interbed sediments and recommended a plutonium  $K_d$  between 300 and 3,500 mL/g for interbed material. Miner, et al. (1982) reported plutonium  $K_d$  values that range from 120 to 5,000 mL/g for batch experiments with Snake River Plain soils.

Cooper, et al. (2006) estimated a plutonium  $K_d$  range of 96 to 12,700 mL/g for alluvium and interbed sediments at INTEC and recommended a plutonium  $K_d$  value of 1,000 mL/g. The minimum and maximum plutonium  $K_d$  values estimated by Cooper, et al. (2006) represented the range of values from batch experiments conducted by Miner, et al. (1982) and Mincher, et al. (2003) and estimated plutonium  $K_d$  values for INL sediments reported by Dicke (1997). The recommended plutonium  $K_d$  value of 1,000 mL/g for alluvium and interbed sediments was based on a lysimeter experiment using a sandy clay sediment roughly comparable to INTEC alluvium and interbed sediments (Kaplan, et al., 2004). Results of the lysimeter experiment indicated a retention factor of 3,000 for Pu(IV), which equated to a  $K_d$  of 1,000 mL/g. Cooper, et al. (2006) estimated a plutonium  $K_d$  range of 0 to 130 mL/g for INTEC basalt and recommended a plutonium  $K_d$  value of 70 mL/g. The plutonium  $K_d$  value of 70 mL/g recommended by Cooper, et al. (2006) for basalt is equal to the minimum value estimated by Dicke (1997).

Researchers have measured plutonium  $K_d$  values in surficial sediments and basalt from the Hanford site. Barney (1992) studied sorption of plutonium in +4, +5, and +6 redox states on a shallow sediment from the Hanford site to elucidate any differences in rate and amount of plutonium sorption in different redox states. A synthetic groundwater was used in the experiments, and initial plutonium concentrations were varied between about  $10^{-11}$  and  $10^{-9}$  M. The data indicated that the  $K_d$  values ranged from 2,100 to 11,600 mL/g; 2,700 to 4,600 mL/g; and 1,000 to 4,600 mL/g for plutonium in +4, +5, and +6 redox states, respectively. The data also indicated that Pu(V) and Pu(VI) upon adsorption were reduced to the tetravalent state.

Ames, et al. (1981) and Salter, et al. (1981) conducted batch equilibrium tests to measure plutonium sorption onto Umtanum Basalt from the Hanford site. Measurements were conducted with synthetic groundwater solutions having compositions representative of the groundwater present in basalt formations at the Hanford site. Ames, et al. (1981) reported a plutonium  $K_d$  value of 20 mL/g, and Salter, et al. (1981) reported plutonium  $K_d$  values ranging from 20 to 25 mL/g.

Measured and recommended plutonium  $K_d$  values are summarized in Table 3-13. Site-specific total plutonium  $K_d$  values for alluvium from INL determined by batch methods range from 28 to 80 mL/g (Mincher, et al., 2003) at 3-hour contact times. These experiments may have been too short to provide reliable  $K_d$  values. Newman, et al. (1996) conducted batch experiments to measure plutonium sorption on INL alluvium at 400-hour contact times and reported Pu(V)  $K_d$  values ranging from 7,800 to 22,000 mL/g; Pu(VI)  $K_d$  values ranging from 1,800 to 4,900 mL/g; and total plutonium  $K_d$  values ranging from 40 to 490 mL/g in the presence of EDTA. Miner, et al. (1982) reported total plutonium  $K_d$  values ranging from 120 to 5,000 mL/g for Snake River Plain soils. Based on the 400-hour batch experiments of Newman, et al. (1996) and considering the range of plutonium  $K_d$  values reported by Miner, et al. (1982), a total plutonium

---

<sup>2</sup>Navratil, J.D. "Idaho Chemical Processing Plant (ICPP)  $K_d$  Studies." Memo (September 5) to R.D. Greenwell, Lockheed Martin Idaho Technologies Company. JDN-001-97. Idaho Falls, Idaho: Lockheed Martin Idaho Technologies Company. 1997.

**Table 3-13. Measured and Recommended Plutonium  $K_d$  Values for Alluvium, Interbed Sediments, and Basalt at the Idaho National Laboratory**

	Measured Plutonium $K_d$ (mL/g)	Test Method	Idaho Nuclear Technology and Engineering Center-Specific Recommended Plutonium $K_d$ (mL/g)*	Recommended Plutonium $K_d$ (mL/g)
Alluvium Pu(V) Pu(VI) Pu(EDTA) Pu(total)	7,800–22,000† 1,800–4,900† 40–490† 28–80‡ 120–5,000§	Batch Batch Batch Batch Batch	1,000	1,000
Sedimentary Interbeds Pu(V) Pu(VI) Pu(EDTA) Pu(total)	5,100–7,900† 110–690† 4–5† >47† >47¶ 0.46¶ (hmf)#	Batch Batch Batch Column Column Column	1,000	500 0.5 (hmf)#
Basalt Pu(V) Pu(VI) Pu(EDTA) Pu(total)	7–130† 12–24† 0.04–0.05† >60† 0.17† (hmf)# >60¶ 0.05–1.14¶ (hmf)#	Batch Batch Batch Column Column Column Column	70	70 0.2 (hmf)#

\*Cooper, D.C., G.D. Redden, and L.C. Hull. DOE/NE-ID-11227, "Operable Unit 3-14 Tank Farm Soil and Groundwater Remedial Investigation/Baseline Risk Assessment—Appendix D: Estimation of  $K_d$  Values for INTEC Groundwater Model." Idaho Falls, Idaho: DOE-Idaho. 2006.

†Newman, M.E., I. Porro, R. Scott, R.M. Dunnivant, R.W. Goff, M.D. Blevins, S.M. Ince, J.D. Leyba, T.A. DeVol, A.W. Elzerman, and R.A. Fjeld. "Evaluation of the Mobility of Am, Cs, Co, Pu, Sr, and U Through INEL Basalt and Interbed Materials: Summary Report of the INEL/Clemson University Laboratory Studies." ER-WAG7-82, INEL-95/282. Idaho Falls, Idaho: Idaho National Engineering Laboratory. 1996.

‡Mincher, B.J., R.V. Fox, D.C. Cooper, and G.S. Groenewold. "Neptunium and Plutonium Sorption to Snake River Plain, Idaho Soil." *Radiochimica Acta*. Vol. 91. pp. 397–401. 2003.

§Miner, F.J., P.A. Evans, and W.L. Polzer. "Plutonium Behavior in the Soil/water Environment." RFP-2480. Golden, Colorado: Rockwell International. 1982.

¶Fjeld, R.A., T.A. DeVol, R.W. Goff, M.D. Blevins, D.D. Brown, S.M. Ince, A.W. Elzerman, and M.E. Newman.

"Characterization of the Mobilities of Selected Actinides and Fission/activation Products in Laboratory Columns Containing Subsurface Material from the Snake River Plain." *Nuclear Technology*. Vol. 135. pp. 92–108. 2001.

#(hmf) denotes a high mobility fraction.



$K_d$  value of 1,000 mL/g is recommended for alluvium at INL. This value is in agreement with the plutonium  $K_d$  value of 1,000 mL/g recommended by Cooper, et al. (2006) for INTEC alluvium.

For sedimentary interbeds at INL, Newman, et al. (1996) conducted batch experiments and reported Pu(V)  $K_d$  values ranging from 5,100 to 7,900 mL/g; Pu(VI)  $K_d$  values ranging from 110 to 690 mL/g; and plutonium  $K_d$  values ranging from 4 to 5 mL/g in the presence of EDTA. Navratil<sup>3</sup> recommended a total plutonium  $K_d$  between 300 and 3,500 mL/g for interbed sediments based on a review of historical studies. Total plutonium  $K_d$  values for interbed sediments determined from column experiments were >47 mL/g (Newman, et al., 1996; Fjeld, et al., 2001). High mobility fractions of plutonium were detected in the column experiments. In the column experiments of Newman, et al. (1996), the high mobility fraction was too small (~1 percent) to determine a  $K_d$ . In the column experiments of Fjeld, et al. (2001), the high mobility plutonium fraction was 1.1 to 2.4 percent and had a  $K_d$  value of 0.46 mL/g. Based on the recommended plutonium  $K_d$  values of Navratil<sup>4</sup> and considering the results of column experiments (plutonium  $K_d$  >47 mL/g), a plutonium  $K_d$  of 500 mL/g is recommended for interbed sediments. This value was chosen to be lower than the alluvium  $K_d$  based on the overall lower values for interbed sediments when compared to alluvium (Table 3-13). Use of the lower Pu(VI) values is not recommended in light of evidence for surface reduction of sorbed plutonium. A  $K_d$  value of 0.5 mL/g is recommended for the high mobility fraction of plutonium in interbed sediments. This high plutonium mobility fraction likely results from colloid-facilitated transport, and its effects should be considered in groundwater dose models.

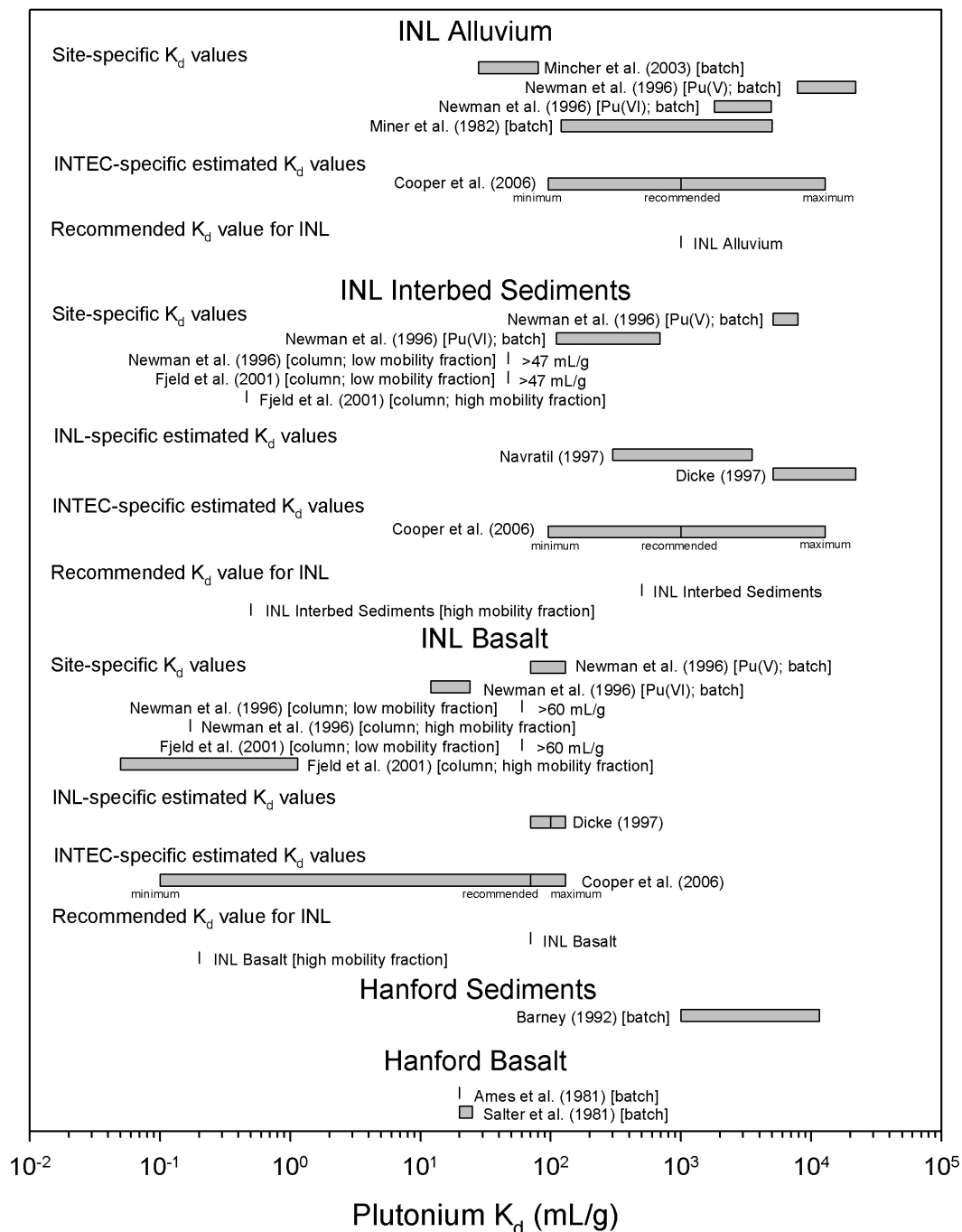
For INL basalt, Newman, et al. (1996) conducted batch sorption experiments and reported  $K_d$  values for Pu(V) ranged from 7 to 130 mL/g, Pu(VI)  $K_d$  values ranged from 12 to 24 mL/g, and plutonium  $K_d$  values in the presence of EDTA ranged from 0.04 to 0.05 mL/g. The Pu(V) and Pu(VI)  $K_d$  values measured by Newman, et al. (1996) are in good agreement with the range of plutonium  $K_d$  values measured for basalt from Hanford (20 to 25 mL/g) using batch techniques (Ames, et al., 1981; Salter, et al., 1981). Total plutonium  $K_d$  values for basalt determined from column experiments were >60 mL/g (Newman, et al., 1996; Fjeld, et al., 2001). In the column experiments of Newman, et al. (1996), the high mobility plutonium fraction was 10 to 55 percent and had an estimated  $K_d$  value of 0.17 mL/g. In the column experiments of Fjeld, et al. (2001), the high mobility plutonium fraction was 17 to 29 percent and had estimated  $K_d$  values ranging from 0.05 to 1.14 mL/g. Based on the basalt column experiments of Newman, et al. (1996) and Fjeld, et al. (2001), a plutonium  $K_d$  of 70 mL/g is recommended for basalt. This value is in agreement with the plutonium  $K_d$  value of 70 mL/g recommended by Cooper, et al. (2006) for INTEC basalt. Use of the lower Pu(VI) values is not recommended in light of evidence for surface reduction of sorbed plutonium. A  $K_d$  value of 0.2 mL/g is recommended for the high mobility fraction of plutonium in basalt. This high plutonium mobility fraction likely results from colloid-facilitated transport, and its effects should be considered in groundwater dose models.

The position of the plutonium  $K_d$  values recommended in this review with respect to measured and estimated site-specific and analogous plutonium  $K_d$  ranges and values is graphically displayed in Figure 3-10. This figure illustrates the uncertainty associated with the plutonium  $K_d$  values recommended for alluvium, interbed sediments, and basalt at INL. Due to available

---

<sup>3</sup>Ibid.

<sup>4</sup>Ibid.



**Figure 3-10. Measured and Estimated Site-Specific and Analogous Plutonium  $K_d$  Ranges and Values and Recommended Plutonium  $K_d$  Values for Alluvium, Interbed Sediments, and Basalt at INL (Table 3-13). Recommended Plutonium  $K_d$  Values Are Associated With Low Uncertainty Due to Available Site-Specific Sorption Data.**

site-specific plutonium sorption data (e.g., Newman, et al., 1996; Fjeld, et al., 2001) and analogous plutonium sorption data from the Hanford site (e.g., Barney, 1992; Salter, et al., 1981), the recommended plutonium  $K_d$  values are associated with low uncertainty.

### 3.4.10 Americium

Am-241 can exist in the +3, +4, +5, and +6 valence states. But, americium predominantly occurs as Am(III) in natural environments. Sorption studies indicate that Am(III) readily sorbs to minerals, crushed rock, and soil materials and, along with plutonium, is considered one of the most immobile actinide elements in the environment (Lu, et al., 1998; Ticknor, et al., 1996). Based on studies of Am(III) on single mineral phases and crushed rock, the adsorption of Am(III) is strongly pH dependent, and increases with increasing pH, with peak adsorption occurring between pH values of 5 and 6. This observed pH dependence is expected, because the dominant aqueous species of americium in the pH range of natural waters are primarily  $\text{Am}^{3+}$  and cationic carbonate complexes at acidic and basic pH values, respectively. High levels of soil organic matter can enhance americium mobility (Artinger, et al., 1998; Schuessler, et al., 2000; Ticknor, et al., 1996). In soil environments, clay minerals are expected to control americium sorption, and  $K_d$  values are expected to correlate with CEC. Studies have shown the potential importance of colloid-facilitated transport of americium in soil systems (Penrose, et al., 1990).

Newman, et al. (1996) summarized results from short-term (400-hour) batch experiments and column tests measuring americium  $K_c$  values for basalt and interbed sediments. The batch and column tests were conducted using a synthetic groundwater formulated to approximate the composition observed in SRPA field samples (ionic strength = 0.0048 M; pH 8.0) (Wood and Low, 1986). For batch tests, americium  $K_d$  values ranged from 70 to 280 mL/g for basalt and from 450 to 1,100 mL/g for interbed sediments. For column tests, americium mobility was characterized by high and low mobility fractions. For basalt, the high mobility fraction (9 to 13 percent) had an estimated  $K_d$  value of 0.18 mL/g and a remaining low mobility fraction with an estimated  $K_d$  of >60 mL/g. For interbed sediments, the high mobility fraction (~1 percent) was too small to determine a  $K_d$ , and the remaining low mobility fraction had an estimated  $K_d$  >49 mL/g.

Fjeld, et al. (2001) performed laboratory column tests to characterize the mobility of americium in a basalt sample and a composite of sedimentary interbed from INL. The solution used in the tests was a low ionic strength (0.004 M) synthetic groundwater (pH 8.0) formulated to approximate the major ion concentration of SRPA groundwater samples (Wood and Low, 1986). For basalt, americium mobility was characterized by two fractions: a high mobility fraction (7 to 12 percent) with retardation factors ranging from 2.6 to 5.8 and a remaining low mobility fraction with a retardation factor >200. For interbed sediments, retardation factors were >800. Based on reported porosities and bulk densities of packed columns, retardation factors for basalt equate to  $K_d$  values of 0.5 to 1.36 mL/g for the high mobility fraction and >57 mL/g for the low mobility fraction, and a  $K_d$  value of >194 mL/g for interbed sediment.

Cooper, et al. (2006) estimated an americium  $K_d$  range of 100 to 10,000 mL/g for alluvium and interbed sediments at INTEC and recommended an americium  $K_d$  value of 400 mL/g for the alluvium and interbed sediments. The minimum and maximum americium  $K_d$  values estimated by Cooper, et al. (2006) represented the range of values from the batch experiments of Newman, et al. (1996) and long-term contact data (see Cooper, et al., 2006, Figure D-3-2),

which indicated that americium  $K_d$  values should range from 100 to 10,000 mL/g in INTEC sediments. The recommended americium  $K_d$  value of 400 mL/g for alluvium and interbed sediments was based on column experiments conducted by Artinger, et al. (2002). Artinger, et al. (2002) reported americium  $K_d$  values ranging from 1,950 to 2,150 mL/g for SDA interbed sediments. Adjusting for CEC (INTEC/SDA = 1:5) lead to the recommended americium  $K_d$  value of 400 mL/g for alluvium and interbed sediments. Cooper, et al. (2006) estimated an americium  $K_d$  range of 0 to 140 mL/g for basalt at INTEC and recommended an americium  $K_d$  value of 0.85 mL/g for basalt. The maximum estimate of 140 mL/g was based on the highest value measured in the batch experiments of Newman, et al. (1996) for basalt and corrected for the sediment/water ratio. The recommended americium  $K_d$  value of 0.85 mL/g was estimated to be the average  $K_d$  reported in the column experiments of Fjeld, et al. (2001).

Americium  $K_d$  values have been determined for Columbia River basalts collected from the Hanford site under experimental conditions similar though not identical to the hydrogeologic system at INL (i.e., alkaline pH, high carbonate concentrations, oxidizing conditions, and similar though not identical basalt mineral compositions). Barney (1981) reported americium  $K_d$  values for Umtanum ranging from 50–315 mL/g. Salter, et al. (1981) reported americium  $K_d$  values for Umtanum ranging from 50–600 mL/g.

Measured and recommended americium  $K_d$  values are summarized in Table 3-14. Measured americium  $K_d$  values for interbed sediments using batch methods range from 450 to 1,100 mL/g (Newman, et al., 1996). Measured americium  $K_d$  values for interbed sediments from column experiments were >49 mL/g and >194 mL/g (Newman, et al., 1996; Fjeld, et al., 2001). In the column experiments of Newman, et al. (1996), a high americium mobility fraction was also detected; however, the high americium mobility fraction was too small (~1 percent) to determine a  $K_d$ . Based on the column experiments of Fjeld, et al. (2001), which indicated an americium  $K_d$  value >194 mL/g, and considering the minimum americium  $K_d$  value reported from the batch experiments of Newman, et al. (1996) (450 mL/g), an americium  $K_d$  value of 400 mL/g is recommended for alluvium and interbed sediments. This value is in agreement with the americium  $K_d$  value of 400 mL/g recommended by Cooper, et al. (2006) for INTEC alluvium and interbed sediments.

For basalt at INL, measured americium  $K_d$  values using batch methods ranged from 70 to 280 mL/g (Newman, et al., 1996). Measured americium  $K_d$  values for basalt from the Hanford site determined by batch methods have similar ranges of 50 to 315 mL/g (Barney, 1981) and 50 to 600 mL/g (Salter, et al., 1981). In column experiments using INL basalts, high and low americium mobility fractions were detected (Newman, et al., 1996; Fjeld, et al., 2001). The high mobility americium fraction in the column experiments had a  $K_d$  range of 0.18 to 1.36 mL/g, and the low mobility fraction had  $K_d$  values of >57 and >60 mL/g. Based on the americium  $K_d$  value from the column experiments of Fjeld, et al. (2001) (>60 mL/g) and considering the minimum americium  $K_d$  value reported from the batch experiments of Newman, et al. (1996) (70 mL/g), an americium  $K_d$  value of 70 mL/g is recommended for basalt. This value is much higher than the americium  $K_d$  value of 0.85 mL/g recommended by Cooper, et al. (2006) for INTEC basalt.

However, the recommendation of Cooper, et al. (2006) considered only  $K_d$  data measured on the high mobility fraction from the column experiments of Fjeld, et al. (2001). The high americium mobility fraction in basalt ranged from 9 to 13 percent in the column experiments of Newman, et al. (1996) and from 7 to 12 percent in the column experiments of Fjeld, et al. (2001). Based on the range of high mobility americium  $K_d$  values measured in the column

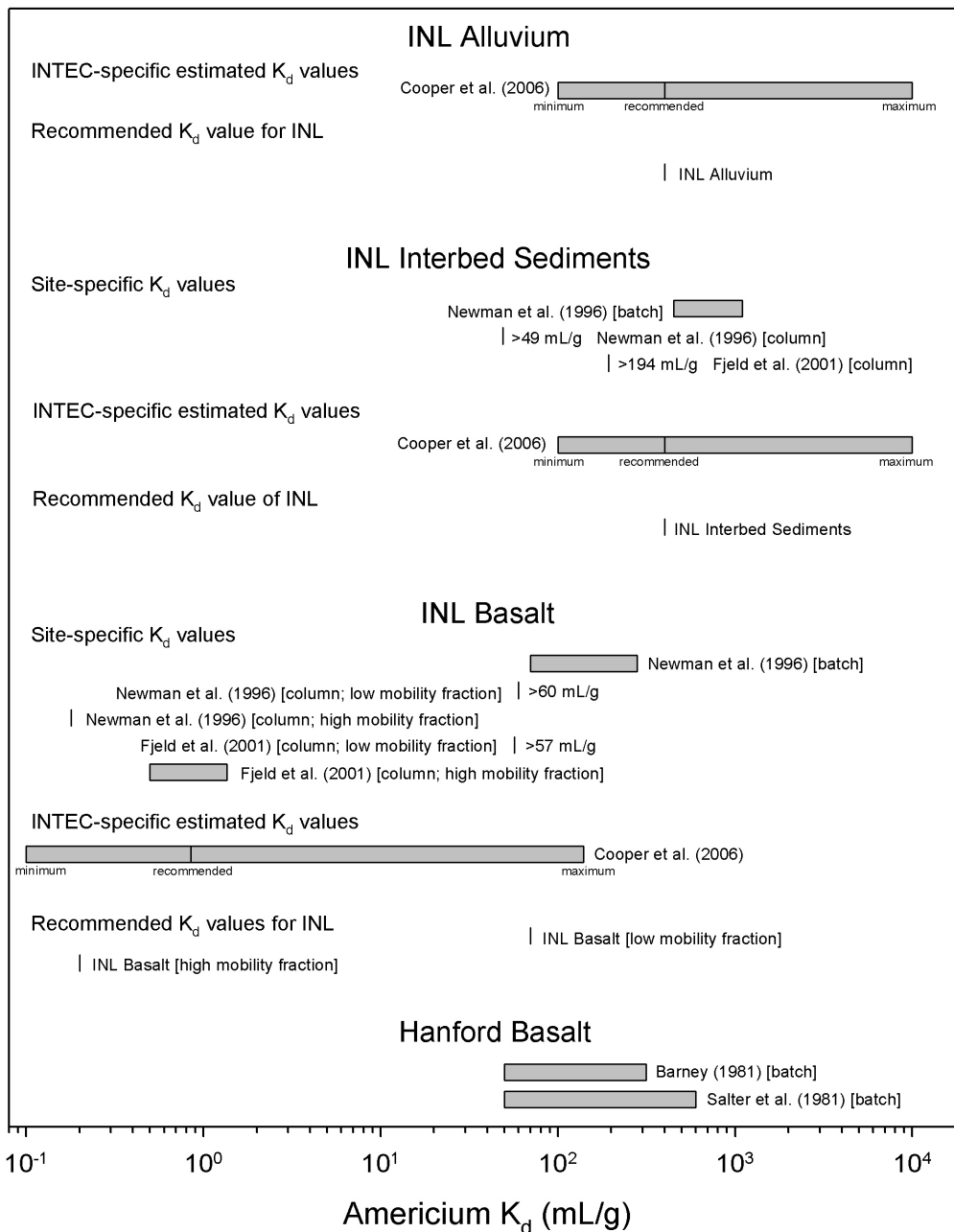
<b>Table 3-14. Measured and Recommended Americium <math>K_d</math> Values for Alluvium, Interbed Sediments, and Basalt at the Idaho National Laboratory</b>				
	<b>Measured Americium <math>K_d</math> (mL/g)</b>	<b>Test Method</b>	<b>Idaho Nuclear Technology and Engineering Center-Specific Recommended Americium <math>K_d</math> (mL/g)*</b>	<b>Recommended Americium <math>K_d</math> (mL/g)</b>
Alluvium	—	—	400	400
Sedimentary Interbeds	450–1,100† >49† >194‡	Batch Column Column	400	400
Basalt	70–280† 0.18† (hmf§) >60† 0.5–1.36‡ (hmf) >57‡	Batch Column Column Column Column	0.85	70 0.2 (hmf)
<p>*Cooper, D.C., G.D. Redden, and L.C. Hull. DOE/NE-ID-11227, "Operable Unit 3-14 Tank Farm Soil and Groundwater Remedial Investigation/Baseline Risk Assessment—Appendix D: Estimation of <math>K_d</math> Values for INTEC Groundwater Model." Idaho Falls, Idaho: DOE-Idaho. 2006.</p> <p>†Newman, M.E., I. Porro, R. Scott, R.M. Dunnivant, R.W. Goff, M.D. Blevins, S.M. Ince, J.D. Leyba, T.A. DeVol, A.W. Elzerman, and R.A. Fjeld. "Evaluation of the Mobility of Am, Cs, Co, Pu, Sr, and U Through INEL Basalt and Interbed Materials: Summary Report of the INEL/Clemson University Laboratory Studies." ER-WAG7-82, INEL-95/282. Idaho Falls, Idaho: Idaho National Engineering Laboratory. 1996.</p> <p>‡Fjeld, R.A., T.A. DeVol, R.W. Goff, M.D. Blevins, D.D. Brown, S.M. Ince, A.W. Elzerman, and M.E. Newman. "Characterization of the Mobilities of Selected Actinides and Fission/activation Products in Laboratory Columns Containing Subsurface Material from the Snake River Plain." <i>Nuclear Technology</i>. Vol. 135. pp. 92–108. 2001.</p> <p>§(hmf) denotes a high-mobility fraction.</p>				

experiments (0.18 to 1.36 mL/g), a  $K_d$  value of 0.2 mL/g is recommended for the high mobility fraction of americium in basalt. This high americium mobility fraction likely results from colloid-facilitated transport, and its effects should be considered in groundwater dose models.

The position of the americium  $K_d$  values recommended in this review with respect to measured and estimated site-specific and analogous americium  $K_d$  ranges and values is graphically displayed in Figure 3-11. This figure illustrates the uncertainty associated with the americium  $K_d$  values recommended for alluvium, interbed sediments, and basalt at INL. Due to available site-specific americium sorption data (e.g., Newman, et al., 1996; Fjeld, et al., 2001) and analogous americium sorption data from the Hanford site (Barney, 1981; Salter, et al., 1981), the recommended americium  $K_d$  values are associated with low uncertainty.

### 3.4.11 Curium

The actinide curium exists in the +3 oxidation state in natural waters. The dominant aqueous species of curium in the pH range of natural waters are primarily cations such as  $\text{Cm}^{3+}$  and



**Figure 3-11. Measured and Estimated Site-Specific and Analogous Americium  $K_d$  Ranges and Values and Recommended Americium  $K_d$  Values for Alluvium, Interbed Sediments, and Basalt at INL (Table 3-14). Recommended Americium  $K_d$  Values Are Associated With Low Uncertainty Due to Available Site-Specific Sorption Data.**

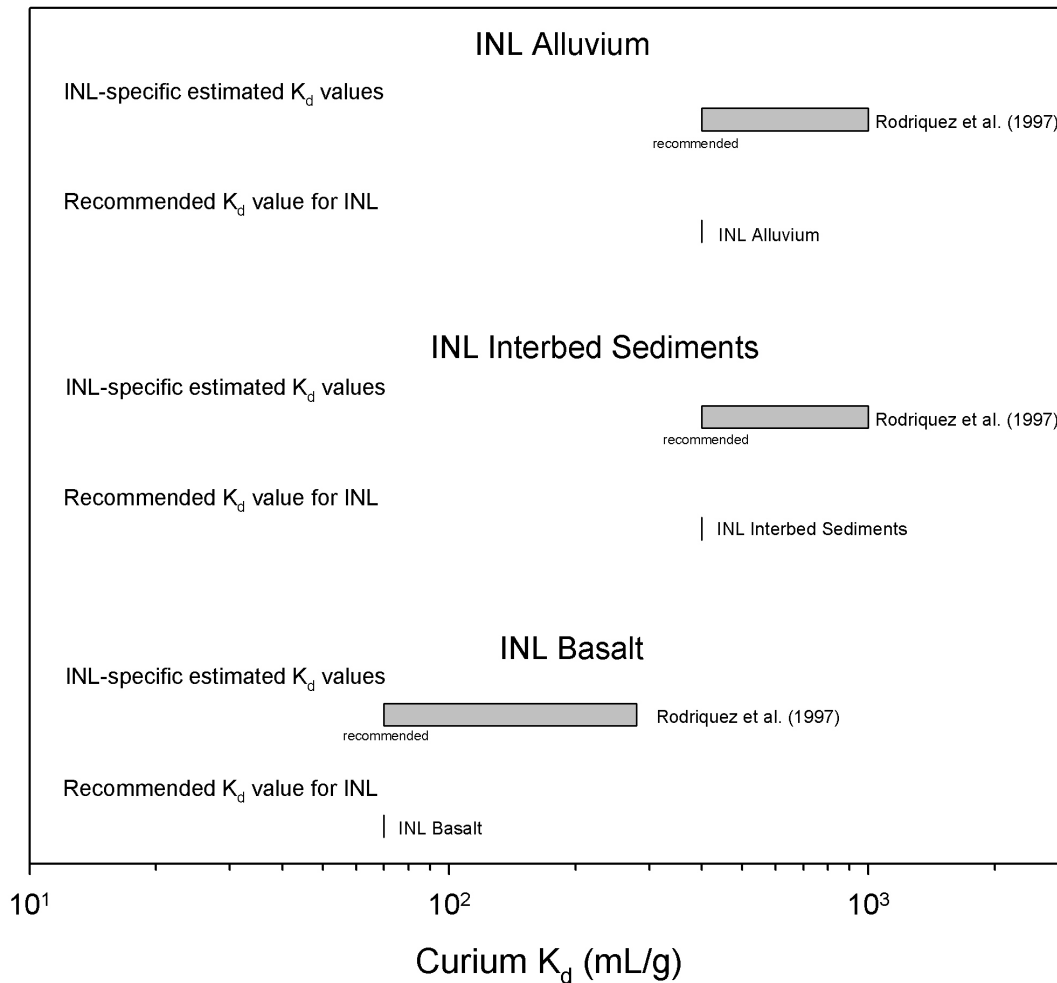
Cm(III) carbonate complexes at acidic and basic pH values, respectively. Available curium sorption studies indicate that sorption of curium is strongly pH dependent and increases with increasing pH with maximum adsorption occurring between pH values of 5 and 6. Curium geochemistry is very similar to that of americium (Guillaumont, et al., 2003). Both are transuranic elements that occur in the +3 oxidation state in natural waters. Both curium and americium form cationic carbonate complexes at acidic and alkaline pH. Both are considered to be immobile in soil environments, and both exhibit high  $K_d$  values. However, the tendency of curium, like americium, to strongly adsorb to soil particles indicates that there is potential for colloid-facilitated transport of curium.

No site-specific sorption data for curium at INL were found in the literature. Using site-specific sorption data for americium from Newman, et al. (1996) as an analog for curium, Rodriguez, et al. (1997) recommended a curium  $K_d$  range of 400 to 1,000 mL/g for sediments at INL and a curium  $K_d$  range of 70 to 280 mL/g for basalt. Rodriguez, et al. (1997) recommended values of 400 mL/g for sediments and 70 mL/g for basalt.

Recommended curium  $K_d$  values are summarized in Table 3-15. No site-specific curium sorption data are available for subsurface materials at INL. Due to similarities in aqueous chemistry, the sorptive characteristics of curium onto alluvium, interbed sediments, and basalt at INL are expected to be very similar to those of americium. Using americium as an analog for curium, a curium  $K_d$  value of 400 mL/g is recommended for interbed sediments and alluvium at INL, and a curium  $K_d$  value of 70 mL/g is recommended for basalt at INL. In addition, the possibility of a high mobility fraction with characteristics similar to that assigned to americium (Table 3-14) should be considered for curium.

The position of the curium  $K_d$  values recommended in this review with respect to estimated site-specific curium  $K_d$  ranges and values is graphically displayed in Figure 3-12. This figure illustrates the uncertainty associated with the curium  $K_d$  values recommended for alluvium, interbed sediments, and basalt at INL. The recommended curium  $K_d$  values are associated with high uncertainty due to the lack of site-specific curium sorption data.

<b>Table 3-15. Recommended Curium <math>K_d</math> Values for Alluvium, Interbed Sediments, and Basalt at the Idaho National Laboratory*</b>				
	<b>Measured Curium <math>K_d</math> (mL/g)</b>	<b>Test Method</b>	<b>Idaho National Laboratory-Specific Recommended Curium <math>K_d</math> (mL/g)</b>	<b>Recommended Curium <math>K_d</math> (mL/g)</b>
Alluvium	—	—	400	400
Sedimentary Interbeds	—	—	400	400
Basalt	—	—	70	70
*Rodriguez, R.R., A.L. Schafer, J. McCarthy, P. Martian, D.E. Burns, D.E. Raunig, N.A. Burch, and R.L. VanHorn. DOE/ID-10534, "Comprehensive RI/FS for the Idaho Chemical Processing Plant OU 3-13 at the INEEL—Part A, RI/BRA Report (Final)." Idaho Falls, Idaho: Idaho National Engineering Laboratory, DOE-Idaho. 1997.				



**Figure 3-12. Estimated Site-Specific Curium  $K_d$  Ranges and Values and Recommended Curium  $K_d$  Values for Alluvium, Interbed Sediments, and Basalt at INL (Table 3-15). Recommended Curium  $K_d$  Values Are Associated With High Uncertainty Due to the Lack of Site-Specific Sorption Data.**



## 4 SUMMARY AND CONCLUSIONS

To satisfy non-high-level radioactive waste determinations for facilities at the Savannah River Site (SRS) and the Idaho National Laboratory (INL) under Section 3116 of the Ronald W. Reagan National Defense Authorization Act, the U.S. Department of Energy (DOE) commonly performs a performance assessment that includes evaluating potential exposure to radionuclides via groundwater transport. Deterministic performance assessment models DOE currently uses to estimate the rate of migration of contaminants at SRS and INL require  $K_d$ s to describe solute retardation along subsurface flow paths. In its consultative role in the Section 3116 waste determination process, the U.S. Nuclear Regulatory Commission (NRC) reviews relevant performance assessments and, therefore, is interested in whether the  $K_d$ s DOE uses for radionuclide transport in the geosphere reasonably reflect expected local conditions.

This report documents a sorption coefficient database tailored to site-specific subsurface conditions for risk-significant radionuclides at SRS and INL and recommends  $K_d$  values for the risk-significant radionuclides that are deemed appropriate for the hydrogeochemical environments found at SRS and INL. A summary of the  $K_d$  recommendations for the risk-significant radionuclides in the hydrostratigraphic units that will be affected by waste releases at SRS and INL is provided in Tables 4-1 and 4-2. The recommended  $K_d$  values are based on knowledge of the sorption behavior of each radionuclide of concern, available data on site hydrogeochemical and mineralogical conditions, and reported  $K_d$  values from site-specific experiments. When site-specific  $K_d$  values were not available for a particular radionuclide,  $K_d$  data on analogous systems to SRS or INL and generic data from the open literature were evaluated to provide a technical basis for the  $K_d$  recommendation. The recommended values tended toward the lower, more conservative end of data ranges. This is because of the uncertainties not only in the appropriate choice of sorption coefficients, but also in the simplified  $K_d$ -based groundwater transport model itself. For example, the fractured basalt strata at INL may contain fast pathways that will make surface sorption processes less effective. The selection of low values is intended to ensure that groundwater pathway models will be unlikely to underestimate potential dose.

These recommendations should be used with care in light of new information that becomes available on site-specific sorption coefficients or on temporal or spatial variability in hydrochemical conditions. This report is not to be construed as providing the technical basis for parameters DOE uses in its performance assessments.

For plutonium, americium, and curium at INL, a high mobility fraction with much lower  $K_d$  values than those in Table 4-2 should be considered in transport models (see Tables 3-13 and 3-14).

The results of this data review can be used in a risk-informed manner to identify potential areas of focused laboratory studies. For each site, starting with the list of radionuclides included in this analysis, staff could narrow the list based on results of performance assessments or other modeling studies. Among this smaller list, those with an insufficient quantity of high-quality, site-specific sorption data (considering both laboratory and field-based studies) may be considered for laboratory analyses that would complement any past and ongoing DOE efforts.

<b>Table 4-1. Summary of Recommended <math>K_d</math> Values (mL/g) for Risk-Significant Radionuclides in Hydrostratigraphic Units at the Savannah River Site</b>					
<b>Radionuclide</b>	<b>Upper Three Runs Aquifer: Upper</b>	<b>Tan Clay Confining Unit</b>	<b>Upper Three Runs Aquifer: Lower</b>	<b>Gordon Confining Unit</b>	<b>Gordon Aquifer</b>
Carbon	2	1	1	1	1
Nickel	10	21	80	150	80
Selenium	425	800	425	800	425
Strontium	5	12	25	50	25
Niobium	160	900	160	900	160
Technetium	0	0.3	0	0.3	0
Tin	500	2,500	500	2,500	500
Iodine	0	0.2	0	0.2	0
Cesium	15	150	50	150	50
Lead	500	2,500	1,500	2,500	1,500
Uranium	100	150	100	300	100
Neptunium	0.2	25	0.6	25	0.6
Plutonium	250	2,500	250	2,500	250
Americium	250	4,250	250	4,250	250
Curium	300	4,250	300	4,250	300

<b>Table 4-2. Summary of Recommended <math>K_d</math> Values (mL/g) for Risk-Significant Radionuclides in Hydrostratigraphic Units at the Idaho National Laboratory</b>			
<b>Radionuclide</b>	<b>Alluvium</b>	<b>Sedimentary Interbeds</b>	<b>Basalt</b>
Carbon	1	1	0
Strontium	12	12	2
Technetium	0	0	0
Iodine	0.1	0.1	0
Cesium	75	200	25
Lead	270	270	10
Uranium	1.6	1.6	0.2
Neptunium	2	5	0.2
Plutonium	1,000	500	70
Americium	400	400	70
Curium	400	400	70

## 5 REFERENCES

Aadland, R.K., J.A. Gellici, and P.A. Thayer. "Hydrogeologic Framework of West-Central South Carolina." PIT-MISC-0112. Report 5. State of South Carolina Department of Natural Resources, Water Resources Division. 1995.

Aadland, R.K., M.K. Harris, C.M. Lewis, T.F. Gaughan, and T.M. Westbrook. "Hydrostratigraphy of the General Separations Area, Savannah River Site (SRS), South Carolina." USDOE Report WSRC-RP-91-13. Aiken, South Carolina: Westinghouse Savannah River Company. 1991.

Alloway, B.J. *Heavy Metals in Soil*. 2<sup>nd</sup> Edition. Glasgow, United Kingdom: Blackie Press. 1995.

Ames, L.L. and D. Rai. "Radionuclide Interactions with Soil and Rock Media— Vol. 1: Processes Influencing Radionuclide Mobility and Retention, Element Chemistry and Geochemistry, Conclusions and Evaluation." EPA 520/6-78-007. Las Vegas, Nevada: EPA, Office of Radiation Programs. 1978.

Ames, L.L., J.E. McGarrah, B.A. Walker, and P.F. Salter. "Sorption of Uranium and Cesium by Hanford Basalts and Associated Secondary Smectite." *Chemical Geology*. Vol. 35. pp. 205–225. 1982.

Ames, L.L., J.E. McGarrah, and B.A. Walker. "Basalt Radionuclide Reactions: FY1981 Annual Report." DOE Report RHO-BW-CR-127-P. Richland, Washington: Pacific Northwest Laboratories. 1981.

Anderson, S.R., M.A. Kuntz, and L.C. Davis. "Geologic Controls of Hydraulic Conductivity in the Snake River Plain Aquifer at and Near the Idaho National Engineering and Environmental Laboratory, Idaho." U.S. Geological Survey Water Resources Investigations Report 99-4033. 1999.

Arnett, R.C., R.C. Martineau, and M.J. Lehto. "Preliminary Numerical Model of Radionuclide Transport in the Snake River Plain Near the Idaho National Engineering Laboratory." EGG-WM-8820. Idaho Falls, Idaho: Idaho National Engineering Laboratory, EG&G Idaho, Inc. 1990.

Artinger, R., B. Kienzler, W. Schuessler, and J. Kim. "Effects of Humic Substances on the Am-241 Migration in a Sandy Aquifer: Column Experiments with Gorleben Groundwater/ Sediment Systems." *Journal of Contaminant Hydrology*. Vol. 35, Nos. 1–3. pp. 261–275. 1998.

Artinger, R., W. Schuessler, F. Scherbaum, D. Schild, and J. Kim. "Am-241 Migration in a Sandy Aquifer Studied by Long-Term Column Experiments." *Environmental Science and Technology*. Vol. 36. pp. 4,818–4,823. 2002.

Baes, C.F. and R.F. Mesmer. *The Hydrolysis of Cations*. New York City, New York: John Wiley & Sons, Inc. 1976.

Baes, III, C.F. and R.D. Sharp. "A Proposal for Estimation of Soil Leaching and Leaching Constants for Use in Assessment Models." *Journal of Environmental Quality*. Vol. 12. pp. 17–28. 1983.

Baes, III, C.F., R.D. Sharp, A.L. Sjoreen, and R.W. Shor. "A Review and Analysis of Parameters for Assessing Transport of Environmentally Released Radionuclides Through Agriculture." ORNL–5786. Oak Ridge, Tennessee: Oak Ridge National Laboratory. 1984.

Barnett, M.O., P.M. Jardine, S.C. Brooks, and H.M. Selim. "Adsorption and Transport of Uranium(VI) in Subsurface Media." *Soil Science Society American Journal*. Vol. 64. pp. 908–917. 2000.

Barney, G.S. "Adsorption of Plutonium on Shallow Sediments at the Hanford Site." WHC–SA–1516–FP. Richland, Washington: Westinghouse Hanford Company. 1992.

———. "Radionuclide Reactions with Groundwater and Basalts from Columbia River Basalt Formations." DOE Report RHO–SA–217. Richland, Washington: Rockwell International. 1981.

Barracough, J.T., J.B. Robertson, and V.J. Janzer. "Hydrology of the Solid Waste Burial Ground as Related to the Potential Migration of Radionuclides, Idaho National Engineering Laboratory." U.S. Geological Survey Open-File Report 76-471. 1976.

Bartholomay, R.C. "Distribution of Selected Radiochemical and Chemical Constituents in Perched Ground Water, Idaho National Engineering Laboratory, Idaho, 1992–95." U.S. Geological Survey Water Resources Investigations Report 98-4026. 1998.

———. "Mineralogical Correlation of Surficial Sediment from Area Drainages With Selected Sedimentary Interbeds at the Idaho National Engineering Laboratory, Idaho." U.S. Geological Survey Water Resources Investigations Report 90-4147. 1990.

Bartholomay, R.C. and B.J. Tucker. "Distribution of Selected Radiochemical and Chemical Constituents in Perched Ground Water, Idaho National Engineering and Environmental Laboratory, Idaho, 1996-98." U.S. Geological Survey Water Resources Investigations Report 00-4222. 2000.

Bartholomay, R.C., L.L. Knobel, and L.C. Davis. "Mineralogy and Grain Size of Surficial Sediment from the Big Lost River Drainage and Vicinity, With Chemical and Physical Characteristics of Geologic Materials from Selected Sites at the Idaho National Engineering Laboratory, Idaho." U.S. Geological Survey Open-File Report 89-384. 1989.

Beasley, T.M., P.R. Dixon, and L.J. Mann. "Tc-99, U-236, Np-237 on the Snake River Plain Aquifer at the Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho." *Environmental Science and Technology*. Vol. 32. pp. 3,876–3,881. 1998.

Bennett, C.M. "Streamflow Losses and Groundwater Level Changes Along the Big Lost River at the INEL, Idaho." U.S. Geological Survey Water Resources Investigations Report 86-4204. 1990.

Bertetti, F.P., R.T. Pabalan, and M.G. Almendarez. "Studies of Neptunium(V) Sorption on Quartz, Clinoptilolite, Montmorillonite, and  $\alpha$ -Alumina." *Adsorption of Metals by Geomedia*. E.A. Jenne, ed. San Diego, California: Academic Press. 1998.

Bibler, J.P. and D.B. Marson. "Behavior of Mercury, Lead, Cesium, and Uranyl Ions on Four SRS Soils." WSRC-RP-92-326. Aiken, South Carolina: Westinghouse Savannah River Company. 1992.

Bittel, J.R. and R.J. Miller. "Lead, Cadmium, and Calcium Selectivity Coefficients on Montmorillonite, Illite, and Kaolinite." *Journal of Environmental Quality*. Vol. 3. pp. 250–253. 1974.

Bledsoe, H.W., R.K. Aadland, and K.A. Sargent. "Baseline Hydrogeologic Investigation—Summary Report." WSRC-RP-90-1010. Aiken, South Carolina: Westinghouse Savannah River Company. 1990.

Buice, J.M., R.K. Cauthen, R.R. Haddock, B.A. Martin, J.A. McNeil, J.L. Newman, and K.H. Rosenberger. "Performance Objective Demonstration Document (PODD) for the Closure of Tank 19 and Tank 18 Savannah River Site." CBU-PIT-2005-00106. Rev. 1. Aiken, South Carolina: Savannah River Operations Office. 2005.

Bunde, R.L., J.J. Rosentreter, and M.J. Liszewski. "Rate of Strontium Sorption and the Effects of Variable Aqueous Concentrations of Sodium and Potassium on Strontium Distribution Coefficients of a Surficial Sediment at the Idaho National Engineering Laboratory, Idaho." *Environmental Geology*. Vol. 34, Nos. 2–3. pp. 135–142. 1998.

Bunde, R.L., J.J. Rosentreter, M.J. Liszewski, C.H. Hemming, and J. Welhan. "Effects of Calcium and Magnesium on Strontium Distribution Coefficients." *Environmental Geology*. Vol. 32, No. 3. pp. 219–229. 1997.

Busenberg, E., L.N. Plummer, M.W. Doughten, P.K. Widman, and R.C. Bartholomay. "Chemical and Isotopic Composition and Gas Concentrations of Ground Water and Surface Water from Selected Sites at and Near the Idaho National Engineering and Environmental Laboratory, Idaho, 1994–97." U.S. Geological Survey Open-File Report 00-81. 2000.

Callahan, M.A., M.W. Slinak, N.W. Gabel, I.P. May, C.F. Fowler, J.R. Freed, P. Jennings, R.L. Durfree, F.C. Whitmore, B. Maestri, W.R. Mabey, B.R. Holt, and C. Gould. "Water-Related Environmental Fate of 129 Priority Pollutants—Vol. 1: Introduction and Technical Background, Metals and Inorganics, Pesticides and PCBs." EPA 440/4-79-029a. Washington, DC: EPA, Office of Water Planning and Standards. 1979.

Christensen, T.H., N. Lehmann, T. Jackson, and P.E. Holm. "Cadmium and Nickel Distribution Coefficients for Sandy Aquifer Materials." *Journal of Contaminant Hydrology*. Vol. 24. pp. 75–84. 1996.

Colello, J.J., J.J. Rosentreter, R.C. Bartholomay, and M.J. Liszewski. "Strontium Distribution Coefficients of Basalt Core Samples from the Idaho National Engineering and Environmental Laboratory, Idaho." U.S. Geological Survey Water Resource Investigations Report 98-4256. 1998.

Cook, J.R., E.L. Wilhite, R.A. Hiergesell, and G.P. Flach. "Special Analysis: Revision of Saltstone Vault 4 Disposal Limits (U)." WSRC-TR-2005-00074. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company. 2005.

Cook, J.R., L. McDowell-Boyer, A.D. Yu, D.C. Kocher, E.L. Wilhite, and K.E. Young. "Radiological Performance Assessment for the E-Area Vaults Disposal Facility." WSRC-RP-94-0218. Rev. 1. Aiken, South Carolina: Westinghouse Savannah River Company. 2000.

Cooper, D.C., G.D. Redden, and L.C. Hull. DOE/NE-ID-11227, "Operable Unit 3-14 Tank Farm Soil and Groundwater Remedial Investigation/Baseline Risk Assessment—Appendix D: Estimation of  $K_d$  Values for INTEC Groundwater Model." Idaho Falls, Idaho: DOE-Idaho. 2006.

Crapse, K.P., S.M. Serkiz, A. Pishko, P.C. McKinsey, R.L. Brigmon, E.P. Shine, C. Fliermans, and A.S. Knox. "Monitored Natural Attenuation of Inorganic Contaminants Treatability Study Final Report." WSRC-TR-2004-00124. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company. 2004.

Dai, M., J.M. Kelly, and K.O. Buesseler. "Sources and Migration of Plutonium in Groundwater at the Savannah River Site." *Environmental Science and Technology*. Vol. 36, No. 17. pp. 3,690–3,699. 2002.

Del Debbio, J.A. and T.R. Thomas. "Transport Properties of Radionuclides and Hazardous Chemical Species in Soils at the Idaho Chemical Processing Plant." WINCO-1068. Idaho Falls, Idaho: Westinghouse Idaho Nuclear Company, Inc. 1989.

Denys, S., G. Echevarria, L. Florentin, E. Leclerc-Cessac, and J.L. Morel. "Availability of Tc-99 in Undisturbed Soil Cores." *Journal of Environmental Radioactivity*. Vol. 70, Nos. 1–2. pp. 115–126. 2003.

Dicke, C.A. "Distribution Coefficients and Contaminant Solubilities for the Waste Area Group 7 Baseline Risk Assessment." INEL/EXT-97-00201. Idaho Falls, Idaho: Lockheed Martin Idaho Technologies Company. 1997.

DOE. DOE-WD-2005-001, "Basis for Section 3116 Determination for Salt Waste Disposal at the Savannah River Site." Washington, DC: DOE. 2006a.

———. DOE/NE-ID-11226, "Basis for Section 3116 Determination for the Idaho Nuclear Technology and Engineering Center Tank Farm Facility." Rev. 0. Washington, DC: DOE. 2006b.

———. DOE-WD-2005-002, "Draft Section 3116 Determination for Closure of Tank 19 and Tank 18 at the Savannah River Site." Rev. 0. Washington, DC: DOE. 2005.

DOE-Idaho. DOE/NE-ID-11227. "Operable Unit 3-14 Tank Farm Soil and Groundwater Remedial Investigation/Baseline Risk Assessment." Rev. 0. Idaho Falls, Idaho: DOE-Idaho. 2006a.

———. DOE/ID-11259. "Annual INTEC Water Monitoring Report for Group 4-Perched Water (2005)." Rev. 0. Idaho Falls, Idaho: DOE-Idaho. 2006b.

———. "Proposed Plan for Tank Farm Soil and Groundwater at the Idaho Nuclear Technology and Engineering Center, Operable Unit 3-14." Idaho Falls, Idaho: DOE-Idaho. 2006c.

———. DOE/ID-10966, "Performance Assessment for the Tank Farm Facility at the Idaho National Engineering and Environmental Laboratory." Errata December 2, 2003. Rev. 1. Idaho Falls, Idaho: DOE-Idaho. 2003

Echevarria, G., J.L. Morel, and E. Leclerc-Cessac. "Retention and Phytoavailability of Radionioabium in Soils." *Journal of Environmental Radioactivity*. Vol. 78. pp. 343-352. 2005.

Elprince, A.M., C.I. Rich, and D.C. Martens. "Effect of Temperature and Hydroxy Aluminum Interlayers on the Adsorption of Trace Radioactive Cesium by Sediments near Water-cooled Nuclear Reactors." *Water Resources Research*. Vol. 13, No. 2. pp. 375-380. 1977.

EPA. "Understanding Variation in Partition Coefficient,  $K_d$ , Values, Volume II: Review of Geochemistry and Available  $K_d$  Values for Cadmium, Cesium, Chromium, Lead, Plutonium, Radon, Strontium, Thorium, Tritium, and Uranium." EPA 402-R-99-004B. Washington, DC: EPA, Office of Air and Radiation. 1999.

———. "Test Methods for Evaluating Solid Waste: Physical/Chemical Methods." SW-846. Washington, DC: EPA, Office of Solid Waste and Emergency Response. 1986.

———. "Draft—Proposed Low-Level Radioactive Waste Standards: Background Information Document, 40 CFR 193, March 13, 1985." Washington, DC: EPA, Office of Radiation Programs. 1985.

Faure, G. and J.L. Powell. *Strontium Isotope Geology*. Berlin, Germany: Springer-Verlag. 1972.

Fjeld, R.A., S.M. Serkiz, P.L. McGinnis, A. Elci, and D.I. Kaplan. "Evaluation of a Conceptual Model for the Subsurface Transport of Plutonium Involving Surface Mediated Reduction of Pu(V) to Pu(IV)." *Journal of Contaminant Hydrology*. Vol. 67. pp. 79-94. 2003.

Fjeld, R.A., T.A. DeVol, R.W. Goff, M.D. Blevins, D.D. Brown, S.M. Ince, A.W. Elzerman, and M.E. Newman. "Characterization of the Mobilities of Selected Actinides and Fission/activation Products in Laboratory Columns Containing Subsurface Material from the Snake River Plain." *Nuclear Technology*. Vol. 135. pp. 92-108. 2001.

Forman, S.L., R.P. Smith, W.R. Hackett, J.A. Tullis, and P.A. McDaniel. "Timing of Late Quaternary Glaciations in the Western United States Based on the Age of Loess on the Eastern Snake River Plain, Idaho." *Quaternary Research*. Vol. 40. pp. 30-37. 1993.



Gerriste, R.G., R. Vriesema, J.W. Dalenberg, and H.P. De Roos. "Effect of Sewage Sludge on Trace Element Mobility in Soils." *Journal of Environmental Quality*. Vol. 11. pp. 359–364. 1982.

Golder Associates, Inc. "Report for the Idaho Chemical Processing Plant Drilling and Sampling Program at Land Disposal Unit CPP-59." Report 893-1195.320. Redmond, Washington: Golder Associates, Inc. 1991.

Goto, M. "Development of a Quantitative Model for Binding Cesium to SRS soils." Masters' Degree Thesis. Georgia Institute of Technology. Atlanta, Georgia. 2001.

Griffin, R.A. and N.F. Shimp. "Effect of pH on Exchange-adsorption or Precipitation of Lead from Landfill Leachates by Clay Minerals." *Environmental Science and Technology*. Vol. 10. pp. 1,256–1,261. 1976.

Grossman, C.J., R.A. Fjeld, J.T. Coates, and A.W. Elzerman. "The Sorption of Selected Radionuclides in Sedimentary Interbed Soils from the Snake River Plain." INEEL/EXT-01-01106. Rev. 0. Idaho Falls, Idaho: Idaho National Engineering and Environmental Laboratory. 2001.

Guillaumont, R., T. Fanghänel, J. Fuger, I. Grenthe, V. Neck, D.A. Palmer, and M.H. Rand. *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*. Nuclear Energy Agency Chemical Thermodynamics Volume 5. Amsterdam, The Netherlands: Elsevier. 2003.

Haji-Djafari, S., P.E. Antommaria, and H.L. Crouse. "Attenuation of Radionuclides and Toxic Elements by in Situ Soils at a Uranium Tailings Pond I Central Wyoming." *Permeability and Groundwater Contaminant Transport*. T.F. Zimmie and C.O. Riggs, eds. ASTM STP 746. Washington, DC: ASTM International. pp. 221–242. 1981.

Hawkins, D.B. and H.L. Short. "Equations for the Sorption of Cesium and Strontium on Soil and Clinoptilolite." IDO-12046. Idaho Falls, Idaho: Atomic Energy Commission, Idaho Operations Office. 1965.

Hemming, C.H., R.L. Bunde, M.J. Liszewski, J.J. Rosentreter, and J. Welhan. "Effect of Experimental Technique on the Determination of Strontium Distribution Coefficients of a Surficial Sediment from the Idaho National Engineering Laboratory, Idaho." *Water Research*. Vol. 31, Issue 7. pp. 1,629–1,636. 1997.

Hochella, J. M.F. and A.F. White, eds. "Mineral–Water Interface Geochemistry." *Reviews in Mineralogy*. Vol. 23. Washington, DC: Mineralogical Society of America. 1990.

Hoeffner, S.L. "Radionuclide Sorption on Savannah River Plant Burial Ground Soil—A Summary and Interpretation of Laboratory Data." DP-1702. Aiken, South Carolina: E.I. du Pont de Nemours and Company, Savannah River Laboratory. 1985.

Hsi, C.K.D. and D. Langmuir. "Absorption of Uranyl Onto Ferric Oxyhydroxides: Application of the Surface Complexation Site-Binding Model." *Geochimica et Cosmochimica Acta*. Vol. 49. pp. 1,931–1,941. 1985.

Hu, Q., Z. Pihong, J.E. Moran, and J.C. Seaman. "Sorption and Transport of Iodine Species in Sediments from Savannah River and Hanford Sites." *Journal of Contaminant Hydrology*. Vol. 78. pp. 185–205. 2005.

Johnson, W.H. "Sorption Models for U, Cs, and Cd on Upper Atlantic Coastal Plain Soils." A Thesis Presented to the Academic Faculty at Georgia Institute of Technology, Atlanta, Georgia. 1995.

Kabata-Pendias, A. and H. Pendias. "Trace Elements in Soils and Plants." Boca Raton, Florida: CRC Press. 1984.

Kaplan, D.I. "Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site (U)." WSRC–TR–2006–00004. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company. 2006.

———. "Recommended Distribution Coefficients,  $K_d$  Values, for Special Analysis Risk Calculations Related to Waste Disposal and Tank Closure on the Savannah River Site (U)." WSRC–TR–2005–00229. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company. 2005.

———. "Recommended Geochemical Input Values for the Special Analyses of the Slit/Engineered Trenches and Intermediate Level Vault." WSRC–RP–2004–00267. Aiken, South Carolina: Westinghouse Savannah River Company. 2004.

———. "Influence of Surface Charge of an Fe-oxide and an Organic Matter Dominated Soil on Iodide and Pertechnetate Sorption." *Radiochimica Acta*. Vol. 91, No. 3. pp. 173–178. 2003.

Kaplan, D.I. and S.M. Serkiz. "Influence of Dissolved Organic Carbon and pH on Anion Sorption to Sediment." WSRC–RP–2006–00005. Aiken, South Carolina: Westinghouse Savannah River Company. 2006.

———. "Influence of Dissolved Organic Carbon and pH on Contaminant Sorption to Sediment." WSRC–RP–2004–00593. Aiken, South Carolina: Westinghouse Savannah River Company. 2004.

———. "In Situ  $K_d$  Values and Geochemical Behavior for Inorganic and Organic Constituents of Concern at the TNX Outfall Delta." WSRC–TR–99–00488. Aiken, South Carolina: Westinghouse Savannah River Company. 2000.

Kaplan, D.I. and R.J. Serne. "Geochemical Data Package for the Hanford Immobilized Low-Activity Tank Waste Performance Assessment (ILAW PA)." PNNL–13037. Rev. 1. Richland, Washington: Pacific Northwest National Laboratory. 2000.

———. "Pertechnetate Exclusion From Sediments." *Radiochimica Acta*. Vol. 81. pp. 117–124. 1998.

———. "Distribution Coefficient Values Describing Iodine, Neptunium, Selenium, Technetium, and Uranium Sorption to Hanford Sediments." PNL–10379. Supplement 1. Richland, Washington: Pacific Northwest National Laboratory. 1995.

Kaplan, D.I., B.A. Powell, D.I. Demirkanli, R.A. Fjeld, F.J. Molz, S.M. Serkiz, and J.T. Coates. "Influence of Oxidation States on Plutonium Mobility During Long-term Transport Through an Unsaturated Subsurface Environment." *Environmental Science and Technology*. Vol. 38, No. 19. pp. 5,053–5,058. 2004.

Kaplan, D.I., R.J. Serne, K.E. Parker, and I.V. Kutnyakov. "Iodide Sorption to Subsurface Sediments and Illitic Minerals." *Environmental Science and Technology*. Vol. 34. pp. 399–405. 2000.

Kaplan, D.I., K.E. Parker, and I.V. Kutynakov. "Radionuclide Distribution Coefficients for Sediments Collected from Borehole 299–E17–21: Final Report for Subtask–1a." PNNL–11966. Richland, Washington: Pacific Northwest National Laboratory. 1998a.

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

Kaplan, D.I., T.L. Gervais, and K.M. Krupka. "Uranium(VI) Sorption to Sediments Under High Ph and Ionic Strength Conditions." *Radiochimica Acta*. Vol. 80. pp. 201–211. 1998c.

Kaplan, D.I., R.J. Serne, A.T. Owen, J. Conca, T.W. Wietsma, and T.L. Gervais. "Radionuclide Adsorption Distribution Coefficients Measured in Hanford Sediments for the Low-Level Waste Performance Assessment Project." PNNL–11385. Richland, Washington: Pacific Northwest National Laboratory. 1996.

Kaplan, D.I., P.M. Bertsch, D.C. Adriano, and K.A. Orlandini. "Actinide Association with Groundwater Colloids in a Coastal Plain Aquifer." *Radiochimica Acta*. Vols. 66 and 67. pp. 181–187. 1994.

Kedziorek, A.M., A.C.M. Bourg, and E. Giffaut. "Hydrogeochemistry of Sn(IV) in the Content of Radioactive Waste Disposal: Solubility and Adsorption on MX–80 Bentonite and Callovo-Oxfordian Argillite." *Physics and Chemistry of the Earth*. Parts A, B, and C. Vol. 32, Issues 8–14. pp. 568–572. 2007.

Knobel, L.L., R.C. Bartholomay, and B.R. Orr. "Preliminary Delineation of Natural Geochemical Reactions, Snake River Plain Aquifer System, Idaho National Engineering Laboratory and Vicinity, Idaho." U.S. Geological Survey Water Resources Investigations Report 97-4093. 1997.

Knobel, L.L., B.R. Orr, and L.D. Cecil. "Summary of Background Concentrations of Selected Radiochemical and Chemical Constituents in Groundwater From the Snake River Plain Aquifer, Idaho—Estimated from an Analysis of Previously Published Data." *Journal of Idaho Academy Sciences*. Vol. 28. pp. 48–61. 1992.

Kuntz, M.A., B. Skipp, M.A. Lanphere, W.E. Scott, K.L. Pierce, G.B. Dalrymple, D.E. Champion, G.F. Embree, W.R. Page, L.A. Morgan, R.P. Smith, W.R. Hackett, and D.W. Rodgers. "Geologic Map of the Idaho National Engineering Laboratory and Adjoining Areas, Eastern Idaho." U.S. Geological Survey Miscellaneous Investigations Map I-2330. Scale 1:100,000. 1994.

Kuntz, M.A., G.B. Dalrymple, D.E. Champion, and D.J. Doherty. "Petrography, Age, and Paleomagnetism of Volcanic Rocks at the Radioactive Waste Management Complex, Idaho National Engineering Laboratory, Idaho." U.S. Geological Survey Open-File Report 80-388. 1980.

Langmuir, D. *Aqueous Environmental Geochemistry*. Upper Saddle River, New Jersey: Prentice Hall. 1997.

Leecaster, M.K. and L.C. Hull. "Spatial Distribution of Neptunium and Uranium Partition Coefficients ( $K_d$ ) for Interbed Sediments at a Radioactive Waste Subsurface Disposal Area." ICP/EXT-03-00088. Rev. 0. Idaho Falls, Idaho: Idaho National Engineering and Environmental Laboratory. 2004.

Lindenmeier, C.W., R.J. Serne, J.L. Conca, A.T. Owen, and M.I. Wood. "Solid Waste Leach Characteristics and Contaminant-Sediment Interactions—Volume 2: Contaminant Transport Under Unsaturated Moisture Contents." PNL-10722. Richland, Washington: Pacific Northwest National Laboratory. 1995.

Liszewski, M.J., J.J. Rosentreter, and K.E. Miller. "Strontium Distribution Coefficients of Surficial Sediment Samples from the Idaho National Engineering Laboratory, Idaho." U.S. Geological Survey Water Resource Investigations Report 97-4044. 1997.

Liszewski, M.J., J.J. Rosentreter, K.E. Miller, and R.C. Bartholomay. "Strontium Distribution Coefficients of Surficial and Sedimentary Interbed Sediment Samples From the Idaho National Engineering Laboratory, Idaho." U.S. Geological Survey Water Resource Investigations Report 98-4073. 1998.

Looney, B.B., M.W. Grant, and C.M. King. "Estimation of Geochemical Parameters for Assessing Subsurface Transport at the Savannah River Plant." Environmental Information Document DPST-85-904. Aiken, South Carolina: E.I. du Pont de Nemours and Company, Savannah River Laboratory. 1987.

Lu, N., K. Kung, C. Mason, I. Triay, C. Cotter, A. Pappas, and M. Pappas. "Removal of Plutonium-239 and Americium-241 From Rocky Flats Soil by Leaching." *Environmental Science and Technology*. Vol. 32, No. 3. pp. 370-374. 1998.

Martian, P., C. Esakkiperumal, and A.L. Schafer. DOE/NE-ID-11227. "Operable Unit 3-14 Tank Farm Soil and Groundwater Remedial Investigation/Baseline Risk Assessment—Appendix A: Groundwater Risk Pathway Model Development, Calibration, and Predictive Results." Idaho Falls, Idaho: DOE-Idaho. 2006.

Mashkin, A.N. and S.L. Shikov. "Effect of Natural and Technogenic Factors on Technetium Behavior in the Environment." *Radiochemistry*. Vol. 42, No. 2. pp. 205-210. 2000.

McConnell, J.W., Jr., R.D. Rogers, J.D. Jastrow, W.E. Sanford, S.R. Cline, T.M. Sullivan, and M. Fuhrmann. "Results After Ten Years of Field Testing Low-level Radioactive Waste Forms Using Lysimeters." ANL/ER/CP 95275. Idaho Falls, Idaho: Idaho National Engineering Laboratory. 1995.

McIntyre, P.F. "Sorption Properties of Carbon-14 on Savannah River Plant Soil." DPST-88-900. Aiken, South Carolina: E.I. du Pont de Nemours and Company, Savannah River Plant. 1988.

Mincher, B.J., R.V. Fox, D.C. Cooper, and G.S. Groenewold. "Neptunium and Plutonium Sorption to Snake River Plain, Idaho Soil." *Radiochimica Acta*. Vol. 91. pp. 397-401. 2003.

Miner, F.J., P.A. Evans, and W.L. Polzer. "Plutonium Behavior in the Soil/water Environment." RFP-2480. Golden, Colorado: Rockwell International. 1982.

Morse, L.H. and M. McCurry. "Possible Correlations Between Basalt Alteration and the Effective Base of the Snake River Plain Aquifer at the INEEL." S. Sharma and J.H. Hardcastle, eds. 32<sup>nd</sup> Symposium on Engineering Geology and Geotechnical Engineering, Boise, Idaho, March 26-26, 1997. Boise, Idaho: Idaho State University. pp. 1-13. 1997

Neiheisel, J. "Prediction Parameters of Radionuclide Retention at Low-Level Radioactive Waste Sites." EPA a520/1-83-025. Washington, DC: EPA, Office of Radiation Programs. 1983.

Newman, M.E., I. Porro, R. Scott, R.M. Dunnivant, R.W. Goff, M.D. Blevins, S.M. Ince, J.D. Leyba, T.A. DeVol, A.W. Elzerman, and R.A. Fjeld. "Evaluation of the Mobility of Am, Cs, Co, Pu, Sr, and U Through INEL Basalt and Interbed Materials: Summary Report of the INEL/Clemson University Laboratory Studies." ER-WAG7-82, INEL-95/282. Idaho Falls, Idaho: Idaho National Engineering Laboratory. 1996.

Nimmo, J.R., J.P. Rousseau, K.S. Perkins, K.G. Stollenwerk, P.D. Glynn, R.C. Bartholomay, and L.L. Knobel. "Hydraulic and Geochemical Framework of the Idaho National Engineering and Environmental Laboratory Vadose Zone." *Vadose Zone Journal*. Vol. 3. pp. 6-34. 2004.

Nishita, H.A., A. Wallace, E.M. Romney, and R.K. Schulz. "Effect of Soil Type on the Extractability of Np-237, Pu-239, Am-241, and Cm-244 as a Function of pH." *Soil Science*. Vol. 135. pp. 25-34. 1981.

Pabalan, R.T., D.R. Turner, F.P. Bertetti, and J.D. Prikryl. "Uranium(VI) Sorption onto Selected Mineral Surfaces: Key Geochemical Parameters." *Adsorption of Metals by Geomedia*. E.A. Jenne, ed. San Diego, California: Academic Press. 1998.

Payne, T.E., R. Edis, B.R. Fenton, and T.D. Waite. "Comparison of Laboratory Uranium Sorption Data with 'In Situ Distribution Coefficients' at the Koongarra Uranium Deposit, Northern Australia." *Journal of Environmental Radioactivity*. Vol. 57. pp. 35-55. 2001.

Penrose, W.R., W.L. Polzer, E.H. Essington, D.M. Nelson, and K.A. Orlandini. "Mobility of Plutonium and Americium Through a Shallow Aquifer in a Semiarid Region." *Environmental Science and Technology*. Vol. 24. pp. 228-234. 1990.

Perkins, K.S. "Measurement of Sedimentary Interbed Hydraulic Properties and Their Hydrologic Influence Near the Idaho Nuclear Technology and Engineering Center at the Idaho National Engineering and Environmental Laboratory." U.S. Geological Survey Water Resources Investigations Report 03-4048. 2003.

Perkins, K.S. and J.R. Nimmo. "Measurement of Hydraulic Properties of the B-c Interbed and Their Influence on Contaminant Transport in the Unsaturated Zone at the Idaho Engineering and Environmental Laboratory, Idaho." U.S. Geological Survey Water Resources Investigations Report 00-4073. 2000.

Plummer, M.A., L.C. Hull, and D.T. Fox. "Transport of Carbon-14 in a Large Unsaturated Soil Column." *Vadose Zone Journal*. Vol. 3. pp. 109–121. 2004.

Porro, I., M.E. Newman, and F.M. Dunnivant. "Comparison of Batch and Column Methods for Determining Strontium Distribution Coefficients for Unsaturated Transport in Basalt." *Environmental Science and Technology*. Vol. 34. pp. 1,679–1,686. 2000.

Powell, B.A., R.A. Fjeld, J.T. Coates, D.I. Kaplan, and S.M. Serkiz. "Plutonium Oxidation State Geochemistry in the SRS Subsurface Environment (U)." WSRC–TR–2003–00035. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company. 2002.

Powell, K.R., S. Serkiz, and D.I. Kaplan. "Evaluation of the D-Area Expanded Operable Unit for Monitored Natural Attenuation of Inorganic Constituents of Concern: Interim Report." WSRC–TR–2001–00574. Aiken, South Carolina: Westinghouse Savannah River Company. 2001.

Prout, W.E. "Adsorption of Radioactive Wastes by Savannah River Plant Soil." *Soil Science*. Vol. 84. pp. 13–17. 1958.

Rathburn, S.L. "Pleistocene Cataclysmic Flooding Along the Big Lost River, East-Central Idaho." *Geomorphology*. Vol. 8. pp. 305–319. 1993.

Read, D., T.A. Lawless, R.J. Sims, and K.R. Butter. "Uranium Migration Through Intact Sandstone Cores." *Journal of Contaminant Hydrology*. Vol. 13. pp. 277–289. 1993.

Reddy, M.R. and S.J. Dunn. "Distribution Coefficients for Nickel and Zinc in Soils." *Environmental Pollution Series B—Chemical and Physical*. Vol. 11, Issue 4. pp. 303–313. 1986.

Reed, M.F. and R.C. Bartholomay. "Mineralogy of Selected Sedimentary Interbeds at or near the Idaho National Engineering Laboratory, Idaho." U.S. Geological Survey Open-File Report 94-374. 1994.

Relyea, J.F. "Theoretical and Experimental Considerations for the Use of the Column Method for Determining Retardation Factors." *Radioactive Waste Management and the Nuclear Fuel Cycle*. Vol. 3. pp. 151–166. 1982.

Rhoads, K., B.N. Bjornstad, R.E. Lewis, S.S. Teel, K.J. Cantrell, R.J. Serne, J.L. Smoot, C.T. Kincaid, and S.K. Wurstner. "Estimation of the Release and Migration of Lead Through Soils and Groundwater at the Hanford Site 218-E-12B Burial Ground. Volume 1: Final Report." PNL-8356. Richland, Washington: Pacific Northwest National Laboratory. 1992.

Rhodes, D.W. "The Effect of pH on the Uptake of Radioactive Isotopes From Solution by a Soil." *Soil Science Society of America Proceedings*. Vol. 21. pp. 389-392. 1957.

Rightmire, C.T. and B.D. Lewis. "Hydrogeology and geochemistry of the unsaturated zone, Radioactive Waste Management Complex, Idaho National Engineering Laboratory, Idaho." U.S. Geological Survey Water Resources Investigations Report 87-4198. 1987.

Robertson, C.G. and P.A. Thayer. "Petrology and Reservoir Characteristics of the Congaree Formation at the Savannah River Site, South Carolina." Proceedings of the Second Bald Head Island Conference on Coastal Plains Geology, Hilton Head Island, North Carolina, November 6-11, 1990. Wilmington, North Carolina: University of North Carolina at Wilmington. pp. 50-51. 1990.

Roddy, M. "Geochemical Study for Perched Water Source Identification at INTEC." EDF-5758. Rev. 0. Idaho Falls, Idaho: Idaho National Laboratory, Idaho Cleanup Project. 2005.

Rodriguez, R.R., A.L. Schafer, J. McCarthy, P. Martian, D.E. Burns, D.E. Raunig, N.A. Burch, and R.L. VanHorn. DOE/ID-10534, "Comprehensive RI/FS for the Idaho Chemical Processing Plant OU 3-13 at the INEEL—Part A, RI/BRA Report (Final)." Idaho Falls, Idaho: Idaho National Engineering Laboratory, DOE-Idaho. 1997.

Rosenberger, K.H., B.C. Rogers, and R.K. Cauthen. "Saltstone Performance Objective Demonstration Document (U)." CBU-PIT-2005-00146. Rev. 0. Aiken, South Carolina: Westinghouse Savannah River Company. 2005.

Routson, R.C., G.S. Barney, and R.M. Smith. "Hanford Site Sorption Studies for the Control of Radioactive Wastes: A Review." WHO-SA-155. Rev. 1. Richland, Washington: Rockwell Hanford Operations. 1980.

Routson, R.C., G. Jansen, and A.V. Robinson. "<sup>241</sup>Am, <sup>237</sup>Np, and <sup>99</sup>Tc Sorption on Two United States Subsoils from Differing Weathering Intensity Areas." *Health Physics*. Vol. 33. pp. 311-317. 1977.

Ryan, J.P. "Batch and Column Strontium Distribution Coefficients With Water-saturated Soil Strata From the Savannah River Plant Burial Ground." Proceedings of the Environmental Migration of Long-Lived Radionuclides International Symposium, Knoxville, Tennessee, 1981. Vienna, Austria: International Atomic Energy Agency. 1982.

Salter, O.F., L.L. Ames, and J.E. McGarrah. "The Sorption Behavior of Selected Radionuclides on Columbia River Basalts." RHO-BWI-LD-48. Richland, Washington: Rockwell International. 1981.

Schmalz, B.L. "Radionuclide Distribution in Soil Mantle of the Lithosphere as a Consequence of Waste Disposal at the National Reactor Testing Station." IDO-10049. Idaho Falls, Idaho: United States Atomic Energy Commission, Idaho Operations Office. 1972.

Schuessler, W., R. Artinger, B. Kienzler, and J. Kim. "Conceptual Modeling of the Humic Colloid-Borne Americium(iii) Migration by a Kinetic Approach. *Environmental Science and Technology*. Vol. 34, No. 12. pp. 2,608-2,611. 2000.

Schwertmann, U. and R.M. Taylor. "Iron Oxides." *Minerals in Soil Environments, Second Edition*. J.B. Dixon and S.B. Week, eds. Madison, Wisconsin: Soil Science Society of America. pp. 379-438. 1989.

Scrudato, R.J. and E.L. Estes. "Clay-Lead Sorption Studies." *Environmental Geology*. Vol 1. pp. 167-170. 1975.

Serkiz, S.M. and W.H. Johnson. "Uranium Geochemistry in Soil and Groundwater at the F and H Seepage Basins (U)." EPD-SGS-94-307. Aiken, South Carolina: Westinghouse Savannah River Company. 1994.

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

Shanbhag, P.M. and G.R. Choppin. "Binding of Uranyl by Humic Acid." *Journal of Inorganic Nuclear Chemistry*. Vol. 43. pp. 3,369-3,372. 1981.

Sheppard, J.C., M.J. Campbell, J.A. Kittrick, and T.L. Hardt. "Retention of Neptunium, Americium, and Curium by Diffusible Soil Particles." *Environmental Science and Technology*. Vol. 13. pp. 680-684. 1979.

Sheppard, M.I. and D.H. Thibault. "Default Soil Solid/liquid Partition Coefficients,  $K_d$ s, for Four Major Soil Types: a Compendium." *Health Physics*. Vol. 59, No. 4. pp. 471-482. 1990.

Sheppard, M.I. and D.H. Thibault. "A 4-Year Mobility Study of Selected Trace-Elements and Heavy-Metals." *Journal of Environmental Quality*. Vol. 25. pp. 1,261-1,267. 1991.

Sheppard, M.I., D.I. Beals, D.H. Thibault, and P. O'Conner. "Nuclide Distribution Coefficients and Their Statistical Distribution." AECL-8346. Pinawa, Manitoba: Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment. 1984.

Stevenson, F.J. and A. Fitch. "Chemistry of Complexation Metal Ions with Soil Solution Organics." *Interactions of Soil Minerals with Natural Organics and Microbes*. P.M. Huang and M. Schnitzer, eds. SSSA Special Publication No. 17. Madison, Wisconsin: Soil Science Society of America, Inc. 1986.

Strom, R.N. and D.S. Kaback. "SRP Baseline Hydrogeologic Investigation: Aquifer Characterization, Groundwater Geochemistry of the Savannah River Site and Vicinity." WSRC-RP-92-450. Aiken, South Carolina: Westinghouse Savannah River Company. 1992.



Thibault, D.H., M.I. Sheppard, and P.A. Smith. "A Critical Compilation and Review of Default Soil Solid/Liquid Partition Coefficients,  $K_d$ , for Use in Environmental Assessments." AECL-10125. Pinawa, Manitoba: Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment. 1990.

Ticknor, K.V. and Y.H. Cho. "Interaction of Iodide and Iodate With Granitic Fracture Filling Materials." *Journal of Radioanalytical and Nuclear Chemistry*. Vol. 140, No. 1. pp. 75–90. 1990.

Ticknor, K., P. Vilks, and T. Vandergraff. "The Effect of Fulvic Acid on the Sorption of Actinides and Fission Products on Granite and Selected Minerals." *Applied Geochemistry*. Vol. 11, No. 4. pp. 555–565. 1996.

Veeresh, H., S. Tripathy, D. Chaudhuri, B.R. Hart, and M.A. Powell. "Sorption and Distribution of Adsorbed Metals in Three Soils of India." *Applied Geochemistry*. Vol. 18. pp. 1,723–1,731. 2003.

Vyas, V.M., A. Roy, W. Strawderman, P.G. Georgopoulos, and D.S. Kosson. "Defining Background Groundwater Quality at the Savannah River Site." Technical Report CCL/CRESP TR01-01. Nashville, Tennessee: Remediation and Exposure Assessment Task Groups, Consortium for Risk Evaluation with Stakeholder Participation (CRESP). 2001.

Waite, T.D., J.A. Davis, T.E. Payne, G.A. Waychunas, and N. Xu. "Uranium(VI) Adsorption to Ferrihydrite: Application of a Surface Complexation Model." *Geochimica et Cosmochimica Acta*. Vol. 24. pp. 5,465–5,478. 1994.

Welhan, J., T. Funderburg, R.P. Smith, and A. Wylie. "Stochastic Modeling of Hydraulic Conductivity in the Snake River Plain Aquifer: 1—Hydrogeologic Constraints and Conceptual Approach." Proceedings of the Symposium on Engineering Geology and Geotechnical Engineering, Boise, Idaho, March 26–28, 1997. Pocatello, Idaho: Idaho State University. 1997.

Westinghouse Savannah River Company. "Environmental Management Program Performance Management Plan." WSRC-RP-2002-00245. Rev 6. Aiken, South Carolina: Westinghouse Savannah River Company. 2002.

Whitehead, R.L. "Geohydrologic Framework of the Snake River Plain Regional Aquifer System, Idaho and Eastern Oregon." U.S. Geological Survey Paper 1408-B. 1992.

Winnfield, K.A. "Spatial Variability of Sedimentary Interbed Properties Near the Idaho Nuclear Technology and Engineering Center at the Idaho National Engineering and Environmental Laboratory." U.S. Geological Survey Water Resources Investigations Report 03-4142. 2003.

Wood, W.W. and W.H. Low. "Aqueous Geochemistry and Diagenesis in the Eastern Snake River Plain Aquifer System, Idaho." *Geological Society of America Bulletin* 97. 1986.

Zimdahl, R.L. and J.J. Hassett. "Lead in Soil." *Lead in the Environment*. W.R. Boggess and B.G. Wixson, eds. NSF/RA-770214. Washington, DC: National Science Foundation. pp. 93–98. 1977.