

SELENIUM SPECIATION ALONG A GROUNDWATER
FLOW PATH IN THE CARRIZO AQUIFER,
SOUTHEASTERN TEXAS, USA.

by

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ABSTRACT

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Selenium concentration and speciation [Se (VI), Se (IV) and Se (-II)] was determined along a flow path in the Carrizo Sand aquifer (southeastern Texas). Groundwater sampling was carried out in March 2006, from ten wells located along the flow path. The collected samples were filtered through 0.45 μm filters and then acidified to pH <2 using ultra pure HCl. Analysis for Se concentration and speciation was done using selective hydride generation – Atomic Absorption spectrometry (HG-AAS). Additional in situ measurements from each well included determination of pH, alkalinity, oxidation-reduction potential (Eh in mV), dissolved iron speciation, dissolved sulfide concentrations and dissolved manganese concentrations. Selenium concentrations in groundwaters of the Carrizo Sand aquifer are

very low (i.e., nanomolar concentrations). Variations in redox condition and geochemical processes appear to exert important controls on the distribution of Se species in Carrizo groundwaters. Redox conditions fluctuate between oxic to mildly reducing environment, in regions proximal to the recharge zone (i.e. ~ 0-15 km). Downgradient at a distance of 15-41 km, Fe (III) reduction is the dominant process, which is followed by sulfate reduction dominating at a distance >41 km along the flow path. Se (VI) and Se (-II) show variable behavior in regions near the recharge zone, whereas Se (IV) dominates in this region. Beyond 26 km, Se (VI) becomes the dominant species. The data are consistent with Fe (II) oxidation, reduction of Fe (III)/ Mn (IV) oxides/oxyhydroxides and pH induced adsorption/desorption as important controlling factors for Se concentrations and speciation within the first 41 km of the groundwater flow path. Further downgradient at a distance >41km (sulfate reduction zone) along the flow path, pH induced desorption appears to lead to the dominance of Se (VI) species in solution. Changes observed in Se concentration and speciation in the Carrizo Sand aquifer are co-relative with the distribution of pH, alkalinity, Eh, and dissolved concentrations of iron, sulfide and manganese, studied along the flow path.

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CHAPTER 1

INTRODUCTION

Selenium occurs naturally as a trace element in both aquatic and terrestrial environments (Stolz and Oremland, 1999). The distribution of selenium in the environment is controlled by various processes that involve physical and chemical as well as biological processes. Processes such as volcanism, combustion (fossil fuels), weathering of selenium-rich rocks and soils, leaching, groundwater flow, adsorption, and oxidation and reduction processes (both biological and chemical) contribute towards the distribution of selenium in the environment (Nriagu and Pacyna, 1988; Besser et al., 1989; Cutter, 1993; Haygarth, 1994; Garbisu et al., 1996; Stolz and Oremland, 1999; Ike et al., 2000; Kulp and Pratt, 2004; Wu, 2004).

The study of selenium in the environment has increased due to its dual nature (as both a nutrient at low concentration and being toxic at high levels) (Robberecht and Van Grieken, 1982; Harrison et al., 1988; Ohlendorf, 1989; Stolz and Oremland, 1999; Amouroux et al., 2001). Studies have been carried out relating to the metabolic importance of selenium in both animals and human beings. Studies relating to plant growth have shown that varying concentrations of selenium can affect plant growth (Fordyce, 2000; Wu, 2004). Deficiency of selenium in animals can result in liver necrosis, muscular dystrophy, Keshan disease as well as white muscle disease (Robberecht and Van Grieken, 1982; Wu, 2004). Exposure to higher concentrations ($2-5 \mu\text{g Se g}^{-1}$) can result in toxic conditions for the animals resulting

in their infertility, deformity of body organs and mortality (Weres et al, 1989; Stolz and Oremland, 1999; Wu, 2004). In relation to human beings, the role of selenium is controversial and is not fully understood (Robberecht and Van Grieken, 1982). Studies conducted by Shamberger (1974-81) relating to human beings have shown that death due to cancer is lower in regions where selenium content is high in the environment. Also the risk of death due to heart disease appears to be lower in selenium rich environments (Robberecht and Van Grieken, 1982). Still at elevated concentrations, selenium is linked to disease in humans such as bronchospasm, irritation of respiratory passages, discoloration of skin and loss of hair and nails.

Selenium is extensively used in industry, as a decolorizing agent in the glass industry, as an additive for stainless steel and vulcanizing agent in the rubber industry. Selenium compounds are used in photography, xerography, in insecticides, photoelectric cells and as an anti-dandruff agent. Selenium is used in agricultural purposes as a dietary supplement in soils having low selenium. Therefore, the concentration of selenium in drinking water supplies resulting from anthropogenic sources is of concern. If the concentration of selenium exceeds the U.S. EPA's Maximum Contaminant Level (MCL) for drinking water ($10 \mu\text{gL}^{-1}$), there is evidence for toxic response in human populations (Robberecht and Van Grieken, 1982; Liu and Narasimhan, 1994). Consuming water with selenium concentration in excess of the U. S. EPA's Maximum Contaminant Level (MCL) i.e., $10 \mu\text{gL}^{-1}$, is thought to be a major contributor to diseases (Liu and Narasimhan, 1994; Fordyce et al., 2000; Vinceti et al., 2000; Lemly and Ohlendorf, 2002; Hoffman, 2002). There are four common forms of selenium in the environment, and each of which exhibits

different chemical behavior in the environment. The hexavalent selenate ion (SeO_4^{2-}) and tetravalent selenite ion (SeO_3^{2-}) are toxic to organisms if they exist at sufficient concentration (Ike et al., 2000). Elemental selenium (Se^0) is non-toxic and organic selenide [$\text{Se}(-\text{II})$] oxidize to form the non-toxic form.

My research work focuses on determining the concentration and chemical speciation of selenium along a specific groundwater flow path in the Carrizo Aquifer, Texas. The flow path chosen for my study has been extensively studied by other researchers for rare earth element concentrations (Tang and Johannesson, 2005; Tang and Johannesson, 2006) and for speciation of elements like Cr and As (Vessely et al., 2004; Haque and Johannesson, 2006). Many wells exist along the flow path and the age of the groundwater along the flow path is relatively well known (Pearson and White, 1967; Stute et al., 1992; Castro et al., 2000; Castro and Goblet, 2003). Collected groundwater samples from ten wells, located along the flow path of the Carrizo Sand aquifer (Fig. 1) were used to study the concentration and speciation of selenium along the flow path, and to infer the geochemical processes that control selenium concentration and speciation in groundwater flow systems. The methodical approach of sampling carried out along the specific flow path in the Carrizo Sand aquifer, is important because it is instrumental in understanding how the concentration and speciation of a trace element changes along a groundwater flow path. The Carrizo Sand aquifer chosen for investigation of selenium contamination, has low selenium concentrations and is unaffected by any anthropogenic sources of selenium. Given, the low concentration of selenium, in groundwaters from the Carrizo Sand aquifer are below the EPA's approved Maximum Contaminant Level (MCL) for selenium i.e., $10 \mu\text{gL}^{-1}$ by orders of magnitude.

CHAPTER 2

LOCATION, GEOLOGY and HYDROGEOLOGY

The Carrizo sand aquifer, which is of Eocene age, is a confined aquifer (Hamlin, 1988; Castro et al., 2000; Castro and Goblet, 2003). The Carrizo sand outcrop is present in the eastern and southern part of Texas and is almost parallel with the Gulf Coast in the southeastern region of Texas (Pearson and White, 1967; Castro and Goblet, 2003). Groundwater samples were collected from the aquifer in the Atascosa and McMullen counties, south of San Antonio city (Fig. 1). The Carrizo sand aquifer is relatively homogeneous and is the dominant part of the Carrizo Formation. It consists of fine to medium grained quartz sand (fluvial deposit) with minor amounts of clay, lignite, calcite and pyrite (Pearson and White, 1967; Hamlin, 1988; Castro et al., 2000; Castro and Goblet, 2003). The aquifer is a part of a regressive sequence that comprises of fluvial, deltaic and marine depositional systems (Hamlin, 1988; Castro and Goblet, 2003). The Carrizo sand, present in the outcrop and shallower regions, correlates with the upper part of the Wilcox Group. In deeper subsurface regions, the overlying unit of the aquifer in the eastern and north-eastern part is the Recklaw Formation which comprises of marine mudstones, whereas in the western part, the non marine mudstone and sandstone form the Bigford Formation (Hamlin, 1988; Castro et al., 2000; Castro and Goblet, 2003). They form a confining unit for the sandy aquifer. The Carrizo-upper Wilcox Group is underlain by the transgressive Middle Wilcox Group which consists of shale, clay and sandy lenticular beds.

The dip of the aquifer is 1.09°- 1.41° towards southeast. The groundwater flow is along the dip direction (Pearson and White, 1967; Castro and Goblet, 2003). The Carrizo aquifer is a freshwater aquifer, but the salinity increases towards the southeast reaching the level of 10g/L at the southern part of the McMullen County (Castro et al., 2000; Castro and Goblet, 2003). The groundwater from the aquifer is used for drinking and irrigational purpose. The porosity of the aquifer ranges from 30% to 40% (Pearson and White, 1967; Castro et al., 2000).

Pearson and White (1967) used the ^{14}C to determine the age of groundwater from the Carrizo sand aquifer. They found that the groundwater from the outcrop areas of the aquifer (i.e. recharge zone) is zero years in terms of ^{14}C ages, whereas down dip at about 35 miles away, the age of the groundwater is 27,000 ^{14}C years (Fig. 1). The Carrizo sand outcrop in the northern part of the Atascosa County, Texas, is recharged by rainfall, and the water flows down dip towards the southeast (along the dip direction) (Hamlin, 1988; Castro et al., 2000; Castro and Goblet, 2003). The hydraulic conductivity varies along the Carrizo sand aquifer, such that in the northeastern and central zones of the aquifer, the hydraulic conductivity is similar i.e. 8.0-66.9ft/day, whereas in the southwestern zone, the conductivity rates are lower, i.e. about 1.3-53.5ft/day (Hamlin, 1988). Thus the sand bodies of the fluvial deposits, having higher hydraulic conductivities are the main pathways for the groundwater flow in the Carrizo aquifer.

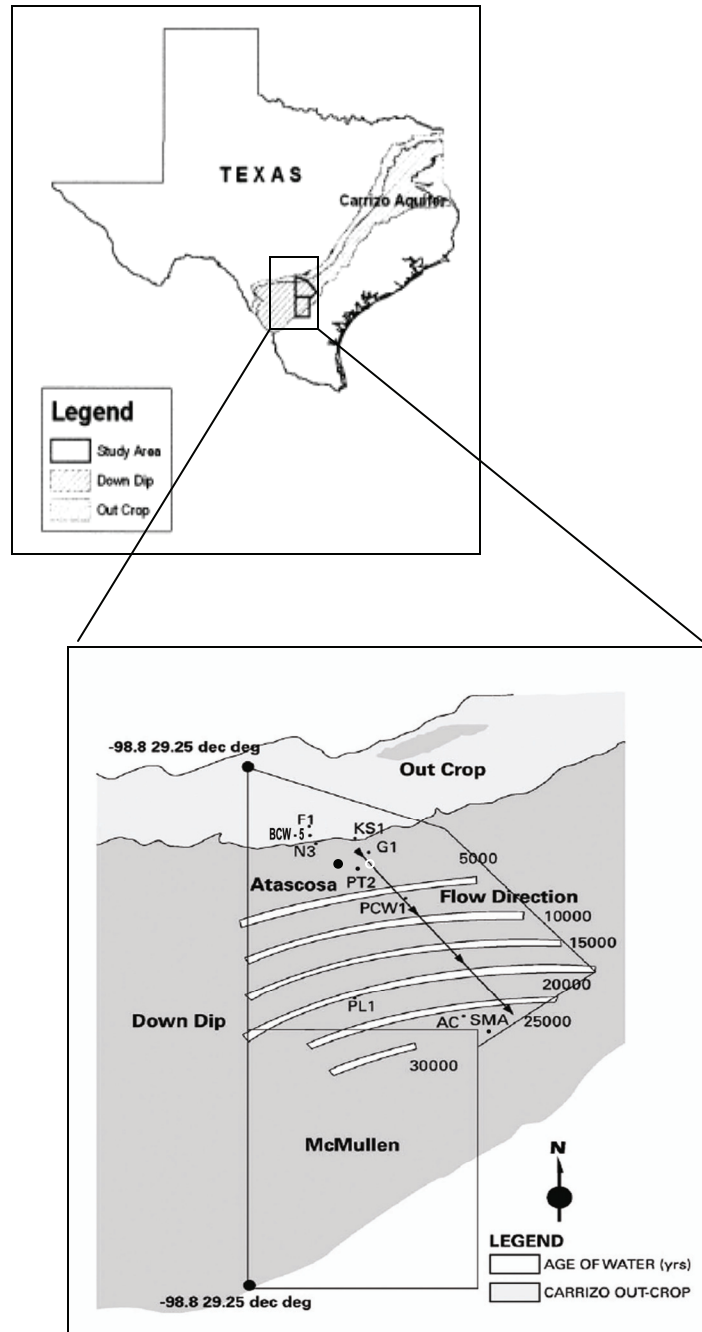


Figure 1: Location of Carrizo Sand aquifer within a map of Texas. Inset showing well locations along the studied groundwater flow path, radiocarbon ages of groundwater (Pearson and White, 1967). Modified from Haque and Johannesson (2006).

CHAPTER 3

BACKGROUND

Selenium concentrations in the Earth's crust are generally less than 1 ppm. The average crustal concentration value ranges from 0.03 to 0.09 ppm (N.A.S., 1976; Stolz and Oremland, 1999). Selenium is combined with other compounds in the environment such as sulfide ores of the heavy metals or with lead and silver [e.g.: Clausthalite (PbSe), Naumannite ((Ag, Pb) Se)]. The concentration of selenium in igneous rocks is about 0.09 ppm (N.A.S., 1976). In sedimentary rocks, the concentration of selenium is higher in shales compared to sandstone and limestone (Nriagu and Pacyna, 1988; Wu, 2004). Research has shown that presence of selenium in oceans and inland waters, also contribute towards the presence of selenium in drinking waters (Measures and Burton, 1978; Robberecht and Van Grieken, 1982; Cutter and Bruland, 1984; Liu and Narasimhan, 1994). Selenium is also associated with volcanic effluents (with sulfur), thus soils surrounding volcanoes are commonly rich in selenium (N.A.S., 1976; Wu, 2004).

Selenium, like sulfur, belongs to group VI of the periodic table and both exhibit similarities in their chemical behavior. Selenium has several oxidation states and its behavior in the environment is largely controlled by its nature of occurrence which is controlled by pH and redox state. The primary oxidation states are +6, +4, 0 and -2 (Weres et al., 1989; Liu and Narasimhan, 1994; White and Dubrovsky, 1994; Ehrlich, 1996; Belzile et al., 2000). Changes

in these oxidation states affect the movement, toxicity and deficiency of this element in the environment.

3.1: Hexavalent selenate ion [Se (VI)]

The hexavalent form of selenium, selenate is soluble in water and is expected to be more common in alkaline environment (Weres et al., 1989; Liu and Narasimhan, 1994). However, in acidic environments the selenate ion may be converted to selenite or elemental selenium, but it is a much slower process than the reduction of selenite ion to elemental selenium (Liu and Narasimhan, 1994). In oxic environments, selenate is one of the primary forms of selenium.

Soluble selenates are present in alkaline soils or in dry areas where weathering of alkaline rocks is prevalent. Selenates present in soil are taken up by plants, which causes toxic concentration of selenium in the plant tissues.

In regard to environmental pollution, the stability of selenate in alkaline environments, its high solubility and its ready uptake by plants, generally leads it to being considered the most dangerous form of selenium in the environment.

3.2: Tetravalent selenite ion [Se (IV)]

The selenite ion is stable under moderately oxidizing conditions and in alkaline waters (N.A.S., 1976; Liu and Narasimhan, 1994). Dissolved selenite is present mainly as biselenite ion (Liu and Narasimhan, 1994). Salts of selenite are less soluble than that of selenates.

Selenite is strongly adsorbed by metal oxides and clays common to soils (Weres et al., 1989; Liu and Narasimhan, 1994). Selenate does not form such surface complexes and is easily dissolved and leached from soils into groundwater. Another important fact in relation to the environmental cycling is that selenite is rapidly reduced to insoluble elemental selenium under acidic conditions. The kinetics of selenite reduction is much faster than the reduction of selenate to selenite or elemental selenium (Liu and Narasimhan, 1994).

Adsorption of selenite to clay minerals, organic matters, and its high affinity to adsorb to Fe-oxides, minimizes the risk of poisoning of organisms. In addition, formation of selenium sulfides, lower solubility of selenite salts, and its rapid reduction to insoluble elemental selenium minimizes hazard due to selenite poisoning (Weres et al., 1989; Velinsky and Cutter, 1991; Ike et al., 2000; Kulp and Pratt, 2004; Wu, 2004).

3.3: Elemental selenium [Se⁰]

In the transition zone of oxic/anoxic environments the disappearance of the soluble oxyanion forms of selenium, i.e., selenate and selenite are replaced by elemental selenium. Consequently, elemental selenium is thermodynamically predicted to be the most dominant species in anoxic environment (N.A.S., 1976; Weres et al., 1989; Liu and Narasimhan, 1994; Stolz and Oremland, 1999; Ike et al., 2000).

Elemental selenium is insoluble in aqueous environments and is the least toxic form of the element (Liu and Narasimhan, 1994; Ike et al., 2000). Elemental selenium occurs under reducing conditions over the whole pH range observed in natural waters (N.A.S., 1976; Weres et al., 1989; Liu and Narasimhan, 1994). Elemental selenium usually coexists with

organic matter and selenium bound to organic matter (Weres et al., 1989). Decomposition of fossil fuels and organic materials at high temperature result in the formation of elemental selenium. Sulfur dioxide and SeO_2 is always formed as a result of the combustion of elemental selenium. The excess sulfur dioxide that is formed during combustion is helpful in the reduction of SeO_2 . Therefore SeO_2 is reduced to elemental selenium by sulfur dioxide (N.A.S., 1976).

In relation to environmental pollution, elemental selenium can be considered as a 'sink' and its contamination in soil or water poses minimum hazard of selenium toxicity.

3.4: Selenide [Se (-II)]

Selenide (Se^{-2}) generally forms a very strong acid, i.e. hydrogen selenide, H_2Se , which is chemically similar to H_2S . The fumes of this acid are very toxic. Hydrogen selenide compound is unstable in natural environment and rapidly decomposes to non-toxic elemental selenium and water in the presence of air (Weres et al., 1989; Liu and Narasimhan, 1994; Ike et al., 2000).

The selenides of heavy metals are very insoluble. Thus metal selenide may also be considered as a 'sink' for detoxification of selenium (White and Dubrovsky, 1994; Wu, 2004).

The different species of selenium can be portrayed in an Eh-pH diagram in relation to their redox conditions (Fig. 2).

3.5: Selenium in Industry

Selenium compounds are widely used in industry for various purposes. Selenium exhibits both photovoltaic action (light is converted directly into electricity) and photoconductive action (electrical resistance decreases with increased illumination), which are useful in both photography and xerography, respectively. Selenium is also used as an additive for stainless steel. In the glass industry, selenium is widely used as a decolorizing agent and in the rubber industry it is useful as a vulcanizing agent. Seleneous acid is used as a gun cleaning chemical. Selenium sulfide is widely used as an anti-dandruff agent in the shampoos.

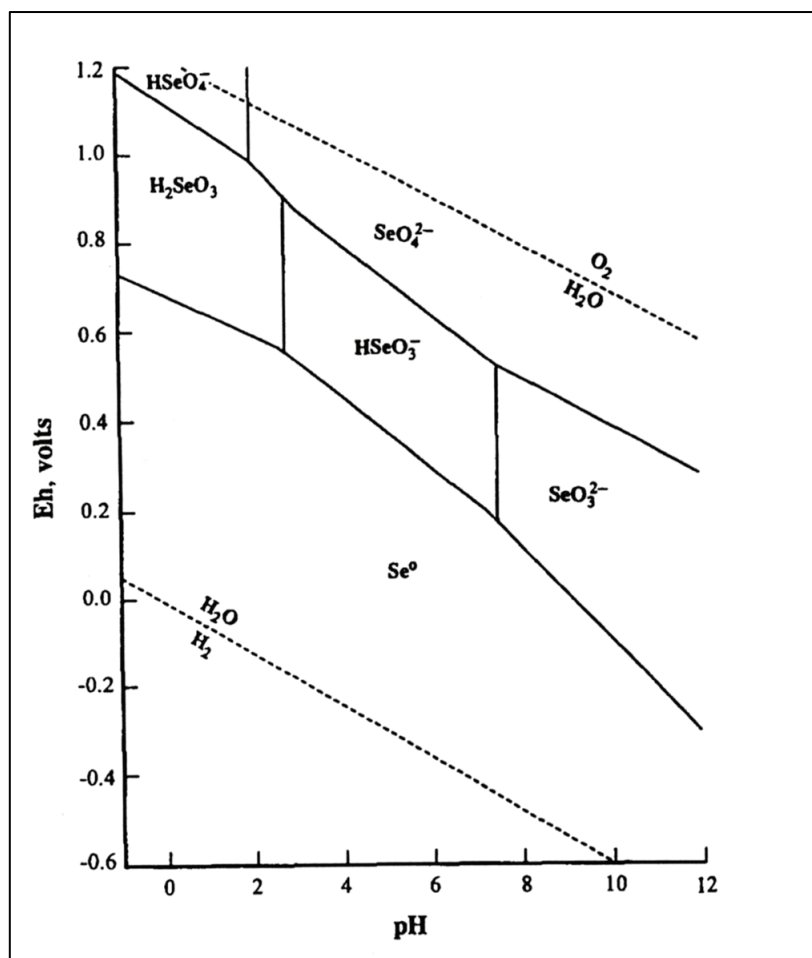


Figure 2: Stability of Se species with respect to Eh-pH conditions in an aqueous environment (From Liu and Narasimhan, 1994).

CHAPTER 4
MATERIALS AND METHODS

4.1: Sample Locations

Groundwater samples were collected from ten well sites located within the Carrizo Sand Aquifer, in the Atascosa and McMullen Counties of Texas. The water samples were collected in March, 2006 along a specific flow path (Fig. 1) that has been previously studied by various authors (Pearson and White, 1967; Castro et al., 2000; Castro and Goblet, 2003; Vessely, 2004; Tang and Johannesson, 2006; Haque and Johannesson, 2006). From each well site, the groundwater samples collected were analyzed for selenium species. Along with the ten samples, a field blank (MilliQ water treated like a sample – filtered & acidified) and three duplicates (wells KS-1, Poteet-2 and AC74R-2) were also collected.

4.2: Preparation of Sampling Materials

Prior to the transportation and collection of field samples all 1 Litre sample bottles (Borosilicate glass bottles with Teflon lined caps; Wheaton), 10 Litre LDPE (low-density polyethylene) cubitainers and Teflon® tubes were acid washed in the laboratory. Each 1L sample bottle was washed three times inside and outside with Milli-Q water (18.2-18.3 MΩ-cm, distilled and deionized). The borosilicate glass bottles were then filled with Milli-Q

water upto the mark of 800 mL. The remaining, 200mL was filled with trace metal grade hydrochloric acid (Fisher Scientific) and allowed to sit for 24 hours. The next day these bottles were rinsed three times with Milli-Q water and then sealed in two plastic Ziploc® bags to keep them uncontaminated prior to sampling. The 10L cubitainers were also triple washed with Milli-Q water and then kept in an acid bath containing 15% (v/v) mixture of reagent-grade nitric acid (Fisher Scientific) and were allowed to soak in the bath for seven days. After a week they were taken out of the reagent bath and rinsed three times with Milli-Q water. The cubitainers were again soaked in a bath tub containing 17% (v/v) mixture of trace metal grade nitric acid (Fisher Scientific). They were again left to soak in the trace bath for seven days. After a week the cubitainers were rinsed three times with Milli-Q water and then sealed in two plastic Ziploc® bags for transportation to the field. The double bagged sample bottles and cubitainers were placed in polyethylene boxes for transportation to the field site. The whole procedure of handling and cleaning of the bottles in the laboratory and field was carried out by wearing two sets of polyethylene gloves.

4.3: Parameters measured in the field

The process of water sampling in the field involved measurement of several parameters. The sampling wells in the Carrizo Sand aquifer are production wells. Prior to collection of groundwater samples, water was pumped out from all the wells for 30 minutes using high capacity pumps. This procedure ensured that the collected water was from the aquifer.

On site measurements included quantifying pH, specific conductance, temperature, oxidation-reduction potential (Eh in mV), and total dissolved solids (TDS) using a Hydrolab MiniSonde5 having a flow through cell. At individual well sites the MiniSonde5 flow through cell was attached to the end of the well outflow unit by means of a polyethylene tube. This process prevented the exposure of groundwater to the atmospheric oxygen and thus provided accurate measurements for the oxidation-reduction potential at each well site. To make sure that the collected water represented the groundwater from the Carrizo Sand aquifer and not from the well bore, measurements for pH, specific conductance and temperature were closely monitored during the flow. All sample waters were collected after the parameters reached a constant value. Titration procedure for measuring alkalinity was carried out in the field site using a digital titrator (HACH, Model 16900).

On site measurements also included quantifying data for iron species, H₂S concentration, manganese concentration, silica concentration, nitrate concentration and ammonia concentration. Measurements were carried out using a portable spectrophotometer (HACH DR/2400). Separate aliquots were used for each method.

Total Iron [Fe_T] was determined using the FerroVer Method (Eaton et al., 1995a) and FerroZine Method. The ferrous species [Fe (II)] was determined using the 1, 10 Phenanthroline Method (Eaton et al., 1995a) and ferric iron [Fe (III)] was calculated by the difference between [Fe_T] and [Fe (II)]. The detection limit for Fe_T and Fe (II) is 0.54 μmol/kg. Hydrogen sulfide was measured using the Methylene Blue Method (Eaton et al., 1995b). Detection limit for H₂S is 0.29 μmol/kg. Manganese, Silica, Nitrate, and Ammonia concentrations were determined using the PAN Method, Heteropoly Blue Method, Cadmiun

Reaction Method and Salicylate Method respectively in the portable DR/2400 spectrophotometer.

4.4: Selenium Collection and Analysis

The handling of the bottles in the field was carried out by wearing two sets of polyethylene gloves. The procedure for groundwater collection was similar at all the well sites. Cubitainers were rinsed three times with pumped out groundwater. The collected water was filtered through 0.45 μm filters (German Sciences, polyether sulfone membrane). The cleaned 1L sample bottles (Borosilicate glass bottles with Teflon lined caps; Wheaton) were rinsed three times with the filtered groundwater from the cubitainer prior to collection of the filtered sample water for laboratory analysis. Groundwater samples for selenium analysis were acidified to $\text{pH} < 2$ with ultra-pure HCL (Seastar Chemicals Inc., sub-boiling, distilled in quartz) to prevent the formation of precipitates, and to preserve the samples. All sample bottles were sealed in two plastic Ziploc® bags.

Total dissolved selenium and selenium species from Carrizo Sand Aquifer, Texas, U.S.A. were analyzed using Hydride generation - Atomic Absorption Spectrometer. This instrument facilitates the precise determination of the different oxidation states of selenium. The method followed for determining the species is described by Cutter (Cutter, 1978; Cutter, 1982). The instrument was calibrated, and the groundwater samples were verified using standard solutions (1000ppm) of sodium selenate and sodium selenite. Using this method of Hydride generation – Atomic Absorption Spectrometer, selenite [Se (IV)] can be determined selectively; and selenate [Se (VI)], from total of [Se (VI) + Se (IV)]

concentration. Applying some modifications to the existing apparatus (Cutter, 1978; Cutter, 1982; Cutter and Bruland, 1984), selenide [Se (-II)] concentrations can be also determined.

CHAPTER 5

RESULTS

The results for the groundwater samples from the Carrizo Sand aquifer are depicted in Table 1, Table 2 and Figs. 3 and 4. The pH values for the groundwater samples range from 6.1 to 8.6 (Fig. 3). Within the first 15 Km along the flow path the pH values show a consistent variation within the range of 6.1 to 6.4. Downgradient along the flow path at a distance > 40 Km the pH in the groundwater samples is > 8. The alkalinity along the flow path in the Carrizo Sand aquifer ranges from 0.63 mmol/kg to 5.76 mmol/kg as HCO_3^- (Fig. 3). Alkalinity varies within the first 15 Km of the flow path ranging from 0.63 mmol/kg to 1.3 mmol/kg as HCO_3^- . At a distance greater than 26 Km, the alkalinity shows a general increase along the flow path reaching 5.76 mmol/kg, at a distance of 65.8 Km (Fig. 3).

Total dissolved iron concentrations (i.e. Fe_T) in groundwaters varies from 0.2 $\mu\text{mol Kg}^{-1}$ to 54 $\mu\text{mol Kg}^{-1}$ (Table 1, Fig. 4). For the region of the aquifer proximal to the recharge zone (i.e., ~ 0 to 15 Km), the Fe_T concentration varies widely from 0.73 $\mu\text{mol Kg}^{-1}$ to 31.6 $\mu\text{mol Kg}^{-1}$. At 0.5 Km (well F-1) along the flow path the Fe_T concentration is 13.8 $\mu\text{mol Kg}^{-1}$. The concentration increases to 15.8 $\mu\text{mol Kg}^{-1}$ at 4.3 Km (well BCW-5) along the flow path. Further down gradient along the flow path at 7.4 Km (well KS-1), the Fe_T concentration drops to 0.73 $\mu\text{mol Kg}^{-1}$. The Fe_T rises again at a distance of 9.4 Km (well N-3) to 11.5 $\mu\text{mol Kg}^{-1}$. With further flow down gradient, the Fe_T concentration increases to 31.6 $\mu\text{mol Kg}^{-1}$ at a

distance of ~ 13.0 Km (well G-1) followed by a decrease in the Fe_T concentration to $24.0 \mu\text{mol Kg}^{-1}$ at a distance of ~ 15 Km (Poteet well). Further along the groundwater flow path, the Fe_T concentrations increase from $19.5 \mu\text{mol Kg}^{-1}$ at a distance of 26 Km (well PCW-1) to $54.4 \mu\text{mol Kg}^{-1}$ at 41 Km (Peeler-1 well) respectively. The remaining flow path shows a sharp decrease in the Fe_T concentration with values of $0.24 \mu\text{mol Kg}^{-1}$ at a distance of 59 Km (well AC74R-2), and $0.96 \mu\text{mol Kg}^{-1}$ at a distance of 65.8 Km (well SMA74R-1). The dominant form of iron (Fe) in the groundwater of the Carrizo Sand aquifer along the observed flow path is ferrous [Fe (II)] form. Fe (II) concentrations range from below detection limit (i.e., $0.36 \mu\text{mol Kg}^{-1}$) to $54.4 \mu\text{mol Kg}^{-1}$ (Table 1, Fig. 4). Ferric [Fe (III)] concentrations [calculated from the difference between Fe_T and Fe (II)] range from $0.01 \mu\text{mol Kg}^{-1}$ to $9.3 \mu\text{mol Kg}^{-1}$ (Table 1, Fig. 4). The regions closer to the recharge zone (~0-15Km) generally exhibit higher concentration of [Fe (II)] relative to [Fe (III)]. The only exception is at 4.2 Km (well BCW-5), where the [Fe (III)] concentration ($8.2 \mu\text{mol Kg}^{-1}$) is greater than [Fe (II)] concentration ($7.5 \mu\text{mol Kg}^{-1}$). Ferrous iron concentration increase down gradient at wells PCW-1 (26.1 Km) and Peeler-1 (41.1 Km) except for wells AC74R-2 at a distance of 59.0 Km and SMA74R-1 at a distance of 65.8 Km, where the [Fe (III)] is higher than the [Fe (II)] concentration.

Hydrogen sulfide concentrations in the groundwaters of the Carrizo Sand aquifer range from below the detection limit ($0.16 \mu\text{mol Kg}^{-1}$) to ~ $20.0 \mu\text{mol Kg}^{-1}$ (Table 1, Fig. 4). Between 0.5 Km (well F-1) and 9.3 Km (well N-3) H_2S concentration remains constant at $0.09 \mu\text{mol Kg}^{-1}$, except at 7.4 Km (well KS-1) where the H_2S concentration is below the detection limit. Down gradient beyond well N-3 the H_2S concentration increases to $0.75 \mu\text{mol Kg}^{-1}$ at a distance of 12.8 Km (well G-1). This increase in

dissolved sulfide is followed by a subsequent decrease in concentration to $0.56 \mu\text{mol Kg}^{-1}$ at 14.5 Km (Poteet well). With flow beyond 14.5 Km, the H_2S concentration in the groundwater increases and finally reaches a concentration of $19.9 \mu\text{mol Kg}^{-1}$ at ~ 66 Km (well SMA74R-1). Between wells AC74R-1 (59 Km) and SMA74R-1 (65.8 Km) the H_2S concentration shows a sharp increase from $5.6 \mu\text{mol Kg}^{-1}$ to $19.9 \mu\text{mol Kg}^{-1}$.

Manganese (Mn) concentration along the flow path in the Carrizo Sand aquifer ranges from $0.2 \mu\text{mol Kg}^{-1}$ to $3.8 \mu\text{mol Kg}^{-1}$. In regions near the recharge zone (~ 0 -15 km), Mn concentration are low and range from $0.2 \mu\text{mol Kg}^{-1}$ to $1.7 \mu\text{mol Kg}^{-1}$. Beyond 15 km the concentration increases and is the highest at the PCW-1 well (26.1 km) i.e., $3.83 \mu\text{mol Kg}^{-1}$. Beyond 26 km the Mn concentration decreases along the flow path, but shows variations with concentrations ranging from $0.45 \mu\text{mol Kg}^{-1}$ to $2.9 \mu\text{mol Kg}^{-1}$ for the last 3 wells i.e., Peeler-1 (41.1km), AC74R-2 (59 km) and SMA74R-1 (65.8 km).

The oxidation-reduction potential (Eh) values for the groundwater of the Carrizo Sand aquifer range from -110 mV to 327 mV (Table 2, Fig. 4). The Eh values for groundwater in close proximity to the recharge zone (~ 0 - 15 Km) are higher than the water flowing down gradient beyond 15 km (Fig. 4). With flow along flow path Eh values drop down to 48 mV at a distance of 26 Km (PCW-1 well). Further down gradient, oxidation-reduction potential drastically decreases reaching negative values.

5.1 Selenium concentrations and speciation

Total dissolved selenium concentration (Se_T) and the concentration of the selenium species are presented in Table 1. The total selenium concentration (Se_T) in groundwater from the Carrizo Sand aquifer ranges from $\sim 0.23 \text{ nmol Kg}^{-1}$ to $0.87 \text{ nmol Kg}^{-1}$. Total selenium concentration (Se_T) initially increases from $0.27 \text{ nmol Kg}^{-1}$ at 0.5

Km (well F-1) to $0.87 \text{ nmol Kg}^{-1}$ at $\sim 4.3 \text{ Km}$ (well BCW-5). With flow beyond 4.3 Km (well BCW-5) to 12.8 Km (well G-1) the total selenium concentration decreases and reaches a value of $0.42 \text{ nmol Kg}^{-1}$. From the distance of 15 Km (Poteet well), until the farthest well (SMA74R-1) at 65.8 Km , the total selenium concentration (Se_T) varies between 0.3 nmol Kg^{-1} and 0.6 nmol Kg^{-1} . The highest value for total selenium concentration (Se_T) is recorded at well BCW-5 at a distance of 4.29 Km ($0.87 \text{ nmol Kg}^{-1}$).

The concentration for the selenate species [Se (VI)] in the groundwaters from the Carrizo Sand aquifer ranges from below the detection limit upto $0.42 \text{ nmol Kg}^{-1}$ (Table 1, Fig. 4). Selenate concentrations continuously increase from 0.5 Km (well F-1) to 7.4 Km (well KS-1) reaching a concentration of 0.4 nmol Kg^{-1} at 7.4 Km . This initial increase is followed by a decrease in the Se(VI) concentration from well KS-1 (7.4 Km) to below the detection limit at well G-1 (12.8 Km). Selenate concentration fluctuates between 0.2 nmol Kg^{-1} and $0.04 \text{ nmol Kg}^{-1}$ between 14.5 Km (Poteet well) and 41.0 Km (Peeler-1 well), followed by an increase in concentration with flow beyond the Peeler-1 well, reaching a value of $0.42 \text{ nmol Kg}^{-1}$ at the farthest location (well SMA74R-1).

Selenite [Se (IV)] concentrations are comparatively stable along specific portions of the flow path (Table 1, Fig. 4). For example, from well F-1 (0.5 Km) to a distance of 26.1 Km (well PCW-1), Se (IV) concentrations range between $0.179 \text{ nmol Kg}^{-1}$ and $0.294 \text{ nmol Kg}^{-1}$. At a distance greater than 26 Km , however the Se (IV) concentration continuously decreases and reaches value below the detection limit at a distance of 59 Km in the farthest two wells (i.e.: well AC74R-2 and well SMA74R-1).

Selenide [Se (-II)] concentrations varies near the recharge zone of the aquifer, i.e. from 0.5 Km at well F-1 to 14.5 Km at well Poteet-2 (Table 1, Fig. 4). In this region of the aquifer the Se (-II) concentrations range from below the detection limit to 0.2 nmol Kg⁻¹. Beyond 26 Km (well PCW-1) Se (-II) reaches a flow path maximum concentration of 0.272 nmol Kg⁻¹ at the Peeler-1 well (a distance of 41.1 Km). Further down gradient, at a distance greater than 41km, Se (-II) concentrations exhibit substantial variation for the last two wells, i.e.: AC74R-2 and SMA74R-1, ranging from below the detection limit to 0.176 nmol Kg⁻¹.

Table 1 : March 2006 data, Carrizo Sand aquifer, Southeastern Texas, USA, Concentration of the elements and their species as measured in the study area.

Sample	Distance (km)	Se _T (nmol kg ⁻¹)	Se VI (nmol kg ⁻¹)	Se IV (nmol kg ⁻¹)	Se -II (nmol kg ⁻¹)	Fe _T (μmol kg ⁻¹)	Fe(II) (μmol kg ⁻¹)	Fe(III) (μmol kg ⁻¹)	H ₂ S (μmol kg ⁻¹)	Mn (μmol kg ⁻¹)
F-1	0.5	0.273±0.013	0±0.04	0.271±0.024	0±0.034	13.84	12.36	1.49	0.09	0.8
BCW-5	4.29	0.878±0.035	0.388±0.021	0.268±0.003	0.222±0.04	15.75	7.52	8.23	0.09	1.02
KS-1	7.4	0.6775±0.02	0.406±0.014	0.1785±0.014	0.093±0.02	0.73	0.72	0.02	BDL	0.2
N-3	9.37	0.454±0	0.1±0.028	0.268±0.028	0.086±0.005	11.57	11.28	0.29	0.09	0.75
G-1	12.8	0.416±0.039	0±0.043	0.294±0.037	0.139±0.044	31.65	30.62	1.03	0.75	0.59
Poteet	14.5	0.5775±0.004	0.229±0.01	0.236±0.005	0.1125±0.009	24.16	17.19	6.97	0.56	1.7
PCW-1	26.1	0.291±0.017	0.048±0.015	0.21±0.013	0.033±0.018	19.51	10.21	9.3	1.15	3.83
Peeler-1	41.1	0.571±0.027	0.199±0.038	0.1±0.004	0.272±0.046	54.44	54.44	BDL	2.56	2.9
AC74R-2	59	0.247±0.018	0.2405±0.024	0	0±0.03	0.24	BDL	0.24	5.61	0.45
SMA74R-1	65.8	0.598±0.057	0.422±0.015	0	0.176±0.058	0.96	0.36	0.6	19.93	1

BDL= Below Detection Limit

Table 2: Groundwater properties of the studied wells

Sample	Distance (km)	Cond (μS cm ⁻¹)	Temp °C	TDS (mg kg ⁻¹)	pH	Eh (mV)	Alk as HCO ₃ (mmol kg ⁻¹)
F-1	0.5	559	24.7	358	6.46	264	1.3
BCW-5	4.29	302	24.61	193.6	6.16	233	0.63
KS-1	7.4	334.6	23.79	214	6.3	327	1.03
N-3	9.37	166.2	26.2	107.8	6.21	190	0.65
G-1	12.8	273.5	25.8	175.2	6.31	133	0.86
Poteet	14.5	386.7	28.24	247.3	6.36	155	0.86
PCW-1	26.1	589.5	34.26	377.5	7.2	48	4.07
Peeler-1	41.1	495	27.3	316.5	8.7	-110	3.38
AC74R-2	59	974	55	623	8.61	-135	5.28
SMA74R-1	65.8	1050	31.82	672.2	8.54	-110	5.76

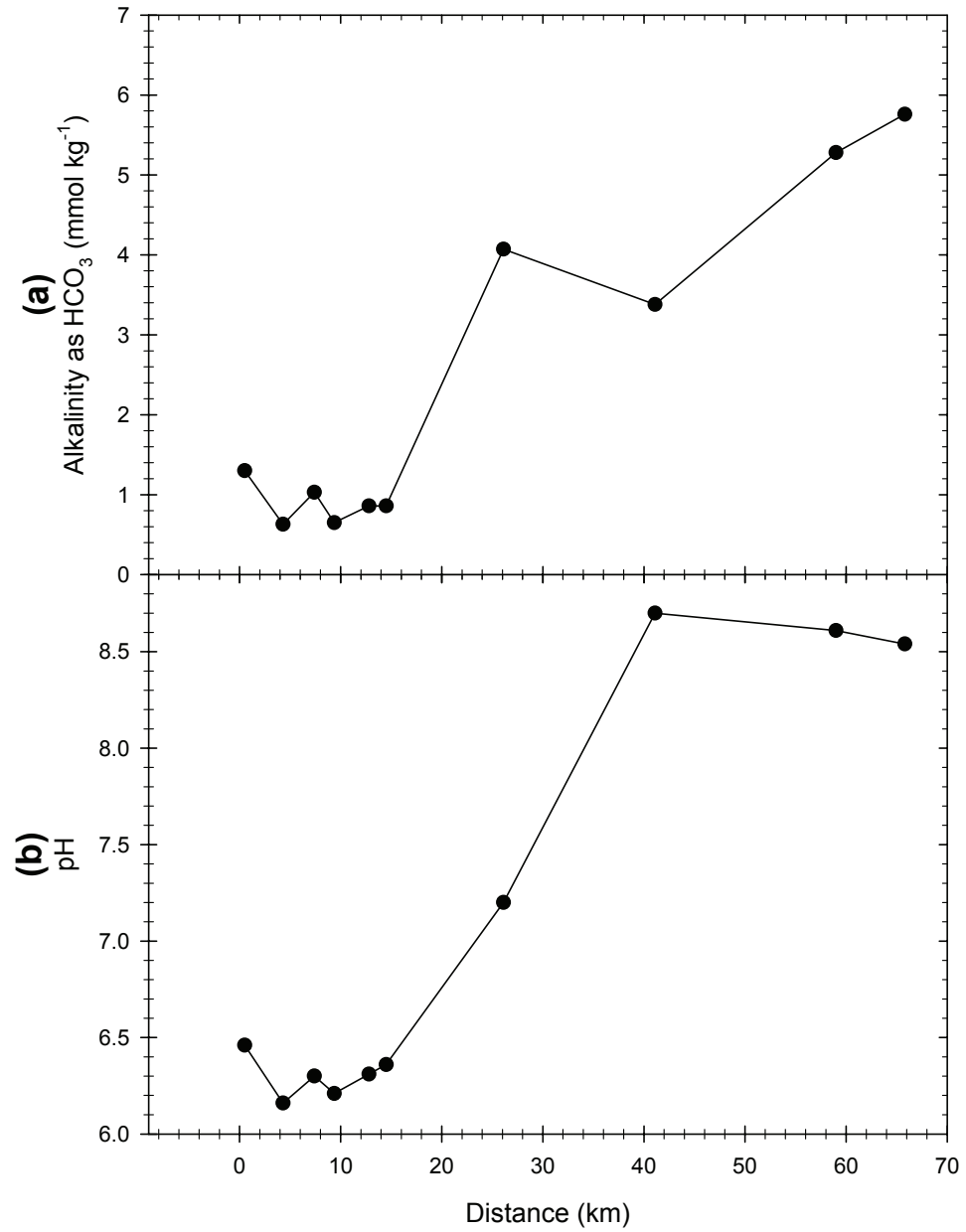


Figure 3: Variation of (a) Alkalinity as HCO₃⁻ (mmol kg⁻¹); and (b) pH in groundwater from Carrizo Sand aquifer (2006) with respect to the distance (km) from the recharge zone.

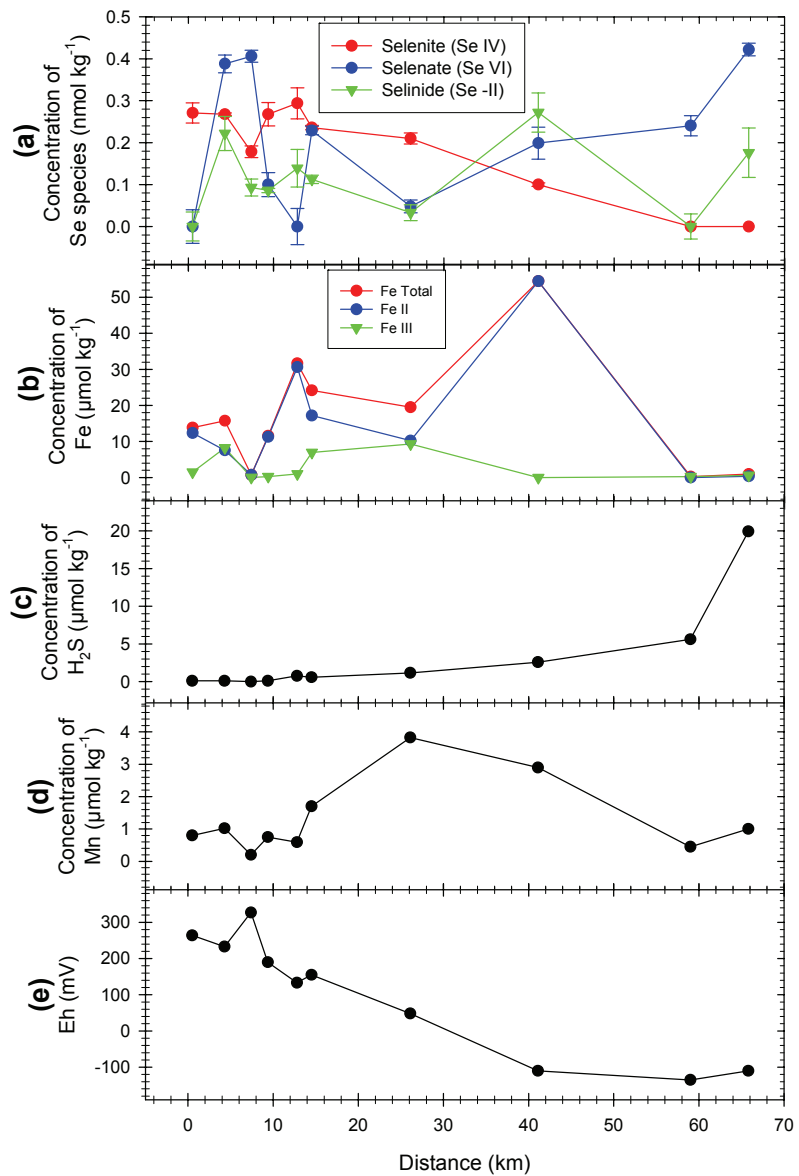


Figure 4: Variation of (a) Se speciation (nmol kg⁻¹); (b) Fe speciation (μmol kg⁻¹); (c) H₂S concentration (μmol kg⁻¹); (d) Mn concentration (μmol kg⁻¹); and (e) Eh in groundwater data from Carrizo Sand aquifer (2006).with respect to the distance (km) from the recharge zone.

CHAPTER 6

DISCUSSION

Selenite concentrations are generally higher in Carrizo groundwater from near the recharge zone and then decrease further down gradient. Selenate and the Selenide show variable behavior in Carrizo groundwater from regions near the recharge zone ranging from below the detection limit up to local maxima (Fig. 4). However, beyond 26 Km (PCW-1 well) Se (-II) concentrations increase at the Peeler-1 well (41.1 Km) followed by a decrease (AC74R-2, 59km), and then increase again (SMA74R-1, 65.8km), whereas Se (VI) shows a general increase in concentration with flow beyond the PCW-1 well (Fig. 4).

From well F-1 (0.5Km) to BCW-5 (4.29Km), the Fe data suggest a zone of Fe (II) oxidation as Fe (II) concentrations drop and Fe(III) concentration increase between these wells (Fig. 4). Both selenate and selenide increase from below detection limit at F-1 (0.5Km) to 0.388 nmol/Kg and 0.222 nmol/Kg, respectively, at BCW-5 (4.29 Km) (Fig. 4). The pH in the two wells F-1 and BCW-5 are 6.46 and 6.16 respectively (Fig. 3). Because selenate is weakly adsorbed for pH >6 (Drever, 1997), a portion of the increase in selenate concentration between wells F-1 and BCW-5 may reflect pH induced desorption of selenate. Selenite concentrations remain constant between wells F-1 and BCW-5 (0.271 ± 0.024 nmol/Kg and 0.268 ± 0.003 nmol/Kg) (Fig. 4), indicating that the inferred oxidation of Fe (II) occurring in this region of the aquifer does not cause significant changes in selenite concentration. The reason for the increase in selenide concentration between these two wells is not clearly

understood with the ongoing Fe(II) oxidation process. Without data for selenium speciation within the aquifer substrate (e.g. speciation of Se adsorbed/co-precipitated with Fe (III) oxides/oxyhydroxides) it is impossible to definitely ascertain why Se (-II) concentrations increase but Se (IV) remains relatively constant between wells F-1 and BCW-5. One possible explanation could be, Fe (II) oxidation may result in breakdown of Fe-sulfides in the sediments, which could lead to release of Se (-II). Another possible explanation for the increase in Se(-II) as well as the substantial increase in Se (VI) concentrations between wells F-1 and BCW-5 is reductive dissolution of Mn (IV) oxides, and subsequent release of sorbed/co-precipitated Se species. This is consistent with the increase in dissolved Mn (II) concentration between these wells (Fig. 4). The redox potential at which Mn (IV) is reduced is higher than the redox potential of Fe (III) reduction (Froelich et al., 1979; Drever, 1997). The measured Eh values for groundwaters from wells F-1 and BCW-5 (233-264 mV) are low enough for Mn (IV) reduction to occur [occurs at a redox level (pe) of 7.5] but too high for Fe(III) reduction [occurs at a redox level (pe) of -1] (Drever, 1997).

Between wells BCW-5 (4.29 km) and KS-1 (7.4 km), Fe_T and Mn concentration drop, reaching local minima that are close to the detection limits for both metals (Fig. 4). Well KS-1 also exhibits the highest Eh value along the flow path (327 mV). The marked drop in dissolved Fe and Mn concentrations in conjunction with the increase in measured Eh values (327 mV) for groundwater from well KS-1 is consistent with the oxic conditions, (Tang and Johannesson, 2006; Haque and Johannesson, 2006). It thus can be concluded that the decrease in total iron (Fe_T) and Mn, in this region of the aquifer reflects Fe (II) and Mn (II) oxidation with subsequent precipitation of Fe (III) and Mn (IV) oxides/oxyhydroxides. The

low H₂S concentration does not support the formation of Fe (II)-sulfide minerals as the mechanism for the low Fe concentration in well KS-1 (Fig. 4). The pH increases slightly from 6.16 to 6.3 with flow from well BCW-5 to the KS-1 well (Fig. 3). Both selenite and selenide decrease, with flow between these wells with Se (IV) decreasing from 0.268 nmol/Kg to 0.179 nmol/Kg and Se (-II) decreasing from 0.222 nmol/Kg to 0.093 nmol/Kg respectively. However, the Se (VI) concentration increases between the wells from 0.388nmol/Kg (well BCW-5) to 0.406 nmol/ Kg (well KS-1), (Table 1, Fig. 4). In general, the distribution of selenium species in the groundwater from well KS-1, as indicated by the Fe, Mn, and Eh data, are consistent with distribution that would be predicted by equilibrium thermodynamics for the oxic conditions at KS-1 groundwater. The decrease in Se (IV) and Se (-II) concentrations between these wells may reflect scavenging of these species by precipitating Fe(III) and/or Mn oxides/oxyhydroxides as Fe(II) and Mn(II) are oxidized. The increase in Se (VI) concentration may also indicate that Se (IV) and/or Se (-II) are being oxidized in groundwater from well KS-1.

With flow beyond well KS-1 (7.4 km) to well N-3 (9.37 km), the increase in Fe and Mn concentrations, and decrease in Eh indicate that redox conditions in the Carrizo Sand aquifer switch from relatively oxidizing to more reducing (Tang and Johannesson, 2006; Haque and Johannesson, 2006). The rise in Fe and Mn concentrations and drop in Eh is consistent with Mn (IV) and Fe (III) reduction in this region of the aquifer (Fig. 4). Selenite concentrations also increase from well KS-1 to N-3, reaching values of 0.268nmol/kg, identical to groundwater up-gradient of well KS-1 (i.e. well BCW-5). In comparison, selenate concentration decreases by a factor of 4 (i.e. 0.406 nmol/kg to 0.1 nmol/kg) with

groundwater flow from well KS-1 to N-3, whereas the selenide concentration remains constant within analytical error (Table 1). The Fe, Mn and Se data suggest that between wells KS-1 and N-3, reduction of Mn (IV), Fe (III) or both, releases adsorbed or co-precipitated Se (IV) back to the Carrizo groundwater. It is possible that the localized oxic conditions for groundwater in the vicinity of well KS-1 led to Se (IV) removal from solution by precipitation with or sorption to Mn (IV)/ Fe (III) oxides/oxyhydroxides that was subsequently re-released back to the groundwater as redox conditions became more reducing with flow beyond well KS-1. The observation that the same amount of selenite is removed from solution between wells BCW-5 and KS-1 as is re-released to solution with flow from well KS-1 to well N-3, supports Se (IV) cycling with oxidative precipitation and reductive dissolution of Fe-Mn oxides/oxyhydroxides in this portion of the Carrizo aquifer. The dramatic decrease in Se (VI) concentration between wells KS-1 and N-3 suggests that pH related sorption along with Fe (III) and or Mn (IV) reduction processes may exert important controls on dissolved Se (VI) concentration in this region of the aquifer. The pH decreases from 6.3 to 6.21 with flow from well KS-1 to well N-3 (Fig. 3). Because Se (VI) is more strongly adsorbed for $\text{pH} \leq 6$ (Dzombak and Morel, 1990; Drever, 1997), as pH decreases toward pH 6, Se (VI) selenate would be expected to strongly adsorb to aquifer mineral surface sites. Another possibility is that Se (VI) is reduced to Se (IV) in this region of the aquifer, which could also explain the increase in Se (IV) concentration observed between wells KS-1 and N-3. Microbes that reduce Se (VI) to Se (IV) have been reported from aqueous environment (Liu and Narasimhan, 1994; Ehrlich, 1996; Stolz and Oremland, 1999; Ike et al., 2000). It should be noted that if Se (VI) reduction is entirely responsible for the

increase in Se (IV) concentration between wells KS-1 and N-3, it would explain only ~ 0.09 nmol/Kg of decrease in Se (VI) concentrations. The remaining 0.217 nmol/kg of Se (VI) that is removed from solution between wells KS-1 and N-3 would require another mechanism (e.g., pH related adsorption).

As the groundwater flows beyond well N-3 to G-1 (12.8Km), the Se (VI) concentration decreases below the detection limit, Se (IV) continues to increase reaching a value of 0.294 nmol/kg, and Se (-II) increases from 0.086 nmol/kg to 0.139 nmol/kg (Table 1, Fig. 4). The increase in the Se (IV) concentration is consistent with its continued release from ongoing reductive dissolution of Fe (III)/ Mn (IV) oxides/oxyhydroxides. The increase in Se (-II) concentration may reflect Se (VI) reduction to Se (-II). Microbes that reduce Se (VI) to Se (-II) are also known from the aqueous environment (Liu and Narasimhan, 1994; Ehrlich, 1996; Stolz and Oremland, 1999; Ike et al., 2000). It should be mentioned that the increase in dissolved Se (-II) concentration in this portion of the aquifer may also reflect release of Se (-II) sorbed to Fe-Mn oxides/oxyhydroxides during reductive dissolution of these oxides/oxyhydroxides.

As the groundwater flows from well G-1 to the Poteet well (14.5 Km), Se (VI) increases from below the detection limit to 0.229 nmol/kg, whereas Se (IV) and Se (-II) concentration decrease (Fig. 4). A noteworthy feature of the Fe data is that although in groundwater Fe (II) concentrations decrease between wells G-1 and Poteet, Fe (III) concentrations increase. The increase in Fe (III) concentration is much greater (i.e., factor of 6) compared to the amount of Fe (II) decrease (i.e., ~ factor of 2) between these wells. The increase in dissolved Fe (III) may indicate a localized region of Fe (II) oxidation. It should be

noted that Mn concentrations increase in this portion of the aquifer, demonstrating that Mn (II) oxidation is occurring consistent with suboxic conditions (Fig. 4). The decrease in selenite and selenide concentrations between wells G-1 and Poteet may reflect scavenging of these species by precipitating Fe (III)/ Mn (IV) oxides/oxyhydroxides. The pH is relatively constant and low (~ 6.3) between G-1(12.8 km) and Poteet (14.5 km), (Fig. 3). Because Se (VI) is weakly adsorbed for pH >6 (Drever, 1997) a portion of the increase in selenate concentration may reflect pH induced desorption of selenate. However, as the pH is approximately the same for G-1 and Poteet groundwaters (6.31 and 6.36 respectively), increase in Se (VI) concentration may indicate that Se (IV) and /or Se (-II) are being oxidized in groundwater from Poteet well.

With flow beyond the Poteet well, Se (IV) continues to decrease at PCW-1 (26.1Km). The Se (VI) and Se (-II) concentration decrease in Carrizo groundwater with flow from the Poteet well to the Pleasanton City well (PCW-1, 26.1 Km), (Fig. 4). The dissolved Fe concentration chiefly Fe (II), also decreases with flow between the Poteet (14.5 km) and PCW-1 (26.1km) wells, which can be explained by the removal of Fe (II) with precipitating sulfide minerals as H₂S concentration in solution increase (Tang and Johannesson, 2006; Haque and Johannesson, 2006). Reduced selenium species can be removed forming Fe-selenides or co-precipitation of Se (-II) with sulfide minerals (Liu and Narasimhan, 1994; Oremland, 1994; White and Dubrovsky, 1994; Belzile et al., 2000). In addition pH increases from 6.36 to 7.2 with flow from the Poteet well to PCW-1 well (Fig. 3). Selenate and selenite desorb from mineral surfaces with increasing pH (Dzombak and Morel, 1990). Decrease in Se (VI) concentration may also be the result of selenate being reduced to selenide species

(selenate getting reduced to selenide, followed by removal of selenide along with sulfide minerals). The reduction kinetics of selenate to selenide is a much slower process than reduction of selenite to selenide (Liu and Narasimhan, 1994). Probably this might be the reason why selenide does not increase in concentration with the following selenate and selenite reduction processes.

Between wells PCW-1 (26.1 km) and Peeler-1 (41.1km) Se (VI) and Se (-II) concentrations increase, whereas Se (IV) concentrations decrease by a factor of 2. The Fe concentration in groundwater from the Peeler-1 well is high compared to our previous investigations (Tang and Johannesson, 2006; Haque and Johannesson, 2006), (Fig. 4). For example, Fe_T concentration in Peeler-1 well groundwater reported in Table 1 is nearly 4 times larger than Fe_T reported in Peeler-1 well groundwater in June 2004 (i.e., 14.3 nmol/kg) (Tang and Johannesson, 2006; Haque and Johannesson, 2006). We suspect that the remarkably high Fe_T concentrations measured for the Peeler-1 well groundwater could be in error as it clearly differs dramatically from our previous analysis. It is important to note that during the sampling of the Peeler-1 well in March 2006, we experienced difficulties with the in situ pump. Moreover, after pumping three well bores from the well, the groundwater remained turbid (i.e., brown in color) and would not clear with continued pumping. For all previous sampling campaigns (e.g., Tang and Johannesson, 2005a, b; Tang and Johannesson, 2006; Haque and Johannesson, 2006) groundwater pumped from the Peeler-1 well was clear. Although the turbidity of the Peeler well groundwater collected in March 2006 was cleared upon filtration through 0.45µm filters (filtration was collected at the well head during sample collection), the marked difference in the character of the water evolved from the Peeler-1

well during the March 2006 sampling compared to our previous sampling suggests that serious problems with this well had developed since our last sampling. Possible explanations for the marked turbidity of the Peeler-1 well groundwater could include 1) a malfunctioning pump that could not remove sufficient water from the well bore to allow sampling of groundwater from the Carrizo aquifer, 2) collapse or some other type of compromise of the well-bore's integrity, or 3) a combination of these issues. For example, it is possible that in addition to Carrizo groundwater, the Peeler-1 well is also sampling groundwater from another aquifer/aquitard owing to some form of failure in the well bore. The high turbidity may reflect high dissolved or more likely colloidal Fe (II) that was mostly removed upon filtration. The high Fe (II) may explain the high Se (-II) concentration in these Peeler-1 well waters, although we might have expected a similar spike in the H₂S concentrations, which is not observed (Fig. 4). Indeed H₂S concentrations are identical to our previous measured dissolved sulfide concentration in the Peeler-1 well (compare Table 1 with Haque and Johannesson, 2006). Assuming that the Peeler-1 well was not malfunctioning during our March 2006 sampling, the increase in pH from 7.2 to 8.7 between wells PCW-1(26.1 km) and Peeler-1 (41.1 km) could explain the increase in Se (VI) concentration owing to pH induced desorption. Decrease in Se (IV) concentrations may reflect reduction to Se (-II).

As the flow continues from Peeler-1 (41.1 km) to AC74R-2 (59 km), Se (IV) and Se (-II) concentration decreases reaching values of below detection limit, whereas the Se (VI) concentration increases by a factor of 1.2 between these wells (Fig. 4). It is important to note that region of the aquifer beyond well PCW-1 (26.1 km), where Se (VI) concentrations dramatically increase corresponds to region where sulfate reduction is the predominant redox

process (Tang and Johannesson, 2006; Haque and Johannesson, 2006). Here dissolved sulfide concentration increase by a factor of 2 between wells Peeler-1 (41.1km) and AC74R-2 (59 km) and by a factor of 4 between wells AC74R-2 and SMA74R-1 (65.8 km), (Table 1, Fig. 4). In between Peeler-1 wells (41.1 km) and AC74R-2 (59 km), the total iron concentration (Fe_T) again decreases dramatically (Fig. 4). Decrease in Fe probably reflects that Peeler-1 well has a problem. We should probably consider the previous Fe data. The total iron decrease and H_2S concentration increases indicating a transitional zone where neither Fe (III) reduction nor sulfate reduction process dominates. This observation is consistent with reports from earlier workers in this region (Tang and Johannesson, 2006; Haque and Johannesson, 2006).

Between Peeler and AC74R-2, total selenium is chiefly Se (VI). Se_T decreases by a factor of 2 between Peeler-1 and AC74R-2, followed by an increase in Se_T concentration between wells AC74R-2 (59 km) and SMA74R-1(65.8km) by a factor of ~2.5 (Table 1). In the groundwaters of the wells AC74R-2 and SMA74R-1, Se (VI) is the dominant species (Fig. 4). The redox condition of water in these wells is buffered by sulfate reduction (Tang and Johannesson, 2006; Haque and Johannesson, 2006). The high concentration of Se (VI) species in comparison to the Se (IV) species in the sulfate reduction zone (Fig. 4) is contradictory to the redox conditions stated by other authors (Cutter, 1982; Robberecht and Van Grieken, 1982; Ohlendorf, 1989; Weres et al., 1989; Calderone et al., 1990; Velinsky and Cutter, 1991; Cutter, 1993; Liu and Narasimhan, 1994; Ehrlich, 1996; Garbisu et al., 1996; Stolz and Oremland, 1999; Ike et al., 2000; Cutter and Cutter, 2004) in their research work relating to various water systems. A possible explanation for this scenario could be pH

related desorption dominant in these two wells. The pH in wells AC74R-2 and SMA74R-1 are 8.61 and 8.54 respectively (Table 1, Fig. 3). Because Se (VI) is weakly adsorbed for pH >6 (Drever, 1997), it can account for the high selenate concentration in these wells.

CHAPTER 7

CONCLUSION

Groundwaters of the Carrizo Sand aquifer of southeastern Texas, USA, shows changes in redox conditions along the chosen flow path. Measurements including pH, alkalinity, dissolved Fe species, H₂S concentration, oxidation-reduction potential along with dissolved selenium species reflect the redox changes. Regions proximal to the recharge zone (0 ~ 15 km) in the northeastern Atascosa County, indicate fluctuating redox regions with conditions ranging from oxic to suboxic. Down gradient down the flow path at a distance ~ 15km – 41 km, dissolved Fe species and H₂S concentration indicates the zone of Fe (III) reduction. This is followed by sulfate reduction zone with groundwater flowing down gradient at a distance > 41 km.

Selenium concentrations in the groundwaters of the Carrizo Sand aquifer are very low and are below the approved U.S. EPA's Maximum Contaminant Level (MCL) for selenium of 133 nmol/kg (i.e. 10 µg/kg). The total selenium along with the selenium species {Selenate [Se (VI)], Selenite [Se (IV)] and Selenide [Se (-II)]} shows variations along the selected flow path within the Carrizo Sand aquifer. Selenate and selenide show variable behavior in regions near the recharge zone. Selenite dominates in the groundwater upgradient near the recharge zone. Beyond 26 km, selenate becomes the dominant species. Processes such as Fe (II) oxidation, reduction of Fe (III) oxides/oxyhydroxides and pH induced

adsorption/desorption (of selenate species) are the controlling factors for the behavior of selenium within the first 41 km of the groundwater flow path. Further down gradient at a distance > 41 km, in the sulfate reduction zone along the flow path, increase in the selenate concentration may be due to pH induced desorption. The pH in these wells increase to 8.6. The geochemical results provide an initial insight into the behavior of selenium within the Carrizo sand aquifer. Further work incorporating the role of microbes can provide more detailed insight for the changes in selenium species along the flow path in the Carrizo Sand aquifer.

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