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Fate and Transport of Selenium and Uranium in the
Upper Arkansas River Valley of
Southwestern Kansas

by

Jill M. Whitmer

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Fate and Transport of Selenium and Uranium in the Upper Arkansas River Valley of Southwestern Kansas

by

Jill M. Whitmer
B.S., Auburn University. 1998

Submitted to the Department of
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ABSTRACT
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The Arkansas River in southwestern Kansas is one of the most saline rivers in the United States. Sulfate is the main contributor to TDS, which averages over 3,000 mg/L. The dissolved constituents, including naturally occurring Se and U, are concentrated in the river in eastern Colorado due to evapotranspiration. Much of the saline water flowing into Kansas seeps into the alluvial aquifer and then the High Plains aquifer due to lowered groundwater levels caused by consumptive pumping. The fate of Se and U in the saline water was examined in the Arkansas River valley in southwest Kansas.

Waters were collected from the river and three multi-level observation well sites along the valley. Eh, pH, DO, and temperature were measured in the ground waters in the field. Major dissolved constituents and Se and U contents were determined in the lab. Se concentrations in Arkansas River water averaged 18 μg/L and ranged from 2.4 μg/L to 20.3 μg/L in the groundwater. U concentrations in the Arkansas River averaged 63 μg/L and ranged from 4.9 μg/L to 41.3 μg/L in the ground water.

Chloride, and to a lesser extent sulfate, behave conservatively in the river corridor. Se and U concentrations were compared to these conservative species and used in geochemical models to evaluate their behavior during movement from the river to the ground waters. In general, Se was more conservative than U during infiltration of saline river water into the subsurface and dilution by fresher ground waters. The modeling indicated that mineral precipitation did not control Se and U contents in the river and ground waters. Sorption of U, and to a smaller degree, of Se, appeared to be the main factor reducing the concentration of these relative to chloride and sulfate concentrations during transport in the aquifer. Leaching from ash layers in the High Plains aquifer may contribute additional amounts to ground waters in selected zones of the aquifer. Se and U contents in the ground waters will most likely continue to increase as more saline river water infiltrates to the subsurface because sorption is not sufficient to attenuate Se and U.

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TABLE OF CONTENTS

Page

ABSTRACT ii

ACKNOWLEDGEMENTS iii

TABLE OF CONTENTS iv

LIST OF TABLES vii

LIST OF FIGURES ix

LIST OF APPENDICES xiv

CHAPTER 1. INTRODUCTION 1

CHAPTER 2. GEOLOGY AND HYDROGEOLOGY 6

2.1 Previous Investigations 6

2.2 Regional Geologic Setting 7

2.2.1 Geomorphology 7

2.2.2 Geologic History 8

2.2.3 Structure and Stratigraphy 9

2.2.4 Description of aquifer sediments 12

2.3 Characteristics of Arkansas River 21

2.3.1 Water quality 21

2.3.2 Flow variations 23

2.4 Hydrogeologic Setting 23

2.4.1 History of water use and irrigation 23

2.4.2 Description of river basin and tributaries 25

2.4.3 Climate 26

2.4.4 Aquifer system and properties 26

2.4.4.1 General groundwater description 26

2.4.4.2 Distribution of aquifer system 26

2.4.4.3 Recharge and river-aquifer interactions 29

2.4.5 Groundwater quality 30

CHAPTER 3. AQUEOUS GEOCHEMISTRY OF SELENIUM AND URANIUM 39

3.1 Previous Investigations 39

3.2 Introduction to Selenium and Uranium Geochemistry 41

3.3 Selenium Geochemistry 41
3.3.1 Chemical properties of selenium 42
3.3.2 Sources, Occurrence and Distribution 43
3.3.2.1 Natural and anthropogenic sources of selenium 43
3.3.2.2 Occurrence and typical concentrations of selenium 44
3.3.2.3 Source and concentrations of selenium in the Arkansas River Valley 46
3.3.3 Aqueous geochemistry 47
3.3.3.1 Behavior and geochemistry of selenium 47
3.3.3.2 Selenium adsorption 49
3.3.4 Toxicity 51
3.4 Uranium Geochemistry 54
3.4.1 Chemical properties of uranium 54
3.4.2 Sources, Occurrence and Distribution 54
3.4.2.1 Natural and anthropogenic sources of uranium 54
3.4.2.2 Occurrence and typical concentrations of uranium 55
3.4.2.3 Source and concentrations of uranium in the Arkansas River Valley 55
3.4.3 Aqueous geochemistry 56
3.4.3.1 Behavior and geochemistry of uranium 56
3.4.3.2 Uranium adsorption 61
3.4.4 Toxicity 64
CHAPTER 4. MULTI-LEVEL WELL SITES 77
4.1 Deerfield 77
4.2 Garden City 78
4.3 Dodge City 79
CHAPTER 5. PROCEDURE AND METHODS 84
5.1 Field Measurements and Sampling Procedures 84
5.2 Laboratory and Analytical Procedures 86
5.3 Geochemical Modeling Procedures 90
CHAPTER 6. RESULTS 101
6.1 Water Chemistry and Site Characteristics 101

6.2 Selenium and Uranium Concentrations....104
6.2.1 Distribution and comparison....105
6.3 Fate and Transport....106
6.3.1 Correlations of groundwater U and Se with water chemistry....106
6.3.2 Conservative and non-conservative behavior....107
6.3.2.1 Ratio comparison at sites with the river....107
6.3.2.2 Ratio changes with depth....109
6.3.2.3 Mixing curves....112
6.3.3 Geochemical modeling....114
6.3.3.1 Species concentration distribution....114
6.3.3.2 Mineral saturation and solubility controls....118
6.3.3.3 Sorption model....120
6.3.3.4 Sensitivity analysis....122
CHAPTER 7. DISCUSSION....179
7.1 Speciation, Mobility, and Solubility....181
7.2 Redox Controls....185
7.3 Conservative Mixing....186
7.4 Sorption....189
7.5 Future Investigations....192
CHAPTER 8. CONCLUSION....193
REFERENCES....196
APPENDIX....203

LIST OF TABLES

Table		Page
Table 1.	Summary statistics of chemical and physical data for the Arkansas River from historical data	35
Table 2.	Typical Se concentrations in rocks and soils	65
Table 3.	Typical Se concentrations in natural waters	66
Table 4.	State of Kansas and United States EPA drinking water standards for total selenium in water	67
Table 5.	Typical U concentrations in rocks and soils	72
Table 6.	Typical U concentrations in natural waters	73
Table 7.	Well locations, depths, and screened intervals for wells included in study	80
Table 8.	Summary of analysis methods and instruments used for major chemistry	93
Table 9.	Concentrations of components in matrix solutions	94
Table 10.	Se and U concentrations in matrix solutions	94
Table 11a.	Amount of Se and U standard added to each group of samples in standard addition analysis	98
Table 11b.	Results and data interpretation from standard addition ICP-MS analysis.	98
Table 12.	Example of input data for geochemical modeling	99
Table 13.	Example of input data for sorption model	100
Table 14.	Major constituent analysis for Arkansas River samples	128
Table 15.	Final field parameters for all the study sites	130
Table 16.	Major constituent analysis for Deerfield groundwater samples	132
Table 17.	Major constituent analysis for Garden City groundwater samples	135
Table 18.	Major constituent analysis for Dodge City groundwater samples	138
Table 19.	Total dissolved Se, U and Mo concentrations as determined using the ^{77}Se, ^{238}U, and ^{95}Mo isotopes by ICP-MS analysis at the KU-PAL	140

Table 20. Correlations between Se and U data with various chemical and physical parameters..... 142

Table 21a. Ratios of Se and U with conservative species for Arkansas River from historical data..... 145

Table 21b. Ratios of Se and U with conservative species for ground water from historical data..... 145

Table 22a. Ratios of Se and U with conservative species for Arkansas River from data collected in this study..... 146

Table 22b. Ratios of Se and U with conservative species for ground water from data collected in this study..... 146

Table 22c. Ratios of Se and U with conservative species for ground water calculated for each study site from data collected in this study..... 147

Table 23. Distribution of Se and U in the Arkansas River in the study area..... 157

Table 24. Distribution of Se and U in the groundwater in the study area..... 158

LIST OF FIGURES

Figure		Page
Figure 1.	Map of the study area in Hamilton, Kearny, Finney, Gray, and Ford counties showing the location of the three sites and the Arkansas River	32
Figure 2.	Generalized stratigraphic column of the sediments in the Upper Arkansas River study area	33
Figure 3.	Map of the study area showing surficial geology features	34
Figure 4.	Mean specific conductance downstream in the Arkansas River from Leadville, Colorado to Coolidge, Kansas	36
Figure 5.	Discharge in the Arkansas River in Coolidge, Kansas near the western edge of the study area over the time of this study. Data from USGS gaging station from 9/30/98 through 9/30/99	37
Figure 6.	Map showing the Arkansas River and other drainages of southwestern Kansas	38
Figure 7.	Map of Cretaceous outcrops high in Se and seleniferous soils in the western United States	68
Figure 8.	Eh-pH diagram for part of the Se-O-H system	69
Figure 9.	Plot showing pH dependence on sorption of Se(IV) and Se(VI) on hydrous ferric oxides	70
Figure 10.	Selenium cycle in nature showing pathway for concentration of Se in natural systems and bioaccumulation in plants and wildlife	71
Figure 11.	Eh-pH diagram for part of the U-O-H system	74
Figure 12.	Eh-pH diagram for part of the U-C-O-H system	75
Figure 13.	Plot showing pH dependence of sorption of U(VI) on ferrihydrite at 25°C	76
Figure 14.	Figure showing well construction, location of clay layers, depth of wells and well screens, and TDS and SO_4 concentrations at the Deerfield site	81
Figure 15.	Figure showing well construction, location of clay layers, depth of wells and well screens, and TDS and SO_4 concentrations at the Garden City site	82
Figure 16.	Figure showing well construction, location of clay layers, depth of wells and well screens, and TDS and SO_4 concentrations at the Dodge City site	83

Figure 17. Picture of flow through apparatus designed for field sampling and parameter measurement in this project.....92

Figure 18. Plot of matrix effects on ^{238}U.....95

Figure 19. Plot of matrix effects on ^{82}Se.....95

Figure 20. Example of sample order used for ICP-MS analysis.....96

Figure 21. Example of template used in data correction and interpretation.....97

Figure 22. Piper diagram showing the water types of groundwaters at the study sites and Arkansas River water.....129

Figure 23.
a. Plot of pH and Eh with depth at Deerfield.....131
b. Plot of DO with depth at Deerfield.....131
c. Plot of SC with depth at Deerfield.....131

Figure 24.
a. Major cation chemistry with depth at Deerfield.....133
b. Major anion chemistry with depth at Deerfield.....133

Figure 25.
a. Plot of pH and Eh with depth at Garden City.....134
b. Plot of DO with depth at Garden City.....134
c. Plot of SC with depth at Garden City.....134

Figure 26.
a. Major cation chemistry with depth at Garden City.....136
b. Major anion chemistry with depth at Garden City.....136

Figure 27.
a. Plot of pH and Eh with depth at Dodge City.....137
b. Plot of DO with depth at Dodge City.....137
c. Plot of SC with depth at Dodge City.....137

Figure 28.
a. Major cation chemistry with depth at Dodge City.....139
b. Major anion chemistry with depth at Dodge City.....139

Figure 29.
a. U, Se, and Mo with depth at Deerfield.....141
b. U, Se, and Mo with depth at Garden City.....141
c. U, Se, and Mo with depth at Dodge City.....141

Figure 30. Plot showing relationship between Se and discharge.....143

Figure 31. Plot of SO_4/Cl downstream in river.....144

Figure 32.
a. Plot of SO_4/Cl with depth.....148
b. Plot of Se/U with depth.....148

Figure 33.
a. Plot of U/Cl with depth.....149
b. Plot of U/SO_4 with depth.....149

Figure 34.
a. Plot of Se/Cl with depth. 150
b. Plot of Se/SO_4 with depth. 150

Figure 35. Plot of Mo/Cl with depth.....151

Figure 36. Plot of relationship between Ca, Mg, Na showing cation exchange in groundwaters.....152

Figure 37.
a. U-Cl mixing curve.....153
b. U-SO_4 mixing curve.....154

Figure 38.
a. Se-Cl mixing curve.....155
b. Se-SO_4 mixing curve.....156

Figure 39.
a. Se species with depth at Deerfield.....159
b. Se species with depth at Garden City.....159
c. Se species with depth at Dodge City.....159

Figure 40. U(VI) complexes with depth at Deerfield.....160

Figure 41. U(VI) complexes with depth at Garden City.....161

Figure 42. U(VI) complexes with depth at Dodge City.....162

Figure 43.
a. Mineral saturation at Deerfield.....163
b. Mineral saturation at Garden City.....163
c. Mineral saturation at Dodge City.....163

Figure 44.
a. Se mineral saturation at Deerfield.....164
b. Se mineral saturation at Garden City.....164
c. Se mineral saturation at Dodge City.....164

Figure 45.
a. U mineral saturation at Deerfield....165
b. U mineral saturation at Garden City....165
c. U mineral saturation at Dodge City....165

Figure 46. Sorption model output for Deerfield....166

Figure 47. Amount of Se and U sorbed from solution....167

Figure 48.
a. pH effects on Se and U....168
b. pH effects on Se species....168

Figure 49.
a. pH effects on U(IV) species....169
b. pH effects on U(V) species....169

Figure 50. pH effects on U(VI) species....170

Figure 51.
a. pH effects on Se mineral saturation....171
b. pH effects on U mineral saturation....171
c. pH effects on mineral saturation....171

Figure 52. Eh effects on Se speciation....172

Figure 53.
a. Eh effects on U(IV) speciation....173
b. Eh effects on U(VI) speciation....173

Figure 54.
a. Eh effects on Se mineral saturation....174
b. Eh effects on U mineral saturation....174
c. Eh effects on mineral saturation....174

Figure 55.
a. SO_4 effects on U(IV) speciation....175
b. SO_4 effects on U(VI) speciation....175
c. SO_4 effects on Se(IV) speciation....175

Figure 56.
a. PO_4 effects on U complexes in the Arkansas River....176
b. PO_4 effects on U complexes in the shallow groundwater at Dodge City....176
c. PO_4 effects on U complexes in the deep groundwater at Dodge City....176

Figure 57.
a. PO_4 effects on U-CO_3 complexes in the Arkansas River.....177
b. PO_4 effects on U-CO_3 complexes in the shallow groundwater at Dodge City.....177
c. PO_4 effects on U-CO_3 complexes in the deep groundwater at Dodge City.....177

Figure 58.
a. PO_4 effects on U mineral saturation in the Arkansas River.....178
b. PO_4 effects on U mineral saturation in the shallow groundwater at Dodge City.....178
c. PO_4 effects on U mineral saturation in the deep groundwater at Dodge City.....178

LIST OF APPENDICES

Appendix 1. Parameters (Eh, pH, DO, SC, temperature) field data taken over time at Deerfield.

Appendix 2. Explanation and data corrections of field Eh values to the standard hydrogen electrode.

Appendix 3. Parameter (Eh, pH, DO, SC, temperature) field data taken over time at Garden City.

Appendix 4. Parameter (Eh, pH, DO, SC, temperature) field data taken over time at Dodge City.

Chapter 1 Introduction

The Arkansas River in southwestern Kansas is one of the most saline rivers in the United States. Total dissolved solids (TDS) in the river at the Colorado-Kansas state line exceeds 3,000 mg/L at the average flow rate of the last decade. The dissolved constituent in greatest concentration in the river is sulfate, which usually ranges between 1,000 and 2,500 mg/L. Elevated dissolved solids levels, including sulfate, in the river are caused by evapotranspirative losses and use and reuse of the water for irrigation in eastern Colorado. Sulfate is also elevated in the groundwater in southwest Kansas because the river recharges the aquifer system and river water diverted for irrigation seeps into the ground. Contents of other naturally occurring constituents in the river water and groundwaters are also locally elevated for the same reasons (Whittemore, 2000).

The broad objective of this project was to assess the fate and transport of selenium (Se) and uranium (U) in the Arkansas River corridor in southwest Kansas based on the hydrogeology and geochemistry of the system. Water samples were collected and analyzed to describe the geochemistry of the river water and groundwater in the study area. The data and geochemical modeling were used to evaluate the behavior of Se and U in the system. Behavior of both constituents relative to sulfate and chloride in the system was a key concern. The data and observations were evaluated within the framework imposed by the river-aquifer interactions and flow regime in the area.

The general study area includes Hamilton, Kearny, Finney, Gray, and Ford counties in southwestern Kansas. Specific investigations for Se and U geochemistry were conducted in Kearny, Finney, and Ford counties. Water samples were collected from wells and the Arkansas River at sites in or near Deerfield, Garden City, and Dodge City. Each site has 4-5 wells screened at various depths.

The saturated parts of the Pliocene Ogallala Formation, undifferentiated Pleistocene deposits, and the Quaternary alluvium form the aquifer system in the area. Water in southwestern Kansas is pumped from the river and alluvial and Ogallala aquifers in the area for many uses. Almost 95% of the water pumped from the Ogallala (High Plains) is used for irrigation. The surface water and groundwaters are important resources and the elevated constituent concentrations are of increasing concern.

Among the many Arkansas River studies, there are a few that are closely related to this project and the upper river corridor in southwestern Kansas. This investigation is part of a larger study of the Arkansas River corridor by the Kansas Geological Survey (KGS). Whittemore (1995, 2000), Young *et al.* (1998), and Tsou (1998) present research, data, maps, modeling results, and progress reports of this project. Zielinski *et al.* (1995, 1997) studied the presence, sources, and transport of uranium in the water of the Arkansas River Valley of southeastern Colorado. Cain (1985) discussed the water quality of the river water and irrigation water in the Arkansas River valley of Colorado. A reconnaissance investigation of the Arkansas River basin in Colorado and Kansas by Mueller *et al.* (1991) provides useful data on high levels of uranium and selenium found in the area.

Recently, interest in dissolved Se and U in surface and groundwaters has increased, and they are becoming a concern in some areas of the country. Sources of Se and U have been identified in Colorado and western Kansas; the most important contribution to the river in eastern Colorado is runoff from Cretaceous marine shales. Dissolved Se and U in water entering the river in Colorado are further concentrated primarily by water loss to evapotranspiration. Se and U were studied together because their behavior is geochemically similar and they are often found in the same environments and have similar sources in this study area. The transport of both elements is redox sensitive and can be affected by sorption.

Therefore, characterizing the chemical and hydrogeological environment was critical to this study.

There are many reasons why the study of Se and U are important locally and regionally. U was investigated in this study because multiple studies have identified elevated levels in the river basin. Zielinski *et al.* (1995, 1997) identified elevated U in the river and investigated the possible sources. They presented Cl/SO_4 ratios that compare to the data collected in Kansas and other similar contaminated areas. These data and historical data from regulatory agencies can be used to track the problem through time and examine changes downstream and with depth in the aquifer. In general, U is elevated throughout the river basin in Colorado. U increases steadily downstream from about 4 μg/L and can exceed 50 μg/L in the river as it crosses into Kansas, which surpasses the proposed drinking water standard of 20 μg/L. Concentrations exceed 100 μg/L in some places along the river (Zielinski *et al.*, 1995). These elevated levels can be a health and safety risk to humans and animals and can also inhibit plant growth when it concentrates in soil (Meyer *et al.*, 1998).

Se was investigated in this study because awareness of problems associated with elevated levels has increased recently and regulatory agencies in the state have begun to examine Se levels in the water. Many studies have been done concerning Se in surface and groundwaters in the last 20 years, especially many focusing on San Joaquin Valley and Kesterson Reservoir in California (White *et al.*, 1991; Tokunaga *et al.*, 1994; Presser, 1994; Fujii and Deverel, 1989; Deverel *et al.*, 1994, Clifton and Gilliom, 1988; Benson *et al.*, 1991). The California studies show that the sources of Se are similar to those in the Arkansas River study area and the geochemical mechanisms controlling the Se are often similar. They also indicate how substantially high Se levels can effect the environment, wildlife, public health, and water supply. The public attention brought about by the effect of Se on wildlife

and migratory birds in Kesterson increased awareness and concern regarding possible problems.

The Kansas Department of Health and Environment (KDHE) has set toxicity limits for wildlife safety in the surface waters of the state. These standards are 5 μg/L as the chronic level and 20 μg/L as the acute level for the protection of aquatic life. The concentration of dissolved Se in groundwater is also a concern since the drinking water standard is 50 μg/L. These limits are necessary because in some chemical forms Se can accumulate in plant and animal tissues and cause disease and death. Elevated levels of Se are also toxic to humans.

Water samples were collected using clean sampling methods to ensure that the samples were not contaminated during collection. The samples were analyzed for major element chemistry using various laboratory and analytical techniques. Se and U analysis was performed on an inductively coupled plasma mass spectrometer (ICP-MS) at the University of Kansas Plasma Analytical Laboratory. The redox environment and pH were determined in the field as precisely as possible since Se and U geochemistry is integrally dependent on these conditions. Geochemical modeling was performed using the USGS reaction path model, PHREEQC to evaluate various geochemical controls, such as solubility, sorption, and mixing (Parkhurst, 1995). The model results were also used to determine speciation and distribution within the system. Behavior of Se and U was evaluated in comparison with the major constituents sulfate and chloride that generally act conservatively in this system.

Important products of this study are the concentration distribution and assessment of Se and U behavior determined through distribution variations in the system, evaluation of conservative mixing behavior, and geochemical model results. The results are valuable to KDHE and other state regulatory agencies for evaluation of potential impacts of Se and U.

The ultimate goal of this study was to determine if Se and U are concentrating in portions of the system and could possibility cause future deterioration of water quality.

Chapter 2 Geology and Hydrogeology

2.1 Previous Investigations

A substantial number of studies on the general geology, hydrogeology, and geochemistry of water of southwestern Kansas have been conducted due to the progressive decline in water levels and water quality. Both the Arkansas River water and groundwater in the High Plains aquifer are important water sources for the area. Efforts to outline the hydrogeologic setting have led to a better understanding of the causes of many water problems.

Smith (1940) conducted an early study of the hydrogeology in southwestern Kansas and Gutentag *et al.* (1981) updated his work. Many studies of specific counties in the area are also available. Waite (1942), and more recently, Spinazola & Dealy (1983) studied the hydrogeology and geology of Ford County. Comprehensive studies of the geology and geohydrology of Finney and Gray counties were done by Latta (1944), Meyer *et al.* (1970), and McGovern & Long (1974). McLaughlin (1943) reported on Hamilton and Kearny counties. Dunlap *et al.* (1985) investigated the stream-aquifer system in Kearny and Finney counties.

Gutentag *et al.* (1984) and Dunlap *et al.* (1985) present a broad overview of the hydrology of the High Plains aquifer. Abbott (1985) and Taylor and Luckey (1974) discuss the water systems and water management in the stream-aquifer setting in the study area. Merriam (1963) provides the regional geologic history and framework that is helpful for understanding the hydrogeology and geology of the study area. Frye and Leonard (1952) and Zeller (1968) also studied the geology and geologic history of Kansas in detail.

2.2 Regional geologic setting

2.2.1 Geomorphology

Location and Setting

The general study area encompasses about 3,560 mi^2 along the Arkansas River in southwestern Kansas (Figure 1). The area extends east from the Colorado state line across Hamilton, Kearny, Finney, Gray, and Ford counties. About 15-20 miles of the Arkansas River alluvium and valley is included in the study area from either side of the river. This land surface slopes gently from the Rocky Mountain front in Colorado and the elevation in the area ranges from about 3,850 feet as the river enters Kansas to about 2,150 feet on the east side of the study area. The land surface has a slope of approximately 12.5 ft/mile toward the southeast (Gutentag *et al.*, 1981).

Southwestern Kansas is in the High Plains section of the Great Plains physiographic province. This area is characterized by little topographic relief between streams. The surface topography varies from flat to the north to rolling sand dunes in the south (Dunlap *et al.*, 1985). The Great Plains province has been defined by Fenneman (1931) as an area of high flat plains situated between an erosional area on either side; Plains Border to the east and the Colorado Piedmont to the west. Drainage from and erosion of the mountains to the west formed the alluvial plain and therefore the geology is mainly sedimentary layers including limestone, shale, sandstone, and unconsolidated sand, gravel, and clay.

This project focuses specifically on three sites, Deerfield in Kearny County, Garden City in Finney County, and Dodge City in Ford County (Figure 1). Four to five wells have been installed at each site allowing characterization of the subsurface hydrogeology. The heterogeneous layers of varying amounts of sand, gravel, and clay form the aquifer system in

the area. In Kansas, typical water movement in the system is from the Arkansas River into the alluvium and then into the High Plains aquifer.

2.2.2 Geologic History

Geologic history

Moderately deep seas during most of the Paleozoic period covered the area in southwestern Kansas. The sea level fluctuated to create numerous cyclothems resulting in the limestone, sandstone, and shale dominated geology in Kansas seen today (McLaughlin, 1943). This cycle between submergence and emergence of land persisted through to the end of the Permian period (Waite, 1942). In late Permian time water subsided resulting in an arid climate and shallow basins allowing the chemical precipitation of salt and evaporites (Latta, 1944). The dissolution of salt created faulting and subsidence in the area. At this time, the clays that form the Permian redbeds were deposited in mud flats (McLaughlin, 1943).

At the end of the Paleozoic era, the area was uplifted causing withdrawal of the shallow seas (Waite 1942). The Cretaceous units are the result of transgressions and regressions of the interior seas that deposited the sandstone, shale, and limestone (Latta, 1944). The orogeny creating the Rocky Mountains at the close of Cretaceous tilted the Cretaceous and older strata to create the regional slope that exists today (McLaughlin, 1943).

The beginning of the Tertiary period was marked by a long period of erosion and some gentle folding creating the Scott-Finney depression, a synclinal trough trending north to south. Much of the Cretaceous sediments were removed by erosion in the southern part of the study area and bedrock valleys were cut prior to the Tertiary period of deposition (Latta, 1944). During the Pliocene there was a change from stream erosion to stream deposition and the bedrock topography was left very uneven at the beginning of this deposition. The Ogallala

was deposited near the end of the Tertiary period on this erosional surface by laterally shifting, braided streams on the broad alluvial plain (McLaughlin, 1943, Waite, 1942). Deposition by the overloaded streams continued until the interstream areas were covered with a mantle of unconsolidated sediment (Waite, 1942). Subsequent erosion removed much of the Ogallala in Hamilton and Kearny counties, especially in the southern part of the area (McLaughlin, 1943).

Beginning in the Quaternary period, loess was deposited by dust storms and eolian sand dunes were deposited contemporaneously (Waite, 1942). From the Quaternary to recent there was deposition of water laid sediments including the Arkansas River alluvium and terrace deposits (Latta, 1944). The thick sequence of stream laid sediments carried from the Rocky Mountain front resembles the Ogallala. Also during the Quaternary there was subsidence causing the Arkansas River to swing north near Hartland, Kansas (McLaughlin 1943).

2.2.3 Structure and Stratigraphy

There is regional structure in this area, but it is not always readily visible on the surface due to erosion or post-deformation deposition. A broad syncline stretches about 15 miles across northwestern Kearny County. This feature probably influenced the drainage system during the post Cretaceous bedrock erosion and subsequent Tertiary deposition and therefore affected the thickness of the Quaternary materials in some places (Gutentag *et al.*, 1981). Another feature is the Scott-Finney depression, an asymmetrical trough extending in a north-south direction from Garden City north through Scott City (Berendsen & Hathaway, 1981).

Extensive salt deposits, deposited by shallow brackish seas during the Permian, can be up to 300 feet thick but in most places were dissolved by groundwater during the late Tertiary and early Quaternary causing subsidence (Spinazola & Dealy, 1983). This area of subsidence is bounded by the Bear Creek Fault in Kearny County to the west and the Crooked Creek-Fowler Fault in Ford County to the east. These two fault zones interrupt the regional structure and define the northwest and southeast limits of the main strata comprising the principal aquifer, the Tertiary Ogallala Formation. The Bear Creek Fault cuts across Stanton, Grant and Kearny counties and the Crooked Creek-Fowler Fault is in Meade and Ford counties. Vertical displacement along the Crooked Creek-Fowler fault can be up to 250 feet (Gutentag *et al.*, 1981).

The geology in this area is dominated by shales, limestones, and sandstones derived from the Pre-Tertiary cyclic transgressive-regressive sequence overlain by Post-Tertiary unconsolidated sedimentary materials from stream deposition (Figure 2). The main aquifer unit is the sand and gravels of the Ogallala Formation and undifferentiated Quaternary deposits. Outcropping units vary with age from Recent alluvium, dunes, and loess through Cretaceous rocks and most often the Cretaceous units form the bedrock (Figure 3). The Cretaceous rocks are divided into upper and lower subdivisions.

Consolidated upper and lower Cretaceous rocks are usually considered to be the bedrock in this area (Young *et al.*, 2000). The bedrock surface is an erosional surface with an average slope toward the southeast of 13.7 feet per mile. As a result of the erosion and subsidence there can be up to 250 feet of relief in some areas (Gutentag *et al.*, 1981). Depth to bedrock varies widely due to erosion creating bedrock channels, dissolution creating bedrock basins and associated faulting. For example, depth to bedrock around the Crooked-

Creek Fowler fault in Ford County ranges from 50 feet to 415 feet (Spinazola & Dealy, 1983).

Cretaceous rocks underlie the principal water-bearing rocks in the area, the Pliocene Ogallala Formation and the undifferentiated Pleistocene deposits. The undifferentiated lower Cretaceous rocks are not always present in this area. When they are present they include the Cheyenne Sandstone, Kiowa Formation, and Dakota Formation (McGovern & Long, 1974). The Upper Cretaceous rocks in the area are the Graneros Shale, Greenhorn Limestone, Carlile Shale, and Niobrara Formation. In the northern part of the study area these Upper Cretaceous rocks retard the vertical flow of water creating an impermeable layer between the Dakota below and overlying aquifer materials (Gutentag *et al.*, 1981). Outcrops of fine grained, lenticular Dakota Sandstone interbedded with clay and shale can be seen along the river in western Kearny County. In some areas outside the study area, the Dakota can be an important source of water (Latta, 1944; Waite, 1942).

Upper Cretaceous rocks outcrop more often than the lower Cretaceous system in southwest Kansas (Smith, 1940). The Graneros Shale outcrops near the river in Hamilton and Kearny counties and conformably overlies the Dakota Formation (Smith, 1940; Waite, 1942). This has been described by many in the study area as dark-colored, fissile shale with sandstone lenses, bentonite beds and sandy shale and limestone. Overlying this is the Greenhorn Limestone consisting of alternating beds of chalky and crystalline limestone, calcareous shale, and bentonite clay (Smith, 1940; McLaughlin, 1943; Latta, 1944; Waite, 1942). The Carlile Shale outcrops along the Arkansas River in northern Hamilton County. The Niobrara Formation has two members; the chalky limestone and shale of the Fort Hays Limestone and the soft chalk beds and chalky shale of the Smoky Hills Chalk (Smith, 1940).

The upper Smoky Hills member has the most volcanic ash and could contain elevated Se content in this area (Rosenfeld and Beath, 1949).

2.2.4 Description of aquifer sediments

Tertiary and Quaternary Systems

The loosely consolidated to unconsolidated sediment of the Pliocene Ogallala, Pleistocene undifferentiated deposits, and Quaternary alluvium form the aquifer system in southwest Kansas. These poorly-sorted, coarse-grained sediments are good water-bearing materials. The Tertiary and Quaternary systems are lithologically similar and are sometimes mapped and described together, especially in the western part of the study area. It is often difficult to define the distribution of the units in the area since they are hard to distinguish (Latta, 1944). However, in most parts of the study area there are some differentiating characteristics that can be used to separate these deposits.

The Ogallala Formation, deposited late in the Tertiary period, can be differentiated in places from the Quaternary system because it has more sand, clay, and caliche and more extensive interbedding (Meyer *et al.*, 1970). The Tertiary deposits outcrop in a few places in the study area and Quaternary deposits outcrop over most of the study area as shown in Figure 3. The alluvial Pleistocene deposits occur mostly in the recent drainage system and consist of discontinuous silt, sand, gravel, and minor but important ash. The Ogallala Formation is cemented by calcium carbonate in some places and the Pleistocene deposits are noncalcareous. Also, the Ogallala Formation is missing the unctuous clays and snail and clam shells common to the Quaternary deposits (Merriam, 1963).

Tertiary System - Ogallala Formation

In southwestern Kansas the Tertiary period is represented solely by the Pliocene Ogallala Formation. The Ogallala Formation is an important aquifer in the region forming a belt 100-250 miles wide from east to west (Smith. 1940). The Ogallala is a heterogeneous mixture of mostly sand, gravel, and silt with minor amounts of chert and limestone that is difficult to correlate accurately over any distance due to much lateral and vertical variation (Gutentag *et al.*, 1981).

Fenneman (1931) supports a fluviatile origin for this formation. Although the sediments appear to be randomly deposited by streams, the gravel can be traced in long, wide winding bands in an east to west direction throughout the area. This suggests that bands were deposited by overloaded streams that continually shifted in a braided stream system moving erosional debris from the mountain front in the west and depositing it as a mantle of permeable material across the broad plain (Fenneman, 1931). The Pliocene Ogallala Formation consists of a mixture of fine to coarse fluvial sediments and lies below Quaternary terrace deposits and loess and above Cretaceous bedrock (McGovern & Long, 1974; McLaughlin, 1943; Waite, 1942; Latta, 1944). The sediment originated as erosional debris from the Rocky Mountains and was transported eastward in streams (Meyer *et al.*, 1970).

The Ogallala is distributed widely over the western 1/3 of the state and in this area it is exposed at or near the surface north of the Arkansas River and is mantled by the Kingsdown silt south of the river in Ford County (Zeller, 1968). It is thin or missing due to erosion in the north-central part of Ford County and reaches the maximum thickness of 250 feet west of Dodge City (Waite, 1942). A thin layer of loess and dune sand overlies the Ogallala and Pleistocene deposits. The Ogallala is probably absent or very thin in much of

Hamilton County, especially to the south and northwestern parts of the county (McLaughlin, 1943).

The lithology of the Pliocene Ogallala Formation is variable over short distances both laterally and vertically. The formation matrix contains poorly sorted arkosic silts, sands, and gravels in varying amounts. Sand is the principle material with significant amounts of silt filling pore spaces (Smith, 1940; Waite 1942). In general, there are clays at the base of the Ogallala, limestone caps at the top, and poorly sorted, structureless layers in the middle. The middle and upper sections are loosely consolidated or cemented with calcium carbonate (Latta, 1944; McLaughlin, 1943). The gravel and clay beds are often lenticular and lenses of sandy silt ranging from inches to 50 feet are common (Smith, 1940; Latta, 1944). Variations such as these can affect water movement in the aquifer. The formation grades upward from pebbles and gravels of limestone, sandstone, ironstone, granite, chert, and igneous rocks to calcareous sands and silts (Waite, 1942; McLaughlin, 1943; Meyer *et al.*, 1970). Typically it varies in color, is massive to cross-bedded, and includes limestone, diatomaceous marl, volcanic ash, opaline sandstone, and bentonitic clay. Small, irregular bodies of chert occur mostly in calcareous beds (Smith, 1940). In Hamilton and Kearny counties the Ogallala has been described as having as much as 80% silt and the Ogallala and undifferentiated Pleistocene sediments are mapped together in these counties because they are so similar (McLaughlin, 1943).

Three members of the Ogallala Formation have been identified in this area, from youngest to oldest as the Kimball, Ash Hollow, and Valentine members. The Kimball member is light gray calcareous sand, gravel and slit with minor opaline chert and caliche. Minor capping limestone is developed locally. The Ash Hollow consists of pink and gray sand, gravel and silt loosely cemented by calcium carbonate to form mortar beds. This

member, that can be as much as 130 feet thick in some places, also includes some limestone and relatively large amounts of volcanic ash, which can be an important source for trace elements in this environment. The Valentine, the lower most member, can be as much as 100 feet and is comprised of unconsolidated sands and gravels with some silica cement, green opaline sandstone, soft limestone, bentonite, and volcanic ash at the base (Merriam, 1963).

Sand, the predominant component, is 95% quartz and feldspar, and occurs as fine to coarse grains in structureless layers. It is often lighter colored than the other sediments, usually gray or white (Waite, 1942). Clays are most common at the base and often range between about 18-29 feet. The color of the finer grained material varies from pink to tan to gray (Latta, 1944). Lenticular bedding and poor sorting are characteristic of the Ogallala Formation and the finer parts are often structureless (Smith, 1940; Waite, 1942).

The gravel fraction of the Ogallala has been studied more thoroughly than the finer fractions. The coarser grained materials can be gray, rusty brown, tan, reddish, yellow. Two gravel facies have been identified by many researchers and described in detail within the Ogallala, the sandstone-ironstone-quartzite facies and the granitic or crystalline igneous and metamorphic facies (Smith 1940; Meyer *et al.*, 1970; Latta, 1944). The sandstone-ironstone-quartzite is common near the base and the granitic facies is more widespread along the river valley in outcrops above the base (Waite, 1942).

The specific lithology of the sandstone-ironstone-quartzite facies varies because it is mostly made from erosion of older rocks. In general this facies is composed of material similar to the Dakota and other Cretaceous formations (Smith, 1940). In Ford County the coarse gravel is mostly of Greenhorn limestone and in Ford and Gray counties is Cretaceous sandstone, limestone, chalk, and shale (Waite, 1942; Latta, 1944). The quartzite was formed from secondary cementation and locally there are also pebbles of Permian gypsum, dolomite

and sandstone present (Smith, 1940). The granitic facies (or the igneous-metamorphic facies) includes grains of granite, graphic granite, pink feldspar, quartzite, several varieties of felsite, and other crystalline igneous and metamorphic rocks (Waite, 1942; Smith, 1940).

Calcium carbonate is present in many forms in this formation and serves as a source of some major constituents, such as Ca, in the groundwater. Mortar beds and caliche are characteristic of the Ogallala (Meyer *et al.*, 1970; McGovern & Long, 1974). Mortar beds are formed where grains are cemented by calcium carbonate cement locally (Zeller, 1968). Abundant, irregular limy concretions higher in the formation and highly cross-bedded caliche beds are common (Waite, 1942; Latta, 1944). Caliche is common as pipy concretions, cementing material, nodules, and irregular beds (Latta, 1944). Also, there is secondary opal and chert in some places (Zeller, 1968).

Locally capping limestone is present at the surface of the Ogallala, but overall limestone is of minor importance to the formation itself. This capping limestone is a maximum of about 5 feet where is occurs (Smith, 1940). The capping limestone that has been also known as the algal limestone is a dense, sand rich limestone with concentric layers having a non-marine origin (Merriam, 1963; Zeller, 1968).

There are discontinuous layers of volcanic ash throughout the Ogallala Formation. Several exposures of this ash outcrop occur in Hamilton County. The calcareous nature of the ash in the Ogallala differentiates it from the more abundant ash layers present in the Pleistocene deposits (Smith, 1940). The greatest thickness of ash is in southeastern Kearny County (McLaughlin, 1943). Pliocene-Pleistocene volcanic ash beds in Kansas have been named Calvert, Reager, Pearlette, and the unnamed Ogallala. These ash layers are important to this study because they are often high in Se (Trelease and Beath, 1949).

Quaternary System - Undifferentiated Pleistocene deposits

The undifferentiated Pleistocene deposits and Quaternary alluvium are the most recent deposits and create an important aquifer system in this area. These unconsolidated sediments are found mostly in the drainage systems and can be several hundred feet thick (Merriam, 1963). There was considerable erosion of the older strata before deposition of Quaternary sediments and the Pleistocene deposits lie unconformably on older rocks (Zeller, 1968).

The Quaternary system in the study area represents channel and floodplain sediments deposited by laterally migrating, low-gradient streams as indicated by stratified layers of mixed clay, silt and sand (Latta 1944; McGovern & Long, 1974). Much of the unit fills cuts in the Ogallala Formation (McLaughlin, 1943). In southwestern Kansas, the Pleistocene deposits are unconsolidated sediments that include dune sand south of the river, loess bluffs north of the river, terrace deposits along the river, and the heterogeneous alluvium.

The unconsolidated, undifferentiated sand, gravel, silt, and local deposits of volcanic ash are usually non-calcareous (McLaughlin, 1943). Although, locally sediments are loosely cemented with calcium carbonate and resemble the mortar beds in the Ogallala (Merriam, 1963). Caliche is common as nodules, concretions, or irregular beds (Latta, 1944). Thickness of these deposits can be several hundred feet (Merriam, 1963).

Terrace deposits

Late Pleistocene terrace deposits are found south of river in the study area (McLaughlin, 1943). Thickness of outcropping deposits reaches a maximum of 20 feet and usually lie 15-25 feet above river level (Smith, 1940). Latta (1944) reports that test holes encountered between 35 and 70 feet of coarse terrace deposits below the surface. The clean,

unconsolidated deposit consists of fine to coarse cross-bedded sand and lenticular gravel beds (Waite, 1942). The gravel and smaller fractions of silt, sand and clay come mostly from igneous rocks but also from nearby Cretaceous limestone outcrops (McLaughlin, 1943). Much of this permeable deposit lies above the water table and therefore does not bear water, but in some places the lower part has provided for a few wells (Latta, 1944).

Recent Alluvium

The Quaternary alluvial deposits are the most important of the Pleistocene deposits for their water bearing qualities (Frye and Leonard, 1952). Near and east of the city of Ford the alluvium lies unconsolidated on the Dakota Formation (Waite, 1942). In general, in the westernmost part of the study area the alluvium lies on Cretaceous bedrock and in the central and eastern part of the study area on undifferentiated Pliocene and Pleistocene deposits. Thickness varies considerably and exceeds about 50 feet in some places in the study area. Usually thickness of alluvium averages 55 feet in Hamilton County and 45 feet in Kearny County (Young *et al.*, 2000).

The undifferentiated Pleistocene river alluvium consists of deposits of poorly sorted, unconsolidated sand, gravel, and silt with small amounts of volcanic ash and coarsens upward from clays to gravels (McLaughlin, 1943). The interbedded lenses have small-scale vertical and lateral variations creating discontinuities over short distances (Latta, 1944, McGovern & Long, 1974). The heterogeneity and abundance of sand and gravel create a very permeable deposit (Waite, 1942).

Lithologically it consists of quartz, feldspar and igneous gravels and some reworked Ogallala and Cretaceous materials (Meyer *et al.*, 1970). Finer grained material is thicker and more persistent near the top 2 to 10 feet of the formation (Latta, 1944). The unit consists of

clean, unconsolidated cross-bedded sand and lenticular gravel beds (McLaughlin, 1943). The finer material is tan to reddish brown calcareous silt, sandy silt and clay-rich silt interbedded with caliche in thin streaks and lenses (Meyer *et al.*, 1970). The coarser sediments include clean, unconsolidated, cross-bedded sand and fine to coarse lenticular gravel beds (Waite, 1942; Smith, 1940).

Dune sand

Dune sand was deposited south of the Arkansas River during the Quaternary period (Smith, 1940). There is a continuous band of dunes south of the river from near Great Bend, Kansas to Colorado and also an area of several square miles in northern Ford County (Waite, 1942). The band expands to a large size, known as the Garden City dune tract, in Finney, south Kearny, and central Gray counties (Frye and Leonard, 1952; Smith. 1940). The eolian dune materials were derived in part from the Quaternary terrace deposits. These dunes range from rugged and active to stable with low, gentle swells. Individual dunes can reach a maximum height of about 70 feet in some places in southwestern Kansas. These highly permeable, well-drained dunes consist of well sorted, moderate to well rounded, usually non-calcareous arkosic sand (Frye, and Leonard. 1952).

Kingsdown Formation

Smith (1940) described this unconsolidated silt dominated sediment as the Kingsdown Formation and Waite (1942) simply named it the Kingsdown silt. In either case this layer has been described and identified south of the river in Ford County and is also present in southeastern Gray County (Smith, 1940). This light colored, even-bedded silty layer grades upward from gravel into loess. It consists of silt, clay, and fine sand, and small

calcareous nodules and is soft and easily eroded (Waite, 1942). The Kingsdown Formation does not reach the maximum thickness of 110 feet in the study area (Smith, 1940).

Loess

A thin deposit of Upper Pleistocene loess covers Pliocene and Pleistocene deposits over most of Hamilton, Kearny and northern Finney counties (McLaughlin, 1943; Smith, 1940). The surface geology map of the study area (Figure 3) shows that loess covers much of the surface and deposits can be very thick in southern Ford County. In general, the thickness ranges from a few feet to about 20 feet. There are few natural exposures of this buff to brown, quartz and feldspar rich silty material. This sediment may have limy concretions and small limestone nodules and forms the soils in the area that have been described as silt loam, clay loam, and silty clay loam. This fine-grained deposit lies above the saturation zone and has very low permeability (Smith, 1940).

Volcanic ash beds

There are surface exposures of thin, compact, white Quaternary volcanic ash beds in southern Hamilton County (McLaughlin, 1943). The volcanic ash is fine grained and calcareous concretions are common (Smith, 1940). McLaughlin reports that the largest ash bed is about 2.5 feet thick. These beds are underlain by clay and overlain by sand and gravel and break off into shabby layers (McLaughlin, 1943). They are a small part of the overall geology in the area but could play a significant role in affecting the geochemistry of the local groundwater.

2.3. Characteristics of the Arkansas River

2.3.1. Water quality

The headwaters of the Arkansas River are in Leadville, Colorado where the subsurface geology is igneous and metamorphic rocks (Mueller *et al.*, 1991). Natural concentrations of major ions such as Ca, Mg and Na, and trace elements such as Se and U derived from these rocks are dissolved in the river. The water is relatively fresh as it enters the Great Plains. However, the natural concentrations of these constituents then become elevated as the water moves downstream and is subject to evapotranspiration, concentration in irrigation return flows, and runoff from saline soils.

In general, the salinity of the Arkansas River increases downstream in eastern Colorado. Most of the streamflow in the Arkansas River downstream of Manzanola, Colorado is irrigation return flow (Cain, 1985). Characteristically, the quality of the water is degraded in irrigation return flows. The quality has been studied in depth, especially from Leadville to the Kansas state line (Mueller *et al.*, 1991; Zielinski, *et al.* 1995; Cain, 1987). Whittemore (2000) collected chemical data for Arkansas River water in southwest Kansas for all the counties of the study area. Data were compiled from the KGS and databases of the United States Geological Survey (USGS), United States Environmental Protection Agency (EPA), and KDHE for the river in the five counties of the study area. Summary statistics for the Arkansas River for this compilation are in Table 1.

The increase in specific conductance (SC) represents well the progressive deterioration in quality. SC is also an indicator of the total dissolved solids (TDS) and sulfate concentration. Generally, specific conductance in the Arkansas River and the alluvial aquifer increases downstream from Leadville to the Kansas state line (Figure 4). The SC increase is about a factor of 50 (to about 3800 μS/cm) (Cain, 1987). However, on a local scale, SC in

the basin varies aerially and seasonally. The TDS content in the river at the Colorado-Kansas line is about 2,000-4,000 mg/L and exceeds 4,000 mg/L during low flows (Whittemore, 2000).

There is a sharp increase in SC downstream of Canon City, Colorado due to the increase in irrigation return flows and inflow of saline groundwater (Cain, 1987). Cain (1985) attributed downstream increases in TDS to consumptive use of the water. When flow is higher in the river the concentration of constituents is lower (Cain, 1985). Recycling irrigation water causes progressive down river increase of TDS because each time the water is used it becomes more saline (Zielinski *et al.*, 1995). Sulfate concentration ranges from 700 to 2,600 mg/L and chloride from about 40 to 200 mg/L at the state line (Whittemore, 2000).

Mean concentrations of Na, K, Ca, Mg, Cl, F, SO_4, HCO_3 also increase downstream (Cain, 1987). The relative order of concentrations of major dissolved ions is sulfate, sodium, calcium, bicarbonate, magnesium, chloride, and silica. Cain (1987) found that dissolved oxygen (DO) ranged from 4-13.2 mg/L in the Arkansas River during an irrigation season. Most DO measurements in the river were more than 5-mg/L. DO concentrations are usually higher in the spring and smaller in the summer in the Arkansas River. The drinking water quality standard for pH is 6.5-9.0 and the measured values for the Arkansas River were between 7.3-8.4 in a study by Cain (1985). Most total phosphate concentrations were less than 0.2 mg/L (Cain, 1985) and Fe was usually less than 0.5 mg/L (Zielinski *et al.*, 1997). Specific water quality data and interpretations for the Arkansas River in southwest Kansas are given by Whittemore (2000).

2.3.2 Flow variations

River discharge varies significantly over short periods of time. Therefore, normally it is the practice to use average data when comparing river data to groundwater data. It is important to understand the flow variations in the Arkansas River and how this affects both river water chemistry and groundwater chemistry from recharge. The Arkansas River has minimal flow in it most of the year and at some points ceases to flow at all. This is most pronounced downstream of the ditch diversions during irrigation season. The smallest streamflow is during the early irrigation season in April and May and the largest streamflows are during June (Cain, 1985). Water diversions to irrigation ditches create nearly a no-flow condition during irrigation season downstream of Manzanola (Zielinski *et al.*, 1995). Pueblo and John Martin reservoirs along the river have regulated flow for about 50 years. Water in the Arkansas River that reaches Kansas has been regulated by John Martin Reservoir since 1946 (Dunlap *et al.*, 1985).

Figure 5 shows the flow variation in the Arkansas River at the Colorado-Kansas state line from several months before to after the fieldwork for this study. The high flows represent a combination of releases from the John Martin Reservoir and sub-regional precipitation events.

2.4 Hydrogeologic setting

2.4.1 History of water use and irrigation in area

Descriptions of the history of water use in the area help in understanding the source and development of the water quality and quantity problems in this area over time. The surface water and groundwaters in western Kansas have many uses, including municipal, industrial, domestic, and stock applications. Almost 95% of water pumped from the High

Plains aquifer is used for irrigation (Gutentag *et al.*, 1981). Most of the water is pumped from the High Plains aquifer and mostly from the Ogallala part of the aquifer in this area. Arkansas River water is diverted for irrigation use in Hamilton, Kearny, and Finney counties.

Irrigation water is important to eastern Colorado and westernmost Kansas because the mean annual precipitation is less than 20 inches. The history of irrigation in this area explains the demand placed on the aquifer system and the beginning of the current water problems in this area where industry and life are so dependent on the sometimes unstable water sources. Water development of the Arkansas River basin in Colorado includes the development of direct diversions, water storage, and groundwater, and importation of water by transit diversion (Abbott, 1985).

Early irrigation ditches on the flood plain were small and since they were on the floodplain required no special engineering to move the water. When the population increased and there were more farmers further from the river, water had to be moved up the terraces to irrigate (Abbott, 1985). In the 1860's, water priorities began to be established and diversion ditches were built in Colorado (Mueller *et al.*, 1991). The first reported appropriation was given in 1859 but water was used for irrigation earlier (Abbott, 1985). This led to large-scale irrigation in the late 1800's along the river in both Colorado and Kansas (Gutentag *et al.*, 1981). By the mid-1880's all the water in the river and tributaries were appropriated for average precipitation and therefore most rights after 1887 were merely flood rights (Abbott, 1985).

The irrigation diversions affected flow in the river and began some of the water level problems that are a concern today. Groundwater development began in earnest after the drought of the 1930's. By the late 1970's 170,000 wells pumped water to irrigate about 13 million acres from the High Plains aquifer (Gutentag *et al.*, 1981). Throughout this time

water managers realized that regulating river flows could help alleviate some of the problem. Times of high flow do not coincide with farming season and the groundwater system and soil moisture can only be recharged to a certain extent. Therefore reservoirs were built to regulate seasonal and annual fluctuations by storing excess and releasing it when needed (Mueller *et al.*, 1991; Abbott, 1985).

Disagreements over quantity and quality of Arkansas River flow entering Kansas from Colorado began in earnest as the population increased and appropriations affected the water in the river-aquifer system. Often there was little water in the river by the time it reached the state line and any water remaining in the river had high salinity due to evapotranspiration and consumptive use. There were various temporary agreements between Colorado and Kansas regarding these issues before 1948 and the final agreement, the Arkansas River Compact, was reached in December 1948 (Abbott, 1985).

2.4.2 Description of river basin and tributaries

Surface water in the Arkansas River originates in Colorado and flows across Kansas and into Oklahoma. The elevation of the Arkansas River at the Kansas-Colorado state line is 3,412 feet (Zielinski *et al.*, 1995). The Arkansas River and tributaries drain 25,410 square miles in Colorado and almost 3,000 square miles between the state line and Garden City (Mueller *et al.*, 1991). Tributaries in the Arkansas River basin in southwest Kansas are shown in Figure 6. There are five main irrigation ditches that divert water from the Arkansas River and substantially affect the flow in Kansas. These are the Amazon ditch, Great Eastern ditch, South Side ditch, Farmer's ditch, Garden City ditch (Dunlap *et al.*, 1985). A smaller diversion, the Frontier ditch, operates in western Hamilton County.

2.4.3 Climate

The mean annual temperature in the study area is 54°F (McLaughlin, 1943). In general the climate in this area is low to moderate precipitation, low humidity, and windy at times (Mueller *et al.*, 1991). Characteristic of the sub-humid to semiarid climate, the rate of evaporation exceeds the rate of precipitation (Smith, 1940; Waite, 1942). In southwestern Kansas the average annual rainfall ranges from about 22 inches in the eastern part (Ford County) to about 17 inches in the western portion (Smith, 1940). About ¾ of the rain falls during the growing season of April through October (Gutentag *et al.*, 1981).

2.4.4 Aquifer system and properties

General groundwater description

In the High Plains aquifer, water flows generally from west to east at a rate of about 1 foot/day (Gutentag *et al.*, 1981), except in areas where the easterly flow is slightly modified by transversing rivers and bedrock highs in this area (Berendsen and Hathaway, 1981). There is no significant local topography in the area affecting the flow of groundwater and creating local groundwater systems. The Rocky Mountains provide a regional groundwater divide, therefore causing the eastward flow of ground and surface water in this area as the land flattens out from the mountain front onto the broad flat plain. The Scott-Finney depression is to the north of the study area, outside the alluvial valley, and may slightly alter flow systems in that area.

Description of aquifer system

The saturated parts of the Pliocene Ogallala Formation, undifferentiated Pleistocene deposits, and the Quaternary alluvium form the main aquifer system in the study area. The

Pliocene and Pleistocene deposits are considered as one aquifer, the High Plains aquifer. Dunlap *et al.* (1985) describe five hydrologic units in the study area: the bedrock aquifer, lower unconsolidated aquifer, confining zone, upper aquifer, and valley aquifer. The aquifer is a multi-layered, heterogeneous, unconsolidated system. The bedrock aquifer is not part of this study and therefore not discussed. The lower and upper aquifers are part of the High Plains aquifer. The valley aquifer is the saturated recent alluvium.

The aquifer sediments vary in their ability to store and transmit water due to the heterogeneity of the deposits (Gutentag *et al.*, 1981). The shallow alluvial aquifer is the hydrostratigraphic unit correlating with the Quaternary Arkansas River alluvium (Figure 2). Parts of the alluvial and High Plains aquifers are lithologically similar and hydrologically connected to some degree in the study area. Groundwater is under confined or semi-confined conditions in the aquifer system (McGovern and Long, 1974).

Depth to water in the alluvium is about 10 feet and can be up to 200 feet in the High Plains aquifer south of the river (Spinazola and Dealy, 1983; Gutentag *et al.*, 1981). The shallow alluvial aquifer extends from near the surface to about 40 feet deep and in general the alluvium is a little deeper to the south of the river. Further descriptions of the distribution and geology of the aquifer system at the study area sites are in Chapter 4. Detailed discussions can also be found in Whittemore *et al.* (2000) and Young *et al.* (2000).

The occurrence and distribution of the High Plains aquifer sediments vary due to the mode of deposition described previously and post-depositional weathering. Also the source area of the High Plains aquifer materials is large and has various rock types, which results in a variable lithology (Berendsen & Hathaway, 1981). The thickness varies because the deposition was on an uneven topographic surface of the underlying bedrock (Smith, 1940; Fenneman, 1931). The areas of greatest thickness are in areas of bedrock basins and areas of

subsidence near the faults (Spinazola and Dealy, 1983). In general, the Ogallala is thinner in the east than in the west and the thickness varies with topography (Smith, 1940).

The High Plains aquifer is discontinuous laterally and horizontally over short distances in some parts of the study area. The maximum thickness of the Ogallala in the region of the river corridor is 360 feet in southern Finney County. The thickness of the Ogallala varies between 0 to 500 feet in Kearny County. This wide range is due to the increase of saturated thickness of about 200 feet over Bear Creek fault zone (Gutentag *et al.*, 1981).

The Arkansas River alluvium is an unconfined aquifer in the corridor. The thickness of this aquifer ranges because it often fills in erosional cuts in the High Plains aquifer and varies because river stage changes. The alluvium is about 15 feet thick in the eastern part of Ford County and about 40 feet thick in the central and western parts of the county. It is about 33-42 feet thick along the south part of the river in Ford County (Waite, 1942). In Kearny County thickness of the alluvium varies between about 10 and 70 feet and is usually about 40-50 feet (McLaughlin, 1943; Dunlap *et al.*, 1985). Near Deerfield, the base of the alluvium is at about 40 feet. Thickness is generally about 50-60 feet in Hamilton County (McLaughlin, 1943). Alluvial thickness varies much more in Gray and Ford counties and can exceed 50 feet in some areas (McLaughlin, 1943). In general, Smith (1940) reports that maximum thickness of the alluvium is about 60 feet in southwestern Kansas. In Kearny County, the river valley is up to about 4 miles wide at the widest point and in Finney County the river valley averages about 2 miles wide (Young, 1998). The river valley is about 1 to 3 miles wide in most parts of Gray and Ford counties.

Recharge and river-aquifer interactions

Knowledge of the recharge and discharge in the study area is relevant to the transportation of chemical constituents. Seepage from the river into the alluvial aquifer and precipitation are the main sources of recharge to the system (Dunlap *et al.*, 1985; Gutentag *et al.*, 1981). The precipitation in the area runs off into the Arkansas River, evaporates, transpires or seeps and recharges the aquifer system (Waite, 1942). Recharge occurs also from seepage from diversion canals and irrigation return flows (Waite, 1942; Latta, 1944; Gutentag *et al.*, 1981). Recharge into the High Plains aquifer is from seepage from the alluvium, and areal and irrigation recharge on land north and south of the alluvium.

Gutentag *et al.* (1981) estimates that recharge is 6 inches/year to the High Plains aquifer in the river valley in southwest Kansas. During high flow the river recharges the alluvium and during low flow the alluvium recharges the river (Gutentag *et al.*, 1981). In Colorado, 75% of the return flow to the river was groundwater return flow during the 1980's (Cain, 1985). Runoff from the land does not contribute much inflow to the river (Dunlap *et al.*, 1985). Zielinski *et al.*, (1995) noted that much of the shallow groundwater returns to the alluvial aquifer.

The interaction between the river and aquifer system in this area is important to understanding the geochemistry of the system and fate and transport of various constituents. The Tertiary and Quaternary units are hydrologically connected (Gutentag *et al.*, 1981). Water leaks from the alluvial aquifer to the underlying Ogallala between Lakin and Garden City (Mueller *et al.*, 1991). Significant flow is lost in the Arkansas River as it flows east from Colorado across the Bear Creek fault and crosses from less permeable Cretaceous sediments into the more permeable sediments of the Ogallala. The fault has displaced younger rocks downward on the east side. As the river crosses over the fault it flows over

less permeable Cretaceous sediments to younger, more permeable rocks of the Ogallala and water can seep into the ground. In Gray County there is fresher water from the south that seems to recharge the river and reduce the salinity of waters from the river valley (Berendsen and Hathaway, 1981).

Discharge from the corridor is through river outflow to the east, groundwater contribution to streams, withdrawal from wells, and evapotranspiration (Gutentag *et al.*, 1981; McLaughlin, 1943). However, water table declines in the High Plains aquifer since the 1970's have substantially reduced the amount of water discharged from the river corridor (Whittemore, 2000).

2.4.5. Groundwater quality

The quality of the groundwater in the area ranges between very fresh and saline. The saline river water is seeping into the groundwater. TDS values usually range from about 300 to 3,000 mg/L in the groundwater in the river corridor. Water from the High Plains aquifer is good enough for irrigation but often is not fresh enough for drinking water (Gutentag *et al.*, 1981). Where affected by river water seepage, the hardness of the water often exceeds 180 mg/L, which classifies it as very hard. Berendsen and Hathaway (1981) report that the groundwater is mainly of the bicarbonate type although sulfate is increasingly important in some areas. McGovern and Long (1974) classify the groundwater in the unconsolidated aquifer as ranging from calcium bicarbonate and calcium magnesium sulfate. Zielinski *et al.* (1997) recorded DO from 6-11 mg/L and Cain (1987) reported DO 7-12 mg/L in the same area. The groundwaters in the river valley are undersaturated with respect to gypsum and other soluble sulfate salts (i.e. thenardite and mirabilite) and quartz, calcite, dolomite, and

Fe^{3+} oxides (Zielinski *et al.*, 1997). Water quality specific to each site in the study area is discussed further in the chapter on multi-level observation well sites.

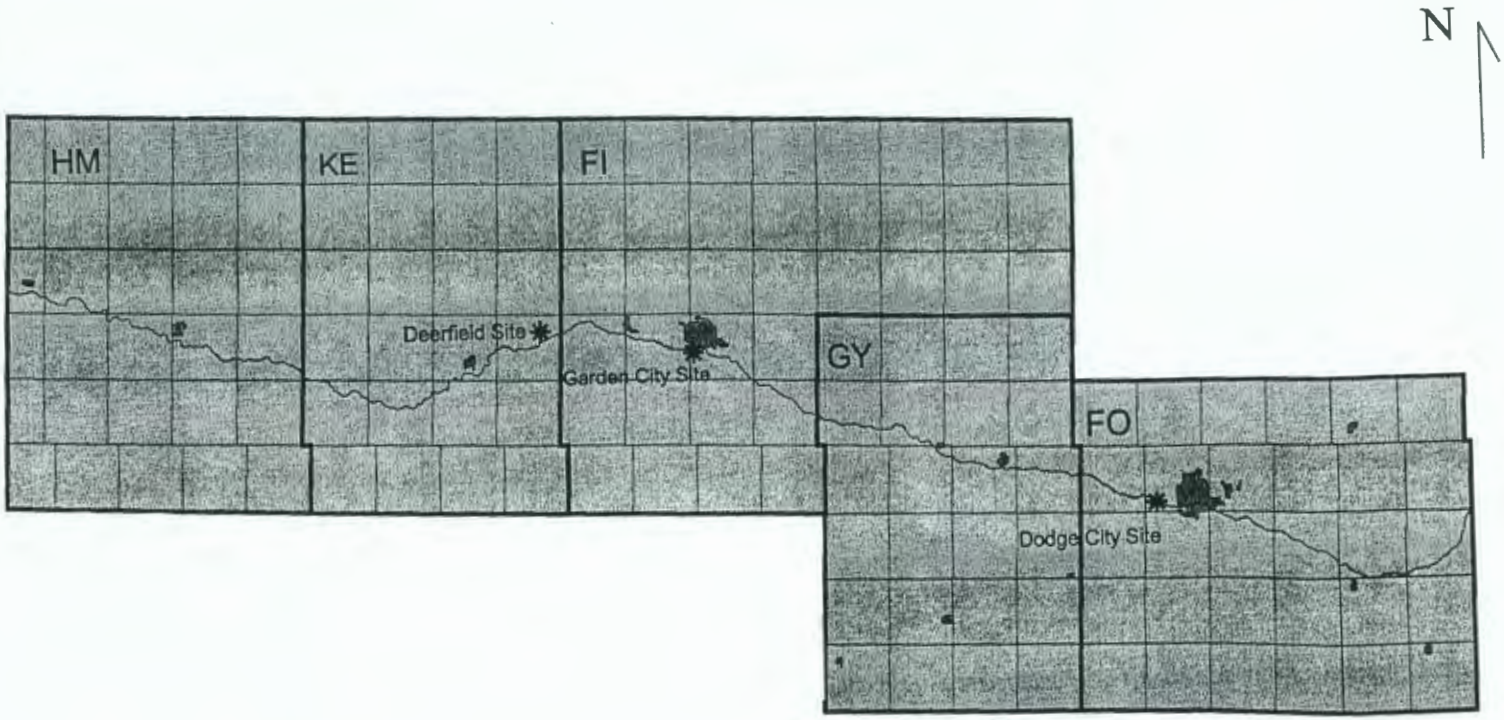


Figure 1. Map of the general study area in Hamilton, Kearny, Finney, Gray, and Ford counties showing the location of the three multi-level well sites and the Arkansas River.

System	Series	Stratigraphic Unit	Thickness (feet)	Hydrogeologic Unit
Quaternary	Pleistocene	Dune sand*	0-75	usually lies above water table and does not yield water to wells
		Loess*	0-45	
		Alluvium*	0-80	Alluvial Aquifer
		Undifferentiated deposits	0-550	High Plains Aquifer
Tertiary	Pliocene	Ogallala Formation	0-500	
Cretaceous	Upper Cretaceous	Niobrara Chalk	0-250	yields little to no water to wells
		Carlile Shale	0-330	
		Greenhorn Limestone	0-200	
		Graneros Shale	0-130	
	Lower Cretaceous	Undifferentiated rocks	0-450	Dakota Aquifer where present

Figure 2. Generalized stratigraphic column of the sediments in the Upper Arkansas River study area.
(Modified From Gutentag *et al*., 1981)

* These three units form the surface layer in different locales and do not lay above one another.
In general, loess exists to the north of the river, dune sand to the south, and alluvium along the river.

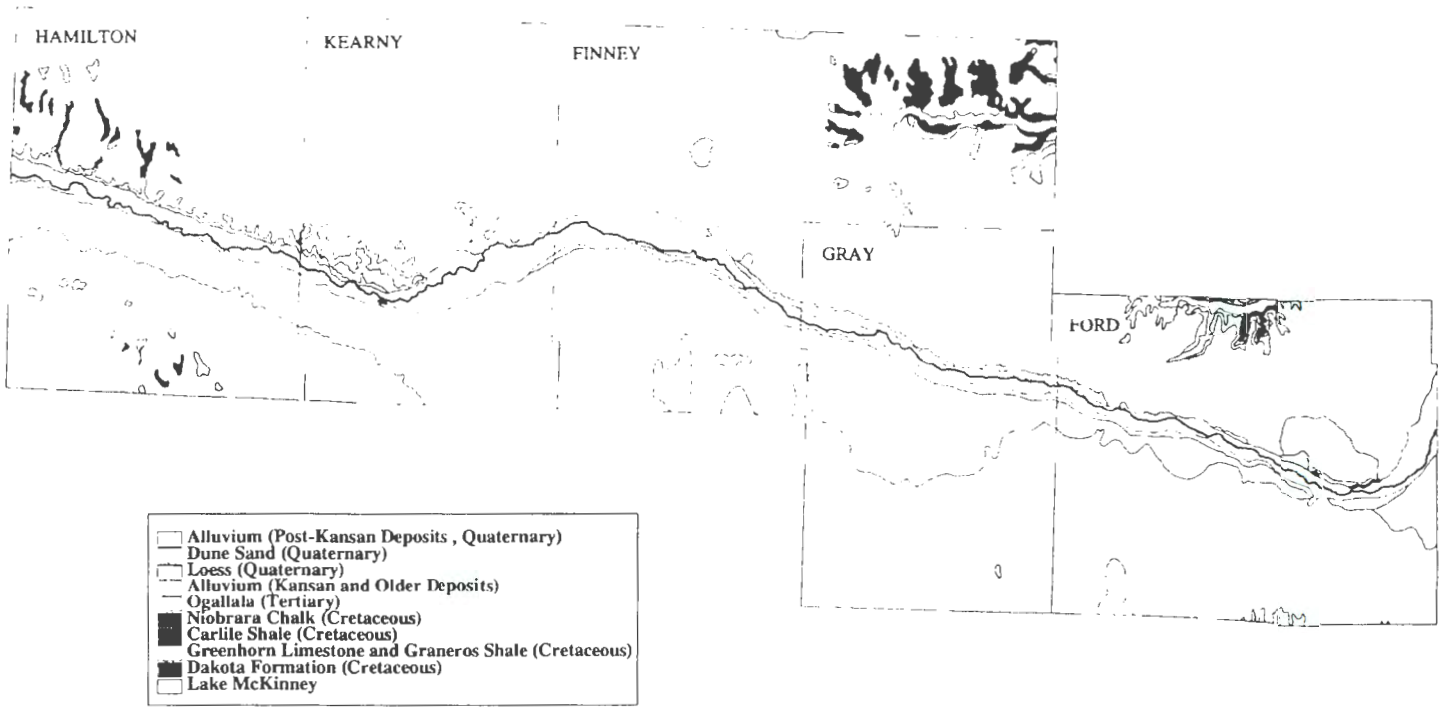


Figure 3. Map of the study area showing surficial geology features.

Table 1. Summary statistics of historical data for the Arkansas River in southwest Kansas compiled from USGS, KDHE, USEPA, and KGS databases. All chemical parameters are given in mg/L except SC and pH.

	Date	discharge (cfs)	SC (uS/cm)	TDS	DO	pH	Se	P
Minimum	11/17/1974	0.84	433	302	5.6	7	1	0
Maximum	11/18/1997	2950	6010	4460	15.2	8.9	35	1.4
Average		215	3634	3092	10	8	16	0.05
Std Deviation		389	1263	1069	2	0	8	0.17

	Ca	Mg	Na	K	Cl	SO_4	F	SiO_2
Minimum	49	13	29	5.5	9	6.9	0.1	5.1
Maximum	450	220	690	35.0	439	2640	1.2	26
Average	299	146	439	10.6	122	1349	0.8	14
Std Deviation	97	53	181	3.1	67	890	0.2	4

	HCO_3	V	Mn	Mo	Sr	NH_4	NO_3
Minimum	276	1	3	1	270	0	2.5
Maximum	344	100	250	19	8300	0.68	14
Average	315	10	43	6	5339	0.12	9
Std Deviation	29	19	46	3	1740	0.12	3

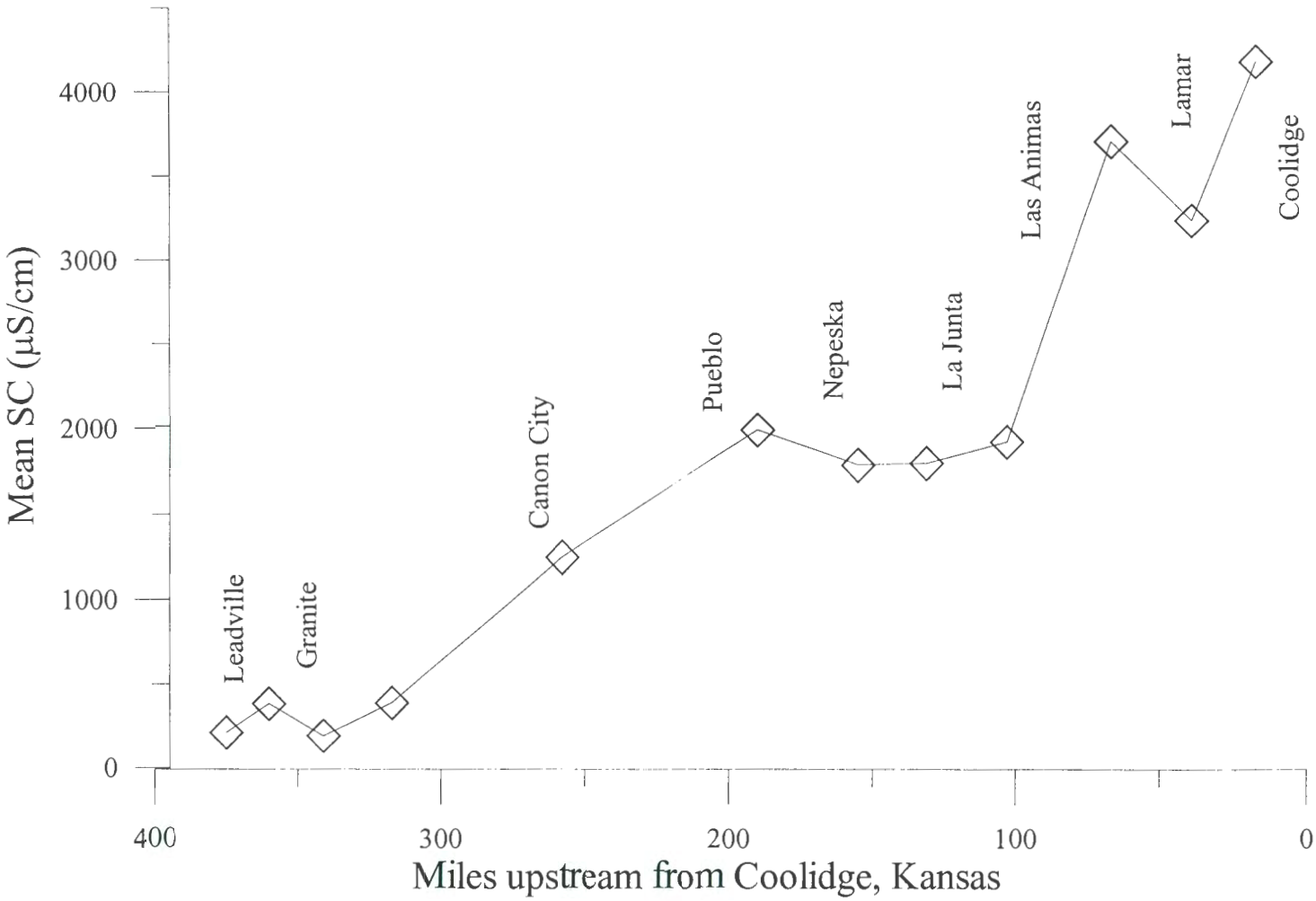


Figure 4. Mean specific conductance downstream in the Arkansas River from Leadville, Colorado to Coolidge, Kansas (From Cain, 1987).

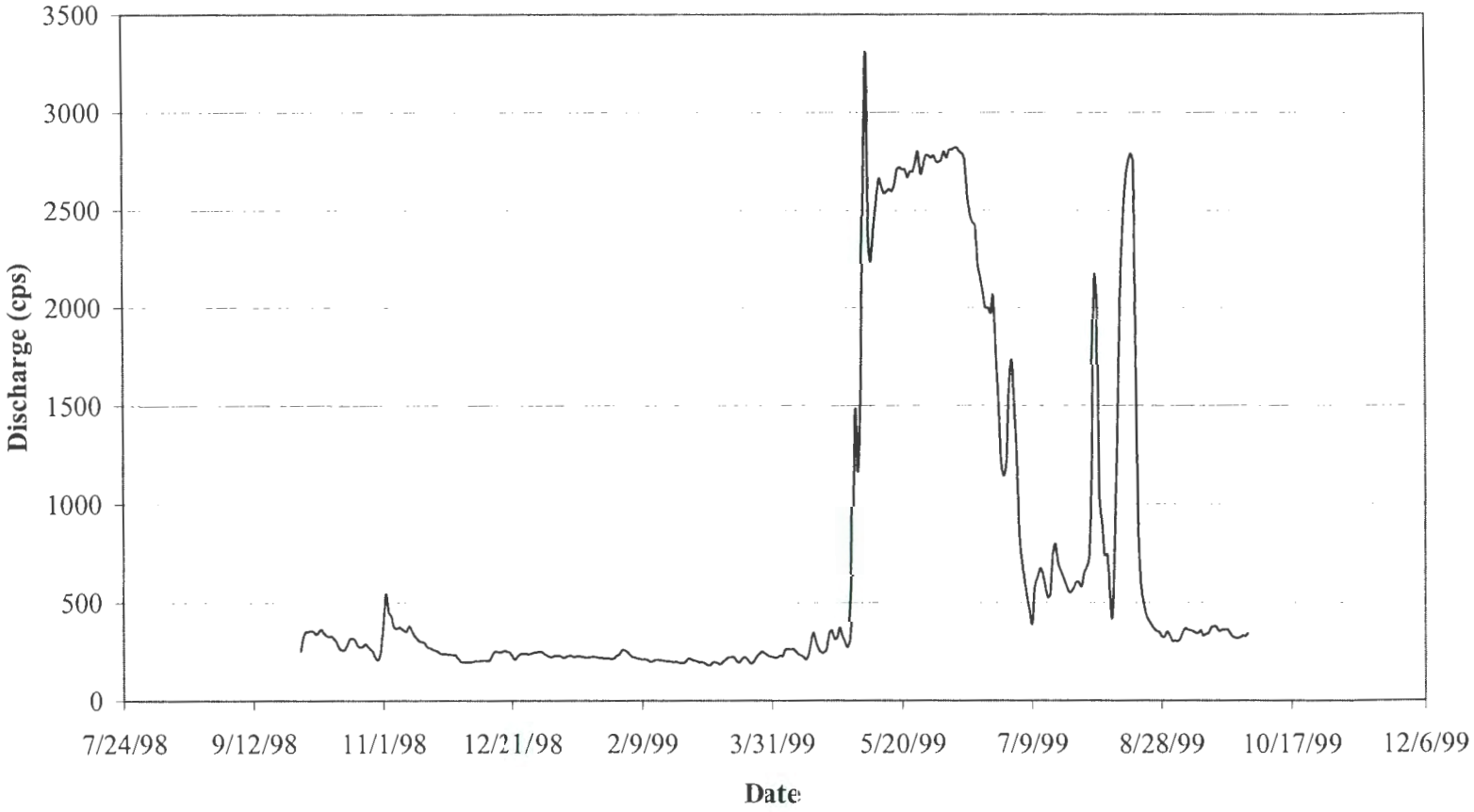


Figure 5. Discharge in the Arkansas River in Coolidge, Kansas near western edge of the study area over the time of this study. Data from USGS gaging station from 9/30/98 through 9/30/99.

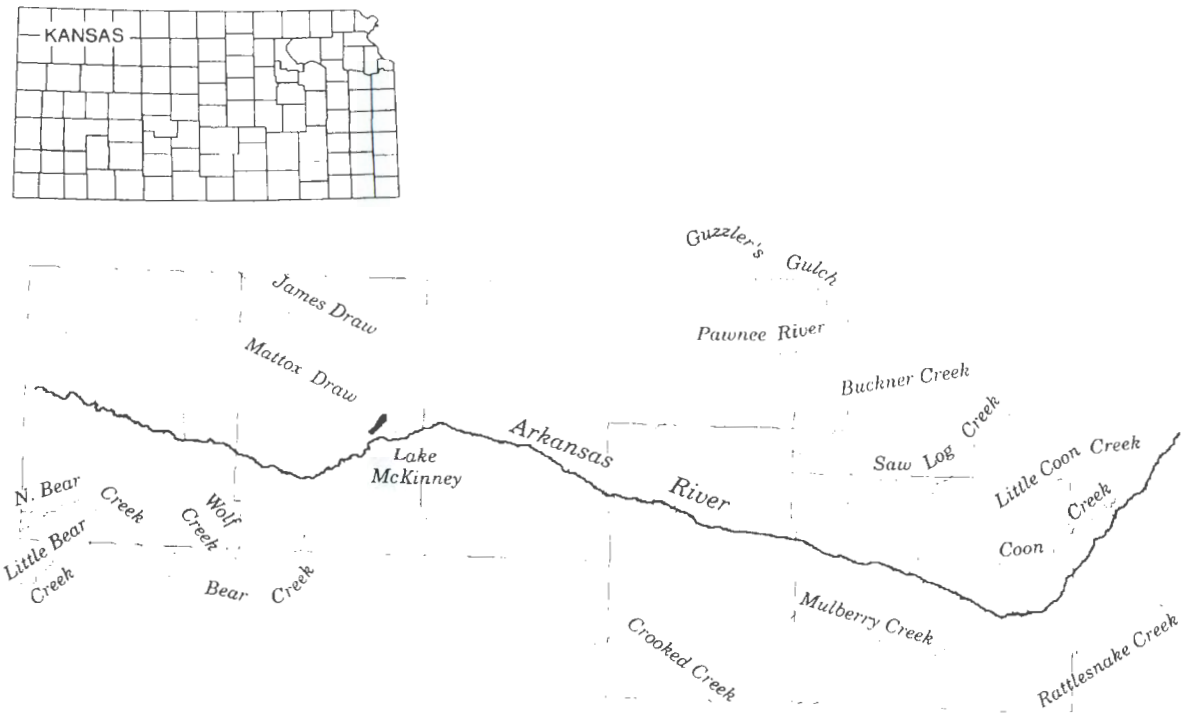


Figure 6. Map showing the Arkansas River and other drainages of southwestern Kansas.

Chapter 3 Aqueous Geochemistry of Selenium and Uranium

3.1 Previous Investigations

The geochemistry of Se and U has been studied thoroughly and many of these studies apply directly to this project. General overviews to site-specific studies help to understand the characteristics of Se and U behavior in natural systems and therefore the fate and transport mechanisms. Some geochemical studies have been done in this study area (Berendsen & Hathaway, 1981; Boon, 1989; Mueller *et al.*, 1991). Berendsen and Hathaway (1981) identify sources of U and concentrations present in the rocks and waters in the study area. The most important part of their study is their evaluation of U in volcanic ash. Evaluation of geochemical changes due to river-aquifer interaction is also important to this study (Jacobs *et al.*, 1988; Leinert *et al.*, 1994; Palmer and Edmond, 1993; Waber *et al.*, 1990).

Many summary studies have been done on Se geochemistry (McNeal and Balistrieri, 1989; Adriano, 1986; Allaway, 1969; Rosenfeld and Beath, 1964; Trelease and Beath, 1949; Chizhikov and Shchastlivyi, 1968; Elrashidi, *et al.*, 1989; Jacobs, 1989; Mayland *et al.*, 1989). The work by Trelease and Beath (1949) and Rosenfeld and Beath (1964) has not been updated but remains two of the most comprehensive studies on seleniferous environments and Se impacts on plants and wildlife. Both works detail areas of seleniferous soils and outcrops of different age rocks that support growth of seleniferous vegetation. Se is present in volcanic ash in the study area and these studies discuss the presence of these ash layers and mechanisms that led to Se concentrations. Langmuir (1997) and Drever (1997) provide general geochemical principles and Langmuir (1978) conducted a thorough study on U thermodynamics and geochemistry.

Se behavior, transport, and mobility have been studied in other environments around the country and these results can be directly compared to this project. Studies done at Kesterson Reservoir and San Joaquin Valley in California are important studies of Se aquatic systems (Benson *et al.*, 1991; Clifton and Gilliom, 1988; Deverel *et al.*, 1994; Fujii and Deverel, 1989; Tokunaga *et al.*, 1994; Presser, 1994). Other studies evaluating Se geochemistry in various environments have been done by Christensen (2000), Coleman and Delevaux (1957), Peterson *et al.*, (1991), and White and Dubrovsky (1994).

U geochemistry in various environments has been studied also but since Zielinski *et al.* (1995, 1997) and others have thoroughly studied U in this study area their studies were considered the most relevant. Bradford *et al.* (1989) looked at U in saline waters in California. The study by Hodge *et al.* (1996) involving the conservative behavior of U in groundwater of the Great Basin of the central United States assists in evaluation of the behavior of various constituents in this study.

Geochemical mechanisms that can lead to toxicity problems, such as bioaccumulation in plant and animal tissues and concentration in water, are important to study. Sorption is one of the most important controlling mechanisms for both Se and U. Sorption behavior with varying conditions and substrates has been studied by many researchers (Boult *et al.*, 1998; Dzombak and Morel, 1990; Howard, 1977; Hsi and Langmuir, 1985; Waite *et al.*, 1994). The Se cycle illustrates how this constituent becomes concentrated in the natural environment and the pathways to bioaccumulation in plants and wildlife (Haygarth, 1994; Lemly and Smith, 1987; Ohlendorf, 1989). Effects of this cycle and subsequent bioaccumulation are described by Underwood (1971), National Research Council (1976), and Wilbur (1983).

3.2 Introduction to Selenium and Uranium Geochemistry

Se and U are geochemically similar in many respects and have often been studied together (Bradford *et al.*, 1989; Henry *et al*, 1982). Historically Se and U have been linked because Se is often found near U ore deposits (Boon, 1989). They are found together in these environments because their redox chemistry is similar. In general both are mobile at more oxidized conditions and immobile under reducing conditions. They are both redox sensitive elements, i.e. the geochemistry of both in aqueous systems is dependent on the redox and pH conditions in the environment.

3.3 Selenium Geochemistry

Investigations of Se occurrence and contamination have become increasingly important over the past decade due to the elevated levels identified in the San Joaquin Valley and Kesterson Reservoir in California and the toxicity effects on wildlife that have been linked to these areas. The well-documented case of Se contamination in the Kesterson Reservoir and San Joaquin Valley of California has been extensively studied and is important to the understanding of Se transport and geochemistry. Irrigation affects the general character of the hydrologic system and geochemistry in the San Joaquin Valley.

The mechanisms leading to Se concentrations in the system are the same in the San Joaquin Valley and the Upper Arkansas River Valley. Evaporative concentration in the area and irrigation effects lead to the concentration of salinity and other constituents such as Se in the groundwater (Deverel *et al.*, 1994). The highest concentrations of Se are often found in surface waters and oxidized groundwaters, such as that in alluvial aquifers because in this environment Se is highly mobile and soluble (Deverel *et al.*, 1994, White *et al.*, 1991, Clifton and Gilliom, 1988). At Kesterson Reservoir the geochemical behavior of Se was linked to

the microbial activity. Se was reduced into a much less mobile form and therefore movement in the system was severely retarded (White *et al.*, 1991). Microbial activity is most likely not a factor in this study area, but the study by White *et al.* (1991) found that it was an important mitigating factor. The sources of Se and pathways of transport in the San Joaquin Valley and Kesterson Valley are very similar to the Upper Arkansas Basin. The problems in California are much more significant in an environmental and public health context, but understanding of the setting is of future value if the problem escalates in Kansas (Presser, 1994).

Recently Se has become a constituent of interest throughout the state. A study by Christensen (2000) investigates the increasing trends in Se in reservoirs in the Solomon River basin in Kansas and Se in irrigation return flows. The potential problem of Se contamination in the Arkansas River has been of recent interest due to examination of surface-water quality by the KDHE. Nearly 50 years ago, Trelease and Beath (1949) noted the toxicity effects of Se and bioaccumulation in plants leading to death of livestock. The interest lately is due to the possibility that consumptive use and irrigation return flows can concentrate Se in natural systems.

3.3.1 Chemical properties of selenium

The study of Se is important because it is one of the most widely distributed elements in the environment. It can concentrate in natural systems to potentially toxic levels, although most natural waters have low Se concentrations (McNeal and Balistrieri, 1989; Presser, 1949; Elrashidi *et al.*, 1989). Se, a nonmetallic element, has an atomic mass of 78.96, an atomic number of 34, and chemical properties that fall between those of metals and nonmetals (Haygarth, 1994; Lemly and Smith, 1987). The six naturally occurring stable isotopes of Se and their natural abundances are (McNeal and Balistrieri, 1989):

^{74}Se (0.87%)	^{78}Se (23.52%)
^{76}Se (9.02%)	^{80}Se (49.82%)
^{77}Se (7.58%)	^{82}Se (9.19%)

The most environmentally important isotopes are ^{77}Se, ^{78}Se, and ^{82}Se, which are the only ones commonly measured. Se chemistry is analogous to that of sulfur and can be found in the same oxidation states and environments in nature (White *et al.*, 1991). Se can substitute easily for S in sulfide minerals such as pyrite in maximum concentrations of 300 mg/kg (ppm) (Presser, 1949). There are five oxidation states of Se: -2, 0, 2, 4, 6 (Chizhikov and Shchastlivyi, 1968).

3.3.2 Sources, Occurrence, and Distribution

Natural and anthropogenic sources of selenium

There are many possible sources for Se in natural systems throughout the world such as volcanic activity, anthropogenic sources, biological interactions, weathering and transport by water (McNeal and Balistrieri, 1989). The Se is usually associated with the clay content in rocks so there are often higher concentrations in shales than in limestones and sandstones (McNeal and Balistrieri, 1989; Mayland *et al.*, 1989). Loamy and clayey soils have a higher content of Se than sandy soils in general (Ihnat, 1989). Drainage from Cretaceous and Tertiary marine sedimentary rocks has been identified as the source of Se in the San Joaquin Valley (Presser, 1949). The elevated Se levels in Kesterson Reservoir are due to runoff and leaching from agricultural soils with elevated amounts of Se and other constituents (Benson *et al.*, 1991). Nicolli *et al.* (1989) identified loess as the most important contamination source in the groundwaters in the Pampa province of Cordoba, Argentina. Loess is an important

surficial geology unit to the north of the river in southwestern Kansas and, therefore, could be an input for Se into the system.

The most important source of Se in Kansas is runoff from Cretaceous marine shales that have high Se concentrations, such as the Niobrara Chalk and Pierre Shale (Christensen, 2000; Trelease and Beath, 1949). The Niobrara Chalk has some of the highest Se concentrations known with a maximum of 103 mg/kg. Shales in general can have up to 45 mg/kg Se. The Se in the Niobrara is concentrated mostly in the upper Smoky Hill Chalk member due to volcanic activity during time of deposition (Trelease and Beath, 1949).

Another important source that has been studied and should be considered in agricultural areas like southwestern Kansas is the application of phosphate fertilizer. Se can be enriched in phosphate rock, the parent material for phosphate fertilizer, and impurities like this remain with the fertilizer (Haygarth, 1994; McNeal and Balistrieri, 1989). Phosphate fertilizer is applied to the fields in the Arkansas River basin in southeastern Colorado and southwestern Kansas (Zielinski *et al.*, 1997). Fertilizer application and other anthropogenic inputs have increased and altered the Se content in both surface and groundwaters (Mayland *et al.*, 1989). Anthropogenic sources such as mobilization as a by-product of industrial activity account for releases of 76,000-88,000 ton per year globally (Haygarth, 1994).

Occurrence and typical concentrations of selenium

Typical concentrations vary widely as a function of soil type, rock type, water, and location. These concentrations vary from less than 1 mg/kg to 300 mg/kg in western seleniferous soils and rocks (Table 2). Trelease and Beath (1949) note that this variance is due to the mode of deposition in this area. Soils or formations derived primarily from other formations high in Se will retain that characteristic. In this study area, the Tertiary Ogallala

was derived from rocks in the Rocky Mountain region, in part from seleniferous Cretaceous rocks, and was deposited under diverse conditions by meandering streams. Se content can range greatly over short distances due to variation in materials and concentration of Se in secondary features such as concretions. Concentration in soils ranges because the content of parent material varies and because some materials such as clay can hold more Se.

Concentrations found in different waters around the world range from less than 1 μg/L in Riverton Basin Wyoming to almost 500 μg/L in some unfiltered water samples from Argentina (Table 3). Maximum concentrations varied between 250 and 400 μg/L in Kesterson Reservoir (White *et al.*, 1991). This shows the possible variation and ability of Se to concentrate to extremely high levels in natural waters.

The drinking water and other standards defined for Se are given in Table 4. The state of Kansas has identified toxicity limits in surface waters for the protection of aquatic wildlife. The wildlife criterion refers to a 4-day average no more than once every 3 years. The one-hour average cannot exceed 20 μg/L more than once every 3 years (Clifton and Gilliom, 1988). These wildlife limits have been set because concentrations higher than these can cause disease, deformity, or death.

Total Se in the environment is a function of the parent material, fertilizer and other anthropogenic inputs minus the amount removed by crops, leached by water and volatized (Haygarth, 1994). Normally Se in natural groundwaters systems is expected to be low due to various geochemical controls that limit mobility (Hem, 1985). Se concentrations show fluctuations due to seasonal effects of irrigation and evaporation (White *et al.*, 1991).

Source and concentrations of selenium in the Arkansas River Valley

The natural and anthropogenic sources are similar in the study area for both Se and U. The main natural source has been identified as runoff from Cretaceous marine shales primarily in Colorado. Se is input to the river in Colorado and begins to be concentrated due to evapotranspiration and leaching of salts and constituents by irrigation. Local Se might also be added due to runoff from seleniferous soils and the Niobrara Chalk in the drainage area of the Arkansas River (Trelease and Beath, 1949). There is elevated Se in the Pierre Shale and the Niobrara Chalk (Mueller *et al.*, 1991; Christensen, 2000). There are outcrops of the Niobrara Chalk in the study area, in northeastern Finney County. Additionally, there are other sources that possibly add small amounts to the waters locally.

Trelease and Beath (1949) identified areas of seleniferous soils in this part of the country and specifically within the river basin north of the study area (Figure 7). They noted than 80% of seleniferous plant specimens have been collected on Cretaceous rocks from the western area of the country. Locally Se and U can be contributed to the water from volcanic ash beds such as those commonly found in Hamilton County (Berendsen and Hathaway, 1981; Smith, 1940; Waite, 1942; McLaughlin, 1943; Merriam, 1963). Se is enriched in volcanic ash beds in southwest Kansas because Se is a constituent of magma and therefore was emitted during the active volcanism before and during the deposition of Cretaceous marine shales. Soils and other formations, such as the Tertiary Ogallala formation, derived from these shales can also be high in Se (Trelease and Beath, 1949).

Furthermore, Se is concentrated in the system by natural processes that could possibly lead to toxic or problematic elevated concentrations. Se is concentrated in the river by evapotranspiration and concentration in irrigation return flows and in the groundwater by recharge of these saline waters (Abbott, 1985; Whittemore, 1995). Lowered water tables in

the High Plains aquifer from increased pumping have allowed the saline waters to enter the subsurface (Whittemore, 2000). Natural levels of many constituents are concentrated as the water is used and reused for irrigation. Se can also be enriched in phosphate fertilizer, which is used on agricultural fields in the area. It is possible that a small amount of Se is contributed in some places from irrigation return flows off fields where phosphate fertilizer is used, but this has not been proven.

Se concentrations can be compared to natural soil and background concentrations to evaluate the extent of the problem. The baseline concentration has been identified in the western United States as 0.23 mg/kg. The average in the Arkansas River as it passes over the state line from Colorado to Kansas near Coolidge was 19 μg/L for 1975-1987. Upstream in the middle Arkansas River basin of Colorado, Se concentrations were found up to 52 μg/L in a tributary to the river (Mueller *et al.*, 1991). The median Se concentration in the Arkansas River as it passes the state line exceeds the chronic toxicity standard for aquatic wildlife and is close to the acute standard described above.

3.3.3 Aqueous geochemistry

Behavior and geochemistry of selenium

Se exists in four oxidation states, II, 0, IV, and VI. These states are commonly in the form of selenide (Se^{-2}) in metals, elemental Se (Se^{0}), selenite (SeO_3^{-2}), and selenate (SeO_4^{-2}) (McNeal and Balistrieri, 1989; Haygarth, 1994). Se is a redox sensitive element and, therefore the relative stability of the oxidation states depend on the environmental conditions present. In the two higher oxidation states, Se(IV) and Se(VI), it occurs in nature as aqueous species or solid compounds (White & Dubrovsky, 1994). Concentration, speciation, and association of Se depend primarily on pH and redox conditions, solubility, and complexing

ability of ligands (McNeal and Balistrieri, 1989). To evaluate the distribution and transportation, one must understand Se speciation and redox chemistry (White *et al.*, 1991). In general, Se is mobile in oxidizing, high pH environments and immobile in reducing, low-neutral pH environments (Ihnat, 1989). Figure 8 illustrates the speciation of Se. This project concentrates on a natural system with mildly oxidizing to oxidizing conditions and therefore only consideration of Se(IV) and Se(VI) are important. The mobility, solubility, and sorption are the most important characteristics of Se(IV) and Se(VI) to this study.

Selenite, the +4 oxidation state, is common under mildly oxidizing conditions. Selenite phases are usually less soluble than the corresponding selenate phases. Selenite is very toxic, but due to this low solubility and mobility, not very dangerous to plants (Ohlendorf, 1989). Selenite has a strong affinity for sorption, which is a function of pH, composition, Se(IV) concentration, and concentration of competing anions such as phosphate (McNeal and Balistrieri, 1989; Haygarth, 1994; Robberecht and Van Grieken, 1982). In soils of moderate redox or humid environments, biselenite ($HSeO_3$-) is the major species at lower pH and SeO_3^{2-} at high pH. At very low pH, Se(IV) is free in solution as H_2SeO_3 (Howard, 1977).

Selenate (Se^{+6}) is the dominant form of Se that forms in well-oxidized, high pH environments and is very mobile (Haygarth, 1994; McNeal and Balistrieri, 1989). Under these conditions it occurs as SeO_4^{2-} (Tokunaga *et al.*, 1994). Due to the mobility and solubility it is easily leached from soil and readily available to plants (Christensen, Ohlendorf, 1989; White *et al.*, 1991), in part because it does not form stable complexes (Robberecht and Van Grieken, 1982). The stability of Se(VI) causes the kinetics of the reactions converting Se(VI) to less mobile forms to be slow, which can be a problem in natural environments because this highly mobile form can be transported easily (McNeal and

Balistrieri, 1989). In moderately oxidizing conditions (Eh ~150-375) selenite stability is dominated by $CaSeO_3^0$ and $HSeO^-$ (White *et al.*, 1991). Selenate is dominant in semiarid areas in well-aerated, alkaline soils (Elrashidi *et al.*, 1989). In soils from arid regions or high redox, selenate is the major species and adsorption controls Se concentration in the soil (Elrashidi *et al.*, 1989). Selenate is the most abundant form of Se in surface water systems. For example, between 54% and 97% of the Se is present as selenate in the San Joaquin River in California (Clifton and Gilliom, 1988).

The relationship between the geochemistry of iron (Fe) and Se is as important to understand as the analogous relationship between Se and S because in some environments $FeSe_2$ can control the solubility of Se. Se geochemistry is controlled by the geochemistry of Fe in some cases since they are associated in both reducing and oxidizing environments (Mayland *et al.*, 1989; Howard, 1977). Se is associated with fine-grained pyrite in sediments at the surface. When ferric hydroxide is present Se(0) can be oxidized at lower Eh (Howard, 1977). When Fe is present, Se can easily be coprecipitated with pyrite or may form ferroselite ($FeSe_2$) (Hem, 1985).

Selenium adsorption

Adsorption of Se onto various particles in aqueous systems is an important controlling mechanism in some environments and under some conditions. Selenite (SeO_3^{-2}) adsorbs much more strongly to soil and other surfaces than does selenate (McNeal and Balistrieri, 1989). The relative amount of SeO_3^{-2} in groundwater decreases relative to that of surface water because it adsorbs easier in groundwater (White *et al.*, 1991). Since selenate (SeO_4^{2-}) is not as strongly adsorbed as selenite it is easily leached from soils and transported to groundwater and most readily taken up by plants (McNeal and Balistrieri, 1989).

Se commonly sorbs onto clay minerals and metal oxides (Tan *et al.*, 1994). Tan *et al.* (1994) found that metal oxides have a much higher ability to adsorb Se than clay minerals, and Howard (1977) reported that ferric oxyhydroxides, i.e. goethite, hematite, are the most important to Se adsorption. In natural systems adsorption by ferric hydroxide often determines Se concentration (Henry *et al.*, 1982). Selenites have affinity for Fe, Al and Mn hydroxides (Robberecht and Van Grieken, 1982).

Conditions such as the pH and other constituent concentrations can affect Se adsorption. At neutral pH, Se(VI) adsorbs only on weak clays, iron oxides, and soil constituents (White *et al.*, 1991). Adsorption of Se (IV) should decrease slightly with an increase in pH up to pH 8 and then decrease sharply above 8 (Figure 9) (Henry *et al.*, 1982). This pH dependence can be explained by the release of H+ prior to ligand exchange due to the required protonation of the adsorption site (Tokunaga *et al.*, 1994).

Boult *et al.* (1998) describes Se(IV) and U(VI) sorption trends on goethite and bentonite with pH, carbonate concentration, and temperature. They found that Se and U adsorb onto goethite and bentonite differently, under different pH conditions, and are affected differently but significantly by the amount of carbonate present. Sorption of Se(IV) on bentonite is important only below pH 7. pH is the most important controlling factor for sorption of Se(IV) on geothite; there is strong sorption below pH 8 and a sharp decrease in the tendency of Se to sorb above pH 8. Bentonite sorbs between 0-20% of Se(IV) and sorption becomes completely insignificant above pH 7. Se(IV) sorption on geothite is strongly pH dependent and decreases sharply above pH 8 (Boult *et al.*, 1998). Sorption is suppressed by competitive effects with SO_4, which is a negative effect since sorption removes Se from groundwater (White *et al.*, 1991).

Se occurs in oxygenated aquifer environments with hydrous Fe oxides. This association is due to strong adsorption of selenite ions on Fe oxide surfaces, which can remove between 95-99% of Se(IV) from solution at below neutral pH. The amount adsorbed depends on the surface character of the ferric oxide. Adsorption to hydrated ferric oxides immobilizes Se(IV) in waters with low to medium pH and increases the Eh range for the stability of Se(IV). In oxidizing waters Se(IV) in the form of $HSeO_3^-$ and SeO_3^{-2} is strongly adsorbed by ferric oxides at pH 2-8. Above pH 8 adsorption decreases until it is completely desorbed by pH 11 because ferric oxides dissociate at high pH. Adsorption lowers Se(IV) concentration in water, which causes an increase in the Eh range over which Se(IV) can be the predominant stable species and therefore a higher Eh is required to oxidize adsorbed Se(IV) (Howard, 1977). This dependence on environmental and chemical conditions is important to consider when evaluating the fate and transport of Se.

3.3.4 Toxicity

The most important reason to study and understand the geochemical behavior of Se in natural systems is the potential toxicity effects for wildlife and humans. The Se cycle showing paths of possible transport in the environment that can lead to bioaccumulation in plants and animal tissue is shown in Figure 10. Concentration of Se due to leaching and transport of indigenous Se has caused problems in many areas of the United States such as the San Joaquin Valley and Kesterson Reservoir (White & Dubrovsky, 1994; Tokunaga *et al.*, 1994; Benson *et al.*, 1991). Se toxicity problems are linked partly to Se mobility (White *et al.*, 1991) because the free metal ion and Se(VI), the most mobile form, are the most toxic to aquatic life (Robberecht and Van Grieken, 1982).

Se is both beneficial and toxic to humans, wildlife, and plant life (McNeal and Balistrieri, 1989). There is a delicate balance between too much and not enough Se intake. Animals require 0.05 to 0.1 mg/kg Se intake but toxicity begins when intake levels exceed 5 to 15 mg/kg Se (Mayland *et al.*, 1989). Se poisoning is due to dietary intake and causes myriad health effects in humans from headache to diarrhea, decrease of blood pressure, and paralysis of the nervous system (Chizhikov and Shchastlivyi, 1968; Haygarth, 1994). High Se content in groundwater has also been linked to carcinogenic effects (Nicolli *et al.*, 1989), but Se also prevents some types of chemically caused cancer in animals (Robberecht and Van Grieken, 1982).

Epidemics of two diseases in China, Keshan disease and Kaschin-Beck disease are found in low Se eco-environments. The study by Tan *et al.* (1994) shows that these diseases are related to Se deficiency in the environment. Human intake is between 20 and 220 μg per day with an average of 60 μg per day (Underwood, 1971). An average daily intake of 2 liters of water with 10 μg/L Se would be most of the necessary daily total intake (Robberecht and Van Grieken, 1982).

When disease and malformity in waterfowl at Kesterson Reservoir in California was linked to Se contamination at the reservoir, awareness of this problem was brought to the forefront in science. Se is a necessary part of the animal diet but is toxic to fish and wildlife when it bioaccumulates (Clifton and Gilliom, 1988). High Se in the water at the reservoir was linked to embryonic deformity in waterfowl (Benson *et al.*, 1991). Se toxicity results in animals when intake is more than 4 mg/kg, but it is also an essential part of animal nutrition (McNeal and Balistrieri, 1989). Se concentration greater than 30 mg/kg dry weight in aquatic bird livers will likely impair reproduction (Peterson *et al.*, 1991). Se affects many organs in

an animal such as liver, kidneys, spleen, heart, pancreas, lungs, hair, blood, muscles, and bones (Chizhikov and Shchastlivyi, 1968).

In the 1930s, some sickness in animals in the western United States was caused by high Se intake and therefore studies of Se began in earnest. Trelease and Beath (1949), Rosenfeld and Beath (1964), and Adriano (1968) were among the first to report these links. Later they established that although high intake causes disease, there is a minimum Se intake required for health reasons (Hem, 1985). Over the last decade there has been increasing concern over high Se areas as potential toxicity effects to humans and wildlife become clearer. Seleniferous soils occur widely distributed throughout the country including on Cretaceous outcrops in eastern Colorado and western Kansas (Figure 7). Seleniferous vegetation occurs on these soils just north of the study area and in southeastern Colorado along the Arkansas River basin (Mayland *et al.*, 1989). In western Kansas, Se seriously affects about 400 square miles of soils, especially in soils on the Niobrara Chalk and Pierre Shale (Trelease and Beath, 1949).

Se accumulates differently in different plants and animals (McNeal and Balistrieri, 1989). Se indicator plants require Se to develop and indicate Se-rich soil (Trelease and Beath, 1949). The amount of Se accumulation in plants depends on the type of plant, speciation of Se, pH, salinity, and $CaCO_3$ content of soil (McNeal and Balistrieri, 1989). In areas of Se-rich soils, plants that can accumulate Se easily can contain hundreds to thousands mg/kg Se (Mayland *et al.*, 1989). Toxic seleniferous soils are often in regions of low rainfall, which explains why Se toxicity problems have been reported in the western United States since 1856 (Boon, 1989; Elrashidi *et al.*, 1989). Se concentrations greater than 4 mg/kg in sediment have the potential to bioaccumulate and cause toxicity problems (Christensen, 2000).

3.4 Uranium Geochemistry

3.4.1 Chemical properties of uranium

U, the most abundant actinide element, has an atomic mass of 238.0289 and an atomic number of 92 (Langmuir, 1997). The behavior and thermodynamics of U have been extensively studied (Langmuir, 1978; Abdelouas *et al.*, 1998; Bradford *et al.*, 1989; Hodge *et al.*, 1996; Klinkhammer and Palmer, 1991). U follows thermodynamically predicted behavior more closely than Se but this may simply be because more is known, studied, and understood about U and its complexing behavior (Henry *et al.*, 1982). There are three important oxidation states of U; U(IV), U(V), and U(VI). U(IV), the uranous ion, and U(VI), the uranyl ion, are the most important in the environment (Langmuir, 1997).

3.4.2 Sources, Occurrence, and Distribution

Natural and anthropogenic sources of uranium

Like Se, the most common sources of U are geologic and anthropogenic materials. Zielinski *et al.* (1995) defined the sources for U in the Arkansas River basin of Colorado as natural leaching of U bearing rocks, leaching by irrigation water, and evaporative concentration. Berendsen and Hathaway (1981) concluded that volcanic ash is the source of U in the groundwater in the Pliocene-Pleistocene sediments in southwestern Kansas. Other studies support this finding near the U deposits in Texas (Henry *et al.*, 1982; Galloway & Kaiser, 1980). Some of the dissolved U in the Arkansas River specifically is due to leaching from U-rich rocks and soils near the source of the river in Colorado (Berendsen & Hathaway, 1981). Mueller *et al.* (1991) noted that both Se and U are elevated due to runoff from marine shales. Anthropogenic sources, most importantly fertilizer application, are an additional

source of U into waters (Palmer and Edmond, 1993). Like Se, phosphate fertilizer has U originating from U enrichment in the phosphate source rocks (Zielinski *et al.*, 1995).

Occurrence and typical concentrations of uranium

Typical concentrations of U in some possible source materials are 2.5 mg/kg in western soils up to 200 mg/kg in phosphate fertilizer (Table 5). Evaporative concentration of water with natural concentrations of U present allows U in waters to reach elevated levels. In general, dissolved U in average surface waters in the western United States is much higher than the average concentration in the country (Table 6). Previously the USEPA had proposed 20 μg/L as the drinking water standard for U but this standard is currently under evaluation and may be revised. In any case higher concentrations of U could pose health and safety risks for wildlife, plants, and humans.

Many researchers discussed different factors related to occurrence of U in the natural environment. Nicolli *et al.* (1989) found the maximum U concentrations were in waters dominated by alkali metals. There is an association between radiogenic Sr and high U concentrations in rocks. There is also a tendency for rivers in shield terrain with high U to have high Rb. Some floodplain rivers have the highest U concentrations measured (Palmer and Edmond, 1993). Leinert *et al.* (1994) showed that U concentrations varied seasonally with a maximum in the summer. Groundwater often holds more U than adjacent streams due to U-soil interactions (Langmuir, 1978).

Source and concentrations of uranium in the Arkansas River Valley

The natural source for U in the study area is probably mainly runoff from Cretaceous marine shales in Colorado (Trelease and Beath, 1949; Zielinski *et al.*, 1995, 1997). Elevated

levels of U in the area have been identified in the Pierre Shale (Mueller *et al.*, 1991). U is also concentrated in the system by evapotranspiration, concentration in irrigation return flows, and by recharge of these saline waters (Abbott, 1985; Whittemore, 1995; Zielinski *et al.*, 1995). U can be enriched in phosphate fertilizer, but Zielinski *et al.* (1997) concluded that most of the U in this area appears to be natural, not fertilizer derived.

A high baseline concentration for U in the western United States (2.5 mg/kg) helps to explain the high concentrations in the water. Zielinski *et al.* (1995) found that groundwater in contact with Cretaceous rocks in the study area is about 18 μg/L. In U-rich areas, such as the Arkansas River basin in Colorado, groundwater concentrations can be up to 120 μg/L. In general, waters in the Arkansas River Valley usually have U concentrations greater than 20 μg/L (Berendsen & Hathaway, 1981). Dissolved U in the Arkansas River at the headwaters in Colorado is about 4 μg/L and 40 μg/L near Lamar, Colorado, just west of the state line with Kansas (Zielinski *et al.*, 1995)

3.4.3 Aqueous Geochemistry

Behavior and geochemistry of uranium

Some work has been done concerning the conservative behavior of U. Hodge *et al.* (1996) concluded that U was acting conservatively in oxygenated groundwaters of the Great Basin based on the covariance of U with Cl, Na, and SO_4. In seawater U exhibits conservative behavior which is shown by the covariance with salinity throughout the oxidized water column (Hodge *et al.*, 1996; Klinkhammer and Palmer, 1991). Osmond and Cowart (1982) found that U behaves conservatively in oxic seawater and Hodge *et al.* (1996) added that it also does in oxygenated groundwater. This behavior is due to the formation of stable carbonate complexes (Klinkhammer and Palmer, 1991).

Under natural groundwater pH conditions, U is relatively insoluble in reducing conditions and soluble under oxidizing conditions. In an oxidizing environment, the solubility of U persists at all pH. This is because soluble complexes of U are generally more stable at higher Eh (i.e. in oxidizing environments) than at lower Eh for a wide range of pH values. Consideration of the U-O-H_2O system presents a simplified interpretation of the possible speciation and the integral redox effects. Brookins (1988) illustrates the predominant species in an Eh-pH diagram (Figure 11). At intermediate to high Eh and low to neutral pH (2-7). the UO_2^{2+} species is the predominant species. At lower Eh and higher pH the solid oxides U_3O_8 and UO_2 are stable. At higher pH and a wide range of Eh, the hydroxide complex, $(UO_2)_3(OH)_5^+$ is common (Drever, 1997).

There are many factors affecting the behavior of U in natural systems. The aqueous speciation of U(VI) is a function of pH and redox (Langmuir, 1997). Other factors that determine concentrations are related to rocks, water, and dissolved constituents in the water. U content in source rocks and proximity of water to U rich rocks and minerals are important controlling factors for contributing dissolved U to water. The presence of U in groundwater systems also depends on the hydraulic connection to fresher aquifers, influence of evapotranspiration, concentration of ligands, and presence of minerals and sediment that can sorb U (McNeal and Balistrieri, 1989).

The uranous ion, U(IV), is dominant at low Eh conditions (Hodge *et al.*, 1996) and is present as UO_2 (Langmuir, 1997). U(IV) is often at very low concentrations in reducing waters due to the low solubilities of the U(IV) solids (Langmuir, 1978, 1997; Hem 1985). Therefore the reduction of U-rich water causes precipitation of U(IV) minerals (Henry *et al.*, 1982). U(IV) is less stable than U(VI) in more oxidizing environments, but uranous

complexes are more stable than uranyl complexes with the same ligand. U(IV) species usually precipitate as insoluble UO_2 or coffinite (Langmuir, 1978).

U(V) is environmentally insignificant and is stable as UO_2^+ at intermediate to low Eh and acidic to neutral pH. It is unstable relative to U(IV) and U(VI) and a weak complexer and therefore U(V) complexes are much less stable than U(IV) or U(VI) complexes with the same ligand. U(V) adsorbs primarily as UO_2OH^+ and $(UO_2)_3(OH)_5^+$ between pH 3-8 (Langmuir, 1978, 1997).

The uranyl ion, U(VI), is the most abundant U species in oxidizing surface water and groundwater and is transported as the uranyl ion (UO_2^{+2}) (Langmuir, 1997). This highly soluble ion exists almost completely as very strong complexes, of which the carbonate is the most important at pH greater than 5 (Langmuir, 1978; Henry *et al.*, 1982). U forms complexes with many different ligands in varying degrees of stability in typical ground or surface waters (Drever, 1997). Langmuir (1997) lists the most common ligands for both the uranyl and uranous ions as carbonate, phosphate, fluoride, sulfate, hydroxide, and silicate. Under most pH conditions carbonate, fluoride, and sulfate form the dominant complexes (Langmuir, 1978). Presence of any U complex will greatly increase the concentration of dissolved U in a water at equilibrium with a U mineral (Drever, 1997).

U is usually complexed in natural systems. Therefore, understanding the speciation behavior of U is critical to a geochemical investigation because the presence of complexes affects mobility, solubility, and concentration of dissolved U in water (Langmuir, 1978). Dissolved carbonate and phosphate greatly increases UO_2 solubility, possibly by several orders of magnitude, by forming complexes (Henry *et al.*, 1982). In reducing environments, U(IV) and its complexes dominate groundwaters (Langmuir, 1997).

When CO_2 is added to the U-O-H_2O system, carbonate complexes become stable (Figure 12). Under normal groundwater pH conditions, the carbonate complexes form with the U(VI) and mostly replace the hydroxyl complexes that are important at low pH (Drever, 1997). Carbonate complexes are the predominant, stable form above pH 5 (Langmuir, 1997; Leinert *et al.*, 1994). U is highly soluble in oxygenated, high pH waters if there is enough carbonate to stabilize U as U-CO_3 complexes (Zielinski *et al.*, 1995). U-CO_3 complexes are most stable at more reducing conditions and higher alkalinity levels and are most stable and dominant in general at pH greater than 5 (Palmer and Edmond, 1993; Langmuir, 1997). They are important because they greatly increase the solubility of U minerals, by facilitating U(IV) oxidation and limiting U adsorption in oxidizing waters (Langmuir, 1997). Most often the uranyl dicarbonate complex dominates and can account for 99% or more of the dissolved U in waters (Henry *et al.*, 1982; Leinert *et al.*, 1994). At slightly acidic and at alkaline pH's $UO_2CO_3^0$ and the tri- carbonate complexes, respectively, are also very important. The stability of U-carbonate complexes decrease as temperature increases which favors the precipitation of uraninite and other U minerals (Langmuir, 1978).

Phosphate complexes also become important species in waters with sufficient concentrations of phosphate. They have the ability, depending on the environmental conditions, to compete with carbonate to be the most important species present. If phosphate is present, uranyl-phosphate complexes become dominant and nearly all available phosphate will complex with U (Galloway & Kaiser, 1980). Similar to carbonate complexes, at intermediate Eh and neutral to alkaline pH, the presence of phosphate complexes will increase the solubility of U minerals by several orders because more than 99% of the dissolved U is in the form of $UO_2(HPO_4)_2^{2-}$. Geochemically, the importance of uranyl-phosphate complexes is often ignored, but $UO_2(HPO_4)_2^{2-}$ is so stable that it is more important

than hydroxyl complexes at pH 4 to 10. This pattern will endure even at low concentrations of phosphate (Langmuir, 1978).

In natural systems without significant amounts of carbonate or phosphate present, U-hydroxyl complexes can become important. The uranyl-hydroxyl complexes are usually present below detectable limits. U(IV)-hydroxyl complexes are stable at higher pH. Significant species are UO_2^{2-}, $UO_2(OH)^+$, $(UO_2)_2(OH)_2^{2+}$, and $(UO_2)_3(OH)_5^+$ (Langmuir, 1978). Other hydroxyl complexes such as $UO_2(OH)_2^0$ and $U(OH)_4^0$ are less stable, but the nature and stability of these complexes as a group depend on the concentration of the dissolved U and the temperature (Langmuir, 1997). As the temperature increases, the UO_2^{2+} and $UO_2(OH)^+$ become more stable and important (Langmuir, 1978).

The complexes that fluoride forms with U(IV) are very limited by the environmental conditions. Uranous-fluoride complexes are important in reducing waters at low pH with only typical amounts of F^- present. In oxidizing waters, the uranyl-F complexes and uranyl ion are important at pH less than 5. These complexes become important when Eh decreases causing precipitation of uraninite. Fluoride and rarely hydroxide complexes are the only species with detectable concentrations under reducing conditions and then only at a limited pH range (Langmuir, 1978).

Relatively minor U complexes form with other ligands. Uranyl sulfate complexes can be important under some conditions. The $UO_2SO_4^0$ complex can be a significant fraction of the U present below a neutral pH and will hinder sorption under these conditions (Langmuir, 1978). Silica also can form weak complexes, such as $UO_2SiO(OH)_3^-$ that is important only near a pH of 6 (Langmuir, 1978).

Uranium adsorption

In a typical system (pH>5), greater than 99% of most trace elements are associated with solid surfaces and less than 1% is dissolved (Langmuir, 1997). In low temperature, oxidizing environments adsorption often influences concentration more than mineral precipitation (Henry *et al.*, 1982, Galloway & Kaiser, 1980, Hsi and Langmuir, 1985, Langmuir, 1978). The pH range of minimum solubility of U(VI) minerals equals the pH range of maximum U(VI) sorption on natural sorbents (Langmuir, 1997). U(VI) adsorption behavior is a function of the aqueous speciation of U and concentration of possible ligands present. Adsorption is the major controlling process in oxidizing groundwater, whereas reduction and precipitation are in control in reducing water (Henry *et al.*, 1982; Galloway & Kaiser, 1980). Quantifying adsorbed material can be important also because the concentration of trace elements in water is usually much lower than calculated or predicted due to adsorption (Drever, 1997). This process is also important because it is the first step in concentration of U mineral deposits (Galloway & Kaiser, 1980).

Adsorption of U by many possible substrates determines concentration and mobility in natural, oxidized groundwater systems (Henry *et al.*, 1982). Amorphous Fe(III) oxyhydroxides have a large sorption capability for U as well as Se and Mo, which are integrally related in many environments (Langmuir, 1997; Henry *et al.*, 1982; Hem, 1985; Hsi and Langmuir, 1985). At neutral pH, most U adsorbs to typical aquifer material (Leinert *et al.*, 1994). Many studies (Read *et al.*, 1993; Abdelouas *et al.*, 1998; Dzombak and Morel, 1990) describe the high sorption capability or affinity of geological materials, such as sandstone or clays, for U. A study by Hsi and Langmuir (1985) on the sorption of uranyl onto various substrates found that uranyl sorbs strongly onto amorphous ferric oxyhydroxide, synthetic and natural hematite, and geothite, particularly above pH 5.

Brown *et al.* (1998) found that in irrigation water U is strongly adsorbed by Fe oxides in the soil before reaching the groundwater, which has important environmental implications in general, and specifically to this study area. However, Abdelouas *et al.* (1998) found that U adsorption from groundwater was negligible. They determined that U was not sorbing from batch and leaching experiments and that U-CO_3 complexes prevailed at high CO_3 concentrations. The U present did adsorb when CO_3 concentration was decreased by dilution and therefore they concluded from this that the presence of CO_3 decreases U sorption (Abdelouas *et al.*, 1998). Langmuir (1997) and Zielinski *et al.* (1995) described how CO_3 present can inhibit adsorption and cause desorption which can lead to formation of U- CO_3 complexes and remobilization (Langmuir, 1997). This adsorption inhibition by carbonate complexing is proportional to the total concentration of carbonate present in the water (Hsi and Langmuir, 1985).

An important study by Boult *et al.* (1998) investigated the sorption capabilities of U(VI) onto different surfaces. They determined that U(VI) strongly sorbs to bentonite between pH 5-8 and that at high pH surface complexation is an important mechanism and at low pH ion exchange is more important. U(VI) sorption onto geothite varies from this model slightly, and surface complexation is still important at high pH but ion exchange is not an important mechanism at low pH. They also determined that there is a competitive effect between sorption of U(VI) and the tendency of U to form carbonate complexes at higher carbonate concentrations. Sorption at intermediate pH involves the $UO_2(OH)^+$ ion (Boult *et al.*, 1998).

Geochemical conditions present, such as pH and alkalinity, and changes in these parameters are intimately related to sorption. Uranyl sorbs the most in the pH range of 5-8.5 (Figure 13) (Hsi and Langmuir, 1985). U(VI) can be desorbed simply by decreasing the pH

(Langmuir, 1997). Langmuir (1978) showed that as the partial pressure of CO_2 increases the adsorption decreases at high pH because this is the pH range where carbonate complexes well with U. Henry *et al.* (1982) report that as SO_4^{2-} or F- concentration increases adsorption decreases at low pH. The maximum adsorption of U begins at about pH 5 and in general adsorption decreases quickly as pH decreases below this point. Since adsorption increases with increasing pH, dissolved U concentration could be expected to decrease with increasing pH (Henry *et al.*, 1982). Above a pH of 6.5, the presence of adsorbed silica may reduce U-ferrihydrite association and humic substances might subdue uranyl adsorption on hematite. At pH 8, U can adsorb onto ferrihydrites and then be released by sunlight (Leinert et al., 1994). Experiments by Hsi and Langmuir (1985) showed that adsorption leveled off at pH greater than 7, which supports Figure 13 because U is completely sorbed above pH 5-7. The presence of sulfate in the waters and formation of uranyl-sulfate complexes favor desorption at low pH (Langmuir, 1978). Hsi and Langmuir (1985) found that Ca and Mg at typical concentration in natural waters (10^{-3}M) did not compete with uranyl for adsorption.

There are other factors influencing and causing fluctuations in sorption. Leinert *et al.* (1994) found that in the summer most U is dissolved, whereas most was adsorbed in winter probably partly due to the higher particle load in the stream. Abdelouas *et al.* (1998) found that temperature could also effect sorption. Their experimental results showed that as temperature increased, U co-precipitated with aragonite and calcite. Overall, understanding the complete sorption picture can be difficult since it depends on many factors, such as concentration of possible substrates, concentration of competing constituents, and many other important geochemical and environmental parameters.

3.4.4 Toxicity

The study of U is important because it can concentrate to become an economic deposit or a public health hazard. In higher concentrations it can be toxic to humans and has been shown to cause disease in livestock animals (Henry and Kapadia, 1980). There is a delicate balance between too much and not enough U in the ground because decreased concentrations will affect the growth of plants due to decreased soil respiration and rates of decomposition (Meyer *et al.*, 1998). U is toxic to kidney function and has other toxicity effects on humans from the associated radioactivity (Zielinski *et al.*, 1997). Also, U accumulates in bone and can persist for a long time (Bradford *et al.*, 1989).

Table 2. Typical selenium concentrations in rocks and soils.

Rock/Soil Type	Concentration (mg/kg)	Source
Phosphate fertilizers	0.5 - 25	Haygarth (1994)
Limestones	1	Haygarth (1994)
Loess	1.1 - 2.3	Nicolli *et al.* (1989)
Upper crust	0.05	Taylor (1964)
Average in Niobrara and Pierre Shale	5.8	Ihnat (1989)
Wyoming shales	1 - 300	Mayland *et al*. (1989)
Se-rich phosphate rocks	1 - 178	Mayland *et al*. (1989)
Kansas and Colorado soils	1 - 10	Mayland *et al*. (1989)

Table 3. Typical selenium concentrations in natural waters.

Water/Location	Concentration (μg/l)	Source
Riverton Basin, Wyoming	<1 to 12	Peterson *et al.* (1991)
Kesterson average	300	Benson *et al*. (1991)
Unfiltered samples in Argentina	119-498	Nicolli *et al*. (1989)
Common drinking water	0.1-100	Mayland *et al*. (1989)
Surface water in Middle Arkansas River	1 - 52	Mueller *et al*. (1991)
Maximum groundwater Middle Arkansas River	29	Mueller *et al*. (1991)
1975-1987 Average in Arkansas River at Coolidge, KS	19	Mueller *et al*. (1991)

Table 4. State of Kansas and United States EPA drinking water standards for total selenium in water. Data is from KDHE (1999).

Water quality standard	Limit or criterion (µg/l)
EPA, Kansas drinking water	50
Kansas livestock drinking water	50
EPA/Kansas groundwater irrigation supply	20
Kansas surface water acute toxicity to aquatic wildlife	20
Kansas surface water chronic toxicity to aquatic	5

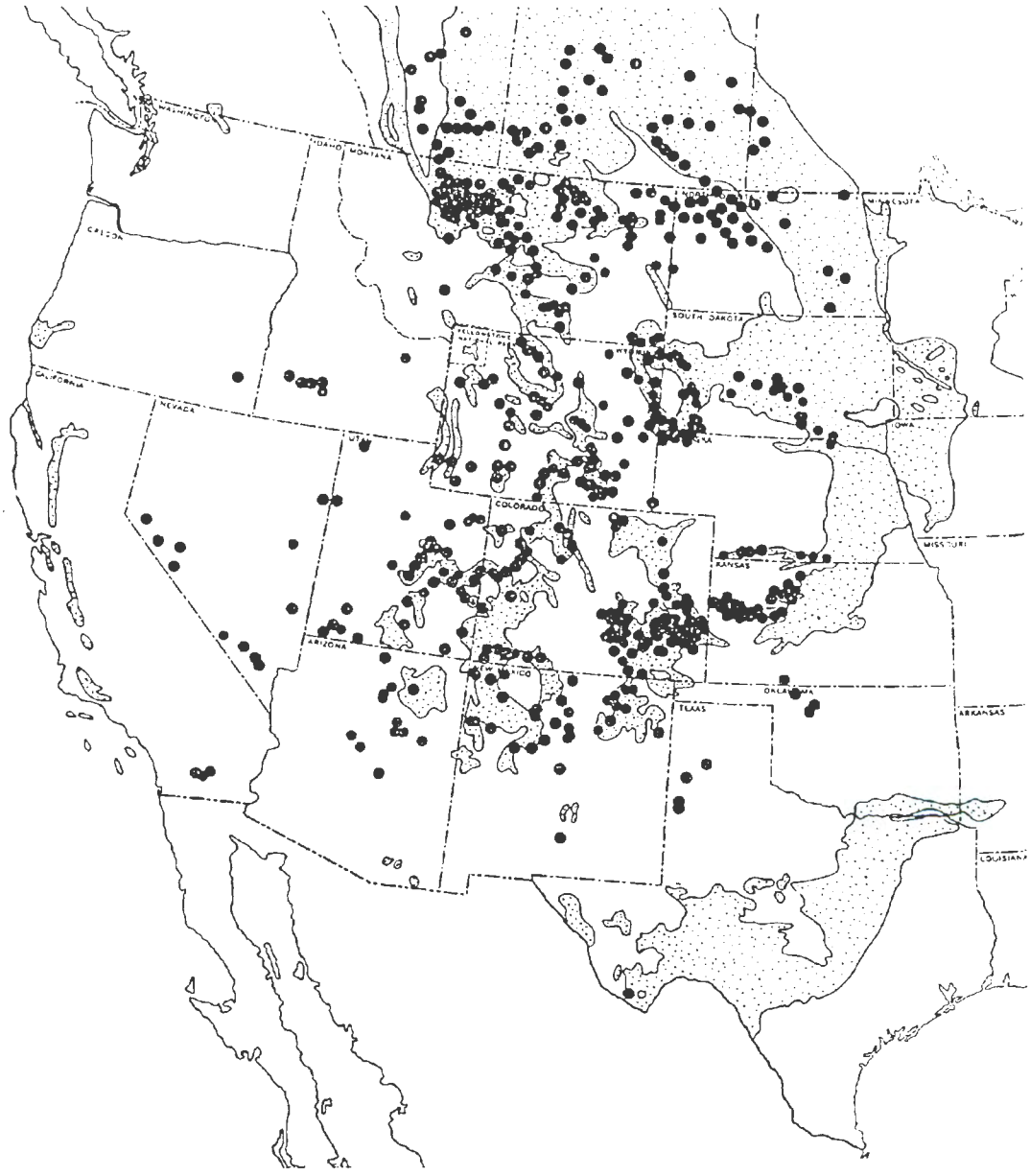


Figure 7. Map of Cretaceous outcrops high in Se (stippled areas) and seleniferous soils (black dots) in the western United States (From Trelease and Beath, 1949).

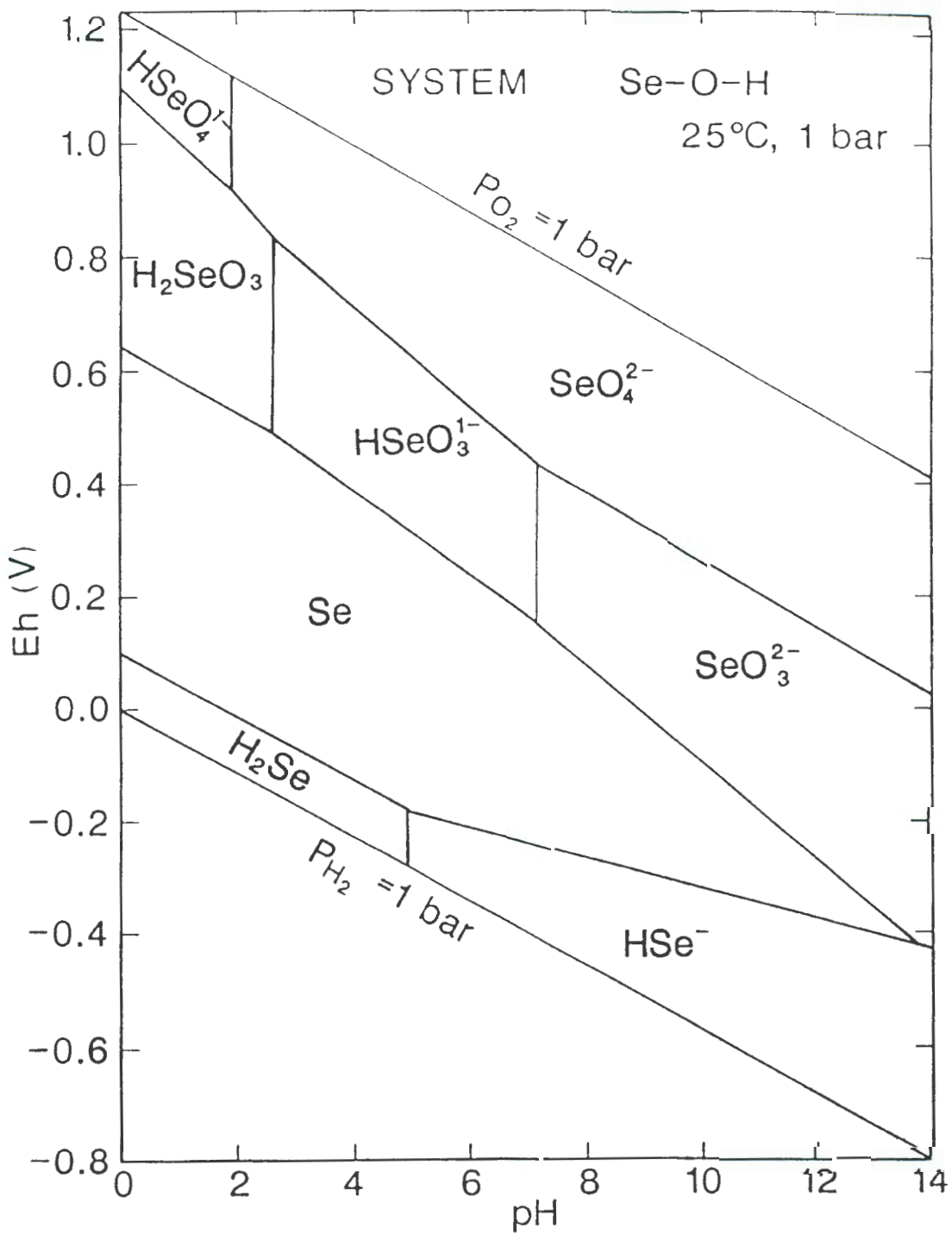


Figure 8. Eh-pH diagram for part of the Se-O-H system (from Brookins, 1988). The activity of dissolved Se = 10^{-6}. Field conditions of the study sites in the Arkansas River valley are plotted as the rectangle on the diagram.

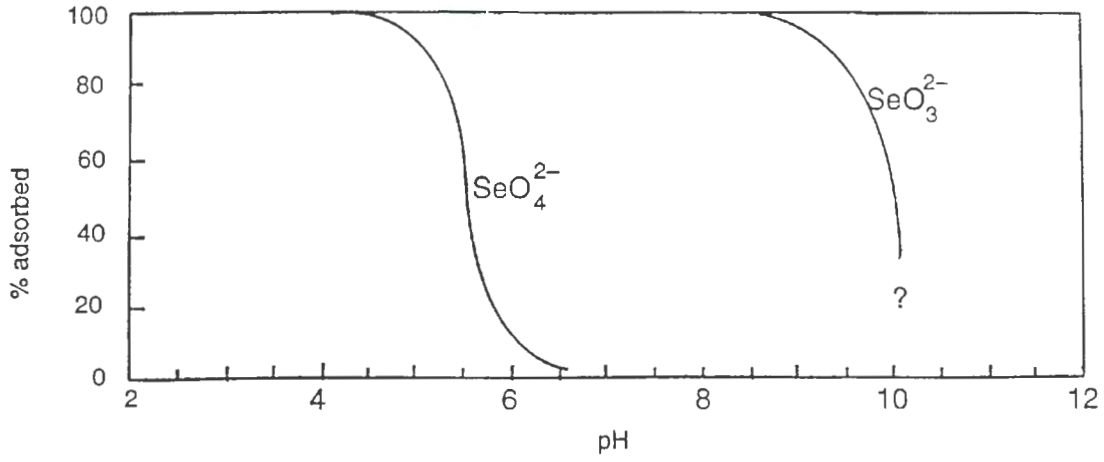


Figure 9. Plot showing sorption pH dependence of Se(IV) and Se(VI) on hydrous ferric oxides (Modified from Drever, 1997).

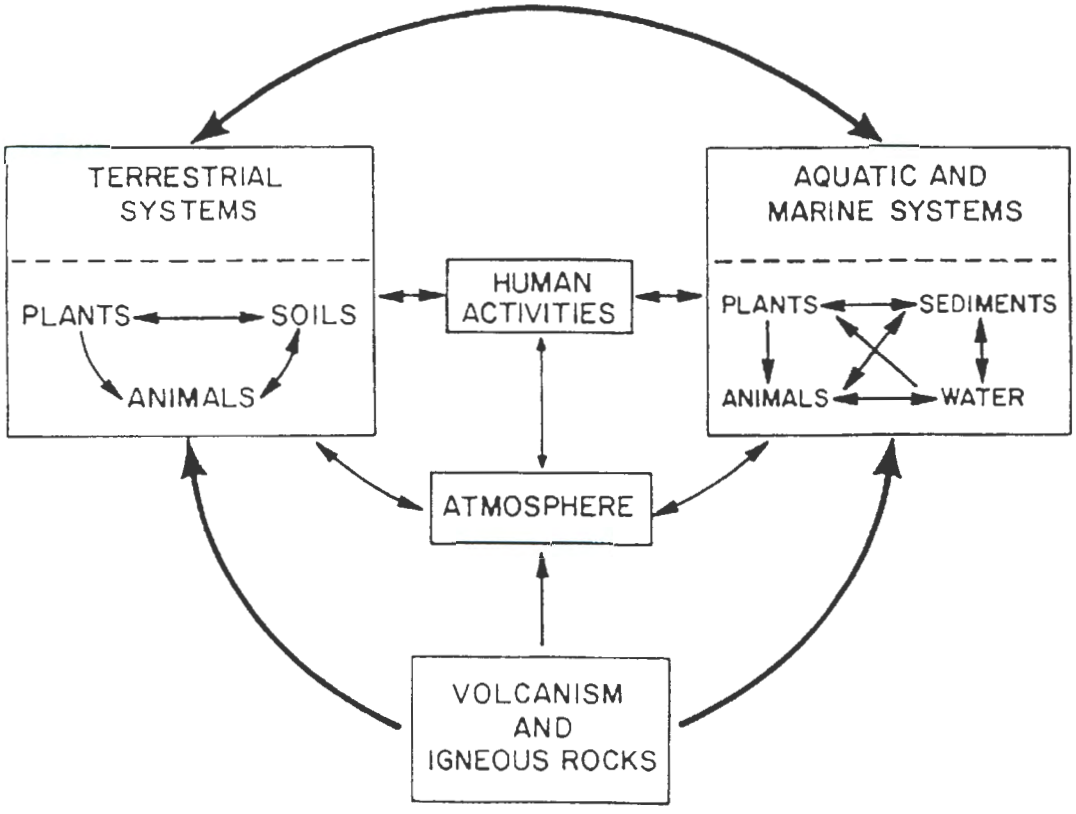


Figure 10. Selenium cycle in nature showing pathway for concentration of Se in natural systems and bioaccumulation in plants and wildlife (From Ohlendorf, 1989).

Table 5. Typical uranium concentrations in rocks and soils.

Rock/Soil Type	Concentration (mg/kg)	Source
Sedimentary rocks	1.2 - 1.3	Langmuir (1997)
Upper crust	2.7	Taylor (1964)
Volcanic ash in western Kansas	6 - 10	Berendsen & Hathaway (1981)
Chert in western Kansas	Up to 106	Berendsen & Hathaway (1981)
Phosphate fertilizer	20 - 200	Zielinski *et al*. (1995)
Baseline for western soils	2.5	Mueller *et al*. (1991)
Average limestones	2	Palmer & Edmond (1993)
Loess	1.2 - 8	Nicolli *et al*. (1989)

Table 6. Typical uranium concentrations in natural waters

Water/Location	Concentration (µg/L)	Source
Average surface waters in US	0.1-7	Langmuir (1997)
Average surface waters, western US	Can be > 20	Langmuir (1997)
Groundwater in U-rich areas	1-120	Langmuir (1997)
Seawater	2-3.7	Langmuir (1997)
Western Kansas groundwater	2-172	Berendsen & Hathaway (1981)
Mean western Kansas groundwater	9.5	Berendsen & Hathaway (1981)
Waters in Ark River valley	> 20	Berendsen & Hathaway (1981)
Background value in US rivers	0.1	Langmuir (1978)
Groundwater in contact with Cretaceous rocks	18	Zielinski *et al*. (1995)

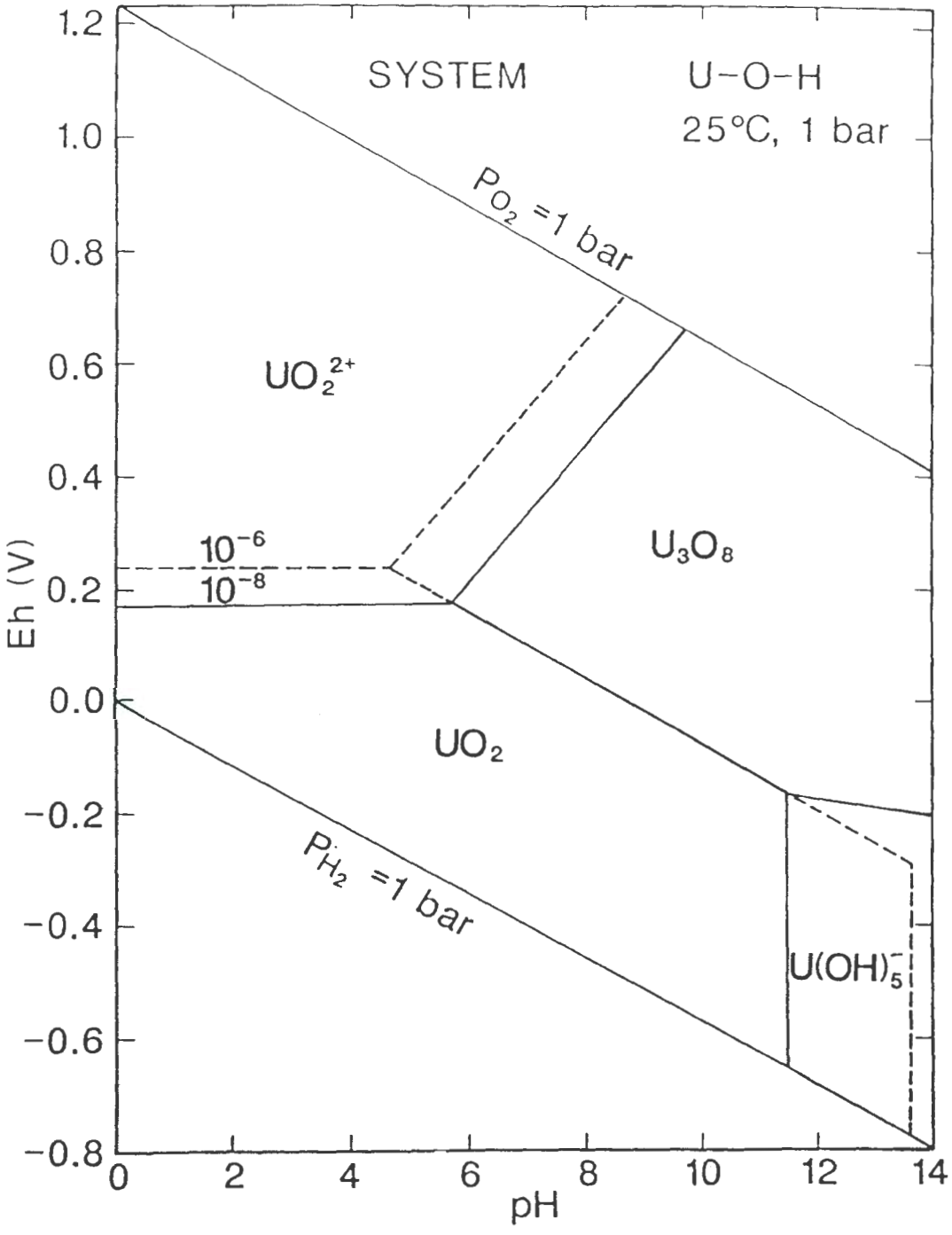


Figure 11. Eh-pH diagram for part of the U-O-H system. Activity for dissolved $U=10^{-6,-8}$. (From Brookins, 1988). Field conditions of the study sites in the Arkansas River valley are plotted as a rectangle on the diagram.

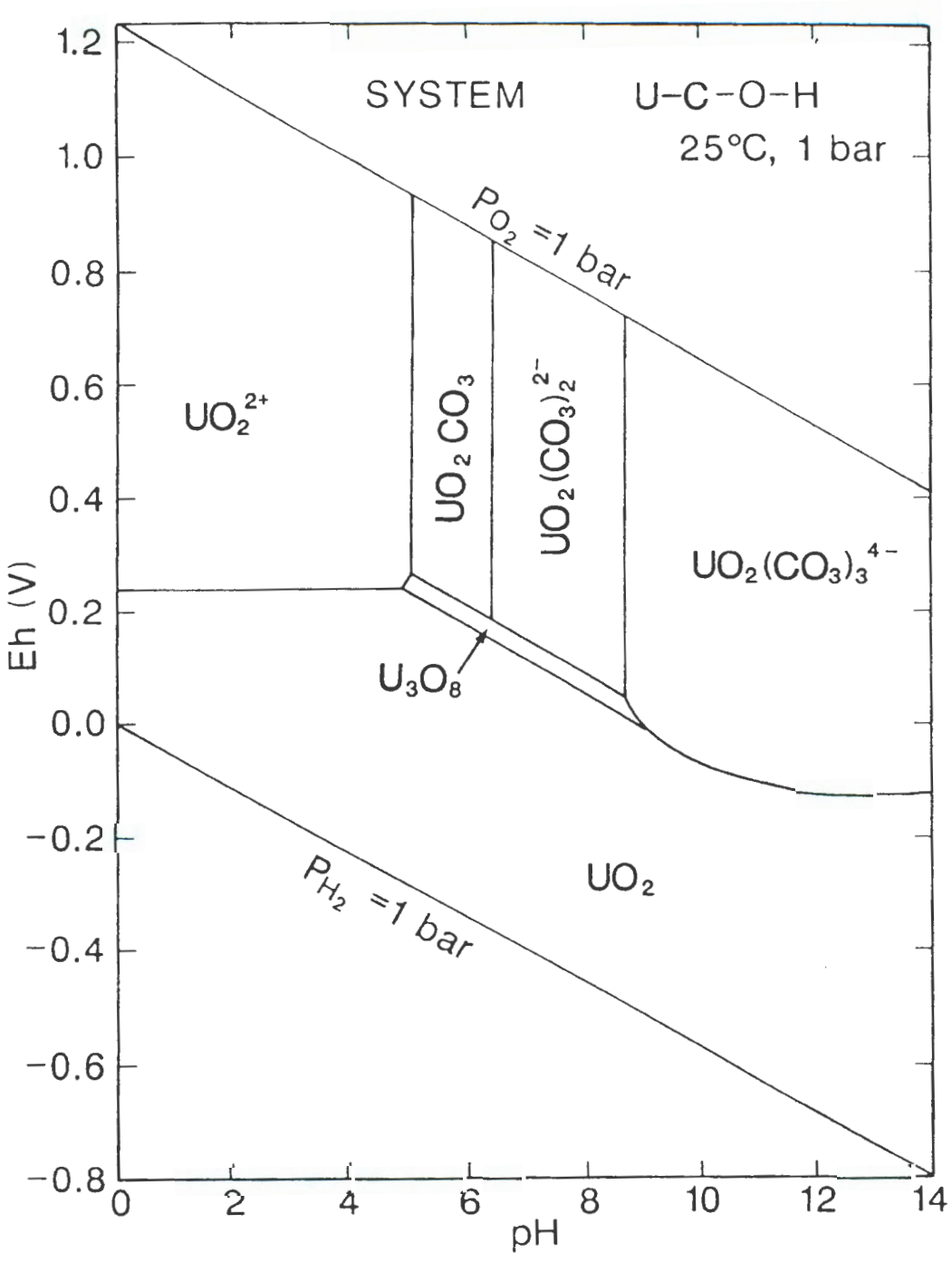


Figure 12. Eh-pH diagram for part of the U-C-O-H system at 25°C (From Brookins, 1988). Assumed activities for dissolved species area: $U=10^{-8,-6}$, $C = 10^{-3}$. Field conditions are shown as a rectangle on the diagram.

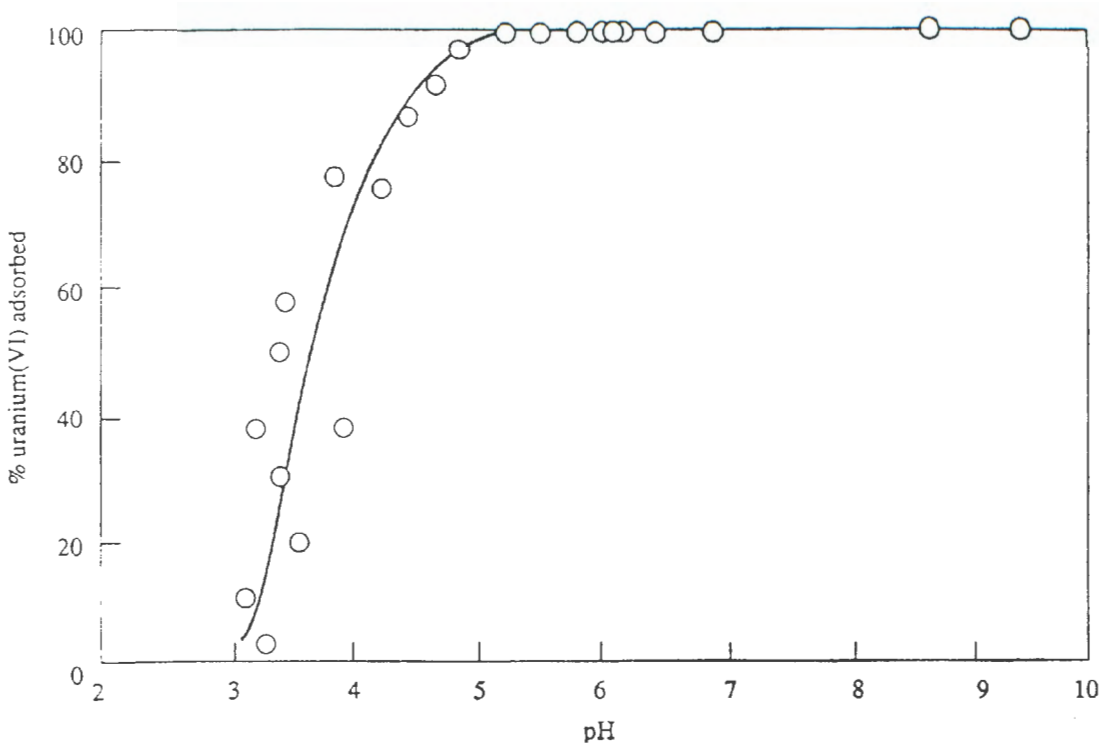


Figure 13. Plot showing pH dependence of sorption of U(VI) on ferrihydrite at 25°C (From Langmuir, 1997).

Chapter 4 Multi-level well sites

Multi-level wells were installed at three sites (Deerfield, Garden City, and Dodge City) for the Arkansas River Corridor Study of the KGS. Detailed site location maps are in Whittemore *et al.* (2000). Each site has 4 to 5 PVC wells with 5- to 10-foot screened intervals at various depths. The well screens were installed in the zones of more permeable sediments. The shallow well at each site is completed in the alluvial aquifer and the deeper wells in the Ogallala aquifer. The sites are located from ¼ to one mile from the Arkansas River. Table 7 shows the legal location, screen depth, and depth to water from the top of casing in each well. A total of 14 wells at three sites were sampled for this study during two different sampling trips in March and May of 1999. Additional data and information are in Whittemore *et al.* (2000).

4.1 Deerfield

The Deerfield site is located in the southwest part of the city in east-central Kearny County, about one mile north of the Arkansas River (Figure 1). There are five wells at this site screened at various depths (Table 7). The site is located at the edge of the alluvial valley and therefore the shallowest well is completed in alluvial terrace deposits. The salinity at the Deerfield site is mostly caused by recharge from the ditch irrigation in the area. The salinity profile gradually decreases in a nearly linear manner with depth. This trend supports a slow migration of salinity and mixing with the fresher water deeper in the aquifer. TDS ranges from 2,700 mg/L in the shallowest well to 460 mg/L in the deepest. In the more saline waters, sulfate contributes most to TDS.

There is a much higher percent of fine-grained sediments at this site and the alluvial aquifer is much thinner than for the other two well sites farther to the east (Figure 14). The

clay layers are relatively homogeneous at the different depths. The change in hydraulic head illustrated in Figure 14 shows the potentially downward movement of water in the aquifer. This is the same for all sites in the study area. The driller's log and gamma and conductivity logs of the deep well at this site show variable lithology and thick clay sequences (Whittemore *et al.*, 2000). Bedrock is 345 feet below the land surface at the site.

4.2 Garden City

The Garden City site is located in southern Garden City, about ¼ mile south of the river (Figure 1). There are five wells ranging in depth from about 59 feet to 250 feet (Table 7). This site is located within the alluvial valley and the sediments at this site are a heterogeneous mix of sand, silt, and gravel (Figure 15). The alluvial aquifer is relatively thin because the water levels are deeper than in other portions of the aquifer. The fine-grained sediments range from sandy clays to clays and are present as lenses and thin layers through the interval of the well depths. The aquifer materials are sand and gravel. The driller's log and gamma and conductivity logs at this site indicate that the sediments are generally coarser grained than at the Deerfield site (Whittemore *et al.*, 2000)

The salinity profile is notably different at this site from that at Deerfield. The TDS ranges from near 3,000 mg/L to about 2,200 mg/L. The sulfate concentrations considerably exceed the drinking water standard. There are not as many clay layers retarding downward movement of the sulfate-dominated salinity and therefore the groundwater in all wells at this site are saline. The water levels measured at this site again show a continuous downward movement of water. Salinity is input into the groundwater at this site by infiltration of the saline river water from the channel into the alluvium and then into the deeper High Plains aquifer.

4.3 Dodge City

The Dodge City multi-level observation well site is located approximately 3 miles west of Dodge City in Ford County (Figure 1). The site is about ¼ mile south of the Arkansas River and is located within the alluvial valley. The stratigraphy at this site is characterized as a well-defined alluvial aquifer between about 5 feet below the surface to about 45 feet deep that is underlain by sands, gravels, silts, and clays of the High Plains aquifer (Figure 16). The four wells at this site are screened at 35-40 feet, 66-72 feet, 106-116 feet, 156-166 feet (Table 7). The hydraulic heads shown in Figure 16 suggest a potential for downward movement of water within the Ogallala aquifer. The driller's log and geophysical well logs for the three deeper wells show relatively continuous thin clay layers between the screened intervals of the two shallowest wells, and another clay zone between the middle two wells. The gamma and conductivity logs show that the relative amount of clays decreases with depth (Whittemore *et al.*, 2000). A nearby irrigation well is screened in the bottom half of the High Plains aquifer.

The salinity profile at this site shows that the high TDS concentration occurs only within the alluvial aquifer. TDS decreases from more than 2,500 mg/L to 279-298 mg/L in the deeper High Plains aquifer. The alluvial water substantially exceeds the sulfate drinking-water standard. Infiltration from the river channel into the alluvium is the source of salinity into the aquifer at this site because the site is near the river and the sediments are coarse.

Table 7. Well locations, depths, and screened intervals for wells included in study.

Site	Well Number	Water level (feet)	Total depth (feet)	Screened depth (feet)	Legal Location
Deerfield	1	17.33	342	330-340	T24S R35W 11 NW NW SW
	2	16.63	247	237-247	T24S R35W 11 NW NW SW
	3	10.57	142	132-142	T24S R35W 11 NW NW SW
	4	8.26	66	58-66	T24S R35W 11 NW NW SW
	5	7.86	44	34-44	T24S R35W 11 NW NW SW
Garden City	1	36.59	253	241-251	T24S R32W 19 NW NE SW
	2	35.48	206	194-204	T24S R32W 19 NW NE SW
	3	29.75	145	135-145	T24S R32W 19 NW NE SW
	4	26.97	86	76-86	T24S R32W 19 NW NE SW
	5	27.37	59	51-59	T24S R32W 19 NW NE SW
Dodge City	1	12.24	168	156-166	T26S R25W 32 NW NW NW
	2	10.97	120	106-116	T26S R25W 32 NW NW NW
	3	9.82	74	66-72	T26S R25W 32 NW NW NW
	4	9.78	42	35-40	T26S R25W 32 NW NW NW

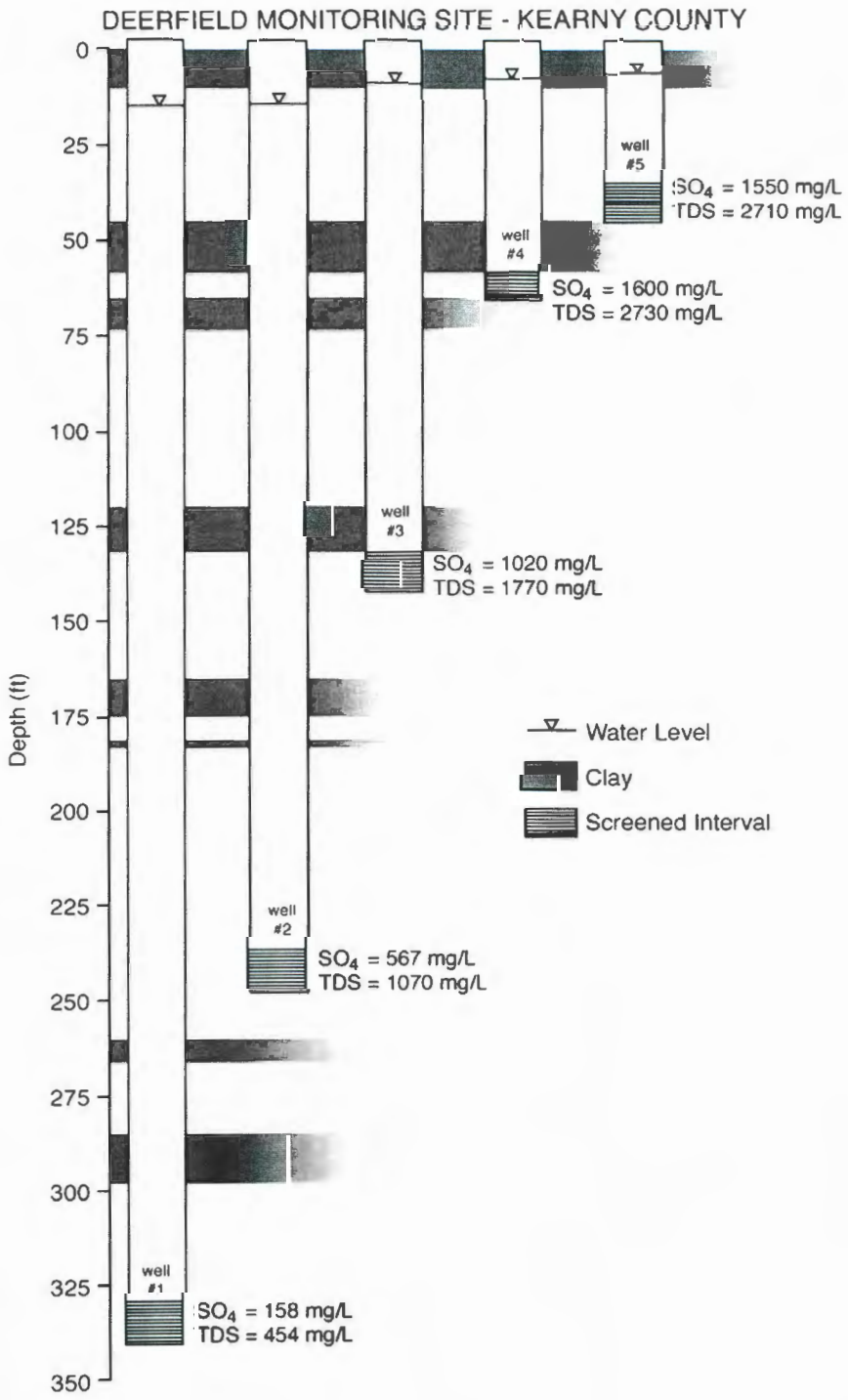


Figure 14. Figure showing well construction, location of clay layers, depth of wells and well screens, and TDS and SO_4 concentrations at the Deerfield site.

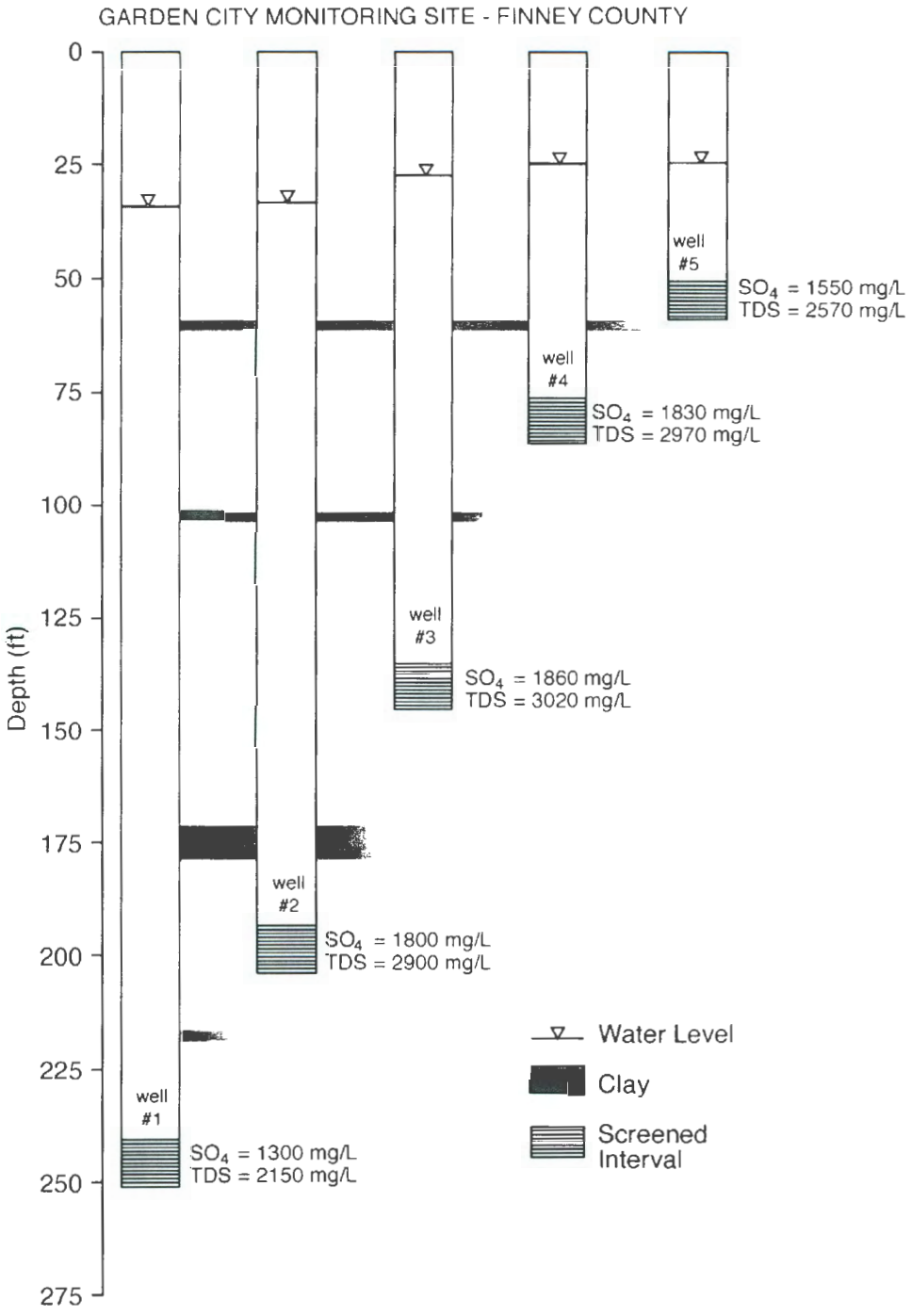


Figure 15. Figure showing well construction, location of clay layers, depth of wells and well screens, and TDS and SO_4 concentrations at Garden City.

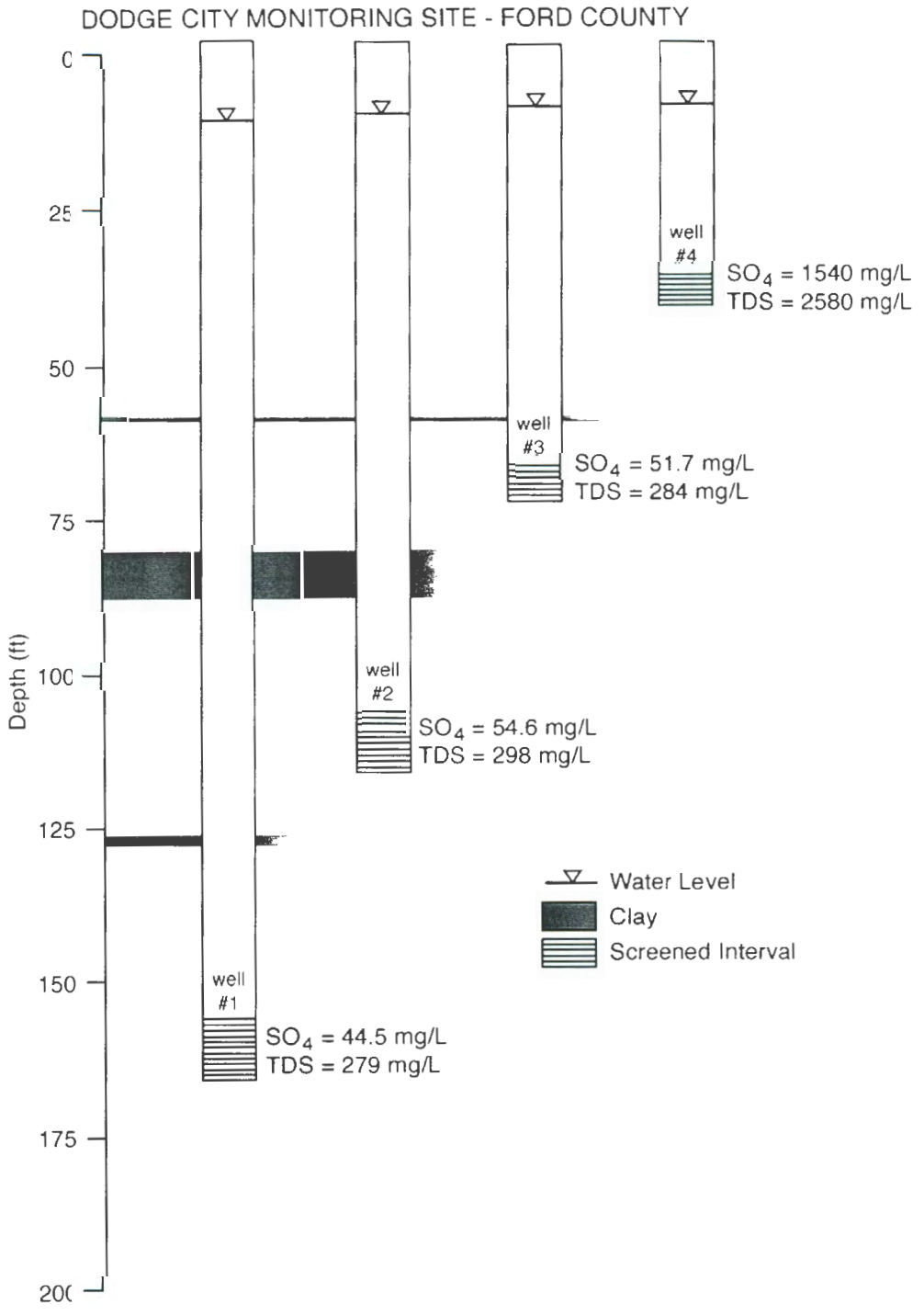


Figure 16. Figure showing well construction, location of clay layers, well and well screen depths, and TDS and SO_4 concentrations at Dodge City.

Chapter 5 Procedure and Methods

5.1 Field Measurements and Sampling Methods

One-time synoptic sampling was done at the 14 wells of the Deerfield, Garden City, and Dodge City sites on March 17 and 18 and May 26, 1999. As shown in Table 7, these wells varied in total depth from 42 to 342 feet. The wells were designed to penetrate only one water-bearing lithological unit. Prior to sampling, the total depth and water levels were measured for each well. The goal was to collect the most representative sample possible and a procedure was followed that theoretically would meet this goal. EPA guidelines suggest that the most representative sample can be attained by flushing out 3-5 well volumes and allowing the field parameters to stabilize to within defined limits before sampling begins. Therefore, each well was purged of more than three well volumes of water using a submersible pump.

A Grundfos Redi-Flo2 submersible pump was used to withdraw water from the wells. This portable pump was moved between wells after each was sampled. The maximum pumping rate was 9 gallons per minute (gpm) for purging but was adjusted to lower rates for sampling. The pump tubing was designed to direct water towards a larger tube for purging and a smaller hose for monitoring field parameters and filtering during final sample collection. Field parameters were constantly measured while the well was purged. The water in the smaller tubing for monitoring could be turned off when the parameters stabilized in order to make final measurements for electrodes that are affected by streaming potential.

Several chemical parameters were measured in the field, i.e., DO, pH, Eh, and temperature. A flow-through apparatus was designed and built for this project (Figure 17). Accurate measurements of these parameters require a flow-through cell that keeps the water from atmospheric contact during monitoring. Two glass U-tubes hand-blown in the Chemistry Department at the University of Kansas were connected by polyethylene tubing

and attached to a ring stand using clamps. The probes were placed in the U-tubes in the following flow order; DO, temperature, pH, Eh. The Eh and pH probes were placed at the end of the line because they theoretically release trace amounts of KCl into water. A rubber stopper was cut to fit each probe and make the device airtight, disallowing groundwater contact with the atmosphere during field parameter measurement. Beginning with the first probe, the tubes were filled with water and then sealed to remove all air. Any air bubbles were removed before monitoring began.

The system was flushed out with the groundwater and monitoring of the Eh, pH, and DO began after about 5-10 minutes. The Eh, DO, pH, and temperature were measured every two minutes until they stabilized. The specific conductance and temperature were also measured at the larger discharge hose about every 15-30 minutes until stabilized. Eh measurements were made using a platinum electrode and a Fisher Scientific Accumet® 1000. ZoBell's solution was used in the field to verify that the Eh probe was working properly. The ZoBell's solution was made in the laboratory before field sampling based on the recipe of Eaton *et al.* (1995). Temperature and pH measurements were determined with a Fisher Accumet® Model 955 meter and DO with the Orion Model 810 series handheld meter. Buffer solutions (pH 4 and pH 7) were used to calibrate the Fisher meter. The Orion meter was calibrated internally per directions for the meter.

After field parameters were stabilized, the flow through the device was turned off and approximately three more minutes of pH and Eh readings were taken for measurements without streaming potential for the model input. About 1000 mL of water was allowed to flow through a capsule with a 0.45-μm membrane filter before samples were collected. The 250-mL polyethylene bottles used to collect samples for ICP-MS analysis were pre-marked for exactly 250-mL volume. Samples for the Se and U analysis were filtered and acidified

with high-purity, concentrated nitric acid in the field to lower the pH to less than 2. One pre-acidified 250-mL polyethylene bottle containing 2 mL of high-purity hydrochloric acid was filled to a 200-mL mark with sample for cation and nutrient determinations. A 500-mL polyethylene bottle was filled with sample for analysis for laboratory pH, specific conductance, and anion concentrations. The bottles were sealed with paraffin film and immediately placed on ice, and then refrigerated in the laboratory until analyses were complete.

The river was sampled twice at Garden City and once near Dodge City on the same three days (March 17 and 18 and May 26, 1999) as for ground-water sampling. The Garden City and Dodge City sites were sampled on consecutive days during the first trip. The second Garden City sample was collected during a period of higher flow (Figure 5) when the main flow of the Arkansas River near the Deerfield site was difficult to sample due to obstruction of small trees and bushes.

5.2 Laboratory and Analytical Procedures

Laboratory procedures

The groundwater and surface-water samples were submitted to the laboratory at the Kansas Geological Survey for major and minor constituent determination. The various methods used to analyze for different constituents are summarized in Table 8.

The water samples were analyzed for Se, U, and Mo on the VG PlasmaQuad II+ XS inductively-coupled plasma mass spectrometer (ICP-MS) at the University of Kansas Plasma Analytical Laboratory using various quality control procedures. ICP-MS includes an argon plasma source with a quadrupole mass analyzer in the standard configuration. An interface between these two parts of the machine extracts ions from the plasma and directs the ion

beam through vacuums into the mass analyzer and detector (Kenison Falkner *et al.*, 1995). In general, the ICP-MS measures a signal that is proportional to the number of ions, actually mass/charge, in multiple sequential sweeps across a selected mass range. These are integrated into a single value for each in units of counts per second for each mass/charge, for a chosen integration period (30 seconds for this study). Each integration period was repeated three times, so that the mean of the three replicate integration periods is reported. In addition, each sample was analyzed at least twice, and final values represent the average of the duplicates. For this study, ^{77}Se, ^{78}Se, ^{82}Se, ^{238}U, and ^{95}Mo all have charges of +1 and thus are measured directly.

^{77}Se was the isotope used in the final geochemical evaluations for the following reasons: ^{82}Kr is an isobaric interference on ^{82}Se; ^{78}Se also has an isobaric interference from Kr as well as a polyatomic interference from the argon dimer, ^{40}Ar^{38}Ar. These two interferences probably contributed to the analytical error calculated when using ^{78}Se that was higher than the error for the other two masses. ^{80}Se, the most abundant isotope of Se, could not be used because of the large amount of the argon dimer, ^{40}Ar^{40}Ar, present. It should be noted that ^{40}Ar^{37}Cl is a possible polyatomic interferent for ^{77}Se, which may explain some of the difficulty in reproducibility in this study. USEPA Method 1638 suggests that ^{77}Se or ^{82}Se can be used, but that ^{82}Se is preferred (USEPA, 1996).

Analytical procedures

The 17 water samples (14 well and 3 river waters) were separated into groups for ICP-MS analysis based on TDS, either fresh or saline. The high TDS samples were diluted 2:1 with 2% HNO_3. Multiple matrix tests were run on the ICP-MS prior to sample analysis to assess matrix effects. A set of standards was made for each group, a high set and a low set, to

mimic the extremes of each group. The 100 ml total volume solutions included Na, Ca, SO_4, and Cl as the matrix, Se, U, and Mo as the analytes, and Bi, Y, and In as the internal standards. Table 9 shows the matrix of the standards used. From these basic matrix solutions, two sets of four solutions were created, set A with high TDS and set B with low TDS. Each set included a low-low, low, medium, and high solution, which refers to the relative concentration of Se, U, and Mo in each solution (Table 10). These concentrations are approximate because the solutions were diluted and then added by mass.

The matrix test showed that the matrix effects differed for different elements (Figures 18 and 19). U238 concentrations were 60% of nominal values in the most saline matrix ("A" matrix), whereas matrix effects on Mo and Se (all isotopes) were insignificant. The severe suppression of the U signal was handled by diluting the samples and using matrix-matched standards according to the "A" and "B" scheme shown above.

The samples were analyzed in sets of 8 unknowns (samples) and an example sample order is shown in Figure 20. This sample order reveals some of the quality control procedures used in the laboratory analysis. These include analyzing samples in a random order and running duplicate analyses on samples. In addition, blanks and drift correctors (the high standard) were included in the analysis to allow for mathematical corrections made on the data after data collection was complete.

Internal standards were added to each sample, blank, and drift corrector as one way of correcting data for drift during the analytical run. Internal standards were chosen by matching masses and geochemical behavior with Se and U. Three internal standards were chosen initially: ^{89}Y, ^{115}In, and ^{209}Bi (10 µg/L each). Based on the goodness of the drift correction of the drift corrector solution (a solution measured every fifth injection during each analytical run), Y corrected the Se analytical data best and Bi worked best for U data. In did

not correct the data well for either Se or U. An example of the template used for data correction and interpretation shows how these conclusions were made (Figure 21). The internal standard that corrected the drift for a particular mass/charge in the drift-corrector solution replicates, so that the replicates had the lowest % relative standard deviation (RSD), was used for drift correction for that mass/charge in the unknowns, standards, and blanks. Although some matrices can be corrected for drift by using a linear interpolation of cps between drift correctors, the matrices of these standards and samples were not corrected well enough. Instead, the drift corrector solution data were used to evaluate the success of the drift correction by internal standards.

A standard addition run was performed to check for accuracy of the data. Standard addition corrects for matrix effects and not spectroscopic effects. A blank, low, medium, and high group of samples were run (Table 11a). In each group Se and U standards were added in increasing concentrations. The results were plotted with concentration of standard added (μg/L) as the x-axes and drift corrected cps as the y-axes. A trend line was then fit through the four points on each plot and the equations of these lines are shown in Table 11b. The results of the standard addition runs shows that there are some small, similar matrix effects in all the samples. Comparing the results from the standard addition in column –x' and results from the original analysis reveals that in general the Se concentrations from the standard addition run were higher at higher Se concentrations. The U concentrations from the standard addition run were lower at all U concentrations. The difference between the original data and standard addition data is fairly constant for all the samples in the standard addition analysis.

5.3 Geochemical Modeling Methods

Geochemical modeling was performed with PHREEQC (Parkhurst, 1995), a USGS reaction path computer model incorporating the WATEQ4F thermodynamic database. The WATEQ4F database was used because it contains the thermodynamic data for uranium and selenium that the PHREEQC internal thermodynamic database lacks. The program simulates geochemical systems and is designed to evaluate quantitative chemical reactions between minerals, waters, gases, and aqueous species.

Data from water analyses performed at the KGS and KU-PAL, and field parameters measured during sampling were used for geochemical modeling. The field measured values for pH and temperature were used for the groundwater models. The average pH value from USGS historical data for groundwater in this area is 7.5 which is similar to the average values obtained from each site in this study, 7.2 at Garden City, 7.4 at Dodge City, and 7.5 at Deerfield. Measured Eh values were converted into pe units using the following equation:

$$pe = \frac{F}{2.303*R*T} * Eh$$

where F = 96.484 kJ/V, R = 8.314e-3 kJ/mol K, temperature is in K, and Eh is in V. For the surface water modeling, pH values determined in the KGS laboratory were used as input. The laboratory values for pH determined in this study are 8.1-8.2, which compares closely with the average pH value of 8.1 from 1974-1995 USGS and EPA historical data. A temperature of 15°C was assumed for the modeling of the river water. A pe value of 7, which corresponds to 400 mV Eh used for modeling of this area by Zielinski *et al.* (1995), is an approximate value for oxidized surface water and was used in this model.

Theoretical parameters were selected to assess the sensitivity of the geochemical model with respect to sulfate, phosphate, and iron concentrations, and pH and Eh. Sensitivity

analyses of pH and Eh were done because Se and U are redox sensitive and there is a small amount of uncertainty in the field measurement of these parameters. The model was run initially with the real data to produce a conceptual model of the system and to evaluate Se and U speciation and mineral solubility and saturation. These models were run with an input file for each well and each river sample. Examples of input data for this type of model are shown in Table 12.

The sorption capability in PHREEQC was also used with the SURFACE keyword simulating sorption. The sorption model helped to evaluate the role of surface complexation of Se and U onto ferric oxyhydroxides in the system and the input file is shown in Table 13. Default values for the surface characteristics were used in the modeling. These values are 0.00005 and 0.0002 for the number of strong and weak sites, respectively, 600 m^2/g surface area, and 0.09 for total mass of surface. The WATEQ4F database was used for general sorption modeling because selenite and uranyl surface species are already included. Thermodynamic data for the surface reactions are from Dzombak and Morel (1990).

The model output was plotted in spreadsheets to evaluate the data with depth in most cases. For all plots, an average of the value in question was calculated for the Arkansas River samples at Garden City and Dodge City and used to represent the average water seeping during different flow conditions from the river to the subsurface.

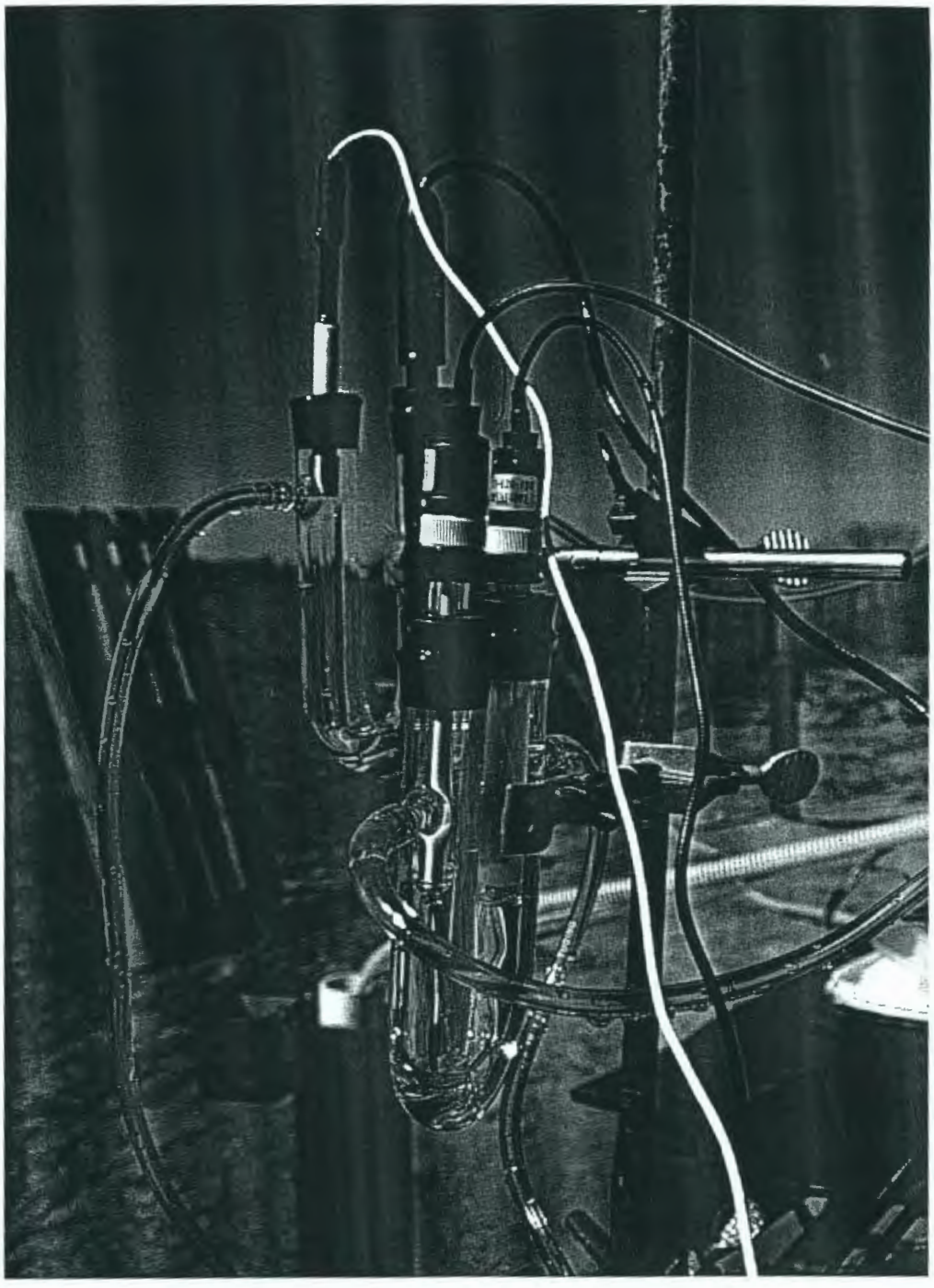


Figure 17. Picture of flow through apparatus designed for field sampling and parameter measurement in this project.

Table 8. Summary of analytical methods and instruments used for major chemistry

Constituent	Analysis instrument	Analysis method
SiO_2, Ca, Mg, Na, K, Sr, B	ICAP, Jarrell-Ash AtomComp 975 and a Mark II/Mark III update kit	
HCO_3	Fisher AutoTitrimeter II System	Electrometric titration
Cl	Alpkem Flow Solution IV System	Ferric Thiocyanate colorimetric method
SO_4	Alpkem Flow Solution IV System	Methyl Thymol Blue colorimetric method
F	Ion selective electrode and a Hach One pH/ISE Meter	
NO_3	Technicon AutoAnalyzer II System	Colorimetric methods and UV-method developed at KGS

Table 9. Concentrations of components in matrix solutions

	Na (mg/L)	Ca (mg/L)	SO_4 (mg/L)	Cl (mg/L)	Y (µg/L)	Bi (µg/L)	In (µg/L)
A matrix (high TDS)	500	300	2200	150	10	10	10
B matrix (low TDS)	20	60	50	10	10	10	10

Table 10. Se and U concentrations in matrix solutions

A and B matrices	Low-low	Low	Medium	High
Se	1 µg/L	5 µg/L	10 µg/L	100 µg/L
U	1 µg/L	1 µg/L	20 µg/L	25 µg/L

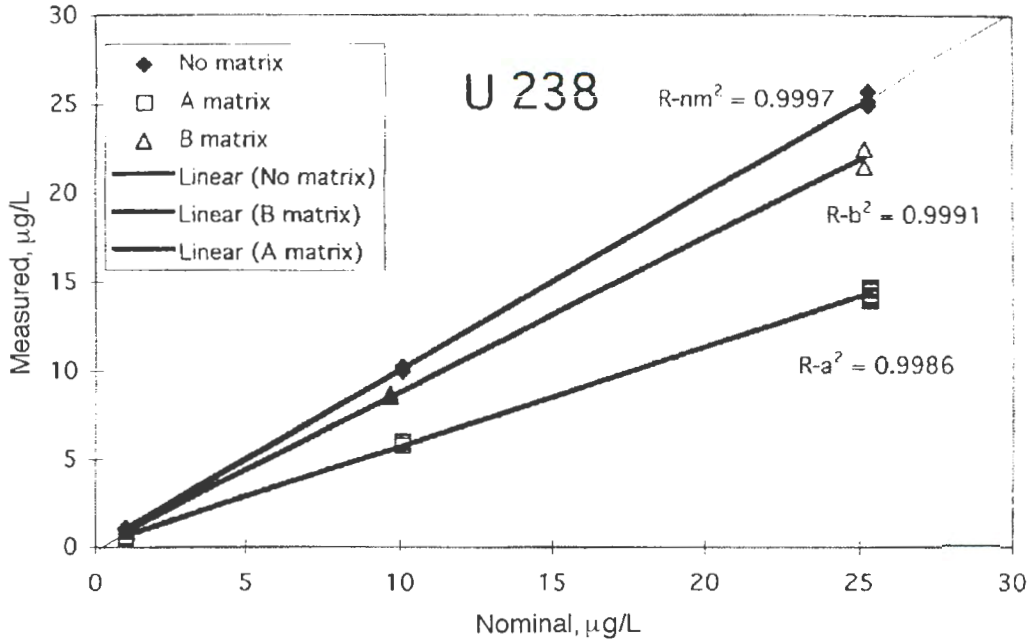


Figure 18. Plot showing matrix effects on ^{238}U.

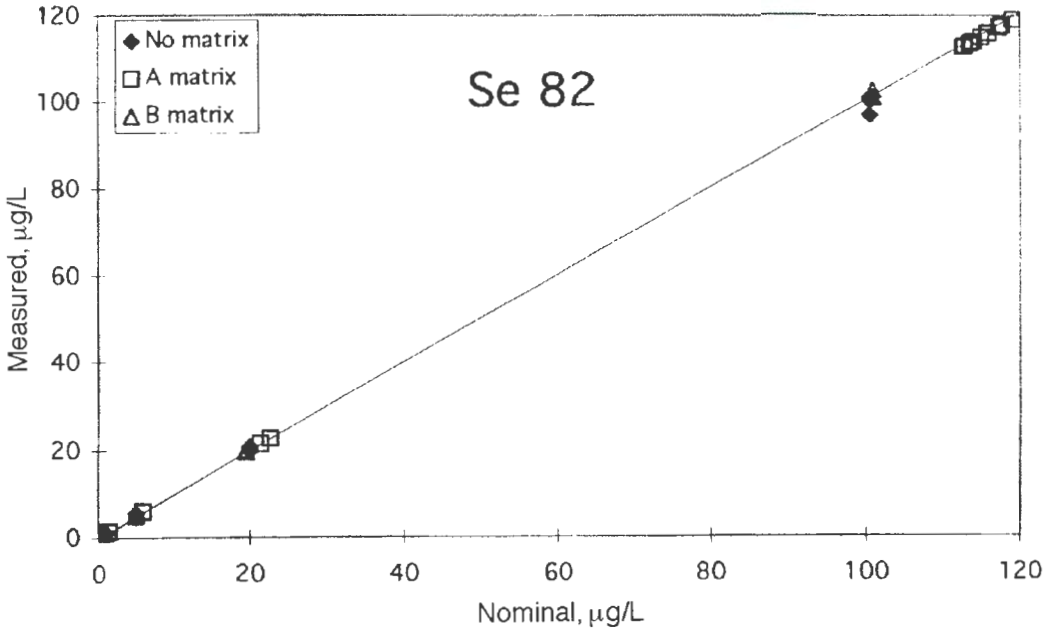


Figure 19. Plot showing matrix effects on ^{82}Se. Matrix effects are the same for all Se isotopes so the ^{82}Se plot shows the matrix effects on ^{78}Se as well.

Figure 20. Example of sample order used during ICP-MS analysis.

1. Blank
2. DCS
3. Medium matrix solution
4. Low matrix solution
5. Lowlow matrix solution
6. Blank
7. DCS
8. High matrix solution
9. Sample 1
10. Sample 2
11. Sample 3
12. DCS
13. Sample 4
14. Sample 5
15. Lowlow matrix solution
16. Sample 6
17. DCS
18. Sample 7
19. Sample 8
20. Medium matrix solution
21. Sample 6
22. DCS
23. Sample 4
24. Sample 2
25. Low matrix solution
26. Sample 5
27. DCS
28. Sample 3
29. Sample 1
30. Sample 7
31. Sample 8
32. DCS
33. High matrix solution
34. Medium matrix solution
35. Low matrix solution
36. Lowlow matrix solution
37. DCS
38. Blank

Figure 21. Example of the template used for Se, U, and Mo ICP-MS data correction. Counts per second data of repeats of the drift corrector solutions are corrected using two internal standards (Y and Bi) and %RSD calculated for each isotope is shown beneath each data block. Se data is best corrected using Y (shown by low %RSD) and U is best corrected by Bi.

	^{77}Se	^{78}Se	^{82}Se	^{83}Kr	^{95}Mo	^{238}U	^{89}Y	^{209}Bi
Corrected with ^{89}Y								
DCS-a	8021	27621	10631	1069	38007	113829	0.97	46729
DCS-b	8068	27382	10667	1139	37856	112592	0.97	46525
DCS-c	7543	25252	10176	990	38638	137317	0.93	55259
DCS-d	7703	25679	10281	1016	38578	135476	0.95	54722
DCS-e	7772	26107	10469	1020	38782	128909	0.99	53275
DCS-f	7817	26260	10461	1044	38708	130581	1.02	53017
DCS-g	7906	26412	10550	1020	38579	127222	1.07	51791
DCS-h	7871	26561	10440	1012	38751	127156	1.14	52091
%RSD	2.2%	3.0%	1.6%	4.5%	0.9%	7.2%		6.4%
Corrected with ^{209}Bi								
DCS-a	8005	27565	10609	1067	37930	113600	101556	0.07
DCS-b	8088	27447	10692	1142	37945	112858	102001	0.98
DCS-c	6366	21312	8588	836	32608	115886	85879	0.78
DCS-d	6565	21884	8761	866	32877	115454	86722	0.81
DCS-e	6803	22853	9164	893	33949	112843	89078	0.87
DCS-f	6876	23098	9202	918	34048	114861	89510	0.9
DCS-g	7119	23782	9500	919	34738	114555	91629	0.96
DCS-h	7046	23779	9346	906	34692	113837	91102	1.02
%RSD	8.8%	9.8%	8.2%	11.2%	5.9%	1.0%	6.8%	

Table 11a. Amount of Se and U standard added to each group of samples in standard addition analysis.

Sample	Se concentrations		U concentrations	
groups	Intended	final added	Intended	final added
blank W	0	0.00	0	0.00
blank X	2	1.93	2	1.94
blank Y	4	3.91	4	3.90
blank Z	6	5.38	6	5.41
low W	0	0.00	0	0.00
low X	2	1.91*	10	9.70
low Y	4	3.82	15	14.1
low Z	6	1.92	20	19.0
med W	0	0.00	0	0.00
med X	10	9.91	20	18.8
med Y	15	14.8	30	28.4
med Z	20	20.4	40	38.1
high W	0	0.00	0	0.00
high X	20	20.3	40	38.6
high Y	30	29.9	60	57.4
high Z	40	40.0	80	75.9

* A mistake was made in the laboratory preparation of this sample and therefore, this point was removed when interpreting standard addition data.

Table 11b. Results and data interpretation from standard addition ICP-MS analysis. y is the signal, x is the concentrations of standard added, and x' is the calculated concentration when the formula is solved for y=0. The percent difference is the difference between the -x' and the original analysis.

sample	sample	formula	-x'	original analysis	percent
name	group	of trendline (y)	(µg/L)	(µg/L)	difference
HNO3	blank Se	=234.46x + 44.516	0.19	0	
DC 3	low Se	=253.38x + 598.26	2.36	2.4	-2%
DC 4	med Se	=158.87x + 2674	16.83	12.55	34%
GC Ark	high Se	=163.74x + 3757.7	22.95	19	21%
HNO3	blank Se	=15124x + 448.47	0.03	0	
DC 3	low U	=16169x + 51404	3.18	5.46	-42%
DC 4	med U	=15982x + 231921	14.51	24.7	-41%
GC Ark	high U	=15788x + 691592	43.80	68.5	-36%

Table 12. Examples of input files for PHREEQC for basic geochemical modeling of groundwater and Arkansas River water at the study sites. The DC1 groundwater input file for Dodge City serves as a representative sample of this type of input.

Title	Deep groundwater	Arkansas River water
Solution 1		
Units	mg/L	mg/L
pH	7.55	8.20
pe	3.57	7.00
density	1.000	1.000
Temp	14.5	15.0
Ca	67.3	311
Mg	9.1	168
Na	18.8	467
K	2.9	11.4
Si	23.9	16.3
Cl	7.4	140
Sr	0.63	6.25
F	0.4	0.96
Br	0.0774	0.8045
I	0.0124	0.0504
B	0.037	0.662
Alkalinity	200 as HCO3	264 as HCO3
S(6)	44.5	2109
N(5)	15.7 as NO3	11.5 as NO3
N(-3)	0.05 as NH4	0.07 as NH4
U	0.0049	0.063
Se	0.003	0.017
O(0)	4.31	

Table 13. Example input file for surface complexation model. The input file for the deep groundwater at Dodge City serves as a representative sample for this type of model. The surface species for Se(IV) and U(VI) are defined in the WATEQ4F database and default values for the surface characteristics were used in this model.

Title	Sorption of Se and U
SURFACE 1	
Hfo_sOH	5e-6 600. 0.09
Hfo_wOH	2e-4
SOLUTION 1	
Units	mg/L
pH	7.55
pe	3.57
density	1.000
Temp	14.5
Ca	67.3
Mg	9.1
Na	18.8
K	2.9
Si	23.9
Cl	7.4
Sr	0.63
F	0.4
Br	0.0774
I	0.0124
B	0.037
Alkalinity	200 as HCO3
S(6)	44.5
N(5)	15.7 as NO3
N(-3)	0.05 as NH4
U	0.0049
Se	0.003
O(0)	4.31
USE solution 1	
USE surface 1	
END	

Chapter 6 Results

6.1 Water Chemistry and Site Characteristics

Arkansas River

Water samples were taken from the Arkansas River near two of the multi-level well sites. Specific conductance (SC) was measured in the field and minor and major element chemistry was determined later. Discharge values for the river were obtained from USGS stream gage data for the two sampling days. The discharges on the sampling dates were 208 cubic feet per second (cfs), 194 cfs, and 2850 cfs for March 17, March 18, and May 26, 1999, respectively. The constituent concentrations in the river water vary with discharge. Major and minor contents are given in Table 14 along with field and laboratory SC and laboratory pH. Historical data from 1974-1995 at Coolidge are also presented for comparison with the data collected in this study. Specific conductance data collected in the field for this study ranges between about 2500 μS/cm and 4400 μS/cm. The average SC for the Arkansas River near Coolidge, Kansas from the USGS historical data for the period 1974-1995 is 3600 μS/cm and the average from the historical USEPA database (KDHE data) for 1975-1995 is 3700 μS/cm. The two samples collected in March 1999 during lower flows contained higher concentrations of major constituents than the average at Coolidge. In contrast, the higher flow of May 1999 was fresher and had lower concentrations than the Coolidge average. The river water is a sulfate dominated type water (Figure 22).

Deerfield

The field parameters measured during pumping of the wells prior to sampling are shown in Table 15. In general the parameters measured in the field decreased steadily over

time (Appendix 1). Eh decreased most sharply at the beginning of pumping and pH was the most stable over time.

These field parameters are also shown with depth to evaluate the redox environment. The pH steadily increases with depth (Figure 23a). The Eh values measured in the field were corrected to the standard hydrogen electrode (SHE). An explanation of the corrections and the corrections are shown in Appendix 2. In general, the Eh decreased with depth to 250 feet and then increased in the deepest well. The DO measured decreased from 3.4 mg/L in the shallowest well to 2.6 mg/L in the deepest well (Figure 23b). The specific conductance trend with depth is shown in Figure 23c. The salinity decreases with depth suggesting that over time the elevated levels of sulfate and other constituents have seeped from the surface deeper into the aquifer.

The major and minor constituent analysis is shown in Table 16. The Ca, Mg, Na, Cl, and SO_4 concentrations range between 58-330 mg/L, 31-122 mg/L, 44-347 mg/L, 24-142 mg/L, and 158-1,597 mg/L, respectively. The groundwater compositions from observation wells D2-D5 are dominated by sulfate and the water from observation well D1 plots on the Piper diagram in an area of no dominance type (Figure 22). The contents of major cations and anions generally decrease with depth (Figure 24a-b). Sulfate decreases most from almost 1,600 mg/L in the shallowest wells to 158 mg/L at depth. Sulfate exceeds the recommended level for drinking water, 250 mg/L, in all but the deepest well at this site.

Garden City

Field parameters were measured until they stabilized before sampling (Appendix 3). The final values measured in the field are presented in Table 15. The Eh values presented in Table 15 are not corrected to the standard hydrogen electrode. The pH ranged between 7.06

and 7.24 and was generally lower in the deeper portion of the aquifer (Figure 25a). The Eh measured increased with depth from about 334 to 356 mV after being corrected to the SHE and suggests an oxidizing environment. The Eh trend is smoother here than at Deerfield. The DO varied between 1.9 and 3.06 mg/L (Figure 25b). The lowest DO content was in the deepest well and the highest in the next deepest well. The groundwater at this site is relatively saline throughout the profile, with specific conductance values between about 2,500 and 4,300 μS/cm (Figure 25c). The highest salinity in the profile is at intermediate depths between 80 and 150 feet.

The water quality analyses are in Table 17. The Ca, Mg, Na, Cl, and SO_4 concentrations were between 302-441 mg/L, 66-131 mg/L, 216-430 mg/L, 94-119 mg/L, and 1,298-1,864 mg/L, respectively. The groundwater composition at this site is predominated by sulfate (Figure 22). The chemistry ranged less at Garden City than at Deerfield as indicated by the much smaller change in concentrations of SO_4 and Cl with depth than at the Deerfield site. The concentrations of Sr, K, Mg, Na, and F follow a similar trend at this site (Figure 26a-b). The SiO_2 and NO_3 contents do not change appreciably with depth.

Dodge City

Field parameters were measured during sampling and their stabilization recorded with time (Table 15) (Appendix 4). The pH was much lower in the shallow contaminated water than in the freshwater from the deeper wells (Figure 27a). The corrected Eh increases slightly with depth suggesting a slightly more oxidizing environment with depth. DO levels measured were between 1.2 and 4.6 mg/L with the lowest in the shallow well and relatively similar contents in the deeper wells (Figure 27b).

At this site the elevated level of sulfate is contained within the alluvial aquifer and probably represents a more recent infiltration of river water. The graph of specific

conductance with depth shows that the river water and groundwater from the shallow well have very high specific conductance (3,000-4,000 μS/cm) and the three deeper wells are still fresh (about 500 μS/cm) (Figure 27c).

The water quality data for the Dodge City site for the samples analyzed by the KGS are in Table 18. Ca, Mg, Na, Cl, and SO_4 vary between 57-352 mg/L, 9-86 mg/L, 19-345 mg/L, 7-97 mg/L, and 45-1,538 mg/L, respectively. The fresh groundwater is a calcium-bicarbonate type water and the water from the shallowest well is sulfate dominated (Figure 22). The concentrations of most constituents such as Sr, K, Mg, Na, Ca, Cl and SO_4 are substantially lower in the High Plains aquifer underlying the alluvium, mirroring the specific conductance trend (Figure 28a-b). Concentrations of SiO_2, F, and HCO_3 remain relatively constant with depth but NO_3 increases with depth.

6.2 Se and U Concentrations

Results for analyses at the KU-PAL are presented in Table 19. Se concentration in the Arkansas River water averaged 18 μg/L for the lower flow samples. The Se concentrations in the river exceeded the EPA chronic toxicity limit for aquatic life and were near the acute level. The Se concentration in the groundwater ranged widely from 2.4 to 20.3 μg/L. Some of the groundwater had higher Se concentrations than the river water. None of the groundwater or river water samples exceeded the drinking water standard for Se. The Garden City site had the highest average Se concentration (16 μg/L). The average Se concentration at the Deerfield site was 14.6 μg/L and, similar to the pattern for U, the Dodge City average was significantly lower (about 6 μg/L).

The U concentration in the Arkansas River in the study area averaged about 66 μg/L during the lower flows sampled and the U in the groundwater samples ranged from 4.9 μg/L

to 41.3 μg/L. The Deerfield site had the highest average U concentration of 28.9 μg/L. The Garden City site had an average concentration of 22.8 μg/L and the highest concentration was are in the next to shallowest well. The Dodge City site had the lowest average U concentration (9.8 μg/L). This trend also corresponds to the average SC, Cl, and SO_4 concentrations at the sites.

6.2.1 Distribution and Comparison

The trends in Se and U concentrations with depth at Deerfield were different from the other sites and also different from the trends in major constituent contents. However, relative changes in the Se and U concentrations were similar at this site (Figure 29a). The concentrations were greatest in the shallowest wells, but also showed a peak at 250 feet deep. A peak in the gamma-ray log shows a clay layer at about 150 feet and bedrock at about 350 feet, which are just below the depths of the wells with low concentrations of Se and U. The range in Mo concentration with depth is much smaller than for Se or U and does not follow the same trend as these two elements at this site.

Except for a larger U content in water from the 88-ft. deep well, there were no substantial trends in Se and U concentration with depth at the Garden City site (Figure 29b). The Mo contents were constant throughout the depth profile. The contamination at the Dodge City site was probably relatively recent and was contained within the alluvial aquifer. The highest concentrations of Se and U were in water from the shallow alluvial well, and the fresher water in the deeper wells contained substantially lower levels of these two elements. Mo values remained relatively constant with depth and were in a similar concentration range as for Se and U in the deeper aquifer (Figure 29c).

6.3 Fate and Transport

6.3.1 Correlations of groundwater Se and U with water chemistry

The relationships between Se and U and various physical parameters and chemical constituents were examined in this study by calculating correlation coefficients and evaluating r-squared values. R-squared values showing the degree of correlation for these relationships are presented in Table 20. The correlative relationships were calculated for the groundwater data set from all the sites (14 points), the groundwaters at each separate site, the Arkansas River samples, and then for the complete data set of river water and groundwater samples.

In the Arkansas River, Se is related to SC and SO_4, and U is related to SO_4. In the river and the groundwater for all the study sites Se and U correlate significantly. At all sites Na, Cl and SO_4 concentrations are strongly related as expected because they are major constituents in the groundwaters. The correlation between the two constituents with the highest concentrations, Na and SO_4, simply indicates the excellent coherence in the behavior of these constituents in the river. When correlations are calculated between chemical parameters using the total groundwater data (14 groundwater samples) Se correlates significantly with SO_4, Cl, and SC and U with Cl and SC.

There are no correlative relationships of Se and U with chemical parameters at the Deerfield or Garden City sites. At Dodge City relationships exist with U and chemical parameters in the groundwater. U is significantly correlated with SC, Na, SO_4, Cl, Ca, Mg, Sr, B, and K. The smaller range in concentrations for Garden City might explain the absence of many significant correlations. However, both the Deerfield and Dodge City sites have large ranges in most constituent concentrations but show marked differences in the number of significant correlations. The significant correlations of U at the Dodge City site may reflect

the large range in concentrations of this element in the fresh and saline waters at the site, in comparison to the smaller range at Garden City. Significant patterns were not found and therefore, other methods, such as the use of change in ratios with depth and changes relative to conservative mixing curves, were better approaches for discerning fate of Se and U in the subsurface.

Se concentrations were compared to discharge values over an extended period of time in the Arkansas River to identify any correlation between concentration and discharge. The historical data collection was used for the Se and discharge data. U concentration was not compared because there were not enough data to plot and find relationships. Figure 30 shows that there is no relationship between Se and discharge. Part of the scatter on this plot is due to analytical error. However, it is apparent that some other factors are more important than just discharge in controlling Se concentration.

6.3.2 Conservative and non-conservative behavior

6.3.2.1 Ratio comparison at sites with river water

Cl and, in general, SO_4 behave conservatively in many environments. However, concentrations of SO_4 are so high in soil moisture irrigated with Arkansas River water in Colorado that gypsum can precipitate. Sulfate concentration increases substantially downstream in the Arkansas River in Colorado as illustrated by Figure 31. The data from Pueblo to Coolidge were taken from Mueller *et al.* (1991) and the Deerfield, Garden City, and Dodge City from data collected in this study. The use of these data is reasonable since the data from this study compares closely to historical data. The SO_4/Cl ratios downstream from Colorado and through the study area decrease slightly after the large sulfate increase between Nepeska and La Junta but remain in a relatively narrow range from below John

Martin Reservoir through southwest Kansas. Therefore, there is no substantial change in SO_4 relative to Cl in the river water.

Se and U concentrations were compared to these conservative species to evaluate their behavior in the river water and groundwaters. Historical data for the study area in southwestern Kansas were collected from STORET, QWDATA, and KGS databases created and maintained by various government agencies, i.e. USEPA, USGS, KGS, and KDHE. These data are for Arkansas River water and groundwater throughout the study area from 1974 to present. Summary statistics for this data collection for the Arkansas River and groundwater are in Tables 21a and 21b, respectively. These historical data can be compared to the data collected in this study. Ratios calculated from data in this study are given in Tables 22a for the Arkansas River, Table 22b for the groundwater in the study area, and Table 22c for each study site calculated separately.

In general, the Se ratios for the river water and groundwaters ranged over 3 to 4 orders of magnitude. Se/Cl for the Arkansas River waters collected in this study was close to the historical average (1.2×10^{-4}) and the average Se/SO_4 ratio for the river based on data from this study was about a factor of two smaller than the historical data. Se ratios from historical data and this study were about 1 order of magnitude greater in groundwater than in Arkansas River water in southwest Kansas suggesting some input of Se relative to Cl and SO_4 in the subsurface. The Se/Cl for the historical groundwater data set averaged 2.2×10^{-3} and for data collected in this study averaged 2.4×10^{-4}. The Se/SO_4 in groundwater is 2.9×10^{-5} for this study compared to 9.9×10^{-4} for historical data. In the historical data there is an increase in Se ratios as the saline water infiltrates from the river into the subsurface and the data from this study show a much smaller increase.

The U ratio data had a smaller range and were more similar than the Se ratio data. The relative differences of the U/Cl and U/SO_4 ratios between the Arkansas River and groundwater were similar. The U ratios have a greater range for the groundwater than the river water data. The average river U/Cl ratio (4.3×10^{-4}) for samples in this study is very close to the historical average and the ratio range for these data is relatively small. The historical U/SO_4 ratio for the river compares well with the U/SO_4 from this study. The U/Cl and U/SO_4 for groundwater in the historical data set average 3.6×10^{-4} and 4.6×10^{-5}, respectively, and these averages are similar for the different data sets. There is little difference in the average U ratios between the saline river water and the groundwater.

These ratios were also calculated for each site from the data collected in this study. Dodge City has the highest ratios but the Se and U are lowest at this site. The ratios can also be contrasted with salinity. The U/Cl and Se/Cl ratios are lowest at Garden City where the Cl concentrations are highest and the ratios are highest at Dodge City where Cl concentrations are lowest.

There is a large range in Se/U in the historical data, and the Se/U data do not compare quite as well as the Se and U ratios between the historical data and data collected in this study. The average Se/U ratio of 0.27 for this study is not substantially different from the value of 0.44 for the historical data for the river. Se/U for data from this study is 0.64 compared to 5.17 for the historical groundwater average. This indicates that there is considerably more Se relative to U in the historical set. In general, the data suggest that Se and U are behaving relatively conservatively in Arkansas River water.

6.3.2.2 Ratio changes with depth

The SO_4/Cl ratio in groundwaters at the study sites generally decreases with depth, reflecting the higher values in the river water than in the deeper, less saline water or

freshwater (Figure 32a). The river water ratio is an average calculated and used for comparison with all the sites. The saline groundwaters throughout the profile at Garden City and in the alluvium at Dodge City have SO_4/Cl ratios similar to that in the Arkansas River. The shallow saline waters at the Deerfield site have SO_4/Cl ratios substantially less than for the river water. The chloride is expected to be more conservative than SO_4. Thus, the lower SO_4/Cl in the saline groundwaters at Deerfield might reflect removal of SO_4 relative to Cl in the source water causing the salinization in the subsurface. The salinity source for the Deerfield site is mainly seepage of diverted river water used for irrigation (Whittemore *et al.*, 2000).

The distribution of ratios of U/Cl, U/SO_4, Se/Cl, and Se/SO_4 with depth at each site was evaluated to determine how Se and U behave relative to the Cl and SO_4 concentrations and the SO_4/Cl ratio. The U/Cl ratio is substantially lower in the shallow groundwater at all sites than in the river water, suggesting U behaves non-conservatively and is removed from solution during recharge (Figure 33a). The ratios of the fresh groundwaters at the Deerfield and Dodge City sites are appreciably greater than in the river water. At Deerfield, the Cl content decreases steadily with depth. The U/Cl ratio begins decreasing at a shallower depth suggesting removal of U relative to Cl, until below 150 feet where the ratio increases. At Deerfield, the U/Cl increases about four times between the shallowest and deepest wells. The U/Cl ratio does not range substantially with depth at the Garden City site.

The U/SO_4 ratio trends are very similar to those for the U/Cl ratio plots. The Deerfield and Garden City sites have similar U/SO_4 ratios to a depth of about 150 feet. The U/SO_4 ratio increases about six times in the groundwater at the sites. The U/SO_4 increases below 150 feet at Deerfield as the waters become fresher, just as the fresh waters of the Dodge City site have much higher U/SO_4 than in the saline alluvial water. The generally

smaller U/SO_4 ratios in the shallow saline groundwater at the sites than in the river water suggests that U is removed during infiltration of the river water into the subsurface (Figure 33b).

Se/Cl ratios with depth indicate that Se is behaving more conservatively at all sites than U and is not being removed from solution very much (Figure 34a). The ratio first decreases slightly and then increases at Deerfield, does not change much at Garden City, and increases and then decreases at Dodge City. The Se/Cl ratios do not change significantly between the river and shallow groundwater. At Deerfield, the increase in Se/Cl relative to the decrease in salinity in the aquifer indicates an input of Se around 150 feet. The Dodge City groundwater ratio increases sharply at about 120 feet and then decreases. Se/SO_4 ratios with depth show the same trends as Se/Cl at each site with the Deerfield site trend slightly less exaggerated (Figure 34b). The Se/SO_4 ratio increases about 12 times at Dodge City in the groundwater, which is three fold over the increase of the Se/Cl ratio.

A plot of the Se/U ratio with depth provides a picture of Se and U behavior relative to each other (Figure 32b). There is no consistent change in the Se/U ratios with depth at the sites. At all three sites the ratio is substantially greater in all groundwaters than in the river water. The range in the Se/U ratio in the groundwaters is about the same or greater than the difference between the river water and the average groundwater at each site.

The Mo/Cl ratio is within a relatively narrow range for the upper 250 feet of the aquifers at Deerfield and Garden City and is also similar to the ratio in the alluvium at Dodge City (Figure 35). The Mo/Cl is smaller in the saline groundwater than in the river water suggesting that a small amount of Mo is removed from solution during transport into the subsurface. The Mo/SO_4 ratio change with depth is similar to that for Mo/Cl.

The change in major cation ratios with depth is useful for assessing ion exchange, and therefore, sorptive properties of the system. The ratio of Na to Ca and Mg represents the relationship between the major cations with a single charge and those with a double charge. Removal of Na from infiltrating river water relative to Ca and Mg appears to be significant in the shallow aquifer (Figure 36). The deeper, fresher waters present at Deerfield and Garden City have substantially lower Na/(Ca+Mg) ratios than the saline waters. The changes in the cation ratio with depth, however, indicate that ion exchange may be occurring in addition to just simple mixing as the control on the ratio. For example, the Na/(Ca+Mg) ratio decreases substantially with depth in the deeper portion of the aquifer at Garden City even though the salinity does not decrease appreciably.

6.3.2.3 Mixing curves

Mixing curves are another geochemical technique valuable for examining changes in Se and U relative to conservative constituents. The approach is especially useful for separating changes in the constituents due to mixing of the saline river water with fresh groundwater from changes due to non-conservative behavior of the Se and U. The ratios of U or Se to Cl and SO_4 are plotted on the y-axis and compared to the conservative constituent concentration on the x-axis in Figures 37 and 38. Theoretically a mixing curve is a line that shows all possible mixing fractions between the two end-member solutions. In this case the end members are the saline river water and the deep fresh groundwater at the sites. Data for the water samples from each well (14 points) were plotted on these graphs along with the two most saline river waters collected during this study (Garden City and Dodge City).

The two mixing plots for U ratios have two mixing lines on them. These represent mixing of the fresh groundwater at Deerfield and Dodge City with river water. The U ratios

for all three freshwaters at Dodge City are similar and effectively serve as one end-member in Figures 37a and 37b. The Garden City data were evaluated with respect to the other lines because there is no fresh groundwater at this site. The Se plots have three mixing lines, two from the river end member to two freshwater end members at Dodge City and to one freshwater end member at Deerfield. Two mixing lines were plotted at Dodge City to show changes in the ratios relative to the end-member range for the three deeper freshwaters.

In general, the U-Cl and U-SO_4 mixing curves show the same trends. The close group of points clustered below the mixing lines on the U/Cl mixing curve suggests at least some removal of U from solution at all sites with the most significant amount of removal at Garden City and secondarily at Deerfield (Figure 37a). The U-Cl mixing curve does show more exaggerated trends than the U-SO_4 curves which is similar to the greater decrease in the ratios on the U-Cl plot with depth (see Figure 33a). The point for the Deerfield groundwater that is slightly saline at about 245 feet plots on the mixing curve but at a significantly higher U/Cl and U/SO_4 ratio relative to the other groundwater points. This suggests an input of U at this horizon (Figure 37b). All of the more saline groundwaters at the Deerfield and Garden City sites, plot at lower U/SO_4 ratios than the ratios of both mixing curves at the sulfate content of the water. Otherwise there is a grouping of all the Garden City waters, 3 Deerfield waters, and the other Dodge City waters below the mixing curves. The Garden City points plot the furthest below the lines, which supports the Se/U plot (see Figure 32b).

The Se mixing curves show somewhat different trends, specifically that conservative mixing is a more important mechanism for Se than for U. The Se-Cl and Se-SO_4 mixing curves show that the point for the saline water in the alluvium at Dodge City falls along one of the mixing curves for that site and that conservative mixing appears to be the main control on the water composition. This suggests that there is no significant removal of Se at this site

(Figure 38a). The Garden City points are mostly clustered near the saline end member but plot relatively near the mixing curves, also suggesting that the Se behaves relatively conservatively at this site. The slightly saline groundwater (61 mg/L Cl) at Deerfield plots above the mixing line and the saline groundwater at about 92 mg/L Cl plots below the line. This suggests that there is a local source inputting Se at about 245 feet deep, which is also where U is input, and significant removal, such as sorption, at the 140-foot depth. This can be compared to the Se/Cl ratio with depth plots. The Se/Cl ratios at Garden City and Dodge City change little to none between the river and groundwater supporting the importance of mixing (Figure 34a). The Deerfield Se/SO_4 ratio increases with depth below 200 feet (Figure 34b). The mixing curve plot (Figure 38b) illustrates better that there is apparently Se input into the system at the 245-foot zone in comparison with the deeper freshwater.

6.3.3 Geochemical modeling

Geochemical modeling using the USGS reaction path model, PHREEQC (Parkhurst, 1995), provides many insights about the speciation, distribution, and mineral saturation at the study sites. The modeling supports the other geochemical evaluations, i.e., the mixing curves and ratio plots.

6.3.3.1 Species concentration distribution

Selenium speciation

For the waters collected from the Arkansas River, the model output shows that 74-83% of the dissolved Se is present as Se(IV) for the Garden City samples and near Dodge City it is only 60% (Table 23). Essentially all of the Se(VI) is in the SeO_4^{-2} form. The Se(IV) is evenly distributed between $HSeO_3^-$ and SeO_3^{-2} in the Dodge City sample and $HSeO_3^-$ is

dominant in the Garden City samples. In general, Eh and pH are the main controls on the species distribution in the system. In this case, the same pH was used for all three river models because the laboratory pH was the same, and the same Eh was used as input because a general value was assumed for this oxidized environment. The different distribution for the different river waters is due to the effects of other constituents in the water.

The distribution of Se species in the groundwater at the sites does not range substantially. In the groundwater at all three sites, essentially 100% of the dissolved Se exists as Se(IV). Se(IV) is the most dominant oxidation state as expected in this mildly oxidizing to oxidizing environment. In the groundwater at the Garden City site, the Se is distributed as mostly (90-93%) $HSeO_3^-$ and some (6-9%) SeO_3^{-2}. At Dodge City and Deerfield, $HSeO_3^-$ is a slightly smaller fraction of the total Se(IV) than at Garden City and SeO_3^{-2} again makes up the rest (Table 24).

Many factors contribute to the redox conditions or Eh measured in groundwater other than simply DO. This often leads to redox disequilibria as described by Langmuir (1997) and Lindberg and Runnells (1984). These authors attribute this disequilibria to either field measurement error or because other redox couples are also contributing to the redox conditions. In this study both Eh and DO were measured in the field and Eh values measured in the field at the study sites in this project (Table 15) do not appear to be in equilibrium with the DO measurements reported; Eh values would be higher if they were in equilibrium. The true Eh is most likely somewhere between the measured Eh and DO, but this depends on what redox couples are affected by Se and U. If a higher Eh assuming equilibrium with DO was used for the geochemical modeling then, in general, the Se distribution would be more similar to the river distribution. Se(IV) would remain the dominant Se species, but some Se(VI) would also be present.

Selenium speciation with depth

The model output was plotted to show Se speciation with depth, which allows evaluation of trends through the subsurface at the sites. Selenite species ($HSeO_3^-$, SeO_3^{-2}) are the most important at all sites. All Se species have less variation with depth at Deerfield than the other sites. A closer look at the Se(IV) species at Deerfield shows that both SeO_3^{-2} and $HSeO_3^-$ have a sinuous trend with depth (Figure 39a). $HSeO_3^-$ is the dominant species and the trend is much more defined at this site.

At Garden City, the concentrations of the major Se(IV) species stay relatively steady in the groundwater with depth (Figure 39b). Se species profiles with depth at Dodge City are somewhat similar to those at Garden City (Figure 39c).

Se species distribution can be compared to Eh or pH conditions with depth. Refer to Figures 23a, 25a, and 27a for the pH and Eh plots with depth at the study sites and Figures 29a, 29b, and 29c for Se and U plots with depth. At Deerfield there is not any similarity between the sinuous Se(IV) trend with depth and the Eh or pH trends. At Garden City, Se(IV) seems to generally follow the pH trend. Although Eh and pH show similar trends with depth at Dodge City, Se does not seem to follow this trend.

Uranium speciation

In the Arkansas River essentially all uranium is present as U(VI). The dominant species is $UO_2(CO_3)_3^{-4}$ (91-95%) and several percent of the U occurs as $UO_2(CO_3)_2^{-2}$ whereas less than 0.1% occurs as UO_2CO_3 and $UO_2(OH)_3$- (Table 23).

U in the groundwater also is mostly in the U(VI) oxidation state as expected in this environment. The U(VI) speciation is dominated by uranyl di- and tri- carbonate complexes as many others have reported (Zielinski *et al.*, 1995; Henry *et al.*, 1982). At all three sites the

U is mostly present (about 50-70%) as the uranyl tri-carbonate, $UO_2(CO_3)_3^{-4}$ (Table 24). The rest of the U is mainly $UO_2(CO_3)_2^{-2}$ and ≤1% UO_2CO_3. The U distribution in the fresh to slightly saline waters at Dodge City and Deerfield differs from the saline waters at the these sites and at Garden City in that the relative amounts of $UO_2(CO_3)_3^{-4}$ and $UO_2(CO_3)_2^{-2}$ are about the same.

Complexes with other constituents were also considered, for example, UO_2F^+ and UO_2SO_4, but these comprised less than 0.001% of the U. PO_4 complexes could be significant also in some wells and possibly the river, but PO_4 was not included in the input because PO_4 was not measured. The effect of PO_4 concentrations on U chemistry using typical river values is described later in the subsection on geochemical modeling.

Redox disequilibrium does not affect U speciation significantly. As discussed above if the Eh values were corrected for equilibrium with DO, Eh would be slightly higher. However, a higher Eh in the geochemical model would have no effect on the U speciation because U is already present in the most oxidized state.

Uranium speciation with depth

U species distribution with depth shows different trends from those for Se. The distribution of U(VI) species in the groundwaters does not change appreciably with depth and is similar to that in the river water. The uranyl di- and tri- carbonates ($UO_2(CO_3)_3^{-4}$ and $UO_2(CO_3)_2^{-2}$) and UO_2CO_3 are the most important followed by the OH- complexes (Figures 40, 41 and 42). The major change in U(VI) species between the river water and the saline water in the alluvium is the decrease in the concentrations of the most important species $UO_2(CO_3)_3^{-4}$. There is a decrease in all predominant U-CO_3 and U-OH complexes except $UO2(CO_3)_3^{-4}$ from the shallow well into the middle of the aquifer at the Deerfield site.

At Garden City the concentration of the uranyl tri-carbonate complex decreases from the river to the shallow groundwater whereas, most of the U(VI) species increase (Figure 41). U speciation at Dodge City is similar to that at Garden City (Figure 42). Looking more closely at differences between the river and saline groundwater in the dominant U(VI) species at Dodge City shows that the only ones to decrease as the water travels from the river into the aquifer are $UO_2(OH)_3^-$ and $UO_2(CO_3)_3^{-4}$. The general trend in the concentrations of the carbonate complexes is the same as that of the U molality with depth trend (Figure 42).

The distributions in the river water and the groundwater are different for various reasons. Differences in pH, Eh, and DO all probably affect the speciation significantly. The distributions are not similar for the saline and fresh groundwaters at Deerfield and Dodge City, therefore the major constituent concentrations appear to control distributions (see Figure 28a).

Comparing U distribution to Eh and pH trends does not reveal much about the behavior of U species (Refer to Figures 23a, 25a, and 27a for the pH and Eh plots with depth at the study sites and Figures 29a, 29b, and 29c for Se and U plots with depth). At Deerfield, U concentrations show the same sinuous trend as Se, but no similarity to either the Eh or pH trends. At Garden City, U concentrations appear to follow a trend similar to Eh, but at Dodge City U concentration does not seem to follow either Eh or pH trends.

6.3.3.2 Mineral saturation and solubility controls

Evaluating the saturation of various minerals gives insight into the general state of the system and the solubility controls at each site. This is an important aspect to understand in this study to accurately describe the behavior of Se and U and their relationship to other major and minor element chemistry. Since there are high levels of SO_4, Ca, and Mg in the

waters, the saturation states relative to sulfate and carbonate minerals were also considered. A water is considered saturated with respect to carbonate minerals if the saturation index is within about 0.3 of saturation and within about 0.1 for gypsum (Langmuir, 1997).

The river water samples at both Garden City and Dodge City were oversaturated with respect to dolomite, calcite, aragonite, magnesite, and chalcedony. The river samples collected during lower flows are close to saturation with respect to gypsum.

The saline water from the shallowest well at Deerfield was substantially oversaturated with respect to aragonite, calcite, dolomite, and magnesite. Waters from the four deeper wells remain close to saturation with respect to aragonite and calcite and slightly supersaturated with respect to dolomite (Figure 43a). The groundwater at Garden City is close to saturation with respect to calcite and aragonite, and slightly to moderately unsaturated with respect to dolomite and gypsum (Figure 43b). The saline groundwater in the alluvium at Dodge City is saturated with respect to dolomite and aragonite, slightly supersaturated with respect to calcite, and very slightly undersaturated with respect to gypsum. The deeper, fresh groundwaters are saturated with respect to calcite and aragonite, somewhat undersaturated with respect to dolomite, and substantially undersaturated with respect to gypsum. At Dodge City, chalcedony, aragonite, calcite, and dolomite are oversaturated. Aragonite and dolomite become slightly undersaturated in the deeper wells. (Figure 43c).

In the Arkansas River, Se minerals are significantly undersaturated (Figures 44a, 44b, and 44c). In contrast, $Se_{(s)}$ is the only Se solid that is close to saturation in any groundwater. Saturation of SeO_2 and $CaSeO_3$ vary the least with depth at all sites. At Deerfield, $Se_{(s)}$ is closest to saturation in wells D2 and D3, which are between 150 and 250 feet deep. There is very little change in $CaSeO_3$ saturation and it remains undersaturated (Figure 44a). At

Garden City, $Se_{(s)}$ is very undersaturated in the river but the shallow groundwater is close to saturation with respect to this mineral (Figure 44b). At Dodge City, $Se_{(s)}$ is closer to saturation in the groundwater than in the river, and the groundwater in the alluvium is nearly saturated with respect to $Se_{(s)}$. This is appropriate since the water is traveling from oxidizing to less oxidizing conditions. Se(0) is a reduced species and will precipitate when the Eh of the water decreases. Saturation with respect to other Se solids at Dodge City is constant and remains substantially low (Figure 44c).

In the oxidized environment of the Arkansas River, saturation with respect to U minerals remains very low (Figures 45a, 45b, and 45c). U minerals precipitate in very reducing environments. In general, saturation with respect to U minerals is the same at the study sites (Figures 45a, 45b, and 45c). Overall, uraninite and coffinite are the U solids closest to saturation but these would not precipitate without a significant change in the redox conditions at the study sites. These two minerals are less undersaturated in the groundwaters than in the river water. Saturation with respect to most U solids is very low and relatively constant with depth. Gummite and UO_3 show no change in saturation with depth at any site.

6.3.3.3 Sorption model

Sorption of Se and U at the Dodge City site was evaluated using the surface complexation capability of PHREEQC. Previous modeling of the groundwater and Arkansas River water at this site showed that the dominant species (90-100%) in the waters were Se(IV) and U(VI). As discussed above, the species of interest, Se and U, in these oxidation states have the strongest tendency to sorb relative to other oxidation states. Therefore, in this project the sorption modeling was limited to these species.

Se and U sorption onto a ferric oxyhydroxide substrate was studied based on an extensive body of research and data available in the PHREEQC and WATEQ4F databases. Sorption onto various clays is also probable at this site but was not studied here due to the limited availability of specific clay descriptions for the High Plains and alluvial aquifers. The goal of this modeling was to gain a clearer picture of the geochemical controls at these sites. A general sorption model was designed to evaluate whether sorption of Se or U onto ferric oxyhydroxides appears to be an appropriate process for the study area and, if so, to quantify the significance.

A strong and weak site is defined for U(VI), but the sorbed species are in different forms, $OHUO_2^{+2}$ and OUO_2^{+}. The surface species for Se(IV) are different from the traditional method of defining a weak and strong site. Both reactions are for sorption to weak sites, suggesting that for some reason this is the way Se(IV) behaves when sorbing to ferric oxyhydroxides. Therefore, the output will be a quantitative picture of the sorption but is not a comparative result. In other words, Se and U can not be quantified simply by comparing the log K's of the reactions.

Surface complexation models were designed for the deep groundwater and the Arkansas River. The hypothesis was that there would be some sorption of both Se and U, but that there would be no competition between these species for sites due to different pH ranges of sorption. Very little U(VI) is adsorbed but nearly all of the Se(IV) is adsorbed on ferric oxyhydroxide surfaces of sediment in the river water. The distribution of Se(IV) and U(VI) in the sorption model output for the deepest well at the Deerfield site is shown in Figure 46. U(VI) sorbs much more onto the weak site (defined as $Hfo_OUO_2^{+}$ in the WATEQ4F database) than the strong site (defined as $Hfo_OHUO_2^{+2}$ in the WATEQ4F database). The amount of free U(VI) is similar to the amount sorbed onto the weak site as it is defined in the

aforementioned database. Very little Se(IV) sorbs onto the weak sites of ferric oxyhydroxides as they are defined in the WATEQ4F database. The distribution of Se between dissolved Se and the two sorption sites is about the same, but overall sorption of Se does not appear to be a major factor at this site. However, at the Deerfield site there are thick clay sequences and this small amount of sorption could become significant when occurring throughout this sequence.

Figure 47 shows these results in the form of the amount (μg/L) sorbed from solution for the groundwater at Deerfield and the Arkansas River in the study area. The difference between the molality of Se or U in solution before and after sorption was calculated. About 5 times more U was sorbed from the groundwater than from the river. Approximately, the same amount, <0.10 μg/L, of Se was sorbed from the surface and groundwaters.

6.3.3.4 Sensitivity analysis

Sensitivity analysis was done on the geochemical model by evaluating the effects of changing some important input parameters; pH, Eh, and PO_4, SO_4 and Fe concentrations. The sensitivity model runs were done on the Dodge City site because it provides a representative example. Eh and pH effects were investigated because of the redox sensitivity of Se and U.

The presence of PO_4 and/or SO_4 can affect the speciation of uranium. With even small amounts of phosphate present U-PO_4 complexes can dominate over U-CO_3 species and all other U complexes (Langmuir, 1978). PO_4 effects were also evaluated because PO_4 concentrations were not measured in this study and the sensitivity analysis provides a way to determine the effect of different PO_4 concentrations. Typical dissolved concentrations of PO_4 obtained from historical USGS data in the study area are 0.02-0.06 mg/L for the Arkansas

River near Coolidge and <0.01-0.03 mg/L for groundwater in Kearny, Finney, Gray, and Ford counties. The maximum PO_4 concentration that can be expected in the study area is 0.1 mg/L. Some SO_4 concentrations can effect Se and U sorption. Due to the relationship between Fe and Se in many environments as discussed in the geochemistry chapter, Fe effects on the model were investigated. Fe concentration was not determined for the water samples, however, the model output showed that typical Fe concentrations in groundwater do not significantly affect the output.

pH effects

The sensitivity analysis for pH in the model was examined for the effect of values between 6.5-8.5 on the deepest (DC1) well at Dodge City. Results show a strong impact on Se and U speciation and the saturation state of some minerals. pH is an important input parameter and strongly affects the output. The results help determine the impact of inaccuracies of the field parameter measurements and the possible variations due to different environmental conditions.

pH effects are different for Se and U and seem to have some dependence on relative importance in the system because there are not any pH effects on the concentrations of the most dominant oxidation states, U(VI) and Se(IV). The plots show that for the less important oxidation states, the Se concentration increases and the U contents decrease with significantly increasing pH (Figure 48a).

The relative importance of the Se species are the same at any given pH until pH above 8.5 where $HSeO_4^-$ becomes more important than H_2SeO_3 (Figure 48b). $HSeO_3^-$, the dominant Se species, shows little pH dependence with the pH range 6.5-8.5. The concentrations of all U(IV) species decrease as pH increases (Figure 49a). The U(V) species

show a different dependence on pH. UO_2^+ concentration decreases relatively sharply with pH and the U(V)-carbonate complex increases slightly (Figure 49b). pH has the greatest effect on the U(VI) species concentrations for two reasons. First, the U(VI) are the dominant species present. Second, in the pH range 7.5-8, the general pH range of the field area, there are some important changes in hierarchy of complexes present. As the complexes increase in importance the slope of the lines decrease. In other words, as the complexes become relatively more important the dependence on pH decreases. The two U-hydroxide complexes have a proportional relationship to pH. An important aspect on this plot is that the predominance of the two most important U(VI) complexes, $UO_2(CO_3)_3^{-4}$ and $UO_2(CO_3)_2^{-2}$, reverse at pH 7.5 (Figure 50).

Calcite, aragonite, and dolomite become oversaturated as pH increases as expected (Figure 51a). The saturation with respect to $Se_{(s)}$ shows strong dependence on pH. The saturation indices of $Se_{(s)}$ decrease in an almost linear trend with increase in pH. $CaSeO_3$ and SeO_2 are less affected by changes in pH. Overall, all Se minerals remain undersaturated throughout the simulation (Figure 51b). The saturation indices of all U minerals evaluated decrease as pH increases. The magnitude of the decrease ranges and is greatest for U_3O_8 and UO_2. Saturation of U minerals is slightly affected by pH but they all remain very undersaturated (Figure 51c).

Eh effects

The redox sensitivity of Se and U, as well as the possibility of small field measurement errors of Eh, are important reasons for evaluating the effect of Eh on the model output. This sensitivity analysis was run on the deep fresh groundwater and the saline shallow water at Dodge City. The pe was the variable changed in the model. The patterns

and Eh effects are the same in both results. This is mostly because Se and U are redox sensitive and therefore react to changes in Eh similarly regardless of the other constituents present. The Eh data corrections relative to the standard hydrogen electrode were made late in this project after the modeling was completed. The uncorrected Eh values shown in Appendix 2 were used in the modeling and these were lower than the corrected data. The trends will be similar, however, this sensitivity analysis only provides a qualitative description of the sensitivity of the model to Eh input values.

In the groundwater, Se(-II) species concentrations (HSe^- and H_2Se) decrease as pe increases because Se(-II) species are the most reduced and are not present in significant concentrations as the water becomes more oxidizing (Figure 52). There is an increase in the concentration of the most oxidized species, Se(VI), with increase in pe. The concentrations of the major Se species in the water, the forms of Se(IV), do not change appreciably with increase in pe. The concentrations of most abundant U species in the groundwater at the sites, U(VI), are not affected with increase in pe. The reduced species, U(IV) and U(V) all decrease in concentration with increasing pe (Figures 53a and 53b).

Eh variations could also affect the saturation state with respect to minerals. $Se_{(s)}$ and U_4O_9 are the only strongly pe dependent minerals. The most important effect is for $Se_{(s)}$ since it is the only one that dissolves back into solution as pe increases (Figure 54a). The decrease in saturation as pe increases is expected because $Se_{(s)}$ is a very reduced mineral phase (see Figure 10). There is little to no difference in the saturation of $CaSeO_3$ and SeO_2. The progressive increase in pe causes no significant change in the saturation of gummite, uranophane, and UO_3 (Figure 54b). U_4O_9 is the most redox sensitive and its saturation decreases substantially as redox conditions increase. In this pe range, uraninite, $UO_{2(a)}$ and

coffinite are the only other U minerals that are significantly affected by pe change (Figure 54c).

Sulfate effects

The effect of sulfate concentration on model output was evaluated due to the high sulfate concentrations in the study area. The sensitivity analysis shows that sulfate concentrations typical of the study area (1,000-3,000 mg/L) do not significantly affect the results for Se and U species and minerals. Sulfate does not inhibit U(IV) or U(VI) complexation with CO_3^{-2} and OH^- (Figures 55a and 55b). The increase in the $UO_2CO_3)_3^{-4}$ concentration with increase in sulfate content might be related to ionic strength effects. Varying the input sulfate concentration in the model has no effect on Se species distributions (Figure 55c).

Phosphate effects

Sensitivity analysis for PO_4 content was performed using the river and shallow and deep well waters at the Dodge City site for a representative sample of the study area. Varying PO_4 concentrations did not affect Se speciation and mineral saturation. Phosphate concentration has no effect on U complexation or U mineral saturation below about 0.01-0.05 mg/L PO_4. Therefore, the phosphate effects are not important in the waters in the study area because typical concentrations are often lower than that.

In the Arkansas River, varying phosphate concentration has no significant effect on any U complex except the U-PO_4 species (Figure 56a). PO_4 concentration has a linear relationship with molality of the U-PO_4 complexes in the groundwaters except that the molality of $UO_2(HPO_4)_2^{-2}$ plateaus at 0.1 mg/L (Figures 56b and 56c). There are no

observable phosphate effects on U-CO_3 complexes in the Arkansas River, but there are effects on the U-CO_3 species in the groundwaters that are similar for both the shallow and deep wells (Figures 57a, 57b, and 57c). U-CO_3 complexes in groundwater decrease substantially in importance at PO_4 concentrations above 0.01 mg/L PO_4. $UO_2(HPO_4)_2^{-2}$ has the strongest dependence on PO_4 concentration and increases as PO_4 is increased. The molality of $UO_2PO_4^-$ slightly increases then decreases when PO_4 concentration is greater than 0.1 mg/L. Increasing PO_4 concentration has no significant effect on U-CO_3 complexes below 0.01 mg/L PO_4. U-CO_3 complexes remain dominant up to about 0.05 mg/L PO_4. At about 0.01 mg/L PO_4, phosphate presence inhibits CO_3 complexation. The effect is the same in the shallow and deep wells and between the di- and tri- uranyl carbonates and UO_2CO_3.

There is no observable effect of PO_4 on the river water, most likely due to the mildly alkaline pH in the water. Phosphate presence has no effect on U mineral saturation in the Arkansas River (Figure 58a). This is possibly due to some CO_2 buffering effect or because PO_4 does not complex under the oxidizing and slightly alkaline conditions of the river water. All U minerals are undersaturated and become more so as PO_4 concentration increases. PO_4 has essentially the same effect on U mineral saturation in shallow and deep well waters (Figures 58b and 58c). There is no substantial impact on mineral saturation up to 0.01 mg/L PO_4.

Table 14. Water quality analysis for Arkansas River samples. Concentrations are given in mg/L. Data for the Arkansas River at Coolidge, Kansas is the historical average.

location	discharge	lab SC	lab pH	measured SC	SiO_2	Ca
Dodge City	208	3950	8.2	4040	16.3	311
Garden City	194	4157	8.1	4350	17.9	360
Garden City 2	2850	2420	8.15	2490	9.4	213
Coolidge			8.1	3651	14.0	301

location	Mg	Na	K	Sr	HCO_3	SO_4
Dodge City	168	467	11.4	6.25	264	2109
Garden City	189	557	13.3	6.42	260	2280
Garden City 2	102	249	9.0	3.56	220	1122
Coolidge	147	441	11	5.34	315	1157

location	Cl	F	NH_4^+	NO_3	B
Dodge City	140	0.96	0.07	11.5	0.662
Garden City	142	1.00	0.07	9.6	0.7490
Garden City 2	70.4	1.04	0.07	1.9	0.393
Coolidge	130	0.81	0.12	8.6	0.4300

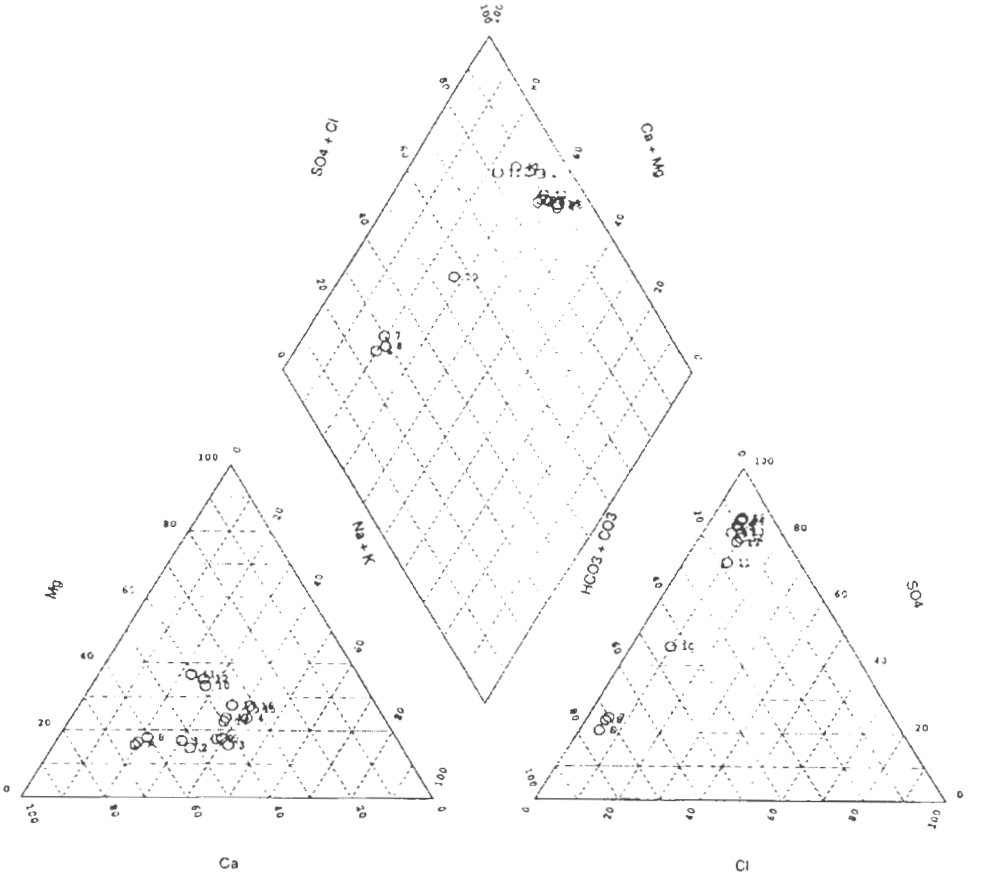


Figure 22. Piper diagram showing water types for the Arkansas River and groundwater at the study sites. The points representing groundwater samples are numbered from 1 to 14 for the shallow to deep groundwaters at Deerfield (1-5), Garden City (6-10), and Dodge City (11-14). The Arkansas River waters are numbered 15 (Garden City), 16 (Dodge City), and 17 (dilute Garden City).

Table 15. Final field parameters measured in observation wells at study sites (D=Deerfield, GC=Garden City, and DC=Dodge City). The DO for wells D-1, D-3, and D-4 were linearly interpolated due to meter problems in the field. Eh values shown here are not corrected to the standard hydrogen electrode as is required with a platinum electrode. The corrected Eh data is shown in Appendix 2.

well number	pH	Eh (mV)	DO (mg/L)	temperature (^{0}C)	SC (uS/cm)
D-1	7.65	133	2.58	17.2	723
D-2	7.47	110	2.79	16.7	1530
D-3	7.31	115	3.00	16.3	2300
D-4	7.23	140	3.21	15.9	3380
D-5	7.21	168	3.42	15.7	3380
GC-1	7.12	146	1.90	14.6	2660
GC-2	7.06	147	3.06	13.5	3440
GC-3	7.19	133	2.60	12.5	3670
GC-4	7.24	132	2.16	13.4	3640
GC-5	7.16	123	2.80	13.5	3180
DC-1	7.55	204	4.31	14.5	449
DC-2	7.65	154	4.63	14.7	467
DC-3	7.64	154	4.63	14.4	446
DC-4	7.24	135	1.22	15.2	3040

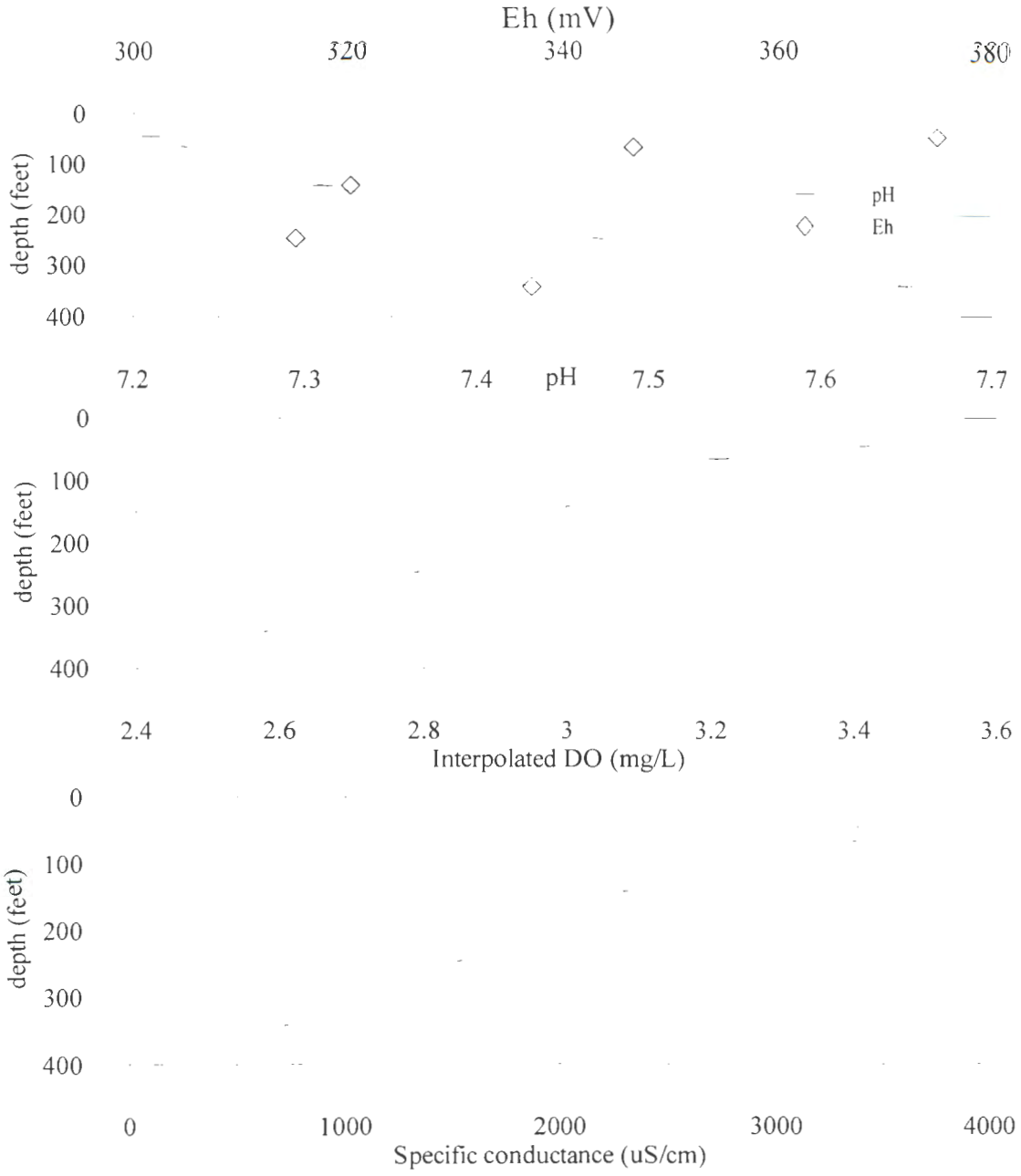
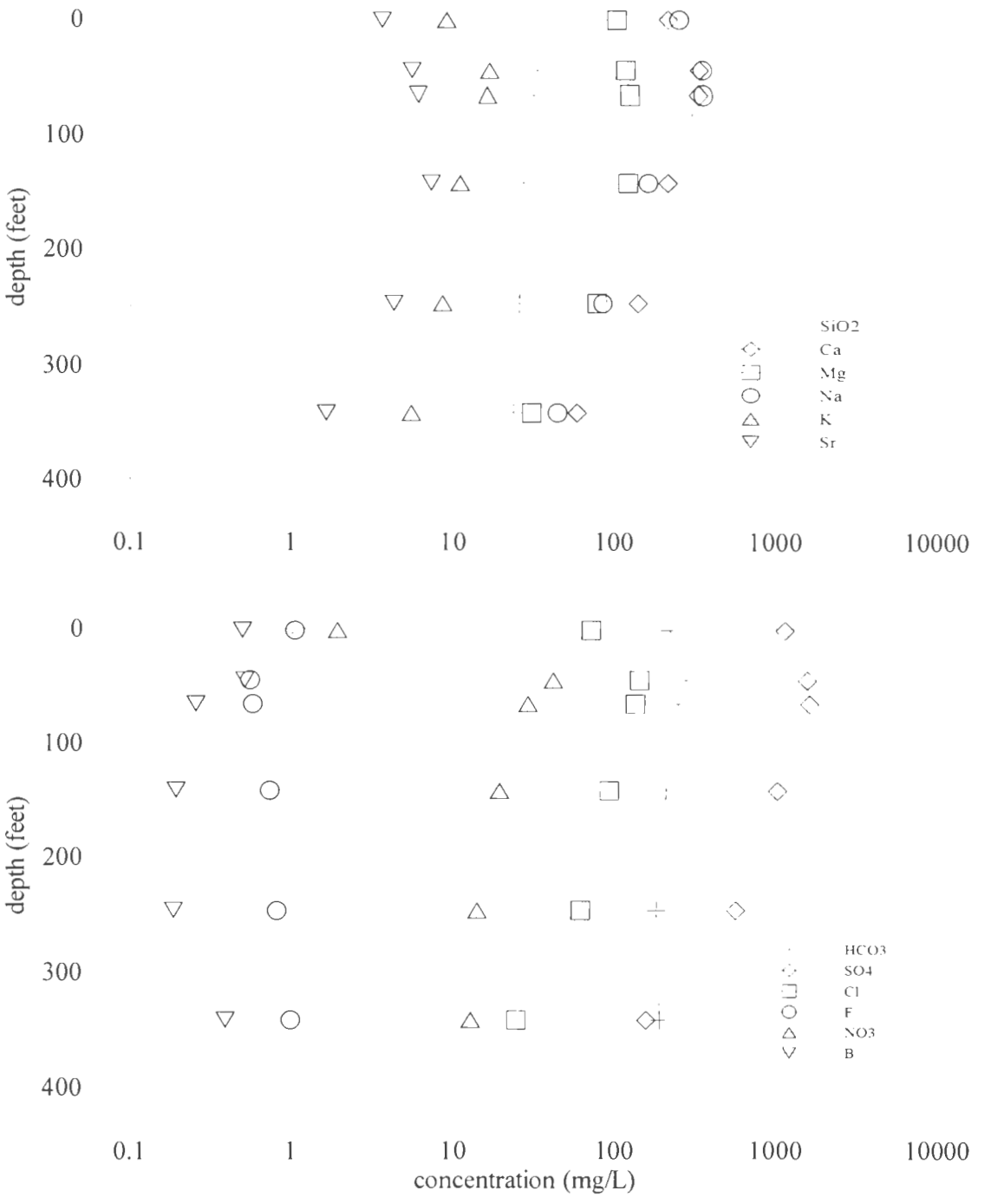


Figure 23. Final field parameters measured at Deerfield. (a) Eh and pH, (b) DO, and (c) SC with depth at Deerfield. DO in wells 2 (340 feet) and 5 (45 feet) were measured in the field and DO values for wells 1, 3, and 4 were linearly interpolated.

Table 16. Water quality analysis for Deerfield groundwater samples. Concentrations are given in mg/L.

sample #	SiO_2	Ca	Mg	Na	K	Sr
D-1	23.4	58.2	30.5	44.1	5.5	1.64
D-2	25.4	140	77.2	83.9	8.5	4.25
D-3	26.6	212	120	160	10.8	7.20
D-4	30.6	324	122	347	15.7	5.96
D-5	32.6	330	116	345	16.3	5.49
Average	27.7	212.8	93.1	196	11.4	4.91

sample #	HCO_3	SO_4	Cl	F	NH_4^+	NO_3	B
D-1	192	158	24.4	0.99	<0.05	12.7	0.185
D-2	182	567	60.8	0.81	<0.05	13.9	0.192
D-3	209	1016	92.3	0.73	<0.05	19.1	0.254
D-4	248	1597	134	0.57	0.05	28.5	0.510
D-5	276	1545	142	0.55	<0.05	41.0	0.493
Average	221	977	90.7	0.73	--	23.0	0.327



Figures 24a-b. Water quality with depth at Deerfield. The symbols at zero depth represent the Arkansas River.

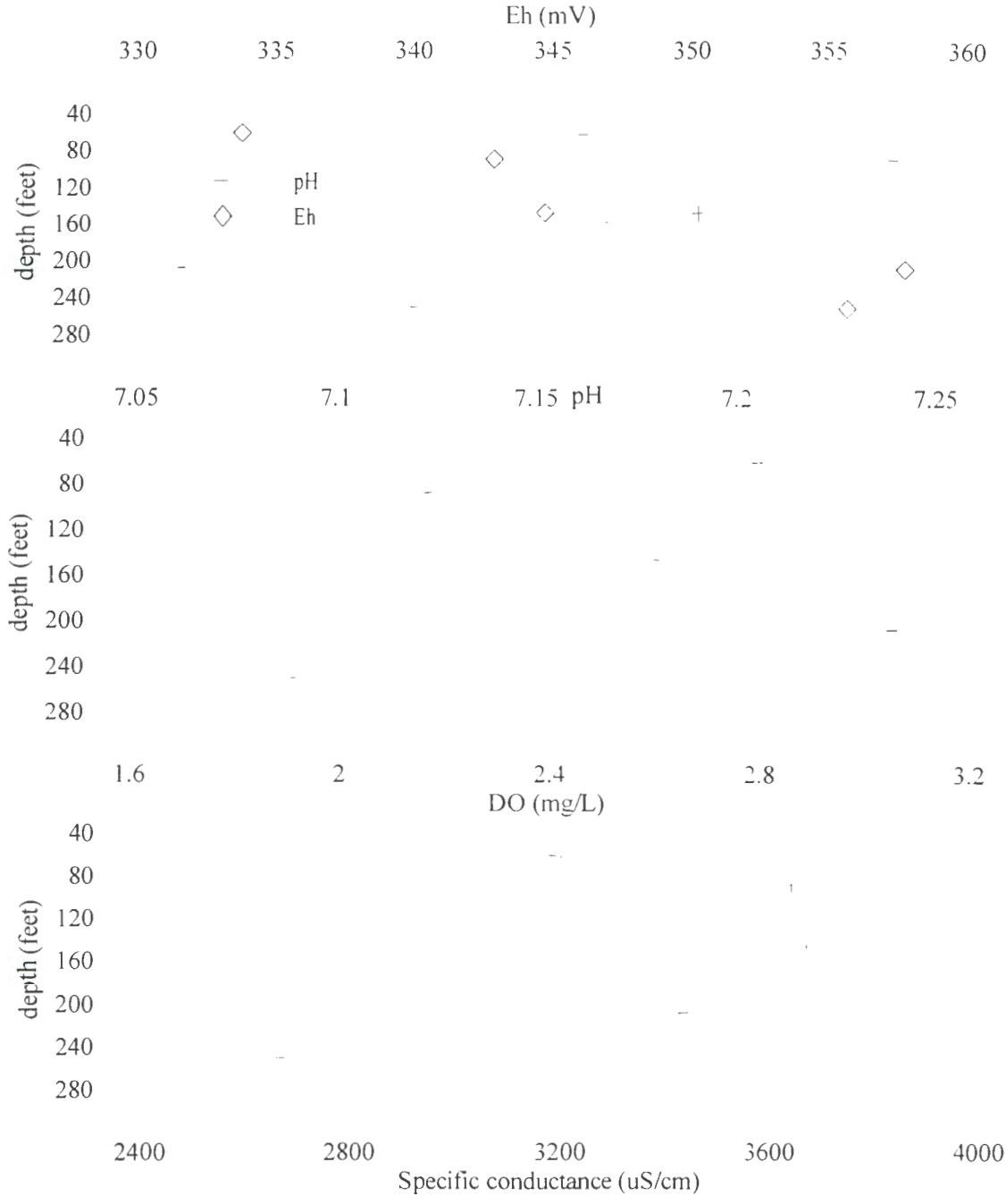
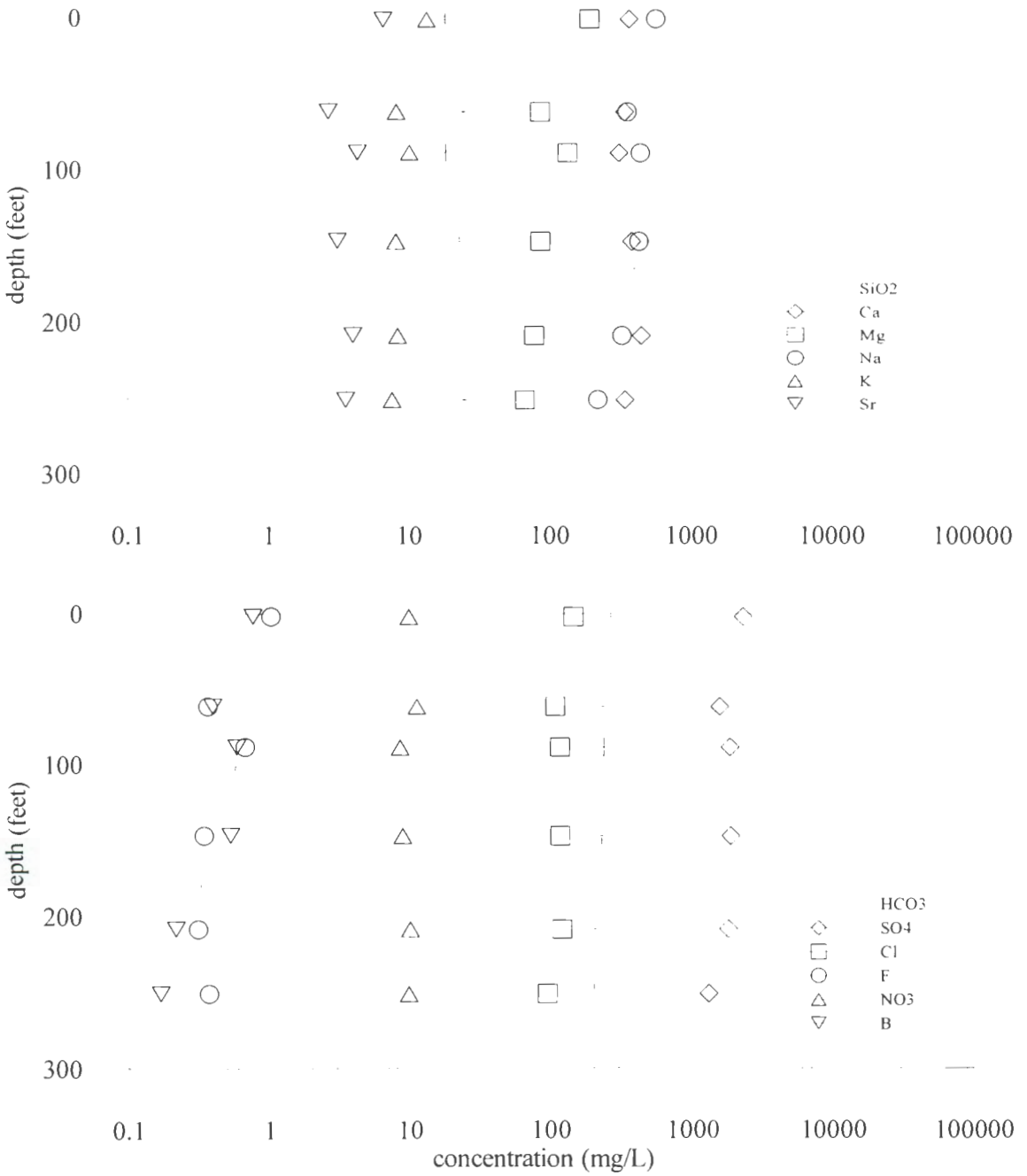


Figure 25. Final field parameters measured at Garden City. (a) Eh and pH, (b) DO, and (c) SC with depth at Garden City.

Table 17. Water quality analysis for Garden City groundwater samples. Concentrations are given in mg/L.

sample #	SiO_2	Ca	Mg	Na	K	Sr
GC-1	24.3	336	66.4	216	7.5	3.49
GC-2	23.9	441	77.5	320	8.2	3.91
GC-3	22.5	375	85.2	422	7.9	3.03
GC-4	17.9	302	131	430	9.8	4.18
GC-5	23.8	330	83.6	344	7.9	2.58
Average	22.5	357	89	346	8.3	3.44

sample #	HCO_3	SO_4	Cl	F	NH_4^+	NO_3	B
GC-1	199	1298	94.2	0.37	<.05	9.7	<0.167
GC-2	202	1795	119	0.31	<.05	9.9	<0.214
GC-3	225	1864	115	0.34	<.05	8.7	0.5230
GC-4	232	1833	114	0.66	<.05	8.3	0.5770
GC-5	228	1547	106	0.36	<.05	11.0	0.3900
Average	217	1667	110	0.41		9.5	0.4967



Figures 26a-b. Water quality with depth at Garden City. The symbols at zero depth represent the Arkansas River.

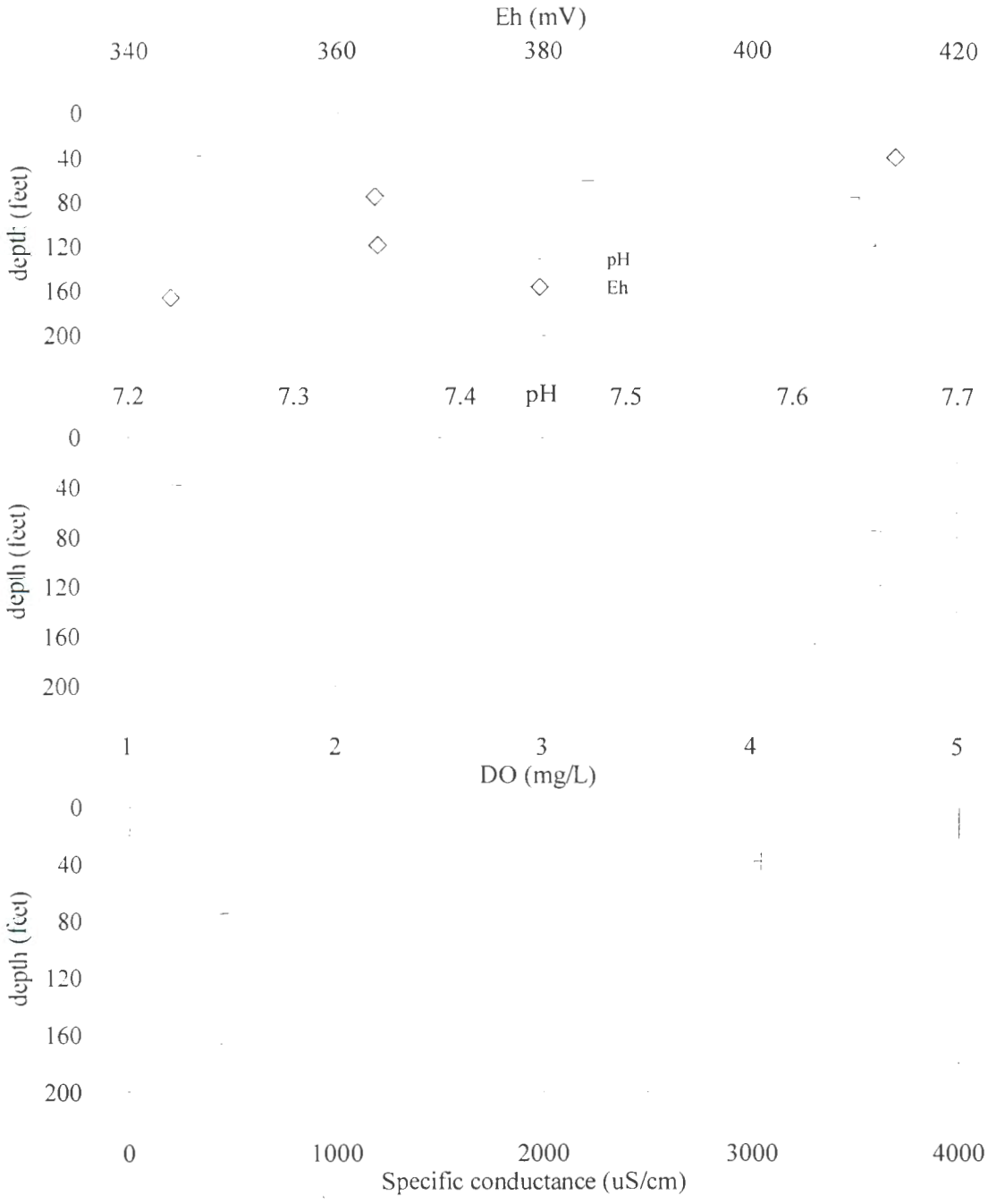
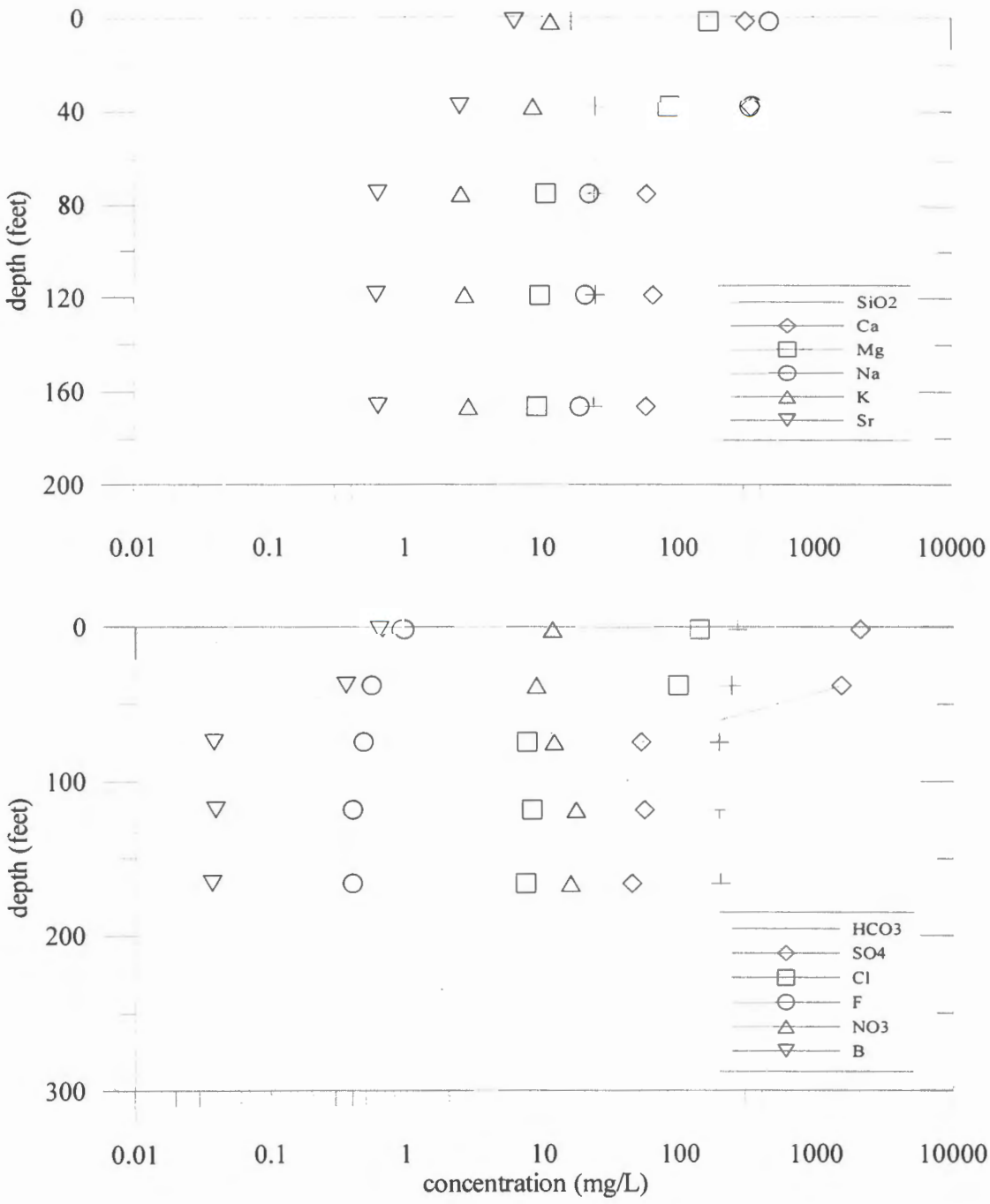


Figure 27. Final field parameters measured at Dodge City. (a) Eh and pH, (b) DO, and (c) SC with depth.

Table 18. Water quality water analysis for Dodge City groundwater samples. Concentrations are given in mg/L.

sample #	SiO_2	Ca	Mg	Na	K	Sr
DC-1	23.9	57.3	9.1	18.8	2.9	0.63
DC-2	24.5	64	9.5	20.5	2.7	0.61
DC-3	23.9	57.4	10.4	21.8	2.5	0.62
DC-4	24.4	352	85.8	345	8.4	2.48
Average	24.2	133	28.7	102	4.1	1.09

sample #	HCO_3	SO_4	Cl	F	NH_4^+	NO_3	B
DC-1	200	44.5	7.4	0.40	<.05	15.7	0.037
DC-2	195	54.6	8.2	0.40	<.05	17.2	0.039
DC-3	194	51.7	7.5	0.48	<.05	11.8	0.038
DC-4	239	1538	96.9	0.55	<.05	8.8	0.356
Average	207	422	30.0	0.46	<.05	13.4	0.118



Figures 28a-b. Water quality with depth at Dodge City. The symbols at zero depth represent the Arkansas River.

Table 19. Total dissolved Se, U and Mo concentrations as determined using the ^{77}Se, ^{238}U, and ^{95}Mo isotopes by ICP-MS analysis at the KU-PAL.

sample name	^{77}Se	^{238}U	^{95}Mo
D-1	8.78	20.5	5.77
D-2	20.1	29.2	3.27
D-3	6.83	16.4	0.86
D-4	17.1	37.2	1.50
D-5	20.3	41.3	2.12
GC-1	16.2	21.3	1.51
GC-2	18.7	19.3	1.29
GC-3	14.5	19.2	1.29
GC-4	14.7	33.2	1.55
GC-5	15.8	21.1	1.38
GC Ark River	19.0	68.5	7.87
GC Ark River2	6.54	25.6	9.69
DC-1	3.01	4.91	2.13
DC-2	6.37	5.20	2.80
DC-3	2.40	5.46	3.95
DC-4	12.6	23.8	1.40
DC Ark River	17.2	62.9	6.63

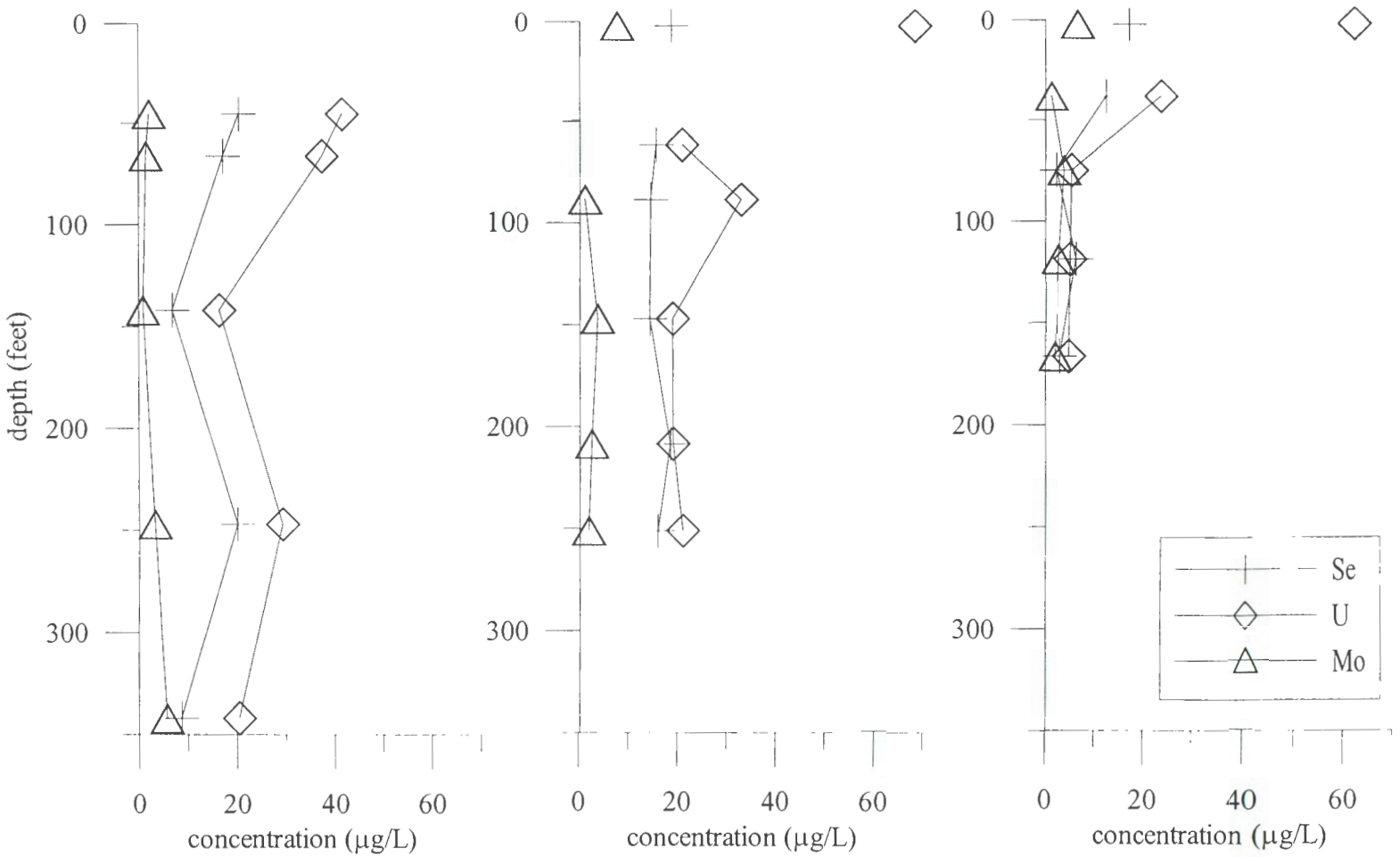


Figure 29. ^{77}Se, ^{238}U, and ^{95}Mo with depth at (a) Deerfield, (b) Garden City, and (c) Dodge City study sites. The symbols at zero depth on the Garden City and Dodge City plots represent the Arkansas River water sampled near these study sites. The legend applies to Figures 29a-c.

Table 20. Summary of correlation relationships between field and chemical parameters. The shaded boxes are significant relationships at the 95% level. Relationships were determined for the groundwaters in the study site (14 points), the groundwater at each separate site (D=Deerfield site,GC=Garden City site, DC=Dodge City site), the Arkansas River, and for all the groundwater and river water samples as a data set (17 points).

#1	#2	Total all	Ark River	D	GC	DC	Total GW
Na	SO_4	0.9588	0.9774	0.9508	0.7676	1.0000	0.9538
Cl	SO_4	0.9197	0.9874	0.9914	0.9196	1.0000	0.9134
Se	pH			0.1586	0.8637	0.7417	0.5247
Se	Eh			0.1546	0.4131	0.4494	0.1397
Se	SC	0.5642	0.9995	0.2178	0.0662	0.8641	0.5671
Se	Mo	0.0146	0.7280	0.0187	0.1352	0.5534	0.1158
Se	Na	0.4666	0.9764	0.2375	0.2958	0.8588	0.4543
Se	SO_4	0.5420	0.9999	0.1955	0.0176	0.8616	0.5344
Se	Cl	0.6546	0.9881	0.2343	0.0194	0.8645	0.6397
Se	Ca	0.5586	0.9608	0.2354	0.5672	0.8736	0.5464
Se	Mg	0.4047	0.9902	0.0725	0.2511	0.8555	0.4513
Se	Sr	0.3642	0.9934	0.0044	0.0642	0.8543	0.3246
Se	Si	0.0347	0.9981	0.3383	0.3064	0.5813	0.0756
Se	B	0.3766	0.9895	0.2492	0.6220	0.8620	0.3882
Se	K	0.2741	0.9023	0.2741	0.0799	0.8620	0.4992
U	pH			0.3592	0.4965	0.9354	0.3045
U	Eh			0.5265	0.0674	0.3846	0.1083
U	SC	0.5501	0.9988	0.5129	0.0860	0.9993	0.4971
U	Mo	0.2049	0.7391	0.0570	0.5962	0.4964	0.0460
U	Na	0.5972	0.9725	0.6216	0.1878	0.9997	0.4445
U	SO_4	0.5379	0.9998	0.4877	0.0545	0.9996	0.4352
U	Cl	0.5626	0.9906	0.5248	0.0096	0.9994	0.6259
U	Ca	0.2671	0.9557	0.5376	0.4543	0.9990	0.3256
U	Mg	0.7984	0.9875	0.1772	0.8397	0.9999	0.6730
U	Sr	0.5556	0.9953	0.0259	0.3418	0.9991	0.4955
U	Si	0.0600	0.9968	0.6938	0.8554	0.2200	0.1564
U	B	0.7536	0.9868	0.6740	0.3195	0.9995	0.6347
U	K	0.5843	0.8948	0.6015	0.8350	0.9934	0.8111
U	Se	0.4633	0.9998	0.7826	0.1962	0.8568	0.6779

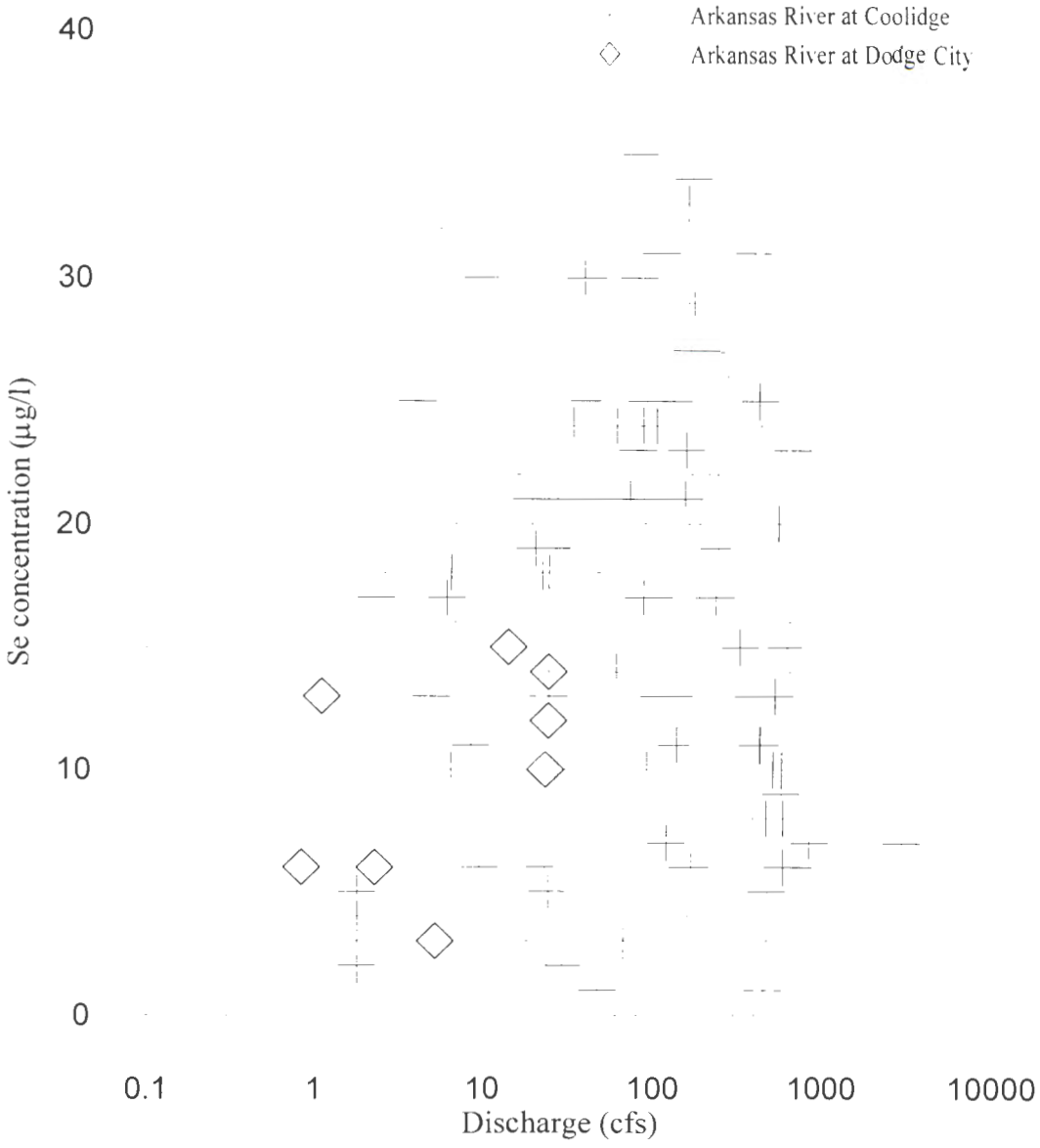


Figure 30. Relationship between Se concentrations and discharge in the Arkansas River in the study area. Discharge data are from USGS river database and Se data are from the historical database collected in this study. The scatter in this plot shows that there is no direct relationship between Se and discharge in this area.

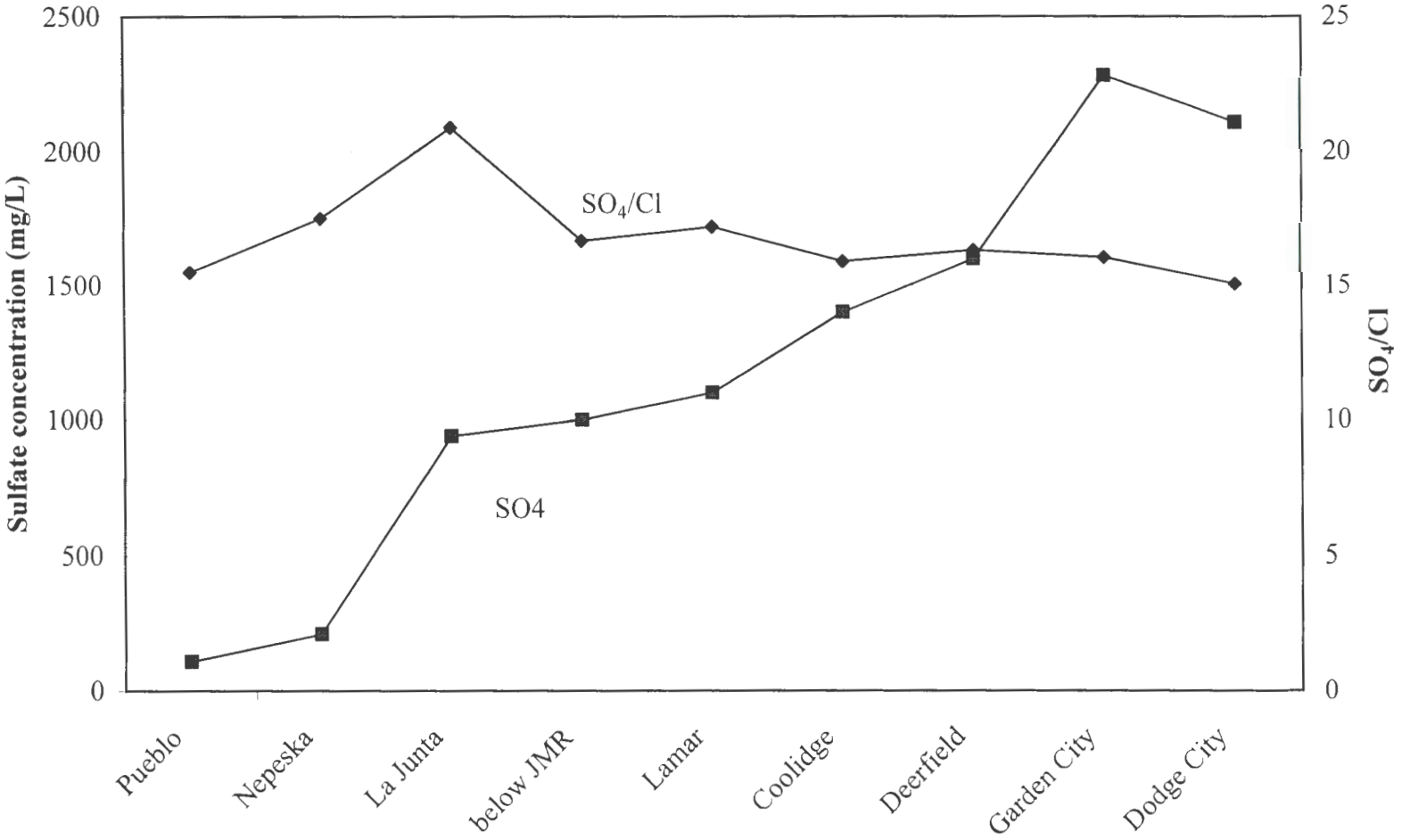


Figure 31. Sulfate and SO_4/Cl ratio downstream in Arkansas River from Pueblo, Colorado and through the study area. Note: JMR = John Martin Reservoir

Table 21a. Summary statistics for historical data for Arkansas River water near Coolidge, Kansas compiled from STORET, QWDATA, and KGS databases. The average, maximum, and minimum values were calculated from the collection of data derived from the above databases.

	U/Cl	U/SO_4	Se/Cl	Se/SO_4	SO_4/Cl	Se/U
Average	3.56E-04	2.21E-05	1.58E-04	1.54E-05	16.10	0.44
Maximum	3.75E-04	2.36E-05	5.63E-04	1.92E-04	15.91	1.50
Minimum	3.37E-04	2.06E-05	9.62E-06	6.71E-07	16.33	0.03

Table 21b. Summary statistics for historical data for groundwater compiled from STORET, QWDATA, and KGS databases. The average, maximum, and minimum values were calculated from the collection of data derived from the above databases.

	U/Cl	U/SO_4	Se/Cl	Se/SO_4	SO_4/Cl	Se/U
Average	4.23E-04	4.62E-05	2.19E-03	9.88E-04	9.17	5.17
Maximum	6.22E-04	6.67E-05	1.67E-02	2.86E-02	9.33	26.79
Minimum	3.02E-04	3.46E-05	9.62E-05	6.71E-05	8.72	0.32

Table 22a. Ratios of Se, U, and Mo with conservative constituents for Arkansas River calculated from data collected in this study.

	U/Cl	U/SO_4	Se/Cl	Se/SO_4	SO_4/Cl	Se/U	Cl	SO_4
Average	4.32E-04	2.76E-05	1.17E-04	7.44E-06	15.69	0.27	117	1837
Maximum	4.82E-04	3E-05	1.34E-04	8.33E-06	16.06	0.28	142	2280
Minumum	3.64E-04	2.28E-05	9.29E-05	5.83E-06	15.06	0.26	70	1122

Table 22b. Ratios of Se, U, and Mo with conservative constituents for groundwater calculated from data collected in this study.

	U/Cl	U/SO_4	Se/Cl	Se/SO_4	SO_4/Cl	Se/U	Cl	SO_4
Average	3.85E-04	4.6E-05	2.43E-04	2.92E-05	11.48	0.64	80	1065
Maximum	8.41E-04	1.30E-04	7.77E-04	1.17E-04	16.21	0.90	142	1864
Minumum	1.62E-04	1.03E-05	7.40E-05	6.72E-06	6.01	0.65	7.4	44.5

Table 22c. Summary statistics of ratios of Se, U, and Mo with conservative constituents in groundwater calculated for each site. D=Deerfield, GC=Garden City, and DC=Dodge City

	U/Cl	U/SO_4	Se/Cl	Se/SO_4	SO_4/Cl	Se/U	Cl	SO_4
D average	4.14E-04	4.95E-05	2.07E-04	2.43E-05	9.92	0.49	76	892
D max	8.41E-04	0.00013	3.60E-04	5.55E-05	11.92	0.43		
D min	1.77E-04	1.61E-05	7.40E-05	6.72E-06	6.48	0.42		
GC average	2.09E-04	1.38E-05	1.47E-04	9.78E-06	15.15	0.71	110	1667
GC max	2.91E-04	1.81E-05	1.72E-04	1.25E-05	16.21	0.69		
GC min	1.62E-04	1.03E-05	1.26E-04	7.78E-06	13.78	0.76		
DC average	5.68E-04	8.17E-05	4.08E-04	5.97E-05	8.86	0.73	30	422
DC max	7.28E-04	1.10E-04	7.77E-04	1.17E-04	15.87	1.06		
DC min	2.46E-04	1.55E-05	1.30E-04	8.16E-06	6.01	0.53		

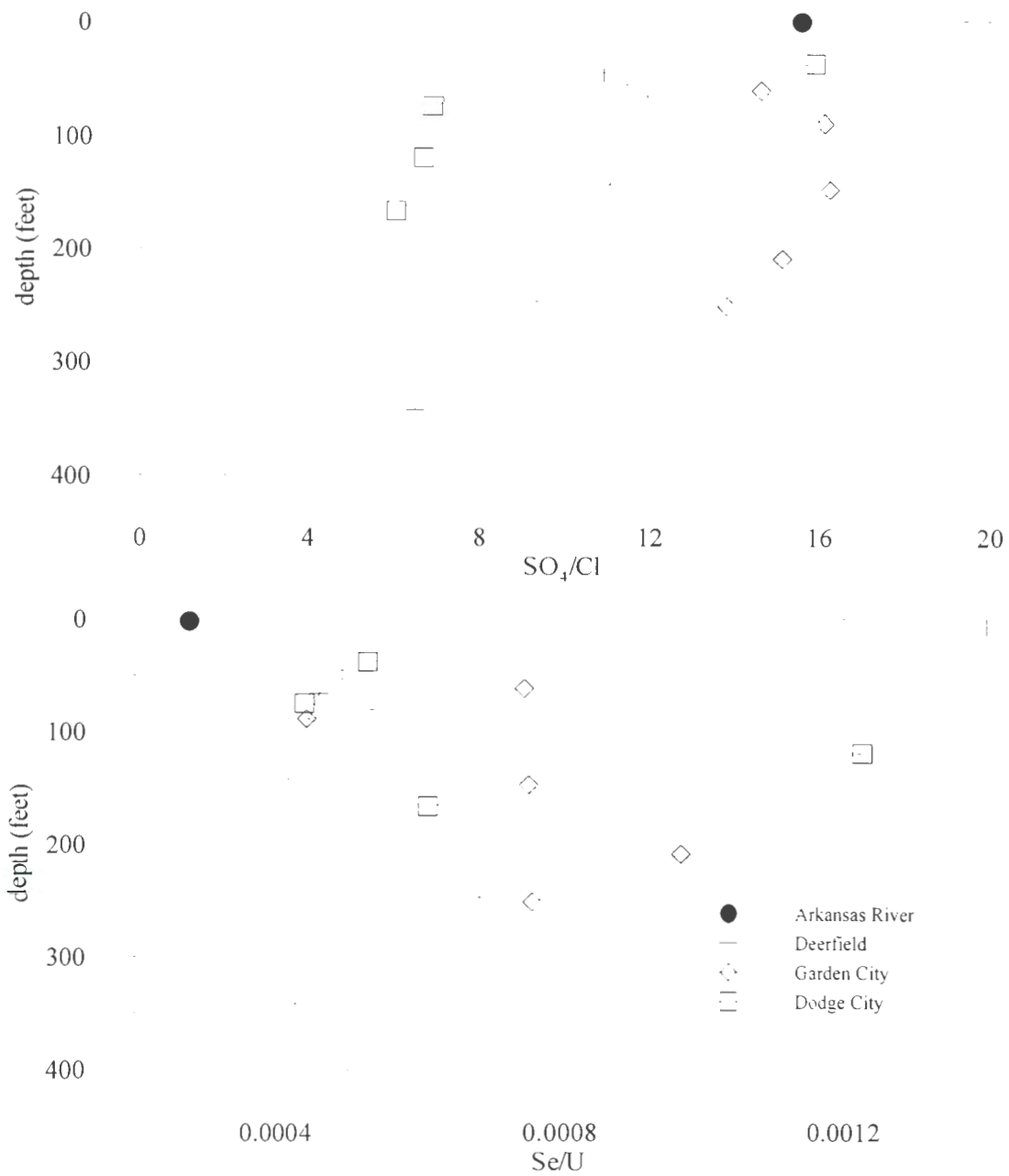


Figure 32a. SO_4/Cl with depth at the study sites.

Figure 32b. Plot of Se/U with depth at the study sites. Note that the legend applies to both graphs and that that the x-axis scales are different.

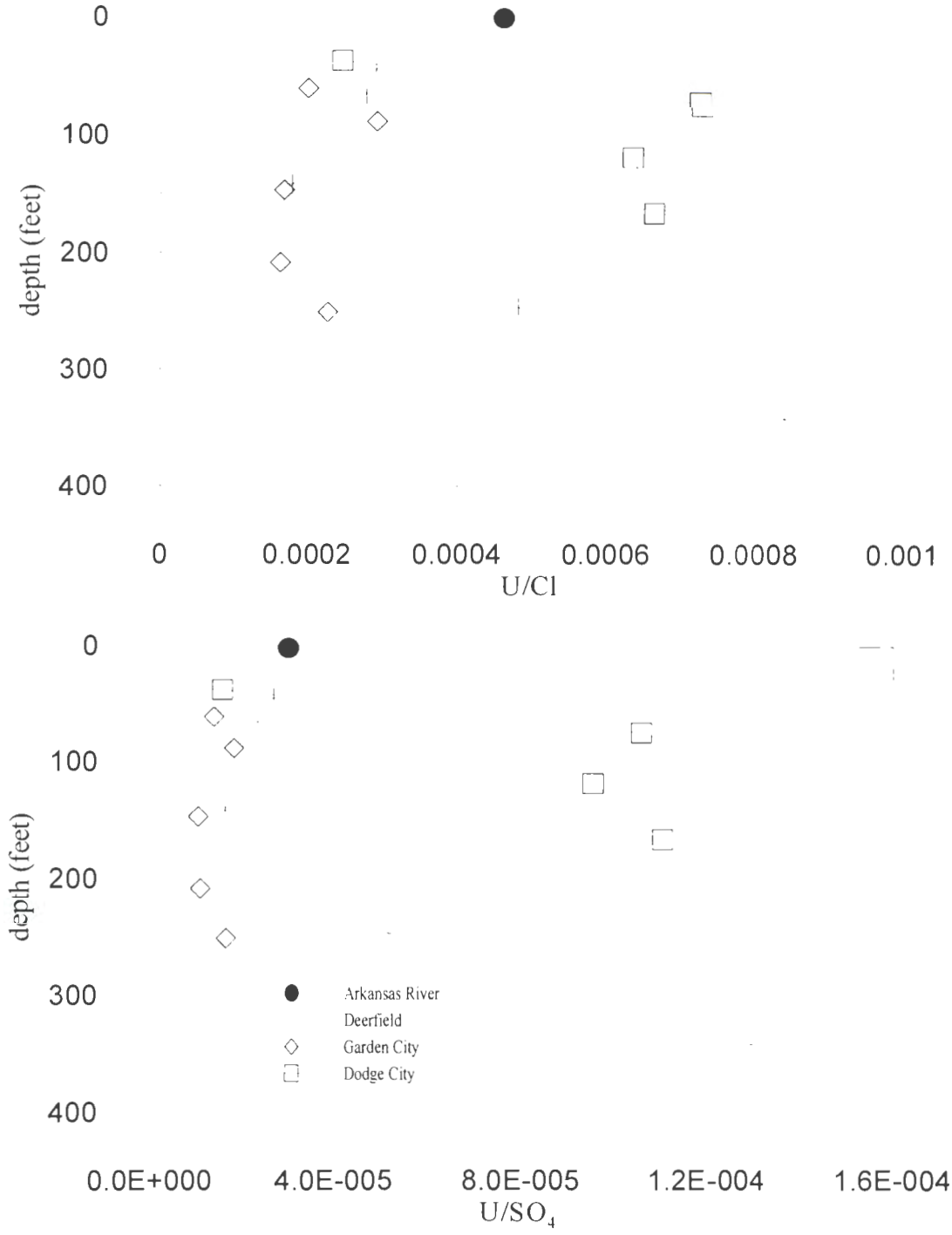


Figure 33a. Plot of U/Cl at the study sites. Note that the legend applies to both graphs.

Figure 33b. Plot of U/SO_4 with depth at the study sites. Note that the scales on the x-axes are different.

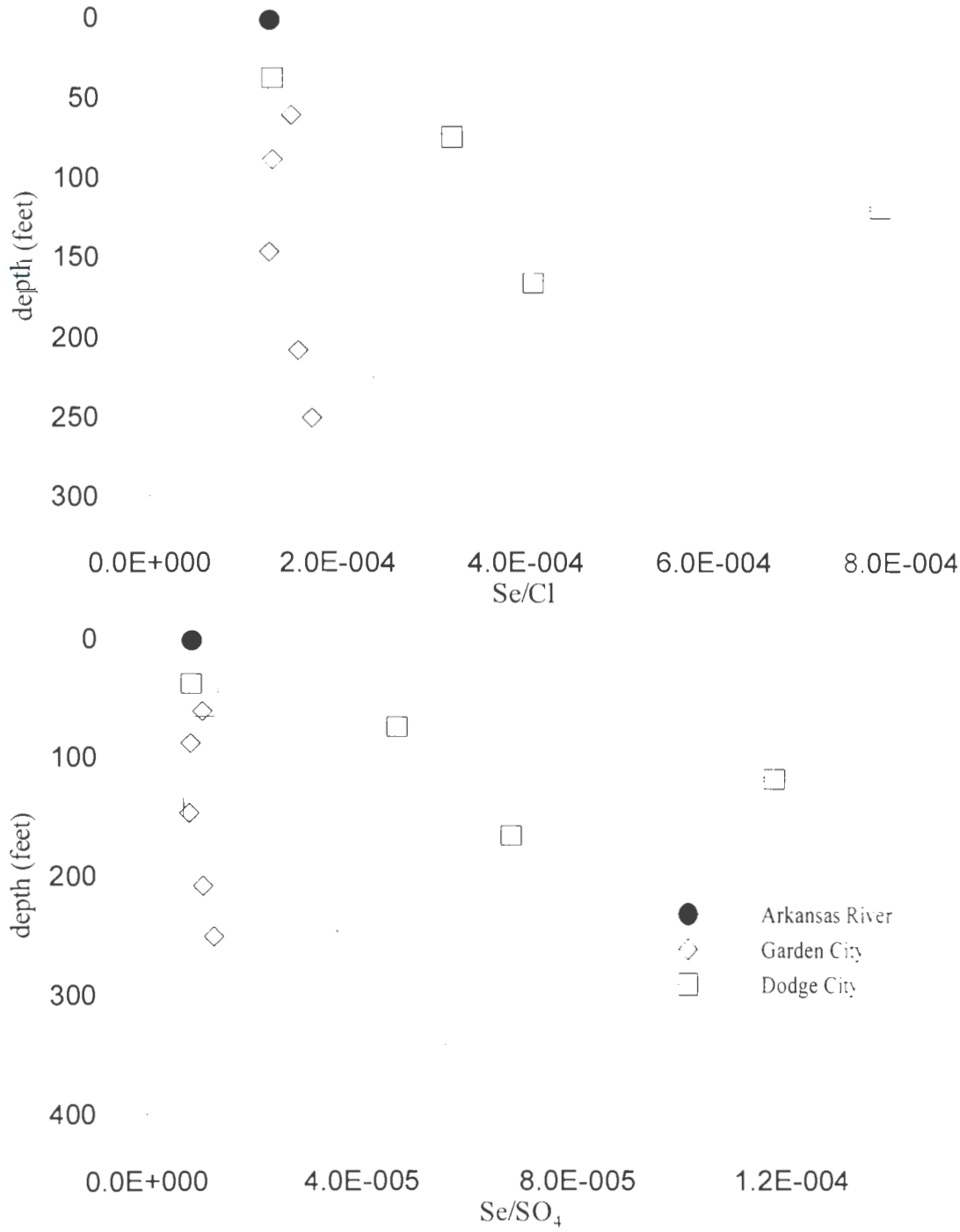


Figure 34a. Plot of Se/Cl with depth at study sites. Note that the legend applies to both graphs.
Figure 34b. Plot of Se/SO_4 with depth at the study sites. Note that the scales on the x-axes are different.

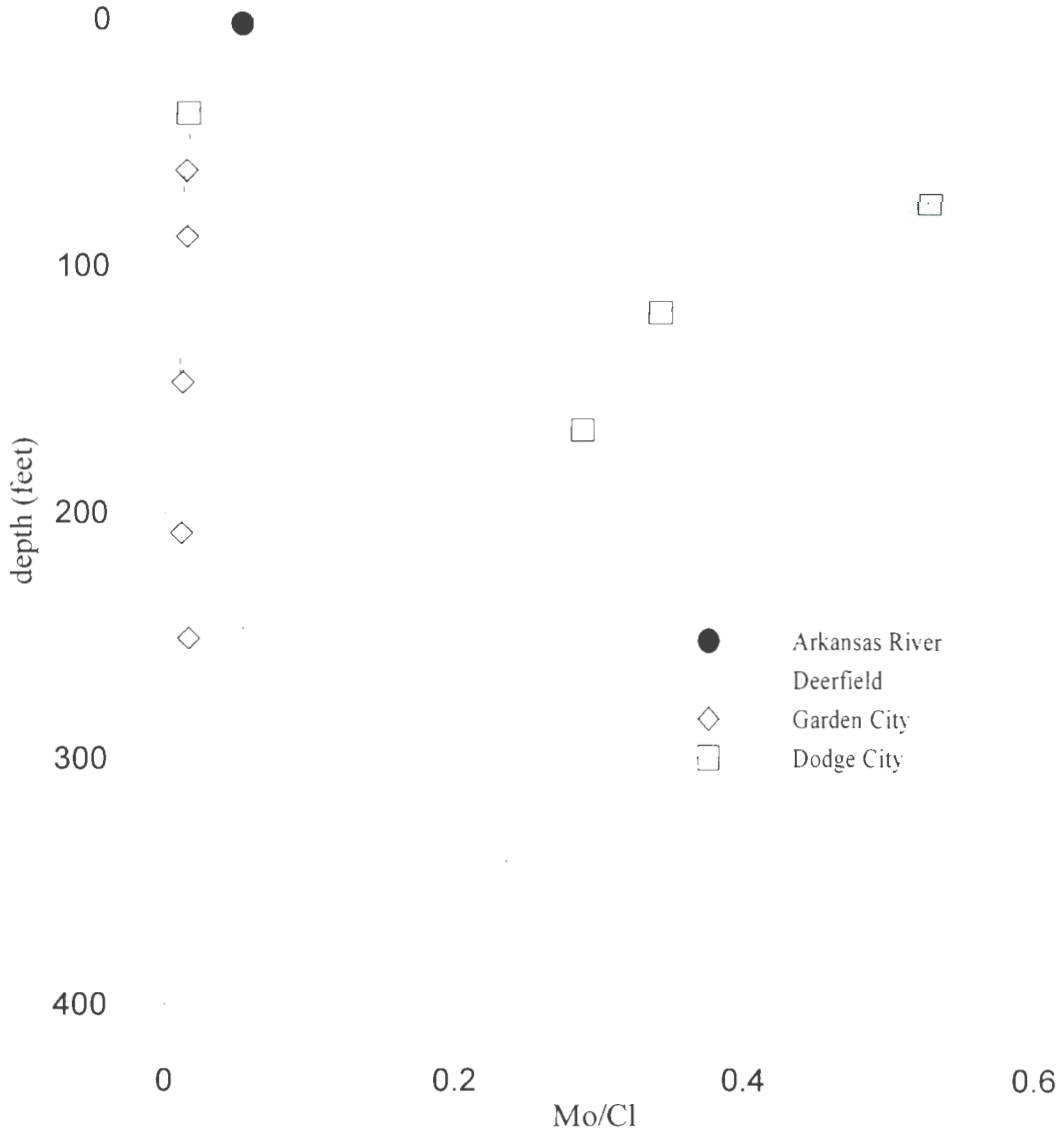


Figure 35. Plot of Mo/Cl with depth at the study sites.

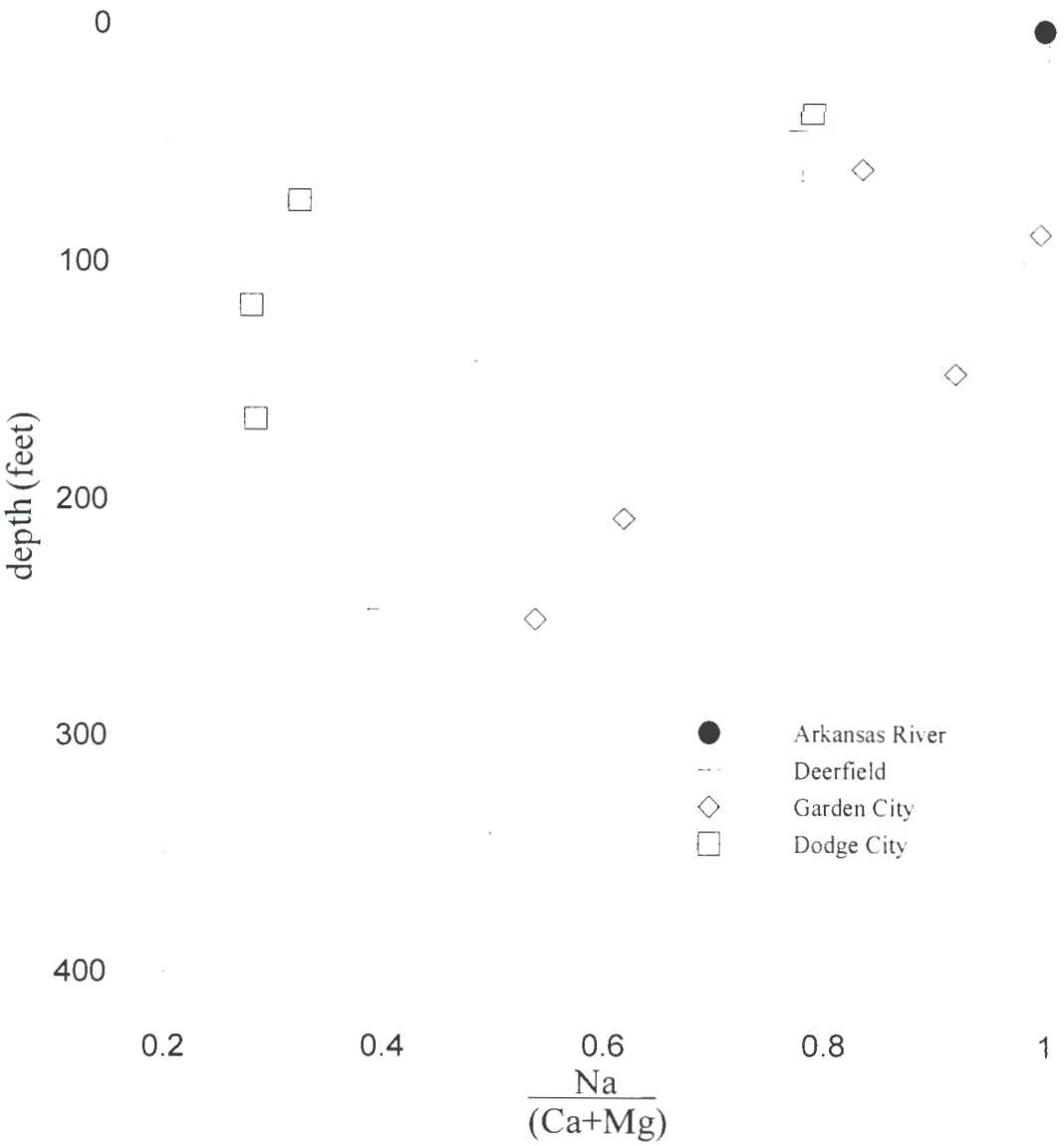


Figure 36. Plot showing the relationship of Na, Ca, and Mg for evaluation of cation exchange as the saline river water infiltrates into the subsurface.

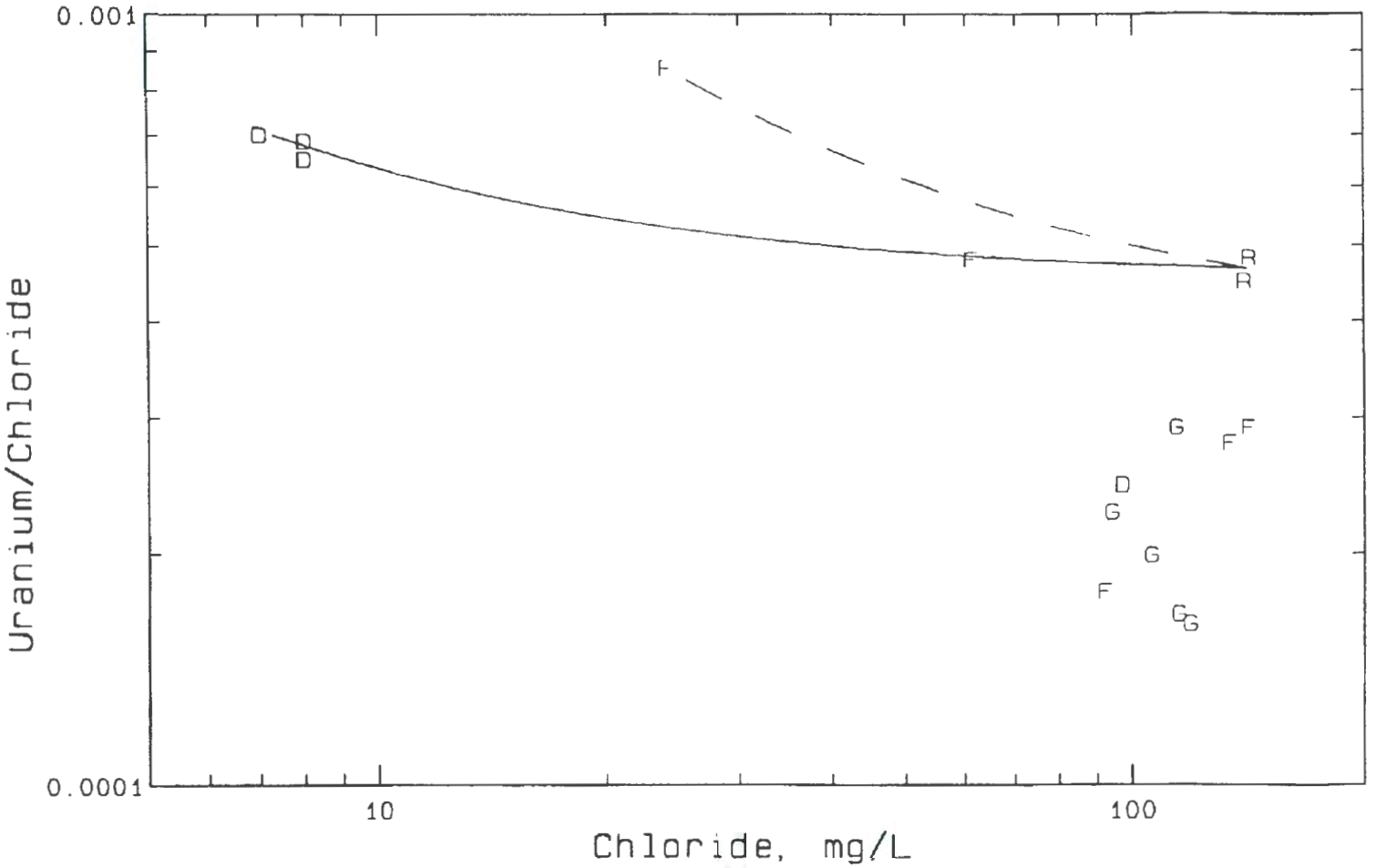


Figure 37a. U/Cl mixing curves for study area. The saline river water serves as the saline end member and the fresh groundwaters at Dodge City and Deerfield as the fresh end member. R=Arkansas River, F=Deerfield groundwaters, G=Garden City groundwaters, and D=Dodge City groundwaters.

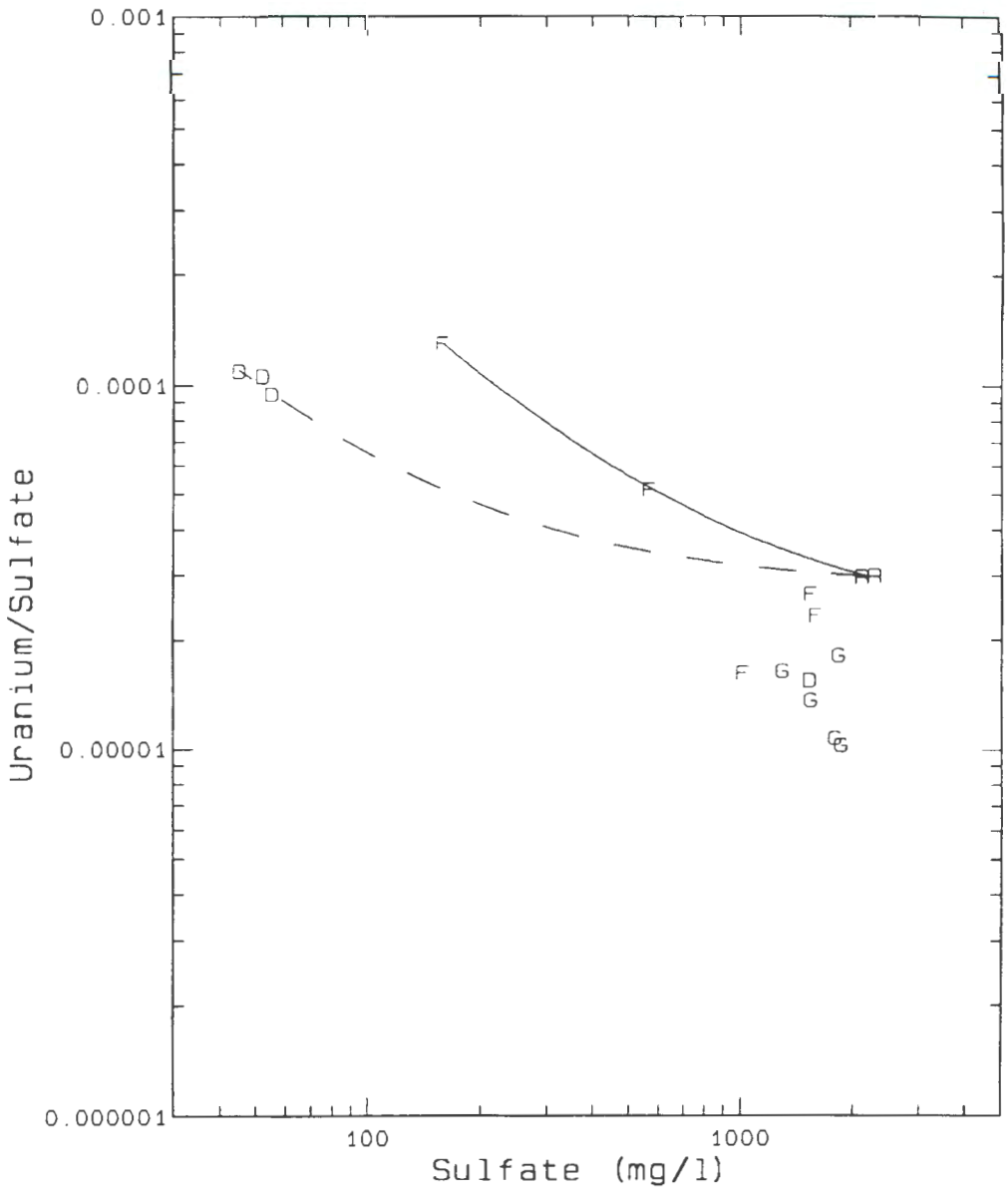


Figure 37b. U/SO_4 mixing curves for study area. The saline river water serves as the saline end member and the fresh groundwaters at Dodge City and Deerfield as the fresh end member. R=Arkansas River, F=Deerfield groundwaters, G=Garden City groundwaters, and D=Dodge City groundwaters.

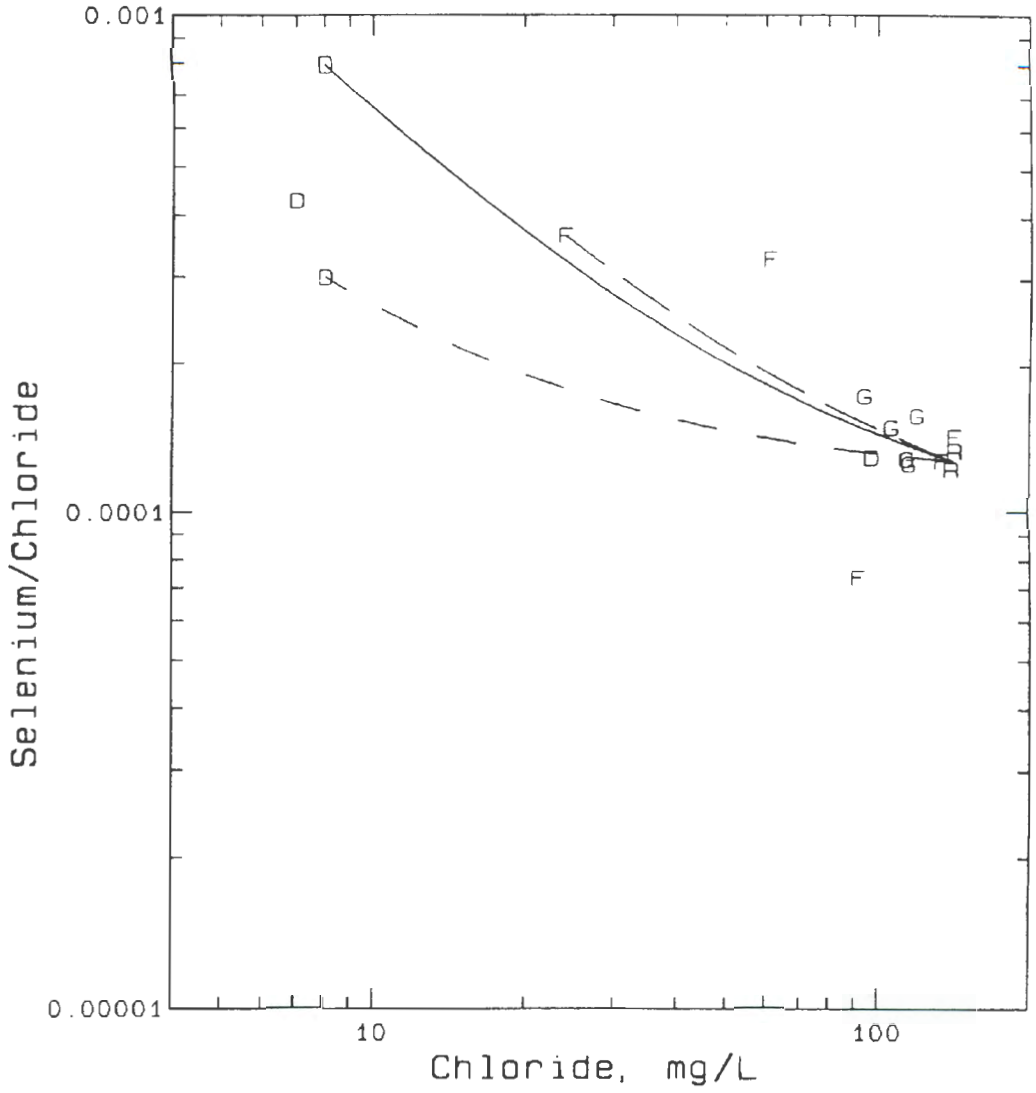


Figure 38a. Se/Cl mixing curves for study area. The saline river water serves as the saline end member and the fresh groundwaters at Dodge City and Deerfield as the fresh end member. R=Arkansas River, F=Deerfield groundwaters, G=Garden City groundwaters, and D=Dodge City groundwaters.

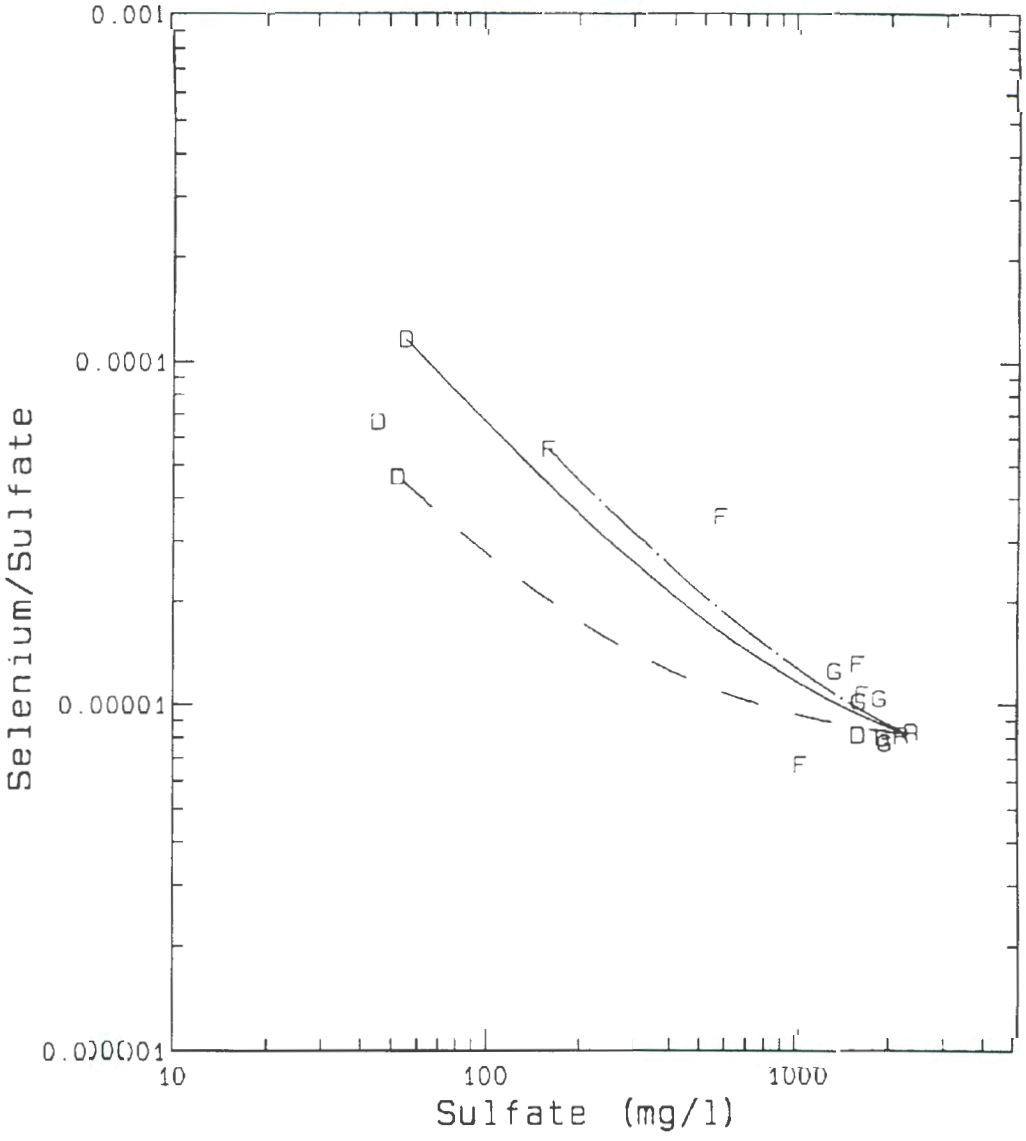


Figure 38b. Se/SO_4 mixing curves for study area. The saline river water serves as the saline end member and the fresh groundwaters at Dodge City and Deerfield as the fresh end member. R=Arkansas River, F=Deerfield groundwaters, G=Garden City groundwaters, and D=Dodge City groundwaters.

Table 23. Distribution of Se and U in the Arkansas River. Concentrations of additional species are shown in Figures 39-42.

	Se(IV)	$HSeO_3^-$	SeO_3^{-2}	H_2SeO_3	Se(VI)	SeO_4^{-2}
GC	83%	51%	31%	<0.00%	17%	17%
DC	60%	31%	29%	<0.00%	40%	40%
GC2*	74%	44%	30%	<0.00%	26%	26%

	U(VI)	$UO_2(CO_3)_3^{-4}$	$UO_2(CO_3)_2^{-2}$	UO_2CO_3	$UO_2(OH)_3^-$	UO_2OH^+
GC	100%	94%	6%	0.01%	0.02%	<0.00%
DC	100%	96%	4%	<0.00%	0.02%	<0.00%
GC2*	100%	91%	9%	0.02%	0.05%	<0.00%

* sample taken at Garden City under low flow conditions

Table 24. Se and U distribution in groundwater in the study area. Concentrations of additional species are shown in Figures 39-42.

	Se(IV)	$HSeO_3$-	SeO_3^{-2}	H_2SeO_3	Se(VI)	SeO_4^{-2}
D1	100%	84%	16%	<0.00%	<0.00%	<0.00%
D2	100%	87%	13%	<0.00%	<0.00%	<0.00%
D3	100%	90%	10%	<0.00%	<0.00%	<0.00%
D4	100%	91%	9%	<0.00%	<0.00%	<0.00%
D5	100%	89%	11%	<0.00%	<0.00%	<0.00%
GC1	100%	93%	7%	<0.00%	<0.00%	<0.00%
GC2	100%	94%	6%	<0.00%	<0.00%	<0.00%
GC3	100%	92%	8%	<0.00%	<0.00%	<0.00%
GC4	100%	91%	9%	<0.00%	<0.00%	<0.00%
GC5	100%	92%	8%	<0.00%	<0.00%	<0.00%
DC1	100%	87%	13%	<0.00%	<0.00%	<0.00%
DC2	100%	85%	15%	<0.00%	<0.00%	<0.00%
DC3	100%	85%	15%	<0.00%	<0.00%	<0.00%
DC4	100%	91%	9%	<0.00%	<0.00%	<0.00%

	U(VI)	$UO_2(CO_3)_3^{-4}$	$UO_2(CO_3)_2^{-2}$	UO_2CO_3	$UO_2(OH)_3$-	UO_2OH^+
D1	100%	53%	47%	0.27%	0.08%	<0.00%
D2	100%	54%	46%	0.40%	0.06%	<0.00%
D3	100%	55%	44%	0.45%	0.03%	<0.00%
D4	100%	63%	36%	0.36%	0.02%	<0.00%
D5	100%	65%	34%	0.33%	0.01%	<0.00%
GC1	100%	52%	47%	0.91%	0.03%	0.01%
GC2	100%	56%	43%	0.95%	0.03%	0.01%
GC3	100%	67%	32%	0.49%	0.02%	<0.00%
GC4	100%	69%	30%	0.38%	0.02%	<0.00%
GC5	100%	62%	37%	0.58%	0.02%	0.01%
DC1	100%	51%	48%	0.46%	0.09%	<0.00%
DC2	100%	56%	43%	0.33%	0.11%	<0.00%
DC3	100%	56%	43%	0.35%	0.11%	<0.00%
DC4	100%	66%	34%	0.39%	0.02%	<0.00%

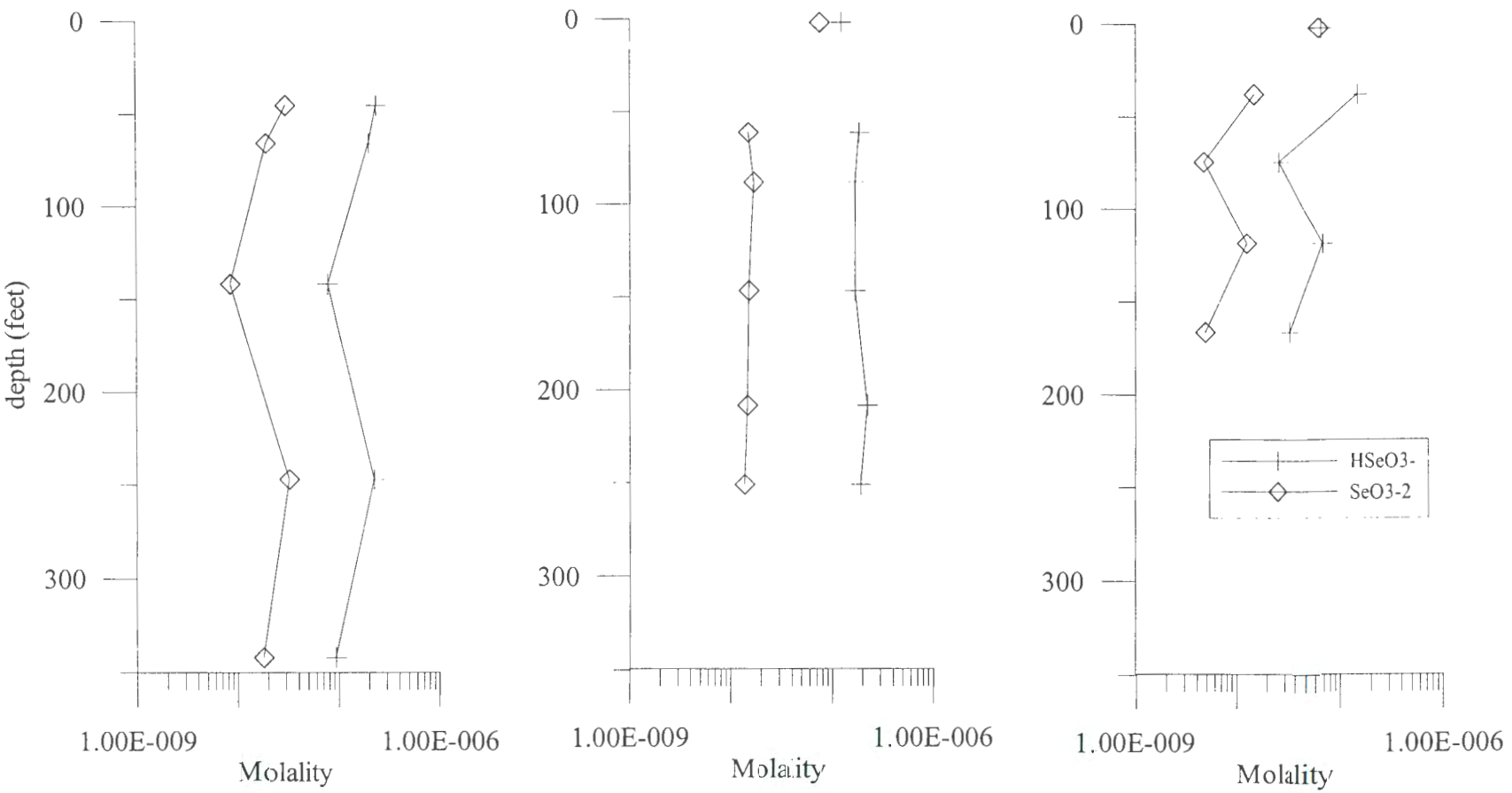


Figure 39. Se species distribution with depth at the (a) Deerfield, (b) Garden City, and (c) Dodge City study sites. Arkansas River speciation is not shown on 39a because a river water sample was not taken near this site. The symbols at zero depth on 39a and 39b represent the Arkansas River near the Garden City and Dodge City sites. Note that the legend applies to 39a-c.

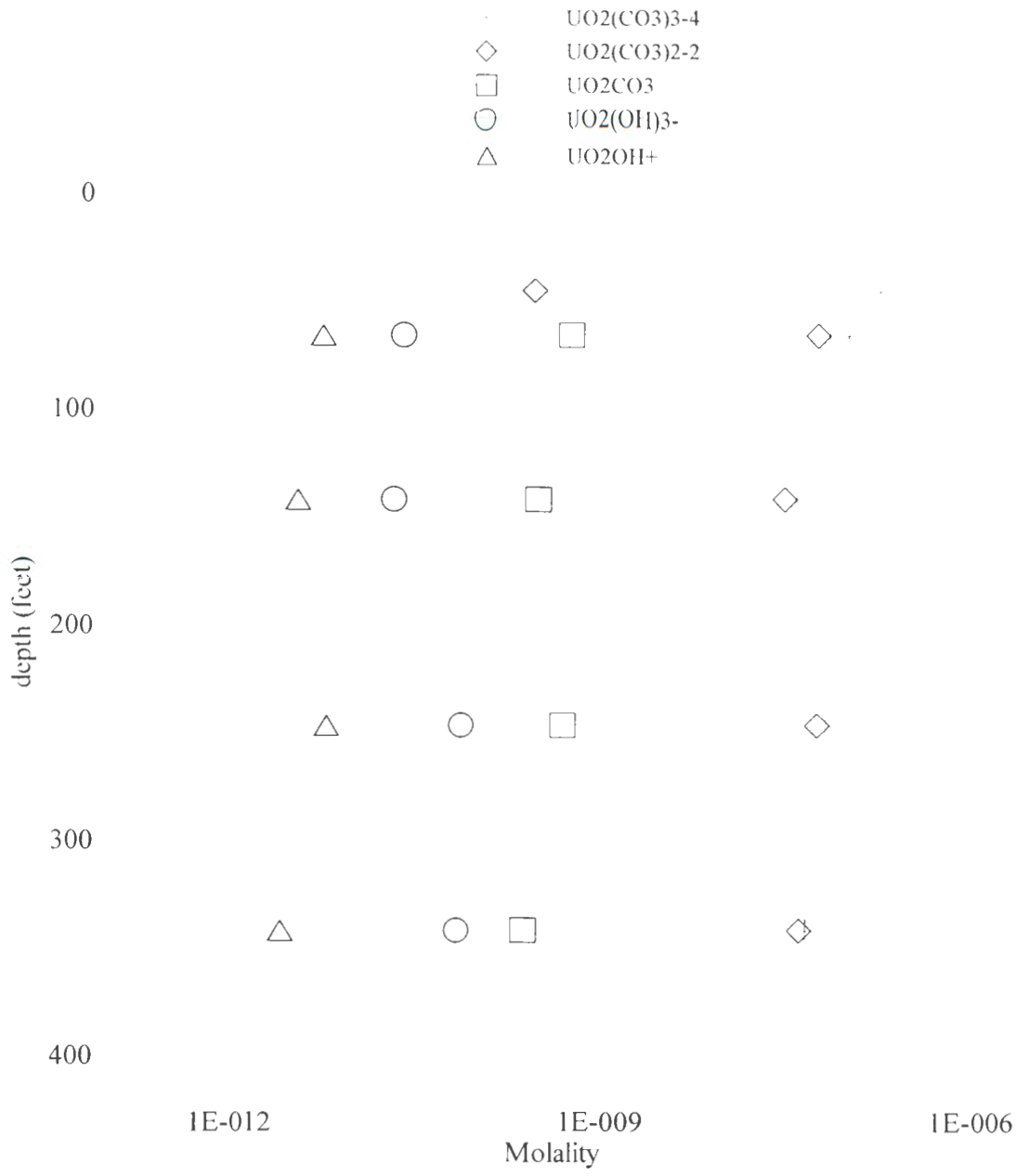


Figure 40. U(VI) speciation with depth at Deerfield. The concentrations of UO_2CO_3, $UO_2(OH)_3^-$, and UO_2OH^+ are less than 10^{-3} m in the shallowest groundwater.

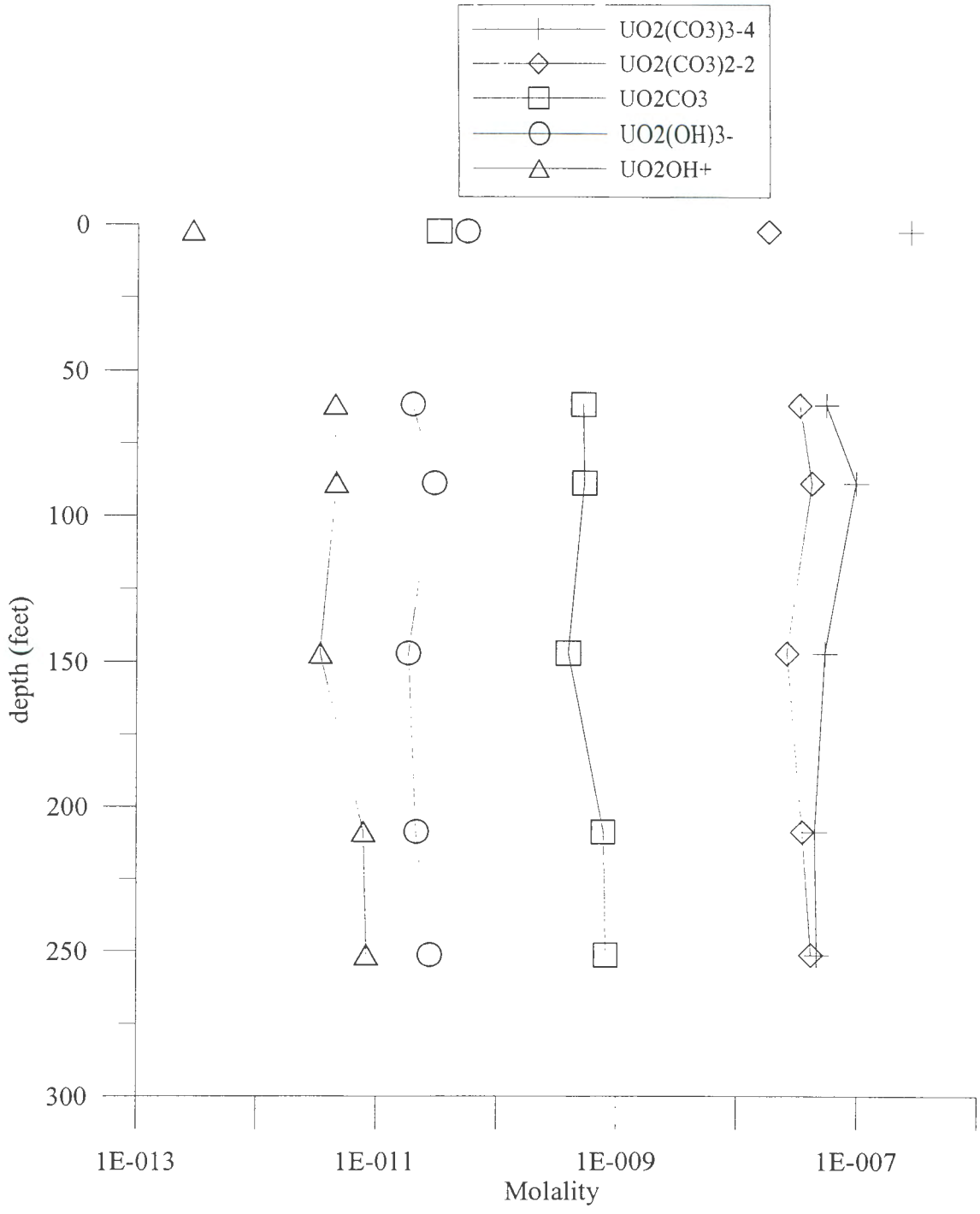


Figure 41. U(VI) speciation with depth at Garden City. The symbols at zero depth represent the Arkansas River.

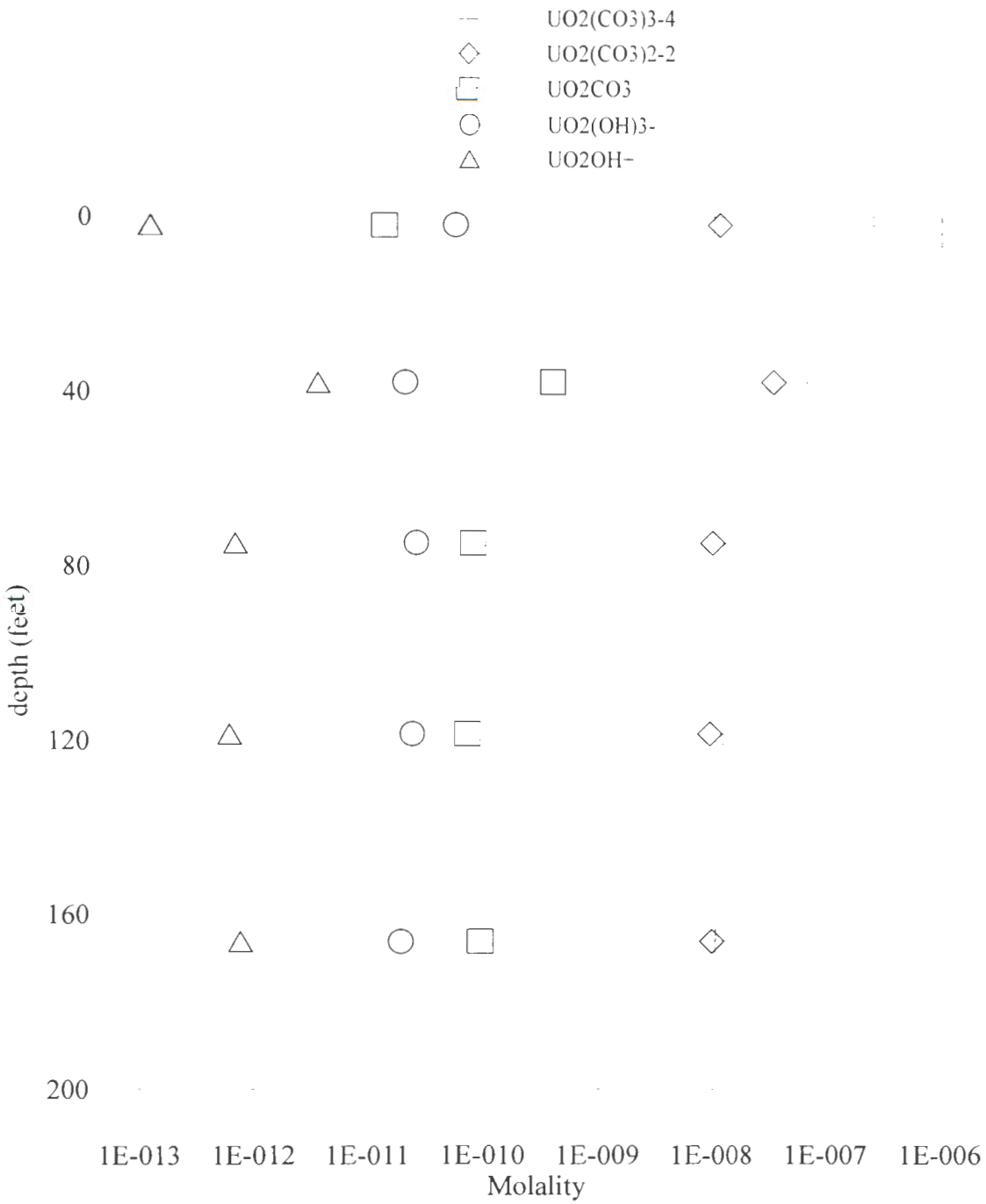


Figure 42. U(VI) speciation with depth at Dodge City. The symbols at zero depth represent the Arkansas River.

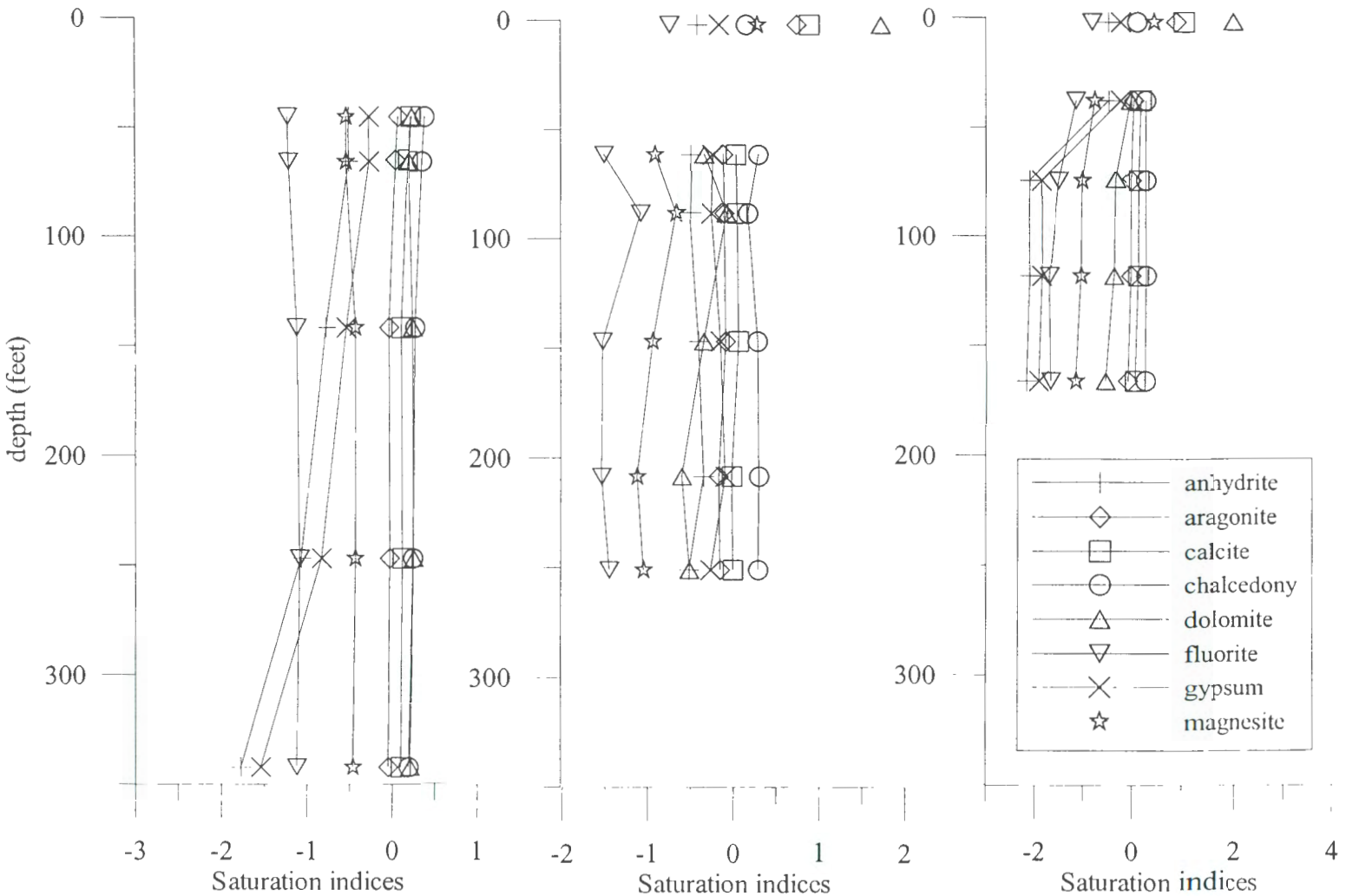


Figure 43. Saturation with respect to various minerals in groundwater at the the (a) Deerfield, (b) Garden City, and (c) Dodge City study sites. The symbols at zero depth on 43a and 43b represent the Arkansas River near Garden City and Dodge City, respecatively. Note that the x-axis scales are different and that the legend applies to 43a-c.

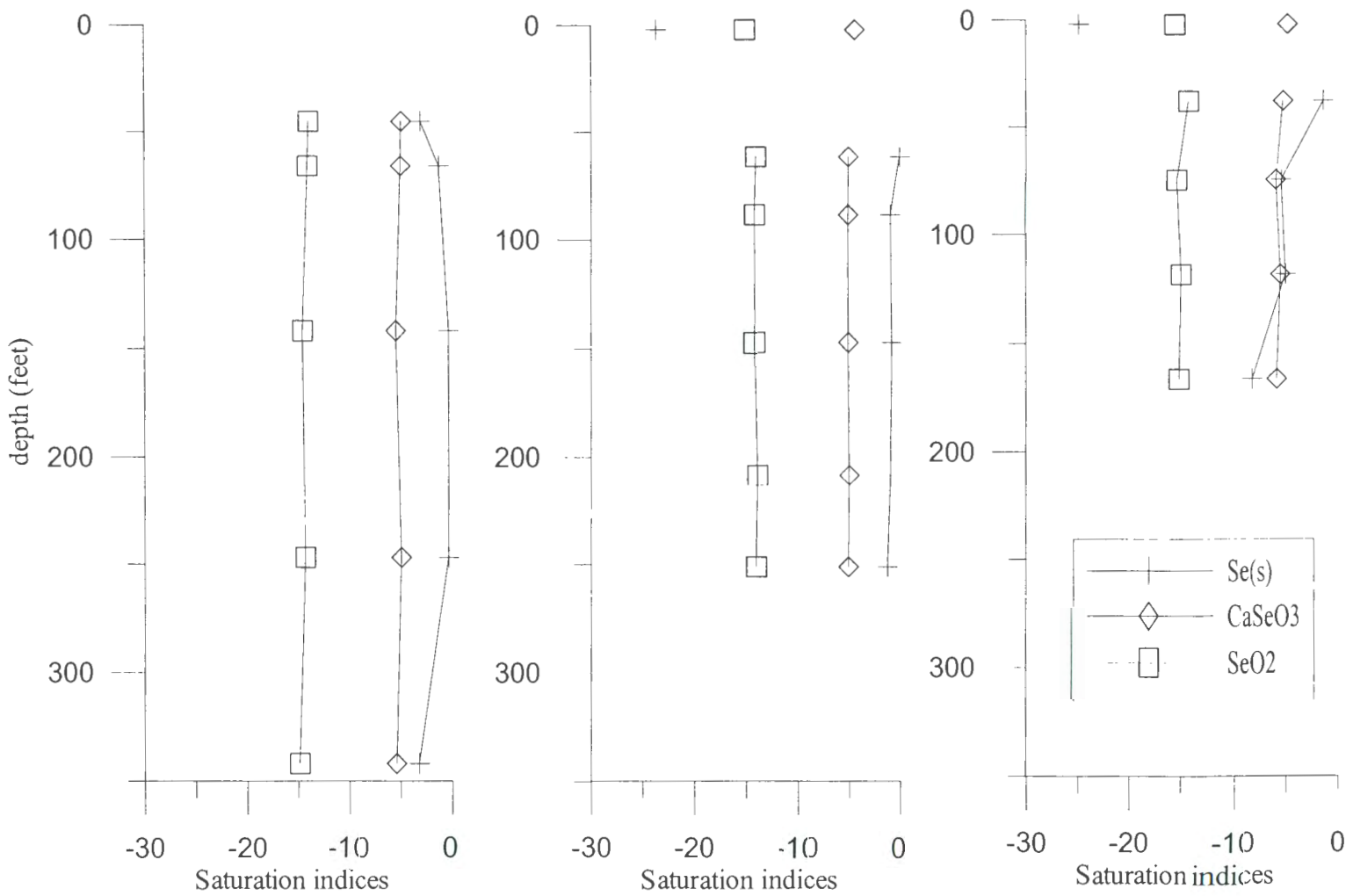


Figure 44. Saturation with respect to Se minerals in the Arkansas River and groundwater at the (a) Deerfield, (b) Garden City, and (c) Dodge City study sites. The symbols at zero depth in 44a and 44b represent the Arkansas River near the Garden City and Dodge City sites. Note that the legend applies to 44a-c.

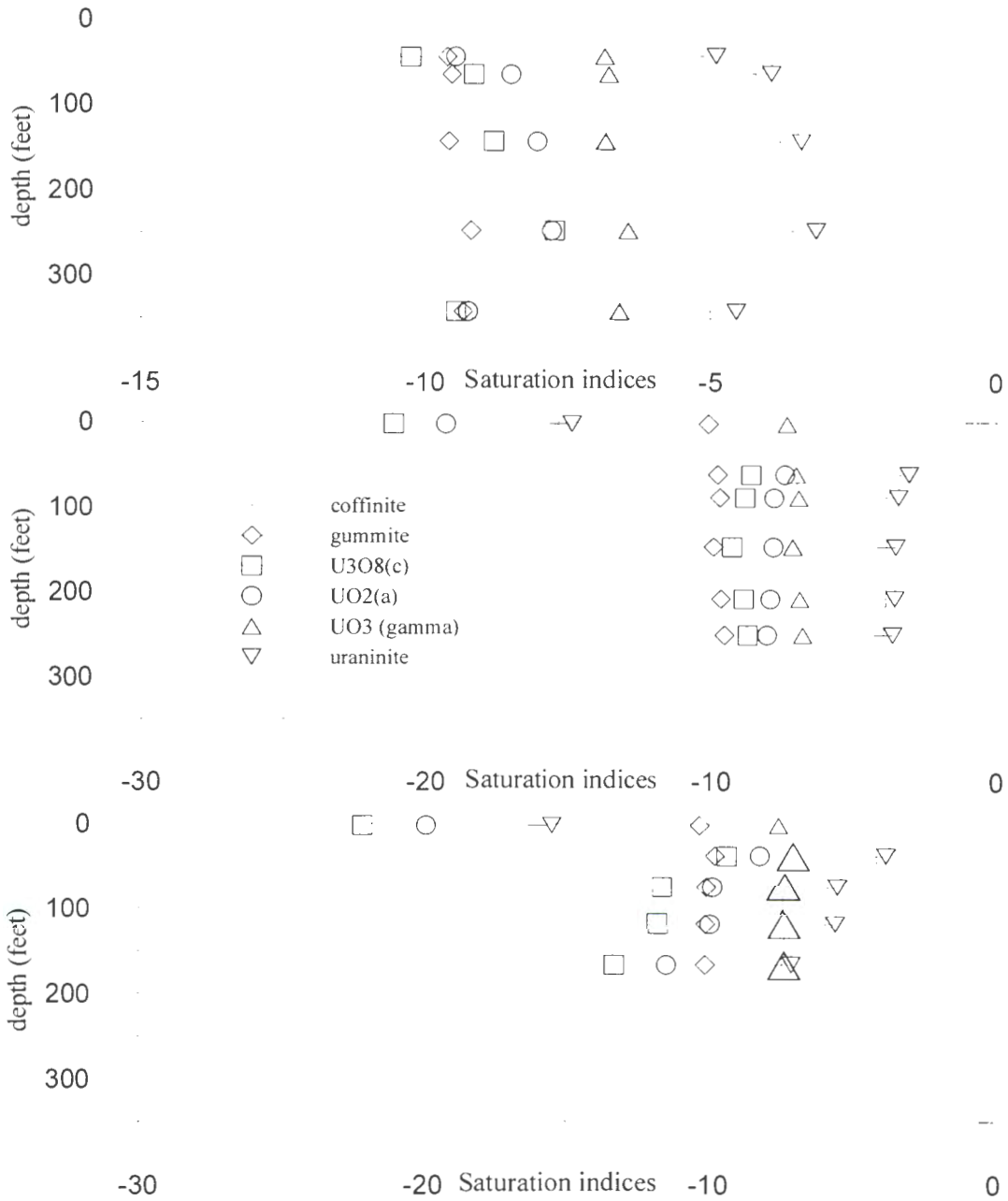


Figure 45. Saturation with respect to U minerals in groundwater at the (a) Deerfield, (b) Garden City, and (c) Dodge City study sites. The symbols at zero depth on 45a and 45b represent the Arkansas River. Note that the legend applies to 45a-c.

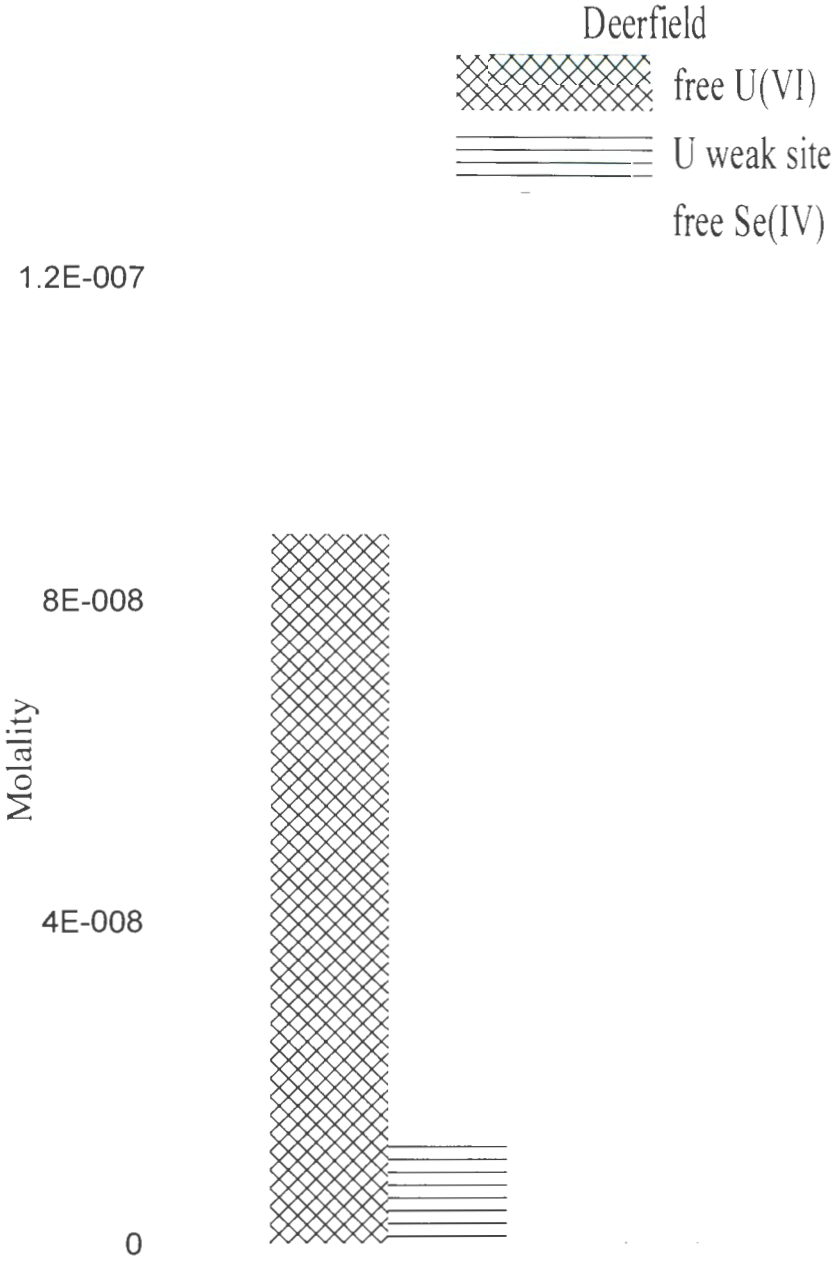


Figure 46. Sorption model output for Deerfield site. Plot shows amount of U(VI) and Se(IV) free in solution and sorbed onto the weak and strong sorption sites as defined in the WATEQF4 database. There is a very small amount of Se sorbed to the sites and U on the strong site relative to Se and U in other forms. Se on sorption sites are not shown on graph because only negligible amounts of Se sorbed.



Figure 47. Sorption model output expressed as amount (µg/l) sorbed from solution. This plot shows that there is significantly more U sorbed than Se and much more sorption taking place at Deerfield than in the Arkansas River.

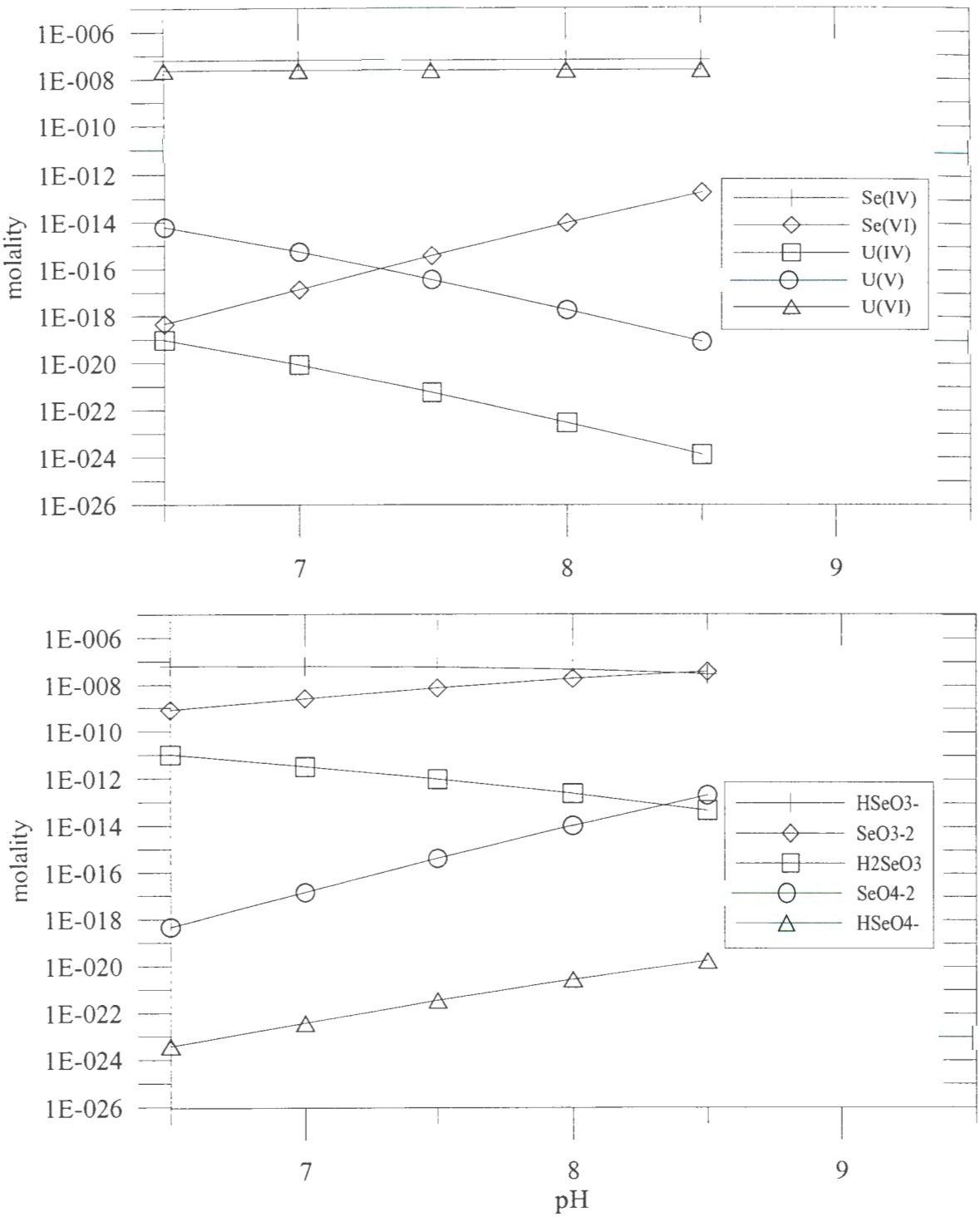


Figure 48. (a) pH effects on major Se and U species at the Dodge City site and (b) pH effects on Se speciation at the Dodge City site.

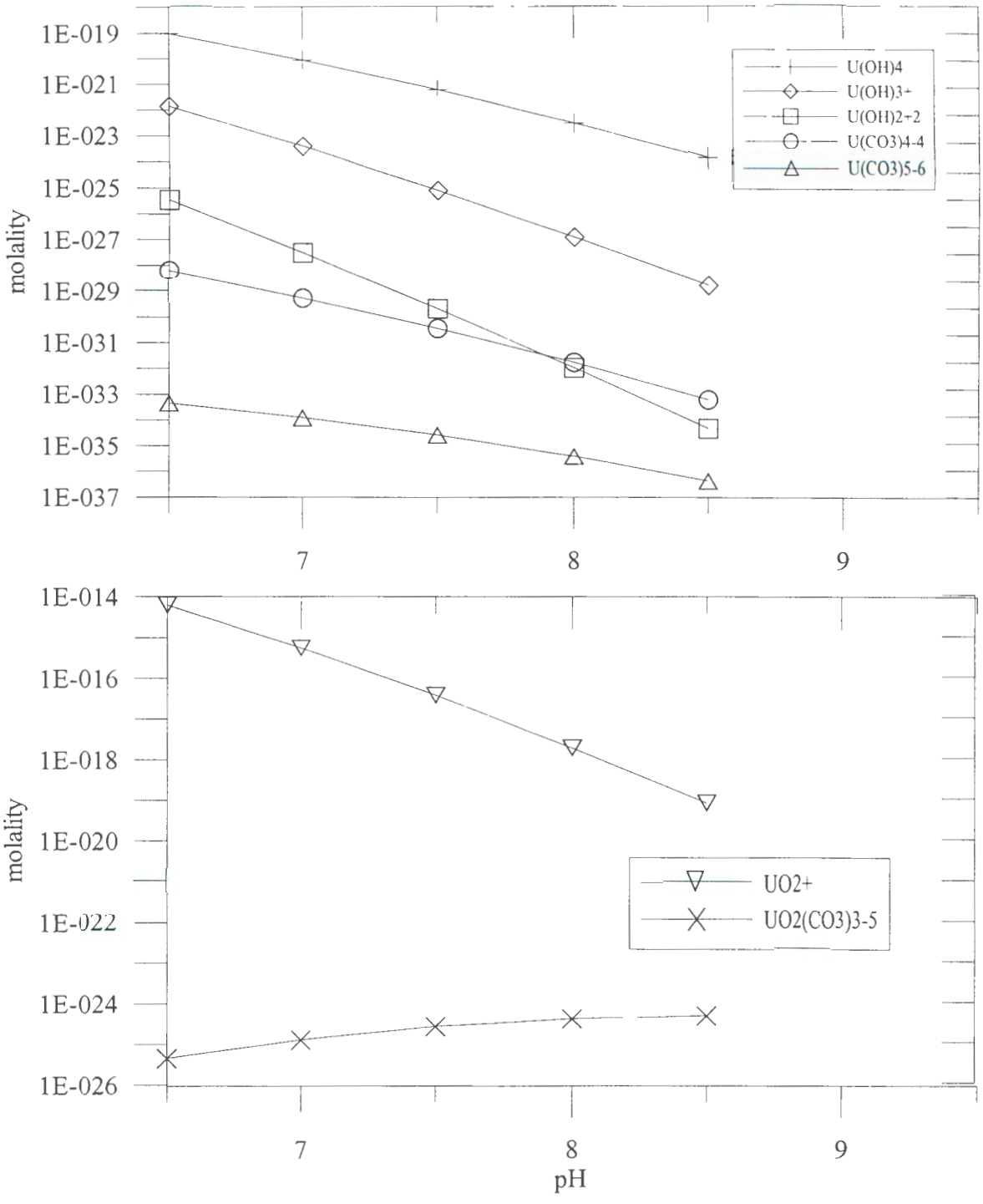


Figure 49. (a) pH effects on U(IV) species at the Dodge City site and (b) pH effects on U(V) species at the Dodge City site.

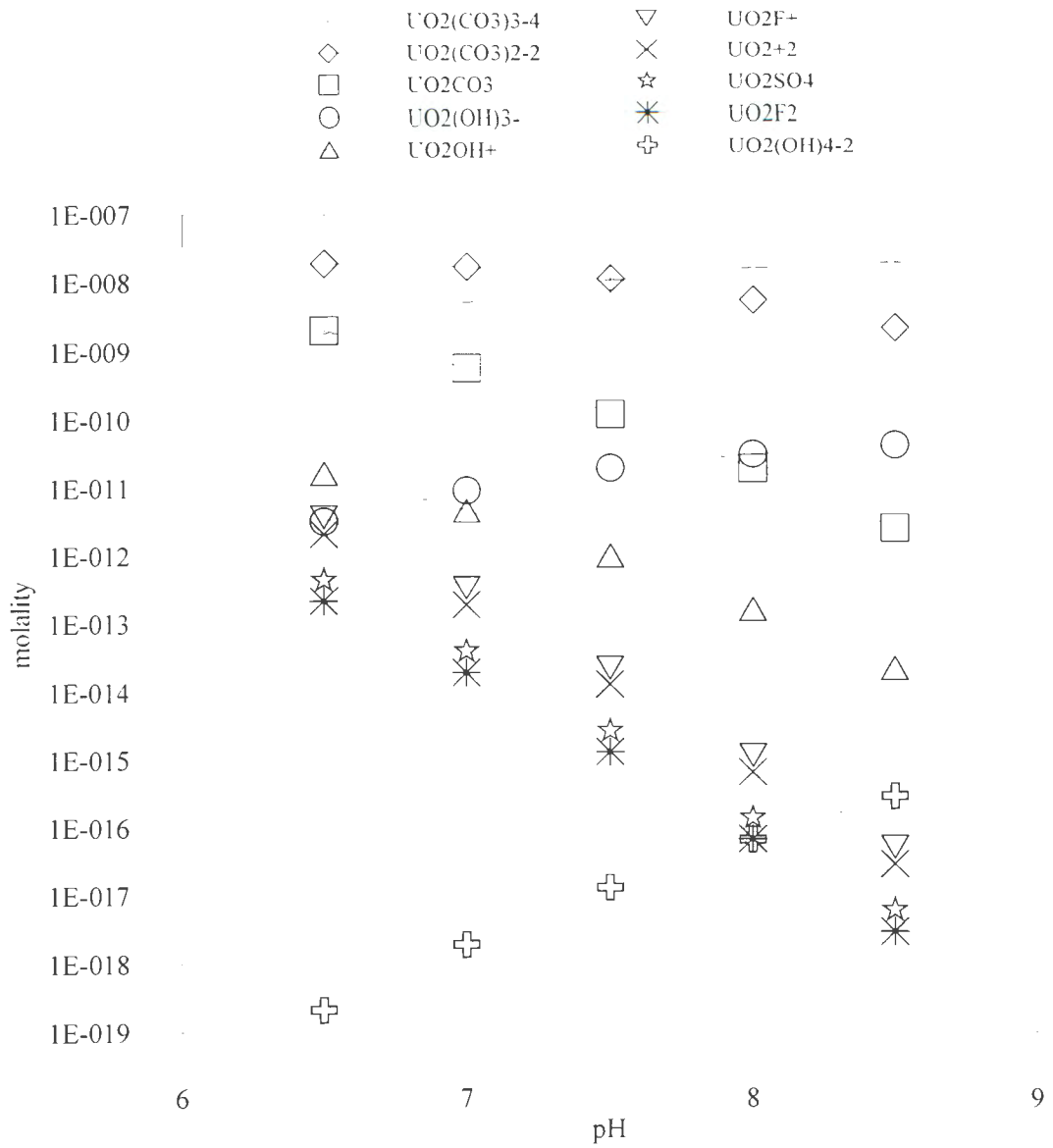


Figure 50. pH effects on U(VI) speciation in deep groundwater at the Dodge City study site.

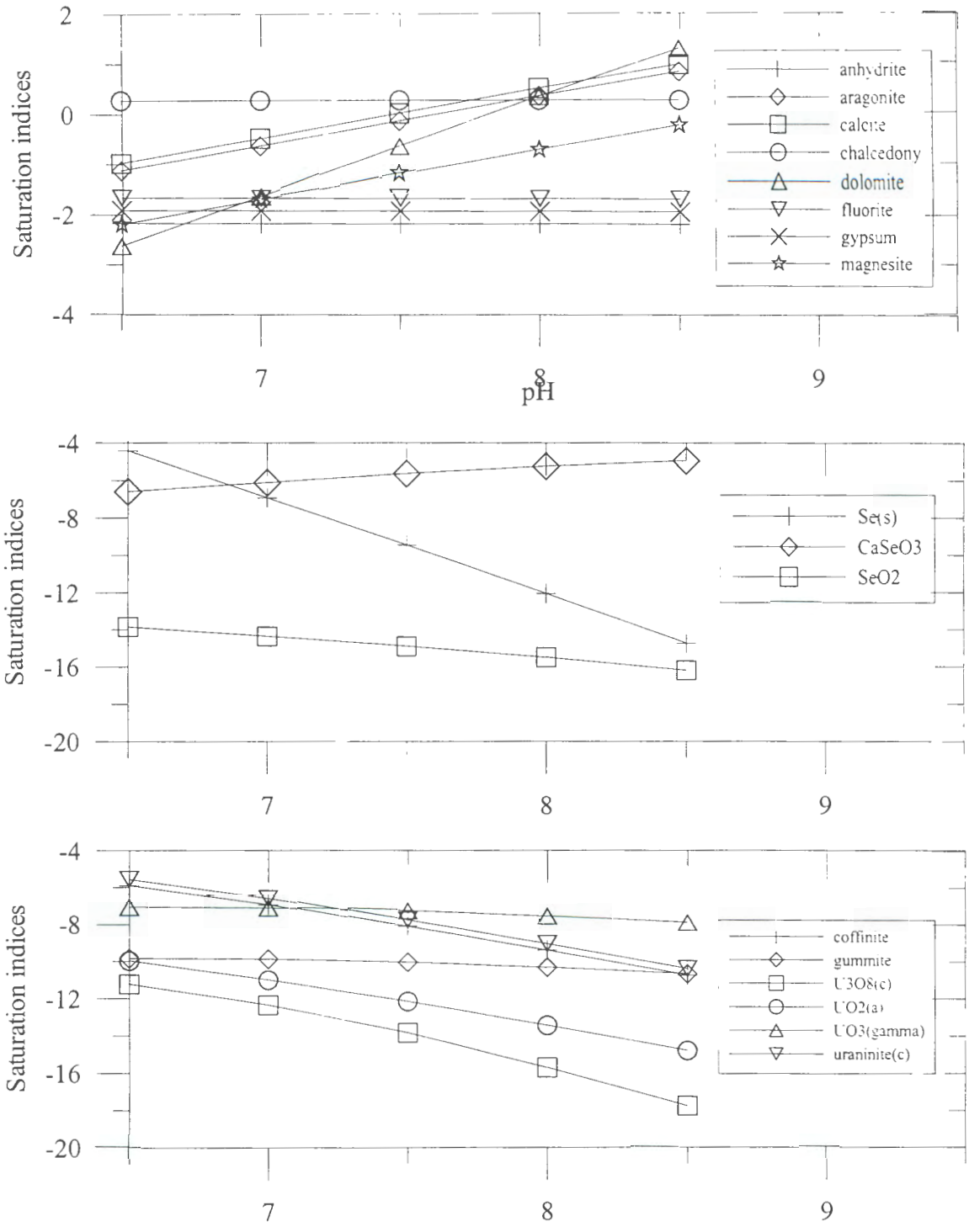


Figure 51. Plot showing pH effects for Dodge City site on saturation with respect to (a) major minerals, (b) Se minerals, and (c) U minerals.

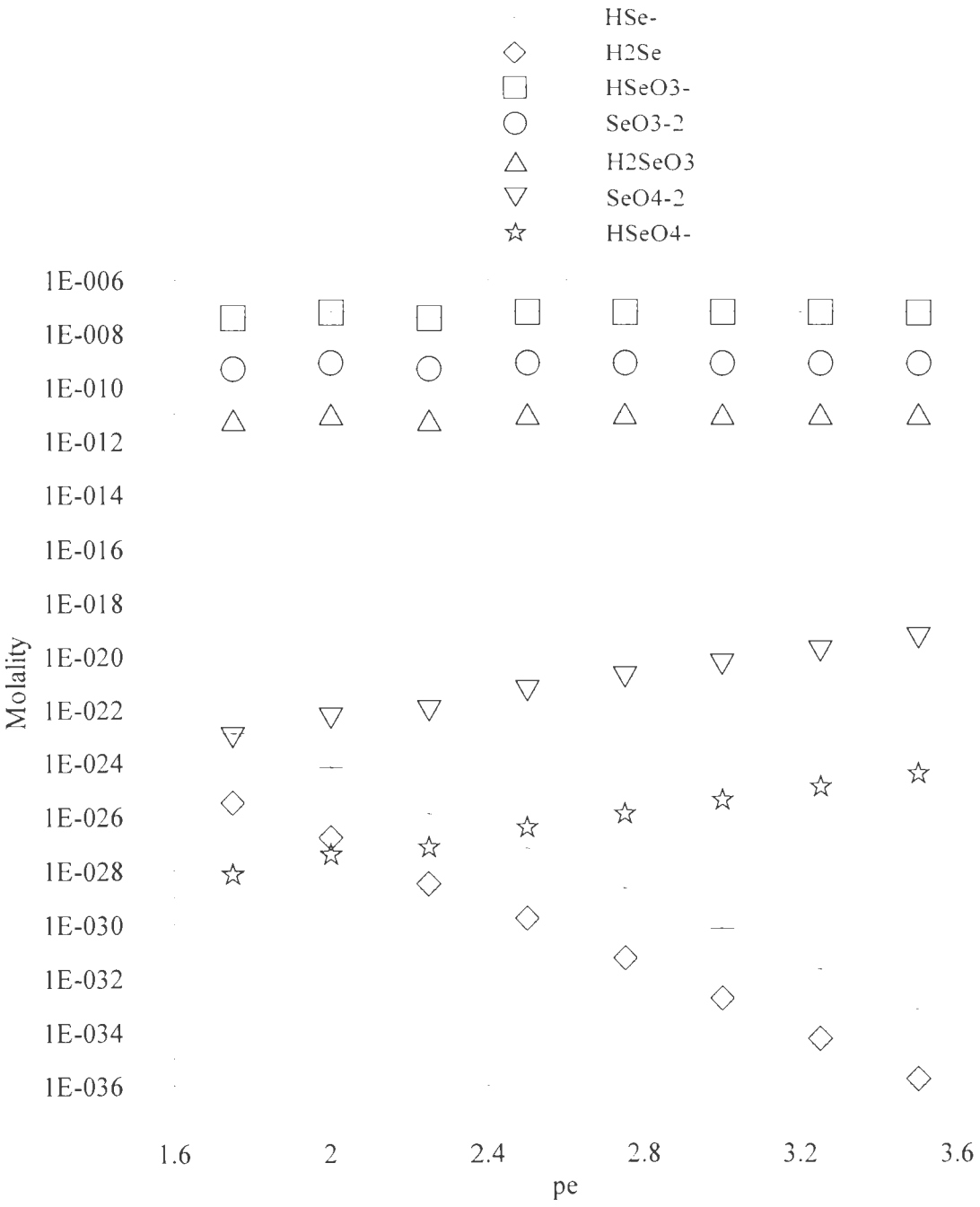


Figure 52. Eh effects on Se speciation in deep groundwater at Dodge City. Se(-II), Se(IV), and Se(VI) species are included on this plot.

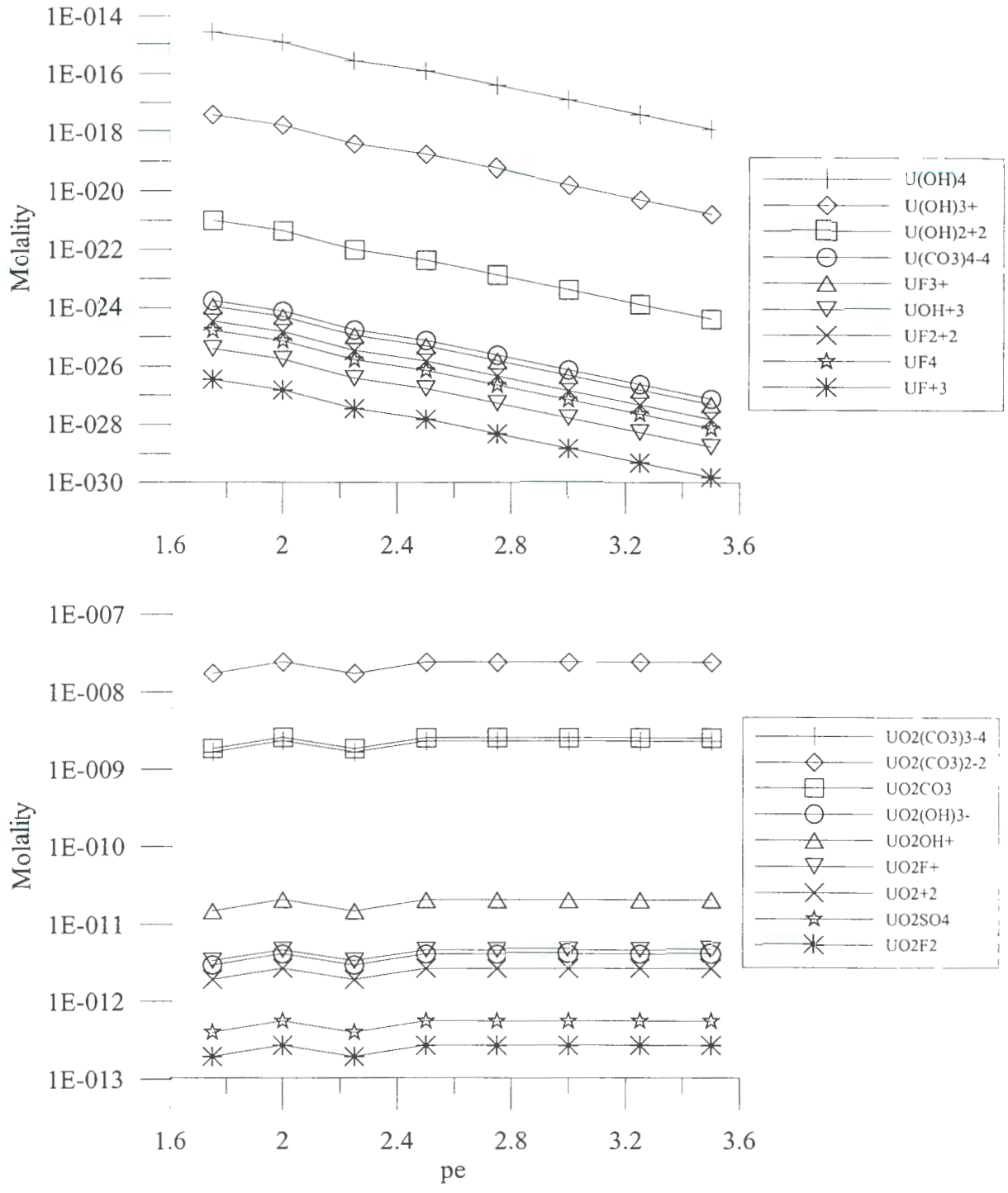


Figure 53. Eh effects on (a) U(IV) speciation and (b) U(VI) speciation.

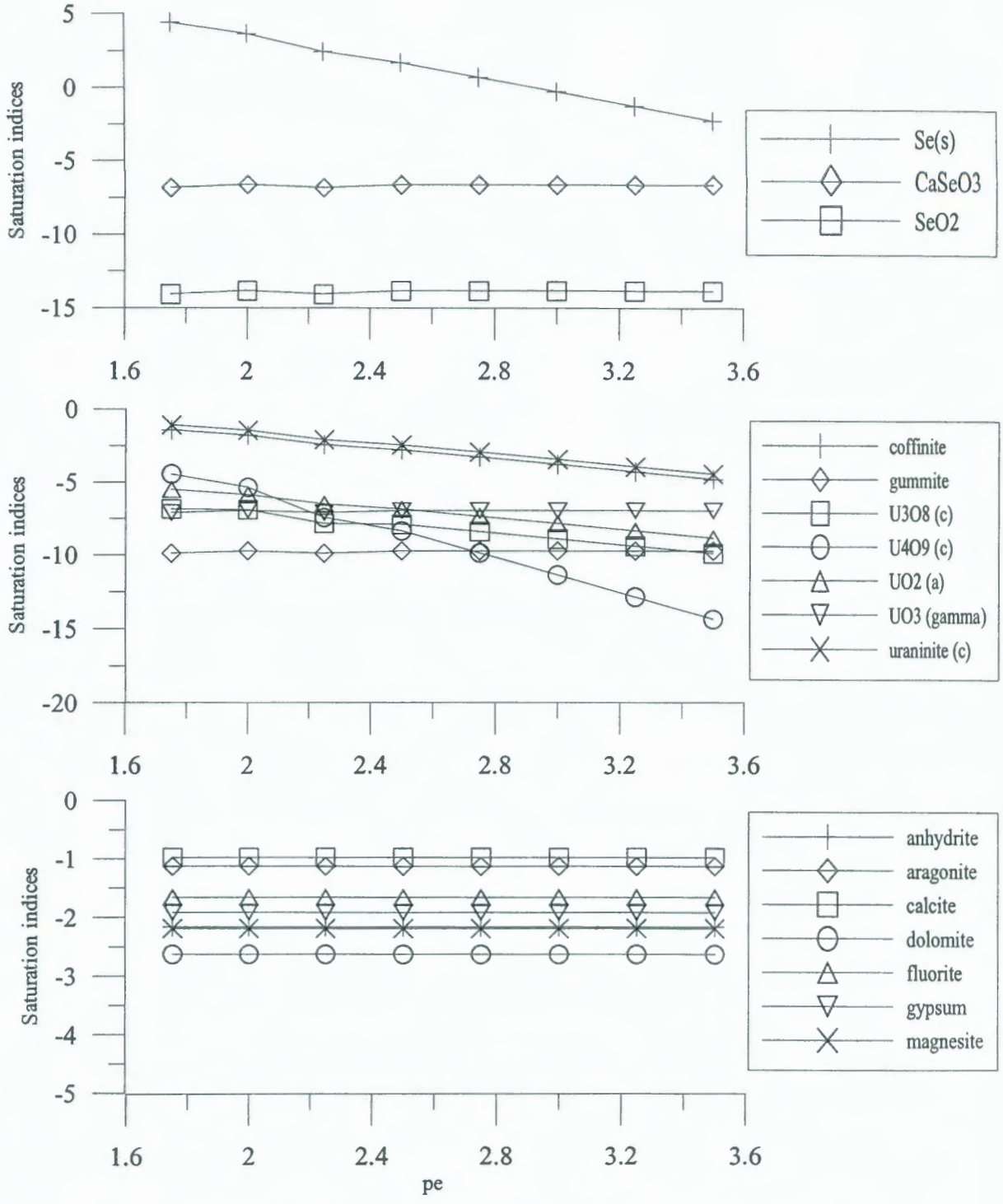


Figure 54. Plots showing Eh effects on saturation with respect to (a) Se minerals, (b) U minerals, and (c) various other minerals.

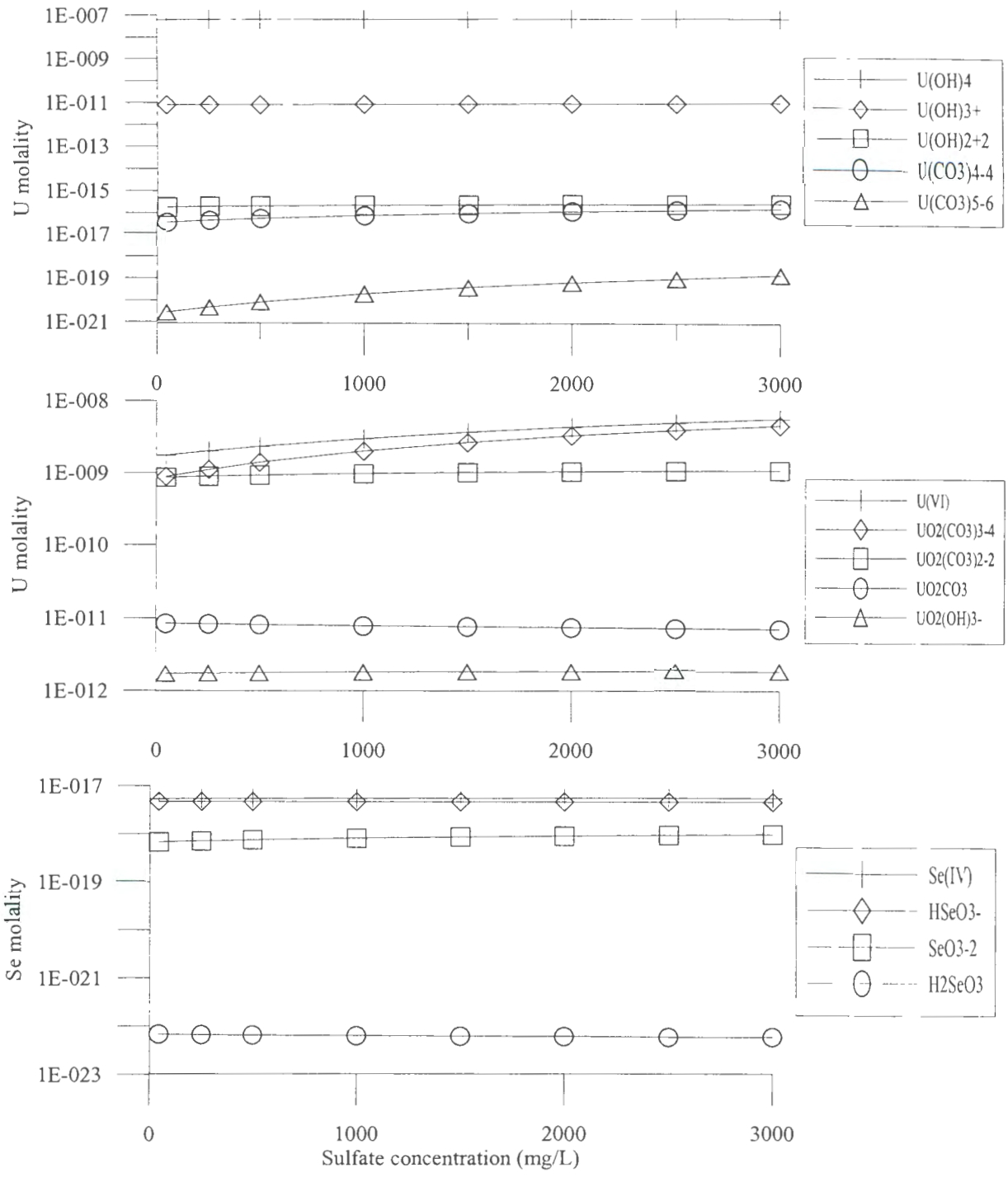


Figure 55. Effect of varying sulfate concentration in the deep groundwater at Dodge City on (a) U(IV) speciation, (b) U(VI) speciation, and (c) Se(IV) speciation.

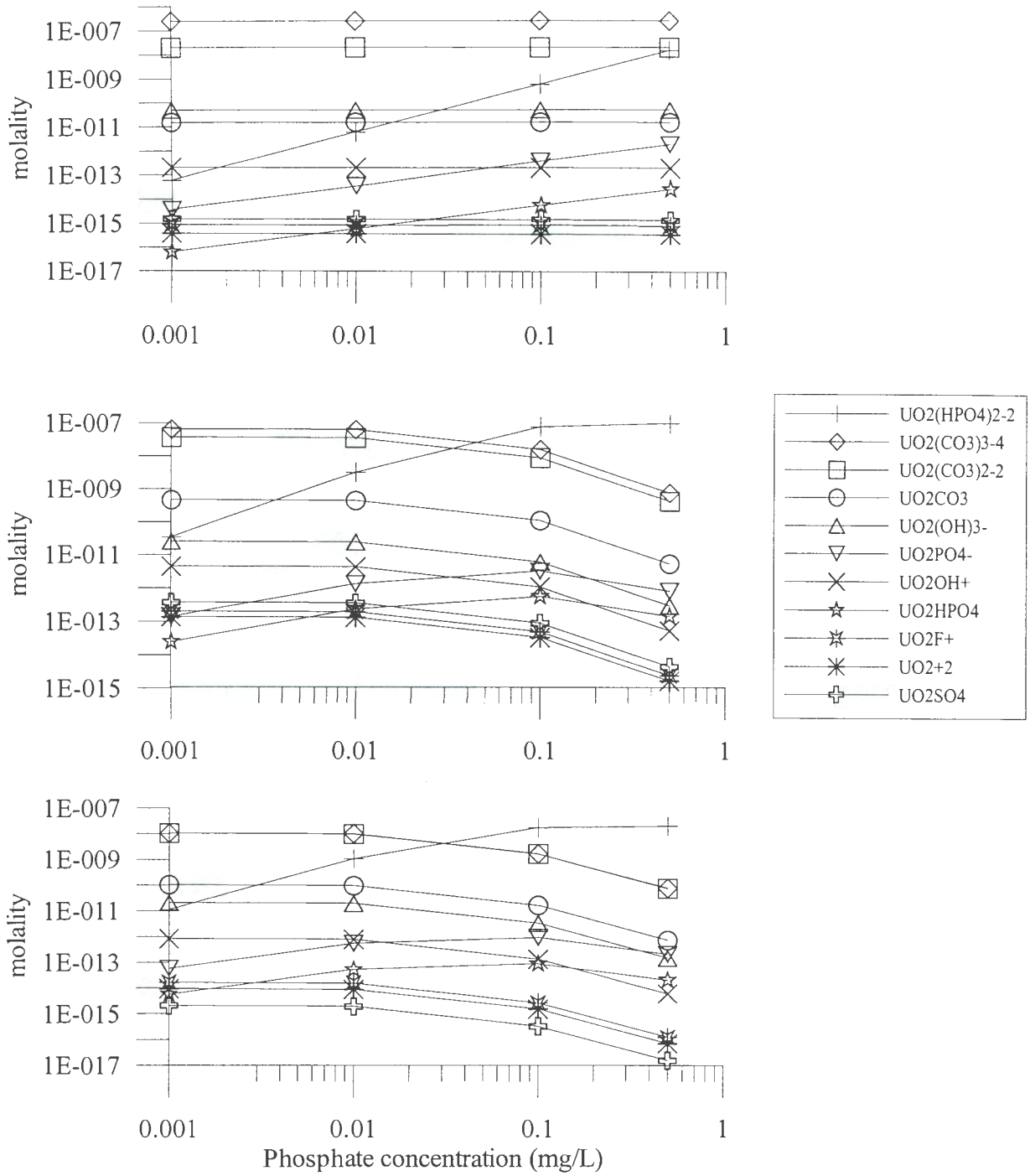


Figure 56. Phosphate effects on U complexes at Dodge City in the (a) Arkansas River, (b) shallow groundwater (DC4), and (c) deep groundwater (DC1). The legend applies to Figures 56a-c.

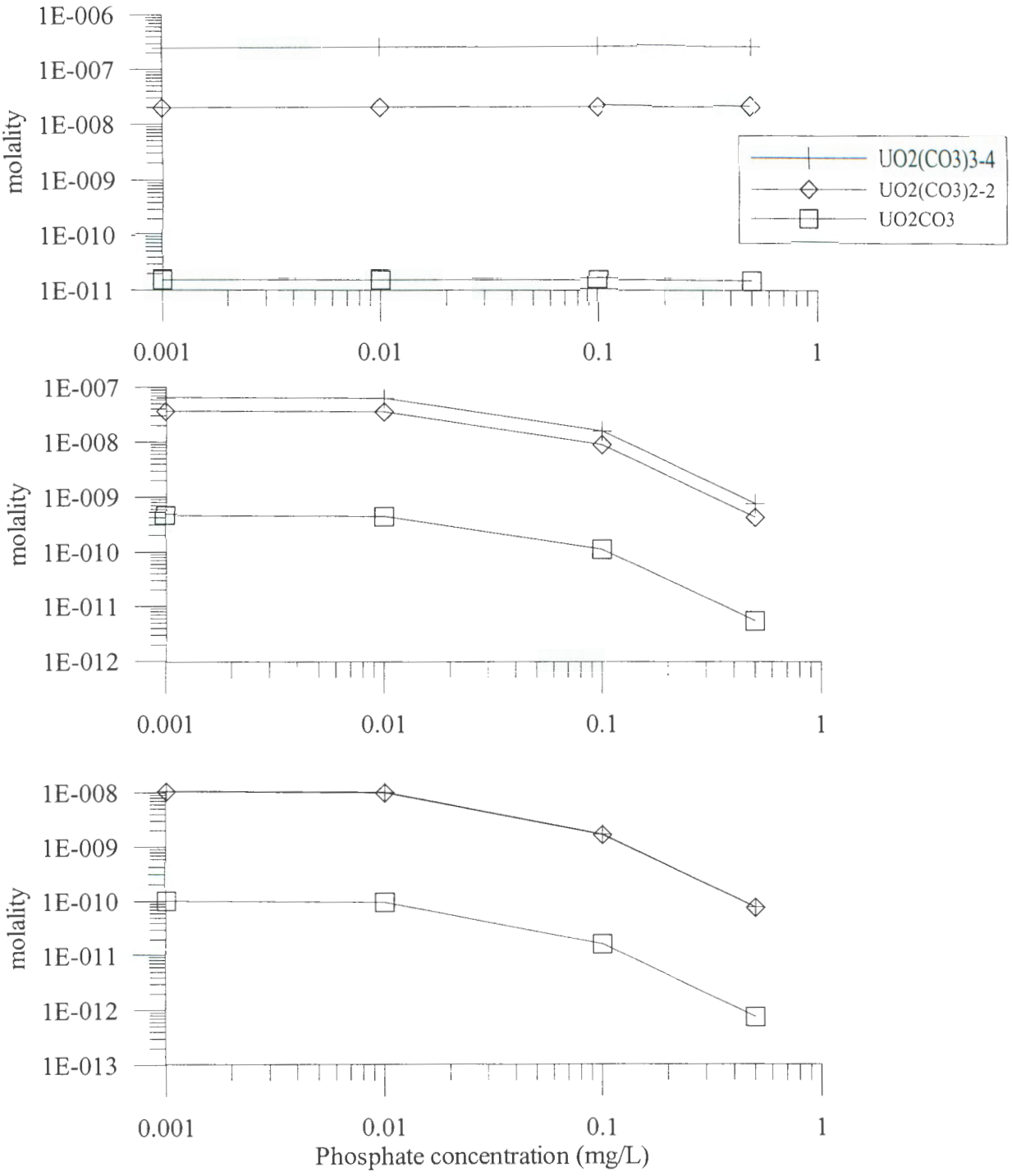


Figure 57. Phosphate effects at Dodge City on U-CO_3 complexes in (a) Arkansas River, (b) shallow groundwater (DC4), and (c) deep groundwater (DC1). The legend applies to Figures 57a-c.

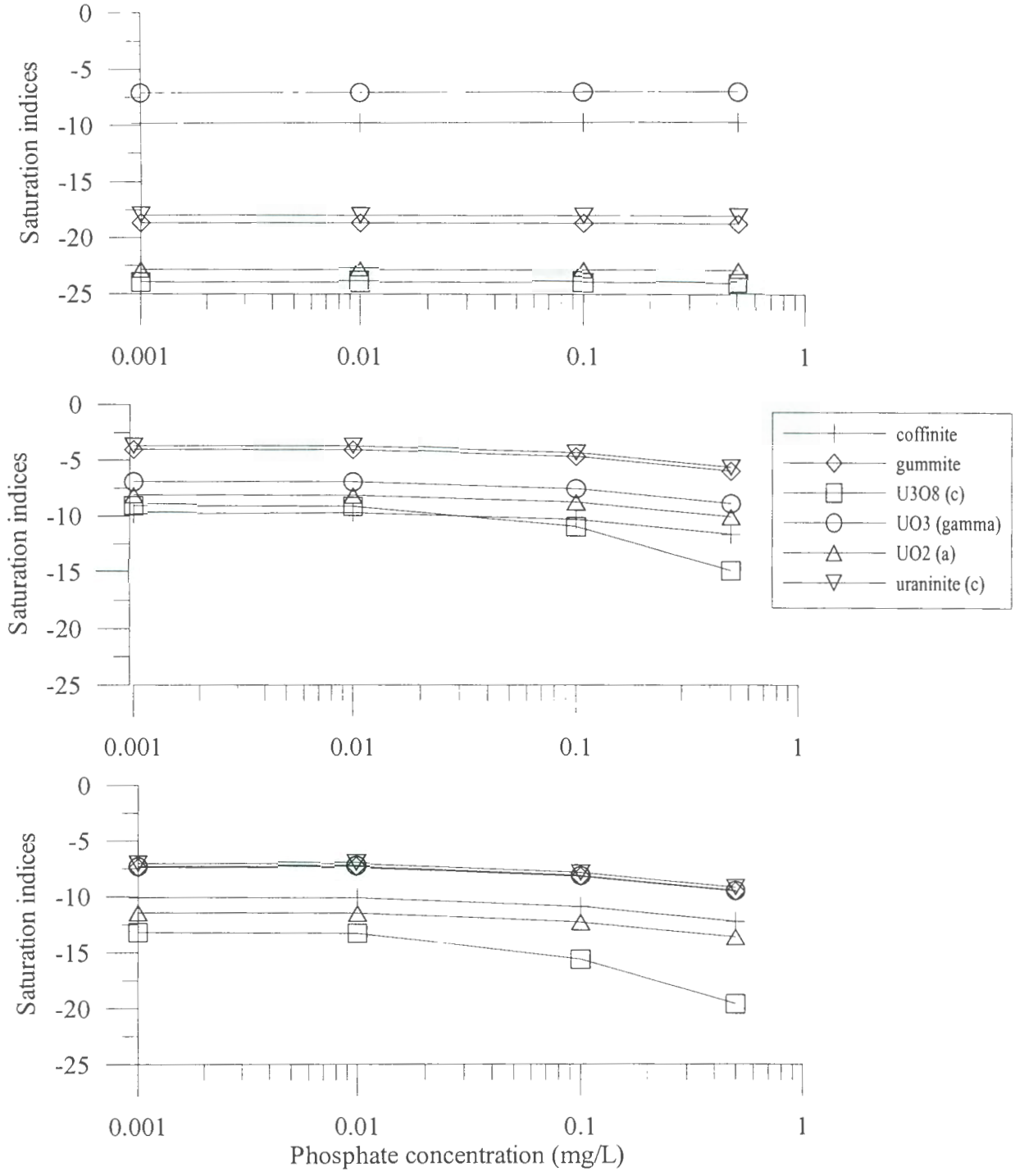


Figure 58. Phosphate effects on U mineral saturation at Dodge City in (a) Arkansas River, (b) shallow groundwater (DC4), and (c) deep groundwater (DC1). The legend applies to Figures 58a-c.

Chapter 7 Discussion

The goal of this project was to combine multiple geochemical, hydrogeological, and analytical techniques to assess the fate and transport of Se and U in the Upper Arkansas River-aquifer system. The hypothesis was that Se and U behave non-conservatively and that mixing was an important physicochemical process affecting both constituents. However, sorption appeared to play a more important role than expected at some sites than in the conceptual model formed early in this study. The solubility controls on the transport and behavior of Se and U were found to be not important because the redox conditions of the system were too oxidizing for Se and U minerals to precipitate. Interpretations of the water chemistry helped place some constraints on important geochemical processes operating in this river-aquifer system.

The ICP-MS data for Se and U collected in this study are similar to other historical values in the study area. In the data from this study, 86% of groundwater samples exceeded 5 μg/L Se and 14% of the water samples were greater than 20 μg/L (Table 19). These limits correspond to the Kansas chronic and acute toxicity limits for aquatic life in surface water. However, none of the water samples exceeded the drinking water standard of 50 μg/L.

U concentrations exceeded 20 μg/L, the drinking water standard previously proposed by the USEPA, in 57% of groundwater samples and all river samples (Table 19). Palmer and Edmond (1993) noted the tendency for some floodplain rivers, such as the Arkansas River, to have high U concentrations. In general, Se and U are higher in the western United States than in other parts of the country. In this study area these constituents exceeded even the western background level, indicating significant inputs (Zielinski *et al.*, 1995; Mueller *et al.*, 1991). The river sample collected during high flow conditions had a U concentration that exceeded the drinking water standard, which suggested that the dilution effect of increased discharge

was not enough to substantially lower elevated concentrations. This will be discussed further in the conservative mixing section of this chapter.

Several factors appear to have played a role in controlling the observed water chemistry and Se and U concentrations in the study area. The main source of Se and U is the weathering of shales known to contain elevated contents of these elements. Evapotranspiration then concentrates dissolved Se and U, as well as major constituents, in residual waters in the river, reservoirs, river water diversions, and the fields irrigated with the diverted water. Agricultural runoff carries the saline water with elevated Se and U into the river. Additionally, there are probably local inputs for Se in the study area, mostly from volcanic ash layers in the Tertiary and Quaternary sediments.

In general, river water quality declines downstream in eastern Colorado. The historical data for 1974-1995 collected from various agencies and studies in the area show that some parameters such as SC and sulfate concentration have increased significantly in the Arkansas River at the Colorado-Kansas state line in recent years (Table 1). Data from wells installed at the Garden City site in 1997 near test holes drilled and sampled in 1961 show that the saline water has been seeping deeper into the aquifer. The sulfate and chloride generally behave conservatively in the river water and groundwaters, both downstream and with depth in the study area. Se and U behavior was evaluated with respect to sulfate and chloride due to the presence of high concentrations and their conservative behavior.

The fate and transport of Se and U can be evaluated in terms of various controlling mechanisms such as sorption, solubility, speciation, and conservative mixing. Several of these factors affecting fate and transport are strongly dependent on the pH and redox conditions present. Many studies (Drever, 1997; Hsi and Langmuir, 1985; Boult *et al.*, 1998) explore these conditions as described in depth in the geochemistry chapter. Speciation and

distribution depend on environmental conditions, which in turn determine mobility, solubility, and toxicity. These factors also contribute to bioavailability, which is one of the main concerns for Se.

7.1 Speciation, Mobility, and Solubility

The speciation of dissolved constituents in the river water is typical of an oxidized environment. The geochemical model indicated that there was more Se present as Se(VI) in the river than in the groundwater (Table 23). Therefore, a substantial proportion of the Se is very mobile in the river and can be transported downstream and through the aquifer system, potentially distributing the contamination. This supports modeling and interpretations made by Clifton and Gilliom (1988) regarding the San Joaquin River in California.

As presented in the results chapter, the modeling output shows that the oxidation state of Se and U in groundwater is essentially the same at all three sites. In the groundwater nearly 100% of the Se is present as Se(IV) and 100% of U as U(VI) (Table 24). This speciation has significant implications for the behavior and transport of these constituents in the study area; U is present as the most mobile form and Se as the most toxic form to plants, aquatic life and humans. This is comparable to Se speciation discussed in various environments by Tokunaga *et al.* (1994); Henry *et al.* (1982) and to U speciation in any oxidized surface water or groundwater. These findings can be contrasted to those by Fujii and Deverel (1989), White *et al.* (1991), and other studies in Kesterson Reservoir and the San Joaquin Valley in California. The groundwater in these areas is more oxidized and, therefore, Se in this environment is mostly present in the Se(VI) oxidation state.

The model output indicated that dissolved U is primarily present as $UO_2(CO_3)_3^{-4}$ in Arkansas River water which is the speciation Leinert *et al.* (1994) reported in the River Glatt

in Switzerland. This is important because Henry *et al.* (1982) found complexation of U to be very important in groundwater in Texas because it limited sorption. Studies in various river environments similar to this project support the data found in this study (Deverel *et al.*, 1994; White *et al.*, 1991; Clifton and Gilliom, 1988). In a study of a similar river environment, Palmer and Edmond (1993) found a similar speciation and reported that this speciation occurs because U-CO_3 complexes are most stable at higher alkalinity levels and at pH greater than 5. Studies in two different stream-aquifer environments found that most often the uranyl bicarbonate complex dominated and accounted for 99% or more of the dissolved U in waters (Henry *et al.*, 1982; Leinert *et al.*, 1994).

This concentration distribution may at first appear to disagree with the speciation expected for the actual field conditions plotted as a box on the U-C-O-H Eh-pH diagram (Figure 12). This seeming difference between the distribution of U-CO_3 complexes on the diagram and in the model output (Tables 23 and 24) is due to differences in the activity coefficients for the -2 and -4 charged complexes. The lines shown on the diagram are drawn for activities and the concentration distribution was evaluated for the model output. There is such a large difference in the activity coefficients for these two U complexes that the predominance of species is reversed between the activity and concentration.

Langmuir (1997) concluded that in oxidizing surface water and groundwaters U(VI) is often the most abundant oxidation state. The speciation and distribution of U is environmentally beneficial for the following reasons. Although U(VI) is the most soluble form of dissolved U, it also forms strong complexes and can sorb to many types of particles present. The strongest U complexes form with carbonate, which is plentiful in the study area as calcium carbonate cement and calcareous sands. The distribution varies slightly in the

groundwaters at the three study sites, but U-CO_3 complexes make up almost all the dissolved U in some proportion.

Se exists as SeO_3^{-2} under the mildly oxidizing conditions present in the groundwaters at these study sites. This form reportedly is the most toxic form of dissolved Se, but often does not bioaccumulate in plants and wildlife because it has low solubility and mobility as discussed by McNeal and Balistrieri (1989). Welch (2000) reports that As(III) is more toxic than As(V), but for drinking water this speciation and relative toxicity does not matter because all As gets turned into As(III) in the stomach. As and Se behavior is often analogous because they are both redox sensitive and behave geochemically similar in some natural environments. This As example may indicate that for drinking water the speciation of Se does not matter for relative toxicity to humans because any Se(VI) present may be converted into the more toxic form, Se(IV) in the stomach. Therefore, a high level of Se in any form may be dangerous to humans.

Several studies have discussed patterns of Se(IV) distribution with depth. Robberecht and Van Grieken (1982) reported that Se(IV) was often uniformly distributed with depth in environmental waters. In the Kesterson Reservoir in California the amount of SeO_3^{-2} in groundwater decreases relative to that of surface water (White *et al.*, 1991). The data in this study are contrary to both of these findings. This result is probably due to differences between the redox environment present in the subsurface at the locations or sorption of Se in the subsurface.

Se and U are present in relatively mobile and soluble forms in the groundwaters at the study sites. There are no apparent solubility controls by mineral precipitation or dissolution on Se and U in the study area because there are no solid U or Se mineral phases present and redox conditions disallow precipitation. Modeling and the conceptual model

formed based on Eh-pH diagrams show that Se and U minerals remain significantly undersaturated throughout the profile at each site. The correlation calculated in this study between SC and U indicates that U is soluble and conserved in solution, which is what Zielinski *et al.* (1995) found in the Arkansas River basin of southeastern Colorado. They also found that in southeastern Colorado the easily measured value of SC could be used to roughly estimate the potential for high U concentration in the study area.

The modeling output also showed that gypsum is close to saturation in some wells. This does not affect Se or U fate and transport but is an important consideration for the study area in general. Sulfate concentration would be controlled by gypsum solubility if the river flows were further concentrated by evapotranspiration. In this instance, sulfate would not behave conservatively. Since high levels of SO_4 are present and concentrations will probably increase further in the future, gypsum could precipitate in the area. Changing sulfate concentration in the model did not affect Se and U speciation significantly, and therefore would not affect precipitation of Se or U minerals or sorption. Thus precipitation of gypsum would only be important if it occluded Se or U in the mineral.

Varying environmental conditions, such as Eh, pH, and increase of constituent concentrations could possibly change the processes presently in control. At Garden City, $Se_{(s)}$ is close to saturation in the shallowest well (Figure 44b) and at Dodge City, the groundwater is nearly saturated with respect to $Se_{(s)}$ in the shallowest well (Figure 44c). At Deerfield, the groundwater is nearly saturated with respect to $Se_{(s)}$ between about 150 and 250 feet deep (Figure 44a). Increasing amounts of Se moving into the subsurface or a slight decrease in the Eh could cause precipitation of $Se_{(s)}$, which could help mitigate this contamination problem at these sites. A higher Eh value assuming equilibrium with DO in the geochemical model would create conditions less likely for $Se_{(s)}$ precipitation.

The saturation with respect to $CaSeO_3$ is also discussed in the previous chapter. Discussions about mineralogy and occurrence of this Se solid were not found in the literature. Therefore, it is simply assumed to be a Se solid used in the modeling program and may or may not be a common species in nature. Several studies, including White *et al.* (1991), using PHREEQC discussed saturation with respect to this mineral similar to the discussion in this study, but none of them discussed the characteristics of the solid.

7.2 Redox Controls

Mo concentrations were determined because Se, U, and Mo are redox sensitive, and because these constituents often behave similarly, Mo concentrations sometimes can help characterize Se and U behavior. In general, Mo behaves much more conservatively with depth than Se or U and the three are only similar when Se and U vary only slightly (Figures 35a and 35b). Therefore, Mo characteristics probably will not assist in constraining behavior. Simple correlation does not show that Mo is related significantly to Se or U (Table 20). Figure 35 indicated that there is some sorption of Mo from solution suggesting that it is behaving similarly to U.

Mo remains constant with depth and does not behave like Se or U at Dodge City so this constituent can not help assess Se and U behavior. At Deerfield, Se and U behave similarly and this is the only site where sorption is important for both constituents. Se and Mo behave most similarly at Garden City, but Se and U are also most constant with depth at this site. Overall, no patterns arose between these three constituents that suggest that Mo could help characterize Se and U behavior.

7.3 Conservative Mixing

Cl and, in general, SO_4 behave conservatively in this system. Comparison of Se and U with these constituents reveals specific information about fate and transport in the system. U behaves non-conservatively relative to these constituents whereas Se behaves conservatively at some but not all of the study sites (Figures 32a, 33 and 34). Other studies report that U sometimes behaves conservatively, especially in oxidized environments (Drever, 1997; Hodge *et al.*, 1996; Klinkhammer and Palmer, 1991). Hodge *et al.* (1996) concluded that U was acting conservatively in oxygenated groundwaters of the Great Basin based on the covariance of U with Cl, Na, and SO_4 but these relationships were not found in this study. Hodge *et al.* (1996) added that U also behaves conservatively in oxygenated groundwater due to the formation of stable carbonate complexes.

Conservative mixing is one of the most important controls in this study area. Dilution of the saline river water during infiltration into the aquifers is important in decreasing the Se and U concentrations in the groundwater. Consideration of mixing is important due to the river-aquifer interactions and seepage of the more saline river water into the subsurface at the study sites. Mixing is also important in the development of the river as it moves downstream from Colorado. The fresh groundwater U/Cl, U/SO_4, Se/Cl, and Se/SO_4 ratios are much higher than surface water ratios (Tables 21 and 22). U/Cl and U/SO_4 are appreciably lower in most of the saline groundwaters of the Arkansas River study sites than in the river water. The Se groundwater ratios are higher than the river Se ratios because there is some Se source in the area but little Cl or SO_4 input in the subsurface of the study area. The sources of SO_4 and Cl are independent of Se at the beginning of the river but in the river water they are affected by the same process of evapotranspiration.

The combination of geochemical processes controlling Se and U concentrations is unique at each study site. Mixing is important at Deerfield where the saline river water and shallow groundwaters are mixing with the fresher, deeper groundwaters, but sorption is also an important control on Se and U at this site, as will be discussed below. The impact of this mixing is evidenced by the almost linear plot of salinity with depth. The mixing curves (Figures 37 and 38) were the strongest method of data interpretation in this study because they allowed determination of where Se and U concentrations were greater or smaller than expected for simple mixing.

The sinuous trend of Se and U and their ratios with Cl in the depth profile also shows deviations from simple mixing. This sinuosity is most evident at Deerfield (Figures 29a and 33a). Other studies linked behavior like this to seasonal trends. Se concentrations show fluctuations due to seasonal effects of irrigation and evaporation in Kesterson Reservoir (White *et al.*, 1991) and U concentrations varied seasonally with a maximum in the summer in the River Glatt in Switzerland (Leinert *et al.*, 1994). However, the periodic nature that Se and U exhibit at the study sites must be due primarily to local inputs and sorption because the rate of vertical groundwater flow is slow. At Deerfield, the sinuous nature with depth may be due to differences in subsurface sources versus sorption. The changes are not due to recharge from the river such as at Garden City because the salinity source at Deerfield is infiltration from the diverted river water used for irrigation. The nature of Se and U concentration changes at Deerfield might strongly be affected by local input from the volcanic ash layers in the aquifer. Several authors identified volcanic ash layers high in Se in this general area and previous studies in southwestern Kansas identified ash layers in Hamilton County near the Deerfield site (Trelease and Beath, 1949; Rosenfeld and Beath, 1964; McLaughlin, 1943; Smith, 1940).

Mixing is the main mechanism controlling the Se concentration distribution with depth and is partly responsible for the U distribution at Garden City. The most important support for this interpretation is the mixing curves (Figures 37 and 38). All of the groundwater points plot on or near the mixing lines at Garden City for Se (Figures 38a and 38b), and in general, mixing is much more important for Se than for U. The sinuosity of the Se and U ratios with Cl at Garden City is due to changes in the salinity of recharge from the river. The discharge and quality of the river water have changed over periods of several years and the sinuosity is probably related to recharge affected by these changes. This is the only site showing evidence of different river salinities from a period of several years (1988-1995) of lower, more saline flows followed by a few years of higher flows with lower salinities (1995-1999) (see data from Whittemore *et al.*, 2000).

Mixing is the main mechanism for fate and transport of Se and U in the subsurface at Dodge City. The mixing curves indicate this because the groundwater points plot on or near one of the two mixing lines plotted for Dodge City (Figures 37 and 38). However, the sinuous trend of Se/Cl and U/Cl ratios with depth is also visible at a smaller scale at Dodge City (Figures 29c and 33a).

The concentrations of Se and U remain high in the river during high flow based on the data collected in this study. The discharge for the high flow sample was approximately 10 times that of the low flow samples, but Se and U decreased by only about one-third. This suggests that conservative dilution is not the only process controlling concentrations in the river water. The flushing of soluble mineral salts and saline water in the soils, as well as in ditches carrying irrigation return flows, could add these constituents to the river water by overland flow.

7.4 Sorption

In low temperature, oxidizing environments adsorption often influences concentration more than mineral precipitation and groundwater often holds more U than adjacent streams due to U-soil interactions (Henry *et al.*, 1982, Galloway & Kaiser, 1980, Hsi and Langmuir, 1985, Langmuir, 1978). Howard (1977) studied Se sorption and concluded that Se occurs with hydrous Fe oxides in oxygenated aquifer environments due to strong adsorption of selenite ions to Fe oxide surfaces often removing between 95-99% of Se(IV) from solution below neutral pH. Se sorption in the Howard (1977) study was not a major control but this could be due to competition with U and pH conditions at the sites.

Sorption attenuates U concentrations, and to a lesser degree, Se concentrations in the Arkansas River study area. Mixing curves, ratios, and geochemical model output indicates that U and some Se are removed from solution by sorption. The most probable substrates are clays and organic material as Boult *et al.* (1998), Dzombak and Morel (1990), and Hsi and Langmuir (1985) concluded. Sorption can be environmentally helpful by lowering constituent concentrations and leaving less in a bioavailable form. However, at these published study sites sorption removed only relatively small amounts of Se and U from solution. This is probably due to pH controls and competitive effects with complexation. White *et al.* (1991) reported that sorption was suppressed by competitive effects with SO_4 in the Kesterson Reservoir in California. This is of potential importance to the Arkansas River corridor since the study area was a similar high-sulfate environment.

The mixing curves and ratio plots clearly show where sorption is attenuating Se and U concentrations. It is not surprising that there are not substantial amounts of Se sorbed because sorption of Se is most important at high pH. Se sorption is only important at the Deerfield site, and primarily for one well water. The geochemical modeling shows that

sorption could play a small role in the fate of Se. However, there is a thicker column of clays at Deerfield than at the other sites, and if this small amount of sorption is continual, significant amounts of Se could be removed. At all three study sites the Se/U ratio increases significantly with depth suggesting that more U is coming out of solution than Se (Figure 32b).

The mixing curves show a very different pattern for sorption of U. U is expected to sorb because at neutral pH 100% of U(VI) sorbs onto ferric oxyhydroxides (Langmuir, 1997). U(VI) has a strong affinity for sorption and Brown *et al.* (1998) found that in irrigation water U was strongly adsorbed by Fe oxides in the soil before reaching the groundwater. The study of Brown *et al.* (1998) has important environmental implications to the southwest Kansas study area because much of the recharging water in both systems is saline irrigation return flow. The U/Cl and U/SO_4 plots with depth show significant removal of U from solution at all study sites. At Deerfield, U sorption is significant in all wells except at the 140-ft depth where there is input of Se and U to the groundwater. This is not surprising because volcanic ash, the source of local Se and U input, is often enriched in Se as reported by Rosenfeld and Beath (1964) and also in U as reported by Berendsen and Hathaway (1981). Alternatively, the relative importance of a Se and U source in ash layers versus sorption could vary with depth.

Sorption is not the dominant geochemical control at Garden City and Dodge City. However, the mixing curves and U ratio plots indicate that sorption is an important mechanism for attenuation of U. U is being removed from solution at all observation well depths at Garden City (Figures 37 and 38). U is being sorbed in the alluvial aquifer at Dodge City. Simple correlations showed that at the Garden City site Se and pH are related at a 90% level. Henry *et al.* (1983) reported that a proportional relationship between pH and Se

suggests that sorption is important. The lack of Se sorption at the Garden City site indicates that pH does not appear to be an important control on sorption of Se for the pH range in the Arkansas River corridor.

Some studies examined the effects of CO_3 presence on Se and U sorption (Hsi and Langmuir, 1985; Boult *et al.*, 1998; Waite *et al.*, 1994). Previously, Langmuir (1978) and Zielinski *et al.* (1995) discussed the limits that U-CO_3 complexation placed on U sorption. However, a later study by Boult *et al.* (1998) found that U-CO_3 complexes are actually sorbed. This has important implications to this study since most of the U is present as U-CO_3 complexes. The mixing curves, ratio profiles, and model results all show that U sorption from infiltrating river water is significant in the subsurface at all the Arkansas River corridor sites. This supports the later literature studies that reported sorption of the complexes.

There are some significant implications for sorption control on Se and U from the analysis of sensitivity to environmental conditions. A slight decrease in Eh or pH could initiate $Se_{(s)}$ precipitation, therefore decreasing Se sorption and in general, Se in solution. It would take a significant decrease in pH or Eh to precipitate U minerals, so the sensitivity analysis did not reveal any implications on U sorption.

As mentioned above, White *et al.* (1991) reported that competitive effects with SO_4 suppressed sorption in the Kesterson Reservoir in California. However, the sensitivity analysis reveals that, theoretically, additional sulfate in the range typical of the Arkansas River study area should not inhibit complexation or sorption of U. PO_4 in the range typical of the study area can affect complexation by causing formation of U-PO_4 complexes that could result in decreasing the concentration of the U-CO_3 complexes. Therefore, the increase of PO_4 concentrations might significantly affect U fate in the study area. However, there was no research found regarding sorption of U-PO_4 complexes to support this conclusion.

7.5 Future Investigations

Throughout the data interpretations it became apparent that some additional studies on the fate and transport of Se and U in the study area could further this work, support these interpretations, and more clearly define the processes in this area. If wells existed and samples could be taken in lines perpendicular to the river, distribution profiles could further explain the distributions of Se and U and the influence of recharge. Depth plots at each sample location showing more of a periodic nature farther from the river could suggest that the effect is due to major variations in long term recharge from the river. This would assist in better evaluation of the effects of recharge from the river into the groundwater. Samples from wells very close to the river during different flow regimes and seasons would help to assess any seasonal or climatic effects. Leinert *et al.* (1994) found a seasonal effect on sorption that also helps explain the periodic nature of the ratio curves with depth and could be explored further in this study area.

The most significant information missing in this study area is a thorough description of the aquifer sediments, including x-ray diffraction to identify the mineralogy of the clay and sand present. Clay mineralogy could be used to further study sorption onto sediments characteristic of the area instead of using a generic ferric oxyhydroxide substrate such as the one used in the modeling in this study. Detailed analysis and description of the location and chemical content of volcanic ash layers could be used to help identify possible local sources of Se and U.

Chapter 8 Conclusions

The goals of this study were met using the data obtained from field measurements, laboratory analyses, historical data collections from government agencies, geochemical modeling, and comparison with conservative constituents in the system. These geochemical techniques, when viewed in conjunction with the hydrogeology and geology of the three sites in this study provide a basic understanding of the fate and transport in the study area.

The following conclusions were drawn from this study:

1. Se concentrations exceed the chronic toxicity limits for aquatic life in the Arkansas River waters but do not exceed the drinking water standard. None of the groundwater samples exceed drinking water standards for Se.
2. U exceeds a proposed drinking water standard of 20 μg/L in all the river waters and in most of the groundwater samples containing sulfate concentrations greater than 1100 mg/L. The two deeper fresh groundwaters at Deerfield also exceed 20 μg/L U.
3. Se and U behave less conservatively than Cl and SO_4 in the groundwaters at the study sites.
4. Se(IV) and U(VI) are the predominant oxidation states present in the groundwater. The predicted occurrence of some Se(VI) with Se(IV) in the river water results from the higher Eh of the river than the groundwater. The use of higher Eh in equilibrium with DO for the geochemical modeling would not significantly affect the speciation of Se and U in these waters.
5. The most important Se species in the groundwater is $HSeO_3^-$ with a small proportion as SeO_3^{-2}. The Se(VI) in the river water occurs essentially all as the SeO_4^{-2} species.

Sensitivity analysis shows that SO_4 and PO_4 typical of the study do not substantially affect Se behavior or complexation.

6. U is mostly in the form of U di- and tri- carbonate species, $UO_2(CO_3)_2^{-2}$ and $UO_2(CO_3)_3^{-4}$. These are the most soluble and mobile forms of U. The sensitivity analysis results from the modeling show that typical PO_4 concentrations in the area groundwater should not substantially affect U speciation.
7. There are no mineral solubility constraints on Se and U at the present conditions at the sites. The redox conditions are not reducing enough for precipitation of Se and U minerals. If pH or Eh is increased saturation with respect to Se and U minerals decreases substantially. The groundwaters are close to saturation with respect to $Se_{(s)}$ between about 150 and 250 feet deep at Deerfield and in the shallowest well at Garden City and Dodge City. Small changes in the Eh and pH conditions or addition of Se into the subsurface could potentially cause precipitation of this solid, thus removing Se from the water.
8. Interpretations and conclusions were made with the data in terms of dilution by mixing saline river water with fresher groundwaters at the study sites compared to the effects of sorption and possible additional sources in the subsurface. The differences between the sources of salinity and heterogeneity of sediments at these sites lead to very different processes controlling the behavior of Se and U at each site.
9. Sorption is the primary mechanism for Se and U attenuation at Deerfield. This is probably because this site has the most abundant clay. There is also a local source of Se and U in one horizon at Deerfield, which is probably leaching from volcanic ash layers present at this site.

10. At Garden City, the fate and transport of Se is controlled mainly by mixing and U by both mixing and sorption. The salinity has permeated most into the High Plains aquifer at this site because there is not as much fine sediment to retard the downward infiltration.
11. Changes in Se and U concentrations at Dodge City are primarily due to mixing of the saline river water with the fresher groundwater and dilution of Se and U. However, sorption of U is also important in the alluvial aquifer.
12. Se should not appreciably concentrate in the system because precipitation is not important and sorption is generally minor. Irrigation practices, consumptive use, and evapotranspiration will continue in this study area. Therefore, due to these human activities, natural sources, and processes controlling the levels of Se in the area, it is probable that concentrations will continue to increase.
13. U in its mobile forms should be transported easily through the system. However, the results from this project indicate that sorption of U is more important than sorption of Se and therefore substantial amounts of dissolved U are attenuated in the subsurface.

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APPENDIX 1

Deerfield Observation Well 1

elapsed time	pH	Eh	DO	temperature	SC (uS/cm)
0:00	7.42	211	3.81	19.9	
0:02	7.52	198	3.95	19.6	
0:04	7.56	185	4.22	19.6	708
0:06	7.62	168	6.61	19.8	
0:08	7.62	157	7.11	19.8	
0:10	7.62	153	7.46	19.8	
0:12	7.62	148	7.67	19.8	
0:14	7.62	142	6.40	19.8	
0:18	7.62	138	6.43	20.1	
0:20	7.62	137	6.50	20.1	723
0:22	7.62	136	6.70	19.8	
0:24	7.62	136	7.05	19.7	
0:31	7.62	138		19.5	
0:36	7.63	138		19.4	723
0:46	7.67	134		19.8	723
0:56	7.65	129		20.6	
1:01	7.64	132		20.4	723
1:06	7.64	133		20.4*	
1:08	7.64	133		20.5	
1:09	7.66	133		21.0	
1:10	7.65	133		21.3	

*Final temperature used for modeling was final flow value.

Deerfield Observation Well 2

elapsed time	pH	Eh	DO	temperature	SC
0:00	7.23	174	2.78	19.1	
0:04	7.44	161	2.66	19.1	1540
0:06	7.44	155	2.68	19.1	
0:08	7.45	149	2.67	19.1	
0:10	7.45	139	2.71	19.1	
0:12	7.45	134	2.70	19.1	
0:14	7.45	126	2.71	19.1	
0:16	7.45	121	2.72	19.3	
0:18	7.45	118	2.73	19.3	1530
0:20	7.45	116	2.77	19.2	
0:22	7.46	114	2.77	19.2	
0:24	7.45	113	2.76	19.2	
0:26	7.45	111	2.78	19.4	
0:28	7.45	111	2.78	19.4	1530
0:30	7.45	111	2.80	19.4	
0:32	7.46	111	2.79	19.3	
0:33	7.46	111	3.85	19.3*	
0:33	7.46	110	2.88	19.4	
0:34	7.47	110	2.55	19.5	
0:34	7.47	111	2.44	19.7	
0:35	7.47	112	2.30	19.8	
0:36	7.46	113	2.26	20.0	
0:45					1530

Deerfield Observation Well 3

elapsed time	pH	Eh	temperature	SC
				2230
0:00	7.20	212	18.8	
0:02	7.29	203	18.9	
0:04	7.30	183	18.9	
0:06	7.32	176	18.8	2280
0:08	7.32	167	18.8	
0:10	7.33	154	18.8	
0:12	7.33	147	19.2	
0:14	7.33	142	19.2	
0:16	7.33	129	19.2	
0:18	7.31	123	19.4	
0:20	7.31	120	19.3	
0:22	7.32	118	19.3	
0:25	7.32	117	19.3	2280
0:28	7.32	115	19.3	
0:30	7.31	115	19.3*	
0:31	7.31	115	19.8	
0:32	7.31	115	20.1	
0:33	7.30	120	21.9	
0:40				
0:43				2300

Deerfield Observation Well 4

elapsed time	pH	Eh	DO	temperature	SC
					3310
0:00	7.09	210	7.76	17.6	
0:02	7.13	203	7.94	17.6	
0:04	7.14	190	8.02	17.6	3370
0:06	7.15	178	9.46	17.6	
0:08	7.15	169	9.81	17.6	
0:10	7.16	158	6.31	17.6	
0:18	7.18	139	6.13	17.5	
0:20	7.18	138	6.25	17.5	
0:22	7.18	137	6.3	17.5	
0:24	7.18	136	6.56	17.5	
0:26	7.18	130	8.20	17.5	
0:28	7.18	132	8.03	17.5	
0:30	7.18	133	7.68	17.7	
0:32	7.18	133	7.58	17.7	
0:34	7.19	134	7.69	17.7	
0:36	7.19	134	7.49	17.7	
0:38	7.19	134	7.63	17.7	
0:40	7.20	134	7.61	17.7	
0:42	7.20	134	7.56	17.7	3380
0:44	7.20	134	7.78	17.7	
0:46	7.21	135	7.85	17.7	
0:50	7.21	136	8.33	17.8	
0:54	7.21	136	8.33	17.8	
0:56	7.21	136	8.35	17.8	
0:58	7.21	136	8.4	17.8	
1:00	7.21	136	8.77	17.8	
1:02	7.21	136	8.78	17.8	
1:03	7.23	137	7.68	17.8	
1:04	7.23	137	8.26	17.8	
1:10	7.22	142	8.08	17.9	
1:12	7.22	141	8.26	17.9	
1:13	7.22	140	5.54	17.9*	
1:13	7.23	140	5.43	18.0	
1:14	7.23	141	5.51	17.9	
1:22					3380

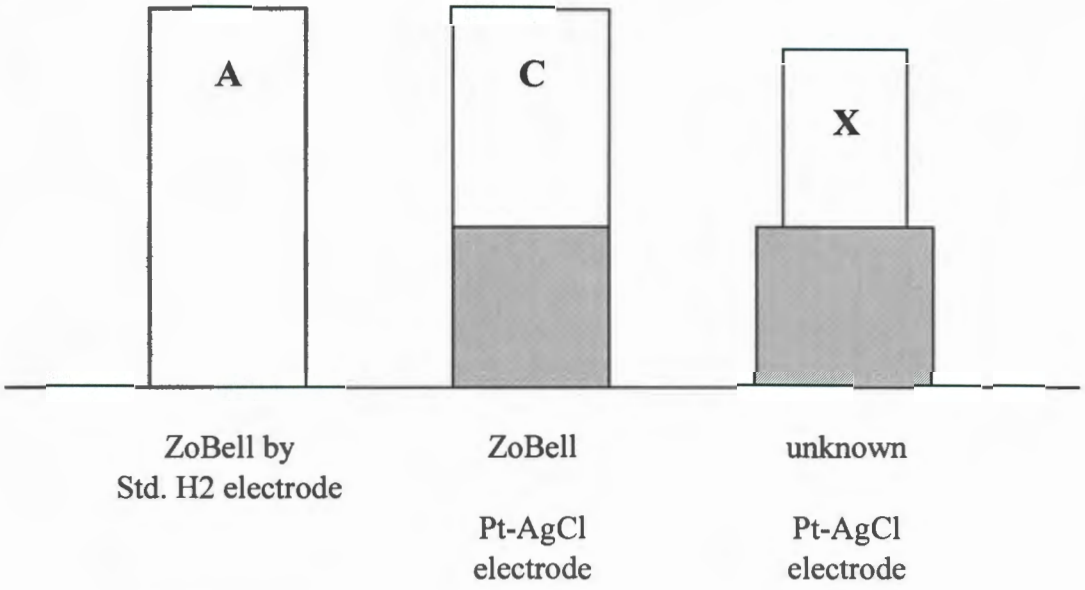
Deerfield Observation Well 5

elapsed time	pH	Eh	DO	temperature	SC
					3350
					3350
0:00	7.06	206	3.69	17.6	
0:02	7.08	196	3.60	17.6	
0:04	7.09	192	4.66	17.6	
0:06	7.13	185	4.51	17.6	
0:08	7.15	180	4.33	17.6	
0:10	7.16	177	4.32	17.6	
0:12	7.16	175	4.24	17.6	3380
0:14	7.17	174	4.23	17.5	
0:16	7.18	171	4.09	17.5	
0:18	7.19	170	4.04	17.5	
0:20	7.19	170	3.94	17.5	3380
0:22	7.20	169	3.78	17.5	
0:24	7.20	169	3.58	17.5	
0:26	7.20	169	3.45	17.5	
0:28	7.20	169	3.44	17.5	
0:30	7.20	169	3.42	17.5	
0:30	7.21	168	2.62	17.5	
0:31	7.21	168	2.44	17.5	3380
0:32	7.21	170	2.42	17.5	
0:33	7.20	173	2.29	17.5*	

APPENDIX 2

After the modeling and data interpretations were made in this project it was pointed out that the Eh values measured in field needed to be corrected to the standard hydrogen electrode (S.H.E). An example of the data correction required with for the Eh meter and probe used in this project is shown below and then a table of the final corrected Eh measurements.

Redox corrections



Eh, t, S.H.E. = X + (A-C)

as long as C is + or - 10 mV of theoretical value

X: measured Eh in unknown

A: ZoBell Eh, relative to S.H.E., at temperature

= 483 - 2.2t, where t = temperature in Celcius

C: ZoBell, relative to Pt-AgCl electrode, at temperature

= 259.2 -1.234t, where t = temperature in Celcius

Correction of Eh values measured in field to S.H.E.

well number	Eh, field	temperature	Eh(mV) , t, S.H.E.	Eh(V) , t, S.H.E.
D-1	133	20.4	337	0.337
D-2	110	19.3	315	0.315
D-3	115	19.3	320	0.320
D-4	140	17.9	347	0.347
D-5	168	17.5	375	0.375
GC-1	146	14.6	356	0.356
GC-2	147	13.5	358	0.358
GC-3	133	12.5	345	0.345
GC-4	132	13.4	343	0.343
GC-5	123	13.5	334	0.334
DC-1	204	14.5	414	0.414
DC-2	154	14.7	364	0.364
DC-3	154	14.4	364	0.364
DC-4	135	15.2	344	0.344

APPENDIX 3

Garden City Observation Well 1

elapsed time	pH	Eh	DO	temperature	SC
					2640
0:00	7.01	222	2.3	14.2	2660
0:02	7.03	212	2.1	14.4	
0:04	7.04	204	2.1	14.9	
0:06	7.04	195	2.0	14.5	2660
0:08	7.05	187	2.0	14.5	
0:12	7.05	179	2.0	14.5	
0:14	7.06	173	2.0	14.6	
0:16	7.07	168	2.0	14.5	
0:18	7.07	163	2.0	14.6	2660
0:20	7.08	161	2.0	14.6	
0:22	7.08	158	1.9	14.5	
0:24	7.08	155	1.9	14.6	
0:26	7.09	153	1.9	14.6	
0:28	7.10	151	1.9	14.5	
0:30	7.10	150	1.9	14.5	
0:32	7.10	149	1.9	14.6	
0:34	7.10	147	1.9	14.6	
0:36	7.10	145	1.9	14.6	
0:38	7.11	144	1.9	14.6	
0:38	7.12	143	1.9	14.5*	
0:39	7.12	144	1.8	14.2	
0:40	7.12	146	1.7	13.4	
0:43					
0:48					2660

*Final temperature used for modeling was final flow value.

Garden City Observation Well 2

elapsed time	pH	Eh	DO	temperature	SC
				14.3	3480
					3450
					3450
0:00	6.91	228	2.94	12.9	
0:02	7.01	218	3.06	13.4	
0:04	7.02	208	3.06	13.4	
0:06	7.03	198	3.08	13.4	3440
0:08	7.03	189	3.08	13.4	
0:10	7.03	179	3.09	13.7	
0:12	7.04	173	3.08	13.6	
0:14	7.04	166	3.07	13.7	
0:16	7.04	161	3.08	13.6	
0:18	7.04	156	3.08	13.6	
0:20	7.04	152	3.09	13.6	
0:22	7.05	150	3.08	13.6	
0:24	7.05	148	3.07	13.7	
0:26	7.05	146	3.08	13.7	
0:28	7.05	144	3.08	13.5	
0:30	7.05	144	3.06	13.5	
0:30	7.06	143	3.15	13.5*	
0:31	7.06	143	2.90	13.3	
0:32	7.06	146	2.74	12.4	
0:32	7.07	146	2.72	12.0	
0:33	7.07	147	2.71	11.4	
0:36					
0:40					3440

Garden City Observation Well 3

elapsed time	pH	Eh	DO	temperature	SC
0:00	7.13	230	2.37	12.1	
0:01	7.15	224	2.37	12.0	
0:03	7.15	215	2.37	12.0	
0:05	7.16	205	2.36	12.0	
0:07	7.16	196	2.36	11.8	
0:09	7.16	181	2.37	12.0	
0:15	7.17	168	2.37	12.0	
0:20	7.17	157	2.37	12.1	
0:23	7.17	153	2.37	12.0	
0:25	7.17	151	2.37	12.1	
0:29	7.17	148	2.36	12.0	
0:31	7.18	146	2.37	11.9	
0:33	7.18	145	2.37	11.9	
0:35	7.18	144	2.37	11.9	
0:37	7.17	142	2.53	12.5	
0:39	7.17	139	2.56	12.6	3660
0:41	7.17	137	2.56	12.6	
0:43	7.17	134	2.58	12.5	
0:45	7.16	133	2.58	12.6	
0:47	7.16	131	2.60	12.6	
0:51	7.16	129	2.60	12.5	
0:53	7.16	128	2.60	12.5	3670
0:56	7.16	127	2.60	12.5*	
0:58	7.17	126	2.88	12.6	
0:58	7.18	127	2.47	12.4	
0:59	7.19	128	2.34	12.0	
0:59	7.19	130	2.28	11.6	
1:00	7.19	131	2.27	11.3	
1:00	7.19	132	2.25	11.1	
1:01	7.19	133	2.26	10.7	
1:09					3670
	7.1				

Garden City Observation Well 4

elapsed time	pH	Eh	DO	temperature	SC
0:00	7.13	230	1.60	12.2	3650
0:02	7.20	223	1.61	12.2	
0:04	7.21	220	1.62	12.1	
0:06	7.22	214	1.60	12.2	
0:08	7.22	210	1.62	12.1	
0:10	7.23	206	1.62	12.1	
0:12	7.22	199	2.03	13.1	
0:14	7.21	186	2.08	13.3	
0:16	7.21	177	2.12	13.3	3640
0:18	7.21	169	2.09	13.4	
0:20	7.20	160	2.12	13.3	
0:26	7.21	144	2.11	13.4	
0:28	7.21	141	2.13	13.3	
0:30	7.21	137	2.15	13.4	3640
0:35	7.22	131	2.15	13.4	
0:37	7.22	130	2.13	13.4	
0:38	7.22	129	2.15	13.4	
0:40	7.22	128	2.16	13.4	
0:42	7.23	127	2.15	13.4	
0:44	7.23	126	2.16	13.4*	
0:45	7.23	126	2.37	13.3	
0:45	7.24	128	1.69	13.1	
0:46	7.24	131	1.58	12.8	
0:46	7.24	132	1.54	12.5	
0:50					
0:55					3640
	7.09				

Garden City Observation Well 5

elapsed time	pH	Eh	DO	temperature	SC
0:00	7.05	230	2.25	11.4	3080
0:04	7.12	200	2.86	13.5	
0:07	7.12	185	2.86	13.5	
0:09	7.12	172	2.87	13.5	3140
0:11	7.12	158	2.86	13.5	
0:15	7.13	142	2.86	13.5	
0:17	7.13	136	2.81	13.4	
0:22	7.13	126	2.81	13.6	3160
0:24	7.13	125	2.84	13.5	
0:26	7.13	123	2.80	13.5	
0:28	7.13	121	2.80	13.5	
0:30	7.13	120	2.82	13.5	
0:32	7.14	119	2.79	13.6	
0:34	7.13	119	2.79	13.5	
0:37	7.14	118	2.80	13.5	
0:40	7.14	117	2.80	13.5	
0:41	7.16	117	3.03	13.5*	
0:41	7.16	117	2.35	13.4	
0:42	7.16	119	2.14	13.1	
0:42	7.16	122	2.07	12.7	
0:43	7.16	123	2.04	12.5	
0:47					
0:51					3180
	7.12				

APPENDIX 4

Dodge City Observation Well 1

elapsed time	pH	Eh	DO	temperature	SC
					436
				14.5	445
				14.5	446
0:00	7.4	159	3.69	14.2	
0:01	7.39	157	3.68	14.3	
0:02	7.39	159	3.83	14.4	
0:06	7.38	160	3.77	14.5	446
0:08	7.4	164	3.69	14.5	
0:10	7.41	168	3.71	14.5	
0:12	7.36	171	4.18	14.3	
0:14	7.36	174	4.24	14.4	
0:16	7.42	178	4.26	14.5	447
0:19	7.46	184	4.29	14.3	
0:24	7.45	189	4.29	14.4	
0:26	7.46	193	4.30	14.4	
0:28	7.48	195	4.31	14.4	
0:30	7.5	196	4.31	14.4	
0:32	7.51	199	4.30	14.5	
0:34	7.52	200	4.30	14.5	
0:36	7.53	201	4.31	14.5	
0:38	7.53	203	4.32	14.4	
0:40	7.53	204	4.31	14.5	
0:41	7.54	205	4.34	14.5*	
0:42	7.56	204	3.68	14.8	
0:43	7.56	204	3.33	15.4	
0:44	7.56	204	3.16	16	448
0:45	7.55	204	3.12	16.5	
0:57					
1:02					449
1:09					

*Final temperature used for modeling was final flow value.

Dodge City Observation Well 2

elapsed time	pH	Eh	DO	temperature	SC
					471
					469
0:00	7.35	192	3.57	14.7	
0:05	7.51	162	4.58	14.7	
0:07	7.52	156	4.6	14.7	
0:10	7.55	151	4.61	14.6	
0:12	7.53	149	4.62	14.6	
0:14	7.55	149	4.61	14.6	
0:16	7.58	149	4.6	14.7	
0:18	7.6	149	4.61	14.7	
0:20	7.61	150	4.61	14.7	
0:22	7.62	151	4.62	14.7	468
0:24	7.62	152	4.61	14.7	
0:25	7.62	152	4.62	14.7	
0:26	7.62	153	4.63	14.7	
0:28	7.62	153	4.62	14.7	
0:30	7.64	154	4.71	14.7*	
0:30	7.65	153	3.08	15.2	
0:31	7.65	153	2.95	15.3	
0:31	7.65	154	2.86	15.5	
0:32	7.65	154	2.76	15.8	
0:38					
0:43					467
0:44					

Dodge City Observation Well 3

elapsed time	pH	Eh	DO	temperature	SC
					436
0:00	7.67	206	4.16	14.4	
0:02	7.65	191	4.36	14.4	442
0:04	7.64	177	4.43	14.4	
0:06	7.64	169	4.38	14.5	
0:08	7.63	161	4.47	14.6	
0:10	7.63	156	4.49	14.6	443
0:12	7.63	153	4.54	14.6	
0:14	7.63	151	4.53	14.7	
0:16	7.62	149	4.58	14.8	
0:18	7.62	149	4.61	14.9	
0:20	7.62	148	4.59	14.9	
0:22	7.62	150	4.61	14.6	445
0:23	7.63	150	4.62	14.5	
0:24	7.63	151	4.63	14.4	
0:25	7.63	151	4.63	14.4	
0:27	7.63	152	4.63	14.4*	
0:29	7.62	150	5.11	14.5	446
0:30	7.64	149	3.75	14.6	
0:30	7.64	148	3.17	14.8	
0:31	7.65	147	3.06	14.9	
0:32	7.64	151	2.98	15.1	
0:33	7.64	154	2.95	15.3	
0:38					
0:42					446

Dodge City Observation Well 4

elapsed time	pH	Eh	DO	temperature	SC
					3090
0:00	7.46	215	1.14	14.9	3070
0:02	7.30	206	1.16	14.9	
0:04	7.26	197	1.17	15.0	
0:06	7.24	188	1.17	15.1	
0:08	7.25	183	1.18	15.2	
0:10	7.24	177	1.19	15.3	
0:12	7.24	170	1.19	15.4	
0:14	7.24	166	1.18	15.5	3050.0
0:16	7.24	162	1.19	15.5	
0:18	7.24	159	1.19	15.5	
0:20	7.24	155	1.20	15.4	
0:22	7.24	151	1.20	15.3	
0:24	7.24	151	1.20	15.2	
0:25	7.24	150	1.20	15.2	
0:26	7.24	148	1.20	15.2	3040
0:28	7.24	146	1.20	15.2	
0:30	7.24	144	1.20	15.0	
0:32	7.24	143	1.20	15.0	
0:34	7.24	141	1.21	15.0	
0:36	7.24	139	1.21	14.9	
0:38	7.24	138	1.21	14.9	
0:40	7.23	137	1.21	14.9	
0:42	7.23	135	1.21	15.1	
0:44	7.23	134	1.21	15.2	
0:45	7.23	133	1.22	15.2	
0:46	7.24	133	1.22	15.2	
0:47	7.24	132	1.62	15.2*	
0:47	7.24	134	0.99	15.3	
0:48	7.24	135	0.89	15.4	
0:48	7.24	135	0.86	15.5	
0:53					
0:57					3040
	7.06				