Analysis of Chemical Storage and Transit Times to Characterize Water Movement Through a Thick Unsaturated Zone Overlying the High Plains Aquifer, Northwestern Kansas

by

Britney S. Katz

Submitted to the graduate degree program in Geology and the Graduate Faculty of the University of Kansas in partial fulfillment of the requirements for the degree of Master of Science.

Randy L. Stotler, Ph.D, Chairman

Daniel R. Hirmas, Ph.D., Committee Member

Jennifer Roberts, Ph.D., Committee Member

Date Defended: September 22, 2014

The Thesis Committee for Britney S. Katz
certifies that this is the approved version of the following thesis:

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Randy L. Stotler, Ph.D, Chairman

Date Approved: September 22, 2014

ABSTRACT

The High Plains aquifer (HPA) is one of the largest aquifers in the world and is critical for agricultural production in both the United States and Kansas. Irrigation has had a large-scale effect on the water resources throughout the HPA, causing steep declines in groundwater levels due to extensive groundwater mining. Work conducted as part of the Kansas Geological Survey (KGS) Index Well Program revealed unexpected increases in water levels in the northwestern Kansas portion of the HPA not associated to precipitation or pumping. This indicated a previously unknown source of recharge to the aquifer and the need to further investigate water movement processes through the thick unsaturated zone above it. The roles of irrigation, land use, and subsurface geology as a possible driving force for water and chemical movement to the aquifer is uncertain due to the thick unsaturated zone above it. The goal of this research was to obtain a better understanding of the relationship between these processes occurring in the unsaturated zone and the aquifer by investigating the storage and transit time of chemicals in the thick 65 meter unsaturated zone in Thomas County, Kansas. Climate, land use changes and the conversion from natural to agricultural irrigated ecosystems within the last century are important controls on chemical movement through the unsaturated zone at this site. Detailed geochemical profiles indicated displaced chloride, nitrate and sulfate reservoirs that were likely mobilized by both an increase in downward water flux during the initial clearing of natural vegetation in the 1920s and again by increased drainage due to the onset of large-scale irrigation in 1984. An average annual water flux of 92 mm/yr was estimated using a chloride mass-balance approach and corresponds with other independent estimates in the area. Calculated chemical transit times through the profile are on the order of hundreds of years and longer than the irrigation history at the field site. However, only chloride mass-balance ages above the predevelopment water table

(above 36 m) are considered accurate since water in the lower profile appears to be remnant water from before the water table declined. This data establishes evidence for complicated flow paths through the unsaturated zone to the aquifer that are influenced by many factors including lithology, climate, land conversion, and irrigation.

ACKNOWLEDGEMENTS

First, I would to thank the Department Of Geology at the University of Kansas for accepting me into their graduate program and providing me with the necessary courses and resources to succeed. This project would not have been possible without funding from the USGS KWRI, Greg Ludvigson at the Kansas Geological survey, and the financial support provided by personal awards and scholarships from the Geological Society of America, the Kansas Geological Foundation, Encana Oil and Gas, Joseph M. Patterson, and the Orth Family.

Without the field assistance and expertise from Joe Anderson and Jake Elder this project would have never been possible. Their patience and persistence during the cold and problematic weeks of drilling in Colby is greatly appreciated and added an interesting, yet hilarious twist to my experience here at KU. I would like to thank Masato Ueshima, Bridget Sanderson, Kevin Fenyak, and Brian Sitek for their assistance with laboratory analyses and sample prep work. I would also like to acknowledge Lon Fram for his cooperation and for allowing myself and the KGS drill team to collect core from his property.

Thank you to my advisor, Randy Stotler, my co-authors, and my thesis committee members. I would like to especially thank my committee member, Daniel Hirmas for providing me with his laboratory space and equipment, for his guidance, and patience. He was always available and extremely helpful when I had questions and I appreciate all of the time he spent teaching and advising me over the past two years.

Thank you to all of the KU graduate students who have provided their feedback, ideas, and support when I was stuck or having a bad day: Erica Dalman, Molly Long, Angela Thompson, Blair Schneider, Logan Byers, and Michelle Mary. A very special thank you to my

family: Mom, Rachel, Sam, Branden, and Divah. They truly believe in my success and have been my biggest support system throughout my entire education.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1. INTRODUCTION

The High Plains region of the United States hosts some of the most productive irrigated agricultural land in the world owing to the vast High Plains aquifer (HPA) that it overlies. This extensively utilized aquifer provides irrigation and, to a much lesser extent, drinking and industrial water that accounts for approximately 23% of all groundwater withdrawals in the United States (Maupin and Barber, 2005). The HPA, which is a critically important resource for Kansas agriculture, extends over much of the western half of the state and undergoes extensive groundwater mining every year (Figure 1). A large portion of the Kansas HPA is on a fundamentally unstable path; large pumping-induced declines in groundwater levels have called into question the viability of the aquifer as a continuing source of water for irrigated agriculture (Dennehy et al. 2002; Waksom et al. 2006).

Water extracted from the aquifer is not being replaced by recharge, thus water levels in these areas are not expected to increase year to year (e.g., Butler et al., 2013). However, work conducted as part of the Kansas Geological Survey (KGS) Index Well Program revealed unexpected increases in water levels within Thomas County (THC) in northwestern Kansas during the 2009-2010 and 2010-2011 recovery period (Stotler et al., 2011). Hydrograph analysis indicated the recovery was not directly associated with precipitation or pumping. This implied an unknown source of recharge to the aquifer in the THC region of the HPA and the need to further investigate water movement processes through the thick unsaturated zone above it.

Water levels in this region are monitored predominately by pumping rates and groundwater well analyses, which can mask changes that are caused or influenced by land use or shifts in land practices. The relative roles of irrigation, land use, and subsurface geology as a possible driving force for water and chemical movement to the aquifer is uncertain due to the thick unsaturated zone above it. A better understanding of the relationship between these processes occurring in the unsaturated zone and those in the aquifer can be attained if the amount of chemical mass available for movement to the water table and chemical transit times through the unsaturated zone are known (McMahon et al., 2006).

The purpose of this research is to investigate water movement and chemical transport throughout the thick unsaturated zone overlying the HPA in northwestern Kansas in order to improve understanding of quality and quantity of water reaching the aquifer. Chemical transit times are established by examining physical hydrologic parameters and chemical tracers, such as chloride and nitrate. Constructing unsaturated zone geochemical profiles in semiarid regions can provide an archive of past environmental changes including climate variability and/or land use change (Jolly et al., 1989; Walker et al., 1991; Cook et al., 1992). A better understanding of these processes occurring throughout the unsaturated zone in northwestern Kansas is critical for assessing future groundwater quality, and the continued use of that portion of the HPA as a water source for irrigated agriculture. It will improve estimates of resource availability and recharge in this part of the aquifer and will expand the quality of information available to water users and managers as they work to slow water-level decline rates and implement enhanced management in this high use area.

2. THOMAS COUNTY FIELD SITE

2.1 Site Characteristics and History

The Thomas County (THC) field site is located in northwestern Kansas approximately 16 miles south of Colby, Kansas (Figure 2). Today, the topographically flat area is used primarily for agricultural farming of corn where development and large-scale irrigation began in 1984. The average thickness of the unsaturated zone at this site ranges between 60 to 65 m and consists of unconsolidated clay, silt, sand, and gravel with scattered layers of cemented zones consisting of calcium carbonate and some silica. Aquifer material was deposited primarily during the Tertiary Period by streams that carried sediments eastward from the Rocky Mountains (Butler et al., 2012).

This site is semi-arid in climate with abundant sunshine, moderate precipitation, frequent winds, and high rates of evaporation. Long-term mean annual precipitation ranges between 0.51 m and an average annual reference evapotranspiration of 1.93 m (NADP 2013; KSRE 2013). Climate history and precipitation rates in more detail are discussed further in section 4.1.

2.2 Irrigation

The field in which samples were collected for this study is approximately 116 ha and has been used to grow corn since going into production in the early 1950s. Groundwater fed irrigation began in 1984 and approximately 53 ha of the field is irrigated using a center-pivot sprinkler. Total reported annual water use from 1990 to 2012 is listed in Table 1. From 1984 to 1990, irrigation practices were poorly documented and therefore not considered for this study. The total average annual water use for irrigation at the site, distributed over 53 ha, is 282 mm/yr since 1990 (WIMAS, 2013).

Detailed fertilizer application records provided by current land owners can be found in Table 2. These records obtained only document fertilizer application since 2011 when current landowners initially purchased and began farming the land. According to these records, NH_3 has been the primary source of nitrogen at the site (approximately 16-21 g/m^2 applied each year) and is applied 8 to 12 inches (203-305mm) below the soil surface. The amount of nitrogen added to the land is determined from soil tests conducted each year. There is no record of products containing calcium sulfate applied. Fertilizer application history before 2011 is unavailable, but regionally, fertilizers were initially applied in large quantities starting in the late 1950s (Cunfer, 2005).

2.3 Hydrogeology

This research builds upon six years (2007-2014) of continuous water level monitoring conducted by the KGS Index Well Program. Groundwater level information was obtained by a pressure transducer in a monitoring well installed at the base of the HPA in THC (Figure 3). Well responses to pumping and changes in barometric pressure indicated that the saturated unconsolidated interval at this site acts as an unconfined aquifer (Butler et al., 2012). This site is an area of moderate well density and groundwater with no significant surface runoff and no fresh-water aquifers below the HPA. The aquifer under current conditions can essentially be considered a closed system, with the primary discharge mechanism being irrigation pumpage. Average annual water use for 2007-2012 over the 32.5 km^2 area centered on the monitoring well was 248 mm/yr (WIMAS, 2014; Butler et al., 2013).

Unlike other monitoring wells within the HPA, the minimum recorded water-level elevation at the THC index well has not declined every year (Butler et al., 2013). Increased water levels were recorded during the 2009 to 2010 recovery season (0.5 m) compared with the previous 2008 to 2009 recovery season. Boundaries limiting regional flow were identified by applying pumping-test interpretation methods to long-term water-level records (Butler et al., 2012). Consistent hydrograph response during the recovery period indicated that a previously unidentified inflow to the area is the primary control on the recovery rather than the amount, duration, or length of pumping. Further evaluation of these water level data indicated that this inflow appears to be relatively steady, vertical flow throughout the year to the unconfined aquifer (Butler et al., 2012).

3. METHODS AND MATERIALS

3.1 Drilling and Sample Collection

Drilling and sampling equipment was provided and conducted by the Exploration Services section of the Kansas Geological Survey. Fieldwork was conducted during March and April of 2013, with samples collected over a total of three weeks. Core samples were collected from beneath an irrigated field located approximately 2 km south of the THC index well (39°13'11.47" N Latitude, 101°00'54.21" W Longitude) (Figure 2). Drilling took place approximately 16 m south of the county road within the irrigated circle.

A complete core profile was obtained through the 63 m unsaturated zone using an Acker soil max, wire-line split-spoon sampler advanced ahead of a hollow-stem auger (8.3 cm diameter) and without drilling fluids (Figure 4a-b). A total of three boreholes (17.8 cm diameter) were drilled within 1 m of each other, with one reaching a depth of 63 m. At that depth, sediment became very incohesive and too saturated to be recovered in the collection tubes due to the proximity to the water table.

3.2 Collection and Analysis of Sedimentary Samples

Core samples (5 cm in diameter by 60 cm long) were collected in plastic core tubes and were labeled with sample depth, top and bottom (Figure 4c). Lithology was estimated and documented while core was retrieved from the auger and tightly sealed with both a rubber cap and vinyl electrical tape to retain moisture (Figure 4d). Once transported back to the University of Kansas, core tubes were stored in a refrigerator set at 13°C.

Particle-size analysis of core samples was completed at the KGS Geoarchaeology and Paleoenvironmental Research Laboratory in Lawrence, Kansas. Particle-size analysis of the core was done through a combination of sieve and pipette analyses. During analysis, 12 determinations were made at one time. Each sample was dispersed and the <20µm, <5µm, and <2µm fractions were determined by pipetting after sedimentation. The <0.2µm fraction is determined by pipetting after centrifugation. The sand was separated from silt and clay by washing the sample through a 300 mesh sieve. The various sand fractions were determined by dry sieving and weighing. The particle-size analysis followed USDA texture classifications and grain-size classes of Udden-Wentworth, where sands are described as 2000-50µm, silts are 50-2µm, and clays <2µm (Wentworth, 1922) (Table 3).

3.3 Collection and Analysis of Water Samples

A total of 56 soil samples were selected for further analysis from the core profile and chosen based on major changes in lithology. Inorganic anions (chloride, nitrate, bromide, fluoride, sulfate, and phosphate) were extracted from sediment samples using a 1:1 saturated paste method as described by Lindau and Spalding (1984) and Herbel and Spalding (1993), with slight modification. Briefly, samples were oven-dried at 60°C for 12 hours and then sieved through a #10, 2 mm sieve to ensure homogeneity. A split sample (~40 g) was collected at this point of the procedure and oven dried at 120°C for 12 hours to calculate the gravimetric water content of each sample. Remaining sediment (~150-200 g) was placed into a 600 mL beaker where deionized water was slowly added and mixed to create a paste-like consistency. The sediment/water mixture was hand stirred for approximately 1 minute and then covered with plastic and left to sit for 4 hours. After sitting, the sediment/water mixture was then slowly filtered through a 0.40-µm filter using a Buchner Funnel and collected in a glass sample vial.

Anion concentrations in the filtered solution were quantified using ion chromatography (IC) with conductivity detection at the Kansas Geological Survey.

Water-extractable ion concentration data, obtained from the IC, were initially reported on a volume basis (mg/L) and were corrected to a dry-weight basis (mg of the ion per kg of dry soil) using sieve weight and air-dried gravimetric water content (θ_g^{ad}) measured at the time of extraction. Ion concentration expressed on a volume basis (mg of the ion per L of the soil pore water) was calculated by dividing the concentrations in mg/kg by the gravimetric water content at field conditions (θ_g^{fc}) and multiplying by the density of water. Chloride, nitrate, and sulfide concentration profiles are detailed in subsequent sections.

3.4 Estimating Water Movement with Environmental Tracers

Chloride is a useful tracer of water movement in the unsaturated zone because it is chemically conservative, nonvolatile (no vapor transport), and generally is not taken up by plants (McMahon et al. 2003). The use of chloride concentrations in pore water and the chloride mass-balance (CMB) method have been widely used to evaluate water fluxes in semi-arid systems (Allison and Hughes, 1978). Required data for CMB include estimates of annual precipitation, total chloride input (from dry fallout and precipitation), chloride input from irrigation water, and pore water chloride concentrations. Some fertilizer applications can also contribute chloride to soil pore water; however, at this location, landowners indicated they did not use fertilizers containing chloride and thus this source was excluded from calculations. The chloride deposition flux at the land surface (q_{cl}) is calculated using Equation 1. It is equal to the product of precipitation and irrigation water and their respective chloride concentrations deposited at the land surface every year:

$$q_{cl} = \mathrm{P\,Cl}_p + \mathrm{I\,Cl}_I \qquad \text{Eq. (1)}$$

where P is annual precipitation [L], I is annual irrigation [L] and $\mathrm{Cl_p}$ and $\mathrm{Cl_I}$ are concentrations of chloride in precipitation and irrigation water [M/V] respectively. Equation 2 was used to estimate the vertical water flux below the root zone (modified from Scanlon et al., 2010a):

$$q = \frac{q_{cl}}{Cl_{uz}} \qquad \text{Eq. (2)}$$

where q is the estimated volumetric water flux below the root zone [L/T], $\mathrm{q_{cl}}$ is the chloride deposition flux at land surface, and $\mathrm{Cl_{uz}}$, is chloride concentrations in unsaturated zone pore water [M/V].

Accumulation times represented by chloride in the unsaturated zone (t) was estimated by dividing the cumulative total mass of chloride for a particular depth interval by the chloride input at the land surface (Equation 3)

$$t = \frac{\int_0^z \theta Cl_{uz}\, dz}{q_{cl}} \qquad \text{Eq. (3)}$$

where t is the average age of the chloride [T], θ is the gravimetric water content, $\mathrm{Cl_{uz}}$ is the concentration of chloride in the pore water [M/V], and $\mathrm{q_{cl}}$ is the chloride deposition flux at land surface. If the chloride deposition flux is assumed uniform, then the chloride concentration in the pore water is inversely proportional to the water flux; low chloride concentrations indicate high water flux, and high chloride concentrations indicate low water flux (Scanlon and Goldsmith, 1997).

4. ANALYSIS OF DEPOSITIONAL SOURCES AND UNCERTAINTY

Chloride is a highly soluble environmental tracer that seldom substitutes in minerals and often constitutes the most dominant ionic species in groundwater and soil water (Whittemore, 1995). Therefore, chloride is a useful way to track water movement and chemical processes in the unsaturated zone. In irrigated agriculture, chloride is derived from the atmosphere through dry and wet fallout, irrigation water, and fertilizers. (Scanlon et al., 2007). Equation 1 calculates the total chloride deposition (q_{cl}) from atmospheric and irrigation sources at land surface. Potential errors in flux, recharge rates, and accumulation time estimates when using the CMB are primarily from large uncertainties in total chloride deposition flux calculations. The following section discusses these three depositional chloride sources at the THC field location and the uncertainties in their analysis.

4.1 Depositional Sources of Chloride

4.1.1 Atmosphere

As mentioned in section 2.1, the THC field site is semi-arid in climate with abundant sunshine, moderate precipitation, frequent winds, and high rates of evaporation. The long-term average annual precipitation rate within the last 100 years is 485 mm/yr (KSRE, 2013). Figure 5, shows the climatic precipitation index for THC over the past century. Chloride deposition on the land surface from the atmosphere come from both wet (precipitation) and dry (dust) fallout. Estimates of atmospheric deposition were determined using the mean annual precipitation rate of 485 mm/yr, which is based on data collected from 1900-2012 at the KSU northwest extension center located about 23 km north of the field site in Colby, Kansas (KSRE, 2013). Measurements of chloride deposition in precipitation were not made in the vicinity of the field site. However, the National Atmospheric Deposition Program (NADP) reported annual chloride values of 0.087

g/m^3 in precipitation from 1984-2012 at a monitoring site in Scott County, located approximately 811 km south of the field site in Scott State Park, Kansas (NADP, 2013). Multiplying the average annual precipitation by the average chloride concentration in precipitation yields an annual average chloride deposition (from the atmosphere) of 0.04 g/m^3.

4.1.2 Irrigation Water

In irrigated agriculture, groundwater is another source of chloride deposition at the land surface and must be included in deposition estimates. Groundwater irrigation essentially redistributes salts from groundwater to soils and can have a large effect on deposition estimates since irrigation water adds a considerable amount of chloride relative to precipitation (Scanlon et al., 2010b). Chloride deposition from irrigation water was estimated using the average concentration of chloride in groundwater (25.3 mg/L) and the total average annual water use for irrigation at the site (282 mm/yr) distributed over 53 ha since 1984 (WIMAS, 2013). This implied an annual chloride deposition flux from irrigation water of about 8.16 g/m^2.

4.2 Uncertainties in Chloride Deposition Estimates

4.2.1 Atmosphere

The main source of uncertainty in estimates of chloride deposition from the atmosphere, is concentrations from wet and dry fallout. Concentrations in precipitation used from NADP only represent the past 30 years and excludes dry chloride from dry deposition (dust). The uncertainty increases if longer time periods (>30 years) and chloride from dry fallout is considered. Variations in climate may also add uncertainty in deposition estimates, such that wet and dry chloride would vary depending on very wet or very dry years. During years of drought, the majority of atmospheric chloride would likely come from large amounts of dust due to dry climatic conditions. Conversely, wet years would yield much less dust and most of the atmospheric chloride would come from precipitation. Therefore, the estimated value of 0.04 g/m^3 should be considered a lower limit. A chloride concentration in precipitation of 0.6 g/m^3 was estimated from bulk precipitation collectors (including dry fallout) by Wood and Stanford (1995). This value can be used as an upper limit because chloride recycles in precipitation collectors (Scanlon and Goldsmith, 1997). Uncertainties in chloride deposition estimates will further affect errors in vertical water flux estimates and chloride accumulation times in the unsaturated zone. However, long-term average precipitation over the past 115 years (485 mm/yr) is relatively close to the mean annual average precipitation over the past 30 years (505 mm/yr). Therefore, large errors in flux and accumulation times may not be as negatively affected by deposition estimates as long as atmospheric chloride depositions values were comparable to current measurements.

4.2.2 Irrigation Water

Many uncertainties are associated with chloride deposition estimates from irrigation water. Volumes were estimated using both pumping rates and the amount of time water was pumped. Although groundwater irrigation began in 1984, the first six years of water use (1984-1989) were poorly documented. If the chloride deposition estimate was recalculated only using reliable and accurate data between 1990 and 2012, the annual chloride deposition flux from irrigation water is 7.11 g/m^2. Both of these deposition values are substantially larger than atmospheric deposition estimates (0.04 g/m^2). The uniformity of water-application rates is controlled by the size of the spray nozzles and by consistent pressure regulation (Stonestrom et al., 2003). Uncertainties in uniformity and volumes of irrigation water is another potential source of error in deposition estimates at this site.

4.2.3 Fertilizer Application

Chloride is also derived from fertilizers commonly applied to the surface of agricultural fields. According to records provided by current landowners, only NH_3 fertilizers have been applied over the past three years. Chloride in fertilizers was not included in deposition estimates for this study due to the lack of application records before 2011 and adds to the error and uncertainty of chloride deposition flux estimates at this site. Fertilizer was applied to the field site approximately three months prior to sample collection. This may add further chemical uncertainties and should be considered when analyzing geochemical profiles.

5. RESULTS AND DISCUSSION

5.1 Sediment Texture

The core profile is dominated by sand (64%), but includes numerous clay and silt rich intervals throughout the profile (Figure 6). The largest clay and silt interval is within the shallow portion of the profile (5 m to 14 m below land surface) with silt ~53% and clay ~42% at these shallow depths. A summary containing detailed particle size distribution results and associated USDA texture classifications are reported in Table 3.

5.2 Gravimetric Water Content

Water content in the unsaturated zone ranged from 0.004 to 0.342 g/g (Table 4 and 5), with an average of 0.114 throughout the profile and showed a general pattern that reflected textural heterogeneities. Measured gravimetric water content through the profile is shown in Figure 7a and the relationship between water content and soil texture with depth is presented in Figure 7b. Lowest water content values were observed in areas dominated predominately by sands and highest water contents correlated with higher amounts of fine-grained sediments. More specifically, higher water content values appear at the uppermost part of the clay and silt intervals, which imply water perched on top of low permeability layers.

5.3 Geochemical Profiles

The concentrations of chemical tracers such as chloride, nitrate, sulfate and bromide are useful in marking the progress, or extent to which various events have occurred and proceeded in the unsaturated zone. Results from chemical analyses are reported as water-extractable concentrations per mass of soil (mg/kg) (Table 4) and as pore water concentrations (mg/L) (Table 5). Geochemical depth profiles for chloride, nitrate, sulfate, and bromide are shown in Figure 8 (water-extractable concentrations, mg/kg) and in Figure 9 (pore water concentrations, mg/L).

Water-extractable concentrations of chloride ranged from 1.0 to 38 mg Cl/kg. The chloride concentration profile (Figure 8b) was initially characterized by low chloride concentrations (~ 8 mg/kg) at shallow depths (< 7 m below land surface). Below this, a chloride peak with maximum concentrations of 38 mg Cl/kg is observed between 8-12 m below land surface. Water-extractable concentrations then decrease (≤ 6 mg Cl/kg) followed by another small peak (8 mg Cl/kg) at depths of 20 m. In the middle section of the profile (22-35 m below land surface), concentrations are low (< 5 mg Cl/kg). The lower portion of the profile (37-53 m) is characterized by fluctuating chloride concentrations between 2 and 27 mg Cl/kg.

Water-extractable concentrations of nitrate in the unsaturated zone ranged from 0.1 to 17 mg NO_3-N/kg and were generally less than chloride concentrations below the root zone (Figure 8c). However, unlike the chloride profile (Figure 8b) with one predominant shallow concentration peak, the nitrate profile is characterized by two distinct nitrate peaks within the upper unsaturated zone. The first peak has a maximum concentration of 12.4 mg NO_3-N/kg and appears between depths of 9-12 m below land surface. The second peak is larger, with a higher maximum concentration of 17 mg NO_3-N/kg, and is observed between 16-21 m depth. Below these two nitrate peaks, concentrations through the middle region of the profile (22-36 m below land surface) are low and do not exceed 1.4 mg NO_3-N/kg. Similarly to the chloride profile, concentrations fluctuate at depths below 36 meters.

Water-extractable concentrations of sulfate ranged from 2.1 to 216 mg SO_4/kg (Figure 8d). The sulfate profile in the unsaturated zone is generally characterized by one, steadily increasing concentration peak starting at a depth of 9 m and reaching a maximum concentration of 216.6 mg SO_4/kg at 25 m below land surface. Below this large sulfate peak, concentrations decrease and generally do not exceed 25 mg SO_4/kg throughout the rest of the profile with the exception of a few enrichments observed between 36 and 50 m (< 50 mg SO_4/kg).

Low water-extractable concentrations of bromide were observed in the unsaturated zone at THC ranging from 0.0029 to 0.1753 mg Br/kg (Figure 8e). The highest bromide concentrations were found between 8 and 12 m in the upper profile (maximum concentrations of 0.156 mg Br/kg) and then again deep within the unsaturated zone between 46 and 51 m below land surface (max concentration of 0.175 mg Br/kg). Lowest concentrations of bromide are observed between 15 and 36 m below land surface.

5.3.1 Upper Unsaturated Zone

Profiles of all four tracers are characterized by relatively large concentration peaks in the upper 25 m of the unsaturated zone (Figure 8). An initial chloride and nitrate peak is observed between 8 and 12 m below land surface. Although bromide concentrations are generally low in the unsaturated zone at THC, a bromide enrichment (maximum concentration of 0.156 mg Br/kg) is observed in the upper profile and also corresponds with the initial chloride and nitrate peak between 8 and 12 m. At depths between 15 and 24 m large nitrate and sulfate peaks are observed (>16 mg/kg) and reach maximum concentrations at 21 m below land surface. In contrast, at this depth chloride and bromide concentrations are relatively small with maximum concentrations < 8 mg/kg). The absence of a corresponding chloride concentration peak is discussed later in this section. Low nitrate/chloride mass ratios in the upper 10 m of the profile correspond with high chloride concentrations and lower nitrate concentrations at 9 m (Figure 9b and 9c). Between 11 and 25 m high nitrate/chloride ratios correspond with depths where concentrations of nitrate and chloride both increase however nitrate concentrations increase at a different rate relative to chloride. Sulfate/chloride mass ratios in the upper unsaturated zone ranged from 0.5 to 26. Initially low sulfate/chloride ratios at 9 m below land surface reflect high chloride concentrations and low sulfate concentrations (Figure 10d). The large sulfate/chloride mass ratio peak that spans between 10 and 30 m reflects sulfate concentrations in the unsaturated zone that are 9 to 16 times larger than chloride concentrations. The bromide/chloride mass ratio curves in the upper unsaturated zone, with ratios (Figure 10b) ranging between 0.001 and 0.007, is not characterized by a distinctive peak, unlike nitrate/chloride and sulfate/chloride mass ratio profiles.

The presence of chloride, bromide, nitrate, and sulfate in the unsaturated zone can be derived from both natural and anthropogenic sources. A large portion of the chloride and bromide in natural groundwater originates from atmospherically transported material, which falls as both wet precipitation and dry fallout (Davis et al., 1998). Nitrate and sulfate is also derived from precipitation as well as by natural chemical interactions between sediment and vegetation (e.g., Scanlon et al., 2010a). Anthropogenic sources, such as irrigation and fertilizers, is another source for large salt and nutrient reservoirs found in the unsaturated zone. Groundwater-fed irrigation redistributes concentrations from the aquifer back to the soil surface. Groundwater bromide/chloride, nitrate/chloride and sulfate/chloride ratio concentrations sampled from nearby irrigation wells in THC (Table 6), are represented by the vertical, green shaded areas on Figure 10. Groundwater nitrate/chloride and sulfate/chloride ratios ranged from 0.32 to 0.39 and 1.44 to 2.47, respectively, and agree with pore-water concentrations observed in the upper unsaturated zone. However, unsaturated zone bromide/chloride concentration ratios (0.001 to 0.007) in the upper 40 m are significantly lower than the groundwater ratios (0.007 to 0.014) applied to the land surface through irrigation from groundwater. In arid and semiarid agricultural environments, a large amount of chloride and nitrate found in the subsurface is derived from fertilizers. Furthermore, high sulfate concentrations will be observed under agricultural land where gypsum-based fertilizers are applied. Elevated bromide concentrations in the upper profile may also be due to the use of pesticides containing methyl bromide. Bromide has been known to form from the decomposition of brominated compounds that are commonly used as pesticides in agricultural fields (Flury and Papritz, 1993; Whittemore, 1995). However, current landowners indicated they have not applied fertilizers containing gypsum or pesticides containing methyl bromide; however, application history before 2011 is unknown. There are a variety of other possible factors that may also affect the chemical storage and transit through the unsaturated zone at the THC site, including evapotranspiration, changes in land use, lithology and climate. The effect of these processes on tracer profiles in the upper 25 m below land surface are discussed further below.

Evapoconcentration is a common natural process affecting subsurface salinity and nutrient buildup in arid and semiarid regions. When water evaporates, or is transpired by plants in the root zone or upper region of the profile, chloride and bromide remains behind and becomes concentrated in proportion to the amount of water removed (Cook, 2000). Lower bromide/chloride mass ratios (<0.003) in the upper profile (Figure 10b) may indicate that the initial chloride and bromide peaks (~9 m depth) reflects salinity generated by evapotranspiration (see Whittemore, 1995). This enrichment due to long-term evapotranspiration at the root zone, also applies for any excess nitrate and sulfate that isn't transpired by plants. Additionally, sulfate/chloride ratios in THC waters are within range of ratios commonly found in waters that formed from evapotranspiration concentration (0.1 to 15) (see Whittemore, 1995). The root zone for corn at the THC site is estimated to reach 2 m below the land surface, similar to other sites with irrigated corn agriculture (e.g., McMahon et al., 2006). Before initial cultivation, the root zone for native grasses would have reached ~ 3 m below land surface. Thus, the expected depth of an evapoconcentration peak is either 2 m or 3 m; however, initial concentration peaks at the THC site are reported at depths of 8 m. This suggests that large chloride, nitrate, sulfate, and bromide concentration peaks, observed between 8 and 21 m (Figure 8) are displaced lower in the profile.

Displaced concentration peaks in thick unsaturated zones have been observed under irrigated fields in the northern, central, and southern High Plains regions, and has been attributed to mobilization due to changes in land use and irrigation return flow (McMahon et al., 2006; Scanlon et al., 2010b). Upon the removal of native vegetation, deep rooted grasses no longer take up water, drainage increases, and salts that had naturally accumulated below the root zone are mobilized.

The presence of a double nitrate peak and large sulfate peak in the upper profile (~ 20 m) may be attributed to processes associated with land conversion to cultivated agriculture. For instance, oxidation of soil organic nitrogen (SON) to nitrate can be initiated by the initial clearing of native grasses (e.g. Scanlon et al., 2010b). The removal of native grasses can increase the oxidation rate of organic matter, and result in higher concentrations of naturally accumulated nitrate in the soil. Chloride is generally unaffected by oxidation (Whittemore, 1995), which would explain the absence of a chloride peak at 20 m below land surface. Similar to nitrate, large sulfate concentrations in the upper profile might also reflect processes associated with initial conversion of the land with sinks from plant uptake and chemical processes with soil organic matter following the removal of natural grasses.

As mentioned previously, bromide/chloride mass ratios in the upper 40 m are significantly lower than the groundwater bromide/chloride ratios distributed through irrigation. If the bromide and chloride in the upper unsaturated zone were primarily sourced from irrigation water, some other process must be affecting them. This might be because, relative to chloride, more bromide is taken up by organic matter, decreasing the amount of bromide, and thus driving the bromide/chloride mass ratio down (Leri and Myneni, 2012; Leri et al., 2014). Additionally, because chloride concentrations are 140 to 400 times larger than bromide concentrations throughout the profile at THC, relatively small changes to the total mass of bromide (even a small amount being taken up by organic matter) will have a significant effect on the bromide/chloride mass ratio.

High nitrate concentrations might also reflect a past fertilizer application event. Excess nitrogen application can produce nitrate by oxidation of reduced nitrogen in the root zone or subsoil (Kreitler and Jones, 1975; McMahon et al., 2006). But ultimately, it is difficult to distinguish if the nitrate observed in the unsaturated zone at the THC site is derived from anthropogenic or natural sources because nitrate reservoirs were likely mobilized by irrigation water (see McMahon and Bohlke, 2006).

At the THC site, the conversion from natural to vegetated land to a plowed agricultural ecosystem roughly began in the 1920s (Cunfer, 2005). Changes in agricultural practices and land use continued through the 1950s with mass applications of fertilizers, potentially contributing additional salt and nutrient sources (Cunfer, 2005). The appearance of an additional nitrate peak between 9 and 12 m below land surface may represent or mark this transition to a rain-fed agroecosystem. The increase in agricultural production and seasonal crops during this time would result in large nitrate uptake by plant roots and may explain why the shallower nitrate peak (~10 m) is smaller than the nitrate peak observed at 20 m. Additionally, more nitrogen in the soil organic matter would be expected after the initial clearing of native land, inferring more nitrogen oxidation to nitrate in those soils, and resulting in a higher nitrate peak during the 1920s. Large scale irrigation at the site began in 1984 converting the land to an irrigated agroecosystem. Irrigated agriculture in semiarid regions generally results in increased recharge from irrigation return flow and causes the mobilization of salt and nutrient reservoirs (Scanlon et al., 2007). High chloride concentrations at depth in most profiles beneath cropland indicate this increased drainage (Scanlon et al., 2007).

Soil texture and lithology may also be controlling salinity and nutrient buildup throughout the upper 20 m of the unsaturated zone. Chloride and bromide peaks centered at 9 m below land surface, correspond with the center of a clay and silt layer (77-95% cumulative clay and silt) located in the upper 5-13 m of the profile (Figure 8a). Finer grained soils retain irrigation water within the root zone for longer periods of time, allowing more time for evapotranspiration and salinity buildup (Scanlon et al, 2010b). Additionally, sorption of up to 10% of the dissolved bromide has been reported on various materials including clay, shale, soil, and organic debris, which would slow down transport (Davis et al., 1998). Nitrate enrichments throughout the entire unsaturated zone are associated with depths that contain >50% cumulative clay and silt distributions (Figure 8c). Additionally, the location of the two largest clay and silt intervals (>90% cumulative) in the upper profile (6-14 m and 21-23 m) align with the depths of the two large nitrate concentrations which could be impeding downward flow and accumulating nitrate. A positive correlation between clay and silt content with high nitrate concentrations in unsaturated sediments was previously observed in both the northern and central HPA (Boyce et al., 1976; McMahon et al., 2006). This correlation could be the result of less flushing and more reduced nitrogen available for oxidation in fine-grained sediments compared to more coarse grain sediments, and thus supports the idea that lithology is at least partially controlling the distribution of large nitrate peaks in the upper 23 m unsaturated zone (e.g., McMahon et al., 2006).

Finally, the shape of the concentration depth profiles shown in Figure 8b might represent a record of recharge and paleoclimate over time. For instance, chloride profiles in northern Senegal, Africa showed climate variability at decadal and century timescales with high chloride concentrations corresponding to drought periods and low concentrations corresponding to periods of high precipitation (Scanlon et al., 2006). In Thomas County, dry drought conditions, such as in the 1930s, would result in high ET causing an increase in salinity buildup. Chloride deposition at land surface from dry fallout might also increase during drought years due to an increase in windblown dust. Unsaturated zone salt inventories after the onset of a major precipitation events may mobilize and appear as chloride bulges (Allison et al., 1994) or give rise to lower chloride concentrations deeper in the profile as a result of larger water fluxes during a wetter climate (McMahon et al., 2003; Scanlon et al., 1991).

5.3.2 Middle Unsaturated Zone

The middle region of the unsaturated zone, between depths ~ 26 to 35 m below land surface, are characterized by low water-extractable chloride, nitrate, sulfate, and bromide concentrations (< 8.1, 0.6, 32, 0.015 mg/kg respectively). At these depths, the profile is dominated predominately by sands (> 70-95%) and low gravimetric water contents (< 0.07 g/g) (Figure 8a and 7b respectively). The decrease in concentration (of all tracers) through this zone may be attributed to dilution, as a result of preferential flow through the coarser grained, sandy material (Scanlon et al., 1991). Additionally, decreased concentrations in this zone may represent a time associated with a wetter climate and higher water fluxes, which is discussed further in section 5.4.1 (McMahon et al., 2003; Scanlon et al., 1991). On the other hand, when pore water concentrations are considered in the sandy interval between 26 and 35 m (Figure 9), chloride, nitrate, sulfate, and bromide concentrations are relatively higher (maximum concentrations 205, 48, 1,722, 0.6 mg/L respectively). This might be a function of low water contents observed in this zone.

5.3.3 Lower Unsaturated Zone

Unlike the predominantly sandy middle region of the profile with low chemical concentrations, the lower portion of the unsaturated zone (below 36 m) reveals fluctuating chemical concentrations and varying lithology. Between 36 and 62 m below land surface, water-extractable concentrations of chloride fluctuate between 2 and 27 mg Cl/kg, nitrate between 0.05 and 3.8 mg NO_3-N/kg, sulfate between 1.6 and 47 mg SO_4/kg, and bromide between 0.01 and 0.2 mg Br/kg (Figure 8b-e). Similar trends are observed in pore-water concentrations (mg/L) in this lower region of the profile, with chloride and sulfate having the largest concentration variances relative to nitrate and bromide (Figure 9b-e). Higher concentrations in the lower region of the unsaturated zone are similar in concentrations reported in groundwater at the THC site relative to groundwater concentrations reported in other areas of the HPA in Kansas.

The lithology changes through this zone, going from a sandy dominated area (26-36 m) to a region (36-63 m) dominated by many fine-grain clay and silt intervals (>50% cumulative clay and silt content) (Figure 8a). Concentration spikes throughout this lower region are all associated with these fine-grained layers, suggesting soil texture is affecting the accumulation or storage of chemical these tracers in the lower unsaturated zone. Elevated concentrations through the lower profile may represent chloride, nitrate, sulfate, and bromide left behind, or perched, on these low permeability layers as the water table rapidly declined. This idea is supported by high water contents (section 5.2) and low water fluxes (section 5.4) at these depths.

Additional evidence that water in this lower unsaturated zone is water from before the water table decline, is provided by mass ratio signatures in the lower unsaturated zone (Figure 10). Below the predevelopment water table line (36 m below land surface), the bromide/chloride ratio steadily increases until concentration ratios remains above 0.005 from a depth of 43 m below land surface to the current water table (Figure 10b). The increasing bromide/chloride ratio between 39 and 44 m may mark a transition zone or front, where new and younger water from the upper unsaturated zone is mixing with water perched as groundwater levels dropped. Within this deeper dewatered zone, all mass ratios (bromide/chloride, nitrate/chloride ratios, and sulfate/chloride) correspond with groundwater ratios. This further suggests that the water observed in this lower region of the unsaturated zone (below 36 m) is remnants of groundwater from before the water table dropped.

The elevated nitrate in the lower profile and groundwater could have been introduced while the deep unsaturated zone was still saturated (prior to the water table decline) through the irrigation well gravel packs in the area. This may have occurred during the initial well installation or gradually over longer timescales. Only a small amount of nitrate would be needed to see this signature and for it to spread, dilute, and affect a large amount of groundwater. Many of the elevated nitrate concentrations (between 36 and 62 m) are associated with layers of high clay and silt content which would have promoted the lateral movement at these depths.

5.4 Flux and Chemical Transit Times

5.4.1 Flux

Chloride concentrations in pore water have been widely used to evaluate water fluxes in semiarid systems (e.g., Allison and Hughes, 1978; Scanlon et al., 2010a). Annual chloride deposition flux at the THC land surface is estimated using Equation 1. Assuming precipitation and irrigation are the only sources of chloride, the chloride deposition flux at the surface is 7.15 $g/m^2/yr$. This deposition flux value is a minimum estimate because chloride from dry fallout (dust) and from fertilizer application has been neglected. Estimated water fluxes in the unsaturated zone ranged from 18 to 296 mm/yr based on the chloride mass-balance approach (Figure 11a). A relationship between flux and pore water chloride concentrations is shown in Figure 11b and the relationship between water flux and soil texture in the THC unsaturated zone is shown in Figure 11c.

Soil texture has a variable control on water flux through the unsaturated zone. A field study in Australia, revealed decreasing recharge rates by an order of magnitude in the Murray Basin, where clay content increased from 0 to 20% under cropland (Kennett-Smith et al., 1994). Yet, studies under several different unsaturated zones in the central High Plains concluded that percolation rates (flux) beneath irrigated agriculture settings are actually independent of the soil texture (Scanlon et al., 2010a). At THC, fluxes generally decrease above or within areas composed of fine-grain clay and silt material and conversely, fluxes increase through coarser textured intervals. The exception to this pattern is observed within the largest silty clay loam layers (57% clay and 42% silt) and the highest water content (0.34) at 22 m below land surface. This depth marks the maximum flux value of 296 mm/yr. Initially, the idea of water moving quickly through a low permeability layer with a large water content seems unlikely. It is possible that these large flux variations in fine-grain soils may be attributed to the hydraulic conductivity and matric potential in unsaturated soils where water is able to move more quickly through water around the smaller grains and cracks in the clay silty layer rather than the larger and (and therefore more spaced out) grains of the unsaturated sand material.

Areas characterized by low water fluxes are associated with high pore water chloride concentrations. Low flux will be associated with large chloride concentrations because water is taken up by vegetation through evapotranspiration and very little water is able to percolate below the root zone (Scanlon et al., 2010a). In contrast, at depths where water flux increases, pore water chloride concentrations decrease. Low concentrations thus represent dilution caused by flushing and increased recharge during wetter climatic conditions (Scanlon and Goldsmith, 1997). Climate variability at inter-annual timescales associated with elevated precipitation, increased recharge in Arizona by a factor of 3 and over decadal timescales resulted in variations in recharge by a factor of 5 in Africa related to drought and non-drought periods (Scanlon et al., 2006).

The calculated average annual water flux at the THC site is 92 mm/yr. This average flux corresponds very well with the inflow rate of 90 mm/yr which was estimated on the basis of water level declines and pumping rates prior to this investigation (Butler et al., 2012). The estimated flux of 92 mm/yr at THC is also within range of fluxes reported under an irrigated field in Yuma County, CO (102 mm/yr) (approximately 190 km northwest of THC) (McMahon et al., 2006). However, the THC water flux estimate is 2 times larger than fluxes reported beneath irrigated fields in southwestern Kansas and 3 times larger than water fluxes in the Texas SHP area (McMahon et al., 2006). This increase from south to north is likely indicative of the influence of a wetter climate in the NHP on water and chloride flux in the unsaturated zone.

5.4.2 Chemical Transit Time

The age of the chloride in the unsaturated zone is estimated using Equation 3 and approximates the length of time for water to move through the profile. This equation assumes that chloride age equals the total mass of the chloride present in the unsaturated zone (above a given depth) divided by the chloride flux at the land surface (Scanlon et al., 2010a; McMahon et al., 2003). Chloride ages throughout the profile, as well as the variation in water flux with corresponding chloride ages, are shown in Figure 12a-b. The average chloride age at the point closest to the water table (~ 61 m below land surface) is about 330 years old. This implies that it has been less than 400 years since water moved through the deeper unsaturated zone. However, as previously discussed (section 5.3.3), mass ratio concentrations in the lower profile correspond with groundwater, suggesting chloride below 36 m is a remnant of older groundwater (prior to irrigation) that was left behind when the water table declined. If this is true, the CMB ages at depths below the predevelopment water table line (below 36 m) are not valid and CMB ages only considered in the upper profile (at depths above 35 m below land surface). However, if water in the lower profile does represent remnants left from the saturated zone prior to the water table decline, current groundwater ^{14}C (Table 7) may provide better insight to water ages within the lower unsaturated zone. The CMB age calculated at 35.6 m below land surface is 182 years. This age predates the time since irrigation began at this site; yet could be attributed to smaller water fluxes over longer-timescales. In comparison, calculated CMB ages in the HPA in southwestern Kansas are 1,600 years old with an average flux of 5.1 mm/yr and ages over 10,000 years old in the Mojave Desert where average fluxes are as low as 0.2mm/yr through thick unsaturated zones (McMahon et al., 2003; Izbicki et al., 2000).

6. CONCLUSIONS

This research evaluated chemical storage and transit times through a 65 m thick unsaturated zone to assess and characterize the possible processes and controlling factors for water and chemical movement to the aquifer in Thomas County, Kansas. A new understanding of processes affecting the storage and transit times of chemicals in the thick unsaturated zone at THC was achieved by using lithologic, hydrologic, and chemical data and further evaluating possible controlling factors at land surface such as climate and changes in land use.

Application of agricultural chemicals at land surface, long-term evapotranspiration and oxidation of organic matter at or below the root zone produced large subsoil chemical reservoirs of chloride, nitrate, and sulfate within the upper unsaturated zone (5-25 m below land surface) at THC. Chemical reservoirs observed within the upper 25 m zone were displaced relative to the estimated root zone at THC and were likely mobilized down through the profile by both an increase in downward water flux during the initial clearing of natural vegetation in the 1920s and again by increased drainage and irrigation return flow following the onset of large-scale irrigation in 1984.

The middle unsaturated zone (26-35 m below land surface) was characterized by decreasing chemical concentrations, low gravimetric water contents, and moderate water fluxes.

Faster paths through this middle region most likely resulted from coarser sandy sediments and larger fluxes during wetter years.

The deep unsaturated zone (36-62 m below land surface) is characterized by elevated chemical concentrations and high gravimetric water contents observed above fine-grain silty clay layers. Elevated concentrations likely represent remnant water left behind on low permeability layers as the water table declined. Mass ratio concentrations of bromide/chloride, nitrate/chloride, and sulfate/chloride in the lower profile correlate with those in the groundwater and further suggest water in this lower region is remnant water from before the water table declined. Increasing bromide/chloride mass ratios below the predevelopment water table line (36-44 m) indicate a transition zone or front where younger water from the upper unsaturated zone may be mixing with older water left behind after the water table declined.

An average annual water flux of 92 mm/yr was estimated at the THC site using the chloride mass-balance method and compares well with a previous estimate of 90 mm/yr which was based off of pumping and water level decline rates. Chemical transit times through the unsaturated zone were on the order of hundreds of years and longer than the irrigation history at the site. Only chloride mass-balance ages above the predevelopment water table (above 36 m) are considered accurate since water in the lower profile appears to be remnant water before the water table declined.

Results from this study establish that land conversion and/changes in land use, irrigation, subsurface geology, and climate are important controls on chemical movement and storage through the thick unsaturated zone at the THC site. Implications of these findings with respect to the aquifer are significant because they indicate that events and processes occurring at land surface are the driving forces controlling both the quality and quantity of water reaching the aquifer.

7. FUTURE WORK

7.1 Isotope Analyses:

7.1.1 Tritium

Tritium analysis can be used as an additional tracer and provide an alternate measure of water movement from the root zone to the deep unsaturated zone. Tritium in the unsaturated zone is generally derived from precipitation and is useful because it substitutes for hydrogen isotopes in the water molecule (McMahon et al, 2003). Because it is radioactive, tritium will be associated with a signature from either before or after atmospheric testing of nuclear weapons. Due to radioactive decay, the activity of tritium in the unsaturated zone decreases over time, and can therefore be used to more accurately evaluate water transit times through the profile. The analysis of pre-bomb and post-bomb tritium in water has been used to track unsaturated zone pore water movement related to irrigation return flow by using a tritium mass-balance approach (McMahon et al, 2006). In one study, tritium-based estimates were compared to chloride flux estimates and further supported their hypothesis that post-bomb water in the deep unsaturated zone had originated from a declining water table (McMahon et al, 2003). Additionally, researchers have used tritium analyses to explain preferential flow in many regions (Nativ et al.,1995; Flint et al., 2002). Due to the uncertainties associated with the chloride mass-balance approach used at the THC site (section 4.2) the addition of tritium analysis will provide a more accurate estimation of recharge rates, water flux, and age of the water throughout the unsaturated zone.

7.1.2 Oxygen and Deuterium

Additional analyses of stable water isotopes $\delta^{18}O$ and $\delta^{2}H$ would improve the characterization of water in the unsaturated zone based on climate. The effect climate variability has on the movement of water and chemicals through the profile can be further evaluated by comparing fractionation signatures associated with precipitation (during wet years) and evaporation (during droughts) to a global meteoric water line.

7.1.3 Nitrogen

It is difficult to identify the source of nitrate observed within the unsaturated zone at THC. Analysis of nitrogen isotopes can be used to distinguish between natural and anthropogenic sources of nitrate in both the unsaturated zone and groundwater. Measurements of $^{15}N/^{14}N$ ratios have been widely used to determine if nitrate was derived from fertilizer, soil, or manure sources (Kreitler, 1979; Kendall, 1998; Bohlke, 2002). McMahon and Bohlke (2006) used nitrogen isotopes to track paleorecharge and identify if groundwater nitrate had been affected by processes of denitrification or NH_3 volatilization, which can contribute to a loss of nitrogen prior to recharge. Therefore, because knowledge of the fertilizer application history at THC is limited, the evaluation and understanding of nitrate in the unsaturated zone would be greatly enhanced by the addition of nitrogen isotope analysis.

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Table 1. Total reported water use at the Thomas County field site from 1990 to 2012. Water use data was provided by the Water Management and Analysis System (WIMAS) through the Kansas Department of Agriculture, Division of Water Resources (DWR) and the Kansas Geological Survey (KGS).

Year	Total Water Used (hectare-meter)	Land Irrigated (hectare)	Hours Pumped	Pump Rate
1990	21.18	52.61	1621	575
1991	21.03	52.61	1610	575
1992	14.12	52.61	1184	525
1993	13.11	52.61	1099	525
1994	16.86	52.61	1649	450
1995	17.31	52.61	1693	450
1996	18.75	52.61	1834	450
1997	15.27	52.61	1680	400
1998	12.53	52.61	1575	350
1999	1.51	17.40	1453	46
2000	14.78	52.61	2168	300
2001	14.01	52.61	2055	300
2002	16.69	52.61	2938	250
2003	15.72	52.61	2768	250
2004	17.24	52.61	3035	250
2005	8.53	52.61	1501	250
2006	20.74	52.61	3652	250
2007	12.83	52.61	2399	250
2008	11.35	52.61	2161	250
2009	8.64	52.61	1698	250
2010	6.66	48.56	1381	250
2011	15.18	50.18	n/a	n/a
2012	21.35	50.18	n/a	n/a

Table 2. Fertilizer application records at the Thomas County field site provided by current landowners. The amount of nitrogen added to the land is based off of soil tests conducted each year by land owners and applied 203-305 mm below the soil surface. Fertilizer application records at the Thomas County field site provided by current landowners. The amount of nitrogen added to the land surface is based off of soil tests conducted each year by land owners and applied 203-305 mm below the soil surface. Fertilizer application data before 2011 is unavailable.

Crop Year	**Application Date** (month/day/yr)	**NH3 Added** (lbs/acre)	**NH3 Added** (g/m^2)	**Crop Area** (acres)	**Crop Area** (m^2)
2011	4/14/2011	145	16.3	130	530000
2012	3/2/2012	191	21.5	130	530000
2013	10/29/2012	150	16.84	130	530000
2014	11/15/2013	191	21.5	130	530000

Table 3. Particle size distribution results and associated USDA texture classifications with depth through the unsaturated zone at the Thomas County field site.

Depth (m)	Total Sand 2000-50µm	CSI 50-20µm	MSI 20-5µm	FSI 5-2µm	Total Silt 50-2µm	CC 2-0.2µm	FC <0.2µm	Total Clay <2µm	Texture USDA Classification
6.4	8.0	50.7	20.4	8.1	79.2	12.5	0.2	12.7	Silt Loam
8.23	4.8	33.7	23.5	16.2	73.4	17.0	4.8	21.8	Silt Loam
9.45	10.9	28.3	9.2	7.4	44.9	31.5	12.7	44.2	Silty Clay
11.89	16.8	30.0	11.4	6.5	48.0	24.0	11.3	35.2	Silty Clay Loam
12.9	22.1	20.7	9.1	8.1	37.8	31.0	9.1	40.1	Clay
13.72	63.8	7.7	4.3	(2.5)	9.5	15.2	11.5	26.7	Sandy Clay Loam
14.02	75.7	6.8	2.2	1.8	10.7	7.1	6.5	13.6	Sandy Loam
14.94	69.2	9.5	3.1	2.1	14.8	8.0	8.1	16.1	Sandy Loam
15.24	64.1	11.7	8.0	3.3	23.0	7.6	5.2	12.9	Sandy Loam
16.76	70.1	9.5	5.8	1.7	17.0	7.5	5.4	12.9	Sandy Loam
21.03	18.4	6.0	25.7	18.2	49.9	25.9	5.8	31.7	Silty Clay Loam
21.34	1.2	9.4	12.8	19.6	41.7	46.2	10.9	57.1	Silty Clay
22.25	15.7	13.0	11.4	10.9	35.4	29.7	19.2	48.9	Clay
22.56	77.1	5.4	4.2	2.3	11.9	6.8	4.2	11.1	Sandy Loam
24.69	77.0	7.3	1.2	0.3	8.8	4.8	9.4	14.2	Sandy Loam
25.30	85.4	4.7	0.9	0.6	6.3	4.3	4.0	8.3	Loamy Sand
25.60	73.7	8.9	7.5	4.2	20.5	3.2	2.6	5.8	Sandy Loam
26.82	78.3	9.7	2.8	1.5	14.0	4.5	3.2	7.7	Loamy Sand
28.04	97.0	1.1	0.3	(0.4)	1.1	1.6	0.3	1.9	Sand
33.53	81.6	6.2	1.0	0.6	7.8	5.1	5.5	10.6	Loamy Sand
34.74	84.6	8.1	1.9	1.0	11.0	2.6	1.9	4.4	Loamy Sand
35.05	79.2	7.5	0.4	1.2	9.1	5.5	6.2	11.7	Sandy Loam
35.36	70.0	5.8	4.0	2.4	12.2	7.9	9.8	17.8	Sandy Loam
35.66	83.5	3.0	1.4	0.6	5.0	4.8	6.7	11.4	Loamy Sand
35.97	87.3	2.6	0.1	1.1	3.7	3.7	5.3	9.0	Loamy Sand
36.88	50.5	16.6	9.7	8.9	35.1	10.5	3.8	14.3	Loam
37.19	47.6	15.9	10.1	7.9	34.0	12.7	5.8	18.5	Loam
38.40	53.7	20.3	11.1	3.4	34.8	9.4	2.2	11.6	Sandy Loam
38.71	84.9	6.0	2.3	1.2	9.5	4.4	1.2	5.6	Loamy Sand
38.71	85.9	7.2	1.8	2.0	11.0	2.9	0.3	3.1	Loamy Sand
39.32	96.9	1.6	0.3	0.6	2.5	0.8	(0.2)	0.6	Sand
39.93	98.3	0.7	0.1	0.4	1.3	0.6	(0.2)	0.4	Sand
40.23	59.8	16.2	6.4	9.5	32.1	3.2	4.9	8.1	Sandy Loam
40.54	37.2	8.8	8.5	21.0	38.3	13.6	10.9	24.6	Loam
44.81	95.8	2.2	0.4	1.0	3.5	0.7	(0.0)	0.7	Sand
46.33	98.9	0.5	0.3	0.1	0.9	0.3	(0.2)	0.1	Sand
46.63	32.0	22.2	12.9	6.9	42.0	19.3	6.8	26.0	Loam
47.24	94.9	3.2	0.4	0.7	4.3	0.6	0.1	0.8	Sand
49.38	74.6	7.2	2.0	0.1	9.4	6.5	9.5	16.1	Sandy Loam
49.99	43.7	13.9	7.8	1.3	23.0	9.1	24.2	33.4	Clay
50.60	45.1	4.5	16.8	9.1	30.5	10.2	14.2	24.4	Loam
51.21	71.5	7.6	7.3	3.3	18.3	5.6	4.7	10.3	Sandy Loam
52.12	92.1	2.4	0.7	0.9	4.0	2.2	1.7	3.9	Sand
53.95	46.1	26.5	13.2	4.6	44.3	7.5	2.0	9.6	Loam
54.56	74.0	15.0	3.9	1.6	20.5	3.9	1.6	5.5	Sandy Loam
55.17	67.7	9.6	1.1	3.1	13.8	9.2	9.3	18.5	Sandy Loam
55.78	74.0	9.4	1.9	1.3	12.6	7.5	5.9	13.4	Sandy Loam
57.30	79.8	7.4	7.2	1.6	16.2	2.6	1.4	4.0	Loamy Sand
59.13	76.2	13.4	3.1	1.0	17.6	4.5	1.7	6.2	Sandy Loam
59.44	42.1	13.3	7.5	12.2	32.9	11.9	13.0	24.9	Loam
60.96	37.1	8.0	6.2	3.1	17.3	21.2	24.4	45.6	Clay
61.26	40.2	6.5	9.3	16.6	32.4	9.8	17.5	27.4	Clay Loam
62.48	61.1	11.3	11.0	7.1	29.4	6.2	3.3	9.5	Sandy Loam

Table 4. Water-extractable concentrations of chloride, sulfate, nitrate, bromide, and fluoride with associated gravimetric water content. Concentrations are on a dry weight-basis (milligram of the ion per kilogram of dry soil). Gravimetric water contents were measured at the time of extraction (DI saturated paste – section 3.3).

Sample Depth Below Surface (m)	Gravimetric Water Content (g/g)	mass of anion per total soil sample (mg/kg)				
		Cl	**SO4**	**NO3-N**	**Br**	**F**
6.40	0.064	8.47	65.87	2.41	0.029	0.291
8.23	0.102	38.44	20.78	4.95	0.125	0.110
9.45	0.018	29.41	38.17	10.05	0.156	0.284
11.89	0.063	13.33	78.62	12.42	0.053	0.398
12.19	0.015	12.66	91.09	10.48	0.044	0.304
13.72	0.016	8.19	101.30	6.40	0.024	0.556
14.02	0.014	6.99	87.97	4.75	0.051	0.391
14.94	0.015	7.06	108.86	5.76	0.026	0.441
15.24	0.011	5.12	109.85	5.54	0.019	0.369
16.76	0.030	5.15	135.05	7.75	0.017	0.438
21.03	0.028	8.26	184.94	16.96	0.029	0.612
21.34	0.066	8.47	216.63	13.09	0.024	1.043
22.25	0.126	4.96	90.98	3.48	0.012	0.755
22.56	0.014	1.80	37.31	1.46	0.006	0.354
24.69	0.029	3.56	53.93	3.25	0.014	0.426
25.30	0.012	3.39	36.84	1.46	0.008	0.354
25.60	0.008	2.39	28.36	1.30	0.010	0.334
26.82	0.013	3.12	23.41	0.64	0.008	0.225
28.04	0.003	1.37	11.52	0.33	0.004	0.227
33.53	0.012	8.10	26.06	0.31	0.020	0.273
34.74	0.007	6.29	17.44	0.13	0.014	0.538
35.36	0.025	6.63	32.07	0.25	0.015	0.523
35.66	0.019	5.36	24.28	0.19	0.007	0.474
35.97	0.015	7.06	29.67	0.28	0.016	0.449
36.88	0.017	8.61	36.17	0.72	0.023	0.608
37.19	0.038	13.45	46.67	1.09	0.033	0.638
38.40	0.023	18.26	39.97	1.40	0.064	0.451
38.71	0.006	6.99	13.18	0.17	0.014	0.229
39.00	0.008	11.77	16.17	0.29	0.033	0.551
39.32	0.001	2.54	4.28	0.07	0.012	0.392
39.93	0.001	2.49	3.23	0.05	0.010	0.272
40.23	0.028	14.91	21.20	0.83	0.043	0.907
40.54	0.032	14.11	28.72	1.08	0.049	1.534
44.20	0.001	1.51	1.58	0.17	0.011	0.341
44.81	0.003	6.49	5.29	0.67	0.043	0.551
46.33	0.001	2.68	2.16	0.30	0.020	0.274
46.63	0.089	25.69	21.18	0.58	0.131	1.750
47.24	0.011	19.86	19.22	3.78	0.172	0.481
49.38	0.048	18.08	16.89	2.47	0.135	0.849
49.99	0.112	22.39	18.63	3.58	0.175	1.963
50.60	0.051	21.37	23.13	1.20	0.170	2.070
51.21	0.022	10.24	8.80	1.68	0.091	1.117
52.12	0.005	5.44	3.05	0.71	0.047	0.616
53.95	0.037	13.03	7.97	2.76	0.118	1.378
54.56	0.005	5.81	3.76	0.95	0.045	0.776
55.17	0.042	11.29	8.20	2.98	0.102	1.427
55.78	0.018	9.93	6.64	1.84	0.059	0.985
57.30	0.004	6.48	4.07	1.49	0.058	0.578
59.13	0.013	14.49	9.09	3.05	0.135	0.969
59.44	0.028	12.66	16.42	3.30	0.092	1.490
60.96	0.066	10.63	14.34	0.82	0.088	2.452
61.26	0.031	8.04	10.66	0.31	0.041	2.457

Table 5. Concentrations of chloride, sulfate, nitrate, bromide, and fluoride in pore water (mg/L) with associated gravimetric water content. Concentrations are reported on a volume basis (mg/L) of the pore water within the unsaturated zone and water contents are representative of the water content at the time samples were collected from the ground at the field site.

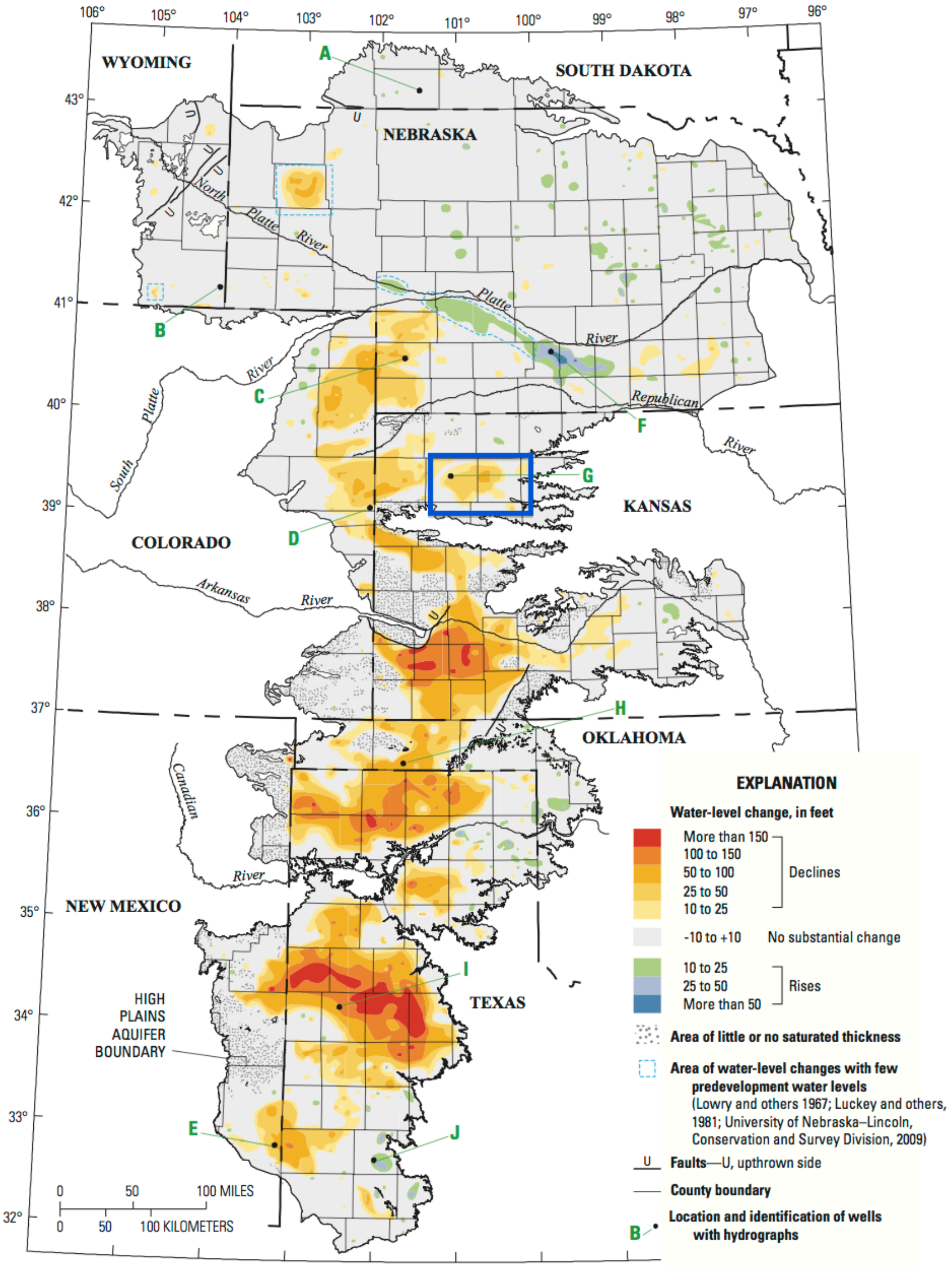
		concentration of anion in pore water (mg/L)				
Sample Depth Below Surface (m)	**Gravimetric Water Content (g/g)**	**Cl**	**SO4**	**NO3-N**	**Br**	**F**
6.40	0.1604	52.82	410.55	15.00	0.179	1.811
8.23	0.1934	198.61	107.37	25.56	0.643	0.569
9.45	0.1624	181.22	235.19	61.92	0.964	1.748
11.89	0.1466	90.66	534.65	84.47	0.361	2.717
12.19	0.1648	76.68	551.68	63.45	0.264	1.844
13.72	0.0920	88.18	1090.17	68.84	0.255	6.040
14.02	0.0744	94.03	1182.57	63.91	0.690	5.256
14.94	0.1040	67.70	1044.47	55.31	0.251	4.239
15.24	0.1019	50.27	1078.70	54.38	0.189	3.623
16.76	0.0903	56.75	1488.98	85.43	0.183	4.857
21.03	0.1892	43.64	977.42	89.61	0.153	3.234
21.34	0.3415	24.81	634.12	38.31	0.070	3.053
22.25	0.2056	24.13	442.65	16.91	0.060	3.673
22.56	0.0616	29.24	606.49	23.70	0.099	5.754
24.69	0.0713	49.92	755.63	45.52	0.203	5.977
25.30	0.0497	68.24	740.65	29.28	0.167	7.117
25.60	0.0303	78.63	933.53	42.88	0.326	11.012
26.82	0.0586	50.97	382.58	10.40	0.137	3.842
28.04	0.0049	204.63	1721.87	48.76	0.598	46.483
33.53	0.0701	115.56	371.76	4.45	0.287	3.888
34.74	0.0339	185.77	514.77	3.83	0.425	15.867
35.36	0.1158	57.30	276.98	2.19	0.133	4.512
35.66	0.0769	69.78	316.06	2.46	0.088	6.167
35.97	0.0740	95.22	400.03	3.83	0.210	6.061
36.88	0.1103	78.12	328.10	6.56	0.213	5.512
37.19	0.1312	102.59	355.87	8.29	0.255	4.860
38.40	0.1093	167.16	365.79	12.80	0.589	4.126
38.71	0.0336	194.70	367.30	4.67	0.402	6.808
39.00	0.0580	202.96	278.90	4.97	0.566	9.510
39.32	0.0102	250.33	421.86	7.07	1.188	38.571
39.93	0.0066	374.72	486.43	7.16	1.523	40.949
40.23	0.1243	119.95	170.55	6.72	0.347	7.298
40.54	0.1632	86.47	175.97	6.64	0.302	9.396
44.20	0.0043	354.64	371.20	39.16	2.492	80.026
44.81	0.0352	184.42	150.27	19.03	1.228	15.679
46.33	0.0069	387.17	312.62	42.75	2.821	39.628
46.63	0.1945	132.09	108.92	2.97	0.675	8.998
47.24	0.1458	136.20	131.80	25.94	1.178	3.298
49.38	0.1607	112.48	105.08	15.36	0.839	5.284
49.99	0.2928	76.48	63.61	12.22	0.599	6.705
50.60	0.2070	103.22	111.72	5.82	0.822	9.997
51.21	0.1151	89.00	76.48	14.58	0.790	9.709
52.12	0.0745	72.94	40.87	9.53	0.633	8.261
53.95	0.1695	76.89	47.03	16.27	0.695	8.133
54.56	0.0818	70.95	45.93	11.56	0.549	9.485
55.17	0.1199	94.16	68.38	24.84	0.850	11.906
55.78	0.1325	74.89	50.10	13.87	0.442	7.435
57.30	0.0386	168.16	105.66	38.56	1.514	15.001
59.13	0.1430	101.27	63.56	21.29	0.942	6.773
59.44	0.1734	73.00	94.70	19.01	0.528	8.593
60.96	0.2192	48.52	65.41	3.72	0.401	11.189
61.26	0.2131	37.74	50.05	1.47	0.194	11.534

Table 6. Groundwater concentrations of chloride, sulfate, nitrogen, nitrate, bromide, and fluoride collected from the irrigation well at the Thomas County field site (10S-33W-04B) and from four other irrigation wells in the surrounding area. Mass concentration ratios of bromide/chloride, nitrate/chloride, and sulfate/chloride were also measured from irrigation wells.

		Milligram per Liter						Mass Ratio		
Thomas County Irrigation Wells	**Sample Date**	**Cl**	**SO4**	**NO3**	**NO3-N**	**Br**	**F**	**Br/Cl**	**NO3-N/Cl**	**SO4/Cl**
10S-33W-04B	3/20/2013	25.27	62.45	35.53	8.03	0.20	1.44	0.0079	0.32	2.47
09S-33W-32BBA	9/1/11	10.66	15.62	18.58	4.20	0.15	1.42	0.0140	0.39	1.47
09S-33W-32A	9/1/11	14.88	24.34	24.64	5.56	0.17	1.37	0.0113	0.37	1.64
09S-33W-32DBC	9/1/11	8.33	17.70	12.55	2.83	0.09	1.47	0.0108	0.34	2.12
09S-32W-29B	9/1/11	14.64	21.14	21.70	4.90	0.15	1.38	0.0104	0.33	1.44
	Average	14.76	28.25	22.60	5.10	0.15	1.42	0.01	0.35	1.83

Table 7. Uncorrected radiocarbon and δ13C data from the Thomas County index well (09S-33W-33BBB), the irrigation well at the Thomas County field site (10S-33W-04B), and four other irrigation wells from the surrounding Thomas County area (modified from Butler et al., 2013).

Well Type	**Location/Well ID**	**Date** (m/d/yr)	**δ^{13}C ‰** (PDP)	**F** (Modern Carbon)	**^{14}C age BP**
Index Well	09S-33W-33BBB	6/15/2011	-6.4	0.5911	4,220
Irrigation Well	09S-33W-32BBA	9/1/2011	-4.1	N/A	3,830
Irrigation Well	09S-33W-32A	9/1/2011	-8.1	N/A	3,960
Irrigation Well	09S-33W-32DBC	9/1/2011	-4.7	N/A	4,600
Irrigation Well	09S-32W-29B	9/1/2011	-3.9	N/A	4,400
Irrigation Well	10S-33W-04B	3/20/2013	-9.9	0.6025	4,070



Base from U.S. Geological Survey digital data, 2001, 1:2,000,000
Albers Equal-Area projection
Standard parallels 29° 30' and 45° 30', central meridian -101°

Figure 1. Historical water-level declines in the High Plains aquifer, predevelopment to 2009. Blue box denotes the northwestern Kansas portion of the HPA and the Thomas County research location in which samples were collected (modified from McGuire, 2009).

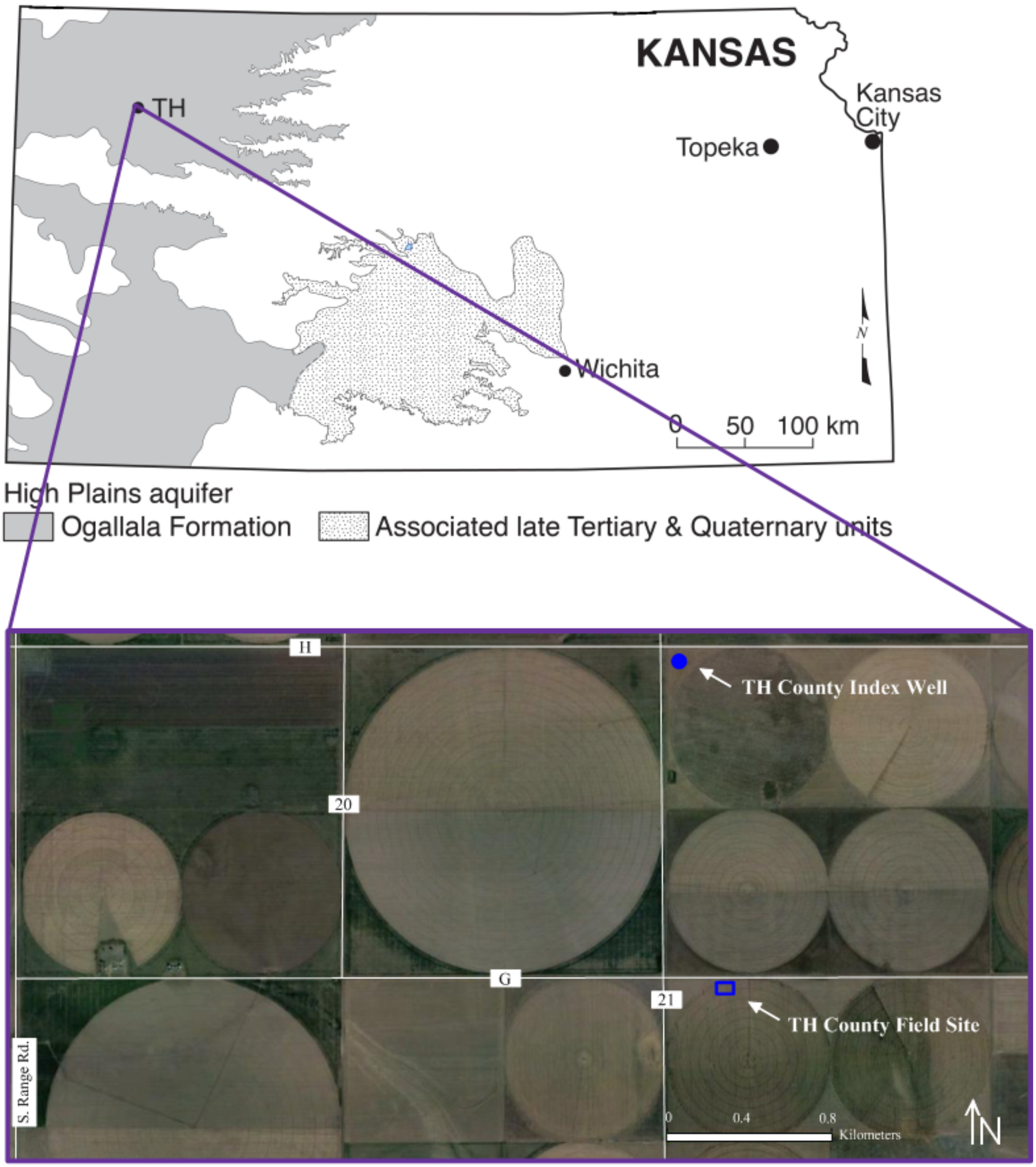


Figure 2. **(a)** The location of the High Plains aquifer within the state of Kansas. Purple outlined section in northwest Kansas represents the Thomas County region (known as GMD4 in KGS index well reports). The approximate study location for this research is marked by the black circle and TH label. **(b.)** Satellite aerial image of the study location in Thomas County (modified from google earth). The Thomas County index well is marked by the blue circle (39°13'11.47" N Latitude, 101°01'05.49" W Longitude) and the blue square marks the field location where samples were drilled and collected for this study (39°13'11.47" N Latitude, 101°00'54.21" W Longitude). Eye elevation of this image is 6.34 kilometers

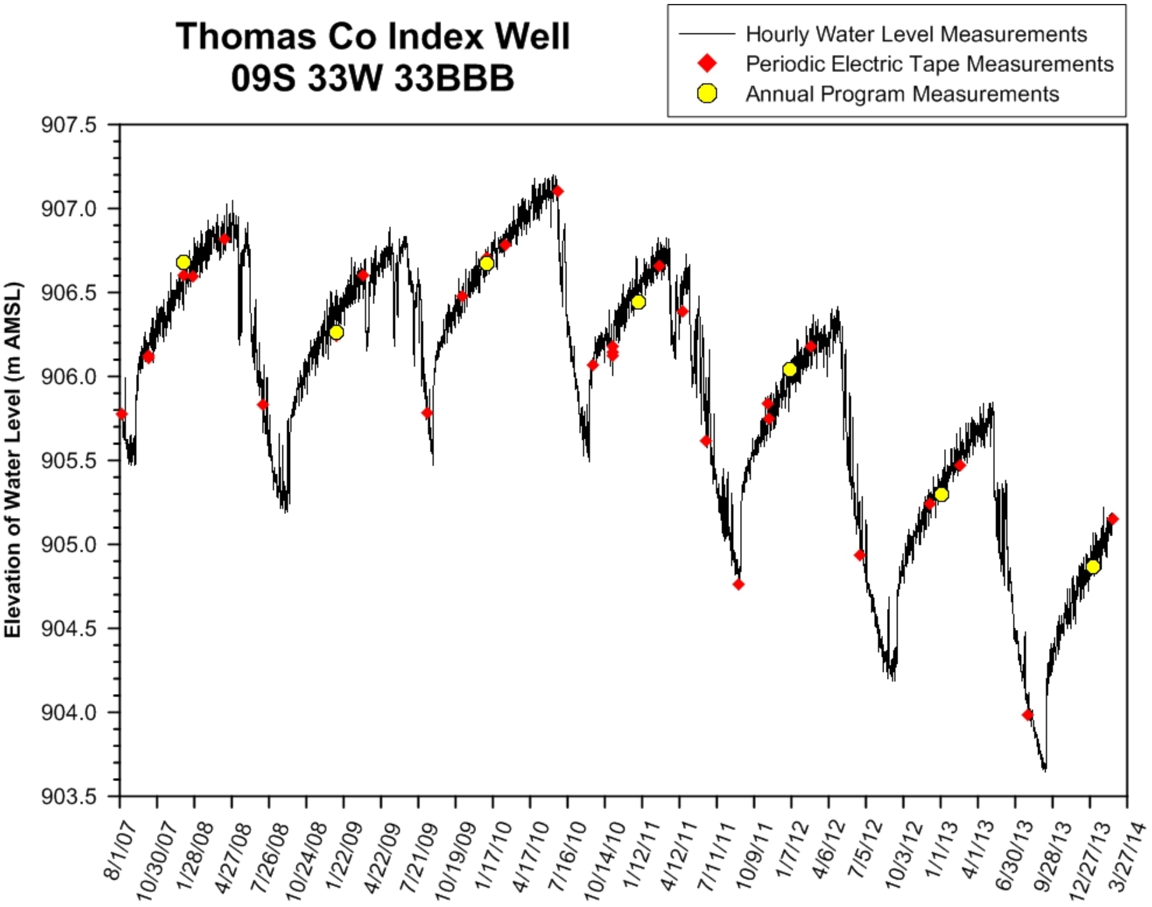


Figure 3. Thomas County index well hydrograph results from August 2007 to January 2014. Figure shows the elevation of water over time. Decreases in water levels are during months of pumping and increases represent recovery time during months without pumping (Modified from Butler et al., 2013).

Figure 4. Photographs showing **(a.)** drill rig and drilling operation at the Thomas County field site on March 25, 2013, **(b.)** hollow-stem auger (8.3 cm diameter) in the ground at the field site, **(c.)** labeled sample cores tubes, and **(d.)** preservation of core samples by tightly sealing both ends with a rubber cap and vinyl electrical tape (to retain moisture). Photographs a., b., and c. taken by Britney S. Katz; photograph d. taken by Randy L. Stotler.

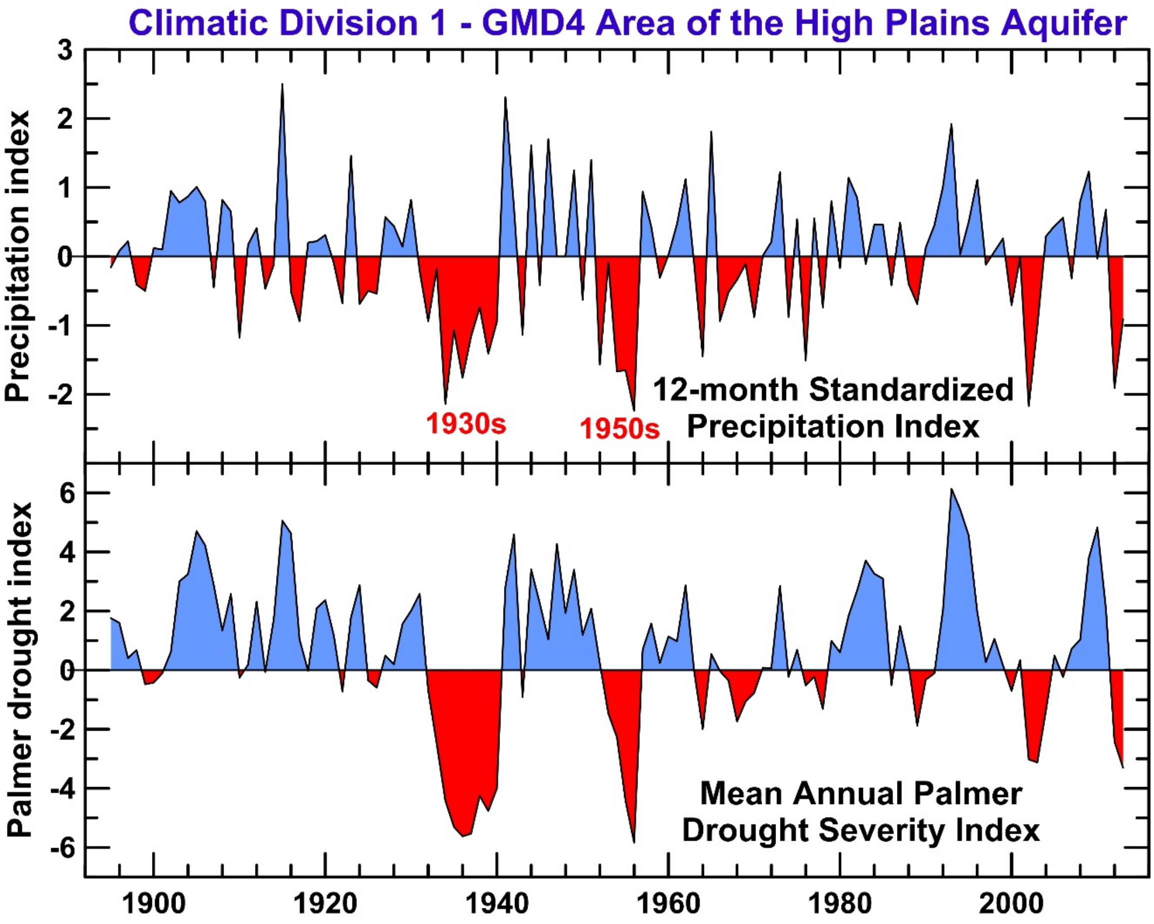


Figure 5. Precipitation index and Palmer drought index for the Thomas County region of the High Plains aquifer over the past century. Both the Palmer drought index and precipitation index reveal large periods of drought in both the late 1930s and 1950s (shaded in red) which would impact salinity buildup in the unsaturated zone at the THC location. Especially wet years in between droughts would promote the mobilization of nutrients and result in larger water-fluxes during those years (D.O. Whittemore, unpublished, data from National Climatic Data Center, 2014, www7.ncdc.noaa.gov/CDO/CDODivisional Select.jsp).

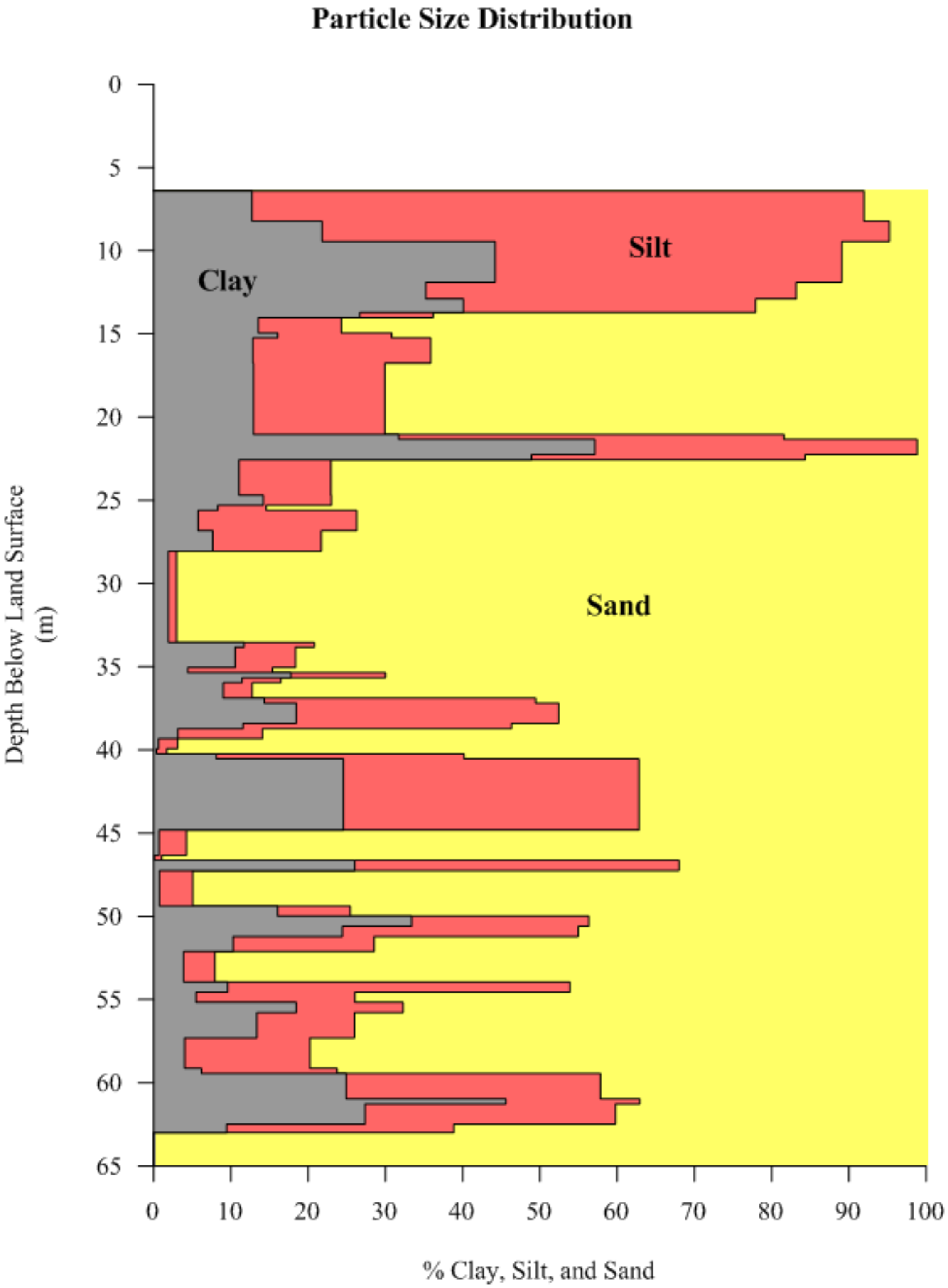


Figure 6. Relationship between depth and particle size distribution (soil texture) through the unsaturated zone at the Thomas County field site. The distribution is reported as % clay (grey), % silt (red), and % sand (yellow). Clay is defined as <2µm, silt as 50-2µm, and sands 2000-50µm. USDA texture classifications through the profile are reported in Table 3.

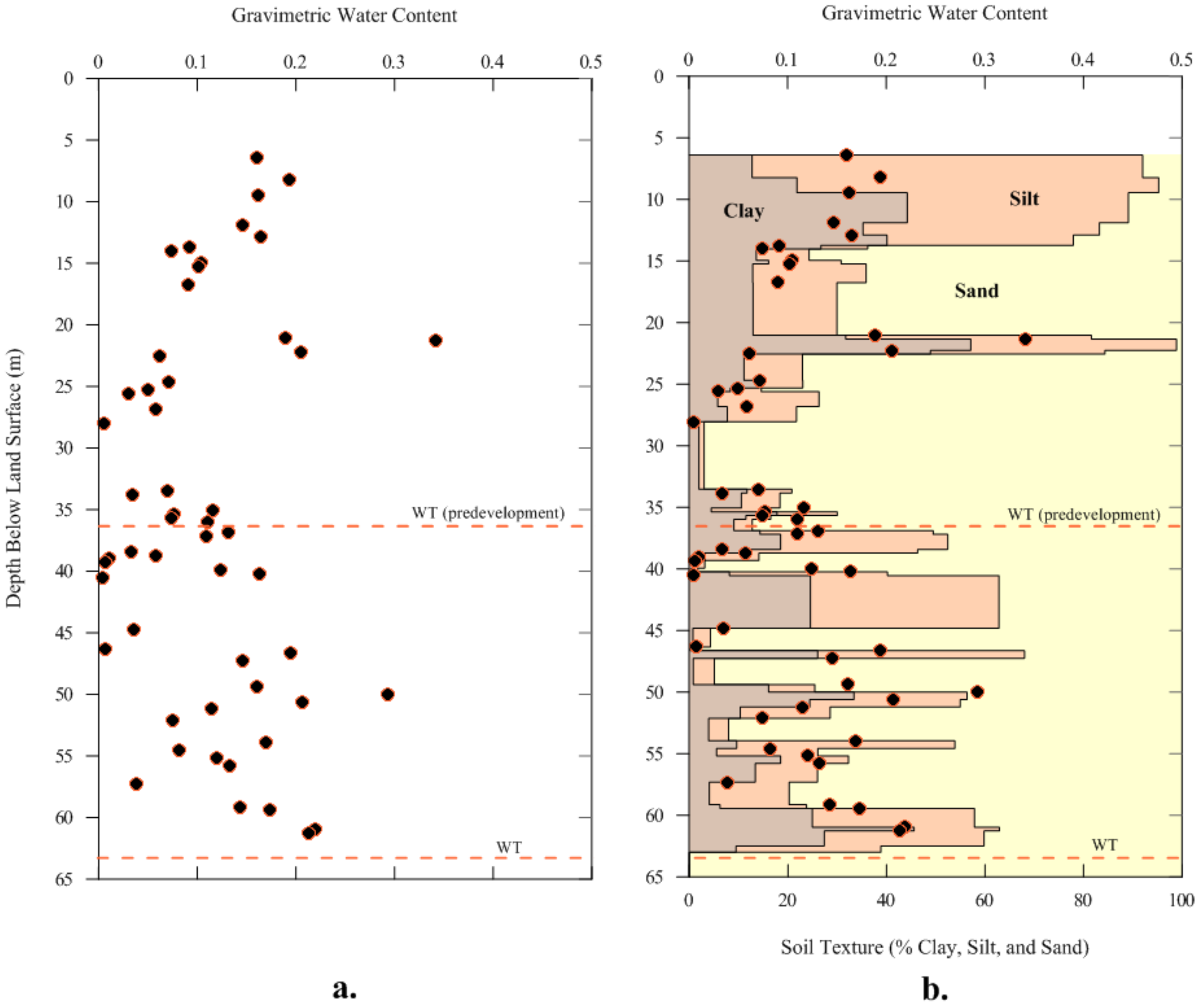


Figure 7. **(a.)** gravimetric water content with depth through the unsaturated zone at the Thomas County field site and **(b.)** relationship between gravimetric water content and soil texture throughout the profile. Horizontal dashed lines are associated with the current water table elevation (WT) and the water table elevation prior to 1984 (WT predevelopment).

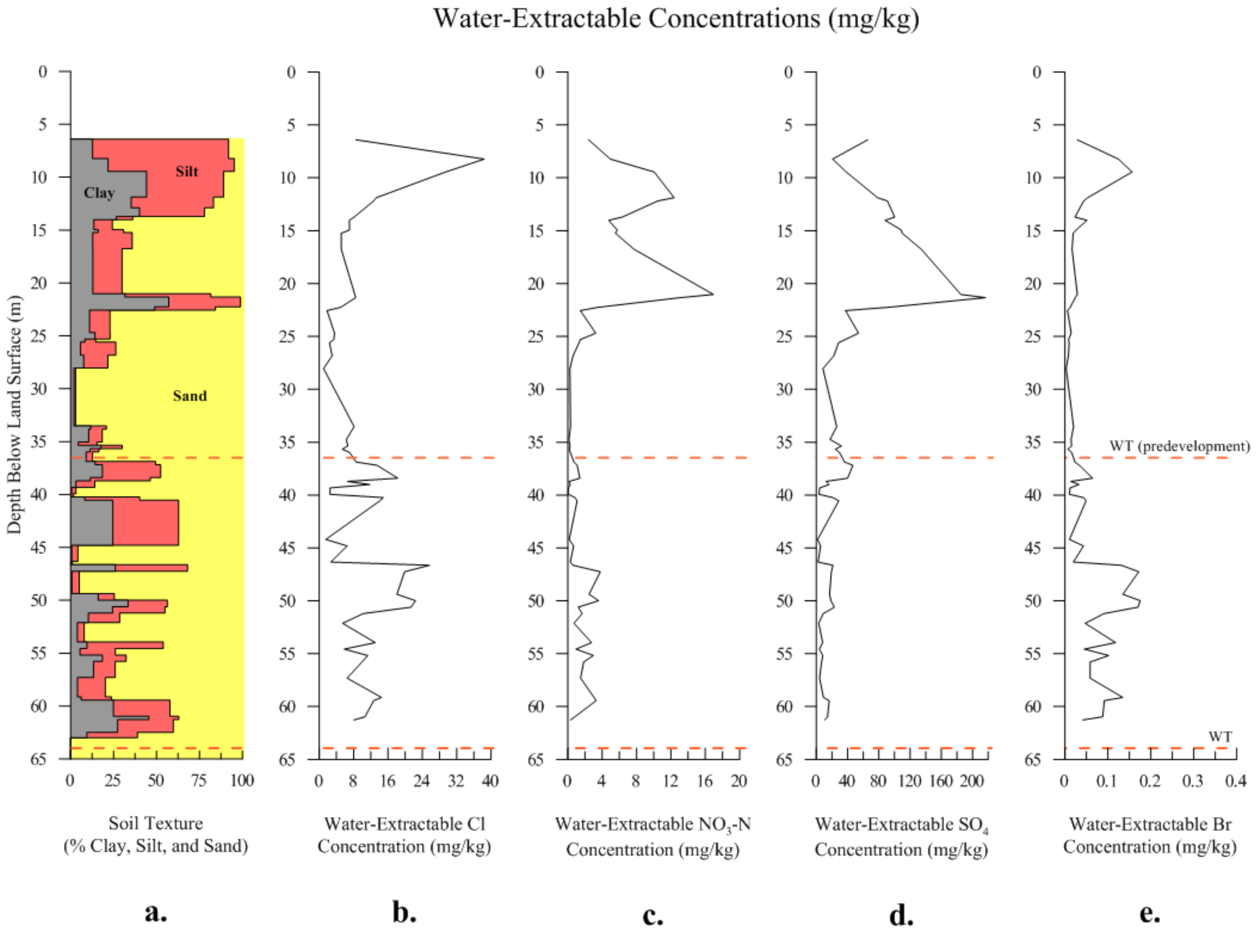


Figure 8. Relationship between depth and **(a.)** soil texture, **(b.)** water-extractable chloride concentrations, **(c.)** water-extractable nitrate concentrations, **(d.)** water-extractable sulfate concentrations, and **(e.)** water-extractable bromide concentrations from the unsaturated zone at the Thomas County field site. These concentrations are on a dry weight-basis (milligram of the ion per kilogram of dry soil) using sieve weight and air dried gravimetric water content measured at the time of DI saturated paste extraction (section 3.3). Horizontal dashed lines are associated with the current water table elevation (WT) and the water table elevation prior to 1984 (WT predevelopment).

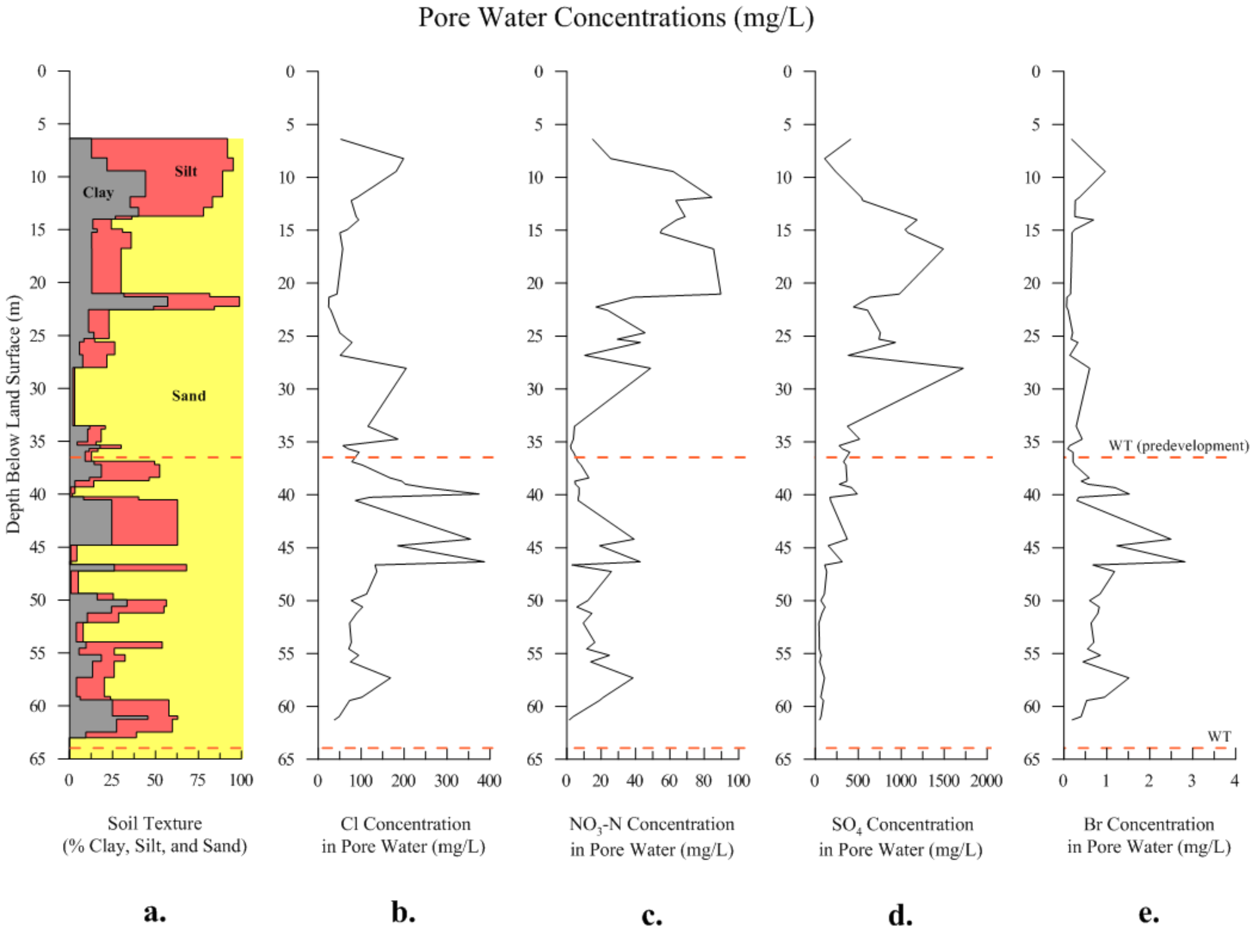


Figure 9. Relationship between depth and **(a.)** soil texture, **(b.)** chloride concentrations in pore water, **(c.)** nitrate concentrations in pore water, **(d.)** sulfate concentrations in pore water, and **(e.)** bromide concentrations in pore water at the Thomas County field site. These concentrations are reported on a volume basis (mg/L) of the pore water within the unsaturated zone. Horizontal dashed lines are associated with the current water table elevation (WT) and the water table elevation prior to 1984 (WT predevelopment).

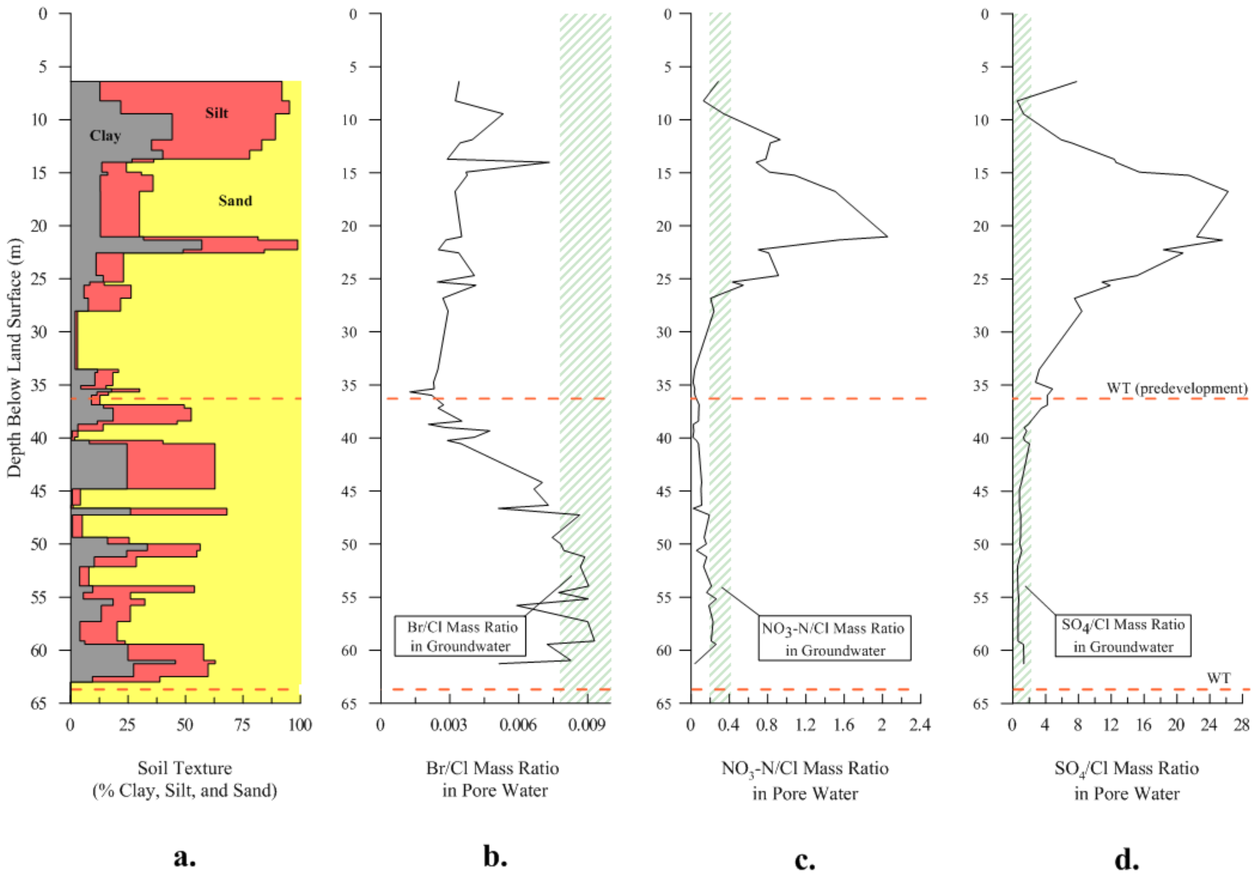
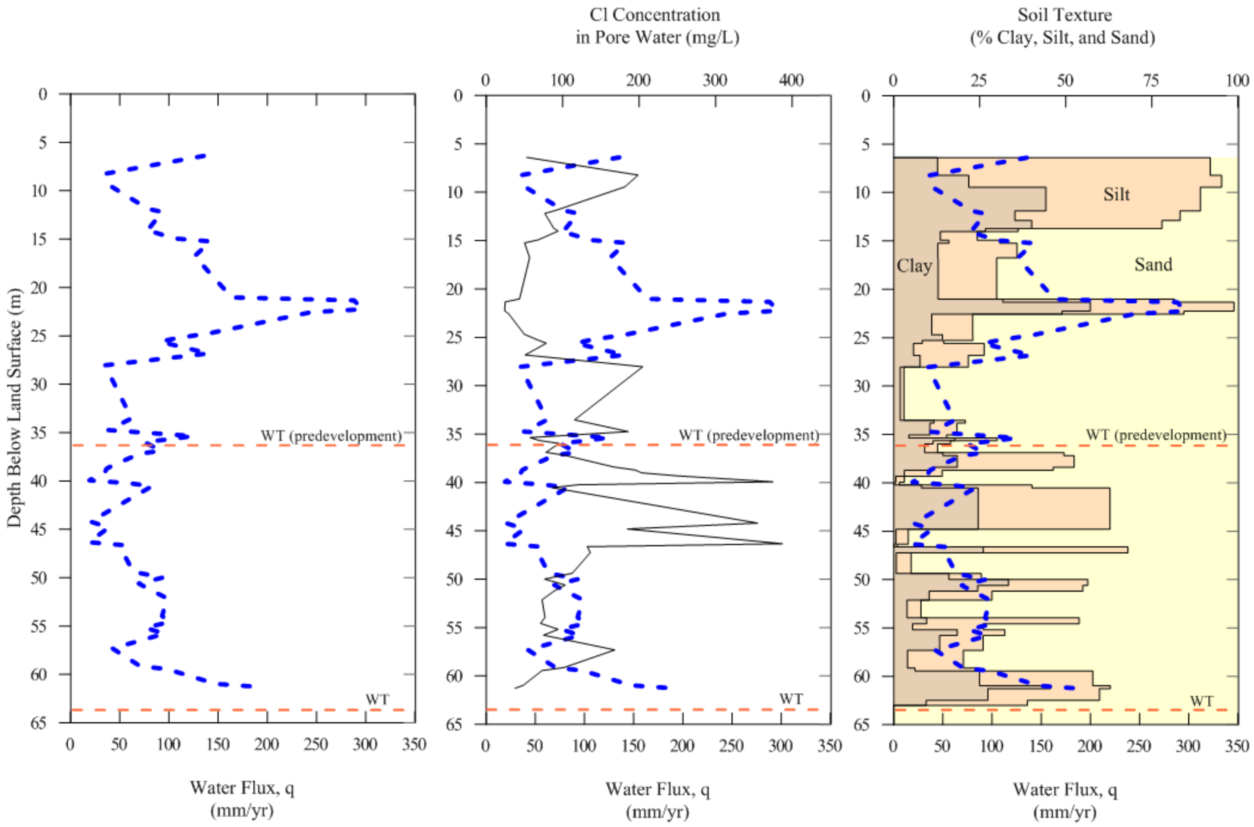
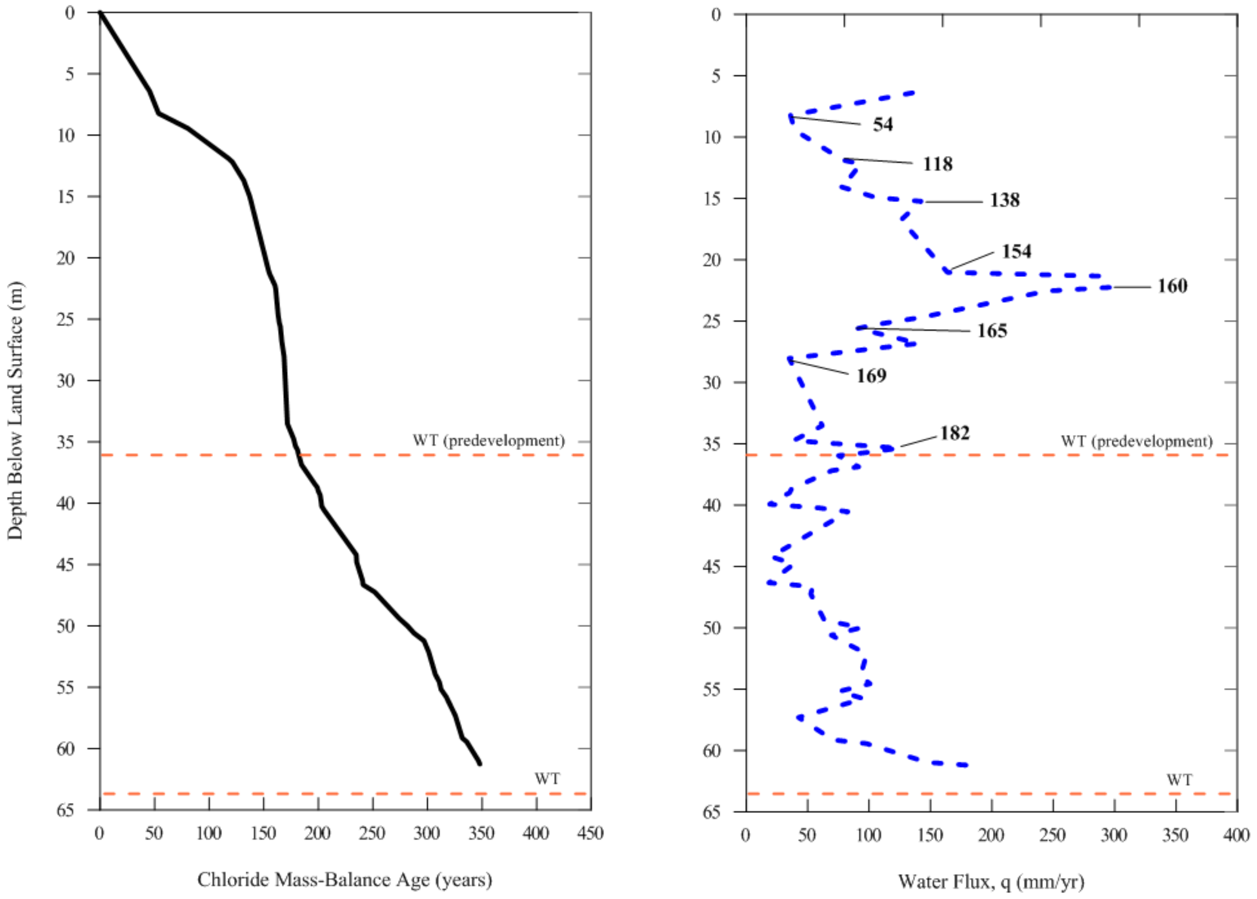


Figure 10. Relationship between depth and **(a.)** soil texture **(b.)** mass ratio concentrations in pore water of Br/Cl, **(c.)** mass ratio concentrations in pore water of NO3-N/Cl, and **(d.)** mass ratio concentrations in pore water of SO4/Cl. Green shaded areas plotted on plots b-c represent the concentration range of those corresponding mass ratios in the groundwater collected from nearby irrigation wells. Horizontal dashed lines are associated with the current water table elevation (WT) and the water table elevation prior to 1984 (WT predevelopment).



a. **b.** **c.**

Figure 11. Relationship between depth and **(a.)** vertical water flux, **(b.)** water flux compared to chloride concentrations in the pore water, **(c.)** water flux in relation to soil texture (PSD) throughout the unsaturated zone in Thomas County. Horizontal dashed lines are associated with the current water table elevation (WT) and the water table elevation prior to 1984 (WT predevelopment).



a.

b.

Figure 12. Relationship between depth and **(a.)** Average chloride mass-balance ages (years) through the unsaturated zone with depth, and **(b.**) vertical water flux (mm/yr) with corresponding chloride mass-balance ages (in years) shown with depth throughout the unsaturated zone in Thomas County. Horizontal dashed lines are associated with the current water table elevation (WT) and the water table elevation prior to 1984 (WT predevelopment.