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Summary of Vadose – Zone Conceptual Models for Flow and Contaminant Transport and 1999 – 2003 Progress on Resolving Deficiencies in Understanding the Vadose Zone at the INEEL

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ABSTRACT

The thick vadose zone that underlies the Idaho National Engineering and Environmental Laboratory has been recognized both as an avenue through which contaminants disposed at or near the ground surface can migrate to groundwater in the underlying Eastern Snake River Plain aquifer, and as a barrier to the movement of contaminants into the aquifer. Flow and contaminant transport in the vadose zone at the INEEL is complicated by the highly heterogeneous nature of the geologic framework and by the variations in the behavior of different contaminants in the subsurface. The state of knowledge concerning flow and contaminant transport in the vadose zone at and near the INEEL IN 1999 was summarized in *Deficiencies in Vadose Zone Understanding at the Idaho National Engineering and Environmental Laboratory* (Wood et al., 2000). These authors identified deficiencies in knowledge of flow and contaminant transport processes in the vadose zone, and provided recommendations for additional work that should be conducted to address these deficiencies. In the period since (Wood et al., 2000) was prepared, research has been published that, to some degree, address these deficiencies. This document provides a bibliography of reports, journal articles, and conference proceedings published 1999 through mid-2003 that are relevant to the vadose zone at or near the INEEL and provides a brief description of each work. Publications that address specific deficiencies or recommendations are identified, and pertinent information from selected publications is presented.

CONTENTS

TABLES

1. INTRODUCTION

A review of existing knowledge about the movement of water and contaminants and non-contaminant substances in the vadose zone beneath the Idaho National Engineering and Environmental Laboratory, and processes that affect water movement and transport, was documented in *Deficiencies in Vadose Zone Understanding at the Idaho National Engineering and Environmental Laboratory* (Wood et al., 2000), hereafter referred to as the *Deficiencies Document*. That document was based, in part, on a workshop held in October 1999 and on research that had been published up to 1999. (Wood et al., 2000) identified deficiencies in the scientific understanding of vadose zone processes and provided recommendations for ameliorating these deficiencies.

Research conducted since publication of the *Deficiencies Document* that is germane to the deficiencies and recommendations identified by (Wood et al., 2000) is summarized in this document. Only research published in the period 1999 – July 2003 was considered in this document. However, preprints of papers that were presented in a conference in October 2003 were reviewed. The relevance of individual publications to specific deficiencies or recommendations is indicated.

This document is a working draft that was prepared by North Wind, Inc., primarily by Robert C. Starr, Dana L. Dettmers, and Brennon R. Orr. The overall organization and content of the document was developed in conjunction with Paul Wichlacz and Tom Wood of Bechtel BWXT Idaho, LLC., the Management and Operations contractor for the Idaho National Engineering and Environmental Laboratory.

This document is organized as follows. Introductory material is presented in Section 1. Relevant research published since preparation of the *Deficiencies Document* are summarized in Section 2. Section 3 provides a tabular listing of the *deficiencies* in understanding of vadose zone processes at the INEEL and the *recommendations* for ameliorating these deficiencies that were presented in the *Deficiencies Document*, and a listing of the recent publications that address individual deficiencies or recommendations. Relevant information from these publications is also provided in Section 3. Section 4 provides a summary. The references cited in this document are presented in Section 5.

Appendix A includes the conceptual model for the vadose zone that was previously published in the *Deficiencies Document*. It is included here to provide background information on the vadose zone beneath and in the vicinity of the INEEL, and so that readers of this document will understand the context of the research summarized herein.

Appendix B is a bibliography of research published 1999-2003 related to the vadose zone at and near the INEEL. These publications were identified by searching the INEEL Technical Library Catalog using the key words *vadose* and *vadose zone*. The catalog was also searched using key words of project titles listed in Table 2-1 of *Deficiencies in Vadose Zone Understanding at the INEEL*. In addition, the general technical literature was searched using several search engines, including Web of Science, Web SPIRS, GeoRef, Engineering Village 2, and PubMed. The searches were performed using one or a combination of the key words *vadose, vadose zone*, *Idaho National Engineering and Environmental Laboratory, INEEL,* and *Idaho*. Also, reference lists in documents published between 1999-2003 were checked for any other pertinent documents published during this time frame. The literature search was performed in August 2002 and hence this review extends only through the first part of 2003. However, preprints of several articles that were published in proceedings of an October 2003 conference are also included.

2. SUMMARY OF INEEL VADOSE ZONE RESEARCH PUBLISHED 1999-2003

The following table provides a brief summary of published research relevant to the INEEL vadose zone. Specifically, it is intended to update the information contained in Table 2-1, pg 2-2 through 2-15, of the Vadose Zone Deficiencies Document (Wood et al., 2000). Publications are grouped in Table 2-1 primarily according to the facility to which they apply and secondarily according to the activity. A very brief summary of these documents is provided in the table. Additional information on these documents is provided in the narrative that follows the table. Full bibliographic citations are provided in Appendix B.

Table 2-1 Summary of publications related to the INEEL vadose zone published 1999-2003

Facility and Dates	**Project**	**Description**
RWMC		
1992-ongoing	Cold Test Investigations	Subsurface exploration to obtain characterization and treatability information to evaluate sonic coring technology to recover hazardous and/or radioactive waste from Pit 9. Bechtel BWXT Idaho, 2000. INEEL/EXT-99-00741. Probehole installation and monitoring within the Cold Test Pit South of the RWMC to allow vapor and moisture characterization of the surrogate waste in the Cold Test Pit South for application to the SDA. Bechtel BWXT Idaho, 2000. INEEL/EXT-2000-01409.
1992-present	Organic Contamination in the Vadose Zone	The selected remedy for OCVZ consists of the extraction and destruction of organic contaminant vapors present in the vadose zone beneath and within the immediate vicinity of the RWMC, and the monitoring of vadose zone vapors and the SRPA in the vicinity of the RWMC. A series of documents have been published detailing environmental and operational results of samples collected. OCVZ End-Year Report 1999. INEEL/EXT-2000-00034, Volumes 1 and 2. OCVZ Mid-Year Report 2000. INEEL/EXT-2000-00640. OCVZ Year-End Report 2000. INEEL/EXT-2001-00023. OCVZ Mid-Year Report 2001. INEEL/EXT-2001-00770. OCVZ End-Year Report 2001. INEEL/EXT-02-00209. OCVZ Mid-Year Report 2002. INEEL/EXT-02-00981.

Facility and Dates	Project	Description
		OCVZ End-Year Report 2002. INEEL/EXT-03-00186. Interim RA Report for OCVZ. INEEL/EXT-02-00862. INEEL/EXT-2000-00040 EDF-ER-126 Supplement 2000, Supplement 2001, Supplement 2002. Site selection details for Units E and F of the vapor vacuum extraction with treatment units. McMurtrey, 2003. EDF-3229. Reporting of damage and repair to Unit C of the vapor vacuum extraction with treatment units. Bechtel BWXT Idaho 1999. INEEL/EXT-98-01102. Nelson, 2001. INEEL/EXT-2000-01682; EDF-ER-251.
1997-ongoing	Active Waste Monitoring	A summary of probe monitoring data collected within the waste zone of the SDA during FY 2002. Myers et al., 2003. INEEL/EXT-03-0001. Collection of samples to test for possible reductive dechlorination within the drums of waste disposed of in the SDA. Hull and Sondrup, 2003. INRA Subsurface Science Symposium.
2000-ongoing	Tensiometer Monitoring	Tensiometers were installed at and near the SDA and field water potential data are collected to monitor moisture conditions and movement in the subsurface. McElroy and Hubbell, 2001. INEEL/EXT-01-01624. McElroy and Hubbell ,2003. INEEL/EXT-02-01276. A study conducted at RWMC and the INEEL Research Center showed that water potential measurements can be used to detect and monitor deep infiltration events at waste disposal sites using tensiometers. Hubbell et al., 2002. ASTM STP 1415.
2001	Reconstruction Of Past Waste Disposal	Research was conducted to reconstruct the past disposal of Rocky Flats Plant 743-series waste buried in the SDA. Miller and Varvel, 2001. INEEL/EXT-01-00034.

Facility and Dates	Project	Description
2001-2002	Laboratory Sorption Experiments	Experiments were conducted to characterize the sorption behavior in sedimentary interbed soils of selected radionuclides buried at the RWMC. Grossman et al., 2001. INEEL/EXT-01-01106. A model has been derived for adsorption of uranium on INEEL sedimentary material using surface complexation theory to predict the range of adsorption conditions to be expected at the SDA. Hull et al., 2002. INEEL/CON-02-00106.
2002	Performance Assessment/ Composite Analysis Monitoring	Reporting of the PA/CA monitoring project results available as of September 2002. Ritter and Parsons, 2002. INEEL/EXT-02-01209.
2000-2002	Risk Analyses	A composite analysis to estimate the projected cumulative impacts to future members of the public from the disposal of low-level radioactive waste at the RWMC and all other sources of radioactive contamination at the INEEL that could interact with that waste. McCarthy et al., 2000. INEEL/EXT-97-01113. Risk analysis of the SDA contaminants of concern performed to support the comprehensive RI/FS study. Holdren et al., 2002. INEEL/EXT-02-01125. Geostatistical study to estimate surficial soil and interbed:basalt contacts, and soil,sediment, and aquifer hydraulic properties near the SDA. Leecaster, 2002. INEEL/EXT-02-00029.
2002	Investigation Of Flow Paths	Updated a previously existing model for simulating flow and transport through the vadose zone at the SDA. Magnuson, 2002. Spectrum conference proceeding PREPRINT INEEL/CON-02-00146. A chemical tracer was applied to seasonally filled infiltration ponds near the SDA to investigate kilometer scale flow paths through the interbedded basalts and sediment. Nimmo et al., 2002. Vadose Zone Journal 1:89-101.

Facility and Dates	Project	Description
		The Nimmo et al. 2002 field experiment was used as one of 23 published studies to assess the extent to which the same properties and processes dominate the observed transport behavior at scales of less than 1 to 1000s of meters. Nimmo, 2002. International Groundwater Symposium.
1997-ongoing	Long-Term Corrosion Test	Corrosion coupons for a variety of metals are buried at 4- and 10-ft depths in a soil berm constructed of Spreading Area B soils. Coupons were recovered following 1 and 3 years of burial. Mizia et al., 1999. INEEL/EXT-99-00678. Alder Flitton et al., 2001. INEEL/EXT-01-00036. Alder Flitton et al., 2001. INEEL/CON-01-01450.
INTEC		
Ongoing	Tank Farm Interim Actions	Work plan for defining the remedial design requirements, preparing the design documentation, and defining and implementing the construction and operations phases of OU 3-13 Tank Farm Interim Action. Bechtel BWXT Idaho, 2000. DOE/ID-10772.
2002	Perched Water	Details the results of fieldwork performed for Phase I of OU 3-13 Perched Water remedy. Bechtel BWXT Idaho, 2002. DOE/ID-10967.
2003	Simulation Of Episodic Flood Events	Research conducted to simulate episodic flood events at the vadose zone research park. Baker and Hull, 2003. INRA Subsurface Science Symposium.
Outside of Facility Boundaries		
1995-ongoing	Box Canyon Investigation	A conceptual model of the fractured basalt vadose zone at Box Canyon was proposed based on the results of lithological studies and a series of ponded infiltration tests. Faybishenko et al., 2000. Water Resources Research 36:3499-3520. A numerical model of the fractured basalt vadose zone at Box Canyon was developed based on the

Facility and Dates	**Project**	**Description**
		conceptual model proposed by Faybishenko et al. 2000. Doughty, 2000. Water Resources Research 36:3521-3534.
General		
2001	National Roadmap For Vadose Zone Science and Technology	A national roadmap was compiled to state the need for vadose zone research and critical research objectives. National Roadmap for Vadose Zone Science and Technology. DOE/ID-10871.

2.1. Summary of RWMC Documents

Publications that describe studies relevant to the vadose zone at the RWMC are summarized in this section.

2.1.1. Cold Test Investigations

Test Plan for Cold Testing of Operable Unit 7-10 Stage I Coring Activities
Bechtel BWXT Idaho, 2002. INEEL/EXT-99-00741.

The OU 7-10 Staged Interim Action was developed to obtain characterization and treatability information for radioactive and hazardous waste at Pit 9. Stage I includes subsurface exploration to obtain materials for characterization and treatability studies. The primary objective of this test is to evaluate performance of sonic coring technology that will be used to recover hazardous and/or radioactive waste samples from Pit 9. Cores will be retrieved using a sonic drilling rig fitted with a coring tool designed to operate in the heterogeneous waste materials anticipated in Pit 9.

Test Plan for Cold Testing of Operable Unit 7-13/14 Type B Probes
Bechtel BWXT Idaho, 2000. INEEL/EXT-2000-01409.

This test plan supports the second phase of the two-phase Probing Project to provide probehole installation and monitoring within the Cold Test Pit South of the RWMC. The installation of Type B probes will allow, through direct sampling, vapor and moisture characterization of the surrogate waste in the Cold Test Pit South for application to the SDA.

2.1.2. Organic Contamination in the Vadose Zone

OCVZ End-Year Report 1999.
INEEL/EXT-2000-00034, Volume 1 and 2.

Approximately 3,981 kg (8,759 lb) of total volatile organic compounds were removed during this operating cycle from July 26, 1999 through December 31, 1999. Of this total mass, 2,490 kg (5,479 lb) was CCl_4.

OCVZ Mid-Year Report 2000
INEEL/EXT-2000-00640.

Approximately 3,838 kg (8,463 lb) of total volatile organic compounds were removed during this operating cycle from January 1, 2000 through June 30, 2000. Of this total mass, 2,414 kg (5,323 lb) was CCl_4.

OCVZ Year-End Report 2000
INEEL/EXT-2001-00023.

Approximately 5,802 kg (12,792 lb) of total volatile organic compounds were removed during this operating cycle from January 1, 2000 through December 31, 2000. Of this total mass, 65% was CCl_4.

OCVZ Mid-Year Report 2001
INEEL/EXT-2001-00770.

Approximately 4,375 kg (9,464 lb) of total volatile organic compounds were removed during this operating cycle from January 1, 2001 through June 30, 2001. Of this total mass, 64.8% was CCl_4.

OCVZ End-Year Report 2001
INEEL/EXT-02-00209.

Approximately 5,317 kg (11,721 lb) of total volatile organic compounds were removed during this operating cycle from July 1, 2001 through December 31, 2001. Of this total mass, 62% was CCl_4.

OCVZ Mid-Year Report 2002
INEEL/EXT-02-00981.

Approximately 6,269 kg (13,820 lb) of total volatile organic compounds were removed during this operating cycle from January 1, 2002 through June 30, 2002. Of this total mass, 57% was CCl_4.

OCVZ End-Year Report 2002
INEEL/EXT-03-00186.

Approximately 6,784 kg (14,958 lb) of total volatile organic compounds were removed during this operating cycle from July 1, 2002 through December 31, 2002. Of this total mass, 57% was CCl_4.

Interim RA Report for OCVZ
INEEL/EXT-02-00862.

Summarizes remedial action activities performed from July 1999 through December 2001.

Volatile Organic Compound Vapor Monitoring Results from Selected Wells at the RWMC
INEEL/EXT-2000-00040 EDF-ER-126 Supplement 2000, Supplement 2001, Supplement 2002.

The purpose of these supplements is to document the OU 7-08 VOC concentrations of vapor samples collected inside and outside the SDA during calendar years 2000, 2001, and 2002.

Considerations and Final Site Selection for Treatment Units E and F for Operable Unit 7-08 Organic Contamination in the Vadose Zone Project
McMurtrey, 2003. EDF-3229.

The thermal oxidizers, Units A and B, have exceeded their functional lifetimes and will be replaced with new catalytic oxidation systems, Units E and F. Several factors were considered in selecting installation sites for Units E and F and are discussed in the report along with details of the selected installation sites.

OCVZ VVET Unit C Failure Root Cause Analysis Report
Bechtel BWXT Idaho, 1999. INEEL/EXT-98-01102.

Unit C was one of three organic Vapor Vacuum Extraction with Treatment units used for removal and destruction of VOCs in the vadose zone beneath and in the vicinity of the SDA. It was inspected after failure on September 11, 1997. Unit C failed because the oxidizer operated at temperatures in excess of design specifications, resulting in damage to the carbon steel mesh and the tubes. It was rebuilt and restarted on June 24, 1998.

Organic Contamination in the Vadose Zone Vapor Vacuum Extraction with Treatment Unit C Damage Report
Nelson, 2001. INEEL/EXT-2000-01682; EDF-ER-251.

The report provides the results of an investigation of the damage to the tubes in the Unit C oxidizer on May 31, 2000. The report concludes that Unit C shut down because of damage resulting from a combination of low flow rate in Tubes 11 and 12 (inadequate equipment design) and high propane concentration in the fume/air/propane mixture fed to Unit C during the training exercises.

2.1.3 Active Waste Monitoring

Fiscal Year 2002 Summary Report for the OU 7-13/14 Probing Project
Myers et al., 2003. INEEL/EXT-03-0001.

The OU 7-13/14 Probing Project involves monitoring within the waste zone of the SDA. All previous monitoring has been between waste disposal locations or at depth in sedimentary interbeds. This report presents the results of data generated during FY 2002. Soil vapor probes were used to collect VOCs, oxygen, hydrogen, methane, carbon dioxide, carbon-14, and tritium data. Data were also collected using lysimeters, tensiometers, soil moisture probes, visual probes, and type A nuclear logging probes.

Degradation of Chlorinated Solvents in the Vadose Zone at the Radioactive Waste SDA
Hull and Sondrup, 2003. INRA Subsurface Science Symposium.

From distribution of gases in the waste disposal pits, the researchers hypothesize that trichloroethene and carbon tetrachloride are undergoing reductive dechlorination by hydrogenolysis under methanogenic conditions within the waste drums. Corrosion of the metal drums is a likely source of hydrogen.

2.1.4 Tensiometer Monitoring

RWMC Tensiometer Status as of November 2000
McElroy and Hubbell, 2001. INEEL/EXT-01-01624.

This report describes the installation, location, startup, and preliminary results for a network of 23 advanced tensiometers installed in 17 boreholes at and near the SDA during FY 2000. In addition, a few tensiometers which were not part of the FY2000 installation were added to the WAG-7 field-monitoring program. Data indicated that steady-state conditions were predominant during the spring and summer of 2000. Only 8 of 22 lysimeters installed in FY 2000 produced a sample, so recommendations for changes during the next round of sampling were made.

Advanced Tensiometer Monitoring in the Deep Vadose Zone at the RWMC
McElroy and Hubbell, 2003. INEEL/EXT-02-01276.

The advanced tensiometer monitoring data supported and expanded upon assumptions in the conceptual model of flow in the unsaturated zone at the RWMC. In addition, the monitoring network provided data for hydrologic flow model calibration and prediction as well as baseline water potential data for use in evaluating remediation activities.

Water Potential Response in Fractured Basalt from Infiltration Events
Hubbell et al., 2002. ASTM STP 1415.

A study was conducted to determine if moisture movement could be detected from natural water infiltration in a dual porosity, fractured basalt. Three boreholes were instrumented with multiple advanced tensiometers to a depth of 31 m and monitored for periods of 1.5 to 3.5 years. One borehole is located at the RWMC and two boreholes are located at the IRC. Water potential measurements were within the tensiometric range, from approximately +100 to –250 cm of water. Typically, water potentials exhibited a near steady-state unit-gradient downward flux. The results of this study indicate that water potential measurements can be used to detect and monitor deep infiltration events at waste disposal sites using tensiometers.

2.1.5 Reconstruction of Past Waste Disposal

Reconstructing Past Disposal of 743-Series Waste in the Subsurface Disposal Area for OU 7-08, OCVZ
Miller and Varvel, 2001. INEEL/EXT-01-00034.

The research objectives included (1) documenting the quantity and disposal locations of buried 743-series waste drums, (2) establishing a defensible estimate of the mass of carbon tetrachloride from 743-series waste buried in the SDA, and (3) establishing a defensible estimate of the mass of total volatile organic compounds (VOCs) from 743-series waste buried in the SDA. A total of 9,691 drums of 743-series waste were initially buried in the SDA, of which 8,676 remain buried following drum-retrieval activities. It is estimated that the mean carbon tetrachloride mass initially contained in the 8,676 remaining drums was 1.8E+06 lb (8.2E+05 kg) with a 95% upper confidence limit of 2.2E+06 lb (1.0E+06 kg). It is estimated that the mean mass of total VOCs initially contained in the 8,676 remaining drums was 2.4E+06 lb (1.1E+06 kg) with a 95% upper confidence limit of 3.1E+06 lb (1.4E+06 kg).

2.1.6 Laboratory Sorption Experiments

The Sorption of Selected Radionuclides in Sedimentary Interbed Soils from the Snake River Plain
Grossman et al., 2001. INEEL/EXT-01-01106.

Experiments were conducted to characterize the sorption behavior of a selected suite of contaminants (uranium, neptunium, americium, and chromium) buried at the RWMC. The principle objective was to characterize the sorption isotherms for the selected radionuclides under conditions representative of actual field conditions and examine variability of sorption behaviors among soils collected at different depths. A second objective is examination of the effect of bicarbonate, sulfate, and fluoride (common groundwater ligands) on sorption behavior. The major conclusion drawn from this research is that sorption behavior of uranium and neptunium was nonlinear at the aqueous phase concentrations. Sorption affinity for uranium and neptunium was observed to vary by less than an order of magnitude among the soils.

Estimating Uranium Partition Coefficients From Laboratory Adsorption Isotherms
Hull et al., 2002. INEEL/CON-02-00106.

An estimated 330 metric tons of uranium have been buried in the SDA. An assessment of uranium transport parameters was performed to decrease the uncertainty in risk and dose predictions derived from computer simulations of uranium fate and transport to the SRPA. A model was used to predict the range of adsorption conditions to be expected at the SDA. Adsorption in the deep vadose zone is predicted to be stronger than in near-surface sediments because the total dissolved carbonate decreases with depth.

2.1.7 Performance Assessment/Composite Analysis Monitoring

Results of Performance Assessment/Composite Analysis Monitoring Program
Ritter and Parsons, 2002. INEEL/EXT-02-01209.

The Performance Assessment/Composite Analysis (PA/CA) Monitoring program was developed and implemented to meet the requirements for monitoring low-level radioactive waste (LLW) disposal facilities. This report presents PA/CA monitoring project results available as of September 2002. Required monitoring includes subsurface monitoring, air pathway surveillance, and subsidence monitoring/control. Subsurface monitoring included near-field (source) monitoring of buried activated metal, monitoring of radionuclide concentrations in the vadose zone, and monitoring of the SRPA. Source monitoring of buried activated metal includes monitoring activated steel and beryllium with a variety of sampling and measurement equipment installed in burial locations. Vadose zone and SRPA monitoring are conducted using the large network of lysimeters and aquifer wells installed in and around the SDA. The regional air surveillance programs at the INEEL have found no measurable airborne radioactivity that is associated with RWMC releases to air, and the amount of subsidence in 2002 was in the historical range for the SDA. Monitoring results are summarized in this report.

2.1.8 Risk Analysis

RWMC Low-Level Waste Radiological Composite Analysis
McCarthy et al., 2000. INEEL/EXT-97-01113.

The composite analysis estimates the projected cumulative impacts to future members of the public from the disposal of low-level radioactive waste at RWMC and all other sources of radioactive contamination at the INEEL that could interact with the LLW disposal facility to affect the radiological dose.

Ancillary Basis for Risk Analysis of the SDA
Holdren et al., 2002. INEEL/EXT-02-01125.

Based on cumulative human health and ecological risk associated with the SDA, 12 radionuclides and four chemical contaminants are identified as human health contaminants of concern: Am-241, C-14, I-129, Nb-94, Nb-237, Sr-90, Tc-99, U-233, U-234, U-235, U-236, U-238, carbon tetrachloride, methylene chloride, nitrates, and tetrachloroethylene. In addition, Pu-238, Pu-239, and Pu-240 were classified as special case contaminants of concern. Ecological risk assessment identified four radionuclides and three chemical contaminants of concern: Am-241, Pu-239, Pu-240, Sr-90, cadmium, lead, and nitrates.

Geostatistic Modeling of Subsurface Characteristics in the Radioactive Waste Management Complex Region, Operable Unit 7-13/14.
Leecaster, 2002. INEEL/EXT-02-00029.

Geostistical techniques were used to predict values at unsampled locations based on the available data measured at specific locations at and near the SDA. This information is used for parameterizing numerical flow and transport models. The variables evaluated include the top and bottom elevation of the surficial soil layer and A-B, B-C, and C-D sedimentary interbeds, porosity and hydraulic conductivity of interbed sediments, and the transmissivity of the aquifer.

2.1.9 Investigation of Flowpaths

Subsurface Pathway and Transport Modeling for INEEL's SDA
Magnuson, 2002. Spectrum conference proceeding PREPRINT INEEL/CON-02-00146

A previously existing model in TETRAD was updated to incorporate additional information obtained from recent characterization activities. Uncertainty was not quantified using parametric approaches; rather conceptual uncertainties were assessed by implementing conceptual variations such as different infiltration rates at the surface, facilitated transport, and different methods to describe hydraulic properties of variable saturated fractured basalts constituting the majority of the subsurface. The primary sensitivity has been the amount of water that actually infiltrates through the waste, thereby mobilizing contaminants. The fluxes out the bottom of the vadose zone model were input into an aquifer model to estimate aquifer concentrations. The estimated aquifer concentrations were used to evaluate human health risks.

Kilometer-Scale Rapid Transport of Naphthalene Sulfonate Tracer in the Unsaturated Zone at the INEEL
Nimmo et al., 2002. Vadose Zone Journal 1:89-101

A chemical tracer, naphthalene sulfonate, was applied to seasonally filled infiltration ponds near the SDA to investigate possible long-range flow paths through the interbedded basalts and sediment of a 200-m-thick unsaturated zone. Within 4 months, tracer was detected in one of 13 sampled aquifer wells and in eight of 11 sampled perched-water wells as far as 1.3 km away. These detections show that (1) low-permeability layers in the unsaturated zone divert some flow horizontally, but do not prevent rapid transport to the aquifer; (2) horizontal convective transport rates within the unsaturated zone may exceed 14 m d^{-1}, perhaps through essentially saturated basalt fractures, tension cracks, lava tubes, or rubble zones; and (3) some perched water beneath the SDA derives from episodic surface water more than 1 km away.

Meter-to-Kilometer Scaling of Preferential Flow in the Unsaturated Zone
Nimmo, 2002. Proceedings of the International Groundwater Symposium

Data from 23 published studies of fast flowpaths in the unsaturated zone, on scales from less than 1 to 1000s of meters, were examined to assess the extent to which the same properties and processes dominate the observed transport behavior at different scales. The INEEL field experiment described in Nimmo et al. 2002 is included. One factor that does not correlate with much wider variation in V_{max} is the water input conditions, particularly if the supply is continuous or intermittent. Results show no clear trend of maximum flow rate with distance spanned by the test, evidence which favors simple scaling. The results are encouraging for the development of models that may represent preferential flow more realistically.

2.1.10 Long Term Corrosion Tests

Long Term Corrosion/Degradation Test First Year Results
Mizia et al., 1999. INEEL/EXT-99-00678.

The Long Term Corrosion/Degradation Test Project is designed to obtain site-specific corrosion rates to support efforts to more accurately estimate the transfer of activated elements to the environment. First year results showed no measurable corrosion for types 304L and 316L stainless steel, Inconel 718, and Zircaloy-4. Corrosion rates for carbon steel and beryllium were the highest. Other metals showing corrosion include Ferralium 255 and aluminum.

Long Term Corrosion/Degradation Test Third-Year Results
Alder Flitton et al., 2001. INEEL/EXT-01-00036.

The test project deploys two proven, industry-standard methods for determining corrosion rates: (1) direct corrosion testing using metal coupons and (2) monitored corrosion testing using electrical/resistance probes. Third-year results showed extremely low measurable rates of general corrosion for most metals being tested. Carbon steel, beryllium, and aluminum showed more evidence of corrosion than other metal alloys. A significant factor of corrosion was the depth at which the coupons were located; more metal loss at greater depths.

Underground Corrosion of Activated Metals in an Arid Vadose Zone Environment
Alder Flitton et al., 2001. INEEL/CON-01-01450.

A long-term corrosion test is being conducted to obtain site-specific corrosion rates to support efforts to more accurately estimate the transfer of activated elements in an arid vadose zone environment. The SDA contains neutron-activated metals from nonfuel nuclear-reactor-core components. Early corrosion rate results after 1 year and 3 years of underground exposure showed that carbon steel and beryllium exhibited the highest corrosion rates, with higher corrosion rates on coupons at greater depth.

2.2 Summary of INTEC and Vadose Zone Research Park Documents

Studies related to INTEC and the Vadose Zone Research Park, which is located near INTEC, are described in this section.

2.2.1 Tank Farm Interim Actions

RD/RA Work Plan for Group 1 Tank Farm Interim Action
Bechtel BWXT Idaho 2000 DOE/ID-10772

This RD/RA Work Plan provides the framework for defining the remedial design requirements, preparing the design documentation, and defining and implementing the construction and operations phases of OU 3-13 Tank Farm Interim Action.

2.2.2 Perched Water

Phase I Monitoring Well and Tracer Study Report, OU 3-13, Group 4, Perched Water
Bechtel BWXT Idaho, 2002. DOE/ID-10967.

This report presents the results of fieldwork performed at INTEC for Phase I of the Waste Area Group 3, Operable Unit 3-13, Group 4, Perched Water remedy. The completed fieldwork includes the drilling and installation of Phase I vadose zone monitoring wells, the collections and analysis of one round of perched water samples, and the completion of 25 weeks of the Phase I tracer study.

2.2.3 Simulation Of Episodic Flood Events

Simulation of Episodic Flood Events at the INEEL Vadose Zone Research Park
Baker and Hull, 2003. INRA Subsurface Science Symposium.

Episodic events occur in the Snake River Plain from snow-melt runoff in the spring. These rapid infiltration events have the potential for transporting contaminants great distances within the subsurface in both a vertical and lateral direction. Long term observations of rapid infiltration at the percolation ponds will provide the information necessary to determine fate and transport of contaminants in the vadose zone.

2.3 Summary of Documents Pertaining to Studies Performed at Areas Outside of Facility Boundaries

Documents that describe studies conducted at the Box Canyon research site, which is located on the Big Lost River slightly upstream of the INEEL are described in this section.

2.3.1 Box Canyon Investigation

Conceptual Model of the Geometry and Physics of Water Flow in a Fractured Basalt Vadose Zone
Faybishenko et al., 2000. Water Resources Research 36:3499-3520.

A conceptual model of the geometry and physics of water flow in the fractured basalt vadose zone was developed based on the results of lithological studies and a series of ponded infiltration tests conducted at Box Canyon. The proposed conceptual model describes the saturation-desaturation behavior of the basalt, in which rapid preferential flow occurs through the largest vertical fractures, followed by a gradual wetting of other fractures and the basalt matrix.

Numerical Model of Water Flow in a Fractured Basalt Vadose Zone: Box Canyon Site, Idaho
Doughty, 2000. Water Resources Research 36:3521-3534.

A numerical model was developed on the basis of the conceptual model proposed by Faybishenko et al. 2000. The numerical model was used to simulate a ponded infiltration test to investigate infiltration through partially saturated fractured basalt. The numerical model adequately reproduces the majority of the field observations and provides insights into the infiltration process that cannot be obtained by data collection alone, demonstrating its value as a component of field studies.

2.4 Summary of General Documents

National Roadmap for Vadose Zone Science and Technology
DOE, 2001. DOE/ID-10871.

This document is a roadmap for all DOE sites. It states the need for vadose zone research and two critical research objectives: (1) improve the understanding of basic physical, chemical, and biological processes and properties, as well as improving the modeling, measuring, and monitoring of flow and transport and (2) identify and discuss activities for cross-cutting issues, such as coupled processes, scaling, measuring and reducing uncertainty, advances in site monitoring systems, and the integration and validation of characterization, monitoring, and assessment tools at the system (field scale) level. For these two research objectives, infrastructure and capabilities required to accelerate progress along the activity pathways are identified.

3. PROGRESS TOWARD ADDRESSING DEFICIENCIES IDENTIFIED IN THE *DEFICIENCIES DOCUMENT* 1999-2003

The *Deficiencies Document* identifies several areas in which there are significant gaps in understanding of vadose zone processes at the INEEL. For each of these areas, specific deficiencies were identified and recommendations for addressing those deficiencies were provided. In this section, the deficiencies and recommendations identified in the *Deficiencies Document* are repeated verbatim, and then material published subsequently that addresses these deficiencies are indicated. However, it cannot be inferred that listing a publication in this series of tables indicates that a deficiency has been completely ameliorated, or that a recommendation has been fully implemented. Rather, tabulating a publication simply indicates that some aspect of a particular publication is relevant to a deficiency or recommendation. In addition, some of the publications listed in Section 2 are not included in the tables in this section because they do not apply to the deficiencies or recommendations identified in the *Deficiencies Document,* although they are relevant to flow and transport in the vadose zone at the INEEL. Selected publications that address a deficiency or recommendation are discussed after the table. The discussions of these publications are arranged in alphabetical order by first author.

3.1. Spatial Variability

Deficiencies and recommendations related to spatial variability that were identified in the *Deficiencies Document*, and documents that report progress related to these deficiencies and recommendations, are shown in the following table.

Table 3-1 Deficiencies, recommendation, and progress related to spatial variability

Deficiencies and Recommendations	**Relevant Publications**
Deficiencies The deficiencies related to spatial variability identified during the Vadose Zone Workshop include the following.	
• Knowledge is inadequate of spatial variability of hydraulic and transport properties and relative significance of spatial scales within INEEL sediment and volcanic rock units	(Leecaster, 2002)
• No validated way exists to scale up laboratory-determined properties to field-scale conditions	
• Ability is inadequate to incorporate spatial variability of lithology and hydrologic and transport properties in numerical models at the scale at which those properties can already be measured	
• Knowledge is inadequate of the interrelationship and interconnectivity of various fracture sets in basalt lava flows and how they constitute the effective permeability	
• Ability is inadequate to effectively assess the site-specific, three-dimensional distribution of basalts and sediments in the subsurface.	(Leecaster, 2002)
Recommendations To address the identified deficiencies, INEEL scientists and managers should develop a field-scale vadose zone test bed or facility equipped for both characterizing the heterogeneities in INEEL-area subsurface materials and assessing the effects of those heterogeneities on transport. The test bed or facility should allow achievement of the following:	
• Develop instruments for site characterization and monitoring and for measuring properties and flux in fast paths	
• Improve understanding of preferential flow mechanisms	(Nimmo, 2002)

Deficiencies and Recommendations	Relevant Publications
	(Nimmo et al., 2002)
• Identify ways to determine the sample distribution required to represent a site	
• Develop, in a generic sense, an understanding of the spatial variability effects on transport of water and contaminants	(Nimmo, 2002) (Nimmo et al., 2002)
• Improve documentation and definition of existing heterogeneity and its impact on models	
• Develop scale-up relationships for combining point measurements to represent a site	
• Develop modeling approaches that account for individual flow paths	
• Improve understanding of the facies distribution of sediments and basalts in the subsurface and obtaining data sets suitable for statistical analyses	
• Develop tracer tests that integrate small-scale effects into large-scale flow and transport	(Nimmo et al., 2002)
• Design laboratory- and field-scale tests together to identify correlations between laboratory- and field-scale results.	

3.1.1. Leecaster 2002

(Leecaster, 2002) describe a geostatistical study performed to estimate values at different locations of some parameters needed to construct a numerical model of the subsurface at the RWMC-SDA. The parameters whose values were predicted were categorized as lithology (essentially the elevation of ground surface and contacts between basalt and sediment layers, down to the bottom of the CD interbed), hydraulic characteristics of interbeds (saturated hydraulic conductivity and porosity), and aquifer permeability (transmissivity of the aquifer).

3.1.2. Nimmo 2002

(Nimmo, 2002) summarize the results of 36 field-scale vadose zone tracer tests, and examined the resulting data sets to ascertain any relationships between the maximum transport velocity, V_{max}, and other characteristics of the system. V_{max} is of particular interest because it is the transport velocity relevant to the first arrival of contaminants or other solutes at a point. They evaluated the type of geologic media, water application method and frequency, test scale (ranging from 0.75 m to 2000 m). They concluded:

- Thirty-six tests show no clear trend of maximum flow rate with distance spanned by the test, evidence which favors simple scaling. [i.e., the tendency for preferential flow to occur is independent of scale]

- Diverse media, for example surface sols and thick layers of fractured rock, clearly have pores of different nature but these differences may not be strongly relevant to the travel time of initial convective transport.

- The dependence [of V_{max}] on water input conditions, particularly whether the supply is continuous or intermittent, may be the dominant influence.

Regarding the last conclusion, they found that the results generally fell into two groups. V_{max} values were greater in tests in which water was applied continuously than in tests in which water was applied intermittently.

3.1.3. Nimmo et al., 2002

(Nimmo et al., 2002) describe a tracer experiment conducted by the USGS during 1999. Tracer was added to water that was diverted from the Big Lost River into Spreading Areas A and B. Wells completed in the aquifer, at the AB and BC interbeds, and in basalt not immediately adjacent to sedimentary interbeds were monitored for the presence of water and tracer.

Some of their observations are paraphrased here.

- Substantial amounts of perched water were found in unsaturated-zone wells.

- Tracer was detected in nine wells.

- In the Snake River Plain aquifer at well USGS-120, tracer was first detected 9 days after tracer introduction.

- In perched water immediately above the BC interbed at UZ98-2, tracer was detected 18 days after tracer introduction.

- In perched water immediately above the BC interbed at the Large-Scale Infiltration Test site, tracer was detected when wells there were first sampled 183 days after tracer introduction.

- In perched water immediately above the CD interbed beneath the Subsurface Disposal Area in well USGS-92, tracer was first detected 91 days after tracer introduction.

Excerpts from their “Discussion” section are paraphrased here.

- The initial detection of tracer in the aquifer well USGS-120 indicates an average vertical movement of at lease 22 m d^{-1} at that location, which is about a factor of 4 greater than the average rate through basalts A and B observed in the Large-Scale Infiltration Test. The measured concentrations suggest that dilution is modest, consistent with a large amount of tracer-tagged water going all the way through the unsaturated zone and at least 0.2 km horizontally. This indicates that under ponded infiltration, the sedimentary interbeds and any other layers expected to have low hydraulic conductivity are not an effective barrier to vertical flow.

- At the BC interbed level, positive detections in seven of eight sampled wells confirm that substantial infiltrated spreading-area water is diverted horizontally be this interbed of flow paths within it or above it. Detections in the Large Scale Infiltration Test wells, 1.3 km east, show that the perched water can move faster than 10 m d^{-1} over considerable distances, with relatively little dilution.

- This experiment provides no confirmation that BC perched water travels from spreading areas to the Subsurface Disposal Area.

- At the CD interbed level, tracer was detected from one of the three sampled wells directly under the Subsurface Disposal Area 1.3 km northeast of Spreading Area B and 2.2 km east of Spreading Area A. The tracer detection suggests an average horizontal flow rate of at lease 14 m d^{-1}. This result demonstrates that perched water beneath the SDA comes in part from subsurface flow of spreading area water.

- The evidence as a whole supports several particular hydrologic phenomena.

  - There can be rapid vertical transport under the spreading areas.

  - Substantial perching of water in the unsaturated zone results directly from the percolation of water from the spreading areas.

  - Over distances of a few kilometers and durations of a few months, horizontal transport occurs in perched water in or above both the BC and CD interbeds.

  - The horizontal spreading in perched zones is not uniform with direction.

- These hydrologic phenomena suggest certain subsurface features that determine the character of flow.

  - Sedimentary interbeds and impeding features of the basalts are imperfect barriers that permit substantial vertical flow, possibly because of interbed discontinuities and basalt fractures.

  - In spite of existing vertical fast flow mechanisms, at least some of the flow-impeding features are sufficiently effective and continuous that they divert substantial flow horizontally for considerable distances.

  - Nonuniformities in both basalt and interbed topography are likely causes of the irregular spatial patterns of tracer detection.

- The long-range horizontal flow requires alteration of previous conceptualizations of subsurface contaminant transport that did not include this sort of flow.

- Horizontal movement by itself does not necessarily imply a greater likelihood that water-borne contaminants will be transported to the aquifer. However, it does put more water under the Subsurface Disposal Area than would occur without spreading –area input.

- This water may facilitate contaminant transport to the aquifer by intercepting water-borne contaminants that would otherwise percolate into and be absorbed by the underlying sedimentary interbeds; it may also transport them downward through preferential flow paths that are active because of the greater amount of water present.

- The horizontal flow is likely to dilute contaminants and disperse them over wider regions of the unsaturated zone, which could provide greater opportunity for sorption, especially within the sedimentary interbeds, by reducing competition for sorption sites, increasing the availability of sorption sites, and changing solution chemistry to favor sorption.

- Therefore, some effects of the inferred horizontal and nonuniform flow are likely to enhance and others to hinder the transport of contaminants to the aquifer.

- Similar behavior concerning fast, long-range flow both horizontally and vertically in the unsaturated zone may occur at other locations with the necessary site characteristics including:

    - Thick vadose zone

    - Highly stratified unsaturated zone

    - Preferential flow paths such as fractures or coarse granular material

    - Ponded water

Some of their conclusions are paraphrased here.

- With a large input of water, the overall structure of the unsaturated zone of the Snake River Plain can generate rapid transport both vertically and horizontally.

- Under ponded infiltration, fine-textured interbeds and layers of particularly dense basalt do not prevent the rapid, high-volume flow that is expected through fractured basalt.

- Some impediments to vertical flow are effective in causing substantial perching and horizontal diversion.

- The observed rapid horizontal flow can persist over distances >1 km, entirely within the unsaturated zone, 100m and more above the aquifer.

- The observed behaviors are likely to enhance the vertical and horizontal spreading of contaminants in the subsurface, although by exposing the contaminants to a greater volume of sedimentary materials they may also have effects that tend to reduce aquifer contamination.

- Because the rapid vertical and horizontal transport in the unsaturated zone seems to be caused by natural features and ponded infiltration, similar phenomena may occur at a variety of sites.

3.2. Data

Deficiencies and recommendations related to data that were identified in the *Deficiencies Document*, and documents that report progress related to these deficiencies and recommendations, are shown in the following table.

Table 3-2 Deficiencies, recommendation, and progress related to data

Deficiencies and Recommendations	**Relevant Publications**
Deficiencies Though the investigations cited above have generated greatly useful hydraulic data that have been valuable in understanding the hydraulic processes occurring in the INEEL vadose zone, deficiencies are associated with the data. The deficiencies in data identified in the Vadose Zone Workshop include the following:	
• An insufficient number of laboratory and in situ measurements of hydrologic properties have been made at the INEEL	
• Current vadose zone characterization and monitoring at INEEL facilities have led to discontinuous data sets that are unable to describe temporal variations in moisture behavior at depth in the vadose zone from transient infiltration events at the surface such as ponding or focused infiltration	(Hubbell et al., 2002)
• The discontinuous data sets are not of sufficient quality for use in calibrating numerical simulations to produce model results with adequate confidence	
• Facilitated transport of actinides in colloidal form has not been evaluated at INEEL disposal sites.	
Recommendations The following monitoring and hydraulic analytical activities are necessary to provide adequate monitoring and sampling of hydraulic data:	
• Develop a process to determine the sufficient amount of data to calibrate and validate transport models	
• Develop a monitoring network that is spatially representative of INEEL facilities.	(Baker and Hull, 2003) (McElroy and Hubbell, 2001; McElroy and Hubbell, 2003)
• Collect data for a sufficiently long time to obtain a temporally representative data set.	(Baker and Hull, 2003) (McElroy and Hubbell,

Deficiencies and Recommendations	Relevant Publications
	2001; McElroy and Hubbell, 2003)
• Develop a consistent set of monitoring parameters that will serve as basic monitoring parameters.	
• Develop better monitoring instrumentation to permit monitoring in the preferred pathways such as fractures, interbeds, rubble zones in the basalts, and alluvial zones in the silty clay materials (e.g., interbeds and surficial sediments). Better monitoring instrumentation also should be developed to efficiently monitor a larger scale, giving information that represents the general vadose zone.	(Hubbell et al., 2002) (McElroy and Hubbell, 2001; McElroy and Hubbell, 2003)
• Standardize monitoring instrumentation, installation, calibration, and data collection (to the extent possible) and adjust calibrations for scale.	(Baker and Hull, 2003)
• Monitor remediated sites to verify modeling and remediation effectiveness.	
• Determine what constitutes the appropriate number and sample size for a representative sample collection, especially at depth.	
• Develop moisture characteristic curves for semi-dense and dense basalts and for gravel.	
• Conduct relatively large-scale natural gradient tracer tests to determine the large-scale effects of preferential pathways.	(Nimmo et al., 2002) (see Spatial Variability, Section ___ for discussion)
• Determine the geochemical conditions that lead to the formation of actinide colloids. The mechanisms for transport of colloids need to be better defined and related to the flow conditions present in the subsurface.	

3.2.1. Baker and Hull, 2003

(Baker and Hull, 2003)describe the Vadose Zone Research Park, located near the Idaho Nuclear Technology and Engineering Center. The VZRP includes a network of instrumentation for monitoring the movement of water and solutes in the vadose zone. This network is located near a pair of new (constructed in ____ and operational in ___) percolation ponds that are used for disposing non-radioactive, non-hazardous wastewater from INTEC. Additional instrumentation is located near the Big Lost River, which is adjacent to the percolation ponds. Although the VZRP has only been operational a short time, (Baker and Hull, 2003) state that the initial data sets

> suggest that infiltration at the ponds is moving rapidly in the vertical direction through layered sedimentary interbeds and fractured basalt layers until reaching impermeable basalt interfaces. Localized ponding has been observed at these interfaces, resulting in lateral transport through the sedimentary interbeds and permeable fractured basalt layers until reaching preferential vertical flow paths. Vertical and lateral transport observed within thick layers of fractured basalt suggest the potential for extensive contaminant transport through basalt layers that have previously been considered impermeable.

Continued collection of data at the VZRP will provide time-series data on water movement in the vadose zone.

3.2.2. Hubbell et al., 2002

(Hubbell et al., 2002) describe water potential data collected in fractured basalt using Advanced Tensiometers^{TM} installed in boreholes. These instruments produce quasi-continuous data sets of matric potential. Interruptions in the data records occurred due to equipment malfunction or because water was depleted in the ceramic tensiometer cups. These data sets provide information on the downward flux of water through the vadose zone, and in particular provide information on water movement following snowmelt events.

The data presented indicate that sharp increases in matric potential, indicative of the passage of a wetting front, occurred fairly rapidly after snowmelt events. However, the pattern of wetting front arrival as a function of depth was not simple, i.e. in some cases the front arrived at deeper monitoring points before it arrived at shallower points. This was interpreted as indicating that preferential flow was occurring. In addition, the pattern of wetting front arrival was not consistent between snow melt events.

Selected excerpts from their “Conclusions” section include the following.

- Water potential measurements were primarily constant with a variation of less than 10 cm and exhibited a near steady-state unit-gradient downward flux, except during periods of episodic infiltration/drainage.

- Spring snowmelt created episodic infiltration that moved rapidly through the fractured basalt.

- These infiltration events produced detectable changes in the water potential to depths up to 15.5 m, in some cases within a few days of the infiltration events.

- During high magnitude infiltration events, preferential saturated channeling of the moisture occurs, bypassing zones within the vadose zone.

- Sedimentary interbeds may have substantially reduced the percolation, acting as either a hydraulic or capillary barrier.

- Unsaturated fracture flow is the major infiltration mechanism through the fractured basalt during much of the year.

- Moisture moves primarily in the fractures during episodic infiltration events and … the episodic events transport significantly more moisture that steady state flow through the basalt matrix.

- Advanced Tensiometers can be used to measure water potentials in deep vadose zones, detect and monitor infiltration events and estimate the contributions of episodic and steady state infiltration flux.

- Instrumentation exists for monitoring water movement below waste disposal sites.

The major contribution of (Hubbell et al., 2002) is that it describes equipment and techniques that may be utilized for generating long-term time series data sets that can be used to infer rates of water movement in the vadose zone. Their advances in equipment design allow tensiometric measurements to be made at any depth, which is a major improvement over the shallow (~ 2 m) depth limitation of conventional tensiometers.

3.2.3 McElroy and Hubbell, 2001, 2003

(McElroy and Hubbell, 2001) describe the installation of a network of 23 Advanced Tensiometers at the Subsurface Disposal Area of the RWMC. Time series plots of water potential measured with these devices starting in late 1999 or early 2000 and continuing through summer or fall 2000, depending on the specific installation, are presented. (McElroy and Hubbell, 2003) report installation of additional instruments and present water potential time series data through summer 2002. They also report spatial and temporal trends in the data, and estimate the flux of water that percolates deeper than the zone influenced by evapotranspiration and hence will ultimately recharge the underlying aquifer.

Excerpts from the conclusions of (McElroy and Hubbell, 2003) include the following.

- The network of advanced tensiometers provided approximately 2-1/2 years of water potential data in basalts and sedimentary interbeds from 6.7 to 73.5 m bls. The majority of the advanced tensiometer locations have been monitored since spring 2000. However, advanced tensiometers in three of the 18 wells have been monitored since 1996, providing over six years of water potential data.

- Measured water potentials from spring 2000 through August 2002 ranged from near saturation (-30 cm of water) in the BC interbed sediments near… to –400 cm of water in the CD interbed sediments, outside of the SDA.

- Water potential data from the majority of the deepest (17 m or greater) advanced tensiometer locations indicated little-to-no change in moisture, suggesting steady state conditions existed at those locations for the past 2-1/2 year monitoring period. These advanced tensiometers were in sediments and basalts at or below the 17-m depth and tended to be located in wells farthest from the main east-west road through the SDA.

- Long-term drying trends were noted in some sediments and basalts. Thelargest overall decrease in water potentials occurred in the shallower sediments and basalts above the 12-m depth. These shallower depths may be responding to decreased infiltration at the surface, from the cumulative effect of less-than-average annual precipitation for the last three years (2000 through 2002).

> Long-term drying of deeper sediments also occurred in the BC interbed sediments…and in the CD interbed sediments….Wells showing long-term drying trends are those located nearest the drainage ditches that parallel the main east-west road through the SDA. These drainage ditches likely focused surface infiltration during years of high run-off from snowmelt. The long-term drying trends in sediments at wells near these drainage ditches may be in response to decreased runoff from three years of less-than-average precipitation (2000 through 2002).

- Average water potentials in the BC interbed sediments suggested wetter conditions inside the SDA compared to outside the SDA. This was attributed to focusing of flow to low-lying areas inside the SDA, such as drainage ditches or open pits or trenches that collect run-off from snowmelt and high-intensity rains.

- Moisture content estimates within the SDA showed greater variability in the BC interbed sediments as compared to the CD interbed sediments. These results suggested nonuniform surface infiltration patterns within the SDA extended to the depth of the BC sedimentary interbed, through predominantly vertical flow, but did not extend to the CD sedimentary interbed. The BC interbed sediments may have dampened and stored the episodic recharge, controlling the deep flux into basalts beneath the sediments. Under these conditions, it was suggested that moisture contents in the CD sedimentary interbed and BC interbed sediments outside the SDA were more representative of long-term, steady-state flow conditions than moisture contents from BC interbed sediments inside the SDA.

- Deep percolation through the BC and CD sedimentary interbeds was estimated from averaged water potentials, using a unit gradient approach. Under the assumption that percolation rates most representative of steady-state flow conditions were based on moisture contents from the CD sedimentary interbed and from BC interbed sediments outside of the SDA, percolation estimates ranged from 1 to 32 cm/yr. the 1- to 32-cm/yr range appeared to be reasonable, given the average annual precipitation of 22 cm, the potential for focused infiltration on the SDA, and the simplifying assumptions used to estimate deep percolation.

3.3. Numerical Modeling

Deficiencies and recommendations related to numerical modeling that were identified in the *Deficiencies Document*, and documents that report progress related to these deficiencies and recommendations, are shown in the following table.

Table 3-3 Deficiencies, recommendation, and progress related to numerical modeling

Deficiencies and Recommendations	Relevant Publications
Deficiencies The deficiencies identified during the Vadose Zone Workshop in vadose zone scientific knowledge that affect the ability to conduct representative simulations of subsurface flow and transport in the vadose zone at the INEEL include the following:	
• The simulation studies have been primarily deterministic with only limited attempts at including uncertainty. This approach limits the usability of the simulation results for making environmental decisions.	
• An emphasis should be placed on using probabilistic modeling and effective representation of the uncertainty in the simulation results. This emphasis will require collecting appropriate data to define parameter distributions.	
• The applicability o f Richard's equation should be evaluated to determine whether it appropriately describes water movement through unsaturated fractured basalts.	
Recommendations The following recommendations are provided to address the identified deficiencies.	
• In terms of simulation capability, develop computationally efficient simulators to allow the discretization necessary to represent flow and transport in the complex and heterogeneous vadose zone at the INEEL. These simulators must be able to include the following: o Kinetic reactive transport o Facilitated transport o Dual-porosity, dual-permeability media o Efficient visual post-processing o Geostatistically based input of spatially varying properties, with explicit accounting and aggregation of uncertainties o Inverse parameter estimation techniques.	(Leecaster, 2002) (see Spatial Variability section for discussion)
• Develop improved data sets obtained at more closely spaced spatial intervals and over long time periods.	
• Establish a process for facilitated approval and adoption of improved simulation codes for use at the INEEL.	

(Magnuson, 2002) briefly describes an effort to evaluate the effect of uncertainty in the conceptual model on simulated movement of water and contaminants. They used a vadose zoned model for the subsurface disposal area of the RWMC that had been previously developed to investigate the effects of :

- Spatial variation in infiltration rate
- Facilitated transport
- Use of alternative formulations of the moisture retention curve of fractured basalt.

They concluded, in part, "Of the sensitivities discussed…the primary sensitivity has been the amount of water that actually infiltrates through the waste, thereby mobilizing contaminants."

3.4. Conceptual Models

Deficiencies and recommendations related to conceptual models that were identified in the *Deficiencies Document*, and documents that report progress related to these deficiencies and recommendations, are shown in the following table.

Table 3-4 Deficiencies, recommendation, and progress related to conceptual models

Deficiencies and Recommendations	**Relevant Publications**
Deficiencies The deficiencies in vadose zone conceptual model scientific knowledge identified during the Vadose Zone Workshop include the following.	
• Improved feedback between field observations and conceptual or predictive models must be implemented to examine the agreement of the data to the conceptual model	(Doughty, 2000)
• Alternative conceptual models describing the following must be developed: o Flow and transport through fractured basalt rocks with sedimentary interbeds o Fracture-matrix interactions o Facilitated transport.	(Faybishenko et al., 2000) (Doughty, 2000)
Recommendations Understanding vadose zone processes sufficiently well to develop accurate conceptual models is the foundation of vadose zone science. To facilitate understanding, the following activities are recommended to address conceptual model deficiencies in scientific understanding:	
• Collect sufficient baseline data for the system to be modeled	(Faybishenko et al., 2000)
• Collect sufficient spatial and temporal data to characterize the modeled system	(Faybishenko et al., 2000)
• Develop and test alternative conceptual models for geologic and hydrologic framework and transport mechanisms	(Faybishenko et al., 2000)

Deficiencies and Recommendations	Relevant Publications
	(Doughty, 2000)

3.4.1. Doughty 2000

(Doughty, 2000) describes a numerical modeling study that was performed in conjunction with the Box Canyon infiltration study (FAYBISHENKO ET AL., 2000). This study is discussed here, as opposed to the section on numerical modeling, because the study is more closely related to developing and testing conceptual models of flow in fractured basalt than it is related to meeting the deficiencies pertaining to numerical modeling that were identified by (Wood et al., 2000).

(Doughty, 2000) used an existing code, TOUGH2, to simulate the movement of water and air beneath the infiltration pond at Box Canyon. Her approach for parameterizing the medium is neither deterministic (in which the location of all fractures in the domain are known) nor stochastic (in which one or more realizations of fracture networks are generated from the spatial statistics of the fracture network). Instead, she used the “quasi-deterministic” approach, in which the fracture network geometry observed in outcrop at the canyon wall was applied to the model beneath the infiltration pond. This approach is based on the assumption that the general characteristics of the fracture network are the same beneath the pond and in the canyon wall. The model was used with two approaches for simulating two phase flow (air and water), and was used both to predict water movement before the tests and to identify important processes using field data.

Based on this simulation study, (Doughty, 2000) presented the following summary and conclusions.

> The numerical model uses an unconventional quasi-deterministic approach that includes a highly simplified representation of the key hydrogeologic features of the fractured basalt vadose zone In particular, the model attempts to maintain fracture network connectivity but omits many smaller-scale details, such as aperture variation within individual fractures and a rigorous treatment of fracture/matrix interactions. The quasi-deterministic model results have been generally consistent with field observations, and modeling has been an effective tool to aid in experiment interpretation….
>
> The pretest simulations which ignore capillarity, suggest that infiltration does not occur uniformly but follows irregular flow paths through the highest=permeability features. Some lateral spreading occurs through vesicular zones and the central fracture zone, but flow through the rubble zone is nearly vertical. Entrapped air is shown to have a large effect, decreasing infiltration rate and creating a less uniform subsurface saturation distribution.
>
> The posttest simulations add realism to the model by considering stable initial conditions in which gravity and capillary forces are balanced. The overall shape of the infiltrated plume is similar for both pretest and posttest simulation, with the flow distribution controlled by the high-permeability features, suggesting that the greatly simplified pretest simulations are useful for studying infiltration through the highly fractured Snake River Plain basalt. However, by incorporating capillarity the model treats fracture/matrix interactions more

> accurately and better illustrates how the system response compares to ambient conditions, which must be appreciated to design effective monitoring devices.
>
> A comparison of observed and modeled natural state conditions was used to estimate values of poorly constrained model parameter4s. Such an inverse analysis would be even more effective if it were expanded to incorporate responses during and after the ponded infiltration test. By optimizing model parameters for both low and high infiltration rates and under wetting and draining conditions, subsequent model predictions could be made with greater confidence.
>
> One of the key questions addressed by the modeling studies is how fracture pattern characteristics and connectivity affect the pattern of water infiltration. Simulations show that strongly preferential gas-phase flow occurs through the subhorizontal rubble zones that exist between basalt flows because the permeability of these zones is several orders of magnitude higher than any other hydrological component at the site. In contrast, widespread lateral liquid flow through the rubble zone only occurs if there are no underlying vertical flow paths because gravity plays such an dominant role in controlling liquid flow. For liquid infiltration from the ground surface the vertical flow paths with the highest effective permeability are active. At the Box Canyon site, there are no vertical rubble zones near the ground surface, so the most permeable flow paths, individual fractures and fracture zones, become the key hydrological component. Under background (low infiltration rate) conditions the largest fractures are drained, leaving the highest effective permeability (intrinsic permeability times relative permeability) in the smaller fractures. Under ponded infiltration conditions the largest fractures wet up and provide the primary vertical flow paths. The tributary structure of the fractures causes the liquid flow to undergo a funneling process with depth, which has been indirectly observed in the field ….
>
> A recurring theme of the field observations at Box Canyon is that the local lithology alone is not enough to predict what kid of response will be observed at a given point in the subsurface. Rather, local responses depend on the entire flow path from the surface ….This finding reinforces the notion that fracture connectivity is of crucial importance in predicting the fate of contaminant migrating downward from the surface with infiltrating water. The quasi-deterministic modeling approach, which is designed to maintain fracture connectivity, has been compared with a more traditional stochastic approach, in which geostatistics is used to construct the permeability distribution as a correlated random field….Results suggest that the stochastic approach is less successful in predicting field behavior because too much information about fracture connectivity is lost in the geostatistical analysis. Consequently, the information available to the resulting stochastic modes is simply not sufficient to capture field behavior. Of course, there are other means of creating stochastic permeability distributions than through traditional variography. One simple modification involves introducing the concept of a neighborhood into the optimization algorithm used to generate the correlated random permeability field, with acceptance rules that encourage connectivity implemented to augment the objective function based on variograms….On the basis of the present study, models that emphasize connectivity over correlation structure are expected to perform better.

3.4.2. Faybishenko et al., 2000

(Faybishenko et al., 2000) performed a series of infiltration experiments in fractured basalt at the Box Canyon field site, located adjacent to the Big Lost River near Arco, Idaho. Based on the results of infiltration experiments conducted during 1996 and 1997, and on the results of the Large Scale Infiltration

Test performed south of the RWMC in 1994, these authors formulated a conceptual model for water flow in fractured media in the vadose zone. The following excerpts from their work describe their conceptual model and some of their conclusions.

> The data obtained during the infiltration tests have confirmed that infiltration is primarily controlled by the characteristics of the fracture system within the basalt flow, leading to strongly preferential, irregular, and nonrepeatable flow patterns in the subsurface. Comparisons between test[s] … show that flow patterns and zones of saturation are highly variable from test to test. Apparently, they do not depend solely on lithological features but are sensitive to both initial conditions and flow history. Beneath the pond, the basalt may be found in unsaturated, saturated, and quasi-saturated conditions with entrapped air. These phenomena confirm the complex character of water flow in a fractured basalt vadose over space and time.
>
> In order to describe such a complex system we propose the multi-geological-component conceptual model illustrated in [Figure ___]. This conceptual model recognizes the connections between individual geological components, each with different hydraulic processes governing water flow. [Figure --] shows the main processes of water flow: preferential flow through conductive vertical fractures, fracture-to-matrix diffusion, vesicular basalt-to-massive basalt diffusion, the funneling effect, and lateral flow (with advective transport) through subhorizontal fractures and rubble zones. This multi-geological-component conceptual model is far more complicated than most existing conceptual models for fractured/porous media….The simpler models cannon account for all the processes necessary to make accurate predictions of flow and transport in the fractured basalt vadose zone. The key features of our conceptual model are summarized in the following paragraphs.
>
> …wetting of the top 0.5 m zone beneath the pond occurred very rapidly. Preferential flow appeared to originate just below this depth, and flow became increasingly localized with increasing depth….Multimodal breakthrough curves that were obtained at the LSIT [Large Scale Infiltration Test], the Box Canyon infiltration tests, and using numerical modeling provide further evidence of a confluence of water flow through different sets of fractures of varying permeability and geometry. In this conceptualization, column-bounding fractures provide the primary pathways for fast vertical infiltration. However, the water supply from the surface into column-bounding fractures is restricted due to limited infiltration through sediments filling near-surface fractures. Some fractures terminate within the basalt flow, either creating dead-end flow paths or indirect flow paths composed of linked column-normal and column-bounding fractures. Furthermore, we expect that water flow within initially dry fractures will show the fingering phenomena that have been identified at the laboratory scale … and in modeling studies… so even conductive column-bounding fractures will not be uniformly wet. Thus simply identifying a monitoring point as being located in a vertical fracture does not enable one to predict the flow response because the response at any point depends on the entire flow path both above the monitoring point and below the monitoring point for nonconductive, dead-end fractures.
>
> Since the largest fractures are vertical, the predominant flow direction under gravity is downward. However, geological features such as the horizontal fractures connecting terminated vertical fractures, the vesicular lenses, the central fracture zone, and the rubble zone promote lateral flow. If the permeability below the rubble zone is low … or if a sedimentary interbed occurs there … perched water zones can be created and

> lateral flow can be widespread. Given the high porosity of the rubble zones … the potential for storage and movement of water (and consequently contaminants) is large. Once positive hydraulic pressure is developed within the perched water in the rubble zone, water may migrate upward into dead-end fractures in the lower part of the basalt flow … and then from there can be imbibed into the matrix.
>
> The decrease in infiltration rate with time observed in all tests is consistent with the theory and experience of infiltration from the land surface….We hypothesize that the main factors affecting the infiltration rate are the topsoil layer, the interface between the sol layer and the fractured basalt, and the near-surface soil-infilled fractures. Small variations of these factors may cause the large range of initial infiltration rates for the tests. Another example of sensitive dependence on local conditions may be the tendency for a pulse-like infiltration rate that was observed during test 97-4. We hypothesize that water penetrates into horizontal fractures only if a critical hydraulic pressure is reached, at which point a hydraulic connection between column-bounding fractures is established. Once a hydraulic connection is made, water begins to flow through the fracture producing a rapid, but short-term increase in the infiltration rate, despite its long-term decreasing trend.
>
> Numerical modeling suggests that the presence of air has a significant effect of infiltration rate and subsurface saturation distribution, and the observation of air bubbles rising through the pond confirms tat entrapment of air does occur. We hypothesize that entrapment of air within the wetted zone beneath the pond occurred in both the vesicular basalt and the fractures infilled with sedimentary material due to the irregular spatial flow pattern.

(Faybishenko et al., 2000)provided the following conclusions.

> The data from the intermediate-scale infiltration tests conducted at Box Canyon combined with those from the LSIT … have shown that it is impossible to identify a priori which fractures will transmit water during an infiltration test, implying that much of the monitoring network will be unused. Instruments that do respond are likely to be sparsely distributed, and their responses difficult to interpret in terms of the scale of the infiltration problem as a whole. Therefore our approach to the development of a conceptual model of water flow in a fractured basalt vadose zone is based on a combination of the lithological information and fracture pattern data together with the results of the infiltration tests. The scale of the Box Canyon experiment was chosen to be relevant to both the scale of geologic variability and the scale of contamination problems, for example, leakage from a single tank.
>
> Even with the geology-based, relevant-scale approach we use, it is impossible to obtain a complete, integrated picture of the movement of water within the multi-porosity system of massive and vesicular basalt and fractures partially infilled with sediments. Point measurements cannot be reliably interpolated for such heterogeneous systems, and geophysical measurements are not of high enough resolution to identify individual preferential flow paths. However, by using a combination of these methods, we can make the following observations. From analysis of the geological setting, we have determined that the fracture pattern exhibits a general increase in the fracture spacing downward. This fracture pattern enables a funneling of flow into progressively fewer flow paths as depth increases; such flow paths may be impossible to locate, and contaminants can move quickly through them. From analysis of the infiltration test data we find that the conventional term “water front,” commonly used to characterize infiltration in sedimentary material, is

> irrelevant for infiltration in fractured rocks. Column-bounding fractures are the primary pathways for preferential flow from the surface toward the rubble zone at a depth of 10 to 12 m. Water flow occurs rapidly through the conducting fracture followed by a gradual saturation of the basalt matrix. Some fractures that are saturated at the beginning of the test desaturate thereafter, suggesting that steady state conditions do not develop.
>
> The field data obtained at Box Canyon can be of general use for hydrogeologists working at other sites composed of fractured basalt and other types of fractured rocks and heterogeneous soils and can be employed to develop investigation strategies, measurement devices, and modeling approaches. For example, the data sets obtained for the Box Canyon infiltration tests were used to build confidence in numerical models used for the Yucca Mountain project ….Moreover, such field data can be interpreted using several alternative models….One exciting new area of research involves conceptualizing flow in the fractured basalt vadose zone as a chaotic dynamical system….The motivation for this approach is twofold: in the temporal regime we recognize that flow through an unsaturated fracture network may be more like a set of dripping faucets that the continuous flow predicted by Darcy's law and Richard's equation. In the spatial regime we recognize that the funneling effect of water flow through the fracture pattern, in combination with the widespread lateral flow in the rubble zone, provides the combination of chaotic processes. The important output provided by a chaotic model is information on how much can be known about the future behavior of a system. A chaotic dynamic approach may provide an entirely new paradigm for describing flow and transport behavior in the fractured basalt vadose zone….For remediation this means knowing what questions are reasonable to ask, rather than oversimplifying a system to the point of uselessness in an attempt to answer all questions.

Salient points made in the paper are summarized below.

- The multi-geological-component conceptual model recognizes the connections between individual geological components, each with different hydraulic processes governing water flow:
    - preferential flow through conductive vertical fractures,
    - fracture-to-matrix diffusion,
    - vesicular basalt-to-massive basalt diffusion,
    - the funneling effect, and
    - lateral flow (with advective transport) through subhorizontal fractures and rubble zones.
- This multi-geological-component conceptual model is far more complicated than most existing conceptual models for fractured/porous media
- Infiltration is primarily controlled by the characteristics of the fracture system within the basalt flow, leading to strongly preferential, irregular, and nonrepeatable flow patterns in the subsurface
- Flow patterns and zones of saturation are highly variable from test to test. Apparently, they do not depend solely on lithological features but are sensitive to both initial conditions and flow history.

- The presence of air has a significant effect of infiltration rate and subsurface saturation distribution

- It is impossible to identify a priori which fractures will transmit water during an infiltration test

- The response at any point depends on the entire flow path both above the monitoring point and below the monitoring point for nonconductive, dead-end fractures.

- Column-bounding fractures are the primary pathways for preferential flow from the surface toward the rubble zone at a depth of 10 to 12 m.

- The fracture pattern exhibits a general increase in the fracture spacing downward. This fracture pattern enables a funneling of flow into progressively fewer flow paths as depth increases; such flow paths may be impossible to locate, and contaminants can move quickly through them

- Since the largest fractures are vertical, the predominant flow direction under gravity is downward. However, geological features such as the horizontal fractures connecting terminated vertical fractures, the vesicular lenses, the central fracture zone, and the rubble zone promote lateral flow.

- If the permeability below the rubble zone is low … or if a sedimentary interbed occurs there … perched water zones can be created and lateral flow can be widespread.

- The conventional term “water front,” commonly used to characterize infiltration in sedimentary material, is irrelevant for infiltration in fractured rocks.

- Water flow occurs rapidly through the conducting fracture followed by a gradual saturation of the basalt matrix. Some fractures that are saturated at the beginning of the test desaturate thereafter, suggesting that steady state conditions do not develop.

- Flow in the fractured basalt vadose zone may be conceptualized as a chaotic dynamical system.

- In the temporal regime flow through an unsaturated fracture network may be more like a set of dripping faucets that the continuous flow predicted by Darcy’s law and Richard’s equation.

- In the spatial regime the funneling effect of water flow through the fracture pattern, in combination with the widespread lateral flow in the rubble zone, provides the combination of chaotic processes

- The important output provided by a chaotic model is information on how much can be known about the future behavior of a system. A chaotic dynamic approach may provide an entirely new paradigm for describing flow and transport behavior in the fractured basalt vadose zone….For remediation this means knowing what questions are reasonable to ask, rather than oversimplifying a system to the point of uselessness in an attempt to answer all questions.

3.5. Source Term

Deficiencies and recommendations related to source term that were identified in the *Deficiencies Document*, and documents that report progress related to these deficiencies and recommendations, are shown in the following table.

Table 3-5 Deficiencies, recommendation, and progress related to source term

Deficiencies and Recommendations	**Relevant Publications**
Deficiencies The deficiencies in vadose zone source term scientific knowledge identified during the Vadose Zone Workshop include the following:	
• Currently, source term models treat water flow through the source term (i.e., the disposal pits) as a spatially uniform process despite the generally accepted conceptual model that water flow is nonuniform, event driven, and episodic.	
• Information about the contaminant release mechanism and rate to the vadose zone is lacking. In the absence of data, conservative assumptions are used that can bias the eventual decision toward unnecessary actions.	(Alder Flitton et al., 2001; Alder Flitton et al., 2002; Ritter and Parsons, 2002)
• Appropriate measurement and model scales have not been determined to adequately characterize and model the source environment.	
• Monitoring programs have not been designed to adequately characterize the source hydrology.	(Myers et al., 2003)
Recommendations The following recommendations are provided to address the identified deficiencies.	
• Conduct laboratory-scale experiments to evaluate model parameters that are relatively insensitive to scale and that may be evaluated adequately at a relatively small scale. If necessary, field-scale experiments should be conducted to evaluate parameters that have large-scale spatial dependency.	
• Conduct a detailed study of near-field processes affecting the source term. The study would improve modeling of contaminant migration from existing buried waste. The timing for such a study is critical because various treatment and remediation methods for this waste are being considered for use at the INEEL. A better fundamental understanding of near-field processes can be used to develop effective treatment and remediation	(Alder Flitton et al., 2001; Alder Flitton et al., 2002; Myers et al., 2003;

Deficiencies and Recommendations	Relevant Publications
methods. Current INEEL projects that will require source term modeling include the Idaho Nuclear Technology and Engineering Center (INTEC) Tank Farm closure (DOE-ID 2000), the Organic Contamination in the Vadose Zone (OCVZ) project (Chatwin et al. 1992), and the Waste Area Group 7 comprehensive remedial investigation/feasibility study for waste disposed of in the SDA pits and trenches (Becker et al. 1998).	Ritter and Parsons, 2002)
• Characterize water movement in the near field. The characterization would require instrumenting containers, waste forms, and backfill material within a few centimeters of the containers, as well as at more distant points within the disturbed backfill. The use of tracers should be considered. Some possible tracers that could be used include tritium as CFA water or a nonhazardous, stable, volatile organic chemical. The objectives of water movement characterization would include the following: o Testing the representativeness of current moisture monitoring of conditions in the near field o Developing a realistic model of water movement through or at the surface of waste o Defining the appropriate conditions for bench-scale tests of waste-material properties o Estimating (with tracers) the fractions of volatile species migrating to the atmosphere from buried waste.	
• Characterize geochemical processes that occur in the near field that influence the mobilization of contaminants. These processes include the following: o The chemical capability of contaminants to form more or less mobile species o Facilitated transport (i.e., the association of contaminants with colloids) o Corrosion processes as they affect buried activated metal objects and containers o Characteristics of grout and waste treated by in situ vitrification o Characteristics of water movement around waste treated by grouting or in situ vitrification.	(Alder Flitton et al., 2001; Alder Flitton et al., 2002)
• Refine analytical methods and models to account for advances in understanding of the processes that are found to substantially affect contaminant releases. A major objective for further study of the release of contaminants from waste forms is to improve the accuracy of source term codes such as DUST. More advanced source term codes should include	

Deficiencies and Recommendations	Relevant Publications
features that allow more realistic modeling of near-field hydrology.	
• Improve understanding of the following processes that would affect releases from grouted or in situ vitrification-treated waste: o The influence of the chemical environment within the grouted or glassified waste form on mobility of contaminant species o The relative importance of diffusional and dissolution-limited releases from grouted or in situ vitrification-treated waste in the initial monolithic form and as cracking and degradation progress o The effects of waste treatment on hydraulic properties within the treated waste at interfaces between treated waste and the surrounding medium and in cracks or other openings through the treated waste.	
• Collect sufficient data to adequately characterize and model the source hydrology.	

3.5.1 Alder Flitton et al., 2001, 2002

(Alder Flitton et al., 2001) and (Alder Flitton et al., 2002) describe a study of the rate of corrosion of metals buried in surficial soil at the RWMC. The first document is an INEEL report and the second is a conference paper. The purpose of this investigation was to

> support the determination of site-specific corrosion rates for metals representing the neutron-activated metals buried at the Subsurface Disposal Area ….The corrosion rates … will be applied to the modeling of the transfer of activated elements from the buried metals to the surrounding environment. The test results will provide site-specific data to satisfy programmatic needs, including radiological fate and transport modeling that will contribute to ongoing radiological composite analyses, performance assessments, and the environmental baseline risk assessments conducted for the SDA.

These documents describe the burial of standard metal coupons and the subsequent excavation and measurement of mass loss and calculation of corrosion rates. Coupons were buried near the Engineered Barrier Test Facility, which is adjacent to the SDA at the RWMC. The coupons are scheduled for recovery after periods of exposure ranging from 1 to 18 years. The metals tested include Types 304L and 316L stainless steels, welded Type 316L stainless steel, Inconel 718, Beryllium S200F, Aluminum 6061, Zircaloy-4, welded Ferralium 255, and carbon steel.

These documents report measured corrosion rates after coupons had been buried for three years.

3.5.2 Myers et al., 2003

(Myers et al., 2003) describe an investigation of the subsurface in the SDA at the RWMC. The purpose of the investigation was "to support the … Remedial Investigation/Feasibility Study … leading to a Record of Decision". In this investigation, probes were driven into the ground to allow insertion and recovery of downhole nuclear measurement tools, collection of water and gas samples, monitoring of soil water potential, and collection of visual images of the subsurface. According to Table 1 of (Myers et al., 2003), the nuclear logging tools include:

- passive gamma detector for identifying gamma-emitting sources
- neutron activation instrument to detect prompt gamma from Cl-35, an indicator for halogenated hydrocarbons
- neutron-neutron detector to evaluate soil moisture
- passive neutron detector for detecting transuranics radionuclides
- shielded, directional gamma detector to identify azimuthal location of gamma-emitting sources

The following are excerpts from their conclusions and recommendations.

- There were analytical problems with VOCs in soil gas and redox gases (oxygen, carbon dioxide, hydrogen and methane)
- The activity of C-14 in carbon dioxide in soil gas near activated steel is elevated by approximately two orders of magnitude relative to natural levels.
- C-14 activities are greater near activated beryllium than near activated steel.
- Lysimeters (devices for collecting water samples from unsaturated materials) "were not consistently collecting sufficient moisture volumes for analysis or no water at all", and recommendations for testing and modification were provided
- Sufficient sample volume were collected twice from one lysimeters to allow analysis for americium, neptunium, plutonium and uranium. There were no positive detections of Am-241, two positive detections of Np-237, two positive detections of Pu-239 and Pu-240, and two positive detections of U- 233/234, U-235, U-236, and U-238.
- The complexity of tensiometer probes caused difficulty with use under field conditions.
- Soil moisture and resistivity probes indicated some locations where moisture contents varied over time and others where there is no clear trend
- Temperature probes indicated that the subsurface temperature varies, with a time lag relative to surface air temperatures that increases with depth.
- The visual probes were very useful for identifying waste:soil interfaces, changes in color of waste and soil matrix, and for imaging waste fragments and pieces.

- Downhole nuclear measurements “have been successfully compiled, organized, and captured in INEEL publications”, and “initial attempts to produce quantitative mass estimates … showed that uncertainties regarding the SDA soil media will have a significant impact on the accuracy of quantitative results.”

3.5.3 Ritter and Parsons, 2002

(Ritter and Parsons, 2002) describe the Performance Assessment/Composite Analysis (PA/CA) Monitoring Program, in which the contaminants of concern identified in the SDA PA/CA. The radioactive contaminants of concern and contaminants of interest identified during the PA, CA, and CERCLA evaluation processes are C-14, Cl-36, I-129, Np-237, U-234, and U-234 (pg. v). In addition, H-3 is a contaminant of interest that is present in activated beryllium (pg. iv), which has been buried in the SDA. The document describes “Source Monitoring Projects”, “Vadose Zone Monitoring”, and “Aquifer Monitoring”.

There were two source monitoring projects, beryllium blocks and activated steel. Beryllium reflector blocks from the Advanced Test Reactor were disposed in the SDA in 1993. The blocks contain about 293,000 Ci of H-3 and 20 Ci of C-14, which is “a substantial fraction of the total C-14 and H-3 inventory of the RWMC” (p. 6). “beryllium in contact with INEEL soil corrodes at about the same rate as carbon steel ….Tritium and C-14 are released from the beryllium by corrosion, and orm environmentally mobile compounds….C-14 in beryllium disposals in the SDA is one of the primary contributors to the total dose estimated for the SDA inventory” (pp 6-7).

This document reports the results of monitoring concentrations of these radionuclides in ambient air above ground surface at the beryllium disposal site, in soil gas and soil moisture in the subsurface adjacent to the disposal site and elsewhere throughout the SDA, and in groundwater distributed around the SDA. Collectively, these data sets provide information on the release of radionuclides from the SDA and the effect of these releases on nearby environmental media.

Ambient air monitoring of tritium concentrations show that estimated doses for air emissions are less than 0.1% of the 10 mrem/r standard,; nevertheless, the RWMC contributes a significant portion of the total dose to a hypothetical receptor (p. v).

Concentrations of tritium and carbon dioxide in soil gas adjacent to the beryllium disposal site exhibit a trend of increasing concentration between 1995 or 1996 and 2001or 2002 (pp 18-20).

Soil moisture samples collected 1997 – 2002 and analyzed for radionuclides have results that can be placed into the following categories (pp 30-41)

- Non-detections: Np-237
- Sporadic detections below the MCL: C-14 and tritium
- Sporadic detections above the MCL: Iodine-129
- Frequent detection with some concentrations above the MCL: U-233/234 and U=238

Aquifer samples collected during 1994 and 2002 (1975 – 2002 for tritium) and analyzed for radionuclides can be placed into the following categories (pp 51-44)

- Non-detection: Cl-36

- Sporadic detections below the MCL: C-14, No-237
- Sporadic detections with some concentrations above the MCL: I-129
- Frequent detections, but all concentrations below the MCL: tritium, U-233/234, U-238

3.6. Geochemistry

Deficiencies and recommendations related to geochemistry that were identified in the *Deficiencies Document*, and documents that report progress related to these deficiencies and recommendations, are shown in the following table.

Table 3-6 Deficiencies, recommendation, and progress related to geochemistry

Deficiencies and Recommendations	**Relevant Publications**
Deficiencies One deficiency in vadose zone geochemical scientific knowledge was identified during the Vadose Zone Workshop:	
• The use of linear, reversible sorption (i.e., the empirical distribution coefficient or K_d) as the mechanism governing the interaction between aqueous and solid phases during transport does not address specific geochemical adsorption processes	
Recommendations Laboratory studies can measure parameters and develop theories of important reactions. Computer models can show the relative importance of processes. However, sampling and analysis of field sites are needed to provide information on the geochemical environment in the vadose zone and verification of the processes occurring in the field. The following specific recommendations are provided to enhance understanding of geochemical issues:	
• Implement the surface complexation and ion exchange models as mass transfer reactions in fate and transport models and use them to replace the empirical K_d approach. A database of exchange constants for minerals and soils must be developed, and the relative selectivity of surfaces for metals and radionuclides should be determined. The models will still be empirical at this time because the selectivity coefficients and types of surfaces are not well known. These types of models are important to advance the level of modeling of pollutants and radionuclides in the environment and the effect of the geochemical environment on contaminant transport.	(Hull et al., 2002)
• Conduct a study of the processes and mechanisms controlling the propagation of pH in the vadose zone and ways to incorporate these processes into a predictive reactive transport code. Most geochemical codes can speciate metals or radionuclides given the pH, but cannot generate these	

Deficiencies and Recommendations	Relevant Publications
environmental factors from mechanisms such as biological activity. The ability to calculate the gas-phase carbon dioxide concentrations mechanistically is important to developing a predictive biogeochemical model of the vadose zone.	
• Evaluate the reaction kinetics and transport rates to select problems and situations in which reaction rates are important to understanding migration. Most vadose zone geochemical reactions important for contaminant transport appear to be relatively fast. Kinetics of adsorption reactions is generally complete in a matter of hours to a few days. This reaction rate is generally faster than the rate of water movement in the vadose zone permitting equilibrium in geochemical reactions to be approached. In the spring, rapid recharge of snowmelt can result in very fast movement of water through coarse-grained materials. Kinetic factors may play an important role in contaminant migration.	
• Measure the potential complexing agents in soil and groundwater to evaluate the presence and identity of these agents. Thermodynamic data to calculate the ability of the complexing agents to sequester contaminants in solution are available for many complexing agents and contaminants. Laboratory work may be needed to develop thermodynamic data for other compounds. The persistence of these complexing agents in the vadose zone then needs to be evaluated to determine their persistence for contributing to transport.	(Grossman et al., 2001).
• Evaluate the biogeochemical reactions in buried waste to assess the development of reducing conditions in waste and the use of other electron receptors than oxygen by microbes. The fate of contaminants in buried waste are closely linked to the oxidation-reduction (redox) environment and the redox state of the contaminants. This information can be used to develop release rates from buried waste.	(Hull and Sondrup, 2003)

3.6.1 Grossman et al., 2001

The work of (Hull et al., 2002) was based on a more extensive sorption study that is reported by (Grossman et al., 2001). The goals of this investigation were “to characterization the sorption of ^{51}Cr, ^{233}U, ^{237}Np, and ^{241}Am in interbed grab samples from the RWMC at the INEEL.” The specific objectives were to characterize sorption isotherms for these isotopes for interbed samples and synthetic groundwater representative of typical INEEL groundwater, to evaluate the variability of sorption among interbed samples, and to determine the effect of anions (bicarbonate, sulfate, fluoride) on sorption; these anions may complex some of these elements. Excerpts of their conclusions are paraphrased here.

1. Sorption of uranium and neptunium was nonlinear at the aqueous phase concentrations examined. A linear distribution coefficient model may be inappropriate to characterize sorption behavior in the traditional transport modeling approach. The Freundlich sorption model was shown to characterize the contaminants' sorption behavior well, and may be a more suitable approach to characterize sorption behavior than the linear model over aqueous concentrations similar to those examined here.

2. The sorption affinity for uranium and neptunium varied by less than an order of magnitude among the soils. The use of a finer spatial scale in transport modeling may not be necessary.

3. Ligand studies were performed to examine the effect of bicarbonate, sulfate, and fluoride on sorption behavior of uranium and neptunium. Uranium is known to form soluble carbonate species. The strong influence of carbonate on uranium behavior masked the effects of sulfate and fluoride in these studies.

4. The sorption behavior of neptunium was similar among the three groundwater simulants, suggesting that carbonate, sulfate, and fluoride had little effect.

5. Chromium's affinity for the soils was small.

6. Solubility studies indicated substantial loss of americium, possibly due to precipitation of $AmOHCO_{3(c)}$.

Excerpts from their "Environmental Significance" section are paraphrased here.

1. The use of linear distribution coefficient model (the K_d approach) in traditional transport modeling may not be appropriate for uranium and neptunium. A more appropriate approach may be the use of the Freundlich sorption model. However, caution should be used because the model may not characterize contaminant sorption behavior beyond the experimental concentration range examined. Nonlinear sorption indicates a decreasing rate of sorption with increasing aqueous phase concentrations, hence at higher concentrations the mobility of a contaminants increases relative to its mobility at lower aqueous concentrations, allowing the contaminant to travel further than would be predicted by a linear sorption model.

2. The variation in sorption affinity among the soil samples was relatively small, suggesting that the use of a finer spatial scale for transport modeling may not be necessary.

3. Perturbations in groundwater chemistry may influence contaminant mobility. Uranium is more mobile in high-carbonate environments than in low carbonate environments. For neptunium, carbonate, sulfate, and fluoride should exert little influence.

4. Precipitation of americium carbonates will likely exert more influence on americium mobility at INEEL than will retardation by geologic media.

5. Sorption of trivalent chromium is expected to be small. Precipitation of chromium hydroxides is likely to be more important than sorption in controlling chromium mobility.

3.6.3 Hull 2002

(Hull et al., 2002) summarize a laboratory study of uranium sorption by sediment samples (surficial soil and sedimentary interbeds) collected at the SDA of the RWMC. They characterized 14 samples and reported the surface area, cation exchange capacity, and Freundlich sorption parameters, n and log K_f, for uranium.

They discuss the n and K_f parameters as follows.

> The commonality in the n values calculated for the uranium adsorption isotherms on the 14 sediment samples from the SDA suggests that the suite of adsorption sites on the sediments is very similar. The n parameter compensates for a decrease in binding affinity to mineral surfaces as sites become filled. Because the mineralogy of the sediments is similar, the suite of adsorption sites might also be expected to be similar.
>
> The Freundlich adsorption constants were significantly different among the sediment samples. The Freundlich K_f is and empirical parameter that is composed of three components, a binding constant, a term related to the number of adsorption sites, and solution composition….We hypothesize that the binding energy parameter is a constant, and the number of surface sites will depend on an extensive material property.

They go on to state "The commonality in the n parameter from the Freundlich isotherms, and the correlation between the K_f parameter and surface area suggests that a more process based model of adsorption can be derived from these data."

They then use surface complexation theory to derive a relationship that has the general form of a Freundlich isotherm and that includes terms that account for "material properties (binding strength, the number of adsorption sites, and the spectrum of binding energies) and water chemistry (the proton stoichiometry of the reaction and the formation of aqueous complexes)." This relationship is empirical because the parameter values were measured on site-specific samples.

They then used this Freundlich isotherm model to investigate the importance of pH and carbonate complexes on uranium sorption. While both variables are important, the range of pH in the subsurface below the SDA does not vary much, due to buffering by calcite. However, the amount of carbonate in solution varies substantially and has a dramatic effect on uranium sorption. Their model showed that the effective partition coefficient, K_d, varies approximately three orders of magnitude with changes in total dissolved carbonate, and that the predicted values were in agreement with the measured values.

This work provides a more robust approach for describing sorption than the more commonly used K_d approach. In addition, their model shows that K_d values for a given solid phase and sorbed species vary dramatically with variations in solution chemistry, and hence the concept of a single K_d value for a sorbing species is not valid.

3.6.3 Hull and Sondrup 2003

(Hull and Sondrup, 2003) presented evidence that redox conditions in the vicinity of drums of buried waste are strongly anaerobic conditions, and that these conditions facilitate anaerobic reductive dechlorination of trichloroethene and carbon tetrachloride. Microorganisms are typically intimately involved in the generation of strongly reducing conditions, and in anaerobic reductive dechlorination.

3.7. Microbiology

Deficiencies and recommendations related to microbiology that were identified in the *Deficiencies Document*, and documents that report progress related to these deficiencies and recommendations, are shown in the following table.

Table 3-7 Deficiencies, recommendation, and progress related to microbiology

Deficiencies and Recommendations	**Relevant Publications**
Deficiencies One deficiency in vadose zone microbiological scientific knowledge in microbiology was identified during the Vadose Zone Workshop:	
• The relative importance of the effects of biological activity on the transport of contaminants is not well understood.	(Hull and Sondrup, 2003) (see Geochemistry section for discussion)
Recommendations Focusing vadose zone microbiological activities on two overarching areas of study clearly will advance the level of knowledge of vadose zone microbiology at the INEEL:	
• Develop an understanding of the basic distribution of microbial physiologies and the abiotic factors that control their distribution	
• Develop an effective and efficient method for determining rates of in situ biologic activity.	
Specific activities required to implement the two areas of study include the following:	
• Thoroughly characterize the vadose zone microbiology of a research site (vertically and horizontally) so that sufficient data are produced to achieve the development of a conceptual model of microbial processes in the vadose zone at a particular site. Given the low-percent culturability of microbes observed in deep vadose core samples from the INEEL, emphasis on culture-independent techniques is particularly warranted to explore basic and applied implications of high numbers of cells that cannot be cultured. In a ranking of environments for microbial activity, deep arid vadose zones rank near the lowest of those investigated (Onstott et al. 1999) and require that special attention be given to	

Deficiencies and Recommendations	Relevant Publications
method detection limits.	
• Conduct temporal studies incorporating alterations in water availability (natural or manipulated) to allow a full appreciation of the range in activities that may be exhibited. This characterization might be tuned to specific issues of concern, for example, microbial corrosion of buried waste containers or contaminant fate and transport.	
• Develop accurate measurement methods for in situ microbial processes. Accurate measurement of microbial processes has proved to be nearly unattainable in all settings including the vadose zone. In the saturated zone, geochemical analyses of groundwater can assist in bounding rates of biological transformation. In the vadose zone, gases or mineralogical alteration could be examined. The work of Wood, Keller, and Johnstone (1993) offers a model for CO_2 measurement in the shallow vadose zone that could be adaptable to greater depths. Innovative approaches for assessment of in situ microbial activities are required for the vadose zone and other microbial habitats.	

No publications relevant to these deficiencies or recommendations were identified in the literature search performed.

3.8. Organization and Communication

Deficiencies and recommendations related to organization and communication that were identified in the *Deficiencies Document*, and documents that report progress related to these deficiencies and recommendations, are shown in the following table.

Table 3-8 Deficiencies, recommendation, and progress related to organization and communication

Deficiencies and Recommendations	Relevant Publications
Deficiencies The specific deficiencies in integration identified during the Vadose Zone Workshop include the following:	
• The INEEL lacks a coordinated, integrated means for coordinating vadose zone sampling, research and modeling above the project level	
• A central archive is required to store and access data and analyses. A central archive would facilitate use of this information by DOE managers and contractors.	
Recommendations Integration of vadose zone activities is required at the INEEL to coordinate science and technology activities between the INEEL Site contractors, universities, other researchers, and the U.S. Geological Survey to guarantee that the deficiencies in understanding about the INEEL vadose zone are addressed. Integration between site programs could ensure complete data collection and model verification. Integration also is needed to oversee the incorporation of new and innovative science and technologies into INEEL vadose zone project approaches and ensure that standardized methodologies and approaches are used to characterize and monitor the vadose zone. In addition, integration should reduce the resource requirements necessary to conduct vadose zone characterization and monitoring at the INEEL and thereby produce cost savings. Some of the specific means to address the deficiencies include the following:	
• Incorporate vadose zone monitoring as an integral part of the assessment and cleanup effort for all major operable units. Currently, levels of vadose zone characterization and monitoring are inconsistent from one operable unit to the another. For instance, a limited effort has been expended for vadose monitoring at Waste Area Group (WAG) 7, the RWMC, yet virtually nothing has been done to collect vital vadose zone data at WAG 3, the INTEC.	
• Coordinate and integrate vadose zone efforts between WAGs and standardize characterization and monitoring methods. An organized effort, funded for	

Deficiencies and Recommendations	**Relevant Publications**
several years, could be used to support the development of nested projects where step-wise progress is made in vadose zone knowledge by causing the results from one test to feed into the next test at another WAG.	
• Improve the collective INEEL ability to predict contaminant migration and in particular actinide mobility in the vadose zone. The observations of plutonium and americium in samples taken from interbeds and groundwater at the INEEL suggest that actinide mobility is greater than normally assumed. Such mobility also has been observed at Los Alamos National Laboratory, the Nevada Test Site (Discover 1999), the Hanford Site (GAO 1998), Clemson University (Newman et al. 1995), and in field- and laboratory-scale experiments conducted at the INEEL (e.g., Wood and Norrell 1996).	
• Apply innovations in vadose zone characterization, monitoring, modeling, and remediation to all ongoing projects at the INEEL.	
• Implement a coordinated effort in landfill cap analysis. This effort would including cap modeling, infiltration monitoring at currently capped sites, and use of the three existing facilities, the Protective Cap/Biobarrier Experiment (see Appendix D), and the Engineered Barrier Test Facility, to develop reliable predictions of long-term cover performance as well as estimates of net infiltration on disturbed sites at the INEEL.	
• Establish closer ties between the INEEL and other DOE sites and the DOE complex-wide Vadose Zone roadmap project to facilitate the exchange of site characterization and vadose-zone transport modeling efforts. The INEEL vadose zone efforts would benefit from more frequent interactions with peers at other Western DOE sites (e.g., the Hanford site, Los Alamos National Laboratory, Yucca Mountain, and the Nevada Test Site) because workers at these sites are currently grappling with many of the same site characterization, monitoring, and modeling challenges as at the INEEL.	
• Evaluate past vadose zone characterization activities, remedial actions, and monitoring at all INEEL sites and at similar sites at other western DOE facilities to determine the current best solution for a variety of sites. A goal of this effort would be to establish a knowledge base from which to direct additional research on monitoring and characterization.	

No publications relevant to these deficiencies or recommendations were identified in the literature search performed.

4. SUMMARY

Research published 1999-2003 has addressed, to some degree, many of the deficiencies and recommendations identified in (Wood et al., 2000). However, many remain to be addressed by research focused on these items. Therefore, (Wood et al., 2000) continues to provide a basis for identifying research needed to improve our understanding of flow and transport in the vadose zone at and near the INEEL.

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APPENDIX A

VADOSE ZONE CONCEPTUAL MODEL

The vadose zone conceptual model in this appendix was originally presented in *Deficiencies in Vadose Zone Understanding at the Idaho National Engineering and Environmental Laboratory* (Wood et al., 2000). It is repeated here to present the synthesis of our understanding of the vadose zone and vadose zone processes at the INEEL at the beginning of the period during which the research described herein was performed.

INSERT APPENDIX C FROM THE DEFICIENCIES DOCUMENT HERE.

APPENDIX B

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Appendix C

Conceptual Models Developed for the Vadose Zone at the Idaho National Engineering and Environmental Laboratory

Appendix C

Conceptual Models Developed for the Vadose Zone at the Idaho National Engineering and Environmental Laboratory

C1. GEOLOGIC FRAMEWORK

C1.1 Regional Geologic Setting

The Idaho National Engineering and Environmental Laboratory (INEEL) is located near the northwestern margin of the Eastern Snake River Plain (ESRP), and lies in an area influenced by two distinct geologic provinces (see Figure 1-1 of the main body of this document). The ESRP is a northeast-trending zone of late Tertiary and Quaternary volcanism that transects the northwest-trending, normal-faulted mountain ranges of the surrounding Basin and Range province. The topographically subdued ESRP, the dominant geomorphic feature of southern Idaho, is a relatively aseismic region in the midst of the high-relief, seismically active Basin and Range province.

Volcanic and sedimentary rocks of the Snake River Plain form a 60 to 100-km-wide belt, extending about 600 km from the Idaho-Oregon border to the Yellowstone Plateau. Volcanic rocks consist of late Tertiary rhyolitic rocks and latest Tertiary to Holocene basaltic lava flows. At least 1 km of basaltic lava flows and intercalated sediments has accumulated in the eastern Snake River Plain following the rhyolitic volcanism related to passage of the Yellowstone mantle plume. About 2 km of subsidence of the eastern Plain in the past 4 million years have allowed the basalts and sediments to accumulate and have confined their emplacement and deposition to the current boundaries of the Plain.

C1.2 Quaternary Basalt, Sediment, and Rhyolite

Basalts and sediments of the ESRP are part of the Snake River Group, composed largely of tholeiitic-basalt lava flows emplaced during the past 4 million years (see Figure C-1). Most eruptions were effusive, and typical landforms of Quaternary mafic volcanism on the ESRP are small shield volcanoes with summit pit craters, fissure-fed lava flows associated with zones of tensional fracturing, and relatively uncommon tephra cones of magmatic or phreatomagmatic origin (Greeley 1982).

Based on field mapping, and limited geochronometry and paleomagnetic data, Kuntz et al. (1990) (see Figure C-2) identified five Quaternary basalt lava-flow groups in the INEEL area, ranging in age from 5,200 years to greater than 730,000 years. Basaltic vents on the ESRP typically form linear arrays of fissure flows, small shields and pyroclastic cones, pit craters, and open fissures, which collectively define northwest-trending volcanic rift zones (see Figure C-3). Volcanic rift zones have similar trends as normal faults in the adjacent Basin and Range province to the north, but are not strictly co-linear with those faults. The most well-known and recently active of ESRP volcanic rift zones is the Great Rift (Kuntz et al. 1988), where eight eruptive episodes occurred at Craters of the Moon, and several smaller, monogenetic lava fields were formed during the past 15,000 years. In the INEEL area, most basaltic rift-zone volcanism seems to have occurred during Pleistocene time, generally between about 0.1 and 0.7 Ma. Most subaerially exposed lavas have normal magnetic polarity and are, therefore, younger than about 730,000 years. Several well-dated Holocene lava fields (Kuntz et al. 1986) erupted from northwest-trending fissures to the south of the INEEL, on the northeast-trending axial volcanic zone.

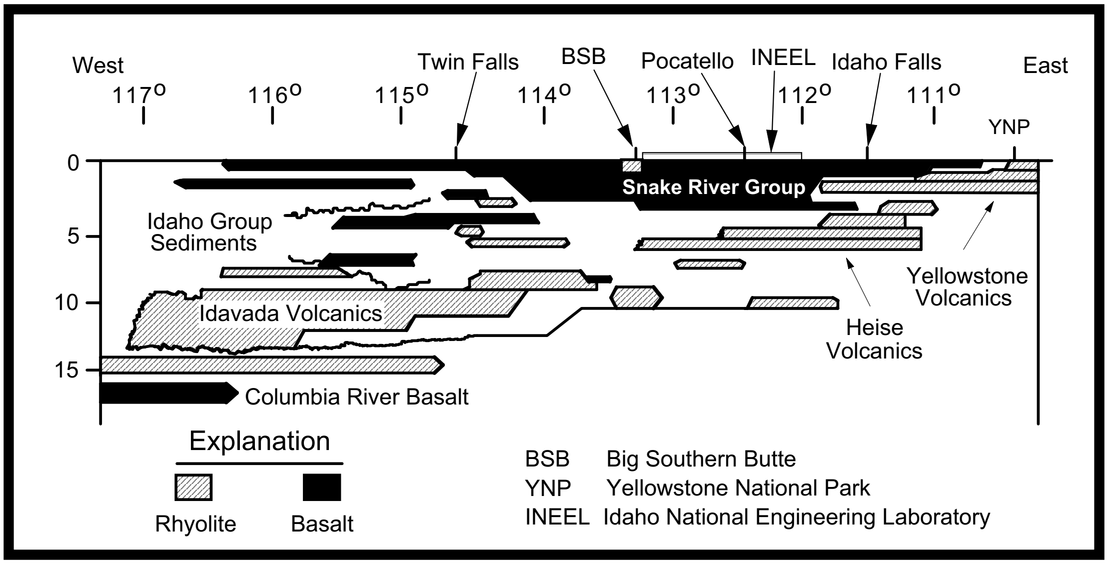
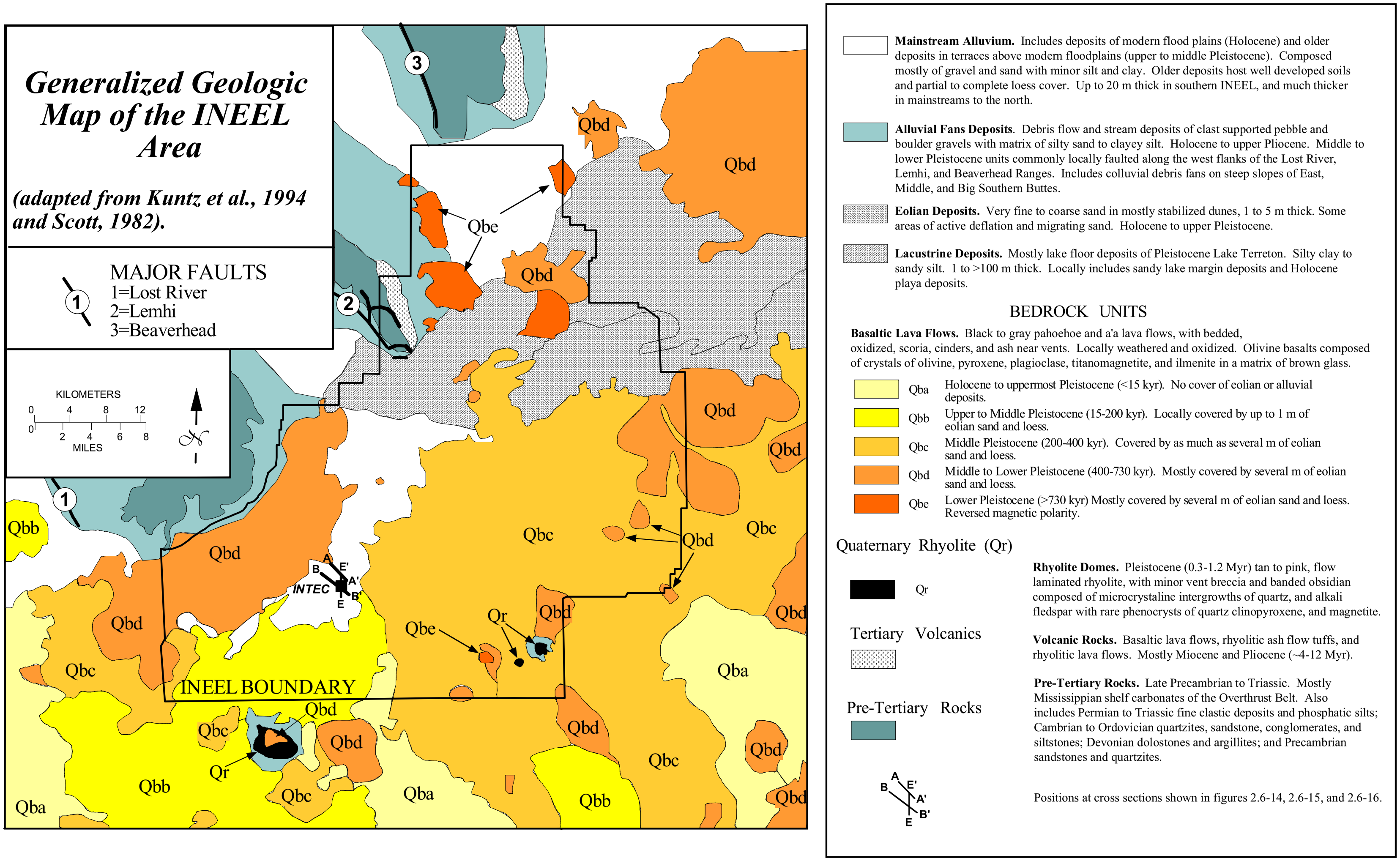


Figure C-1. Diagram of age versus longitude for Snake River Plain Volcanic Rocks (modified from Armstrong, Leeman, and Malde 1975).



□ **Mainstream Alluvium.** Includes deposits of modern flood plains (Holocene) and older deposits in terraces above modern floodplains (upper to middle Pleistocene). Composed mostly of gravel and sand with minor silt and clay. Older deposits host well developed soils and partial to complete loess cover. Up to 20 m thick in southern INEEL, and much thicker in mainstreams to the north.

🟦 **Alluvial Fans Deposits**. Debris flow and stream deposits of clast supported pebble and boulder gravels with matrix of silty sand to clayey silt. Holocene to upper Pliocene. Middle to lower Pleistocene units commonly locally faulted along the west flanks of the Lost River, Lemhi, and Beaverhead Ranges. Includes colluvial debris fans on steep slopes of East, Middle, and Big Southern Buttes.

▨ **Eolian Deposits.** Very fine to coarse sand in mostly stabilized dunes, 1 to 5 m thick. Some areas of active deflation and migrating sand. Holocene to upper Pleistocene.

▨ **Lacustrine Deposits.** Mostly lake floor deposits of Pleistocene Lake Terreton. Silty clay to sandy silt. 1 to >100 m thick. Locally includes sandy lake margin deposits and Holocene playa deposits.

BEDROCK UNITS

Basaltic Lava Flows. Black to gray pahoehoe and a'a lava flows, with bedded, oxidized, scoria, cinders, and ash near vents. Locally weathered and oxidized. Olivine basalts composed of crystals of olivine, pyroxene, plagioclase, titanomagnetite, and ilmenite in a matrix of brown glass.

🟨	Qba	Holocene to uppermost Pleistocene (<15 kyr). No cover of eolian or alluvial deposits.
🟨	Qbb	Upper to Middle Pleistocene (15-200 kyr). Locally covered by up to 1 m of eolian sand and loess.
🟧	Qbc	Middle Pleistocene (200-400 kyr). Covered by as much as several m of eolian sand and loess.
🟧	Qbd	Middle to Lower Pleistocene (400-730 kyr). Mostly covered by several m of eolian sand and loess.
🟥	Qbe	Lower Pleistocene (>730 kyr) Mostly covered by several m of eolian sand and loess. Reversed magnetic polarity.

Quaternary Rhyolite (Qr)

■ Qr

Rhyolite Domes. Pleistocene (0.3-1.2 Myr) tan to pink, flow laminated rhyolite, with minor vent breccia and banded obsidian composed of microcrystaline intergrowths of quartz, and alkali fledspar with rare phenocrysts of quartz clinopyroxene, and magnetite.

Tertiary Volcanics

▨

Volcanic Rocks. Basaltic lava flows, rhyolitic ash flow tuffs, and rhyolitic lava flows. Mostly Miocene and Pliocene (~4-12 Myr).

Pre-Tertiary Rocks

🟦

Pre-Tertiary Rocks. Late Precambrian to Triassic. Mostly Mississippian shelf carbonates of the Overthrust Belt. Also includes Permian to Triassic fine clastic deposits and phosphatic silts; Cambrian to Ordovician quartzites, sandstone, conglomerates, and siltstones; Devonian dolostones and argillites; and Precambrian sandstones and quartzites.

A E' B A' B' E

Positions at cross sections shown in figures 2.6-14, 2.6-15, and 2.6-16.

Figure C-2. Geologic map of the INEEL area showing five Quaternary lava-flow groups.

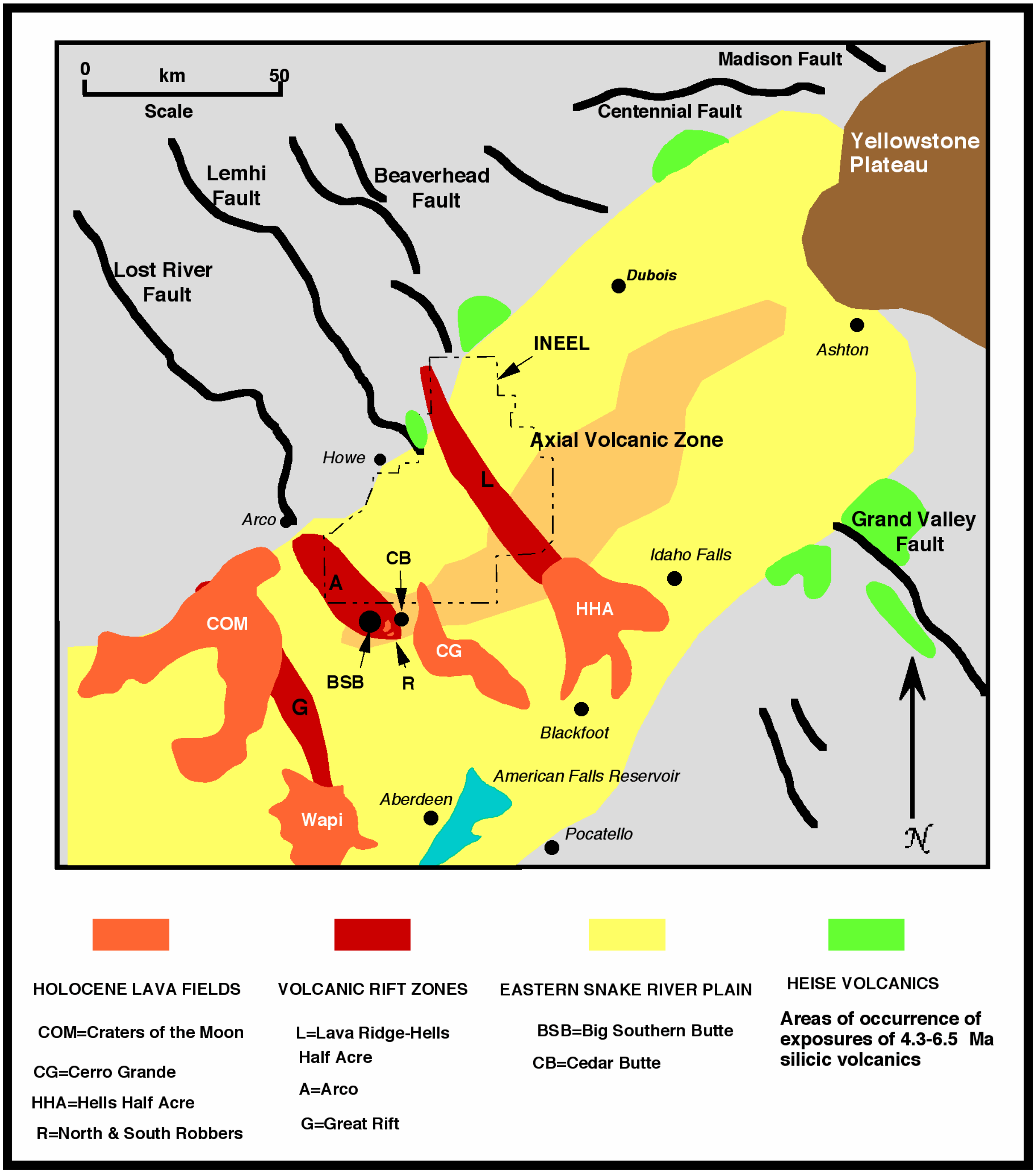


Figure C-3. Map of the Eastern Snake River Plain showing locations of volcanic rift zones, young lava flows and major faults.

C1.3 Quaternary Surficial Deposits and Sediment Interbeds

Most lava flows in the INEEL region are Pleistocene in age, have been subaerially exposed for several hundred thousand years, and are, therefore, blanketed with unconsolidated sedimentary deposits of eolian, alluvial, and lacustrine origin (Scott 1982) (see Figure C-2). Though little is known of the detailed Quaternary lithostratigraphy of the ESRP subsurface, data from INEEL drillcores (Figure C-4) generally indicate that relatively long (10^5-year) periods of sedimentation and volcanic quiescence, represented by major sedimentary interbeds, were punctuated by relatively brief ($<10^2$- to 10^3-year) episodes of basaltic volcanism, the latter represented by rapidly emplaced lava-flow groups (Kuntz and Dalrymple 1979; Kuntz et al. 1979, 1980; Champion, Lanphere, and Kuntz 1988; Anderson and Lewis 1989; Anderson 1991). The present distribution of surficial deposits is probably qualitatively analogous to that of subsurface deposits, involving intermittent blanketing of lava flows by loess, and the deposition of fluvial/lacustrine sediments in low-lying areas between constructional volcanic zones.

The following discussions provide information derived from examination of surficial deposits in the INEEL area, but they can be viewed as models for depositional processes responsible for sediment interbeds between lava flows at depth.

C1.3.1 Alluvial Deposits

Alluvial deposits of two types are found in the INEEL area: alluvial-fan deposits and mainstream alluvium. Alluvial fans are developed on the steep lower flanks of basin-and-range mountains and contain clastic material of local origin, commonly subangular or subrounded, moderately sorted gravel, dominated by Paleozoic carbonate clasts.

Mainstream-alluvial deposits are associated with the channels of the Big Lost River, Little Lost River, and Birch Creek, which longitudinally drain the northern Basin and Range province and flow southward onto the ESRP (Pierce and Scott 1982). None of these streams reaches the Snake River to the south. Instead, their ephemeral waters percolate into permeable lava flows and sediments at the Lost River Sinks of the northern INEEL, a local recharge area for the Snake River Plain aquifer. Mainstream deposits are generally better sorted, rounded, and bedded than those of alluvial fans, and clasts are predominantly quartzite, chert, silicified Eocene volcanic rocks, and other resistant lithologies.

C1.3.2 Lacustrine Deposits

Volcanic eruptions and tectonism have periodically impounded the Snake River and its tributaries, forming lacustrine basins or areas of impeded drainage (Malde 1982; Howard, Shervais, and McKee 1982; Scott et al. 1982; Hackett and Morgan 1988). In the INEEL region, the axial volcanic zone obstructed drainage from areas north of the ESRP. During glacial/pluvial periods, the resulting basins received more runoff than now, and contained large shallow lakes, in contrast to the present small playas of the Lost River Sinks. One such basin in the area that is now the northern INEEL was occupied by Lake Terreton, from which Pleistocene deposits have been cored in the upper part of Drillhole 2-2A (see Figure C-2). Lake Terreton formerly covered a wide area near the present Mud Lake. Its shoreline generally follows the 4,800-ft topographic contour on the ESRP and is marked by beaches, bars and deltas. Lake Terreton sediments are the major source of material for Holocene dunes to the northeast.

C1.3.3 Eolian Deposits

Pleistocene loess deposits are widespread on the ESRP, and reach their greatest thickness along its southeastern margin. Several episodes of loess deposition are inferred from studies of loess stratigraphy and paleopedology (Pierce et al. 1982; Lewis and Fosberg 1982; Scott 1982). Holocene basalt

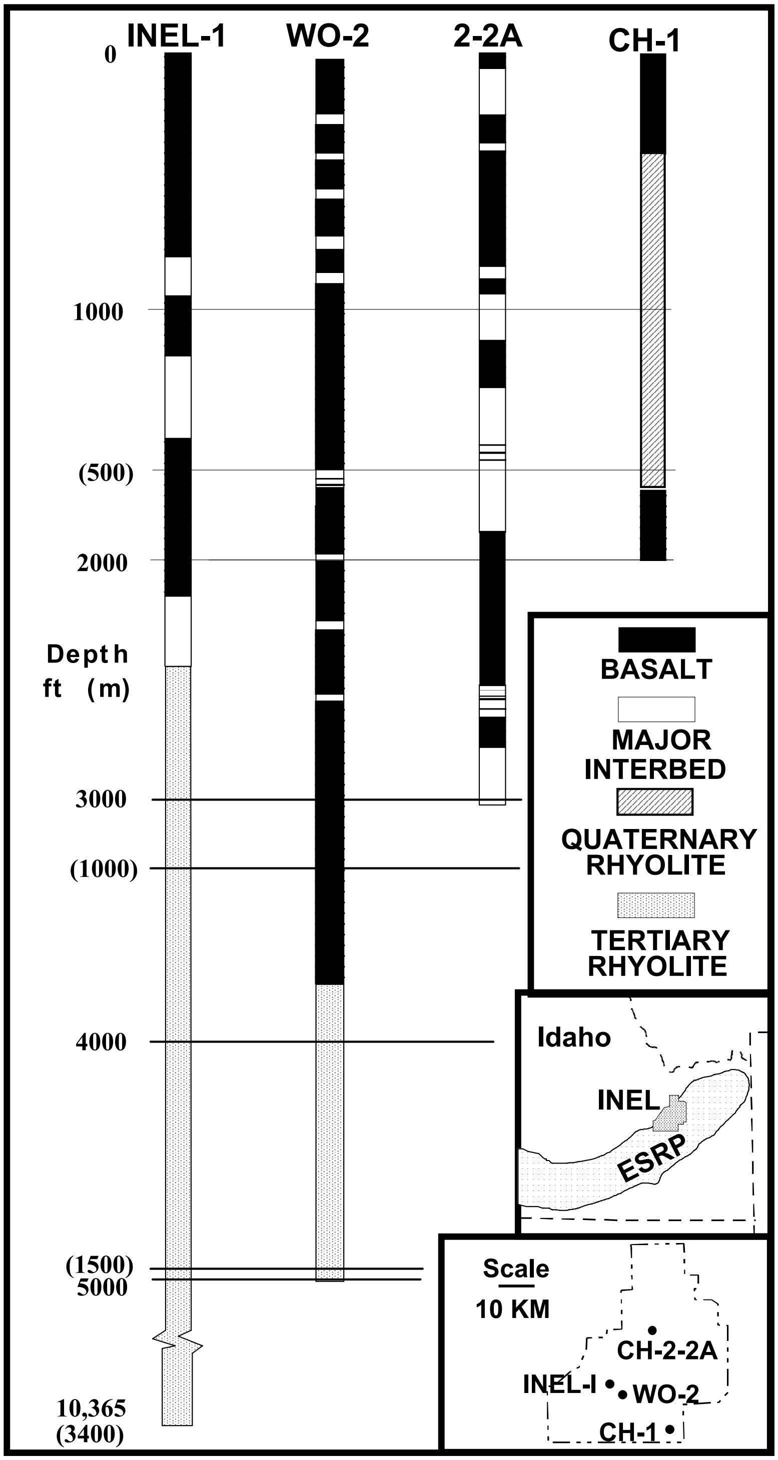


Figure C-4. Simplified lithologic logs of four deep INEEL drill holes.

flows on the ESRP have accumulated little or no loess (Kuntz et al. 1986), indicating that major loess deposition ceased about 10 to 15 ka. Late Pleistocene basalt flows and geomorphic surfaces are overlain by a single loess blanket, whereas older surfaces are generally mantled by several loess units, separated by paleosols or erosional surfaces. Pierce et al. (1982) identified two widespread loess units in southeast Idaho: the upper loess (Unit A) was deposited about 10 to 70 ka, while the lower (Unit B) is dated less specifically but probably accumulated about 140 to 200 ka. Dunes and sheets of Holocene eolian sand near Mud Lake (see Figure C-2) are deflated from the alluvial surfaces of the Lost River Sinks, and from the abandoned shoreline, and floor of former Lake Terreton to the southwest.

C1.4 Sediment Interbed Distribution and Thickness

The distribution and lithology of sedimentary interbeds within the basalt section beneath the INEEL area exerts a strong influence on the flow of groundwater in both the vadose and saturated zones. It has been postulated that a thick sequence of fine-grained, relatively impermeable, lake sediments in the Mud Lake area impede groundwater flow and cause the steep gradient in the water table there (Lindholm et al. 1983; Lindholm and Goodell 1986; Garabedian 1989). In contrast, interbed distribution and lithology may enhance aquifer flow in the central part of INEEL. The distributions of interbeds in a cross section that traverses the Big Lost River and extends from the Plain margin to East Butte (see Figure C-5) shows that there are numerous interbeds beneath the present course of the river, and that they become less numerous and thinner with distance from the river. There is likely to be a mixture of both coarse-grained (sands and sandy gravels representing channel and terrace deposits) and fine-grained (silts and silty clays laid down as overbank deposits) interbeds deposited by the Big Lost River as it was pushed back and forth by lava-flow emplacement during the past several million years. Eolian deposits of both loess and sand also are likely to be present. Based on drillhole information from throughout the INEEL, two interpretations of interbed distribution are shown in Figure C-5, one assuming a very short horizontal continuity of interbeds (more of a river channel interpretation), and one assuming a long horizontal continuity of interbeds (perhaps representing broad flood-plain development such as the river exhibits today). In either case, however, there is a concentration of northward-elongated (perpendicular to the plane of the cross section) alluvial interbeds in the central portion of INEEL. The presence of these interbeds beneath most of the major facilities at INEEL provides important controls on transport of water and contaminants in the vadose zone.

The thickness of sediment interbeds is extremely variable at both local (even within individual interbeds) and regional scales (see Figure C-6 and Table C-1). Thickness statistics were developed from the electronic database of well lithologies developed by Anderson et al. (1996). Additional analysis shows that there is a tendency for interbed thickness to be greater in the northern than in the southern portions of the INEEL because of the presence of thick lake sediments there. There may be significant aliasing of the data because no attempt was made to account for different depths of wells. Some of the thickest beds occur only deep in the deepest boreholes, and because there are only a few deep boreholes, the data set is likely skewed toward thinner interbeds.

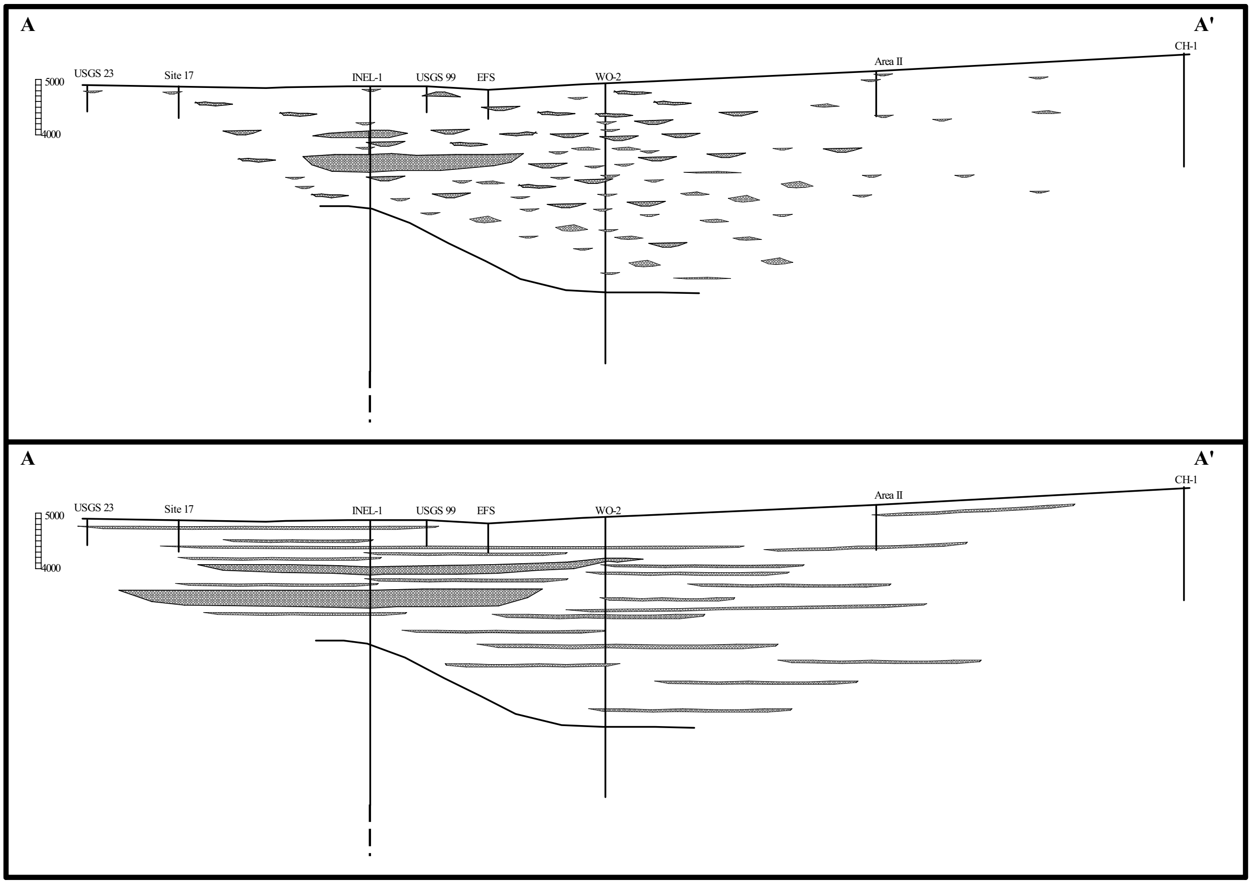


Figure C-5. Sediment interbed distribution across the INEEL.

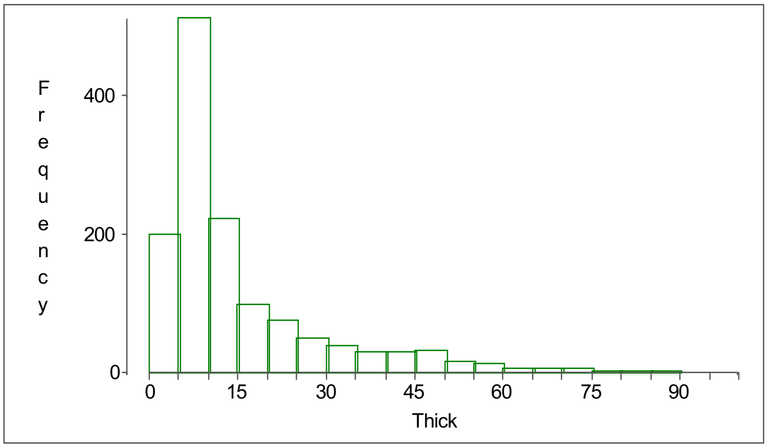


Figure C-6. Histogram for sediment interbeds from all INEEL wells.

Table C-1. Thickness statistics for sediment interbeds from all INEEL wells.

Minimum	1
Maximum	533
Median	9.0
Mean	10.9
Standard deviation	0.403277

C1.5 Characteristics of Basalt Lava Flows

C1.5.1 Lava Flow Facies

During emplacement of ESRP basalt lava flows, molten rock is continuously supplied to the advancing flow front through lava tubes. The solidified crust on the top, bottom, and ends of the lava flows is kept inflated by the pressure of the molten material in the interior of the flow. As the flow front advances, the crust at the end of the flow is laid down and overridden by the new lava, and the upper crust is stretched, broken, and fissured by movements of magma beneath. This “bulldozer tread” type of emplacement mechanism produces distinctive facies within each lava flow. An idealized section showing distribution of vertical and horizontal facies variation in ESRP basalt lava flows is shown in Figure C-7. From bottom to top, basalt lava flows typically are composed of a basal rubble zone, a lower vesicular zone, a massive columnar jointed zone, an upper vesicular and fissured zone, and a cap of platy-jointed crust.

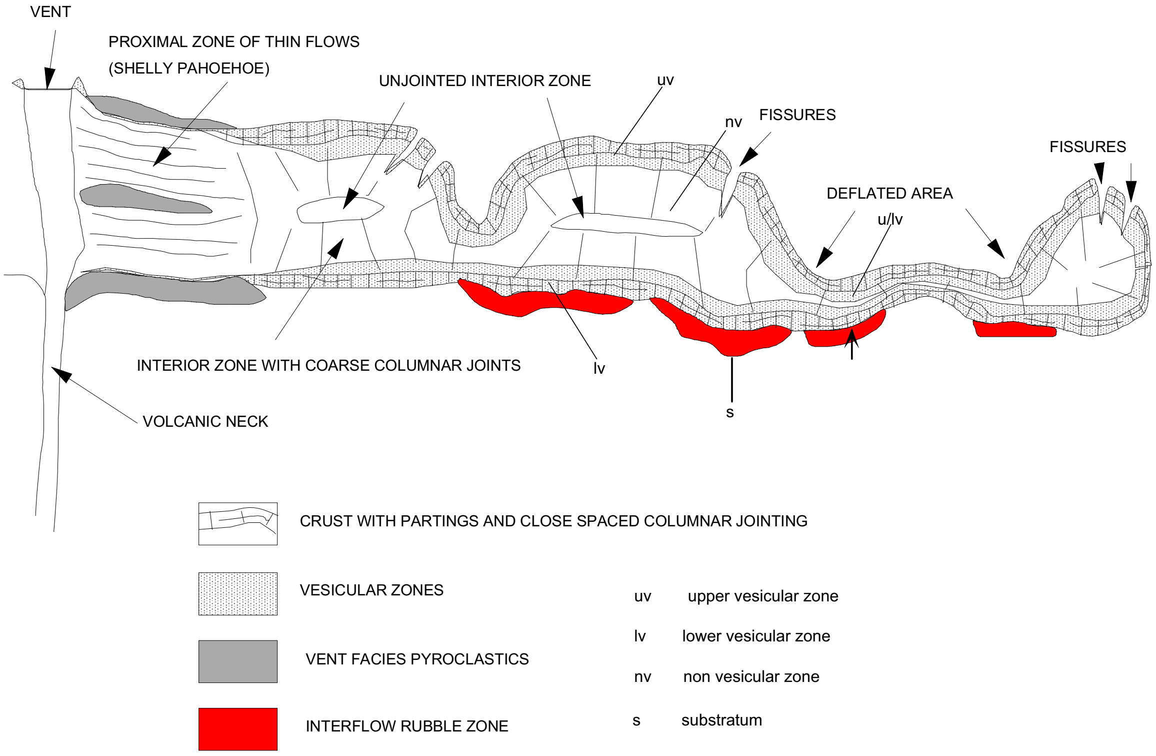


Figure C-7. Longitudinal cross section of a typical basalt lava flow on the Eastern Snake River Plain.

The near vent facies of lava flows is typified by thin, vesicular, platy flows (shelly pahoehoe). Also pyroclastic ash and breccia layers are commonly interleaved within the thin flow layers. With distance from the vent, the shelly pahoehoe grades rapidly into the layered facies structure, described above, which typifies the medial and distal portions of the lava flow (see Figure C-7). Deflation pits, in which solidified crust has subsided over areas where lava has drained away, are common throughout the flow but more numerous near the terminus.

C1.5.2 Lava Flow Dimensions

There is a great range in length, area, and thickness of lava flows in the INEEL area (see Table C-2). The length and area measurements are for lava flows exposed at the surface, and are measured from geologic maps (Hackett, Smith, and Khericha 2000). The thickness measurements are mostly from drill hole information in the Radioactive Waste Management Complex area, augmented by measurements made of lava flow thickness in cliff faces in the Box Canyon area, to the west of INEEL (Knutson et al. 1989, 1992).

Table C-2. Statistics of lava flow dimensions.

	Length (km)	Area (km^2)	Thickness (m)
Minimum	0.1	0.5	1
Maximum	31	400	34
Range	30.9	399.5	33
Mean	12.4	96.5	?
Median	10	70	7
Standard deviation	7.9	94.2	?
Number of measurements	46	43	641

C2. VADOSE ZONE HYDROLOGIC CONCEPTUAL MODEL

This section presents the current level of understanding of water movement in the subsurface at the INEEL. The section is organized in terms of the general movement of water in the subsurface, following the path of water from land surface to the Snake River Plain Aquifer. Figure C-8 graphically shows the vadose zone at the INEEL, the sources of water, and the movement of water in different parts of the vadose zone. This conceptual model is derived from both field observations from a variety of investigations conducted at the INEEL since the 1960s and from hypotheses. By including hypotheses, the conceptual model will not necessarily agree with the conceptual models of each and every researcher working on vadose zone issues at the INEEL. However, it will contain enough common elements to be satisfactory to most researchers.

In general, the movement of water in the INEEL subsurface is extremely complex to describe because of spatial variability of hydraulic properties, temporal changes in the hydrologic regime caused by seasonal changes, limited access locations with vertical wells in areas where horizontal permeability is a dominant control, heterogeneous waste disposal, lack of integrated sampling opportunities in the vadose zone like pumping tests in the aquifer, and limited duration of monitoring activities. With these limitations in mind, the remainder of this section describes a vision of water movement in the subsurface.

C2.1 Sources of Water at Surface

Several sources of water contribute to water movement in the vadose zone. Direct precipitation contributes some water to the subsurface. The annual precipitation at the INEEL is approximately 22 to 23 cm/year. A variable portion of this annual precipitation is received as snow, which accumulates until a melting event occurs. Runoff of precipitation can occur during substantial rain events or from snowmelt events. Flooding from runoff in local basins on the INEEL can supply substantial amounts of water when those events occur.

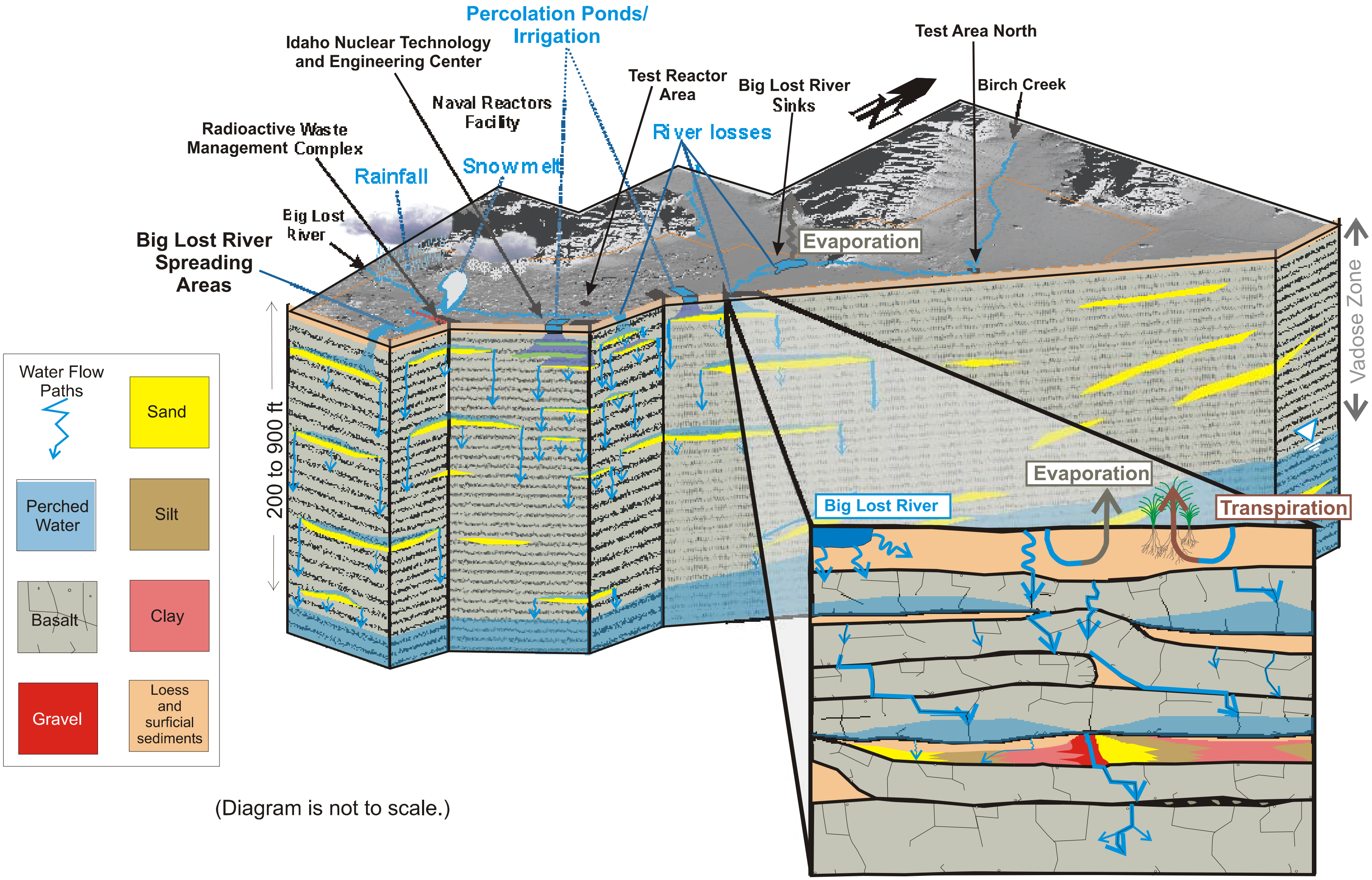
In addition to precipitation, another source of water is surface water that flows onto the INEEL from several drainages to the northwest. These drainages are the Big Lost River, the Little Lost River, and Birch Creek. Depending on the snow pack and precipitation that occur in a particular year, these water sources may flow all year, or they may be completely used up for irrigation prior to reaching the INEEL. The amount of water reaching the vadose zone from these surface water sources depends on the proximity to the surface sources.

A third source of water that contributes to water movement in the vadose zone is anthropogenic activities at the INEEL facilities. These sources include sewage treatment ponds, infiltration galleries, and disposal of process water at some facilities. Where these anthropogenic sources exist, they usually supply a far greater amount of water to the subsurface than precipitation.

C2.2 Surface Infiltration

Infiltration of water from the surface into the subsurface is known to be spatially and temporally variable. At the INEEL, infiltration primarily occurs in early spring, when the accumulated snow pack melts and there is essentially no evapotranspiration. Exceptions to this, however, include infiltration resulting from summer thundershowers.

The primary controls on where, when, and how much water infiltrates at any one place are the following:



(Diagram is not to scale.)

Figure C-8. Geohydrologic conceptual model of the vadose zone at the INEEL.

- The degree of soil freezing (results from cold weather conditions and a lack of snow pack)
- Disturbances of natural layering in soils that disrupts low permeability layers, or disrupts high permeability layers that act as capillary barriers
- Depressions in surface topography that collect meltwater
- The magnitude of potential evapotranspiration that is occurring and the depth to which evapotranspiration affects water movement
- Spatial variability in hydraulic properties
- Presence of preferential pathways that allow rapid infiltration.

The controls on infiltration listed above are primarily for infiltration that is occurring as a result of widespread precipitation or snowmelt. In addition to this infiltration mechanism, infiltration occurs from the surface sources and anthropogenic sources under saturated conditions. The controls on this type of infiltration include the following:

- Hydrologic properties of the sediments under the river, spreading areas, or infiltration ponds
- Height of water or head
- Duration of water being present.

Once the water infiltrates into the surficial sediments past a depth where it can be affected by evapotranspiration, it primarily continues to move downward under the influence of gravity, though capillarity can exert an influence that can move water laterally from wetter to drier locations.

C2.3 Water Movement from Surface Sediments into Basalt

As water moves downward through the surficial sediments, it eventually encounters an underlying fractured basalt flow. Multiple mechanisms are possible by which water can continue moving downward into this lithologic unit. These are illustrated graphically in Figure C-9. All these mechanisms likely occur to varying degrees. The difficulty is in assessing their relative contribution to net water movement under a range of hydrological conditions from dry to wet.

The first mechanism illustrated in the figure is movement from the pore space of the sediments into the pore space of the matrix. This process likely takes place predominantly in locations where there is not sufficient water to elevate moisture conditions at the interface.

The second mechanism is closely related to the first and consists of water movement from the pore space in the sediments into a very small aperture fracture that exerts a capillary imbibition force on the sediment pore water. This process, similar to the first, also likely takes place in predominantly drier locations.

The third mechanism describing water movement at this interface consists of lateral movement of water along the interface. This movement would occur when the moisture flux moving vertically through the surficial sediments is greater than the hydraulic conductivity of the underlying basalt matrix, and when there are no open fractures in the basalt. This lateral movement could occur with or without the

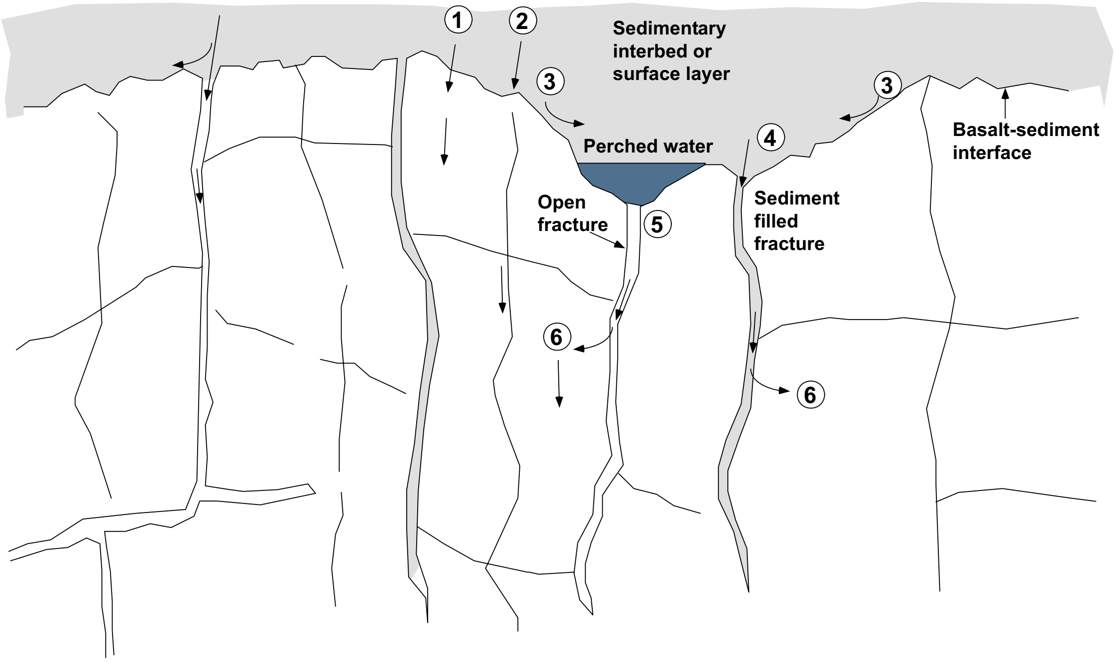


Figure C-9. Possible mechanisms by which water can move across a sediment/basalt interface.

presence of perched water. If perched water conditions form, the magnitude of the lateral flux could be greater. This horizontal movement of perched water is believed to have been observed in neutron access tube moisture monitoring in the CFA landfills (Keck et al 1995). Because the vertical permeabilities of the basalt matrix are generally less than the overlying sediments, it is likely that some horizontal movement occurs frequently.

A fourth possible mechanism of water movement across this interface is when water moving laterally or vertically encounters a sediment-filled fracture into the underlying basalt. The sediment in the fracture is derived from the sediment overlying the fracture and will have a similar hydraulic conductivity allowing water to move vertically downward through it.

The fifth, and potentially dominant, mechanism by which water crosses the sediment-basalt interface occurs when perched water accumulates at the interface and encounters an open fracture. Depending on its aperture, the fracture will likely not allow water to enter until perched conditions occur. Once perched conditions occur, an air-entry potential is reached and a pulse of water will enter the fracture. Depending on the conditions, this pulse may have a greater magnitude of water than all the previous mechanisms combined.

This presentation of water movement from the surficial sediments into the basalt conveniently ignores some complications, such as the presence of a low-permeability clay layer at some locations, such as is often found at the base of the surficial sediments inside the Subsurface Disposal Area. In these cases, the dominant mechanisms may be different, or they may be the same but even more dominant because water may perch and move laterally even farther until it encounters a fracture or preferential pathway into the fractured basalt.

C2.4 Water Movement Within Basalt Flows

The movement of water within the fractured basalt is the least-understood portion of the subsurface pathway. Any conceptual model for this portion of the subsurface is primarily based on hypothesis. Part of the reason for this is the limited number of observations that are available from which to draw conclusions. Several hypotheses are viable for describing water movement in this fractured basalt region including both Darcian and non-Darcian flow. These conceptual models are likely applicable under different conditions.

Under saturated conditions (e.g., flooding or high surface infiltration), the primary water movement in this region will be within the system of fractures. The fracture will control the movement of water because of their high permeability compared to the basalt matrix. This type of water movement will result in a rapid advance of a wetting front through the entire fractured basalt portion of the subsurface. Monitoring of the advance of the wetting front in the Large Scale Infiltration Test (Wood and Norrell 1996) confirmed this rapid movement. If this movement is the dominant mechanism that is being considered, it may be appropriate to represent this portion of the subsurface as an equivalent high-permeability, low-porosity media. The degree to which this approach is representative is subject to qualitative discussions. For risk assessment purposes, the approach may be adequate. For actually understanding and representing the physical mechanism, this approach almost certainly is invalid.

Under less than saturated conditions, the mechanism of water movement in the fractured basalt is less certain. One hypothesis is that the open fractures will act as capillary barriers and water existing as films on the fracture walls will be imbibed into the fracture matrix. (mechanism 6 in Figure C-9) (Wang and Narasimhan (1985). In this case, water movement would be primarily within the low-permeability basalt matrix and would behave as Darcian flow. Other hypotheses that have non-Darcian flow regimes as their basis include film flow along the walls of the fractures and chaotic falling drips.

No matter what the mechanism of water movement in the fractures, there will still be some interaction with basalt matrix. The basalt matrix has been observed to have matric potentials in tensiometric range at the INEEL, indicating relatively wet conditions. This increases the likelihood of interaction between water in the basalt matrix with water moving in fractures. In the cases where water and contaminants interact between the fractures and the basalt matrix, a dual continuum representation is required for numerical simulation.

Under extremely dry conditions, it seems reasonable that the majority of water movement will be within the basalt matrix by Darcian flow. Under these conditions, some movement of water could still occur along fracture walls, however, as a result of heterogeneity and preferential pathways in the fractured basalt.

In any case, the fractured basalt is extremely heterogeneous with preferential pathways caused by the presence of fractures. When water movement occurs in the preferential pathways, only a limited portion of subsurface is involved in transmitting water. Some portions of basalt flows are more fractured than others, according to the geologic model (Knutson et al. 1992).

The extent to which water moves horizontally while vertically transiting the fractured basalts is uncertain. Under conditions of a wetting front resulting from ponding in the Large Scale Infiltration Test, evidence of lateral water movement in the region under the basin was observed. However, on a larger scale there was no evidence of lateral migration even 50 ft outside the basin as water moved primarily vertically downwards. This was the case until the infiltrating water encountered a sedimentary interbed, perched, and then spread laterally.

If no sedimentary interbeds are present at a location where infiltration occurs, rapid water movement down to the aquifer will occur. This rapid movement down through the vadose zone has been observed in USGS monitoring wells on the INEEL (USGS 1963). At one location on south central portion of the INEEL, Well 5 showed a definite rise in water level about 15 to 20 days after the beginning of the spring thaw that was attributed to infiltration of snowmelt in local basins at land surface.

C2.5 Water Interaction with Sedimentary Interbeds

Where sedimentary interbeds are present in the subsurface, they have a large effect on downward movement of water. This occurs because of a permeability contrast between the interbed, the fractures, and basalt matrix. One primary result of this contrast is the development of perched water in association with the interbeds.

The exact mechanism causing perching is unknown but is hypothesized to include the following:

- Low permeability lenses within interbeds
- Low permeability of interbeds compared to fractured basalt
- Infilling of fractures both above and below the interbeds with clay particles.

Most fractures in the subsurface have a clay lining (Rightmire and Lewis 1987). These clay particles can be hypothesized to migrate with pulses of infiltrating water. It is easy to conceptualize these particles migrating downward to the interbed through the open fractures where they then get filtered out when the water encounters the interbed. As these particle accumulate above the interbed, they fill up the fracture. Because these particles are primarily fine-grained clay, they have a low permeability. If the basalt matrix over the interbed has a low enough permeability, the combination of the basalt matrix and the clay-filled fracture also will have a low permeability and will lead to development of perched conditions. An example of this situation has likely been observed at the SDA. As a vadose zone monitoring well (Well USGS-92) was being drilled at the SDA, perched water was observed while the well was being drilled in basalt above an interbed at a depth of approximately 200 ft. As the drilling just proceeded into the interbed at this location, the perched water drained into the interbed. Drilling stopped and the interbed portion of the wellbore was sealed. Perched water recovered and has been present since 1972.

Infilling of fractures below the interbeds could result by several methods. Mobilization of fine clay-particles could occur as a result of transient pulses of water impact the interbeds. More likely is that the infilling occurred when the basalt flows were first exposed at land surface as surficial sediments were laid down to become future interbeds.

Because the interbeds are composed of porous sediments, Darcian flow is believed to describe water movement across the interbeds. Though they are limited in vertical extent, the interbeds do have some capacity to store transient pulses of water from above and release them more slowly to the underlying fractured basalt. This storage capacity results in a damping of transient infiltration pulses as water from an infiltration event moves vertically across a sequence of interbeds. This conceptual damping has been captured in numerical simulations of subsurface flow and transport performed for the SDA and INTEC facilities.

Water that transits the interbeds will enter the underlying basalts via the same mechanisms that were discussed above for the migration of water from the surficial sediments down into the fractured basalt.

C2.6 Infiltrating Water Reaches Snake River Plain Aquifer

Eventually, water infiltrating at the surface of the INEEL will reach the underlying Snake River Plain Aquifer. Though the aquifer is not technically part of the vadose zone and, therefore, not in the scope of this document, nonetheless some important interactions occur as the water that infiltrated at the surface encounters the aquifer.

In the majority of locations, this encounter between infiltrated water and the aquifer is expected to occur within fractured basalt because fractured basalt comprises the majority of the vadose zone. The presence of fractures makes a large capillary fringe zone unlikely. The degree of interaction between the infiltrating water and water flowing horizontally within the aquifer depends on water velocity within the aquifer. This horizontal velocity is spatially variable because of spatial variability of hydrologic properties and preferential pathways within the aquifer.

Changes in water levels in the aquifer have been observed over periods of weeks to months. As the water level rises or falls, the movement of water (and contaminants) from the vadose zone into the aquifer will be affected. Within the aquifer, horizontal permeability generally becomes more important than the vertical permeability.

C2.7 Summary

This section provides a discussion of the various mechanisms that are thought to control water movement in the various portions of the subsurface. The level of confidence varies between the sediment portions of the subsurface where the flow mechanisms are reasonably well understood and the fractured basalt portions where the mechanisms are less well known.

C3. PHYSICAL PROCESSES OF CONTAMINANT TRANSPORT IN THE VADOSE ZONE

Contaminant mass transport in the vadose zone is affected by a number of processes including the physical phase that the contaminant occupies and the transport mechanisms within each phase. These processes are mathematically described in numerical transport models in an attempt to predict contaminant distribution, concentration, or flux, both spatially and temporally. Concurrent with the physical transport, chemical processes transform the contaminant during its transport, further complicating the prediction. It is important to conceptually understand the possible transport mechanisms and chemical transformation of the contaminant along with the correct mathematical description in the numerical model to correctly predict the contaminant distribution. Furthermore, an understanding of the processes and the scale in which they are applicable is required to make the necessary parameter measurements needed for the numerical predictive model. This section briefly describes the physical processes of contaminant transport. Chemical processes are described in the following section.

The type of contaminant, method of release, and vadose zone properties all determine the physical phases that the contaminant occupies for mass transfer. Potential physical mechanisms for contaminant transport include (1) mass flux of the dissolved chemical movement within the soil-water, (2) gaseous mass flux through the void space, (3) pure liquid mass flux through the soil pores, and (4) the sorbing of contaminants onto colloidal particles and subsequently transport with the soil-water. An illustration of the source term and contaminant migration conceptual model for the INEEL vadose zone is provided in Figure C-10.

Advection and dispersion in the water phase transport contaminants dissolved in the pore water. The rate of advective transport is equal to the average linear velocity of the water. Dispersion describes the spreading phenomenon of a contaminant in a porous medium. It is a nonsteady irreversible process in the sense that if the flow were reversed, the initial distribution of the contaminant could not be recreated. The current state of scientific knowledge assumes that dispersion comprises two processes: mechanical dispersion and molecular diffusion. The mechanical dispersion is created by velocity variations at the microscopic level. Molecular diffusion is caused by the random movement of contaminant molecules in a fluid creating a flux from higher to lower concentrations.

Organic liquids and some inorganic materials have the potential for transport in the gas phase. In addition, some radionuclides (mainly ^{14}C as CO_2 or as CH_4, and ^{3}H as water vapor) also can be transported in the gas phase. Contamination within the gas phase usually results from the partitioning of the contaminant from a liquid or dissolved phase by vaporization or biological processes and is highly dependent on the temperature. Mass transport within the gas phase occurs by diffusion and by convection (if the gas phase is moving). A common assumption is that no gas advection occurs. However, researchers have suggested that this may not be the case in fractured systems because of barometric pressure fluctuation.

Nonaqueous-phase liquids (NAPLs) can be transported through the vadose zone as a pure phase. A NAPL is an organic liquid that is immiscible with water and, therefore, exists as a liquid phase that is separate from water. Nonaqueous phase liquids can be classified based on their density relative to that of water. A light nonaqueous phase liquid (LNAPL) is less dense than water, and a dense nonaqueous phase liquid (DNAPL) is more dense than water. Because of these density contrasts, the behavior of LNAPLs and DNAPLs in the subsurface is quite different. Light nonaqueous phase liquids float at the water table and thus their depth of penetration is limited, while DNAPLs sink below the water table and thus can penetrate to great depths in groundwater systems.

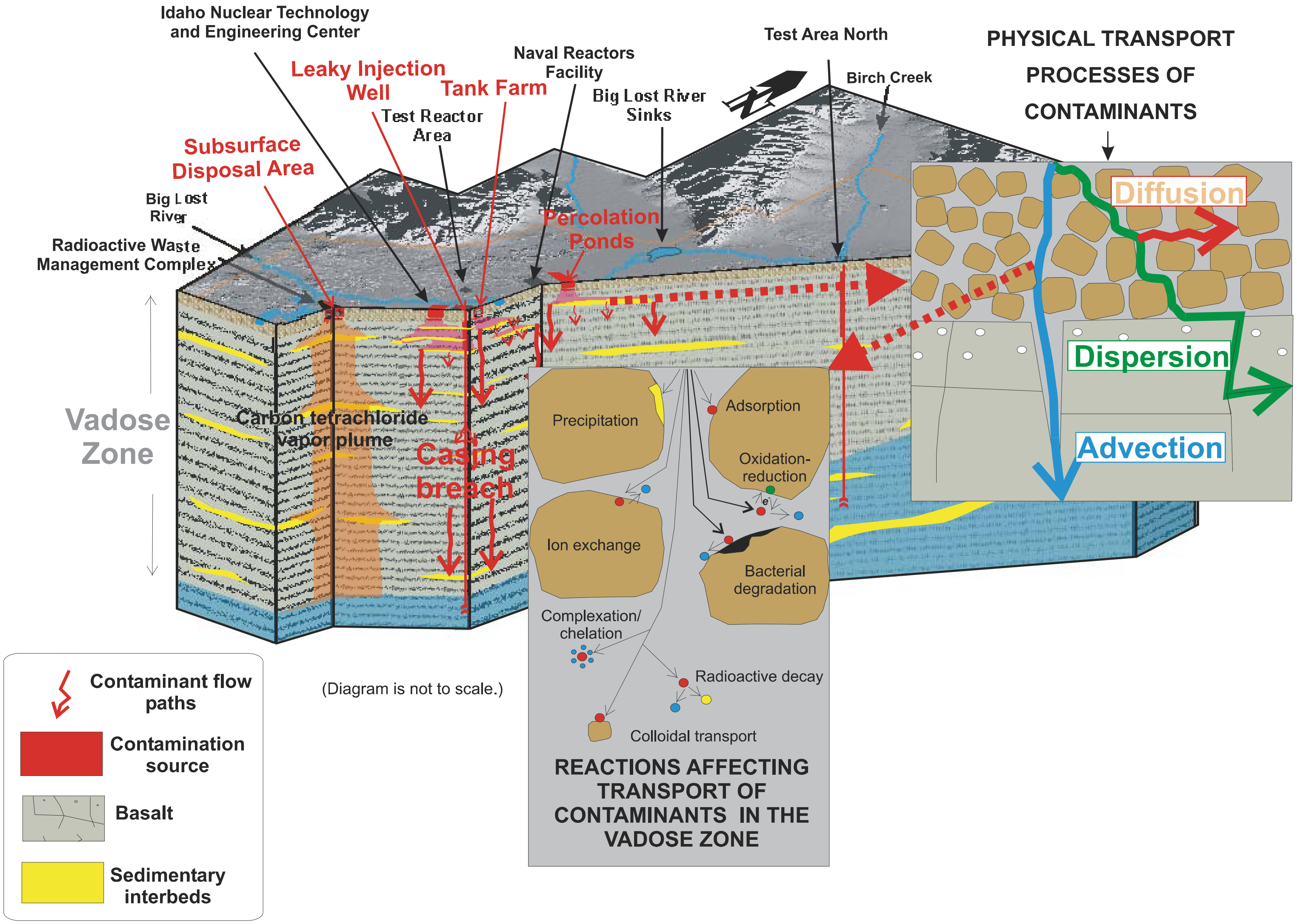


Figure C-10. Source term and contaminant migration conceptual model of the vadose zone at the INEEL.

Pressure and gravitational gradients drive NAPL transport in the vadose zone. The movement of a NAPL away from the initial source area can subsequently serve as an additional source for dissolved or gas phase transport. The extent of NAPL transport is dependent on the volume of the NAPL release, the area of infiltration, the time duration of the release, properties of the NAPL and the media, and subsurface flow conditions (Mercer and Waddell 1993). Residual NAPLs can be a source of subsequent gas and dissolved phase transport.

Colloidal transport of contaminants can be viewed as special case of contaminant transport. Colloidal transport of contaminants occurs when contaminants sorb onto small particles (10^{-6} to 10^{-9} m) and are subsequently transported with the advective flux of the water. Plutonium and ^{60}Co and possible ^{137}Cs migration have been attributed to colloidal-assisted transport at Hanford (Boutin 1999). Chemically and physically, colloids behave differently from dissolved species. Some researchers have concluded that contaminated colloids can be transported faster than if the contaminant were in its dissolved form. Conversely, colloids may be retarded by filtration in the soil. Colloidal transport becomes more likely in saturated or unsaturated fracture flow (Parsons, Olague, and Gallegos 1991).

Multi-phase transport must be considered in evaluating the overall mass transport of a contaminant within vadose zone environments. A contaminant can occupy one or multiple phases and the rate of transport within each of these phases can vary in both direction and magnitude. Contaminant transport is further complicated by the interaction between the phases and the chemical processes that occur in each phase. Care must be taken to incorporate all of the processes involved in contaminant transport within vadose zone environments.

C4. VADOSE ZONE GEOCHEMICAL CONCEPTUAL MODEL

As water moves through the soil matrix, reactions transfer dissolved constituents between solution (aqueous phase) and solid, vapor, and biological phases. Biogeochemical reactions can significantly alter the rate at which contaminants move relative to the rate at which water moves. These phase transfers generally retard the rate of contaminant movement; however, transfers to the vapor phase (^{14}C, tritium, and volatile organic compounds) can increase the rate of migration.

C4.1 Biogeochemical Processes

The important processes in biogeochemistry are surface adsorption, dissolution – precipitation, oxidation – reduction, complexation, volatilization, and biotransformation. Biogeochemical reactions are described by the law of mass action that indicates that chemicals react in definite proportions and that matter is conserved during reactions. The applicability of the law of mass action to a wide range of biogeochemical reactions is illustrated by the decrease in uranly ion ($UO2^{+2}$) adsorption above a pH of 8 (Figure C-11) as a side effect of the decomposition of organic matter by microbes.

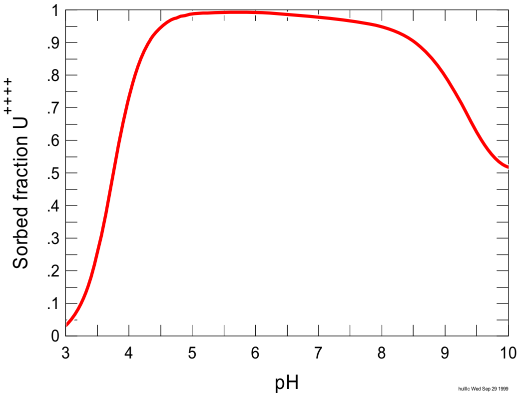


Figure C-11. Fraction of uranium adsorbed from solution as a function of pH. At low pH, hydrogen ion competes for exchange sites with uranyl. At high pH, carbonate complexing with uranyl inhibits adsorption. ΣU = 10^{-6} molar, ΣC = 10^{-3} molar.

Microbes oxidize organic matter [CH_2O] to water [H_2O] and carbon dioxide [CO_2] using dissolved oxygen [O_2] and releasing energy that the microbes use to live.

$$CH_2O + O_2(aq) \xrightarrow[\text{microbes}]{} CO_2(aq) + H_2O$$

$$O_2(g) \longleftrightarrow O_2(aq)$$

$$CO_2(aq) \longleftrightarrow CO_2(g)$$

Oxygen is dissolved from the vadose zone vapor phase and carbon dioxide released to the vapor phase to compensate for the changes in aqueous concentrations from the reaction. The presence of a vapor phase is important to this reaction, and so vadose zone biogeochemical activity is tied to hydrology as the water content controls the gas-filled porosity and the transport of nutrients. If the rate of oxygen consumption exceeds the rate of oxygen replenishment, reducing conditions will develop. Under reducing conditions, microbes can use other electron receptors to survive.

Carbon dioxide in the vadose zone reacts with water to form carbonic acid [H_2CO_3]. Carbonic acid reacts with soil minerals such as calcite [$CaCO_3$ (s)], dissolving the minerals and releasing solutes to the aqueous phase.

$$CO_2(aq) + H_2O \longleftrightarrow H_2CO_3$$

$$CaCO_3(s) + H_2CO_3 \longleftrightarrow Ca^{+2} + 2HCO_3^-$$

Some of these reactions are reversible, and when vadose zone water is lost by evapotranspiration, minerals can precipitate from solution.

The dissolution of minerals by carbonic acid consumes hydrogen ion, raising the pH, and increases the concentration of dissolved carbonate $[HCO_3^-]$. Dissolved carbonate forms aqueous complexes with metals such as uranyl $[UO_2^{+2}]$. Geochemical reactions depend on the concentration of the free ions in solution. As carbonate complexes the uranyl ion, the concentration of free ion in solution decreases, though the total amount of uranium in solution remains the same:

$$UO_2^{+2} + nHCO_3^- \longleftrightarrow UO_2(CO_3)_n^{-2(n-1)} + nH^+$$

$$UO_2^{+2} + \equiv SOH^0 \longleftrightarrow \equiv SOUO_2^+ + H^+$$

By decreasing the free uranyl concentration in solution, carbonate complexing decreases the amount of uranyl that can be removed by forming surface complexes on mineral adsorption sites in the soil $\left[\equiv SOH^0\right]$.

Uranium buried in waste can be present in a variety of forms. Frequently, metallic uranium has been oxidized to uraninite (UO_2) or U_3O_8 prior to disposal at the Subsurface Disposal Area. Uranium oxides are not stable in oxidizing conditions in contact with water with respect to uranium hydroxide (Schoepite) (see Figure C-12), and hydration reactions will occur in the waste.

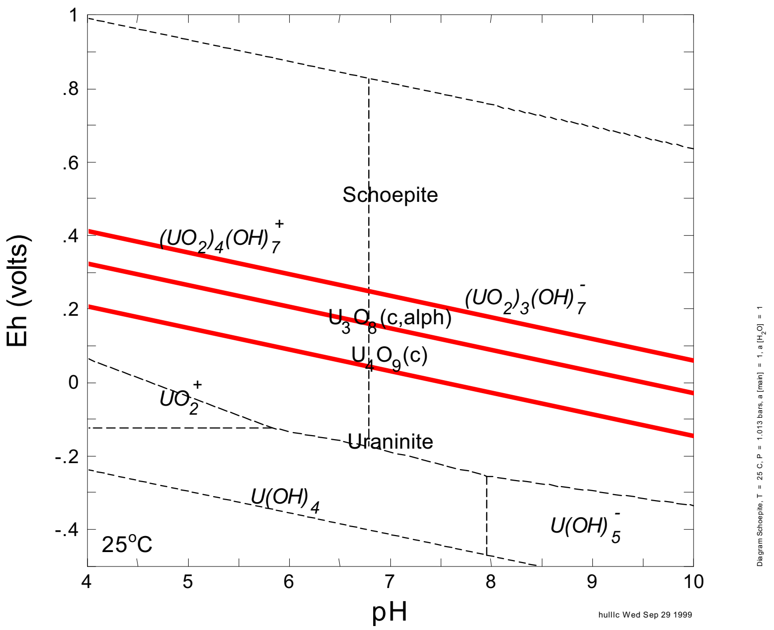


Figure C-12. Eh-pH diagram of uranium stability relations. Italicized text indicates aqueous species, standard text indicates solid phases, dotted lines separate stability fields for aqueous species, and solid lines separate stability fields of solid phases. The upper diagonal dashed line represents the upper boundary of the stability field of water.

In oxidizing conditions, the concentration of free uranium in solution is controlled by Schoepite mineral solubility. The concentration of uranium in solution is on the order of 10^{-6} to 10^{-5} molar at a neutral pH (see Figure C-13). If microbial action depletes the dissolved oxygen in the waste and conditions become reducing, then Schoepite will not be stable relative to the oxides, and uraninite is likely to control the concentration of uranium in solution. Under reducing conditions, the concentration of uranium in solution in equilibrium with uraninite will be lower than 10^{-8} molar (see Figure C-14). Where the solubility of a uranium mineral phase controls the concentration of uranium in leachate migrating from a waste, reducing conditions in the waste will result in a two order of magnitude decrease in the release of uranium from the waste.

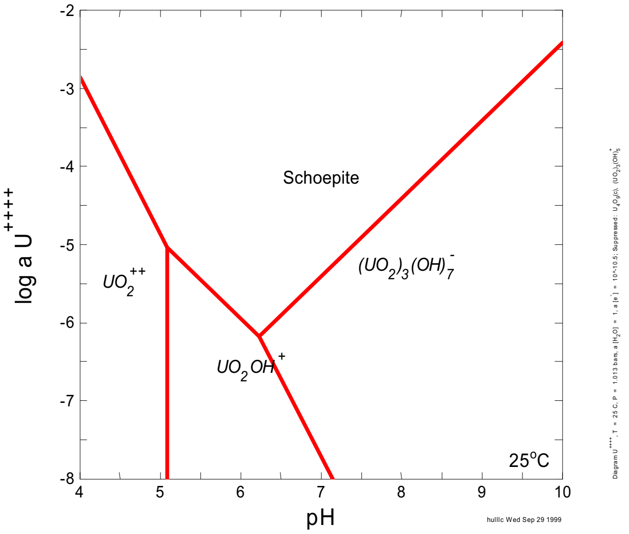


Figure C-13. Solubility of uranium in solution in equilibrium with Schoepite under oxidizing conditions.

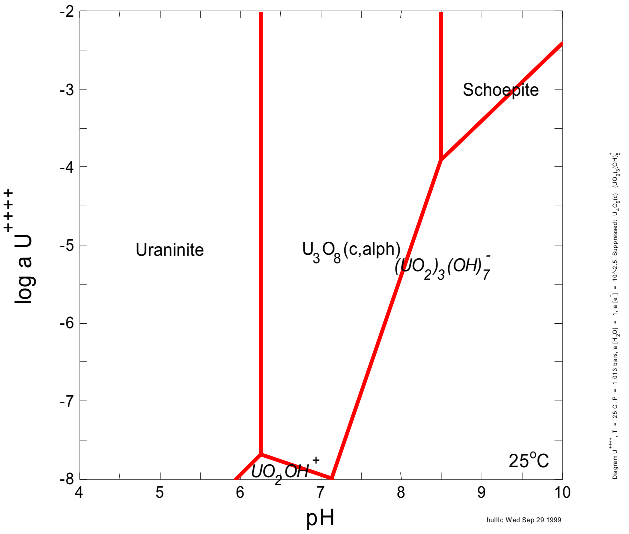


Figure C-14. Solubility of uranium in solution in equilibrium with uraninite and U_3O_8 under reducing conditions.

$$U_3O_8 + \frac{1}{2}O_2 + 9H_2O \longleftrightarrow 3\,UO_2(OH)_2 \bullet 2H_2O \quad (\textit{Schoepite})$$

C4.2 Mineral and Solution Equilibria

Thermodynamic data to describe equilibrium between species in solution and between solutions and solid mineral phases are reasonably well developed, even for actinide radionuclides (Grenthe et al. 1992; Silva et al. 1995; Spahiu and Bruno 1995). The aqueous model describes the interaction of inorganic and organic chemicals in aqueous solution. The aqueous model calculates the activities of species in solution and the reactions between solution and inorganic chemicals.

C4.2.1 Speciation Model

The most common aqueous geochemical model is a chemical speciation model where ions in solution are speciated based on an ion pairing model (Serne, Arthur, and Krupka 1990; Steefel and MacQuarrie 1996; Lieser 1995). Ion activities are determined using the Debeye-Huckel or Davies equations. These equations limit the model applicability to relatively low ionic strength solutions. The model could be extended to higher ionic strengths using the Pitzer equations (Harvie, Moller, and Weare 1984; Suarez and Simunek 1996, 1997). For soil waters in an arid environment, or for waste disposal situations, the ability to model high ionic strength solutions could be advantageous. The availability of data for the Pitzer equations for heavy metals and radionuclides is not known and the availability of thermodynamic data may significantly hinder the implementation of Pitzer equations.

C4.2.2 Equilibrium Processes

For geochemical reactions that are rapid and reversible, an equilibrium model is used. Chemical reactions that take place within the aqueous phase usually occur quickly enough that equilibrium is maintained (Morel 1983). For other reactions, the rate of reaction must be compared to the time scale of interest. Often partial equilibrium models or pseudoequilibrium models are acceptable. To be able to predict biogeochemical changes with time in a soil-water system, however, a kinetic description of biogeochemical reactions is needed.

C4.2.3 Redox

Oxidation-reduction reactions are driven by microorganisms. The reactions microorganisms use for energy must be thermodynamically favorable (Chapelle 1993). This depends on the geochemical environment of the subsurface. Electron exchanges between redox pairs will be driven by the availability of food and substrate. There are a few inorganic redox reactions, such as oxidation of ferrous iron by ferric iron, that are likely to occur (Scharer et al. 1993). There should be a very close link between the biological degradation model and the inorganic solution model because all components will have to be conserved across both types of reactions (Yeh and Salvage 1997; McNab and Narasimhan 1994, 1995; Humphreys et al. 1995). This suggests that setting up the biological reactions and the inorganic reactions in the same form and solving together with the same algorithm is the most efficient way to run the model.

C4.3 Adsorption on Mineral Surfaces

Over a number of years, a theoretical basis for describing adsorption reactions onto mineral surfaces has been developed. An extensive base of experimental data on the adsorption of metals and anions onto single minerals in laboratory experiments is available. However, this approach has not been extended to deal with mixtures of minerals or to natural vadose zone materials. This application of mechanistic adsorption to natural materials is currently the largest gap in our ability to model the migration of contaminants in the environment.

The K_d approach provides an empirical description of the retardation of a contaminant moving with groundwater. Mechanistic models have been developed to describe the adsorption process (Appelo 1996; Appelo and Postma 1996; Davis and Kent 1990; Dzombak and Morel 1990). While these mechanistic models have not yet been widely applied in radioactive waste site assessments, applications are being developed for Yucca Mountain (Triay et al. 1997) and the Nuclear Regulatory Commission (Kent et al. 1988). The empirical K_d approach cannot address the effects of large pH changes during neutralization of waste solutions or changes in solution composition as high ionic strength waste solutions are diluted. The mechanistic models can explicitly account for changes in solution chemistry. On the other hand, the mechanistic models are computationally very intensive, and are not suitable for complex three-dimensional transport simulations. Therefore, mechanistic models and geochemical codes can be used to model the release and transport of contaminants near the source where solution chemistry is changing rapidly. Mechanistic models and geochemical codes can be used to calculate K_d values for use in the fate and transport code away from the source where solution chemistry is stable.

Mechanistic models describe interactions between aqueous species and mineral surfaces that occur through electrostatic and covalent bonds. Ion exchange reactions are primarily electrostatic and depend on the attraction between negatively charged mineral surfaces and cations in solution. Surface complexes form a covalent chemical bond between a site on the mineral surface and an ion, and can form even when the surface and the ion have opposite charges.

C4.3.1 Ion Exchange

Clay minerals are the most common ion exchange media in soil and develop a fixed, negative surface charge by lattice substitution of trivalent cations for silica (Al^{+3} for Si^{+4}) in tetrahedral sites and substitution of divalent cations for aluminum (Mg^{+2} for Al^{+3}) in octahedral sites. The negative charge is balanced by attracting cations from solution to the surface of the clay. Exchange sites on clays are preferentially filled by ions with higher charge density (small hydrated size, large charge). Some ions that are themselves fairly small (lithium, sodium) are hydrated, and the hydrated ion is larger than some of the larger cations (cesium, strontium). The order of preference for ion exchange depends primarily on ionic properties, not clay properties. The clay determines the total capacity, but the preference depends on the ion. The general order of selectivity for exchange sites for divalent cations is (Deutsch 1997)

$$Pb^{+2} > Ba^{+2} \approx Sr^{+2} > Cd^{+2} \approx Zn^{+2} \approx Ca^{+2} > Mg^{+2} \approx Ni^{+2} \approx Cu^{+2} > Mn^{+2} > Fe^{+2} \approx Co^{+2}.$$

Divalent cations have a greater selectivity than monovalent cations.

An ion exchange reaction is written as a mass-balance chemical reaction:

$$Na^{+} + 1/2CaX_2 \leftrightarrow 1/2Ca^{+2} + NaX$$

with

$$K_{Na/Ca} = \frac{[NaX][Ca^{+2}]^{0.5}}{[CaX_2]^{0.5}[Na]^{+}}$$

where

X = Cation exchange site concentration (moles/L)

$K_{Na/Ca}$ = Selectivity coefficient for sodium – calcium exchange.

Ion exchange reactions are written as if all the exchange sites were filled at all times. The exchange coefficients, therefore, represent the relative strength of the ion exchange reaction. Selectivity coefficients have been determined and are published in the literature (Appelo and Postma 1996). These coefficients are not thermodynamic equilibrium coefficients. Site-specific data are needed to develop selectivity coefficients for INEEL materials. An ion exchange approach was successfully used to model strontium-90 migration in the presence of competing cations for a glacial outwash aquifer (Kipp, Stollenwerk, and Grove 1986).

Because strontium is one of the most preferred cations for ion exchange, it will compete successfully with other cations for exchange sites. Hydrogen ion is hydrated, and has a fairly low charge density. As a result, hydrogen ions do not compete well for exchange sites. Using the selectivity coefficients determined for INEEL soils, and ion exchange theory, the effects of low pH and competing cations can be explicitly included in a calculation of strontium adsorption.

C4.3.2 Surface Complexation

Surface complexation is the formation of a chemical bond between an ion and a reactive surface site on a mineral surface. There are several levels of complexity in mechanistic surface complexation models. At the simplest level, a mineral surface can have a surface charge that depends on the pH of solution. The surface hydroxide groups on the mineral surface act as a diprotic acid and can gain or loose hydrogen ions:

$$\equiv SOH_2^+ \leftrightarrow \equiv SOH^0 + H^+$$

$$K_{a1} = \frac{[\equiv SOH^0][H^+]}{[\equiv SOH_2^+]}$$

$$\equiv SOH^0 \leftrightarrow \equiv SO^- + H^+$$

$$K_{a2} = \frac{[\equiv SO^-][H^+]}{[\equiv SOH^0]}$$

where

$\equiv SOH^0$ = Surface hydroxide group on a soil oxide mineral (moles/L)

K_{a1}; K_{a2} = Apparent acidity constants.

The mineral surface can have a positive, neutral, or negative charge depending on solution pH. The equilibrium constants for gain and loss of a proton (K_{a1} and K_{a2}) have been measured for soil oxide phases such as FeOOH, AlOOH, and SiO_2.

Cations in solution form complexes with the surface site as described by a chemical mass-balance reaction:

$$\equiv SOH^{0} + M^{+m} \leftrightarrow \equiv SOM^{+(m-1)} + H^{+}$$

$$K_i = \frac{[\equiv SOM^{+(m-1)}][H^{+}]}{[\equiv SOH^{0}][M^{+m}]}$$

where

K_i = intrinsic equilibrium constant for adsorption.

This reaction releases a hydrogen ion into solution, and so the equilibrium between the free metal in solution and the adsorbed metal on the surface will depend on pH. At low pH, the metal may not be able to replace a hydrogen ion on the surface, and adsorption will be decreased (see Figure C-11). The adsorption equation is written in terms of the concentration of the free metal in solution. If complexing agents are present in solution, they will take some of the free metal ion and sequester it in solution in the form of a complex. The complexed metal is “hidden” from the surface reaction, and does not take part in the formation of the surface complex. This simple mechanistic approach can address pH effects and solution chemistry effects on adsorption of metals onto minerals. It has been applied to laboratory studies (Kohler et al. 1996) and field investigations (Furrer, von Gunten, and Zobrist 1996; Kent et al. 1999; Kent and Maeder 1999). This approach would permit addressing the low pH of the waste solutions, complexing with organic chelating agents, and the formation of inorganic complexes with fluoride, phosphate, carbonate, or other ligands in solution.

C4.3.3 Modeling and Implementation

A surface complexation model should be used for solid phases where the surface charge is dependent on pH and ionic strength (Dzombak and Morel 1990). Surface complexation is a common module in geochemical codes (Parkhurst 1995; Allison, Brown, and Novo-Gradac 1991; Serne, Arthur, and Krupka 1990). Surface complexation modeling is less commonly implemented in reactive transport codes (Yeh and Salvage 1997). Implementation of surface complexation depends on development of a partition coefficient between the aqueous activity and the surface activity of species. Because surface oxy-hydroxide sites have such a range of site energies, a single partition coefficient does not describe the solution-surface interaction well. A number of papers have addressed the development of coefficients to describe surface complexation reactions in complex soil systems with multiple sites (Westall et al. 1995; Cernik, Borkovec, and Westall 1995). This is an area that requires additional investigation, but one that could have significant benefits to predictive modeling of radionuclides and heavy metals.

C4.4 Mineralogy

Adsorption is a surface phenomenon and depends on mineral surfaces. The mineralogy of sediments and basalts has been investigated at the INEEL. The mineralogy of the Big Lost River alluvium is quartz (32 to 45%), plagioclase feldspar (16 to 30%), clay minerals (8 to 14%), potassium feldspar (6 to 18%), pyroxene (8 to 14%), and calcite or dolomite or both (2 to 6%) (Bartholomay 1990). The clay minerals identified in the alluvium are illite, smectite, mixed-layer illite-smectite, kaolinite, and chlorite. The clay minerals are detrital and have not formed in place by weathering (Knobel, Bartholomay, and Orr 1997). At some locations, the gravel is lightly cemented or coated by secondary calcite. Analysis of coatings on the alluvium indicates that the composition is 45% silica, 45% calcite, 5% iron oxide, and 5% aluminum oxide (Nace et al. 1975).

The carbonate (calcite and dolomite) grains and coatings provide rapid acid neutralization and pH buffer capacity, as well as ion exchange sites for strontium. The clay minerals provide sites for adsorption of cationic contaminant species such as Sr^{+2} and PuO_2^{+2}, and the iron and aluminum oxide coatings provide a range of sites having positive, negative, and neutral charges. At very low pH (i.e., pH of less than 3), the surfaces of oxides are positively charged, and cation adsorption reactions are inhibited. As the pH of solution rises, cation adsorption increases significantly in the pH range of 4 to 6. Oxide coatings also provide sites for adsorption of both cations and anionic contaminant species such as $PuO_2(CO_3)_2^{-2}$.

Beneath the surficial alluvium lie 600 to 900 m (2,000 to 3,000 ft) of layered basalt flows and interbedded sediments (Nace et al 1975). The basalt flows are characterized as overlapping lobes of basalt intermixed with larger basalt flows of relatively uniform thickness beneath the INTEC. The sediments found between the basalt flows are often discontinuous and characterized by sequences of sand, silt, clay, and lesser amounts of gravel (Mundorf, Crosthwaite, and Kilburn 1964).

A number of studies of basalt mineralogy are summarized by Knobel, Bartholomay, and Orr (1997). Key findings of these studies are that the mineralogy of the Snake River Plain basalt is remarkably uniform in composition, and that very little weathering of basalt is noted in this section. Fractures and vesicles in basalt can contain sediments washed into the basalt after cooling. These sediments are generally fine-grained silt- and clay-sized particles consisting of quartz and clay minerals with lesser amounts of feldspar, calcite, and pyroxene.

The sedimentary interbeds are primarily composed of sand and silt, with some small clay lenses. The majority of the interbeds are thin (0.3 to 1.5 m [1 to 5 ft]) layers of silt that were deposited in eolian or fluvial environments between the major basalt flows. The mineralogy of the interbeds is similar to the alluvium, with the composition of quartz (18 to 39%), plagioclase and potassium feldspar (26 to 42%), clay minerals (0 to 42%), and pyroxene (0 to 41%). Dolomite is absent and calcite is variable (0 to 28%). Identified clay minerals include illite, smectite, mixed-layer illite-smectite, kaolinite, and chlorite (Knobel, Bartholomay, and Orr 1997). Clay minerals were identified as detrital and commonly have reddish coatings of ferric oxyhydroxides (Rightmire 1984; Rightmire and Lewis 1987).

Clay and iron oxide minerals provide the greatest amount of radionuclide retardation within the interbed portion of the groundwater flow path. A complication, however, is that the percentage of these minerals spatially varies, as does the thickness of the interbeds. Multiple pathways exist for water infiltrating through the vadose zone because infiltrating water may be deflected and move laterally along an interbed for some distance before resuming a vertical path. The actual distance traversed by infiltrating water through the interbeds and the amount of sorptive surfaces encountered by infiltrating water within the interbeds are not accurately predictable.

C4.5 Reaction Kinetics

For geochemical reactions that are rapid and reversible, equilibrium among reactants can be assumed. Chemical reactions that take place within the aqueous phase usually occur quickly enough that equilibrium is maintained. For other reactions, the rate of reaction must be compared to the time scale of interest. Often partial equilibrium models or pseudoequilibrium models are acceptable. For geochemical reactions that are slow or irreversible, data for a kinetic model are needed. Kinetic processes have been incorporated into a number of geochemical transport and reaction codes (Lichtner 1996; Suarez and Simunek 1996, 1997; Yeh and Salvage 1997). Generally, these codes deal with a carefully selected set of potential geochemical reactions to study well-defined systems. Lichtner (1996) modeled weathering of silicate rocks and Suarez and Simunek (1996, 1997) modeled the system calcium-carbonate-sulfate in soils under irrigated agriculture. When dealing with well-constrained systems, a kinetic approach can be successfully applied. Generally, kinetic data that can be applied to field conditions are lacking for inorganic geochemical systems (Morel 1983). The many variables present in soil environments are not usually addressed in laboratory kinetic investigations.

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