

THE OCCURRENCE OF CHROMIUM IN THE
CENTRAL OKLAHOMA AQUIFER AND
ITS RELATIONSHIP TO OTHER
MAJOR ELEMENTS

By

DINA MULIATI ELISABETH SULISTIO

Sarjana Strata 1

Bandung Institute of Technology

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Thesis Approved:

M. H. Hunsler

Thesis Adviser

Gary J. Stewart

Douglas C. Kent

Thomas C. Collins

Dean of the Graduate College

PREFACE

This thesis attempts to determine the areal distribution of the elevated chromium concentrations, the processes responsible for mobilization of chromium, and chromium relation to other major elements in the Central Oklahoma aquifer. Chromium is present in the ground water in areas with neutral to alkaline environment. This condition is enacting oxidation of the Cr^{3+} , which is normally found adsorbed, to Cr^{6+} , which is mobile and toxic.

Chemplot was used to portray the areal distribution of elevated chromium concentrations and other major elements involved in the study. Factor analysis was used to evaluate the ionic relationships of chromium and major elements in the aquifer, whereas Piper plot was used to look at water-type in the area of elevated chromium concentrations. Then, literatures on Eh-pH study of As, Cr, Fe, Mn, Se, U, and V enabled the writer to make a reasonable conclusions.

I wish to express my gratitude and appreciation to Dr. Arthur W. Hounslow, thesis adviser, for his guidance and assistance. I would like to thank Dr. Gary F. Stewart and Dr. Douglas C. Kent for serving as committee members. Appreciation is also expressed to Mr. Scott C. Christenson at Oklahoma Geological Survey for his help to sharing the data. Acknowledgement is also rendered to Mr. Wilmer, Rick, and Doug for helping me to prepare the transparencies and slides; and to Betsy Little, for helping me with typing and printing.

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two years. Finally, and most importantly, I would like to thank Sofian Sulistio and Rusianty for their patience and understanding. I dedicate this thesis to them whose love has nurtured my life.

*The earth is our workshop
we may not curse it,
we are bound to sanctify it.*

- Mazzini -

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CHAPTER I

INTRODUCTION

Many of the elements in the periodic system affect mankind in three ways, and therefore can be discussed from three perspectives. First, they can serve as important raw materials to meet the technological need for societies; thus, they contribute to the living standard of populations and to the quality of life. Second, elements can present problems of toxicity to human beings and to other forms of life on which people depend for food. Such toxicity may result from man's own activities or from natural processes in the environment. Third, they may be essential for various forms of life, including human beings. Chromium is one of the few elements in the periodic system for which these three aspects are important and for which an adequate data base is available.

Toxic effects due to human contact with chromium compounds were known from about 1798. Results from animal experiments with chromium compounds were published by Gmelin as early as 1824. The first paper published in 1932, connected exposure to chromium compounds with development of lung cancer. Most of the literature on the toxic and carcinogenic effects of chromium compounds were published after 1932. The next major development in the growing knowledge of the effects of chromium compounds was in 1959. It was documented that certain organic chromium-containing compounds are essential to human beings (Langard, 1982).

During the past few years anomalous large amounts of chromium (total, dissolved, and dissolved Cr^{6+}) were observed in the water from some wells in

the western part of the Central Oklahoma aquifer. These amounts exceeded the EPA's mandatory upper limit of 0.05 mg/l. This occurrence said to be of natural origin (Oklahoma Geological Survey, 1992). It was unique, since chromium - especially Cr(VI) - in ground water has usually been associated with a pollution-type source (Hem, 1989).

Purpose and Scope of Study

The purpose of this study was (1) to determine the areal distribution of the elevated chromium concentrations (total, dissolved, and dissolved Cr⁶⁺), and (2) to evaluate the processes responsible for mobilization of this potentially toxic, naturally (?) occurring trace substance. Figure 1 shows the diagram of the whole problem, purpose and scope of study.

Objective (1) was pursued by retrieving all chromium data from Oklahoma Geological Survey's data base and by plotting the elevated chromium concentrations onto a map (Figure 12, p. 72). Chemplot v. 1.31 (Hounslow, 1991) was used to look at areal distribution of chromium and other major elements - as histograms on each wells - on rotated plane. The data were also analyzed by factor analysis to evaluate the ionic relationships between chromium and other major elements, and the relationships between chromium and other parameters within the aquifer. WATEVAL (Hounslow, 1990) was used to identify the water type of Central Oklahoma aquifer. Then, the results were plotted onto Piper diagram.

Additional depth information was secured from chemical and X-ray analyses of solid samples from nine test holes located in the study unit (Breit et al., 1990). One of the holes was located in an area of generally good water quality (NOTS 4); the remaining eight were located in areas known to have

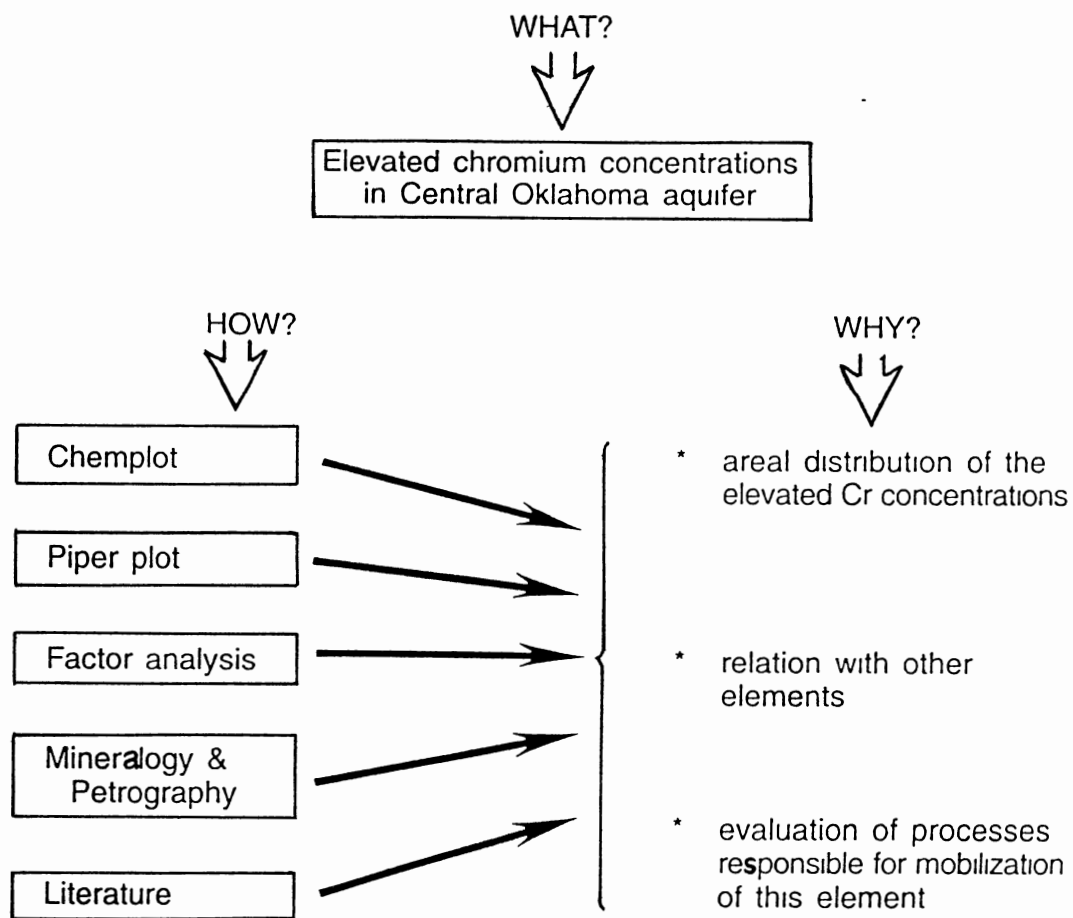


Figure 1. Problem, Purpose, and Scope of Study

large concentrations of one or more of the potentially toxic metals (Figure 3). All analytical and X-ray work was done by Oklahoma Geological Survey. Several literature studies on continental red beds, Permian red beds in Oklahoma, and chromium were also done. To evaluate the processes responsible for mobilization of chromium, the redox behavior of chromium was integrated with the results from Piper plot, Chemplot, factor analysis, mineralogy, and petrography study of rocks in the study unit.

Physical Setting

The Central Oklahoma aquifer underlies about 3,000 square miles of central Oklahoma, including most of the Oklahoma City metropolitan area (Christenson et al., 1987). The aquifer underlies all or parts of Canadian, Cleveland, Kingfisher, Logan, Lincoln, McClain, Oklahoma, Payne, Pottawatomie, and Seminole Counties (Figure 2). The study unit is bordered by T19N, T6N, R4W, and R6E. The aquifer is within the Osage Plains section of the Central Lowland Physiographic Province of the Interior Plains division of the United States (Fenneman, 1946).

The eastern part of the study unit is characterized by low hills, generally covered by blackjack and post oaks, with relief of 30 to 200 feet. The western part of the study unit is characterized by gently rolling grass-covered plain with relief of less than 100 feet (Christenson et al., 1987). Elevations within the study unit generally are higher in the west than in the east. The highest elevations are about 1,400 feet above sea level in the western part of the study unit, along the drainage divide between the Canadian and North Canadian Rivers. The lowest elevations are about 800 feet above sea level, along the Cimarron River.

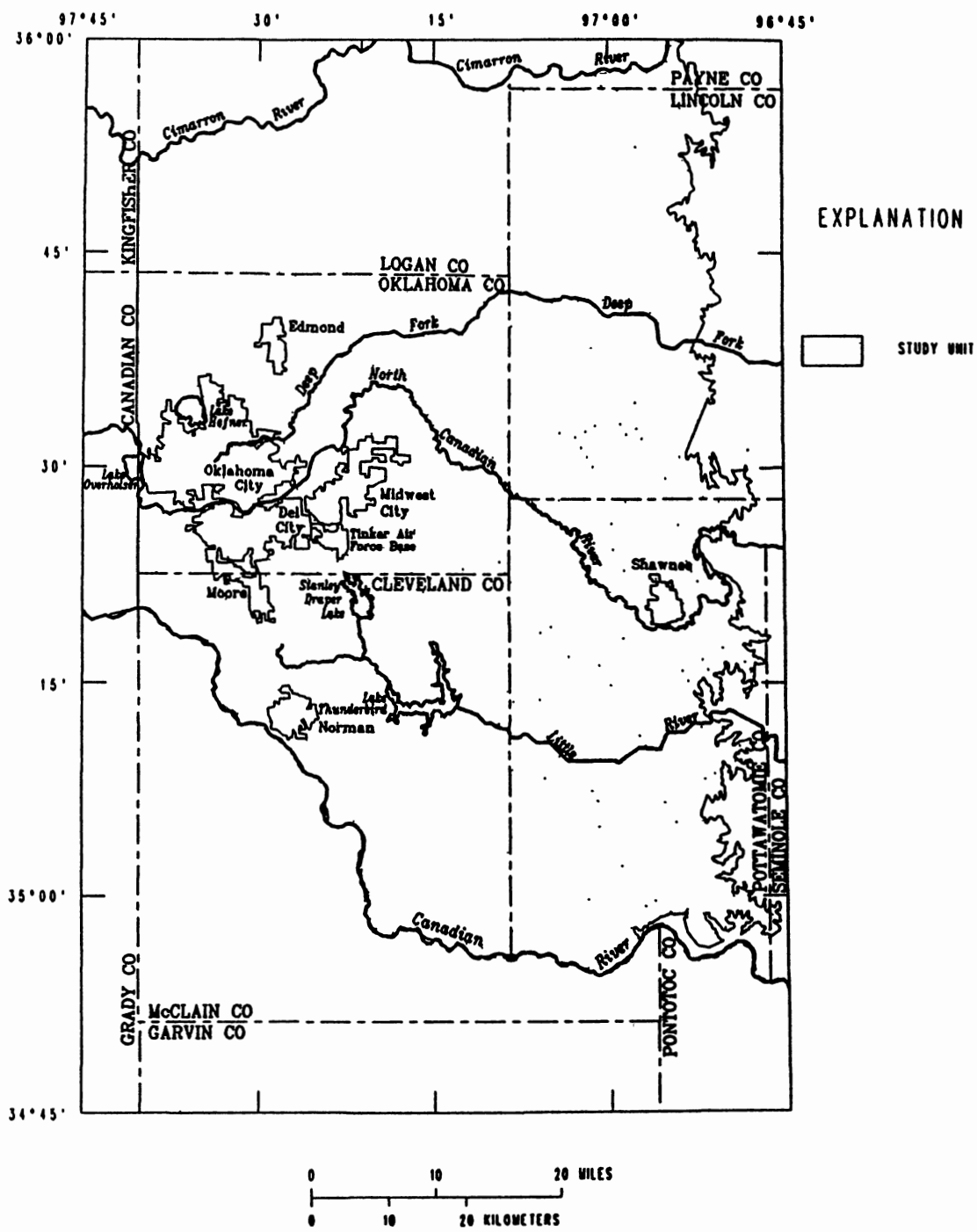


Figure 2. Geographic Features of Study Unit (Christenson et al., 1987)

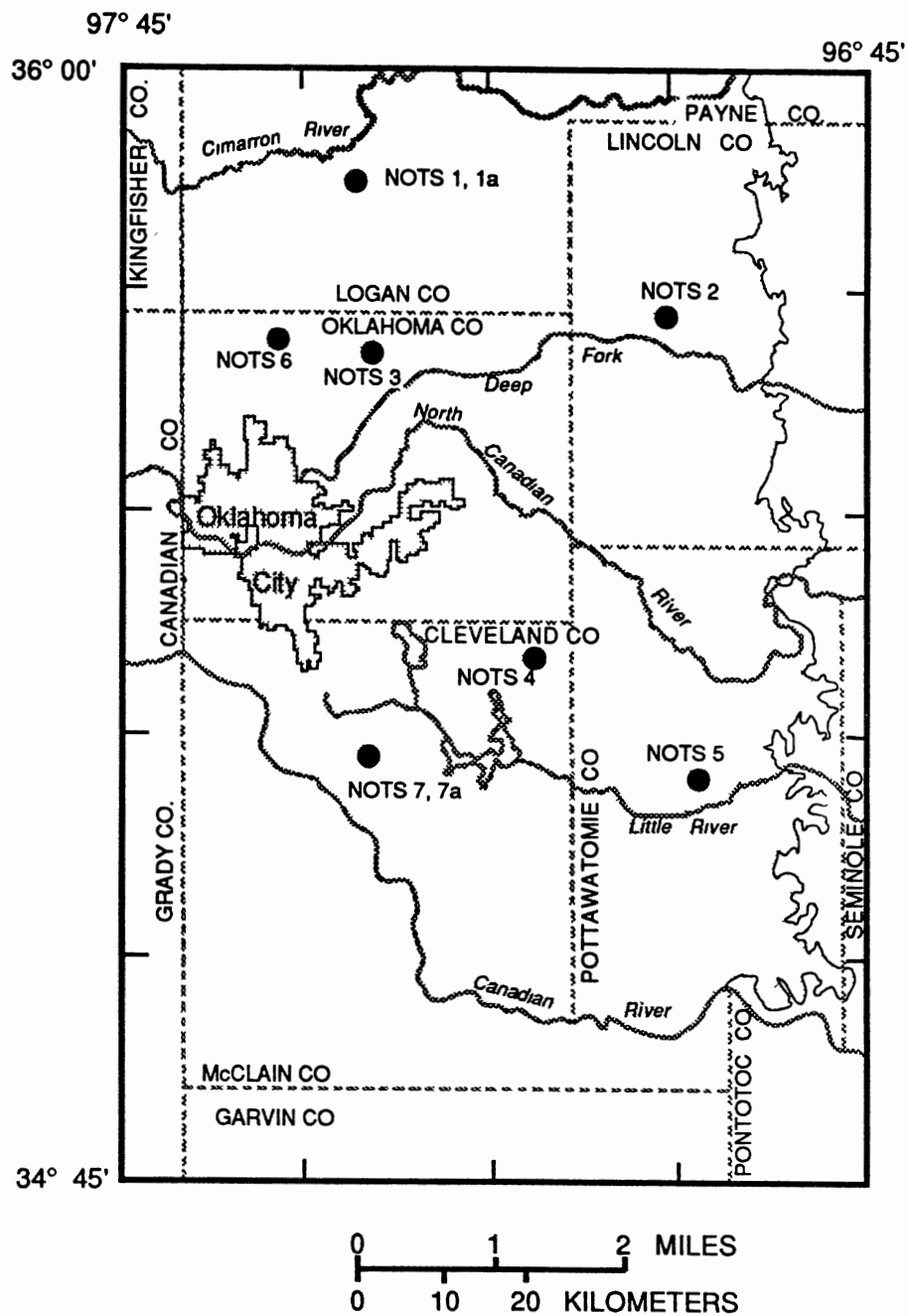


Figure 3. Location of the Study Unit Containing the Central Oklahoma Aquifer and Test Wells Sampled for Mineralogy and Petrography Study (Breit et al., 1990)

The major streams in the study unit are the Cimarron River, the Deep Fork River, the North Canadian River, the Little River, and the Canadian River (Figure 2). These streams, which flow from west to east across the study unit, have formed broad, flat alluvial valleys. The Little River is a tributary to the Canadian River and the Deep Fork River is a tributary to the North Canadian River. The headwaters of the Little River and the Deep Fork River are within the study unit. The Cimarron River is the northern boundary of the study unit. The Canadian River is its southern boundary.

Climate

The average annual temperature in the study unit is about 16°C. The average annual precipitation is approximately 30 inches, most of which falls from April through October. Precipitation decreases from east to west. It ranges from 30 inches in western Logan County to 38 inches in southeastern Pottawatomie County. Estimated 2.5% to 10% of the total precipitation recharges the Central Oklahoma aquifer (Pettyjohn et al., 1982). Average annual snowfall ranges from 6 to 10 inches (Pettyjohn et al., 1982). Average annual evapotranspiration ranges from 28 to 32 inches from west to east across the study unit.

Previous Investigations

The physiography, geology, and hydrogeology of the study unit are well documented in the literature.

Geology

The first study of geology and water resources of Oklahoma was that of Charles N. Gould (1905). Later, a voluminous amount of literature accumulated on the regional geology of Oklahoma and on the local geology of all counties in Oklahoma. Muehlberger (1967) stated that basement rocks in central Oklahoma are Spavinaw Granite and Central Oklahoma granite group. These intrusive units were uplifted relative to the other rock units some time prior to Cambrian sedimentation. In central Oklahoma, basement wells penetrate Central Oklahoma granite group. This group is characterized by both microcline and oligoclase (plagioclase).

Gould (1926), Bale (1928), Merritt and Minton (1930), Travis (1930), Patterson (1933), Green (1936) Anderson (1941), and Ham and Merritt (1944), described Permian sediments in central and west-central Oklahoma. The Permian rocks in central Oklahoma consist of red beds and non-red sediments. The red beds are composed chiefly of red clay shales with interbedded sandstones, gypsum, dolomites, and beds of rock salt. The non-red sediments consist chiefly of limestones and shales.

They concluded that: (1) the Wellington Formation and Garber Sandstone cannot be separated south of northern Oklahoma County; (2) in Cleveland County the Garber-Wellington section is the thickest and is 90% sandstone, southward it grades rapidly to a predominance of shale in northern Garvin County; (3) the Wellington Formation is defined as the alternating beds of red shales and red sandstones; (4) the Garber Sandstone is described as a series of red clay shales, red sandy shales, and red sandstones; (5) the Hennessey Shale boundaries are the transgression (stratigraphic) boundaries and are described as the distinctive blocky red clay shales; (6) barite rosettes occur at

many horizons, but are well developed in the upper part of the Garber-Wellington section in Cleveland County; (7) carbonates occur erratically throughout Garber-Wellington and are likely to be found in conglomeratic zones where the pebbles consist chiefly of dolomite.

Tasch (1964), Olson (1967), Simpson (1979), and Shelton (1979) concluded that Garber-Wellington sediments were deposited under deltaic conditions, and the basinward sediments indicate a transition from evaporitic to brackish to fresh water environments. The environment of the deposition was a broad delta on which was deposited both marine and nonmarine sediments. The marine phases were represented by dolomitic-clay intraformational conglomerates and dolomitic sandstones.

MacLachlan (1967) made an effort to investigate the paleotectonic of the Permian System in Oklahoma. Permian rocks record environmental changes from normal marine (interval A), to restricted marine (interval B), to marine mudflat (interval C-D) conditions. Rocks of Permian age are exposed across much of central and western Oklahoma. Recent alluvium covers the Permian rocks along major stream courses. In northern Oklahoma the lowest part of the Permian is divided into the Admire, Council Grove, and Chase Groups. Several of the limestone units are distinguishable in the subsurface of northern Oklahoma, but farther south group names are more applicable because of the increased thickness of rocks and the presence of detrital materials.

The contact of the Heringtone Limestone with the overlying Wellington Formation is designated as the upper boundary of interval A. In western Oklahoma this contact represents a transition from normal marine limestone below to dolomite, anhydrite, and mudstone of the Wellington Formation above. The contact is also transitional in central Oklahoma. Limestone beds of interval A contain progressively more sand southward from the Kansas border toward

source areas in the Wichita and Arbuckle Mountains. Interval A is composed of fine-grained sandstone, mudstone, and limestone. The area by central Oklahoma contains the coarsest material because arkosic sediment derived from the mountains was spread northward.

Formations between northern Oklahoma and the Wichita Mountains assigned to interval B. Fine-grained detrital rock dominates interval B, except in parts of northern Oklahoma where it is interbedded with evaporites. Elsewhere in Oklahoma evaporites form less than 20% of the interval.

East of the Anadarko Basin and south of the Wichita Mountains the sequence, consecutively from oldest to youngest, consists of the Wellington Formation, Garber Sandstone, Hennessey Shale, and El Reno Group. The base of Wellington Formation is divided into two parts. The lower part is a thick evaporite sequence, mostly anhydrite but including some salts; the upper part is red mudstone containing small amounts of evaporite. The Garber Sandstone is a coarse-grained red sandstone and sandy mudstone. The sandstone coarsens eastward. The Hennessey Shale consists of red mudstone, with tongues and lenses of sandstone, and a few beds of gypsum. The Hennessey was probably formed as a nearshore deposits.

During the time of interval B, thick gypsum beds and interbedded mudstone had accumulated. Widespread thick anhydrite deposits and associated red beds of the Wellington Formation make up the basal part of interval B in the Anadarko Basin. Eastward, red beds containing small amounts of sandstone are predominant in interval B, whereas normal marine limestone characterizes interval A in the same areas. During deposition the change in sediment type was gradual. As a result, brown dolomite now separates normal marine limestone of interval A from the lower part of the Wellington Formation

(evaporite rock). Circulation of water within the basin apparently becomes more restricted than before, and the water shallower.

Interval C-D in Oklahoma has been eroded to such an extent that the history of tectonic activity during its deposition can only be inferred in a very general way. The interval is thickest just north of the Wichita Mountains and thins progressively northward and eastward. A gradual westward migration of the shoreline is postulated because Permian rocks record a change in the dominant lithologies of each interval. In western Oklahoma a normal marine basin which received carbonate deposits during the time of interval A later became an evaporitic basin. Interval C-D includes the youngest Permian strata in Oklahoma. It was deposited in the most restricted basic. This interval comprises evaporite rock, sandstone, and mudstone.

Hydrogeology

Gould (1905) gives a brief description of the water usage within the Permian red beds, over its outcrop area, in Oklahoma. The parameters used were depth to water and supply capabilities of scattered wells. Bingham and Moore (1975) published a hydrologic map of Oklahoma City Quadrangle. Wood and Burton (1968), Carr and Marcher (1977), and Wickersham (1979) studied and published papers about the hydrogeology of the Central Oklahoma aquifer for Cleveland and Oklahoma Counties, for southern Logan and northern Oklahoma Counties, and for southern Cleveland, southern Oklahoma, and parts of Pottawatomie Counties, respectively. The parameters used were total saturated thickness, transmissivity, storage coefficient, and yield. Total fresh water stored in the Central Oklahoma aquifer was estimated by Wickersham

(1979) as 50 million acre-feet based on a specific yield of 0.20. Average recharge was estimated as 5%-10% of total precipitation.

Geochemistry

In terms of major-ion chemistry, water within the Central Oklahoma aquifer generally is suitable for use as public water supplies. The concentrations of chloride, sulfate, and dissolve solids (Carr and Marcher, 1977; Bingham and Moore, 1975) generally are less than the recommended concentrations of the US EPA's (1982) secondary standards. Water in the Hennessey Group generally has large concentrations of sulfate and dissolved solids that make the water unsuitable for most uses (Carr and Marcher, 1977; Bingham and Moore, 1975).

The availability of potable water is controlled by the depth to the fresh water-salt water interface. Dissolved solids content of the Central Oklahoma aquifer was generally less than 500 mg/l and seldom exceeded 1,000 mg/l, except in areas where oil field activities contaminated the aquifer (Carr and Marcher, 1977; Bingham and Moore, 1975). Wickersham (1979) found that the water quality varies with depth, and the best water quality was found at depths of 500-800 feet.

Bloch, Gay, and Dunbar (1981) found that concentrations of selenium, chromium, and uranium have been contaminating municipal wells. Christenson and Parkhurst (1987) stated that those potentially toxic elements have occurred naturally in geologic formations within the study unit. Breit, Rice, Esposito, and Schlottman (1990) published "Mineralogy and Petrography of Permian Rocks in the Central Oklahoma Aquifer" and proposed that the large concentrations of

arsenic, chromium, selenium, uranium, and large gross-alpha-particle activities were the result of rock-water interaction within the aquifer.

CHAPTER II

DESCRIPTION OF THE CENTRAL OKLAHOMA AQUIFER

Water Use

The predominant water use in the Central Oklahoma aquifer is for public supplies. The quantity of ground water withdrawn from the Central Oklahoma aquifer approximately doubled during 1970 and 1985. Water use for public supplies tripled from about 10,000 acre-feet in 1970 to about 30,000 acre-feet in 1985, while uses other than public stayed approximately the same (Parkhurst et al., 1989).

In 1985, water use from the Central Oklahoma aquifer was reported to be 40,000 acre-feet, of which 73% was used for public supplies. All the major communities in central Oklahoma, except Oklahoma City, depend either entirely on ground water from the Central Oklahoma aquifer or on a mixture of ground water and surface-water supplies. The other water uses are for industrial (15%), commercial (5%), irrigation (5%), and all other combined uses (<2%).

Hydrogeology

The Central Oklahoma aquifer consists of those geologic formations that yield substantial volumes of water to wells. The ground water comes from the extensive, continuous flow system centered around Oklahoma, Cleveland, and Logan Counties in central Oklahoma. Most of the circulation in this flow system

is in the Garber Sandstone and Wellington Formation. Substantial circulation also occurs in the Chase, Council Grove, and Admire Groups and the alluvium and terrace deposits along major streams in the study unit (Figure 4). The circulation of ground water is mainly in the Garber Sandstone and the Wellington Formation; thus, the Central Oklahoma aquifer commonly has been called the "Garber-Wellington aquifer". This terminology has problems associated with it: (1) the Garber Sandstone and the Wellington Formation are not everywhere an aquifer, because of a decrease in transmissivity; and (2) the water in the Chase, Council Grove, Admire Groups, and the overlying alluvium and terrace deposits are part of the same flow system. However, for purposes of this thesis, the term "Central Oklahoma aquifer" is used.

The Central Oklahoma aquifer (Figure 2, p. 5) extends from the Canadian River on the south to the Cimarron River on the north. It also extends from the Oklahoma-Canadian and Logan-Kingfisher County lines on the west to the contact of the Pennsylvanian Vanoss Formation with the Permian Chase, Council Grove, and Admire Groups on the east. The limit of freshwater circulation coincides approximately with the Oklahoma-Canadian and Logan-Kingfisher County lines. The depth of the aquifer is variable and defined by the base of fresh water (<5,000 mg/l total dissolved solids), which ranges between 100 and 1000 feet below the land surface (Parkhurst et al., 1989).

The aquifer underlies all of Cleveland and Oklahoma Counties and parts of Lincoln, Logan, Payne, and Pottawatomie Counties (Figure 2, p. 5). Stratigraphic units that comprise the Central Oklahoma aquifer include Quaternary alluvial and terrace deposits and Permian sedimentary rocks. Permian sedimentary rocks include the Garber Sandstone, the Wellington Formation, and the Chase, Council Grove, and Admire Groups (Table I). Most

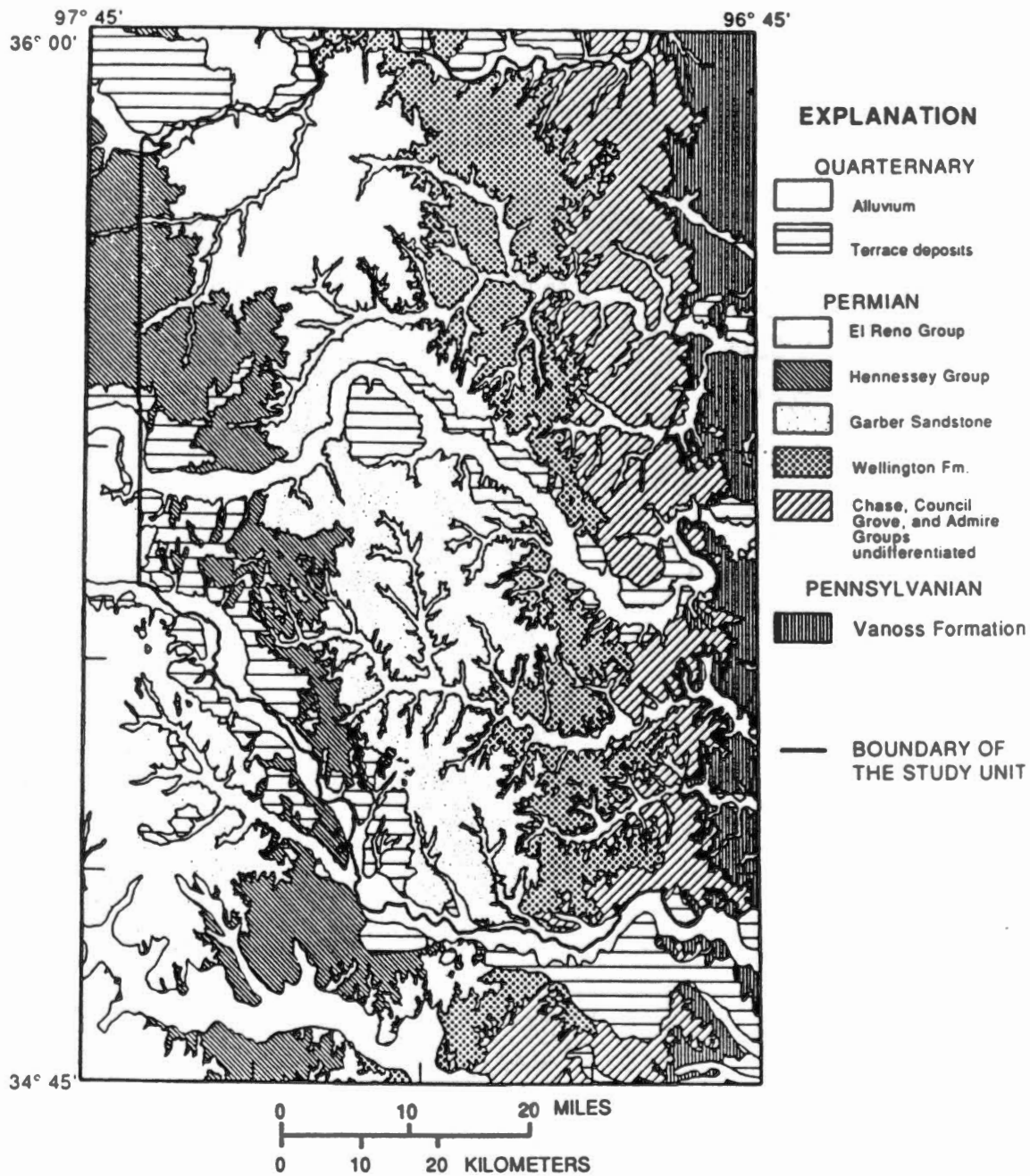


Figure 4. Geologic Map of Central Oklahoma (Parkhurst et al., 1989)

water within the aquifer is produced from the Garber Sandstone and the Wellington Formation. Substantial amounts of water are also contained in the Permian Chase, Council Grove and Admire Groups, which underlie the Wellington Formation. Outside the study unit, the permeability of these Permian rocks decreases. The Permian rocks in the aquifer are overlain by the Permian Hennessey Group as a confining layer.

TABLE I
THE STRATIGRAPHIC UNITS OF THE
CENTRAL OKLAHOMA AQUIFER

Erathem	System	Series	Geologic Unit
Cenozoic	Quaternary	Holocene	Alluvium
		Pleistocene	Terrace deposits
Paleozoic	Permian	Lower	El Reno Group
			Hennessey Group
			Garber Sandstone and Wellington Formation (undivided)
			Chase, Council Grove, and Admire Groups (undivided)
	Pennsylvanian	Upper	Vanoss Formation

Alluvium

Alluvium associated with the streams is the youngest geologic deposit in the study unit. Sediment is constantly being eroded, transported, and deposited by streams. Alluvium is present along most of the perennial streams in the study unit, but the most extensive deposits are present along the North Canadian and Canadian Rivers. Here the alluvium is as much as 3 miles wide along these rivers. The alluvium consists of lenticular beds of clay, silt, sand, and gravel. The thickness of the alluvium ranges from 0 to about 100 feet. The thickest deposits usually contain beds of gravel, and wells completed in them may produce as much as 700 gpm (Bingham and Moore, 1975).

Terrace Deposits

The terrace deposits associated with streams in the study unit are Pleistocene alluvial deposits. Erosion has deepened the stream valleys, leaving the terrace deposits above the present flood plains. Terrace deposits along the Cimarron, North Canadian, and Canadian Rivers may be as much as 8 miles wide. The terrace deposits consist of lenticular beds of clay, silt, sand, and gravel. The thickness of the terrace deposits in the study unit ranges from 0 to 100 feet and wells completed in the most productive deposits may yield up to 300 gpm (Bingham and Moore, 1975).

El Reno Group

Rocks of the El Reno Group of Permian age crop out in the western part of the study area. Rocks in the El Reno Group are not considered in this thesis because they are separated from the Central Oklahoma aquifer by low permeability rocks in the Hennessey Group (Christenson et al., 1987).

Hennessey Group

The Hennessey Group (undifferentiated in this thesis) of Permian age consists of reddish-brown shale and siltstone with a few thin beds of very fine-grained sandstone. The Hennessey Group has little transmissivity, because it is composed mainly of shale and siltstone. Thus, it is not considered to be part of the Central Oklahoma aquifer. The Hennessey Group overlies the aquifer in the western one-third of the study unit, but has been removed by erosion in the eastern two-thirds. The Hennessey Group forms a confining unit where it overlies the Central Oklahoma aquifer. Though it has little transmissivity, a few small-yield wells, such as domestic and stock wells, are completed in the Hennessey Group (Christenson et al., 1987).

Garber Sandstone and Wellington Formation

In central Oklahoma, it is difficult to distinguish between the Garber Sandstone and the Wellington Formation of Permian age. Although it is possible to map the contact between the two geologic units on the land surface (Bingham and Moore, 1975), it is virtually impossible to detect the contact in the subsurface (Carr and Marcher, 1977). Thus, the two geologic units are not differentiated in this thesis.

According to Dott (1941), the Wellington Formation consists of an alternating, intergrading and interfingering succession of red shales and red, cross-bedded sandstone. The top of the Pennsylvanian Heringtone Limestone is its lower boundary. The lowest sandstone of the Garber Sandstone is its upper boundary. The estimated thickness of Wellington Formation is 500 feet in Logan and Oklahoma Counties, and 400 feet in Cleveland County. Patterson (1933) described its sand as fine-grained, friable, micaceous, and cross-

bedded. Dolomitic conglomerates often mark the base of the formation and occur throughout at shale-sandstone transition zones.

According to Aurin et al. (1926), the Garber Sandstone consists of interstratified series of red clay shales, red sandy shales, and massive, cross-bedded red sandstone. The Hennessey Shale is its upper boundary. The lower Garber Sandstone consists primarily of red fissile clay shales interstratified with thin seams of red sandstone. The upper of Garber Sandstone is composed of heavy ledges of massive red sandstone. The sandstone is lenticular, generally cross-bedded and not uncommonly conglomeratic, interstratified with beds of fissile shale and sandy shale. Its combined thickness is about 600 feet. Barite rosettes are the common features throughout the Garber Sandstone, but are abundant at the base and top of it.

The Garber and Wellington sequence generally is thought to have been deposited in a deltaic environment (Carr and Marcher, 1977). It consists of lenticular beds of fine-grained, cross-bedded sandstone interbedded with siltstone and shale. The sand grains are predominantly quartz, and they are friable. The geologic units dip to the west into the Anadarko Basin in western Oklahoma about 50 feet per mile.

In southeastern Oklahoma County, about 75% of the total thickness of the sequence is sandstone. In all directions from southeastern Oklahoma County, the percentage of sandstone decreases and the percentage of siltstone and shale increases. For example, in southern Cleveland County, only 25% of the total thickness is sandstone (Wood and Burton, 1968). The thickness of the Garber Sandstone and Wellington Formation is approximately 1,165-1,600 feet, with medium value of 1,510 feet (Parkhurst et al., 1989).

Shallow wells may be completed in either the Garber Sandstone or Wellington Formation, but wells with the largest yields from the Central

Oklahoma aquifer are completed in both geologic units. A few wells completed in both units will yield as much as 600 gpm. Maximum well yields generally range from 200 to 400 gpm because of the fine-grained nature of the sandstone in both geologic units.

Chase, Council Grove, and Admire Groups

The Chase, Council Grove, and Admire Groups (undifferentiated in this thesis) of Permian age consist of beds of fine-grained, cross-bedded sandstone, shale, and thin limestone. In surface exposures, these groups appear to be virtually identical to the overlying Garber Sandstone and Wellington Formation. The combined thickness of these groups ranges from 570 to 940 feet with a median of 745 feet (Parkhurst et al., 1989).

In the eastern part of the study unit, wells are completed in the Wellington Formation and in one or more of the underlying Chase, Council Grove, and Admire Groups. East of the outcrop of the Wellington Formation, wells completed only in the Chase, Council Grove, and Admire Groups generally yield 10 to 100 gpm, with a few wells yielding as much as 120 gpm.

Bingham and Moore (1975) referred to this stratigraphic sequence of the Chase, Council Grove, and Admire Groups as the "Oscar Group", and assigned it to the Pennsylvanian System. In a recently published correlation chart, Lindberg (1987) refers to Bingham's and Moore's Oscar Group as the Chase, Council Grove, and Admire Groups. This terminology follows the usage of the U.S. Geological Survey and is used in this thesis.

Vanoss Formation

The Vanoss Formation of Pennsylvanian age underlies the Chase, Council Grove, and Admire Groups. The Vanoss Formation consists mainly of shale and a few thin, fine-grained sandstone beds. The Vanoss generally does not yield substantial volumes of water to wells and is not considered part of the Central Oklahoma aquifer (Christenson et al., 1987).

Hydrologic Properties

The size, shape, and sorting of the sand grains, and the type and amount of cement contained in the sandstone beds determine the hydraulic characteristics of the beds. Jacobsen and Reed (1944) found the average size of sand grains in Garber Sandstone and Wellington Formation to be 0.006 inches - fine sand -. The average shape of the sand grains is angular to subangular. The aquifer sands are also well sorted with an average value of sorting coefficient of 1.26 (Carr and Marcher, 1977).

The aquifer test data from the southeastern part of the study unit in Oklahoma and Cleveland counties are used to determine transmissivities and storage coefficients. Wood and Burton (1968) found that transmissivity ranges from 300 to 7,000 gallons per day per foot (gpd/ft), with an average of 5,000 gpd/ft. Wickersham (1979) calculated average transmissivity to be 3,300 gpd/ft. A storage coefficient for the confined portion of the aquifer was determined by Wood and Burton (1968) to be 2.0×10^{-4} . Wickersham (1979) obtained an average specific yield of 0.20 for the unconfined sediments. Specific capacities of wells in the Central Oklahoma aquifer range from 0.6 (Wood and Burton, 1968) to 2.3 (Wickersham, 1979) gallons per minute per foot (gpm/ft) of drawdown. Variability in specific capacity is commonly a reflection of well

design and construction, thus, is not a reliable indicator of the productivity of the aquifer.

Mineralogy and Petrography

To evaluate the processes responsible for accelerating chromium release into the Central Oklahoma aquifer, the mineralogy and petrography of the rocks were examined by Oklahoma Geological Survey (U.S.G.S. Open File Report 90-678), from which the following summary was compiled. If it is assumed that the changes in composition of ground water within the aquifer are the result of rock-water interaction, then a characterization of solid constituents of the aquifer is also important.

As much as 60% of the solid constituents of the aquifer are clay- and fine silt-sized particles. Quartz and illite are the dominant minerals in all 9 cores (Figure 3, p. 6). Gypsum was not detected in any sample, but calcite and dolomite are irregularly distributed throughout the cores. Major constituents of the clay-size fractions are illite, kaolinite, chlorite, chlorite-smectite, illite-smectite, smectite, and vermiculite. The assemblage of clay minerals is similar in all test holes and apparently independent of stratigraphic unit.

The sandstones are mainly quartz arenites to sublitharenites with a significant amount of matrix; they are very fine to medium grained and well to poorly sorted. The relatively few medium-grained sandstones are well rounded, whereas most of the finer grained materials are subangular to angular. The sandstones in the aquifer have as much as 36% void space. White and gray-green sandstones occur in distinct reducing zones, most often as layers between darker colored sandstones and shales. Pore-filling matrix is a variable

mixture of silt-sized quartz and clay minerals with the dominant constituent of the matrix composed of illitic clays.

Only two cores (NOTS 6 and NOTS 7) were examined in details because they are within the area of elevated chromium concentrations (Table II). The Hennessey Group core (NOTS 7) has the highest content of plagioclase and contains chlorite that is consistently detectable over the length of that core. It also contains a higher percentage of illite than the core from the Garber-Wellington sequence (NOTS 6). A regularly intrastratified illite-smectite and sparse occurrence of kaolinite are found in NOTS 7. Biotite is least abundant in NOTS 6 and 7. Only samples from NOTS 6 contain detectable calcite and dolomite is most abundant in NOTS 7. Barite was found in only two samples in NOTS 6.

TABLE II
LOCATION AND DESCRIPTION OF TEST HOLES
USED FOR THIS STUDY (U.S.G.S. OPEN FILE
REPORT 90-678)

Test Hole	Local Identifier	Station Number	Total Depth (ft)	Geologic Unit
6	14N-03W-07DAA2	354208 973302	587	Garber Sandstone
7	09N-02W-29DCA5	351315 972543	456	Hennessey

Several samples were examined to identify As, Cr, Se, U, and V. These samples were selected because of the large concentrations of these metals detected by chemical analyses of the whole-rock samples and by observations of thin sections and core materials (Breit et al., 1990). Many of the samples that have high trace metals can be characterized as reduction zones. Preliminary results of these examinations are presented in Table III.

Detrital Minerals

Fragments of vein quartz and quartz with inclusions of biotite, chlorite, or tourmaline are common in samples from all test cores. Quartz grains are cemented by hematite, manganese oxides, and dolomite (the most abundant cement). Polycrystalline quartz grains are abundant in some sandstones. Sericitized and partly dissolved plagioclase were identified but the plagioclase species could not be estimated. Orthoclase and microcline are constituents of sandstones from all cores. Most grains of potassium feldspar have been partly or extensively dissolved.

Chert, metamorphic rocks, shale rock fragments and dolostone intraclasts were observed in samples from all cores. Chert is present as well-rounded grains. Some of which have been extensively dissolved. Schist fragments consist mainly of muscovite and quartz. In most sandstones, the shale fragments are green and are rimmed by dark iron-oxide coatings. Nodules and detrital clasts of dolomite were detected in all cores. The micritic dolostone nodules were found mainly within mudstones. Although the majority of the nodules are micritic, some are rimmed, veined, or cored with sparry dolomite.

TABLE III
 PRELIMINARY IDENTIFICATION OF RESIDENCES
 OF As, Cr, Se, U, AND V IN PERMIAN ROCKS OF
 THE CENTRAL OKLAHOMA AQUIFER

Test Hole	Depth (ft)	Phase
1a	65.4	<i>Arsenic</i>
1	82.4	brown iron oxides, goethite?
		brown iron oxides, and pyrite
1	82.4	<i>Chromium</i>
2	131.1	brown iron oxides
Hennessey	outcrop	detrital chromite
		smectite?
2	131.1	<i>Selenium</i>
6	404.3	unidentified Cu-Se-S phase
6	502.3	clausthalite (Pb-Se)
		native selenium
2	131.1	<i>Uranium</i>
6	502.3	unidentified U-Ti phase
6	502.3	tyuyamunite?
7	152.1	uranium-silica spheres
		tyuyamunite (Ca(UO ₂) ₂ -(VO ₄) ₂ •7-10H ₂ O)
2	86.4	<i>Vanadium</i>
2	211.1	haggite (V ₂ O ₃ (OH) ₃)
5	120.5	haggite and volborthite (Cu ₃ (VO ₄) ₂ •3H ₂ O)
6	404.6	haggite
6	502.3	tyuyamunite?
6	502.3	vanadium oxides
7	152.1	vanadium oxides

From: USGS Open File Report 90-678.

The heavy minerals recovered from the cores included tourmaline, zircon, epidote, martite, titanium oxide, and a rare phosphate mineral. Other unidentified heavy minerals were also found and detected in thin laminae within sandstones from all test cores. Detrital iron-titanium oxide grains are rare in green sandstones where grains of relict titanium oxides are common.

Both muscovite and biotite are minor to trace constituents of samples from most of the cores. Muscovite is ubiquitously distributed. Most muscovite grains have silt or smaller sizes, though some are as large as medium sand. The biotite in sandstones is typically rimmed by a thick coating of iron oxide. A few grains of green biotite were detected as inclusions in quartz grains.

Authigenic Constituents

Barite occurs as elongate, clear prisms within voids that lack other authigenic minerals. Locally the aquifer is cemented by barite rosettes. Tiny kaolinite and hematite grains are present as inclusions within the calcite cement. Contacts between calcite and dolomite are abrupt and irregular. A significant percentage of the Permian sandstones examined are cemented by dolomite. Usually, micritic dolomite is outlined by iron oxides. Most of dolomite cement is sparry. Sparry dolomite locally cements sandstones and is dispersed in clay-rich matrix layers, particularly near dolomite conglomerates. It commonly contains inclusions of hematite and a few percent of manganese.

Areas of sample that contain abundant goethite lack carbonate cements and are very friable. Usually goethite forms relatively thin coatings on other grains. Some examinations revealed that aggregates of goethite are cored by hematite. Hematite is a common constituent of most of the rocks examined and

is responsible for the red and purple colors. Dendrites of manganese oxide were visible in green sandstone and mudstone intervals in most cores.

The presence of hematite and goethite is lithologically controlled. It is predominant in ironstone layers and nodules and in the red-colored shales. Analysis of a sample of red shale from the Wellington Formation indicated appreciable quantities of Cr, Ni, Sr, and Zn (McBride, 1985). She also mentioned that analysis of a red shaly conglomerate containing dolomite, quartz, hematite and goethite exhibited elevated levels of As, Mn, and U, and enrichment in Pb and Zn. In a gray shaly conglomerate, Ba, Cr, Mn, S, and Sr were found to be elevated. Kaolinite is ubiquitous within the aquifer's sandstones and is present as pore-filling aggregates and as inclusions in dolomite and calcite. Incipient quartz overgrowths were detected in most sandstone samples. Quartz overgrowths are abundant on quartz grains cemented by calcite but are absent in grains surrounded by dolomite cement.

CHAPTER III

GEOCHEMISTRY OF CHROMIUM

General Physical and Chemical Properties

Chromium [7440-47-3] is the 21st element in the earth's crust in relative abundance, ranking with V, Zn, Ni, Cu, and W. With atomic number 24 and relative atomic mass 51.996, it belongs to Group VIB (transition series) of the periodic table whose other members are Mo and W. Its neighbors are V and Mn. Its configuration is $(Ar)3d^54s^1$. Its physical properties are listed on Table IV. Chromium is one of the essential trace elements.

Chromium was first isolated and identified as a metal by French chemist Nicolas-Louis Vauquelin. In 1798 he was working with a rare mineral, Siberian red lead (crocoite, $PbCrO_4$). He chose to name it *Chromium* from the Greek word chroma meaning color, because of the wide variety of brilliant colors displayed by compounds of the new metal (Burns and Burns, 1975).

An early application of chromium compounds was as pigments, particularly chrome yellow, $PbCrO_4$. Basic chromium sulfate was used for tanning of hides where the reaction of chromium with collagen raises the thermal stability of the leather and renders its resistance to bacterial attack. During the 19th century, the most important application of chromium is as an alloying element. This particular application was gradually developed, mainly in France, and led to chromium steels. Chromite was employed as a furnace refractory as early as 1879 (Encyclopedia of Chemical Technology, v. 6, 1979).

TABLE IV
PHYSICAL PROPERTIES OF CHROMIUM

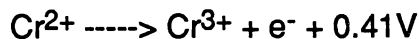
Property	Value
Isotopes, %	
50	4.31
52	83.76
53	9.55
54	2.38
Atomic radii, Angstrom	0.76
Density at 20°C, g/cm ³	7.19
Melting point, °C	1875
Boiling point, °C	2680
Vapor pressure, 130 Pa, °C	1610
Specific heat at 25°C, kJ/(mol.K)	23.9
Thermal conductivity at 20°C, W/(m.K)	91
Electrical resistivity at 20°C, μohm.m	0.129
Standard electrode potential, valence 0 to +3, V	0.71

From Udy, 1956.

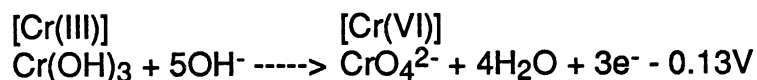
Chromium occurs in each of the oxidation states from -2 to +6, but only the 0 (elemental) +2, +3, and +6 states are common. Cr²⁺ is unstable in most compounds, as it is easily oxidized to Cr³⁺ form by air. Only the Cr³⁺ and Cr⁶⁺ oxidation states are common and important for human health. It is of great importance to realize that these two oxidation states have very different

properties and biological effects on living organisms, including human beings. Therefore, they must always be examined separately. A valid generalization of the biological effects of chromium as an element cannot be made (Langard, 1982).

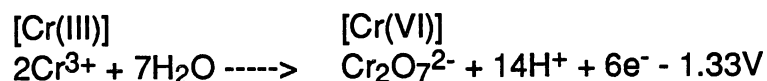
In acid solution chromium occurs as Cr^{2+} (chromous), Cr^{3+} (chromic), and $\text{Cr}_2\text{O}_7^{2-}$ (dichromate) ions and in basic solution as $\text{Cr}(\text{OH})_2$, CrO_2^- (chromite), and CrO_4^{2-} (chromate). Chromium metal is highly acid resistant and is only attacked by HCl , HF , and H_2SO_4 . The chromous ion is rapidly oxidized to $\text{Cr}(\text{III})$ by air and slowly by H^+ .



In its highest oxidation state chromium forms exclusively oxy-compounds that are all potent oxidizing agents. In basic solution the chromate ion is less oxidizing



than the dichromate ion in acidic solution



The difference of electric potential between these two states (+3 and +6) in acidic solution reflects the strong oxidizing properties and the substantial energy needed to oxidize the $\text{Cr}(\text{III})$ to the $\text{Cr}(\text{VI})$ form. For practical purposes, it can be stated that this oxidation never occurs in biological systems. The reduction of the $\text{Cr}(\text{VI})$ occurs spontaneously in the organism, unless present in an insoluble form (Merian, 1984). Living matter does not produce the energy necessary to oxidize $\text{Cr}(\text{III})$ to $\text{Cr}(\text{VI})$ in the organism; therefore, it can be stated that nearly all $\text{Cr}(\text{VI})$ in the environment is produced by human activities. The industrial use of chromium and the oxidation to $\text{Cr}(\text{VI})$ state on an industrial

scale did not begin until 1816. Thus, man's experience with this form is relatively short.

The most stable ionic state of chromium is Cr(III). It usually bonds with oxygen, nitrogen, sulfur, and many organic complexes. Although CrF₆ is well known, the most common forms of Cr(VI) are almost always bound to oxygen. The formation of metal hydroxides plays an important role in the chemistry of chromium in soils and water systems. Cr(III) coprecipitates with many of the metal hydroxides. Cr(VI) coprecipitates with aluminum hydroxide over the pH range 7 to 9.4 (Langard, 1982). The presence of Cr(VI) in our environment is important because in this oxidation state chromium is most toxic (NIOSH, 1975) and very water soluble.

Abundance, Natural Occurrence, and General Geochemical Character

Chromium is ubiquitous in nature. It can be detected in all matter in concentrations ranging from less than 0.1 µg/m³ in air to 4 g/kg in soils. It is found mainly in ultrabasic rocks (plutonic associations) and laterites (sedimentary associations). Areas underlain by ultrabasic or basic rocks may have elevated levels of chromium, causing toxicity in cereal crops. The development of specialized floras tolerant of very high levels of chromium over serpentinites in various parts of the world is well known (WHO, 1988); e.g., *Allysium markgrafi* (Yugoslavia), lichen (New Zealand), *Phormium colensoi*, *Liliaceae*, and *Gentiana corymbifera*.

Elemental chromium is not found in nature. The most important naturally occurring chromium mineral is chromite (FeCr₂O₄). Besides in chromite, Cr(III) is also found in some other minerals, e.g., uvarovite (Ca₃Cr₂(SiO₄)₃), crocoite

(PbCrO_4), fuchsite ($\text{K}(\text{Al,Cr})_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$). Cr(VI) may exist naturally (Robertson, 1975; Bartlett and James, 1979), but is less stable in reducing environments than Cr(III). Cr(VI) is a strong oxidizing agent in acidic solutions.

The average concentration of chromium in the earth's crust, basalt, granite, and shale is 100, 200, 20, and 100 ppm, respectively (Krauskopf, 1979).

Vinogradov (1962) gave a world average concentration of chromium in ultramafic, mafic, intermediate, and felsic rock as 2,000, 200, 50, and 25 ppm, respectively. Rock samples of Hawaiian lavas ranged from less than 1 ppm to 1,750 ppm chromium (Wager and Mitchell, 1953). About the same range in chromium concentration was reported in rocks from Skaergaard intrusion in Greenland (Wager and Mitchell, 1951) and in the tertiary lavas of northeastern Ireland (Patterson, 1952).

Rocks

Most of the sources of chromium in the earth's crust are in the Cr(III) state. The most important and the only commercial mineral deposits being in the form of chromite (FeCr_2O_4) which is rarely pure. It has the ideal composition of 68% Cr_2O_3 and 32% FeO or approximately 46% chromium. Actually the Cr/Fe ratio varies considerably and the ores are better represented as $(\text{Fe,Mg})\text{O} \cdot (\text{Cr,Fe,Al})_2\text{O}_3$.

Chromite deposits occur in olivine and pyroxene rich rocks and their weathered products. Geologically, chromite occurs in stratiform deposits several feet thick. Usually, the deposits are covering a very wide area and are mined by underground methods. Podiform deposits, i.e., isolated lenticular, tabular, or pod-shaped bodies ranging in size from a kg to several millions tons. These deposits are mined by both surface and underground methods,

depending on size and occurrence. Chromium also can be found in coal (5-10 mg/kg) (Merian, 1984). Inorganic carcinogens such as As, Be, Cd, Co, Cr, Ni, Se, and U exist in coal, but most will be removed by electrostatic precipitation. Chromium is a common guest constituent (<1%) in sphalerite (ZnS) and chalcopyrite (CuFeS₂).

Chromium concentrations in igneous rocks are positively correlated with concentrations of Si, Mg, and Ni. The high chromium concentration in sedimentary rocks is of agricultural importance where the element is present in phosphorites (Table V). Phosphorites are used as a phosphates fertilizer in agriculture and are a significant source of chromium for agricultural soils. Chromium-containing rocks and ores are found in all regions of the world, but the major sources of the world's chromium supplies are the ultrabasic rocks of South Africa, Turkey, the Soviet Union and Zimbabwe (US NAS, 1974).

Soils

While underlying rocks contribute little chromium to the vegetation directly, the chromium content in vegetation is strongly correlated with that of the underlying soils. The composition of soil is influenced by the composition of the parent rock from which it is formed. Thus, the background level of chromium in soil varies greatly.

In most soils, chromium occurs in low concentrations. However, chromium concentration in soils ranges from 5 to 1,500 µg/g (Bowen, 1979). Wedepohl (1969) found that chromium contents in basaltic soil and bauxite are 160 µg/g and 260 µg/g, respectively. The highest concentrations, as high as 3.5 g/kg, are always found in serpentine soils (Bowen, 1979). Al, Cr, Fe, Mn, and Pb have low to very low mobilities and thus would be enriched in soils. More

TABLE V
RANGE AND MEAN CONCENTRATIONS OF
CHROMIUM IN IGNEOUS AND
SEDIMENTARY ROCKS

Rocks	Concentration (ppm)		Mean
	Range		
Ultramafic igneous	1,000	- 3,400	1,800
Basaltic igneous	40	- 600	220
Granitic igneous	2	- 90	20
Shales & Clays	30	- 590	120
Black shales	26	- 1,000	100
Limestones		-	10
Sandstones		-	35
Phosphorites	30	- 3,000	300
Coals (ash)	10	- 1,000	20

From: US NAS, 1978.

chromium will be available to plants growing in a neutral to basic soil than in acidic soil. This is probably due to the mobility of Cr(VI). Navrot and Singer (1976) concluded that Cr is more mobile in soil than Fe or Al but not as mobile as Mn, Ca, or K.

The weathering of rocks produces chromium complexes that are almost exclusively in Cr(III) state. Under extreme conditions weathering may be accelerated by oxidation of Cr(III) to Cr(VI). Cr(VI) is relatively stable and mobile in soils that are sandy or contain low organic matter concentrations (Frissel et al., 1975; Bloomfield and Pruden, 1980). The reduction of Cr(VI) by organic matter in soils has been demonstrated by Bloomfield and Pruden (1980), who suggest that the movement of chromium through soil is dependent on soil

texture, pH, and organic matter type and content. Thus, as a small amount of Cr(III) in soil may be oxidized to Cr(VI) and become mobile, some of that Cr(VI) will be sorbed, some will be reduced, and some may be leached into ground water or drainage water.

The primary mode of occurrence of chromium in rocks is as the mineral chromite (FeCr_2O_4). Chromium is an isomorphous substitute for Fe or Al in other minerals of the spinel group. Chromium is also one of the adsorbed trace metals in illites and smectites (secondary soil minerals). For contaminated soils, chromium undergoes redox reactions. The one way in which redox reactions can influence the chemical forms of trace metals in the soils is directly through a change in the oxidation state of the trace metal itself, i.e., Cr(III) to Cr(VI) (Bartlett and James, 1979).

Water

It is now generally agreed that high chromium levels in water arise from industrial sources (US NAS, 1974). Except for areas bearing chromium deposits or in highly industrialized areas, most surface and ground waters contain very low levels of chromium. In surface and ground waters chromium occur in two oxidation states: Cr(III) and Cr(VI). Cr(III) occurs as the cation Cr^{3+} and Cr(VI) as the oxy-anion CrO_4^{2-} . These two ions behave differently from one another in natural waters. The anionic form is more soluble, more toxic, and has been implicated as carcinogen. The total concentration of chromium is regulated by federal statutes. It is 50 $\mu\text{g/l}$ for public and private uses (US EPA, 1988).

Naturally occurring chromium concentrations in water arise from mineral weathering processes, soluble organic chromium, sediment load, and

precipitation. Chromium from industrial pollution will also be present and generally is inseparable. Out of 170 lakes sampled in the high Sierra Mountains in California, only two contained as much as 5 ppb chromium. The pH of these lakes ranged from 4.7 to 7.3 with a mean and median value of 6.0 (Bradford et al., 1968). Robertson (1975) reported that Cr(VI) presented in ground water of the Paradise Valley, Arizona, at concentrations as high as 220 ppb. The presence of Cr(VI) was attributed to silicate hydrolysis and low CO₂ levels. The pH of this water ranged from 7.8 to 9 with Eh values from -0.4V to +0.9V (Figure 5).

Kopp and Kroner (1968) detected chromium in 25% of surface water samples from sources in the USA, with a range of 1-112 µg/l, and a mean concentration of 9.7 µg/l. The remaining 75% contained less than 1 µg/l, the detection limit. Another survey of 15 rivers in the USA revealed levels ranging from 0.7 to 84 µg/l, the majority of samples containing between 1 and 10 µg/l (Durum and Haffty, 1963). Chromium contents in natural water of up to 215 µg/l were reported by Novakova et al. (1974). Although modern methods of water treatment remove much of the naturally present chromium, it should be noted that chlorinated drinking-water usually contains traces of Cr(VI). The mean level in the drinking-water supplies in 100 cities in the USA was only 0.43 µg/l, with a range from barely detectable to 35 µg/l (Durfor and Becker, 1964).

Battelle Pacific Northwest Laboratories under the SWES (Solid Waste Environmental Studies) project shows that precipitation of Cr(OH)₃ over the pH range 6.5-10.5 may maintain the aqueous Cr(III) concentrations at levels well below the National Interim Primary Drinking Water Standard for chromium. Thermodynamic data in Table VI shows considerably higher Cr(III) solubility. It was estimated that the concentrations could be well above the drinking water limit, except between pH 8.3-9.3, where concentrations equaled the standard.

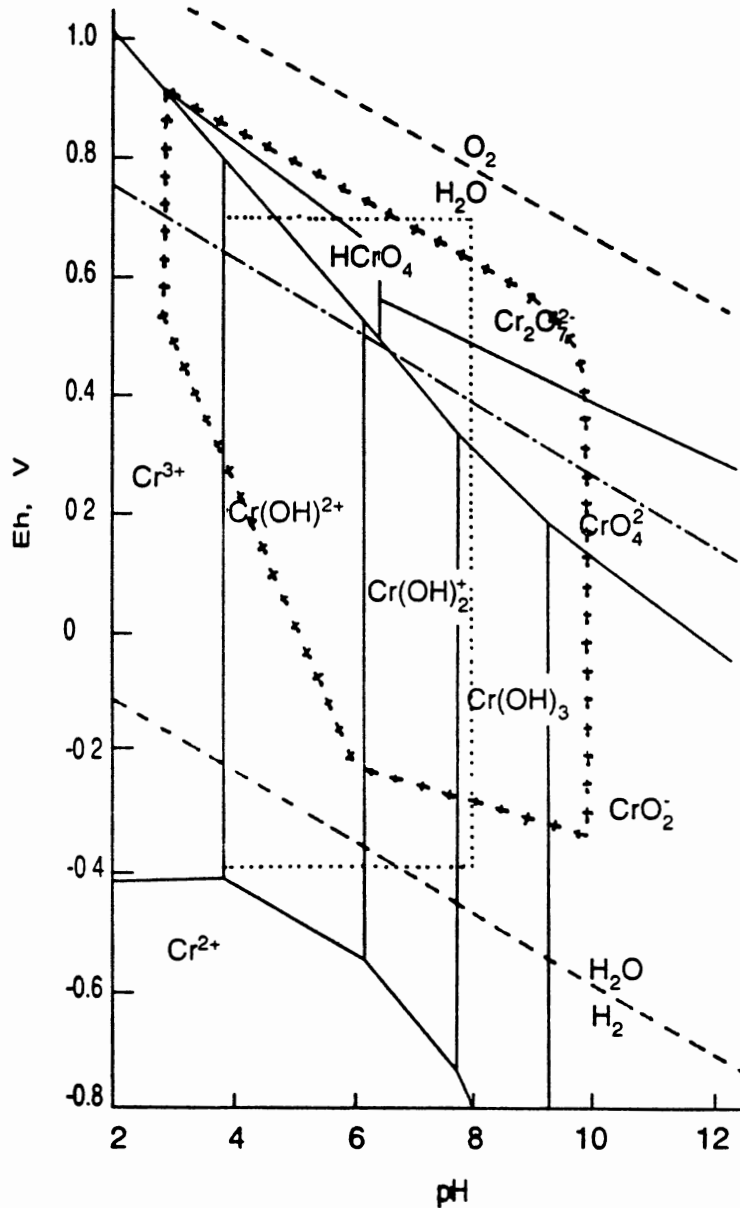


Figure 5. Eh-pH equilibrium diagram for 10^{-6} M chromium in water. Solid lines (—) between two species indicate equal concentrations of each species. Dashed lines (---) represent the thermodynamic limits for the stability of water. Dotted lines (-.-.-) represent the relationship for water in contact with the atmosphere (Garrels and Christ, 1965). The region enclosed with the dotted line is where most soil Eh-pH measurements will fall (Frissel et al., 1975). The region enclosed with plus (+) signs is where most Eh-pH measurements of natural waters will lie (Robertson, 1975). From: Langard (1982).

TABLE VI
 SWES THERMODYNAMIC DATA FOR Cr(III)
 (log₁₀ OF EQUILIBRIUM CONSTANTS)

Reaction	SWES/EPRI Research
Cr(OH) ₃ (s) + 3H ⁺ <=> Cr ³⁺ + 3H ₂ O	< 9.62
Cr(OH) ₃ (s) + 2H ⁺ <=> Cr(OH) ₂ ⁺ + 2H ₂ O	5.62 ± 0.18
Cr(OH) ₃ (s) + H ⁺ <=> Cr(OH) ₂ ⁺ + H ₂ O	< 0.75
Cr(OH) ₃ (s) <=> Cr(OH) ₃	< -7.13
Cr(OH) ₃ (s) + H ₂ O <=> Cr(OH) ₄ ⁻ + H ⁺	-18.15 ± 0.27
2Cr(OH) ₃ (s) + 4H ⁺ <=> Cr ₂ (OH) ₂ ⁴⁺ + 4H ₂ O	< 13.3
3Cr(OH) ₃ (s) + 5H ⁺ <=> Cr ₃ (OH) ₄ ⁵⁺ + 5H ₂ O	< 17.1
4Cr(OH) ₃ (s) + 6H ⁺ <=> Cr ₄ (OH) ₆ ⁶⁺ + 6H ₂ O	< 20.9

From: EPRI Technical Brief, 1986.

This research has also quantified the formation of (Cr,Fe)(OH)₃ solids, in which the presence of small amounts of iron controls Cr(III) solubility. The formation of such solids is important, particularly at pH values below 6, where Cr(III) solubility is not as strongly limited by Cr(OH)₃. Adsorption of Cr(III) controlled by Cr(OH)₃ or (Cr,Fe)(OH)₃ solids can further reduce its aqueous concentration below the NIPDWS levels .

Furthermore, this research has also stated that amorphous iron oxide (Fe₂O₃•H₂O(am)) has a particularly high adsorption capacity for Cr(VI). The adsorption of Cr(VI) can be reduced by competing solutes, especially the

common anions (e.g., sulfate and bicarbonate). These anions consume adsorption sites and render the solid surface more negative in charge. The effect of sulfate on Cr(VI) adsorption is shown in Figure 6. The presence of dissolved silica (H_4SiO_4) also reduces the adsorption of Cr(VI), with Cr(VI) adsorbed decreases with time.

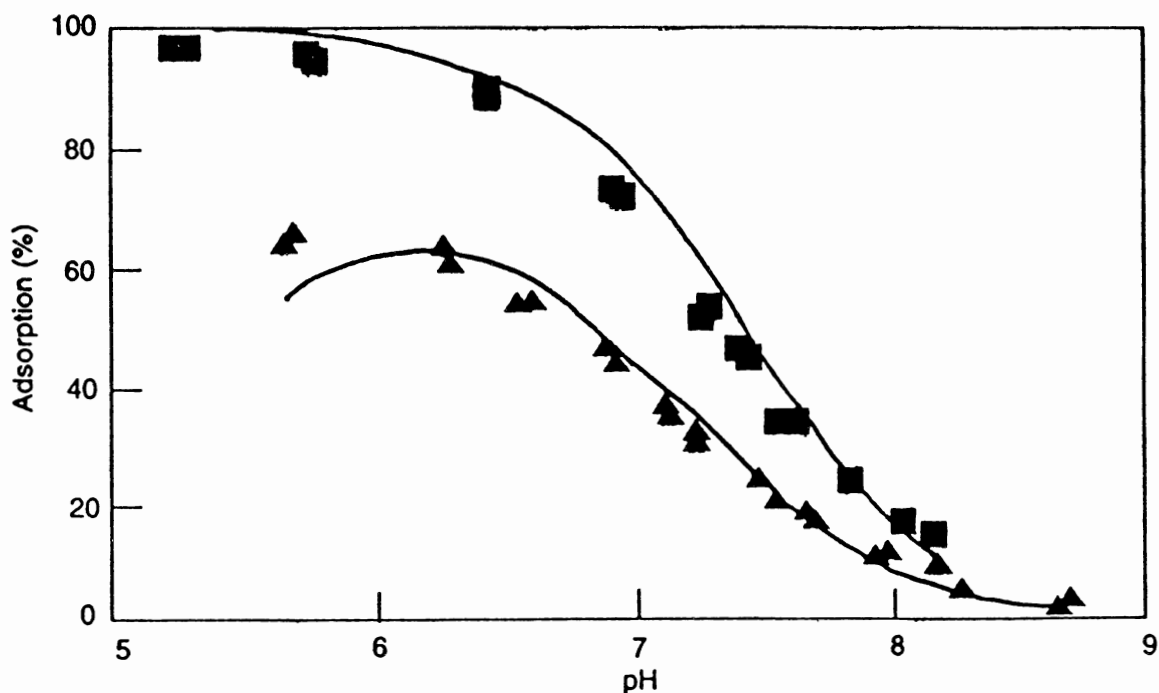


Figure 6. Adsorption of Cr(VI) on amorphous iron oxide. $\text{CrO}_4^{2-} = 5 \times 10^{-6}\text{M}$; $\text{Fe}_t = 0.87 \times 10^{-3}\text{M}$. The data points associated with the upper curve indicate the percentage of total Cr(VI) that is adsorbed. The points associated with the lower curve show the adsorption of Cr(VI) that occurs in the presence of $2.5 \times 10^{-3}\text{M}$ sulfate. The continual curves are the results of SWES model calculations (EPRI Technical Brief, 1986).

This research has also developed rate data (kinetic data) for the interconversion of Cr(III) and Cr(VI). The oxidation of Cr(III) to Cr(VI) has been shown to occur by reaction with pyrolusite (beta-MnO₂), a mineral coating of soil particles. The reaction is dependent on the surface area of the beta-MnO₂ present and to a lesser degree on pH and on Cr(III) concentration. The reaction appears to be surface-catalyzed, with the slow desorption of the newly formed Cr(VI) from the beta-MnO₂ surface limiting the overall reaction rate.

The reduction of Cr(VI) to the much-less-soluble Cr(III) was also studied. Cr(VI) is quickly reduced to Cr(III) by small amounts of iron, in the form Fe(II) in solution. Even in oxygen-rich waters, the small amounts of Fe(II) occurring in predominantly Fe(III)-containing minerals such as hematite appear to be adequate to cause the rapid reduction of Cr(VI) to Cr(III). The rates of these reactions increase with increasing H⁺ concentration (i.e., decreasing pH).

Eary and Rai (1987) studied the kinetics of Cr(III) to Cr(VI) by reaction with manganese dioxide. Their experiments indicate that the oxidation of aqueous Cr(III) does not occur by surface-catalyzed reactions with dissolved oxygen but by direct reaction with beta-MnO₂(s). Furthermore, they noticed that soil forms of MnO₂(s) are likely to have lower zero points of charge and higher surface energies, implying that these forms may cause more rapid oxidation of Cr(III) than the beta-MnO₂(s) used in their experiments.

The extent of Cr(III) oxidation is limited by anionic Cr(VI) adsorption in acidic solutions and by Cr(OH)₃(s) precipitation in neutral to alkaline solutions. The high solubilities of Cr(VI) solids in oxidizing environments imply that chromium may be attenuated only by adsorption rather than by precipitation of a solubility-controlling solid. The ready oxidation of Cr(III) to Cr(VI) by manganese oxides indicates the need to examine the mineralogy and oxidation potential of both the elevated chromium-bearing materials and the underlying

soils. The presence of manganese oxides would indicate the potential for greater transport of aqueous chromium as Cr(VI) species in ground waters. Without manganese oxides the oxidation of aqueous Cr(III) is unlikely to occur.

Zachara et al. (1987) studied the chromate adsorption on amorphous iron oxyhydroxide in the presence of major ground water ions. They concluded that major ground water anions bind to the surface of $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (am), reduce positive charge, and compete directly with CrO_4^{2-} as sites become limited. The surface reaction of these anions reduces CrO_4^{2-} adsorption. Cations have little influence on CrO_4^{2-} adsorption. Later they stated that chromate adsorption in the subsurface environment may be significantly suppressed by the presence of common anionic constituents in ground water. Thus, elevated levels of dissolved $\text{CO}_2(\text{g})$, H_4SiO_4 , and SO_4^{2-} may all dramatically reduce CrO_4^{2-} adsorption.

Schroeder and Lee (1975) have shown in simulated natural water systems that Cr(III) can be oxidized rapidly by MnO_2 and more slowly by oxygen. The oxidation can be inhibited by substances in natural water. Cr(VI) is reduced by Fe(II), dissolved sulfide, and organic sulfhydryl groups. Lovett and Lee (1976) suggested that organic matter is important in the reduction of Cr(VI) and that some of the chromium in river water is organically bound. Yamazaki (1980) pointed that the rate of formation of Cr(III) complexes will be relatively slow if only Cr(III) is present but might be much more rapid if Cr(VI) is reduced in the presence of organic molecules.

Air

Chromium occurs in the air of non-industrialized areas in concentrations of less than $0.1 \mu\text{g}/\text{m}^3$. The natural sources of airborne chromium originates from

atmospheric fallout, vulcanism and wind-borne aerosols, soil, and organic particulates. Man-made sources include all types of combustion and emissions by the chromium industry (WHO, 1988). The chemical forms of chromium in the air are not known. It is usually assumed that part of the air-borne chromium exists in the hexavalent form, especially that is derived from high-temperature combustion. Some of this will be reduced by organic matter in the air and some will be deposited on vegetation, soils and in the water. CrO_3 may be the most important compound in the air (Sullivan, 1969).

Wildlife and Plants

Cr, As, Ni, Sn, and V are essential to animals, but the biological role of most of these elements in plants remains to be established. The designation of chromium as an essential element to animals and man is recent. An adult human contains about 6 mg chromium. Cr(VI) is better absorbed in the upper gastrointestinal track than Cr(III), but only Cr(III) is biologically active as an essential element. "Glucose Tolerance Factor (GTF)" is reported to be biologically active form of chromium. Cr(III) as GTF is apparently absorbed much better (WHO, 1988).

Anionic complexes occur in aquatic environments and may be important in metal transport into micro-organisms. Energy dependent uptake of chromate (CrO_4^{2-}) has been described in the fungus, *Neurospora crassa*. Binding and transport of sulphate by *Salmonella typhimurium* was inhibited by anions structurally similar to the tetrahedral sulphate ion with an inhibition sequence as follows: $\text{CrO}_4^{2-} > \text{SeO}_4^{2-} > \text{MoO}_4^{2-} > \text{WO}_4^{2-} > \text{VO}_4^{2-}$ (WHO, 1988).

Sources of Chromium

Chromium concentrations found in soil, water, and air above background levels (Parkin and Tilles, 1968) are due to the redistribution of chromium containing minerals by wind, water, and human being (Table VII). Wind and water erosion of soils derived from ultramafic igneous rocks, shales and clays will result in increased chromium loads in air and water in comparison to erosion of soils derived from granitic igneous rocks, limestones, and sandstones.

TABLE VII
THE GLOBAL SOURCE OF CHROMIUM
IN THE ENVIRONMENT

Inputs	Percentage
Volcanic emissions	<1
Biological cycle:	
extraction from soils by plants	15
weathering of rocks and soils	15
Man-made emissions:	
general ore and meal production	3
metal use	60
coal burning and other combustion processes	7

From: Merian (1984).

Chromite mining is a source of airborne chromium and, due to particulate fallout, will also affect chromium concentrations in water and soil. In the United

States this is not a factor because no chromite has been mined since 1961, thus, elevated chromium concentrations in the United States arise almost entirely from industrial use and end-product use (Sullivan, 1969).

Metallurgy

Chromium is alloyed with Fe, Ni, Co, and other metals. These are then used in making various steels (US NAS, 1974). Most of the chromium released to the environment from these operations would be elemental or trivalent chromium. These will have little biological impact on the environment, unless they are oxidized to Cr(VI).

Chemical Industry

Chromates are manufactured from chromite ore and are the primary product from which other compounds are manufactured (Sullivan, 1969). Cr(III) dust is emitted during initial stages of the conversion of ore to chromate. Chromate dusts are emitted after oxidation of the ore. Chromate concentration in air originating from chromate producing plants ranged as high as 1.48×10^5 $\mu\text{g}/\text{m}^3$ and the geometric mean particle sizes in air sampled were 0.32-0.37 μm (Gafafer, 1953).

Chromium will enter the environment from many industries that use chromates or dichromates as raw materials. Some of these uses include: catalyst, paint, pigment, textile, graphic arts, fungicide, corrosion inhibitor, paper match, fireworks, and dry cell battery industries (Table VIII, p. 47). Cement contains up to 60 ppm chromium and as much as 13% of that can be Cr(VI) (Keenan and Perone, 1957). Cr(VI) is probably formed during the kiln processing under alkaline conditions. This points to the possibility of the

inadvertant production of chromate in other manufacturing processes not related to the chromium industry.

Coal

Abernethy and Gibson (1963) reported that coal contains from 7-20 ppm chromium. Furr et al. (1977) collected representative fly ash from 12 coal-fired electric generating plants in the United States. These samples contained from 43 ppm chromium in fly ash from Montana to 259 ppm chromium in fly ash from New Hampshire.

Chromium has been shown to be concentrated in the smaller particle size fractions (Davidson et al., 1974; Phung et al., 1979). Davidson et al. (1974) found 740 ppm chromium in the size fraction greater than 11.3 μm and 3,300 ppm chromium in the 1.1-2.2 μm size fraction. Natusch and Wallace (1974) showed that the distribution of this chromium favored the particle surface. Thus, the surface areas exposed to possible reaction are maximized. Metal concentrations in fly ash show a size-density distribution. It has been noted that Ca, Mg, Fe, Mn, Co, Cr, V, and Zn tend to concentrate in heavier density fractions. In strongly alkaline fly ash the formation of Cr(VI) could be expected. Phung et al. (1979) did not report the presence of Cr(VI) in fly ash but showed that the chromium presence increased in solubility as the pH changed from 12 to 9 and was constant from pH 9 to pH 6.

Toxicity

Chromium also can cause illness in human beings. Severe and prolonged allergic contact dermatitis to chromium contained in cement can be a disabling process in workers exposed to cement. Water soluble Cr(VI) is the

TABLE VIII
 MAJOR CHROMIUM USES AND KEY CHROMIUM
 CHEMICALS INVOLVED

Chromium chemical use area	Key chromium chemical involved
Paints and pigments	Chrome yellow Chrome orange Chrome oxide green Molybdate orange Chrome green
Leather tanning liquor	Basic chromium sulfate
Metal finishing and plating	Chromic acid
Corrosion inhibitors	Zinc chromate Zinc tetroxychromate Strontium chromate Lithium chromate
Catalysts	Cadmium chromate Copper chromate Magnesium dichromate Nickel chromate Copper chromite
Drilling muds	Chromium lignosulfonate
Wood preservatives	Chrome copper arsenate Chrome zinc chloride
Textile mordants and dyes	Chromic chromate Chromic chloride (hydrated) Chromic fluoride Chromic lactate

From: US EPA, 1990.

sensitizer at concentrations of 5 µg/g or more. It means that some effects can result from exposure to airborne chromium including irritative lesions of the skin and upper respiratory tract, allergic reactions, and cancers of the respiratory tract. This chromium can be reduced to the non-sensitizing Cr(III) by the addition of FeSO₄, but must be added at the time mortar or concrete is made (WHO, 1988).

Electroplating can release chromic acid spray and air-borne Cr₂O₃, both of which can result in direct damage to skin and lungs. Chromium dust has long been incriminated as a potential cause of lung cancer and chromium has been shown to be mutagenic in micro-organisms, causing infidelity (misreading) during synthesis of DNA copies (Baetjer, 1950).

Soil amendments such as metallurgical slags have very high concentrations of Co, Cr, Cu, Ni, Pb, and Zn. Use of these slags clearly poses a potential metal pollution problem. It is estimated that the current rates of mining equal or exceed natural rates of cycling for several metals. For heavy metals, such as Cd, Cu, Cr, Hg, Mn, Pb, and Zn, the rates of mobilization from mining are estimated to exceed by a factor of ten or more the rates of mobilization from natural cycling (WHO, 1988). One of the consequences of such human activity is pollution or prospect of contamination of proximate soils. Inorganic carcinogens, such as As, Be, Cd, Cr, Co, Ni, Se, and U exist in coal, but most will be removed by electrostatic precipitation.

Six epidemiological studies, five of which were at different locations (Taylor, 1966; Enterline, 1974; Davies, 1978; Langard & Norseth, 1979; Mancuso & Hueper, 1951; Baetjer, 1950), of up to 1,200 chromate workers strongly indicate that inhalation of Cr(VI) produces lung cancer. These studies, supported by the production of local carcinogenic responses in rats and hamsters at the site of implantation of injection (Laskin, 1970).

The extent to which ingested Cr(VI) induces cancer is not clear, both because of the lack of experimental evidence and because there is the possibility that Cr(VI) is reduced to Cr(III) in the stomach. Because of these uncertainties, no dose data for Cr(VI) exist on which to base a quantitative risk estimate of oral carcinogenicity. Therefore, the criterion concentration for Cr(VI) of 50 µg/l, based on its toxicity, should be regarded as a strict upper limit. It does not include any consideration of the carcinogenicity of Cr(VI) (WHO, 1988).

The effect of salinity and temperature on Cr(VI) toxicity to grass shrimp is reported by Fales (1978). At fixed salinities of 10 and 20 g/kg toxicity increased with increasing temperature between 10 to 25°C. At fixed temperature toxicity decreased with increasing salinity from 10 to 20 g/kg. Detailed analysis of toxic effects is complicated by the occurrence of many different compounds of the metal, e.g. chromium in different valence states. Chromium in excess amounts can be toxic, dependent upon the chemical species of chromium and the route of exposure. In general, Cr(III) is much less toxic than the Cr(VI) form (WHO, 1988).

CHAPTER IV

CHROMIUM SOLUBILITY AS A FUNCTION OF Eh AND pH

The solubility of a chemical compound (or mineral) in water is controlled in part by such factors as temperature, pressure, hydrogen ion concentration (pH), and the redox potential (oxidation potential or Eh). Temperature and pressure rarely affect mineral solubilities under most ground water conditions (Hem, 1989). The pH, however, has a profound effect on the presence and mobility of elements. Most elements are soluble only in a specific pH range. The solubility of some elements may also depend upon their oxidation state, which is determined by the Eh of the environment. Eh is a measure of the intensity of oxidizing or reducing conditions in a solution. Eh's values are expressed in volts relative to the hydrogen electrode at zero.

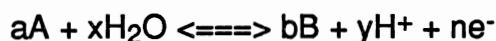
Chromium, for example, is very insoluble and immobile in the trivalent state, but becomes very soluble when oxidized to the hexavalent state. Therefore, the understanding of occurrence of such elements in ground water can be enhanced by interpretation of Eh and pH measurements of the ground water, and development of Eh-pH stability field diagrams.

The purpose of this chapter is to discuss the Eh-pH field stability diagrams of iron and manganese because iron hydroxides, iron and manganese oxides are assumed to be responsible for the mobilization of chromium in the Central

Oklahoma aquifer. Chromite solubility is given because detrital chromite was found at a depth of 131.2 feet in test hole 2 (Figure 3, p. 6).

Eh-pH Stability-Field Diagrams

Eh-pH diagrams are constructed on the basis of individual chemical equations and certain thermodynamic properties related to such equations. Most Eh-pH diagrams in this chapter were taken from Hem (1977). Given any reaction in which substance A is changed into substance B, and which can be written in such a form that hydrogen ions (H^+), water molecules, and electrons (e^-) are involved, the laws of equilibrium can be applied to express the reaction in two independent variables (Garrels, 1960): Eh and pH. pH determines the influence of the hydrogen ions and Eh determines the influence of electrons. Such reaction would have the following general form:



where A is the reactant, B is the product, ne^- is the number of electrons released, and a, b, x, and y are the concentrations of each in moles or gram-ions. In case a reaction is independent of Eh or pH, n or y respectively will be 0.

The Nernst equation defines the fundamental relationship between Eh and pH:

$$Eh = Eo + \frac{RT}{nf} \ln \frac{[B]^b [H^+]^y}{[A]^a [H_2O]^x}$$

where

Eh = redox potential, volt

R = universal gas constant, $8.31434 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

T = absolute temperature, 273.15 K

n = number of electrons released

f = the Faraday constant, $9.64867 \times 10^4 \text{ C}\cdot\text{mol}^{-1}$

E_o = standard potential of reactants, defined by:

$$E_o = \frac{\Delta G_R^o}{nf}$$

where ΔG_R^o = standard free energy of reaction.

pH is the negative logarithm of the hydrogen ion activity, and the activity of water and solids are unity, so, the significant variables become Eh, pH, and the activities of the ions under consideration. It should be remembered that these calculated stability-fields represent minimum solubilities because of the difference between the activity (thermodynamic concentration) and the molar concentration (actual concentration). This discrepancy is usually not a serious problem when dealing with very diluted waters (Garrels, 1960).

Many of the relationships used in constructing Eh-pH diagrams are half-reactions, and in natural systems chemical equilibrium will be established only by combining or coupling oxidation half-reactions with reduction ones. Techniques for preparing Eh-pH diagrams and their limitations have been described in detail in numerous papers (Garrels and Christ, 1965; Hem and Cropper, 1959; Pourbaix, 1949). A concentration of 10^{-3} moles/l of dissolved carbon species (equivalent to about 61 mg/l as HCO_3^-) and of 10^{-4} moles/l of dissolved sulfur species (equivalent to about 9.6 mg/l as SO_4^{2-}) has been specified for the diagrams presented here. Metal sulfide solubility effects are not considered in detail. The bicarbonate and sulfate concentrations specified are near those of Livingstone's (1963) "average river water". Effects of ionic strength have not been considered in most of the graphs.

Standard Gibbs free energies of formation used in preparing Eh-pH diagrams are given in Table IX. Most were taken from Wagman et al. (1968). These were supplemented with values calculated from solubility data. Solubility based values used for iron and manganese species are essentially

the same ones used in compilations by Langmuir (1969), and Crerar and Barnes (1974), respectively. For chromium the ΔG° values were taken from Naumov et al. (1971). Measurement of the Eh of water, using inert metal and standard electrodes, is seldom possible in many natural environments. However, this difficulty sometimes can be evaded by estimating an Eh from other data. Hem and Cropper (1959) have used dissolved iron and pH for this purpose.

To be an index of Eh, the participating reactants must be available in sufficient amounts and also must react reversibly, at reasonably fast rates. The iron system appears to fulfill these requirements in the stability field of $\text{Fe}(\text{OH})_3(\text{c})$ where ferrous iron or complexes are the dominant dissolved forms. Determinations of dissolved iron, which exclude colloidal or particulate forms, will serve as an approximate index of ferrous activity and the calculated Eh should represent conditions near a ferric hydroxide surface.

Eh-pH Diagrams for Iron, Manganese and Chromium

Eh-pH Diagram for Combinations of Iron and Manganese

In natural environments we are concerned with understanding the mobility, geochemical characteristics, and chemical behavior of trace elements in a variety of modes of occurrence. Important modes of occurrence for trace elements are as major elements in trace minerals, as trace constituents of unweathered dominant minerals from the parent material, as trace constituents in minerals formed during weathering, and as ions adsorbed to colloidal particles or in the exchange layer of clays. The behavior of trace elements in these occurrences can be understood in terms of solubility of trace minerals and

TABLE IX
STANDARD GIBBS FREE ENERGY OF FORMATION
USED IN PREPARING Eh-pH DIAGRAMS

Species	ΔG° kcal/mole	Source of Data
<i>Chromium</i>		
Cr ₂ O ₃ (c)	-253.2	Naumov et al. (1971)
Cr(OH) ₃ (c) ppt.	-202.4	Naumov et al. (1971)
FeCr ₂ O ₄ (c)	-323.28	Naumov et al. (1971)
Cr ₂ O ₇ ²⁻ (aq)	-307.75	Naumov et al. (1971)
CrO ₄ ²⁻ (aq)	-172.29	Naumov et al. (1971)
Cr ³⁺ (aq)	-48.74	Naumov et al. (1971)
CrOH ²⁺ (aq)	-100.0	Naumov et al. (1971)
Cr(OH) ₂ ⁺ (aq)	-149.1	Naumov et al. (1971)
Cr(OH) ₄	-237.28	Naumov et al. (1971)
<i>Iron</i>		
Fe(OH) ₃ (c) ppt	-166.0	Feitknecht & Schindler (1963)
Fe(OH) ₂ (c) ppt	-114.6	Leussing & Kolthoff (1953)
FeCO ₃ (c) siderite	-159.35	Wagman et al. (1969)
FeS ₂ (c) pyrite	-39.9	Wagman et al. (1969)
Fe ₂ O ₃ (hematite)	-177.4	Wagman et al. (1969)
Fe ₃ (OH) ₈	-450.0	Ponnamperuma et al. (1967)
Fe ³⁺ (aq)	-1.1	Wagman et al. (1969)
FeOH ²⁺ (aq)	-54.83	Wagman et al. (1969)
Fe(OH) ₂ ⁺ (aq)	-104.7	Wagman et al. (1969)
Fe ²⁺ (aq)	-18.85	Wagman et al. (1969)
FeOH ⁺ (aq)	-64.2	Leussing & Kolthoff (1953)
Fe(OH) ₃ ⁻ (aq)	147.0	Wagman et al. (1969)
Fe ₃ O ₄ (magnetite)	-242.7	Bricker (1965)
<i>Manganese</i>		
MnO ₂ (c) (pyrolusite)	-118.18	Wagman et al. (1969)
MnO ₂ (birnessite)	-108.3	Bricker (1965)
Mn ₂ O ₃ (bixbyite)	-210.6	Wagman et al. (1969)
MnOOH (c) (manganite)	-113.3	Bricker (1965)
Mn ₃ O ₄ (hausmannite)	-306.7	Wagman et al. (1969)
Mn(OH) ₂ (c) amorphous	-147.0	Wagman et al. (1969)
MnCO ₃ (c) pp.	-194.3	Latimer (1952)
MnCO ₃ (c) (rhodochrosite)	-195.2	Wagman et al. (1969)
MnS (c) (alabandite)	-52.14	Robie & Waldbaum (1968)
Mn ²⁺ (aq)	-54.5	Wagman et al. (1969)
MnOH ⁺ (aq)	-96.8	Wagman et al. (1969)
HMnO ₂ ⁻ (aq)	-120.9	Hem (1963)

From: Hem, 1977.

host minerals, ion exchange reactions, and surface chemistry of colloidal particles. To review the methods for selectively removing trace elements in the iron oxide, manganese oxide, organic, and exchangeable sites, Rose (1975) did some experiments on a wide variety of partial extraction methods. These experiments can be used to imitate the processes in natural environment.

Trace metals contained in the lattice of minerals composed of major elements are dependent on stability of the major phases. So, major phase stabilities must be considered in any discussion of partial extraction methods. The minerals formed during weathering tend to be fine grained and relatively sensitive to changes in their environment. Minerals that have resisted weathering are usually resistant to chemical treatments (Rose, 1975). For this reason, the stability of clays, Fe-Mn oxides, and organic materials must be considered in the effect of partial precipitation on release of trace elements. So, treatments to remove (to dissolve) one or more minerals can be controlled for studying the mobility and modes of occurrence of trace elements.

The stability of iron and manganese oxides in water as a function of Eh and pH is summarized in Figure 7. The iron oxides (hematite and magnetite) are stable under all conditions except very acid solutions or relatively reducing conditions. Manganese oxides are stable (at $Mn^{2+} < 10^{-6} M$) only under very oxidizing, neutral to basic conditions. Because of the variety of organic compounds, no single stability can be specified. Most organic compounds are truly stable only near the H_2-H_2O line near the bottom of the diagram, though metastability is obviously pronounced (Rose, 1975).

The clay minerals vary in their stability from one mineral to another, but dissolution of clay (as contrasted to conversion of one clay to another) will be controlled largely by solubility of aluminum. Within the pH range of 5-8, aluminum solubility is low (Parks, 1972) and pH effects on clay minerals are

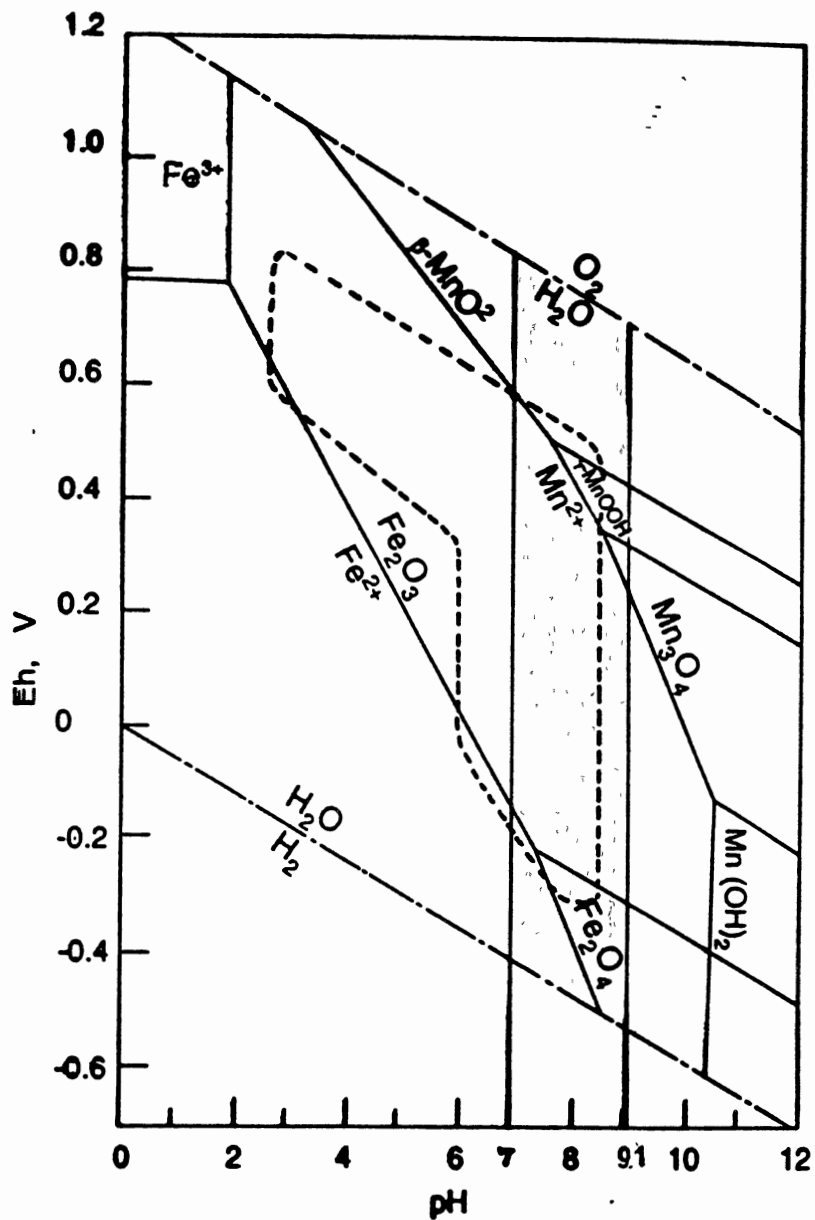


Figure 7. Eh-pH diagram in relation to stability of iron and manganese oxides and oxyhydroxides at 25°C and 1 atm. Dotted lines enclose the Eh-pH range of the natural environment. Data for iron and manganese species are listed in Table IX. Assumed activity of dissolved iron and manganese is 10^{-6} M (Rose, 1975). Red-shaded region indicating species present given the range of pH values found in wells containing elevated levels of chromium.

expected to be at minimum. At more acid pH values (3 and less), clays dissolve significantly, and trace elements in their lattices will be released at a significant rate.

Based on solubility data of this sort, Rose (1975) formulated procedures for selectively dissolving one constituent of a sediment or soil without affecting others. For instance, moderately reducing conditions at neutral pH will dissolve manganese oxides with minimal effect on clays, iron oxides, and organic matter. More strongly reducing conditions, preferably at a slightly acid pH, would be chosen to remove iron and manganese oxides without dissolving clays. Strongly acid conditions, especially if not highly oxidizing, would dissolve iron and manganese oxides, clays, and most trace minerals.

Once the host mineral is dissolved, the behavior of the trace metal depends on its solubility in the medium. In order for the minerals to dissolve in reasonable times, a considerably undersaturated solution is needed. Undersaturated solution is needed because of the possible slow reaction of the trace mineral and because of possible difficult accessibility of the solution to the trace mineral, owing to its occurrence within composite grains.

Eh-pH Diagrams for Iron and Manganese

Freshly precipitated and disordered ferric hydroxide and manganese oxides are highly active sites for immobilizing many dissolved ionic species. Two processes by which the immobilization occurs are specific adsorption and coprecipitation. Sorption and lattice substitution are recognized widely as important mechanisms. Extensive reviews of the literature on sorption of trace metals by hydrous oxides have been published by Jenne (1968).

The remainder of this chapter reviews the thermodynamics of coupled oxidation and reduction reactions of substrate and solute ions, and certain other reactions that may occur among chromium ions at surfaces of freshly precipitated ferric hydroxide. The probable effects on solubilities are indicated by Eh-pH diagrams and related calculations and graphs. Where it is used in this thesis the term "ferric hydroxide" represents metastable poorly crystallized material having a standard free energy of formation of -166 kcal/mole, and a solubility product of $10^{-38.2}$. This is within the range of published values for this material cited by Langmuir (1969).

Redox conditions in aqueous iron systems are illustrated in the Eh-pH diagrams in Figure 8. The diagram shows by shading the fields of stability for precipitated ferric hydroxide, siderite, pyrite, and ferrous hydroxide. Superimposed on these stability fields are solubility contours showing total dissolved iron activity in moles per liter between 10^{-3} M (56 mg/l) and 10^{-9} M (0.056 μ g/l).

The uncharged aqueous species $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ are thought by some investigators (Lengweiler et al., 1961) to be mainly colloidal solids and reported ΔG values may be unreliable. Polynuclear ferric species summarized by Mesmer and Baes (1975) are not significant when iron concentrations are 10^{-3} M or less. The species $\text{Fe}(\text{OH})_4^-$, for which stability data were reported by Schindler (1967), could be dominant at a pH above 8, but its concentration could exceed 10^{-7} M only above pH 12.

A mixed-valence iron hydroxide $\text{Fe}_3(\text{OH})_8(\text{c})$ was reported by Ponnampetuma et al. (1967) to occur in reduced soil zones. If this species was included in Figure 8, it would replace the $\text{Fe}(\text{OH})_2(\text{c})$ stability domain and would have minor effects on solubility in the reducing region above pH 9. Jones et al. (1974), after careful studies of dissolved iron in stream water, concluded that

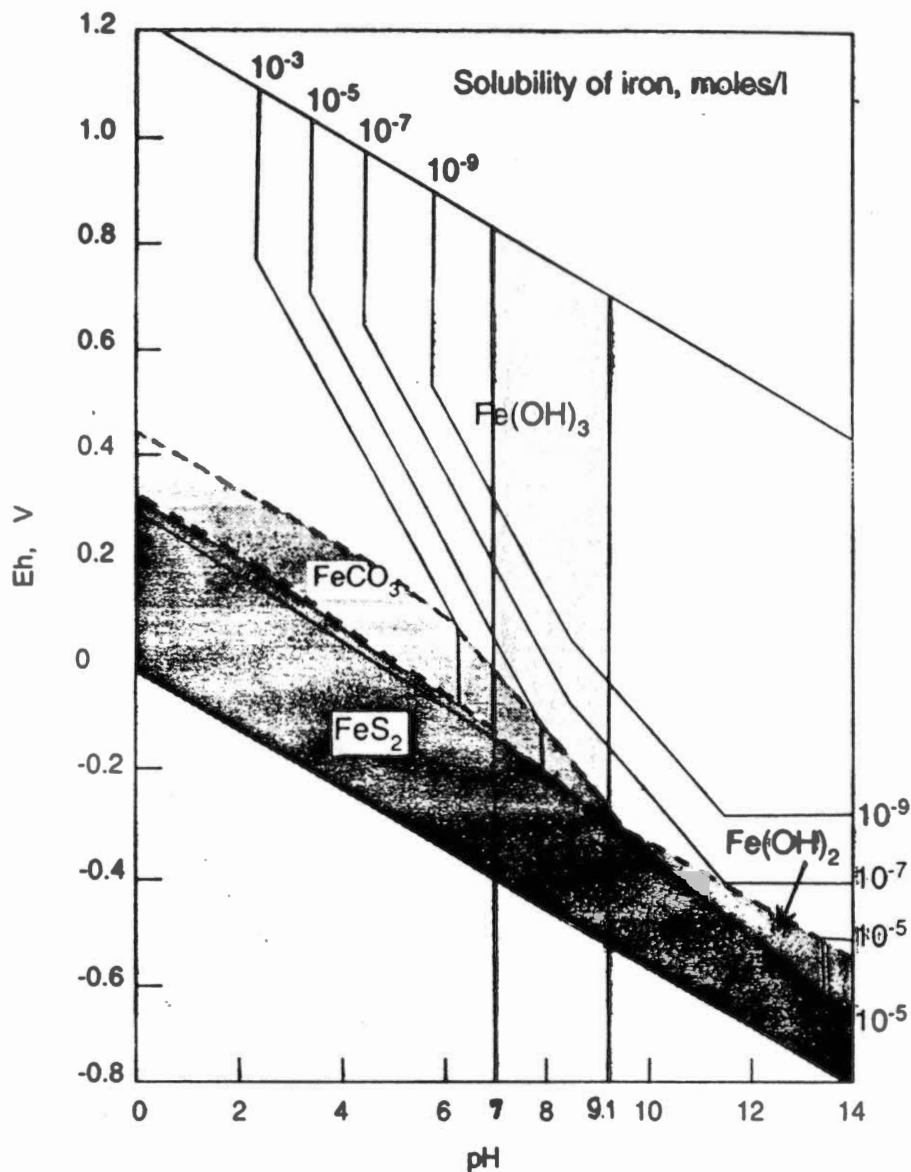


Figure 8. Equilibrium relationship in system $\text{Fe} + \text{H}_2\text{O} + \text{O}_2$, at 25°C and 1 atm. Stability domains for ferric and ferrous hydroxide, siderite, and pyrite, and total equilibrium dissolved iron activity ($10^{-7}\text{M} = 5.6 \mu\text{g/l}$), with fixed total sulfur species activity = 10^{-4}M (or 9.6 mg/l as SO_4^{2-}) and CO_2 species activity = 10^{-3}M (or 61 mg/l as HCO_3^-) (Hem, 1977). Red-shaded indicating species present given the range of pH values found in wells containing elevated levels of chromium.

cryptocrystalline $\text{Fe}(\text{OH})_3$ is the probable form of $\text{Fe}_3(\text{OH})_8(\text{c})$ in stream sediments.

Chemical behavior of chromium and manganese may be influenced by reactions involving iron (Hem, 1977). The Eh-pH and solubility graphs for those elements are shown in Figures 9, 10, and 11. There are several processes that must be considered in studying the mobility of major elements in the environment. For example, the solubility of Ag, Cr, and Cu decreases when reduction of these metal ions is coupled with the oxidation of Fe^{2+} . The oxidation of Mn by aqueous O_2 is catalyzed at $\text{Fe}(\text{OH})_3$ surface. Coprecipitation of Cr, Cu, Ni, and Zn may occur by local alterations in $\text{Fe}(\text{OH})_3$ crystal structure. Ferric hydroxide accompanies manganese oxides in various natural precipitates. Most oxidized manganese species have low solubilities, and manganese oxide precipitates may themselves be a substrate for redox processes. Figure 9 shows stability regions for solids and the solubility of manganese.

The only significant manganese solute species in natural systems are forms of Mn^{2+} . At a specified HCO_3^- activity the MnHCO_3^+ complex is never a dominant species. MnOH^+ occurs above pH 10 and HMnO_2^- above pH 12 but neither is particularly significant in natural water systems. Figure 9 also shows a very large stability field for rhodochrosite (MnCO_3) if a high concentration of dissolved manganese is present. A freshly precipitated form of MnCO_3 , reported by Garrels et al. (1960), would have a smaller stability field. Boundaries for oxide species were calculated for the most stable forms where Table IX (p. 54) lists more than one ΔG° value.

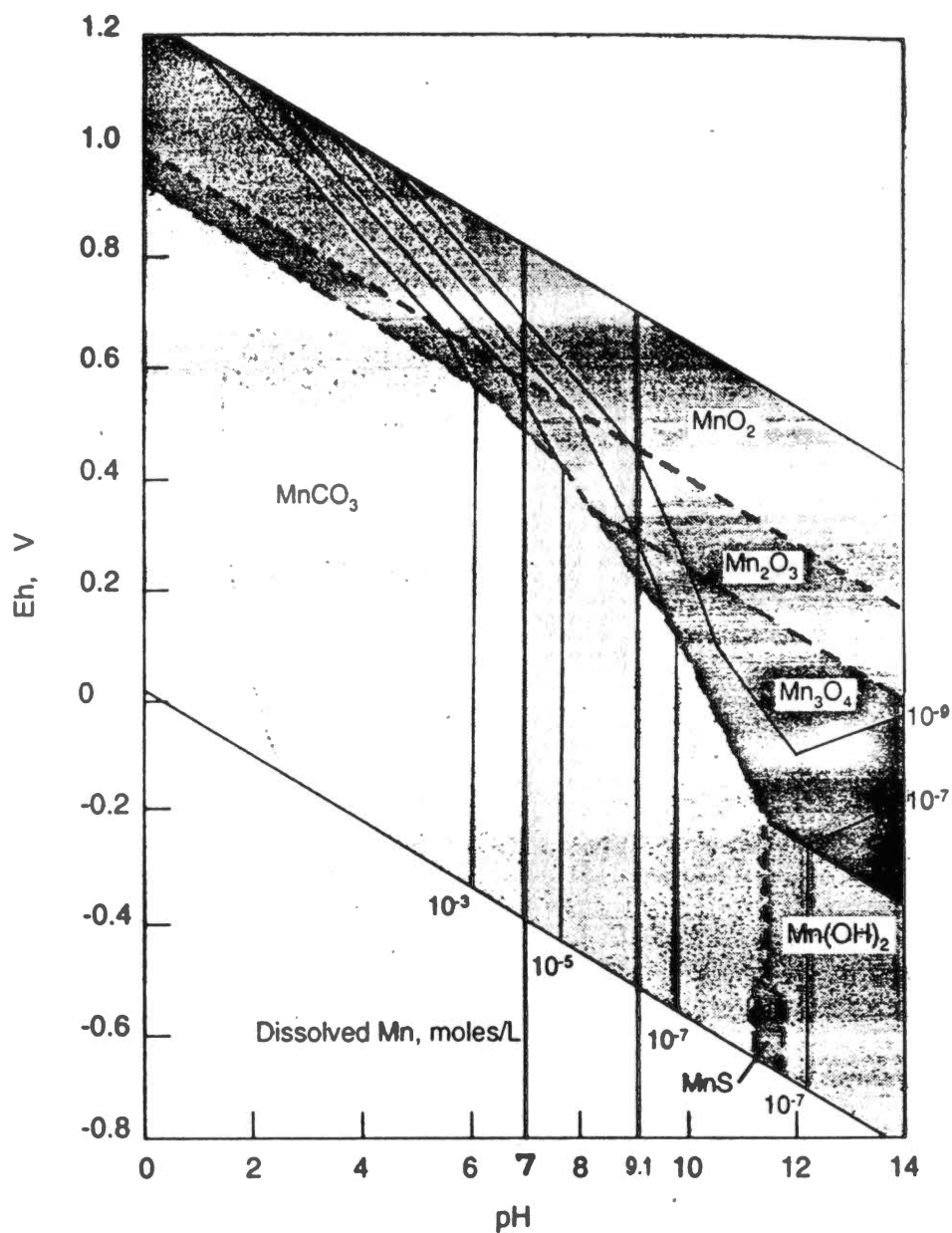


Figure 9. Stability domains for solids and equilibrium activity of dissolved manganese in system $\text{Mn} + \text{H}_2\text{O} + \text{O}_2$, with fixed total activity of sulfur = 10^{-4}M and carbon = 10^{-3}M at 25°C and 1 atm, assumed activity for manganese = 10^{-7}M (Hem, 1975). Red-shaded region indicating species present given the range of pH values found in wells containing elevated levels of chromium.

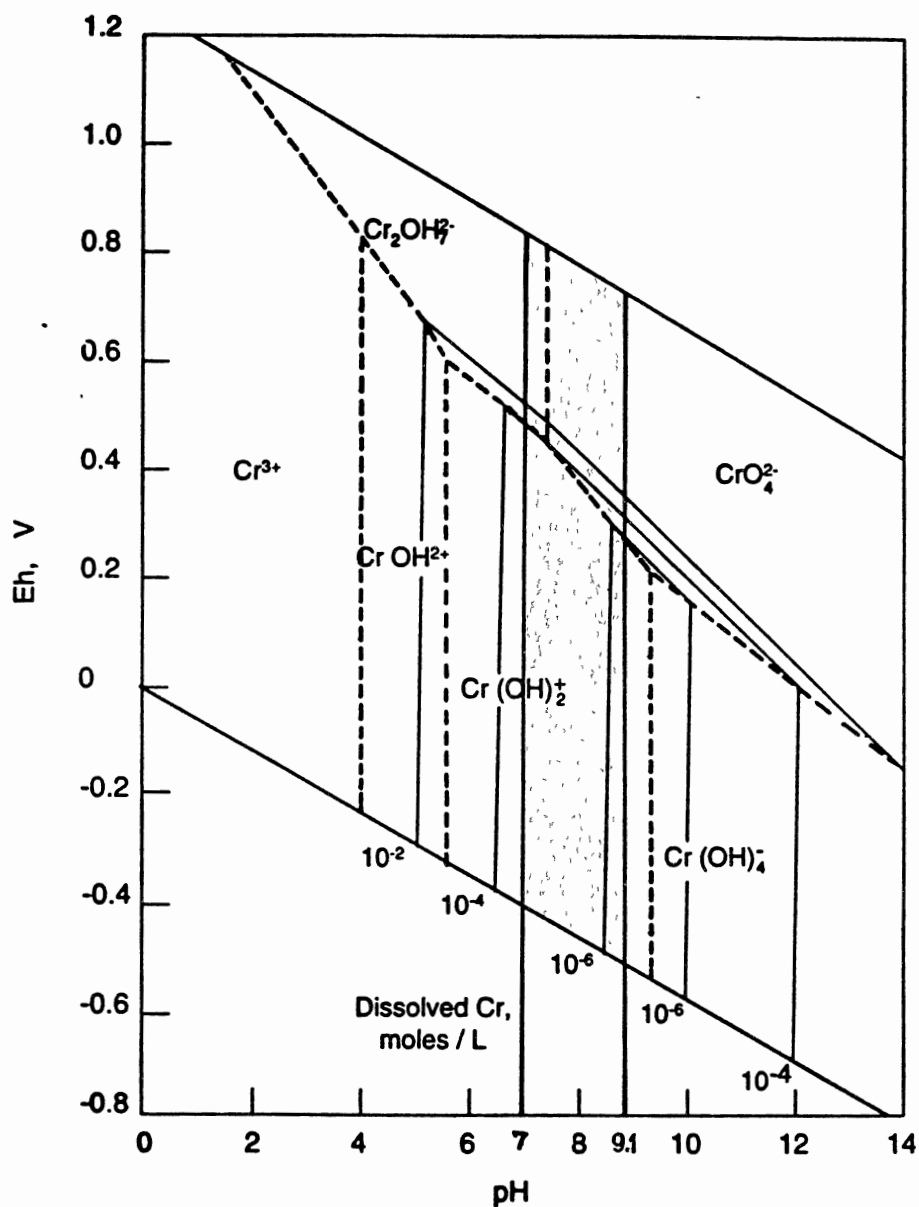


Figure 10. Equilibrium relationships in system Cr + H₂O + O₂ with fixed total activities of sulfur = 10⁻⁴M and carbon = 10⁻³M at 25°C and 1 atm. Areas of dominance of solute species (dashed lines) and dissolved chromium activity (solid lines) in presence of Cr(OH)₃(c) (10⁻⁷M = 5.2 μg/l Cr) (Hem, 1977). Red-shaded region indicating species present given the range of pH values found in wells containing elevated levels of chromium.

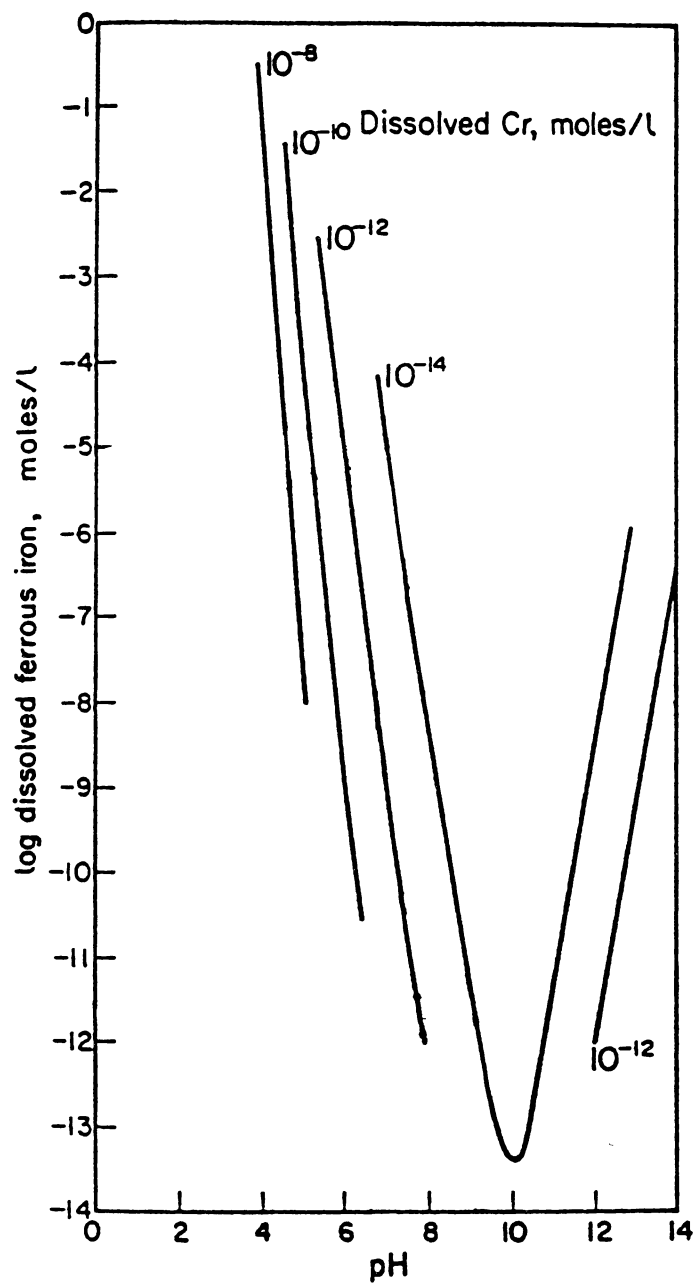
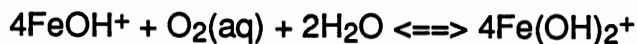


Figure 11. Equilibrium solubility of chromite (FeCr_2O_4) at 25°C and 1 atm (Hem, 1977).

Oxidation of ferrous to ferric ionic species in alkaline aerated water can be represented:



for which the mass-law expression is:

$$\frac{[\text{Fe}(\text{OH})_2^+]^4}{[\text{FeOH}^+]^4 [\text{O}_2(\text{aq})]} = 10^{35.57} \quad (1)$$

Or, at a ferric hydroxide surface:



$$\frac{[\text{H}^+]^4}{[\text{FeOH}^+]^4 [\text{O}_2(\text{aq})]} = 10^{49.09} \quad (2)$$

A parallel reaction for manganese oxidation could be written:



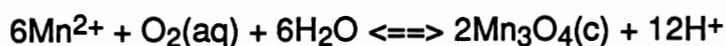
$$\frac{[\text{H}^+]^4}{[\text{Mn}^{2+}]^2 [\text{O}_2(\text{aq})]} = 10^{2.84} \text{ to } 10^{-1.38}$$

The larger of the two equilibrium constants is for the most stable oxide, pyrolusite form, and the smaller is for birnessite form (Table IX, p. 54).

Laboratory studies by Bricker (1965) and Morgan (1967) identified the initial product of oxidation of divalent dissolved manganese in alkaline aerated solutions as a less oxidized species generally having the Mn_3O_4 composition.

Bricker (1965) has shown that this form can be converted to MnO_2 by aging.

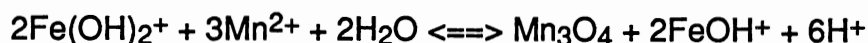
Thus the initial step in manganese oxidation is:



$$\text{This gives: } \frac{[\text{H}^+]^{12}}{[\text{Mn}^{2+}]^6 [\text{O}_2(\text{aq})]} = 10^{-36.54} \quad (3)$$

A stronger thermodynamic driving force is indicated for ferric hydroxide precipitation, and kinetic studies reported by Stumm and Morgan (1970) indicate that reaction (3) is slower than reaction (2) at a given pH. Thus, where

both iron and manganese are present the iron would be oxidized more rapidly than the manganese. A part of the ferric iron might react with Mn^{2+} , however, by a process such as:



This reaction gives the mass-law expression:

$$\frac{[FeOH^+]^2 [H^+]^6}{[Fe(OH)_2^+]^2 [Mn^{2+}]^3} = 10^{-36.06} \quad (4)$$

At the boundary between the dominant fields for those two iron species at pH 8.5, this expression can be shortened to:

$$[Mn^{2+}] = 10^{12.02}[H^+]^2.$$

If $[HCO_3^-]$ is below 10^{-3} , the stable solids in this system would be $Fe(OH)_3(c)$ and Mn_3O_4 . The manganese concentration would be $10^{-4.95}$ M (580 $\mu g/l$) at equilibrium. If the pH is greater than 8.5 or if the ferrous/ferric ratio is less than one, then the solubility of manganese would be much lower. To have a substantial catalytic effect, however, the recycling mechanism in which $FeOH^+$ is converted to $Fe(OH)_2^+$ by oxygen and returned to $FeOH^+$ by reacting with Mn^{2+} would have to be relatively fast because only small amounts of dissolved iron could be present.

Some investigators have reported a noticeable catalytic effect on manganese oxidation rates when ferric hydroxide surfaces and thus some ferrous and ferric dissolved ions are present. Other surfaces such as feldspar (Hem, 1964), silica (Crerar and Barnes, 1974), and clays, or previously deposited manganese oxide having a negative charge evidently can offer improved opportunity for nucleation of manganese oxide.

Manganese oxidation processes cause high redox potentials at oxide surfaces. Manganese oxide species in which all or a part of the manganese is at the 3+ oxidation state can be disproportionate.

For example,



At equilibrium:

$$\frac{[\text{Mn}^{2+}]}{[\text{H}^+]^2} = 10^{8.79}$$

This calculation uses the free energy assigned to birnessite, reported by Bricker (1965) to be the form of MnO_2 in in deep-sea manganese nodules. The forward reaction is more rapid at pH less than 6. If the pH of the system was buffered at 8.5 the equilibrium activity of Mn(II) would be $10^{-8.21}$ (0.34 $\mu\text{g/l}$). This is less than 1/1000 of the solubility calculated for the manganese-iron redox mechanism at this pH [equation (4)].

It is evident that after a manganese oxide, or mixed iron and manganese oxide surface has been formed, the removal of soluble manganese from water moving past the surface can be readily occur if oxygen is available. In many environments the rate of oxide accumulation may be controlled principally by the rate at which the reactants are brought into the system.

Conditions favoring oxide deposition include availability of a negatively charged surface, low dissolved bicarbonate activity, relatively high concentrations of manganese in solution, a high pH and a plentiful oxygen supply. In systems where there is a continuing input of Mn^{2+} , the oxidation step previously cited will continue to generate Mn_3O_4 . As the pH, manganese and iron contents of the water fluctuate, the solids deposited will have differing proportions of ferric hydroxide, MnO_2 and Mn_3O_4 , and various impurities.

Eh-pH Diagram for Chromium

Stability fields for the various species of chromium occurring in water shown in Figure 10 (p. 62). The boundaries separate the domains of the predominant solutes (ions), except the solid-solute boundaries where 10^{-6} moles/liter was chosen. The species are displayed as solid or crystalline forms ($\text{Cr}(\text{OH})_3$) or ions (Cr^{3+}). The free energy values used in the calculation of the free energy of reactions are from Naumov et al. (1971, 1974).

Chromium forms anionic species when oxidized and cationic species when reduced (except at pH greater than 12). Figure 10 shows the domains of the anionic hexavalent and cationic trivalent dissolved species and chromium solubility for amorphous $\text{Cr}(\text{OH})_3$. The anhydrous crystalline species Cr_2O_3 is much less soluble below 10^{-8} M (1.1 $\mu\text{g/l}$) over the pH range from 4.7 to 14 (Hem, 1977). The Eh-pH diagram of this kind might apply to the residual trivalent chromium oxide minerals in resistate rocks or stream sediments.

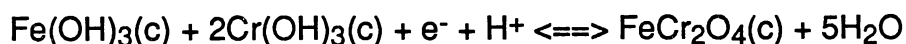
Solubilities for $\text{Cr}(\text{OH})_3$ probably are more realistic for natural reducing aqueous systems to which Cr(VI) might be introduced by disposal of waste. The dominant areas of anionic oxidized chromium species occur within the dominant areas of ferric dissolved species. However, chromate reduction can be coupled to ferrous ion oxidation (Hem, 1975). In ground water systems where iron is abundant chromium will tend to be immobilized as Cr^{3+} form.

Dissolution of Cr(III) minerals could occur in oxygenated waters that have a low concentration of equilibrium-controlled chromate anions. The slope of chromate solubility contours in Figure 10 is steeper than the dissolved oxygen redox slope, thus the occurrence of CrO_4^{2-} would be favored by pH greater than 7.3. Robertson (1975) found 100-200 $\mu\text{g/l}$ (about $10^{-5.5}$ M) of Cr(VI) in ground water in a part of Paradise Valley, near Phoenix, Arizona. The higher

concentrations were in water having a pH between 8.5 and 9.0. Measured redox potentials were in oxidizing condition and they gave a CrO_4^{2-} solubility close to equilibrium values shown in Figure 10. It would appear that the chromate results from oxidation of Cr(III) in minerals in the basin fill of the valley.

Solubility of Chromite

From published free energy data the most stable solid mineral species of chromium appears to be chromite (FeCr_2O_4). It is doubtful whether chromite can be precipitated from aqueous solutions under surface conditions. The reduction of



gives a standard potential of 1.57 volts, and implies that the stability field for chromite would cover most of the water stability region. Chromite could perhaps be formed as an impurity or admixture where reduced chromium was precipitated with ferric hydroxide.

Figure 11 (p. 63) is a plot of the solubility of chromite as a function of activity of dissolved ferrous species and pH. This diagram was developed from equilibria of the type:



using appropriate ferrous and chromic hydroxide complexes. The presence of ferric hydroxide is assumed throughout, and solubility contours are terminated when they begin to involve ferrous ion activities that are out of equilibrium with $\text{Fe}(\text{OH})_3$ at the specified pH. The extremely low chromium solubilities which are shown in Figure 11 suggest that these conditions may be a mechanism by which ferric hydroxide precipitates may scavenge traces of chromium from solution.

Chromite has the crystal structure of spinel (MgAl_2O_4), an arrangement with a very high degree of chemical thermodynamic and physical stability. Spinel structures seem to be formed most readily by crystallizing from a melt. A reversible precipitation from solutions at 25°C is seldom observed. However, Barnes and Clarke (1969) identified Mn_3O_4 with a spinel structure in precipitates that had formed on well casings, after mixing of ground water from different parts of the aquifer or where corrosion of the metal surface was occurring nearby.

CHAPTER V

RESULTS AND DISCUSSION

Appraisal of Chromium Data in the Central Oklahoma Aquifer

The chemical analyses used in this thesis are presented in Appendix A and B. It can be seen from Appendix B that in most places pH values exceeded 7 and at some places even reached 9, indicating the alkaline nature of the water. In the majority of the samples carbonate and bicarbonate are not analyzed, and when reported, are present only in small quantities. The same lack of measured data was found for temperature, dissolved organic carbon (DOC), dissolved oxygen (DO), SiO₂, NO₂+NO₃, As, Ba, Ca, Mg, K, and F. Data for pH, total Cr, Se, Cl, SO₄, specific conductance (SC), and hardness were available for most locations. The rest of variables such as sampling depth, alkalinity, Na, Fe, Mn, dissolved Cr, and dissolved Cr(VI) were determined less often than the previous group (Table X). Overall, the bulk of the data were reported as either a value of "less than" that required for a particular standard or no data at all.

The maximum contaminant level (MCL) for chromium is 50 µg/l. The MCL was exceeded in 54 wells of 58 wells where chromium (total, dissolved, and dissolved Cr⁺⁶) was analyzed. Figure 12 shows the locations where chromium was analyzed and where concentration equals or exceeds the MCL for

TABLE X
DATA APPRAISAL BASED ON PARAMETERS'
PERCENTAGE USED IN THE STUDY

Parameters	Amount of Data	Percentage (%)
Sampling depth	21	23.3
Temperature	16	17.8
Specific Conductance	76	84.4
Dissolved Oxygen	15	16.7
pH	67	74.4
Alkalinity	20	22.2
CO ₃	6	6.7
HCO ₃	6	6.7
NO ₂ + NO ₃	8	8.9
Dissolved Organic Carbon	8	8.9
Hardness	80	88.9
Ca	20	22.2
Mg	20	22.2
Na	24	26.7
K	17	18.9
Cl	76	84.4
SO ₄	78	86.7
F	19	21.1
SiO ₂	15	16.7
As	14	15.6
Ba	14	15.6
Dissolved Cr	24	26.7
Dissolved Cr(VI)	21	23.3
Total Cr	72	80.0
Fe	20	22.2
Mn	20	22.2
Se	87	96.7

chromium. Most of the locations where the MCL was exceeded are in the western third of the study unit.

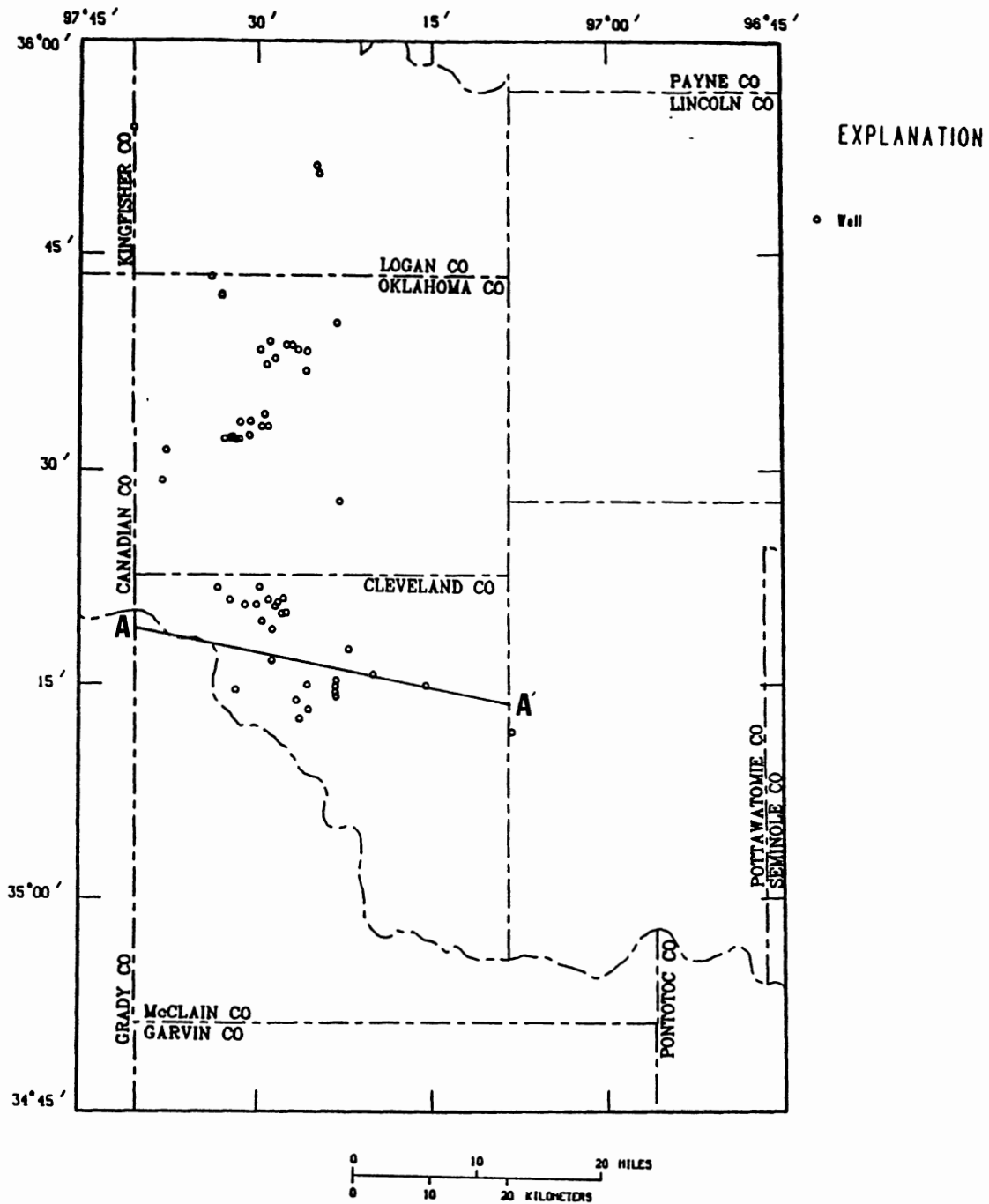


Figure 12. Locations of wells where chromium (dissolved, dissolved Cr^{6+} , and total) equals or exceeds $50 \mu\text{g/l}$

There are 104 wells whose waters have elevated chromium concentrations after the first data sorting from Oklahoma Geological Survey data base. This sorting was based on 50 µg/l (MCL) chromium. Thus, those 104 data points have chromium values that equal or exceed the MCL. Careful data sorting gave only 90 data. The rest of them (14 data points) were not considered to be useful because they lack analyses of most major ions.

Of the 90 data points reported only 21 have dissolved Cr⁶⁺ concentrations, 24 have dissolved chromium concentrations, and 72 have total chromium concentrations (Appendix A). The detection limit for dissolved chromium, dissolved Cr⁶⁺, and total chromium are 5 µg/l, 1 µg/l, and 10 µg/l, respectively. The average of chromium concentrations in the study unit were calculated from dissolved chromium, dissolved Cr⁶⁺, and total chromium values. The detection limit values were not counted to make the average chromium contents because they are not reliable in making the calculations. The average chromium concentrations were used in Chemplot and Piper analyses.

Relationship of pH and Chromium Concentrations

The pH range of water samples from the study unit is between 6.0 to 9.5 (Parkhurst et al., 1989). Almost 25.6% of those data (23 of 90 data points) did not have the pH values reported. The lowest pH value is 7.6 and the highest is 9.1, with the average of 8.3, indicating the alkaline environment. When pH was plotted against chromium, the points exhibit an appreciable degree of scatter (Figure 13). All elevated chromium concentrations lie above pH 7.6. The regression line is: $\text{pH} = -0.0044 \text{ Cr} + 8.3945$. The line itself indicates that the chromium concentration decreases very little as the pH increases. This result

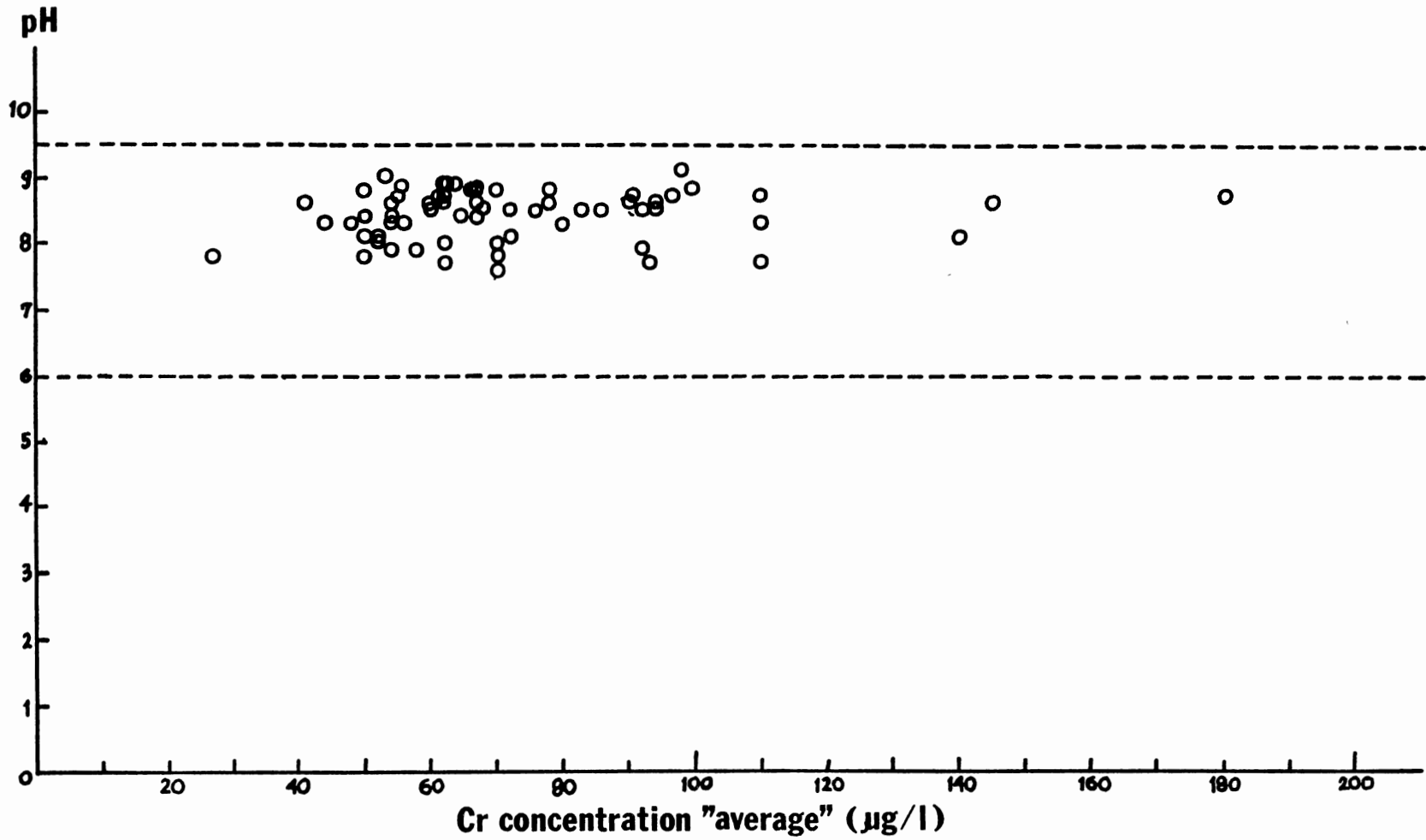


Figure 13. Chromium Concentration "Average" vs. pH

indicates that the effect of pH on the chromium concentration in the Central Oklahoma aquifer was not very significant.

The Results from Chemplot v. 1.31

The Chemplot v. 1.31 (Hounslow, 1991) was used to look at "histograms" areal distributions of elevated chromium concentrations and other variables. The data used to input into the program were listed in Appendix C. The results of Chemplot v. 1.31 were areal distributions of Cr (averaging of dissolved, total, dissolved Cr⁶⁺), pH, Fe, Mn, As, Se, Ca, Mg, Ba, Na, K, Cl, SO₄, temperature, hardness, and specific conductance (Appendix C).

Tabulated data on areal distributions of those parameters are listed in Table XI. Each cross (x) in this table represents significant (high) value of each parameter. Only 44 data points were used as inputs into Chemplot v. 1.31. These data points represent 44 wells that have elevated chromium concentrations. Each well has several data that come from different sampling depth (Appendix A and B). For wells which have more than one data point, the average value from different sampling depths was used for that particular data point (well).

Elevated chromium concentrations are clustered around wells in Edmond, northern Oklahoma City, around Moore, northern Norman, and near Lake Thunderbird. Some were found on several places, i.e., at the border of Kingfisher-Logan County, in Oklahoma County, in Cleveland County, and in Pottawatomie County. Cleveland County has 44 data of elevated chromium concentrations, followed by Oklahoma County (37 data), Logan County (8 data), and Pottawatomie County (1 data), respectively (Appendix B). Chromium areal distribution was similar to the areal distributions of As, and specific

TABLE XI
RESULTS FROM CHEMPLOT V. 1.31

Parameters	Areal Distribution				
	Edmond	OKC	Moore	Norman	Lake Thunderbird
pH	X	X	X	X	X
Temperature	X	X			
Specific Conductivity	X	X	X	X	X
Hardness	X	X	X	X	X
Cr	X	X	X	X	X
Fe					X
Mn					X
As	X	X	X	X	X
Se	X	X	X	X	X
Ca	X	X	X	X	X
Mg	X	X	X	X	X
Ba	X	X	X	X	X
Na		X		X	X
K				X	X
Cl	X	X			X
SO ₄		X		X	X

conductance. The areal distribution of Fe was similar to that of Mn and was distributed near Lake Thunderbird (the highest). The areal distribution of Ca, Mg, Ba, and hardness are alike. The areal distribution of K is similar to that of southern part of specific conductance areal distribution. The areal distribution of Na is similar to the areal distribution of Cl and SO₄.

Most of the elevated chromium concentrations occurred in wells completed in Hennessey Group, the other elevated concentrations of major ions and parameters were found in wells completed in the Garber Sandstone and terrace

deposits. The highest dissolved Cr(VI) concentration was found in the Hennessey Group, whereas the highest dissolved, total, and average chromium concentrations were found in the Garber Sandstone.

The location of the maximum value of each parameter involved in the study are listed in Appendix D. This grouping of major parameters based on their maximum values were used in conjunction with Chemplot results. The results of grouping of major ions and parameters based on their maximum values were not identical with the results from Chemplot, but some similarities were found. For example, grouping (Appendix D) has shown that the highest Fe and Mn are found in well 09N-01W-13 CDC 1. Results from Chemplot also have shown the highest Fe and Mn at this location (near Lake Thunderbird). The same similarity also was found for Ca, Mg, Ba, and hardness. Their highest concentrations are found in well 07N-04W-31 CCC 1 or the upper right corner on Chemplot (Appendix D and C). These similarities are not identical because (1) average value used in Chemplot (44 data) would not have the same value as any individual data used in grouping effort (90 data); (2) Chemplot looks at the pattern of clustering of each major ions and parameters; (3) grouping effort could not give the pattern of clustering of each major ions and parameters.

The Results from Piper Plot

A Piper plot of 18 water analyses from the Central Oklahoma aquifer that have elevated chromium concentrations is presented in Figure 14. These 18 water analyses (20% of 90 total data) were used because the analyses were complete. The rest of the water analyses (72 data points) were not included in the Piper analysis because most of them only have hardness, pH, specific conductance, and detection limits of Cl and SO₄ reported. The two lower

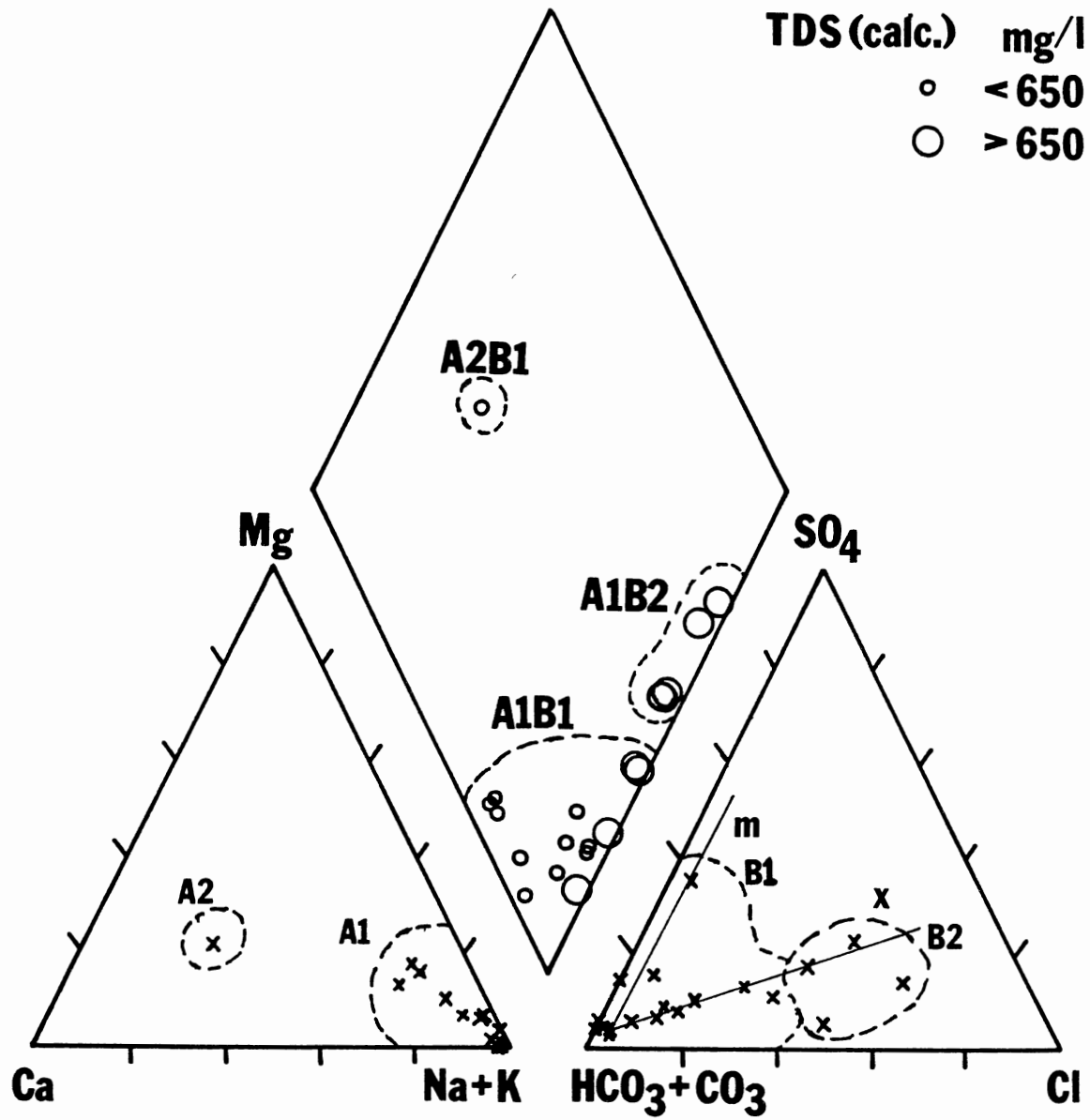


Figure 14. Piper Plot of Area of Elevated Chromium

triangles represent relative percentages of cations and anions (meq/l), respectively. Points in the upper diamond translate each cation-anion pair into a single point representing the entire analyses.

Cations plot in two distinct parts of the triangle (A1 and A2). Area A1 containing most of the 18 water data is characterized by a high percentage of Na+K, with Ca and Mg accounting for a minor percentage of the total cations. The series of water analyses in area A1 are likely lying on a straight line. This line passes through Na+K corner when extrapolated. This trend indicates addition or removal of Na+K, Ca, and Mg. Area A2, containing only one data, is characterized by approximately 27% Na+K, 52% Ca, and 21% Mg. Cation exchange process might exist but no data in between area A1 and A2 to support the interpretation.

The majority of points in the anionic triangle plot in the two regions: (1) Area B1 is where HCO_3+CO_3 comprises more than 50% of the total anion with a minor percentage of Cl and SO_4 ; (2) Area B2 is where Cl comprises more than 40% of the total anion with a minor percentage of HCO_3+CO_3 and SO_4 . Both extrapolated lines in this triangle pass through HCO_3+CO_3 corner with the other end of lines going to SO_4 corner and near Cl corner. B1 likely has a relation with B2. Trends in this triangle suggest mixing process (line m and x) (Figure 14).

Area A1B1 is alkali-carbonate water. This area is characterized by predominant Na and HCO_3+CO_3 with minor Cl and SO_4 . Waters represented by these points may be involved in ion exchange and mixing. Cation exchange process provides sodium to substitute calcium and magnesium after carbonate dissolution. This would infer the presence of sodic-rich clays in the sediments. In Chapter II, it was shown that kaolinite and illite were the only clays detected in the cores. Chloride might occur as chloride contamination from brines or

halite dissolution. Thus, a change in mineralogy of the subsurface environment must be assumed if cation exchange is taken to be the mechanism responsible for high sodium concentrations in the water. In the Garber Sandstone and Wellington Formation, the source of sodium may have been weathering of plagioclase which are found associated with dolomite (McBride, 1985; Breit et al., 1990).

Area A1B2 is saline water. This area is characterized by predominant Na and Cl with minor SO_4 and HCO_3+CO_3 . The analyses may represent areas where dissolution of halite and/or brine contamination contribute to the ionic make-up of the water. Areas A1B1 and A1B2 show continuous straight line on the lower right side of diamond shape diagram. This would also infer the mixing process and ion exchange processes in the study area.

Point A2B1 is water that has temporary hardness. This point is characterized by predominant Ca and HCO_3+CO_3 with moderate Cl and minor Na, Mg and SO_4 . This water might come from the dissolution of carbonate rocks.

Carbonate dissolution and plagioclase weathering play an important role in making up water type in the Central Oklahoma aquifer. Both processes provide calcium, HCO_3+CO_3 , and sodium to the subsurface environment. Usually montmorillonite must be present to provide sodium for exchanging with calcium. Depth to the base of fresh water in the Central Oklahoma aquifer range from 500 to 1,000 feet below the land surface. Some water samplings in the study area reach 796 feet below the land surface. Thus, in some places brine might cause chloride contamination (mixing process) with the fresh water. Small amounts of sulfate may come from barite or gypsum dissolution. This small percentage may happen because sulfate is used as a competing solute to consume adsorption sites, in this case amorphous iron oxides surfaces (see

Discussion). Sulfate consumes adsorption sites and renders the iron oxides surfaces more negative in charge, so, the surfaces become more limited for the adsorption of Cr(VI). The presence of sulfate, bicarbonate or dissolved silica can decrease Cr(VI) adsorption on amorphous iron oxides surfaces (Chapter III).

A wide variety of water compositions were observed in the shallow zone and the patterns are closely related to the geologic units (Parkhurst et al., 1989). Overlaying Figure 12 on the map of shallow-zone ground water, the elevated chromium concentrations mostly lie on Na-HCO₃ water-type (I), moderate amount of data lie on Ca-Mg-HCO₃ water-type (II), a few data lie on Ca-Mg-Na-HCO₃-Cl-SO₄ water-type (III), and one data point represents the Ca-Mg-Na-HCO₃-Cl water-type (IV) (Figure 15). The first, the second, and the third water-type are almost always found in the Hennessey Group. The fourth water-type (Ca-Mg-Na-HCO₃-Cl) is found exclusively in Garber Sandstone and Wellington Formation. Several of the second water-type can be found in Garber Sandstone and Wellington Formation; very little water has the first and the third water-type.

Only wells completed in the Garber Sandstone and Wellington Formation were included in the deep zone because almost no wells are completed in the other geologic units (Parkhurst et al., 1989). The deep zone also exhibits a variety of water compositions as shown on Figure 16. In west-central Oklahoma County, large concentrations of sulfate, chloride, and bicarbonate are common. Along the southwestern edge of Cleveland County, sulfate is found in large concentrations and bicarbonate concentrations are larger than elsewhere in the study unit. In this zone, most of the data lie on Hennessey Group that has most of the water-type (Ca-Mg-HCO₃, Na-HCO₃, Ca-Mg-Na-HCO₃, Na-HCO₃-SO₄,

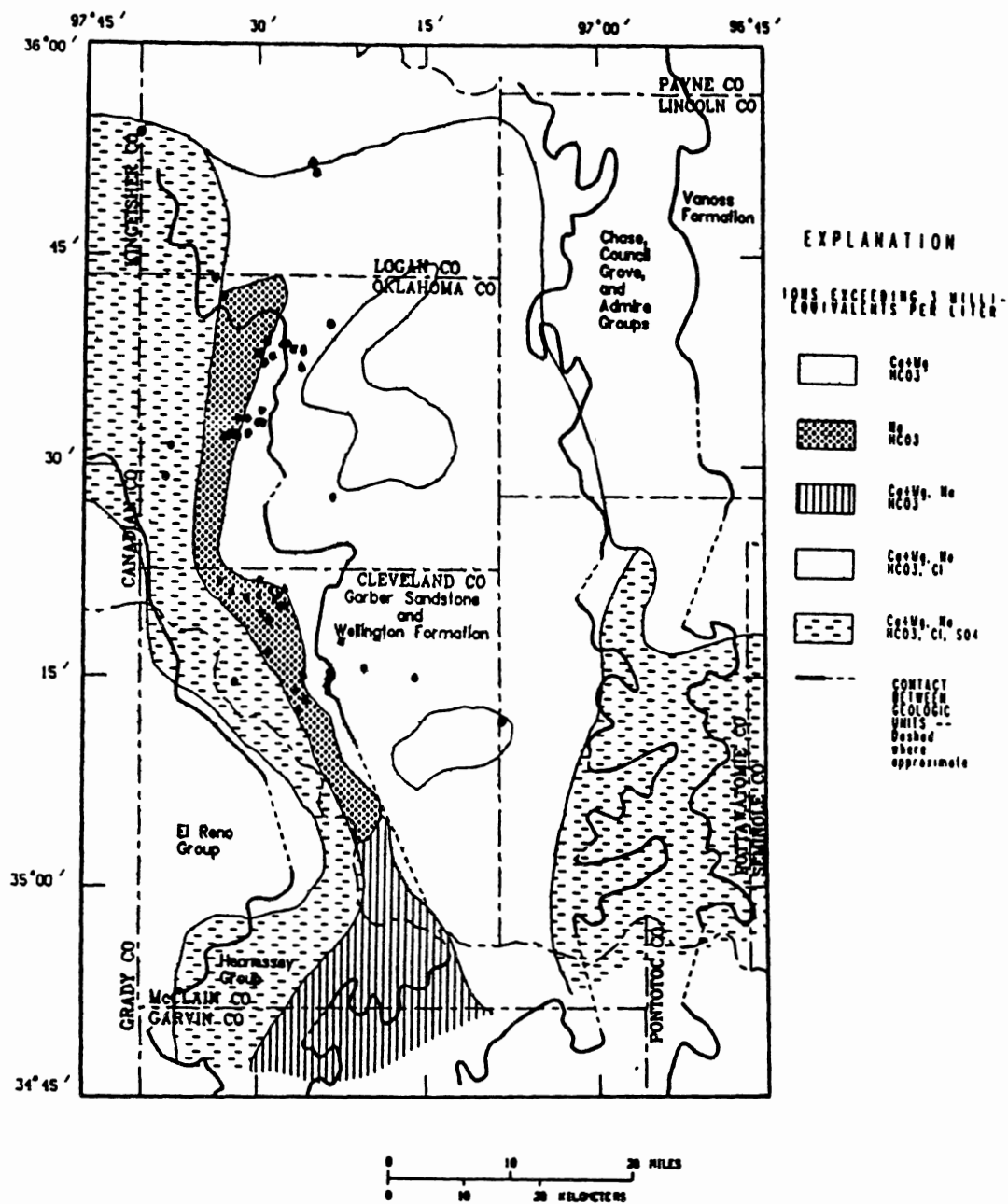


Figure 15. Major-ion chemistry in the shallow zone of the study unit. • represents wells that have elevated chromium (dissolved, dissolved Cr⁶⁺, and total) concentrations (Parkhurst et al., 1989 and author, 1992)

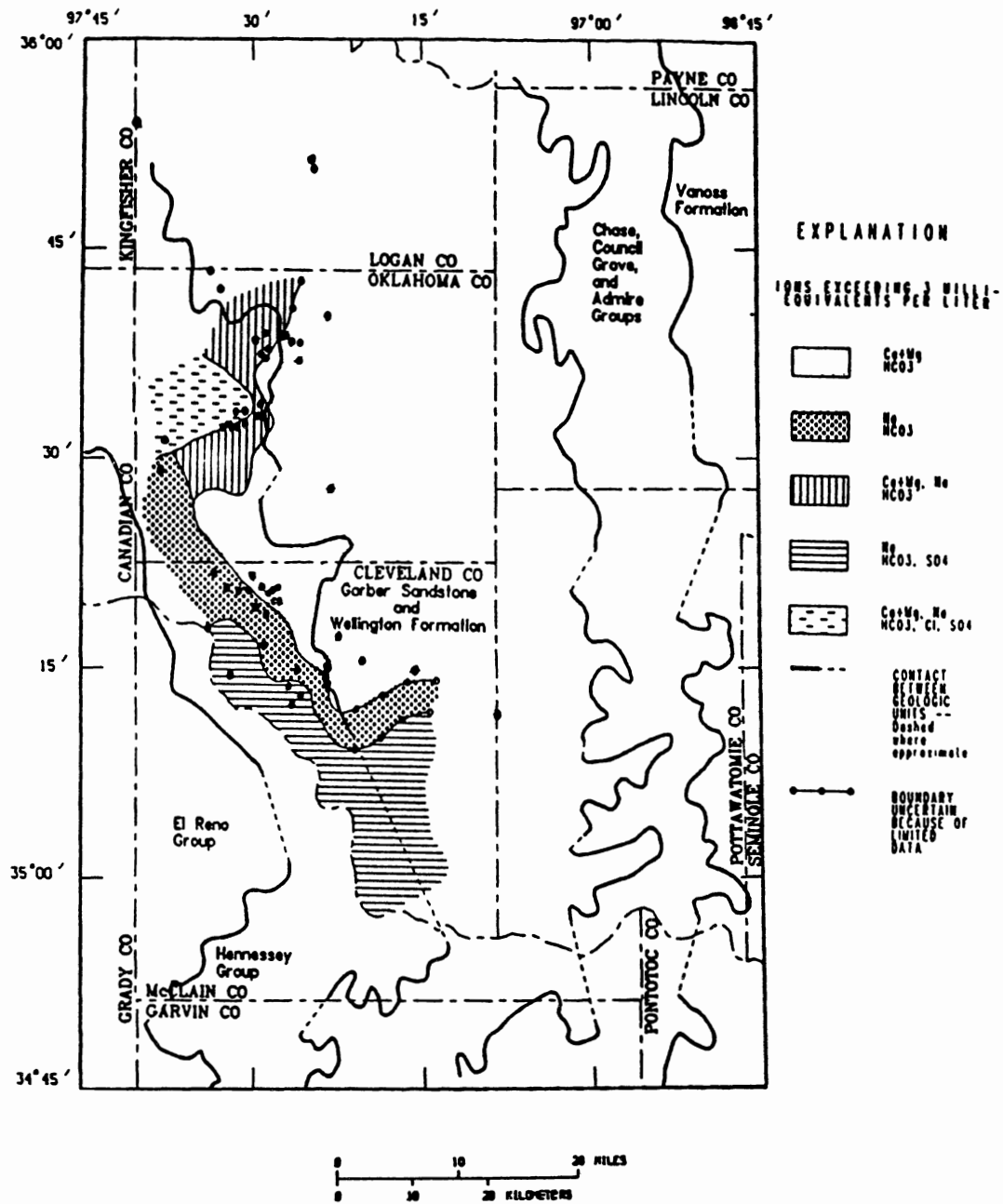
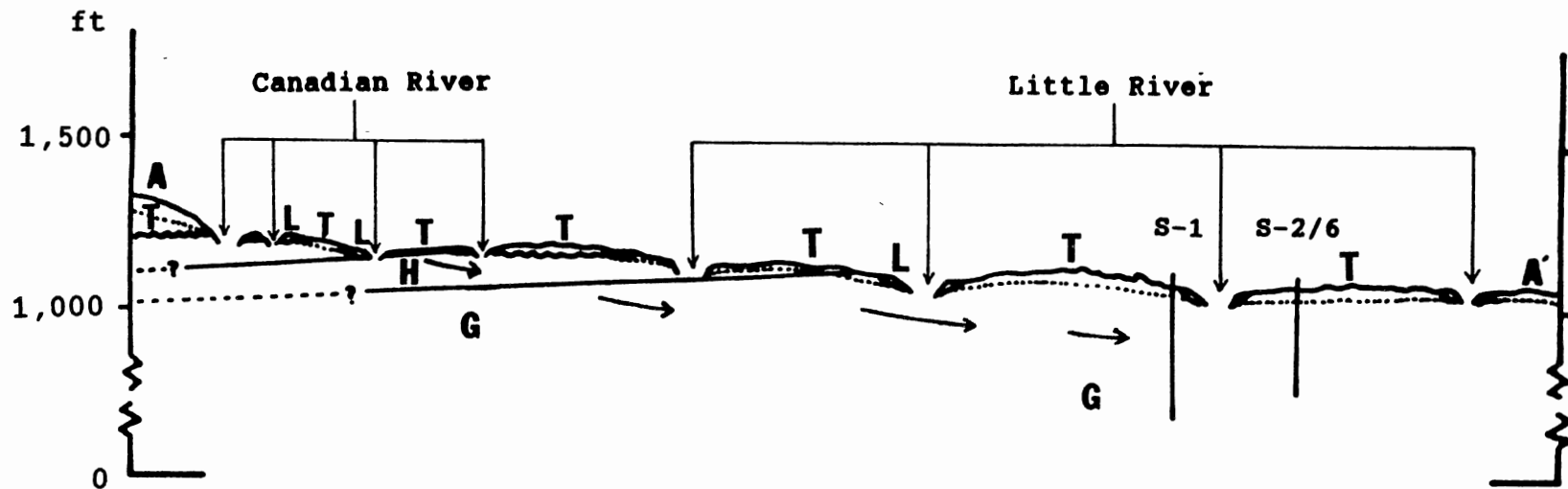


Figure 16. Major-ion chemistry in the deep zone of the study unit. • represents wells that have elevated chromium (dissolved, dissolved Cr^{6+} , and total) concentrations (Parkhurst et al., 1989 and author, 1992)

and Ca-Mg-Na-HCO₃-Cl-SO₄). Most data in Garber Sandstone and Wellington Formation is the Ca-Mg-HCO₃ watertype.

Geologic cross-section (A-A') (Figure 17) passes two wells on the eastern part of the study unit: (1) well 09N-01W-08 CCC 1 has sampling depth of 695 feet; (2) well 09N-01W-13 CDC 1 has sampling depth from 455 to 615 feet. In southern Cleveland County about 25% of the total thickness of the sequence is sandstone (Wood and Burton, 1968). If this statement is taken as an assumption, then 695 feet and 615 feet sampling depth would have 521.3 feet and 461.3 feet of red clay shales and red sandy shales from the Garber Sandstone sequence. With the geologic units dip 50 feet per mile to the west and recharge direction to the east, recharge likely affects the precipitation or dissolution and adsorption or desorption process in this part of the Central Oklahoma aquifer. Later, the combination of these processes affects the fluctuation of chromium concentration releases into the Central Oklahoma aquifer (see Discussion).

Results from Piper analysis are not exactly the same as the previously mentioned figures (Figures 15 and 16). Piper analysis shows three water-types: Na-HCO₃, Na-Cl-HCO₃, and Ca-Na-Cl-HCO₃. Figures 15 and 16 show more water-type varieties with more major ions taken into several water types, such as Ca-Mg-HCO₃ water-type, Na-HCO₃-SO₄ water-type, Ca-Mg-Na-HCO₃ water-type, Ca-Mg-Na-HCO₃-Cl water-type, and Ca-Mg-Na-HCO₃-Cl-SO₄ water-type. This difference might occur because the Piper analysis in this thesis only considered 18 complete water analyses, each having elevated chromium, in the Central Oklahoma aquifer. However, Figures 15 and 16 use all water analyses in the Oklahoma Geological Survey data base.



Horizontal scale: 1 : 250,000
 Vertical scale : 1 : 6,000

Explanation:

- L = alluvium
- T = terrace deposits
- H = Hennessey Group
- G = Garber Sandstone
- S-1 = sample no. 1 at well no. 1 (see Appendix A)
- S-2/6 = sample no. 2-6 at well no. 2 (see Appendix A)
- = water table
- = ground water flow

Figure 17. Geologic Cross-Section (A-A')

Results from Factor Analysis

Factor analysis used in this work was performed by using a standard program developed by Hounslow (1990) on an IBM-compatible PC installed at the School of Geology, Oklahoma State University. It is used to explain the trend or relationship of major constituents within the Central Oklahoma aquifer. Five attempts were made in order to get the ionic relationships between chromium and other major elements or other variables, but only three groups display more reasonable relationships.

Group 1 (Cr, Ca, Mg, Na, K, Ba, Hardness)

Appendix B listed all the variables that were loaded into factor analysis group 1. The results are listed on Table XII. Two factors explain about 68.4% of the total variance of the data set and the following observations were made.

TABLE XII
FACTOR LOADINGS OF GROUP 1

Variable	Factor 1	Factor 2
Cr	-0.2465	0.5413
Ca	0.9293	0.0473
Mg	0.9238	0.2463
Na	0.2109	0.7908
K	0.3668	0.6283
Ba	0.9052	0.1086
Hardness	0.6434	-0.4549
Variance explained by each factor		
	45.5718%	22.7816%

Factor 1, accounting for 45.57% of the total data variability predominantly measures the Ca, Mg, Ba, and hardness. Factor 2, accounting for 22.78% of the total data variability predominantly measures the Na and K. Both variables have positive loadings.

Factor analysis of Group 1 indicates dolomite, calcite, gypsum, and barite solution results in the appearance of ionic Ca, Mg, and Ba, and water hardness in the Central Oklahoma aquifer. The relationship of Na and K is not clear and can only be explained as either the product of micas and alkali feldspars alterations under alkaline conditions or halite dissolution and brine mixing near the base of fresh water.

Group 2 (Cr, Fe, Mn, Ca, Na, Cl)

Appendix B listed all the variables that were loaded into factor analysis Group 2. The results were listed on Table XIII. Three factors explain about 81.8% of the total variance of the data set and the following observations were made.

Factor 1, accounting for 34.80% of the total data variability predominantly shows close relationship of Fe and Mn in the study area. Both variables have high positive loadings. Factor 2, accounting for 28.69% of the total data variability predominantly measures the Na and Cl. Both variables have high positive loadings. At last, factor 3 consists of moderate positive Cr loading and moderate negative Ca loading. Both variables account for 18.31% of the total variability data.

In the Central Oklahoma aquifer there is one factor (Ca) that directly controls the mobility of chromium in the environment. Ionic Ca likely comes

TABLE XIII
FACTOR LOADINGS OF GROUP 2

Variable	Factor 1	Factor 2	Factor 3
Cr	0.2610	0.2496	0.7129
Fe	0.9784	0.1367	0.0614
Mn	0.9819	0.1497	0.0184
Ca	0.1252	0.2807	-0.7631
Na	0.2868	0.8354	-0.0624
Cl	0.0215	0.9171	0.0186
Variance explained by each factor			
	34.7988%	28.6882%	18.3143%

from the dissolution of carbonate rocks (dolomite or calcite) in the aquifer. This assumption is supported by the evidence of their irregular existence throughout the nine test cores in the study unit. Moreover, the quartz grains usually cemented by hematite, manganese oxides, and dolomite. Waters characterized by high Na-Cl are most likely the result of dissolving localized halite deposits or of mixing with salt water at the base of the aquifer.

In Chapter III it was shown that Ca is more mobile than Fe, Mn, and Cr; that iron oxide accompanies manganese oxides in various natural precipitation; that oxidation of Cr(III) to Cr(VI) occurs by reaction with pyrolusite (beta-MnO₂); and that the adsorption of Cr(VI) on the iron oxide surface can be reduced by sulfate and bicarbonate in the environment. Thus, this factor illustrates the indirect relationship between Cr and Fe-Mn oxides in the Central Oklahoma aquifer. It is likely that sulfate and bicarbonate, available from gypsum, barite,

and dolomite dissolutions, consume the adsorption sites on the Fe-Mn oxides and allow Ca to be present with oxidized chromium.

Group 3 (Cr, Fe, As, Se, Ca, Na)

Appendix B listed all the variables that were loaded into factor analysis Group 3. The results were listed in Table XIV. Three factors explain about 74.8% of the total variance of the data set and the following observations were made.

TABLE XIV
FACTOR LOADINGS OF GROUP 3

Variable	Factor 1	Factor 2	Factor 3
Cr	0.2579	0.5926	-0.5532
Fe	-0.1003	0.8894	0.1116
As	0.8778	-0.1175	0.1999
Se	0.8306	0.1469	-0.2751
Ca	0.0530	0.1087	0.7734
Na	0.5139	0.5256	0.4310
Variance explained by each factor			
	30.0654%	24.4261%	20.3002%

Factor 1, accounting for 30.06% of the total data variability predominantly measures the Se and As of study area. Both variables have high positive

loadings. Factor 2, accounting for 24.43% of the total data variability predominantly measures the Cr and Fe. Fe has high positive loading while Cr has moderate positive loading. Factor 3 consists of moderate negative Cr loading and moderate positive Ca loading. Both variables account for 20.3% of the total variability data.

Once again Cr and Ca show a direct relationship. Fairly large area of Ca's stability in the environment enables it to be present with oxidized Cr. Fe and Cr relationship emerges as the result of adsorbed Cr on Fe oxide surfaces. As and Se are enriched in the hydrolyzate sediments, specifically, adsorbed onto aluminum hydroxides (clays). Under most natural Eh-pH conditions in ground water, they would be tied up in the sediments and not released to the water. The desorption of these elements is accomplished primarily under high oxidizing condition (Rankama and Sahama, 1950). This process also holds true for Cr. Thus, As and Se existence may also relate to Cr existence in the Central Oklahoma aquifer although factor analysis failed to show it.

The Eh of the Central Oklahoma Aquifer

The Eh-pH diagrams for Fe, As, Se, U, and V (from Brookins, 1988) were used in conjunction with data listed on Table II (p. 24). Estimation of Eh range on those diagrams can be pointed out by giving the pH range that is existed in the Central Oklahoma aquifer and by combining it with the trace minerals or ions found in the aquifer.

Arsenic occurs in brown iron oxides and pyrite in test hole 1. Pyrite (FeS_2) is a widespread mineral under reducing environment. The Eh required for the formation of pyrite decreases with increasing pH, and it can be seen from Figure 8 (p. 59) that at the given pH values, the Eh of the system need only be between

-0.15 and -0.32 volts for pyrite to form. At these ranges of Eh and pH, HAsO_4^- is likely found (Figure 18). Arsenic in some minerals is present as As(II), in which case it substitutes readily for S(II).

Detrital chromite (FeCr_2O_4) was found in test hole 2 at a depth of 131.1 feet. Chromite ion (CrO_2^-) can only be found at reducing and very high pH (>13) environment, and it is not likely the case in the Central Oklahoma aquifer. From Figure 10 (p. 62), it is clear that at the given pH range, Cr(VI) ions will appear if the range of Eh falls near or beyond 0.26 to 0.47 volts. It indicates the oxidizing environment.

Native selenium was found in test hole 6. The field of native selenium encompasses a large area on the Eh-pH diagram (Figure 19). At the given pH range, slightly oxidizing environment (-0.03 to 0.17 volts) is sufficient to develop native selenium. McBride (1985) found that the Eh of the Central Oklahoma aquifer need only be between 0.26 and 0.36 volts for selenate (SeO_4^{2-}) to form, giving the pH range of 8.1-9.2. These conditions did not indicate a uniform redox process in the Central Oklahoma aquifer.

Using Figure 20, it is not easy to predict the Eh of uranium species in the Central Oklahoma aquifer. The test-holes data does not give much information on what minerals really exist in the Central Oklahoma aquifer. Uranium-silica spheres were found in test hole 6, tyuyamunite ($\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 7-10\text{H}_2\text{O}$) was found in test hole 7, and an unidentified uranium-titanium phase was found in test hole 2. In the presence of Si, an important field of coffinite (as USiO_4) appears. At pH 7.6 to 9.1, the Eh needed to build this phase will be in the range of -0.05 to -0.27 volts (at $a_{\text{Si}} = 10^{-1}$). Some cogenetic coffinite-pyrite is likely found if the sulfide-sulfate line crosses this phase at pH 7 and 8.

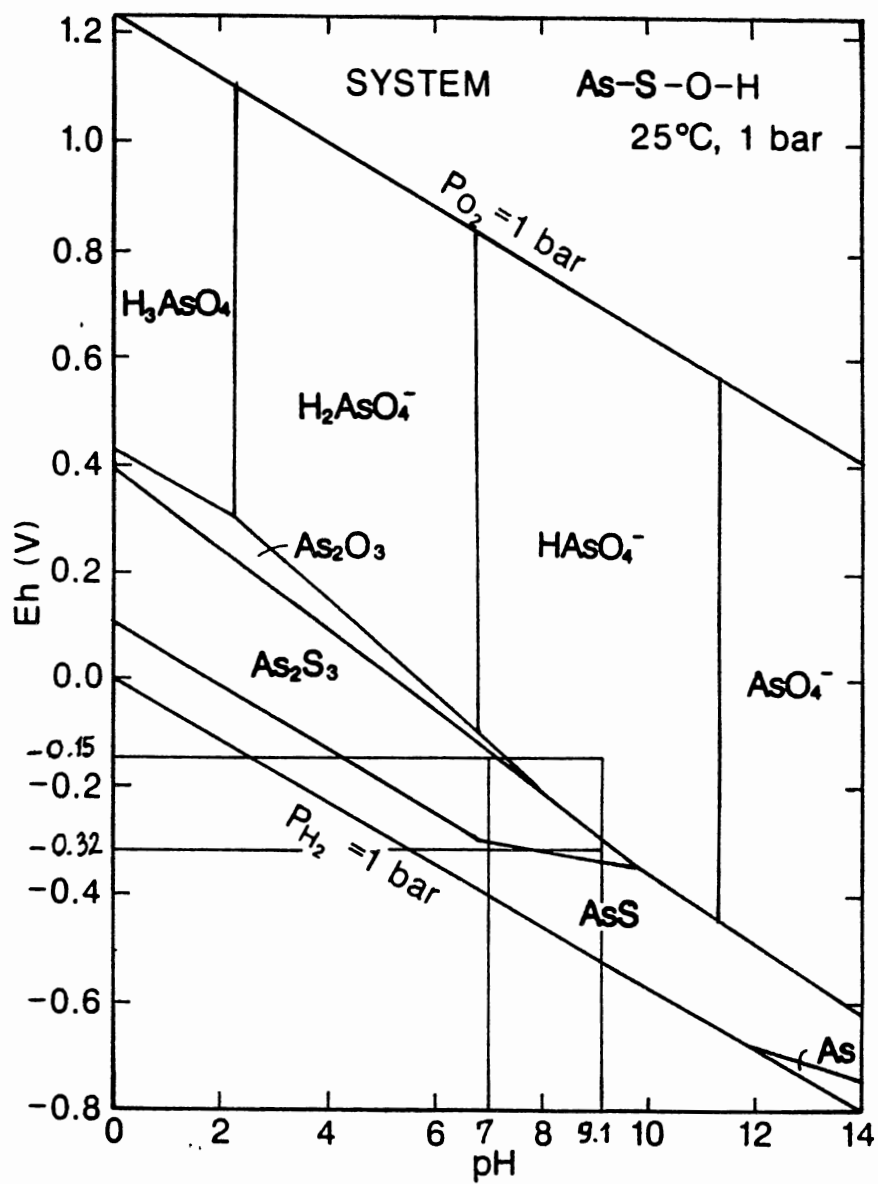


Figure 18. Eh-pH diagram part of the system As-S-O-H.
The assumed activity of dissolved As= 10^{-6}
(Brookins, 1989)

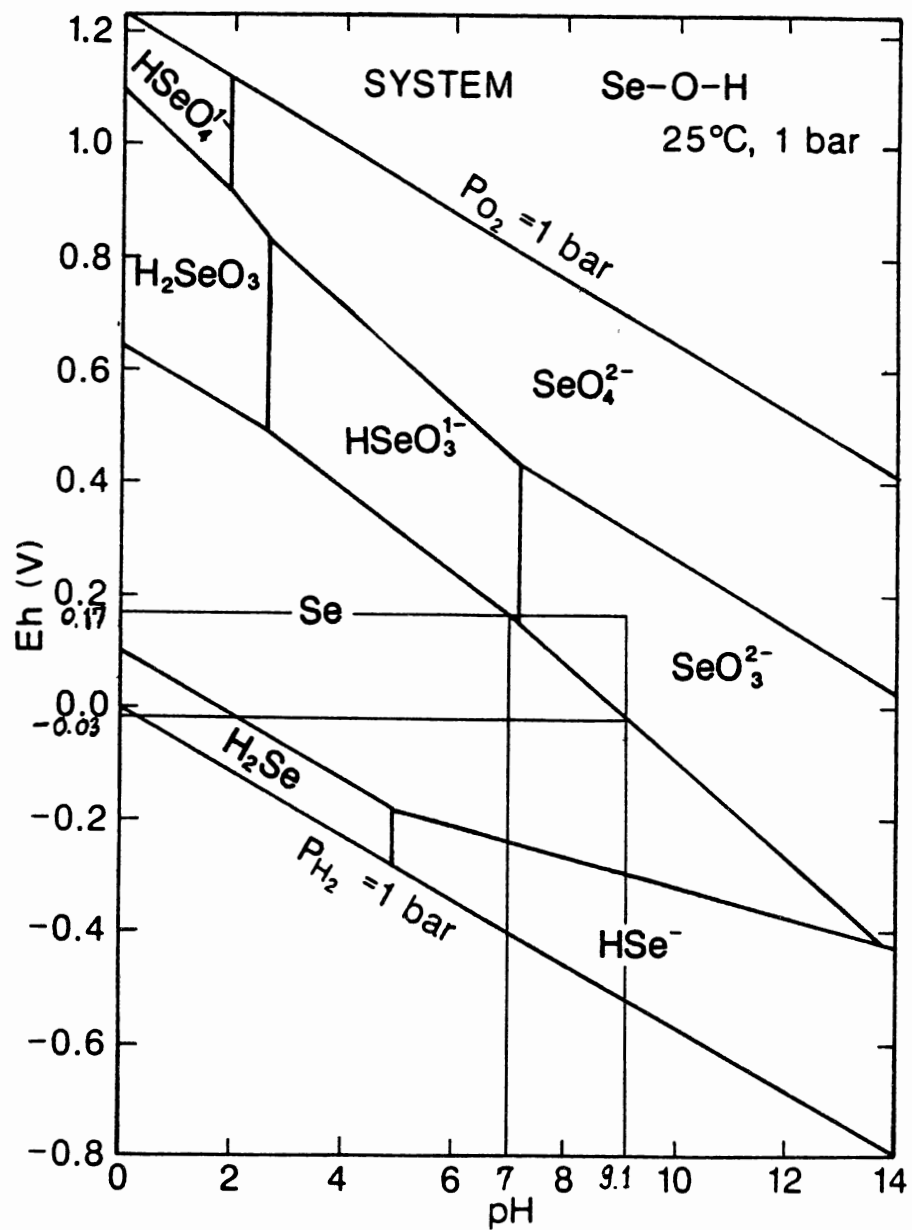


Figure 19. Eh-pH diagram for part of the system Se-O-H. The assumed activity of dissolved Se= 10^{-6} (Brookins, 1989)

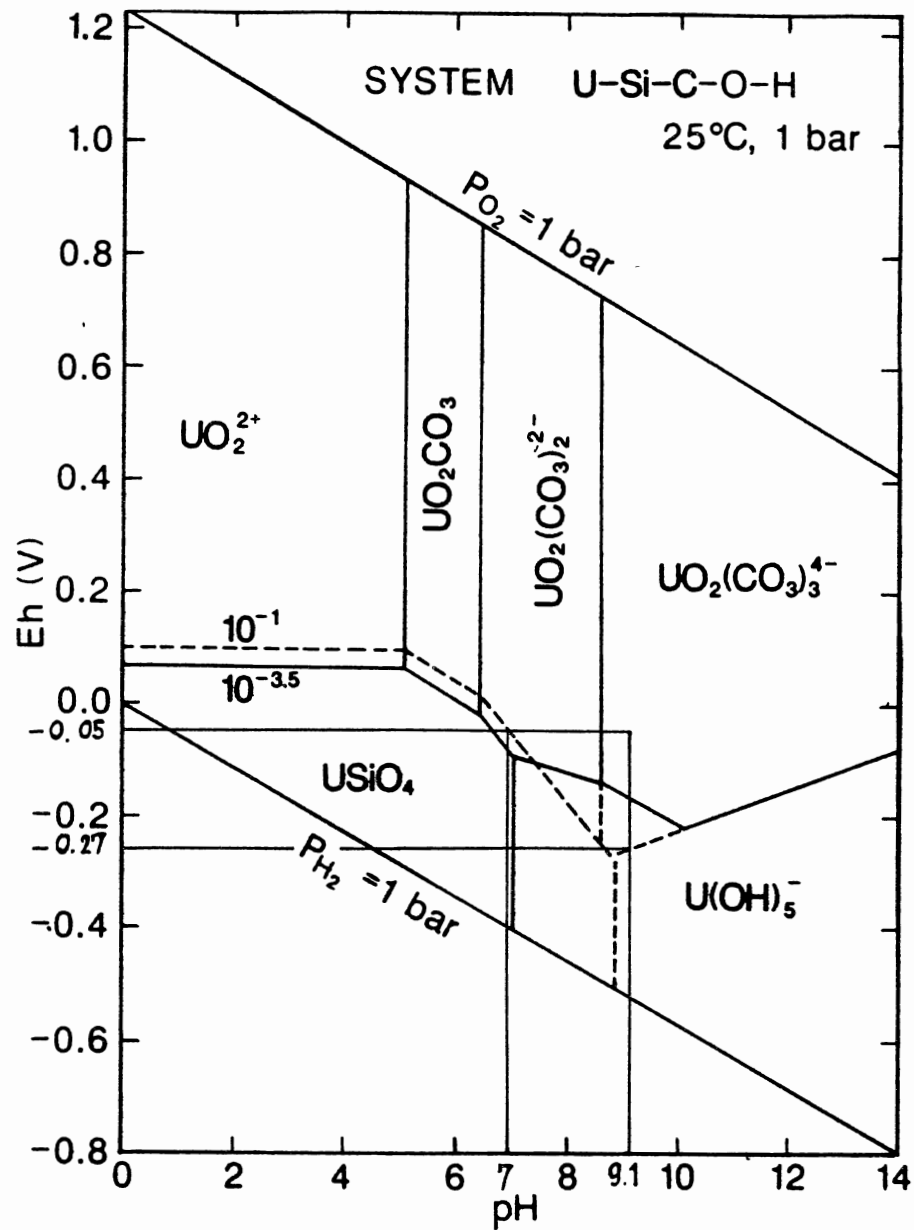


Figure 20. Eh-pH diagram for part of the system U-Si-C-O-H. Assumed activities for dissolved species are: $U=10^{-8}$, $C=10^{-3}$, $Si=10^{-3.1}$ (Brookins, 1989)

Vanadium oxides were found in test holes 6 and 7. In many instances, the V(III, IV) does not enter separate oxides but is rather incorporated into the octahedral sites of clay minerals (Brookins, 1988). The Eh values will be found in the range of -0.13 to -0.27 volts (Figure 21).

In summary, the Eh of the Central Oklahoma aquifer lies in the range of -0.27 to -0.15 volts and in the range of 0.26 to 0.36 volts, indicating both reducing and oxidizing environments. In the western third of the Central Oklahoma aquifer, chromium and selenium more likely occur in the oxidizing environment as chromate and selenate ions, respectively. Arsenic, uranium, and vanadium are more likely released into the Central Oklahoma aquifer in the reducing conditions. Thus, redox conditions of this aquifer control the mobility of trace metals that are adsorbed on the iron oxyhydroxides surfaces.

Discussion

The general composition of most common rock types in the Central Oklahoma aquifer is predictable. Limestones and associated dolomites are largely calcium and magnesium carbonates. Shales and clays are rich in aluminum silicates and usually have a complex trace-element chemistry because of the wide range of metal substitutions that are possible. Sandstones, in absence of matrix and cement, are rich in silica and commonly have low abundances of trace elements because of their relatively high permeability. Low contents of already existing trace elements may be leached by percolating water.

Approximately 60% of solid constituents of the aquifer consist of clay- and silt-sized particles. In southeastern Oklahoma County, about 75% of the total thickness of the sequence in the Garber Sandstone and Wellington Formation

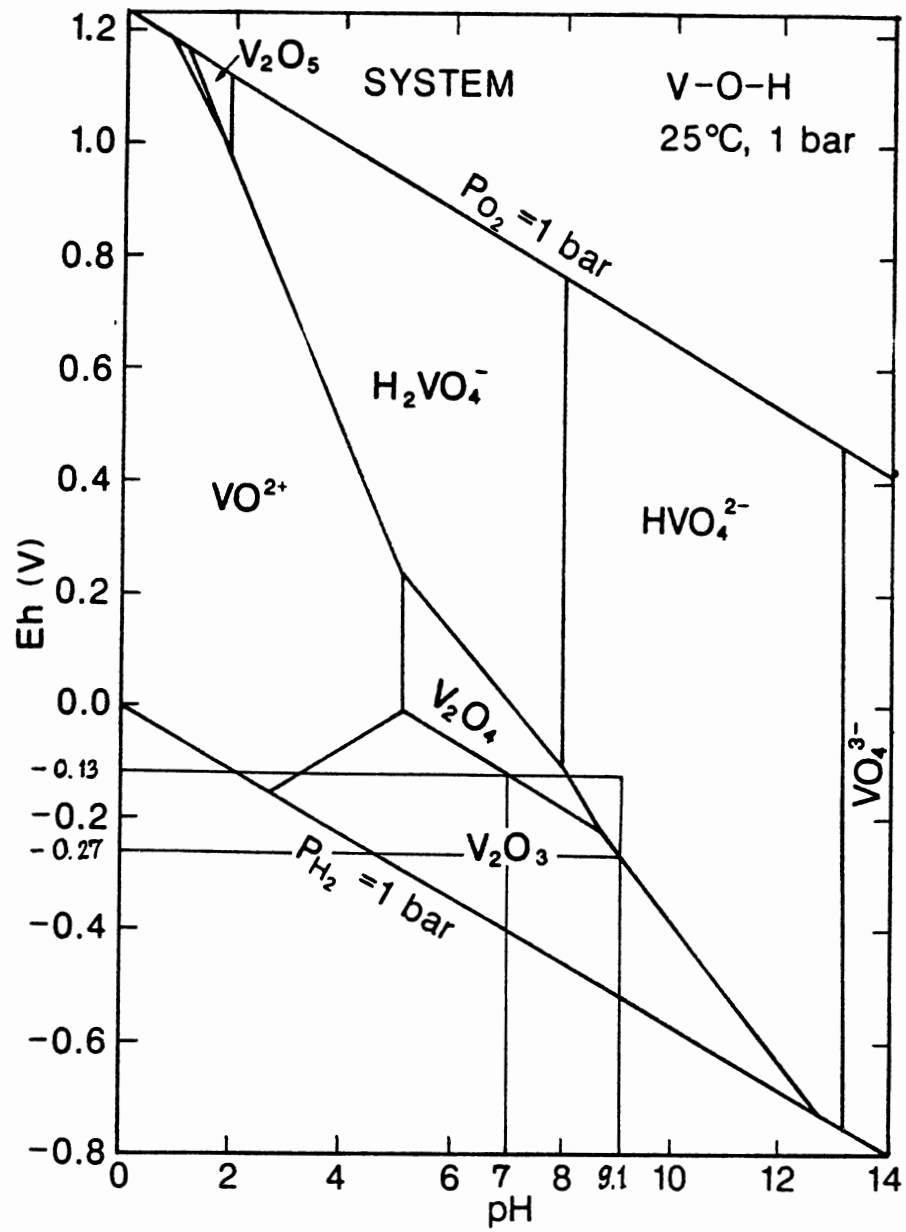


Figure 21. Eh-pH diagram for part of the system V-O-H. The assumed activity for dissolved V=10⁻⁶ (Brookins, 1989)

is sandstone; however, beyond this area the percentage of sandstone decreases, and the percentage of siltstone and shale increases. From Chapter III, it was known that chromium most likely being concentrated on smaller particle-sized fractions. Moreover, lithology of the western third of the study unit is controlled by the distribution of Hennessey Group and Garber Sandstone, which primarily consists of fine-sized particles. Therefore, the area of elevated chromium contents is closely related to the geologic units.

Water-type results from WATEVAL (Piper plot) do not perfectly coincide with the major-ion chemistry map of the study unit either in the shallow zone (Figure 15, p. 82) or in the deep zone (Figure 16, p. 83). Piper analysis comes up with three water-types: Na-HCO₃, Na-Cl-HCO₃, and Ca-Na-Cl-HCO₃. Figures 15 and 16 show more water-type varieties with more major ions taken into several water types, such as Ca-Mg-HCO₃ water-type, Na-HCO₃-SO₄ water-type, Ca-Mg-Na-HCO₃ water-type, Ca-Mg-Na-HCO₃-Cl water-type, and Ca-Mg-Na-HCO₃-Cl-SO₄ water-type. This difference might occur because Piper analysis in this thesis only considered 18 complete water analyses with elevated chromium contents in the Central Oklahoma aquifer. The other 72 data points are not sufficient because they lack bicarbonate, carbonate, silica, chloride, density, and total dissolved solid (TDS) data. However, Figures 15 and 16 use all water analyses in the Oklahoma Geological Survey data base. WATEVAL (Piper Plot) and water-type maps approaches lead to the conclusion that Na-HCO₃ and Ca-Mg-HCO₃ water types occur in the area of elevated chromium concentrations. Sodium chloride water also was found in the western third of the study unit. Those water types in the western third of the Central Oklahoma aquifer indicate: dissolution of sodium chloride, barite, and gypsum; mixing processes with brine; and cation exchange processes.

Chemplot shows similar areal distributions for Cr, As, and specific conductance. Other similarities also occur for Fe-Mn, Ca-Mg-Ba-hardness, and Na-Cl-SO₄. Factor analysis provides similar relationships for Fe-Mn, As-Se, Cr-Ca, Ca-Mg-Ba-hardness, and Na-Cl-K. Eh-pH diagrams and factor analysis suggest that the reducing process produces Fe, Mn and As, oxidizing process produces Cr(VI) and Se. Effects of dolomite, calcite, barite and gypsum dissolutions are shown by Ca, Mg, Ba, and hardness relationships. Effect of halite dissolution is shown by Na, K, and Cl relationships. Those ions and parameters are most likely controlling chromium occurrence in the Central Oklahoma aquifer.

Test holes in the study area suggest that the water has been in reducing as shown by several reducing zones in all test holes. However, the existence of chromate and selenate ions suggest that the aquifer, alkaline in nature, is now becoming oxidizing. These facts indicate that the Central Oklahoma aquifer, especially the western third area, is experiencing fluctuations of reduction and oxidation processes.

Uniform redox processes do not prevail in the Central Oklahoma aquifer. It is supported by the Eh-pH evaluation on some trace elements residing in the Central Oklahoma aquifer. On the one side a moderate oxidizing environment causes the release of chromium and selenium, on the other side reducing conditions controlled the mobility of Fe, Mn, As, U, and V. Thus, a combination of pH and Eh plays an important role in releasing chromium into the environment.

Metal ions can occur as trace constituents in the lattice of a mineral formed during weathering, or occluded as a trace mineral in such a phase, or adsorbed on such a mineral and covered over by further precipitation. One of the examples is chromium in the presence of iron or manganese oxides. Controls

on such material will be the stability and properties of the host phase (dolomite and iron or manganese oxides). Because these phases are formed during weathering, they are likely to be chemically stable in many surficial environments. Also, because of the fine-grained size and imperfect crystal lattices of most of these phases, elements in such sites tend to be somewhat accessible to the surrounding solutions.

Most minerals coatings consist of hematite, manganese oxide (MnO_2), and dolomite. Amorphous iron oxides provide large surface area to adsorb Cr(VI), but the capacity is reduced by the existence of bicarbonate, sulfate, and dissolved silica. Interaction between manganese oxide and Cr(III) accelerates the Cr(VI) formation, which depends on pH, Cr(III) concentrations, and availability sites on the manganese oxide's surfaces. On the other hand, small amounts of iron oxyhydroxide can slowly reduce Cr(VI) to Cr(III). Thus, chromium mobility more likely depends on the availability of iron oxyhydroxides, manganese oxide, bicarbonate, and sulfate in the Central Oklahoma aquifer.

From all previous discussion, it is clear that the original source of chromium in the Central Oklahoma aquifer comes from ferromagnesian minerals in red bed sediments. However, processes responsible for releasing elevated chromium concentrations in the western third of the Central Oklahoma aquifer are complex. There are two processes that play important roles: (1) redox process; (2) adsorption/desorption process.

Water recharge to the subsurface with its dissolved CO_2 controls the pH of ground water in the Central Oklahoma aquifer. Reaction between water and dissolved CO_2 produces carbonic acid (H_2CO_3). H_2CO_3 in ground water dissociates into HCO_3^- and H^+ species. Silicate hydrolysis can also control pH. Then, bicarbonate species in the ground water reacts with red bed sediments. Gradually, calcite, dolomite, halite, gypsum, and barite are dissolved. This

dissolution process releases Ca, Mg, Na, Ba, Cl⁻, HCO₃⁻, and SO₄²⁻ ions into the ground water.

Montmorillonitic clays provide exchange surfaces to remove calcium and release sodium. Plagioclase dissolution found in the study unit contributes sodium. The excessive amount of sodium and bicarbonate in the ground water produces the Na-HCO₃ water type. Near the base of fresh water, mixing process between brine and fresh water may occur. Thus, chloride contamination most likely occurs near this area. From the previous paragraph, it is clear that bicarbonate and silicate hydrolyzate use H⁺ which results in alkaline ground water in the western part of the Central Oklahoma aquifer.

Hematite (iron oxide) cement and manganese oxide coatings provide adsorption surfaces for chromium, especially Cr(VI). Manganese oxide will oxidize Cr(III) to Cr(VI), which in turn is adsorbed by iron oxide. Afterward, desorption process can release adsorbed Cr(VI) to the environment, and high pH likely controls the desorption process. Ferrous oxide can reduce Cr(VI) to Cr(III) if pH decreases. SO₄²⁻ and HCO₃⁻ ions can reduce chromium adsorption on the iron oxide surfaces. Major ground water anions such as SO₄²⁻ and HCO₃⁻ ions that are bound to the surface of iron oxide, reduce positive charge, and compete directly with CrO₄²⁻ as sites become limited. The surface reaction with these anions reduces CrO₄²⁻ adsorption. Elevated levels of dissolved CO₂(g) and H₄SiO₄ are known to reduce CrO₄²⁻ adsorption dramatically (Chapter III). High pH then helps to release CrO₄²⁻ to the environment.

Industrial activities almost always provide a major contribution to the concentration and distribution of metals and other substances in the environment. Thus, major chromium-users and chromium-processing industries are often considered to be the main source of elevated chromium

concentrations in the environment. This was not proven in this case because of lack of data by state and county.

In practice, the frequency of reporting is irregular. More importantly, the only information sought is whether certain constituents exceed state or federal standards. As a result, the bulk of data are being reported as a value of "less than" that required for a particular standard, and this does not provide usable information for the researcher. Other equally important factors are: (1) no requirement by the state on elements other than those for which there are specific limitations or standards; (2) no cross-checks for water quality data among various agencies that have conducted the analyses. Consequently, little information is available on those trace elements for which there are currently no standards, and little information is accessible on anions at all, except chlorides, nitrates, sulfates, bicarbonates, and possibly phosphates.

CHAPTER VI

CONCLUSIONS

The conclusions resulting from this study are as follows:

1. The elevated chromium concentrations reported in the Central Oklahoma aquifer are found in the Na-HCO₃, Na-Cl, and Ca-Mg-HCO₃ water-types. These water types occur in the western part of the study unit, in the Garber-Wellington Formation and the Hennessey Group.
2. The ground water of the Central Oklahoma aquifer has experienced cation exchange processes; dissolution of calcite, dolomite, barite, halite, and gypsum; and mixing with brine, which released as major ions Ca, Mg, Na, HCO₃⁻, Cl⁻, and SO₄²⁻.
3. Most elevated chromium concentrations lie almost exclusively in the Hennessey Group and near the Hennessey Group - Garber Sandstone boundary in the western part of the study unit. Chromium has been shown to be concentrated in the smaller particle-size fractions. This size exclusiveness might be caused by the type of lithology and grain size of Hennessey Group (shales and siltstones) and Garber Sandstone (red clay shales, red sandy shales, and red sandstone).
4. Chemplot results show four groups of similar areal distributions of major ions and parameters in the western part of the study unit. These groups are (1) Cr, As, and specific conductance; (2) Fe and Mn; (3) Ca, Mg, Ba, and hardness; and (4) Na, Cl⁻ and SO₄²⁻.

5. From the tabulated data in Appendix D, it is clear that the highest Fe, Mn, dissolved Cr, pH, and dissolved organic carbon (DOC) occur in Cleveland County (well 09N-01W-13 CDC 1). The highest Ca, Mg, Na, Ba, and hardness occur in Logan County (well 17N-04W-31 CCC 1); the highest Se, total Cr, and average Cr occur in Oklahoma County (well 14N-03W-07 DAA 2); the highest Cl⁻, F⁻, and specific conductance occur in Cleveland County (well 09N-01W-08 CCC 1). The highest dissolved Cr(VI), As, dissolved oxygen (DO), temperature, K, and SO₄²⁻ are present in several different wells from those previously mentioned.

6. Factor analysis suggests that several ionic relationships occur. They are Cr-Fe, Cr-Ca, As-Se, Fe-Mn, Na-Cl, Ca-Mg-Ba-hardness, and Na-K. All these major ions control the occurrence of chromium although only Fe, Mn, SO₄²⁻, and HCO₃⁻ affect its mobility.

7. Dolomite, calcite, barite, gypsum, and halite dissolution result in Ca-Mg-Ba-hardness relationships and the Na-Cl relationship in the Central Oklahoma aquifer. Na-K relationship can be explained as either the product of mica and alkali feldspar alterations under alkaline conditions, or halite dissolution and brine mixing near the base of fresh water. Usually, iron oxyhydroxides accompany manganese oxides in the rocks, and factor analysis confirms this relationship. Sulfate, bicarbonate, and silica hydrolysis, available from gypsum, barite, dolomite, and calcite dissolution, consumes the adsorption sites on the Fe-Mn oxides and allows Ca to be present with oxidized Cr. As and Se usually are adsorbed onto clays. The desorption of As and Se occurs primarily under high oxidizing conditions.

8. Uniform redox conditions are uncommon in the Central Oklahoma aquifer. Alkaline, reducing environments readily release arsenic, uranium, and vanadium that are adsorbed on the iron oxyhydroxides surfaces. Alkaline,

oxidizing conditions release chromium and selenium as chromate and selenate ions, respectively. The production of Cr(VI) species by the oxidation process between manganese oxides and Cr(III) is countered by iron oxyhydroxides that reduce Cr(VI) to Cr(III). Cyclic Fe-Mn redox processes control the Cr(VI) mobility in the environment.

9. Oxidation of chromium from the Cr(III) state - which is immobile due to adsorption onto clays and amorphous iron oxyhydroxides - to Cr(VI) state, is occurring as a result of the high pH and the oxidizing conditions in the aquifer. Desorption processes resulting from high pH are responsible for the release of adsorbed Cr(VI) species.

10. From points 3 to 8, it is clear that the original source of chromium in the Central Oklahoma aquifer comes from ferromagnesian minerals in red bed sediments. Iron and manganese oxides provide adsorption surfaces for chromium, especially Cr(VI). Manganese oxides will oxidize Cr(III) to Cr(VI), which in turn is adsorbed by iron oxyhydroxides. Then, high pH controls the desorption process that can release adsorbed Cr(VI) to the environment.

11. The frequency of reporting data is erratic. The only information generally recorded is whether certain constituents exceed the state or federal standards. As a result, the bulk of the data are being reported as a value of "less than" that required for a particular standard, and this does not provide usable information for the researcher.

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APPENDIXES

APPENDIX A

CHROMIUM DATA BASE

CLEVELAND COUNTY

NO.	LOCAL IDENTIFIER	STATION NUMBER	DATE	TIME	SAMPLING DEPTH (ft)	Cr dissolved (ug/l)	Cr(VI) dissolved (ug/l)	Cr total (ug/l)	Cr average (ug/l)
1	09N-01W-08	CCC 1	351543097200601	07-29-86	1216	695	80	-	80.0
2	09N-01W-13	CDC 1	351455097153301	09-23-86	1208	455	110	-	110.0
3	09N-01W-13	CDC 1	351455097153301	09-23-86	1209	475	120	-	120.0
4	09N-01W-13	CDC 1	351455097153301	09-23-86	1210	515	130	-	130.0
5	09N-01W-13	CDC 1	351455097153301	09-23-86	1211	595	80	-	80.0
6	09N-01W-13	CDC 1	351455097153301	09-23-86	1212	615	80	-	80.0
7	09N-02W-15	ADD 1	351518097231801	12-06-84	-	-	-	-	58 58.0
8	09N-02W-15	ADD 1	351518097231801	04-20-83	-	-	-	-	92 92.0
9	09N-02W-15	DDD 1	351452097232201	12-06-84	-	-	-	-	70 70.0
10	09N-02W-17	DCC 1	351458097254901	04-20-83	-	-	-	-	66 66.0
11	09N-02W-17	DCC 1	351458097254901	12-06-84	-	-	-	-	62 62.0
12	09N-02W-22	ADD 1	351426097232201	12-06-84	-	-	-	-	50 50.0
13	09N-02W-22	DDA 1	351409097231801	12-06-84	-	-	-	-	92 92.0
14	09N-02W-22	DDA 1	351409097231801	07-29-87	1120	-	80	-	80.0
15	09N-02W-29	DCA 5	351315097254301	02-17-89	1100	263	<5	-	98 98.0
16	09N-02W-30	ABA 1	351353097264501	12-06-84	-	-	-	-	62 62.0
17	09N-02W-30	ABA 1	351353097264501	10-17-85	-	-	-	-	93 93.0
18	09N-02W-31	DAA 1	351236097262801	04-25-88	1330	-	100	93	- 96.0
19	09N-03W-02	DCA 5	351643097285004	10-17-82	1200	796	-	-	140 140.0
20	09N-03W-20	AAD 1	351438097315101	12-16-77	1500	-	60	-	- 60.0
21	10N-02W-36	CCC 2	351729097221302	10-22-87	1601	-	80	-	- 80.0
22	10N-02W-36	CCC 2	351729097221302	10-22-87	1600	-	70	-	- 70.0
23	10N-03W-07	ABB 3	352148097332101	01-07-85	-	-	-	-	60 60.0
24	10N-03W-10	AAB 1	352148097295201	04-14-83	-	-	-	-	54 54.0
25	10N-03W-12	DDC 1	352100097275001	04-14-83	-	-	-	-	72 72.0
26	10N-03W-12	DDC 1	352100097275001	12-20-84	-	-	-	55	55 55.0
27	10N-03W-12	DDC 1	352100097275001	01-29-85	-	-	-	<50	67 67.0
28	10N-03W-13	BBD 1	352043097282001	04-19-88	0900	-	60	65	- 62.5
29	10N-03W-13	CBB 1	352028097283201	12-20-84	1200	-	-	52	56 54.0
30	10N-03W-13	CBB 1	352028097283201	01-29-85	-	-	-	<50	27 27.0
31	10N-03W-14	BAA 1	352055097290601	12-20-84	1200	-	-	54	57 55.5
32	10N-03W-14	BAA 1	352055097290601	01-29-85	-	-	-	<50	44 44.0
33	10N-03W-15	ACC 1	352035097300701	01-29-85	-	-	-	<50	48 48.0
34	10N-03W-16	ACA 1	352034097310501	01-29-85	-	-	-	<50	41 41.0
35	10N-03W-17	BAA 1	352054097322101	10-24-85	-	-	-	99	100 99.5
36	10N-03W-22	DAD 1	351926097293001	04-18-83	-	-	-	-	76 76.0
37	10N-03W-22	DAD 1	351926097293001	10-17-85	-	-	-	-	83 83.0
38	10N-03W-22	DAD 1	351926097293001	08-04-87	1030	-	70	-	- 70.0
39	10N-03W-24	AAA 1	352001097273601	04-19-83	-	-	-	-	70 70.0
40	10N-03W-24	ABB 1	351957097275901	04-18-83	-	-	-	-	78 78.0
41	10N-03W-24	ABB 1	351957097275901	12-20-84	-	-	-	62	62 62.0
42	10N-03W-24	ABB 1	351957097275901	01-29-85	-	-	-	55	79 67.0
43	10N-03W-26	ADB 1	351853097284701	12-21-84	-	-	-	59	60 59.5
44	10N-03W-26	ADB 1	351853097284701	01-29-85	-	-	-	<50	68 68.0

LOGAN COUNTY -

NO.	LOCAL IDENTIFIER	STATION NUMBER	DATE	TIME SAMPLING DEPTH (ft)	Cr dissolved (ug/l)	Cr(VI) dissolved (ug/l)	Cr total (ug/l)	Cr average (ug/l)
45	14N-03W-06 BB 1	354326097335401	01-15-87	1003	280	-	-	50 50.0
46	14N-03W-06 BB 1	354326097335401	01-15-87	1007	360	-	-	70 70.0
47	16N-02W-21 BAA 3	355118097250001	04-20-88	1301	229	60	-	- 60.0
48	16N-02W-21 BAA 3	355118097250001	04-20-88	1300	229	60	58.00	74 64.0
49	16N-02W-21 BAA 3	355118097250001	04-21-88	1600	176	80	110.00	82 90.7
50	16N-02W-21 BAA 3	355118097250001	04-21-88	1601	176	90	-	- 90.0
51	16N-02W-21 DBD 1	355045097244801	11-14-84	0800	-	-	-	94 94.0
52	17N-04W-31 CCC 1	355355097402301	06-06-88	1400	-	<100	-	<10 50.0

OKLAHOMA COUNTY

NO.	LOCAL IDENTIFIER	STATION NUMBER	DATE	TIME	SAMPLING DEPTH (ft)	Cr dissolved (ug/l)	Cr(VI) dissolved (ug/l)	Cr total (ug/l)	Cr average (ug/l)	
53	11N-02W-02	BAB 1	352750097230001	02-12-85	0956	-	-	-	110	110.0
54	12N-03W-04	CCD 1	353214097313401	12-11-79	1000	-	-	-	61	61.0
55	12N-03W-04	CCD 1	353214097313401	05-20-86	-	-	-	130	160	145.0
56	12N-03W-04	DAD 1	353229097304301	04-25-83	-	-	-	-	56	56.0
57	12N-03W-05	BDA 1	353221097322001	03-13-85	-	-	-	-	66	66.0
58	12N-03W-05	BDA 2	353218097321801	12-04-79	-	-	-	-	150	150.0
59	12N-03W-05	CCC 1	353216097324701	01-30-86	1205	533	50	-	-	50.0
60	12N-03W-05	DCA 1	353223097320501	04-24-86	-	-	-	-	110	110.0
61	12N-03W-05	DDD 1	353213097315001	12-11-79	1000	-	-	-	92	92.0
62	12N-04W-09	CDD 1	353126097374101	01-01-86	1206	720	-	-	67	67.0
63	12N-04W-09	CDD 1	353126097374101	01-01-86	1208	796	-	-	61	61.0
64	12N-04W-09	CDD 1	353126097374101	01-01-86	1207	760	-	-	180	180.0
65	12N-04W-09	CDD 1	353126097374101	05-07-87	0830	-	-	-	75	75.0
66	12N-04W-28	BCA 1	352917097380001	01-01-86	1207	786	-	-	50	50.0
67	13N-02W-08	DBA 1	353658097255301	04-20-83	-	-	-	-	78	78.0
68	13N-02W-08	DBA 1	353658097255301	01-17-85	0925	-	-	-	54	54.0
69	13N-02W-08	DBA 1	353658097255301	10-07-85	-	-	-	<50	62	62.0
70	13N-03W-01	CBA 1	353750097283101	12-11-84	0945	-	-	-	52	52.0
71	13N-03W-11	BAA 1	353724097291401	04-18-83	-	-	-	-	90	90.0
72	13N-03W-11	BAA 1	353724097291401	12-11-84	0910	-	-	-	86	86.0
73	13N-03W-26	CCD 1	353358097292601	04-25-83	-	-	-	-	54	54.0
74	13N-03W-26	CCD 1	353358097292601	03-02-85	-	-	-	<50	53	53.0
75	13N-03W-33	CAB 1	353325097313001	12-04-79	-	-	-	-	85	85.0
76	13N-03W-34	CBA 1	353329097304001	12-11-79	1000	-	-	-	99	99.0
77	13N-03W-35	CCC 1	353308097294001	04-25-83	-	-	-	-	50	50.0
78	13N-03W-35	DCC 2	353308097290701	04-25-83	-	-	-	-	50	50.0
79	14N-02W-23	CCB 1	354014097231401	10-28-77	1500	-	50	-	-	50.0
80	14N-02W-31	BCC 1	353845097273401	04-18-83	-	-	-	-	94	94.0
81	14N-02W-31	BCC 1	353845097273401	12-11-84	1100	-	-	-	110	110.0
82	14N-02W-31	CAA 1	353843097270601	01-17-85	0915	-	-	-	72	72.0
83	14N-02W-31	DDA 1	353826097263501	04-18-83	-	-	-	-	50	50.0
84	14N-02W-32	DCD 1	353819097254901	01-17-85	0900	-	-	-	62	62.0
85	14N-03W-07	DAA 1	354213097330101	04-27-88	0807	480	-	-	210	210.0
86	14N-03W-07	DAA 2	354208097330201	12-07-88	0900	475	40	<1	89	64.5
87	14N-03W-34	DDA 1	353825097294701	04-20-83	-	-	-	-	52	52.0
88	14N-03W-34	DDA 1	353825097294701	12-11-84	0945	-	-	-	54	54.0
89	14N-03W-35	ABA 2	353859097285801	10-27-77	1500	-	120	-	-	120.0

POTTAWATOMIE COUNTY

NO.	LOCAL IDENTIFIER	STATION NUMBER	DATE	TIME SAMPLING	Cr DEPTH (ft)	Cr dissolved (ug/l)	Cr(VI) dissolved (ug/l)	Cr dissolvd (ug/l)	Cr average (ug/l)
90	08N-02E-06 CAB 2	351140097081402	12-11-77	0900	-	50	-	-	50.0

APPENDIX B

DATA BASE FOR OTHER MAJOR ELEMENTS

CLEVELAND COUNTY

NO.	LOCAL IDENTIFIER	STATION NUMBER	Cr average (ug/l)	DO (mg/l)	pH	DOC (mg/l)	Fe dissolved (ug/l)	Mn dissolved (ug/l)	As dissolved (ug/l)	Se dissolved (ug/l)	Temperature of water (degree C)
1	09N-01W-08	CCC 1 351543097200601	80.0	-	-	-	1100	20	-	150	-
2	09N-01W-13	CDC 1 351455097153301	110.0	-	-	-	4000	70	-	35	-
3	09N-01W-13	CDC 1 351455097153301	120.0	-	-	-	5200	90	-	39	-
4	09N-01W-13	CDC 1 351455097153301	130.0	-	-	-	6100	100	-	44	-
5	09N-01W-13	CDC 1 351455097153301	80.0	-	-	-	2800	30	-	47	-
6	09N-01W-13	CDC 1 351455097153301	80.0	-	-	-	1300	20	-	39	-
7	09N-02W-15	ADD 1 351518097231801	58.0	-	7.9	-	-	-	-	5	-
8	09N-02W-15	ADD 1 351518097231801	92.0	-	7.9	-	-	-	-	12	-
9	09N-02W-15	DDD 1 351452097232201	70.0	-	8.0	-	-	-	-	<5	-
10	09N-02W-17	DCC 1 351458097254901	66.0	-	8.3	-	-	-	-	12	-
11	09N-02W-17	DCC 1 351458097254901	62.0	-	8.7	-	-	-	-	29	-
12	09N-02W-22	ADD 1 351426097232201	50.0	-	8.1	-	-	-	-	<5	-
13	09N-02W-22	DDA 1 351409097231801	92.0	-	8.5	-	-	-	-	<5	-
14	09N-02W-22	DDA 1 351409097231801	80.0	5.9	8.3	1.8	23	1	2	<1	18.5
15	09N-02W-29	DCA 5 351315097254301	98.0	2.6	9.1	-	87	4	33	12	17.0
16	09N-02W-30	ABA 1 351353097264501	62.0	-	8.0	-	-	-	-	<5	-
17	09N-02W-30	ABA 1 351353097264501	93.0	-	7.7	-	-	-	-	<5	-
18	09N-02W-31	DAA 1 351236097262801	96.5	2.4	8.7	0.4	<3	<1	42	73	19.0
19	09N-03W-02	DCA 5 351643097285004	140.0	-	8.1	-	-	-	-	110	-
20	09N-03W-20	AAD 1 351438097315101	60.0	3.6	-	-	<10	<2	5	1	11.0
21	10N-02W-36	CCC 2 351729097221302	80.0	-	-	-	-	-	-	-	-
22	10N-02W-36	CCC 2 351729097221302	70.0	13.2	7.6	2.1	10	9	28	31	17.0
23	10N-03W-07	ABB 3 352148097332101	60.0	-	8.5	-	-	-	-	18	-
24	10N-03W-10	AAB 1 352148097295201	54.0	-	7.9	-	-	-	-	64	-
25	10N-03W-12	DDC 1 352100097275001	72.0	-	8.5	-	-	-	-	<5	-
26	10N-03W-12	DDC 1 352100097275001	55.0	-	8.7	-	-	-	-	12	-
27	10N-03W-12	DDC 1 352100097275001	67.0	-	8.8	-	-	-	-	<5	-
28	10N-03W-13	BBD 1 352043097282001	62.5	6.4	8.9	1.1	<3	<1	32	29	18.5
29	10N-03W-13	CBB 1 352028097283201	54.0	-	8.6	-	-	-	-	12	-
30	10N-03W-13	CBB 1 352028097283201	27.0	-	7.8	-	-	-	-	<5	-
31	10N-03W-14	BAA 1 352055097290601	55.5	-	8.8	-	-	-	-	15	-
32	10N-03W-14	BAA 1 352055097290601	44.0	-	8.3	-	-	-	-	12	-
33	10N-03W-15	ACC 1 352035097300701	48.0	-	8.3	-	-	-	-	11	-
34	10N-03W-16	ACA 1 352034097310501	41.0	-	8.6	-	-	-	-	7	-
35	10N-03W-17	BAA 1 352054097322101	99.5	-	8.8	-	-	-	-	130	-
36	10N-03W-22	DAD 1 351926097293001	76.0	-	8.5	-	-	-	-	50	-
37	10N-03W-22	DAD 1 351926097293001	83.0	-	8.5	-	-	-	-	30	-
38	10N-03W-22	DAD 1 351926097293001	70.0	5.0	8.8	2.1	<3	<1	19	63	19.5
39	10N-03W-24	AAA 1 352001097273601	70.0	-	7.8	-	-	-	-	40	-
40	10N-03W-24	ABB 1 351957097275901	78.0	-	8.8	-	-	-	-	18	-
41	10N-03W-24	ABB 1 351957097275901	62.0	-	8.9	-	-	-	-	7	-
42	10N-03W-24	ABB 1 351957097275901	67.0	-	8.9	-	-	-	-	10	-
43	10N-03W-26	ADB 1 351853097284701	59.5	-	8.6	-	-	-	-	8	-
44	10N-03W-26	ADB 1 351853097284701	68.0	-	8.5	-	-	-	-	8	-

CLEVELAND COUNTY

NO.	LOCAL IDENTIFIER	STATION NUMBER	Cr average (ug/l)	Cl dissolved (mg/l)	F dissolved (mg/l)	SO4 dissolved (mg/l)	NO2 + NO3 dissolved (mg/l)	HCO3 dissolved (mg/l)	CO3 dissolved (mg/l)	Specific Conductance (us/cm)
1	09N-01W-08	CCC 1 351543097200601	80.0	490	1.8	160	-	-	-	2590
2	09N-01W-13	CDC 1 351455097153301	110.0	14	0.20	13	-	-	-	602
3	09N-01W-13	CDC 1 351455097153301	120.0	26	0.20	17	-	-	-	699
4	09N-01W-13	CDC 1 351455097153301	130.0	39	0.20	25	-	-	-	729
5	09N-01W-13	CDC 1 351455097153301	80.0	170	0.30	97	-	-	-	1320
6	09N-01W-13	CDC 1 351455097153301	80.0	280	0.30	180	-	-	-	1850
7	09N-02W-15	ADD 1 351518097231801	58.0	<10	-	<20	-	-	-	504
8	09N-02W-15	ADD 1 351518097231801	92.0	<10	-	<20	-	-	-	509
9	09N-02W-15	DDD 1 351452097232201	70.0	<10	-	<20	-	-	-	484
10	09N-02W-17	DCC 1 351458097254901	66.0	11	-	<20	-	-	-	532
11	09N-02W-17	DCC 1 351458097254901	62.0	21	-	100	-	-	-	807
12	09N-02W-22	ADD 1 351426097232201	50.0	<10	-	25	-	-	-	504
13	09N-02W-22	DDA 1 351409097231801	92.0	<10	-	<20	-	-	-	474
14	09N-02W-22	DDA 1 351409097231801	80.0	3	0.40	10	0.160	-	-	426
15	09N-02W-29	DCA 5 351315097254301	98.0	16	1.0	44	-	256	15	563
16	09N-02W-30	ABA 1 351353097264501	62.0	<10	-	<20	-	-	-	353
17	09N-02W-30	ABA 1 351353097264501	93.0	<10	-	<20	-	-	-	425
18	09N-02W-31	DAA 1 351236097262801	96.5	24	1.2	190	0.400	-	-	1100
19	09N-03W-02	DCA 5 351643097285004	140.0	46	-	37	-	-	-	1080
20	09N-03W-20	AAD 1 351438097315101	60.0	-	-	24	-	-	-	450
21	10N-02W-36	CCC 2 351729097221302	80.0	-	-	-	-	-	-	-
22	10N-02W-36	CCC 2 351729097221302	70.0	200	0.60	31	0.480	-	-	1250
23	10N-03W-07	ABB 3 352148097332101	60.0	11	-	<20	-	-	-	489
24	10N-03W-10	AAB 1 352148097295201	54.0	<10	-	<20	-	-	-	489
25	10N-03W-12	DDC 1 352100097275001	72.0	<10	-	<20	-	-	-	455
26	10N-03W-12	DDC 1 352100097275001	55.0	<10	-	<20	-	-	-	602
27	10N-03W-12	DDC 1 352100097275001	67.0	<10	-	<20	-	-	-	456
28	10N-03W-13	BBD 1 352043097282001	62.5	8	0.50	10	0.430	-	-	563
29	10N-03W-13	CBB 1 352028097283201	54.0	<10	-	<20	-	-	-	614
30	10N-03W-13	CBB 1 352028097283201	27.0	<10	-	<20	-	-	-	445
31	10N-03W-14	BAA 1 352055097290601	55.5	<10	-	<20	-	-	-	614
32	10N-03W-14	BAA 1 352055097290601	44.0	<10	-	<20	-	-	-	434
33	10N-03W-15	ACC 1 352035097300701	48.0	<10	-	<20	-	-	-	500
34	10N-03W-16	ACA 1 352034097310501	41.0	<10	-	<20	-	-	-	521
35	10N-03W-17	BAA 1 352054097322101	99.5	37	-	<20	-	-	-	708
36	10N-03W-22	DAD 1 351926097293001	76.0	<10	-	<20	-	-	-	489
37	10N-03W-22	DAD 1 351926097293001	83.0	<10	-	<20	-	-	-	555
38	10N-03W-22	DAD 1 351926097293001	70.0	7	0.70	13	0.530	-	-	563
39	10N-03W-24	AAA 1 352001097273601	70.0	<10	-	<20	-	-	-	522
40	10N-03W-24	ABB 1 351957097275901	78.0	<10	-	<20	-	-	-	543
41	10N-03W-24	ABB 1 351957097275901	62.0	<10	-	<20	-	-	-	614
42	10N-03W-24	ABB 1 351957097275901	67.0	<10	-	<20	-	-	-	543
43	10N-03W-26	ADB 1 351853097284701	59.5	<10	-	<20	-	-	-	553
44	10N-03W-26	ADB 1 351853097284701	68.0	<10	-	<20	-	-	-	543

LOGAN COUNTY

NO.	LOCAL IDENTIFIER	STATION NUMBER	Cr average (mg/l)	DO (mg/l)	pH	DOC (mg/l)	Fe dissolved (mg/l)	Mn dissolved (mg/l)	As dissolved (mg/l)	Se dissolved (mg/l)	Temperature of water (degree C)
45	14N-03W-06	BB 1 354326097335401	50.0	-	-	-	-	-	-	-	<5
46	14N-03W-06	BB 1 354326097335401	70.0	-	-	-	-	-	-	-	19
47	16N-02W-21	BAA 3 355118097250001	60.0	0.2	-	-	-	-	-	-	18.0
48	16N-02W-21	BAA 3 355118097250001	64.0	0.2	8.9	0.8	8	4	69	245	18.0
49	16N-02W-21	BAA 3 355118097250001	90.7	1.7	8.7	1.4	15	7	53	75	17.5
50	16N-02W-21	BAA 3 355118097250001	90.0	1.7	-	-	-	-	-	-	17.5
51	16N-02W-21	DBD 1 355045097244801	94.0	-	8.6	-	-	-	-	100	-
52	17N-04W-31	CCC 1 355355097402301	50.0	-	-	-	21	<20	<10	6	17.0

LOGAN COUNTY

NO.	LOCAL IDENTIFIER	STATION NUMBER	Cr average (ug/l)	Ca dissolved (mg/l)	Mg dissolved (mg/l)	Na dissolved (mg/l)	K dissolved (mg/l)	Ba dissolved (ug/l)	SiO2 dissolved (mg/l)	Hardness total (mg/l)	Alkalinity (mg/l)
45	14N-03W-06	BB 1 354326097335401	50.0	-	-	-	-	-	-	-	-
46	14N-03W-06	BB 1 354326097335401	70.0	-	-	-	-	-	-	-	-
47	16N-02W-21	BAA 3 355118097250001	60.0	-	-	-	-	-	-	-	-
48	16N-02W-21	BAA 3 355118097250001	64.0	2.1	0.83	190	0.50	40	10	9	-
49	16N-02W-21	BAA 3 355118097250001	90.7	3.1	1.5	140	0.60	54	11	14	-
50	16N-02W-21	BAA 3 355118097250001	90.0	-	-	-	-	-	-	-	-
51	16N-02W-21	DBD 1 355045097244801	94.0	-	-	-	-	-	-	23	-
52	17N-04W-31	CCC 1 355355097402301	50.0	100	24	59	1.6	370	-	360	217

LOGAN COUNTY

NO.	LOCAL IDENTIFIER	STATION NUMBER	Cr average (ug/l)	Cl dissolved (mg/l)	F dissolved (mg/l)	SO4 dissolved (mg/l)	NO2 + NO3 dissolved (mg/l)	HCO3 dissolved (mg/l)	CO3 dissolved (mg/l)	Specific Conductance (us/cm)
45	14N-03W-06	BB 1 354326097335401	50.0	-	-	-	-	-	-	-
46	14N-03W-06	BB 1 354326097335401	70.0	-	-	-	-	-	-	-
47	16N-02W-21	BAA 3 355118097250001	60.0	-	-	-	-	354	12	907
48	16N-02W-21	BAA 3 355118097250001	64.0	54	0.30	39	0.510	354	12	907
49	16N-02W-21	BAA 3 355118097250001	90.7	29	0.80	27	0.350	303	10	607
50	16N-02W-21	BAA 3 355118097250001	90.0	-	-	-	-	303	10	607
51	16N-02W-21	DBD 1 355045097244801	94.0	12	-	26	-	-	-	678
52	17N-04W-31	CCC 1 355355097402301	50.0	93	-	42	-	-	-	885

OKLAHOMA COUNTY

NO.	LOCAL IDENTIFIER	STATION NUMBER	Cr average (mg/l)	DO (mg/l)	pH	DOC (mg/l)	Fe dissolved (ug/l)	Mn dissolved (ug/l)	As dissolved (ug/l)	Se dissolved (ug/l)	Temperature of water (degree C)
53	11N-02W-02	BAR 1 352750097230001	110.0	-	8.3	-	-	-	-	-	50
54	12N-03W-04	CCD 1 353214097313401	61.0	-	-	-	-	-	-	-	44
55	12N-03W-04	CCD 1 353214097313401	145.0	-	8.6	-	-	-	-	-	43
56	12N-03W-04	DAD 1 353229097304301	56.0	-	8.3	-	-	-	-	-	10
57	12N-03W-05	BDA 1 353221097322001	66.0	-	8.8	-	-	-	-	-	<5
58	12N-03W-05	BDA 2 353218097321801	150.0	-	-	-	-	-	-	-	71
59	12N-03W-05	CCC 1 353216097324701	50.0	-	7.8	-	-	-	-	-	<5
60	12N-03W-05	DCA 1 353223097320501	110.0	-	7.7	-	-	-	-	-	<5
61	12N-03W-05	DDD 1 353213097315001	92.0	-	-	-	-	-	-	-	46
62	12N-04W-09	CDD 1 353126097374101	67.0	-	8.6	-	-	-	-	-	5
63	12N-04W-09	CDD 1 353126097374101	61.0	-	8.7	-	-	-	-	-	17
64	12N-04W-09	CDD 1 353126097374101	180.0	-	8.7	-	-	-	-	-	28
65	12N-04W-09	CDD 1 353126097374101	75.0	-	-	-	-	-	-	-	7
66	12N-04W-28	BCA 1 352917097380001	50.0	-	8.4	-	-	-	-	-	9
67	13N-02W-08	DBA 1 353658097255301	78.0	-	8.6	-	-	-	-	-	28
68	13N-02W-08	DBA 1 353658097255301	54.0	-	8.6	-	-	-	-	-	8
69	13N-02W-08	DBA 1 353658097255301	62.0	-	8.6	-	-	-	-	-	23
70	13N-03W-01	CBA 1 353750097283101	52.0	-	8.0	-	-	-	-	-	17
71	13N-03W-11	BAA 1 353724097291401	90.0	-	8.6	-	-	-	-	-	12
72	13N-03W-11	BAA 1 353724097291401	86.0	-	8.5	-	-	-	-	-	<5
73	13N-03W-26	CCD 1 353358097292601	54.0	-	8.4	-	-	-	-	-	<5
74	13N-03W-26	CCD 1 353358097292601	53.0	-	9.0	-	-	-	-	-	<5
75	13N-03W-33	CAB 1 353325097313001	85.0	-	-	-	-	-	-	-	120
76	13N-03W-34	CBA 1 353329097304001	99.0	-	-	-	-	-	-	-	55
77	13N-03W-35	CCC 1 353308097294001	50.0	-	8.4	-	-	-	-	-	<5
78	13N-03W-35	DCC 2 353308097290701	50.0	-	8.4	-	-	-	-	-	<5
79	14N-02W-23	CCB 1 354014097231401	50.0	4.0	-	-	<10	2	21	1	17.5
80	14N-02W-31	BCC 1 353845097273401	94.0	-	8.5	-	-	-	-	-	34
81	14N-02W-31	BCC 1 353845097273401	110.0	-	8.7	-	-	-	-	-	69
82	14N-02W-31	CAA 1 353843097270601	72.0	-	8.1	-	-	-	-	-	25
83	14N-02W-31	DDA 1 353826097263501	50.0	-	8.8	-	-	-	-	-	3
84	14N-02W-32	DCD 1 353819097254901	62.0	-	7.7	-	-	-	-	-	11
85	14N-03W-07	DAA 1 354213097330101	210.0	-	-	-	-	-	-	-	350
86	14N-03W-07	DAA 2 354208097330201	64.5	0.2	8.4	0.4	6	8	65	385	18.0
87	14N-03W-34	DDA 1 353825097294701	52.0	-	8.1	-	-	-	-	-	16
88	14N-03W-34	DDA 1 353825097294701	54.0	-	8.3	-	-	-	-	-	15
89	14N-03W-35	ABA 2 353859097285801	120.0	4.8	-	-	<10	<2	27	0	19.0

OKLAHOMA COUNTY

NO.	LOCAL IDENTIFIER	STATION NUMBER	Cr average (ug/l)	Ca dissolved (mg/l)	Mg dissolved (mg/l)	Na dissolved (mg/l)	K dissolved (mg/l)	Ba dissolved (ug/l)	SiO2 dissolved (mg/l)	Hardness total (mg/l)	Alkalinity (mg/l)
53	11N-02W-02	BAB 1 352750097230001	110.0	-	-	-	-	-	-	66	-
54	12N-03W-04	CCD 1 353214097313401	61.0	-	-	-	-	-	-	-	-
55	12N-03W-04	CCD 1 353214097313401	145.0	-	-	-	-	-	-	<10	-
56	12N-03W-04	DAD 1 353229097304301	56.0	-	-	-	-	-	-	93	-
57	12N-03W-05	BDA 1 353221097322001	66.0	-	-	-	-	-	-	25	-
58	12N-03W-05	BDA 2 353218097321801	150.0	-	-	-	-	-	-	-	-
59	12N-03W-05	CCC 1 353216097324701	50.0	-	-	-	-	-	-	14	-
60	12N-03W-05	DCA 1 353223097320501	110.0	-	-	-	-	-	-	300	-
61	12N-03W-05	DDD 1 353213097315001	92.0	-	-	-	-	-	-	-	-
62	12N-04W-09	CDD 1 353126097374101	67.0	-	-	110	-	-	-	16	280
63	12N-04W-09	CDD 1 353126097374101	61.0	-	-	160	-	-	-	18	326
64	12N-04W-09	CDD 1 353126097374101	180.0	-	-	150	-	-	-	26	344
65	12N-04W-09	CDD 1 353126097374101	75.0	-	-	-	-	-	-	-	-
66	12N-04W-28	BCA 1 352917097380001	50.0	-	-	140	-	-	-	32	288
67	13N-02W-08	DBA 1 353658097255301	78.0	-	-	-	-	-	-	12	-
68	13N-02W-08	DBA 1 353658097255301	54.0	-	-	-	-	-	-	31	-
69	13N-02W-08	DBA 1 353658097255301	62.0	-	-	-	-	-	-	45	-
70	13N-03W-01	CBA 1 353750097283101	52.0	-	-	-	-	-	-	95	-
71	13N-03W-11	BAA 1 353724097291401	90.0	-	-	-	-	-	-	27	-
72	13N-03W-11	BAA 1 353724097291401	86.0	-	-	-	-	-	-	50	-
73	13N-03W-26	CCD 1 353358097292601	54.0	-	-	-	-	-	-	<10	-
74	13N-03W-26	CCD 1 353358097292601	53.0	-	-	-	-	-	-	47	-
75	13N-03W-33	CAB 1 353325097313001	85.0	-	-	-	-	-	-	-	-
76	13N-03W-34	CBA 1 353329097304001	99.0	-	-	-	-	-	-	-	-
77	13N-03W-35	CCC 1 353308097294001	50.0	-	-	-	-	-	-	35	-
78	13N-03W-35	DCC 2 353308097290701	50.0	-	-	-	-	-	-	<10	-
79	14N-02W-23	CCB 1 354014097231401	50.0	26	13	130	-	140	-	120	328
80	14N-02W-31	BCC 1 353845097273401	94.0	-	-	-	-	-	-	28	-
81	14N-02W-31	BCC 1 353845097273401	110.0	-	-	-	-	-	-	47	-
82	14N-02W-31	CAA 1 353843097270601	72.0	-	-	-	-	-	-	130	-
83	14N-02W-31	DDA 1 353826097263501	50.0	-	-	-	-	-	-	16	-
84	14N-02W-32	DCD 1 353819097254901	62.0	-	-	-	-	-	-	160	-
85	14N-03W-07	DAA 1 354213097330101	210.0	-	-	-	-	-	-	<10	-
86	14N-03W-07	DAA 2 354208097330201	64.5	3.6	1.4	260	0.70	28	11	15	-
87	14N-03W-34	DDA 1 353825097294701	52.0	-	-	-	-	-	-	88	-
88	14N-03W-34	DDA 1 353825097294701	54.0	-	-	-	-	-	-	68	-
89	14N-03W-35	ABA 2 353859097285801	120.0	4.0	1.5	360	-	40	-	16	470

OKLAHOMA COUNTY

NO.	LOCAL IDENTIFIER	STATION NUMBER	Cr	Cl	F	SO4	NO2 + NO3	BCO3	CO3	Specific
			average	dissolved	dissolved	dissolved	dissolved	dissolved	dissolved	Conductance
			(ug/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(us/cm)
53	11N-02W-02	HAB 1	352750097230001	110.0	88	-	28	-	-	652
54	12N-03W-04	CCD 1	353214097313401	61.0	-	-	-	-	-	-
55	12N-03W-04	CCD 1	353214097313401	145.0	52	-	28	-	-	682
56	12N-03W-04	DAD 1	353229097304301	56.0	100	-	25	-	-	734
57	12N-03W-05	HDA 1	353221097322001	66.0	60	-	41	-	-	869
58	12N-03W-05	BDA 2	353218097321801	150.0	-	-	-	-	-	-
59	12N-03W-05	CCC 1	353216097324701	50.0	28	-	44	-	-	519
60	12N-03W-05	DCA 1	353223097320501	110.0	210	-	29	-	-	944
61	12N-03W-05	DDD 1	353213097315001	92.0	-	-	-	-	-	-
62	12N-04W-09	CDD 1	353126097374101	67.0	8	0.29	17	-	-	-
63	12N-04W-09	CDD 1	353126097374101	61.0	12	0.64	36	-	-	-
64	12N-04W-09	CDD 1	353126097374101	180.0	13	1.0	37	-	-	-
65	12N-04W-09	CDD 1	353126097374101	75.0	-	-	-	-	-	-
66	12N-04W-28	BCA 1	352917097380001	50.0	16	0.41	37	-	-	-
67	13N-02W-08	DBA 1	353658097255301	78.0	28	-	<20	-	-	588
68	13N-02W-08	DBA 1	353658097255301	54.0	33	-	<20	-	-	652
69	13N-02W-08	DBA 1	353658097255301	62.0	70	-	31	-	-	743
70	13N-03W-01	CBA 1	353750097283101	52.0	<10	-	<20	-	-	504
71	13N-03W-11	BAA 1	353724097291401	90.0	12	-	<20	-	-	730
72	13N-03W-11	BAA 1	353724097291401	86.0	<10	-	35	-	-	595
73	13N-03W-26	CCD 1	353358097292601	54.0	21	-	<20	-	-	565
74	13N-03W-26	CCD 1	353358097292601	53.0	11	-	<20	-	-	543
75	13N-03W-33	CAB 1	353325097313001	85.0	-	-	-	-	-	-
76	13N-03W-34	CBA 1	353329097304001	99.0	-	-	-	-	-	-
77	13N-03W-35	CCC 1	353308097294001	50.0	35	-	<20	-	-	565
78	13N-03W-35	DCC 2	353308097290701	50.0	<10	-	<20	-	-	791
79	14N-02W-23	CCB 1	354014097231401	50.0	-	-	19	-	-	760
80	14N-02W-31	BCC 1	353845097273401	94.0	30	-	<20	-	-	811
81	14N-02W-31	BCC 1	353845097273401	110.0	32	-	37	-	-	655
82	14N-02W-31	CAA 1	353843097270601	72.0	<10	-	<20	-	-	597
83	14N-02W-31	DDA 1	353826097263501	50.0	<10	-	<20	-	-	614
84	14N-02W-32	DCD 1	353819097254901	62.0	82	-	28	-	-	760
85	14N-03W-07	DAA 1	354213097330101	210.0	120	-	-	-	-	-
86	14N-03W-07	DAA 2	354208097330201	64.5	110	1.6	72	0.470	398	1160
87	14N-03W-34	DDA 1	353825097294701	52.0	<10	-	24	-	-	509
88	14N-03W-34	DDA 1	353825097294701	54.0	<10	-	31	-	-	504
89	14N-03W-35	ABA 2	353859097285801	120.0	-	-	78	-	-	1410

POTTAWATOMIE COUNTY

NO.	LOCAL IDENTIFIER	STATION NUMBER	Cr average (ug/l)	DO (mg/l)	pH	DOC (mg/l)	Fe dissolved (ug/l)	Mn dissolved (ug/l)	As dissolved (ug/l)	Se dissolved (ug/l)	Temperature of water (degree C)
90	08N-02E-06 CAB 2	351140097081402	50.0	7.3	-	-	<10	<2	1	0	14.5

POTTAWATOMIE COUNTY

NO.	LOCAL IDENTIFIER	STATION NUMBER	Cr average (ug/l)	Ca dissolved (mg/l)	Mg dissolved (mg/l)	Na dissolved (mg/l)	K dissolved (mg/l)	Ba dissolved (ug/l)	SiO2 dissolved (mg/l)	Hardness total (mg/l)	Alkalinity (mg/l)
90	08N-02E-06 CAB 2	351140097081402	50.0	9.2	5.4	150	-	130	-	45	276

POTTAWATOMIE COUNTY

NO.	LOCAL IDENTIFIER	STATION NUMBER	Cr average (ug/l)	Cl dissolved (mg/l)	F dissolved (mg/l)	SO4 dissolved (mg/l)	NO2 + NO3 dissolved (mg/l)	HCO3 dissolved (mg/l)	CO3 dissolved (mg/l)	Specific Conductance (us/cm)
90	08N-02E-06 CAB 2	351140097081402	50.0	5	-	10	-	-	-	490

Detection limit:

Cr dissolved	=	5 $\mu\text{g/l}$
Cr(VI) dissolved	=	1 $\mu\text{g/l}$
Cr total	=	10 $\mu\text{g/l}$
Fe dissolved	=	3 $\mu\text{g/l}$
Mn dissolved	=	1 $\mu\text{g/l}$
Se dissolved	=	1 $\mu\text{g/l}$
Cl dissolved	=	10 mg/l
SO ₄ dissolved	=	20 mg/l
K dissolved	=	2 mg/l
Hardness	=	10 mg/l

APPENDIX C

INPUT DATA FOR RUNNING CHEMPLOT v. 1.31
AND THE RESULTS FROM CHEMPLOT v. 1.31

Cr-Fe-Mn-As-Se-pH-Ca-Mg-Hardness

0

9,Cr,ug/l,Fe,ug/l,Mn,ug/l,As,ug/l,Se,ug/l,pH,dim,Ca,mg/l,Mg,mg/l,Hardness,mg/l

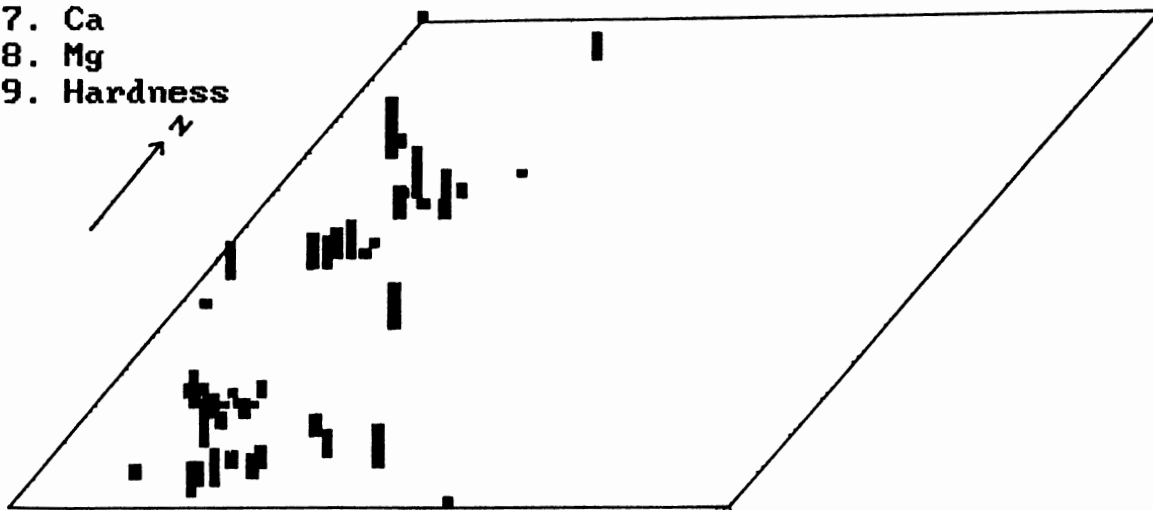
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 6,4,14,8,98,87,4,33,11.5,9.1,2.5,1,10
 7,4,13,8,77.5,1.5,0.5,5,2.5,7.9,0,0,105
 8,4,13,7,96.5,1.5,0.5,42,73,8.7,3.9,1.5,16
 9,4,11,12,140,1.5,0.5,5,110,8.1,0,0,5
 10,4,8,9,60,5,1,5,1,7,4,2,1,7,0
 11,4,18,13,75,5.8,4.8,16.5,16.8,7.3,2.8,1.5,13
 12,4,7,17,60,1.5,0.5,5,18,8.5,0,0,87
 13,4,10,17,54,1.5,0.5,5,64,7.9,0,0,170
 14,4,12,17,65,1.5,0.5,5,5,7,8.7,0,0,27
 15,4,12,16,48,1.5,0.5,14,14.5,8.4,4.7,4,126.7
 16,4,11,16,50,1.5,0.5,5,13.5,8.6,0,0,85.5
 17,4,10,16,48,1.5,0.5,5,11,8.3,0,0,110
 18,4,9,16,41,1.5,0.5,5,7,8.6,0,0,71
 19,4,8,16,99.5,1.5,0.5,5,130,8.8,0,0,88
 20,4,10,15,76.5,1.5,0.5,9.7,47.7,8.6,4.7,4.3,90.3
 21,4,12,15,69.5,1.5,0.5,5,18.8,8.6,0,0,54.5
 22,4,11,14,64,1.5,0.5,5,8,8.6,0,0,52
 23,4,7,42,60,1.5,0.5,5,10.8,7,0,0,0
 24,4,15,51,80,5.5,2,3,27.4,85.8,1,0.5,9.2
 25,4,1,55,50,21,10,5,5.5,7,100,24,360
 26,4,17,24,110,1.5,0.5,5,50,8.3,0,0,66
 27,4,9,30,87.5,1.5,0.5,5,32.3,8,0,0,32.7
 28,4,8,30,94,1.5,0.5,5,24.9,7.7,0,0,67.8
 29,4,3,29,96,1.5,0.5,5,14.3,8.3,0,0,15
 30,4,3,26,50,1.5,0.5,5,9,8.4,0,0,32
 31,4,14,35,65,1.5,0.5,5,19.7,8.6,0,0,14.3
 32,4,12,36,52,1.5,0.5,5,17,8,0,0,95
 33,4,11,35,88,1.5,0.5,5,4.8,8.6,0,0,38.5
 34,4,11,32,53.5,1.5,0.5,5,2.5,8.7,0,0,26
 35,4,9,31,85,1.5,0.5,5,120,7,0,0,0
 36,4,10,31,99,1.5,0.5,5,55,7,0,0,0
 37,4,11,31,50,1.5,0.5,5,2.5,8.4,0,0,20
 38,4,17,39,50,5,2,21,1,7,26,13,120
 39,4,13,37,81.5,1.5,0.5,5,32.6,8.5,0,0,55.3
 40,4,14,37,62,1.5,0.5,5,11,7.7,0,0,160
 41,4,7,41,137.5,3.8,4.3,35,367.5,7.7,1.8,0.7,10
 42,4,10,37,53,1.5,0.5,5,15.5,8.2,0,0,78
 43,4,11,37,120,5,1,27,0,7,4,1.5,16
 44,4,31,6,50,5,1,1,0,7,9.2,5.4,45

Cr-Fe-Mn-As-Se-pH-Ca-Mg-Hardness

CHEMPLOT - Version 1.31 A. W. HOUNSLOW Oklahoma State University

1. Cr
2. Fe
3. Mn
4. As
5. Se
6. pH
7. Ca
8. Mg
9. Hardness

Maximum value of Cr is 140 ug/l
Minimum non-zero value is 41 ug/l



[F1] single/set
[F2] background
[F3] NW [F4] NE
[F5] SW [F6] SE
[F7] FULL VIEW
[F8] WELL PLOT
MAG Z = .25
[F9] Z - MIN Z
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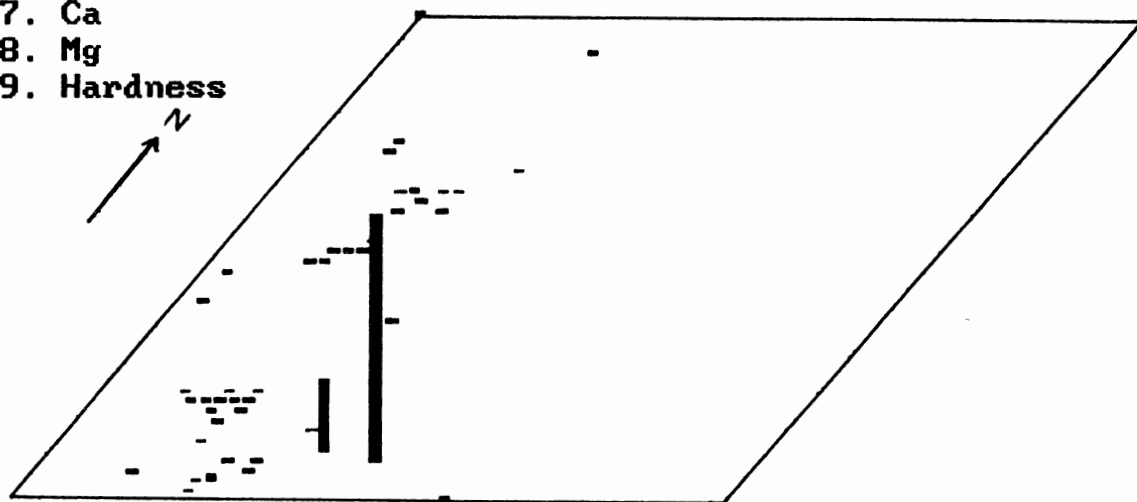
Press E(nd), H(elp), S(ummary), compound # and toggles + ENTER to continue █

Cr-Fe-Mn-As-Se-pH-Ca-Mg-Hardness

CHEMPLOT - Version 1.31 A. W. HOUNSLOW Oklahoma State University

1. Cr
2. Fe
3. Mn
4. As
5. Se
6. pH
7. Ca
8. Mg
9. Hardness

Maximum value of Fe is 3880 ug/l
Minimum non-zero value is 1.5 ug/l



[F1] single/set
[F2] background
[F3] NW [F4] NE
[F5] SW [F6] SE
[F7] FULL VIEW
[F8] WELL PLOT
MAG Z = 1
[F9] Z
[F10] GRID OFF

Press E(nd), H(elp), S(ummary), compound # and toggles + ENTER to continue █

Cr-Fe-Mn-As-Se-pH-Ca-Mg-Hardness

CHEMPLOT - Version 1.31 A. W. HOUNSLOW Oklahoma State University

1. Cr
2. Fe
3. Mn
4. As
5. Se
6. pH
7. Ca
8. Mg
9. Hardness

Maximum value of Mn is 62 ug/l
Minimum non-zero value is 0.5 ug/l



[F1] single/set
[F2] background
[F3] NW [F4] NE
[F5] SW [F6] SE
[F7] FULL VIEW
[F8] WELL PLOT
MAG Z = 1
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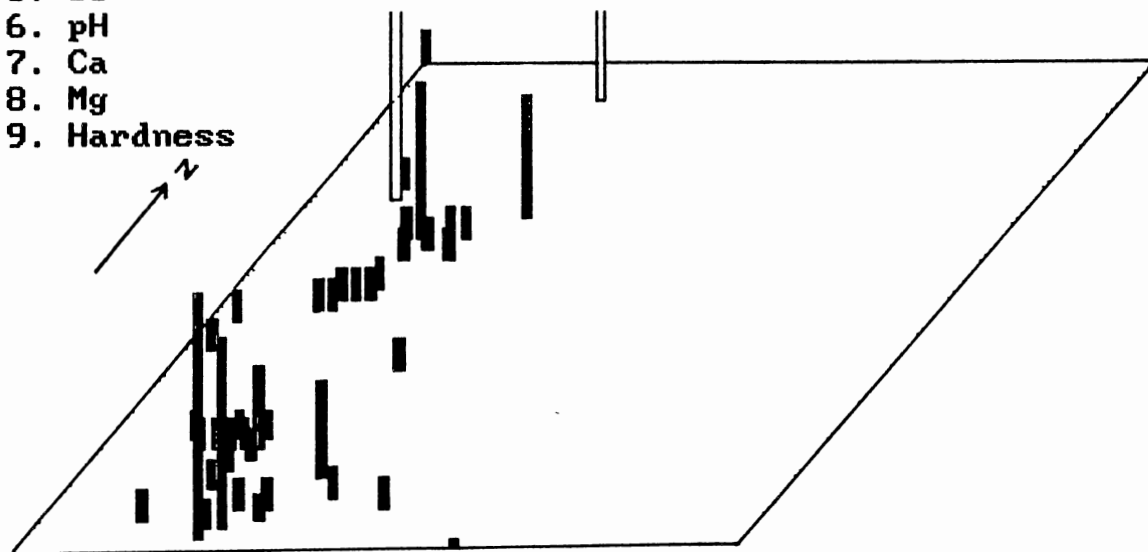
Press E(nd), H(elp), S(ummary), compound # and toggles + ENTER to continue █

Cr-Fe-Mn-As-Se-pH-Ca-Mg-Hardness

CHEMPLOT - Version 1.31 A. W. HOUNSLOW Oklahoma State University

- 1. Cr
- 2. Fe
- 3. Mn
- 4. As
- 5. Se
- 6. pH
- 7. Ca
- 8. Mg
- 9. Hardness

Maximum value of As is 42 ug/l
Minimum non-zero value is 1 ug/l



- [F1] single/set
- [F2] background
- [F3] NW [F4] NE
- [F5] SW [F6] SE
- [F7] FULL VIEW
- [F8] WELL PLOT
- MAG Z = 1
- [F9] Z
- [F10] GRID OFF

Press E(nd), H(elp), S(ummary), compound # and toggles + ENTER to continue █

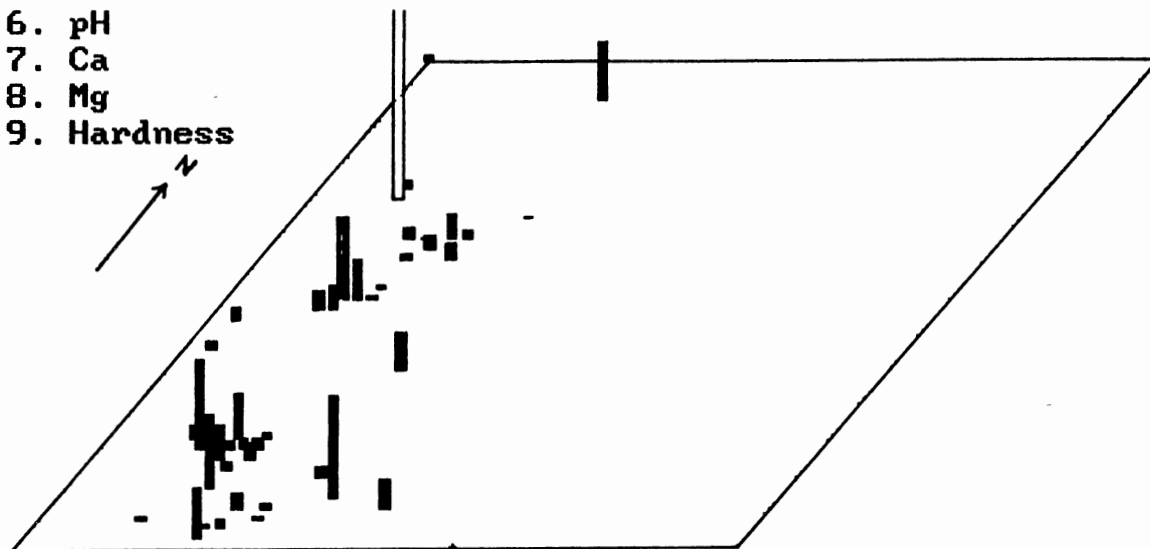
Cr-Fe-Mn-As-Se-pH-Ca-Mg-Hardness

CHEMPLOT - Version 1.31 A. W. HOUNSLOW Oklahoma State University

1. Cr
2. Fe
3. Mn
4. As
5. Se
6. pH
7. Ca
8. Mg
9. Hardness

Maximum value of Se is 367.5 ug/l

Minimum non-zero value is 1 ug/l



[F1] single/set
[F2] background
[F3] NW [F4] NE
[F5] SW [F6] SE
[F7] FULL VIEW
[F8] WELL PLOT
MAG Z = 1
[F9] Z
[F10] GRID OFF

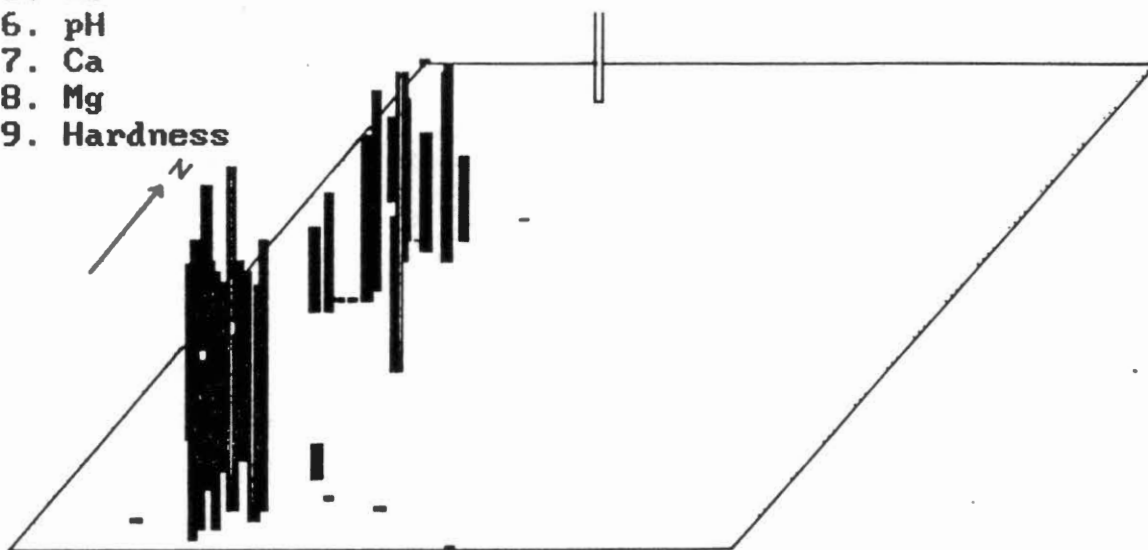
Press E(nd), H(elp), S(ummary), compound # and toggles + ENTER to continue █

Cr-Fe-Mn-As-Se-pH-Ca-Mg-Hardness

CHEMPLOT - Version 1.31 A. W. HOUNSLOW Oklahoma State University

1. Cr
2. Fe
3. Mn
4. As
5. Se
6. pH
7. Ca
8. Mg
9. Hardness

Maximum value of pH is 9.1 dim
Minimum non-zero value is 7 dim



[F1] single/set
[F2] background
[F3] NW [F4] NE
[F5] SW [F6] SE
[F7] FULL VIEW
[F8] WELL PLOT
MAG Z = 1
[F9] Z - MIN Z
[F10] GRID OFF

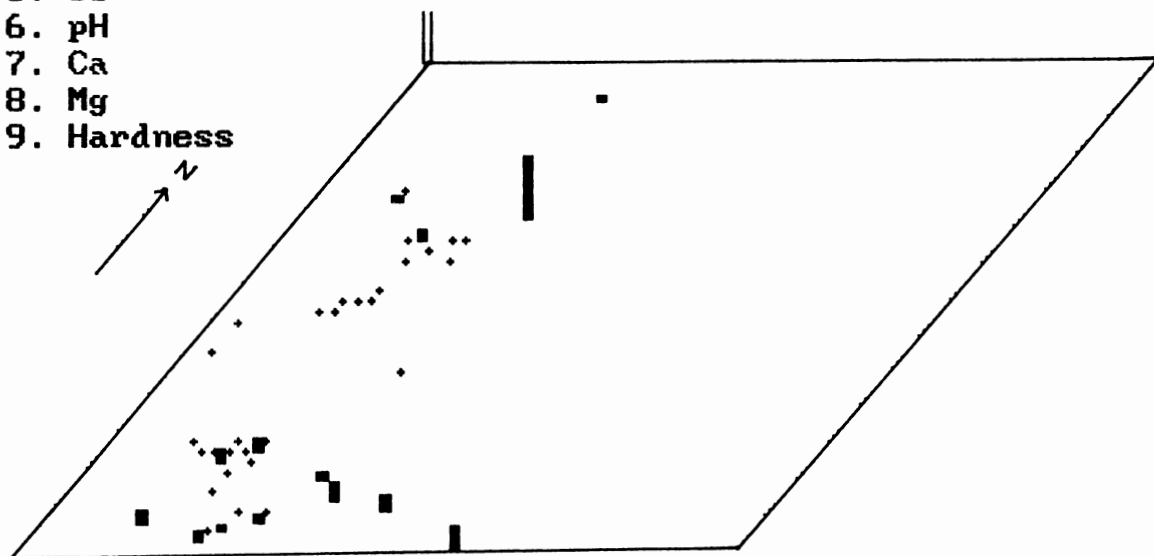
Press E(nd), H(elp), S(ummary), compound # and toggles + ENTER to continue █

Cr-Fe-Mn-As-Se-pH-Ca-Mg-Hardness

CHEMPLOT - Version 1.31 A. W. HOUNSLOW Oklahoma State University

1. Cr
2. Fe
3. Mn
4. As
5. Se
6. pH
7. Ca
8. Mg
9. Hardness

Maximum value of Ca is 100 mg/l
Minimum non-zero value is 1 mg/l



[F1] single/set
[F2] background
[F3] NW [F4] NE
[F5] SW [F6] SE
[F7] FULL VIEW
[F8] WELL PLOT
MAG Z = 1
[F9] Z
[F10] GRID OFF

Press E(nd), H(elp), S(ummary), compound # and toggles + ENTER to continue ■

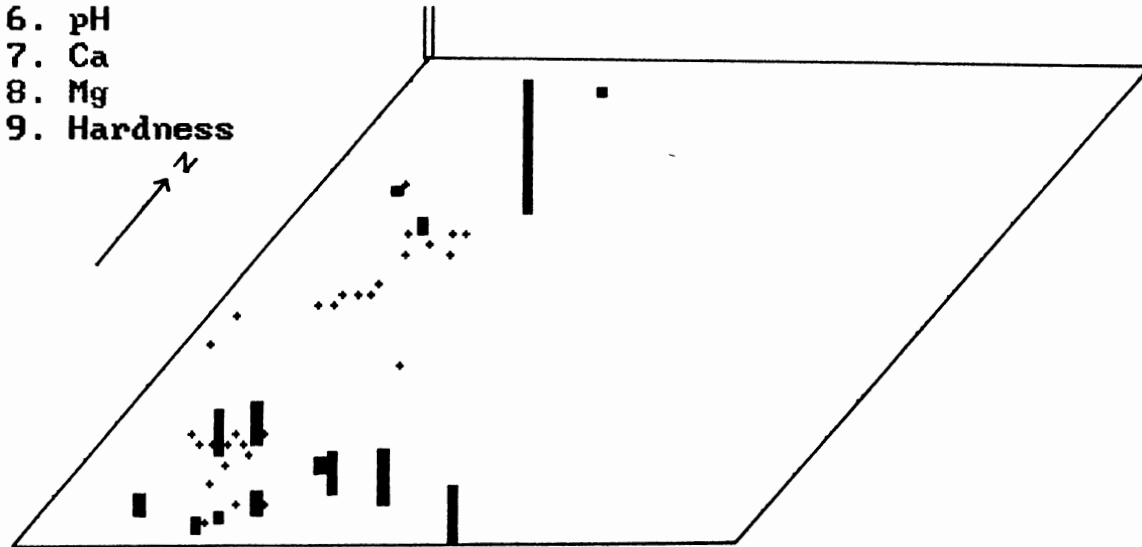
Cr-Fe-Mn-As-Se-pH-Ca-Mg-Hardness

CHEMPLOT - Version 1.31 A. W. HOUNSLOW Oklahoma State University

1. Cr
2. Fe
3. Mn
4. As
5. Se
6. pH
7. Ca
8. Mg
9. Hardness

Maximum value of Mg is 24 mg/l

Minimum non-zero value is 0.5 mg/l



[F1] single/set
[F2] background
[F3] NW [F4] NE
[F5] SW [F6] SE
[F7] FULL VIEW
[F8] WELL PLOT
MAG Z = 1
[F9] Z
[F10] GRID OFF

Press E(nd), H(elp), S(ummary), compound # and toggles + ENTER to continue █

Cr-Fe-Mn-As-Se-pH-Ca-Mg-Hardness

CHEMPLOT - Version 1.31 A. W. HOUNSLOW Oklahoma State University

1. Cr
2. Fe
3. Mn
4. As
5. Se
6. pH
7. Ca
8. Mg
9. Hardness

Maximum value of Hardness is 360 mg/l
Minimum non-zero value is 5 mg/l



[F1] single/set
[F2] background
[F3] NW [F4] NE
[F5] SW [F6] SE
[F7] FULL VIEW
[F8] WELL PLOT
MAG Z = 1
[F9] Z
[F10] GRID OFF

Press E(nd), H(elp), S(ummary), compound # and toggles + ENTER to continue █

Ba-SO4-T-Na-Cl-K-SC

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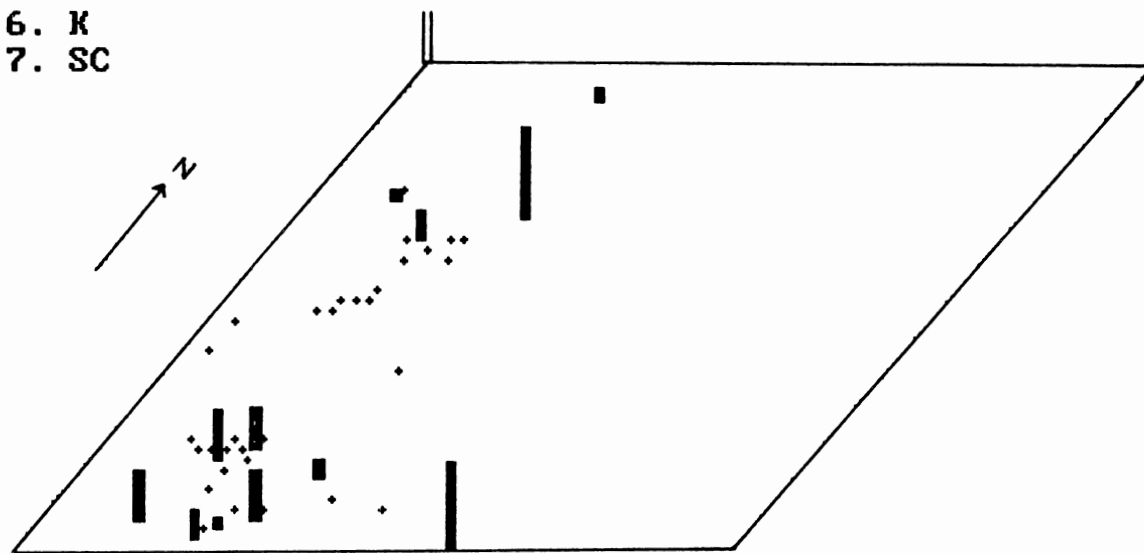
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 9,14,11,12,0,37,0,0,46,1,1080
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 11,14,18,13,26,20.5,17,125,102.5,2.8,625
 12,14,7,17,0,10,0,0,11,1,489
 13,14,10,17,0,10,0,0,5,1,489
 14,14,12,17,0,10,0,0,5,1,497.7
 15,14,12,16,60,10,18.5,36.7,6.1,0.4,540.7
 16,14,11,16,0,10,0,0,5,0,524
 17,14,10,16,0,10,0,0,5,0,500
 18,14,9,16,0,10,0,0,5,0,521
 19,14,8,16,0,10,0,0,37,0,708
 20,14,10,15,73.3,11,19.5,33.3,5.8,0.4,535.7
 21,14,12,15,0,10,0,0,5,0,555.5
 22,14,11,14,0,10,0,0,5,0,548
 23,14,7,42,0,10,0,0,5,0,0
 24,14,15,51,18.8,22.4,17.8,66,21,0.2,741.2
 25,14,1,55,370,42,17,59,93,1.6,885
 26,14,17,24,0,28,0,0,88,0,652
 27,14,9,30,0,20.7,0,0,52.3,0,708
 28,14,8,30,0,26.8,0,0,61.6,0,777.3
 29,14,3,29,0,25,0,105,9.5,0,0
 30,14,3,26,0,37,0,140,16,0,0
 31,14,14,35,0,17,0,0,43.7,0,661
 32,14,12,36,0,10,0,0,5,0,504
 33,14,11,35,0,22.5,0,0,8.5,0,662.5
 34,14,11,32,0,10,0,0,16,0,554
 35,14,9,31,0,10,0,0,5,0,0
 36,14,10,31,0,10,0,0,5,0,0
 37,14,11,31,0,10,0,0,20,0,678
 38,14,17,39,140,19,17.5,130,5,0,760
 39,14,13,37,0,16.8,0,0,18,0,669.3
 40,14,14,37,0,28,0,0,82,0,760
 41,14,7,41,14,41,18,130,115,0.4,1160
 42,14,10,37,0,27.5,0,0,5,0,506.5
 43,14,11,37,40,78,19,360,5,0,1410
 44,14,31,6,130,10,14.5,150,5,0,490

CHEMPLOT - Version 1.31 Ba-SO4-T-Na-Cl-K-SC
A. W. HOUNSLOW Oklahoma State University

1. Ba
2. SO4
3. T
4. Na
5. Cl
6. K
7. SC

Maximum value of Ba is 370 ug/l
Minimum non-zero value is 14 ug/l



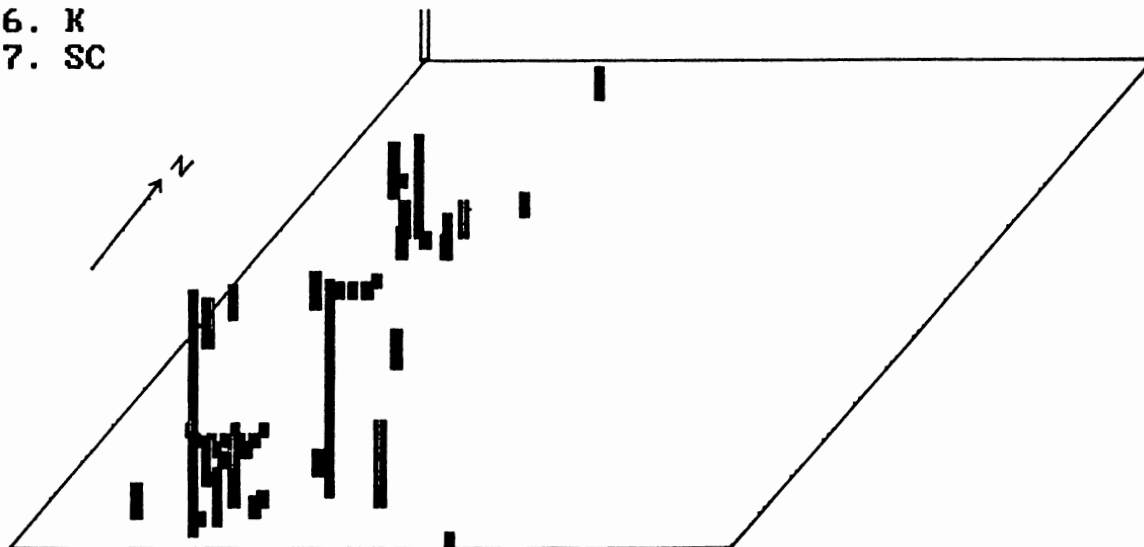
[F1] single/set
[F2] background
[F3] NW [F4] NE
[F5] SW [F6] SE
[F7] FULL VIEW
[F8] WELL PLOT
MAG Z = 1
[F9] Z
[F10] GRID OFF

Press E(nd), H(elp), S(ummary), compound # and toggles + ENTER to continue █

CHEMPLOT - Version 1.31 Ba-SO4-T-Na-Cl-K-SC A. W. HOUNSLOW Oklahoma State University

- 1. Ba
- 2. SO4
- 3. T
- 4. Na
- 5. Cl
- 6. K
- 7. SC

Maximum value of SO4 is 190 mg/l
Minimum non-zero value is 10 mg/l



[F1] single/set
[F2] background
[F3] NW [F4] NE
[F5] SW [F6] SE
[F7] FULL VIEW
[F8] WELL PLOT
MAG Z = 1
[F9] Z
[F10] GRID OFF

Press E(nd), H(elp), S(ummary), compound # and toggles + ENTER to continue █

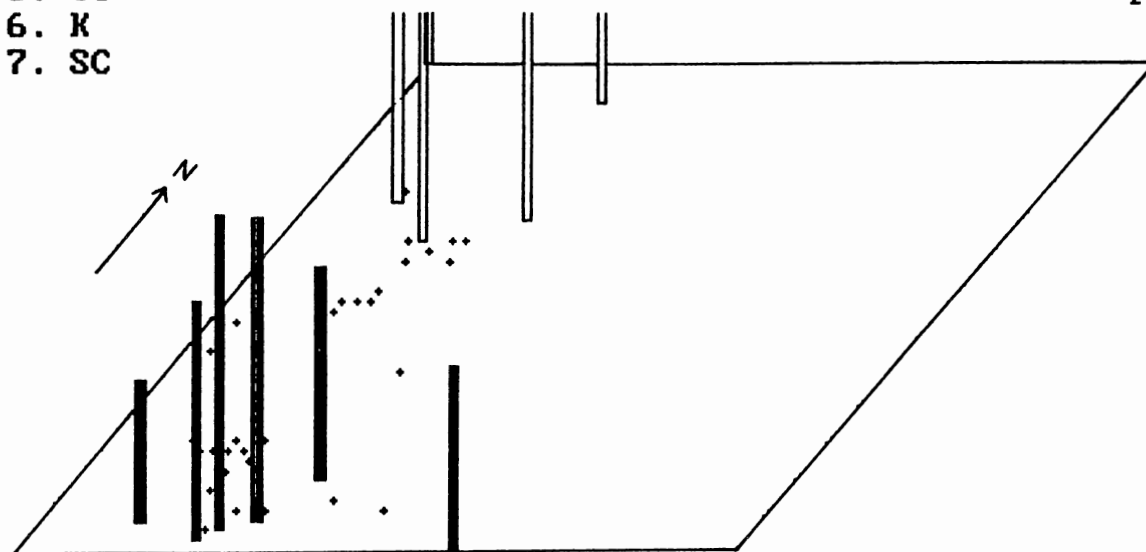
Ba-SO4-T-Na-Cl-K-SC

CHEMPLOT - Version 1.31 A. W. HOUNSLOW Oklahoma State University.

1. Ba
2. SO4
3. T
4. Na
5. Cl
6. K
7. SC

Maximum value of T is 19.5 deg.C
Minimum non-zero value is 11 deg.C

T = temperature



[F1] single/set
[F2] background
[F3] NW [F4] NE
[F5] SW [F6] SE
[F7] FULL VIEW
[F8] WELL PLOT
MAG Z = 1
[F9] Z
[F10] GRID OFF

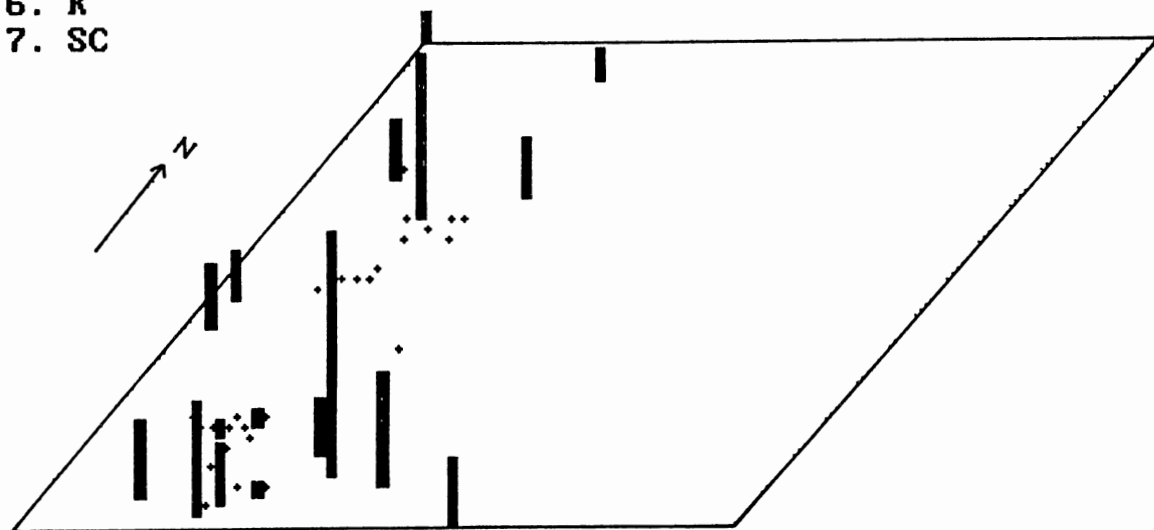
Press E(nd), H(elp), S(ummary), compound # and toggles + ENTER to continue █

Ba-SO4-T-Na-Cl-K-SC

CHEMPLOT - Version 1.31 A. W. HOUNSLOW Oklahoma State University

1. Ba
2. SO4
3. T
4. Na
5. Cl
6. K
7. SC

Maximum value of Na is 540 mg/l
Minimum non-zero value is 30.3 mg/l



[F1] single/set
[F2] background
[F3] NW [F4] NE
[F5] SW [F6] SE
[F7] FULL VIEW
[F8] WELL PLOT
MAG Z = 1
[F9] Z
[F10] GRID OFF

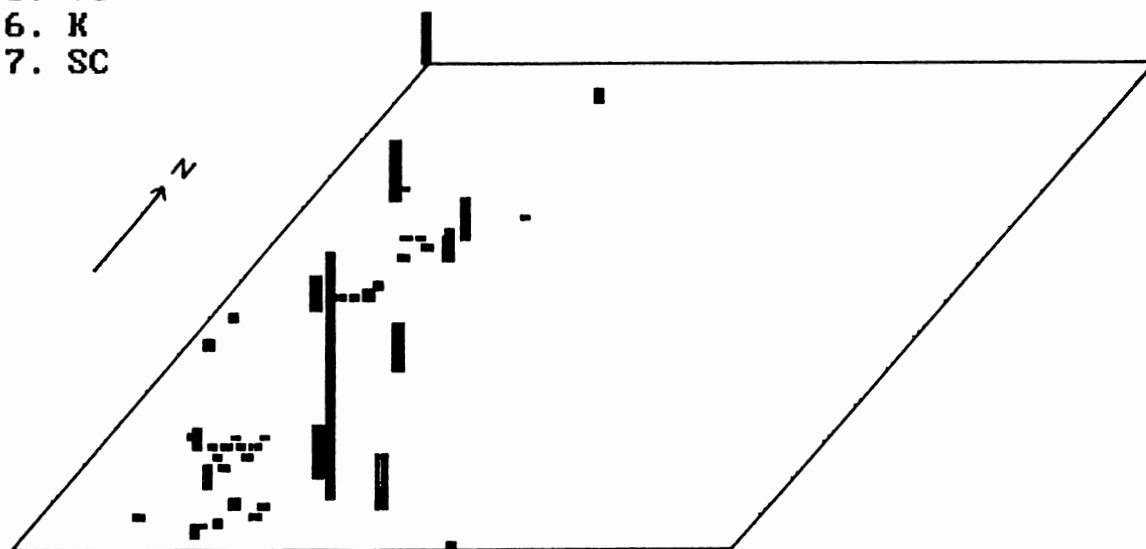
Press E(nd), H(elp), S(ummary), compound # and toggles + ENTER to continue █

Ba-SO4-T-Na-Cl-K-SC

CHEMPLOT - Version 1.31 A. W. HOUNSLOW Oklahoma State University

1. Ba
2. SO4
3. T
4. Na
5. Cl
6. K
7. SC

Maximum value of Cl is 490 mg/l
Minimum non-zero value is 4.3 mg/l



[F1] single/set
[F2] background
[F3] NW [F4] NE
[F5] SW [F6] SE
[F7] FULL VIEW
[F8] WELL PLOT
MAG Z = 1
[F9] Z
[F10] GRID OFF

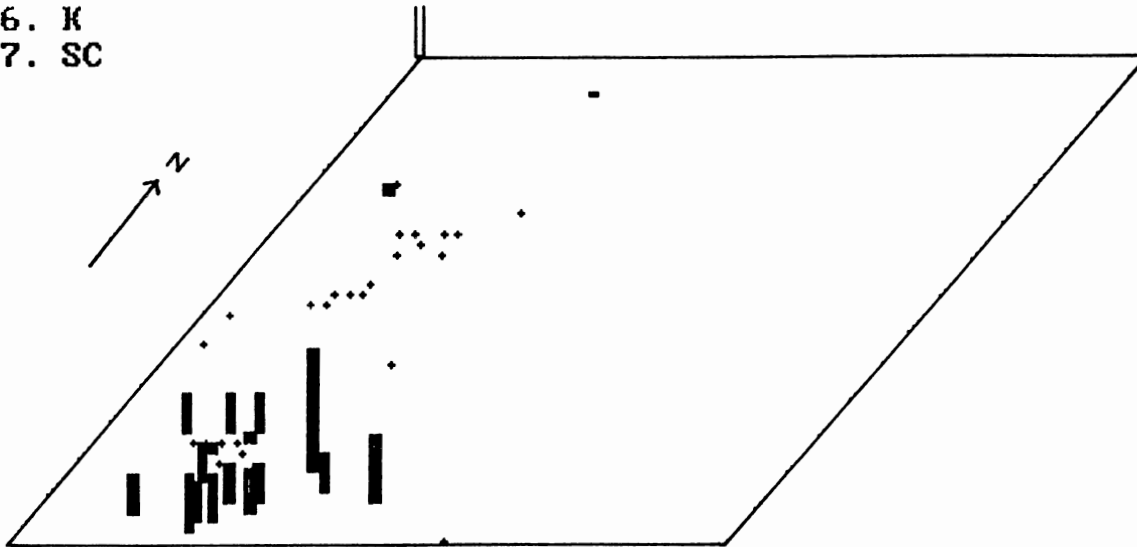
Press E(nd), H(elp), S(ummary), compound # and toggles + ENTER to continue █

Ba-SO4-T-Na-Cl-K-SC

CHEMPLOT - Version 1.31 A. W. HOUNSLOW Oklahoma State University

1. Ba
2. SO4
3. T
4. Na
5. Cl
6. K
7. SC

Maximum value of K is 2.8 mg/l
Minimum non-zero value is 0.2 mg/l



[F1] single/set
[F2] background
[F3] NW [F4] NE
[F5] SW [F6] SE
[F7] FULL VIEW
[F8] WELL PLOT
MAG Z = .5
[F9] Z - MIN Z
[F10] GRID OFF

Press E(nd), H(elp), S(ummary), compound # and toggles + ENTER to continue █

Ba-SO4-T-Na-Cl-K-SC

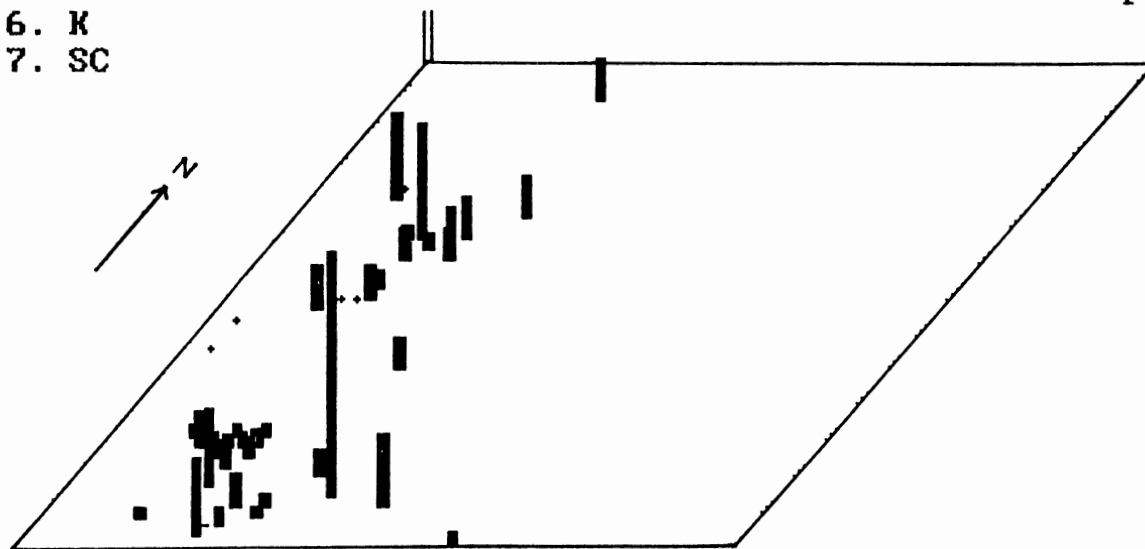
CHEMPLOT - Version 1.31 A. W. HOUNSLOW Oklahoma State University

1. Ba
2. SO4
3. T
4. Na
5. Cl
6. K
7. SC

Maximum value of SC is 2590 us/cm

Minimum non-zero value is 389 us/cm

SC = specific conductance



[F1] single/set
[F2] background
[F3] NW [F4] NE
[F5] SW [F6] SE
[F7] FULL VIEW
[F8] WELL PLOT
MAG Z = 1
[F9] Z - MIN Z
[F10] GRID OFF

Press E(nd), H(elp), S(ummary), compound # and toggles + ENTER to continue █

APPENDIX D

**GROUPING OF MAJOR ELEMENTS BASED ON
THEIR MAXIMUM AND MINIMUM VALUES**

GROUPING OF MAJOR ELEMENTS BASED ON
THEIR MAXIMUM AND MINIMUM VALUES

Variables	Range	County	Local Identifier
Cr dis.	5 - 130 ug/l	Cleveland	09N-01W-13 CDC 1
Fe	3 - 6,100 ug/l		
Mn	1 - 100 ug/l		
pH	7.6- 9.1		
DOC	0.4- 2.1 mg/l		
Ca	2.5- 100 mg/l	Logan	17N-04W-31 CCC 1
Mg	0.8- 24 mg/l		
Ba	10 - 370 ug/l		
Na	59 - 540 mg/l		
Hardness	5 - 360 mg/l		
Se	1 - 385 ug/l	Oklahoma	14N-03W-07 DAA 2
Cr*	27 - 210 ug/l		
Cr tot.	10 - 210 ug/l		
Cl	10 - 490 mg/l	Cleveland	09N-01W-08 CCC 1
F	0.2- 1.8 mg/l		
SC	353 -1,590 us/cm		
Cr(VI)	1 - 130 ug/l	Oklahoma	12N-03W-04 CCD 1
As	10 - 69 ug/l	Logan	16N-02W-21 BAA 3
K	0.5- 4.5 mg/l	Cleveland	10N-02W-36 CCC 2
SO ₄ ²⁻	9.9- 190 mg/l	Cleveland	09N-02W-31 DAA 1
T	11 - 17.5°C	Cleveland	10N-03W-22 DAD 1
DO	0.2- 13.2 mg/l	Cleveland	10N-02W-36 CCC 2

Explanation:

Cr dis. = dissolved chromium
 Cr* = average chromium
 Cr tot. = total chromium
 Cr(VI) = dissolved hexavalent chromium
 DOC = dissolved organic carbon
 SC = specific conductance
 T = temperature
 DO = dissolved oxygen

VITA²

Dina Muliati Elisabeth Sulistio

Candidate for the Degree of

Master of Science

Thesis: THE OCCURRENCE OF CHROMIUM IN THE CENTRAL OKLAHOMA
AQUIFER AND ITS RELATIONSHIP TO OTHER MAJOR ELEMENTS

Major Field: Geology

Biographical:

Personal Data: Born in Palembang, South Sumatera, Indonesia, October 16, 1963, the daughter of Sofian Sulistio and Rusianty.

Education: Graduated from Sancta Ursula High School, Jakarta, Indonesia, in June 1983; received Sarjana Strata 1 (Bachelor of Science) degree in Geology and Exploration Geophysics from Bandung Institute of Technology, Bandung, Indonesia, in March 1989; completed requirements for the Master of Science degree at Oklahoma State University, Stillwater, in December 1992.

Professional Experience: Research assistant, Krakatau Expedition, Department of Geology, Bandung Institute of Technology, Indonesia, 1984-1985; research assistant, Geomagnetic Study on Lembang Fault, Department of Geology, Bandung Institute of Technology, Indonesia, August-December 1987; teaching assistant, Geophysics and Volcanology Laboratory, Department of Geology, Bandung Institute of Technology, Indonesia, January 1987-June 1989; teaching assistant, Department of Geology, Oklahoma State University, 1990-1991.

Professional Organization: National Ground Water Association.