

INEEL Subregional Conceptual Model Report

*Volume 2: Summary of Existing Knowledge
of Geochemical Influences on the Fate and
Transport of Contaminants in the Subsurface
at the INEEL*

September 2003



*Idaho National Engineering and Environmental Laboratory
Bechtel BWXT Idaho, LLC*

INEEL Subregional Conceptual Model Report

**Volume 2: Summary of Existing Knowledge of Geochemical Influences on the
Fate and Transport of Contaminants in the Subsurface at the INEEL**

September 2003

**Idaho National Engineering and Environmental Laboratory
Idaho Falls, Idaho 83415**

**Prepared for the
U.S. Department of Energy
Assistant Secretary for Environmental Management
Under DOE Idaho Operations Office
Contract DE-AC07-99ID13727**

CONTENTS

1.	INTRODUCTION	1-1
2.	OVERVIEW OF GEOCHEMICAL CONCEPTUAL MODELS	2-1
3.	PROCESSES THAT CONTROL GEOCHEMICAL EVOLUTION AND TRANSPORT IN THE SUBSURFACE.....	3-1
3.1	Advection and Dispersion.....	3-1
3.2	Dissolution and Precipitation	3-1
3.2.1	Thermodynamic Controls on Dissolution and Precipitation	3-2
3.2.2	Kinetic Controls on Dissolution and Precipitation.....	3-3
3.2.3	Congruent and Incongruent Dissolution	3-3
3.2.4	Coprecipitation.....	3-3
3.3	Sorption/Desorption	3-4
3.3.1	Effect of Sorption and Desorption on Contaminant Transport	3-4
3.3.2	Alternative Approaches for Describing Sorption.....	3-5
3.4	Matrix Diffusion	3-10
3.5	Transformation.....	3-11
3.5.1	Aqueous Speciation Based on pH-Eh Conditions.....	3-12
3.5.2	Complex Formation	3-15
3.5.3	Biologically-Mediated Transformations	3-16
3.6	Facilitated Transport	3-16
3.6.1	Complex Facilitated Transport.....	3-18
3.6.2	Colloid-Facilitated Transport.....	3-18
3.7	Equilibrium versus Kinetic Models	3-19
4.	GEOCHEMICAL COMPOSITION OF UNCONTAMINATED GROUNDWATER BENEATH THE INEEL	4-1
4.1	Geochemical Evolution.....	4-1
4.2	Observed Composition of Uncontaminated Groundwater Beneath the INEEL and Vicinity.....	4-2
4.2.1	Olmsted 1962	4-2
4.2.2	Robertson et al., 1974	4-6
4.2.3	Curtis 2000.....	4-8
4.3	Vertical Variation in Solute Composition.....	4-8

4.3.1	Olmsted	4-8
4.3.2	Robertson et al.	4-8
4.3.3	Mann 1986	4-9
4.4	Sources of Water and Solutes in the Aquifer Beneath the INEEL.....	4-15
4.4.1	Precipitation	4-15
4.4.2	Tributary Basins (including both underflow and surface water).....	4-16
4.4.3	Water Diverted for Irrigation	4-20
4.4.4	Thermal Waters.....	4-20
4.4.5	Water – Rock Interaction / Diagenesis.....	4-20
4.5	Geochemical Models Incorporating Mixing and Diagenesis that Account for Solute Geochemistry in Groundwater Beneath the INEEL and Vicinity	4-21
4.5.1	Robertson et al. 1974	4-21
4.5.2	Wood and Low.....	4-23
4.5.3	McLing.....	4-26
4.5.4	Knobel et al.	4-27
4.5.5	Busenberg et al.....	4-35
4.6	Groundwater Age Studies and Evidence for Fast Flow Paths	4-36
4.6.1	Luo et al.	4-36
4.6.2	Johnson et al.....	4-38
4.6.3	Roback et al.....	4-40
4.6.4	Busenberg et al. 2001.....	4-44
5.	EFFECT OF WASTE DISPOSAL ON GROUND WATER QUALITY	5-1
5.1	Survey by Robertson et al.	5-1
5.1.1	Nonradioactive Waste	5-1
5.1.2	Radioactive Components	5-3
5.1.3	Apparent Influences Observed on the Subsurface Behavior and Distribution of Wastes	5-4
5.1.4	Summary of Robertson et al. 1974.....	5-8
5.2	Disposal Methods Used at the INEEL	5-10
5.2.1	Injection Wells	5-10
5.2.2	Buried Waste.....	5-11
5.2.3	Infiltration Ponds and Ditches.....	5-11
5.2.4	Contaminated Surface Soils	5-11
5.3	Wastes and Contaminants Disposed in the INEEL Subsurface	5-12
5.3.1	Summary of types of wastes disposed at INEEL	5-12
5.4	Contaminants Observed in Perched Water and Groundwater Beneath the INEEL and Vicinity.....	5-17

6.	GEOCHEMICAL BEHAVIOR OF INEEL CONTAMINANTS OF CONCERN.....	6-1
6.1	Solubility of Contaminants at the Radioactive Waste Management Complex	6-1
6.2	Sorption Measurements for INEEL Contaminants of Concern and INEEL Media	6-4
6.2.1	Newman et al., 1996	6-4
6.2.2	Landa et al., 2000.....	6-6
6.2.3	Liszewski et al., 1997.....	6-8
6.2.4	Liszewski et al 2000.....	6-9
6.2.5	Pace et al 2001	6-11
6.3	Actinide Speciation and Sorption Calculations using Surface Complexation Models	6-14
6.4	Segregation of INEEL Contaminants of Concern into Classes with Similar Expected Behavior	6-18
6.4.1	Newman et al. 1995	6-18
7.	GEOCHEMICAL CONCEPTUAL MODELS DEVELOPED FOR INDIVIDUAL WASTE AREA GROUPS.....	7-1
7.1	Subregional Geochemistry	7-1
7.1.1	Contaminant Distribution.....	7-1
7.2	Test Area North.....	7-2
7.2.1	TSF-05 Injection Well	7-2
7.2.2	TSF-07 Disposal Pond	7-3
7.3	Test Reactor Area.....	7-3
7.3.1	Groundwater Geochemistry	7-3
7.3.2	Vadose Zone	7-3
7.3.3	Perched Water.....	7-4
7.4	Idaho Nuclear Technology and Engineering Center	7-5
7.4.1	Groundwater	7-5
7.4.2	Vadose Zone	7-5
7.5	Radioactive Waste Management Complex	7-5
7.5.1	Vadose Zone	7-6
7.5.2	Perched and SRPA Water	7-6
7.5.3	Conceptual Model.....	7-7
7.6	Naval Reactors Facility.....	7-9
7.6.1	Geochemical Transport Mechanisms.....	7-9

7.7	Argonne National Laboratory-West.....	7-10
8.	SUMMARY AND CONCLUSIONS.....	8-1
9.	REFERENCES.....	9-1

FIGURES

3-1.	Freundlich and Langmuir isotherm models.....	3-6
3-2.	Alternative speciation diagrams for iron.....	3-13
3-3.	Speciation diagrams for chromium (a) aqueous species (b) aqueous and solid species.....	3-14
4-1.	Spatial distribution of geochemical classes of groundwater.....	4-3
4-2.	Water temperature profile for INEL-1 test hole.....	4-11
4-3.	Chemical quality of water for open intervals in Water-Supply well and INEL-1 test hole.....	4-13
4-4.	Hydrochemical zones of groundwater at the NRTS and sources of chemically distinct recharge to the eastern Snake River Plain (shaded area).....	4-17
4-5.	Rock dissolution rate and groundwater residence time based on U Th decay series disequilibrium.....	4-37
4-6.	Contour plots of (A) $^{87}\text{Sr}/^{86}\text{Sr}$ and concentrations of (B) Li, (C) Si, (D) Na, and (E) Mg in groundwater, and (F) sampled well locations and locations of river channels.....	4-39
4-7.	(a) Important features and wells sampled (b) $^{234}\text{U}/^{238}\text{U}$ ratios in parts per million.....	4-41
4-8.	Location of natural and artificial recharge to the eastern Snake River Plain Aquifer at and near the Idaho National Engineering and Environmental Laboratory.....	4-47
4-9.	Flow velocity vector of ground water calculated from tritium/helium-3 ages of water from selected wells at and near the Idaho National Engineering and Environmental Laboratory.....	4-48

TABLES

4-1.	Water classification system (after Olmsted 1962).....	4-2
4-2.	Selected water-quality data from the INEL-1 water-supply well and INEL-1 test hole.....	4-12
4-3.	Dissolved species in precipitation near INEEL and in groundwater at the INEEL.....	4-16
4-4.	Reaction models used for interpreting the natural geochemistry of the Snake River Plain aquifer system.....	4-30
4-5.	Summary of conceptual models that account for the natural solute geochemistry of the Eastern Snake River Plain Aquifer.....	4-31

5-1. Liquid waste disposed to injection wells. 5-12

5-2. Liquid waste disposed to ponds and ditches. 5-13

5-3. Buried solid wastes. 5-15

5-4. Contaminated soil and buried waste sites. 5-15

5-5. Groundwater contaminants, sources, and maximum concentrations as listed by INEEL Waste Area Group. 5-17

5-6. Contaminant concentrations in the SRPA. 5-23

5-7. Contaminants listed by type (i.e., inorganic, radionuclide, organic, NAPL, DNAPL). 5-24

6-1. Summary of pH and redox regimes that minimize solubility for each of the contaminants of potential concern. 6-3

ACRONYMS

ARA	Auxiliary Reactor Area
BET	Branaur-Emmett-Teller (method)
BORAX	Boiling Water Reactor Experiment
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFA	Central Facilities Area
CFC	chlorofluorocarbon
DOC	dissolved organic carbon
EDL	electrical double-layer (theory)
ICPP	Idaho Chemical Processing Plan
INEEL	Idaho National Engineering and Environmental Laboratory
INTEC	Idaho Nuclear Technology and Engineering Center
IRA	Interim Risk Assessment
LPIT	large-scale pumping and infiltration test
MTR-ETR	Materials Testing Reactor – Engineering Test Reactor
NRF	Naval Reactors Facility
NRTS	National Reactor Testing Station
PBF	Power Burst Facility
RWMC	Radioactive Waste Management Complex
SC	surface complexation
SCM	surface complexation model
SDA	Subsurface Disposal Area
SI	saturation index
SRPA	Snake River Plain Aquifer
TAN	Test Area North
TC	total clays

TDS	total dissolved solids
TRA	Test Reactor Area
TSF	Technical Support Facility
USGS	United States Geological Survey
VOC	volatile organic compound
WAG	waste area group

INEEL Subregional Conceptual Model Report— Summary of Existing Knowledge of Geochemical Influences on the Fate and Transport of Contaminants in the Subsurface at the INEEL (Draft)

1. INTRODUCTION

This document summarizes previous descriptions of geochemical system conceptual models for the vadose zone and groundwater zone (aquifer) beneath the Idaho National Engineering and Environmental Laboratory (INEEL). The primary focus is on groundwater because contaminants derived from wastes disposed at INEEL are present in groundwater, groundwater provides a pathway for potential migration to receptors, and because geochemical characteristics in and processes in the aquifer can substantially affect the movement, attenuation, and toxicity of contaminants. The secondary emphasis is perched water bodies in the vadose zone. Perched water eventually reaches the regional groundwater system, and thus processes that affect contaminants in the perched water bodies are important relative to the migration of contaminants into groundwater. Similarly, processes that affect solutes during transport from near-surface disposal facilities downward through the vadose zone to the aquifer are relevant. Sediments in the vadose zone can affect both water and solute transport by restricting the downward migration of water sufficiently that a perched water body forms, and by retarding solute migration via ion exchange.

Geochemical conceptual models have been prepared by a variety of researchers for different purposes. They have been published in documents prepared by INEEL contractors, the United States Geological Survey (USGS), academic researchers, and others. The documents themselves are INEEL and USGS reports, and articles in technical journals. The documents reviewed were selected from citation lists generated by searching the INEEL Technical Library, the INEEL Environmental Restoration Optical Imaging System, and the ISI Web of Science databases. The citation lists were generated using the keywords ground water, groundwater, chemistry, geochemistry, contaminant, INEL, INEEL, and Idaho. In addition, a list of USGS documents that pertain to the INEEL was obtained and manually searched. The documents that appeared to be the most pertinent were selected for further review. These documents are tabulated in the citation list.

This report summarizes existing geochemical conceptual models, but does not attempt to generate a new conceptual model or select the “right” model.

This document is organized as follows. Geochemical models are described in general in Section 2. Geochemical processes that control the transport and fate of contaminants introduced into groundwater are described in Section 3. The natural geochemistry of the Eastern Snake River Plain Aquifer (SRPA) is described in Section 4. The effect of waste disposal on the INEEL subsurface is described in Section 5. The geochemical behavior of the major contaminants is described in Section 6. Section 7 describes the site-specific geochemical models developed for various INEEL facilities.

2. OVERVIEW OF GEOCHEMICAL CONCEPTUAL MODELS

The National Research Council (2001) defines a conceptual model as “an evolving hypothesis identifying the important features, processes, and events controlling fluid flow and contaminant transport of consequence at a specific field site in the context of a recognized problem.” A geochemical conceptual model can be described as the combination of solid, aqueous, and gaseous phases that comprise the system of interest, and the equilibrium and kinetic reactions that control the distribution and concentrations of species of interest in the system. A conceptual model identifies the components and processes that are most important to the particular question that is being investigated. Hence, there could be multiple conceptual models for the same physical system, depending on the particular question of interest.

The first type of geochemical models considered here, the natural system models, describes the natural geochemical system in the Eastern SRPA, and attempts to account for the type and concentration of solutes in groundwater that is unaffected or minimally affected by the presence of anthropogenic contaminants. The second type, the contaminated system models, describes interactions between contaminants introduced into the aquifer and the solutes and solid (mineral and amorphous) phases present before the contaminant was introduced. The latter type of model is of greater interest in this document. This type of model provides the basis for developing mathematical models that can be used for explaining and predicting the movement and fate of contaminants in groundwater, from the source to potential receptors. Predictions of this type are made in assessing the effects of historical and proposed activities, particularly waste disposal and environmental remediation activities.

A different classification scheme for geochemical models is equilibrium versus kinetic models. Equilibrium models are based on the assumption that geochemical systems are at thermodynamic equilibrium, and hence that the distribution of various components of the system can be calculated based on a relatively small number of measured system parameters and thermodynamic data for the species of interest. In contrast, kinetic models are based on the assumption that geochemical systems are not at thermodynamic equilibrium, although they tend to react in ways that bring them closer to thermodynamic equilibrium. Kinetic models are inherently more difficult to parameterize than equilibrium models, and are more difficult to cast into numerical schemes for quantifying the system. Hence, equilibrium models are more common than kinetic models.

3. PROCESSES THAT CONTROL GEOCHEMICAL EVOLUTION AND TRANSPORT IN THE SUBSURFACE

This section presents a general discussion of the major processes that control the transport and fate of contaminants in the subsurface. Many of these processes are also important in the natural geochemical evolution of groundwater. These processes include advection and dispersion (Section 3.1), dissolution, precipitation, and coprecipitation (Section 3.2), sorption (Section 3.3), matrix diffusion (Section 3.4), and transformation (Section 3.5). Facilitated transport is discussed in Section 3.6. Equilibrium and kinetic approaches are discussed in Section 3.7.

3.1 Advection and Dispersion

Advection and dispersion affect all wastes released into the subsurface at INEEL. Advection is the movement of contaminants dissolved in water caused by the bulk movement of that water. Dispersion is the spreading of contaminants in water, and is caused by differences in the length of the flow path traversed by different parcels of water (and the contaminants dissolved in that water) and differences in flow velocity in different flow paths. Dispersion mixes a plume of contaminated groundwater or vadose zone water with surrounding uncontaminated water, and acts to reduce maximum contaminant concentrations and concurrently increasing the volume of contaminated water.

Advection and dispersion are primary transport mechanisms for aqueous wastes that were discharged directly into the SRPA. Advection and dispersion are also important for aqueous contaminants discharged into percolation ponds. Typically, some of the water discharged into percolation ponds infiltrates and flows downward through the vadose zone until it reaches the underlying aquifer, or it may temporarily reside in perched water bodies in the vadose zone.

Water from precipitation that comes in contact with either buried waste or contaminated soils may become contaminated due to mass transfer of contaminants from these sources. This contaminated water can then move downward through the vadose zone and ultimately reach the underlying aquifer. Given the low average precipitation rate and the corresponding low infiltration rate, advection and dispersion are usually of minor importance relative to transport of contaminants from these waste sources. However, when these sources are flooded, advection and dispersion may become important.

3.2 Dissolution and Precipitation

Dissolution refers to the conversion of a solid phase into dissolved constituents, and precipitation is the formation of a solid phase from dissolved constituents.

Dissolution is important in natural geochemical evolution because it is a major mechanism in water-rock interaction. Dissolution of mineral or amorphous phases by groundwater and vadose zone water is the source of most solutes in these waters.

With regard to waste disposal and contaminant transport, dissolution is probably most important in disposal facilities as a process that converts buried waste into dissolved contaminants. It could also be important if soluble solids were disposed via injection wells, or if aggressive solutions were injected into the subsurface. Situations in which dissolution would be important include leaching of soluble salts in buried waste, or corrosion of metals in buried waste. Dissolution may also be important if contaminants are precipitated, coprecipitated, or sorbed to minerals that are stable under one set of geochemical conditions, and are subsequently released due to changes in geochemical conditions, such as change in pH

or redox state. An example of this is dissolution of pre-existing minerals following disposal of acidic waste in the subsurface.

Precipitation could be an important contaminant sequestering mechanism if contaminants were precipitated or coprecipitated in minerals that formed after wastes were introduced into the subsurface. An example is incorporation of strontium or other metals in calcite via coprecipitation. A second example is precipitation of solid phases following release of concentrated solutions that have extreme pH. Neutralization of pH by reactions with native minerals in the subsurface could cause other minerals to precipitate and thereby sequester contaminants. Precipitation is also important if phases such as clay minerals or metal oxides or hydroxides are precipitated and subsequently sorb contaminants.

3.2.1 Thermodynamic Controls on Dissolution and Precipitation

Dissolution and precipitation of minerals is controlled by both thermodynamic and kinetic constraints.

The thermodynamic constraint is described here. Consider the dissolution of anhydrite, $CaSO_4$:



The equilibrium condition for this reaction is

$$K_{eq} = \frac{[Ca^{2+}][SO_4^{2-}]}{[CaSO_4]} \quad \text{Equation 3-2}$$

where

terms enclosed in square brackets = activities.

The activity of the solid phase (the denominator) is equal to 1, and thus the expression reduces to:

$$K_{eq} = [Ca^{2+}][SO_4^{2-}] = K_{sp} \quad \text{Equation 3-3}$$

where

K_{sp} = is the equilibrium constant for dissolution or the solubility product.

The saturation state of a solution can be described by the saturation index (SI).

$$SI = \log \left(\frac{IAP}{K_{sp}} \right) \quad \text{Equation 3-4}$$

where

IAP = the ion activity product, which is the product of the activities of the aqueous species in the dissolution reaction.

For the case of anhydrite dissolution, the expression is:

$$SI_{\text{anhydrite}} = \log \left(\frac{[Ca^{2+}][SO_4^{2-}]}{K_{sp}} \right) \quad \text{Equation 3-5}$$

Saturation index values equal zero for saturated solutions, and greater than zero for supersaturated solutions, and are less than zero for undersaturated solutions. Precipitation of a mineral phase is thermodynamically possible if and only if the SI for that mineral is greater than zero, while dissolution is thermodynamically possible if and only if the SI for that mineral is less than zero. In practice, SI values between -0.5 and +0.5 are often taken to be saturated, given the uncertainty in the thermodynamic data needed for calculating K_{sp} values and activity coefficients used for relating the activity of an aqueous species to its concentration.

Examples where saturation indices are calculated for minerals in the Eastern SRPA groundwaters include (Wood & Low 1988) and (Knobel et al 1997).

3.2.2 Kinetic Controls on Dissolution and Precipitation

Thermodynamic calculations can be used to evaluate whether a mineral can dissolve or precipitate, but they do not address the rate at which these processes take place, i.e. precipitation or dissolution kinetics. This is important because some phases do not precipitate or dissolve at appreciable rates in the environment, even though these processes are thermodynamically possible.

3.2.3 Congruent and Incongruent Dissolution

Congruent dissolution is a process in which a solid phase dissolves to yield only aqueous species. The dissolution of anhydrite (Equation 3-1) is an example.

In contrast, incongruent dissolution is a process in which a solid phase reacts and yields both aqueous species and solid species. The weathering of feldspars to yield dissolved ions and solid clay minerals is an example. Incongruent dissolution is important relative to the geochemistry of the Eastern SRPA because this process is the source of clay minerals in the aquifer, as suggested by the studies of Knobel et al. (1997). Clay minerals are typically strong sorbents for cations, including the radioactive cationic forms of Cs, Co, and Sr.

3.2.4 Coprecipitation

During the precipitation of a mineral phase, trace amounts of elements other than the major constituents of the mineral can be incorporated into the mineral structure by replacing the major constituent in some lattice sites. This process is known as coprecipitation. For example, during precipitation of calcite, CaCO₃, some other cations can replace Ca in the calcite lattice. In order for this replacement to occur, the competing ion must be similar in size and charge to the predominant cation. Several cationic metals can be coprecipitated during calcite precipitation, including strontium. If radioactive strontium, Sr-90, is coprecipitated in calcite, then it may be immobilized long enough for radioactive decay to reduce concentrations to levels below regulatory concern. This approach is being developed by a team of researchers at INEEL, Idaho State University (ISU), and the University of Toronto (Fujita et al. 2000).

3.3 Sorption/Desorption

3.3.1 Effect of Sorption and Desorption on Contaminant Transport

Sorption is the partitioning of dissolved constituents to solids. Conversely, desorption is the release of materials from solids to the aqueous phase. Sorption includes *adsorption*, in which the partitioning is a surface phenomenon, and *absorption* in which partitioning occurs in the interior of the solid. A common example of adsorption is cation exchange, in which positively charged ions are attracted to negatively charged mineral surfaces by electrostatic forces. An example of absorption is the incorporation of potassium ions in interlayer positions of illite, a clay mineral. In this discussion, *sorption* is used as a global term that includes both adsorption and absorption.

Sorption is important primarily because it can drastically retard the movement of ionic contaminants. Cations are generally retarded much more than anions because most common minerals have negatively charged surfaces, which attract positively charged ions. Ions that are sorbed move more slowly than water is moving through the medium. The ratio of the rate of water velocity to contaminant velocity is the retardation coefficient, R . An unretarded solute, which moves at the same velocity as water, has a retardation coefficient of 1. Retarded solutes, which move slower than water, have retardation coefficients greater than 1. Some strongly sorbed contaminants have retardation coefficients on the order of 10,000 and are essentially immobile. Most contaminants have much lower retardation coefficients, and although they move more slowly than water, they are not immobile.

Sorption of contaminants has several effects. First, as previously discussed, it retards the migration rate. Second, it reduces concentrations in water. Third, it increases concentrations in the sorbed phase.

At some point, waste in the subsurface will no longer release contaminants into water, and concentrations in water downgradient of the waste will decline. If contaminants have previously been sorbed by the solid phase downgradient of the waste, they will desorb as the flux of contaminants from the primary source decreases, and thus the minerals that previously sorbed contaminants from groundwater will now act as a secondary source of contaminants. Hence, sorption/desorption is a two-edged sword. It slows contaminant transport and reduces concentrations during the active life of a primary source, but it can also extend the time needed for concentrations to attenuate naturally and can extend the time needed for active remediation. Like diffusion in dual porosity media, desorption can cause long tails on elution curves during remediation activities.

Sorption can be an important mechanism that removes contaminants from water discharged to percolation ponds. Cationic contaminants can be sorbed by the surficial sediments in which the pond was constructed, or by sediments in interbeds transited by water that infiltrated from percolation ponds. Sorption is also an important mechanism that binds some contaminants (e.g., cesium) to mineral surfaces in contaminated soils.

Desorption may also be important in the generation of dissolved contaminants from buried waste, from sediments in percolation ponds, or from contaminated soils. If uncontaminated water comes in contact with these materials, desorption transfers contaminant mass from the waste into water.

Sorption is particularly important for radioactive contaminants attenuating radioactive contaminants. Retardation due to sorption slows the velocity of contaminant migration and increases the length of time needed for a mass of contaminant to migrate a given distance along a flowpath. The longer travel time provides additional time in which radioactive decay reduces concentrations more than it would if the contaminant were not retarded. This effect is more significant as travel times of a retarded radionuclide become longer relative to the radioactive decay half-life. Hence, longer-lived nuclides must

be more strongly sorbed than shorter-lived nuclides for the increased decay due to retarded transport to be significant.

Various approaches for conceptualizing and describing the sorption process are presented in Section 3.8. Studies in which the sorptive characteristics of geologic media from the INEEL were measured are discussed in Section 6.2.

3.3.2 Alternative Approaches for Describing Sorption

Sorption is defined as the retention of dissolved species by solid particles. If the reaction between dissolved and solid species occurs at the surface of the particle, the process is termed “adsorption”, while if the reaction occurs in the interior of the particle it is referred to as “absorption.” The term “sorption” is a more global term that includes both adsorption and absorption. A common example of adsorption is the electrostatic attraction of cations to negatively charged silicate mineral surfaces. Examples of absorption include the incorporation of potassium ions into interlayer positions of illite, a clay mineral, and the retention on non-polar organic compounds in the interior of granular activated carbon particles.

Sorption is important both in natural geochemical evolution of groundwater and in the transport of contaminants. Sorption typically causes the majority of the mass of many species to be associated with the solid phase and for only a small portion to be in the dissolved phase. Sorption and desorption attenuate changes in concentration of ionic species. Sorption can substantially slow the transport of strongly sorbed species. For example, the transport velocity of a strongly sorbed cation may be many orders of magnitude slower than the velocity of groundwater. Desorption that occurs during the elution or leaching phase of groundwater remediation project can act to maintain elevated concentrations in groundwater for long periods, and thereby extend the period during which remedial actions must be operated.

The importance of sorption in retarding contaminant migration has generated substantial interest in quantifying sorption, and in incorporating the effects of sorption into mathematical models used for predicting the transport of contaminants in groundwater. Alternative approaches for describing sorption are described (Sections 3.8.1 and 3.8.2) and the results of sorption measurements using geologic material from the INEEL subsurface and contaminants relevant to INEEL are described in Section 6.2.

Various methods are used for describing the sorption of dissolved species by solid phases. Common approaches include isotherm models, ion exchange models, and electrostatic adsorption models.

3.3.2.1 Isotherm Approach

An isotherm is defined as “a plot that describes the amount of a species sorbed... as a function of its concentration in solution, measured at constant temperature” (Langmuir 1997). Essentially, a sorption isotherm is a plot of the concentration in the sorbed phase as a function of the concentration in the dissolved phase. Two commonly used mathematical models for describing sorption isotherms are the Freundlich isotherm model and the Langmuir adsorption isotherm model.

The Freundlich isotherm model is the equation:

$$\frac{x}{m} = KC^n \quad \text{Equation 3-6}$$

where

- x/m = is the mass of the sorbed species per unit mass of the solid phase
- K = is a constant
- C = is the aqueous concentration of the sorbed species
- N = is a constant (Langmuir 1997).

If the exponent n is equal to 1, then the isotherm is linear with slope equal to K , which is called the distribution coefficient and denoted K_d . Hence, the commonly used K_d approach for describing sorption is a special case of the Freundlich equation. An important feature of the Freundlich isotherm is that the number of sorption sites is assumed to be infinite, and hence there is no upper bound on the sorbed mass.

The Langmuir adsorption isotherm model is described by

$$\frac{x}{m} = \frac{bCN_{\max}}{1 + bC} \tag{Equation 3-7}$$

where

- b = is a constant
- N_{\max} = is the maximum possible sorption by the solid phase (Langmuir 1997).

The major characteristic that distinguishes the Langmuir isotherm model from the Freundlich model is that the number of sorption sites is limited, and hence there is an upper bound on the sorbed mass (Figure 3-1).

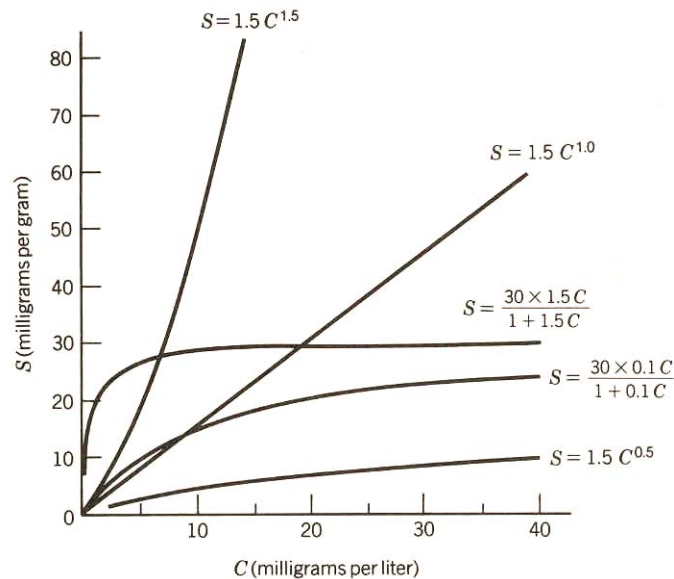


Figure 3-1. Freundlich and Langmuir isotherm models.

There are several advantages in the use of isotherm models. One advantage is that they are relatively easy to parameterize via laboratory batch tests. A second advantage is that the linear Freundlich model (the K_d model) is very easy to incorporate into mathematical transport models.

The major disadvantage is that isotherm models are applicable only to the conditions at which the measurements were made (i.e., at the same temperature, pH, ionic strength, and concentration of major and minor constituents). Differences in solution chemistry will result in different amounts of sorption, even without varying the sorbing mineral surface or the sorbed contaminant. This issue is discussed by (Reardon 1981), and is examined in the context of the INEEL by Landa et al. (2000). This is a potentially major impediment to the use of sorption isotherms for predicting the migration of contaminants because (1) solution chemistry in waste liquids may be very different from the solution chemistry of uncontaminated groundwater, (2) the solution chemistry will vary in time and space due to mixing between waste liquids and the surrounding groundwater, and (3) reactions between waste liquids and both groundwater and minerals in the aquifer framework may cause the solution composition to vary in time and space.

The use of the K_d approach for describing sorption applies to isotherm approaches in general, with the exception that sorption sites are unlimited does not apply to Langmuir isotherms, as discussed in Curtis et al. 2000.

A significant limitation of the K_d approach is that it does not account for the possible variability in chemical conditions nor for the possibly limited number of sorption sites. The surface complexation model (SCM) is one approach that can account for these effects. In this approach, the adsorbing surface is considered to possess surface functional groups that can form surface complexes analogous to the formation of aqueous complexes with ligands in solution (p. 4-3).

Landa et al. (2000) (p. 5-1) also comments on the applicability of the K_D approach for describing sorption.

Although K_d s are widely used, their application implicitly assumes that all factors affecting K_d s are constant. However, these factors, which include pH, the concentration of complexing ligands, the concentration of competing adsorbates, and the availability and types of adsorption sites, generally are not constant in field environments such as the INEEL. Therefore, K_d s may not adequately describe the transport and fate of waste constituents in some environments.

They further comment (Landa et al 2000) (p. 5-3):

The K_d value determined for a given constituent in the laboratory is unique to the solution properties (pH, competing ions, complexing ligands, etc.), and sorbent properties (mineralogy, organic matter content and character, surface area, etc.) being investigated. It may also vary with the method used to determine the K_d – batch column, or in situ – as well as with intra-method variations, such as the solid-solution ration in bench testing, flow-rates in column studies, and particle-size fractions measured for in-situ studies. Extrapolation from laboratory to field conditions must be done with caution. Where solution composition is variable, for example, in a contaminated ground water system, solute transport modeling based on a single K_d value may have inherent problems. Despite these limitations, K_d -based solute transport modeling has been widely used in the study of organic, inorganic, and radioactive contaminants in the subsurface.

One of the reasons that the K_D approach is widely used is that it is very easy to incorporate linear sorption into contaminant transport equations and computer codes used for simulating contaminant transport. K_D values are incorporated via use of a retardation coefficient, R (Equation 5-3 and 5-4), by dividing the advective velocity of water by R to get the velocity of the retarded solute.

$$R = \frac{V_w}{V_s} \quad \text{Equation 3-8}$$

where

- R = the linear retardation coefficient
- V_w = the advective velocity of water
- V_s = the apparent velocity of the retarded solute.

The retardation coefficient is related to the distribution coefficient by:

$$R = 1 + \frac{\rho_b}{\theta} K_D \quad \text{Equation 3-9}$$

where

- ρ_b = the bulk density of the medium
- θ = the volumetric water content, or porosity in a water-saturated medium
- K_D = the distribution coefficient.

Some authors (e.g., [Landa et al. 2000]) define a term K_R as:

$$K_R = \frac{\rho_b}{\theta} \quad \text{Equation 3-10}$$

and hence:

$$R = 1 + K_R \quad \text{Equation 3-11}$$

This formulation allows a very easy conversion between the sorption parameter and the retardation coefficient.

3.3.2.2 *Electrostatic Adsorption Models / Surface Complexation Approach*

Isotherm models for describing sorption have the limitation that they are generally applicable only to the conditions under which the sorption measurement was made. Hence, it is difficult to extrapolate measurements made in a laboratory under one set of conditions to the field, where conditions such as temperature, pH, the concentration of major ions in solution, and the concentration of minor constituents that compete for sorption sites may differ from those in the laboratory. In large part, this is because isotherm models are simply empirical and are not based on the mechanisms involved in sorption.

These limitations are summarized by Langmuir (1997) (p. 369), as follows:

The adsorption-isotherm and ion-exchange models are of limited applicability when modeling complex and variable natural systems, particularly when the sorbates of interest are minor or trace ionic species ($<10^{-4}$ to 10^{-5} mol/kg), and the sorbents exhibit pH-dependent surface charge. For such conditions, the adsorption of trace ionic species often takes place against the net surface charge of the sorbent. This is the behavior of most toxic trace metal cations, including those of the heavy metals and radionuclides when adsorbed by positively charged metal oxyhydroxides, for example.

Langmuir (1997) (p. 370) continues:

Changes in aqueous speciation are not readily accommodated by isotherm and ion-exchange models. Multivalent species often occur in aqueous complexes: adsorption depends on the sorptive behavior of the complexes. For example, cation-OH complexes are often strongly adsorbed by oxides and hydroxides of Fe(III), Mn(IV), Ti(IV), and AL(III). In contrast, fluoride, chloride, sulfate, and carbonate complexes of the same cations are usually weakly adsorbed, if at all, by the same solids.

The conditions of interest in groundwater beneath the INEEL include the presence of trace metal cations, particularly actinides, and sorption by iron oxyhydroxides. Hence, it is to be expected that isotherm sorption models may have limited utility for modeling sorption of actinides and other cations at the INEEL.

A more robust model for describing sorption that is based on chemical mechanisms, instead of simply being an empirical approach, is referred to as either the electrostatic adsorption model or the SCM. "They can consider simultaneously such important system properties as changes in pH, aqueous complex formation and solution ionic strength (solution speciation), and the acid-base and complexing properties of one or more sites on several sorbing surfaces simultaneously" (Langmuir 1997) (p. 371).

Surface complexation models account for variable surface charge of minerals by accounting for the reaction between metal cations in the solid sorbent surface, S , with protons, H^+ , to form surface species whose charge varies with pH. These surface species are represented as SOH_2^+ (a positively charged surface site), SOH (a neutral surface site), and SO^- (a negatively charged surface site). The relative proportions of these surface sites varies with pH, with the positively charged sites predominating at lower pH. Hence, this model accounts for the pH dependence of surface charge. Sorption of a cation from solution to a surface site can be represented by



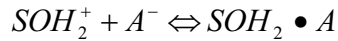
where

SO^- = a sorbing site on the mineral surface

M^+ = a cation in solution

$SO M^+$ = a surface complex (i.e., the cation sorbed to the surface sorption site).

Similarly, sorption of an anion A^- can be represented by



Equation 3-13

The variation in surface charge with pH accounts for the differing ability of surfaces to sorb cations and anions under different pH conditions.

The following description of SCMs is taken from Langmuir (1997) (pp. 372-373). The different SCMs referred to are based on different conceptualizations of the electrical double layer near a charged surface.

The surface complexation (SC) or electrostatic models differ conceptually and mathematically from the simpler isotherm and ion exchange models in several important ways. As used in MINTEQA2, all the models consider solution speciation and aqueous ion activities. In addition, the SC models employ electrical double-layer theory (EDL) theory...The SC models thus consider the adsorption process in a relatively more atomistic and mechanistic way than do the simpler models. This provides the SC models with a greater capability than the simple models have of predicting adsorption for conditions beyond those used to determine model parameters.

Some common assumptions inherent in the SC models include:

1. The sorbing surface is composed of specific functional groups that react with sorbing solutes to form surface complexes ... in a manner analogous to the formation of aqueous complexes in the bulk solution.
2. Surface complexation and ionization reactions can be described with mass-action equations, corrected for electrostatic effects using EDL theory.
3. Surface charge ... and electrical potential ... are consequences of chemical reactions involving the surface functional groups.
4. The apparent binding constants determined for the mass-law adsorption equations are empirical parameters related to thermodynamic constants ... via activity coefficients of the surface species.

3.4 Matrix Diffusion

Matrix diffusion is a physical-chemical process that substantially affects solute transport and reaction in some environments, which are referred to as *dual porosity media*. Dual porosity media are systems in which zones with strongly contrasting permeability are adjacent to one another, and both the more and less permeable zones have significant porosity. Examples of dual porosity media include fluvial aquifers with interbedded sand and silt or clay, fractured clay, and fractured sandstone or shale. In these media, the sand (or fractures) are the more permeable zones and the silt, clay, or rock matrix are the porous, less permeable zones. At the INEEL, fractured vesicular basalt and interflow zones have these characteristics. In dual porosity media, water moves much faster in the more permeable zones than in the less permeable zones. Therefore, solute concentrations can change much more rapidly in the more permeable zones than in the less permeable zones. Differences in solute concentrations cause diffusion to transport mass from high-concentration zones to low concentration zones. This process attenuates the migration of sharp solute breakthrough fronts and causes extensive tailing during elution curves. This phenomenon is a major transport process in some environments, especially porous rocks, but has received

little attention at the INEEL. The term *matrix diffusion* refers to the process of diffusion between more permeable zones and the less permeable matrix, and is synonymous with transport in dual porosity media.

Newman et al. (1995) briefly discuss matrix diffusion in their description of radionuclide sorption studies. They performed column experiments using both crushed basalt and intact basalt cores. Breakthrough curves for the crushed basalt columns could be fit using either the advection-dispersion equation with equilibrium sorption, but a better fit was obtained using a model that included either kinetic sorption or porosity whose access is limited by mass transport (e.g., diffusion into immobile water).

In contrast, breakthrough curves generated in column studies with intact basalt cores were very different from breakthrough curves generated in columns studies using crushed basalt.

The breakthrough curves observed for intact basalt cores do not resemble those expected based on advective-dispersive flow through a uniform porous media. The breakthrough curves obtained from the intact basalt cores show rapid breakthrough of approximately 60% of the input concentration ...followed by extensive tailing (or extremely slow breakthrough)...Fitting data from bromide breakthrough curves with the two site/two region CXTFIT model indicated that up to 90% of the saturated porosity was immobile....It is possible that contaminant transport in the intact cores is controlled by diffusion into and out of the basalt matrix rather than by sorption reactions (pp. 62,68).

Diffusion between water in different parts of the medium, as described by Newman et al. (1995) is the characteristic feature of transport in a dual porosity medium.

3.5 Transformation

Transformation refers to the change in chemical species. It includes both abiotic and biologically-mediated processes.

Transformations can be very important relative to the mobility, toxicity, and solubility of contaminants. Common transformations change in speciation due to redox reactions (i.e., Fe-II \leftrightarrow Fe-III or Cr-VI \leftrightarrow Cr-III), and due to change in pH (i.e., Pb). Hexavalent chromium forms oxyanions that are soluble, not significantly retarded, and toxic. Trivalent chromium forms cationic species that are much less mobile, less soluble, and less toxic than hexavalent chromium species. The characteristics of many metals vary with pH and redox state. Hull & Pace (2000) present activity diagrams for contaminants of potential concern at the Radioactive Waste Management Complex (RWMC).

Biologically-mediated transformations are also important factors that affect the release of contaminants from waste and subsequently the transport and fate of contaminants in the subsurface. For example, biodegradation of organic matter (i.e., paper, cardboard, and wood containers) in landfills such as the RWMC can generate strongly reducing conditions that are favorable to release of some metals, and the inorganic and organic acids produced by organic matter biodegradation may accelerate corrosion of waste metals and complexation of metals. Biotransformation is important in converting nitrate into innocuous nitrogen. Biotransformation is very important in the fate of organic contaminants in the subsurface. For example, tetrachloroethene (PCE) and trichloroethene (TCE) in the groundwater plume emanating from Technical Support Facility (TSF)-05 at Test Area North (TAN) are being biotransformed into less chlorinated ethenes and ultimately into innocuous products, ethene, chloride, bicarbonate, and water. Biodegradation also commonly degrades contaminants derived from petroleum into innocuous products.

Radioactive decay is important in that it reduces the mass of radioactive contaminants. If the daughter products are stable or long-lived, then radioactive decay reduces the amount of contaminants present. Conversely, if the daughter products are radioactive with half-lives shorter than or comparable to those of the parents, then the overall amount of activity does not substantially change over short time scales.

3.5.1 Aqueous Speciation Based on pH-Eh Conditions

Hull & Pace (2000) describe speciation and solubility of contaminants of potential concern at the RWMC. Their work is described in more detail in Section 6.1. Curtis et al. (2000) describe the effect of speciation on the transport of uranium and selected transuranics. Their work is discussed in more detail in Section 4.2.3.

Most elements occur as several aqueous species and mineral phases under the range of pH and redox conditions that exist in water. At thermodynamic equilibrium, the distribution of a species (including both dissolved and solid phases) is controlled by the pH and redox conditions, concentration of the element in solution, and the overall solution chemistry. For a given solution composition at thermodynamic equilibrium, the distribution of an element among various species can be calculated. The distribution is often presented on activity diagrams such as pH-pe, pH-Eh, or pH-a_{O₂} diagrams. An example of each of these diagrams for iron is shown in Figure 3-2. In these diagrams, the vertical axis represents three commonly-used methods of describing redox conditions. In all cases, more oxidizing conditions occur farther from the horizontal axis and more reducing conditions occur closer to the horizontal axis.

In these diagrams, the individual fields represent the range of conditions under which a particular species is the major species. Other species are present, but at lower concentrations than the predominant species. The boundaries between aqueous species does not depend on the dissolved concentration of the element, but the boundaries between solid and dissolved phases do depend on dissolved concentrations, with the size of the solid phase stability increasing as the dissolved concentration increases.

Redox-pH speciation is important with respect to the transport and fate of contaminants in the subsurface because (1) different aqueous species can have quite different mobility in the subsurface, (2) the solubility of can vary with pH-redox conditions, and (3) the speciation of one element can affect the mobility of other species in the subsurface.

Redox-pH speciation affects mobility as a result of the major species under different conditions having different charge (i.e., being polyvalent or monovalent, anionic, cationic, or neutral). In general, neutral species are not retarded by sorption, anionic species are retarded by sorption to a limited number of minerals, and cationic species are retarded under almost all conditions due to the common occurrence of minerals with negatively-charged surfaces. Polyvalent cations (e.g., ions with charge of +2, +3, etc.) are generally more strongly sorbed, and hence retarded, than are monovalent cations (ion with a charge of +1).

If different species of an element have different charges under different pH-redox conditions, then the mobility would vary with pH-redox state. For example, the major aqueous species of chromium are anions in the Cr-VI oxidation state that prevails under oxidizing conditions, while the predominant Cr-III aqueous species under more reducing conditions are cations (Figure 3-3). Hence, dissolved chromium species would typically be more mobile under oxidizing conditions than under reducing conditions.

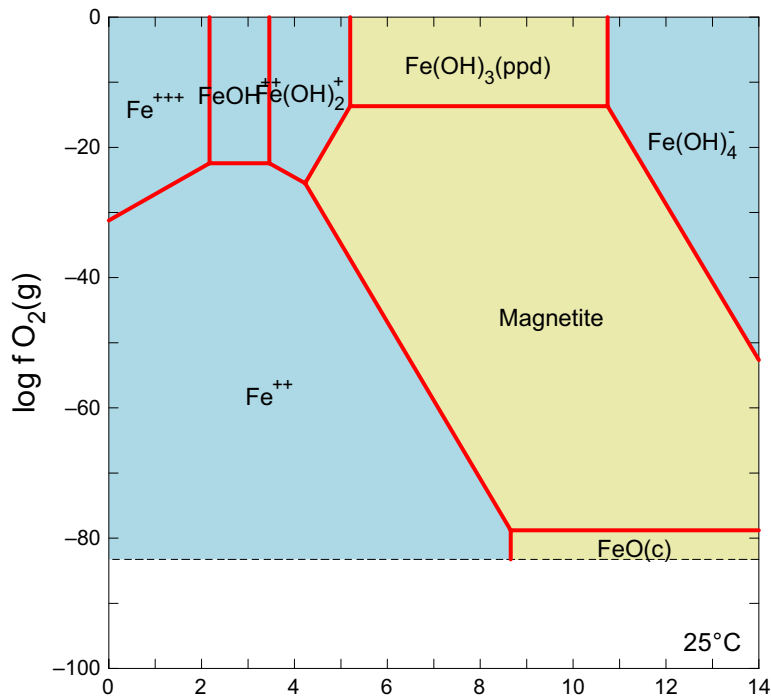
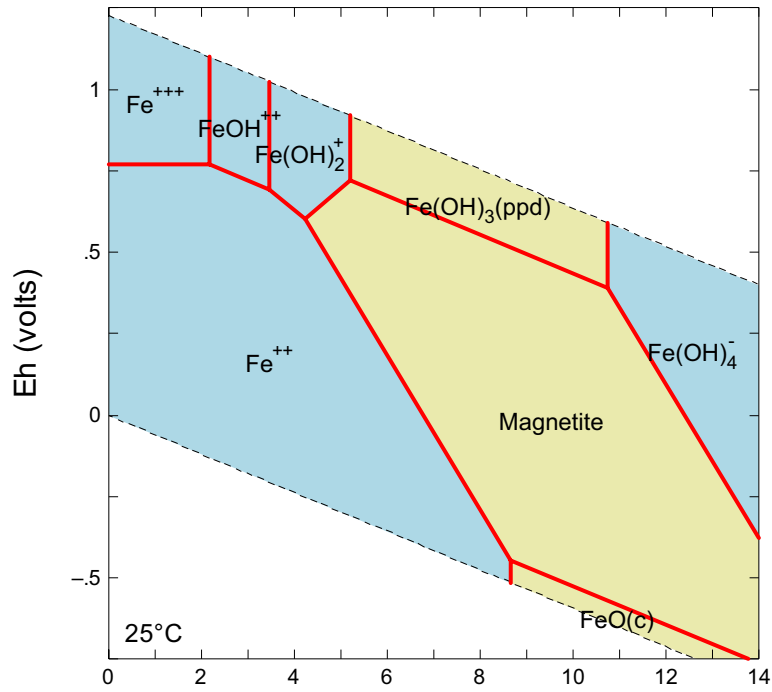


Figure 3-2. Alternative speciation diagrams for iron.

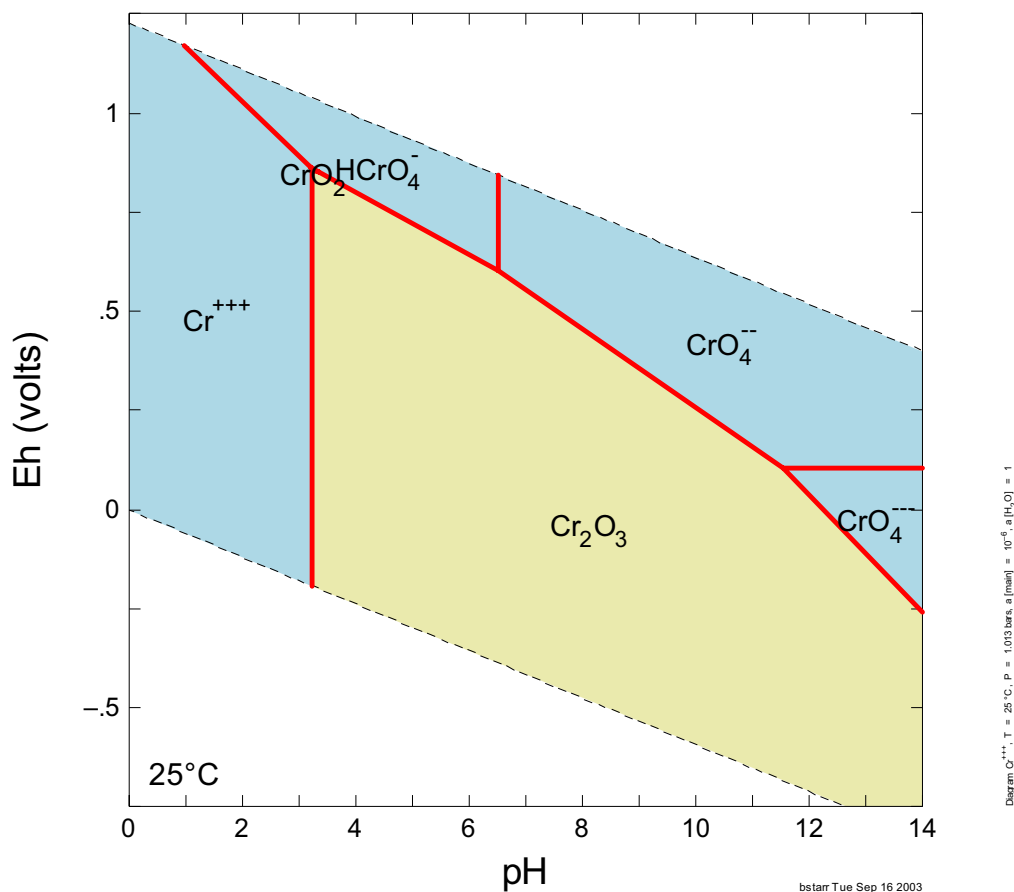


Figure 3-3. Speciation diagrams for chromium (a) aqueous species (b) aqueous and solid species.

A second effect of pH-redox state on chromium mobility is that dissolved Cr-III concentrations are limited by the solubility of solid phases. Hence, the oxidation state is very important in controlling the mobility and concentration of chromium in the subsurface. This behavior is common among many elements, although the conditions under which a particular element is more or less mobile vary between elements.

A third effect of pH-redox state on contaminant mobility in the subsurface is the interaction between different elements. For example, the behavior of iron and manganese can affect the transport of cationic and under some conditions, anionic species. In contrast to chromium, iron and manganese form solid phases under oxidizing conditions. These solid phases are important because they have relatively large ion exchange capacities and hence can substantially retard the migration of dissolved ions of other elements. Their surface charge varies with pH, and they sorb cations at higher pH and anions at lower pH. The pH at which the transition between sorbing anions and cations occurs is different for different mineral phases. The net surface charge of common iron and manganese minerals is negative at the slightly alkaline pH typical of the INEEL subsurface, they tend to have large cation exchange capacities, and therefore they are important sorbents for cations. Therefore, the presence or absence of these solid phases, which is controlled by their concentration and pH-redox conditions, can substantially affect the mobility of other contaminants.

A pH-Eh diagram for iron shows the stability fields for aqueous species in blue and the stability fields for solid phases in green. A similar diagram is shown for strontium. The boundaries of the iron stability fields are shown as faint dashed lines on the strontium speciation diagram. Assuming that the iron mineral hematite has a net negative surface charge at all pH, then Sr^{++} would be sorbed by hematite. If we further assume that hematite is the major cation sorbent in a system, then Sr^{++} sorption would be tied to the presence of hematite. Hence, Sr^{++} would be sorbed and retarded under the pH-redox conditions in which hematite is stable. These conditions are shown as the shaded region on the Sr speciation diagram.

Hematite is stable under oxidizing conditions, but unstable under strongly reducing conditions at circa-neutral pH. If a system evolved from oxidizing conditions where hematite was stable to reducing conditions in which hematite was not stable, then hematite would dissolve and the cations sorbed to hematite surfaces would be released into solution. Similarly, if the system remained aerobic but became very acidic, then the system would shift to the stability field of Fe^{3+} and hematite would dissolve. Again, sorbed cations would be released into solution.

This example illustrates how the redox behavior of one element, iron in this case, can affect the mobility of other elements, even when those elements have limited changes in speciation with pH-redox conditions. Although iron was used in this example, other elements also affect the behavior of other elements. Elements that commonly affect the mobility of other elements include sulfur (through the formation of low solubility metal sulfides), carbon (through the formation of carbonate complexes), phosphorus (through the formation of phosphate complexes and phosphate minerals), and manganese and aluminum (through precipitation of mineral phases that have large cation exchange capacities).

Another mechanism through which the pH-redox behavior of one element can affect the transport of other elements is formation of colloidal particles. Colloidal particles are so small that they are readily transported in groundwater. Ions that are sorbed to colloidal particles are transported at the same rate as the colloidal particle, which can be orders of magnitude faster than the sorbed ion would be transported if it were sorbed to a stationary mineral particle. Again using iron as an example, colloidal particles could precipitate in the pH-redox conditions in which solid phases such as hematite are stable. Colloidal particles of silica, iron, manganese, and aluminum oxides and hydroxides, carbonate minerals, and clay minerals have all been observed in groundwater at various field sites. Colloidal transport in the INEEL subsurface is discussed in more detail in Section 3.6.

3.5.2 Complex Formation

A complex can be defined as “a dissolved species formed from two or more simpler species, each of which can exist in aqueous solution” (Drever 1997) (p. 34). Alternatively, a complex typically is an association between a metal atom and one or more ligands (Langmuir 1997) (pp. 82-83). An anion or neutral molecule that can combine with a cation to form a complex is known as a ligand.

The ligands are typically anions (e.g., Cl^- , F^-), or neutral species (e.g., H_2O , NH_3) that are arranged in a definite geometric pattern around the central metal atom (Drever 1997) (p. 34). Common inorganic ligands include carbonate, bicarbonate, sulfate, phosphate, hydroxide, fluoride, and chloride. Natural organic ligands include citrate, humic and fulvic acids, and others. Synthetic organic ligands (e.g., ethylenediaminetetraacetic (EDTA), which is commonly used as a decontaminating agent) can also be important chelating agents in some situations, particularly when they are disposed in the subsurface.

Complexes are important for the following reasons (Langmuir 1997) (pp. 82-83):

- Some elements occur in solution more often in complexes than as free ions. Uranium in the IV oxidation state is an example.
- Adsorption of cations or anions may be greatly favored or inhibited when they occur as complexes rather than as free (uncomplexed) ions. For example, the hydroxide complexes of uranyl ion (UO_2^{2+}) are strongly adsorbed by oxide and hydroxide minerals, whereas uranyl carbonate complexes are poorly adsorbed by these minerals.

The significance of complex formation includes (1) complex formation can increase the solubility of metals, and (2) complex formation can increase the mobility of a contaminant. For example, Hull & Pace (2000) (Figure 3-60, p 3-47) plot the solubility of uranium as a function of pH and redox condition. Under oxidizing conditions, U-carbonate complexes are the most soluble species, except at high pH. Plutonium is generally strongly sorbed in the subsurface (see Newman et al. 1995). However, kilometer-scale transport of Pu at Los Alamos National Laboratory has been attributed to the formation of Pu-EDTA complexes, which are much less retarded than uncomplexed Pu.

3.5.3 Biologically-Mediated Transformations

Biologically-mediated transformations are changes brought about by micro- or macro-organisms in the chemical form of an element. Biotransformations typically accelerate the rate of thermodynamically feasible reactions that occur slowly abiotically. Examples of biologically-mediated transformations that have been observed at INEEL include the transformation of dissolved silica into silica precipitates in ponds at TRA (Robertson et al. 1974), possibly the reduction of hexavalent chromium to trivalent chromium in organic sediments at the same location (Hull 1989), and conversion of PCE and TCE into less chlorinated chloroethenes in groundwater at TAN (Peterson et al. 2000).

The major significance of biologically-mediated reactions is that organisms can cause reactions to occur at rates that are significant relative to the transport and remediation of contaminants, that would otherwise not occur at meaningful rates.

3.6 Facilitated Transport

Facilitated transport can be defined as the movement of a contaminant in the subsurface at a rate that is significantly faster than expected as a result of the contaminant being associated with a mobile phase. In other words, if a contaminant is expected to be substantially retarded by sorption to mineral surfaces in the vadose zone or aquifer, but in fact moves more quickly than predicted, the faster transport is attributed to facilitated transport. The mechanisms responsible for facilitated transport include preferential flow, complex formation, and colloids.

In their discussion of sorption studies performed using synthetic groundwater and INEEL geologic media, Newman et al. (1995) observed that a fraction of each of the radionuclides they studied exhibited substantially more rapid transport than the majority of that radionuclide. They discussed this behavior as follows.

Enhanced mobility fractions of ^{60}Co , ^{239}Pu and ^{241}Am were observed within the first 5 pore volumes eluted... The percentages of the total radionuclide observed in the enhanced mobility fractions were 3% for ^{60}Co , 9 to 13% for ^{241}Am , and 10 to 55% for ^{239}Pu . Three possible explanations for the observed enhanced mobility fractions are: 1) association of these elements with a mobile colloidal phase, 2) formation of a more mobile complex, or 3) kinetically limited sorption. All three of these radionuclides have been observed to form or be associated with

colloidal material ...²³⁹Pu and ²⁴¹Am are thought to form neutral or negatively charged complexes with carbonate....It is not possible to conclude which of these three mechanisms is most probable from the results reported here (p. 28).

A fraction of ²⁴¹Am, ⁶⁰Co, or ²³⁹Pu moving at a much faster rate than predicted by use of a single, equilibrium based, distribution coefficient may significantly alter predicted arrival times and peak concentrations of these three radionuclides downgradient from their source. Enhanced transport may change risk calculations or the importance of perceived risk. Consequently, the frequency and magnitude of enhanced transport, as well as the mechanisms controlling enhanced transport were explored.

The enhanced mobility fraction observed in column tests was greatest for plutonium. Therefore, initial efforts to elucidate the mechanism causing this enhanced transport were directed at plutonium. Studies were performed to test each of the three possible mechanisms for enhanced mobility identified...Oxidation state analyses of plutonium equilibrated with synthetic groundwater showed that colloidal plutonium can be formed under the conditions in the INEL subsurface...Also, Estes and McCurry (1994) found 2.3 to 9.8 ppm of colloidal material (<0.45 μ m) in three wells near the Idaho Chemical Processing Plant (ICPP). This colloidal material was made up primarily of calcium, magnesium, and silica. Both plutonium...and americium...have been shown to sorb strongly to silica. Both of these facts support but do not prove the hypotheses of colloid associated transport as a mechanism for the observed enhanced transport.

In order to examine the possibility of enhanced transport due to the formation of negatively charged carbonate complexes, the total alkalinity of the plutonium spiked synthetic groundwater applied to a crushed basalt packed column was varied...An increase in total alkalinity from 0.05 to 1.1 g/L as CaCO₃ increased the apparent enhanced mobility fraction from 52.2 to 78.0%. This supports the hypotheses that carbonate complexation may result in enhanced transport of plutonium.

Finally, the effect of flowrate on enhanced transport of americium was examined...An increase in flowrate from 0.1 mL/min to 10 mL.min increased the apparent enhanced mobility fraction from 1.3 to 42.9%. Increased flowrates may increase the mass of mobilized colloidal material and/or reduce the fraction of contaminant, which is in equilibrium with the solid surfaces (by decreasing the contact time).

Although these initial studies indicate enhanced transport can occur in laboratory columns, they do not clearly elucidate either the mechanism(s) causing the apparent enhanced transport or the significance of this phenomena under field conditions. Further study is needed in this area in order to provide an effective assessment of the frequency and magnitude of enhanced transport and resulting risk (pp. 36-39).

3.6.1 Complex Facilitated Transport

The importance of complex formation on the mobility of actinides in the INEEL subsurface is discussed by Curtis et al. (2000). In Section 4.3 and Figure 4-2, Curtis et al. (2000) show that the distribution coefficient for UO_2^{2+} predicted using surface complex modeling is strongly (orders of magnitude) affected by the concentration of ligand, resulting in greater mobility of U as the amount of complexation increases. In Section 4.3.1.1, Curtis et al. (2000) discuss the chemical speciation of Pu, and indicate that “unless F, P, and SO_4^{2-} concentrations are very high, oxide, hydroxide and carbonate complexes of Pu can be expected to be the dominant species” (Curtis et al. 2000, p.4-7). However, they do not further discuss oxide and hydroxide complexes, and state that “there is no information at present on the possible occurrence of these (carbonated) complexes. This is unfortunate given the ubiquity of the carbonate system in most ground-water environments.” Thus, experimental data needed to quantify the importance of Pu complexation to what is probably the dominant ligand in INEEL groundwater are lacking. However, in Section 4.3.2.1 they present the results of speciation calculations, which show that the predominant (three most abundant) Pu species in some INEEL waters are exclusively carbonate complexes.

The behavior of Np is discussed in Section 4.3.1.2. of Curtis et al. (2000). The authors indicate that Np forms complexes with carbonate, but provide little detail. However, in Section 4.3.2.1 they present the results of speciation calculations, which show that the predominant (three most abundant) Np species in some INEEL waters include carbonate complexes.

The behavior of U is discussed in substantially more detail in Section 4.3.1.3 of Curtis et al. (2000). They note that at pH values above 6, that the predominant U(VI) species are carbonate complexes, and as a result the extent of U sorption by common mineral surfaces declines by orders of magnitude between pH ~7 and 9. Hence, formation of carbonate complexes substantially increases the mobility of U in the INEEL subsurface. Carbonate formation is similarly important for Am (Section 4.3.1.4; Curtis et al 2000).

The major conclusions to be drawn from this portion of the work presented by Curtis et al. (2000) are that actinides form complexes with carbonate species that are common constituents of INEEL groundwater, and that this complexation can substantially enhance their mobility in the subsurface.

3.6.2 Colloid-Facilitated Transport

Curtis et al. (2000) also discussed the importance of colloids on actinide transport beneath the RWMC. Although various authors define colloidal-size particles differently, a common definition is that colloids are particles that are so small that they remain in suspension due to Brownian motion, and thus they remain suspended indefinitely. With respect to contaminant transport, colloids are important because they can be composed of a solid phase of the contaminant itself, or a contaminant can be sorbed by a colloidal particle. Colloidal particles can be transported in groundwater at velocities similar to that of the groundwater itself (i.e., with a retardation coefficient of 1). Hence, contaminants that are associated with colloids may be transported much faster than they would otherwise, assuming that they are otherwise strongly retarded via sorption to mineral surfaces. Therefore, if colloidal particles have contaminants associated with them and move from shallow contaminant sources through the vadose zone into the underlying groundwater, then the transit time into groundwater could be drastically reduced. If contaminants are associated with colloids in the groundwater system, then the contaminants could be transported in the aquifer much more quickly than would be predicted by conceptual models that include only equilibrium sorption to stationary mineral surfaces.

Curtis et al. (2000) (p. 4-41) summarize their review of the importance of colloid-facilitated transport as follows.

There is evidence for the formation of actinide colloids in batch and column experiments, and in the field...Experiments have demonstrated that actinides elute from columns packed with interbed sediments from the Subsurface Disposal Area (SDA) at a much faster rate than would be predicted from equilibrium sorption of aqueous species. This enhanced mobility fraction has been attributed to colloid facilitated transport...It has not been determined what percentage of actinides in column breakthrough curves might be associated with colloids and what percentage might be in the form of soluble complexes.

The fractures and vesicles in basalt beneath the INEEL do exhibit evidence of colloid transport. However, there is a question whether colloids at deeper basalt intervals represent transport from the surface of from interbeds immediately above the basalts. Colloids measured at depth could have been emplaced as interbeds were forming.

The strongest evidence for colloid facilitated transport comes from the detection of Pu in the 110 and 240 ft interbeds. Further evidence needs to be collected to determine if these detections represent natural transport from waste buried at the SDA, contamination from boreholes, or analytical problems.

Hence, there is evidence that colloid facilitated transport may be important in actinide transport in the subsurface beneath INEEL, but this evidence is not conclusive.

3.7 Equilibrium versus Kinetic Models

Curtis et al. (2000) discuss the applicability of the concept of local chemical equilibrium (Section 4.4). They state that the “distribution coefficients theoretically apply only to reversible first-order reactions at local equilibrium,” and that “actinide sorption and desorption reactions with minerals are often affected by several kinetic processes.” They list the following kinetic processes, which may cause disequilibrium to exist.

- Chemical or physical sorption reactions between an actinide and a mineral surface. These are generally relatively fast, although there is often a slow component that may require weeks to achieve equilibrium.
- Diffusion to or from reaction sites in zones of immobile water. Immobile water can be a layer on the grain surface, within a grain, between grains, in fractures, or in interlayer positions of expandable clay minerals.
- Mineralogical changes in the sorbing phase.

They also point out that the rate of approach to equilibrium in laboratory sorption experiments depends on experimental conditions, including:

- The amount of agitation, which could grind particles and expose fresh mineral surfaces that have different sorption characteristics than aged surfaces. Insufficient agitation may not completely mix sediment and solution, leading to diffusion limited transport
- Lack of chemical equilibrium between sediment and the aqueous phase.
- Lack of chemical equilibrium in the dissolved phase
- Rock type.

Rapid groundwater velocities can prevent attainment of chemical and physical equilibrium. Transport through interbeds is likely to be sufficiently slow that equilibrium is approached, but rapid transport of pulses of water through basalt fractures may not allow sufficient time for equilibrium to be achieved (Section 4.4.2). Note that this discussion applies to the vadose zone, but probably not to the groundwater zone.

They summarize as follows.

- There is insufficient information to reliably assess whether chemical equilibrium between actinides and sediments at the INEEL exists...However,...sorption of actinides by interbed sediments at the INEEL should be relatively rapid, with most sorption occurring within 24 hours...for the purpose of risk assessment analysis, the assumption of chemical equilibrium appears to be reasonable. Flow velocities through the interbed layers appear to be slow enough to allow sufficient time for sorption reactions to attain equilibrium.
- There may be insufficient time for equilibrium to occur in basalt fractures because of higher flow velocities. Also, there is evidence ... for diffusion into zones of stagnant water, which will increase times needed to attain equilibrium. However, considering the relatively low amount of rainfall and infiltration at INEEL, sustained rapid flow through fractures may be limited. The slower velocities associated with short intermittent periods of recharge could allow enough time for reactions to approach equilibrium.

4. GEOCHEMICAL COMPOSITION OF UNCONTAMINATED GROUNDWATER BENEATH THE INEEL

The geochemical characteristics of groundwater beneath the INEEL are the result of natural processes that govern the evolution of water chemistry and man-made perturbations to those processes, particularly the disposal of waste in the subsurface. This section is organized as follows. A general description of geochemical evolution is provided in Section 4.1. The composition of uncontaminated or minimally contaminated groundwater, as reported in several investigations, is summarized in Section 4.2. This section focuses on lateral variations in solute composition of groundwater in the upper part of the aquifer where virtually all of the wells are completed. The much smaller body of information available on vertical variations in solute composition of groundwater is discussed in Section 4.3. These two initial sections present a picture of what can be seen in terms of the solute geochemistry of groundwater beneath the INEEL. The remaining parts of this section describe how this situation came to be. The sources of water to the aquifer and solutes in that water are described in Section 4.4. After water enters the Eastern SRPA, the solute composition of groundwater can change due to reactions between groundwater and the rocks that host the aquifer. Geochemical and mixing models proposed by various investigators to account for spatial variations in solute composition of groundwater beneath the INEEL are described in Section 4.5. Studies in which environmental tracers were used to ascertain groundwater ages are discussed in Section 4.6.

4.1 Geochemical Evolution

The natural geochemical composition of groundwater, that is the type and concentration of solutes in groundwater, reflects the concentrations of solutes in water when it fell as precipitation and changes that occurred afterwards. These changes include evaporation, changes caused by plants and microorganisms in the soil zone, and changes that occur in the vadose zone and saturated zone below the root zone. The changes that occur below the root zone are collectively referred to as “water-rock interactions”. Water-rock interactions include:

- Dissolution and exsolution of gases
- Dissolution and precipitation of mineral phases, including incongruent dissolution that occurs during weathering reactions of minerals that yield both solid and dissolved products such as the weathering of feldspars into clay minerals
- Coprecipitation, in which an ion is incorporated as a minor constituent into the crystal lattice of a mineral via substitution of the predominant ion
- Interactions between dissolved species and solid phase surfaces, such as sorption, ion exchange, and surface complex formation.

In addition to reactions between the dissolved phase and solid phases, reactions that occur only in the dissolved phase are important in the evolution of the geochemical composition of groundwater. These reactions include processes such as acid-base reactions, hydrolysis, redox reactions, and complex formation.

Finally, many reactions that control the geochemical composition of groundwater are facilitated by microorganisms. Microorganisms are particularly important in facilitating redox reactions, and for transforming organic matter in the subsurface (Chapelle 1993).

4.2 Observed Composition of Uncontaminated Groundwater Beneath the INEEL and Vicinity

Two investigations of the solute composition of uncontaminated groundwater beneath the INEEL have are presented here. These investigations include Olmsted (1962) (Section 4.1.1), Robertson et al. (1974) (Section 4.1.2).

4.2.1 Olmsted 1962

An early investigation of water quality of groundwater beneath the INEEL (called the National Reactor Testing Station [NRTS] at the time) was performed by the USGS (Olmsted 1962). This study utilized water analysis data from 148 groundwater samples collected from 92 wells during the period 1949-1961 (p. 11). Major ion values for these water samples were plotted on Piper trilinear plots, and the samples were classified into four categories based on cation and anion concentration ratios. Their classification system is shown in Table 4-1, and the spatial distribution of water types is shown in Figure 4-1. Note that water types A and B are uncontaminated groundwater, while types C and D have been contaminated by human activities.

Table 4-1. Water classification system (after Olmsted 1962).

Category	Cations	Anions
Type A	Ca and Mg \geq 85% of cations	HCO ₃ ⁻ and CO ₃ ²⁻ \geq 70% of anions
Type B	Na and K > 15% of cations	HCO ₃ ⁻ and CO ₃ ²⁻ \geq 70% of anions
Type C	No limits	HCO ₃ ⁻ and CO ₃ ²⁻ < 70% of anions, and SO ₄ ²⁻ \leq 30% of anions
Type D	No limits	SO ₄ ²⁻ > 30% of anions

Type A and B waters as defined by Olmsted (1962) underlie most of the INEEL.

Type A water...underlies the western or northwestern half of the Station {INEEL} adjacent to the Lost River, Lemhi, and Beaverhead Ranges, and the intervening valleys drained by the Little Lost River and Birch Creek...Type B water...underlies the eastern or southeastern half of the NRTS and probably underlies much of the plain to the east and south. Type B water also underlies two small areas surrounded by type A water...these bodies...are believed to reflect upward flow of deep water in which natural cation exchange has occurred. Before these wells were deepened to their present depths, the water in them was lower in sodium and potassium – more like the surrounding type A water (p. 34).

Type A and B water are thought to reflect uncontaminated groundwater, and the difference in the cation ratios reflects different sources.

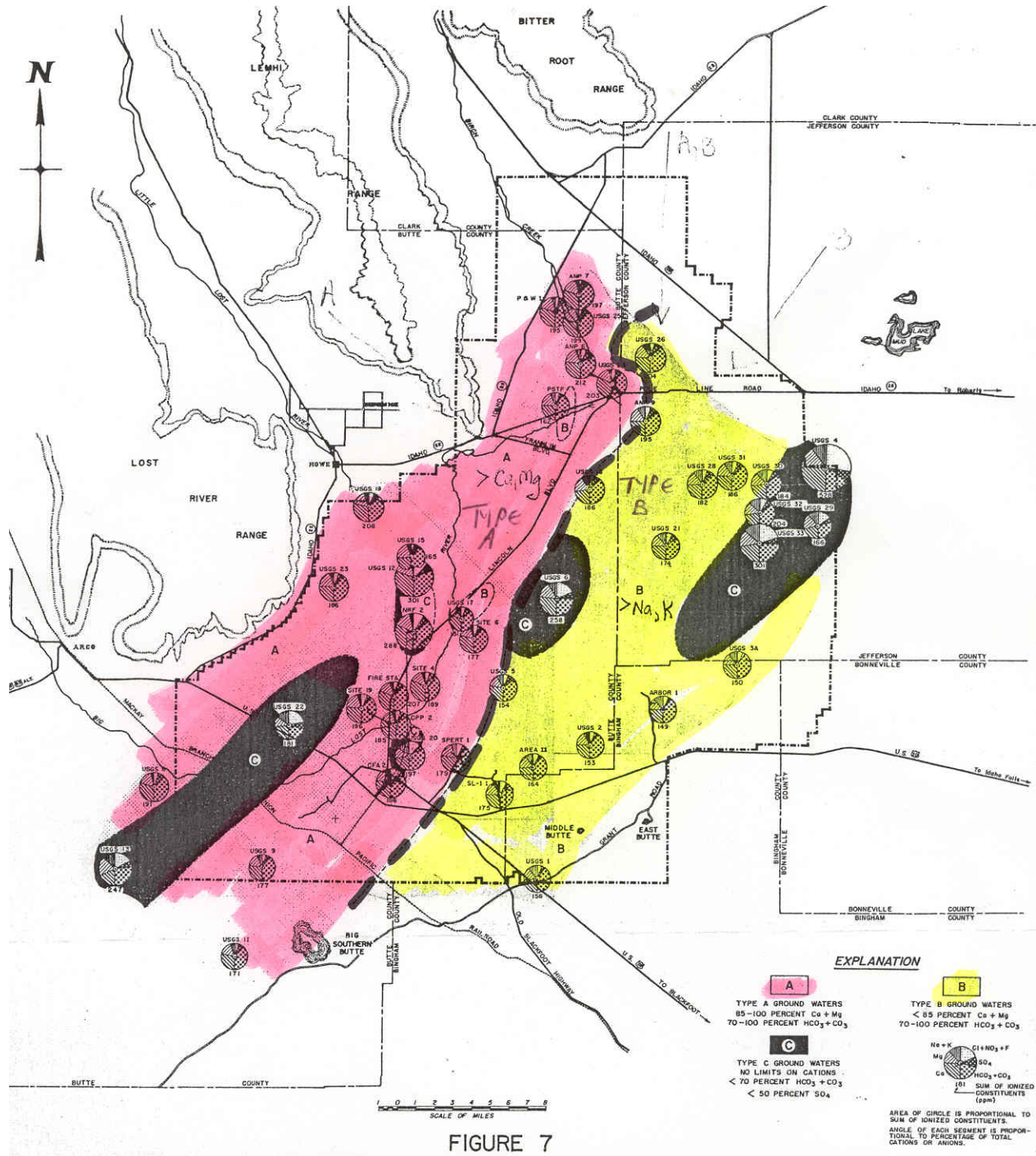


FIGURE 7

Figure 4-1. Spatial distribution of geochemical classes of groundwater (modified from Olmsted 1962).

The ... type A ... water is characteristic of carbonate rocks (limestone and dolomite) which underlie large areas in the mountains, in the drainage basins of the Little Lost River and Birch Creek to the northwest...the chemical character of type A water clearly indicates its derivation from the drainage basins to the northwest.. Type B water is derived from the region north and northeast of the NRTS. This region is underlain by silicic volcanic rocks which have a much higher content of sodium, potassium, and silica than most of the rocks in the source regions for water of type A. The greater abundance of these constituents in water of type B may be due in part to the fact that this water has moved farther through the basalt beneath the plain than has type A water, and in part to the fact that some water of type B has moved through considerable volumes of fine-grained sediments....Some water of type B has been affected by seepage from irrigated lands in the Mud Lake area (p. 38).

Type C and D waters have been affected by anthropogenic contamination.

A change in the proportions of the anions is believed to be the best indication of contamination in the waters of the NRTS. Water of type C is the principal type of contaminated water. An increase in the percentage of chloride and a decrease in the percentage of bicarbonate, accompanied by an increase in the sum of the dissolved solids, indicate contamination from one or more of several sources, chiefly aqueous waste discharged at facilities such as the ICPP, or drainage from irrigated tracts such as the Mud Lake area. High-chloride water of unknown origin, probably a natural occurrence, is evidently entering the reservoir system in some localities (p. 39).

The easternmost body of type C water is derived in part from return flow of irrigation water in the Mud Lake area to the northeast. The source of contamination in the next area to the west, around well USGS 6, is not known, nor is it known in the area still farther west, represented by wells USGS 12 and NRF 2 (p. 39).

The water of type C in the remaining two areas contains a significantly higher percentage of sodium and potassium...than the adjacent water of type A. In the smaller area, extending southward from the ICPP, sodium chloride waste water is the obvious source of contamination...The source of contamination in the larger area, occupied by wells USGS 13 and 22, is not known. There may be a natural origin, or the water may be derived in part from seepage in irrigated areas in the valley of the Little Lost River (p. 39).

Type D water, represented by only six analyses, has a unique chemical character in that sulfate is the predominant anion. Five of the samples...represent the body of perched water that has infiltrated from the Materials Testing Reactor – Engineering Test Reactor (MTR-ETR) waste-disposal pond. Four of these samples have higher concentrations of dissolved constituents than any other waters sampled in the NRTS. The sixth sample ...is peculiar in that it is high in sulfate yet has the lowest concentration of dissolved constituents of any water sampled in the Station. The source of this water and the reason for its peculiar character are not known (p. 24).

Olmsted (1962) summarizes his work as follows:

On the basis of the proportions of ionized constituents the ground waters were subdivided into four chemical types, designated A, B, C, and D. Types A and B, which are the most extensive, are essentially uncontaminated native waters in which bicarbonate and carbonate (chiefly bicarbonate) equal or exceed 70% of the anion total. Types C and D, which are considered to be contaminated waters, are distinguished from types A and B by the lower percentage of bicarbonate and carbonate (less than 70% of the anion total) and higher percentage of sulfate, chloride, nitrate, and fluoride. Chloride is the chief contaminant in type C water; sulfate is the predominant anion in type D water.

Type A water, in which calcium and magnesium equal or exceed 85% of the cation total, underlies the western half of the Station and is derived chiefly from the drainage basins of the Little Lost River and Birch Creek to the northwest. The low percentage of sodium and potassium, and the low concentration of silica in this water reflect the scarcity of these constituents in the source areas, which are underlain extensively by limestone and dolomite.

Type B water, in which sodium and potassium exceed 15% of the cation total, underlies the eastern half of the Station, originated in the mountains to the north and northeast, and probably is affected by irrigation in the Mud Lake region. The mountainous intake area is underlain by silicic volcanic rocks which are much higher in sodium, potassium, and silica than most of the rocks in the source region for type A water; this difference is indicated by the larger amounts of these constituents in type B water.

In types A and B waters the sum of the dissolved constituents averages slightly more than 200 ppm. The low mineralization reflects the moderate to abundant precipitation in the mountainous source areas, the absence of extensive deposits containing highly soluble minerals, and the low solubility of the basalt that forms the principal aquifer system. The source of contamination in type C water, which is known to occur in five areas within the Station, include drainage from irrigated areas (chiefly the Mud Lake region), aqueous-waste discharged to wells at operational facilities (notably the ICPP), and probably, waters of various natural origins including thermal springs. Increase in chloride in type C water generally is accompanied by an increase in total dissolved solids (TDS) and may or may not be associated with a concomitant increase in sodium and potassium.

Type D water is rare; most of it occurs in a body of perched water derived from seepage from the waste-disposal pond at the MTR-ETR facility. Some of this water is the most highly mineralized water in the NRTS; the sum of dissolved constituents approaches 1,000 ppm in samples from wells near the disposal pond.

Areal variations in chemical character confirm the regional south-southwestward direction of ground-water movement indicated by the configuration of the water table. Changes in relative amounts of replenishment from different sources, reflected by changes in direction of ground-water flow lines, result in blending of types A and B waters in a broad transition zone that extends south-southwestward across the Station. Variations in chemical character of the water with time are significant in some wells within the transition zone. However, in most wells remote from waste-discharge facilities, changes in water quality with time are small....

Changes in the chemical character of ground water as it moves through the aquifer system are caused by dilution, sorption, and chemical precipitation. Dilution probably is the most important process, at least on a regional scale. Cation exchange, an adsorption process, is important only where thick masses of sediment are present. Anion adsorption, absorption, and chemical precipitation may explain in part the attenuation of the contaminated water down gradient from Mud Lake (pp. 67-69).

4.2.2 Robertson et al., 1974

The geochemical composition of groundwater beneath the INEEL and vicinity was described by Robertson et al. (1974). They present the spatial distribution of inorganic constituents and temperature in the upper portion of the aquifer, and also describe their geochemical conceptual model that accounts for the observed solute distributions. Their discussion of each parameter is summarized below.

4.2.2.1 Dissolved Solids

Their data (p. 60) show a general trend of lower dissolved solids concentrations toward the southeast and higher concentrations toward the northwest, closer to the carbonate terrains in the mountains northwest of the INEEL. They speculate that the distortion of the 2000 mg/L contour in the southern portion of the site is caused by heterogeneity in transmissivity. High TDS values southwest of Mud Lake are probably due to evaporative concentration during irrigation (p. 59).

4.2.2.2 Temperature

Temperature contours (p 61) are generally parallel to groundwater flow lines. Anomalously warm areas are attributed to recharge of irrigation water near Mud Lake, and either to recharge of irrigation water from the Big and Little Lost River valleys or to discharge of thermal waters (p. 59, 61).

4.2.2.3 Calcium and Magnesium

Calcium and magnesium (pp. 63-64) show a similar pattern, with concentrations generally increasing along a SE-NW trend, presumably reflecting the input of these cations from dissolution of carbonates in the mountains northwest of the site. High concentrations near Mud Lake are attributed to recharge of evaporative-concentrated irrigation water (p. 62).

4.2.2.4 Sodium

The SE-NW sodium (p. 65) concentration trend is opposite that of calcium and magnesium. High concentrations near Mud Lake are attributed to recharge of irrigation water, with speculation that thermal water is a possible source of sodium. Attenuation is attributed to dilution and possibly ion exchange. Isolated elevated concentrations are attributed to thermal water, irrigation recharge, or waste disposal (p. 62).

4.2.2.5 Chloride

The distribution of chloride (p. 66) shows a quasi-constant background with three high-concentration areas superimposed. The two areas near the southwestern portion of the INEEL are attributed to recharge of irrigation water, thermal water, or waste disposal. The high concentration zone near Mud Lake is not attributed to recharge of irrigation water. Instead, "the only conclusion drawn from

these data is that hydrochloric acid and sulfuric acid constitute the most probable sources of the excess chloride and sulfate....A reasonable source for this quantity of acid is not apparent at this time” (p. 68).

4.2.2.6 Potassium

The distribution of potassium (p. 69) “appears random except for a crude parallelism of contours to direction of groundwater flow. There may be a tendency for a decrease from east to west which ... could be explained as westerly dilution of high potassium water related to the breakdown of silicic volcanics in the northeastern recharge area” (p. 69). High concentrations near Mud Lake were attributed to irrigation.

4.2.2.7 Bicarbonate

The distribution of bicarbonate (p. 71) shows a general pattern of increasing concentrations from SE to NW, consistent with the predominant source of bicarbonate being dissolution of carbonate rocks in the mountains northwest of the site. Superimposed on this regional pattern are an area of elevated concentration near Mud Lake, which is attributed to irrigation, and two areas of elevated concentration in the southern portion of INEL that are attributed to waste disposal activities (p. 70).

4.2.2.8 Sulfate

The distribution of sulfate (p. 72) shows a trend of increasing concentrations from SE to NW, and is attributed to a source of sulfate in the Medicine Lodge Creek drainage basin in the northern recharge area (p. 70). The high concentration zone near Mud Lake is not attributed to recharge of irrigation water. Instead, “the only conclusion drawn from these data is that hydrochloric acid and sulfuric acid constitute the most probable sources of the excess chloride and sulfate....A reasonable source for this quantity of acid is not apparent at this time” (p. 68).

4.2.2.9 Nitrate

The distribution of nitrate (p. 73) shows generally low values “with a crude parallelism with direction of flow” (p. 70). The elevated values near Mud Lake are attributed to the use of nitrogenous fertilizer. However, “the source of isolated nitrate highs near the central and northern part or the NRTS is not known” (p. 70).

Author’s note – a reasonable explanation for the elevated nitrate concentrations near TAN is nitrification of sewage disposed in the aquifer. A reasonable explanation for the elevated concentrations near the Naval Reactors Facility (NRF), Test Reactor Area (TRA), and ICPP is also disposal of sewage.

4.2.2.10 Fluoride

The spatial distribution of fluoride (p. 75) shows a general trend of increasing concentrations to the SE. This is attributed to fluoride-rich water recharging the Eastern SRPA from the northeastern recharge zone, and being progressively diluted with recharge from other areas. Concentrations may be controlled by precipitation of fluorite or fluoroapatite (p. 74).

4.2.2.11 Silica

The spatial distribution of silica (p. 76) shows a general trend of increasing concentration to the SE. This is attributed to high silica water recharging from the northeastern recharge area (p. 74).

4.2.3 Curtis 2000

The following summary description of the geochemical conditions typical of the subsurface beneath the RWMC is taken from a review prepared by Curtis et al. (2000).

To summarize some of the geochemical characteristics at the site that can have a large impact on some or all of the actinides considered {U, Np, Pu, Am – ed}. Specifically, the waters from perched zones below the SDA and ground water from the SRPA have the following characteristics that may be significant for actinide transport: (1) a pH with a range of 7.8 to 8.4, (2) dissolved oxygen concentrations that are nearly saturated to slightly supersaturated with respect to air, (3) saturation indices that indicate the water is typically slightly saturated {supersaturated – ed.} with respect to calcite, and (4) dissolved organic carbon (DOC) concentrations that are generally below 1 mg/L (Knobel and others 1992a) or near 1 mg/L (Busenberg, 1999, USGS written communication). Generally, higher DOC values are obtained in wells that are contaminated by drilling fluid surfactants or show evidence of other anthropogenic organic contamination (Busenberg, 1999, verbal communication). In a previous study, Leengen and Bagby (1982) had measured significantly higher DOC concentrations in INEEL ground waters ranging from 1.6 to 18 mg/L. In addition, investigations of cores taken at the site indicate: (1) calcite commonly occurs in both fractures and in the sedimentary interbeds, (2) iron oxyhydroxides, which can adsorb actinides strongly under certain conditions, are commonly observed on fracture surfaces and in the interbed sediments, and (3) clay minerals, most commonly identified as illite, account for an average of 20% of the sediment interbed material analyzed (Bartholomay, 1990c). Both smectite and mixed layer smectite clays have also been observed in some interbed samples. Each of these characteristics can impact the aqueous speciation, the surface speciation, and/or the redox state of an actinide.

4.3 Vertical Variation in Solute Composition

Several workers have described vertical variation in solute concentrations in groundwater beneath the INEEL.

4.3.1 Olmsted

Olmsted (1962) briefly mentioned vertical variations in solute composition of groundwater.

Except for a top layer of relatively fresh water as much as 50 feet thick which occurs in many parts of the NRTS, changes with depth in the chemical quality of the water are small in most wells not located near waste-discharge facilities. The top layer of fresher water is believed to be derived from infiltration of precipitation and local runoff on the plain.

4.3.2 Robertson et al.

Robertson et al. (1974) (pp. 74-77) describe vertical variations in solute concentration as follows.

The first indication of a significant change in water composition with depth came from in-place, water-resistivity studies (inverse of conductance) made with a mobile logging unit on several wells. These studies show the presence of a body

of relatively fresh water (specific conductance of 100 to 200 micromhos at 25°C) at the top of the water table, as much as 50 ft thick through usually much thinner, underlain by normal groundwater with a specific conductance of 300 to 400 micromhos. This fresh zone was first interpreted as an accumulation of rainfall and snowmelt that had percolated directly to the water table with little reaction in rocks of the plain. It was then noticed, however, that the fresh zone occurred only in cased holes and then only above the level of perforations in the casing. Further, although thief samples showed lower concentrations of dissolved solids in the fresh zone, tritium values were much higher than in deeper zones.

A satisfactory interpretation of these data has not been achieved. An alternative explanation envisions fresh water accumulating within the well casing by condensation of warm, humid, tritium-rich surface air on the cold steel casing. The fresh zone, therefore, may be only an artifact, but the data does raise serious questions about the suitability of thief samples to represent the groundwater body.

A second example of vertical compositional variation concerns a single deep well. A pumped sample taken on June 7, 1952, from Well 7 represented water from a depth of 214 ft (the water table) to 698 ft....Later the hole was deepened and on August 9, 1952 a pumped sample represented the water from 212 to 1,200 ft....In spite of the fact that the deep sample contains some unknown proportion of the same water contained in the shallow sample, the deep sample shows some significant changes. Compared to the shallower sample, deeper water exhibits a doubling of sodium, and eightfold increase in fluoride, a doubling of silica, together with small reductions in calcium, magnesium, and bicarbonate and a ninefold decrease in nitrate....

The compositional changes noted in Well 7 do, however, lead to the suggestion that deep water under the NRTS may contain more sodium, silica, and fluoride than does shallow water. These constituents, especially when not accompanied by abundant chloride, point to the breakdown of silicic rocks as a source. Well 7 may be tapping water that reacts with silicic rocks at depth. The closeness of Well 7 to the margin of the plain means that silicic rocks may not be buried as deeply as they are farther out on the plain. This evidence provides additional support for the inference, based on geologic reasoning, that silicic volcanic rocks underlie the basalt and sediments of the plain.

4.3.3 Mann 1986

Mann (1986 #190) reports water quality variations in a deep (10,365 ft) corehole drilled at the INEEL. The purpose and significance of this corehole is described by [Mann, 1986 #190].

A 10,365-ft deep test hole was drilled in 1979 at Idaho National Engineering Laboratory. The main purpose of the test hole was to ascertain whether a hydrothermal resource existed beneath INEL and, if so, whether it would be economically feasible to develop the resource....

Few drill holes penetrate the rocks underlying the INEL more than 1,000 ft and most holes are less than 750 ft in depth. Because the test hole penetrated more than 7,000 ft of rocks that had not previously been explored by drill holes, the

test hole also yielded new information on the physical, chemical and hydraulic properties of the rocks and the chemical characteristics of the ground water contained therein (p. 2).

Mann (1986 #190) describe vertical variations in temperature with depth in this corehole as follows. Figure 4-2 is a plot of temperature as a function of depth from his report.

The physical and chemical properties of water pumped from the INEL-1 test hole differ with depth. Water temperature in the INEL-1 test hole gradually increased from 26°C at 600 ft below land surface to 144°C at 9,985 ft....The temperature of water in the test hole, however, had not come to equilibrium after being undisturbed for slightly more than one month. The temperature at a depth of 600 ft below land surface was still about 13°C greater than the temperature of water at the same depth in the SRPA. The greater temperature may be the result of the circulation of water in response to convection currents within the well bore. The temperature gradient in the test hole was nearly linear and averaged slightly less than 1.3 °C per 100 ft of depth below land surface. From 600 to about 4,000 ft, the temperature gradient was not as uniform as it was below 4,000 ft....In the interval from 1,300 to 1,600 ft, the temperature increased about 1°C or about 0.3 °C per 100 ft. This decrease in gradient corresponds to the thick zone of sand, silt and clay....From 2,450 to 2,750 ft, the temperature increased about 1°C ,...also about 0.3 °C per 100 ft. This decrease was near the contact between the tuffaceous interbeds that immediately underlie the lowermost basalt and the underlying welded tuff....The relatively low temperature gradient in the two intervals may result from the rocks having a slightly greater hydraulic conductivity than adjacent rocks (p. 15).

Mann (1986 #190) then discuss variations in chemical properties of water with depth. Table 4-2 provides the water quality data he reported, and Figure 4-3 shows Stiff diagrams of water analyses from four depth intervals.

The dissolved solids and chemical composition of the water pumped from INEL-1 change markedly with depth. Water from the Water-Supply well, which taps the upper 200 ft of the SRPA, contained 381 mg/L ... of dissolved solids and had a calcium bicarbonate type of chemical composition with significant amounts of magnesium and chloride....

The dissolved solids concentration increases from 350 to 915 mg/L in the interval between 2,206 and 3,559 ft. Whether the increase is gradual or abrupt is not known, because this interval was neither pumped nor was the water sampled. If the increase is abrupt, it may occur at the contact between the altered basalt and tuffaceous interbeds at about 2,160 ft below land surface; the vertical and horizontal hydraulic conductivity also would likely decrease at this depth. From 3,559 to 10,365 ft, the dissolved solids increase from 915 to 1,020 mg/L – a relatively small increase when compared to the 565 mg/L increase that occurs between 2,206 and 3,559 ft.

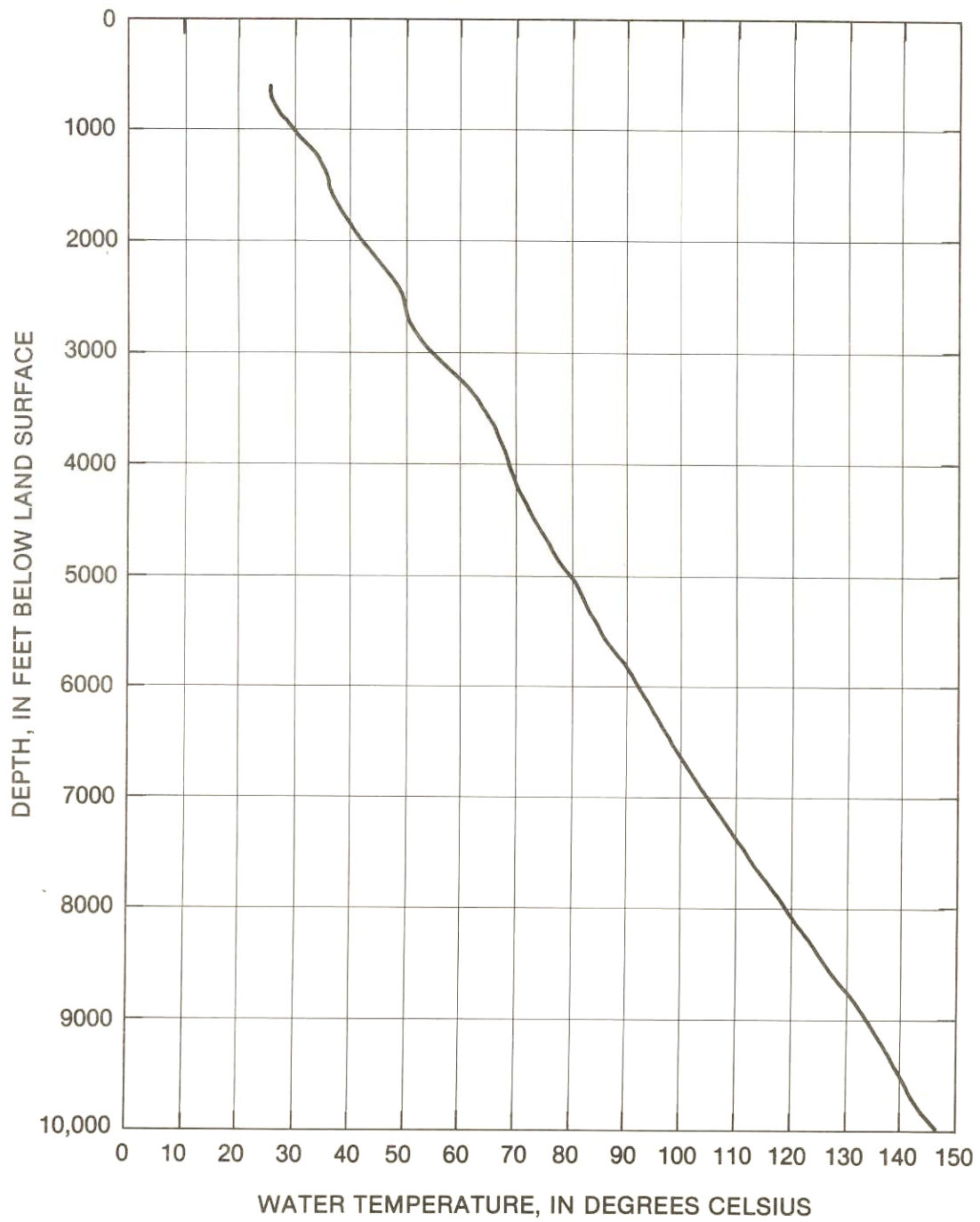
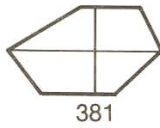


Figure 4-2. Water temperature profile for INEL-1 test hole (after Mann 1986).

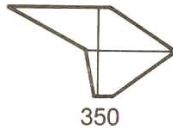
Table 4-2. Selected water-quality data from the INEL-1 water-supply well and INEL-1 test hole (after Mann 1986).

[Analyses are in milligrams per liter unless otherwise noted. Constituent concentrations in dissolved state unless otherwise noted. Abbreviation, $\mu\text{g/L}$, represents micrograms per liter.]

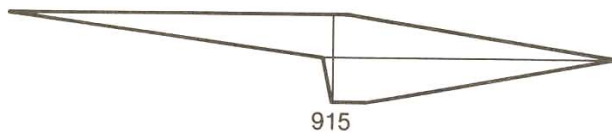
Water-Supply Well		INEL-1 Test Hole			
Interval tested (feet below land surface)	395- 595	1,511 2,206	3,559- 3,713	3,559- 4,878	4,210- 10,365
Alkalinity	160	210	720	670	740
Arsenic ($\mu\text{g/L}$)	1	20	24	73	--
Bicarbonate	190	220	780	820	900
Boron ($\mu\text{g/L}$)	280	900	580	530	560
Calcium	76	10	8.1	8.9	7.3
Chloride	74	17	17	13	12
Chromium-total ($\mu\text{g/L}$)	20	20	10	10	0
Fluoride	0.2	1.1	12	13	13
Iron ($\mu\text{g/L}$)	0	0	770	1,200	1,100
Lead ($\mu\text{g/L}$)	0	0	0	0	--
Lithium ($\mu\text{g/L}$)	5	50	290	280	--
Magnesium	28	2.0	1.1	1.1	0.5
Manganese ($\mu\text{g/L}$)	0	20	110	60	50
pH	7.8	8.2	8.2	8.3	7.9
Potassium	3.0	10	9.2	8.1	7.5
Dissolved solids (calculated)	381	350	915	957	1,020
Selenium ($\mu\text{g/L}$)	2	1	0	0	--
Silica	24	60	33	39	47
Sodium	12	92	330	370	390
Strontium ($\mu\text{g/L}$)	370	100	120	140	150
Sulfate	50	32	69	97	99
Water temperature ($^{\circ}\text{C}$)	12	34	38	50	57



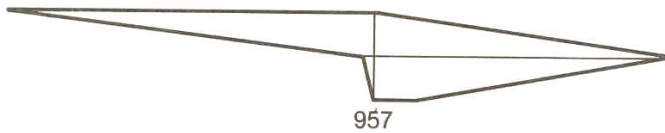
Water-Supply well
Open interval:
395 to 595 feet



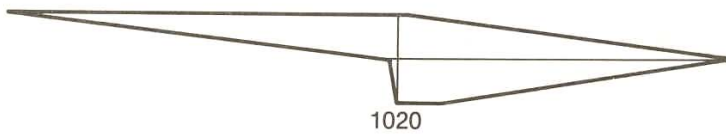
INEL-1 Test Hole
Open interval:
1511 to 2206 feet



Open interval:
3559 to 3713 feet



Open interval:
3559 to 4878 feet



Open interval:
4210 to 10,365 feet

EXPLANATION

CHEMICAL-QUALITY DIAGRAM—Shows major constituents in milliequivalents per liter. The diagrams are in a variety of shapes and sizes, which provides a means of comparing, correlating, and characterizing similar or dissimilar types of water. Number, 381, is the dissolved solids concentration in milligrams per liter.

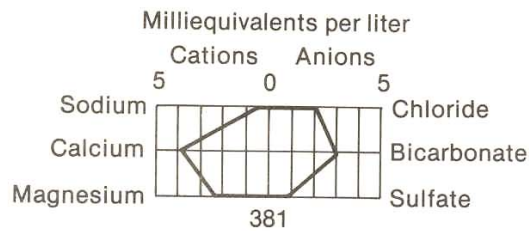


Figure 4-3. Chemical quality of water for open intervals in Water-Supply well and INEL-1 test hole (after Mann 1986).

The smaller concentration of dissolved solids in the upper 2,200 ft of rocks tapped by INEL-1 is attributed to dilution by the infiltration of streamflow, rainfall and snowmelt and underflow from upgradient recharge areas. Streamflow in the Big Lost and Little Lost rivers has a calcium bicarbonate type of chemical composition....The infiltration of streamflow along the channels of these rivers constitutes a significant part of the recharge to rocks that underlie the INEL.

The transition from a calcium bicarbonate to sodium bicarbonate type of chemical composition occurs in the interval between 595 and 1,511 ft below land surface....It is not known whether the transition is gradual or abrupt because the interval was not pumped and samples were not collected. The transition most likely occurs in the interval from 850 to 1,220 ft which is mainly sand, silt, and clay....The change in chemical composition is caused by an increase in sodium and a decrease in calcium in the water. Dilution of the sodium type of water with a calcium type of water, ion exchange, and precipitation of calcite accounts for the change in the chemical composition of water. In the vicinity of the INEL-1 test hole, dilution is the prime controlling factor. The sodium-type water at depths greater than 1,511 ft below land surface vertically moves upward in response to a higher hydraulic head. It is diluted by the calcium-type water present in the shallow basaltic rocks.

Water samples collected from the Water-Supply well and INEL-1 test hole were analyzed for selected trace elements in addition to dissolved solids and common ions....In general, the concentration of trace elements increased with depth. The larger concentrations are likely associated with the higher water temperature and the hydrothermal alteration of rock units below a depth of 1,600 ft.

Chromium and selenium, on the other hand, were present in slightly greater concentrations in water from the Water-Supply well which taps the upper 200 ft of the SRPA than in the deeper rock units tapped by INEL-1...Strontium was present in a significantly greater concentration in the aquifer – 370 µg/L ... than in deeper units – 100 to 150 µg/L. For the observed concentrations in water from the SRPA, chromium, selenium and strontium are likely introduced into the ground-water flow system via water recharged along the major stream channels or is derived from minerals in the sand, silt and clay deposits that are intercalated with the basalts.

Boron and silica concentrations were greater in the interval from 1,511 to 2,206 ft than in underlying or overlying units....The reasons for these greater concentrations are not known, but probably are associated with the altered and mineralized basaltic rocks that occur from 1,600 to 2,100 ft below land surface (pp. 15-20).

4.4 Sources of Water and Solutes in the Aquifer Beneath the INEEL

The water and solutes in the aquifer beneath the INEEL are derived from several sources. The sources of water include precipitation that falls directly on the INEEL, and underflow and infiltration from tributary basins. Solutes dissolved in these waters enter the aquifer beneath the INEEL, and solutes can be added to or removed from groundwater as it moves beneath the INEEL via reactions with the solid phases present in the aquifer. Water and solutes in precipitation are discussed in Section 4.2.1, and tributary basin underflow and infiltration are discussed in Section 4.2.2. The effect of irrigation on solutes is discussed in Section 4.2.3. Water-rock interaction is introduced in Section 4.2.4, and a detailed discussion of this topic is presented in Section 4.3. Finally, groundwater age studies and their implications are discussed in Section 4.4.

4.4.1 Precipitation

Mundorff et al. (1964) estimates that recharge from precipitation may vary from 0.02 ft/year in the central part of the Eastern SRPA to as much as 0.3 ft/year near Craters of the Moon. Kjelstrom (1995) estimates an average recharge rate of 0.08 ft/year from a basin water-budget analysis.

Cecil et al. (1992) used environmental tracer data and neutron logging data to estimate net water infiltration rates through soils at one site near the RWMC at the INEEL. Chlorine-36 and tritium concentrations and neutron logs in shallow boreholes indicated that net infiltration ranges from 2 to 5% of the annual precipitation. Busenberg et al. (2001) suggest that areal recharge occurs both as continuous spatially distributed diffuse recharge resulting from widespread percolation through the entire unsaturated zone and occasional concentrated recharge resulting from short-term penetration of water along distinct pathways through the unsaturated zone.

Ackerman et al. (in preparation) uses 2 to 5% of precipitation, as determined by Cecil et al. (1992) to estimate a recharge rate of 0.02 to 0.04 ft/year. They estimated that recharge would be about 70 ft³/s over the entire subregion using the upper value of 0.04 ft/year. Ackerman et al. determined that the net effect of recharge from precipitation is probably very small when compared to other sources of inflow; it is a less important consideration than more concentrated sources such as streamflow infiltration.

Arnett and Smith (2001) state that direct precipitation on the plain locally recharges the aquifer to a limited degree, particularly when snow melts rapidly in the spring. The present Waste Area Group (WAG)-10 conceptual model uses the Cecil et al. (1992) estimate of approximately 2 to 5% of the annual precipitation.

The concentrations of major ions in precipitation at Craters of the Moon National Monument, located about 25 km west of the INEEL, was reported by Busenberg et al. (2001) and compared to concentrations in groundwater collected from well USGS 101, near the southeastern corner of the INEEL. Busenberg et al. (2001) consider that water from well USGS 101 represents uncontaminated regional groundwater (p. 41). Comparison of solute concentrations indicates that concentrations in groundwater are much higher than concentrations in precipitation. The larger concentrations result from reaction with solid phases present in soil, the vadose zone, and the groundwater zone, and potentially from human activities such as addition of agricultural chemicals, road salt, and waste disposal.

Table 4-3. Dissolved species in precipitation near INEEL and in groundwater at the INEEL (Busenberg et al., 2001).

[Units concentration are in milligrams per liter except for (1) temperature is in degrees Celsius (°C); pH is the negative base-10 logarithm of the hydrogen-ion activity in moles per liter; 3H is in tritium units (TU); carbon-14 is in percent modern carbon (pmc); and carbon-13, deuterium, and oxygen-18 are in permil. Blank spaces, data not available. *, estimated concentration]

Characteristic or constituent	Precipitation ¹	USGS 101 ²
Temperature	10 °C	14.7 °C
pH	5.61	8.16
DO	9	9
HCO ₃	58	168
³ H		5.99 TU
Ca	.379	36.9
Mg	.058	15.3
Na	.315	15.5
K	.055	2.8
Cl	.45	21
SO ₄	.761	21.5
F	.01	.79
SiO ₂		30.4
NO ₃	.988	4.8
HN ₄	.273	
Sr	.002*	.172
Al		.02
δ ¹³ C	-12* permil	-9.29 permil
¹⁴ C	100* pmc	58.6 pmc
δ ₂ H	- 140* permil	-135.5 permil
δ ¹⁸ O	-18.2* permil	-17.61 permil

¹ Average concentrations in precipitation from 1988 to 1999 from Craters of the Moon, Idaho.

² Busenberg and others, 2000

4.4.2 Tributary Basins (including both underflow and surface water)

Robertson et al. (1974) discuss the solute composition of water that enters the Eastern SRPA as underflow from tributary basins in their section entitled “Composition of Recharge”. They group underflow spatially into the following categories (Figure 4-4; their figure 18): northwest, west, east, north, northeast, and thermal water. Water from their “west” category enters the ESRP aquifer downgradient of the INEEL and is not discussed herein. They also discuss water-rock interaction, and recharge of irrigation water. Their paradigm is described as follows (p. 42). “Using the hypothesis that the mineralogy of the enclosing rocks provides the dominant control on the composition of a groundwater, particularly groundwaters with short and simple histories, the unique chemical characteristics of different sources of recharge to the eastern Snake River Plain, and the possible mineralogic controls on these unique compositions were explored and related to the unique compositions in groundwater beneath the NRTS.” Their postulated reactions are presented in the following subsections.

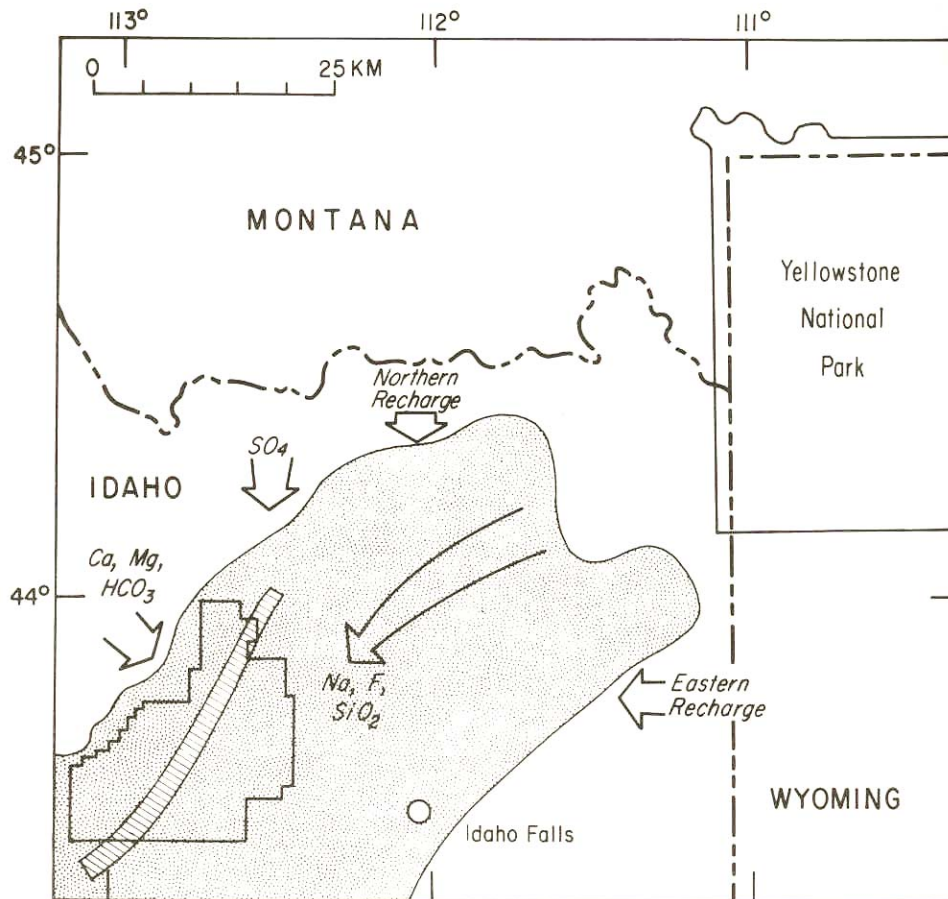


Figure 4-4. Hydrochemical zones of groundwater at the NRTS and sources of chemically distinct recharge to the eastern Snake River Plain (shaded area) (after Robertson et al. 1970).

4.4.2.1 *Northwestern Tributary Basins*

Robertson et al. (1974) group the Big Lost River, Little Lost River, Birch Creek, and Medicine Lodge Creek into the “Northwest” category. The rock types in this region include quartzitic sediments, limestones, dolomites, sandstone, and shale. “The areal predominance of carbonate rocks, their ability to imbibe and carry all surface water, and their simple highly reactive composition consisting of relatively soluble calcite and dolomite, make them the most important geochemical controls on the northwest side of the Snake River Plain” (p. 45).

They postulate that the following set of reactions is responsible for the solutes in groundwater that enters the Eastern SRPA from these tributary basins.

- Calcite dissolution
- Dolomite dissolution
- Hydrolysis of potassium feldspar to muscovite

- Hydrolysis of sodium feldspar to montmorillonite
- Hydrolysis of muscovite and montmorillonite to kaolinite
- Hydrolysis of kaolinite to gibbsite.

4.4.2.1.1 Big Lost River

Carkeet et al. (2001) describe the geochemistry of the Big Lost River drainage system. This drainage system consists of contributing mountainous streamflow basins tributary to the Big Lost River. Groundwater in this system moves as underflow into the SRPA near Arco. This area is characterized by carbonate rocks.

Carkeet et al. (2001) based their geochemical description on water-chemistry analyses from ten wells. Water from the Big Lost River drainage system characteristically is enriched in calcium, magnesium, and bicarbonate. The predominant chemical reactions in this groundwater system are related to interaction of water with calcite and dolomite. These predominant reactions are supported by the abundance of carbonate rocks in the basin and by the calcium-magnesium bicarbonate nature of the water. The postulated reactions are as follows:

- Precipitation and dissolution of calcite
- Dissolution of dolomite.

4.4.2.1.2 Little Lost River

Swanson et al. (2002) describe the geochemistry of the Little Lost River drainage basin. This drainage system consists of contributing mountainous streamflow basins tributary to the Little Lost River. The geology of this area is characterized by carbonate rocks. Groundwater in this basin enters the SRPA as underflow near Howe.

Swanson et al. (2002) described geochemical reactions between rocks and groundwater in the Little Lost River drainage basin using water-chemistry data from six wells and two surface-water sites. Water typically is enriched in calcium, magnesium, and bicarbonate. The predominant chemical reaction is the dissolution of dolomite. Plausible chemical reactions are defined as follows.

- Precipitation of calcite
- Either precipitation or dissolution of dolomite
- Dissolution of halite
- Dissolution of gypsum

4.4.2.1.3 Birch Creek

The Birch Creek drainage basin consists of contributing mountainous streamflow (Shawn Swanson personal commun 2002). The geology of this area, similar to the Big Lost River and Little Lost River drainages, is characterized by carbonate rocks and a basalt barrier to groundwater flow in the central part of the basin. Groundwater in this basin enters the SRPA as underflow northwest of TAN.

Water in the Birch Creek drainage basin typically is enriched in calcium, magnesium, and bicarbonate. The predominant chemical reaction is the dissolution of dolomite. Plausible chemical reactions are defined as follows.

- Dissolution or precipitation of calcite
- Dissolution of dolomite
- Dissolution of gypsum
- Reactions associated with the basalt barrier, to include dissolution of olivine, diopside, labradorite, potassium feldspar, and illite.

4.4.2.2 *Northeastern Tributary Basins*

Robertson et al. (1974) discuss inputs from northeastern tributary basins (p. 52). This area includes the Henry's Fork of the Snake River and the Fall River drainage basins. The rock type in this area is rhyolitic volcanic rocks. The postulated reactions are as follows (p. 49).

- Hydrolysis of potassium feldspar and sodium feldspar
- Hydrolysis of calcium feldspar to yield montmorillonite and gibbsite
- Weathering of pyroxene and amphibole minerals
- Dissolution of silica minerals
- Dissolution of fluorite
- Devitrification of volcanic glass.

4.4.2.3 *Eastern Tributary Basins*

Robertson et al. (1974) discuss inputs from east of the eastern Snake River Plain (p. 50). The rock types in this area are similar to those in the northwestern tributary basins, and consist of carbonates, siltsstones, and shales, and contain coal, anhydrite, gypsum, phosphate, and fluoride. The same reactions proposed to occur in the Northwestern tributary basin are proposed to occur here, as well as the following additional reactions.

- Dissolution of anhydrite and gypsum
- Hydrolysis of fluorapatite
- Hydrolysis of siderite
- Oxidation of pyrite and marcasite
- Precipitation of ferric hydroxide.

4.4.2.3.1 Northern Tributary Basins / Camas Creek / Mud Lake

Robertson et al. (1974) discuss inputs from northern tributary basins (i.e., the Camas Creek / Mud Lake drainage basin) (p. 52). The rock types in this area and consequently the reactions that occur there are similar to those in the eastern tributary basins (Section 4.2.2.3).

In the Mud Lake area, “water from Camas Creek is used for irrigation and eventually reaches Mud Lake. The analysis of water from Mud Lake ... shows an approximate doubling in the concentration of most constituents due to evaporation during irrigation” (p. 52).

4.4.3 Water Diverted for Irrigation

Robertson et al. (1974) address recharge of irrigation water (p. 58). “The effect of crop irrigation on a groundwater composition... consists of evaporative concentration of most dissolved constituents, an additional increase in sodium and chloride, increase in fertilizer-based constituents, and a regulation of silica concentration by some external control. Evaporation rates necessary to achieve the doubling and tripling of dissolved constituents frequently observed require repeated or prolonged exposure of the water to sun and wind at the earth’s surface, resulting in a rise in water temperature. Such multiple exposure commonly occurs in regions of intensive irrigation, as along the Snake River where downstream reuse of water is common. Pumping of water for irrigation from a perched body of recharged irrigation water, as occurs at Mud Lake, produces the same recycling effect. Leaching of highly soluble sodium chloride, originating from the fallout of atmospheric dust, could account for some additional increases of sodium and chloride ions” (p. 58).

4.4.4 Thermal Waters

Robertson et al. (1974) discuss contributions from thermal waters (p. 55). “Hot springs bordering the plain on concealed bounding faults, as well as possible hot springs beneath the plain on buried basin and range faults, may contribute thermal water to the groundwater. Recognition of the contribution of thermal water to ordinary groundwater may be difficult. Where the proportion of thermal water is large, it will be indicated by a large temperature increase in the groundwater. Before significant dilution has occurred, a high dissolved solids content, particularly of sodium and chloride, as well as high concentrations of constituents such as fluoride, boron, lithium, and ammonia, may denote a thermal contribution” (p. 55).

4.4.5 Water – Rock Interaction / Diagenesis

Robertson et al. (1974) briefly address water – rock interaction (p. 57). “Rocks underlying the station might affect the composition of that part of the precipitation that infiltrates. Moreover, as the chemically distinct recharges enter the Snake River Plain and move through the rocks, changes in composition effected by reaction with Snake River Plain rocks would be expected” (p. 57). Their geochemical model includes:

- Hydrolysis of olivine to chlorite, montmorillonite, and goethite
- Weathering of pyroxene
- Precipitation of calcite
- Hydrolysis of plagioclase feldspars
- Alteration of ilmenite to goethite and rutile.

4.5 Geochemical Models Incorporating Mixing and Diagenesis that Account for Solute Geochemistry in Groundwater Beneath the INEEL and Vicinity

At least three investigators have attempted to account for the geochemical processes that have yielded the observed composition of INEEL groundwater. In chronological order, these are Robertson et al. (1974), Wood and Lowe (1988) McLing 1994, Knobel et al. (1997), and Busenberg et al. (2001)

4.5.1 Robertson et al. 1974

Robertson et al. (1974) briefly describe the geochemical processes that affect solute composition in the Eastern SRPA. The processes they considered are mineral-water equilibrium and sorption (pp. 77-83).

Their discussion of mineral-water equilibrium follows.

Results show that groundwaters at the NRTS approach saturation with respect to calcite and dolomite, and that slight supersaturation occurs in groundwater from the northwest part of the station....

Numbers ... indicating degree of supersaturation of the groundwater with respect to calcite and dolomite, range from 1.0 to 1.5 for calcite and 1.0 to about 5.0 for dolomite. An exception is a saturation of 2.3 time with calcite and 13.4 times with dolomite at one of the TRA wells. Precipitation of a solid phase depends upon kinetic factors as well as the existence of a saturated solution. Experience indicates that precipitation of calcite requires supersaturations of about 4 times or more...and dolomite seems to require supersaturations of 10 to 30 times or more to overcome the kinetic barriers that obstruct precipitation...Based on this experience, no calcite or dolomite should precipitate from groundwaters beneath the NRTS under the temperature and pressure conditions prevailing in the ground. Well-crystallized calcite does form joint and vesicle coatings in the rocks above the water table where evaporation can effect a concentration of solutes.

Although supersaturation with respect to the other minerals considered does not occur, examination of the extent of dissolution of olivine in the various groundwater compositions provides an approximate measured of the degree to which the Snake River basalts react with groundwater....Olivine should be the first mineral in the basalt to react to yield weathering products such as chlorite....Unfortunately thermodynamic solubility data for chlorite were unavailable for analysis. For the compositionally closest available substitute, the degree of saturation of several groundwaters with respect to magnesium serpentine was evaluated...No water listed in Table III is saturated with respect to magnesium serpentine; however, the difference between the composition of the water and the theoretical composition of a saturated water indicates the extent of approach toward saturation. If the groundwater reacts with appreciable amounts of olivine to form serpentine (or a serpentine-like mineral), smaller differences should exist in samples that have been in contact longer with basalt (downgradient along flowlines), between the water sample compositions and the theoretical equilibrium compositions....The northeast-southwest transaction...

(parallel to groundwater flow) shows an erratic pattern of undersaturation with respect to magnesium serpentine. The lack of a pattern showing an increasing approach toward saturation to the southwest argues against there being any significant reaction between the basalt and groundwater.

Perhaps the major reason for this lack of reaction between the groundwater and rock is the relatively brief period of time that the two have been together. Groundwater within 200 ft of the water table seems to be moving quite rapidly with short-term rates as high as 54 ft per day and the long-term rates averaging 6 to 8 feet per day....Therefore, groundwater beneath the NRTS probably has not had sufficient time to equilibrate with minerals in the basalt. Very deep groundwater beneath the NRTS may, however, move much more slowly through the rocks and thus approach a composition in equilibrium with the minerals.

Their discussion of sorption is as follows.

The composition of groundwater at the NRTS can be affected in a limited way by the phenomenon of cation sorption...The frequently amorphous, hydrous oxides of iron and manganese exert the dominant control over sorption of heavy metals....Carbonate minerals exercise a strong control over the sorption of strontium....In natural groundwater systems, changes in water composition tend to be slight and extend over such long periods that exchangeable cations on solids always approach equilibrium with the surrounding solution. Only relatively large changes in water composition of extended duration will produce major changes in the ratio of cations held by exchange.

Recharge of recycled irrigation water containing sodium in a greater ratio to the other cations than exists in the groundwater tends to remove exchangeable calcium, magnesium, and potassium from the rocks or soil and replace them with equivalent amounts of sodium. When sufficient sodium has been removed from the percolating water to restore the original cation ratios, the process of removing sodium will stop. Of course, while sodium is being removed from solution, the other cations are displaced into solution, thus tending to create a new solution with cation ratios closer to the original groundwater. If the groundwater moves rapidly, dispersal of recharged irrigation water into the groundwater will tend to make compositional differences less apparent. Both these processes tend to buffer any extensive changes in the ratios of cations sorbed by the solid phases.

Discharge of waste through a well may effect a more drastic change in the naturally sorbed cations. This is because waste discharge passes through very limited areas as it leaves the well. Waste that is grossly different in composition from the groundwater may produce large changes in sorbed cations; however, unless waste discharge continues, rapid groundwater flow, like that under the NRTS, will reestablish the original pattern of exchangeable cations on the solids.

If concentrated sodium solution (a few thousand mg/L or more) were to be discharged into groundwater at the NRTS, they could produce deleterious local effects. However, no such discharges presently occur or are anticipated. Montmorillonitic clay minerals that are presently dominantly saturated with calcium and magnesium may obtain sufficient sodium by exchange to become dispersed, mobile, and plug rock pores. Additionally, the calcium and

magnesium removed from exchange sites and put into solution may provide the additional supersaturation required to precipitate calcite and dolomite in rock pores near the well. Either phenomenon might reduce the specific capacity of a well. Although the amount of calcite or dolomite precipitated from a given volume of groundwater might not be sufficient to measurable plug rock pores, episodic disposal of waste in which the boundary between waste and groundwater fluctuates may cause recurrent precipitation in the same rock interval and, consequently, cause serious plugging of the formation.

4.5.2 Wood and Low

Wood & Low (1988) examined groundwater in the Eastern SRPA, and attempted to identify the processes responsible for its geochemical composition. Their study was part of the USGS Regional Aquifer-System Analysis. The following is excerpted from the “Summary and Conclusions” section of their report (pp. D44-D45).

Four independent geochemical techniques were used to quantify the solute chemistry of the eastern Snake River Plain regional aquifer system: (1) calculation of a regional solute balance within the aquifer, (2) identification of mineralogy in the aquifer framework to compare with the postulated mineralogy, (3) comparison of thermodynamic mineral saturation indices with plausible solute reactions, and (4) comparison of stable-isotope ratios of the ground water with those in the aquifer framework. Because each of these techniques gave consistent results, it is assumed that the proposed reactions realistically reflect the solute geochemistry of the system....

Examination of the mineralogy ... identified major primary and alteration minerals in two major lithologies that constitute the aquifer framework.... Probable equations were written for precipitation of calcite and silica, weathering of olivine, pyroxene, pyrite anhydrite, and plagioclase. These proposed reactions were compared with saturation indices of the ground water to ensure that the minerals proposed to be dissolving were thermodynamically under saturated and that water was in equilibrium or was saturated with respect to minerals proposed as precipitating. The proposed reactions were evaluated by the stable isotopes $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$. Favorable comparison of the calculated $\delta^{13}\text{C}$... in ground water with the observed $\delta^{13}\text{C}$... suggests that the proposed carbonate reactions are consistent with isotopic constraints. The relative proportion of sulfur from each source was calculated by assuming that sulfate originated from oxidation of pyrite ... and anhydrite (gypsum)....

About 20% of the total solute load leaving the eastern plain is derived from weathering of the aquifer framework. The remainder is introduced from tributary drainage basins; thus, the solute load in the Snake River Plain regional aquifer system is sensitive to input from tributary drainage basins. Mass-balance calculations indicate precipitation of calcite and silica, which is consistent with the observed secondary deposits of these products filling vesicles in the basalt. The sources of sodium, chloride, and sulfate are believed to be from fluid inclusions and flushing of grain boundaries and pores of detrital marine sediments in interbeds.

Minor and trace solute concentration, although composing less than 5% of the TDS, are an important consideration with respect to water use. Concentrations of lithium, strontium, and nitrite plus nitrate as nitrogen probably are controlled by the availability in the aquifer framework. Concentrations of barium, fluoride, lead, iron, and manganese appear to be controlled by mineral precipitation. Beryllium, cadmium, chromium, cobalt, copper, molybdenum, and vanadium also may be controlled by mineral precipitation.

The effects of human activities on solute concentration and isotope ratios in specific areas were identified by solute concentrations and isotopes along several flowpaths that traversed irrigated areas. Evapotranspiration of irrigation water appears to have enriched the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of the ground water in irrigated areas and to have slightly increased the concentrations of calcium and bicarbonate. The data indicate that TDS in Blue Lakes Spring, which has experienced a large increase in discharge, have increased with time. However, the effects of irrigation on solute concentrations are small because of the chemical similarity of irrigation water with that present naturally in the aquifer, rapid ground-water movement, and large dispersivity of the aquifer.

Silica and Na-K-Ca geothermometers were used to evaluate water samples from 79 wells and springs from a large area underlying the cold-water system. The geothermometers suggest that the geothermal system is regionally extensive: approximately one-half of the silica-quartz water temperatures were greater than 90°C . Dissolved solute concentrations from the geothermal system are similar to those from the overlying Snake River Plain regional aquifer system. The reaction-controlling solutes in the geothermal system are assumed to be similar to the reactions in the cold-water system, except that ion-exchange processes combined with increased temperature and hydrolysis reaction increased sodium, bicarbonate, silica, and pH and decreased calcium and magnesium concentration relative to the Snake River Plain regional aquifer system. The pH of the water probably is controlled by the silica dissociation reaction and is maintained between 9 and 9.5 in the system. The presence of hydrogen sulfide and hydroxide prevents increases in concentration of many solutes from insoluble sulfide and hydroxide minerals. Fluoride concentration appears to be controlled by thermodynamic saturation with the mineral fluorite, whereas silica concentration appears to be controlled by precipitation of quartz. Dating of geothermal water in the Salmon Falls River basin by ^{14}C methods adjusted for carbonate solution suggests that the residence time is about 17,000 years. Isotopes of oxygen and hydrogen in the geothermal water indicate that the water is of local origin. Lighter values of $\delta^2\text{H}$, compared with $\delta^2\text{H}$ in the cold water, were observed in several geothermal samples and may indicate that water recharged the geothermal system during a cooler climate in the past.

Their conceptual model of the geochemical system in the shallow, cold-water portion of the aquifer can be summarized as follows.

- Approximately 80% of the solutes in groundwater that discharges from the Eastern SRPA at King Hill, ID, are present in groundwater that enters from tributary basins. Details for major ions are presented in Table 7 of Wood & Low (1988).
- The remaining 20% of the solutes are generated from weathering reactions that occur in the aquifer.

- The major reactions that control solute composition are dissolution and precipitation of minerals in the aquifer framework, and additions of solutes by human activities such as application of fertilizer and road salt
- The main processes / reactions are:
 - Addition of NaCl from fluid inclusions, detrital marine sediments, and man's activities
 - Dissolution of olivine
 - Weathering of plagioclase to smectite
 - Dissolution of pyroxene
 - Dissolution of detrital anhydrite
 - Oxidation of pyrite
 - Precipitation of calcite
 - Precipitation of silica.
- This suite of reactions is not unique (i.e., other combinations of reactions could account for the observed solute compositions). Isotopic, thermodynamic, and mineralogic arguments were used to constrain the proposed reactions.
- Stable carbon isotopic data are consistent with calcite precipitation occurring in the aquifer.
- Stable sulfur isotopic data were used to constrain the relative contribution of anhydrite dissolution and pyrite oxidation.
- Irrigation has had little effect on groundwater geochemistry.
- The deeper geothermal system contributes little flow to the shallow, cold-water system.

A geochemical conceptual model was also developed for the deeper geothermal system. The major processes in this conceptual model are as follows (Wood & Low 1988; Table 18):

- Dissolution of NaCl from fluid inclusions, grain boundaries, and pores of detrital marine sediments
- Fluorite dissolution
- Anhydrite dissolution
- Pyrite oxidation
- Calcite dissolution
- Weathering of feldspar to gibbsite
- Ion exchange.

The essential feature of the Wood & Low (1988) conceptual model is that the solute geochemistry of the shallow groundwater system is due primarily to input of solutes from tributary basins and secondarily to dissolution and precipitation reactions that occur in the aquifer.

4.5.3 McLing

McLing (1994) considered two conceptual models for accounting for the observed water chemistry in INEEL groundwater. The first, the diagenetic model, is the same conceptual model utilized by Wood and Low (1988) and Knobel et al. (1997), and is based on the assumption that the solutes in INEEL groundwater are derived from reactions between the solid matrix (i.e., mineral phases in sediments and rocks that host the aquifer). The second conceptual model, the mixing model, is based on the assumption that relatively little interaction between water and rocks occurs in the aquifer, and that observed changes in water chemistry along a flow path result primarily due to mixing of groundwater derived from multiple sources, in this case water from the Birch Creek drainage, from Mud Lake, and geothermal water from depth.

McLing (1994) argues that the diagenetic model is inconsistent with some of the observed characteristics of the INEEL groundwater system, including: thermodynamic calculations indicate that substantial silica should precipitate in the aquifer, while little is observed; changes in concentration of sulfate and chloride in uncontaminated water along a flowpath are not accounted for by the diagenetic model.

McLing (1994) presents an alternative conceptual model to account for changes in water chemistry as groundwater transits the INEEL. His model is that mixing between Ca-Mg bicarbonate water derived from the Birch Creek drainage, and with water from the Mud Lake area that has higher proportions of sodium and potassium relative calcium and magnesium than does Birch Creek groundwater, largely accounts for observed changes in water chemistry. In addition to these major sources of water, a minor amount of sulfate- and chloride-rich geothermal water was needed in his mixing model to account for the observed behavior of sulfate and chloride. His mixing model did not require that significant rock-water interaction (i.e., diagenesis) occur in the aquifer. McLing (1994) concluded that the mixing model provided a better description of the geochemical evolution that occurs in groundwater beneath the INEEL than does the diagenetic model.

McLing (1994) criticized the diagenetic conceptual model suggested by Wood & Low (1988) and in his own work on the following bases.

- Wood & Low (1988) suggested that fluid inclusions and marine sediments are the sources for Cl⁻ in the aquifer...However, these are inconsistent with observations of aquifer material (p. 41).
- The aquifer beneath the INEL is undergoing extensive diagenesis similar to that described by Wood and Low (1986). However, there is very little observable evidence to support a model that requires extensive diagenesis in the aquifer at the INEL (p. 43).
- The exclusion of sulfate and chloride alone invalidates the results of the water rock interaction model (p. 43).
- The NETPATH calculations indicate that the groundwater precipitated more SiO₂ than calcite. This is inconsistent with the lack of secondary silica in the aquifer (p. 43).

- The water-rock interaction {model} is incapable of accounting {for} SO_4^{2-} or Cl^- behavior in the SRPA at the INEL (p. 43).
- The relatively small amount of predicted weathering is consistent with observations of aquifer host rock. First, alteration reactions are sluggish at the cold temperature of the aquifer ($< 15^\circ\text{C}$). Second, residence time for groundwater in the SRPA allows little time for the water to interact with the host rock. Third, core samples taken from the aquifer at the INEL do not exhibit extensive weathering (p. 46).

4.5.4 Knobel et al.

Knobel et al. (1997) developed a geochemical conceptual model that is very similar to the Wood & Low (1988) conceptual model. They identified the predominate minerals present in sediments and basalt, the major ions present in INEEL groundwater, and postulated a set of geochemical reactions between minerals and groundwater that were likely to be occurring and partially responsible for the composition of groundwater.

The geochemical conceptual model that accounts for the natural solute makeup of groundwater beneath the INEEL is described in the following excerpts from Knobel et al. (1997).

The concentrations of naturally occurring inorganic constituents in ground water are controlled by the type, abundance, and reaction rates of minerals in the aquifer (p.11).

It is assumed ... that SRPA water chemistry is dominated by the faster reacting, more abundant minerals and that the effects of slow-reacting minerals are negligible (p. 13).

The distribution of major ions in ground water is partially controlled by the solubilities of minerals in the aquifer and by the ground-water flow system. Concentrations of solutes in ground water generally increase in the direction of ground-water flow until equilibrium between the solid, liquid, and gaseous phases is established. Once equilibrium is established, concentrations remain relatively constant until the equilibrium of the system is disrupted by other factors such as microbial activity, industrial or agricultural waste disposal, a change in mineralogy, or mixing with water from another source (pp. 13-14).

The mean concentrations of constituents in 424 samples from sites in the entire eastern Snaker River Plain ... were larger than the mean concentrations associated with the INEL samples not affected by waste disposal ($n=5$). The increases in mean concentration in these samples probably reflect the inclusion of more downgradient samples in the statistical analysis. The mean concentrations of the constituents from the 59 samples collected exclusively downgradient of the INEL ... were similar to or larger than the mean concentrations of the 424 samples reported by Wood and Low (1988). The increases in mean concentrations of chemical constituents mimic the generalized configuration of the flow system in the Eastern SRPA (p. 15).

From these excerpts, it is apparent that the Knobel et al. (1997) geochemical model assumes that the solute composition of groundwater in the Eastern SRPA is controlled by dissolution and precipitation of minerals that is ongoing in the aquifer (i.e., their conceptual model is essentially the same as the [Wood & Low 1988] diagenesis conceptual mode). Unlike the McLing (1994) conceptual model, mixing of water from different sources is not considered to be important.

A condensed version of their summary follows (pp. 44-46):

- Groundwaters from INEEL are generally of calcium-magnesium bicarbonate type. Water samples from TAN have higher relative concentration of sodium and chloride and smaller concentrations of calcium and bicarbonate than other waters evaluated, and have been affected by waste disposal activities.
- The major thermodynamically unstable minerals in the aquifer include:
 - Labradorite (a calcium-sodium feldspar)
 - Pyroxene
 - Olivine.
- The major thermodynamically stable minerals in the aquifer include:
 - Smectite
 - Calcite
 - Ferric oxyhydroxide.
- Silica phases (quartz, cryptocrystalline quartz, and amorphous silica) can be either stable or unstable. Thermodynamic calculations show that quartz and chalcedony (cryptocrystalline quartz) are slightly supersaturated, while silica glass (amorphous silica) is slightly undersaturated, but the saturation index is so close to zero that its stability is uncertain.
- Minerals directly observed as secondary products in association with basalt or with minerals in basalt include:
 - Smectite
 - Ferric oxyhydroxides
 - Calcite
 - Silica.
- The link between the mineral assemblage and the aqueous solution is the thermodynamic condition of the chemical system. Saturation indices calculated from 22 representative water samples indicate that the following minerals are unstable and should dissolve, if present.
 - Anhydrite
 - Pyroxene
 - Olivine
 - Amorphous silica (possibly unstable).
- The following minerals are oversaturated and would be expected to precipitate:

- Calcite
- Ferric oxyhydroxides.
- Labradorite can weather to form calcium montmorillonite (smectite).
- Plausible chemical reactions that are likely to occur in the aquifer include:
 - Congruent dissolution of olivine, diopside (a pyroxene mineral), and anhydrite
 - Incongruent dissolution of labradorite leaving a residuum of calcium montmorillonite
 - Precipitation of calcite
 - Oxidation of ferrous iron and precipitation of ferric oxyhydroxides
 - Precipitation or dissolution of silica.

Table 5 of Knobel et al. (1997) presents “preliminary reaction models used for interpreting the natural geochemistry of the SRPA system, Idaho”, and is reproduced here as Table 4-4.

Knobel et al. (1997) also addressed the effect of waste disposal on the natural geochemical system.

Waste-disposal practices modify the natural chemistry in the SRPA system, but the rates and amounts of modification are dependent on the type of disposal practice. For example, when wastes are injected directly into the saturated part of the systems, they bypass many of the natural geochemical barriers that would immobilize some of the waste constituents; hence, they arrive in the aquifer at waste-stream concentrations. Conversely, when wastes are discharged to infiltration ponds, many constituents are retarded during downward infiltration of waste fluid. Cation exchange is an effective process for such retardation.

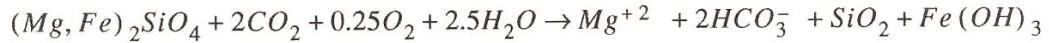
The net effect of cation exchange is that the multivalent, heavier cations in waste streams tend to be removed from solution by adsorption and replaced by lower-charged cations that are less stable on solid-phase exchange sites. The cation-exchange capacities of aquifer-system materials are sufficiently large to provide a significant retardation effect on liquid wastes discharged to infiltration ponds at the INEL (p. 46).

The Wood & Low (1988), McLing (1994), and Knobel et al. (1997) geochemical models are summarized in Table 4-5. The models are arranged with the diagenetic models together.

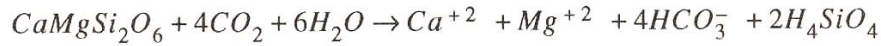
Table 4-4. Reaction models used for interpreting the natural geochemistry of the Snake River Plain aquifer system (Knobel et al., 1997).

CONGRUENT DISSOLUTION REACTIONS

(2) Dissolution of olivine



(3) Dissolution of diopside

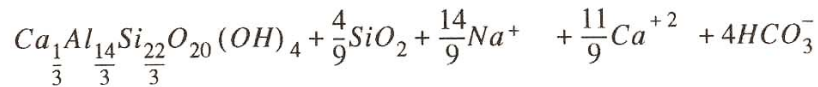
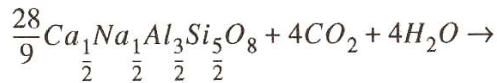


(4) Dissolution of anhydrite



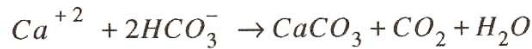
INCONGRUENT DISSOLUTION OF FELDSPAR

(5) Weathering of labradorite to calcium montmorillonite (calcium smectite)

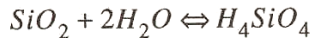


PRECIPITATION-DISSOLUTION REACTIONS

(6) Precipitation of calcite

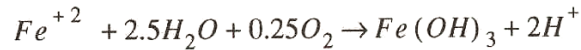


(7) Silica dissolution and/or precipitation



OXIDATION-REDUCTION REACTIONS

(8) Oxidation of ferrous iron



(9) Oxidation of pyrite

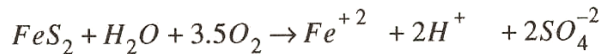


Table 4-5. Summary of conceptual models that account for the natural solute geochemistry of the Eastern Snake River Plain Aquifer.

Reference	Conceptual Model Type	Sources Of Solutes	Dissolution Reactions Or Water Sources	Precipitation Reactions	Source Of Chloride	Source Of Sulfate
(Robertson et al 1974)	Equilibrium with kinetically limited precipitation	Mainly present in inflow from tributary basins.	Discounted significant dissolution in the ESRP	Calcite and dolomite are saturated, but kinetic limitations prevent precipitation in the saturated zone.		
(Wood & Low 1988)	Diagenesis	80 % of solutes in groundwater that discharge from the ESRP are present in inflow from tributary basins (Big and Little Lost Rivers, Birch Creek, Camas Creek) The remaining 20% of solutes are derived from reactions that take place in the aquifer and human activities	Addition of NaCl from fluid inclusions, detrital marine sediments, and man's activities Dissolution of olivine Weathering of plagioclase {a feldspar mineral} to smectite Dissolution of pyroxene Dissolution of detrital anhydrite Oxidation of pyrite	Precipitation of calcite Precipitation of silica Weathering of plagioclase to smectite	Dissolution from fluid inclusions in basalt, and leaching from marine detrital particles in sedimentary interbeds	Dissolution of anhydrite and oxidation of pyrite

Table 4-5. (Continued).

Reference	Conceptual Model Type	Sources Of Solutes	Dissolution Reactions Or Water Sources	Precipitation Reactions	Source Of Chloride	Source Of Sulfate
(Knobel et al 1997)	Diagenesis	Origin of solutes other than processes in the ESRP aquifer and human activities were not addressed	<p>Dissolution of olivine</p> <p>Dissolution of diopside (a pyroxene mineral)</p> <p>Dissolution of anhydrite</p> <p>Dissolution of labradorite {a feldspar mineral} to calcium smectite</p> <p>Silica dissolution and/or precipitation</p> <p>Oxidation of pyrite</p>	<p>Precipitation of calcite</p> <p>Silica dissolution and/or precipitation</p> <p>Oxidation of ferrous iron {and subsequent precipitation of Fe(OH)₃}</p>	Not addressed.	Dissolution of anhydrite and oxidation of pyrite
(McLing 1994)	Diagenesis model	Water from Birch Creek tributary basin and diagenesis in the ESRP	<p>Dissolution of feldspar</p> <p>Ion exchange</p>	<p>Precipitation of calcite</p> <p>Precipitation of silica</p>		

Table 4-5. (Continued).

Reference	Conceptual Model Type	Sources Of Solutes	Dissolution Reactions Or Water Sources	Precipitation Reactions	Source Of Chloride	Source Of Sulfate
	<p>Mixing model</p>	<p>Mixing of waters from three different sources that have different solute compositions. Dissolution / precipitation reactions in the aquifer are relatively unimportant.</p>	<p>Ca-Mg bicarbonate water derived from the Birch Creek drainage</p> <p>Water from the Mud Lake area that has higher proportions of sodium and potassium relative to calcium and magnesium</p> <p>A minor amount of sulfate- and chloride-rich geothermal water</p> <p>Dissolution of olivine, pyroxene, and potassium feldspar</p>	<p>Precipitation of calcite</p>	<p>Small (0.4 %) fraction of geothermal water</p>	<p>Not addressed. Sulfate concentrations declined along the flowpath studied, and hence a sulfate sink, not a source, was needed.</p>

Table 4-5. (Continued).

Reference	Conceptual Model Type	Sources Of Solutes	Dissolution Reactions Or Water Sources	Precipitation Reactions	Source Of Chloride	Source Of Sulfate
(Busenberg et al 2001)	Mixing and diagenesis	Very shallow young water, deeper and older regional groundwater, diagenesis, anthropogenic inputs	Nitrate, sodium chloride, carbon dioxide, pyrite, Forsterite (insert class of mineral) potassium feldspar, anorthite, basalt, and (presumably sodium – calcium) feldspar,	Calcium smectite, sodium smectite, and Fe(OH) ₃ . Calcite dissolved in some models and precipitated in others	Pyrite	Sodium chloride

4.5.5 Busenberg et al.

A groundwater age dating study performed by the USGS (Busenberg et al. 2001) includes a brief section on geochemical modeling. They used the code NETPATH to calculate a series of mixing and reaction models that could account for the observed solute content of INEEL groundwater in different wells. They mixed “regional background water”, and precipitation that had reacted with carbon dioxide and minerals present in the INEEL subsurface. Their “regional background water” is uncontaminated groundwater whose composition was that determined at well USGS 101. The solute content of precipitation used was that of precipitation at Craters of the Moon. They present five models generated by NETPATH that account for the observed solute composition in each of eight groundwater analyses. Multiple models were generated because there is not a unique solution to the problem of inferring processes that generated an observed water chemistry. These models typically show dissolution of nitrate, sodium chloride, carbon dioxide, pyrite, Fosterite (insert class of mineral) potassium feldspar, anorthite, basalt, and (presumably sodium – calcium) feldspar, and precipitation of calcium smectite, sodium smectite, and $\text{Fe}(\text{OH})_3$. Calcite dissolved in some models and precipitated in others. Cation exchange occurred in some models. Basically, these models are in general agreement with the reaction portion of the geochemical conceptual models of Knobel et al. (1997) and Wood & Low (1988). In addition, they present a correlation between fluoride and strontium concentrations in groundwater (Figure 27, p 47) and interpret this data as a falling on a mixing line between one end member with high F and low Sr concentrations (regional background groundwater) and a ‘young fraction’ end member with low F and high Sr (presumably water that originated in the carbonate mountains to the north and northwest of the INEEL or in water that entered the INEEL portion of the aquifer from the north east). The mixing component of the NETPATH simulations is consistent with the McLing (1994) mixing conceptual model. The NETPATH models had fractions of “young water” that ranged from 0.21 to 0.44, with the balance being “regional water”.

The following was excerpted from the Summary and Conclusions section of Busenberg et al. (2001) (pp. 54-55).

- Water in ... the southeastern part of the INEEL appears to be a binary mixture of local recharge and very old, regional groundwater, and samples from most of the wells are about 20 to 50% young water that is 14 to 21 years old.
- Two main mechanisms of recharge of the young fraction of ground water were recognized in samples from the northern part of the INEEL. Water recharged by rapid, focused recharge through the thick, unsaturated zone, and water recharged by slow infiltration through the thick unsaturated zone.
- Water samples from wells that contained a young fraction of water that recharged in the central, western, and southwestern parts of the INEEL are complex mixtures of regional ground water, agricultural return flow, natural recharge, and artificial recharge from infiltration ponds and injections wells at the various facilities at the INEEL.
- Three natural ground-water types were identified from their He, Li, and F concentrations: (1) northeastern regional water with very high He, Li, and F concentrations; (2) recharge from the southeast with moderate He and high Li and F concentrations; (3) recharge from mountain valleys in the western part of the INEEL with low concentrations of He and Li and high concentrations of Ca, Mg, and alkalinity. The water was modified locally by mixing with agricultural runoff and wastewater from INEEL facilities.

- The young recharge water composes a very small fraction of the total volume of water in the SRPA, and this young water was sampled because most of the wells at and near the INEEL are completed in the upper 15 m of the aquifer.
- Recharge by dispersed infiltration, rapid, focused recharge along flowpaths, and an intermediate mechanism of recharge were recognized at the INEEL.
- Ground water of the SRPA at the INEEL is stratified, and the ground-water age increases with depth.
- A preferential ground-water flowpath was identified that extends from the Little Lost River and Big Lost River Sinks southward through central INEEL past Big Southern Butte. Flow velocities of about 3 m/day were typical in the preferential flowpath but decreased to about 1 m/day for the rest of the INEEL.

In the context of this review, the Busenberg et al. (2001) conceptual model includes mixing of water from different sources and reactions between water and minerals in the subsurface.

4.6 Groundwater Age Studies and Evidence for Fast Flow Paths

Several groundwater age dating studies have been performed at the INEEL and vicinity using various environmental tracers. These studies are relevant because they can provide insight into the probable origin of groundwater in different portions of the aquifer, and provide information on groundwater flow paths. Three articles that describe isotopic and geochemical studies for age dating of groundwater in the Eastern SRPA are Johnson et al. (2000), Luo et al. (2000), and Roback et al. (2001).

4.6.1 Luo et al.

Luo et al. (2000) describe a study in which uranium and thorium decay series members were analyzed in groundwater samples collected from the INEEL and vicinity. They interpreted this data set to quantify the rates of adsorption / desorption, dissolution / precipitation, and groundwater flow rate. They determined the following.

- Adsorption of Ra and Th takes place on time scales of a few tenths of a minute to several minutes. Desorption times are several days for radium and several years for thorium. These time constants lead to estimates of retardation factors on the order of $> 10^6$ for Th 10^4 for ^{226}Ra , and 10^3 for ^{238}U .
- Rocks in contact with newly-recharged groundwaters in the north dissolve at a rate of $\sim 800 \text{ mg L}^{-1} \text{ y}^{-1}$, and rocks in contact with older groundwaters in the south dissolve at $\sim 70 \text{ mg L}^{-1} \text{ y}^{-1}$. Precipitation occurs on time scales on the order of hours to days for thorium, months for radium, and years for uranium.
- Groundwater transit times range from ~ 1 year in the north to ~ 100 years in the central and southwestern parts of the INEEL.
- There are two preferential flow zones in the INEEL, one originating from the Birch Creek Valley and the other from the Little Lost river valley, and extending southward into the SRPA.

Their plots of rock dissolution rate and groundwater residence time are presented here (Figure 4-5). The tongues that extend roughly southward from the Birch Creek and Little Lost River valleys in both plots are interpreted to be zones of preferential flow.

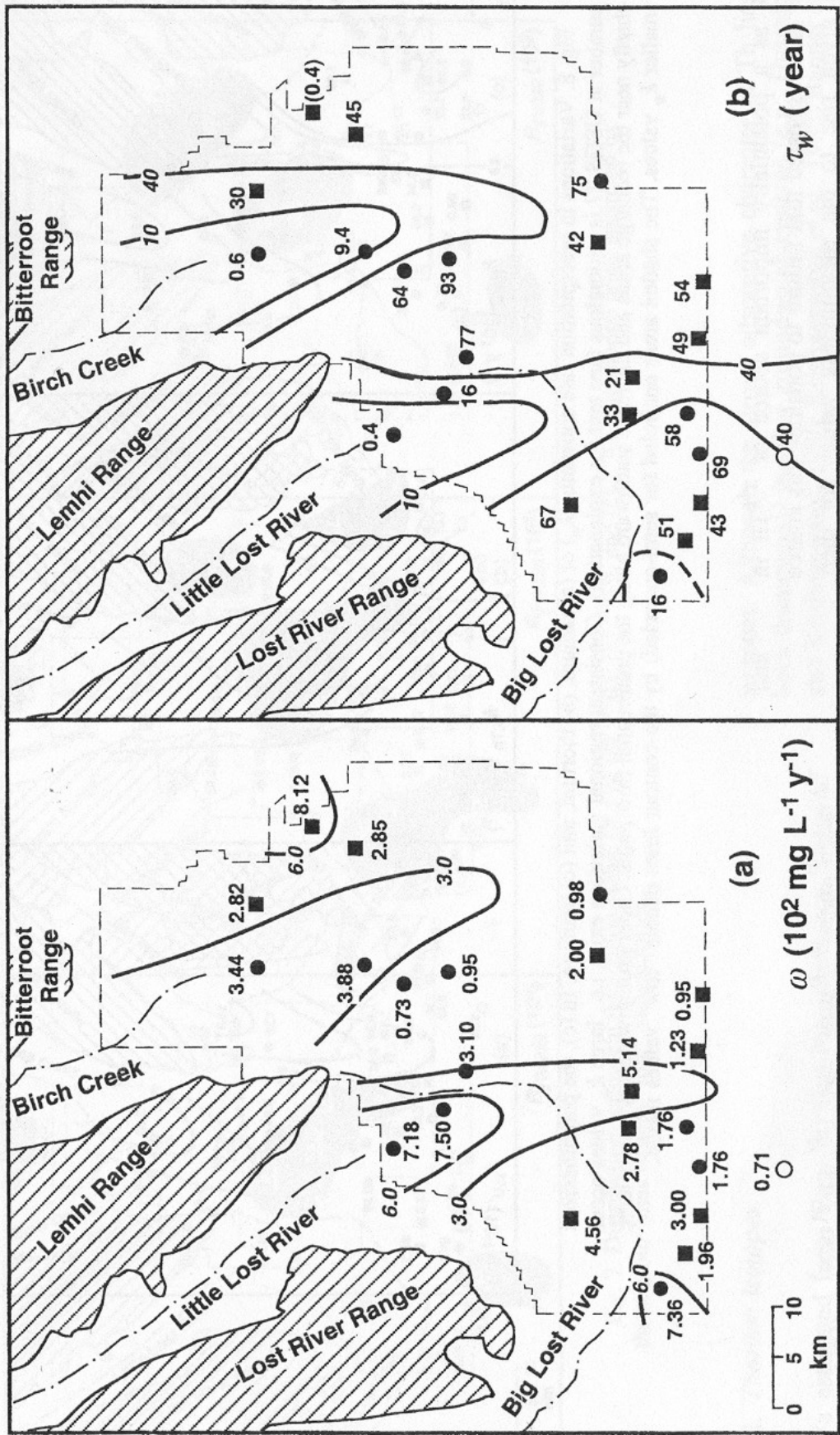


Figure 4-5. Rock dissolution rate and groundwater residence time based on U Th decay series disequilibrium (Luo et al., 2000).

4.6.2 Johnson et al.

A similar study is described by Johnson et al. (2000), who used concentrations of Li, Si, Na, and Mg, and stable strontium isotopes to characterize groundwater flow patterns in the aquifer beneath INEEL and vicinity. The spatial distribution of chemical constituents Li and Si (Figure 4-6) illustrates a systematic variation of solute geochemistry from NW to SE, which is generally consistent with the pattern originally identified by Olmsted (1962) and further discussed by McLing (1994). The pattern of Na may indicate contamination by agricultural fertilizer, and the pattern of Mg roughly mimics the Sr isotopic data. The spatial patterns of chemical constituent concentrations reflect both the input in underflow and recharge, and the effects of water-rock interaction in the aquifer. Stable strontium isotope ratios, $^{87}\text{Sr}/^{86}\text{Sr}$, reflect the evolution from the ratio in water entering the aquifer toward the value in equilibrium with rocks that form the aquifer framework. Longer residence times correlate with a closer approach to the equilibrium value.

Thus, isotope ratios provide a record of water-rock interaction that is more easily interpreted than that obtained from solute concentration data” (p. 874). “The pattern exhibited by the $^{87}\text{Sr}/^{86}\text{Sr}$ data is striking. Water entering the aquifer from the Birch Creek and Little Lost River valleys to the north has high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (>0.71100) relative to waters originating east of the INEEL; the high ratios are inherited from Paleozoic sediments to the north. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios decrease along all possible southwestward flow paths, but in some areas they decrease strongly, whereas in other areas they decrease less. Particularly well defined is a relatively narrow zone of high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (the high isotope-ratio zone) that extends southward from the Little Lost River valley through the southern boundary of the INEEL. Zones with relatively $^{87}\text{Sr}/^{86}\text{Sr}$ ratios occur near the center of the INEEL (central low isotope-ratio zone) and in the western part of the INEEL (western low isotope-ratio zone). Visually, the $^{87}\text{Sr}/^{86}\text{Sr}$ patterns in Figure 2A (see Figure 4-6) suggest a channeling of the high-ratio northern groundwater through preferential flow zones between and around the western and central low isotope-ratio zones (p. 872).

One process that controls groundwater chemistry in this area is regional mixing of contrasting water masses....Mixing between the northern water masses entering from the Little Lost River valley and Birch Creek valley and waters originating east of the INEEL results in a northwest to southeast gradient in water chemistry. This gradient is apparent in all solute concentration and isotope-ratio plots, particularly in the Li data....Mixing thus plays a role in defining the $^{87}\text{Sr}/^{86}\text{Sr}$ patterns, both the shapes and locations of the high and low isotope-ratio zones cannot be produced by this process alone. The narrowness of the high isotope-ratio zone cannot be explained by regional mixing; the water entering from the Little Lost River valley would spread out into a relatively wide zone were it not channeled by hydrologic heterogeneity” (p. 872).

Channeling of groundwater flow through the high isotope-ratio zone and relatively slow flow in the western and central low isotope-ratio zones can readily produce the observed isotope-ratio pattern. In this scenario, the high isotope-ratio zone is a fast-flow zone, where high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios originating in the Little Lost River valley and the Birch Creek valley persist far to the south because the water has relatively brief contact with the host rock. In the low $^{87}\text{Sr}/^{86}\text{Sr}$ zones, the same groundwater evolves closer to the isotopic composition of the host rock ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7070 \pm 0.0003$...) because of slower groundwater flow, prolonged contact with the rock, and greater rock dissolution” (p. 872).

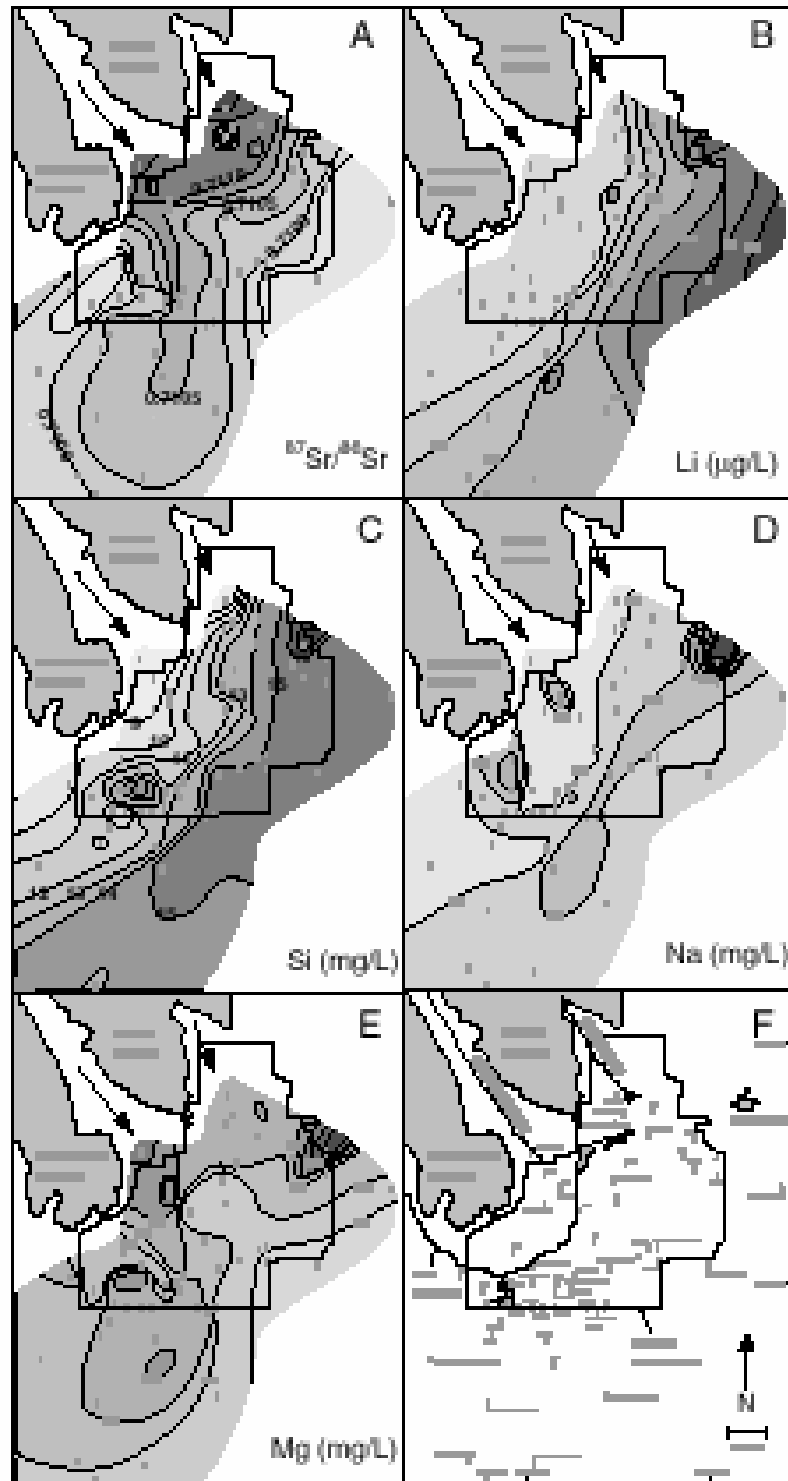


Figure 4-6. Contour plots of (A) $^{87}\text{Sr}/^{86}\text{Sr}$ and concentrations of (B) Li, (C) Si, (D) Na, and (E) Mg in groundwater, and (F) sampled well locations and locations of river channels (after Johnson et al. 2000).

A concurrent study has measured $^{234}\text{U}/^{238}\text{U}$ ratios in the same groundwater samples (Roback et al. 1997). The spatial pattern in the data is very similar to that of the $^{87}\text{Sr}/^{86}\text{Sr}$ data. This is especially significant because the systematics of U isotopes are different from those of Sr isotopes...the similarity of the U and Sr isotope results suggests that radiogenic isotope ratios in general are effective groundwater tracers” (p. 872).

4.6.3 Roback et al.

Roback et al. (2001) used uranium isotopes ($^{234}\text{U}/^{238}\text{U}$) to examine chemical evolution and flow patterns in groundwater beneath the INEEL and vicinity. They collected groundwater samples from INEEL and vicinity and analyzed them for $^{234}\text{U}/^{238}\text{U}$. The wells sampled and the measured $^{234}\text{U}/^{238}\text{U}$ ratios are shown in Figure 4-7. They also used strontium isotopic data from Johnson et al., 2000.

A general description of the data reported by Roback et al. (2001) is taken from their article.

$^{234}\text{U}/^{238}\text{U}$ ratios show systematic lateral variations across the study area...Groundwater entering the aquifer from the Birch Creek, Little Lost River, and Big Lost River valleys to the north and west have high $^{234}\text{U}/^{238}\text{U}$ ratios relative to regional groundwater represented by samples in the eastern and southeastern parts of the INEEL. Water masses with these distinct isotopic signatures persist tens of kilometers away from their sources. For example, a narrow zone with high $^{234}\text{U}/^{238}\text{U}$ ratios extends southward from the mouth of the Little Lost River and remains well defined to the southern boundary of the INEEL. Two zones with relatively low $^{234}\text{U}/^{238}\text{U}$ ratios occur near the center and western parts of the INEEL” (p. 1137).

A first-order observation of the isotopic data is that $^{234}\text{U}/^{238}\text{U}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are higher in waters that emanate from the Little Lost River and Birch Creek valleys on the northwest edge of the aquifer than they are elsewhere in the aquifer...In recent years, most of the surface water from the Little Lost River and Birch Creek valleys ... has been diverted for irrigation such that only small amounts reach the INEEL. Uranium and strontium isotope data are taken as evidence that these drainages do supply a significant volume of groundwater to the aquifer and thus constitute important recharge sources” (p. 1137).

The Big Lost River intermittently flows westward onto the INEEL ... and rapidly infiltrates, via the riverbed, playas that mark its terminus and spreading areas to recharge the aquifer...Two areas with low $^{234}\text{U}/^{238}\text{U}$... and $^{87}\text{Sr}/^{86}\text{Sr}$... isotope ratios lie near (but below) the terminal playas of the Big Lost River and the spreading centers, and thus may reflect infiltration of Big Lost River Water. Johnson et al. (2000) termed these two areas the central low-isotope ratio zone and the western low-isotope zone...Uranium and strontium isotopic ratios from these samples define a distinct field...that plots below the trend defined by the rest of the aquifer samples...The greatest uranium and strontium isotope ratios in both of these zones are nearly identical to those of the Big Lost River. Samples from the western low-isotope ratio zone form an array that trends away from the isotopic composition of the Big Lost River toward U and Sr isotope ratios that are closer to those of the host basalt ... consistent with water-rock interactions ...These observations, combined with the physical evidence that the Big Lost River supplies a significant amount of water to the aquifer, argue that the two zones are dominated by infiltrated water from the Big Lost River” (p. 1137).

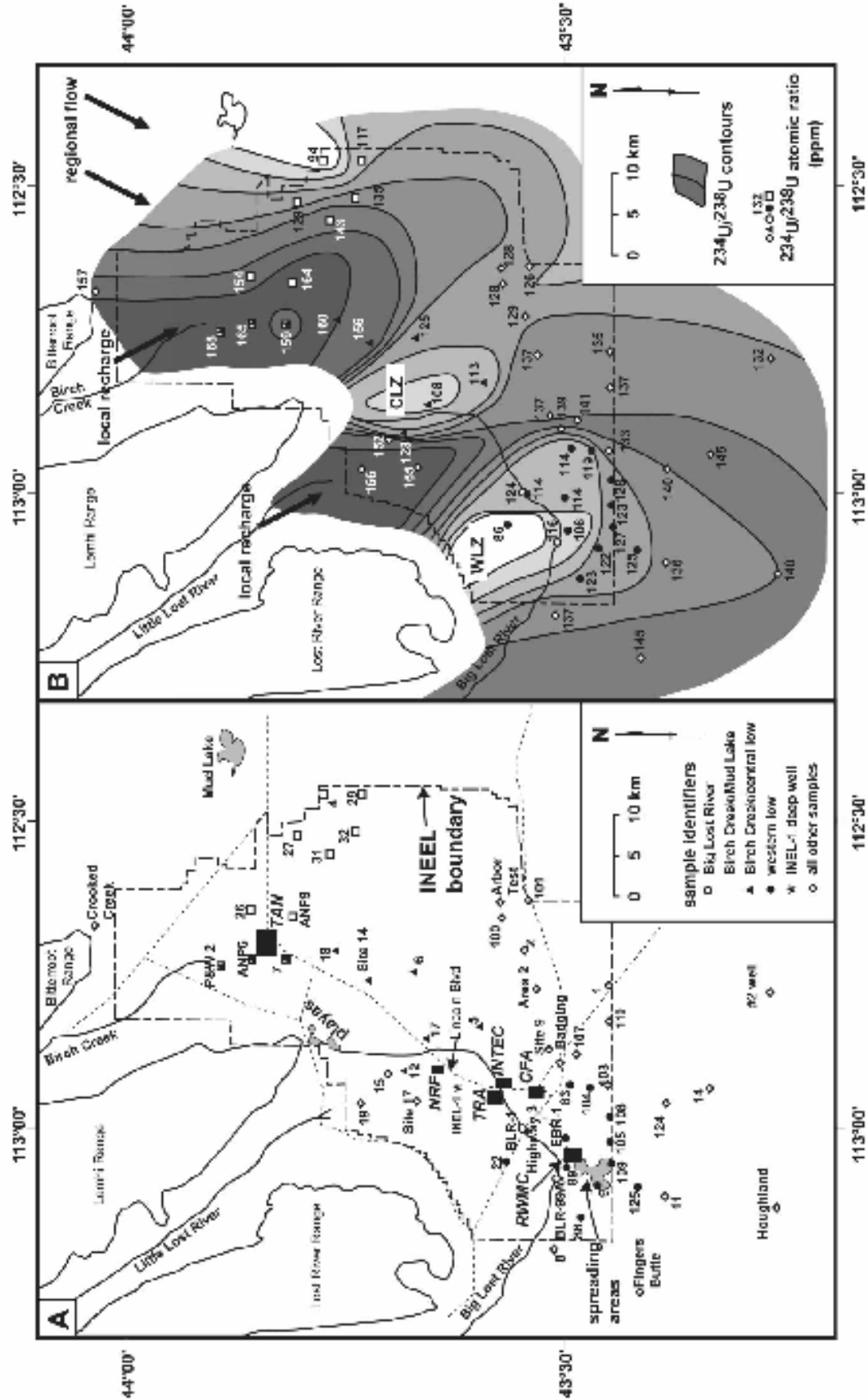


Figure 4-7. (a) Important features and wells sampled (b) $^{234}\text{U}/^{238}\text{U}$ ratios in parts per million (after Roebuck et al., 2002).

The contrast in $^{234}\text{U}/^{238}\text{U}$ isotope ratios between waters emanating from the Little Lost River and Birch Creek valleys and the rest of the aquifer reflects the markedly different geology and hydrology of these recharge valleys when compared to those of the basalt aquifer. The recharge areas are in basin-and-range type valleys that are filled with Quaternary gravel, sandstone, and shale of alluvial and fluvial origin...A significant component of groundwater flow in these recharge valleys is likely to be through intergranular pores. In contrast, the SRPA consists dominantly of Quaternary basalt, and flow is fracture dominated. The clastic material that fills the recharge valleys is likely to have higher uranium concentrations ... than does the basalt of the Snake River Plain aquifer... Thus, the marked difference in $^{234}\text{U}/^{238}\text{U}$ isotope ratios between the groundwater in the local recharge valleys and that in the basalt aquifer can be attributed to differences in flow mechanisms (porous vs. fracture flow), host rock lithology, and the age of aquifer material" (p. 1138).

Given that the SRPA in the vicinity of the INEEL comprises different water masses with distinct $^{234}\text{U}/^{238}\text{U}$ ratios and that uranium should behave as a relatively conservative tracer in this aquifer, uranium isotopes may be useful in determining mixing patterns and relative volumes" (p. 1138).

Another potential source of recharge water in the aquifer is upwelling of water from depth; a mechanism that has been suggested to occur in both of the low-isotope-ratio zones... If upwelling waters did mix with the aquifer, the effect would most readily be noticed in the low-isotope-ratio zones, which are suspected to be regions of lower water flux relative to the rest of the aquifer ... and which have the lowest uranium concentrations of aquifer samples...

Mass balance considerations require large volumes of upwelling water relative to aquifer water in order to greatly influence the uranium isotope ratios anywhere in the aquifer. No physical ... or chemical ... evidence supports this. Thus, the above considerations suggest that upwelling thermal waters do not constitute a significant proportions (more than a few percent) of the aquifer in the low-isotope-ratio zones (although small proportions are likely), nor is it likely that these waters greatly influence the uranium isotope ratios elsewhere in the aquifer" (p. 1138).

Given that the SRPA in the vicinity of the INEEL comprises different water masses with distinct $^{234}\text{U}/^{238}\text{U}$ ratios and that uranium should behave as a relatively conservative tracer in this aquifer, uranium isotopes may be useful in determining mixing patterns and relative volumes. Mixing relations are manifested as linear trends on a plot of $1/\text{U}$ concentration vs. $^{234}\text{U}/^{238}\text{U}$ ratio... The results are consistent with a strong influence of mixing across some of the mapped isotope gradients.... Mixing between groundwater from the local recharge valleys to the northwest and the groundwater of the regional aquifer to the east is to be expected and is evident from gradients in solute concentrations.... Samples along the transect extending from north of the TAN to the eastern boundary of the INEEL south of Mud Lake ... display a crude linear trend ... suggesting that mixing between these two water masses is an important factor in the observed gradient in $^{234}\text{U}/^{238}\text{U}$ ratios. The mixing trend highlights the persistence of Birch Creek groundwater to a distance of about 10 km southeast of the TAN and then dilution by regional aquifer water near the site

boundary. Deviations of the data from a perfectly linear array, however, indicate that two-component mixing alone does not explain the trend, and either multi-component mixing or water-rock interaction must be invoked to explain modifications to the uranium data. The plot of $^{234}\text{U}/^{238}\text{U}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$... also shows a good correlation that is also consistent with two-component mixing....

Roback et al. (2001) discuss water-rock interaction as follows.

Uranium systematics along the transect from the mouth of Birch Creek to the central low-isotope-ratio zone also display a linear trend ... consistent with mixing of two water masses. The most likely sources of the second mixing component are upwelling of deep groundwater and/or infiltration of Big Lost River surface water However, ... uranium isotopic data and mass balance considerations argue against large volumes of upwelling water in the low-isotope-ratio zones. It is more likely that the decrease in $^{234}\text{U}/^{238}\text{U}$ along this trend is produced by mixing of groundwater in the northeast with water that originated as surface water from the Big Lost River and was subsequently modified by water-rock interaction” (pp. 1138-1139).

Uranium isotope-ratios are closely mimicked by $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.... The good correlation displayed by these two isotopic systems indicates that dissolution of rock with near equilibrium $^{234}\text{U}/^{238}\text{U}$ ratios dominates over selective leaching and alpha recoil in controlling the $^{234}\text{U}/^{238}\text{U}$ ratios of the groundwater. $^{234}\text{U}/^{238}\text{U}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ also define a trend toward the isotopic composition of the basalt, ... which implies that U and Sr isotopics were modified through water-basalt dissolution....

The data ... suggest that incongruent dissolution of basalt plays an important role in modifying the chemical and isotopic composition of groundwater in the aquifer.... Increasing water-rock interaction results in the release of uranium in secular equilibrium from the basalt by dissolution, and a removal of relatively greater amounts of uranium from solution by precipitation and/or ion exchange” (p. 1139).

Roback et al. (2001) discuss groundwater flow patterns and preferential flow paths as follows.

Although groundwater mixing and water-rock interaction affect the uranium and strontium isotope ratios of the SRPA in this region, neither of these processes readily explains the observed spatial pattern of isotope ratios. Mixing of groundwater from the recharge valleys with water from the regional SRPA to the east may partially explain the general northwest to southeast trend in uranium systematics and solute concentration data.... Mixing, however, does not readily explain the shape or location of the zones with either high or low isotope ratios....

We interpreted the two zones with high isotope ratios as preferential flow pathways along which groundwater from the Birch Creek and Little Lost Rivers is channeled.... The low-isotope-ratio zones are interpreted as zones of relatively stagnant groundwater that are physically isolated from the more rapidly flowing zones elsewhere in the aquifer by low-permeability zones....

Flow channeling through primary volcanic features is a likely cause of the preferential pathways delineated by isotope data....Groundwater that emanates from local recharge valleys of the Little Lost River and Birch Creek is funneled through high-transmissivity zones that correspond to ...primary volcanic structures in the Snake River Plain basalts. Channeling effects are most obvious nearest the recharge valleys, where volumes of the recharge groundwater are greatest. With increasing distance along flow pathways, these preferential pathways are deflected to more southward and southwestward directions and become more diffuse because of dilution and dispersion (pp. 1139 1140).

Roback et al. (2001) provided the following summary of their study.

Radiogenic isotope ratios in groundwater provide powerful tools for understanding chemical and physical processes in aquifers. We have used natural variations in $^{234}\text{U}/^{238}\text{U}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in groundwater from the SRPA in the vicinity of the INEEL to identify *chemically distinct water masses*, to assess *mixing* and *water-rock interaction*, and to delineate detailed *groundwater flow pathways*. Mixing of groundwater from the mouth of Birch Creek with groundwater to the east and to the south appears to be an important process. Mixing of groundwater elsewhere...is difficult to document....The uranium and strontium isotopic composition of groundwater evolves toward that of the host rock along flow pathways. Incongruent dissolution of the basalt ...and can explain the observed isotopic modification.

Two preferential flow pathways extending southeast from the mouths of Birch Creek and the Little Lost River valleys remain distinct for tens of kilometers into the regional aquifer. It is likely that these preferential flow zones follow high-permeability volcanic features....The data also delineate two regions with low isotopic ratios that we interpret as relatively stagnant areas. Mixing between these stagnant areas and the regional aquifer appears to be limited. Both low-isotope-ratio zones are influenced by infiltrated water from the Big Lost River (p. 1140).

4.6.4 Busenberg et al. 2001

Groundwater flow velocities are not uniform throughout the Eastern SRPA beneath the INEEL. Busenberg et al. (2001) calculated the age of the young fraction of groundwater using $^3\text{H}/^3\text{He}$ environmental tracers, and used spatial distribution of groundwater age to illustrate (Figure 25, p. 44) groundwater flow velocities in the upper part of the aquifer.

A preferential ground-water flowpath was identified that extends from the Little Lost River and Big Lost River Sinks southward through central INEEL past Big Southern butte. Flow velocities of about 3 m/day were typical in the preferential flowpath but decreased to about 1 m/day for the rest of the INEEL” (Busenberg et al 2001) (p 55).

Busenberg (2001 #191) used environmental tracers to characterize shallow groundwater at the INEEL and in the vicinity. The justification for this study provided by Busenberg (2001 #191) follows.

In 1949, the U.S. Atomic Energy Commission, later to become the U.S. Department of Energy...requested that the USGS investigate the water resources

of ... the INEEL....Since that time, the USGS has maintained a monitoring network at the INEEL to determine hydrologic and geochemical trends and to delineate the movement of facility-related radiochemical and chemical wastes in the SRPA.

As part of continuing investigations at the INEEL, ... a detailed study of the ground water at and near the INEEL was done ... to estimate the age of the ground water, sources of water, flow velocities, and mixing fractions of the water from various sources....Understanding the age and recharge mechanisms of ground water at the INEEL is important for determining how waste discharged at facilities will move within the Snake River Plain aquifer system in the future (pp. 3-4)

Busenberg (2001 #191) described the purpose and scope of their investigation as:

The purpose of this report is to use selected environmental tracer data collected at and near the INEEL ... to estimate ages and sources of the young fraction of ground water in the SRPA at the INEEL. The young fraction of ground water is defined as all water that has recharged since the 1940s. The young recharge water composes a very small fraction of the total volume of water in the Snake River Plain aquifer, and this young water was sampled because most of the wells at and near the INEEL are completed in the upper 15 m of the aquifer. Concentrations of chlorofluorocarbons (CFCs), sulfur hexafluoride (SF₆), and hydrogen (H₂) and helium (He) isotopes in water samples from 86 wells at and near the INEEL ... were measured and used to calculate the fraction and age of young water in the samples. Concentration of nitrogen (N₂), oxygen (O₂), argon (Ar), methane, and carbon dioxide (CO₂) dissolved in groundwater were measured ... and used to evaluate the temperature and mechanisms of recharge of groundwater at the INEEL. Concentrations of gases, isotopic ratios, and other chemical constituents ... were measured to determine the source of the water and to calculate the fraction of water from different sources and the fraction of young water in the samples (p.4).

One of Busenberg's (2001 #191) objectives was to identify recharge mechanisms. They discuss recharge mechanisms as follows.

In arid and semiarid regions, the mechanisms of ground-water recharge can significantly affect the apparent CFC ages. Gee and Hillel (1988) recognized two mechanisms of recharge in arid regions: (1) continuous spatially distributed diffuse recharge resulting from widespread percolation through the entire unsaturated zone, and (2) occasional concentrated recharge resulting from the short-term penetration of water along distinct pathways through the unsaturated zone that bypass the greater part of its volume....both mechanisms of recharge occur on the eastern Snake River Plain. Fractured volcanic rocks exposed at the surface in the southwestern part of the INEEL present avenues for rapid focused recharge. At some of these locations, rapid infiltration of water is known to occur....Rapid recharge occurs along the channel of the Big Lost River at the INEEL, ... at the INEEL spreading areas, and at the Big and Little Lost River Sinks....The surface-to-aquifer recharge mechanisms ... along with ground-water movement through the system as underflow from tributary valleys and as

regional underflow define the predominant mechanisms for recharge of water that is sampled from the aquifer at the INEEL (pp. 7-8).

Busenberg (2001 #191) determined the spatial distribution of selected trace constituents of groundwater beneath and near the INEEL, and presented this information in a series of maps. The constituents they presented are lithium, boron, strontium, tritium, CFC-11, CFC-12, and CFC-113. Their discussion of these constituents follows.

The areal distribution of selected chemical constituents and dissolved gases in the SRPA provides an insight into the source of the ground water. Concentrations of Li and B ... illustrate the major separation of the two principal types of water (Olmstead 1962, types A and B). Concentrations of both B and Li in the eastern part of the INEEL are larger than concentrations in other parts of the INEEL. Concentrations of B at the mouth of the Little Lost River are larger than upstream concentrations, which may indicate an addition of B from agricultural practices....The B anomaly in the western part of the INEEL ... suggests that surface water recharges the SRPA at the Little Lost River Sinks east of Howe. The chemistry of the Little Lost River drainage was significantly different between that of ... underflow ...and from the mixture of underflow and agricultural runoff....

Strontium (Sr) concentrations ... can be used to distinguish the different sources of water that are recharging the SRPA at the INEEL. Concentrations of Sr were larger in the northeastern part of the INEEL than in the southeastern part. The areas of higher Sr concentrations correspond to the areas of high HCO_3^- concentrations..., and areas of lower Sr concentrations correspond to areas of low HCO_3^- concentrations. These relations suggest that the Sr and HCO_3^- are of similar origin (p. 9).

Tritium (^3H) concentrations are present in most ground water at the INEEL except in an area of very low to no ^3H in the northern and northeastern part....This area has received virtually no post-1950 water and has not been contaminated by ^3H released or discharged from facilities at the INEEL. This area also has low concentrations of CFC-12, CFC-11, and CFC-113....Normally, the ^3H in precipitation can be calculated from {for ? ed.} the geographic location from historical areal distribution of ^3HThis was not possible at the INEEL because the site has been a significant local environmental source of ^3H . Thousands of curies of tritium were disposed of or discharged....Tritium concentrations in the aquifer are larger in the disposal areas....Concentrations of CFCs are also larger in the disposal areas....(p. 9).

Busenberg (2001 #191) used the ratio of tritium concentration to the concentration of ^3He , its daughter product, to calculate groundwater ages. Based on these and other data, they have inferred the “probable location of natural and artificial recharge of the SRPA” (Figure 4-8) and “the flow velocity of water in the upper part of the SRPA calculated from the $^3\text{H}/^3\text{He}$ age and the probable location of recharge” (Figure 4-9).

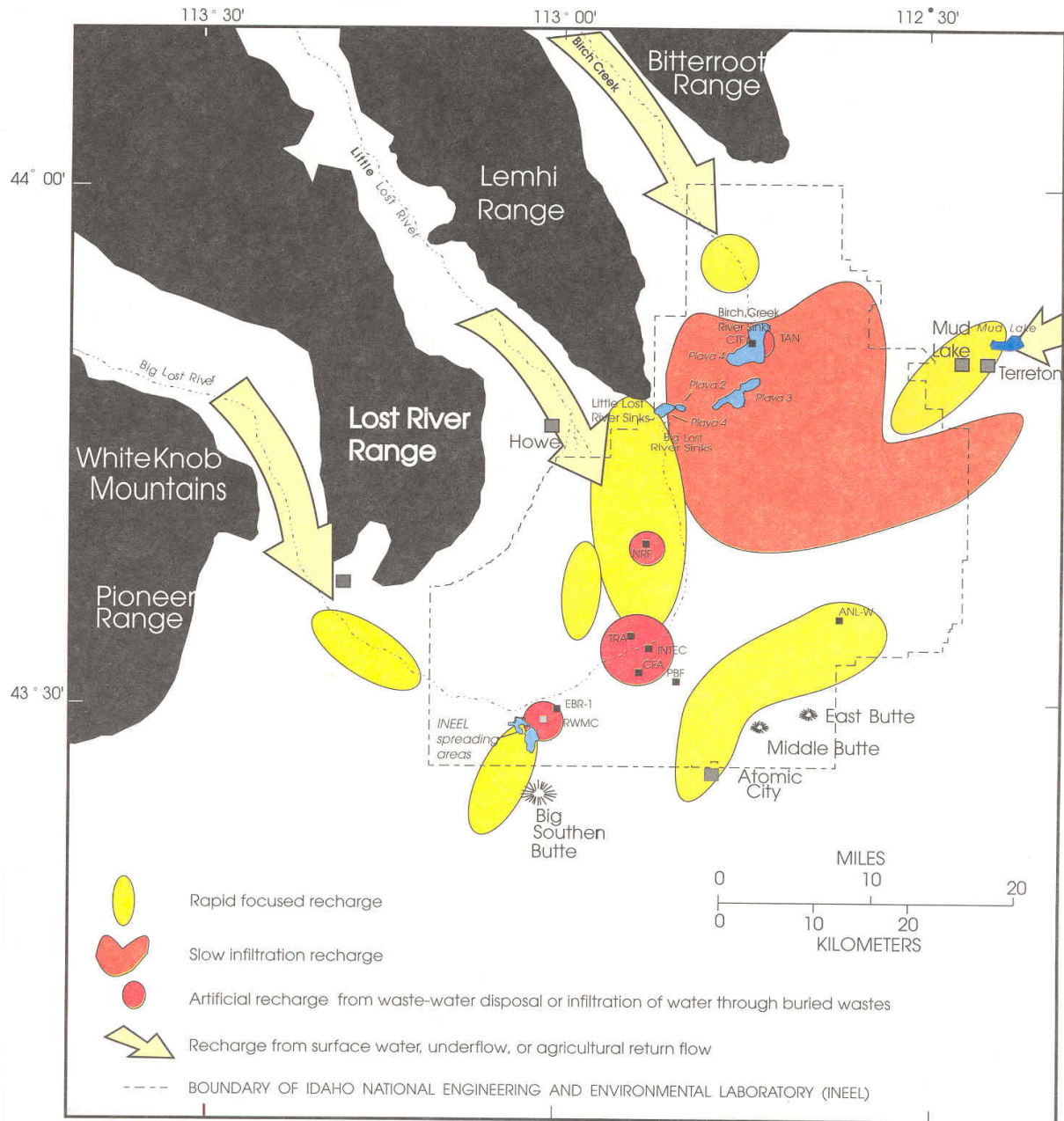


Figure 4-8. Location of natural and artificial recharge to the eastern Snake River Plain Aquifer at and near the Idaho National Engineering and Environmental Laboratory (after Busenberg et al. 2001).

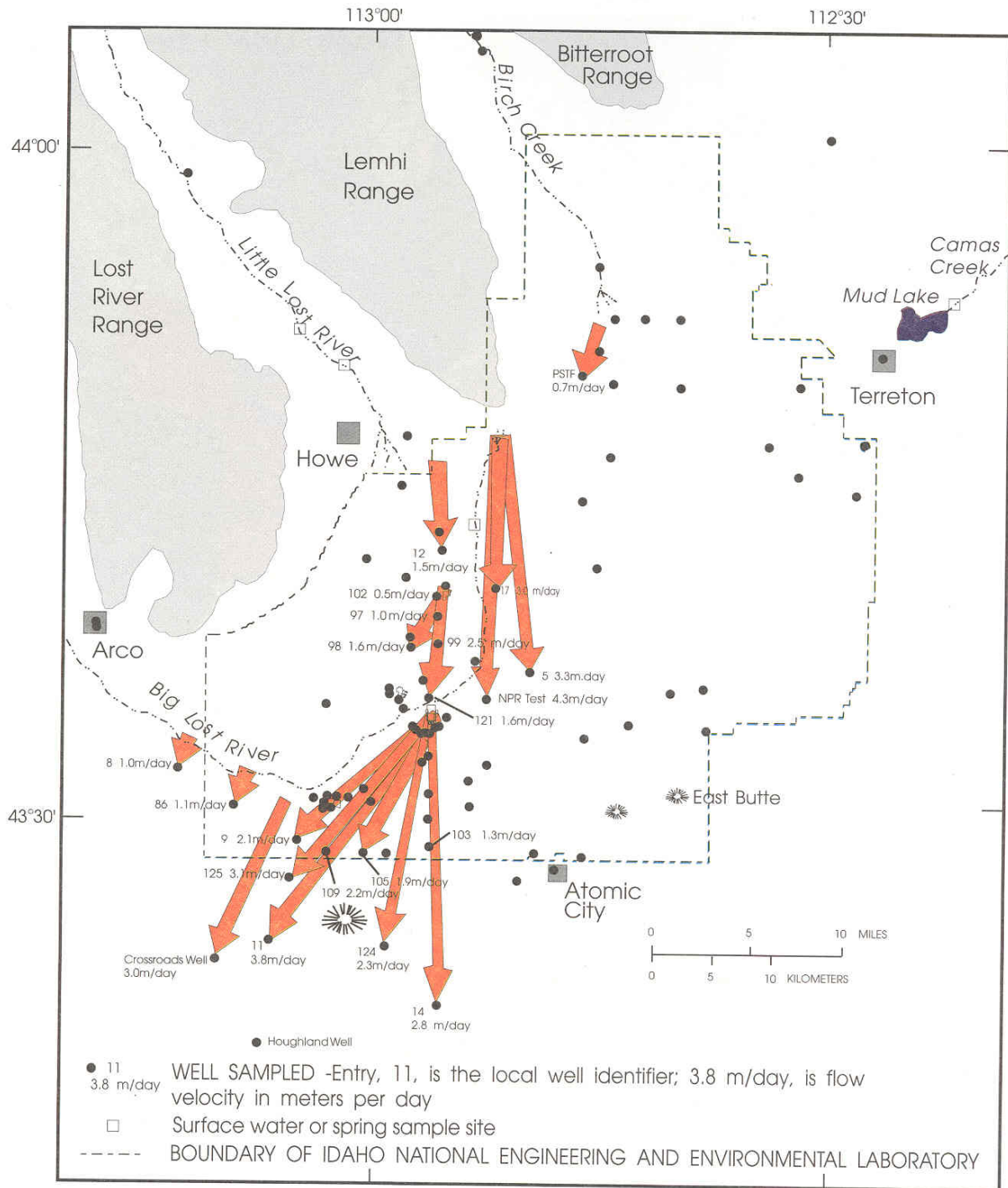


Figure 4-9. Flow velocity vector of ground water calculated from tritium/helium-3 ages of water from selected wells at and near the Idaho National Engineering and Environmental Laboratory (after Busenberg et al. 2001)

Busenberg (2001 #191) describe the rationale for developing a geochemical model in the context of groundwater dating, and the geochemical model they developed.

Wells at the INEEL commonly have very large, open intervals...and sample ground water of different origin and ages. Because water of different origin has different chemical and isotopic compositions, the fraction of water of different origin can, in theory, be determined by geochemical modeling. NETPATH is a mass-balance geochemical model that is suitable for this purpose...NETPATH can determine geochemical reactions occurring along a flowpath, the extent of the reactions, the composition of reacting phases, the isotopic evolution of C, S, hydrogen (H), O, and nitrogen (N) along the flowpath, and the ^{14}C age of the ground water. The net geochemical reactions, mass transfer, isotopic evolution, and mixing fractions were determined for water samples from the INEEL...

5. EFFECT OF WASTE DISPOSAL ON GROUND WATER QUALITY

Previous sections have discussed the natural geochemical evolution of groundwater beneath the INEEL and vicinity. Disposal of wastes in the aquifer, or in the vadose zone followed by transport to the aquifer, results in geochemical interactions that can affect the waste itself, other solutes in groundwater, and the solid phase. The effects of waste disposal on subsurface water quality was examined by Robertson et al. (1974), which is discussed in Section 5.1. Since his report, numerous investigations of subsurface contamination have been performed at the INEEL to comply with environmental regulations that became effective afterwards. These investigations are summarized in Section 5.2, and the geochemical conceptual models developed during these investigations are summarized in Section 7. The disposal methods and types of wastes disposed are described in Sections 5.3 and 5.4, and groundwater contaminants derived from these waste disposal practices are described in Section 5.5.

5.1 Survey by Robertson et al.

Robertson et al. (1974) summarized the liquid wastes that had been disposed in the subsurface at various INEEL facilities between 1952 and 1970 and described the effects that this waste disposal had on groundwater quality. Their study did not include wastes disposed at the RWMC, which are primarily solid wastes. The following excerpts illustrate their geochemical conceptual model.

After waste products enter the regional groundwater of the SRPA, their fate is controlled by two general influences – the natural properties of the aquifer system and artificial, or man-induced, influences. Natural factors which control the movement and behavior of waste products include velocity and direction of groundwater flow, dispersion properties of the aquifer, degree and distribution of anisotropy and heterogeneity in the aquifer system, sorption and heat-transfer properties of the aquifer minerals, chemical equilibria of the aquifer system, and others. The man-induced influences consist primarily of the hydraulic effects on the aquifer from pumping and injecting wells. Secondary effects might include upsets in the natural chemical equilibrium by waste water and changes in the viscosity of the aquifer water by the injection of warmer waste water. The latter could cause an increase in the hydraulic conductivity of the aquifer in the zone transmitting the warmer water (p. 143).

The following sections parallel those in Robertson et al. (1974) and provide excerpts that illustrate their geochemical model.

Although Robertson et al. (1974) discuss inorganic contaminants and radioactive contaminants, it is interesting to note that they do not mention the organic contaminants that were later recognized as common groundwater contaminants at INEEL and elsewhere.

5.1.1 Nonradioactive Waste

Robertson et al. (1974) describe transport of nonradioactive contaminants in groundwater. These contaminants include chloride, sodium, and chromium.

5.1.1.1 Chloride

Robertson et al. (1974) discussed chloride transport in the aquifer as follows.

Although many chemical waste products are discharged to the subsurface, only sodium chloride, chromate, and heat have produced significantly detectable changes in the water quality of the SRPA (p. 150).

Sodium chloride is the most significant chemical waste product dosed to the subsurface at the NRTS. Consequently, sodium and chloride are among the most wide-spread waste products in the regional groundwater (p. 150).

Ion exchange or sorption can significantly affect solute flow rates. If a waste ion is reversibly sorbed while flowing through the aquifer, it will travel at a slower rate than the average groundwater flow rate. The permeability (and porosity) features of the SRPA are large-scale features. Consequently, a very small amount of basalt surface area is exposed to the water, in comparison to, say, a sand aquifer. Sorption or exchange reactions are highly dependent on available mineral surface area. Many other factors control the magnitude of sorption effects such as the species and charge of the ion, the minerals present and their crystal structure, and the total chemical makeup of the water. The sorption effects on chloride are believed to be insignificant for two reasons. First, and most important, the anion exchange capacity of earth materials is much less than the cation exchange capacity; second, is the small amount of available mineral surface area. The latter effect may be somewhat offset by the presence of clay coatings on some of the basalt fracture and void surfaces. This conclusion is supported by other data later in this section such as materials balance studies and comparisons with tritium and other waste product behavior. It should be pointed out however, that the positively charged waste cations, Cs-137, Sr-90, and sodium, do show significant influence by sorption. The principal sorption reactions in this case are probably reversible exchange reactions; that is, they generally do not permanently remove solutes from solution (p. 153).

Important points made by Robertson et al. (1974) in this section include:

- Recognition of the importance of surface area, mineralogy, and water composition on sorption
- Cation exchange capacity is typically greater than anion exchange capacity
- The importance of clay minerals as sorbents
- Ion exchange is reversible.

5.1.1.2 Sodium

Robertson et al. (1974) discussed sodium transport in the aquifer as follows.

Although the sodium data generally follow patterns similar to the chloride data, the sodium concentrations generally are lower than the normal 3:2 chloride:sodium ratio. The apparent ratios are more near 4:2, in most cases. The reasons for this are uncertain; however, ion exchange or other sorptive reactions are probably responsible. Cationic sodium is more retarded by ion exchange on the basalt and sediments than anionic chloride. No quantitative information is known about the ion exchange characteristics of the aquifer, primarily because of its large-scale features. It is not feasible to extrapolate the results of laboratory

studies on small samples to the whole aquifer. However, exchange or other forms of sorption could adequately account for sodium reduction of this magnitude. Cationic strontium-90 and cesium-137 also appear to have been strongly affected by sorption or ion exchange in the aquifer (p. 159).

5.1.1.3 Chromium

Robertson et al. (1974) discussed chromium transport in the aquifer as follows.

The only facility from which waste chromium in the aquifer has been observed is TRA. Chromium contamination in the SRPA at NRTS was first studied by the Geological Survey in 1966....That study showed that less than 10% of the chromates were reduced from hexavalent form to trivalent or other forms in the ground....It also showed that chromium served as a useful tracer to distinguish TRA wastes from ICPP wastes in the aquifer because the ICPP has not discharged any significant amounts. Therefore, the presence of chromium in groundwater downgradient from the TRA and ICPP is indicative of TRA wastes, as there is no detectable natural chromium in the water (p. 164).

An important point in this section is that little hexavalent chromium is reduced to trivalent chromium in the subsurface. This statement contradicts / invalidates an assumption made that chromium discharged to the TRA Ponds is reduced to the trivalent form and hence is not mobile in the subsurface (Hull 1989).

5.1.2 Radioactive Components

Robertson et al. (1974) introduce their discussion of radioactive contaminants in the aquifer as follows.

Only two waste radioisotopes, Sr-90 and tritium, are detectable in the SRPA over a significant area of distribution. Other radioactive waste products such as Cs-137 are not detectable for one or more of the following reasons: (a) their discharge concentration is too low, (b) their half-life is too short, (c) their concentration is rapidly reduced by sorption reactions (p. 166).

Note that Robertson et al. (1974) did not identify ³⁶Cl or ¹³¹I as widely distributed radioactive contaminants. These radioisotopes have been identified as mobile contaminants in INEEL groundwater by Mann et al. (1994).

5.1.2.1 Strontium-90 and Cesium-137

The geochemical conceptual model developed by Robertson et al. (1974) is described in the following excerpts.

Although significant amounts of Sr-90 have also been disposed to the ground at the TRA, none has been detected in the SRPA from these releases...The Sr-90 is apparently sorbed on the sediments as it percolates downward from the disposal ponds. Although the Sr-90 has passed through the surface alluvium into the perched water in the basalt, it has not passed through the lower interbedded sediments into the SRPA.

The ICPP Sr-90 distribution patterns indicate that this waste product has not migrated as far as some of the other solutes such as chloride and tritium... This can be explained by several factors. First, the original concentration of the Sr-90 in the effluent is relatively low.... Second, Sr-90 concentration decreases with time because of radioactive decay. However, the long 28-year half-life diminishes the significance of this factor. Third, and most importantly, Sr-90 is susceptible to ion exchange on earth materials. The mineral exchange sites in the NRTS subsurface are largely calcium saturated because of the relatively high ratio of dissolved calcium content of the water. Dissolved strontium tends to exchange with calcium on exchange sites. Even though a relatively small amount of mineral surface area is available to the groundwater, it is believed that ion-exchange is largely responsible for the retarded migration of waster Sr-90. This belief is strongly supported by the materials balance data ... and by the Sc-137 distribution data....

The production of waste cesium-137 (Cs-137) is closely related to Sr-90; consequently, it has been discharged in nearly parallel quantities at the ICPP.... Cs-137 also has a similar half-life (30 years). Although many analyses have been run, Cs-137 has never been detected in aquifer water below the ICPP region, apparently because of ion exchange. Cesium ions have a greater selectivity coefficient for ion exchange than any other ionic species. The small quantities of Cs-137 injected in the aquifer seem to be almost totally removed from solution by exchange reactions within a distance of a few hundred feet (p. 168).

Important points in this section include:

- Sorption is an important attenuative mechanism for ⁹⁰Sr
- Sediments are implicated as important sorbents
- Co-precipitation is not mentioned as an important mechanism in Sr retardation
- Cs is sorbed more strongly than is Sr, and hence it is highly retarded in the aquifer.

5.1.2.2 Tritium

Robertson et al. (1974) did not identify and geochemical processes that would affect tritium transport. Assuming that tritium would be present almost exclusively as tritiated water, then it would not be significantly affected by geochemical reactions in most setting and would therefore be transported conservatively in groundwater.

5.1.3 Apparent Influences Observed on the Subsurface Behavior and Distribution of Wastes

Excerpts from Robertson et al. (1974) describe their geochemical conceptual model.

There are many factors that control the actual and apparent migration and distribution patterns of the waste products underground, both in the unsaturated and saturated zones. Among these factors are: hydraulic dispersion, which is related to the physical and hydraulic characteristics of the aquifer; groundwater

flow rates; anisotropy, heterogeneity, and porosity of the aquifer; sorption-desorption reactions; biological activity of algae and bacteria; radioactive decay; chemical equilibria reactions; effects of pumping and injection wells; natural recharge influences such as seepage from the Big Lost River and local run-off; numbers, locations, construction and hydraulic characteristics of the monitor wells....The interdependency and complexity of these factors, combined with limited data or poor understanding of them, prevents complete quantitative assessment of their effects on the disposed NRTS wastes. However, current interpretations and appraisals of these controls are presented below (p. 184).

Sorption reactions, which are used herein to include ion exchange, have been shown to be a significant influence on the behavior of some waste products in the subsurface (namely Sr-90 and Cs-137). This influence is probably most pronounced on the pond wastes in the perched water system at TRA but is also significant in the SRPA and the ICPP perched water system.

Nearly all the pertinent sorption studies of NRTS have been oriented toward the exchange capacities and distribution coefficient of the sediments with very little attention to the basalt phases....Practically nothing quantitative is known about the in-place sorption capacity of the basalts in the SRPA.

Hawkins and Short (1965) determined cation exchange capacities and distribution coefficients for a variety of conditions on the Big Lost River alluvium, through which the TRA pond wastes drain. A distribution coefficient of a particular solute is defined for a given solid-liquid chemical system as the ratio of the solute concentration on the adsorbent to the solute concentration in the solvent, expressed in ml/g.

Schmalz (1972) indicates that the distribution coefficients for Sr-90 and Cs-137 in TRA was-water-alluvium system are on the order of 10 ml/g and 500 ml/g, respectively, for a typical waster water composition. In addition, his studies tentatively indicate that Big Lost River alluvial layer beneath the pond has reached its capacity to adsorb additional Sr-90 and perhaps Co-60. However, it appears that the alluvium still retains considerable capacity for the sorption of more Cs-137. These conclusions are fairly well substantiated by the observed distribution of dissolved waster products in the perched water beneath the TRA pond. The large perched waste water body in the basalt section (beneath the surface alluvial layer) contains no detectable Cs-137, but in recent years has shown small but increasing Sr-90 concentrations and relatively high and widespread Co-60 content....These data would support the idea that Sr-90 and Co-60 have "broken through" the ion-exchange column of the Big Lost river sediments beneath the ponds, but that Cs-137 has not.

In addition to the surface layer of Big Lost River alluvium, other interbedded layers of finer grained sediments between the ground surface and the SRPA provide ion-exchange opportunities for waster nuclides percolating downward toward the aquifer. One example of this is the sediment zone upon which the large TRA perched water body reposes. That bed and others through which the percolating waste water must pass have adsorbed essentially all of the Sr-90, Cs-137, and Co-60 so that no detectable concentration of these isotopes have reached the SRPA. However, other less sorbable waster products, such as tritium

and NaCl, have reached the aquifer in low but significant concentrations. It is not known when Sr-90, Cs-137, and Co-60 will saturate the sorption capacity of the lithologic column between the ponds and aquifer and begin to contaminate the SRPA. This will partly depend on future changes in the chemical characteristics of the water.

Even if these TRA wastes do reach the aquifer, sorption will continue to take place. However, the magnitude of the sorption process in the SRPA would be considerably smaller than in the overlying sediment beds. This is because the aquifer is primarily basalt with a specific wetted surface area several orders of magnitude smaller than that of fine-grained sediments. Nevertheless, significant sorption apparently does occur in the aquifer, as evidenced by the data from ICPP, where Sr-90 and Cs-137 have been discharged directly to the aquifer for many years. Sr-90 contamination is apparent to a limited extent in the aquifer, but no Cs-137 has been observed.

In much the same way as the TRA pond wastes, the ICPP pit wastes have to pass through several sediment layers in their downward percolation toward the regional aquifer. The same is true for the waste products in the perched water body within the basalt beneath ICPP, which have been recharged recently by the collapsed disposal well.

In conclusion, then, it is apparent that sorption processes (principally ion exchange) play a significant role in controlling the behavior of some waste products in the subsurface. The products most affected are the cationic isotopes Cs-137, Sr-90, and Co-60. Ordinary sodium also appears to have been retarded in its aquifer migration. Tritium and anionic products such as chloride and I-131 do not appear to be significantly influenced by ion-exchange processes. Because sorption delays the migration of some radionuclides, it provides the additional benefit of allowing more time for those nuclides to decay radioactively (pp. 193-195).

Robertson et al. (1974) discuss the importance of chemical equilibrium reactions on the behavior of wastes in the subsurface as follows (p. 195):

Only limited conclusions can be made regarding this influence {equilibrium reactions} on subsurface waste behavior. The processes involved include solution-precipitation and oxidation-reduction reactions. There is no evidence to indicate any significant oxidation-reduction influences on subsurface waste products. Cr(VI), for instance, undergoes little reduction to Cr(III) underground.

The TRA pond situation is the only apparent instance where chemical reactions may have had an effect on the migration of liquid wastes underground. Chemical precipitation was previously pointed out as a factor which decreased the permeability of the TRA pond bottoms. A chemical equilibrium study of several TRA pond water analyses indicates that at a pH of 8 or less the water is generally not saturated with any mineral species. However, if the pH increases to 9 or 10 or higher, the waste water may become supersaturated in several mineral species such as calcium carbonate, magnesium carbonate, iron carbonate, ferric hydroxide, and several other species. Several measurements have shown pond water pH values in the range of 9 to 11, so without doubt there has been occasional supersaturation of some components in the water.

Although a full chemical analyses of the typical ICPP disposal well effluent has never been run, a computer analysis of the chemical equilibrium of an approximate but hypothetical composition of that water indicated it is generally not saturated in any significant mineral species. Therefore it is apparent that precipitation reactions are probably not a significant influence on this waste before or after it enters the aquifer. However, corrosion has certainly played an indirect but very significant role in the fate of ICPP disposal well wastes. The well effluent with its increased salt content, high dissolved oxygen, and occasional low pH, caused corrosion of the steel well casing which led to the well collapse. This in turn caused the wastes to enter a perched water zone instead of going directly into the aquifer which changed many of the factors affecting the waste products (i.e., ion exchange) and also increased contamination of the production wells (p. 195).

Robertson et al. (1974) address “Other Factors” that affect the fate of wastes in the subsurface as follows (pp. 195-196).

Radioactive decay certainly has a bearing on the distribution and concentrations of waste radionuclides in the groundwater. Given enough time, all radioactive wastes have the unique property of self-obliteration. For instance, if disposal of tritium were curtailed, the quantity of tritium in the groundwater would gradually decline so that after 86 years (7 half-lives) more than 99% of the originally present waste tritium would be gone.

The waste disposal summary indicates that about 70,000 Ci of liquid radioactive waste had been discharged at NRTS and of that amount, only about 13,000 Ci now remain. The loss is due almost entirely to radioactive decay. Radioactive decay, of course, has no influence on nonradioactive waste products such as NaCl and chromates. As long as these products are discharged, their inventory in the groundwater will continue to increase in an irreversible process.

Certain biological factors can, in some instances, have limited effects on the behavior and fate of liquid waste products discharged at the NRTS. These influences might include bacterial, algae, and higher plant and animal actions. The only instance where this is known to be a factor is at the TRA ponds, and has been described previously in this report. Other organisms at the pond, including water fowl, aquatic vegetation, and insects, may have some influences on the nuclides disposed there, but it is probably insignificant. Conversely, the effects of the waste products on the life system are also unknown (pp. 195-196).

Salient points regarding geochemistry recognized by Robertson et al. (1974) in this section include:

- Sorption – desorption reactions affect contaminant transport
- Equilibrium chemical reactions affect contaminant transport
- The importance of biological processes on contaminant fate and transport in the subsurface was not recognized
- Sediments are more important as sorbents than are basalts and hence substantially affect contaminant transport, particularly in the vadose zone

- Cs is more strongly sorbed than Sr
- Anions and tritium are not significantly sorbed
- Cr-VI is not substantially reduced to Cr-III
- Precipitation was discounted as an attenuation mechanism, except in the TRA pond
- Co-precipitation was not recognized as a potential attenuation mechanism for Sr
- The importance of subsurface biological processes was not recognized.

5.1.4 Summary of Robertson et al. 1974

The following excerpts are from the summary provided by Robertson et al. (1974).

Groundwater in the SRPA beneath the NRTS contains low levels of dissolved solids and is of good quality for most purposes. The compositions of this groundwater reflect the compositions of various sources of surface and groundwater recharge from mountains and valleys bordering the Plain. The compositions of the different sources of recharge can be explained by reaction of rain and snowmelt with the dominant reactive minerals believed to be present in the rocks of each recharge area. In addition, longer residence time of groundwater in rocks of the recharge areas, than in rocks of the Snake River Plain, allows reactions between minerals and groundwater to proceed and, in some cases, to equilibrate. Deep groundwater beneath the NRTS contains more sodium, fluoride, and silica than shallow groundwater, perhaps reflecting the presence of silicic volcanic rocks at depth and longer residence times to promote reactions between minerals and water.

Recharge water derived from areas of intensive irrigation can be recognized by its high content of dissolved solids, warm temperature, and high levels of fertilizer-based constituents such as nitrate. Irrigation recharge water quickly loses its identity in the SRPA due to rapid dispersion.

Near-saturation of the groundwater beneath the NRTS with respect to calcite and dolomite requires that care be used in utilization of the water, where concentration or mixing may occur, to avoid precipitation of solids.

The quantitative record of liquid wastes released to the subsurface at NRTS is incomplete. Available information indicates that from 1952 (when disposal began) through 1970 about 1.9×10^{10} gallons of liquid waste containing 7.0×10^4 curies of radioactivity and about 1×10^8 pounds of chemical waste have been discharged to the ground at the NRTS. Most of this has been to the ICPP deep well, the TRA seepage ponds and deep well, and the NRF seepage ponds. Migration and distribution of wastes after release depends on a variety of complex influences. Wastes discharged above the SRPA at the NRTS form temporary perched water bodies, but eventually percolate to the regional water table.

The subsurface influence of waste disposal has been analyzed for only two facilities at NRTS – the TRA and ICPP. For other facilities, waste disposal is either insignificant or, as in the case of the NRF, sufficient data has not been collected to prepare an analysis.

The principal waste products at TRA have been NaCl, chromate, tritium, Cs-137, Sr-90, and Co-60. Distribution of these products in the perched water system has been fairly well defined. The upper sedimentary layers at TRA have been very effective in removing most or all of the cationic waste products (Cs-137, Sr-90, and Co-60) except sodium and chromium. Significant quantities of the other wastes (tritium, NaCl, hexavalent chromium), however, have entered and been dispersed in the SRPA beneath the NRTS. Their distribution in the aquifer is only partly defined because of the lack of observation wells to the south and southwest of TRA.

Because of better observation-well coverage, the behavior and distribution of ICPP wastes in the regional aquifer have been much more thoroughly studied. The principal ICPP waste products include NaCl, tritium, Sr-90, Cs-137, and heat. Analysis of the observed behavior of these products in the aquifer over the 18-year (1952-1970) discharge period indicates that dispersion is a very significant mechanism in spreading and diluting the waste plume, more so than classical dispersion theory would predict. This extraordinary dispersion process may be due largely to differential vertical anisotropy in the aquifer, although channel branching and turbulent mixing in the relatively fast-flowing groundwater may be involved. Basalt has relatively poor ion-exchange capacity (compared to fine sediments); nevertheless, exchange or sorption has a prominent influence on cationic waste products in the aquifer (namely Cs-137, Sr-90, and sodium). Cs-137, for instance, has been removed below detection limits from the aquifer water by sorption. Decay of radionuclides has also been a significant factor in reducing the extent of the waste plume. Additional factors, such as pumping-wells, have lesser, but significant, influences on the migration of NRTS wastes in the aquifer.

Tritium and NaCl, the most widespread wastes in groundwater at the NRTS, have been carried downgradient in detectable quantities about 4.5 miles and have contaminated an area of at least 12 to 15 square miles of the aquifer. Concentrations of these wastes are very small however, and no groundwater contamination has been detected close to the southern boundary of the NRTS. The use of water from three supply wells (Wells CP-1, NRF-2, and S5G production) has required restriction or prohibition because of contamination by waste products. (The CP-1 well has recently been restored to unrestricted use.)

Materials-balance analyses and other data indicate that most of the wastes discharged at the NRTS remain in the upper 250 ft of the SRPA, as they migrate downgradient. Waste tritium and heat in the groundwater appear to be maintaining an equilibrium inventory, dissipating by decay and conduction, respectively, at a rate equal to their recharge.

Data available at this time indicate that liquid waste discharged to groundwater in the SRPA beneath the NRTS attenuates rapidly due to dispersion in the flowing groundwater, sorption of some cationic wastes, and decay of all radionuclides.

However, there are many significant limitations in the data at this time (pp. 199-201).

To summarize (Robertson et al 1974):

- The natural solute composition of groundwater in the Eastern SRPA reflects the composition of groundwater and surface water in tributary basins.
- Recharge of irrigation water is recognizable because the natural solutes have been concentrated by evaporation and addition solutes from agricultural fertilizer have been added
- Limited water-rock interaction in the Eastern SRPA, and mixing between waters that have different origins, modify the solute composition of water in the Eastern SRPA.
- Liquid wastes disposed at TRA and ICPP/Idaho Nuclear Technology and Engineering Center (INTEC) were studied.
- The predominant liquid chemical wastes are derived from water treatment, and include sodium chloride, acids and bases, and hexavalent chromium.
- The predominant radioactive wastes are tritium, C0-60 Sr-90, and Cs-137.
- For liquid wastes discharged at the ground surface or in the vadose zone, sorption by sediments substantially attenuates the migration of cationic contaminants. However, sorption does not substantially attenuate anions (e.g., chloride, hexavalent chromium) or tritium (in the form of tritiated water).
- Sorption is much weaker in basalt than in sediments due to the much smaller surface area available in fractured basalt than in the granular sedimentary interbeds and differences in mineralogy.
- Sorption retards transport rates and thereby provides more time for radioactive decay to reduce concentrations of sorbed radionuclides
- Sorption is reversible.
- Anionic contaminants are not significantly sorbed.

5.2 Disposal Methods Used at the INEEL

This section provides a high-level summary description of the methods used for disposing liquid and solid wastes at the INEEL. This report focused primarily on liquid wastes because these have a rapid effect on the quality of water in the subsurface, while non-liquid wastes affect subsurface water quality only after they dissolve and exit the disposal facility.

5.2.1 Injection Wells

Starting in the 1950s, injection wells were constructed at the INEEL for disposing wastewaters directly into the SRPA or in some situations into the vadose zone. These injection wells provided a historical means of waste disposal, but are no longer used; injections ceased in the 1980s. The types of waste and volumes injected into each well varied based on location of the injection well in relation to contaminant sources.

5.2.2 Buried Waste

Disposal of wastes by shallow land burial has been an accepted standard practice in industry. Waste burials in general pose a threat to groundwater because the wastes are typically placed directly into the vadose zone, and any contaminant release from the waste is then available for transport in the vadose zone and, potentially, to the underlying aquifer. Wastes have been disposed of through burial at the INEEL since the site was originally established in the early 1950s.

Burial of wastes can be roughly classified into two broad categories, convenience disposal and managed disposal. Convenience disposal typically occurred during short-term projects, such as construction activities. Managed disposal is typified by the presence of acceptance criteria for the wastes being disposed and active management (e.g., placement, cover) of the disposal area. Managed buried waste disposals were typically performed in planned locations and conducted over longer durations or, for specific projects, over a shorter time frame to meet clean up goals.

5.2.3 Infiltration Ponds and Ditches

Wastewater generated by INEEL operations has been discharged since the early 1950s to a series of unlined ponds and ditches. Wastewater disposed to these surface-disposal facilities has contained small concentrations of dissolved radioactive and/or nonradioactive chemical constituents. The release of contaminants from ponds and ditches is controlled by the hydraulic and geochemical properties of the geologic materials that make up the pond or ditch bottom. Typically, the hydraulic conductivity of pond bottom materials is large and wastewater disposed to ponds and trenches rapidly infiltrates. Under these conditions, the release of wastewater and chemically conservative contaminants to the underlying vadose zone nearly approximates the rate of discharge to the ponds. Less conservative constituents may be sorbed to pond-bottom sediments. These sorbed constituents may provide a later source of release to the vadose zone under altered geochemical conditions. Shallow perched groundwater bodies commonly form in alluvial deposits directly beneath the pond in response to infiltration. These perched groundwater bodies also constitute a point of attenuated contaminant source-term release to the vadose zone.

5.2.4 Contaminated Surface Soils

Contaminated soil sites are a common feature at many historical industrial facilities, including the INEEL. Past practices including surface discharges of contaminated liquids, fallout from air emissions, as well as accidental discharges resulting from failed underground piping, leaking underground basins and tanks, or simple spills, created numerous areas where surface and subsurface soils contained hazardous and radiological contaminants at varying concentrations.

Accidental releases generally were cleaned up at the time of the incident to protect facility workers. Those sites that were not cleaned up immediately, or that were a part of the facility operations, were incorporated into the environmental restoration program during the early 1990s. In general, the contaminated soil sites were evaluated as part of facility scale remedial investigations according to the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) process. Most of those that were deemed to pose unacceptable risk have been remediated. In only a few cases are the CERCLA investigations ongoing. Although literally hundreds of sites have been identified, only contaminated soils at the INTEC tank farm have been determined to have the potential to impact aquifer water quality.

5.3 Wastes and Contaminants Disposed in the INEEL Subsurface

This section summarizes the types of wastes disposed in the subsurface at the INEEL. The information is presented in tabular form. Table 5-1 lists the types of wastes discharged by each facility, and Table 5-2 categorizes wastes by type.

5.3.1 Summary of types of wastes disposed at INEEL

Table 5-1. Liquid waste disposed to injection wells.

Type of Wastes	WAG/INEEL Location	Disposal Location	Description
Industrial and sanitary	TAN	TSF-05	Organic, inorganic, and low-level radioactive constituents
Treated sanitary sewage and process wastewater	TAN	IET-06	
Treated sanitary sewage and liquid chemical waste	TAN	WRRTF-05	
Noncontaminated and cold wastewater	TAN	LOFT-04	
Cold wastewater, secondary cooling water from reactors, nonradioactive wastewater	TRA	TRA-05	
Chemical	TRA	USGS-53	
Low-level radioactive and chemical	INTEC	CPP-23 and USGS-50	
Low-level radioactive and raw coolant	PBF	PBF-05	
Discharge from regeneration of reactor demineralizers and secondary reactor coolant water	PBF	PBF-15	

Table 5-2. Liquid waste disposed to ponds and ditches.

Type of Wastes	WAG/INEEL Location	Disposal Location	Description
Low-level radioactive, condensate from two evaporator systems, wastewater from regeneration of water softeners and boiler blowdown operations (past disposal), cold process water and treated sewage effluent (ongoing disposal)	TAN	TSF-07 Disposal Ponds	Wastewater contained chemical cleaners, paint thinners, and paint strippers. Some liquids were corrosive and consisted of acids and caustics.
Low-level radioactive wastewater	TRA	Warm Waste Ponds	Cooling tower blowdown waste, wash waste from hot cell drains, laboratory solutions, and floor drainage from the Advanced Test Reactor
Nonradioactive wastewater	TRA	Chemical Waste Pond	Industrial chemicals associated with ion-exchange columns and waste softeners
Cooling-tower blowdown water	TRA	Cold waste pond	Cooling water from blowdown during reactor operations, discharge from air conditioning units, secondary system drains, floor drains, and other non-radioactive drains throughout TRA.
Sanitary wastewaters	TRA	Sewage Leach Ponds	
Radioactive and chemical	INTEC	Unlined service waste disposal ponds	
Wastewater generated in the ARA-I shop and maintenance building	PBF/ARA	ARA-I Chemical Evaporation Pond	Small quantities of radionuclides, acids, bases, and volatile organic compounds
Low-level waste from reactor research and facility surface runoff	PBF/ARA	ARA-III Radioactive Leach Pond	

Table 5-2. (Continued).

Type of Wastes	WAG/INEEL Location	Disposal Location	Description
Radiologically contaminated and nonradioactive overflows from SPERT-I reactor pit	PBF/ARA	PBF SPERT-I Leach Pond	
Effluent from a demineralizer, water softener waste, emergency shower drain water, and discharges from reactor-building floor drains	PBF/ARA	PBF SPERT-II Leach Pond	
Primary coolant water and sump pump discharges	PBF/ARA	PBF SPERT-III Large Leach Pond	
Radioactively contaminated wastewater, emergency shower water and primary coolant effluents from the SPERT-IV reactor	PBF/ARA	PBF SPERT-IV Leach Pond	
Uncontaminated secondary coolant water from the SPERT-IV reactor and uncontaminated effluent from Three Mile Island studies	PBF/ARA	PBF SPERT-IV Lake	
Wastewater from BORAX II through V reactor experiments	BORAX	BORAX Leach Pond and Drainage Ditch	
Surface water from runoff and facility drains	ANL-W	Industrial Waste Pond	
Surface water from runoff and facility drains	ANL-W	Ditches and Canals	
Sanitary wastewater and photo processing solutions	ANL-W	Sanitary Sewage Lagoons	
Cooling tower blowdown, sanitary effluent, cooling condensates, and radioactive effluent	ANL-W	Leach Pit	
Nonradioactive, non-sewage, industrial, and storm water discharge	NRF	Industrial waste ditch	
Low-level radioactive effluent	NRF	SI W Tile Drainfield	
Low-level radioactive effluent	NRF	AIW/ECF Wastewater Disposal Facilities	
Sewage wastewater	NRF	Sewage Lagoons	

Table 5-3. Buried solid wastes.

Type of Wastes	WAG/INEEL Location	Disposal Location	Description
Buried waste does not include hazardous wastes	PBF/ARA	SL-1	
Buried waste does not include hazardous wastes	BORAX	BORAX-I	
Buried waste does not include hazardous wastes	CFA	CFA	
Reactor components, structural metals, jet engines, heavy equipment, clothing, wood, other metal objects, glassware and laboratory equipment, biological wastes, production equipment (e.g., lathes, furnaces), wastewater treatment sludges, and solidified organics	RWMC	SDA	

Table 5-4. Contaminated soil and buried waste sites.

WAG/INEEL Location	Contaminated Soil Site	Description
TAN	Nearly 100 sites including TSF-07 Clarifier Pits, TSF-03 and WRRTF-01 Burn Pits, and the TSF-29 Acid Pond	Contaminated by historic operations
TAN	TSF surface ponds, drainage ditches, railroad tracks and areas used for equipment storage	Large contaminated areas
TAN	IET Valve Pit and the mercury spill sites associated with the Heat Transfer Reactor Experiment (HTRE)-III engine	Unintentional releases of radioactive and hazardous materials
TAN	TSF-07 Disposal Pond	Contaminated by low levels of radionuclides, corrosive wastewater, chromium and lead
TRA	15 sites with surficial soil contamination	Primarily associated with radiological waste tanks
TRA	Hot Tree Site	An anonymous spruce was allegedly involved in the rupture of a low-pressure acidic transfer line originating from the gamma facilities building

Table 5-4. (Continued).

WAG/INEEL Location	Contaminated Soil Site	Description
INTEC (WAG 3 FS Final)	Tank Farm soils	Various contaminated soil sites from spills, ruptured transfer lines, leaking lines, release of contaminated condensate, leaks from tanks, etc.
	Soils under buildings/structures	Located under buildings or structures and limited or no information about the extent or volume of the contaminant releases.
	Other surface soil sites	Various contaminated soils sites from spills, small landfills, leaking lines, break in line, percolation ponds, boxes of soil, trenches, old sewage treatment plant, grease pit, area used to discard used paint solvents, and buried gas cylinders
CFA	13 sites	Waste generating processes from industrial support facilities including vehicle maintenance, welding and other crafts, an industrial waste landfill, radiological laboratories, and radiological laundry facilities
PBF/ARA	55 sites	Past practices including small unlined impoundments used to dispose of research wastewater, septic leach fields, reactor coolant water blow down pits, and windblown contaminated soils from the SL-1 reactor accident
BORAX		Soils and buried debris contaminated primarily by heavy metals and fission products from reactor operations
RWMC	SDA	Buried waste
RWMC	Acid pit	Liquid wastes, primarily organic solvents and radiologically contaminated acids and cleaning solutions
NRF	SI W Retention Basins, the SI W Radiography Building Collection Tanks, the Hot Storage Pit, the ECF Water Pit Release, the AI W/SI W Radioactive Line Near BB19, and the AI W Processing Building Area Soil	Accidental radiological discharges have occurred at NRF resulting from corroded underground piping, leakage from underground basins, and releases from radiological tanks
NRF	Old Sewage Treatment Plant, Seepage Basin Pump Out Area, and Sewage Lagoons	
NRF	Old Ditch Surge Pond and S5G Basin Sludge Disposal Bed	Potentially radiologically-contaminated
ANL-W	Industrial waste pond	Contained concentrations of cesium-137, trivalent chromium, mercury, selenium, and zinc

5.4 Contaminants Observed in Perched Water and Groundwater Beneath the INEEL and Vicinity

Contaminants observed in perched water bodies and in groundwater beneath the INEEL are listed below. Table 5-5 lists sources, contaminants, and maximum concentrations by INEEL WAG. Table 5-6 lists contaminant concentrations in the SRPA. Table 5-7 lists contaminants by type.

Table 5-5. Groundwater contaminants, sources, and maximum concentrations as listed by INEEL Waste Area Group.

WAG	Source of Contamination/ Location Description	Contaminants	Observed Concentrations (listed as ranges or max value, unless noted as different)
1	TSF-05 Injection Well (DOE-ID 2001)	TCE	12,000-32,000 ppb
		PCE	110 ppb
		cis-DCE	3,200-7,500 ppb
		trans-DCE	1,300-3,900 ppb
		tritium	14,900-15,300 pCi/L
		Sr-90	530-1,880 pCi/L
		Cs-137	1,600-2,150 pCi/L
1	Widespread, concentrations above background (from TSF- 05 and WRRTF-05 (sulfate and chloride only) (Wymore et al. 2000)	nitrate	Approx. max 4 mg/L
		sulfate	Approx. max 40 mg/L
		alkalinity	Approx. max 1200 mg/L
		Chloride	Approx. max 100 mg/L
1	Widespread (in accordance with the Wastewater Land Application Permit) (Orr et al. 2003)	Total dissolved solids, sulfate, sodium, coliform	Detected in the aquifer
1	TSF-07 Pond- Perched Water- bodies (DOE-ID 2003)	Gross alpha	3.2-120 pCi/L
		Gross beta	0-120 pCi/L
		Sr-90	1-136 pCi/L

Table 5-5. (Continued).

WAG	Source of Contamination/ Location Description	Contaminants	Observed Concentrations (listed as ranges or max value, unless noted as different)
2	TRA-05 Injection Well and USGS-53 Injection Well and infiltration to the groundwater (Burns et al. 1997)	chromium	209-321 ug/L (max range)
		tritium	30.3-37.6 pCi/mL (max range)
2	Other groundwater contaminants, source not specified	See Table A2 in this document	
2	Perched groundwater from wastewater disposals to the radioactive-waste, chemical-waste, cold-waste, and sanitary-waste ponds (Bartholomay and Tucker 2000)	tritium	0.8-365 pCi/mL shallow 0.41-116 pCi/mL deep
		Sr-90	23.5-6800 pCi/L shallow 1.6-59 pCi/L deep
		Cs-137	1,200-42,300 pCi/L shallow
		Cr-51	2,700-24,500 pCi/L shallow
		Co-60	7,700-44,000 pCi/L
		Dissolved Cr	<5-26 ug/L shallow 9.8-98 ug/L deep
		Hexavalent chromium	1-5 ug/L shallow
		sodium	7.6-20 mg/L shallow 6.1-1000 mg/L deep
		chloride	9.3-27 mg/L shallow 3.1-43 mg/L deep
		sulfate	18-3200 mg/L deep 340 mg/L shallow

Table 5-5. (Continued).

WAG	Source of Contamination/ Location Description	Contaminants	Observed Concentrations (listed as ranges or max value, unless noted as different)
3	CPP-23 Injection Well	Hg, Am-241, Co-60, Cs-137, tritium, I-129, Np-237, Pu, Sr-90, U	NA
3	Other groundwater contaminants, source not specified	See Table A2 in this document	
3	USGS-50 Perched Groundwater	Tc-99, tritium, Sr-90, U-234	NA
3	Perched groundwater from two wastewater infiltration ponds (Bartholomay and Tucker 2000)	tritium	<3-11.3 pCi/mL deep
		Sr-90	< reporting level-2.8 pCi/L deep 142-190 pCi/L
		sodium	170 mg/L shallow 105-197 mg/L deep
		chloride	270 mg/L shallow 135-386 mg/L deep
		Sulfate	30 mg/L shallow 14-41 mg/L deep
		Nitrate (measured as nitrite plus nitrate (as nitrogen))	1.3-59 mg/L
4			Detection of 25 contaminants, some possibly migrated from INTEC, some local sources but extent not defined, zinc from well components
5			Detection of beryllium, iron, arsenic, lead, nitrate, organic compounds

Table 5-5. (Continued).

WAG	Source of Contamination/ Location Description	Contaminants	Observed Concentrations (listed as ranges or max value, unless noted as different)
6		None	
7	Aquifer and vadose zone near SDA (human health contaminants of concern) (Holdren et al. 2002)	Am-241	0.006-9.6 pCi/g (vadose, core samples) 0.041-9 pCi/L (vadose, lysimeters) 0.011-5 pCi/L (aquifer)
		C-14	Not detected (vadose, core samples) 11-26 pCi/L (vadose, lysimeters) 1.8-28 pCi/L (aquifer)
		I-129	Not detected (vadose, core samples) 22-53 pCi/L (vadose, lysimeters) 0.59-17 pCi/L (aquifer)
		Nb-94	Not detected (vadose) Not detected (aquifer)
		Np-237	Not detected (vadose) Not detected (aquifer)
		Sr-90	0.13-1.2 pCi/g (vadose, core samples) 2.2-52 pCi/L (vadose, lysimeters) 0.12-58 pCi/L (aquifer)
		Tc-99	1.08-4.2 pCi/g (vadose, core samples) 5.8-46 pCi/L (vadose, lysimeters) 1.0-35 pCi/L (aquifer)
		U-233/234	1.7 pCi/g (vadose, core samples) 1.7-111 pCi/L (vadose, lysimeters) 0.40-1.84 pCi/L (aquifer)
		U-235/236	0.120 pCi/g (vadose, core samples) 0.35-8.2 pCi/L (vadose, lysimeters) 0.020-0.18 pCi/L (aquifer)

Table 5-5. (Continued).

		U-238	1.7-7.5 pCi/g (vadose, core samples) 0.26-53 pCi/L (vadose, lysimeters) 0.21-0.88 pCi/L (aquifer)
		Carbon tetrachloride	14-2400 µg/L (vadose, perched water) 1.9-1000 µg/L (vadose, lysimeters) <0.21-8 µg/L (aquifer)
		Methylene chloride	Not detected-23 µg/L (vadose, perched water) Not detected-6.8 µg/L (vadose, lysimeter) <0.21-8 µg/L (aquifer)
		Nitrates	0.21-2.94 mg/kg (vadose, core samples) 0.12-242 mg/L (vadose, lysimeters) 0.28 mg/L-2.9 g/L (aquifer)
		Tetrachloroethylene	2.6-230 µg/L (vadose, perched water) Not detected-27 µg/L (vadose, lysimeter) Not detected-0.4 µg/L (aquifer)
7	Other groundwater contaminants, source not specified	See Table A2 in this document	

Table 5-5. (Continued).

WAG	Source of Contamination/ Location Description	Contaminants	Observed Concentrations (listed as ranges or max value, unless noted as different)
7	Perched groundwater from solid and liquid radioactive and chemical buried waste at SDA (Bartholomay and Tucker 2000 (Table 7))	Plutonium-238	above reporting level
		Americium-241	Above reporting level
		chloride	69-78 mg/L
		Carbon tetrachloride	260-1800 µg/L
		1,2-Dichloroethane	0.96-1.8 µg/L
		Chloroform	540-920 µg/L
		Toluene	<0.2-0.29 µg/L
		Methylene chloride	<0.2-5.3 µg/L
		Tetrachloroethylene	50-180 µg/L
		1,1-dichloroethane	7.7-15 µg/L
		1,1-dichloroethylene	0.95-2.2 µg/L
		1,1,1-trichloroethane	55-170 µg/L
		1,1,2-trichloroethane	<1.7-0.6 µg/L
		1,2-dichloropropane	3.2-6.7 µg/L
		Trichloroethylene	360-1400 µg/L
Cis-1,2-dichloroethene	0.32-0.8 µg/L		
Freon-113	1.3-3.6 µg/L		
8	NRF Groundwater	tritium	15-308 pCi/L
		chloride	7-213 mg/L
		nitrate	0.45-2.04 mg/L
		chromium	6.79-35.20 ug/L
8	Other groundwater contaminants, source not specified	See Table A2 in this document	
9		None	

Table 5-6. Contaminant concentrations in the SRPA (Bartholomay et al. 2000).

Contaminant	Sources	General Location	Concentration Range
Tritium	Injection of wastewater through disposal well at INTEC and discharge of wastewater to the infiltration ponds at INTEC and TRA		0.29-18.7 pCi/mL
		North of CFA	14.8 pCi/mL
		Near TRA	15.9 pCi/mL
		South of INTEC	18.2 pCi/mL
		At the boundary	0.31 pCi/mL
		South of the boundary	0.3 pCi/mL
Sr-90	Wastewater disposal into a pit at INTEC, direct injection and discharged to infiltration ponds at INTEC, infiltration and evaporation ponds at TRA, and infiltration ponds at INTEC	INTEC	2.1-41.1 pCi/L
Gross alpha and beta		general	6-39 pCi/L
chromium	Chromium was discharged to infiltration ponds at TRA and INTEC, to an injection well at TRA and INTEC, and in wastewater at PBF	South of TRA	168 ug/L
		general	<14-26 ug/L
sodium	Sodium was discharged to the INTEC infiltration ponds, the TRA chemical waste infiltration pond, the NRF industrial-waste ditch, and at CFA	INTEC	96 mg/L
		RWMC	42-48 mg/L
		TRA	42 mg/L
chloride	Infiltration ponds at the INEEL	TRA	<15-18 mg/L
		RWMC	20-84 mg/L
		NRF	20-209 mg/L
Sulfate	Sulfate was discharged to infiltration ponds at the TRA, infiltration ponds at INTEC, and the NRF industrial-waste ditch	NRF	41-145 mg/L
		RWMC	59 mg/L
		TRA	54-147 mg/L
Nitrate	Injected into the INTEC disposal well and discharged to the INTEC infiltration ponds	INTEC	<5-49 mg/L
		CFA	17 mg/L
		RWMC	5.7-8.7 mg/L
		TRA	7.0 mg/L
		NRF	Greater than 5 mg/L
Fluoride	Discharged to infiltration ponds at INTEC	INTEC	0.2-0.3 mg/L
Many trace elements and purgeable organics			

Table 5-7. Contaminants listed by type (i.e., inorganic, radionuclide, organic, NAPL, DNAPL).

Inorganic	Organic	Radionuclides	Trace	NAPL	DNAPL
nitrate	TCE	Tritium	Hg		TCE
sulfate	PCE	Sr-90	Cr		PCE
chloride	cis-DCE	Cs-137	Pb		cis-DCE
sodium	trans-DCE	U-234			trans-DCE
Cr	coliform	Gross alpha			
	hydrazine	Gross beta			
	carbon tetrachloride	Co-60			
	methylene chloride	U			
		Tc-99			
		I-129			
		Am-241			
		Np-237			
		Pu			

6. GEOCHEMICAL BEHAVIOR OF INEEL CONTAMINANTS OF CONCERN

The preceding section identified the contaminants that have been identified in groundwater beneath the INEEL and vicinity. This section discusses the geochemical behavior of these contaminants as it affects their transport. An investigation of the solubility of contaminants present at the RWMC is discussed in Section 6.1. Sorption is widely recognized as an important process that retards the migration of many contaminants in the INEEL subsurface. The results of sorption studies using INEEL geologic media and contaminants are discussed in Section 6.2. These studies are primarily laboratory measurements of sorption isotherms, and hence the results are applicable only to the conditions under which the measurements were made. An alternative approach for describing sorption is surface complexation modeling, in which interactions between solutes and surfaces are described as a set of reversible reactions. Application of this approach for predicting sorption of selected INEEL contaminants is described in Section 6.3. Contaminants are grouped into separate classes based on their probably transport behavior in the subsurface in Section 6.4.

6.1 Solubility of Contaminants at the Radioactive Waste Management Complex

Hull & Pace (2000) used equilibrium geochemical modeling to predict the solubility of contaminants of potential concern in soil moisture (i.e., vadose zone water) at the RWMC. Although they were primarily concerned with dissolution of contaminants from disposed wastes, their findings are generally applicable to the groundwater environment as well. The contaminants they considered are:

- Carbon tetrachloride
- Methylene chloride
- Tetrachloroethylene
- Nitrate
- Actinium-227
- Americium-241
- Carbon-14
- Chlorine-36
- Cesium-137
- Iodine-129
- Niobium-94
- Neptunium-237
- Protactinium-231

- Lead-210
- Plutonium-239 and -240
- Radium-226
- Strontium-90
- Technetium-99
- Uranium-233, -234, -235, -236, and -238.

They used the geochemical program Geochemist's Workbench, Version 3, to generate speciation diagrams and to calculate the solubility of these contaminants, except for the organic compounds, as a function of pH and P_{O_2} , in a solution considered typical of soil water at the RWMC. Their results were summarized in their Table 4-1, which is repeated here as Table 6-1. Excerpts from their summary are as follows.

- The effect of oxidation/reduction potential on the solubility of these contaminants is varied. There is no single set of redox and pH conditions that will minimize the solubility of all of the contaminants.
- Many of these contaminants do not show an effect of redox regime on solubility.
- The contaminants whose solubility does vary with redox regime, the reduced form is generally less soluble. This is particularly true for the actinides.
- In general, a moderately reduced environment ... would be the best redox regime for the waste
- The contaminants show a wide range of solubility variation with pH. Carbonate complexing, and complexing with hydroxide ions increase with increasing pH. This sequesters more of the contaminant in solution and increases solubility. The amount of carbonate or hydroxide in solution also decreases the solubility of carbonate or hydroxide phases. The relative strength of these two competing reactions is different for each of the contaminants, leading to the wide variation in solubility behavior with increasing pH. In general, a pH in the neutral to slightly basic range (pH 7 to 8.5) would be better than high pH values (pH > 9).
- Soil waters in the SDA where the pH is controlled by equilibrium between $CO_2(g)$ - Calcite and dissolved carbonate will have a pH between 7.2 and 8.2 depending on the partial pressure of the $CO_2(g)$. The natural buffering capacity of the system will help to maintain a slightly alkaline pH. Soil water between the trenches contains dissolved oxygen. High partial pressures of $CO_2(g)$ in the soil gas phase suggest a significant amount of biological degradation of organic matter in the trenches and pits. This degradation will consume oxygen in the waste and will help maintain reduced conditions in the pits and trenches. The natural tendencies of the water buried at the SDA will be to reach a condition that may be near optimum for minimizing the solubility of the contaminants.

Table 6-1. Summary of pH and redox regimes that minimize solubility for each of the contaminants of potential concern (from Hull and Pace 2000).

Contaminant of Potential Concern	pH regime ¹	Redox regime ²
Chlorinated volatile organic compounds	No information.	No information on solubility, but moderate to strongly reduced conditions contribute to reductive dechlorination reactions.
Nitrate	Moderate pH range contributes to ion exchange of ammonia under reduced conditions.	Moderate to strongly reduced conditions do not affect solubility, but contribute to denitrification to N ₂ (g) and conversion to ammonia with adsorption on clays.
Actinium-227 and Americium-241	Moderate pH has the lowest solubility, carbonate complexing increases solubility as pH increases	No effect.
Carbon-14	High pH has the lowest solubility as calcite precipitates	Only under strongly reduced conditions does dissolved carbonate change to methane with a gas phase controlling solubility.
Chlorine-36	No effect.	No effect.
Cesium-137	No effect.	No effect.
Iodine-129	No effect.	No effect.
Lead-210	Moderate pH has the lowest solubility	No effect
Niobium-94	Moderate pH has the lowest solubility	No effect.
Neptunium-237 and Protactinium-231	High pH has the lowest solubility	Moderate to strongly reduced environments have the lowest solubility
Plutonium-239, and 240	High pH has the lowest solubility	Moderate to strongly reduced environments have the lowest solubility
Radium-226	Moderate pH has the lowest solubility	Strongly reducing conditions can reduce sulfate to sulfide increasing solubility at moderate pH.
Strontium-90	Moderate pH has the lowest solubility	No effect
Technetium-99	Moderate pH has the lowest solubility	Moderate to strongly reducing conditions have lowest solubility
Uranium-233, 234, 235, 236, and 238	High pH decreases solubility	Moderate to strongly reducing conditions have lowest solubility
1. pH regime	moderate high	pH 7 to 9 pH 9 to 13
2. Redox regime	oxidized moderately reduced strongly reduced	log a O ₂ (aq) -3 to -40 log a O ₂ (aq) -40 to -70 log a O ₂ (aq) -70 to -86

6.2 Sorption Measurements for INEEL Contaminants of Concern and INEEL Media

6.2.1 Newman et al., 1996

Newman et al. (1995) summarize sorption studies performed at INEL and Clemson University. These studies measured sorption isotherms for several radionuclides that are present in the INEEL subsurface (Am, Cs, Co, Pu, Sr, U) using basalt and granular media collected from sedimentary interbeds.

They used equilibrium K_d models and kinetic models to obtain distribution coefficients from batch experiments. They discussed these approaches as follows.

Distribution coefficients were determined from partitioning of the radionuclide at 400 hours and from first-order and dual rate models. . . . Distribution coefficients based on concentrations at 400 hours were generally higher than values determine from the other two methods. The dual rate model appears to provide a better approximation to the data than the single rate model . . . indicating heterogeneity among sorption sites. It appears that incorporation of an additional rate may be needed to explain ^{60}Co sorption to interbed. . . . This observation may be due to a change in the redox state of cobalt possibly mediated by a subsurface component.

Generally, the sorption rate constant was larger with interbed than basalt. ^{90}Sr appeared to sorb slowly to both basalt and interbed. This apparent slow sorption may have been caused by large amounts of naturally occurring strontium in the basalt and interbed material which reached equilibrium with the synthetic groundwater during the washes prior to spike addition (pp. 39, 49).

They discussed the importance of oxidation state on Pu transport as follows.

Because of its important role in subsurface transport, plutonium oxidation states were measured in the synthetic groundwater solution. This was accomplished by allowing plutonium to equilibrate in the synthetic groundwater solutions for 14 days and monitoring the oxidation state(s) over time. . . . Within the first 24 hr. the majority of plutonium remaining in solution was Pu(V) with smaller amounts of Pu(IV), Pu(VI), and Pu(III). Also within this time frame the total plutonium activity in the solution phase decreased to 60 to 70% of the initial value, due primarily to a decline in Pu(IV). However, when the container was shaken at the end of the 14-day period, the solution phase activity increased to 90% of the initial value. Thus, the initial decline in solution phase activity was attributed to settling of polymerized or precipitated Pu(IV). The distribution of plutonium between the oxidation states remained relatively constant throughout the remainder of the 14-day period.

These results indicate that colloidal plutonium can be formed under the conditions in the INEL subsurface. Also, because the majority of Pu(IV) was removed fro solution by polymerization or precipitation, Pu(IV) is not expected to be mobile (other than possibly through colloidal transport) and a distribution coefficient is not appropriate for this form of plutonium (p. 49).

They then discussed their measured values for distribution coefficients for Pu in the V and VI oxidation states.

The following observations can be made regarding the magnitudes of the distribution coefficients. First, distribution coefficients were higher in surface soil (collected near the Radioactive Waste Management Area) and interbed material than in basalt. This was expected due to the higher content of clay, iron and manganese minerals in surface soils and interbed material which can sorb and/or reduce plutonium to the least mobile IV state. Second, results are consistent with the belief ... that Pu(VI) complexes most strongly with carbonate, which yields a negatively charged ion. Finally, plutonium K_d values were over an order of magnitude lower in the presence of EDTA. EDTA is a strong chelating agent that forms (negative or neutral) complexes with metals.

An important observation was made regarding the oxidation state of solution phase plutonium in the interbed material batch tests. At the slow suspended solids concentrations, plutonium remained in the initial state (either V or VI). However, at high suspended solids concentrations, transformation from V to IV and from VI to V and IV was observed. This was likely due to reduction mediated by iron and/or manganese minerals. Since actual solid to liquid ratios in the subsurface are much higher than those in batch tests, it is likely that plutonium will be in reduced forms in the field, i.e. IV and V. Plutonium (IV)...does not stay in solution but tends to form polymers or precipitates, and to stick to surfaces. In this form it is highly immobile unless colloidal forms are transported (pp. 51-51).

Newman et al. (1995) drew the following conclusions from their study.

Equilibrium distribution coefficients were determined for Am, Cs, Co, Sr, U, Pu(V) and Pu(VI) with interbed and crushed basalt materials collected from the INEL....The values obtained ...did not vary greatly from values reported in the literature for, similar though not identical, conditions....

However, a fraction of the ^{241}Am (9-13%), ^{60}Co (3%) and ^{239}Pu (10-55%) applied to crushed basalt packed columns was transported at a much faster rate than the bulk of these three radionuclides. The enhanced mobility fractions of ^{241}Am , ^{60}Co , and ^{239}Pu were observed to a lesser degree (~1%) in interbed material packed columns....This enhanced mobility may alter predicted arrival times and peak concentration of these three radionuclides downgradient from their source. Thus enhanced mobility may change risk calculations....

Equilibration of plutonium with synthetic groundwater indicated that within 24 hours the majority remaining in solution was Pu(V). Also within this time frame the total plutonium activity in the solution phase decreased to 60 to 70% of the initial value. This was due primarily to a decline in Pu(IV) and was attributed to settling of polymerized or precipitated Pu(IV). Because the majority of Pu(IV) was removed from solution by polymerization or precipitation, it is not expected to be mobile (other than possibly through colloidal transport) and a distribution coefficient is not appropriate for this form of plutonium. Finally, in batch studies using high interbed material suspended solids concentrations, Pu(V) was reduced to Pu(IV), and Pu(VI) was reduced to Pu(V) and Pu(IV). This reduction

indicates that at the high suspended solids concentrations found in the field, plutonium may be present in its reduced and less mobile forms (again, with the possible exception of colloidal transport).

Batch studies indicated that the buffering capacity of both interbed and crushed basalt materials from the INEL are sufficiently high to make significant variations in subsurface pH at distances more than a few meters from perturbations (waste sources) unlikely. Therefore, pH variations are not expected to be a significant factor in predicting subsurface transport. However, ionic strength and specific ion effects on the sorption of cesium and uranium were observed. Specifically, increasing K^+ concentrations were shown to reduce sorption of cesium to both crushed basalt and interbed materials. Increasing Ca^{2+} concentrations were observed to decrease uranium sorption to basalt surfaces, while increasing sorption to interbed surfaces. Increasing K^+ concentrations decreased uranium sorption to interbed surfaces. The effects of K^+ and Ca^{2+} on the sorption of uranium to interbed materials may result from the effects of these two cations on the surface charge and structure of expandable clays.

Sorption rate constants were determined for Cs, Co, Sr, and U. Comparisons of the estimated times required to reach equilibrium with basalt (61 to 329 hr.), ...to the average flow velocity estimated ... from the large-Scale Aquifer Pumping and Infiltration Test (5 m/day), indicates that these elements might not be in equilibrium with basalt surfaces under large-scale pumping and infiltration test (LPIT) conditions. The times required to reach equilibrium estimated for interbed materials were considerably shorter (4 to 219 hr.). The faster sorption rates for interbed materials coupled with the much slower average flow velocities observed for sedimentary interbeds indicate that the assumption of equilibrium may be valid for sedimentary interbeds....

Tests to evaluate the validity of using distribution coefficients measured under saturated conditions for estimating retardation under unsaturated conditions ... indicated that distribution coefficients measured under saturated conditions may be used ... to estimate retardation under unsaturated conditions. The results from both of these tests indicate that laboratory determined distribution coefficients may be applicable under field subsurface conditions.

Experiments were conducting using intact basalt cores as well as crushed basalt packed columns. Results indicated that contaminant transport in intact basalt cores, and possibly in fractured basalt, did not follow traditional patterns assumed by advective-dispersive flow models and may be dominated by preferred flow paths and diffusion into and out of the basalt matrix rather than by sorption reactions. These last results indicate the complexity of field conditions and emphasize the need for caution in data interpretation and application (pp. 78-80).

6.2.2 Landa et al., 2000

Distribution coefficients and their use in transport calculations for actinides at the RWMC have been recently been reviewed (Landa et al. 2000). The following is excerpted from their introductory section (Section 5.1).

The transport and fate of waste constituents in geologic material is dependent on chemical and physical processes that govern the partition of constituents between the solid, stationary phase and an aqueous, mobile phase. This partition often is quantified by an empirically determined parameter called the distribution coefficient (K_d). Many transport models for radionuclides use K_d s to predict the extent to which the migration of the constituent will be lessened relative to the mean ground-water velocity. Although K_d s are widely used, their application implicitly assumes that all factors affecting K_d s are constant. However, these factors, which include pH, the concentration of complexing ligands, the concentration of competing adsorbates, and the availability any types of adsorption sites, generally are not constant in field environments such as the INEEL. Therefore, K_d s may not adequately describe the transport and fate of waste constituents in some environments.

The following is excerpted from their summary section (Section 5.7):

- The distribution coefficient is a measure of the amount of a solute sorbed from solution by a solid phase
- Advantages of the K_d approach are its mathematical simplicity and ease of obtaining experimental values.
- A limitation of the K_d approach is that a measured K_d is a unique function of the aqueous and solid phase compositions.
- Sorption is affected by:
 - Mineralogy
 - Competition between solutes for sorption sites
 - Formation of aqueous complexes, hence concentrations of ligands
 - pH-dependent aqueous speciation and surface charge
 - Solution ionic strength
 - Concentration (non linear sorption will yield concentration dependent K_d values).
- The K_d approach may adequately describe contaminant migration and reversible sorption in ground water systems in which the aquifer regions occupied by the contaminant plume and by the background water each have uniform mineralogical and chemical compositions, which remain uniform through the time scale of interest. In general, the reactive sorption of the contaminant of interest must also be adequately described by the local equilibrium assumption.
- The K_d approach will generally not properly describe contaminant migration in ground-water systems undergoing dynamic chemical evolution.

They identified nine “specific concerns regarding the K_d s recommended for use in the risk assessment model”, and summarized as follows.

There is not enough data from WAG7 to quantify all of the uncertainty associated with the K_{ds} for Am, Np, Pu, and U used in the Interim Risk Assessment (IRA) model. The data...show that sorption of Am, Np, Pu, and U generally varies as a function of pH, carbonate concentration, and sorption site type and concentration. For 11 different waters from the INEEL, thermodynamic modeling indicates that sorption of Am can vary by 400%, Np by 25%, Pu by 55%, and U by 3000%. For a constant water composition, the K_{ds} selected for the IRA model could vary by as much as 1500% for the range in concentration of surface sites measured in interbed sediments and fracture fill collected from the INEEL. In conclusion, the experimental conditions used to measure K_{ds} for the IRA model do not adequately represent the aqueous and solid phase variability at WAG 7.

6.2.3 Liszewski et al., 1997

Liszewski et al. (1997) describe a study performed by the USGS and ISU in which the distribution coefficient (K_d) for strontium was measured in surficial sediment samples collected from various locations at the INEEL. They reported that K_d values for strontium ranged from 36 ± 1 to 275 ± 6 ml/g (p. 13). They noted "in general, K_d 's were larger from samples collected near the RWMC (204 ± 6 to 275 ± 6 ml/g) and lowest from samples near the TRA (66 ± 3 to 94 ± 2 ml/g). One exception was sample BC-11 at the north end of the site, which had a K_d of 36 ± 1 ml/g. K_d 's for samples collected near the ICPP and TAN facilities ranged from 61 ± 3 to 134 ± 4 ml/g and 118 ± 3 to 203 ± 5 ml/g, respectively. K_d 's from samples collected remote from facilities ranged from 36 ± 1 to 209 ± 5 ml/g" (p. 13).

They observed that both sediment and solution properties can affect K_d values, as follows (p. 13).

These results indicate that significant variability exists in strontium K_d 's of surficial sediment at the INEL. Some of this variability can be attributed to physical and chemical properties of the sediment itself; however, the remainder of the variability may be due to compositional changes in the equilibrated solutions after being mixed with the sediment...The extent to which variability in strontium K_d 's can be explained by differing properties of either the sediment or solution is as yet unquantified and is the subject of future study.

They describe the importance of sorption on transport (p 13).

The variability in strontium K_d 's ... has important implications relative to the transport of strontium beneath waste disposal ponds at the INEL. Sediment beneath waste disposal ponds having large K_d 's, such as that near the RWMC, can be expected to effectively lessen strontium movement relative to sediment having small K_d 's, such as that near the TRA, other factors that affect transport being equal.

They also recognize that the concentration of the sorbed species is important (p.13). "The results of this study should be used with caution when applied to radioactive strontium, which normally is present at concentrations far less than the concentration of stable strontium used in this study."

Although they provide this caution, they do not point out that isotherms typically are concave downward, and therefore the ratio of sorbed to dissolved concentrations is larger at lower dissolved concentrations.

6.2.4 Liszewski et al 2000

Liszewski et al. (2000) report further investigation of the samples evaluated in Liszewski et al. (1997). In this study, they examined the correlation between strontium K_d values and properties of the solution and solid phases. Their findings and interpretations are illustrated in the following excerpts:

The Branaur-Emmett-Teller (BET) method surface area of the sediment samples...had a correlation coefficient of 0.7022...indicating a strong correlation with strontium K_d s. To explain this relation, it is necessary to recognize that sorption is a surface-limited phenomenon and, therefore, is controlled largely by the available surface area. The fact that the strontium K_d s correlated more strongly with surface area than with any other property indicates that strontium K_d s are more dependent on bulk surface area than on the character or composition of the sediment samples. Other researchers have identified this relationship for strontium and other cationic species....This independence from the composition of the sediment samples indicates that chemisorption may play a primary role in the strontium sorption process (p. 420).

None of the mineralogical phases correlated strongly with strontium K_d s; however, the mineralogical phase with the strongest correlation with strontium K_d s was weight percent of total clay minerals (0.3748)....One possible explanation for the observed correlation between total clay minerals and strontium K_d s is size and shape of the grains....Sediment samples with high percentages of total clay minerals have higher total surface areas and K_d s than sediment samples with small amounts of clay minerals. The correlation coefficient for total clay minerals and surface area was 0.4623...which suggests a moderate correlation between the two properties (p. 420).

A second possible explanation for the correlation between total clay minerals and strontium K_d s is cation exchange. Soil clays often are colloidal, and have a predominantly negative charge. This negative charge has the ability to retain cations from an aqueous solution ...therefore, when a clay mineral is placed in contact with an aqueous solution, the negative charge of the mineral can be partially neutralized. In this experiment, it is possible that the clay minerals retained some strontium from the synthetic aqueous solutions. This retention may have increased the amount of strontium sorbed by the sediment and, therefore, increased the strontium K_d s. The number of cations that are retained on the surface of the clay mineral is dependent on the surface area and charge of the clay colloid. This relation is consistent with the surface area of the sediment sample being a primary control of strontium K_d s" (p. 420).

The strong negative correlation between strontium K_d s and the size fraction greater than 4.75 mm is consistent with the correlation of strontium K_d s with surface area identified previously. The sediment samples with high percentages of large size fractions had small surface areas per unit mass and, therefore, have correspondingly small K_d s. This again suggests that the specific identity or composition of the sediment is not as important as the actual surface is to the sorption process. This relation suggests that a positive correlation should exist between strontium distribution coefficients and small-diameter size fractions. The moderate positive correlations determined for the two smallest diameter size fractions supports this theory (p. 421).

The sediment samples were analyzed for the following elements: silicon, titanium, aluminum, iron, manganese, magnesium, calcium, sodium, potassium, strontium, and barium....All elements are reported as oxides except strontium and barium....MnO correlated strongly with strontium K_{ds} ... TiO_2 , Al_2O_3 , Fe_2O_3 , and MgO correlated moderately with strontium K_{ds}There were strong correlations among TiO_2 , Al_2O_3 , Fe_2O_3 , and MgO ... except for the correlation between Al_2O_3 and MnO ..., which indicates that these four oxides are associated. the four oxides also have moderate to strong correlation coefficients with surface area....One possible explanation for these correlations is that the oxides TiO_2 , Al_2O_3 , Fe_2O_3 , and MgO are predominant in total clay minerals. A high percentage of TiO_2 , Al_2O_3 , Fe_2O_3 , and MgO in a sample, therefore, is a characteristic interrelated to weight percent of total clay minerals. The moderate correlation of these four oxides with total clay mineral ... supports this explanation....the presence of surface oxides on the sediment samples is another possible explanation for correlation of Fe_2O_3 and MnO with strontium K_{ds} . While the presence of surface oxides may be an indication of the magnitude of the surface area of the sediment samples, it may also have the effect of decreasing the cation-exchange capacity of the samples (p. 421).

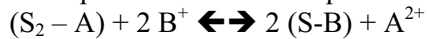
Equilibrium calcium and pH correlations with strontium K_{ds} are important because they are two correlations that indicate the effect of the solution composition on strontium K_{ds} . These effects are expected because the number of available surface binding sites is influenced largely by the other ions in solution. The negative correlation of calcium with strontium K_{ds} indicates that as equilibrium calcium increase, strontium K_{ds} decrease...The importance of equilibrium-solution concentrations of calcium and magnesium on strontium sorption can be understood by considering the principle of cation exchange. Calcium and magnesium both carry a positive two charge when in ionic form. Although the ionic radius of magnesium ... is smaller than that of either calcium ...or strontium...magnesium may compete for similar sites because of its positive two charge in ionic form....Cations can be retained on the surface of a negatively charged particle. This mechanism may be responsible for calcium's negative correlation with strontium K_{ds} . Many cations in the aqueous solution, including Sr^{2+} , Ca^{2+} , and Mg^{2+} , can be retained on the sedimentary surface. Cation-exchange equilibrium between the divalent cations is established on the sedimentary surface. A simplistic representation of this equilibrium is given by $(S-M_1) + M_2 \rightleftharpoons (S-M_2) + M_1$

where

$(S-M_1)$ = a surface site with ion M_1
 $(S-M_2)$ = a surface site with ion M_2 , and M_1 and M_2 are the free ions in solution.

If M_1 is Ca^{2+} ion, and M_2 is the Sr^{2+} ion, as solution concentration of calcium increase,...the equilibrium will be forced to the left, and therefore, a larger amount of Ca^{2+} will be retained at the surface than Sr^{2+} . So, when the equilibrium solution concentrations of calcium is significantly larger than the equilibrium-solution concentration of strontium, more calcium than strontium will be retained on the surface. Larger concentration of equilibrium calcium will, therefore, lead to decreased strontium sorption and subsequently lower strontium K_{ds} , as was observed in this study (pp. 421-423).

The second equilibrium-solution property that correlated with strontium K_{ds} was equilibrium pH. Over the narrow equilibrium pH, the larger the pH, the larger the strontium K_d . This correlation may be due to cation exchange between the divalent cation, Sr^{2+} , and the monovalent cation, H^+ , at the sedimentary surface. A simplistic view of this equilibrium is...



where

(S₂-A) = a surface site with a divalent cation
 (S-B) = a surface site with a monovalent cation
 B⁺ and A²⁺ = the free ions in solution.

As with the calcium-strontium equilibrium, when there is a larger amount of H^+ in solution, the equilibrium is forced to the right, and a larger number of H^+ ions are retained on the surface than Sr^{2+} ions. At larger pH, the amount of H^+ in solution is decreased, leading to a decrease in retention of H^+ at the sedimentary surface, and accordingly, to an increase in the amount of Sr^{2+} retained at the surface. This brings about an increase in strontium sorption, and therefore, larger strontium K_d (pp. 423 – 424).

Excerpts from their summary section are as follows.

While the composition and character of the sediment sample can affect the sorption process, data presented in this report indicates that the most important property that affected strontium sorption was the bulk-surface area. Many of the other sediment properties that correlated with strontium K_{ds} can be explained by their relationship to surface-area (p. 425).

The effects of solution properties on strontium K_{ds} cannot be explained in the same manner. These effects were interpreted as being due primarily to competition among similarly charged and sized cations for sorption sites as part of normal ion-exchange processes by shifting the ion-exchange equilibrium (p. 425)

Multivariate analyses were performed on the five sediment and solution properties that strongly correlated with strontium K_{ds} . The highest r^2 of 0.8071 was obtained using all five properties; however, an r^2 of 0.8043 was obtained using just three properties: equilibrium pH, MnO, and BET surface area. This suggests that strontium K_{ds} may be predicted using as few as three sediment and solution properties (p. 425).

In conclusion, the lack of correlation between any one factor and the experimentally determined K_d values indicates that the strontium sorption process is a multifaceted phenomenon (p. 425).

6.2.5 Pace et al 2001

Pace et al. (2001) performed a multiple regression analysis on data generated in a study of strontium sorption by sediment-infill material (sediment collected from vesicles and fractures in basalt core samples). They identified solution and sediment properties that were strongly correlated with measured K_d values for strontium, and developed predictive equations based on these variables. In addition, they summarized the K_d values measured previously on INEEL materials. Excerpts from this study follow.

They cite K_d values for various INEEL media measured by others.

The range of K_{ds} of basalts determined by Colello et al. (1998) and Pace et al. (1999) is relatively narrow when compared with that of K_{ds} of surficial, interbed, and vesicle- and fracture-infill sediments at the INEEL (Liszewski et al. 1997, 1998; Pace et al. 1999). The basalt K_{ds} ranged from 1.3 ± 8.4 to 29.4 ± 1.6 ml/g; the surficial-sediment K_{ds} ranged from 26 ± 1 to 275 ± 3 ml/g, the interbed sediments K_{ds} ranged from 38 ± 7 to 32841 ml/g; and infill-material K_{ds} ranged from 201.58 ± 10.79 to 356.16 ± 8.43 ml/g. These results suggest that ion exchange was the primary sorption mechanism in the sediment experiments. In contrast, basalts have low strontium sorption and show little evidence of exchangeable ions in the equilibrium solutions. The primary sorption mechanism for basalts, therefore, is thought to be physisorption (pp. 996-997).

They discuss some of the general factors that affect sorption.

The sorption process is a surface phenomena and, therefore, is related to the surface area (SA) of a substance. Substances that have small SA per unit mass, such as basalt, have smaller K_{ds} ; substances that have large SA per unit mass, such as the fine-grained fracture- and vesicle-infill material and clay minerals, which have large K_{ds} . Sorption also is influenced by ion exchange. Materials that have large cation-exchange capacities, such as sediment infill and clays, have large sorption capacities. The K_{ds} of the geological materials ... indicate that most sorption probably occurs in the sediments, and that the finer grained sediments, such as those in fractures and vesicles of basalt, have the largest sorption potential (pp. 994-995.)

Their overall approach was to use statistical methods to identify the variables that were most strongly related to measured K_{ds} , and to generate a predictive equation that could be used to estimate K_{ds} from easily-measured solution and solid phase media property values.

Multiple-linear-regression models were produced to select variables important in predicting strontium K_{ds} (p. 997). The prediction equation for this study was statistically derived from the sediment-infill and standard-material data. The equation derived ... for predicting K_{ds} of sediment-infill and standard-material samples is listed below:

$$SrK_d = 31.887 (SRI) + 1714.116(MNO) - 68.324(KI) + 938.750(FEI) + 372.720$$

where

SRI = is the initial strontium in solution
MNO = is manganese oxide
KI = od initial potassium in solution
FEI = is initial iron in solution.

SRI was determined to be an important variable in the prediction equation because it is the element of interest...Variables that describe the solid material, such as the whole-rock composition or the mineralogy, tended to be selected when SRI was included in the prediction equation. The second variable selected into the prediction equation was MNO, which is part of whole-rock composition data.MNO is important in the prediction equation probably because it represents a wide array of solid-phase characteristics. MNO was present as a trace constituent in all of the tested samples...therefore , it is unlikely than MNO directly affected the sorption process. MNO correlated with several mineralogy

types...specifically the amount of total clays (TC)...The TC correlates well with SA {surface area} ...Liszewski et al. (2000) also showed that SA was an important variable in predicting strontium K_d s. For the data presented here, SSA values represent a surplus of binding sites relative to the small number of ions in the initial solutions...SA may not have been selected in this study as an important prediction variable because of the numerous sorption sites in all samples. The results of normalizing the strontium K_d s to SA indicated that the sorption process involved variables in addition to SA....{and} it was concluded that the sorption process involved additional variables. NO represents the variables SA and mineralogy of the solid sample....MNO is a physical indicator and was not directly involved in the reactions....The variable MNO correlates with a variety of solid-phase characteristics including sample mineralogy and SA....

Initial potassium (KI) was the third variable selected into the prediction equation...Potassium is a univalent cation and would be expected to be less important than divalent cations in predicting strontium K_d s. Divalent cations compete directly with strontium for sorption sites. For univalent cations to compete for sorption sites with strontium, two univalent cations must sorb. Previous studies have shown that potassium, although a stronger competitor ion than the more ubiquitous sodium ion, is a weak competitor ion when compared with various divalent cations...Because of the relative concentrations of univalent and divalent cations in solution, it is possible that the excess potassium competed mechanistically for surface site. Although this is an empirical formula and KI may have been chosen because of non-mechanistic protocols, a more robust model is likely to have selected a mechanistically important variable. That KI was nearly constant in all the batch experiments indicates either that KI represents an important sorption variable, or that the prediction equation had reached the accuracy limits of the experimental data. The initial concentration of iron in solution was the fourth variable selected into the prediction equation. FEI is another nearly constant solution variable, which may suggest that solution chemistry is important in predicting strontium K_d s when working with a specific type of sediment such as sediment infills, clays, and calcite. Iron, like potassium, could have a mechanistic effect on the sorption or it could be a strong empirical indicator (pp. 998-999).

Their summary of this article includes the following.

The variables important in predicting strontium K_d s are the concentration of strontium in the initial solution, the amount of manganese oxide present in the solid phase, and the potassium in solution (p. 1001).

The statistical analysis of batch-experiment results shows that:

1. Strontium initial, manganese oxide, and potassium initial are important variables in predicting strontium K_d s of sediment samples
2. Strontium in the initial solution is important in predicting K_d s because it is the limiting factor in surficial sorption

3. Manganese oxide is important because it represents not only the mineralogy of the sediment, but also the surface area
4. Potassium in the initial solution is the only univalent cation that inversely affects the sorption of strontium
5. Most of the variables selected after the third variable (potassium initial) did not significantly improve the prediction equation (p. 1001).

6.3 Actinide Speciation and Sorption Calculations using Surface Complexation Models

In a review of radionuclide transport processes beneath the RWMC prepared by the USGS, Curtis et al. (2000) (Section 4.3) used the SCM approach to simulate the effect of actinide concentration, pH, and ligand concentration on the mobility of actinides in INEEL groundwater. For the case of uranium, their simulations show that the distribution coefficient (K_D) for UO_2^{2+} has orders of magnitude variation due to changes in uranium concentration, pH, and ligand (e.g., carbonate species) concentrations. This large variation in K_D due to changes in solution chemistry alone is in sharp contrast to the general assumption that K_D values are constants, and certainly calls into question the applicability of the K_D approach for describing sorption of actinides.

Curtis et al. (2000) (Section 4.3.1.3) used the SCM approach, coupled with aqueous speciation modeling, to examine the effect of sorption site concentration, pH, and P_{CO_2} on sorption of U(VI) by several minerals. Their results (Figure 4-4) show that K_r values for U(VI) sorption by ferrihydrite, an iron oxyhydroxides that is common in the INEEL subsurface and potentially a major sorbent, varied over six orders of magnitude ($10^{-2} - 10^4$) throughout the assumed range of conditions, which are not an unreasonable range to be expected in the INEEL subsurface (including both the immediate vicinity of disposed wastes and the minimally affected vadose zone and aquifer). This suggests that retardation factors (see Equation 3-9) could vary over approximately four orders of magnitude ($\sim 10^0 - 10^4$), and again indicates that the use of single-valued K_D values to describe sorption may be inadequate to account for spatial and temporal variations in the geochemical system.

Curtis et al. (2000) (Section 4.3.1) examined the chemistry and speciation of several actinides: Pu, Np, U, and Am. They summarize the thermodynamic data available for these elements, the aqueous complexation with inorganic and organic ligands, the effect of redox conditions on speciation and complexation,

Their discussion of plutonium chemistry and speciation (Section 4.3.1) can be summarized as follows:

- There are many sources of uncertainty in describing and/or predicting the chemical behavior of Pu in groundwater.
- There is uncertainty in the thermodynamic data available for Pu.
- Polymerization and depolymerization of Pu(IV) occurs, but is poorly understood, and the kinetics of these reactions is important.
- Complexation with natural organic matter is poorly understood.
- Complexation with organic ligands “may well dominate” the speciation of trivalent actinides (e.g., Am-III).

- Complexation with inorganic ligands (hydroxide and carbonate species) dominate the speciation of pentavalent and hexavalent forms (Np, U, Pu).
- The presence of organic matter may facilitate actinide reduction.
- The oxidation state of actinide ions strongly determines their chemical interactions.
- In general, trivalent, tetravalent, and hexavalent states are strongly complexed by carbonate, hydroxide, and humic ligands; moderately complexed by sulfate and fluoride; and weakly complexed by chloride. Actinides in the pentavalent state (e.g., Np and Pu) “show considerable aqueous stability even in the absence of complexing anions such as carbonate”, which is interpreted to mean that pentavalent actinides are not strongly complexed by carbonate..
- There are numerous measured K_D values, but these results are generally applicable only to the specific conditions under which the measurements were made and “may consequently be difficult to use in the prediction of radionuclide transport”.
- Many reactions that affect Pu speciation and transport are kinetically limited, and hence the equilibrium approach may not be valid.
- Predicting the transport behavior of Pu is difficult because of the natural complexity and chemical and physical heterogeneity of the ground-water environment. In particular the variability of the redox environment, and the redox sensitivity of Pu, makes accurate transport predictions very difficult.
- Pu exists in multiple oxidation states in most groundwater environments. Pu(III) and Pu(IV) are important under reducing conditions, and Pu(IV), Pu(V) and possibly Pu(VI) under oxidizing conditions.
- The dominant Pu species are expected to be oxide, hydroxide, and carbonate complexes, unless F, P, or SO_4^{2-} concentrations are very high.
- Pu sorption on different minerals varies with pH.
- Pu-carbonate surface complexes are likely to be important, by analogy with U behavior, but data on their occurrence are lacking.

The discussion by Curtis et al. (2000) of neptunium chemistry and speciation (Section 4.3.1.2) can be summarized as follows.

- Np(IV) and Np(V) are the main oxidation states in most groundwaters.
- Under the oxidizing conditions typical of INEEL groundwater, Np(V) would predominate.
- Np sorption is pH dependent, with greatest sorption at ~8 – 8.5.
- Np(V) complexes with carbonate, which reduces sorption.
- Surface complexation data at higher than atmospheric P_{CO_2} values are lacking. By analogy with U, Np-hydroxy-carbonate surface complexes could be important at elevated subsurface P_{CO_2} values.

Their discussion of uranium chemistry and speciation (Section 4.3.1.3) can be summarized as follows:

- U(IV) and U(VI) are the primary oxidation states in the subsurface.
- U(IV) minerals have very low solubility.
- U(VI) is the more mobile oxidation state.
- U(VI) thermodynamic data have been summarized, but there are known lacks, including data on solid phases that are known to exist, and data on organic ligands.
- U(VI) forms multiple hydrolysis species and carbonate complexes. This indicates that both pH and P_{CO_2} affect U(VI) speciation.
- Sorption of U(VI) by various minerals has been studied by several workers.
- Sorption is dependent upon pH and P_{CO_2} .
- Surface complex modeling has been used to describe U(VI) sorption by different minerals.
- Values of K_r determined using surface complexation models differ by many orders of magnitude with reasonable variation in mineral type, pH, P_{CO_2} , ligand concentration, and surface site concentration.

Their discussion of americium chemistry and speciation (Section 4.3.1.4) can be summarized as follows:

- The only important oxidation state of americium in groundwater is Am(III)
- Am(III) species include a suite of hydrolysis products and carbonate species
- Am(III) speciation is dependent upon pH and P_{CO_2}
- Sorption has been studied experimentally and simulated using SCM
- Sorption is dependent upon mineralogy, pH, and P_{CO_2} .

These authors (Curtis et al. 2000) used a geochemical modeling code, PHREEQC, to simulate the aqueous speciation of Np, Pu, Am, and U waters with a range of compositions, which were taken from surface waters and groundwaters at or near the INEEL (Section 4.3.2). Water composition affects speciation due to variations in pH, P_{CO_2} , ionic strength, and concentration of other species, particularly inorganic species that complex the actinides.

The simulation results show the following for plutonium and neptunium.

- Most of the waters were near saturation or slightly supersaturated with calcite, slightly supersaturated with respect to atmospheric P_{O_2} , and have P_{CO_2} values about three times atmospheric.
- Most of the Pu was present as Pu(V), with minor amounts ($\ll 1\%$) present as Pu(IV) and Pu(VI).
- The most common Pu species in all waters were carbonate complexes.
- Np was present at significant concentrations in two oxidation states. In most samples, Np(V) dominated (60-90%) with the balance being Np(VI).

- The most common Np species were NpO_2^+ and carbonate complexes.
- There was so little sulfate, nitrate, fluoride, and phosphate in the waters simulated that complexes with these ligands were insignificant.
- Waters in direct contact with wastes probably have substantially different water chemistry from the natural water chemistry simulated, and may have high concentrations of nitrate, phosphate, organic chelate complexants that may increase the aqueous solubility of Np and Pu.
- The strong aqueous phase complexation of Pu with carbonate impedes its sorption to goethite and surface complexation.
- Np is strongly sorbed to goethite in INEEL groundwater.
- Sorption of Np and Pu is generally proportional to the amount of goethite surface present.
- Uncertainty in the concentration of sorption sites leads to a corresponding uncertainty in the magnitude of retardation factors.
- Pu is more mobile than Np under oxidizing conditions.
- Reducing conditions, such as might occur in the vicinity of disposed wastes or possibly in clayey, organic-carbon rich interbeds, would be expected to significantly limit the mobility of Pu.
- Uncertainties in thermodynamic data for Np and Pu lead to uncertainty in their aqueous speciation and sorption.
- The...speciation results presented...illustrate the significant uncertainties that remain concerning aqueous thermodynamic data for Pu and Np speciation. The uncertainties involved in thermodynamic modeling of Pu and Np sorption, and in any predictions of Np and Pu transport using such thermodynamic models, can be expected to be even greater, because the results depend not only of the aqueous thermodynamic data, but also on even more uncertain sorption data, and on bibulous estimates of the properties of INEEL interbed sediments and basalts. Nevertheless, thermodynamic speciation results can serve the important purpose of illustrating the potential dependencies of sorption processes on aqueous and surface chemical compositions and on mineralogical parameters, and do offer potentially useful estimates of the effects of compositional and mineralogical changes. (Section 4.3.2.2)

Their speciation calculations for uranium show the following (Section 4.3.2.3).

- The amount of sorption of U(VI) depends on the sorbing minerals, the concentration of sorption sites, pH, and P_{CO_2} .
- The predominate U(VI) species in INEEL waters are carbonate complexes.
- Complexes with other inorganic ligands were insignificant due to the low concentrations of these ligands.
- While it may be difficult to extrapolate ...the results suggest that U(VI) may be mobile at the site because of the formation of soluble U(VI) carbonate complexes and that pH and P_{CO_2} , and the nature of the adsorbing site are important in controlling the mobility of U(VI) (Section 4.3.2.3).

Their speciation calculations for americium show the following (Section 4.3.2.4):

- The calculated K_r values depend on the solution composition, sorbing mineral, pH and P_{CO_2} .
- The calculated K_r values vary greatly between water compositions and mineralogy.
- Am(III) is sorbed more than U(VI).
- The SCMs for Am derived from lab studies have considerable uncertainty, and hence these SCMs are of little value in assessing potential mobility. The range in calculated values suggests that there is great uncertainty in the potential mobility of Am.

Their summary of this analysis includes the following (Curtis et al. 2000)(Section 4.3.3):

Speciation can be important in controlling the mobility of actinides below the SDA {Subsurface Disposal Area – ed.}. Critical factors involving speciation that impact actinide mobility include ... the redox state of the actinide...the solution species and ... the surface species...the calculated K_r values for Am can vary by 400%, Np by 25%, Pu by 55%, and U by 3000%. These variations are only due to differences in solution composition.

These authors used K_r instead of the more familiar K_D to describe sorption, where K_r is defined in equation 5-6.

6.4 Segregation of INEEL Contaminants of Concern into Classes with Similar Expected Behavior

6.4.1 Newman et al. 1995

Newman et al. (1995) provide the following summaries of the environmental geochemistry of selected elements. The following section headings follow their organization.

6.4.1.1 Americium

The predicted americium species in solution under oxidizing conditions and alkaline pH are $Am(CO_3)_2^-$, $Am(CO_3)_3^{-3}$, and $AmCO_3^+$The pH of water in the SRPA beneath the INEL has been observed to range from 7.0 to 9.1. Fied et al. (1974) found the distribution coefficient for americium to decrease with increasing Na^+ , Ca^{2+} , Sr^{2+} , La^{+3} , and Zr^{+4} , suggesting exchange as a sorption mechanism. Other researchers have found americium to be associated with colloidal material, and in some instances appeared to be irreversibly sorbed to these colloids....Moulin et al. (1991) and Nash et al. (1988) suggest that sorption on SiO_2 and formation of silicate pseudo-colloids may be an important mechanism in controlling americium distribution (p. 3).

6.4.1.2 Cesium

In natural waters, cesium in solution exists primarily as the monovalent cation Cs^+ with little tendency to form complexes. The solubility of most cesium compounds in aqueous solutions is quite high. The mechanism of cesium sorption is believed to be ion exchange, and other monovalent ions such as K^+ , Na^+ , and NH_4^+ compete with Cs^+ for available sites.

6.4.1.3 Cobalt

Two oxidation states have been observed for cobalt in nature, Co(II) and Co(III), where Co(II) predominates in most natural waters. In soil/water systems, sorption of ^{60}Co has been shown to increase with increases in pH between pH 6 and 9...Additionally, the solubility of cobalt decreases with increasing pH primarily due to the precipitation of $\text{Co}(\text{OH})_2$ ($K_{sp} = 1.09 \times 10^{-15}$)...The aforementioned increase in ^{60}Co sorption with increasing pH may be explained by the hydrolysis of Co^{+2} and the subsequent formation of cobalt colloids...In sorption studies...found that cobalt was associated with particles from 0.2 to 2 μm in diameter. The cobalt was correlated with organic and/or manganese oxide coatings of clay minerals within this size range...proposed that ^{60}Co was sorbing to iron oxide coatings and that the ^{60}Co sorption mechanism was ion exchange. However, 80% of the sorbed ^{60}Co in his study was “fixed” and was not removed in desorption experiments, thus contradicting the proposed mechanism of ion exchange (p. 4).

6.4.1.4 Plutonium

The aqueous speciation of plutonium is complex in that it may coexist in solution in different oxidation states (III, IV, V, and VI). Since the environmental behavior of plutonium depends on its oxidation state, it is critically important to know the oxidation states(s) of plutonium for determination of its distribution coefficients. In aqueous solutions plutonium exists as the hydrated ions Pu^{3+} , Pu^{4+} , PuO_2^+ , and PuO_2^{2+} . The III and IV states (Pu^{3+} and Pu^{4+}) of plutonium predominate under reducing and low pH conditions, and the V and VI states (PuO_2^+ and PuO_2^{2+}) predominated under oxidizing and alkaline pH conditions (Ames and Rai, 1978). The Pu(IV) oxidation state is insoluble at high pH where it tends to hydrolyze and form polymers. These polymers may be either neutral or positively charged and may remain in solution for significant time periods. Penrose et al. (1990) showed that plutonium exists in solution as predominately uncharged (91-99%) or anionic (2-10%) species in groundwater migrating from the Los Alamos National Laboratory, NM. Furthermore, this research showed plutonium was tightly or irreversibly associated with colloidal material 25 to 450 μm in size.

Carbonate complexation of actinides including plutonium may lead to increased solubility and formation of anionic species (Guillaumont and Adloff 1992; Nash et al. 1988). The transuranics in general tend to form stable neutral and anionic carbonate complexes. The Up(IV) carbonate complexes neither undergo disproportionation nor redox reactions (IAEA, 1991; Sanchez et al. 1985). Pu(V) and Pu(VI) may form carbonate complexes as well (Yamaguchi 1993; Salter et al. 1981a and b) (pp. 4-5).

6.4.1.5 Strontium

The average content of stable strontium in basaltic rock is 465 ppm (Ames and Rai 1978). This concentration is high considering the amount of ^{90}Sr that may come in contact with the basalt from waste sites. Therefore, the resident stable strontium concentration must be considered in regards to the concentration of strontium used in distribution coefficient determinations. Strontium shows little tendency to form colloidal or anionic species (Ames and Rai 1978). The mechanism of strontium sorption is believed to be ion exchange, and Ca^{2+} has been shown to compete for sorption sites with Sr^{+2} (Barney 1982; Salter et al. 1981a and b) as their ionic radii are similar, 1.18 and 1.32 Å, respectively (Huheehy 1983) (p. 5).

6.4.1.6 Uranium

Uranium has three stable oxidation states: IV, V, and VI. The divalent uranyl cation, UO_2^{2+} , is the most stable form of uranium in neutral aerated aqueous solutions (Langmuir 1978; Seaborn and Katz 1957). Under these conditions uranium is believed to form anionic or neutral species (Early et al. 1984; Jensen, 1980; Ames et al., 1981). At alkaline pH's the uranyl ions may become hydrolyzed to form uranyl hydroxides and carbonates. Negative surface charges, such as those found on most subsurface materials, can repel these negatively charged ions and reduce the extent of sorption (p. 5).

7. GEOCHEMICAL CONCEPTUAL MODELS DEVELOPED FOR INDIVIDUAL WASTE AREA GROUPS

Groundwater beneath some of the facilities at INEEL has been contaminated by historical operations, principally waste disposal in the shallow subsurface or via injection into the aquifer. Each facility has been included in a CERCLA WAG, and remedial investigations have been performed for contaminated groundwater in these WAGs. A geochemical conceptual model was generated as part of the remedial investigation for each WAG. These geochemical conceptual models describe the contaminants present in groundwater and in some cases, the geochemical processes that affect the transport and ultimate fate of these contaminants. The geochemical conceptual models have been further developed at WAGs where extensive groundwater remediation has been performed. This section summarizes the geochemical conceptual models developed for the INEEL subregion and for each WAG at which contaminants have been introduced into groundwater. The following facilities / WAGs are excluded from this discussion because historical activities there did not cause significant groundwater contamination: WAG 4 Central Facilities Area (CFA), WAG 5 Power Burst Facility/Auxiliary Reactor Area (PBF/ARA), and WAG 6 Boiling Water Reactor Experiment (BORAX).

7.1 Subregional Geochemistry

The chemical nature of water in the SRPA is in part dependent on chemical interactions with the basalts and sediments in the aquifer. Olmsted (1962) characterized groundwater at the INEEL into several chemical compositions. The first, derived from mountainous carbonate drainages to the west, is enriched in calcium, magnesium, and bicarbonate and occurs over much of the western part of the INEEL (Busenberg et al. 2001). The second, derived from the area northeast of the INEEL, is characterized by increased occurrence of rhyolitic and andesitic rocks and is enriched in calcium, magnesium, and bicarbonate, but with a larger equivalent fraction of sodium, potassium, fluoride, silica, and chloride. This water composition is typical of much of the eastern part of the INEEL. A third composition, characterized by increased concentrations of nitrate and chloride and decreased concentrations of bicarbonate, is derived from recharge of irrigation water and wastewater at the INEEL (Orr et al. 2003).

7.1.1 Contaminant Distribution

Geochemical data can be used to provide an understanding about the transport of contaminants. The distribution of small concentrations of selected contaminants at the subregional scale is dependent on the capability of those contaminants to persist in the flow system. The ion exchange and sorption capacity of geologic materials affects the persistence of dissolved constituents in groundwater moving through those materials. Those contaminants that are more reactive to the processes of sorption and ion exchange are less likely to be detected at any distance from the source. Contaminants moving within basalt will be less likely to be affected by ion exchange because the ion-exchange capacity of basalt is relatively small (Nace et al. 1975). However, the presence of clays enhances ion exchange. Montmorillonite, the most abundant clay mineral associated with the rocks of the Eastern Snake River Plain at the INEEL, is one of the more efficient ion-exchange minerals (Nace et al. 1975). Tritium, because it composes part of the water molecule, is nonreactive and provides a measure of advective flow. Detectable concentrations over a large area of the INEEL are attributed to the conservative nature of this radionuclide and to the quantities disposed to the subsurface since 1952. Much smaller quantities of chlorine-36 and iodine-129 were disposed to the aquifer. These relatively conservative contaminants persist and are detectable at very small concentrations in groundwater. INEEL researchers believe that contaminant transport is dependent on contaminant source strength, release rates, and processes of sorption and decay (Orr et al. 2003).

7.2 Test Area North

Groundwater at TAN is enriched in calcium and bicarbonate. The chemical composition of groundwater at TAN reflects the clastic and carbonate rocks of source areas to the north and northwest (Kaminsky et al. 1994).

7.2.1 TSF-05 Injection Well

The primary source of contamination is the TSF-05 injection well (Kaminsky et al. 1994). The release mechanism is simply injection of contaminants directly into the aquifer, along with long-term dissolution of nonaqueous contaminants and sorption/desorption of radionuclides. Advective flow is the predominant contaminant transport mechanism. The release is complicated by the presence of injected sludge, which appears to trap even aqueous contaminants such as tritium for long periods of time (Sorenson et al. 1996; Sorenson 2000); therefore, the sludge acts as an ongoing, secondary source of contamination sustaining the radiological and organic plumes. Sorenson et al. (1996) also implicated the TSF-07 disposal pond for some radionuclide contamination reaching the aquifer because downward migration of water pumped to the pond through the vadose zone and a perched water body have allowed contaminants to reach groundwater.

7.2.1.1 Radionuclides

The radionuclides present at TAN are limited to tritium because sorption has severely limited the transport of all other radionuclides (Sr-90, Cs-137, and U-234). Tritium does not sorb at all and has the shortest half-life of these radionuclides, but it is present only in concentrations below the drinking water standard. Because of this, tritium makes a good conservative tracer for groundwater movement when its radioactive decay is taken into account. Sr-90 is intermediate between H-3 and the long-lived radionuclides in terms of sorption. In the case of Sr-90, another mechanism that may affect transport is substitution into the crystal structure of calcite. While this mechanism has not been studied extensively at TAN, an ongoing research project at the INEEL, funded by the Environmental Management Science Program, is looking to induct the process as a potential remediation strategy for Sr-90. During enhanced ISB in the residual source area at TAN, it was noted that Sr-90 increased significantly in wells near TSF-05 along with calcium and magnesium, but that all of these cations quickly returned to baseline levels based on downgradient monitoring well data (Sorenson et al. 2000a). The significance of this mechanism is not currently well understood. Radionuclides, including Cs-137, U-234, and a few other very low concentration radionuclides present at TAN, appear to sorb very strongly to the basalt and perhaps to the sludge around TSF-05. The only well in which these radionuclides have been detected in groundwater above drinking water standards is TSF-05 (Sorenson et al. 1996). Because the distribution of long-lived radionuclides is so limited at TAN, and because the risk driver for TAN is TCE, no effort has been made to determine actual sorption coefficients.

7.2.1.2 Organic Plume

The organic plume consists of volatile organic compound (VOC) contaminants. In the source area of TSF-05, anaerobic biodegradation is an important process impacting the fate of VOCs, but the downgradient part of the aquifer is quite aerobic. TCE degradation appears to be occurring even in the aerobic aquifer and has been attributed to a cometabolic process, but further work is needed to demonstrate the occurrence of the process directly. Sorption is not believed to be significant for these compounds based on experiments with TCE and basalt (Ingram et al. 1998). Prior to the start of remediation activities, it was found that the organic material in the sludge had stimulated a process known as reductive dechlorination within about 250 ft of TSF-05 (Sorenson et al. 2000a). This process allows chlorinated ethenes to be sequentially dechlorinated to ethene when the process goes to completion

(Freedman and Gossett 1989); however, it was only observed to proceed as far as dichloroethene in the field. Based on the success of laboratory studies, a field evaluation to further stimulate this process was conducted and successful transformation of TCE to ethene was achieved in the field. This process has now been incorporated into the long-term remediation of the site (DOE-ID 2001).

Biological degradation, however, impacts these contaminants significantly. Downgradient of the residual source area, insufficient carbon was present to drive reductive dechlorination and the system is quite oxygenated. In spite of this, it was found that concentrations of TCE were decreasing relative to those of PCE and tritium in the plume (Sorenson et al. 2000b). This rate of decrease was quantified as a pseudo-first order process yielding a half-life for TCE between 9 and 22 years, depending on the assumptions used. It was hypothesized that aerobic cometabolism of TCE is occurring in the plume in spite of the oligotrophic conditions of the aquifer. Several factors were identified that corroborate this hypothesis, including laboratory studies demonstrating that bacteria capable of the process are present in the plume, the dissolved oxygen distribution, and the relative behavior of TCE and PCE (DOE-ID 2000). Based on these findings, MNA was incorporated into the long-term remediation strategy for the dissolved contaminant plume (DOE-ID 2001).

7.2.2 TSF-07 Disposal Pond

Selected trace elements were present in concentrations exceeding EPA drinking water standards in two wells completed in the perched water-bodies in sediments below the TSF-07 Disposal Pond. Activity ranges for gross alpha, gross beta, and strontium-90 are shown in Table 8-1. It is believed that metals and radionuclides present in perched water generally are being attenuated through adsorption and cation-exchange in pond bottom sediments and in the vadose zone and do not pose a threat to the SRPA (Orr et al. 2003).

7.3 Test Reactor Area

Sources of contamination at TRA included direct injection into the aquifer at TRA-05 and USGS-53 injection wells and discharges to the TRA Warm Waste Pond. Discharges to the Warm Waste Pond caused contamination of sediments; therefore, infiltration of water through the pond caused the migration of contaminants to the TRA Perched Water bodies and ultimately the SRPA.

7.3.1 Groundwater Geochemistry

The composition of the groundwater beneath TRA is a result of the natural geochemical interactions between the aquifer matrix and the additions of chemically dissimilar disposal waters. Groundwater at TRA has been classified as calcium-bicarbonate type, which is indicative of recharge from the clastic and carbonate sedimentary rocks to the north and northwest (Robertson et al. 1974). Mechanisms that control transport in the aquifer include radioactive decay, sorption, groundwater dispersivity, effective porosity, and the velocity of flow (Orr et al. 2003).

7.3.2 Vadose Zone

Mechanisms considered to be important for the transport of contaminants in the vadose zone at TRA include radioactive decay, sorption, rate of infiltration from different sources of recharge, and effective porosity.

7.3.3 Perched Water

Water located in the deep perched water zone at TRA is groundwater that has been pumped from the aquifer, used for various purposes, then discharged to ponds on the surface. Based on a comparison of perched water composition to groundwater composition, the most significant component added to perched water is sulfate, which is likely derived from sulfuric acid used to regenerate ion exchange columns. The pH of water in the perched water zone is about 8, so any acid disposed is neutralized (Hull 1989).

Although large quantities of sodium hydroxide and sodium chloride were added to the wastewater at TRA, there is not a significant change in the relative cation composition of the perched groundwater or in the chloride content of the water. The maximum increase in the percent of sodium in the perched groundwater is 10%. The buffering of groundwater composition relative to waste stream water composition may reflect a significant reservoir of calcium and magnesium in surficial sediments for ion exchange with sodium and hydrogen ions from the wastewater (Hull 1989).

7.3.3.1 Hexavalent Chromium

Chromium strongly adsorbs to surficial sediments in the warm-waste pond bottoms (Orr et al. 2003). Therefore, the hexavalent chromium discharged to the Warm Waste Ponds at TRA, could have been reduced, particularly by organic matter in the pond sediments, removed from the infiltrating water, and deposited on sediments surfaces by ion exchange or precipitation. Hexavalent chromium can be reduced to the trivalent state in the presence of reduced iron and sulfur species or by readily oxidizable organic matter. Trivalent chromium will oxidize slowly in the presence of oxygen or manganese dioxide, which is a common constituent of INEEL soils (Hull 1989).

Movement hexavalent chromium discharged to the Warm Waste Pond probably passed directly to the aquifer during the first short period of operations. As algae grew in the pond, died, and built up a mat of organic matter on the bottom of the pond, hexavalent chromium would react with the organic matter and reduce chromium to the trivalent state. Once in the trivalent form, chromium would be precipitated, sorbed, or exchanged on solid surfaces and removed from solution. Therefore, most of the chromium discharged to the pond is still in pond sediments in the trivalent state. Hexavalent chromium that passed through the pond remained in the hexavalent state and moved with the water as an anion (Hull 1989).

7.3.3.2 Tritium

Factors affecting the distribution of H-3 in perched water at TRA include proximity to radioactive waste disposal ponds, depth of water below the ponds, variable tritium disposal rates, radioactive decay of tritium, and dilution effects of the CP and Big Lost River recharge.

7.3.3.3 Absence of Other Radionuclides

Selected radionuclides strongly adsorb to surficial sediments in the warm-waste pond bottoms (Orr et al. 2003). The absence of an Sr-90 plume in the SRPA at TRA can be attributed to the fact that Sr-90 was only discharged at the surface in disposal ponds and was sorbed onto sediments in the vadose zone. Reduced disposal rates and the sorption of Cs-137 to soil particles are the most probable causes of the general lack of detections of Cs-137 in perched water at the TRA. The absence of Cr-51 in the perched water at TRA is most likely due to the decreased disposal rates and the relatively short half-life of Cr-51 (27.7 days) (Bartholomay et al. 2000). The limited presence of Co-60 in the perched water at the TRA is most likely due to proximity to the former leaking Retention Basin and the presence of a large amount of suspended sediment in the water samples collected (Bartholomay and Tucker 2000).

7.4 Idaho Nuclear Technology and Engineering Center

7.4.1 Groundwater

Water from the SRPA in the southern half of the INEEL typically is enriched in calcium, magnesium, and bicarbonate (Knobel et al. 1997). Aquifer water underlying INTEC is similar in composition. The background concentrations of sodium, chloride, sulfate, and nitrate are 10, 15, 10 to 40, and 5 mg/L, respectively (Robertson et al. 1974). Wastewater disposed to the injection well and percolation ponds has increased the concentrations of these and other ions in groundwater downgradient from INTEC (Bartholomay et al. 2000), but the source term input estimates of available process water and contaminant mass are uncertain. Estimates also are uncertain of those physical properties that have a primary influence on flow and contaminant transport domain.

Mechanisms that control transport in the aquifer include radioactive decay, sorption, groundwater dispersivity, effective porosity, and the velocity of flow (Orr et al. 2003). Effective porosity estimates have been made from inverse modeling of contaminant distributions (tritium and iodine-129). These estimates are dependent on the assumed thickness of the aquifer and vertical mixing of the contaminant throughout the aquifer thickness.

7.4.2 Vadose Zone

Perched groundwater bodies have formed in response to wastewater disposal at INTEC. Wastewater originates from the SRPA, but chemical processes at INTEC modify the water chemistry. The chemistry of water in perched groundwater bodies is chemically different depending on the location and source (DOE-ID 2000b). Water-level and water-chemistry data indicate that upper perched groundwater zones beneath the north and south parts of INTEC are separated and chemically different. The actual extent of these perched water bodies is not well defined and the connections between the perched water bodies are not well understood (Orr et al. 2003).

Mechanisms considered to be important for the transport of contaminants in the vadose zone at INTEC include radioactive decay, sorption, rate of infiltration from different sources of recharge, and effective porosity (Orr et al. 2003). Transport of contaminants from spills that were contained in surficial sediments is facilitated by water for release to the deeper subsurface from those soils. Water may originate from landscape irrigation, piping losses, and shallow infiltration from percolation ponds (DOE-ID 1997a). The dye tracer test presently underway (DOE-ID 2000c) is designed to improve understanding of the distribution and source of water in the vadose zone.

7.5 Radioactive Waste Management Complex

Low concentrations of carbon tetrachloride, nitrates and C-14 are affecting the aquifer near the SDA. Carbon tetrachloride has been identified slightly above the MCL and nitrate levels in the southeast corner of the SDA are steadily increasing. Low concentrations of C-14 also have been detected in the region.

Several contaminants have been detected at low concentrations in the vadose zone and may be migrating. The most frequently detected contaminants include nitrates, carbon tetrachloride, C-14, Tc-99, and uranium isotopes. In addition, Am-241, I-129, Pu-238, and Pu-239/240 have been detected sporadically at concentrations near the detection limits (Holdren et al. 2002).

7.5.1 Vadose Zone

Geochemistry, as it affects movement of contaminants through the vadose zone and aquifer, has been modeled primarily using distribution coefficients applied to the sedimentary structures. Because flow through the basalts is considered to occur through the fracture network, relatively little reaction is expected between dissolved contaminants and the basalt matrix. Some evidence exists of sedimentary infilling and precipitated minerals inside of the basalt fractures, which could retard contaminant movement. A conceptual approach to model this interaction was presented in Magnuson and Sondrup (1998), but was discontinued in the most recent model because the relatively limited fracture surface area resulted in negligible sorption (Orr et al. 2003).

A key parameter for estimating future fate and transport of contaminants is chemistry of the infiltrating water and subsequent leaching of contaminants from the waste. In the surficial soils, precipitation can be altered by soil minerals and in some cases by the presence of the waste itself. Groundwater geochemistry has been investigated repeatedly, as reported in Olmstead (1962); Robertson et al. (1974); Rightmire and Lewis (1987); Rawson and Hubbell (1989); Rawson et al. (1991); Cleveland and Mullin (1993); Knobel et al. (1997); and Hull and Pace (2000).

In the RWMC area, hydrogen potential is about 8 ± 0.5 , buffered by calcite-water-CO₂ interactions. Caliche, an impermeable, concrete-like soil naturally cemented by calcite, is common in the area. The oxidation-reduction potential is oxidizing and equivalent to air. The soil moisture is saturated with respect to calcite and super-saturated with dolomite (Wood and Norell 1996).

As described previously, a network of lysimeters was installed in the SDA to monitor water chemistry near the waste zone. As identified by Hull and Pace (2000), however, certain lysimeter results were apparently affected by a magnesium chloride solution that was used as a dust suppressant on roads; additionally, bromide tracer installed with some lysimeters may have also contaminated some samples. After eliminating suspect samples, Hull and Pace (2000) compiled water chemistry results from 90 samples taken from 13 lysimeters in the SDA. They found little variation with time, but significant spatial variability with no apparent correlation to specific areas within the SDA. The most “representative” water chemistry for the SDA is defined in Hull and Pace (2000). Oxidized conditions persisted with dissolved oxygen in the range of 4.8 to 7.8 mg/L. Soil zone CO₂ levels are very high (up to 10%) in the SDA waste area. The pH of soil moisture is found to be only slightly alkaline (ranging from 7.2 to 8.2), possibly due to high concentrations of CO₂ in soil gas resulting from organic decomposition of waste materials. Pore water is saturated with respect to calcite (Orr et al. 2003).

7.5.2 Perched and SRPA Water

As summarized by the USGS (1999), perched water samples have been shown to be oversaturated with zeolite and clay minerals. Perched water has been described as either sodium chloride or sodium bicarbonate (Rawson and Hubbell 1989). Perched water chemistry for the RWMC has also been presented in Barraclough et al. (1976); Rightmire and Lewis (1987); Knobel et al. (1992); Knobel et al. (1997); Rawson et al. (1991); Tucker and Orr (1998); Bartholomay (1998); and Rawson et al. (1991).

The SRPA water samples from near the RWMC are typically calcium-magnesium bicarbonate in character and supersaturated with respect to aragonite, calcite, and dolomite, and undersaturated with respect to fluorite, sulfate minerals, and silicate minerals (Knobel et al. 1997). Aquifer water chemistry in the RWMC region is also presented in Mann and Knobel (1988), Liszewski and Mann (1993), and Burgess et al. (1994).

Chemical characteristics that affect transport of actinides are summarized by the USGS (1999) as 1) a pH ranging from 7.8 to 8.4; 2) dissolved oxygen concentrations nearly saturated to slightly supersaturated with respect to air; 3) slightly saturated with respect to calcite; and 4) dissolved organic carbon near or below 1 mg/L (Orr et al. 2003).

7.5.3 Conceptual Model

Recent contaminant transport simulations indicate that low levels of contamination will impact the aquifer in the future, but the resulting risk to humans and the environment will be relatively low (Holdren et al. 2002). Although the current conceptual model is generally considered an adequate and conservative tool for assessing risk, uncertainties remain in the representation of the subsurface hydrologic and geochemical systems. Holdren et al. (2002) summarizes, “Contaminants of particular interest for model calibration, such as C-14, uranium, and other actinides, are detected sporadically and at very low concentrations that do not describe migration trends. The low concentrations coupled with lack of trends cannot be emulated with any confidence” (Orr et al. 2003).

The current INEEL conceptual model uses an equilibrium, reversible distribution coefficient to emulate the various geochemical factors affecting retardation of the transport codes. Distribution coefficients (i.e., Kds) are commonly used in computer modeling as a mathematically simple representation of sorption. Kd values encompass all processes that remove a contaminant from solution. They are a bulk term representing the ratio of adsorbed to dissolved concentrations, typically given in units of mL/g. Typically, the value is obtained by fitting a linear isotherm to results of batch or column experiments, neglecting the actual mechanisms responsible for contaminant removal (Dicke 1997). Kds are incorporated into a constant retardation factor in the advection-dispersion equation enabling modelers to simulate a reduction in contaminant concentration as the solution passes through the various vadose zone structures.

Use of distribution coefficients, or Kds, is widely accepted as a defensible method to simplify transport calculations. However, where there exists significant temporal and spatial heterogeneities in the geochemical environment, the use of Kds becomes problematic. For example, Hull (2001) comments that multiple water types have been identified in the RWMC subsurface, indicating that geochemical conditions are not uniform.

There are a number of limitations with using the Kd approach. For example, spatial or temporal variability in chemical conditions and solubility potentials cannot be addressed with singular partition coefficients. Additionally, it is difficult to accurately represent actual field conditions in batch sorption experiments (Hull and Pace 2000). Or as stated by the USGS (1999), the measured Kd values are applicable only to the specific conditions under which the experiments were conducted. Other problems with the use of Kd values include poor design of batch experiments, competition between species for sorption sites, and non-linear response to increasing aqueous concentration. To date, facility-specific simulations have relied on the linear isotherm approach using a limited set of site-specific data. Although the results are generally considered conservative for purposes of risk assessment, a number of investigators have suggested that long-term evaluations be conducted to provide a basis for more representative geochemical modeling.

The literature regarding the use of Kd values is extensive. As a starting point, the reader is referred to the discussions developed by Landa, Glynn, Stollenwerk, and Curtis (USGS 1999). These researchers reviewed the use of Kds at RWMC for four specific contaminants (Am, Np, Pu and U) and concluded that “the experimental conditions used to measure Kds for the IRA model do not adequately represent the aqueous and solid phase variability at {the RWMC}.” The reviewers proposed the use of a surface complexation model, as specific surface-complexation and ion-exchange constants are important

parameters to utilizing K_d measurements. In order to support the simulation work specifically for the RWMC, a comprehensive set of K_d s and solubility limits were compiled in Dicke (1997) for RWMC contaminants. This compilation utilized literature values and results of batch tests on RWMC cores where available. The paucity of site-specific data prompted testing on additional samples in the 1999 timeframe.

7.5.3.1 Geochemical Reactions

In the ABRA conceptual model, all geochemical reactions between dissolved contaminants and the vadose zone matrix are represented by partition coefficients assigned to the sedimentary interbeds. This approach was practical from a computational perspective, and is thought to be conservative from a risk assessment perspective (Holdren et al. 2002). During the earlier IRA modeling work, researchers modeled chemical interactions between contaminants and sedimentary and precipitated mineral coatings lining the basalt fracture surfaces (Magnuson and Sondrup 1998). However, because the relatively small surface area coupled with rapid rate of water through the basalts resulted in negligible sorption, this approach was not carried forward to the ABRA conceptual model.

Surficial and interbed sediment sorption has been modeled using linear reversible isotherms, described by partition coefficients. A set of partition coefficients has been assembled for the RWMC contaminants and sediments using a combination of literature values and site-specific data. Due to the complexity of the geochemical factors affecting the concentration of contaminants in solution, as well as the limited site-specific data, the sorption process is an uncertainty in the current conceptual model. In addition to difficulties obtaining representative sorption data, non-dissolved transport is also a possibility. Transport of contaminants in non-dissolved states (particulate forms) has been investigated in laboratory tests and, by way of sensitivity studies, has been incorporated into the conceptual model (Orr et al. 2003).

To develop sedimentary sorption coefficients for the ABRA, analyses were conducted on approximately 60 interbed core samples to estimate particle size distributions; surface area; exchangeable cations and anions; clay mineralogy; and extractable silica, iron, manganese, and aluminum, and sorption isotherms for uranium and neptunium. Comparison of partition coefficients from the sorption isotherms to the values from Dicke (1997) supported the conclusion that the partition coefficients elected for the uranium and neptunium are physically plausible and conservative because they are on the lower end of the measured partition coefficient distribution. The sorption isotherms measured from the core samples were nonlinear, but for risk assessment purposes, the more conservative linear values were implemented (Holdren et al. 2002).

A key parameter controlling the sorption reactions is the oxidation state of the contaminant of interest. It has been shown that the transport and adsorptive characteristics of contaminants, particularly actinides, are strongly affected by their initial oxidation state and by oxidation/reduction reactions within the vadose zone (Hull and Pace 2000; USGS 1999). Oxidation states and associated potential for organic and inorganic complexation controls, in part, the fraction of contaminant entering and remaining in solution. Speciation of contaminants (i.e., their form as disposed and as altered by waste zone characteristics), as well as redox state of the water, is not well known and thought to be highly variable.

The RWMC contaminants display a wide range of geochemical properties. Chemical interactions with pore water, sediments, and basalt matrices are complex and supported by a small set of empirical data. Solubility calculations on a contaminant-by-contaminant basis indicate that the effect of oxidation/reduction potential and hydrogen potential on the solubility of these contaminants varies. However, for many contaminants (particularly actinides) the ambient SDA conditions, with moderately reduced environment and approximately neutral pH, may minimize solubility (Hull and Pace 2000).

Although dissolved phase transport is generally considered the predominant transport mechanism, transport may be facilitated by movement of suspended particulate forms of contaminants. Experiments have given evidence that actinides elute from interbed sediment columns at a greater rate than those attributable to equilibrium sorption of aqueous species. This enhanced mobility fraction has been attributed to colloidal transport (Fjeld et al. 2000). As summarized by the USGS (1999), colloidal particles originating from mineral fragments, precipitates, and other mechanisms exist in RWMC basalt fractures and groundwater. Their mobility is controlled by the stability of colloids in groundwater, chemical interactions between colloids and matrix surfaces, and other hydrological and physical factors. In the SDA vadose zone, filtration of colloids by interbed sediments is hypothesized as a mechanism of removing colloids from solution. Further evidence for particulate transport facilitated by colloids comes from the detection of actinides in the interbeds (USGS 1999).

A series of sensitivity studies was performed as part of the ABRA to explore the impact of a small fraction of highly mobile, particulate forms of Pu-238 and Pu-239 on groundwater risk. The results of the sensitivity studies appeared to greatly over-predict aquifer concentrations (Holdren et al. 2002).

As discussed previously, geochemical characteristics also vary significantly between and within geologic structures. Use of single, constant retardation coefficients clearly is not representative of the natural system. The question of whether to use an isotherm approach (linear or other) or to use surface complexation theory in a geochemical reactive transport code remains unresolved. A number of investigators have suggested that long-term evaluations be conducted to provide a basis for more representative geochemical modeling. Hull (2001) recommended a course of action to incorporate geochemistry in to INEEL fate and transport models with both short- and long-term research activities. These types of recommendations should be further evaluated as part of the INEEL conceptual model development.

Although Holdren et al. (2002) concludes that upgradient facilities do not influence contaminant concentrations in the aquifer in the SDA vicinity, the assessment is not necessarily definitive. The interpretation of nitrate and chromium concentrations in the aquifer in Section 5.2.4 of the ABRA leaves open the possibility of upgradient influences. In addition, facilitated transport mechanisms are potential contributors, although their contribution is thought to be minor. Also, it is unclear to what extent chromium serves as an indicator of dissolved phase transport through the vadose zone beneath the SDA.

7.6 Naval Reactors Facility

The background chemistry of groundwater at NRF generally is similar to water chemistry elsewhere on the INEEL. Olmsted (1962) noted that groundwater derived from mountainous carbonate drainages to the west is enriched in calcium, magnesium, and bicarbonate (Busenberg et al. 2001). A second water composition, derived from the area northeast of the INEEL, is characterized by increased occurrence of rhyolitic and andesitic rocks and is enriched in calcium, magnesium, and bicarbonate but with a larger equivalent fraction of sodium, potassium, fluoride, silica, and chloride. Minor changes in groundwater chemistry at NRF may be attributed to the temporal changes in flow direction and water source.

7.6.1 Geochemical Transport Mechanisms

Contaminant transport through sediments and basalts at NRF is affected by chemical processes and conditions that occur in the subsurface. These processes and conditions include sorption, pH, colloid filtration, and oxidation/reduction.

Sorption processes affect the persistence of contaminants released to the subsurface at NRF (Westinghouse Electric Corporation 1996). The distribution coefficient (K_d) provides a measure of these processes. Site-specific values of K_d were determined for different constituents and different soil types at NRF. Inorganic constituents included chromium, lead, mercury, and silver. The K_d value for chromium ranged from 0.5 to 4.6, depending on the soil type. The K_d for lead exceeded 388. The K_d for mercury ranged from 110 to 3,049 and the K_d for silver ranged from 78 to 463. Contaminants tend to persist longer with larger K_d values. Radioactive constituents, including cesium-137, are believed to have sorbed to surficial sediments and are not migrating to the aquifer. Activities of radioactive contaminants released to the subsurface at NRF will be reduced with radioactive decay (Westinghouse Electric Corporation 1996). The persistence of these contaminants is affected by the length of the parent half-life.

The pH of water in the vadose zone and SRPA will affect the persistence of a contaminant in those systems. Solubility increases with increased pH. Colloidal particles may form when contaminated solutions react with groundwater or the soil. Colloidal particles, which may contain contaminants, may be filtered out in the surficial loess and other fine-grained sedimentary deposits. A large percentage of inorganic contaminants released to the subsurface at NRF is believed to have been transformed into more insoluble forms through oxidation and reduction reactions in the soil. These contaminants would not migrate to the aquifer but would be retained as oxide, hydroxide, and oxyhydroxide minerals or coatings on minerals.

7.7 Argonne National Laboratory-West

Water from the SRPA at ANL-W is enriched in calcium and bicarbonate (Argonne National Laboratory 2002). Wastewater disposed to ditches, ponds, and pits also is enriched in sodium. Processes of sorption tend to inhibit transport through the vadose zone; these processes are evident in subsequent discussion of contaminant distribution in the subsurface at ANL-W.

8. SUMMARY AND CONCLUSIONS

Variations are observed in the natural chemical character of water in the SRPA within the INEEL subregion. Several geochemical conceptual models have been developed to explain these variations.

The mixing/diagenesis model incorporates mixing of chemically different waters derived from drainage basins tributary to the eastern Snake River Plain and rock/water interactions within the basaltic SRPA. This conceptual model is broadly accepted.

- In this model, most of the solutes in groundwater (as much as 80%) are contained in inflows to the SRPA from tributary basins.
- The remainder of the solutes (20%) is generated from weathering reactions that occur in the aquifer. The major reactions that control solute composition are dissolution and precipitation of minerals in the aquifer framework

An alternative conceptual model has been developed that suggests that mixing of waters from geochemically different tributary basins alone is sufficient to account for variations in water chemistry within the INEEL subregion.

- In the mixing model, observed changes in water chemistry at the INEEL can be explained completely by mixing between Ca-Mg bicarbonate water that is derived from the Birch Creek drainage and water from the Mud Lake area that contains higher proportions of sodium and potassium relative to calcium and magnesium.
- In this model, the observed behavior of sulfate and chloride requires a minor amount of sulfate- and chloride-rich geothermal water.

Variations in solute concentrations also are attributed to anthropogenic addition of solutes within the INEEL subregion.

- Areas hydraulically upgradient to the INEEL are characterized by agricultural activity. In these areas, solutes may be added by the application of fertilizers or by evaporative concentration of existing solutes.
- Variations in chemical character of groundwater also are attributed to waste disposal practices at the INEEL. Disposal of water and solutes to injection wells and to infiltration ponds has resulted in detectable contaminant plumes in the aquifer.

Geochemical processes have been identified that affect the transport of contaminants in groundwater.

- Ion exchange processes control attenuation of most of the radioactive cations. Sorption due to cation exchange slows transport of these solutes through the vadose zone and the SRPA.
- Biodegradation processes affect concentration of specific organic constituents. At TAN, remediation of the TCE plume is utilizing these processes.
- Co-precipitation has been identified as a process that may attenuate strontium.

9. REFERENCES

- Bunde RL, Rosentreter JJ, Liszewski MJ. 1998. Rate of strontium sorption and the effects of variable aqueous concentrations of sodium and potassium on strontium distribution coefficients of a surficial sediment at the Idaho National Engineering Laboratory, Idaho. *Environmental Geology* 34: 135-42
- Bunde RL, Rosentreter JJ, Liszewski MJ, Hemming CH, Welhan J. 1997. Effects of calcium and magnesium on strontium distribution coefficients. *Environmental Geology* 32: 219-29
- Busenberg E, Plummer LN, Bartholomay RC, United States. Dept. of Energy., Geological Survey (U.S.). 2001. *Estimated age and source of the young fraction of ground water at the Idaho National Engineering and Environmental Laboratory*. Idaho Falls, Idaho: U.S. Geological Survey. vii, 144 pp.
- Carkeet C, Rosentreter JJ, Bartholomay RC, Knobel LL. 2001. *Geochemistry of the Big Lost River Drainage Basin, Idaho. Rep. Water Resources Investigations Report 01-4031*, United States Geological Survey, Idaho Falls, Idaho
- Chapelle FH. 1993. *Ground-Water Microbiology & Geochemistry*. New York: John Wiley & Sons, Inc. 424 pp.
- Curtis GP, Glynn PD, Stollenwerk KG, Bartholomay RC. 2000. TASK 2: Radionuclide transport processes. In *Review of the Transport of Selected Radionuclides in the Interim Risk Assessment for the Radioactive Waste Management Complex, Waste Area Group 7 Operable Unit 7-13/14, Idaho National Engineering and Environmental Laboratory, Idaho*, ed. JP Rousseau. Idaho Falls, Idaho: United States Geological Survey
- Drever JI. 1997. *The Geochemistry of Natural Waters, Surface and Groundwater Environments*. Upper Saddle River, NJ: Prentice Hall. 436 pp.
- Fjeld RA, DeVol TA, Goff RW, Blevins MD, Brown DD, et al. 2001. Characterization of the mobilities of selected actinides and fission/activation products in laboratory columns containing subsurface material from the Snake River Plain. *Nuclear Technology* 135: 92-108
- Fujita Y, Ferris EG, Lawson RD, Colwell FS, Smith RW. 2000. Calcium carbonate precipitation by ureolytic subsurface bacteria. *Geomicrobiology Journal* 17: 305-18
- Hull, L.C. 1989. Conceptual model and description of the affected environment for the TRA warm waste pond. EGG-ER-8644.
- Hull L, Pace MN. 2000. *Solubility Calculations for Contaminants of Potential Concern, OU 7-13/14. Rep. INEEL/EXT-2000-00465*, Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho
- Johnson TM, Roback RC, McLing TL, Bullen TD, DePaolo DJ, et al. 2000. Groundwater "fast paths" in the Snake River Plain aquifer: Radiogenic isotope ratios as natural groundwater tracers. *Geology* 28: 871-4.

- Knobel LL, Bartholomay RC, Orr BR, United States. Dept. of Energy., Geological Survey (U.S.). 1997. *Preliminary delineation of natural geochemical reactions, Snake River Plain aquifer system, Idaho National Engineering Laboratory and vicinity, Idaho*. U.S. Geological Survey WRIR-97-4093.
- Landa ER, Glynn PD, Stollenwerk KG, Curtis GP. 2000. TASK 3: Distribution Coefficients (Kds) and Their Application to Transport Analysis. In *Review of the Transport of Selected Radionuclides in the Interim Risk Assessment for the Radioactive Waste Management Complex, Waste Area Group 7 Operable Unit 7-13/14, Idaho National Engineering and Environmental Laboratory, Idaho*, ed. JP Rousseau: United States Geological Survey
- Langmuir D. 1997. *Aqueous Environmental Geochemistry*. Upper Saddle River, New Jersey: Prentice Hall. 600 pp.
- Liszewski MJ, Rosentreter JJ, Miller KE, Bartholomay RC. 2000. Chemical and physical properties affecting strontium distribution coefficients of surficial-sediment samples at the Idaho National Engineering and Environmental Laboratory, Idaho. *Environmental Geology* 39: 411-26
- Liszewski MJ, Rosentreter JJ, Miller KE, Idaho State University., United States. Dept. of Energy., Geological Survey (U.S.). 1997. *Strontium distribution coefficients of the surficial sediment samples from the Idaho National Engineering Laboratory, Idaho*. U.S. Geological Survey Water Resources Investigations Report 97-4044. 33 p.
- Luo SD, Ku TL, Roback R, Murrell M, McLing TL. 2000. In-situ radionuclide transport and preferential groundwater flows at INEEL (Idaho): Decay-series disequilibrium studies. *Geochimica Et Cosmochimica Acta* 64: 867-81
- Mann LJ, Beasley TM, United States. Dept. of Energy., Geological Survey (U.S.). 1994. *Iodine-129 in the Snake River Plain aquifer at and near the Idaho National Engineering Laboratory, Idaho, 1990-91*. U.S. Geological Survey Water Resources Investigations Report 94-4053. 27 p.
- McLing TL. 1994. *The Pre-Anthropogenic Groundwater Evolution at the Idaho National Engineering Laboratory, Idaho*. Master of Science in Geology thesis. Idaho State University, Pocatello, Idaho. 62 pp.
- Newman ME, Porro I, Scott R, Dunnivant FM, Goff RW, et al. 1995. *Evaluation of the Mobility of Am, Cs, Co, Pu, Sr, and U through INEL Basalt and Interbed Materials: Summary Report of the INEL/Clemson University Laboratory Studies. Rep. INEL-95/282*, Idaho National Engineering Laboratory, Idaho Falls, Idaho
- Olmsted FH. 1962. *Chemical and Physical Character of Ground Water in the National Reactor Testing Station, Idaho. Rep. IDO-22043-USGS*, U.W. Department of the Interior, Geological Survey, Idaho Falls, Idaho
- Orr BR, Cecil LD, Knobel LL, United States. Dept. of Energy., Geological Survey (U.S.). 1991. *Background Concentrations of Selected Radionuclides, Organic Compounds, and Chemical Constituents in Ground Water in the Vicinity of the Idaho National Engineering Laboratory*. U.S. Geological Survey Water Resources Investigations Report 91-4015. 52 p.

- Pace MN, Rosentreter JJ, Bartholomay RC. 2001. Determination of variables in the prediction of strontium distribution coefficients for selected sediments. *Environmental Geology* 40: 993-1002
- Peterson LN, Sorenson KS, Starr RS. 2000. Field demonstration report, Test Area North Final Groundwater Remediation, Operable Unit 1-07B. DOE/ID-10718, Revision 0.
- Rawson SA, Walton JC, Baca RG. 1991. Migration of Actinides from a Transuranic Waste-Disposal Site in the Vadose Zone. *Radiochimica Acta* 52-3: 477-86
- Reardon EJ. 1981. Kd's - can they be used to describe reversible ion sorption reactions in contaminant migration? *Ground Water* 19: 279 - 86
- Roback RC, Johnson TM, McLing TL, Murrell MT, Luo SD, Ku TL. 2001. Uranium isotopic evidence for groundwater chemical evolution and flow patterns in the eastern Snake River Plain aquifer, Idaho. *Geological Society of America Bulletin* 113: 1133-41
- Robertson JB, Schoen R, Barraclough JT, Geological Survey (U.S.). Water Resources Division. 1974. *The influence of liquid waste disposal on the geochemistry of water at the National Reactor Testing Station, Idaho, 1952-1970*. Idaho Falls: U. S. Geological Survey Water Resources Division. xii, 231 pp.
- Swanson SA, Rosentreter JJ, Bartholomay RC, Knobel LL. 2002. *Geochemistry of the Little Lost River Drainage Basin, Idaho. Rep. Water Resources Investigation Report 02-4120*, United States Geological Survey, Idaho Falls, Idaho
- Swanson SA, Rosentreter JJ, Bartholomay RC, Knobel LL. 2003. *Geochemistry of the Birch Creek drainage basin, Idaho DRAFT. Rep. DRAFT*, United States Geological Survey, Idaho Falls, Idaho
- Wood WW, Low WH. 1988. *Solute Geochemistry of the Snake River Plain Regional Aquifer System, Idaho and Eastern Oregon. Rep. 1408-D*, United States Geological Survey, Washington D.C.