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Hydrogeology and Chemical Characterization of Hydrocarbon in Domestic Water Wells, Rancho Villa Subdivision, Rogers, Arkansas

Janelle Renee Sherman
University of Arkansas, Fayetteville

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HYDROGEOLOGY AND CHEMICAL CHARACTERIZATION OF HYDROCARBON IN DOMESTIC WATER WELLS,
RANCHO VILLA SUBDIVISION, ROGERS, ARKANSAS

Hydrogeology and Chemical Characterization of Hydrocarbon in Domestic Water Wells,
Rancho Villa Subdivision, Rogers, Arkansas

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Geology

by

Janelle Renee Sherman
Wayne State University
Bachelor of Science in Geology, 2010

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University of Arkansas

This thesis is approved for recommendation to the Graduate Council.

Dr. Phillip Hays
Thesis Director

Dr. Matthew Covington
Committee Member

Mr. Erik Pollock
Committee Member

Abstract

This project is centered on the Rancho Villa community in Rogers, Arkansas where several residents have had hydrocarbon contamination in their domestic water wells. The goal of this project was to understand the hydrogeology in the study area, characterize the contaminant chemically, and determine the source of the contaminant. The hydrogeology of the area was determined from previous theses. Seventeen samples were taken from the wells in the Rancho Villa community; each sample was analyzed for geochemical parameters and by Gas Chromatography/Mass Spectrometry (GC/MS) for organic compounds analysis. Four of the 17 samples had a visible non-aqueous layer of hydrocarbon on top of the water.

Qualitative analyses of the GC chromatograms for the hydrocarbon samples indicate the presence of abundant gasoline and diesel range n-alkanes. Synthetic fuel additives also were detected in the samples. These findings suggest the contamination is from a fuel spill and is not naturally occurring. The carbonate aquifer in the study area is karstified, with anisotropic flow. The contaminant has persisted in the area for the past six years and is localized in the Rancho Villa community. No reported spill sites are near the community, and no possible physical sources have been identified. The study area is located on the up thrown block of a normal fault; stress fractures associated with the normal fault are likely conduits for the contaminant, and allow focused migration of the hydrocarbon. The water samples with visible hydrocarbon had some emulsification, indicative of microbial degradation. The source of the contaminant was not determined; however this study is a foundation for further investigation in the area.

Acknowledgements

Special thanks to the Rancho Villa community, Ms. Caroline Eastman of the Arkansas Department of Health, Mr. Roger Miller of the Arkansas Department of Environmental Quality, and Dr. Michael Formolo of University of Tulsa, Department of Geosciences. Their help and input was invaluable to this project.

Also many thanks to my advisor and my committee members for their help, suggestions, and patience.

Dedication

This thesis is dedicated to my late grandmother Mrs. Eleanor McIntosh, I would not have made it here without your unending love and support. I hope that I have made you proud.

Table of Contents

I. Problem Statement and Site Description..... 1

II. Geology..... 3

III. Structure..... 5

IV. Hydrologic Setting..... 7

V. Hydrogeology..... 9

VI. Hydrocarbon Fingerprinting..... 10

 A. Distinguishing Background Hydrocarbon from Hydrocarbon
 Introduced into the Environment..... 11

 B. Hydrocarbon Fingerprinting Methods..... 12

VII. Methodology..... 19

 A. Well Sampling..... 19

 B. Water Sample Preparation and GC/MS Analysis..... 20

 C. Hydrocarbon Sample Preparation and GC/MS Analysis..... 21

VIII. Results and Discussion..... 23

 A. ADEQ Water Analysis..... 23

 B. ADEQ Organic Compound Analysis..... 27

 C. GC/MS Water Sample Analysis..... 29

 D. GC/MS Pure Phase Hydrocarbon Sample Analysis..... 31

 E. Contaminant Source..... 34

 F. Contaminant Degradation and Distribution..... 38

IX. Conclusions..... 46

X. References..... 49

XI. Appendices..... 54

I. Problem Statement

In Rogers, Arkansas, a subdivision community, Rancho Villa, has reported problems with their domestic water wells since 2006. Several residents in the community have reported to the Arkansas Department of Health (ADH) the presence of a viscous brown hydrocarbon causing an oily sheen and strong fuel odor in their domestic water wells. Contaminated drinking water poses a serious problem for this rural community, many residents do not have access to an alternative drinking water source. Connecting households in this community to the municipal water supply would be costly. Representatives from the ADH interviewed many residents in the Rancho Villa community and surrounding communities and recorded reports of contaminated well water and associated water, plumbing, and health problems. Ms. Caroline Eastman from the ADH contacted Dr. Phillip Hays in the department of Geosciences at the University of Arkansas who suggested that the issue be investigated as a Master's thesis project.

Most of the affected residents continue to use their well water with or without treatment. Numerous health effects are associated with acute and chronic exposure to various hydrocarbon compounds, including those found in fuels. By way of example, exposure to polycyclic aromatic hydrocarbons (PAH), common fuel constituents, can cause erythema, respiratory complications, gastrointestinal issues, and in the most severe cases leukemia and lymphoma (U.S. EPA, 1984). However, the nature of the contamination at Rancho Villa is not yet well characterized and as such the total effects are not known. The goals of this project were: 1. To characterize the contaminant chemistry, 2. Understand the hydrology of the contaminant site and 3. If possible, identify the source of the contamination.

Site Description

The Rancho Villa community is located less than a mile east of the more heavily populated area of Rogers. The community is situated on a bluff above Beaver Reservoir at an elevation of 1,300 feet and comprises about 45 single-family residences. Public water supply is not available in the area. The study area is situated on the up thrown block of a normal fault that is trending northeast-southwest. Stress fractures resulting from the normal fault are likely conduits for subsurface flow. The surficial geological unit of the study area is the Boone Formation, a karstified limestone with interbedded chert (Dowell, 2005).

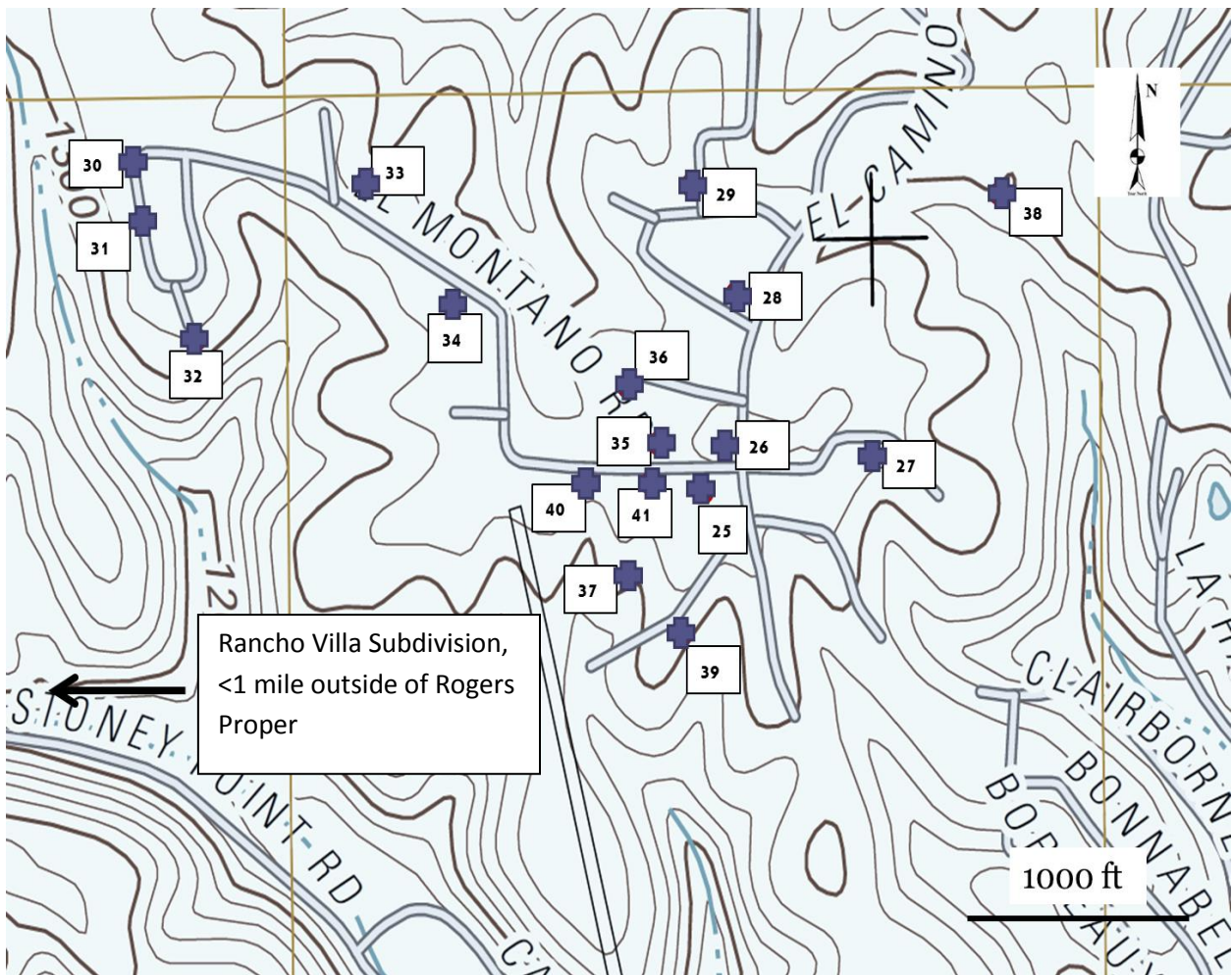


Figure 1. Map of the study area and distribution of sampled wells

II. Geology

The Boone Formation is the dominant surficial geological unit in the study area east of Rogers, Arkansas, and controls the topography of the area. The Boone Formation is a Mississippian age limestone with interbedded chert, exposed across approximately fifty percent of Benton County (Dowell et. al, 2005). The Boone Formation is a part of the Mississippian system comprising the Boone, St. Joe, Batesville, and Fayetteville Formations (Hunt, 1974) (Fig. 2). In Missouri, the Boone Formation is divided into four formations, whereas in northwest Arkansas these units cannot be reliably discriminated as a result of the changes in depositional textures due to cementation, recrystallization, silicification, dolomitization, and stylolite development (Rezaie, 1979).

Within the Boone in northwest Arkansas, two distinct intervals exist. The Lower Boone is a crystalline, argillaceous and bioclastic limestone with a large amount of dark, discontinuously bedded chert, and the Upper Boone is a white to gray oolitic limestone containing a large amount of light, continuously bedded chert (Hunt, 1974). The Boone has a regional thickness of approximately 300 feet (Hunt, 1974). The Rancho Villa community is located near the shores of the Beaver Lake Reservoir upon the bluff forming Boone. The U.S. Geological Survey classifies the St. Joe Limestone as a part of the Boone Formation; however, many local authorities name the St. Joe as a separate formation (Manger and Shanks, 1976 and Adamski, 2000). For this study, the St. Joe Limestone will be regarded as a separate formation. The St. Joe Limestone is also of Mississippian age, underlies the Boone and is composed of gray to pink, fine-grained, crinoidal, relatively pure limestone, and light-gray crystalline chert, as well as 15 to 35 percent clay (Hunt, 1974). The thickness of the St. Joe Limestone varies regionally from six feet to 84 feet, with an average thickness of 45 feet (McFarland, 1975). The Devonian Chattanooga Shale is the geologic unit that underlies the St. Joe Formation, composed of dark colored shale that is fissile and argillaceous, and has an average thickness of 30 feet (Hunt, 1974). The upper part

of the Chattanooga is jointed, with pyrite and kerogen disseminated throughout (Hunt, 1974). The Chattanooga is relatively impermeable and serves as a regional confining unit between the overlying and underlying aquifers. The Clifty Formation is middle Devonian in age and underlies the Chattanooga; the Clifty is a bluff forming sandstone with limestone lenses and ranges in thickness from five to 20 feet (Stanton, 1993). Some of the wells in the study area extend into the Ordovician age formations, which include the Everton, Powell, and Cotter Formations. The Everton Formation underlies the Clifty Formation, and is not well exposed in the study area, the Everton is primarily dolomite, sandy dolomite, sandstone, and thin lenses of limestone (Frezon and Glick, 1959). The Late Ordovician Cotter and Powell Formations are both chert-bearing dolomites (Stanton, 1993). The Cotter Formation is up to 400 feet thick, and is difficult to distinguish from the Powell Formation in some areas. The Powell Formation is thinner than the Cotter and ranges in thickness from less than 10 to up to 95 feet (Stanton, 1993).

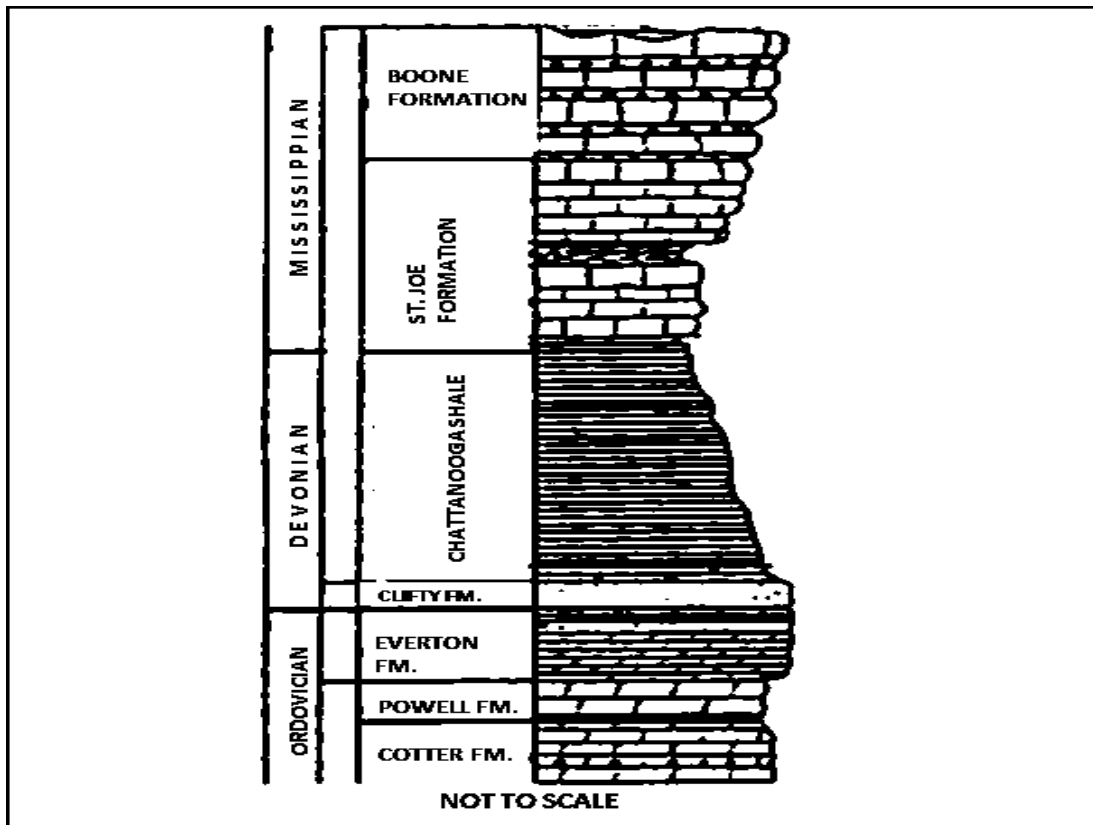


Figure 2. Stratigraphic Column of Rogers Quadrangle, Benton County, AR, Modified From Dowell, Hutchinson, Boss (2005)

III. Structure

In Benton County, AR the strata are essentially flat lying and follow a gentle (less than one degree), regional dip to the south (Stanton, 1993). The dip of the units in northwest Arkansas is a result of the uplift of the Arkansas Dome, which extends into southern Missouri, northern Arkansas, northeastern Oklahoma, and southeast Kansas (Shinn, 1979). Greater dip magnitudes are observed near faults. Croneis (1930) described two structures local to Rogers, AR, the Price Mountain and Glade Faults, which are located six miles to the southeast and five miles to the northeast respectively. Both the Price Mountain Fault and the Glade Fault trend southwest to northeast, and are normal faults downthrown to the southeast of their fault traces (Dowell et al, 2005). Deformation in Northwest Arkansas is a result of compression from the northeast and southwest. Structural deformation in the area is not obvious or readily observed, and is covered with regolith in most places in Benton County (Martin, 1999). The study area is situated on the up thrown block of a northeast to southwest trending normal fault (Fig. 3)

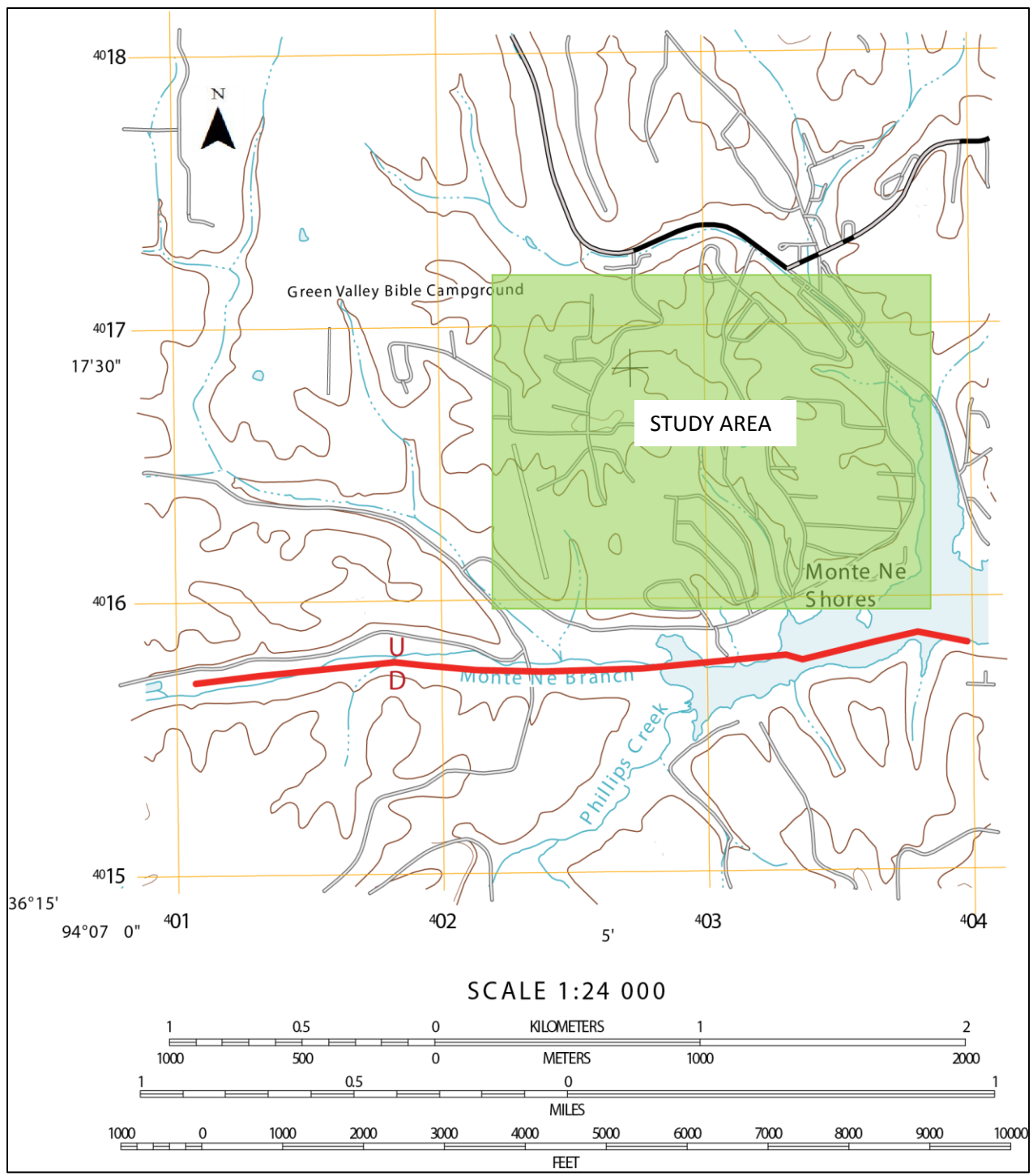


Figure 3. Structure map, Rogers Quadrangle, showing a normal fault in the study area
 Modified from Dowell, Hutchinson, Boss, 2005

IV. Hydrologic Setting

The study area is in the city of Rogers in Benton County, Arkansas. Benton County is drained by the White River which subsequently drains to the Arkansas River. Mean annual rainfall in Benton County is about 43 inches per year, and the ratio of surface water use to ground-water use is 41.1 to 8.8 million gallons per day (Adamski, 1995). Runoff and stream flow vary annually; changes are due to differences in seasonal evapotranspiration and precipitation. Runoff in the study area ranges from 11 to 14 inches per year (Adamski, 1995). The domestic wells in the Rancho Villa community range in depth from 200-600 ft. The wells of greater depth span the Boone, St. Joe, Chattanooga, and underlying Ordovician age Formations.

The Boone Formation along with the underlying St. Joe Limestone is a part of the regional Springfield Plateau aquifer which extends through northwest Arkansas, southwest Missouri, southeast Kansas, and northeast Oklahoma. The Boone and St. Joe Formations are characterized by low primary porosity (less than 1 percent) and low primary permeability (less than 0.001 millidarcies) (Van de Heuvel, 1979). Porosity present along chert layer bedding planes and along fractures in the limestones allows for initiation of dissolution. (Stanton, 1993). The Chattanooga Shale underlies the Springfield Plateau aquifer and acts as a confining layer (Martin, 1999). Dissolution of the limestone in the Boone Formation has created secondary porosity and permeability. The limestone in the Boone Formation is marked by dissolution karst features such as caves and sinkholes. The wells sampled for this study are 0.65 to 1.24 miles away from Beaver Reservoir (Fig. 4). Beaver Reservoir was dammed by US Army Corp of Engineer in 1966 to serve as a stored water source for drinking water, hydroelectric power, and flood control (Davis and Shepherd, 2010).

V. Hydrogeology

Stanton (1993) established a conceptual model for groundwater flow in the Boone-St. Joe aquifer, studying a number of locations in northwest Arkansas by establishing flow communication between wells and recording various parameters and properties of flow. Stanton determined that flow in the Boone-St. Joe aquifer at his study locations during high flow has a minimum velocity of 2.34 feet per hour. Flow in the Boone-St. Joe aquifer is dynamic, non-steady state, anisotropic, and is dominantly controlled by the stratigraphy and dissolution of the formations that comprise the aquifer (Stanton, 1993). Groundwater flow in the Boone-St. Joe aquifer is complex and heterogeneous, continuous flow is typically localized in conduits formed from dissolution and occurs in vertical joints and fractures (Martin, 1999 and Stanton, 1993). Horizontal flow often occurs perched atop chert layers in the aquifer (Rezaie, 1979). Flow conditions in the Boone-St. Joe aquifer can be significantly influenced by large rain or storm events, which cause episodic increases in flow volume and flow rate. Conversely, periods of drought decrease flow in the aquifer. Flow in karst aquifers occurs along fractures and openings formed by dissolutions, which store and convey water to be discharged at springs and stream baseflow. Porosity and permeability in karst aquifers decrease with depth. As water infiltrates karst aquifers to great depth, dissolution and potential for water storage increases (Driscoll, 1986 and Martin, 1999). Fractures and dissolutions increase permeability and throughput times, allowing faster flow over longer distances than what would be observed in non-karst aquifers.

Martin (1999) conducted pumping tests in the Boone-St. Joe aquifer to constrain the transmissivity and specific capacity of the aquifer. Martin conducted pumping tests in Avoca, AR, Clear Creek, AR, and in Bella Vista, AR in order to accrue regionally representative data of the aquifer. The average discharge at the Avoca location was measured to be 1.53 gpm, and transmissivity ranged from 1.87 to 5.92 ft²/day. At the Clear Creek site, the transmissivity of the Boone-St. Joe aquifer was measured to be 222 ft²/day, and the specific capacity to be 1.72 gpm/ft at a discharge of 6.3 gpm then

decreased to 1.41 gpm/ft at a discharge rate of 10.3 gpm. The change in specific capacity with an increase in discharge indicates turbulent flow at the Clear Creek site (Driscoll, 1986). The Bella Vista pumping test in the Martin study yielded an average discharge rate of 264 gpm. Transmissivity at the Bella Vista site was determined to be 3,876 ft²/day (Martin, 1999). Stanton (1993) also studied the factors influencing flow in the Boone-St Joe aquifer at a number of locations in northwest Arkansas using pumping tests, and calculated transmissivity to be 220 ft²/day with a discharge rate of 6.3 gpm. Stanton's values for specific capacity and discharge are 1.84 gpm/ft and 258 gpm respectively. The large range of values for the discharge, transmissivity, and specific storage for the Boone-St. Joe aquifer at various sites within Northwest Arkansas indicate that flow in the aquifer is very complex and heterogeneous.

VI. Hydrocarbon Fingerprinting

Hydrocarbon fingerprinting techniques were developed to determine the origins of spilled petroleum products in the environment, and are used in oil characterization and environmental forensics. Quantitation and identification of organic compounds that constitute petroleum are used to characterize hydrocarbon released in the environment. Success in oil fingerprinting depends on sampling method, analytical approach, and data interpretation strategies (Wang and Fingas, 2003). Gas chromatography-mass spectrometry (GC-MS) is the most commonly used analytical method for hydrocarbon fingerprinting and is utilized in this study.

Target analytes used in determining the source of petroleum spills depend on the type of oil spilled and the expected needs for data comparison (Wang and Fingas, 2003). The main target analytes are as follows: Individual saturated hydrocarbons, volatile hydrocarbons, EPA priority parent PAHs and petroleum specific homologues, biomarker terpane and sterane compounds, and measurements of total petroleum hydrocarbons and stable carbon isotope ratios (Wang and Fingas, 2003). Upon exposure to the environment, the effects of weathering and degradation have a significant impact on the chemical

signature of hydrocarbons. The loss of chemical constituents from petroleum in the environment begins with the loss of n-alkanes, then cyclic alkanes, low molecular weight aromatics, and then higher molecular weight compounds as degradation progresses (Hostettler et al, 2007). Cyclohexanes are compounds that are more persistent than n-alkanes in the environment, and often are used to differentiate fuel types released into the environment (Hostettler et al, 2007).

A. Distinguishing Background Hydrocarbon from Hydrocarbon Introduced into the Environment

Naturally occurring organic matter in soils contains hydrocarbons that have similar volatility to hydrocarbons in petroleum, and the presence of naturally occurring hydrocarbons can contribute to total hydrocarbons present at a spill site (Stout and Wang, 2007). Biogenic hydrocarbons exist as background in contaminated areas, and can interfere with the chemical signature of the contaminating hydrocarbon. Sources of biogenic hydrocarbon include metabolic products and degradation products of plants, phytoplankton, bacteria, and algae (Wang and Fingas, 1999). Biogenic hydrocarbons show an n-alkane distribution pattern of odd-numbered alkanes at higher abundance compared to even-numbered alkanes in the range of n-C₂₁ to n-C₃₃, an unresolved complex mixture (UCM) hump is typically absent in GC chromatograms of biogenic hydrocarbon (Wang and Fingas, 1999).

Lorenson et al (2009) studied the chemical signature of tar balls that washed up on the coastline of California from various marine oil seeps as well as crude oil spills that occurred off of the California coast. The goal of the Lorenson study was to determine whether the source of the tar balls was from crude oil spills or natural oil seeps. The tar balls that were formed by the natural oil seeps had a number of chemical characteristics in common, (1) $\delta^{13}\text{C}$ values of -23‰ v PDB, (2) aliphatic biomarker parameters of high 28,30 bisnorphane and high C₃₅ ab-hopane 22S and 22R epimers compared to C₃₄, (3) the presence of gammacerane, (4) consistent oleanane, (5) low diasteranes relative to regular steranes, and (6) abundant monoaromatic steranes relative to triaromatics, (7) a value that is less than 3 for the

triplet biomarker parameter C_{24} tetracyclic terpane, C_{26} tricyclic terpane (S), and C_{26} tricyclic terpane (R), and (8) prominent sulfur polycyclic aromatic hydrocarbons. The letters R and S indicate compound stereochemical organization or handedness of the compound (Lorenson et al, 2009).

Sesquiterpanes are a class of compounds that are used to distinguish the origin of hydrocarbon released in the environment (Yang et al, 2009). Sesquiterpanes are common in crude oils and ancient sediments, the concentration of these compounds is diagnostic of petroleum maturation and refinement (Yang et al, 2009). Sesquiterpanes are bicyclic biomarker alkanes. During thermal evolution the concentration of C_{14} sesquiterpanes decreases as organic matter matures and the concentration of C_{15} drimane and C_{16} homodrimane is increases as maturation progresses. (Wang and Fingas, 2007). Sesquiterpanes are typically concentrated in light petroleum products with diesel range compounds, while pentacyclic terpanes and sterane are absent or in low abundance in light petroleum (Wang and Fingas, 2007).

B. Hydrocarbon Fingerprinting Methods

Wang et al, 2011, used forensic oil fingerprinting and data interpretation to characterize the chemical composition of an oil spill in Sarnia, Ontario, Canada using GC and GC/MS analyses of oil biomarkers to compare diagnostic ratios of source specific marker compounds. To determine the source of hydrocarbon contamination, Wang et al 2011, characterized the distribution patterns of bulk hydrocarbon groups ,including n-alkanes, quantified biomarker and alkylated polycyclic aromatic hydrocarbon (PAH) compounds, compared distribution profiles, and then compared diagnostic ratios of PAH and biomarker compounds (Fig 5). The results of the Wang 2011 study revealed that the n-alkanes fell within the diesel carbon chain range of n- C_8 to n- C_{24} with almost no resolved peaks in the heavier lube oil carbon range of n- C_{24} to n- C_{50} . The UCM GC results showed one hump in the diesel range and

another hump in the lube oil range. The samples contained varying proportions of a diesel-lube oil mixture.

A paper by Wang and Fingas, 1999, summarized investigations of a number of oil spills and the methods used in identification. Methods used in oil spill source determination studies fall into two categories: non-specific methods and specific methods for detailed component analysis. Only specific methods generate individual component and petroleum source specific information (Wang and Fingas, 1999). Gas Chromatography-Flame Ionization Detection (GC-FID) chromatograms describe major oil components and weathering extent of the spilled oil. N-alkane biodegradation indicators such as pristane and phytane can be compared to monitor the microbial degradation of hydrocarbons at a spill site (Wang and Fingas, 1999). Comparing n-alkane profiles in hydrocarbon samples can reveal differences in weathered fuels, and identify different fuel types. Another method for oil spill identification described in the 1999 paper by Wang and Fingas is PAH fingerprint analysis. PAH are more persistent and resistant to environmental weathering than saturated hydrocarbons, the persistence of PAH compounds makes them ideal as identification fingerprints. PAH fingerprints are distinctly different for petrogenic, pyrogenic, and refined petroleum hydrocarbons (Alimi, 2003). Even petroleum products that are of similar type can have distinctive PAH distribution profiles.

Petroleum biomarker fingerprints are also used in identification, environmentally persistent biomarkers are chemically analyzed to determine the source of spilled oil and to monitor degradation of spilled oil (Wang and Fingas, 1999). Biomarker compounds used in fingerprinting include tricyclic, tetracyclic, and pentacyclic terpanes, methylhopanes, sterane, methylsteranes, and diasteranes (Wang and Fingas, 1999). GC analysis of petroleum biomarkers sterane and terpane can yield information about source, extent of weathering, and efficacy of potential treatment methods (Wang and Fingas, 2003).

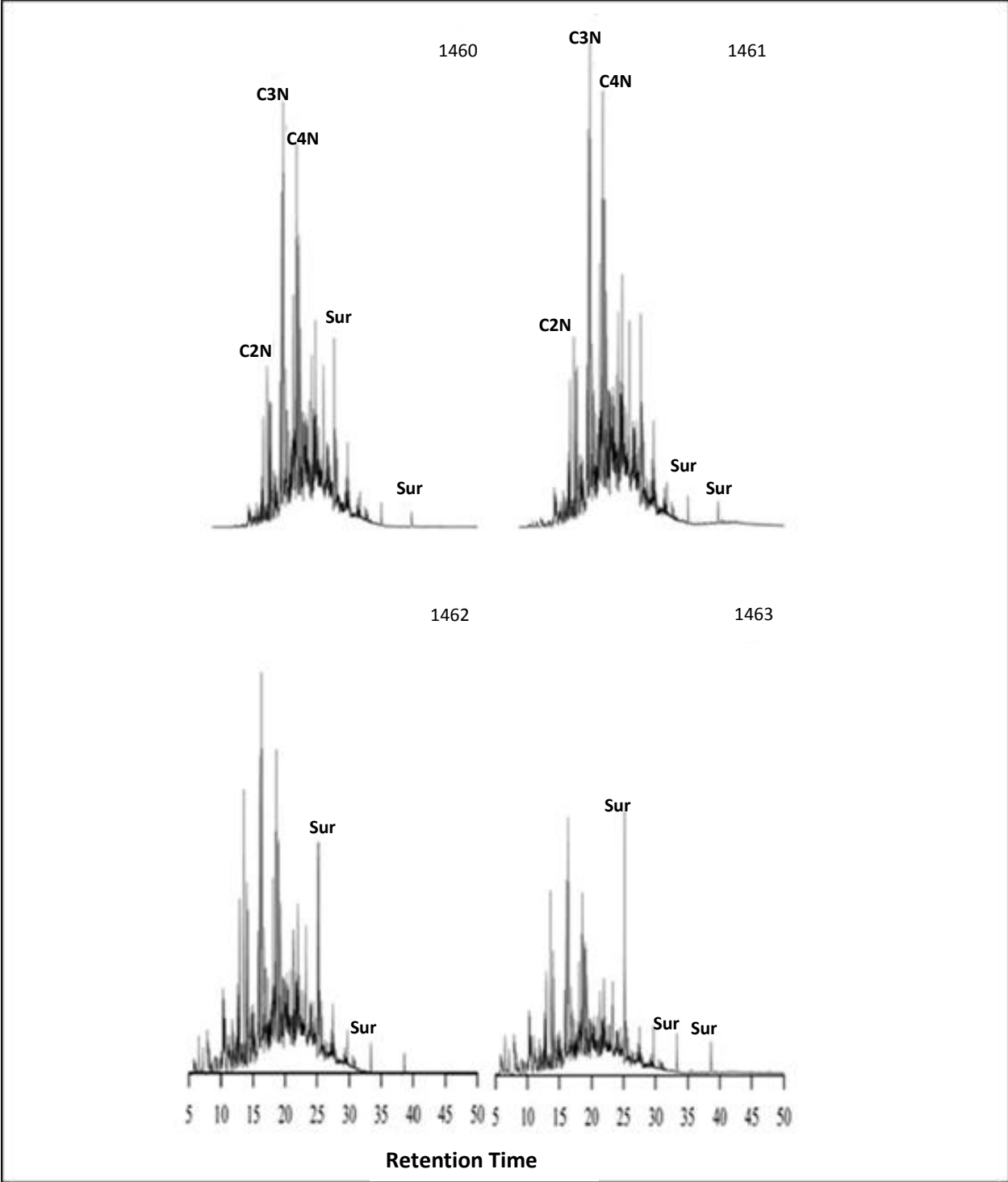


Figure 5, Example of a PAH biomarker chromatograms for oil samples, used to compare profile distributions in hydrocarbon fingerprinting, retention time increases along the x-axis and abundance increases along the y-axis, from Wang et. al., 2011

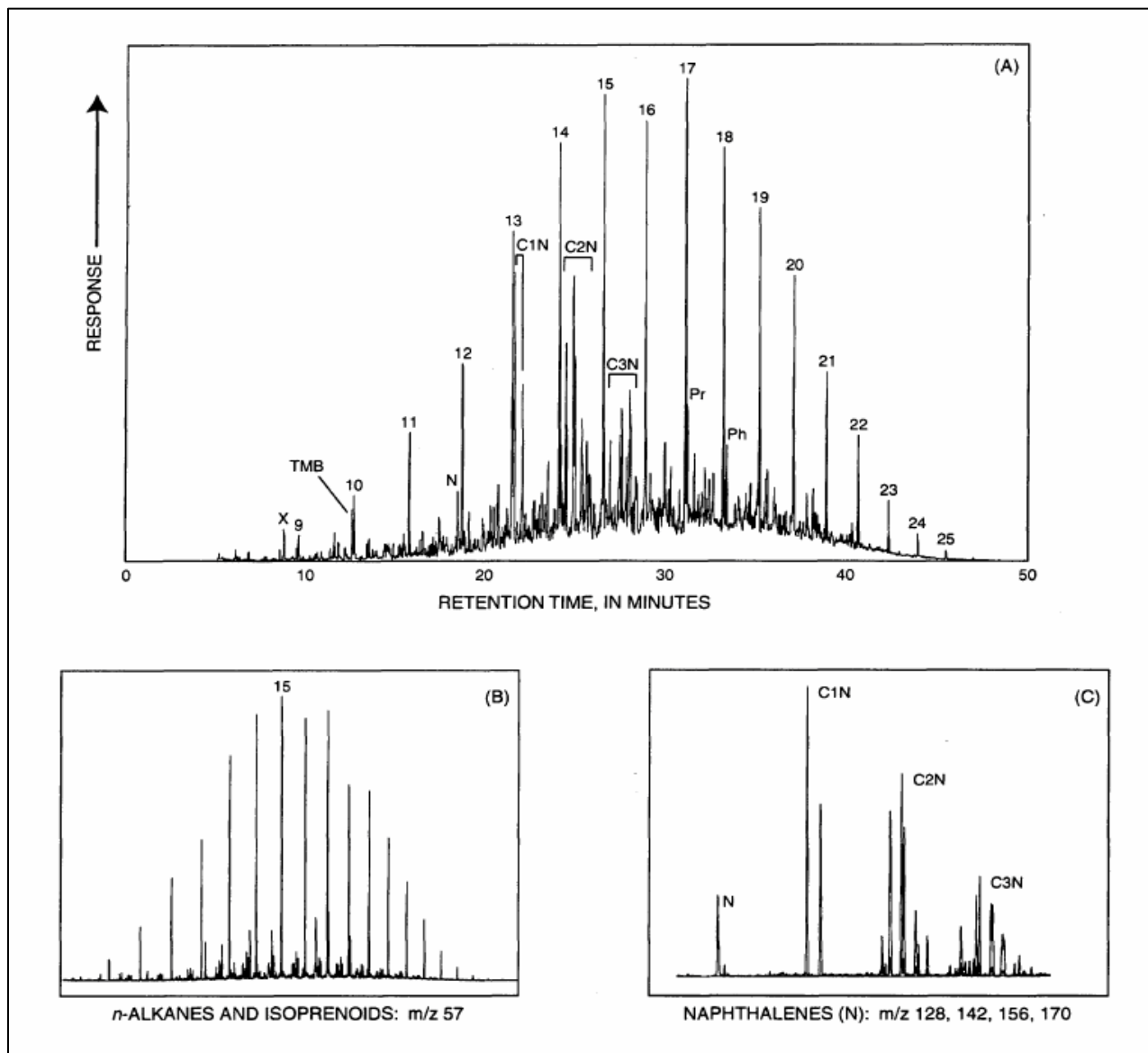


Figure 6, Example of n-alkane chromatogram used in the Hostettler and Rostad (2001) study, for comparison of diagnostic ratios and profile distributions to identify sources of spilled oil

In 1989 the Exxon Valdez oil spill occurred in Prince William Sound, Alaska, releasing 258,000 barrels of crude oil (Bence, Page, and Boehm, 2007). Multiple sources contributed to the hydrocarbons recovered from the Prince William Sound marine environment, the hydrocarbons were from anthropogenic as well as natural sources. The types of hydrocarbons that contributed to the Prince William Sound environment comprised a complex mixture and included: weathered residues from the Exxon spill, hydrocarbons from eroding organic sediments and oil seep sources near the area, refined product from recreational activity in the environment, pyrogenic hydrocarbon from the burning of petroleum products, and biogenic hydrocarbons from natural biologic processes (Bence, Page, and Boehm, 2007). The sources were identified using fingerprinting of PAH and petroleum biomarkers. The PAH distributions of the hydrocarbons found in the Prince William Sound environment were diagnostic of the source type and were the most important tool for identifying sources in this study. In the more degraded samples, PAH distributions were not helpful in identifying hydrocarbon sources and instead the aromatic biomarkers were used. The petrogenic hydrocarbons were characterized by naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes, and chrysenes in crude oil and refined products (Bence, Page, and Boehm, 2007). Biogenic hydrocarbons found in the spill environment were identified by the presence of the compounds perylene and retene, while the pyrogenic hydrocarbon was identified by a PAH distribution dominated by fluoranthene, pyrene, and benzopyrene (Bence, Page, and Boehm, 2007). Comparisons of ratios of dibenzothiophenes to phenanthrenes in PAH distributions resolved the natural background levels of hydrocarbon in the environment before the Exxon Valdez spill. However the individual components of the background hydrocarbons could not be identified in the Prince William Sound environment.

In a study by Hostettler et al (2001), the goal was to characterize the free phase hydrocarbons in an alluvial aquifer in Mandan, North Dakota. A contaminant plume of LNAPL 20 feet below surface had a thickness of six feet and an areal extent of 657,000 ft². Purge and trap GC/MS, isotope ratio mass

spectrometry, and liquid chromatography/mass spectrometry were used to characterize the contaminant plume (Hostettler et al, 2001). A number of parameters derived determined the character of the contaminant and include: ratios of pristane to phytane and alkane to pristane, $n-C_{max}$ (the n-alkane at the highest peak height), and a number of other compound ratios that are specific to diesel fuel and diesel fuel at various stages of degradation (Hostettler et al, 2001) (Fig. 6).

The Mandan study concluded that the samples recovered from the contaminant plume were all diesel, with a considerable loss of lower molecular weight n-alkanes from biodegradation. The parameter ratios analyses indicated that the contaminant in all of the samples were from the same source; however, differences in chemical distribution were apparent which were attributed to variations in the fuel composition over a long period of usage (Hostettler and Rostad, 2000).

In January of 2000, a heavy fuel oil spill occurred in Guanabara Bay, in Rio de Janeiro, Brazil, releasing 8,177 barrels of fuel oil due to a pipeline rupture (Meniconi and Barbanti, 2007). In a study by Meniconi and Barbanti in 2003, the goal was to distinguish between the background hydrocarbons in the environment and the hydrocarbons released i to the environment by the pipeline rupture. After the initial oil spill response, samples were taken from the Guanabara Bay area and characterized by measuring the concentrations of n-alkanes, PAH, and petroleum biomarkers. The results for the Guanabara Bay study included an analysis of 16 EPA priority PAHs from the samples. The concentrations of the PAHs varied in each sample, and ranged from 184 to 5,110 ng/g; however, the differences between the concentrations were not statistically significant (Meniconi and Barbanti, 2007). The authors also found that the PAH concentrations in the samples Guanabara Bay sediment were similar to various analogous marine environments around the world, some of which did not experience oil spill conditions, indicating that the PAHs in the Guanabara Bay sediment are due to anthropogenic sources (Meniconi and Barbanti, 2007).

Using PAH diagnostic ratios including phenanthrene to anthracene, the authors were able to distinguish between the different sources of hydrocarbon in the Guanabara Bay samples and determined that samples taken closest to the rupture had petrogenic character and samples with pyrogenic character were taken from subtidal environments. The majority of the samples could not be chemically correlated with the oil spill in the bay, and instead revealed that the PAH were due to chronic anthropogenic input, the spilled oil had a very different biomarker distribution pattern than the hydrocarbon in the samples (Meniconi and Barbanti, 2007).

In this study, GC/MS is used to identify the presence of diesel range n-alkanes in the aqueous and non-aqueous phases. No potential sources have been identified in a 1.5 mile radius.

VII. Methodology

A. Well Sampling

Seventeen domestic wells in the Rancho Villa subdivision community were sampled for this study (Fig. 1). The majority of the domestic wells that were sampled were chosen based on the 2007 ADH resident reports. Twenty five domestic wells were included in the ADEQ report; eight of the 25 well owners were contacted and agreed to sampling for this study. Nine other domestic wells were sampled based on recommendations from the residents, and reconnaissance of the Rancho Villa subdivision area. From the eight in the original report that agreed to sampling and the nine that were gathered by reconnaissance, 17 wells were sampled in total.

Well sampling was completed in tandem along with Mr. Roger Miller of the ADEQ in Little Rock, AR. Well sampling was completed in three separate trips on October 23rd, October 30th, and November 27th 2012. Care was taken to ensure that the samples were collected from an unfiltered source so that each sample would be representative of the groundwater. Four of the 17 wells had a visible non-aqueous phase layer on top of the water. Well samples were collected either from a spigot or by using a bailer. Visibly contaminated wells were sampled by bailer, the non-aqueous hydrocarbon floated above the water. An emulsified horizon existed between the water and hydrocarbon, the water was collected separately from the hydrocarbon so that they could be analyzed individually. To prevent cross contamination, all wells with free product were sampled after those wells that did not have free product. The pH, specific conductance, temperature, and dissolved oxygen were measured at each well site using a YSI MPS 556 multi parameter meter. The quality assurance protocol of ADEQ and this project included calibration of the conductivity meter each morning before sampling by rinsing twice with distilled water, rinsing twice with conductivity standard solution, then adjusting the conductivity reading to the value of the standard. The pH meter was calibrated by rinsing the probe twice with distilled water and twice with pH standard solution 7.00. The calibration cup was filled with enough pH 7.00 solution to

cover the probe, and a reading was taken when the temperature stabilized. The pH meter was then calibrated with the pH 10.00 standard. The DO probe was rinsed twice with tap water, and barometric pressure measured to calculate correct DO percent saturation using the following formula: $\text{Barometric Pressure}/760 = \text{_____} * 100$ (YSI, 2009).

Wells which had a working pump installed were pumped, and water was allowed to discharge until specific conductance readings stabilized, at which point field parameters were recorded. Between samplings, the instrument probes were stored in a neutralizing solution to protect the probe and insure reliable measurements. For wells that were pumped during sampling, measurements were made in a flow-through chamber; for the wells that were sampled by bailer, parameters were measured in sampling bottles. The water well samples were submitted to the ADEQ laboratory for the following analyses: alkalinity (EPA Method 310.2), major cations were measured by inductively coupled plasma mass spectrometry (ICP-MS) and anion concentrations by ion chromatography (EPA Method 300), total dissolved solids (EPA Methods 160.1 and 160.2), total organic carbon (EPA Method 5310 B), dissolved metals (EPA 200.8), and also volatile organic compounds by GC/MS (EPA 8260 C) by ADEQ.

B. Water Sample Preparation and GC/MS Analysis

The water from the 17 well samples was prepared by a liquid-liquid extraction technique for GC/MS. For the liquid-liquid extraction, 250 mL of sample was transferred into 500 mL amber glass bottles that had been cleaned in a HCl solution, deionized water, and precombusted prior to use. After adding 20 mL of hexane to the 500 mL bottle, the bottle was placed on a shaker table for 30 minutes. The hexane layer was then removed and placed into a 20 mL scintillation vial, and dried under a gentle stream of N₂ gas. The addition of 20 mL of hexane, shaking, and hexane removal process was repeated twice more, and the 20 mL scintillation vial was dried under N₂ gas to a volume of about two mL.

For GC/MS analysis, 100 μL of the dried sample was transferred into a 2 mL GC vial with a 200 μL vial insert and 50 μL of hexane was added into the vial which was then crimped. The extracts of the water samples were analyzed by GC/MS using a Hewlett Packard 7890 series GC and a 5975 series MSD. Prepared hexane was run along with the water extract extracts. A 30m x 250 μm x 0.25 μm HP-5MS column (95% dimethyl 5% diphenyl polysiloxane) was used for GC/MS analysis. The concentrated samples were analyzed under the following conditions: 1.0 μL splitless injection, constant flow of 1.0 mL/min, solvent delay of 6.0 min, injector temperature of 150°C, interface at 300°C, temperature program of 70 to 300°C at 4°C/min and a hold at 300°C for 15 min, after Orem et. al.(2007).

C. Hydrocarbon Sample Preparation and GC/MS Analysis

In four of the 17 samples a visible non-aqueous hydrocarbon layer was visible and separable (Fig. 15). Each of the four non aqueous samples was transferred into 5 mL amber vials. Before GC/MS analysis, the hydrocarbon samples were separated into three fractions by column chromatography. The neck of a 10 mL pipette was plugged with a small amount of quartz wool, then filled with combusted deactivated silica. After filling the column with the deactivated silica, the side of the pipette was tapped until there was a flat surface on top to allow for better elution.

Ten milliliter glass pipettes were used for chromatography. To saturate the silica and remove air bubbles, about 3 mL of hexane was run through the column and then discarded. About 4-5 drops of the hydrocarbon sample was added to the top of the column, hexane was used for elution of the F1 fraction (n-alkanes), a 1:1 solution of hexane and dichloromethane for the elution of the F2 fraction (polycyclic aromatic hydrocarbons), and a 1:1 solution of dichloromethane and methanol for the elution of the F3 fraction (polar compounds). The F3 fraction was not analyzed, having no compounds of interest to this study, fractions 1-3 were captured in separate respective vials. The vials for fractions 1 and 2 were then dried to completion under a gentle N_2 stream. Once the vials dried, 500 μL of hexane was added. For

GC/MS analysis, 75 μL of redissolved sample was added to a 2 mL vial with a 200 μL insert along with 75 μL of hexane, and the vials were crimped for analysis. Prepared hexane blanks were run along with the water extracts. The concentrated hydrocarbon samples were analyzed by GC/MS using a Hewlett Packard 7890 series GC and a 5975 MSD. A 30m x 250 μm x 0.25 μm HP-5MS column (95% dimethyl 5% diphenyl polysiloxane) was used for GC/MS analysis. The samples were analyzed under the following program: 40°C to 140°C at 15°C/min and then from 140°C to 300°C at 1.8°C/min, and held at 300°C for 30 minutes, after Wang and Philp, (1997).

The GC/MS program implemented on the well samples were from previous studies with similar goals. Determining the correct program to use in this study was a challenge; many variables need to be considered when using GC/MS for hydrocarbon fingerprinting. In many of the papers mentioned here, the authors had a number of potential sources in mind before the analyses; the goal in these papers was then to match the compound distribution in the chromatograms to the source chromatograms.

VIII. Results and Discussion

A. ADEQ Water Analysis

The water samples were measured for general geochemical parameters (Table 8, and Figs 7-11). The pH of the waters in this study range from 5.89 to 7.06 with a median of 6.66; the range for CaCO_3 , determined by alkalinity titration, is 131 to 247 mg/L, with a median of 137.5 mg/L. Chloride in the water samples for this study range from 1.69 to 5.86 mg/L with a median value of 2.83 mg/L (Fig 7). Dissolved solid concentrations in the water samples for this study are 193 to 277 mg/L with a median value of 217 mg/L. Nitrate concentrations in the water samples range from less than 0.03 to 9.65 mg/L with a median value of 0.10 mg/L. Sulfate concentrations found in the water samples range from 0.71 to 9.54 mg/L, with a median of 1.96 mg/L (Fig. 8). Calcium is the dominant cation in the water samples. The concentrations of major ions, Ca^+ , Mg^{2+} , CaCO_3 , Na^+ , K^+ , Cl^- , and SO_4^{2-} , were converted to milliequivalents, normalized, then plotted on piper diagrams to determine water type; the water in the Rancho Villa wells is calcium bicarbonate type water (Fig. 25).

In previous studies where ground water quality was continuously monitored in the Boone-St. Joe and Cotter Formation aquifers, Stanton (1993) determined a median pH value of 7.33, median specific conductance of 423 mg/L, and median temperature of 15° C. Adamski (2000) determined the median concentration for chloride in the Springfield Plateau aquifer to be 3.8 mg/L, and median dissolved solid concentration in the Springfield Plateau aquifer to be 220 mg/L. Median nitrate concentration in the Springfield Plateau aquifer is 2.0 mg/L (Adamski, 1995 and 2000). Sulfate concentrations in the Springfield Plateau aquifer typically range from 5 to 10 mg/L with a median value of 7.5 mg/L. In the Adamski (1995) study, waters in the Springfield Plateau aquifer are classified as calcium-bicarbonate type water.

In comparison with the Adamski study, the major ion concentrations in Rancho Villa waters were higher than values for the regional Springfield Plateau aquifer. The values representing concentrations of dissolved constituents in the Adamski (2000) study are from a much broader area, as the Springfield Plateau aquifer extends into Nebraska, Oklahoma, Arkansas, and Missouri and include data for confined areas of the aquifer. The median values for dissolved solids concentration and geochemical parameters for the broader Springfield Plateau aquifer in the Adamski (2000) study, represent a larger range of retention times and flow distances than what are observed in the Stanton (1993) study.

The pH and specific conductance in the Stanton study are lower than the values for these same parameters in the Rancho Villa waters. Values for concentrations of TDS and nitrate are higher in the Rancho Villa waters than in the regional Springfield Plateau aquifer (Adamski 1995 and 2000). The differences in the concentrations of dissolved constituents and pH are related to flow rates and retention times, and therefore the degree of geochemical evolution of the waters in their respective settings (Chowdhury, 2008). Groundwater movement along flow paths can provide information on chemical concentrations and residence time of the groundwater; ion and anion concentrations in groundwater come from solutes in precipitation, and water-rock interactions (Chowdhury, 2008). In comparison with values from the Stanton 1993 study, the low values for pH and specific conductance of the Rancho Villa waters can indicate shorter travel times than the wells in the Stanton study, resulting in water that is less buffered, with lower concentrations of dissolved constituents (Chowdhury, 2008).

Boxplots indicate the minimum, 25th percentile, median, 75th percentile, and maximum value

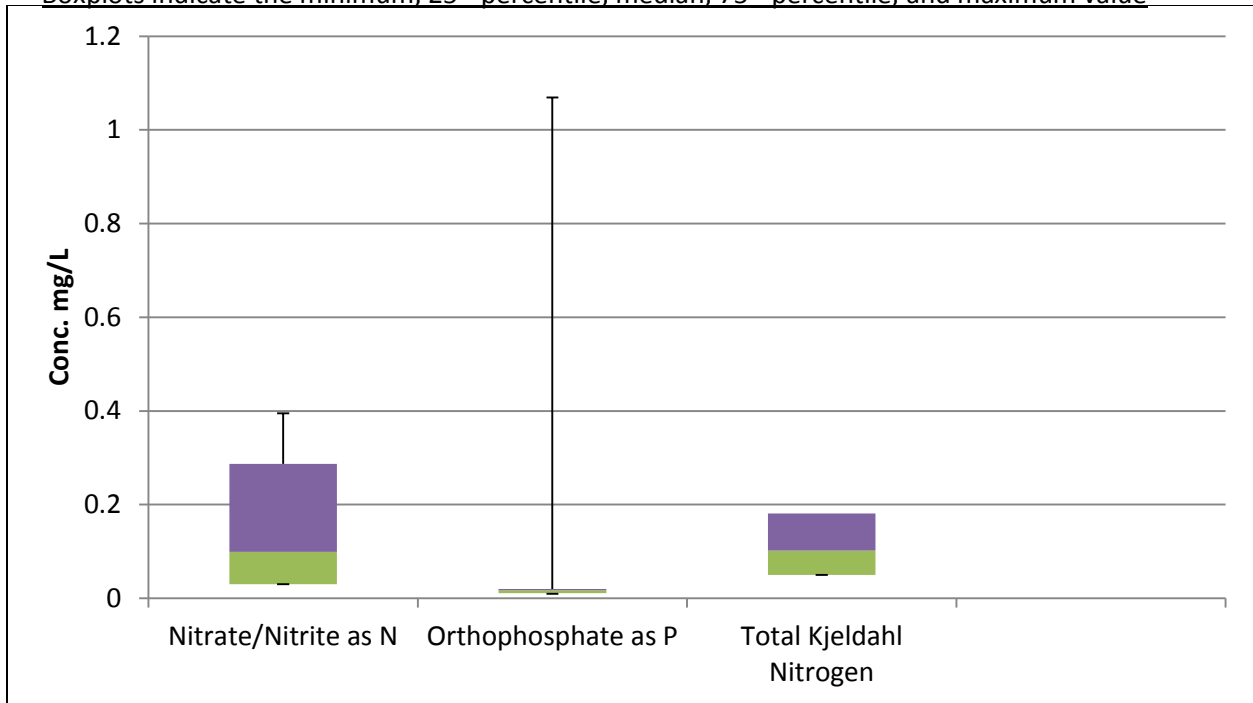


Figure 7, Concentrations of Nitrate, Phosphate, and Organic Nitrogen in Rancho Villa groundwater from ADEQ Water Sample Analysis, 12/2012

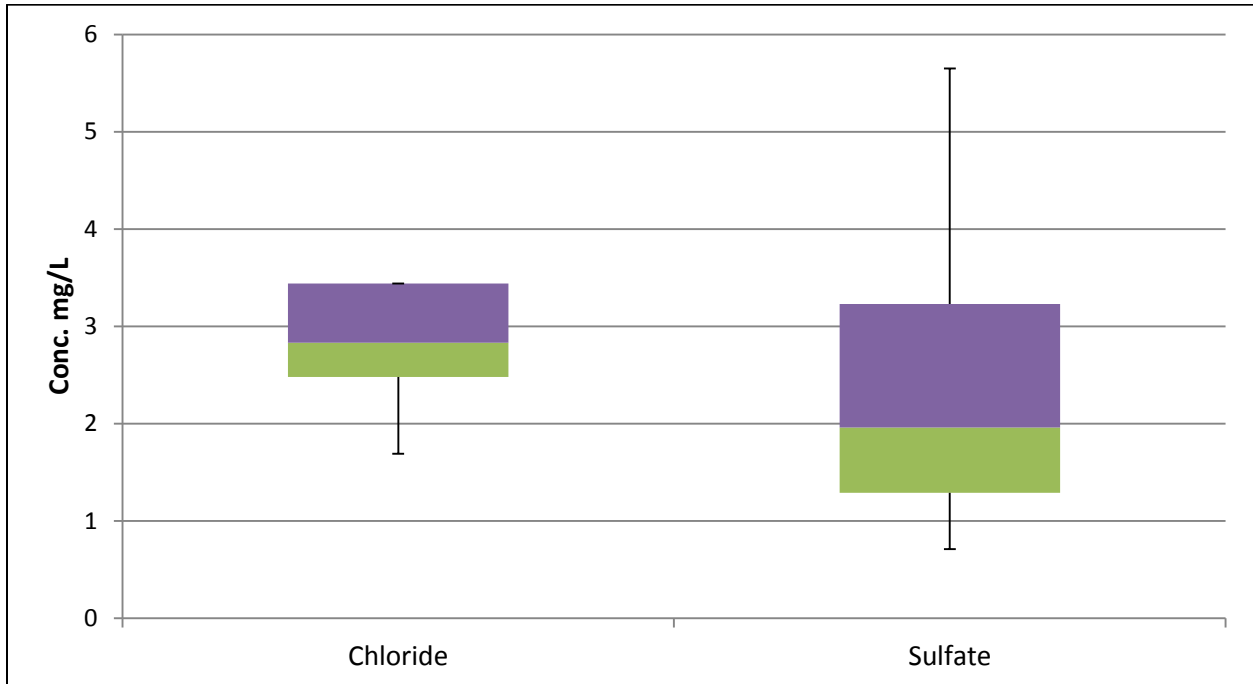


Figure 8, Concentrations of Chloride and Sulfate in Rancho Villa groundwater from ADEQ Water Sample Analysis, 12/2012

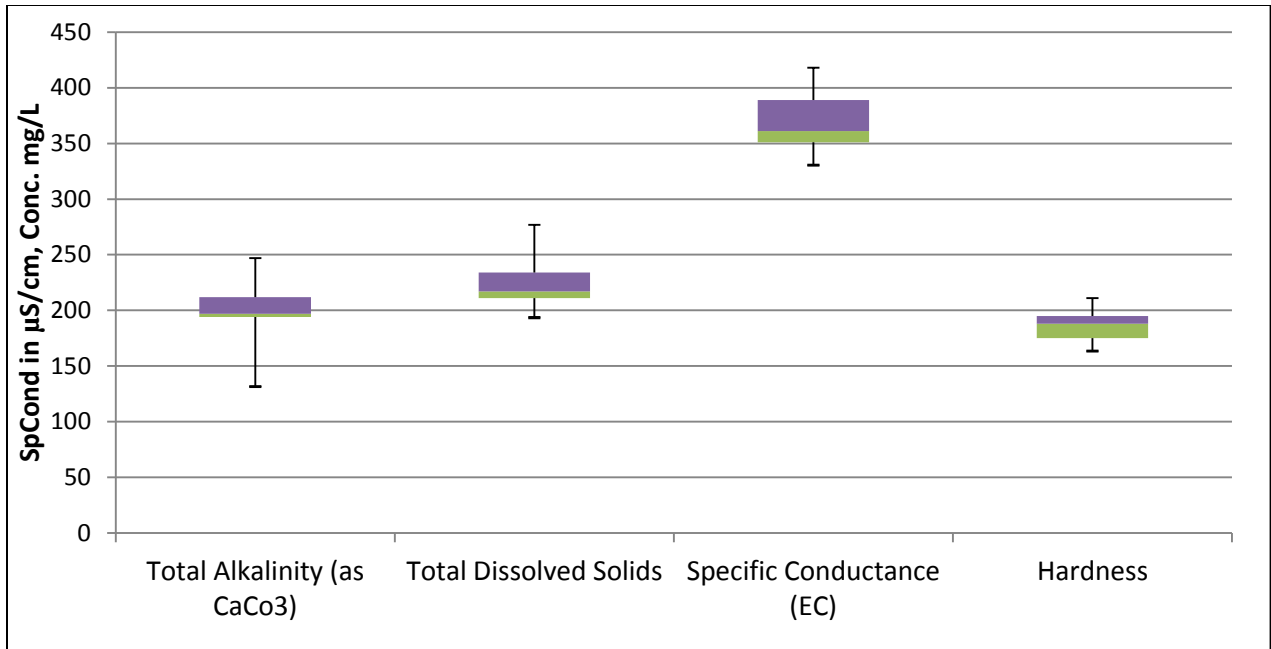


Figure 9, Concentrations of CaCO₃, TDS, and Hardness, and Specific Conductance of Rancho Villa groundwater from ADEQ Water Sample Analysis, 12/2012 (Specific conductance in micro siemens/cm, all other parameters in mg/L)

Boxplots indicate the minimum, 25th percentile, median, 75th percentile, and maximum value

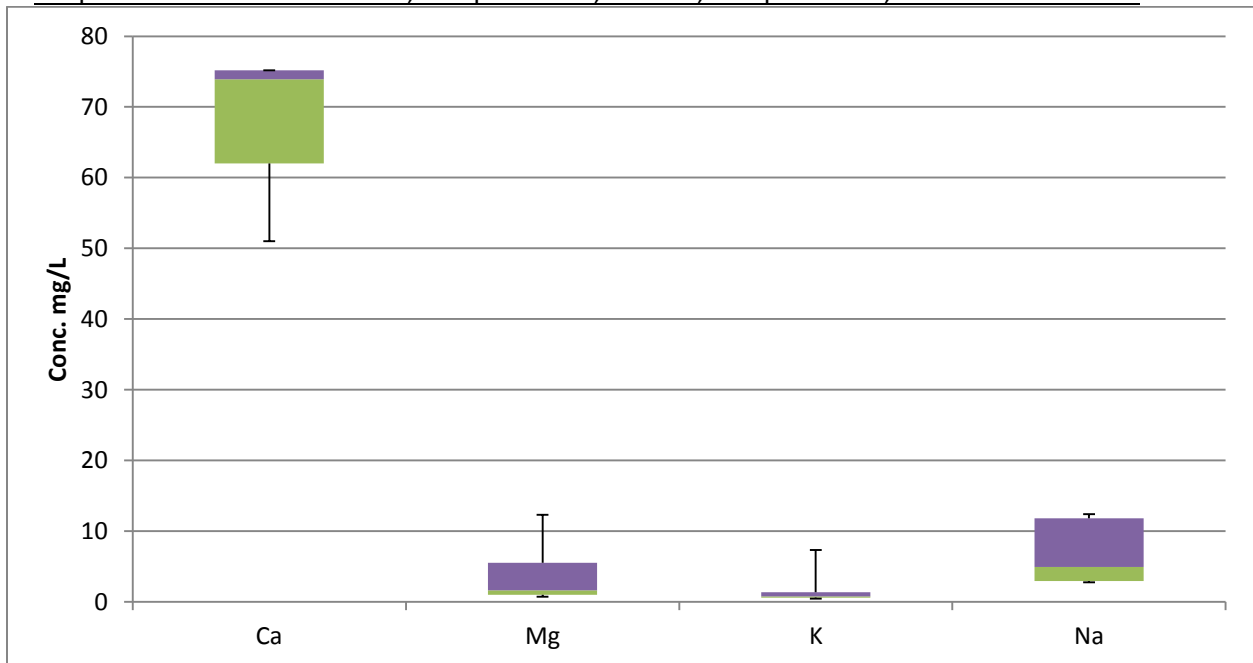
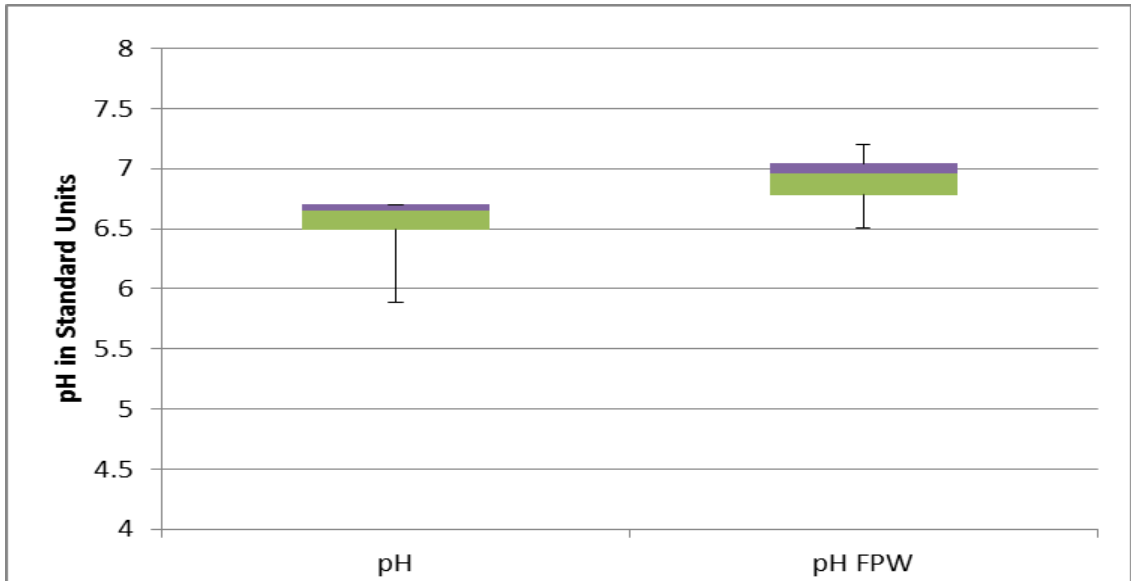


Figure 10, Concentrations of selected ions in Rancho Villa groundwater, from ADEQ Water Sample Analysis, 12/2012



Boxplots indicate the minimum, 25th percentile, median, 75th percentile, and maximum value

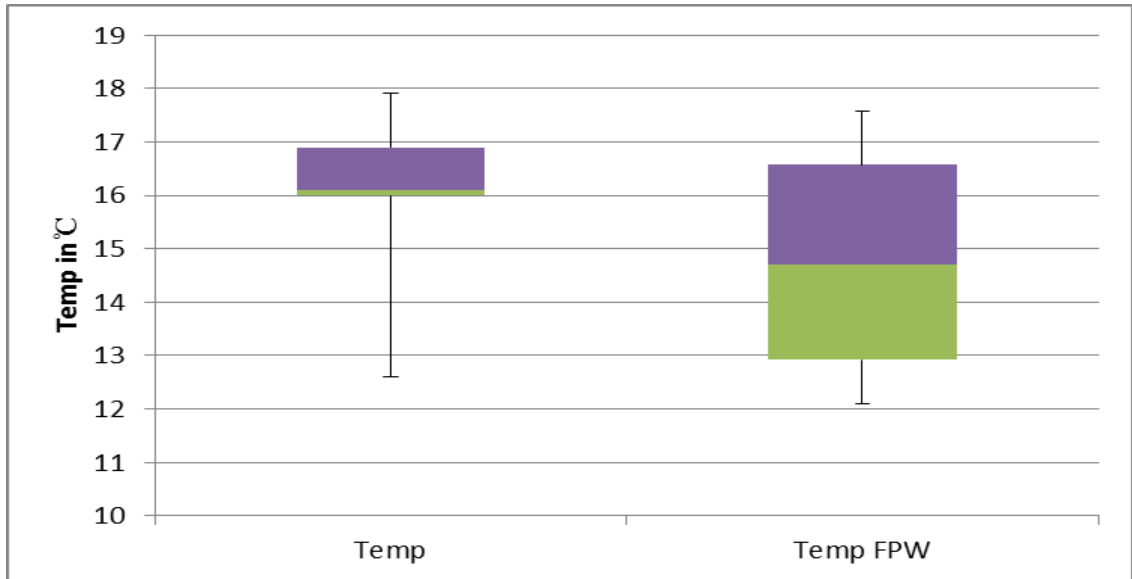


Figure 11, pH, and temperature in free product wells and non-free product wells ADEQ

B. ADEQ Organic Compounds Analysis

The results of the water analyses yielded no VOC concentrations above the ADEQ reporting limit for 14 of the 17 samples. However for water samples from wells 35, 37, and 38, the concentrations of a number of volatile organic compounds were detected at significant levels (Fig 12). In wells 35, 37, and 38, a layer of non-aqueous hydrocarbon was visible in the samples, and a zone of emulsification of the

hydrocarbon was apparent at the base of the organic liquid immediately above the water-organic interface. A maximum contaminant limit of 700 µg/L has been established for trimethylbenzene, and the concentrations of trimethylbenzene in samples from wells 35 and 38 are well below that limit at 7 µg/L and 371 µg/L respectively (ASTDR, 1999 and EPA, 2007). Trimethylbenzene occurs naturally in crude oil, and is also added directly to gasoline. Trimethylbenzene is typically exposed to the environment from releases to land, air, groundwater, and surface water; it evaporates when exposed to air and is slightly soluble in water. Trimethylbenzene exposure can cause nervous system disorders upon prolonged exposure (ASTDR, 1999).

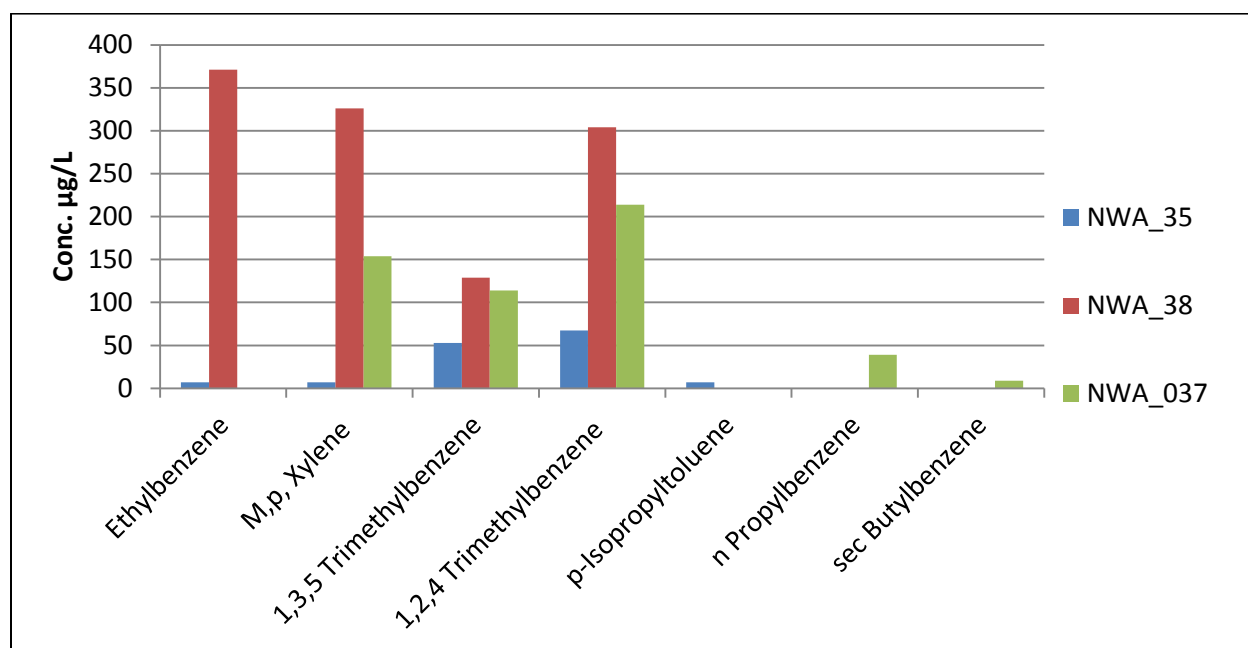


Figure 12, VOC concentrations in ADEQ Analyses from visibly contaminated wells in Rancho Villa community 12/2012

The maximum contaminant limit for xylene is 10,000 µg/L, xylene was detected in wells 35, 37, and 38 at concentrations of 7 µg/L, 154 µg/L, and 326 µg/L respectively (Fig. 12) (EPA, 2007). Major sources of xylene in the environment are from petroleum. Similar to trimethylbenzene, xylene occurs naturally in crude oil, is used as a solvent, and is added to gasoline (ATSDR, 2005). Xylene evaporates quickly from soil and surface water, the low concentrations of xylene found in the water samples is well

below the MCL and have not been proven to have adverse health effects (ATSDR, 2005). Owners of the majority of the wells sampled had reported complaints to the Arkansas Department of Health in 2007; at the time of the sampling in the Fall of 2012 many of the residents who had previously reported problems with their water said they had no current problems.

C. GC/MS Water Sample Analysis

The aqueous-phase component of the well water samples were analyzed using GC/MS to determine the relative abundances of any organic compounds dissolved in the water. The aqueous-phase portions of samples from wells 35, 37, and 38 were so heavily emulsified, they were treated as oil samples and not as water samples and are discussed in the next section. The results of the GC/MS analysis were separated by ions 57, 91, and 217 (Fig. 13, Fig. 14). Mass chromatograms identify compounds that respond to a selected compound with a given m/z ratio. Peaks in the chromatogram for ion 57, are responses for compounds that have a mass corresponding to butyl radical compounds (C_4H_9), which include saturated hydrocarbons (Hites, 1997). Peaks in the chromatogram for ion 91 indicate responses for compounds that have a mass corresponding to benzyl radical compounds (C_7H_7), which include aromatic hydrocarbons (Hites, 1997). Electron impact ionization causes molecules to fragment in to characteristic ions. GC allows separation of molecules according to retention column interaction and hence retention time and MS allows for separation of fragmentation based on ion mass-to-charge ratio (m/z); this allows for compound identification (Issacman et al, 2012). In the chromatograms of this study, ions with m/z 57 identify the saturated fraction, and ions with m/z 91 identify the aromatic fraction. Many of the peaks in the chromatograms existed in the ion 57 fraction, which represents the saturated hydrocarbons. In the sample from NWA_031, a number of compounds present are characteristic of diesel fuel (C_9 - C_{25}) (Kaplan et al, 1997 and EPA, 2007). Although the gas

chromatogram has a total of 46 peaks, only the peaks indicated in Table 3, have compounds that are identified with a percent confidence of 90% or greater.

Numerous compounds exist in NWA_040, however several of the peaks in the ion 91 chromatogram indicate the presence of diethyl phthalate, a common lab contaminant, with over 90% confidence, which indicates that contamination occurred at some time during the sample preparation (Fig. 14).

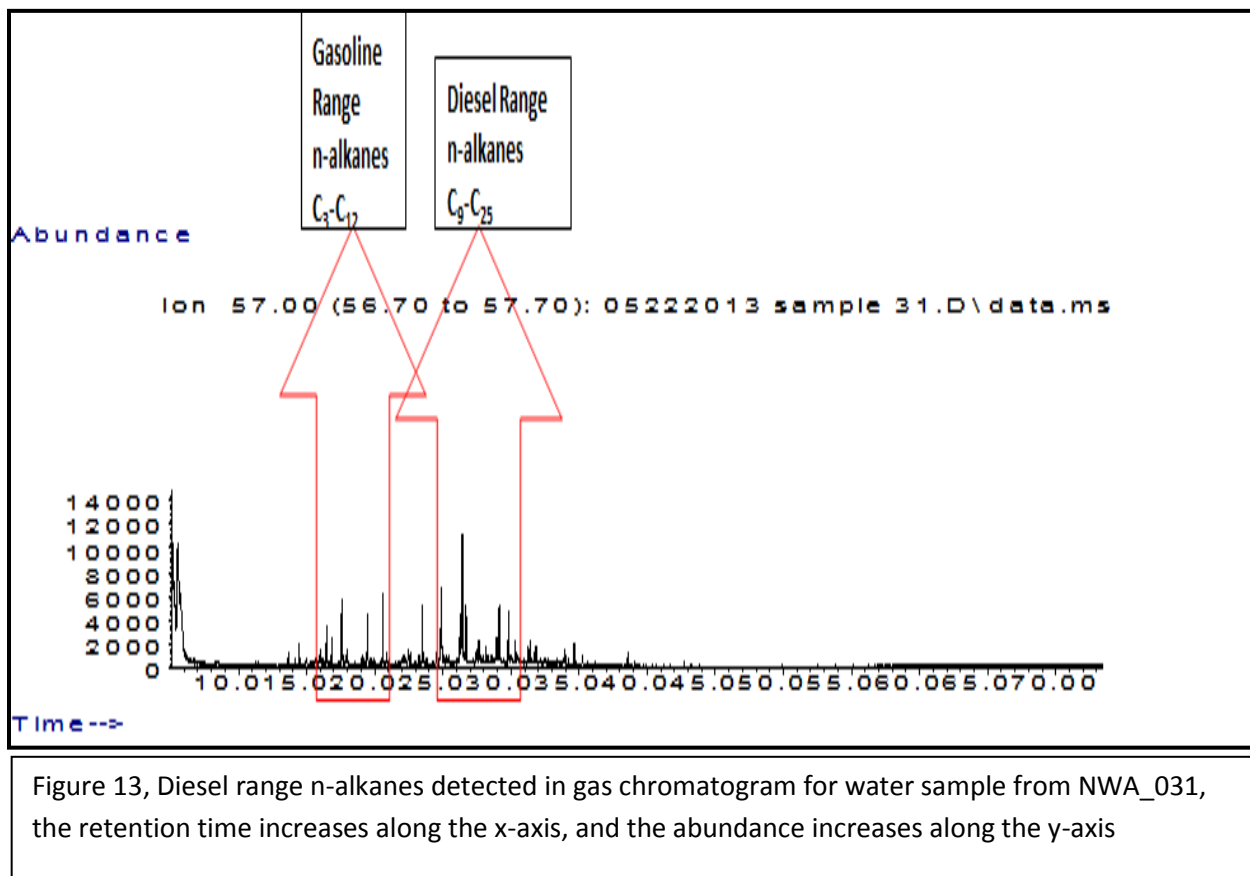


Figure 13, Diesel range n-alkanes detected in gas chromatogram for water sample from NWA_031, the retention time increases along the x-axis, and the abundance increases along the y-axis

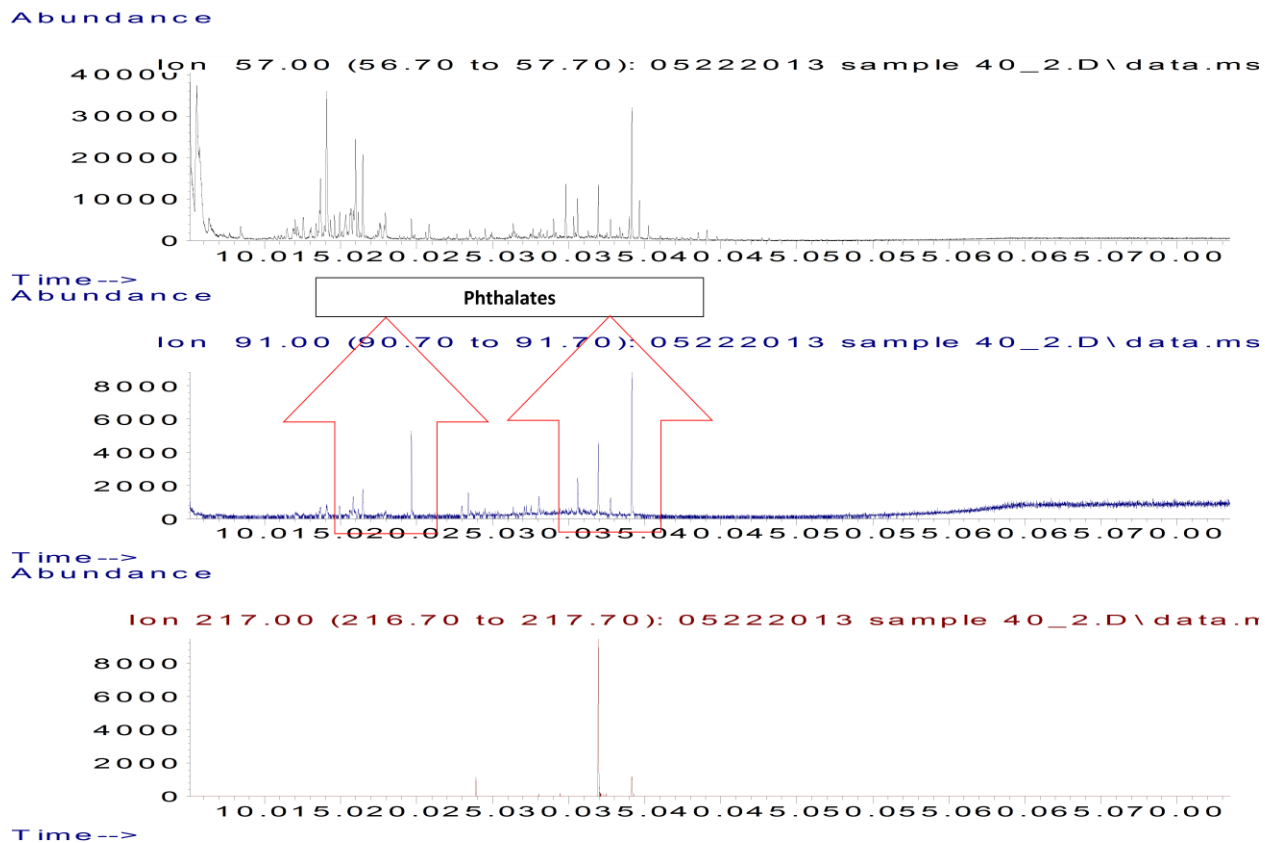


Figure 14, Phthalate contamination detected in Gas Chromatogram for Water Sample NWA_040, the retention time increases along the x-axis, and the abundance increases along the y-axis

D. GC/MS Pure-Phase Hydrocarbon Sample Analysis

Four wells had a visible layer of hydrocarbon on top of the aqueous phase; these wells were NWA_035, NWA_037, NWA_038, and NWA_039 (Fig. 15). Like the water samples, compounds were identified by ions 57, 91, and 217. In the final analysis, only the saturated hydrocarbon fraction was informative.

Well Sample	Total % Peak Area of Diesel Range n-alkanes in Chromatogram
NWA_35	70%
NWA_37	75%
NWA_38	61%
NWA_39	52%

Table 1, Total Peak Areas of Diesel Range n-alkanes in Hydrocarbon

For NWA_35 (Table 4), nearly all of the compounds were diesel range n-alkanes. The lowest n-alkane peak in the chromatogram for NWA_35 was tetradecane (C₁₄) which is well within the range for diesel n-alkanes (C₉-C₂₅). The majority of the compounds for the sample from well NWA_37 were diesel range n-alkanes, the lowest n-alkane compound is dodecane (C₁₂). The samples from wells NWA_38 and NWA_39 also had chromatograms with a number of compounds identified as diesel range n-alkanes. The chromatograms show abundant saturated hydrocarbon compounds within the range of that expected for a typical refined diesel. Hydrocarbon compounds in the lighter-than diesel (<C₉) and heavier-than-diesel (>C₂₅) ranges have notably low peak area indicating low concentrations. Refined diesel fuel can have minor amounts of the lower- and higher- range compounds. In addition, microbial degradation within an aquifer can change the saturated hydrocarbon distribution, typically imparting higher relative concentrations of heavier compounds. However, the chromatogram result is characteristic of a refined diesel.

The distribution of the wells with free product are shown in Figure 15, the wells that currently have non-aqueous phase contamination are labeled with yellow and those that have been reported to have contamination in the past but did not at the time of sampling are labeled with green. The general orientation of all wells that have had free product trends northeast-southwest; however, wells that are not contaminated are located next to wells that are; such a distribution is indicative of aquifer

heterogeneity and is consistent with interpretation of fracture or focused flow control of contaminant migration (Fig. 15). Well NWA_035 has visible contamination and is up gradient from well NWA_037 which is also contaminated; however the wells between them have no visible contamination; this indicates that the contaminant is traveling on preferential flow paths presented by the highly fractured framework of the Boone-St. Joe aquifer. The study area is situated upon the up thrown block of a normal fault (Fig 3). Numerous fractures associated with the normal fault likely provide conduits for the LNAPL contaminant migration.

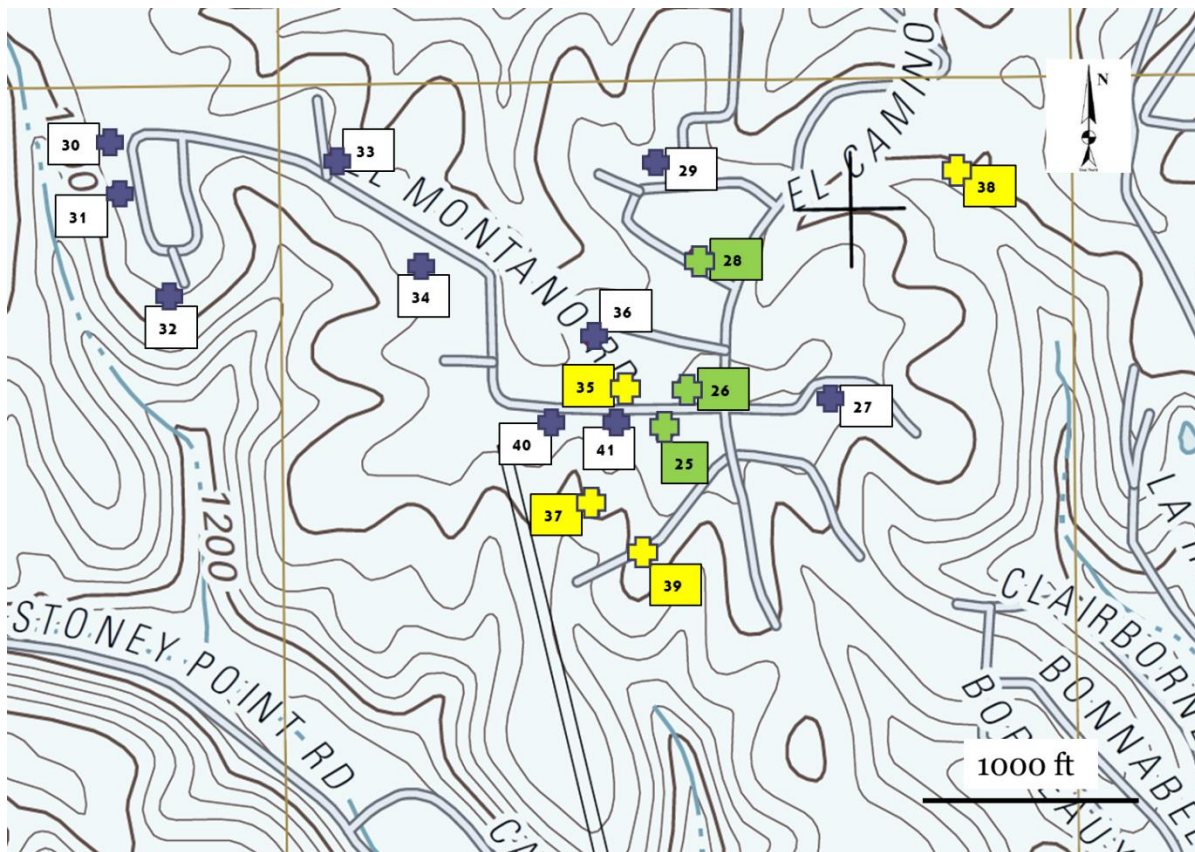


Figure 15. Map of visibly contaminated wells in study area (highlighted in yellow) and previously contaminated wells (highlighted in green)

E. Contaminant Source

The contaminant pathway may be considered at two different scales, based on distance of the source from the area of groundwater contamination. If the contaminant is coming from a source immediately adjacent to the community, the source could be one of the fueling stations along Beaver Lake reservoir, which is 0.52 miles away and 300 feet down gradient from Rancho Villa; however diesel is not a common fuel for lake craft. The contamination that exists in the wells is a Light Non Aqueous Phase Liquid (LNAPL) that has a density less than water and floats above the water table. LNAPLs are typically a mixture of volatile hydrocarbons with low molecular weight; common examples of LNAPL contaminants in groundwater are heating oil, gasoline, and diesel fuel (Vesper, 2003). In karst aquifers, LNAPLs float on top of underground water pathways and can move up gradient in response to changes in the water table (Hardisty, 2003). The conduits in fractured karst aquifers allow LNAPL to lift with rising water and press against the ceiling, often becoming trapped in pockets in the conduit ceiling (Vesper, 2003). Due to the lack of possible sources in a reasonable radius (1-1.5 miles) in the down gradient direction, the more likely scenario is that the contaminant is coming from some more distant source, and is being degraded as it travels within the aquifer to the study area.

A sample of free product from one of the contaminated wells in the study was analyzed by the ADEQ in 2007 (Table 2); results of the analysis showed significant concentrations of tert-Butylbenzene (262,000 µg/L) and trimethylbenzene (1,220,000 µg/L), both of which are commonly used as synthetic fuel additives. Whereas certain isomers of butylbenzene occur naturally in crude oil (e.g. sec-butylbenzene), tert-Butylbenzene does not occur naturally in crude oil and is exclusively a synthetic compound added to fuels (NIOSH, 1983 and Wang and Fingas, 1995). Trimethylbenzene is also found occurring naturally in crude oil (often ranging 0-2 wt % of crude oil) (EP Energy, 2012). Tert Butyl benzene was not detected in either the Hartgers (1994) study or the Eganhouse (1993) study, which both

involved using GC/MS to determine the chemical composition of crude oil. Hartgers (1994) states that tert Butyl substituted alkylbenzenes are not biosynthetic, and their presence in hydrocarbons is due to anthropogenic input. Acetone is also present in the 2007 ADEQ analysis at a concentration of 458,000 µg/L (Table 2). Acetone occurs naturally in the environment, and is not a compound found in crude oil. However, owners of diesel vehicles often use acetone as a fuel additive in order to increase mileage (Brown, 2011). The presence of acetone and synthetic tert-Butylbenzene in the ADEQ analysis indicates that the contaminant is not from a natural petroleum source.

ADEQ Analysis			
Report Date	4-May-07		
Sample ID			
Lab #	2007-1415		
4-Chlorotoluene	< 16000	µg/L	5/2/2007
1,3,5-Trimethylbenzene	1220000	µg/L	5/2/2007
tert-Butylbenzene	262000	µg/L	5/2/2007
1,2,4-Trimethylbenzene	3140000	µg/L	5/2/2007
sec-Butylbenzene	76800	µg/L	5/2/2007
1,3-Dichlorobenzene	< 14000	µg/L	5/2/2007
1,4-Dichlorobenzene	< 10600	µg/L	5/2/2007
p-Isopropyltoluene	< 11800	µg/L	5/2/2007
1,2-Dichlorobenzene	< 14000	µg/L	5/2/2007
n-butylbenzene	217000	µg/L	5/2/2007
1,2-Dibromo-3-chloropropane	< 17200	µg/L	5/2/2007
1,2,4-Trichlorobenzene	< 22800	µg/L	5/2/2007
Napthalene	32100	µg/L	5/2/2007
Hexachlorobutadiene	<19200	µg/L	5/2/2007
1,2,3-Trichlorobenzene	< 26000	µg/L	5/2/2007
Acetone	458000	µg/L	5/2/2007
2-Butanone	< 256000	µg/L	5/2/2007
4-Methyl-2-pentanone	1060000	µg/L	5/2/2007
2-hexanone	< 190000	µg/L	5/2/2007
Diesel Range Organics	45	%	5/2/2007

Table 2, Adapted from 2007 ADEQ Analysis on NWA_038, VOC concentrations

Further evidence for a diesel fuel source is the distribution of n-alkanes in the gas chromatograms for the wells with free product. In each of the chromatograms for the wells with free product the highest n-alkane identified is heneicosane (C_{21}), the range for diesel n-alkane compounds is C_9 - C_{25} (Tables 3-7) (Kaplan et al, 1997). Chromatograms for mid-continent region crude oil from the Anadarko Basin in Oklahoma and Texas have n-alkanes ranging from C_{20} to C_{45} (Fig 16) (Wang and Philp, 1997).

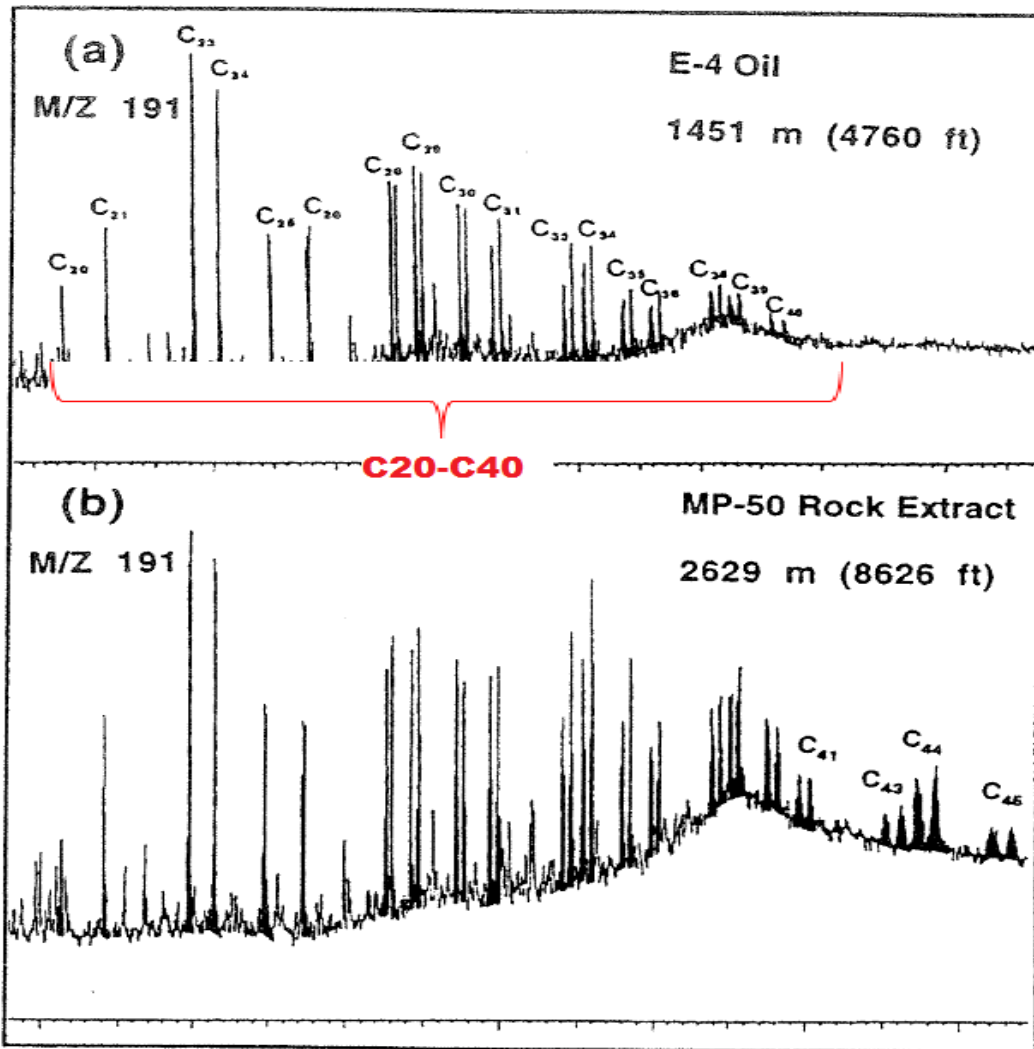


Figure 16. Chromatograms for crude oil from the Anadarko Basin, high molecular weight n-alkanes consistent with crude oil, From Wang and Philp, 1997. Retention time increases to the right on the x-axis, abundance increases going up the y-axis

In the crude oil chromatogram from the Anadarko Basin, the molecular weight of the compounds are consistent with what is found in crude which can include compounds with a carbon chain length of C_{60} (Kaplan et al, 1997). Figure 25 is an example chromatogram, kindly supplied by Agilent Technologies, for a diesel fuel analyzed on a DB 5MS column, which is the same column used in the free product analysis for this study. In the chromatograms for the Agilent diesel fuel and the chromatogram for the free product in this study, the compounds are consistent with n-alkanes found in diesel fuel (Figs 25 and 26). The lack of high molecular weight n-alkanes ($>C_{25}$) identified in the chromatograms of the free product wells in this study, indicate that the hydrocarbon contamination is a refined petroleum product and is not from a natural source (Fig 18).

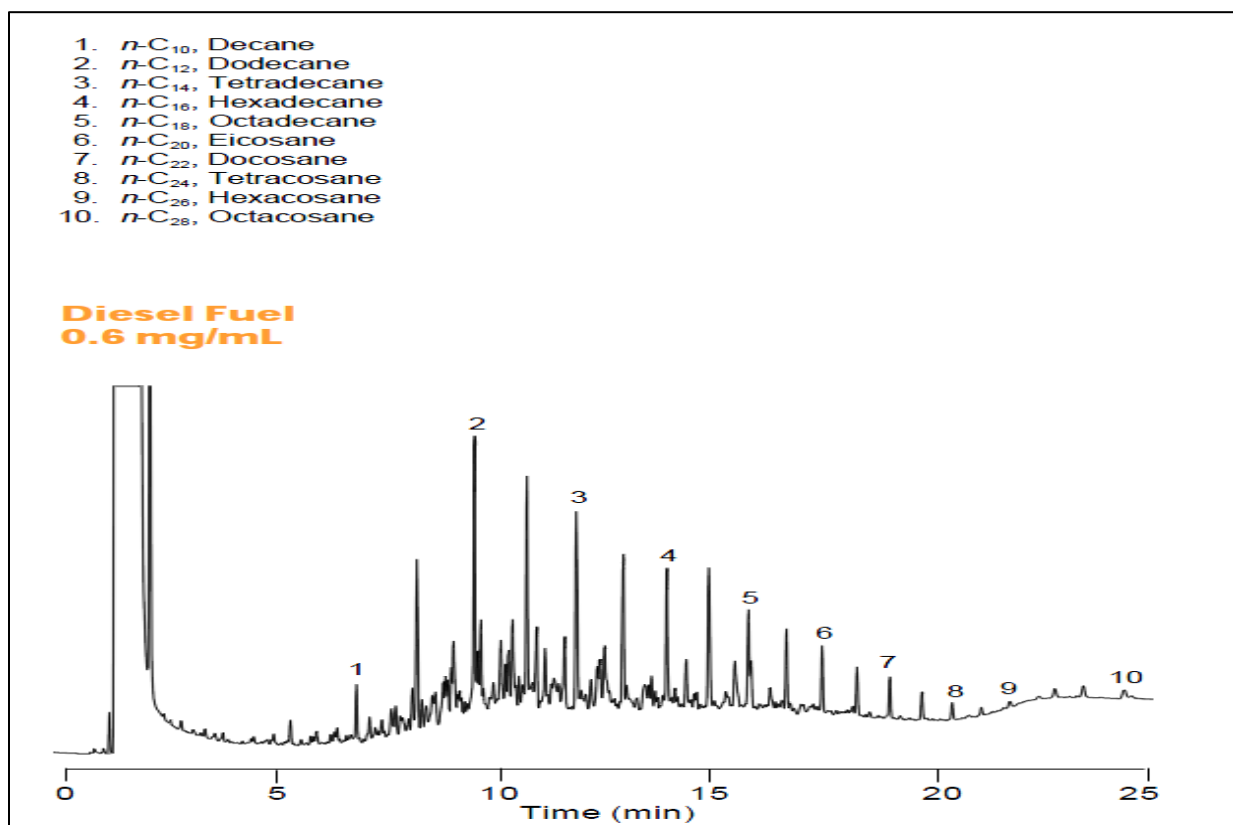


Figure 17. Example Diesel Fuel Chromatogram from Agilent Technologies, with time increasing along the x axis, and abundance increasing along the y-axis

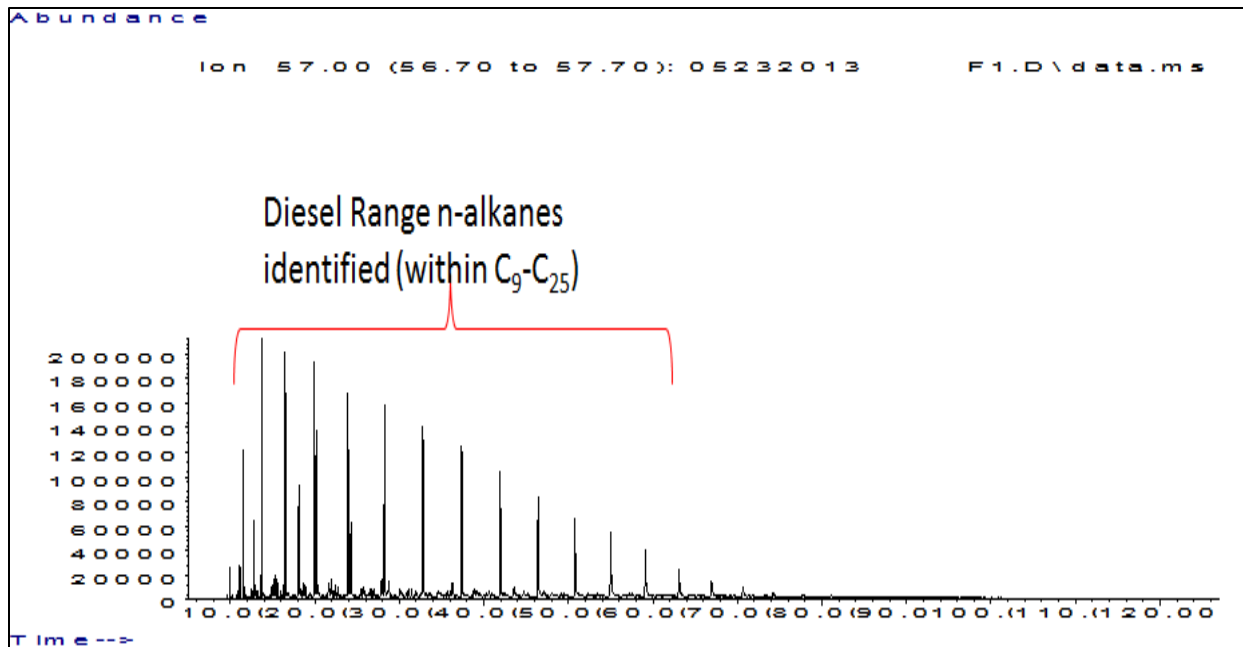


Figure 18. Chromatogram for free product from well 38. The chromatogram for well 38 is very similar to the chromatograms for the other free product wells in this study

D. Contaminant Degradation and Distribution Discussion

Microbial degradation of hydrocarbon compounds in the groundwater environment can diminish concentrations of compounds, alter relative abundance ratios of compounds, and generate intermediate degradation compounds (Chapelle, 2001). Microbial degradation is an important mechanism for ameliorating organic contamination of groundwater. For this study, consideration of the extent of the hydrocarbon degradation is important, particularly in the samples with free product the hydrocarbon emulsified with the water to some extent. Hydrocarbons are commonly immiscible in water; persistent emulsification can indicate microbial degradation and production of biosurfactant (Fleck et al, 2000). Hydrocarbons can be degraded by various microbial mechanisms, and associated microbial populations in groundwater. Once aerobic microorganisms have consumed molecular oxygen in a system, anaerobic organisms become active using other available terminal electron acceptors (Drever, 1997). In particular, anaerobic degradation of hydrocarbon occurs when nitrate is available; other electron acceptors in anaerobic degradation include ferric iron, sulfate, or bicarbonate (Drever,

1997). When external electron acceptors are no longer available, methanogens convert organic material into methane using CO₂ (Drever, 1997). While the water itself in the visibly contaminated wells is quite oxic and acts as an oxidant delivery mechanism for hydrocarbon-degrading microbes (Fig. 19), the non-aqueous phase is anoxic, potentially causing a restricted zone of anoxia in water in contact with the hydrocarbon, and the hydrocarbon may have been degraded by other terminal electron acceptor processes such as nitrate-, iron-, or sulfate- reducing bacteria based on the geochemical data (Fig 7, Fig 8) (Drever, 1997).

Boxplots indicate the minimum, 25th percentile, median, 75th percentile, and maximum value

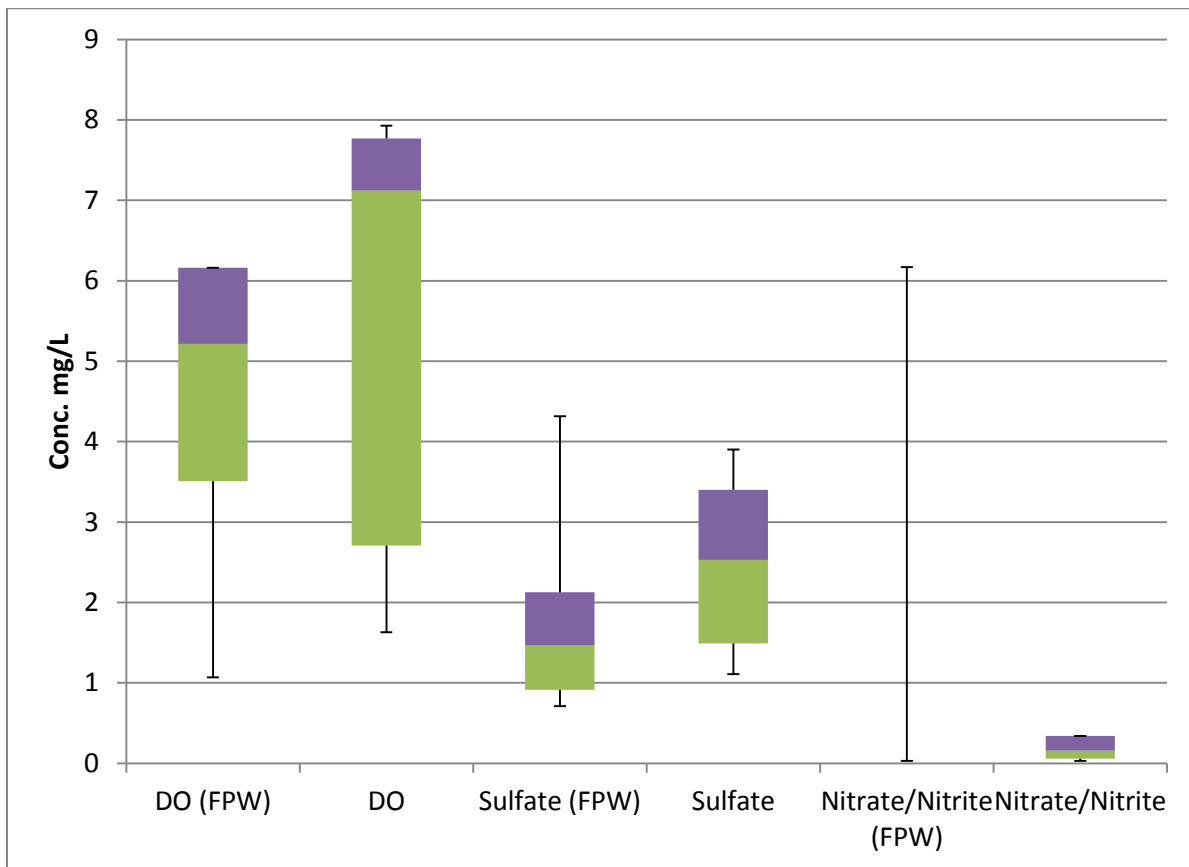


Figure 19, Medians of sulfate, nitrate, and DO concentrations in free product wells and wells without free product indicate a reducing environment favoring microbial degradation in the free product wells

Median dissolved oxygen concentration in the wells with free product is lower than the dissolved oxygen concentrations in the other wells; aerobic microbial degradation gives rise to depleted dissolved oxygen in groundwater (Fig. 19). In the free product wells, the medians of the nitrate and sulfate concentrations are lower than in the wells that are not visibly contaminated; this could indicate that the sulfate and nitrate act as electron acceptors during microbial degradation (Fig. 19). Statistical analysis indicates no statistically significant difference between the medians of DO ($P=0.335$) and sulfate ($P=0.157$) in the free product wells versus those wells without free product. The median values of nitrate between free products wells and those without free product were statistically significant ($P=0.007$). Dissolved oxygen and nitrate concentrations between non-free products wells and wells that previously had free product indicates no statistically significant difference (DO, $P=0.201$ and NO_3^{2-} , $P=0.325$), suggesting geochemical parameters in wells that previously had free product have returned to background concentrations. A P-value less than 0.05 denotes a statistically significant difference between two groups given that the groups are independent (Ott, 1984).

Fifteen of the wells had iron concentrations below the reporting limit; however in two of the free product wells, the dissolved iron concentrations were 213 $\mu\text{g/L}$ and 128 $\mu\text{g/L}$ (Fig 20). In reducing environments iron becomes soluble in water; the presence of dissolved iron in the water indicates that anaerobic bacteria may contribute to hydrocarbon degradation. Methane is present in six of the wells in the study area, in four of those wells the $\delta^{13}\text{C}$ value is near -60‰ v PDB, indicating methane of biogenic origin, potentially originating from microbial degradation of hydrocarbon (Fig 21). Methanogenesis occurs in the absence of other more energetic available electron acceptors.

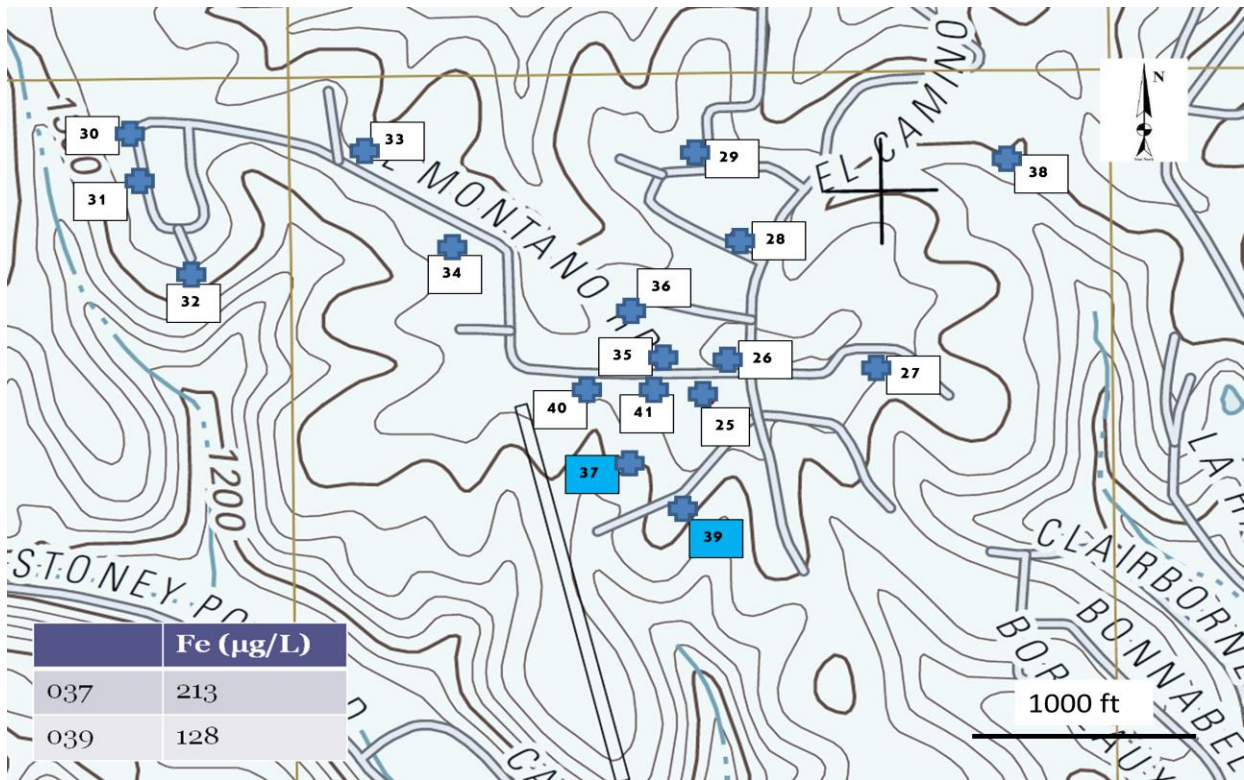


Figure 20 Map of study area showing the only two wells with dissolved Fe, which indicate a reducing environment, depleted DO

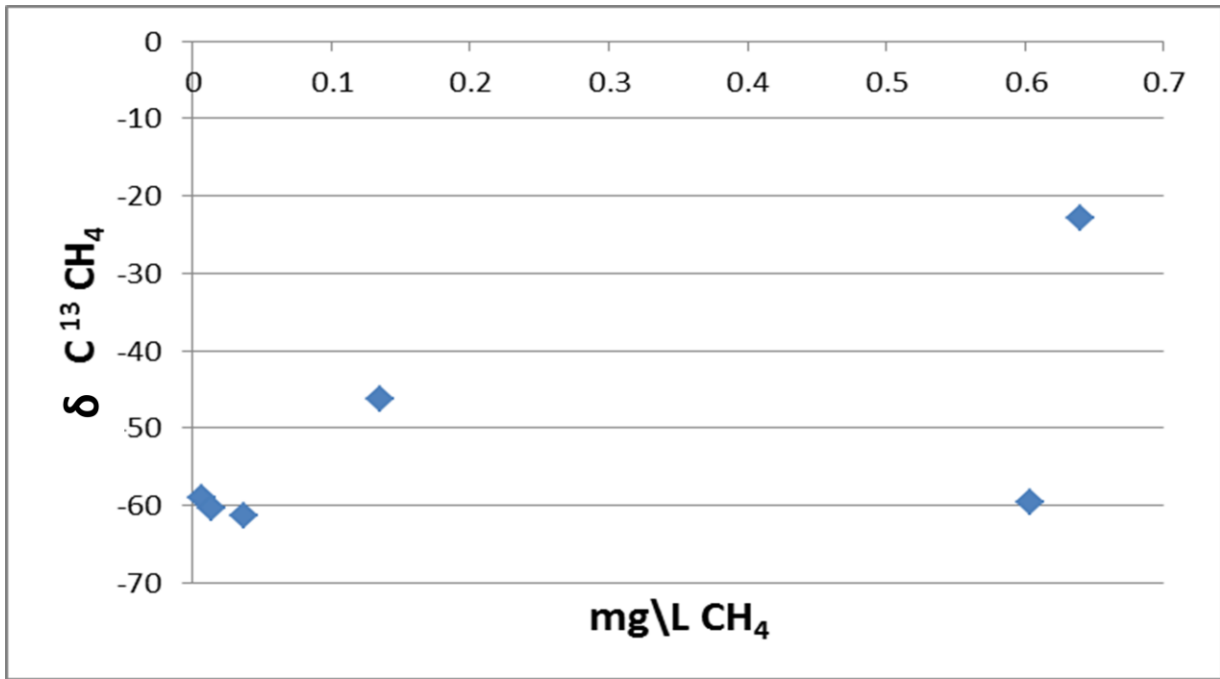


Figure 21. δ C¹³ values indicate that CH₄ is microbially derived. (Analyses were done at the UASIL by membrane extracted cavity ring down spectrometry using a Picarro G2201.)

Four of the wells in the study area have a non-aqueous hydrocarbon layer, with emulsification apparent at the aqueous-non aqueous interface (Fig. 15). However, geochemical data for groundwater samples from only three of the free-product wells corroborate microbial degradation of hydrocarbon, this variation may be explained by the depths at which the water samples were collected. Water within each well bore and in the aquifer is likely geochemically stratified with more anaerobic conditions prevalent nearer the zone of non-aqueous phase hydrocarbon. Hydrocarbon degradation occurs more rapidly when oxygen is present, rate of degradation decreases as oxygen is depleted (Drever, 1997). The DO concentration is likely depleted closest to the water-hydrocarbon interface, the same is true for nitrate and sulfate as well; such stratification or other geochemical gradients heterogeneities may also explain the inconsistent statistical significance for terminal electron acceptors (DO, nitrate, sulfate) in the samples.

Figure 23 compares the relative abundances of diesel range n- alkanes in each sample, with increasing carbon chain length. The susceptibility to degradation of hydrocarbon compounds is a function of the n-alkane carbon chain length (Wang and Philp, 1997). Lighter n-alkanes tend to be more labile and degrade more rapidly; heavier n-alkanes tend to be more refractory and persistent (Alimi et. al., 2003 and Kaplan et. al., 1997). Among the free product wells, which include wells 35, 37, 38, and 39, well 35 has the lowest abundance of lower molecular weight diesel range n-alkanes (Fig 23), this could indicate the sample from this well has a greater extent of degradation among the free product wells. The extent of degradation decreases in the visibly contaminated well samples in the following order: 35, 39, 37, and 38 (Figs 15 and 23). The distribution of VOCs, diesel n-alkanes, and methane from microbial degradation defines two, parallel northeast-southwest trends the study area (Fig. 22). The study area is situated on the up thrown block of a normal fault that trends northeast-southwest (Fig 3); fractures that accompany the fault have the same orientation and could be conduits for localized flow resulting in the observed distribution. Three wells that were initially reported to have contamination in 2007 no longer

had contamination during sampling for this study; this suggests southwest movement of the contaminant plume through time (Fig. 15), or more efficient degradation at these locations.

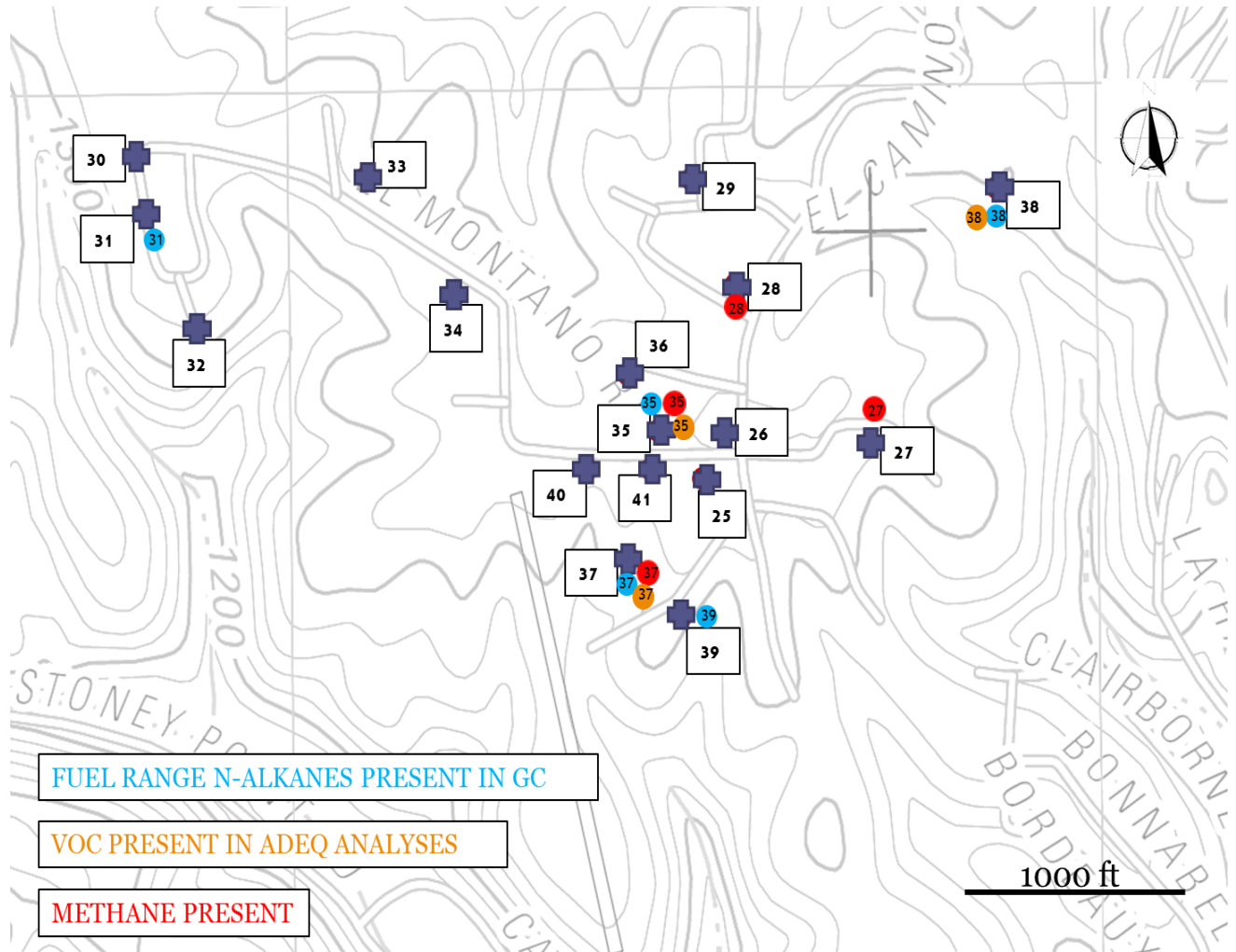


Figure 22. Spatial distribution of n-alkanes, VOC, and methane in the Rancho Villa Wells

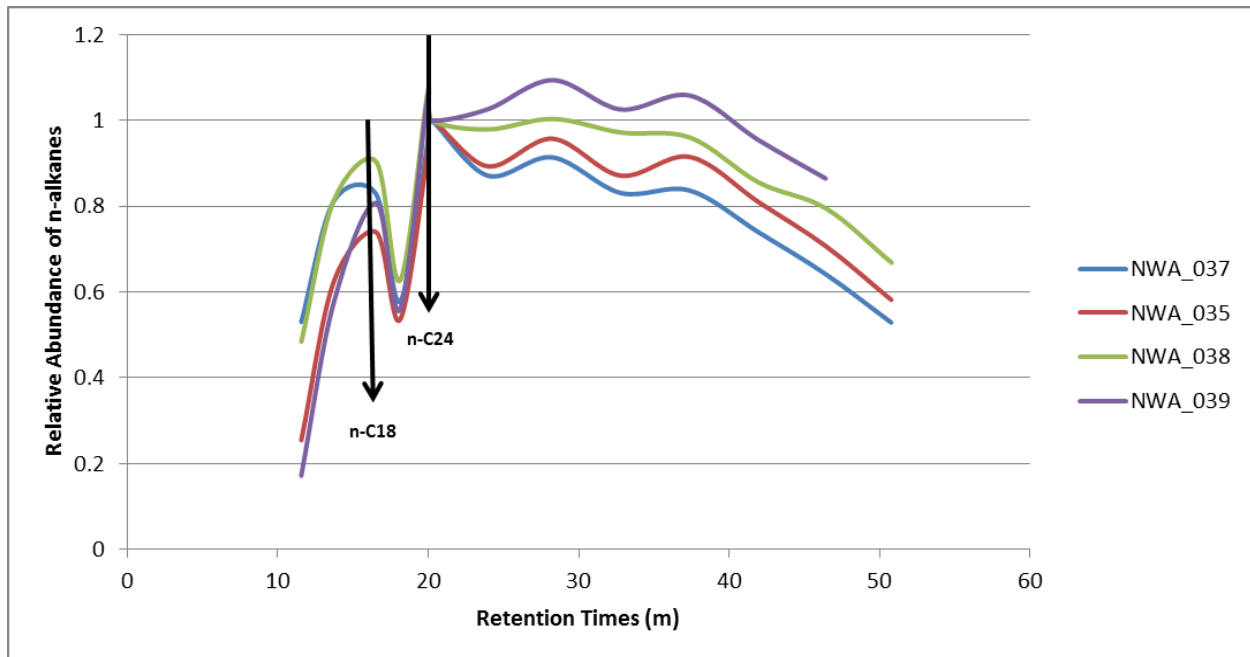


Figure 23. Relative abundances of diesel n-alkanes in visibly contaminated wells

Although three wells no longer exhibit contamination, the contamination has persisted in the Rancho Villa community since 2007 and is severe at some well locations; wells 35 and 37 were observed to have three feet or more free product over the water table. In 2007, several residents reported contamination to the ADH. Sampling for this study was completed in Fall 2012, at which time three of the wells that were reported to have contamination no longer had any problems; this suggests that the contaminant plume has degraded or migrated within the community from 2007 to 2012. The presence of acetone and tert Butyl benzene in the hydrocarbon indicates that the contaminant is not from a natural source, and is from a fuel spill that has migrated to the area. GC/MS analysis of the hydrocarbon indicates that compounds present in the contaminant are consistent with diesel fuel. Emulsification observed at the water-hydrocarbon interface indicates active microbial degradation. Geochemical data show that sulfate and nitrate are more depleted in the wells with free product, which indicates that sulfate and nitrate are acting as electron acceptors facilitating anaerobic degradation. The occurrence of biogenic methane in four wells may also indicate microbial degradation of hydrocarbon by various

terminal electron acceptor processes, from aerobic through nitrate, iron, sulfate, and CO₂ reduction indicate the variability, stratification, and heterogeneity of the geochemical environment of the aquifer. The community is situated upon a bluff that is about 300 feet up gradient from Beaver Reservoir, where fueling stations along the shore were initially considered as a possible source for the contamination; however, diesel is rarely used as a fuel for lake craft. No potential sources were identified in a reasonable radius (within 1.5 miles), the contaminant more likely is travelling from a greater distance along dissolution pathways and is being degraded along the way. The facts that the contamination has likely traveled more than 1.5 miles, occurs in very focused areas-often in close proximity to uncontaminated wells, suggest that faults in the subsurface allow focused migration of the hydrocarbon.

IX. Conclusions

The goals of the study were, (1) to constrain the hydrogeology of the site as relates to contaminant migration, (2) to characterize the contaminant chemically, and (3) to determine the source of the contaminant. The hydrogeology of the area was determined from previous theses (Stanton, 1993, Hunt, 1974, Rezaie, 1978, and Martin, 1999), additional data and observations during this study provided site-specific detail. The area is characterized by a carbonate karst aquifer – the Boone and St. Joe Limestones – with dynamic, non-steady state, anisotropic flow, and extensive dissolution typical of karst. In karst environments, dissolution along fractures offers high permeability and preferential flow zones; this allows for rapid fluid movement to occur over greater distances. Wells in the Rancho Villa community are completed in the karst aquifer. The study area is situated on a bluff near the shores of Beaver Reservoir. Generally the potentiometric surface of the unconfined Springfield Plateau aquifer is a subdued reflection of topography, so the general local groundwater flow direction can be assumed to be down away from the bluff toward the reservoir (Fig. 19).

An analysis of the hydrocarbon contaminant determined significant concentrations of tert Butylbenzene and acetone, which are fuel additives that do not naturally occur in crude oil. Qualitative analysis of the GC chromatograms for the contaminant indicated the presence of diesel range n-alkanes, which suggest that the contaminant is from a refined diesel fuel source. The source most likely is located greater than 1.5 miles away from Rancho Villa, as a detailed survey of the local area (less than 1.5 miles radius) revealed no potential sources; however, the contaminant has persisted since about 2007. No reported fuel spills or RCRA permitted sites documented in the area could be identified as a potential source of the contaminant. Three fueling stations with RCRA permitted storage tanks are 0.52 miles from the domestic wells, located down gradient along the shores of Beaver Reservoir however, these serve recreation boating, and diesel is not commonly used for that purpose. The analyses help to constrain the type of hydrocarbon found in the wells as a diesel fuel; analyses from this study are a

significant basis for further study of this site. In 2007, the ADEQ analyzed a sample from a well in the community, labeled as NWA_038. The results of the analysis reported trimethylbenzene at a concentration of 1,220,000 µg/L, acetone at a concentration of 458,000 µg/L, tert Butylbenzene at a concentration of 262,000 µg/L, and an overall composition that is 45% diesel range organics (Table 2). The total peak area percentage of diesel range organics in the free product samples ranged from 52-70%. No federal regulatory limit has been established for trimethylbenzene, a synthetic fuel additive that also occurs naturally in crude oil (US EPA, 1994). Tert Butylbenzene is a synthetic compound that does not occur naturally in crude oil, and is added to diesel fuel (Brown, 2011 and Hartgers, 1994). Acetone is not present in crude oil, and is often added to diesel fuel. Considerably high concentrations of tert Butylbenzene and acetone in the hydrocarbon indicate it is not likely from a natural petroleum source. Analysis of the hydrocarbon from wells with free product using GC/MS revealed that the molecular weights of n-alkanes identified in the analysis are consistent with diesel fuel. However, the hydrocarbon product recovered from the wells appears to be in an unrefined state. An explanation for this appearance is that the contaminant has been degraded en route to its present location.

Further, intervals of emulsification appear at the water-hydrocarbon interface; indicating microbial reduction of oxygen, nitrogen, and sulfate. Methane is also present two of the wells with free product, which suggests that external electron acceptors have been depleted, allowing methanogens to convert organic material to methane and CO₂ (Drever, 1997) . Geochemical data show that sulfate and nitrate are more depleted in the wells with free product, which indicates that sulfate and nitrate are acting as electron acceptors facilitating anaerobic degradation. The occurrence of biogenic methane in four wells may also indicate microbial degradation of contaminant hydrocarbon through methanogenesis at some locations. This evidence of microbial degradation of hydrocarbon by various terminal electron acceptor processes, from aerobic through nitrate, iron, sulfate, and CO₂ reduction indicate the variability, stratification, and heterogeneity of the geochemical environment of the aquifer.

The orientation of wells that have or have had free product is on a northeast-southwest trend, indicative of the travel direction and movement along discrete fractures. The contamination seems to be localized and is not widespread, also indicating focused migration of the contaminant along fractures associated with normal faults in the area.

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XI. Appendices

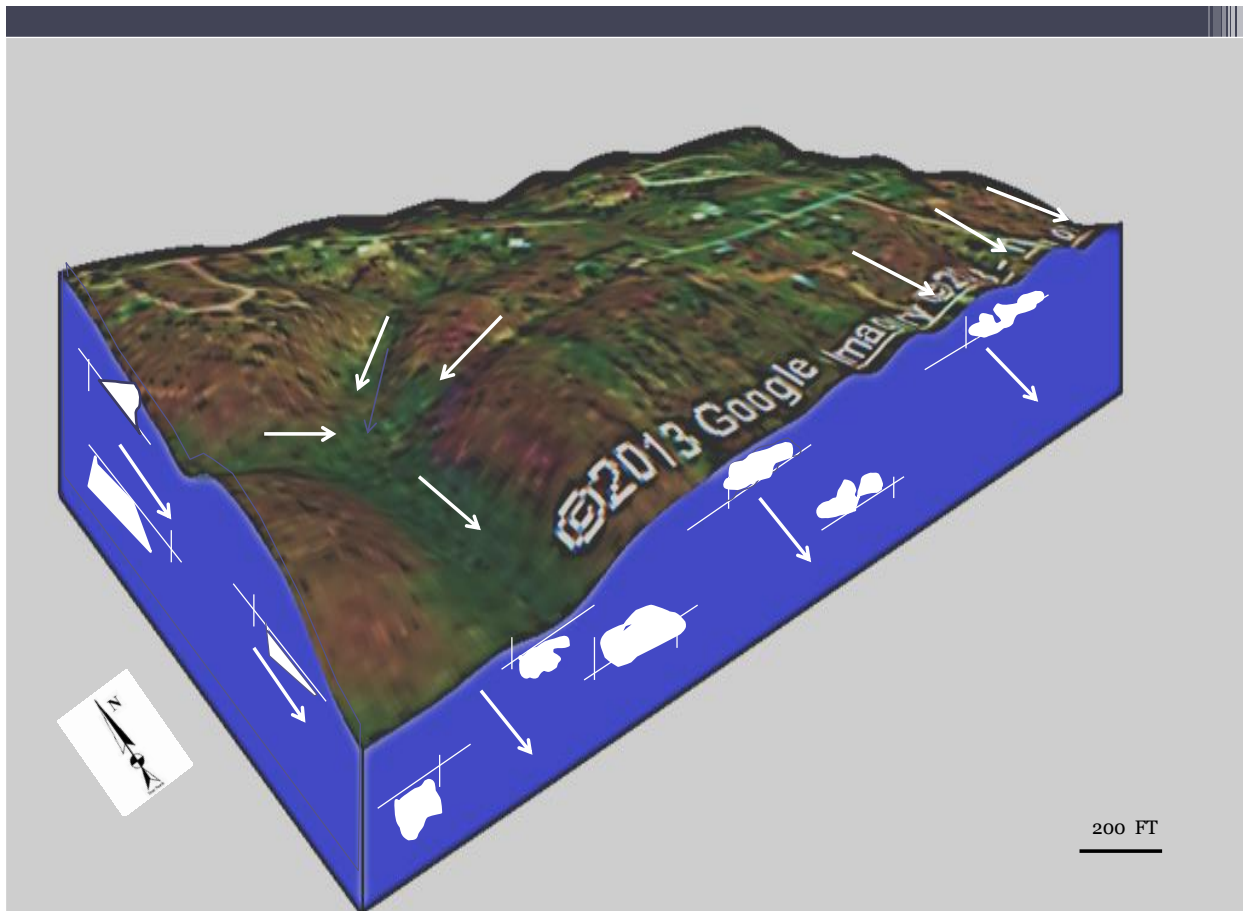


Figure 24, Conceptual Model of Surface and Subsurface Flow

NWA_031			
Peak #	Peak Area %	Gasoline Range	Quality
12	1.35	Dodecane, 2,6,10-trimethyl-	91
		Nonane, 5-(1-methylpropyl)-	72
		Dodecane, 2,6,11-trimethyl-	72
Diesel Range			
14	2.61	Hexadecane	87
		Tetradecane	87
		Tridecane	83
19	3.51	Heptadecane, 2,6,10,15-tetramethyl	86
		Hexadecane, 2,6,10,14-tetramethyl-	86
		Nonadecane	86
20	2.52	Pentadecane	96
		Pentadecane	93
		Pentadecane	91
25	2.63	10-Methylnonadecane	90
		Tetratetracontane	87
		Nonadecane	87
28	2.23	Tritetracontane	91
		Tetratetracontane	91
		Heptacosane, 1-chloro-	87
30	8.22	Pentadecane, 2,6,10,14-tetramethyl	91
		Pentadecane, 2,6,10,14-tetramethyl	90
		Hexadecane, 2,6,10,14-tetramethyl-	90
36	4.48	Heptacosane	87
		Tetratetracontane	86
		Tetratetracontane	86

Table 3, Peak Identification of Water Sample

NWA_035			
Peak #	Peak Area %	Diesel Range n-alkanes	Quality
1	2.42	Tetradecane	96
		Tetradecane	94
		Hexadecane	91
2	6.4	Pentadecane	96
		Pentadecane	95
		Pentadecane	93
3	7.56	Hexadecane	95
		Hexadecane	95
		Hexadecane	94
4	5.48	Pentadecane,	91
		Heptadecane,	80
		Hexadecane,	80
5	9.51	Pentadecane,	91
		Heptadecane,	80
		Hexadecane	80
6	10.52	Pentadecane,	91
		Pentadecane	91
		Dodecane, 2-methyl-8-propyl-	90
7	9.05	Octadecane	98
		Octadecane	96
		Pentadecane	95
8	9.69	Nonadecane	98
		Nonadecane	92
		Heneicosane	91
10	9.3	Heneicosane	99
		Heptadecane,	
		2,6,10,15-tetramethyl	95
		Pentadecane	95

Table 4, Peak Identification of Water Sample

NWA_37			
Peak #	Peak Area %	Diesel Range n-alkanes	Quality
1	2.03	Tridecane	97
		Tridecane	96
		Hexadecane	91
2	1.68	Dodecane, 2,6,10-trimethyl-	91
		Hexadecane, 2,6,10,14-tetramethyl-	90
		Dodecane, 2,6,10-trimethyl-	80
3	4.65	Tetradecane	96
		Tetradecane	94
		Tridecane	90
4	3.32	Heptadecane, 2,6,10,14-tetramethyl	90
		Hexadecane, 2,6,10,14-tetramethyl-	86
		Heptadecane, 2,6,10,15-tetramethyl	80
5	7.15	Pentadecane	98
		Pentadecane	97
		Pentadecane	96
6	7.15	Hexadecane	96
		Hexadecane	95
		Hexadecane	93
7	5.07	Pentadecane, 2,6,10-trimethyl-	91
		Tridecane, 5-propyl-	87
		Hexadecane, 2,6,10,14-tetramethyl-	86
8	7.67	Heptadecane	98
		Heptadecane	98
		Pentadecane	91
9	8.04	Pentadecane, 2,6,10,14-tetramethyl	91
		Pentadecane, 2,6,10,14-tetramethyl	91

		Octadecane, 2,6-dimethyl-	90
10	7.69	Octadecane	98
		Octadecane	97
		Heptadecane	91
11	5.91	Hexadecane, 2,6,10,14-tetramethyl-	98
		Nonane, 5-butyl-	90
		Hexadecane, 2,6,10,14-tetramethyl-	89
12	8.03	Nonadecane	96
		Tridecane, 6-propyl-	94
		Nonadecane	92
15	6.53	Nonadecane	95
		Docosane	93
		Hexadecane	93

Table 5, Peak Identification of Water Sample

NWA_038			
Peak #	Peak Area %	Diesel Range n-alkanes	Quality
1	1.03	Tridecane	97
		Tridecane	95
		Tridecane	93
2	1.04	Dodecane, 2,6,10-trimethyl-	91
		Hexadecane, 2,6,10,14-tetramethyl-	86
		Dodecane, 2,6,11-trimethyl-	80
3	3.66	Tetradecane	96
		Tetradecane	94
		Tetradecane	91
6	2.54	Heptadecane, 2,6,10,14-tetramethyl	90
		Dodecane, 2,6,10-trimethyl-	86
		Hexadecane, 2,6,10,14-tetramethyl-	86
7	6.14	Pentadecane	97
		Pentadecane	96
		Pentadecane	96
10	6.83	Hexadecane	96
		Hexadecane	95
		Hexadecane	91
11	4.64	2-Bromo dodecane	94
		3,5-Dimethyldodecane	87
		Pentadecane, 2,6,10-trimethyl-	86
13	8.08	Heptadecane	98
		Heptadecane	98
		Pentadecane	91
14	7.56	Pentadecane, 2,6,10,14-tetramethyl	93
		Octadecane, 2,6-dimethyl-	86
		Dodecane, 2-methyl-8-propyl-	86

16	7.37	Octadecane	98
		Octadecane	98
		Pentadecane	94
17	4.84	Hexadecane, 2,6,10,14-tetramethyl-	98
		Hexadecane, 2,6,10,14-tetramethyl-	91
		Tridecane, 7-hexyl-	90
18	7.59	Nonadecane	98
		Nonadecane	92
		Octacosane	91

Table 6, Peak Identification of Water Sample

NWA_039			
Peak #	Peak Area %	Diesel Range n-alkanes	Quality
1	1.45	Tetradecane	96
		Tetradecane	94
		Tetradecane	91
2	1.61	Heptadecane	90
		Tridecanol	90
		Pentadecane	87
3	4.97	Pentadecane	98
		Pentadecane	96
		Pentadecane	95
4	6.84	Hexadecane	96
		Hexadecane	94
		Hexadecane	93
5	4.7	Tridecane	93
		Heptadecane	83
		Heptacosane	83
6	8.84	Heptadecane	98
		Heptadecane	98
		Pentadecane	91
7	8.41	Pentadecane	96
		Pentadecane	95
		Octadecane	86
8	8.63	Octadecane	98
		Octadecane	96
		Heptadecane	91
9	6.26	Hexadecane, 2,6,10,14-tetramethyl-	98
		Dodecane, 2,6,10-trimethyl-	87
		Tetratetracontane	86

Table 7, Peak Identification of Water Sample

	Zn ug/L	Cu mg/L	Fluoride mg/L	Chloride mg/L	Sulfate mg/L	Total Alkalinity (as CaCO ₃) mg/L	Nitrate/Nitrite as N mg/L
NWA_024	3.68	<0.05	0.06	2.97	3.23	131	9.65
NWA_025	12.6	3.44	0.27	3.73	3.53	191	0.105
NWA_026	7.88	3.42	0.41	3.55	3.4	197	0.054
NWA_027	4290	6.55	0.05	1.69	3.07	219	<0.03
NWA_028	140	14.3	0.06	2.36	1.85	192	0.158
NWA_029	8.99	18.6	0.08	5.86	1.73	167	0.626
NWA_030	24.5	2.43	0.05	3.64	1.11	194	0.458
NWA_031	4.46	6.95	0.05	2.48	1.18	195	0.287
NWA_032	16.6	5.5	0.05	2.05	1.29	196	0.17
NWA_033	23.8	38.3	0.05	2.94	1.49	197	0.34
NWA_034	3.21	1.3	0.07	2.6	9.54	209	0.099
NWA_035	4.86	1.99	0.36	3.44	1.96	220	<0.03
NWA_037	1.02	<0.05	0.37	3.2	0.71	212	<0.03
NWA_038	3.62	<0.05	0.05	2.36	2.63	197	<0.03
NWA_039	1.37	<0.05	0.65	2.83	0.98	247	<0.03
NWA_040	37.7	4.22	0.1	2.65	4.77	202	0.06
NWA_041	18	5.69	0.39	2.79	2.53	223	0.054

Table 8, Geochemical Data from ADEQ

	Orthophosphate as P mg/L	Total Kjeldahl Nitrogen mg/L	Total Organic Carbon mg/L	Phosphorus- total mg/L	Total Dissolved Solids (mg/L)	Dissolved Oxygen mg/L
NWA_024	0.039	0.25	0.597	0.065	277	9.96
NWA_025	0.017	<0.05	0.218	<0.02	211	2.18
NWA_026	0.015	<0.05	<0.2	0.026	213	1.83
NWA_027	0.011	<0.05	<0.2	<0.02	242	1.63
NWA_028	0.016	<0.05	<0.2	<0.02	211	7.12
NWA_029	0.021	<0.05	<0.2	<0.02	193	7.68
NWA_030	0.02	0.134	<0.2	<0.02	211	8.06
NWA_031	0.019	0.148	<0.2	<0.02	211	7.77
NWA_032	0.023	0.102	<0.2	<0.02	214	7.99
NWA_033	0.019	0.181	<0.2	<0.02	217	7.45
NWA_034	0.017	0.12	<0.2	<0.02	234	3.83
NWA_035	0.013	0.193	<0.2	<0.02	238	1.07
NWA_037	0.128	0.628	0.516	<0.02	217	6.32
NWA_038	<0.01	1.23	0.75	0.074	224	6.11
NWA_039	<0.01	0.102	0.658	<0.02	242	4.32
NWA_040	<0.01	<0.05	<0.2	<0.02	230	5.06
NWA_041	<0.01	<0.05	<0.2	0.025	214	2.71

Table 8 (Cont), Geochemical Data from ADEQ

	pH	Temperature °C	Specific Conductance (EC) μ S/cm	Ca mg/L	Mg mg/L	K mg/L	Na mg/L	Fe ug/L	Hardness mg/L
NWA_024	6.28	16.1	418	62	2.06	1.46	19.1	<20	163
NWA_025	6.53	17	361	62.5	5.52	1.15	8.05	<20	179
NWA_026	6.84	18.3	369	54.4	7.95	1.37	11.8	<20	169
NWA_027	5.89	16	409	82	1.64	0.439	4.93	<20	211
NWA_028	6.33	16.9	357	74.2	0.98	0.57	2.75	<20	189
NWA_029	6.49	17.6	330	66.2	1.51	0.568	3	<20	172
NWA_030	6.72	16.3	351	75.7	0.76	0.614	2.93	<20	192
NWA_031	6.7	16.2	336	73.9	0.74	0.558	2.88	<20	188
NWA_032	6.66	15.2	347	75.2	0.82	0.598	3.03	<20	191
NWA_033	6.58	16	351	76.4	0.99	0.66	2.81	<20	195
NWA_034	6.7	16.1	381	74.8	4.63	0.759	5.01	<20	206
NWA_035	6.51	17.7	405	72.4	1.63	0.694	17.2	<20	187
NWA_037	7.04	16.2	389	51	11.5	1.95	13.3	213	175
NWA_038	6.87	13.2	345	78.4	1.09	0.796	2.9	<20	200
NWA_039	7.06	12.1	433	53.4	9.26	1.86	18.8	128	171
NWA_040	6.65	15.8	343	75	4.05	0.838	4.41	<20	204
NWA_041	6.85	12.6	346	54.6	10.5	1.8	10.8	<20	179

Table 8(Cont), Geochemical Data from ADEQ analysis

Triplot Results:

18 points (Converted to MEq).

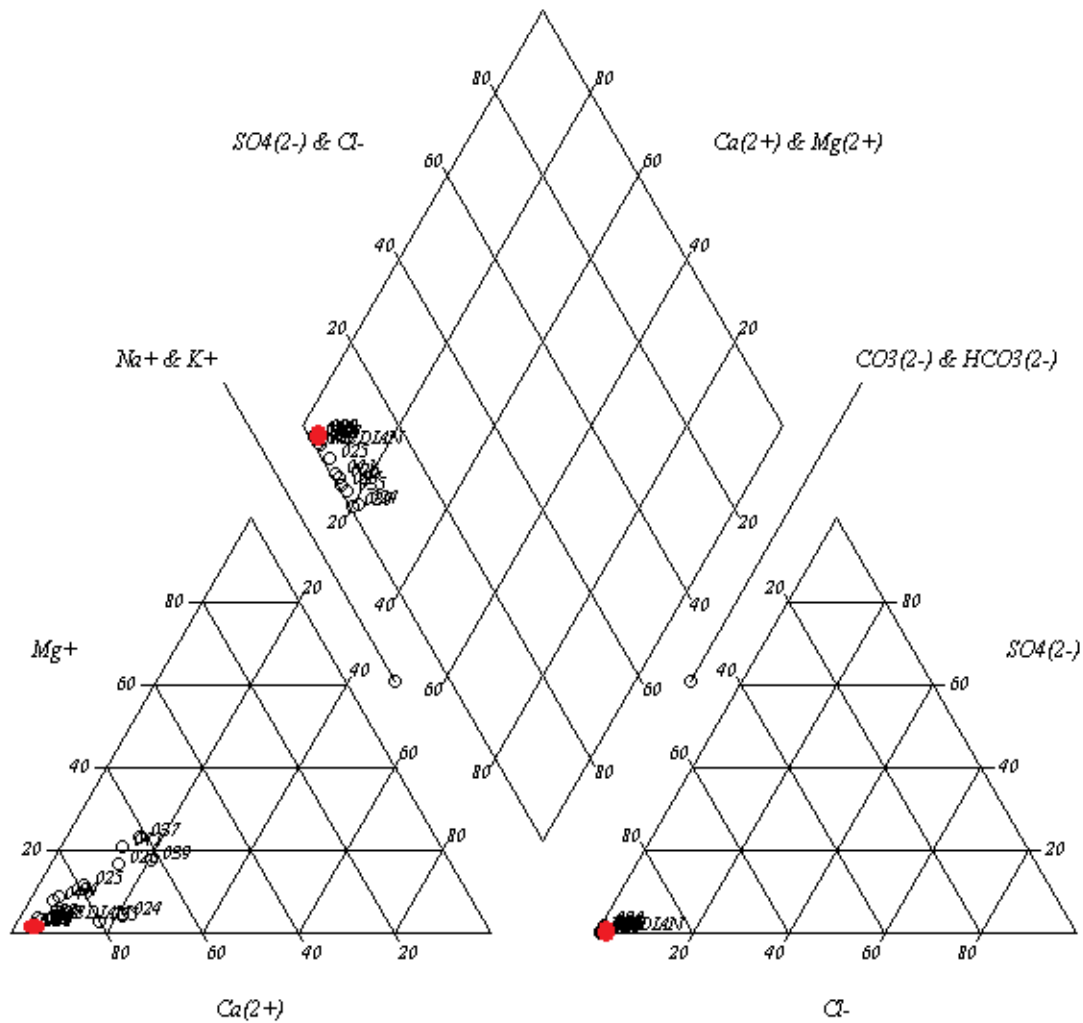


Figure 25. Piper Diagram Plot of Water Type, Ca-Bicarbonate (Trilinear Plot Java Applet) Median Value in Red
From <http://www.rime.com.au/triplot/triplot.html>