BASELINE GROUNDWATER QUALITY TESTING NEEDS IN THE EAGLE FORD SHALE REGION

By

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ABSTRACT

As the pace of drilling in the Eagle Ford shale increases, so does the potential for groundwater contamination incidents. The goals of this analysis are (1) to determine whether existing baseline groundwater quality data in the Eagle Ford shale region of southern Texas is adequate to provide a comparison to potential future contamination from oil and gas development and (2) to define an appropriate and cost-effective list of parameters that will aid in strategic planning of baseline groundwater quality testing in the Eagle Ford shale region for the same goal.

First, a list of potential testing parameters is defined using case studies of proposed groundwater contamination. Second, formation water chemistry in the Eagle Ford shale region is compared to groundwater chemistry in the counties of the Eagle Ford shale region to determine which chemical indicators demonstrate potential to consistently detect contamination. Third, statistical power analysis is used as a guideline to decide whether more samples are needed for each testing parameter in each county in the Eagle Ford shale region. Next, known health effects of each testing parameter are described in order to highlight potential pollutants that should be prioritized in a sampling initiative. Finally, testing costs are reported to introduce a perspective about microeconomic choices affecting which stakeholders take responsibility for baseline groundwater quality testing.

These tasks led to the findings that some of the most dangerous potential pollutants, including methane, total petroleum hydrocarbons, nitrate, volatile organic compounds, polycyclic aromatic hydrocarbons, alpha particles, beta particles, and gamma radiation, are poorly characterized in the region, if at all. Furthermore, testing these parameters is more expensive than testing less hazardous ones. Water well owners may be unable to afford the expense of testing these parameters. Therefore, a testing initiative facilitated by agencies, industry, or other organizations may be more efficient at establishing a regional baseline for these high priority, expensive tests. As such, the framework and analysis presented here can be used by groundwater managers in the Eagle Ford shale region to develop baseline sampling strategies tailored to specific counties in the region.

Acknowledgements

The idea for this project came from concerns expressed by residents of a small community in Webb County, Texas called “Los Botines.” After hearing about cases of potential groundwater contamination linked to hydraulic fracturing, the residents approached a non-profit organization I was working for, the Rio Grande International Study Center (RGISC), with questions about how to get baseline water quality tests taken for water wells in Los Botines. After some research, my colleagues and I at RGISC found that comprehensive baseline groundwater quality testing would cost more than the non-profit could afford, and we speculated that the expense would deter residents from pursuing testing on their own. With this in mind, the analysis presented here seeks to enable water well users, oil and gas companies, and agencies to better understand groundwater resources in the Eagle Ford shale region of South Texas.

Much gratitude is owed to Tricia Cortez, Executive Director of RGISC, who has not only been an outstanding mentor, but also provided me with opportunities to work with stakeholders on the ground. Additionally, my thanks go out to my fellow students at the Nicholas School of the Environment, especially those who are members of the Drilling, Environment, and Economics Network; and to members of the Laredo, Texas-based Safe Fracking Coalition, who engaged in open-minded discussions about oil and gas development and were always willing to share their expertise on relevant topics. Finally, I greatly appreciate the time and feedback offered by my advisor, Dr. Robert B. Jackson, who offered careful and thoughtful guidance throughout the process of writing this analysis.

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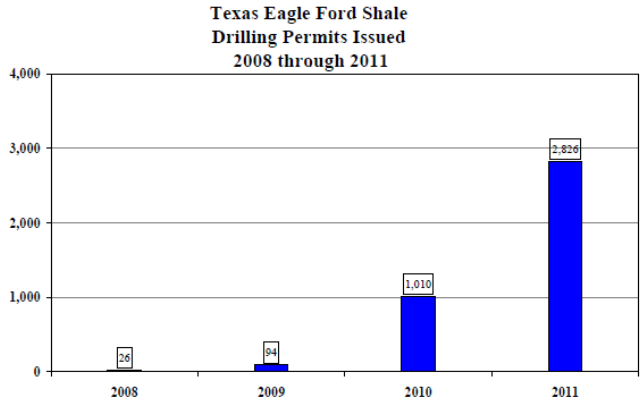
I. Introduction

Rapid increases in the pace of drilling activity in the Eagle Ford shale play (Figure 1) have created dual pressures for landowners who also own mineral rights in the region. These landowners theoretically have a desire to collect income from leasing their mineral rights, but also have a preference for protecting their water quality. Recent developments in the technologies of horizontal drilling and hydraulic fracturing have allowed oil and gas extraction from low permeability formations, such as shale, to become more economically viable (Hughes 2011). In shale plays[1] across the United States, drilling rates have increased (Lippman Consulting and U.S. Energy Information Administration 2010). This increase in drilling activity could be problematic however, because chemicals that flow back[2] out of oil and gas wells during extraction could potentially cause groundwater to become contaminated with toxic materials (Colborn, Kwiatkowski et al. 2011).

FIGURE 1 ACCELERATION OF DRILLING ACTIVITY IN THE EAGLE FORD SHALE (RAILROAD COMMISSION OF TEXAS 2012)



Recent proposed cases of groundwater contamination occurring after increases in the rate of hydraulic fracturing in Texas, Pennsylvania, Wyoming, and other states have remained contentious because of the lack of background water quality data available. "Background" water quality refers to the chemical characteristics of the water before a change is made to the water body that could affect its chemical characteristics[3]. On the one hand, oil and gas companies (industry) are aware of the opportunity for landowners to falsely claim that contamination has occurred when if water quality problems already exist. On the other hand, landowners have been unable to find compensation for groundwater remediation when no comparison to background water quality is available to indicate the source of contamination.

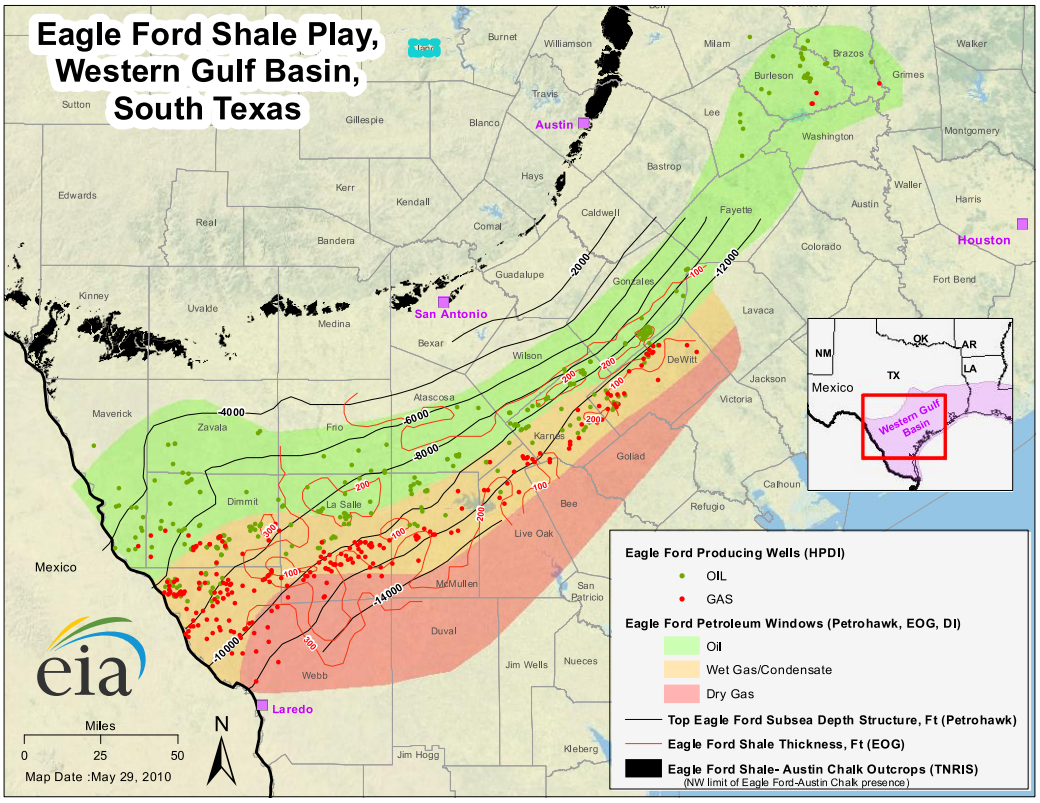
As a shale play that is rich in liquids such as oil and condensate (Figure 2), drilling activity in the Eagle Ford is expected to continue accelerating. This is because liquids are currently more valuable than dry gas (U.S. Energy Information Administration 2011; U.S. Energy Information Administration 2012). In

[1] In oil and gas exploration, a "play" is a region where significant quantities of oil and gas are expected to occur. Schlumberger. (2012). "Oilfield Glossary." Retrieved April 24, 2012, from http://www.glossary.oilfield.slb.com.
[2] The term "flowback" is used to describe the mixture of hydraulic fracturing fluids that returns to the surface when the well is producing. Flowback may contain produced water, hydraulic fracturing chemicals, and petroleum hydrocarbons.
[3] In this report, the term "baseline" will be used interchangeably with the term "background."

fact, the Energy Information Administration recently noted the Eagle Ford as a contributor in Texas' significant gains in production for the year of 2011 (U.S. Energy Information Administration 2012).

In light of the potential for groundwater contamination to occur in the Eagle Ford shale region, it is important to assess the strength of existing background water quality datasets in accurately predicting a regional baseline of water quality. Additionally, it is important to determine geographic locations in the region where more information is needed and what kind of chemical data is needed. The analysis presented in this report finds that current available baseline groundwater quality data is not adequate to assess potential groundwater contamination from oil and gas exploration in the Eagle Ford shale region.

FIGURE 2 WINDOWS OF OIL, CONDENSATE, AND GAS IN THE EAGLE FORD SHALE (U.S. ENERGY INFORMATION ADMINISTRATION 2010)



Current regulations and programs exist to facilitate baseline groundwater quality characterization, but to my knowledge no widespread initiative exists to assist landowners or the oil and gas industry in the Eagle Ford shale region in acquiring the appropriate tests needed to assess baseline water quality for the purpose of detecting potential future contamination from oil and gas drilling, extraction, and production activities (hereafter termed "oil and gas development"). Yet assessing potential contamination of groundwater wells caused by oil and gas development relies on groundwater stakeholders, those who consume groundwater and those who have the capacity to pollute groundwater, having access to appropriate and reliable background water quality data (Texas Administrative Code 2006).

Studies assessing baseline groundwater quality have ranged from testing few parameters to testing extensive lists of potential contaminants and indicators. Baseline groundwater quality testing should include a

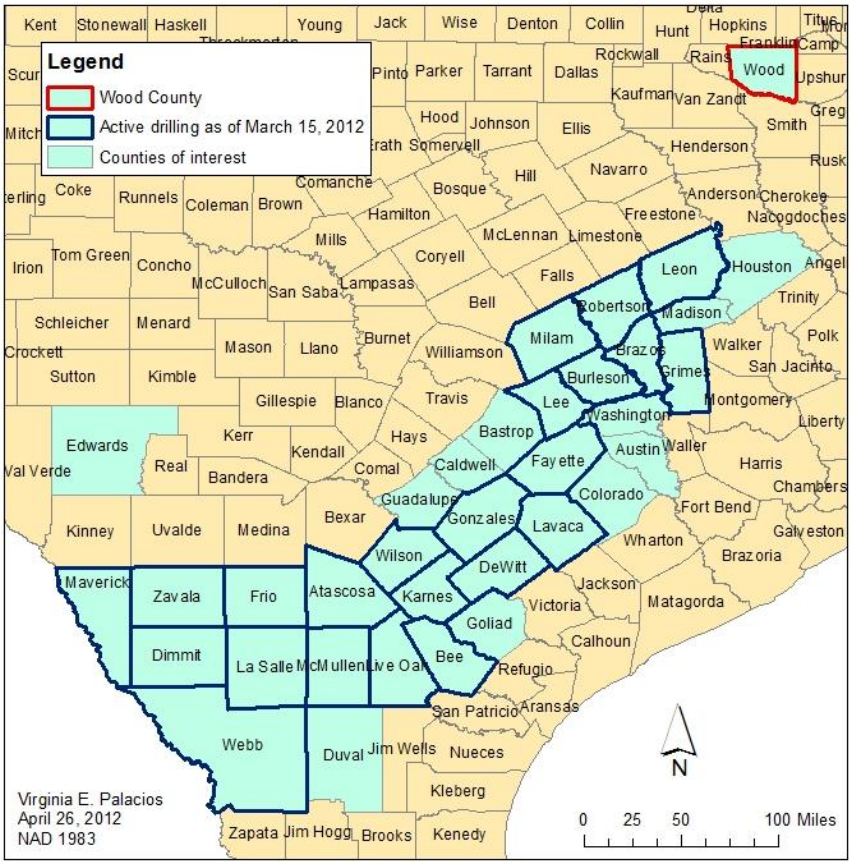
comprehensive list of parameters in order to be effective at detecting a wide range of potential contaminants after oil and gas drilling takes place. However, the expense of testing a comprehensive list of analytes[4] serves to dissuade some water well owners from volunteering to conduct background water quality testing on their water well. Considering this potential reaction, limited resources should be spent on the most essential tests that are effective in detecting constituents specific to oil and gas contamination.

Therefore, the purpose of this analysis is (1) to determine whether existing baseline water quality data in the Eagle Ford shale region is adequate to provide a comparison to potential future contamination from oil and gas development and (2) to define an appropriate and cost-effective list of parameters that would aid in strategic planning of baseline water quality testing in the Eagle Ford shale region for the same goal.

Geographic Scope

The data used in this analysis represents all Eagle Ford shale counties listed by three sources: Railroad Commission, Energy Information Administration, and the website EagleFordShale.com. The 35 "counties of interest" used in this analysis are depicted in Figure 3 and are listed in Appendix I.

FIGURE 3 COUNTIES INCLUDED IN THIS ANALYSIS.

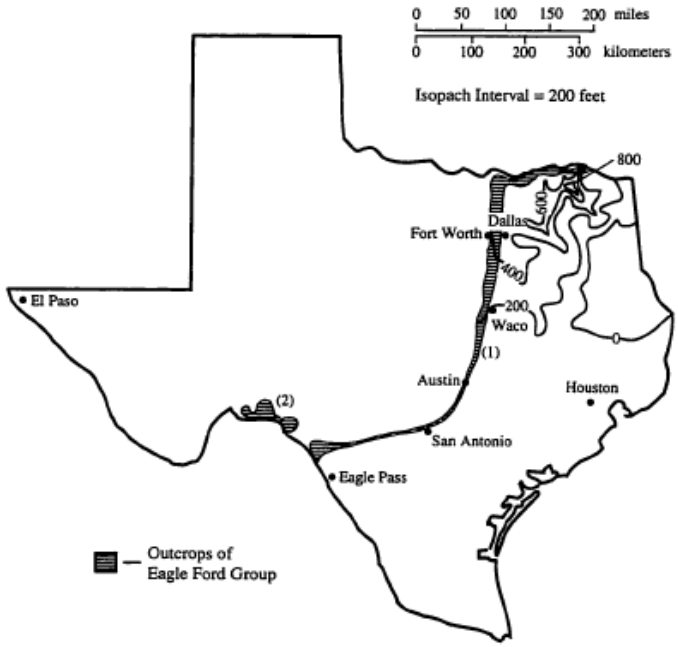


[4] The term analytes refers to a chemical parameter which must be analyzed, or tested, in a laboratory.

One county included in this analysis, Wood County, is not in geographic proximity to the area of current active Eagle Ford shale drilling. However, Wood County is included in this analysis because it is the only county for which U.S. Geological Survey (USGS) produced water chemistry data for the Eagle Ford shale formation was available. Produced water chemistry was documented in the USGS produced waters database between the years of 1951 and 1975. The age of this data, and Wood County's distance from the current active drilling region of the Eagle Ford shale demands further supporting evidence that the formation examined in Wood County is still taxonomically considered to be a part of the Eagle Ford formation.

Figure 4 depicts isopachs (lines of equal thickness) for the Eagle Ford shale. The area of Wood County, depicted in Figure 4 East of Dallas, and in Figure 3 outlined in red, includes regions where the Eagle Ford shale is known to exist at a thickness between 200 and 800 feet. Therefore, although the USGS produced waters data is old, Lai (1997) confirms that Wood County has been considered to contain portions of the Eagle Ford formation more recently than 1975. However, considerable uncertainty still exists as to whether produced water chemistry of the Eagle Ford formation in Wood County matches produced water chemistry of the Eagle Ford formation in other counties.

FIGURE 4 ISOPACHS IN THE EAGLE FORD SHALE. (ADAPTED FROM SELLARD ET AL. 1932 AND SURLES, 1987, CITED IN LAI 1997)



Pathways and detection

This report does not include analysis of the potential pathways through which groundwater contamination from oil and gas extraction activities could occur. However, for the sake of understanding a comparison between baseline groundwater quality and potentially contaminated groundwater quality, these pathways are outlined in this section. A pathway can be defined as a continuous space between a hydrocarbon-bearing

formation and a groundwater aquifer. Four potential pathways have been postulated in previous research (U.S. General Accounting Office 1989; Environmental Protection Agency 2011; Osborn, Vengosh et al. 2011)[5]:

1. Natural migration of fluids and gases from the formation to the aquifer
2. Leaky oil or natural gas well casings
3. Induced fractures connecting with or enlarging existing natural fractures
4. Induced fractures connecting with abandoned oil and gas wells

If the pathways are present, fluids and/or hydrocarbon gases that were naturally occurring or which were injected into the oil and gas formation could mix with groundwater. In order to detect potential contamination, the concentration of potential contaminants flowing from the hydrocarbon-bearing formation into the groundwater aquifer must be higher than the concentration of the same pre-existing chemicals in the groundwater aquifer. Additionally, the potential contaminant must enter the aquifer at a rate that is greater than the groundwater flow rate, or else the contaminant would be diluted to a level that is not different from the pre-existing background water quality. Although expected concentrations are compared in this report, groundwater flow modeling is outside the scope of the analysis presented here.

Mixing of petroleum-hydrocarbon gases, such as methane, in an aquifer can be detected through measurements of total organic carbon. However, carbon-13 (^{13}C) isotopes have been used in numerous cases to detect contamination from hydrocarbons. A description of how ^{13}C isotopic signatures are measured is provided in Appendix II. The change in concentration of ^{13}C isotopes in an aquifer can help to determine whether gas found in the aquifer was sourced from a specific formation that was explored for natural gas. Although this test provides a useful indication of whether contamination was caused by oil and gas development activities, without a strong dataset of background carbon isotope values it is difficult to prove whether the post-drill $\delta^{13}C$ concentrations matching those found in a shale formation were pre-existing or not.

Categories

The case studies that are described below list potential groundwater quality parameters that can be used to detect potential contamination from oil and gas development. Those parameters have been grouped into the following seven categories:

1. Gas hydrocarbons
2. Liquid hydrocarbons
3. Salts
4. Metals
5. Radionuclides
6. Volatile organic compounds (VOC)
7. Polycyclic aromatic hydrocarbons (PAH)

The complete list of parameters attributed to each category can be found in Appendix III, Table 20. A characterization of the data available for these parameters, their efficacy for the intended purpose, their known health effects, and costs of testing each parameter will be described in the results section. All of this information is used to generate a list of the most essential baseline groundwater quality parameters for the Eagle Ford shale region and to support recommendations for future testing initiatives.

[5] Cited in Sumi, L. (2005). Our Drinking Water at Risk. Durango, CO, Oil and Gas Accountability Project,.

Case Studies

In the past decade, several prominent studies have linked groundwater quality changes to potential migration of hydraulic fracturing fluids, produced water, and/or petroleum hydrocarbons into aquifers. The results of these studies were questioned, however, because baseline water quality data was not available for a comparison with potentially contaminated groundwater samples. The cases described here are used to generate a list of potential baseline groundwater quality testing parameters for the Eagle Ford shale region. This discussion is not intended to provide a comprehensive analysis of all cases of potential groundwater contamination that have been linked to hydraulic fracturing. Rather, these cases point to the complex nature of proving contamination through the scientific process, and the need for more baseline ground water quality testing of specific chemicals.

i. Emergency Administrative Order: Range Resources (EPA 2010)

In the summer of 2010 the EPA issued an emergency order to Range Resources Company to investigate and remediate contamination of two domestic water wells lying within the Barnett shale in Parker County, Texas (Environmental Protection Agency 2010). Private tests, RRC tests, and EPA tests of one water well indicated that concentrations of volatile organic compounds (VOC) and gas hydrocarbons including benzene[6] (C_6H_6), toluene (CH_3), propane (C_3H_8), hexane (C_6H_{14}), ethane (C_2H_6), and dissolved methane (CH_4) were present (Wilson, Sumi et al. 2011). Tests by the RRC showed benzene and toluene levels in excess of federal Maximum Contaminant Levels (MCL) for drinking water (Environmental Protection Agency 2012a; Environmental Protection Agency 2012b). Subsequent tests by the EPA returned lower values than the RRC found, however toluene concentrations were still above the MCL. Additionally, the EPA's analyses of methane isotopes ($\delta^{13}C–CH_4$ and $\delta D–CH_4$) in the water well returned values nearly identical to the isotopic signature of methane and hydrogen that was produced from two nearby gas wells, as seen in Table 1 (Environmental Protection Agency 2010).

TABLE 1 EPA ISOTOPIC FINGERPRINT ANALYSIS OF ALLEGEDLY CONTAMINATED DOMESTIC WELL IN PARKER COUNTY, TEXAS COMPARED TO COMMINGLED GAS FROM THE BUTLER AND TEAL GAS WELLS.

	Domestic water well	Natural Gas well
$\delta^{13}C–CH_4$	-47.05	-46.60
$\delta D–CH_4$	-188.5	-183.9

Critics of the EPA's actions toward Range Resources state that the gas was pre-existing, and that no lack of wellbore integrity was found, implying that there was no possible way for the fluid and gas migration to have occurred as a result of Range Resources' activities (Smitherman and Porter 2012). Background water quality data for the hydrocarbons found in the investigation may have allowed a more robust conclusion. As such, this analysis includes a characterization of known background concentrations for the following VOC and gas hydrocarbons:

[6] Benzene, toluene, ethylbenzene, and xylene (BTEX) are volatile organic compounds (VOCs) which are generally known to occur in oil and gas formations. BTEX are also found in diesel fuel, which is sometimes used in hydraulic fracture treatments. Source: Leusch, F. and M. Bartkow (2010). A short primer on benzene, toluene, ethylbenzene and xylenes (BTEX) in the environment and in hydraulic fracturing fluids. G. University and S. W. R. Centre.

Category	Potential baseline chemical analytical parameter
Gas hydrocarbons	Methane Ethane Propane Hexane
VOC	Benzene Toluene

ii. Investigation of Ground Water Contamination near Pavillion, WY (EPA 2011)

The EPA recently issued a draft report analyzing results from alleged cases of contamination in Pavillion, WY (Environmental Protection Agency 2011). In this study, the EPA performed tests for an extensive list of water quality parameters. Categories describing these parameters are listed below.

- Major anions and alkalinity
- Semi-Volatile Organic Compounds (sVOC)
- Pesticides
- Polychlorinated Biphenyls (PCB)
- Total Inorganic Carbon (TIC)
- Metals
- Gasoline Range Organics (GRO)
- Diesel Range Organics (DRO)
- Total petroleum hydrocarbons (TPH)
- Total phase-separated hydrocarbons
- Alcohols and Volatile Organic Compounds (VOC)
- Bacteria
- Low molecular weight acids
- Fixed gas isotopes

Elevated levels of methane and DRO were found in domestic water wells in the vicinity of natural gas wells in Pavillion, WY (Environmental Protection Agency 2011). The EPA installed two monitoring wells into the groundwater aquifer in order to determine the presence of potential contaminants in the aquifer. Tests of the two monitoring wells found VOC, synthetic compounds, and components of compounds that had been used in hydraulic fracturing at the site (Appendix III, Table 20).

The EPA concluded that leaching from hydraulic fracturing fluid disposal pits and possibly leaks in the wellbore cement casing had allowed contaminants to migrate to the aquifer. Critics have asserted that the EPA's conclusions were based on limited data and that installation of the monitoring wells may have been the sources of contamination that the EPA found (Railroad Commission of Texas 2012).

Not surprisingly, the final paragraph of the EPA draft investigation of Pavillion, WY states:

> *"Collection of baseline data prior to hydraulic fracturing is necessary to reduce investigative costs and to verify or refute impacts to groundwater…this investigation supports recommendations made by the U.S. DOE Panel on the need for collection of baseline data, greater transparency on chemical composition of hydraulic fracturing fluids, and greater emphasis on well construction and integrity requirements and testing."*

This conclusion arises from speculation that the organic and inorganic contaminants found at the site might be expected to occur naturally, considering that the region has been targeted for oil and gas exploration (U.S.

Energy Information Administration 2010). Such speculation underscores the importance of baseline testing. However, testing for all of the categories described above is not necessary. From the list of testing categories described above, sVOC, TIC, Pesticides, PCB, bacteria, and low molecular weight acids were not included in this analysis, but the other parameters are included. Reasons for omitting these parameters from the analysis are explained below.

First, sVOC are an indication of the presence of dispersed oil droplets in water (Neff, Sauer et al. 2011). While a test for sVOC would provide an indication of the presence of petroleum hydrocarbons in water, VOC are non-essential parameters for baseline groundwater quality testing if petroleum hydrocarbons are tested in other ways.

Next, TIC is a category that is used to detect products of chemical interactions between produced water and groundwater (Environmental Protection Agency 2011). TIC includes parameters such as bicarbonate (HCO_3^-) and calcite ($CaCO_3$). Bicarbonate is characterized in this analysis, but only in the context of an expected change in concentration if produced water breaches an aquifer. TIC, including $CaCO_3$, are not considered as parameters in this analysis, because a baseline groundwater quality analysis only needs to look for pre-contamination constituents, rather than examining expected products of chemical interactions between the potential contaminants and background water components.

Finally, Pesticides, PCB, bacteria, alcohols and low molecular weight acids are not included in the categories that will be characterized in this report, because they either represent potential contamination from sources other than oil and gas; or these parameters would provide non-essential supporting evidence of contamination that can be determined more simply by a sample's comparison with the one or more of the other essential baseline water quality parameters.

Considering these factors, this analysis includes a characterization of known background data availability, and some background concentrations, for the following parameters which correspond to the seven categories previously listed[7]:

Category	Potential baseline chemical analytical parameter
Gas hydrocarbons	Fixed gas isotopes (carbon isotopes)
Liquid hydrocarbons	Total Petroleum Hydrocarbons (TPH) Gasoline Range Organics (GRO) Diesel Range Organics (DRO)
Salts	Major anions and alkalinity (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, F^-, NO_3^-)
Metals	Al, Ag, B, Ba, Be, Ca, Co, Fe, K, Mn, Mo, Na, Sb, Sr, Ti, Zn, S, P, As, Cd, Cr, Cu, Hg, Ni, Pb, Se, U
VOC	Benzene, toluene, ethylbenzene, xylene (BTEX)

iii. Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing (Osborn et al. 2011)

One example of the difficulty that is presented in using $\delta^{13}C$ isotope concentrations for determining whether groundwater contamination occurred is offered by Osborn et al. (2011) and Molofsky et al. (2011). Osborn et al. (2011) found a correlation between the concentrations of dissolved methane found in domestic water wells and the proximity of those water wells to hydraulically fractured natural gas wells. The researchers

[7]Analytical parameters described here are based on those tested in the Pavillion, WY EPA Investigation.

concluded that water wells within 1 km of a hydraulically fractured natural gas well were more likely to have high concentrations of methane in their water wells, sometimes dangerously high, and that this contamination may have been caused by shale gas extraction (Osborn, Vengosh et al. 2011). Table 2 lists the tests that were used to reach this conclusion. Among the tests used, carbon isotopic values for methane ($\delta^{13}C\text{-}CH_4$) indicated that methane sourced from the Marcellus shale was present in high concentrations in water wells that were in close proximity to hydraulically fractured natural gas wells.

TABLE 2 ANALYTICAL TESTS USED BY OSBORN, ET AL. (2011) TO DETECT POTENTIAL GROUNDWATER CONTAMINATION CAUSED BY SHALE GAS EXTRACTION.

Test	Purpose	Conclusions of Osborn et al.
Methane, ethane, and propane isotopes and concentrations	Indicates whether gas contamination is present Isotopes, and ethane/propane ratios help to determine the source of the gas	Isotopic signature of the methane found in the water wells matched the isotopic fingerprint of gas from the Marcellus formation, indicating that contamination had occurred; presence of ethane and propane in the ratios found supports the conclusion that gas migrated from the shale.
$\delta^{13}C$-DIC, $\delta^{18}O$, and $\delta^{2}H$	Indicators of microbial methane	No positive correlation between $\delta^{13}C$-DIC and $\delta^{13}C\text{-}CH_4$, indicating that methane was not formed by microbes. No correlation between $\delta^{2}H$ found in water and $\delta^{2}H$ found in methane at the site, indicating that the methane was not formed in the shallow aquifer; $\delta^{18}O$ composition was of modern meteoric origin, indicating that it did not come from an older, deeper formation.
$\delta^{11}B$, $\delta^{226}Ra$ **Major cations (Na^{+}, Ca^{+2}, Mg^{+2})** **Major anions (Cl^{-}, Br^{-}, NO_3^{-} SO_4^{-2})** **Trace metals** **Alkalinity as HCO_3^{-}**	Additional indicators of potential mixing with deep formation waters	Samples matched background data, therefore no contamination from formation fluids could be verified.

Molofsky et al. (2011) have questioned the conclusions of Osborn et al. (2011) that higher concentrations of methane in water wells near natural gas wells indicated that contamination had occurred after drilling. Rather, Molofsky et al. (2011) contended that water wells positioned in valleys tend to have higher concentrations of methane than water wells in uplands. Therefore, they posit that this relationship may have skewed the results of Osborn et al. (2011). Additionally, they questioned the interpretation that the isotopic signatures of methane found in the water wells were sourced from the Marcellus shale, and offered an interpretation that suggested the methane was from a separate nearby formation. Nonetheless, Molofsky et al. (2011) cite the need for background isotopic data in order to determine if potential contamination has occurred as a result of gas extraction and production (Molofsky, Connor et al. 2011).

Taking this into consideration, baseline groundwater testing of carbon isotopes is an essential tool for assessing whether oil and gas drilling activities have affected an aquifer. Contrastingly, parameters that are non-essential for baseline groundwater quality testing are water isotopes ($\delta^{18}O$ and $\delta^{2}H$) and boron isotopes ($\delta^{11}B$). Water and boron isotopes are used with concentrations of $\delta^{13}C$ isotopes as additional supporting evidence that defines which formation the hydrocarbons were sourced from (Osborn, Vengosh et al. 2011); therefore, knowing the concentration of water and boron isotopes is non-essential if $\delta^{13}C$ concentrations from a background water quality test are available for comparison to a potentially contaminated sample of water. As such, the following parameters are considered in this analysis:

Category	Potential baseline chemical analytical parameter
Gas hydrocarbons	Methane Ethane Propane Carbon isotopes
Salts	Major cations and anions (Na^{+}, Ca^{+2}, Mg^{+2}, Cl^{-}, Br^{-}, NO_3^{-} SO_4^{-2}) Alkalinity as HCO_3^{-}
Metals	Trace metals, although not listed in Osborn et al. (2011) or supplemental information, this category corroborates that metals should be tested.

iv. Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources (EPA 2011)

The EPA is currently conducting a study on the potential impacts of hydraulic fracturing on drinking water resources (Office of Research and Development 2011). In an attempt to be comprehensive, the final study plan contains a list of chemicals found in hydraulic fracturing fluids and flowback water that spans 25 pages. The list is long primarily due to the extensive number of potential chemicals that have been or will be used in hydraulic fracturing at the sites considered in the study.

Due to the expense of testing so many parameters, the EPA has selected five retrospective case studies out of a list of 45 nominated cases, and two prospective case studies out of a list of seven possible candidates[8]. The retrospective case studies will examine cases where hydraulic fracturing was alleged to have caused groundwater contamination, and in the prospective case studies the EPA will examine sites where drilling has not yet occurred. The prospective case studies will allow the EPA to gain understanding of all possible pathways of contamination and how to detect when contamination has occurred if that is the case.

The EPA plan to study the potential impacts of hydraulic fracturing on drinking water resources points out that interferences can complicate analytical approaches used to characterize samples associated with hydraulic fracturing:

> *"Some gases and organic compounds can partition out of the aqueous phase into a non-aqueous phase (already present or newly formed), depending on their chemical and physical properties. With the numbers and complex nature of additives used in hydraulic fracturing fluids, the chemical composition of each phase depends on partitioning relationships and may depend on the overall composition of the mixture. The unknown partitioning of chemicals to different phases makes it*

[8] The rationale behind the EPA's selection of case studies is available in their report titled "Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources" and will not be discussed here.

difficult to accurately determine the quantities of target analytes. In order to address this issue, EPA has asked for chemical and physical properties of hydraulic fracturing fluid additives in the request for information sent to the nine hydraulic fracturing service providers." (EPA 2011, p.166)

These complications are illustrative of the challenge that landowners and agencies are faced with in conducting post-drill water quality testing for the purpose of detecting potential contamination from oil and gas drilling, extraction, production, and waste storage activities. Although the EPA has access to the list of chemical and physical properties of hydraulic fracturing fluid additives from these nine service providers, this kind of information is not publically available for all wells in the United States. Even Texas' landmark disclosure bill passed in the summer of 2011, H.B. 3328, allows oil and gas companies not to disclose chemicals considered to be trade secrets[9] (H.B. 3328, 2011). Additionally, a well operator is not required to disclose the list of chemicals used in the hydraulic fracturing treatment until after the well has been completed. Therefore, if a hypothetical landowner in Texas desires to test her water well for hydraulic fracturing fluid components before drilling takes place, she must choose her baseline groundwater quality tests using a general list of hydraulic fracturing fluids known to have been used in her region. Testing for region-based hydraulic fracturing fluids would not only be expensive, but it might also be irrelevant since hydraulic fracturing fluid mixtures vary from well to well and because chemical formulas for hydraulic fracturing fluids are constantly changing. Based on this reasoning, baseline groundwater quality testing would be greatly enhanced if oil and gas well drillers conducted the tests before drilling using a list of parameters tailored to the hydraulic fracturing fluid mixture that is used at each site.

The list of intended testing parameters, not including hydraulic fracturing fluids, for the EPA's prospective case studies is provided in Table 3.

TABLE 3 EPA TIER 2 INITIAL TESTING: SAMPLE TYPES AND TESTING PARAMETERS (OFFICE OF RESEARCH AND DEVELOPMENT 2011)

Sample Type	Testing Parameters
Surface and ground water	• General water quality parameters (e.g., pH, redox potential, dissolved oxygen, TDS) • General water chemistry parameters (e.g., cations and anions, including barium, strontium, chloride, boron) • Metals and metalloids (e.g., arsenic, barium, selenium) • Radionuclides (e.g., radium) • Volatile and semi-volatile organic compounds • Polycyclic aromatic hydrocarbons
Soil	• General water chemistry parameters • Metals • Volatile and semi-volatile organic compounds • Polycyclic aromatic hydrocarbons
Produced water from waste pits or tanks where available	• General water quality parameters • General water chemistry parameters • Metals and metalloids • Radionuclides • Volatile and semi-volatile organic compounds • Polycyclic aromatic hydrocarbons • Fracturing fluid additives/degradates

Out of the parameters listed for groundwater in Table 3, redox potential and dissolved oxygen will not be

[9] Landowners, neighbors and agencies are allowed to challenge a trade secret provision within two years from the date the well completion report is filed.

considered in this analysis because neither would provide definitive evidence of contamination if concentrations with a potentially contaminated sample were compared with background water quality. Rather, both redox potential and dissolved oxygen are non-essential parameters that serve to support conclusions drawn from other analyses. Additionally, sVOC are not considered for the same reason. Based on these decisions, the parameters listed below will be considered in this analysis.

Category	Potential baseline chemical analytical parameter
Salts	TDS
	Cations and anions
	Barium
	Strontium
	Chloride
	Boron
Metals	Arsenic
	Barium
	Selenium
Radionuclides	Radium
VOC	BTEX
PAH	Not reported

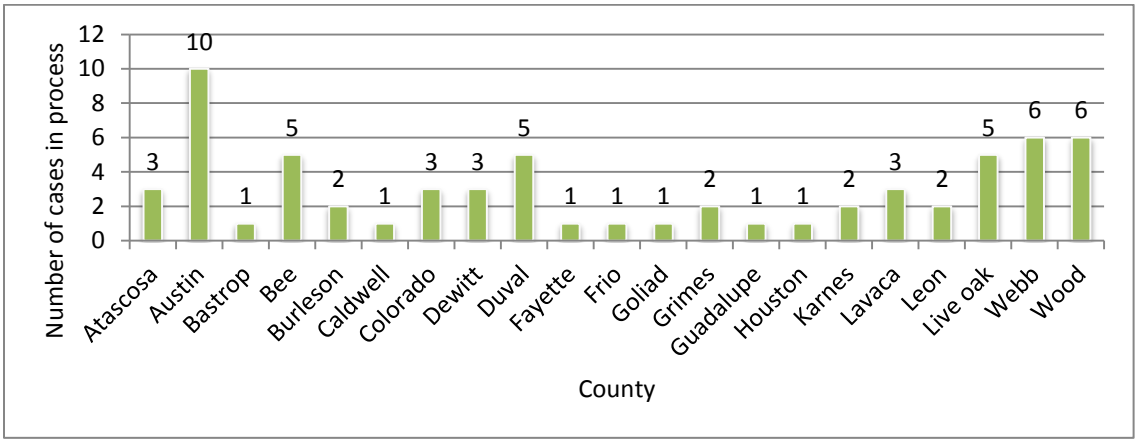
v. Reported Groundwater Contamination in the Eagle Ford shale region

The Railroad Commission of Texas (RRC) is the agency that has jurisdiction over contamination of groundwater associated with exploration, development, or production, including storage or transportation, of oil and gas (Texas Groundwater Protection Committee 2011). As a part of the Texas Groundwater Protection Council (TGPC), the RRC submits an annual compilation of all pending or completed cases of contamination[10] in the state of Texas (Texas Groundwater Protection Committee 2011). This is useful for determining which contaminants are expected and should be tested for in a baseline groundwater quality test.

Here, all of the cases reported by the RRC for the 35 counties of interest in the Eagle Ford shale region were compiled. However, cases of contamination were listed for only 21 out of the 35 counties (Figure 5). The counties with the most cases of contamination were Austin, Webb, Wood, Bee, Duval, and Lavaca. The counties in which no contamination was reported are depicted in Appendix IV, Figure 20.

[10] These cases represent incidents where "the detrimental alteration of the naturally occurring physical, thermal, chemical, or biological quality of groundwater" has occurred according to TAC, Title 31, Part 18, Chapter 601, Subchapter A, Rule §601.2.

FIGURE 5 NUMBER OF PENDING CASES OF GROUNDWATER CONTAMINATION ATTRIBUTED TO OIL AND GAS ACTIVITIES IN COUNTIES OF THE EAGLE FORD SHALE REGION IN 2010



Contaminants found in these cases are listed in Table 4, below. In compiling the reported cases for analysis, some reported contaminants were consolidated into one category that most accurately represented that contaminant (Appendix IV, Table 22). Out of the 64 cases of reported contamination, only four were new cases in the year 2010. The status of the case investigations can be found in Appendix IV, Figure 15.

TABLE 4 CONTAMINANTS REPORTED IN GROUNDWATER CONTAMINATION CASES ATTRIBUTED TO OIL AND GAS ACTIVITIES IN 2010 (TEXAS GROUNDWATER PROTECTION COMMITTEE 2011)

Contaminant	Count	EPA MCL
Liquid hydrocarbons	27	NA
BTEX	25	0 - 10 mg/l
Chlorides	7	250 mg/l*
Gas hydrocarbons	2	NA
Arsenic	1	0 mg/l
Barium	1	2 mg/l
Metals (not defined)	1	NA
Total	**64**	

*National Secondary Drinking Water Standard

BTEX chemicals and liquid hydrocarbons were the most frequent contaminants reported in 2010 (Table 4). Included in Table 4 are the EPA MCLs and Secondary Standards for each of the contaminants found in the counties of interest in the 2010 report[11]. However, it should be noted that no concentrations of the chemical contaminants are provided in the joint report. Therefore, no comparison can be made between an expected concentration that would be found in the shale formation and the expected concentration that would be found in groundwater. Nonetheless, out of the list of potential contaminants in Table 4, all are included in this analysis, and are represented by the following parameters:

Category	Potential baseline chemical analytical parameter

[11] Potential hazards and human health effects attributed to each of these contaminants are discussed in the results section.

Gas hydrocarbons	Methane
Liquid hydrocarbons	Total petroleum hydrocarbons[12]
Salts	Chloride
	Sodium
Metals	Arsenic
	Barium
Radionuclides	Radium
VOC	BTEX
PAH	Not reported

II. Data and Methods

As stated in the introduction, the objectives of this analysis are (1) to determine whether existing baseline groundwater quality data in the Eagle Ford shale region is adequate to provide a baseline for comparing to potential future contamination from oil and gas drilling, and (2) to define an appropriate and cost-effective list of parameters that would aid in strategic planning of baseline groundwater quality testing in the Eagle Ford shale region for the same goal. To achieve these objectives, a list of essential parameters was established first, using the case studies described in the previous section. Second, using the list of essential parameters, the available groundwater data for those contaminants in the counties of interest is described; when possible, this data is compared to concentrations of the same parameters known to occur in the Eagle Ford shale formation. Finally, recommendations for testing efforts are made based on data needs, whether health effects are known to occur for each parameter, and the cost of each test.

In characterizing the baseline data available for each county, the number of samples available in each county is given for each parameter, and general statistical principles are used to determine whether enough samples are present. If an EPA Maximum Contaminant Level (MCL) or Secondary Standard[13] for drinking water has been set for the parameter of interest, a map was drawn depicting the known concentration at each sample location. Additionally, maps are depicted for selected parameters of interest that have not been assigned an MCL or Secondary Standard by the EPA, but which are particularly useful in detecting potential contamination.

In order to define which general chemistry parameters would be the best indicators of an influx of flowback or hydrocarbons into a groundwater well, chemical concentrations from the USGS Produced Waters database were statistically compared to groundwater quality for the counties of interest. This allowed for some chemical tests to be removed from the list of recommended tests because the parameters are neither

[12] TPH encompasses all of the contaminants listed in Appendix IV, Table 29.

[13] Maximum Contaminant Levels (MCLs) are "National Primary Drinking Water Regulations (NPDWRs or primary standards) are legally enforceable standards that apply to public water systems." and "National Secondary Drinking Water Regulations (NSDWRs or "secondary standards") are non-enforceable guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water. EPA recommends secondary standards to water systems but does not require systems to comply."
Environmental Protection Agency. (2012, March 6, 2012). "List of Contaminants & their MCLs." Drinking Water Contaminants Retrieved March 13, 2012, 2012, from http://water.epa.gov/drink/contaminants/index.cfm.

dangerous to human health nor are they expected to cause a substantial change in concentration when mixed with groundwater.

In addition to comparisons made between the TWDB groundwater database and the USGS produced waters database, a systematic literature review was conducted to determine whether additional potential contaminants that might be found in the Eagle Ford shale. Additionally, this served to establish expected concentrations for known contaminants expected to occur in the Eagle Ford formation. Although the results of this attempt were generally not substantial enough to use in a statistical comparison with groundwater, some references that were found in this process are used throughout the sections to support various findings. The lack of findings in this attempt demonstrates that more publically available data is needed about the produced water chemistry of the Eagle Ford shale formation.

Finally, quotes were requested from all laboratories listed by the Texas Commission on Environmental Quality (TCEQ) as certified to test samples in the drinking water category in the state of Texas. These 83 labs[14] are certified under the National Environmental Laboratory Accreditation Program (NELAP). Twenty of the 83 labs replied to the request. These data are used qualitatively to make general recommendations about whether organizations or landowners should be expected to conduct a sampling effort. For more expensive tests, it might be less likely that landowners will actively pursue a water analysis for those tests. For this reason, a strategic sampling effort in regions that have less publically available information on these more expensive analytes might best be taken on by an agency, industry, or other organizations.

Produced Water Data

Produced water can be defined as the water that is naturally occurring in the formation where oil and gas exploration occurs. During the production phase of an oil and gas well, produced waters flow out of the well, along with hydraulic fracturing fluids that were used in the well, and any hydrocarbons present in the formation. Produced water contains a variety of chemicals that occur naturally in a formation. Since produced water is known to occur in the Eagle Ford shale formation at moderate to high volumes(Lai 1997; Hsu and Nelson 2002; Mullen 2010; Mullen, Lowry et al. 2010)[15], it is conceivable that if a pathway between a hydrocarbon-bearing formation and an aquifer exists, then produced water chemistry would cause a change in chemical concentrations found in the aquifer. A comparison between the chemistry of produced water and the chemistry of groundwater in the counties of interest is used to identify which chemical parameters are expected to be the most different, and will therefore serve as good indicators of contamination.

The USGS provides a database of concentrations of general chemistry parameters for produced waters from multiple formations in each state (Breit, Skinner et al. 2006). Procedures used to prepare the dataset for analysis are listed in Appendix V. The information contained in the database was offered voluntarily by various companies (U.S. Geological Survey 2002). Only 36 records were available for the Eagle Ford formation, although 1606 records were available for other formations in the counties of interest. The

[14] Some labs were not considered if they did not test any of the chemicals of interest for this report (e.g. if the lab only tested for total coliforms).

[15] According to Lai (1997), Hsu and Nelson (2002), Mullen 2010, and Mullen, Lowry et al. (2010), the average water content of the Eagle Ford shale formation is 16 to 19 percent. Additionally, Mullen, Lowry et al. (2010) reported a case where high water volumes in the Eagle Ford shale at depths of 15,230 feet prevented flow of gas from the well.

samples for the Eagle Ford formation were taken between the years of 1951 and 1975, while samples for other formations in the counties of interest were taken between 1929 and 1980.

Water quality parameters that are provided in both the produced waters database and the groundwater database include:

- pH
- Bicarbonate
- Calcium
- Chloride
- Magnesium
- Potassium
- Sodium
- Sulfate
- TDS

Nonetheless, using this dataset for the Eagle Ford shale formation may not be an accurate representation of Eagle Ford shale produced water chemistry in other counties, because all of the data representing the Eagle Ford formation are from wells drilled in Wood County[16]. This is problematic, since Wood County is not currently in the active drilling area of the Eagle Ford shale. This fact raises doubts about whether the data that was labeled as "Eagle Ford" in the USGS produced waters dataset is still considered to be from a formation that is within the boundaries of the Eagle Ford formation.

As it turns out, the samples taken for Wood County represent depths ranging from 4200 feet – 5800 feet. Although oil and gas wells have recently been drilled in Wood County at those depths, the wells are categorized in the Woodbine and Sub-Clarksville formations[17]. The Sub-Clarksville formation underlies the Eagle Ford (Holbrook 1985), but the Woodbine formations and Eagle Ford are undivided in portions of northeast Texas (U. S. Geological Survey ; Condon and Dyman 2006)[18]. Therefore, although the produced waters data for the Eagle Ford are in fact representing the Eagle Ford formation, the fact that portions of the Eagle Ford and Woodbine are undivided could mean that Eagle Ford produced water samples are chemically different in Wood County compared to counties in the active drilling area.

Although a statistical comparison of produced waters and groundwater in Wood County is described in this analysis, it should be understood that a high level of uncertainty is embodied in the analysis. More produced water data is needed for the active drilling area in order to draw a relevant and accurate comparison between Eagle Ford shale produced water and groundwater in the counties of interest.

In order to understand, in a general sense, how produced water chemistry differs from groundwater chemistry, data from other formations in the counties of interest was compared to groundwater chemistry in the counties of interest. Such an analysis is useful for guiding future research, but more chemical data from Eagle Ford produced water is still needed to learn which parameters will be most useful for baseline testing in the active drilling region.

In addition, other sources provide some indication of expected elements in the Eagle Ford formation, but the only available data is for core samples. Kearns (2011) provides geochemical analysis of Eagle Ford core samples for major elements, trace elements, and isotopes. This data is described further in appendix V.

[16] One record in the Eagle Ford shale was documented in Houston County, but this record was not used to allow for a simpler comparison of Wood County produced water and groundwater data.
[17] The RRC approved 55 drilling permits for Wood County wells from 01/01/2009 to 01/01/2012, and six of those wells were within the depth range of 4200 – 5800 feet. Records on the Railroad Commission W-1 Permit Application database indicate that these wells were drilled into a Sub-Clarksville and Woodbine formation.
[18] Eagle Ford stratigraphy is shown in Appendix VI, Figure 20.

Other sources indicate the presence of sulfur (S), nickel (Ni), vanadium (V), aluminum(Al), iron (Fe), calcium (Ca), silicon (Si), and zircon(Zi) in core samples(Comet, Rafalska et al. 1993; Mullen 2010). Although this information could guide future research, it is not as useful for comparing to liquid concentrations since the solubility of the elements in the core samples is unknown. However, values of $\delta^{13}C$ isotopes in the Eagle Ford provided by Kearns (2010) and Comet (1993) could be useful for a comparison with groundwater $\delta^{13}C$ isotopes. This comparison is described in the results section.

Groundwater Data

Data from the Texas Water Development Board's (TWDB) groundwater quality database[19] was used to determine if enough samples are available to establish a reliable distribution of potential baseline concentrations, where comparisons can be made between baseline groundwater quality and groundwater samples that have potentially been contaminated by oil and gas activities. Additionally, as mentioned above, the groundwater quality data was compared to produced water concentrations when possible to determine which chemicals in each county exhibit the greatest differences and are therefore more likely to serve as a reliable indicator of contamination.

Table 5 depicts the number of samples available for each county in the Eagle Ford shale region. The samples were taken between the years of 1988 and 2011. Additionally, the number of samples taken with reliable methods, the number of individual wells that are represented in the pools of samples, and the number of wells with more than one sample are provided. Not depicted in the table are the total numbers of groundwater wells recorded by the TWDB for each county, but this information is included in each data availability table as needed (Table 16 and Appendices X through XIV). The total number of groundwater wells for each county of interest is a count of state well numbers listed in the TWDB "Well Location Shapefile" (TWDB GISa; TWDB GISb).

Parameters such as those listed in Table 5 can be assessed with statistical principles to determine if the number of wells that have been sampled is adequate to define reliable mean concentrations for each parameter in the region. As such, power analysis was used for each parameter in each county of interest to determine the statistical power of the sample size with a pre-defined effect size (ES) and significance level (α)[20]. A larger statistical power indicates greater accuracy (Cohen 1992), and a power of 0.80 is recommended[21]. Cohen (1992) uses a calculation that recommends between 26 and 38 samples for a power of 0.80, allowing a large effect size and $\alpha = 0.05$ or 0.01 for the difference in means, respectively.

Notably, Caldwell and Guadalupe Counties have the fewest number of samples. Additionally, counties with less than 26 wells that have been sampled (out of those with reliable samples) include Guadalupe, Caldwell, Madison, Dewitt, McMullen, Washington, Fayette, and Bee. Adding to that list, those counties with fewer than 38 samples include Goliad, Austin, Karnes, Grimes, Lee, Leon, Houston, and Wood. . Contrastingly, the counties with the strongest statistical power, containing more than 26 individual water wells that also have more than one sample attributed to the well are Atascosa, Duval, Frio, Gonzalez, LaSalle, Webb, and Zavala.

A list of each general water chemistry parameter found in the database is provided in Appendix VIII. Additionally, the TWDB database contains EPA STORET data with concentrations of infrequent constituents. Over 270 different infrequent constituents are listed in the data base (see Appendix IX). Selected constituents are described in forthcoming sections of this analysis, as they relate to detecting contamination from oil and gas activities.

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[19] TWDB Groundwater Database available at: http://www.twdb.state.tx.us/groundwater/data/gwdbrpt.asp

[20] In this case, ES is zero when there is no difference between a given sample and the distribution mean for the sample size being considered. ES ranges infinitely upward from zero when the residuals are not equal to zero Cohen (1992). Therefore, a small ES renders a more precise statistical value. Additionally, alpha (α) refers to the probability of falsely rejecting the null hypothesis.

[21] Cohen (1992) chose the value 0.80 as the optimal power, because a greater power would require an infeasible sampling effort, and a lower number would increase the chance of a false prediction too greatly.

TABLE 5 NUMBER OF SAMPLES AVAILABLE IN THE TWDB GROUNDWATER DATABASE FOR GENERAL WATER QUALITY PARAMETERS IN EACH COUNTY OF THE EAGLE FORD SHALE REGION.

County	Records in database	Individual wells	Records with reliable sampling methods	Individual wells with reliable samples	Wells with multiple reliable samples	Youngest record in reliable samples	Oldest record in reliable samples
Atascosa	784	370	182	87	49	2010	1990
Austin	214	104	68	27	16	2009	1992
Bastrop	563	266	84	38	18	2010	1988
Bee	387	243	44	25	11	2009	1990
Brazos	395	222	73	45	18	2010	1992
Burleson	455	297	85	60	16	2011	1992
Caldwell	410	273	26	14	7	2011	1992
Colorado	394	155	108	44	22	2009	1988
Dewitt	357	243	40	17	8	2009	1988
Dimmit	414	198	100	54	24	2010	1990
Duval	452	247	129	75	32	2009	1990
Edwards	166	70	81	42	20	2011	1993
Fayette	615	337	60	24	15	2010	1988
Frio	486	239	143	81	34	2010	1990
Goliad	263	185	42	27	9	2009	1990
Gonzales	588	244	277	68	40	2011	1988
Grimes	292	225	41	30	7	2009	1992
Guadalupe	239	170	18	10	3	2010	1992
Houston	204	95	82	33	21	2010	1993
Karnes	496	356	43	28	10	2009	1988
LaSalle	276	119	85	43	27	2010	1990
Lavaca	204	115	103	49	17	2009	1992
Lee	257	149	74	32	10	2011	1989
Leon	175	74	75	32	21	2010	1992
Live Oak	212	115	65	39	18	2009	1990
Madison	109	41	38	17	11	2011	1993
Maverick	92	72	66	56	9	2002	1992
McMullen	188	70	48	19	13	2010	1992
Milam	379	192	79	39	19	2010	1988
Robertson	529	352	97	48	22	2011	1989
Washington	324	246	38	22	10	1992	2009
Webb	254	115	127	67	35	2010	1989
Wilson	438	185	100	50	24	2010	1990
Wood	326	203	55	35	13	2010	1989
Zavala	563	230	115	62	31	2011	1988
Totals	**10329**	**5555**	**2503**	**1240**	**569**		

Geospatial Analysis

Maps depicting the concentration of selected groundwater quality parameters at each well site were created using a graduated color scheme for each concentration range (see Appendix V for procedures used). It is possible to interpolate water concentrations across the region for spaces where no water quality data was available. However, this kind of analysis was not attempted because even simple water chemistry parameters such as total dissolved solids (TDS) exhibited cases of regional heterogeneity across short distances of the landscape (Appendix XI, Figure 19). Therefore, a regional interpolation may imply that concentrations can be predicted, but true concentrations could still vary significantly from the mean. For this reason, it may also not be reasonable to assume that counties with a quantity of samples exhibiting strong statistical power are able to predict the concentration of various chemical parameters in their region. This point serves to encourage additional sampling when possible, considering that the mass of samples already compiled only serves to establish a potential range of concentrations, whereas concentrations that vary significantly from the mean could occur in any water well.

III. Results

The purpose of characterizing the baseline is to determine which chemical parameters are already well construed across the landscape, and to identify geographic regions and chemical parameters where testing efforts should be focused. Earlier, certain counties were highlighted as having particularly few groundwater samples recorded in the TWDB database, while others were highlighted as having a statistically acceptable number of samples. Although records may exist in the TWDB database for the specified number of wells, not every well owner has conducted all of the baseline groundwater quality tests that are necessary for comparison with a potentially contaminated sample. Therefore, although some counties may seem to have enough samples recorded in the TWDB database, closer inspection may reveal deficiencies in baseline groundwater quality data.

Additional analysis described below uses the USGS produced waters database and geochemical concentrations found in the literature for the Eagle Ford shale, to compare concentrations of various chemical parameters to groundwater chemical concentrations. This analysis helped to determine which parameters are likely to show changes in groundwater concentrations if an influx of produced water occurs. As discussed earlier, high levels of uncertainty are embedded in the produced waters dataset, but a broad comparison of produced water and groundwater is presented in section C, below. More data is needed to develop an accurate comparison, but the data presented here serve as a useful guide for future research.

Testing priority codes

For most of the categories that follow, codes are used to describe whether increasing the number of samples for a particular parameter should be a high priority each county. The codes used are based on the number of samples required by power analysis to achieve a power of 0.80, as described in the Groundwater Data section. For counties with less than 26 samples of a particular parameter, the code "T" is used to recommend that testing be a high priority. In this situation, a region-wide testing initiative is strongly recommended to enhance the baseline dataset. For counties that have between 26 and 38 samples, the code "R" is used to indicate that testing is recommended. In this situation, testing initiatives are recommended to enhance the baseline dataset. Finally, for counties that have more than 38 samples, the code "A" is used to indicate that testing should take place as needed. In this situation, testing initiatives are not necessary, but those interested in the water quality of a specific well that has not yet been tested should understand that the groundwater chemistry of the well could vary significantly from the baseline even if more than 38 samples exist for a given county; if financially possible, testing is recommended.

A. Gas Hydrocarbons

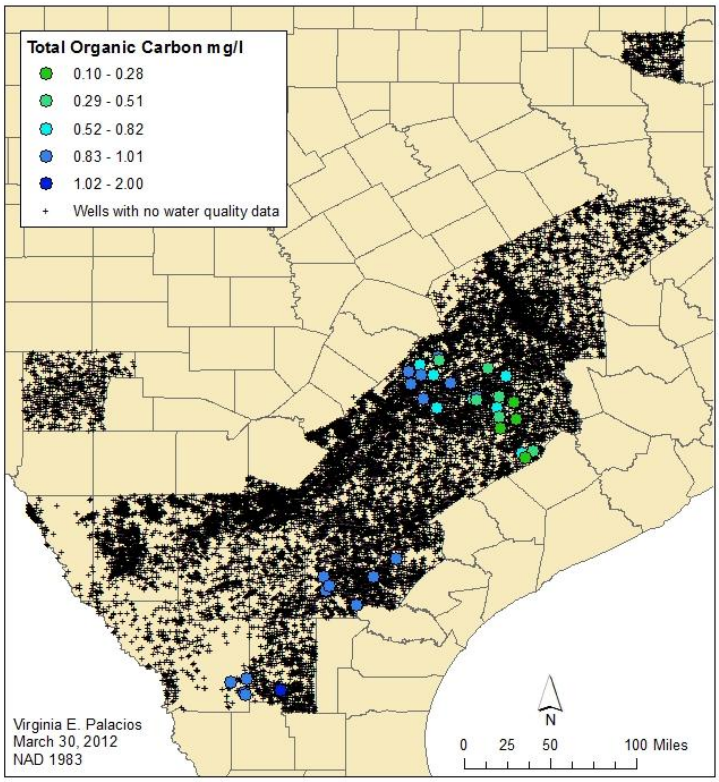
Baseline characterization

Natural gas is made up mostly of methane (CH_4), but may include hydrocarbon gases such as propane (C_3H_8), hexane (C_6H_{14}), and ethane (C_2H_6) (Union gas 2012). No samples for methane, ethane, propane, or hexane were available in the Texas Water Development Board groundwater quality database. However, all of these cases contain organic carbon. Therefore, a test for total organic carbon (TOC) would encompass measurements for these gases in a baseline water quality test.

Out of the 35 counties examined, eight counties have samples for total organic carbon (TOC), and 13 counties have samples for $^{13}C/^{12}C$ stable isotope ratios. Appendix X, Table 23 depicts the total number of samples of each of these constituents that are found in the sixteen counties for which samples of these parameters are available.

Although the total number of samples known to exist in the entire Eagle Ford shale region conforms to the power analysis guidelines presented by Cohen (1992), a map depicting the sample locations (Figure 9) indicates that most of the region lacks geographically relevant samples for TOC. More samples taken over a broader geographic region are recommended to help verify whether hydrocarbons are pre-existing in certain water wells.

FIGURE 6 TOTAL ORGANIC CARBON CONCENTRATIONS IN THE COUNTIES OF INTEREST.



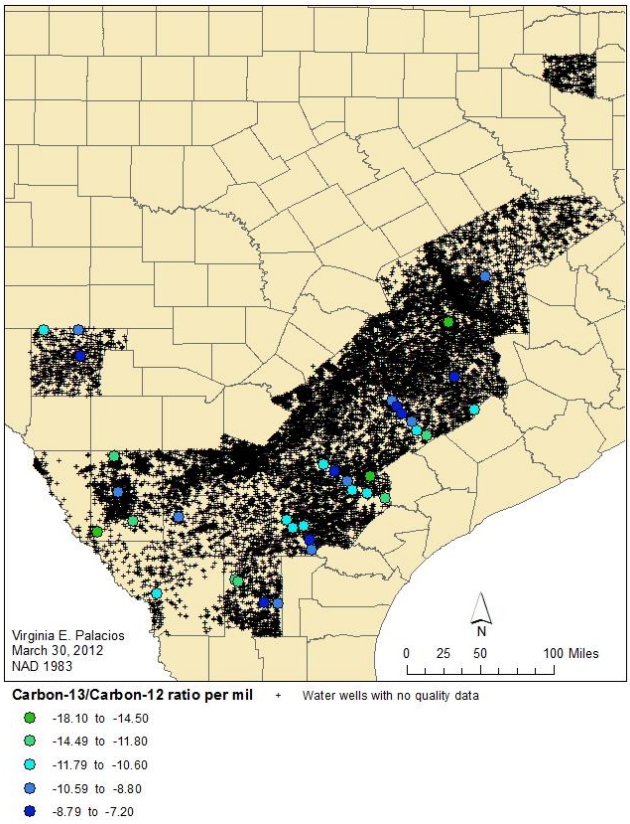
Testing for TOC over a broader geographic region is recommended, and would provide data necessary for comparing baseline water samples to those that are potentially contaminated from oil and gas. However, establishing this dataset will take time, and since heterogeneity in TOC concentrations might exist across the landscape a reading at any one well has a high probability of Type I or II error[22]. Simply put, the dataset is not yet large enough or well distributed enough to be able to accurately depict when a sample concentration is a true representation of what is expected. Therefore, as the dataset for TOC is being established, these concentrations should be supported with a carbon isotopic signature. This will enable a more accurate

[22] Type I and II error indicate that a sample was mistakenly thought to be different or similar, respectively, when compared the average, when in fact the opposite is true.

assessment of whether hydrocarbons occurring in a well without background TOC concentrations were pre-existing or were sourced from a petroleum hydrocarbon-bearing formation.

Only 35 samples are available in the TWDB Infrequent Constituents database for $^{13}C/^{12}C$ stable isotope ratios in groundwater across the entire Eagle Ford shale region (Appendix X, Table 23). However, these samples were more geographically distributed across the region[23] than the TOC sample sites. Interestingly, the $\delta^{13}C$ concentrations found in groundwater for the counties of interest were less negative than $\delta^{13}C$ concentrations found in the Eagle Ford shale, indicating that the methane found in these groundwater samples could also be thermogenic (e.g. sourced from a deep formation which potentially bears petroleum hydrocarbons) (Schoell 1980; Barker and Fritz 1981).

FIGURE 7 GEOGRAPHIC DISTRIBUTION OF CONCENTRATIONS AND SAMPLES OF $^{13}C/^{12}C$ STABLE ISOTOPE RATIOS.



The range of $^{13}C/^{12}C$ stable isotope ratios in groundwater is between -7.2 ‰ and -18.1 ‰ (Appendix X, Table 23)[24]. In a single sample t-test, the mean of $^{13}C/^{12}C$ stable isotope ratios is -10.57391, with a p-value of less than 0.01, and 95 % confidence intervals of -11.687710 and -9.462116. These results indicate that regional variation exists in the $^{13}C/^{12}C$ stable isotope ratio of groundwater in the counties of interest. This result

[23] Exploration of the dataset reveals that these samples were taken between the years 2002 and 2009. Some of the samples that appear in lines across the landscape were taken within the same month, implying a coordinated sampling effort.

[24] A boxplot shown in Appendix X, Figure 20 indicates that the $^{13}C/^{12}C$ stable isotope ratio of -18.1 ‰ could be an outlier.

implies that the probability of Type I or II error is high when comparing groundwater samples to potentially contaminated samples, and underscores the importance of additional testing.

In order to compare these groundwater samples to expected $\delta^{13}C$ concentrations found in the Eagle Ford shale formation, a strategic literature search was conducted, and is described in Appendix V. Out of the references returned, only two provided values for $\delta^{13}C$ in the Eagle Ford shale formation. Kearns (2011) reports $\delta^{13}C$ values between a range of -24.094 ‰ and -26.023 ‰ for five core samples taken in DeWitt County in the Eagle Ford Formation, while 40 Eagle Ford samples taken in Gonzales County at varying depths exhibited a $\delta^{13}C$ range of -27.07 ‰ to -26.78 ‰. Additionally, Comet (1993) documents $\delta^{13}C$ values in whole oil, postulated to have been sourced from the Eagle Ford (Table 6) which overlap with the range found by Kearns (2011). However, the locations of Comet's $^{13}C/^{12}C$ samples are not provided. Therefore, it is not possible to discern whether the samples given represent a range of $^{13}C/^{12}C$ ratios relevant to the geographic scope of this paper.

TABLE 6 VALUES OF 13C/12C ISOTOPE RATIOS FOUND IN POTENTIAL EAGLE FORD SOURCE FORMATIONS COMET (1993)

Formation	Mean ‰ (range ‰) number of samples
Mississippi Delta Oils	-26.7 (-27.9 to -25.4) n=50
Louisiana Wilcox	-26.8 (27.4 to -26.2) n=24
Austin Chalk*	-28.0 (-29.1 to -25.4) n=29

The carbon isotope values for Dimmit and Guadalupe Counties differ by up to 3 ‰. When Comet's data is included, the difference is up to 5 ‰. These data offer a more well-defined carbon isotope signature for the Eagle Ford formation than can be said for groundwater across the landscape, where the range is up to 10 ‰ different[25] . One reason for the broader range of $^{13}C/^{12}C$ isotope ratios in groundwater could be that more than one aquifer is included in the analysis. To test this hypothesis, $^{13}C/^{12}C$ stable isotope ratios were plotted against depth, but no trend was discovered (see Appendix X, Figure 20). The wide distribution of values in groundwater, and the lack of trend with depth further support the notion that more baseline data is needed on $^{13}C/^{12}C$ isotope ratios. In order to assess whether C^{13}/C^{12} stable isotope ratios in produced water of the Eagle Ford shale have a unique enough signature from those in aquifers of the region, a paired t-test comparing core sample C^{13}/C^{12} stable isotope ratios from Kearns (2011) to groundwater ratios was conducted. The t-test indicates that the mean of differences was 16.2 ‰ with a p-value less than 0.01. This indicates that groundwater C^{13}/C^{12} stable isotope ratios are distinct enough from C^{13}/C^{12} stable isotope ratios values found in the Eagle Ford shale formation to serve as an indicator of contamination from gas leaks into aquifers. However, the groundwater samples of $^{13}C/^{12}C$ isotope ratios do not represent data from Gonzales or Dewitt Counties, where the core samples for the Eagle Ford formation were taken (see Appendix XI, Figure 19 and Table 23). Additionally, for 23 counties in the area of interest, no carbon isotope data for groundwater is available. Considering the limitations of the sample size and the geographic distributions of

[25] If the outlier of -18.1 ‰ is removed, the range of $^{13}C/^{12}C$ stable isotope ratios in groundwater is -15.3 ‰ to -7.2 ‰, with a difference of about 8 ‰.

data, a general comparison can be made between expected concentrations in the Eagle Ford and the overlying groundwater aquifers, but the chance of Type I or Type II error remain.

Health effects

The human health effects of methane are poorly researched. Neither the EPA nor the Agency for Toxic Substances and Disease Registry list any potential human health effects of methane exposure. However, methane gas present in high enough concentrations in groundwater could pose an asphyxiation or explosion hazard if allowed to build up in an enclosed space (Osborn, Vengosh et al. 2011).

Cost of testing

Testing for total organic carbon is a much cheaper test than a carbon isotope test (Table 7). Additionally, relatively few of the labs surveyed conduct carbon isotope testing.

TABLE 7 COST OF TESTING FOR CARBON ISOTOPE RATIOS AND TOTAL ORGANIC CARBON WITH LABS CERTIFIED TO TEST DRINKING WATER IN THE STATE OF TEXAS.

Test	Min of Cost	Mean of Cost	Max of Cost	Number of Labs
$^{13}C/^{12}C$	133	171	240	3
TOC	25	35	42	7

Recommendations

Both TOC and $^{13}C/^{12}C$ stable isotope ratios should be sampled more thoroughly in groundwater across the region of the Eagle Ford shale. Additionally, more samples of $^{13}C/^{12}C$ stable isotope ratios for hydrocarbons in the Eagle Ford formation are needed to establish expected regional variation for $^{13}C/^{12}C$ ratios across the region. These are important tests to undertake because of the hazards that are posed when water is contaminated by gas hydrocarbons.

TOC sampling is a high priority for baseline water quality testing because it can serve as a primary indicator of potential contamination from petroleum hydrocarbons, because it is poorly construed across the landscape for the counties of interest, and because no one county has enough TOC samples to be considered statistically powerful. Also, testing for TOC is relatively affordable, so establishing a more robust baseline of TOC in groundwater across the Eagle Ford shale region is achievable.

That being said, TOC sampling will be ineffective to use as a regional baseline if anomalies in TOC concentrations exist across the landscape. In order to support TOC concentration findings, more samples of $^{13}C/^{12}C$ stable isotope ratios are needed.

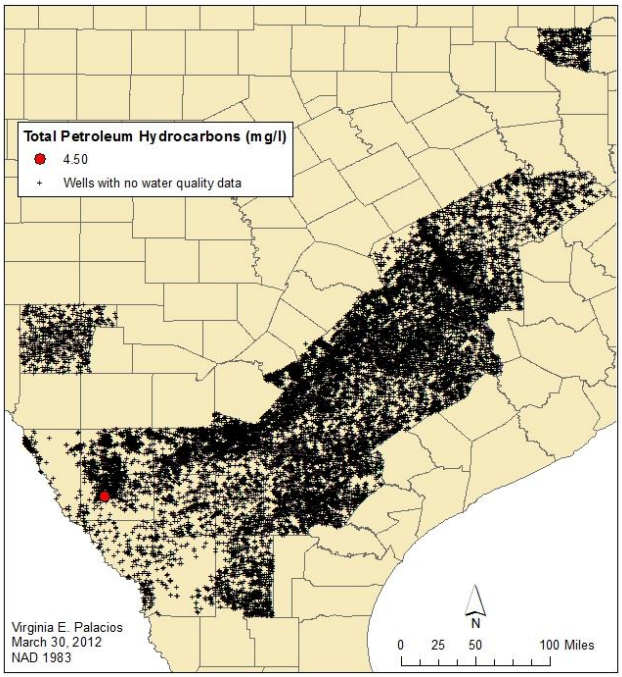
B. Liquid Hydrocarbons

Baseline characterization

Gasoline range organics (GRO) and diesel range organics (DRO) represent liquid petroleum products that have a specific number of carbons chained together; $C_6 – C_{10}$, and $C_{10} – C_{28}$, respectively (Environmental Protection Agency 1999). No samples exist in the TWDB database for either GRO or DRO. However, a test for total petroleum hydrocarbons (TPH) would include hydrocarbons in the range of both GRO and DRO. In the TWDB database, only two samples exist for the counties of interest. Those samples were taken in

Dimmitt County, and both samples bear the same concentration (see Figure 12). It is unclear whether the values provided in the database represent background water quality data or a case of contamination that was reported through the EPA STORET database[26] (Rein and Hopkins 2008).

FIGURE 8 GROUNDWATER CONCENTRATIONS OF TOTAL PETROLEUM HYDROCARBONS IN THE COUNTIES OF INTEREST. TWO DATAPOINTS ARE FOUND IN THE DATABASE, BUT THEIR LOCATIONS OVERLAP ON THE MAP.



Health effects

Health effects associated with some TPH compounds include headaches and dizziness, numbness in the feet and legs. Additionally effects on the blood, immune system, lungs, skin, and eyes are known to occur for some TPH compounds(Agency for Toxic Substances and Disease Registry 1999).

Cost of testing

The cost of testing for TPH is less expensive than testing for both GRO and DRO at the same time (Table 8). The test is moderately expensive, but more labs test for TPH than GRO or DRO.

TABLE 8 COST OF TESTING FOR LIQUID HYDROCARBONS WITH LABS CERTIFIED TO TEST DRINKING WATER IN THE STATE OF TEXAS.

Test	Min of Cost	Mean of Cost	Max of Cost	Number of Labs
Diesel Range Organics	68	82	97	3
Gasoline Range Organics	72	84	91	3

[26] TPH concentrations were reported in the infrequent constituents portion of the TWDB groundwater quality database. Most data in the infrequent constituents database came from the EPA STORET database.

TPH	50	89	138	4

Recommendations

Considering these potential health impacts and the lack of current baseline groundwater quality data for liquid hydrocarbons, it is clear that more background water quality data is needed to determine whether cases of existing liquid hydrocarbon leaks into groundwater exist in counties that make up the Eagle Ford shale region. Although liquid hydrocarbons are not expected to occur in groundwater, additional background data would aid in preventing false claims that contamination was either present or not present before oil and gas extraction activities began. Since virtually no baseline groundwater quality data is available for TPH, and testing is relatively expensive, it is recommended that an agency, industry, or other organization take on a groundwater sampling initiative for TPH that is geographically representative of the Eagle Ford shale region.

C. Salts

Relevant parameters in produced water

The concentration of like constituents in groundwater and produced water can be compared in order to determine whether the mean difference in each is statistically significant. If produced water concentrations of any particular salt are always much higher than the concentrations in the groundwater, that particular salt can be considered an effective parameter to use for detecting a change in groundwater chemistry caused by oil and gas activities.

In this analysis, Eagle Ford shale formation produced water samples are compared to groundwater samples for Wood County, for the parameters that are available in the produced waters database. However, given the uncertainties associated with how closely Wood County data resembles the geochemistry of the Eagle Ford in the current active drilling area, additional produced water samples from other formations were compared to groundwater samples to establish a generally applicable range of how greatly produced water differs from groundwater. These additional produced water samples were compiled from only the counties of interest, and represent all formations that are listed for those counties.

A paired t-test was used to determine whether the differences in produced water quality of the Eagle Ford were statistically significant when compared to groundwater. First, data for Wood County indicates that all analyte concentrations were significantly greater in produced water except for pH and sulfate (Appendix XI, Table 24). Total dissolved solids (TDS), chloride, and sodium return the greatest mean of differences. Additionally, for all three analytes, the maximum values found in groundwater do not overlap with the minimum values found in produced water (Appendix XI, Table 25).

Although only Wood County data was available for the Eagle Ford shale in the produced waters database, produced water chemistry for all the counties of interest was compared to groundwater chemistry for all the counties. Slight differences from the Wood County data are observed when these additional data points are considered.

First, pH and sulfate are statistically significant when results for all counties are considered (Appendix XI, Table 26). Notably, pH in groundwater exhibits a broader range of values than produced water (Appendix XI, Table 27), and would be a poor indicator of post-drill contamination without a baseline water quality test for the actual well at which potential contamination is experienced. Therefore, a baseline of pH in groundwater would not be expected to be higher or lower than produced water pH unless both produced water and baseline groundwater quality for the site were known prior to the potential influx of contaminants to the aquifer.

Next, data for potassium were not available in the Wood County dataset; whereas 143 produced water samples recorded potassium concentrations for other formations in the counties of interest (Appendix XI, Table 27). Nonetheless, potassium concentrations are not likely to be a useful indicator of contamination, considering that the maximum groundwater concentration of potassium is close to the value of the third quantile of the potassium concentration for produced water. Also, the maximum concentration of potassium in produced water is an order of magnitude higher than the third quantile, indicating that the dataset may contain outliers that skew the distribution of potassium concentrations (Appendix XI, Table 27).

According to the produced waters data for all counties of interest, sulfate concentrations in produced water are higher than in groundwater by a statistically significant amount (Appendix XI, Table 26). However, the

range of concentrations in groundwater indicates that the maximum concentration of sulfate in groundwater is greater than the third quantile in produced water (Appendix XI, Table 27). Similar to potassium, the high sulfate concentrations found in the upper quantile of the produced waters may be skewed by outliers.

Baseline characterization

Only Caldwell and Guadalupe counties have poor statistical power for all of the general water chemistry parameters that are listed in the produced waters dataset, although testing is recommended for some of these parameters in Madison (Appendix XI, Figure 27) and Washington (Appendix XI, Figure 28) counties. Every other county has strong statistical power based on the number of samples it has.

Other salts that have not yet been discussed, but which were indicated as important in the case studies, include bromide, nitrate, and selenium. Number, percent, and groundwater testing recommendations for these parameters are given in Appendix IX, Figure 29. Power analysis indicates that most counties have an acceptable number of samples for bromide and selenium, but many counties need more samples for nitrate in order to adequately characterize the baseline for these parameters.

Health effects

Although a change in chemistry could occur from an influx of produced water into an aquifer, the constituents found in the produced waters database are not necessarily harmful. No Maximum Contaminant Levels (MCL) exist for the chemicals listed in the produced waters database. However, the EPA has defined National Secondary Drinking Water Standards (Secondary Standards) for pH, chloride, sulfate, and Total Dissolved Solids (TDS) (Table 9). Alternatively, MCLs are defined for bromate[27], nitrate, and selenium. The known health effects of these parameters are listed in Table 9.

TABLE 9 EPA MCLS AND SECONDARY STANDARDS FOR SALTS AND PH IN GROUNDWATER (ENVIRONMENTAL PROTECTION AGENCY 2012).

Chemical	MCL (mg/l)	Health effects
pH	6.5 – 8.5*	
Chloride	250*	
Sulfate	250*	
TDS	500*	
Bromate	0.01	Increased risk of cancer
Nitrate	10	Infants below the age of six months who drink water containing nitrate in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome.
Selenium	0.05	Hair or fingernail loss; numbness in fingers or toes; circulatory problems

*EPA Secondary Standard for drinking water

[27] Bromate is a common byproduct of bromide interactions with disinfectants in surface water. Source: New York State Department of Health. (2011, April 2011). "Bromate in Drinking Water - Information Fact Sheet." Drinking Water Protection Program.

Cost of testing

Magnesium, potassium, and bromide are the most expensive parameters to test out of the salt category. However, on average, salts are less expensive to test than other parameters. There are also a greater number of laboratories that test salts than there are that test some of the other parameters discussed in this analysis (Table 10).

TABLE 10 COST OF TESTING, IN USD, FOR VARIOUS SALTS WITH LABS CERTIFIED TO TEST DRINKING WATER IN THE STATE OF TEXAS.

Test	Min of Cost	Mean of Cost	Max of Cost	Number of Labs
Bromide	13	30	60	7
Calcium	9	11	15	3
Chloride	13	22	43	7
Magnesium	9	35	60	2
Nitrate	13	22	43	9
Potassium	9	35	60	2
Selenium	10	17	20	5
Sodium	9	11	15	3
Sulfate	13	23	58	11
TDS	12	21	33	11

Recommendations

If contamination does occur, the baseline for TDS, chlorides, and sodium has already established across most of the Eagle Ford shale region[28], and concentrations in groundwater as high as what would be found in produced water would imply contamination in a post-drilling test. Therefore, rather than spend limited resources to test all of the potential analytes in the produced waters database, only the produced water parameters that deviate substantially from the mean found in groundwater should be a high priority for testing. Also, considering that there is no secondary standard listed for sodium, TDS and chloride should take higher priority than sodium in a list of analytes for baseline groundwater quality testing. Likewise, parameters such as bromide, selenium, and nitrate should be a high priority for testing in counties where poor statistical power is available. Considering that the cost of testing these parameters is relatively low, and that the baseline is partially established in all counties of the Eagle Ford shale region, testing for salts could feasibly be taken on by water well owners.

[28] Locations of where TDS, chlorides, and sodium have been tested are depicted in Appendix XI, Figure 19.

D. Metals

Baseline characterization

Every case study mentioned in this analysis considers trace metals in either baseline groundwater quality testing or in testing for potential post-drill contamination. Concentrations of trace metals in produced waters of the Eagle Ford shale formation were either not found in the literature, or did not represent enough samples to warrant a comparison with groundwater concentrations. Therefore, it is unclear how necessary trace metal samples are to background water quality testing in the Eagle Ford shale region in particular. Nonetheless, a list of trace metals was compiled from the case studies discussed in the introduction. With the exception of phosphorus, for each trace metal identified every county has at least one sample[29]. The number of samples varies by county and parameter, but testing recommendations based on power analysis can be found for each parameter and county in Appendix II, Tables 36 to 42.

Health effects

Table 11 lists the potential health effects of metals, metalloids, and additional salts that are known to occur in oil and gas flowback fluids. No MCL or health effects were listed for Boron, Cobalt, Molybdenum, Nickel, Phosphorus, Silicon, or Strontium.

TABLE 11 EPA MAXIMUM CONTAMINANT LEVELS (MCL) AND SECONDARY STANDARDS FOR METALS IN DRINKING WATER AND ASSOCIATED HEALTH EFFECTS.

Element	MCL (mg/l)	Health effects
Aluminum	*0.05 to 0.2	
Antimony	0.006	Increase in blood cholesterol; decrease in blood sugar
Arsenic	0.01	Skin damage or problems with circulatory systems, and may have increased risk of getting cancer
Barium	2	Increase in blood pressure
Beryllium	0.004	Intestinal lesions
Cadmium	0.005	Kidney damage
Chromium	0.1	Allergic dermatitis
Copper	1	
Iron	*0.3 mg/L	
Lead	0.015	Infants and children: Delays in physical or mental development; children could show slight deficits in attention span and learning abilities; Adults: Kidney problems; high blood pressure
Manganese	0.05*	
Mercury	0.002	Kidney damage
Selenium	0.05	Hair or fingernail loss; numbness in fingers or toes; circulatory problems
Silver	*0.10 mg/L	

*EPA Secondary Standard

[29] Silicon was not included in the database.

Cost of testing

Testing metals is generally not expensive (Table 12). Additionally, many metals can be tested together in a batch, making the cost of testing multiple parameters more affordable.

TABLE 12 COST OF TESTING, IN USD, FOR METALS WITH LABS CERTIFIED TO TEST DRINKING WATER IN THE STATE OF TEXAS.

Test	Min of Cost	Mean of Cost	Max of Cost	Number of Labs
Metals package	175	175	175	1
Metals single	10	20	35	5

Recommendations

More data is needed on the concentrations of trace metals that are expected to be found in produced water of the Eagle Ford shale region. Without this information, defining a narrow list of baseline groundwater testing for metals is difficult. Although the baseline is well characterized for some metals, the dataset is less robust for others. When it comes to metals, baseline testing must be considered on a county-by-county basis for each parameter. At a minimum, it is safe to say that metals which are known to cause health effects should be considered as a higher testing priority than other metals.

E. Naturally-Occurring Radioactive Materials (NORM)

Baseline characterization

Various kinds of radionuclides are known to occur naturally in oil and gas formations including uranium-238, uranium-235, thorium-232, and their daughter products: radium-226, radium-228, lead-210, and polonium-210 (NORSEDECOM 2003)[30]. Generally, the concentrations of radionuclides found in produced water are not expected to be very high, but waste handling methods can lead to higher concentrations of long-living radionuclides being stored at the surface(Valeur and Ramboll Oil and Gas 2010) .

In the Eagle Ford shale formation, very high in-situ gamma radiation from potassium-40, thorium, and uranium have been observed (Fertl 1979). At the surface however, the RRC reports that one Eagle Ford drilling field in Wood County documented radiation greater than 500 microroentgen/hour (µR/hr)[31] (Railroad Commission of Texas 2000). Aside from the case in Wood County, groundwater contamination from uranium and radon-226 has been documented in Live Oak, Karnes, and Gonzales Counties (Wukasch and Cook 1971 or later; McConnell, Ramanujam et al. 1998). These cases of contamination are related to historical uranium mining and waste disposal, activities which have also taken place in Duval, Karnes, Webb, Live Oak, Bee, and Fayette Counties (Pirson 1970; Annamalai and McGarvey 1980; Fishman and Huang 1980; Jones 1981; Otto Jr. 1984; McConnell, Ramanujam et al. 1997). The possibility of encountering historical radionuclide contamination underscores the importance of baseline testing for radioactive elements or

[30] Cited in Valeur (2010)

[31] According to the RRC website, a microroentgen is a measurement of exposure to x-ray or gamma ray radiation in the air, whereas picocuries (pCi) measure the amount of a substance that decays over time RRC (2000). 500 µR/hr is one order of magnitude greater than the regulatory standard (50 µR/hr) for release of materials for uses other than oil and gas activities.

particle emissions in the Eagle Ford shale region to avoid false assumptions about the presence or absence of radioactive materials before oil and gas drilling begins.

Knowing which parameters are the most important ones to test for, however, is more complicated. Out of the radionuclides discussed here, radium-226 and -228 are the most common, and the most long lived (Fertl 1979; Lawrie, Desmond et al. 2000; Valeur and Ramboll Oil and Gas 2010). Given this evidence, it at first seems appropriate to focus baseline water quality testing on radium-226 and radium-228; however, given the fact that potassium, thorium, and uranium are known to exist in high concentrations in the Eagle Ford formation, only testing for radium would be insufficient.

Yet, testing for all of these parameters is not necessary, because radionuclides each give off a certain kind of radiation that is sometimes the same for other radionuclides, and the number of baseline analytical tests can be significantly reduced if only the appropriate kinds of radiation are tested. Three kinds of radioactive emissions exist: alpha, beta, and gamma radiation. All of the radionuclides discussed give off alpha or beta particle emissions, except for potassium-40 which emits gamma radiation (Table 13).

TABLE 13 TYPES OF RADIOACTIVE EMISSIONS KNOWN TO OCCUR FROM VARIOUS RADIONUCLIDES (FERTL 1979)

Radionuclide	Type of emission
Uranium-238	Alpha
Thorium-232	Alpha
Radium-226	Alpha
Radium-228	Beta
Radon-222	Alpha
Potassium-40	Gamma
Lead-210	Beta
Polonium-210	Alpha

The numbers of wells with reliable samples that have tested radionuclides in the counties of interest are listed in Appendix XIII, Table 43. Radium-226 and Radium-228 have been tested in most counties, but radon, thorium and potassium-40 have been tested in fewer than 10 counties. Additionally, lead-210, polonium-210, and gamma radiation are not recorded anywhere in the database.

Every county has tested for alpha or beta radiation (Appendix XIII, Table 34). However, most of the counties have poor statistical power due to the low number of samples that have been reported, and additional sampling is needed. Additionally, some records indicate concentrations that are greater than the EPA MCL (see Figure 15). It is unclear whether these data points were taken in response to a case of contamination, or whether they represent unaffected background data.

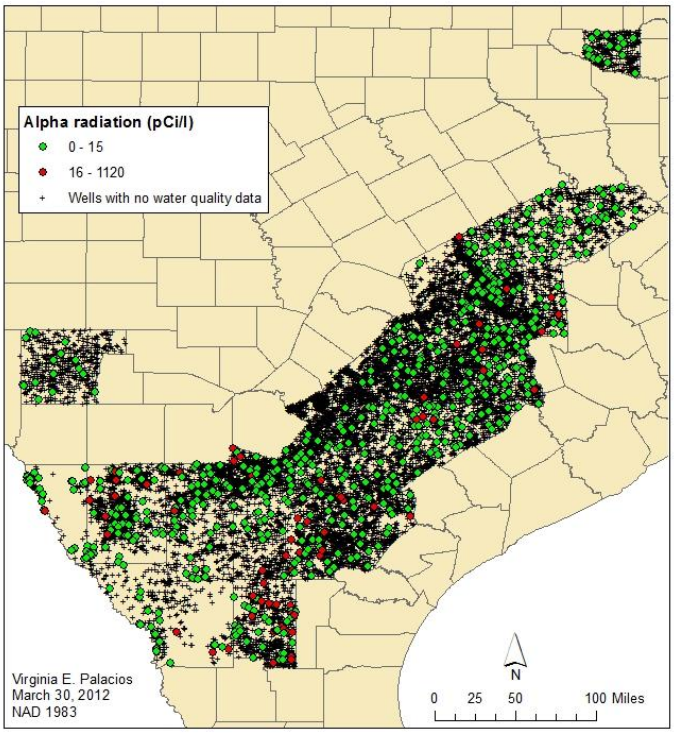
Health effects

Although alpha and beta particles are the most easily shielded from skin contact, ingestion of alpha and beta particles is known to carry greater risk than external exposure to these particles (Smith and Argonne National Laboratory 1992). Gamma radiation, however, is able to penetrate through thick protective layers, and is generally considered to be the most harmful (Environmental Protection Agency 2012). The EPA lists MCLs for uranium, radium, alpha particles, and beta particles, and all are associated with an increased risk of cancer (Table 14) (Environmental Protection Agency 2012). Potassium-40 and thorium are also known to cause cancer (Argonne National Laboratory 2005; Environmental Protection Agency 2012) , but are not regulated in drinking water.

TABLE 14 EPA MAXIMUM CONTAMINANT LEVELS FOR RADIOACTIVE ELEMENTS/PARTICLES IN DRINKING WATER

Radioactive element	MCL
Uranium	30 µg/l
Radium	5 pCi/l
Alpha particles	15 pCi/l
Beta particles	4 millirems/year

FIGURE 9 ALPHA PARTICLE CONCENTRATIONS IN THE COUNTIES OF INTEREST. RED POINTS REPRESENT VALUES GREATER THAN THE EPA MCL.



Cost of testing

On average, the cost of testing alpha and beta particle emissions together is less expensive than testing these parameters separately. Additionally, it is clear that testing for specific radionuclides is much more expensive. Similarly, testing gamma emissions is less expensive than testing for potassium-40, the only gamma radiation emitter on the list.

TABLE 15 COST OF TESTING, IN USD, FOR RADIONUCLIDES WITH LABS CERTIFIED TO TEST DRINKING WATER IN THE STATE OF TEXAS.

Test	Min of Cost	Mean of Cost	Max of Cost	Number of Labs
Alpha	16	37	50	3
Alpha/Beta	50	54	65	4
Beta	16	37	50	3
Gamma	84	84	84	1
Potassium-40	250	250	250	1
Radium 226	65	92	125	4
Radium 226 and 228	150	168	185	4
Radium 228	85	102	125	4
Radon 222	35	96	200	4
Uranium	20	107	255	8

Recommendations

Considering the health effects associated with radionuclides, regional heterogeneity of alpha concentrations (Figure 13), and the low statistical power of the available sample sizes more testing is recommended. Testing for alpha, beta, and gamma radiation is recommended, since these parameters encompass the effects of multiple radionuclides, and because these tests cost less than test for individual radionuclides.

F. Volatile Organic Compounds (VOCs)

The volatile organic compounds (VOCs) most commonly associated with oil and gas are the BTEX chemicals: benzene, toluene, ethylbenzene, and xylene. These chemicals are not generally thought to occur in groundwater, but determining background concentrations is necessary to verify this speculation. A comprehensive national study seeking to determine baseline concentrations of VOCs in groundwater found toluene in at least 1 % of samples, although concentrations greater than the MCL were not found (Wukasch and Cook 1971 or later). The study area, however, did not include samples within counties of the Eagle Ford shale region, and ethylbenzene and xylene were not considered in the research.

Baseline characterization

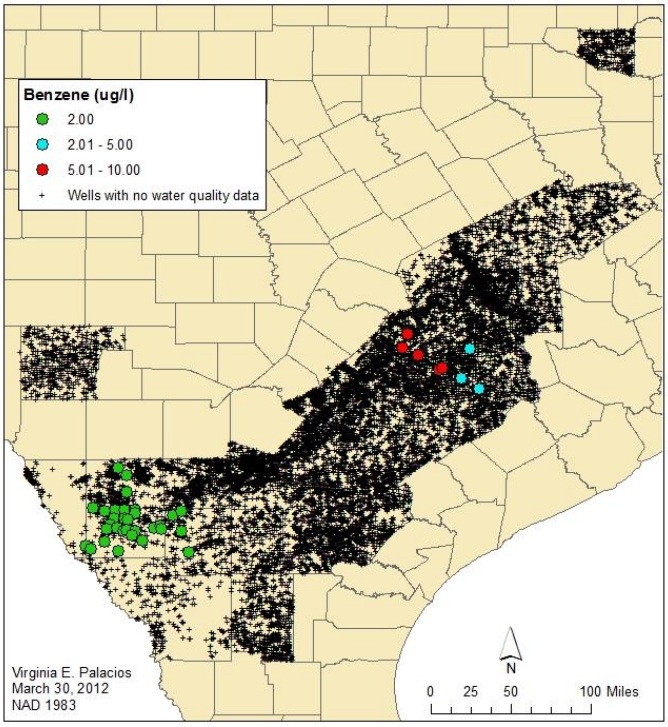
For this analysis, concentrations of BTEX chemicals are only provided for six counties in the TWDB groundwater quality database. All counties have less than 26 samples, indicating insufficient statistical power (Table 16). Additionally, geospatial analysis indicates that the available samples are not evenly spaced

enough to establish a reliable baseline across the region (Figure 13), and some samples exceeded the MCL. In three counties, no samples were taken for xylene; whereas benzene, ethylbenzene, and toluene were tested at the same time in all the other samples. It is unclear whether these samples were taken in response to a case of potential contamination, or if they were intended to represent baseline groundwater quality.

TABLE 16 NUMBER AND PERCENT OF WELLS WITH RELIABLE SAMPLES FOR WHICH CONCENTRATIONS OF BTEX CHEMICALS ARE FOUND IN THE TWDB GROUNDWATER DATABASE.

County	Total wells	Benzene		Ethylbenzene		Toluene		Xylene	
Bastrop	791	3	0.4%	3	0.4%	3	0.4%	NA	
Colorado	574	1	0.2%	1	0.2%	1	0.2%	NA	
Dimmit	527	24	4.6%	24	4.6%	24	4.6%	24	4.6%
Fayette	863	4	0.5%	4	0.5%	4	0.5%	NA	
La Salle	362	4	1.1%	4	1.1%	4	1.1%	4	1.1%
Zavala	748	3	0.4%	3	0.4%	3	0.4%	3	0.4%
Grand Total	3865	39	1.0%	39	1.0%	39	1.0%	31	0.8%

FIGURE 10 BENZENE CONCENTRATIONS IN THE COUNTIES OF INTEREST. POINTS MARKED IN RED INDICATE CONCENTRATIONS THAT EXCEED THE EPA MCL FOR BENZENE.



Health effects

All four VOCs listed here are regulated by the EPA in drinking water. All of the BTEX chemicals are considered to present serious health effects (Table 21).

TABLE 17 HEALTH EFFECTS OF VOLATILE ORGANIC COMPOUNDS COMMONLY FOUND IN OIL AND GAS FLOWBACK (ENVIRONMENTAL PROTECTION AGENCY 2012).

Chemical parameter	MCL (mg/l)	Health Effects
Benzene	0.005	Anemia; decrease in blood platelets; increased risk of cancer
Toluene	1	Nervous system, kidney, or liver problems
Ethylbenzene	0.7	Liver or kidneys problems
Xylene	10	Nervous system damage

Cost of testing

The cost of testing BTEX chemicals is high Table 18). This cost is conceivably not affordable for some water well owners.

TABLE 18 COST OF TESTING, IN USD, FOR VOC WITH LABS CERTIFIED TO TEST DRINKING WATER IN THE STATE OF TEXAS.

Test	Min of Cost	Mean of Cost	Max of Cost	Count of Lab
BTEX	40	87	125	5
VOC	50	149	200	8

Recommendations

Considering the potential health impacts of BTEX chemicals, the fact that they are frequently listed as contaminants from oil and gas activities in the counties of interest, that they could occur naturally, and because so few samples have been taken across the landscape it is highly recommended that a strategic baseline groundwater sampling initiative for VOC, including BTEX, take place by an agency, industry, or other organization.

G. Polycyclic Aromatic Hydrocarbons (PAHs)

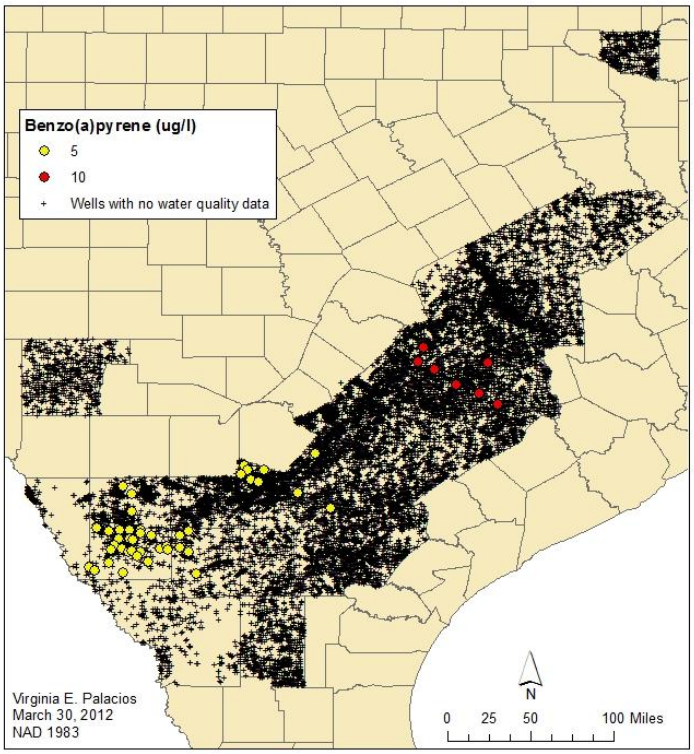
Baseline characterization

PAHs are known to occur in oil and gas flowback water (Bojes, Pope et al. 2007; Joa, Panova et al. 2009). All counties of interest have tested PAHs fewer than 26 times, indicating poor statistical power (Appendix XIV, Table 45). Geospatial analysis indicates wide geographical gaps in sampling (Figure 14). All of these tests were taken at the same time, and seven of the 49 samples exceeded the EPA MCL for benzo(a)pyrene (Tables 25 and 26). Therefore, it is unclear whether these samples represent background concentrations or if they were taken in response to potential contamination.

Health effects

Animal testing has shown that PAHs cause reproductive and developmental health effects. Additionally, detrimental effects to the skin, body fluids, and immune system have been observed in animals (Agency for Toxic Substances and Disease Registry 1996). The EPA has listed 16 priority-pollutant PAHs (Appendix 14, Table 45), but only Benzo(a)pyrene is regulated in drinking water (Bojes, Pope et al. 2007; Joa, Panova et al. 2009; Environmental Protection Agency 2012). Seven of the 16 priority-pollutant PAHs have been listed as probable carcinogens by the EPA (NTP 2005)[32]. Points marked in red in Figure 14 exceed the EPA MCL of 10 µg/l of Benzo(a)pyrene.

FIGURE 11 BENZO(A)PYRENE CONCENTRATIONS IN THE COUNTIES OF INTEREST.



Cost of testing

All 16 priority PAH can be tested at the same time in a package. In fact, laboratories do not offer individual tests of these parameters. Nonetheless, the cost of testing for PAH is expensive, and may be unaffordable to some well owners.

TABLE 19 COST OF TESTING, IN USD, FOR PAH WITH LABS CERTIFIED TO TEST DRINKING WATER IN THE STATE OF TEXAS.

Test	Min of Cost	Average of Cost	Max of Cost	Number of Labs
PAH	120	148	176	2

[32] Cited inBojes, H. K., P. G. Pope, et al. (2007). "Characterization of EPA's 16 priority pollutant polycyclic aromatic hydrocarbons (PAHs) in tank bottom solids and associated contaminated soils at oil exploration and production sites in Texas." Regulatory Toxicology and Pharmacology **47**(3): 288-295.

Recommendations

Considering the serious health effects associated with PAHs, their association with oil and gas flowback, and the lack of available data in the Eagle Ford shale region, a strategic sampling effort for PAHs is recommended for the counties of interest. Because the cost of testing is so high, such an initiative might best be taken on by an agency, industry or other organization.

IV. Discussion

This analysis employed five different strategies to determine which parameters should be tested prior to oil and gas drilling to establish a functional baseline for comparison to potentially contaminated samples. First, a list of potential parameters was defined using prominent case studies of oil and gas contamination cases. Second, known concentrations of parameters found in produced water were compared to known concentrations of those same parameters for the same geographic region, in order to determine if differences could reasonably be expected. Third, statistical power analysis was used to determine whether the minimum number of samples needed to establish confidence in a range of concentrations for any given parameter had already been acquired for each county and parameter of interest. Next, health effects were considered to highlight potential pollutants that should be prioritized in a sampling initiative. Finally, cost of testing was considered to introduce a perspective about whether a well owner might be expected to voluntarily participate in baseline groundwater quality sampling, or whether an organized and geographically strategic sampling initiative should be led by an agency, industry, or other organization.

The results of employing these strategies reveal that some of the most dangerous chemicals are not adequately characterized in baseline water quality, if at all. These high priority baseline tests include TOC, $^{13}C/^{12}C$, TPH, nitrate, alpha particles, beta particles, gamma radiation, VOC, and PAH. The average cost of testing all of these parameters is approximately $1000.

Contrastingly, with the exception of Caldwell and Guadalupe counties, most salts are well characterized across the region. In counties where more tests are needed, TDS, chlorides, bromide, nitrate, and selenium are the most essential testing parameters. On average, the cost of testing all of these parameters would total less than $250.

For the most part, metals are also well characterized, but each county has a slightly different number of tests for each parameter, indicating that testing initiatives for metals will be more localized and tailored to each county than testing for high priority baseline parameters mentioned above. Another aspect of metals is that some of the metals analyzed are regulated in drinking water, because of health effects that are associated with their presence at or above threshold concentrations. For counties and well owners faced with many baseline water quality needs, these regulated metals are higher priority parameters than other metals or salts. The cost of testing these 14 metals listed in table 12 would be about $300 if the average price is true, or it could be $140 if the lowest price is true; in which case, the package price would be more expensive. Counties seeking to enhance current baseline datasets can use the testing priority codes listed in Appendix XII to determine which metals need to be tested the most in that particular county.

In conclusion, background water quality data is an essential component of assessing potential groundwater pollution. Considering that cases of potential groundwater contamination linked to oil and gas activities have been contentious due to lack of background water quality data, groundwater stakeholders in the newly and rapidly developing Eagle Ford shale region would be wise to quickly establish regional initiatives to conduct baseline water quality testing for the parameters recommended here.

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Appendix I – Counties

The data used in this analysis represents all Eagle Ford shale counties listed by three sources: Railroad Commission [R], Energy Information Administration [E], and the website EagleFordShale.com [S].

- Atascosa [R, E, S]
- Austin [E, S]
- Bastrop [E, S]
- Bee [R, E, S]
- Brazos [E, S]
- Burleson [R, E, S]
- Caldwell [R]
- Colorado [S]
- Dewitt [R, E, S]
- Dimmit [R, E, S]
- Duval [E, S]
- Edwards [R]
- Fayette [E, S]
- Frio [R, E, S]
- Goliad [E, S]
- Gonzales [R, E, S]
- Grimes [R, E, S]
- Guadalupe [R]
- Houston *
- Karnes [R, E, S]
- LaSalle [R, E, S]
- Lavaca [R, E, S]
- Lee [R, E, S]
- Leon [R, S]
- Live Oak [R, E, S]
- Madison [S]
- Maverick [R, E, S]
- McMullen [R, E, S]
- Milam [R, E, S]
- Robertson [S]
- Washington [E, S]
- Webb [R, E, S]
- Wilson [R, E]
- Wood *
- Zavala [R, E, S]

* Houston and Wood Counties were mentioned in EagleFordShale.com as having been listed by the RRC in a list of Eagle Ford shale counties. Although they are no longer listed on the RRC's webpage for the Eagle Ford shale, there is reason to suggest that Eagle Ford drilling is not entirely ruled out for Houston and Wood counties.

The Railroad Commission of Texas (RRC) reports that drilling in the Eagle Ford shale is taking place in 16 fields in 24 counties (Railroad Commission of Texas 2012a). However, this analysis includes 35 counties in the Eagle Ford shale region. The reason for including more counties than the RRC lists as existing in the Eagle Ford shale is that both the Energy Information Administration (EIA) (Figure 1) and the website EagleFordShale.com[33] have included some counties in the Eagle Ford shale region that are not listed by the RRC. Additionally, the RRC includes counties in the Eagle Ford shale that have not been listed by these other sources (Figure 4) (U.S. Energy Information Administration 2010; Dukes, DuBose et al. 2012). Considering that both the EIA and EagleFordShale.com are websites that seek to predict trends in drilling activity, it is possible that some counties not listed by the RRC, but which are listed by these other sources, will experience drilling in the foreseeable future. Therefore, the decision to include counties not listed by the RRC is intended to ensure that this analysis is relevant to future audiences.

[33] EagleFordShale.com is currently hosting a website for the Eagle Ford Task Force, a group formed by current Railroad Commissioner David Porter to help overcome economic and logistical obstacles of developing the Eagle Ford shale play. This website provides detailed and referenced information about Eagle Ford shale counties. Since this website is about development of the shale, it makes sense that the list of counties the website offers might include counties that the business community expects to see drilling at in the near future.

Appendix II – Carbon isotope values

Carbon-13 (^{13}C) isotope concentrations are calculated by comparing the ratio of ^{13}C to ^{12}C isotopes of carbon in a given sample of gas, to a predefined standard, Pee Dee Belemnite (PDB). The following equation (Farquhar, O'Leary et al. 1982) describes this comparison:

$$\delta^{13}C\ (‰) = ((R_{sample}/R_{standard}) - 1) \times 1000 \qquad \text{Equation 1}$$

In equation 1, R_{sample} represents the ratio of $^{13}C/^{12}C$ found in the sample, while $R_{standard}$ represents the ratio of $^{13}C/^{12}C$ found in the PDB standard (Farquhar, O'Leary et al. 1982). The PDB standard has a ^{13}C isotope ratio that is less than one (Slater, Preston et al. 2001). Therefore, if the concentration of ^{13}C in a sample is less than the concentration of ^{13}C in the standard, the resulting concentration of $\delta^{13}C$ (‰) would be more negative than it would have been if the ^{13}C sample concentration were higher than the standard.

Methane has a specific $\delta^{13}C$ concentration (corresponding to when and how it was formed), which is also referred to as an isotopic signature or "fingerprint." Naturally occurring methane in a groundwater aquifer could come from recent microbial degradation of organic matter, termed biogenic methane. However, methane in groundwater could also come from an aquifer's connection with a deeper source of methane that was formed from high temperatures and pressures, also called "thermogenic" methane. Thermogenic gas tends to have a less negative $\delta^{13}C$ concentration than biogenic methane (Schoell 1980; Barker and Fritz 1981)[34].

When thermogenic methane from a shale formation reaches an aquifer that contains more biogenic gas than thermogenic gas, it would likely make the overall concentration of $\delta\ ^{13}C$ in the aquifer less negative. If only small amounts of biogenic gas were present before the thermogenic methane leaked into the aquifer, then the concentration of methane gas found in the aquifer would very closely resemble the isotopic ratio found in gas that is produced from the natural gas formation. The extent to which the groundwater $\delta^{13}C$ concentrations change depends on the quantity and type of thermogenic gas that enters the aquifer.

[34] Schoell 1980 Cited in Osborn et al. (2011)

Appendix III – Starting list of potential testing parameters

This list represents the initial list of potential baseline groundwater quality analytes. From this list, data availability for each parameter are assessed for each of the counties of interest, and recommendations for future testing are made based on data availability, health impacts, and cost associated with testing each parameter.

TABLE 20 CATEGORIES OF POTENTIAL BASELINE GROUNDWATER CHEMISTRY PARAMETERS.

Category	Potential baseline chemical analytical parameters
1. Gas hydrocarbons	Methane
	Ethane
	Propane
	Hexane
	Total organic carbon
	Carbon isotopes
2. Liquid hydrocarbons	Total Petroleum Hydrocarbons
	Gasoline range organics
	Diesel range organics
3. Salts	Bicarbonate
	Bromide
	Calcium
	Chloride
	Magnesium
	Nitrate
	Potassium
	Selenium
	Sodium
	Sulfate
	Total Dissolved Solids
4. Metals	Aluminum
	Antimony
	Arsenic
	Barium
	Beryllium
	Boron
	Cadmium
	Chromium
	Cobalt
	Copper
	Iron
	Lead
	Manganese
	Mercury
	Molybdenum

	Nickel Phosphorus Potassium Silver Strontium Sulfur Titanium Uranium
5. Radioactive elements/parameters	Alpha Beta Gamma Uranium Thorium Radium 226, 228 Radon 222 Potassium-40
6. Volatile organic compounds (VOCs)	Benzene Toluene Ethylbenzene Xylene
7. Polycyclic aromatic hydrocarbons (PAHs)	Acenaphthene Acenaphthylene Anthracene Benzo(a) anthracene Benzo-(a)-pyrene Benzo(b)fluoranthene Benzo(ghi)perylene Benzo(k)fluoranthene Chrysene Dibenzo (a,h) anthracene Fluoranthene Fluorene Indeno (1,2,3-cd) pyrene Naphthalene Phenanthrene Pyrene

Appendix III – Pavillion, WY test results

TABLE 21 CONTAMINANTS FOUND IN MONITORING WELLS DRILLED BY THE EPA IN PAVILLION, WY

Component found in groundwater	Hydraulic fracturing ingredient the component was used in at the site
· **Acetate and benzoic acid**	· "Natural breakdown products of organic contaminants like BTEX and glycols"
· **Benzene, Toluene, Ethylbenzene, and Xylene (BTEX)** · **Trimethylbenzenes**	· "Aromatic solvent (usually a BTEX solution) used in a breaker" · "Toluene and xylene were used in flow enhancers and a breaker"
· **Chloride**	· Potassium chloride used in carbon dioxide foam hydraulic fracturing · Ammonium chloride used in a crosslinker
· **Diesel range organics (DRO)**	· "Diesel oil (mixture of saturated and aromatic hydrocarbons including naphthalenes and alkylbenzenes) was used in a guar polymer slurry/liquid gel concentrate and in a solvent." · "Petroleum raffinates (mixture of paraffinic, cycloparaffinic, olefinic, and aromatic hydrocarbons) were used in a breaker." · "Heavy aromatic petroleum naphtha (mixture of paraffinic, cycloparaffinic and aromatic hydrocarbons) was used in surfactants and in a solvent." · guar polymer · solvent
· **Diethylene glycol**	· foaming agent · solvent
· **Isopropanol**	· biocide · surfactant · breakers · foaming agents

· **Potassium hydroxide (KOH)** · **Potassium metaborate**	· crosslinker · solvent
· **Triethylene glycol**	· solvent
· **Tert-butyl alcohol**	· "Breakdown product of methyl *tert*-butyl ether (a fuel additive), and *tert*-butyl hydroperoxide (a gel breaker used in hydraulic fracturing)"

Appendix IV – RRC groundwater contamination report

In the joint groundwater monitoring and contamination report, the RRC indicates that BTEX stands for Benzene, Toluene, Ethylbenzene, and Xylene; NG stands for natural gas; but COND is not described. Here it is assumed that COND stands for Condensate. These codes were consolidated into their respective categories for analysis as described in Table 4.

TABLE 22 CONSOLIDATED CATEGORIES OF RRC REPORTED CONTAMINANTS

Consolidated category	Reported contaminant
BTEX	Benzene, dissolved benzene, BTEX
Liquid hydrocarbons	hydrocarb, hydrocarb seep, PSH, total petroleum hydrocarbons (TPH), COND, condensate, crude oil
Gas hydrocarbons	NG, methane
Chlorides	Chloride, sodium chloride

FIGURE 12 ACTIVITY STATUS FOR PENDING CASES OF GROUNDWATER CONTAMINATION ATTRIBUTED TO OIL AND GAS ACTIVITIES IN 2010 (TEXAS GROUNDWATER PROTECTION COMMITTEE 2011).

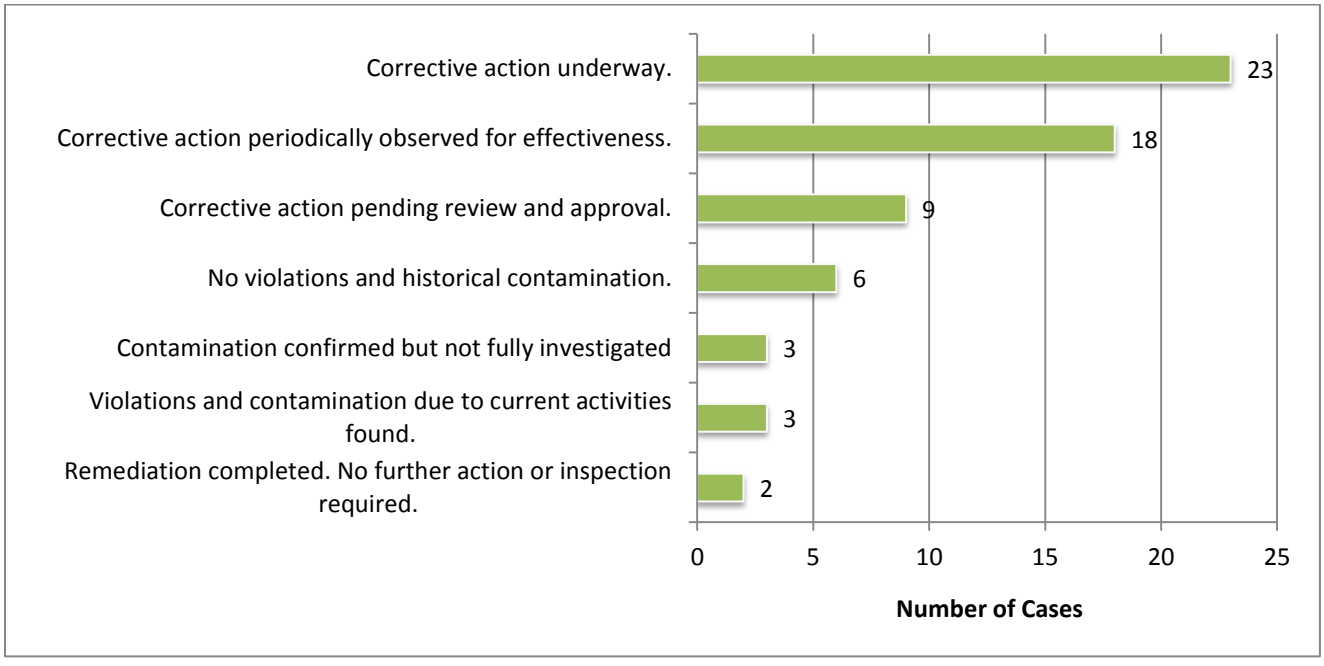
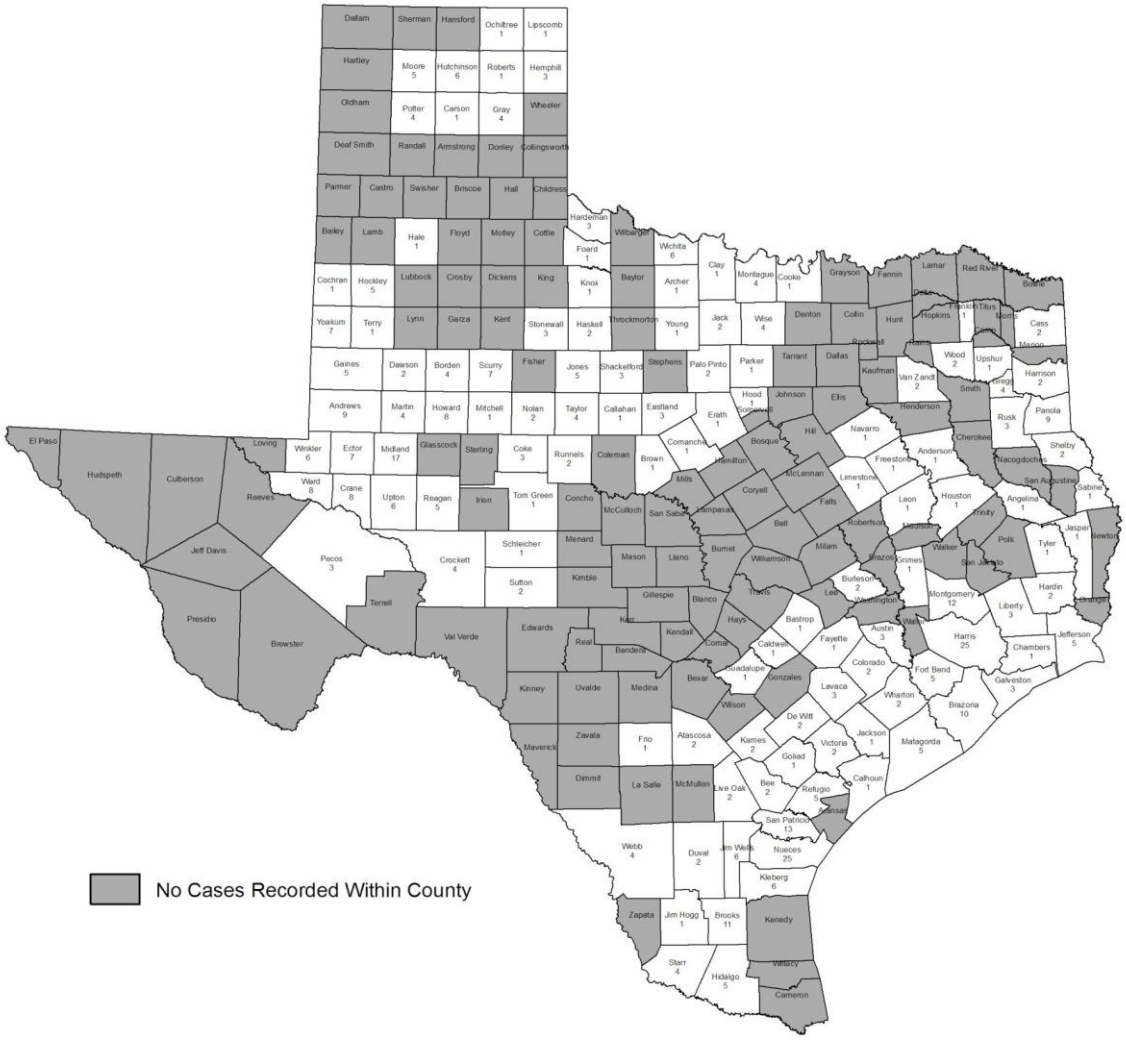


FIGURE 13 MAP OF THE NUMBER OF PENDING GROUNDWATER CONTAMINATION CASES CAUSED BY OIL AND GAS ACTIVITIES REPORTED IN 2010 (TEXAS GROUNDWATER PROTECTION COMMITTEE 2011).



Appendix V – Data preparation

USGS Produced Water Database

The database was filtered for "EAGLEFORD" under the category "RevSAMPFORM." According to the user manual, REVSAMPFORM stands for "Revised sample formation name," and indicates the following: "Geologic units from which the samples was [sic] produced. Corrections to SAMPFORM made to be consistent with stratigraphic columns in the USGS 1995 National Oil and Gas Assessment and the USGS Geologic Names Lexicon http://ngmdb.usgs.gov/Geolex/geolex_home.html" Additionally, some records in the database were codes for "null" entries, where no concentration was available. In preparing the dataset for analysis, values of zero in the USGS produced waters database were interpreted as null entries, as were values of -3, -2, and -1, because the USGS produced waters database description reads "values of -3 replace original character entries of "ND", "NA" or null entries; -2 replace original character entries of "none", "negative", or "nil", -1 replaces original character entries of "trace" and "minor". (Null entries: 0)." (U.S. Geological Survey 2002)

Kearns (2010)

Geochemical analysis of Eagle Ford core samples taken by Kearns (2010) include major elements, trace elements, and isotopes listed below. The data were taken at two sites: one in Gonzales County, and one in De Witt County. The samples in Gonzales County (n=72) represent depths from 8090.5 to 8173.5 feet, while the samples taken in DeWitt (n=42) County represent depths of 13700.5 to 13828.5 feet (Kearns 2011).

- N %
- TOC %
- C/N
- δ15N
- δ13C
- TIC %
- S %
- Mg %
- Al %
- Si %
- P %
- K %
- Ca %
- Ti %
- Mn %
- Fe %
- V ppm
- Cr ppm
- Ni ppm
- Cu ppm
- Zn ppm
- Th ppm
- Rb ppm
- U ppm
- Sr ppm
- Zr ppm
- Mo ppm

TWDB Groundwater Database

The following procedures were used to extract data from the TWDB groundwater quality database:

1. Data for each county was extracted using the "Water Quality Publication Report Query" and each county code.
2. The data was filtered for reliability codes 08 – 14 and 16 using the column labeled "reliability rem." (see Appendix VII – Reliability codes)
3. Flags indicating quantity boundaries, such as greater than ">" or less than "<," were ignored when preceding a concentration.
4. Blanks were revised as "NA" for functionality with statistical and geospatial analysis software.
5. Zeros were set to "NA" if they deviated substantially from the range of other values in the dataset.
6. Zero values for carbonate were changed to NA values when they made up most of the samples in a county. For example, no data for carbonate was provided for Wood County.

Geospatial Analysis

ESRI was the data source for Texas county boundaries data (ESRI 2000). Location data for water wells in Texas was acquired from the TWDB's GIS Data webpage (TWDB GISa; TWDB GISb). The groundwater quality data tables were added to the map and then joined by state well number with the TWDB "Well Location Shapefile". Finally, the data were projected in NAD 1983 with no UTM Zone. For displaying graduated colors, in some cases the natural breaks (Jenks) method was used to display the range of concentrations. However, if significant thresholds, such as an MCL, were known for a specific chemical, the displayed concentration ranges were altered to depict this threshold.

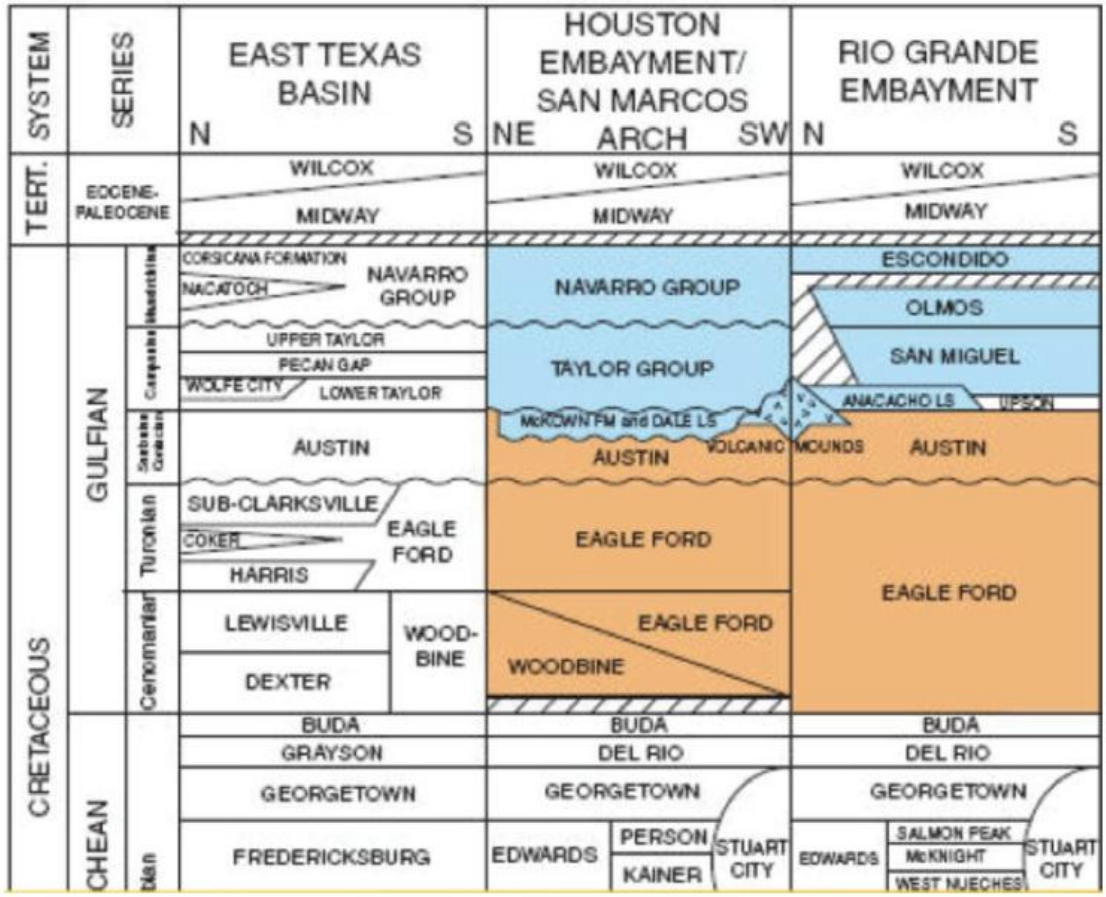
Literature Review

Literature was systematically queried using two databases: ISI Web of Knowledge, and OnePetro. Additional literature may be included that the author found through other sources. Search terms for the literature searches were as follows:

- "Eagle Ford" AND formation
- "Eagle Ford" AND shale
- "*County Name* County" Texas

Appendix VI – Stratigraphic column

FIGURE 14 STRATIGRAPHIC COLUMN OF THE EAGLE FORD FORMATION (CONDON AND DYMAN 2006, CITED IN MULLEN 2010).



Appendix VII – Reliability codes for groundwater quality samples in Texas Water Development Board database.

Code	Description
01	Not indicative of aquifer quality. Data should be used carefully.
02	Sample collected from well not sufficiently pumped; and not filtered or preserved. Data should still be used carefully.
03	Sample collected from well sufficiently pumped but not filtered or preserved. Holding time probably not honored.
04	Chemical analysis taken from a report. Sample collection and preservation procedures unknown.
08	Sample filtered in the field. Temperature, conductivity, and pH measured in the field. Alkalinity measured in the lab. Nutrient sample not preserved and included in anion sub-sample. Sample kept cold until delivered to the lab.
09	Same as #08, but not filtered in the field.
10	Sampled in accordance with the TWDB's A Field Manual for Ground-Water Sampling, 2003. Samples are collected when temperature, conductivity, and pH have stablized. Sample was filtered and field tested for alkalinity. Samples are preserved as applicable, kept chilled, and delivered to the lab. Holding times are honored. Organic sub-samples are not filtered.
11	Same as #10 but not filtered.
12	Sample collected by TCEQ staff following prescribed QA-QC procedures.
13	Cation sample preserved and run thru TDH lab. Anion and nutrient sub-samples sent to lab at Texas Tech lab and run within 24 hours. Field test completed as described in #10.
14	Similar to #10 but sample results determined by using a Hach DR-2000 lab.
15	Collection procedures not documented, results obtained by use of a Groundwater Conservation District's Hach equipment.
16	Sample collected by USGS for NAWQA program using "Clean Sample" technique.
99	Reliability unknown, not available, or not yet entered into database. Sample collected from tank, distribution, or bailed from well.

Appendix VIII – TWDB Groundwater Database Listed Parameters

Concentrations for the following chemicals and parameters are provided in the Texas Water Development Board groundwater database:

pH	Boron	Lead	Silicon
Temperature	Bromide	Lithium	Silver
Conductivity	Cadmium	Magnesium	Sodium
Sodium Adsorption Ratio	Calcium	Manganese	Strontium
Total Dissolved Solids	Calcium Carbonate	Mercury	Sufate
Alkalinity	Carbonate	Molybdenum	Tellurium
Aluminum	Chloride	Nitrate	Uranium
Antimony	Chromium	Nitrite plus Nitrate	Vanadium
Arsenic	Cobalt	Oxygen	Zinc
Barium	Copper	Phosphorus	
Beryllium	Fluoride	Potassium	
Bicarbonate	Iron	Selenium	

Appendix IX – All Infrequent Constituents Identified in the TWDB Groundwater Database

1,1,1-TRICHLOROETHANE, TOTAL, UG/L
1,1,2,2-TETRACHLOROETHANE, TOTAL, UG/L
1,1,2-TRICHLOROETHANE, TOTAL, UG/L
1,1-DICHLOROETHANE, TOTAL, UG/L
1,1-DICHLOROETHYLENE, TOTAL, UG/L
1,2,4-TRICHLOROBENZENE, TOTAL, UG/L
1,2-DICHLOROBENZENE, TOTAL, UG/L
1,2-DICHLOROETHANE, TOTAL, UG/L
1,2-DICHLOROPROPANE, TOTAL, UG/L
1,2-DIPHENYLHYDRAZINE, TOTAL, UG/L
1,3-DICHLOROBENZENE, TOTAL, UG/L
1,4-DICHLOROBENZENE, TOTAL, UG/L
2, 4, 5-T, WATER, DISSOLVED, UG/L
2, 4-D, WATER, DISSOLVED, UG/L
2,4,5-T, TOTAL, UG/L
2,4,5-TP INCLUDES ACIDS & SALTS IN WATER, UG/L
2,4,6-TRICHLOROPHENOL, TOTAL, UG/L
2,4-D, TOTAL, UG/L
2,4-DICHLOROPHENOL, TOTAL, UG/L
2,4-DIMETHYLPHENOL, TOTAL, UG/L
2,4-DINITROPHENOL, TOTAL, UG/L
2,4-DINITROTOLUENE, TOTAL, UG/L
2,6-DINITRO-2-CRESOL, TOTAL, UG/L
2,6-DINITROTOLUENE, TOTAL, UG/L
2-CHLOROETHYL VINYL ETHER, TOTAL, UG/L
2-CHLORONAPHTHALENE, TOTAL, UG/L
2-NITROPHENOL, TOTAL, UG/L
3,3'-DICHLOROBENZIDINE, TOTAL, UG/L
4,4'-DDD, TOTAL, UG/L
4,4'-DDE, TOTAL, UG/L
4,4'-DDT, TOTAL, UG/L
4-BROMOPHENYL PHENYL ETHER, TOTAL, UG/L
4-CHLORO-3-CRESOL, TOTAL, UG/L
4-CHLOROPHENYL PHENYL ETHER, TOTAL, UG/L
4-NITROPHENOL, TOTAL, UG/L
A-BHC-ALPHA, TOTAL, UG/L
ACENAPHTHENE, TOTAL, UG/L
ACENAPHTHYLENE, TOTAL, UG/L
ACROLEIN, DISSOLVED, UG/L
ACRYLONITRILE, DISSOLVED, UG/L
ALACHLOR, TOTAL, UG/L
ALDRIN, TOTAL, UG/L
ALKALINITY PHENOLPHTHALEIN FIELD DATA (MG/L)
ALKALINITY, FIELD, DISSOLVED AS CACO3
ALKALINITY, TOTAL (MG/L AS CACO3)
ALPHA, DISSOLVED (PC/L)
ALPHA, TOTAL (PC/L)
ALUMINUM, DISSOLVED (UG/L AS AL)
ALUMINUM, TOTAL (UG/L AS AL)
ANION/CATION CHG BAL, PERCENT
ANTHRACENE, TOTAL, UG/L
ANTIMONY, DISSOLVED (UG/L AS SB)
ANTIMONY, TOTAL (UG/L AS SB)
ARSENIC, DISSOLVED (UG/L AS AS)
ARSENIC, TOTAL (UG/L AS AS)
BANVEL (DICAMBA), TOTAL, UG/L
BARIUM, DISSOLVED (UG/L AS BA)
BARIUM, TOTAL (UG/L AS BA)
B-BHC-BETA, TOTAL, UG/L
BENZENE, VOLATILE ANALYSIS, TOTAL, UG/L
BENZIDINE, TOTAL, UG/L
BENZO(A) ANTHRACENE, TOTAL, UG/L
BENZO-(A)-PYRENE, TOTAL, UG/L
BENZO(B)FLUORANTHENE, TOTAL, UG/L
BENZO(GHI)PERYLENE, TOTAL, UG/L
BENZO(K)FLUORANTHENE, TOTAL, UG/L
BERYLLIUM, DISSOLVED (UG/L AS BE)
BERYLLIUM, TOTAL (UG/L AS BE)
BETA, DISSOLVED (PC/L)
BETA, TOTAL (PC/L)
BIS (2-CHLOROETHOXY) METHANE, TOTAL, UG/L
BIS (2-CHLOROETHYL) ETHER, TOTAL, UG/L
BIS (2-CHLOROISOPROPYL) ETHER, TOTAL, UG/L
BIS(2-ETHYLHEXYL) PHTHALATE, TOTAL, UG/L
BISPHENOL, TOTAL, UG/L
BORON, DISSOLVED (UG/L AS B)
BROMIDE, DISSOLVED, (MG/L AS BR)
BROMIDE, DISSOLVED, (UG/L AS BR)
BROMODICHLOROMETHANE, TOTAL, UG/L
BROMOFORM, TOTAL, UG/L

BROMOMETHANE, TOTAL, UG/L
BUTYLBENZYL PHTHALATE, TOTAL, UG/L
CADMIUM, DISSOLVED (UG/L AS CD)
CADMIUM, TOTAL (UG/L)
CALCIUM, DISSOLVED (MG/L AS CA)
CARBON DIOXIDE (MG/L AS CO2)
CARBON TETRACHLORIDE, TOTAL, UG/L
CARBON, TOTAL (MG/L AS C)
CARBON, TOTAL INORGANIC (MG/L AS C)
CARBON, TOTAL ORGANIC (MG/L AS C)
CARBON-13 / CARBON-12 STABLE ISOTOPE RATIO PER MIL
CARBON-14 DISS APPARENT AGE (YEARS BP)
CARBON-14 FRACTION MODERN
CHLORDANE, TOTAL, UG/L
CHLORIDE, TOTAL (MG/L AS CL)
CHLOROBENZENE, TOTAL, UG/L
CHLORODIBROMOMETHANE, TOTAL, UG/L
CHLOROETHANE, TOTAL, UG/L
CHLOROFORM, TOTAL, UG/L
CHLOROMETHANE, TOTAL, UG/L
CHLOROPHENOL, TOTAL, UG/L
CHROMIUM, DISSOLVED (UG/L AS CR)
CHROMIUM, FIELD ACIDIFIED W/HNO3, FILTERED, UG/L
CHROMIUM, TOTAL (UG/L AS CR)
CHRYSENE, TOTAL, UG/L
CIS-1,3-DICHLOROPROPENE, TOTAL, UG/L
CIS-1,3-DICHLOROPROPYLENE, TOTAL, UG/L
COBALT, DISSOLVED (UG/L AS CO)
COPPER, DISSOLVED (UG/L AS CU)
COPPER, TOTAL (UG/L AS CU)
CYCLOHEXANONE, TOTAL, UG/L
DACTHAL (DCPA), TOTAL, UG/L
DDD, TOTAL, UG/L
DDE, TOTAL, UG/L
DDT, TOTAL, UG/L
DELTA-BHC, TOTAL, UG/L
DEUTERIUM, EXPRESSED AS PERMIL VSMOW
DIAZINON, TOTAL, UG/L
DIBENZO (A,H) ANTHRACENE, TOTAL, UG/L
DIBROMOCHLOROMETHANE, TOTAL, UG/L
DIELDRIN, TOTAL, UG/L
DIETHYL PTHALATE, TOTAL, UG/L
DIMETHYL PTHALATE, TOTAL, UG/L
DI-N-BUTYL PHTHALATE, TOTAL, UG/L
DI-N-OCTYL PHTHALATE, TOTAL, UG/L
DIPHENYLAMINE, TOTAL, UG/L
DURSBAN (CHLOROPYRIFOS), TOTAL, UG/L
ENDOSULFAN - ALPHA, TOTAL, UG/L
ENDOSULFAN - BETA, TOTAL, UG/L
ENDOSULFAN SULFATE, TOTAL, UG/L
ENDOSULFAN, TOTAL, UG/L
ENDRIN ALDEHYDE, TOTAL, UG/L
ENDRIN, TOTAL, UG/L
ETHYL PARATHION, TOTAL, UG/L
ETHYLBENZENE IN WATER, UG/L
FLUORANTHENE, TOTAL, UG/L
FLUORENE, TOTAL, UG/L
FLUORIDE, TOTAL (MG/L AS F)
GAMMA-BHC (LINDANE), TOTAL, UG/L
GROSS ALPHA RADIATION,TOTAL, PRODUCED WATER(pCi/L)
GROSS BETA RADIATION, TOTAL, PRODUCED WATER(pCi/L)
HALOGEN, TOTAL ORGANIC, UG/L
HARDNESS, NON-CARBONATE (MG/L AS CACO3)
HARDNESS, TOTAL (MG/L AS CACO3)
HEPTACHLOR EPOXIDE, TOTAL, UG/L
HEPTACHLOR, TOTAL, UG/L
HEXACHLOROBENZENE (HCB), TOTAL, UG/L
HEXACHLOROBUTADIENE, TOTAL, UG/L
HEXACHLOROCYCLOPENTADIENE, TOTAL, UG/L
HEXACHLOROETHANE, TOTAL, UG/L
HYDROGEN ION CONCENTRATION, TOTAL (MG/L)
HYDROGEN SULFIDE, MG/L
HYDROXIDE ION (MG/L AS OH)
INDENO (1,2,3-CD) PYRENE
IODIDE (MG/L AS I)
IRON, DISSOLVED (UG/L AS FE)
IRON, TOTAL (UG/L AS FE)
ISOPHORONE, TOTAL, UG/L
LEAD, DISSOLVED (UG/L AS PB)
LEAD, FIELD FILTERED, ACIDIFIED W/HNO3, UG/L
LEAD, TOTAL (UG/L AS PB)
LINDANE, TOTAL, UG/L

LITHIUM, DISSOLVED (UG/L AS LI)
LITHIUM, TOTAL (UG/L AS LI)
MAGNESIUM, DISSOLVED (MG/L AS MG)
MAGNESIUM, TOTAL (MG/L AS MG)
MALATHION, TOTAL, UG/L
MANGANESE, DISSOLVED (UG/L AS MN)
MANGANESE, TOTAL (UG/L AS MN)
MERCURY, DISSOLVED (UG/L AS HG)
MERCURY, TOTAL (UG/L AS HG)
METHOXYCHLOR, TOTAL, UG/L
METHYL PARATHION, TOTAL, UG/L
METHYLENE CHLORIDE, TOTAL, UG/L
MOLYBDENUM, DISSOLVED, UG/L
NAPHTHALENE, TOTAL, UG/L
NICKEL, DISSOLVED (UG/L AS NI)
NICKEL, TOTAL (UG/L AS NI)
NITRATE NITROGEN, DISSOLVED (MG/L AS N)
NITRATE NITROGEN, TOTAL (MG/L AS N)
NITRITE NITROGEN, DISSOLVED (MG/L AS N)
NITRITE NITROGEN, TOTAL (MG/L AS N)
NITRITE NITROGEN, TOTAL (MG/L AS NO2)
NITRITE PLUS NITRATE, DISSOLVED (MG/L AS N)
NITRITE PLUS NITRATE, TOTAL (MG/L AS N)
NITROBENZENE, TOTAL, UG/L
NITROGEN, AMMONIA, DISSOLVED (MG/L AS N)
NITROGEN, AMMONIA, TOTAL (MG/L AS N)
NITROGEN, KJELDAHL, DISSOLVED (MG/L AS N)
NITROGEN, ORGANIC, TOTAL (MG/L AS N)
N-NITROSODIMETHLAMINE, TOTAL, UG/L
N-NITROSO-DI-N-PROPYLAMINE, TOTAL, UG/L
N-NITROSODIPHENYLAMINE, TOTAL, UG/L
OXIDATION REDUCTION POTENTIAL (ORP), MILLIVOLTS
OXYGEN, DISSOLVED (MG/L)
OXYGEN, DISSOLVED, ANALYSIS BY PROBE (MG/L)
OXYGEN-18, EXPRESSED AS PERMIL VSMOW
OXYGEN-18/OXYGEN-16 OF SULFATE (RATIO PER MIL)
PCB - 1221, TOTAL, UG/L
PCB - 1232, TOTAL, UG/L
PCB - 1242, TOTAL, UG/L
PCB - 1248, TOTAL, UG/L
PCB - 1254, TOTAL, UG/L
PCB - 1260, TOTAL, UG/L
PCB - 1262 (ARACLOR), TOTAL, UG/L
PCB- 1016, TOTAL, UG/L
PENTACHLOROPHENOL (PCP), TOTAL, UG/L
PH (STANDARD UNITS) LAB
PH (STANDARD UNITS), FIELD
PHENANTHRENE, TOTAL, UG/L
PHENOL, TOTAL, UG/L
PHOSPHORUS, DISSOLVED (MG/L AS P)
PHOSPHORUS, DISSOLVED ORTHOPHOSPHATE (MG/L AS P)
PHOSPHORUS, IN TOTAL ORTHOPHOSPHATE (MG/L AS P)
PHOSPHORUS, TOTAL (MG/L AS P)
PHOSPHORUS, TOTAL AS PO4 (MG/L)
PICLORAM, TOTAL, UG/L
POTASSIUM 40 (K-40), DISSOLVED, PC/L
POTASSIUM, DISSOLVED (MG/L AS K)
PURGEABLE ORGANIC CARBON, UG/L
PYRENE, TOTAL, UG/L
RADIUM 226 + RADIUM 228, DISSOLVED, PC/L
RADIUM 226 + RADIUM 228, TOTAL, PC/L
RADIUM 226, DISSOLVED, PC/L
RADIUM 226, DISSOLVED, RADON METHOD, PC/L
RADIUM 226, TOTAL, PC/L
RADIUM 228, DISSOLVED (PC/L AS RA-228)
RADIUM 228, TOTAL, PC/L
RADON 222, DISSOLVED, PC/L
RESIDUE, TOTAL FILTERABLE (DRIED AT 180C), MG/L
SELENIUM, DISSOLVED (UG/L AS SE)
SELENIUM, TOTAL (UG/L)
SILVER, DISSOLVED (UG/L AS AG)
SILVER, FIELD FILTERED, ACIDIFIED W/HNO3, UG/L
SILVER, TOTAL (UG/L AS AG)
SILVEX, TOTAL, UG/L
SODIUM CHLORIDE (NACL), MG/L
SODIUM PLUS POTASSIUM (MG/L)
SODIUM, DISSOLVED (MG/L AS NA)
SOLIDS, SUSPENDED, RESIDUE ON EVAP AT 180C, MG/L
SPECIFIC CONDUCTANCE, FIELD (UMHOS/CM AT 25C)
STRONTIUM, DISSOLVED (UG/L AS SR)
STRONTIUM, ISOTOPE OF MASS 86 AND 87 RATIO
SULFATE, TOTAL (MG/L AS SO4)
SULFIDE, DISSOLVED (MG/L AS S)
SULFUR-34/32 OF SULFATE, DISSOLVED, PER MIL

TEMPERATURE, WATER (CELSIUS)
TETRACHLOROETHYLENE, DISSOLVED, UG/L
THALLIUM, DISSOLVED (UG/L AS TL)
THALLIUM, TOTAL (UG/L AS TL)
THORIUM, NATURAL, DISSOLVED PC/L
TIN, TOTAL (UG/L AS SN)
TOLUENE, VOLATILE ANALYSIS, TOTAL, UG/L
TOTAL PETROLEUM HYDROCARNON mg/L
TOXAPHENE, TOTAL, UG/L
TRANS-1,2-DICHLOROETHYLENE, TOTAL, UG/L
TRANS-1,3-DICHLOROPROPENE, TOTAL, UG/L
TRANS-1,3-DICHLOROPROPYLENE, TOTAL, UG/L
TRICHLOROETHYLENE, TOTAL, UG/L
TRICHLOROFLUOROMETHANE, TOTAL, UG/L
TRITIUM COUNTING ERROR
TRITIUM IN WATER (TRITIUM UNITS)
TRITIUM, DISSOLVED (TRITIUM UNITS)
TRITIUM, TOTAL (TRITIUM UNITS)
TURBIDITY, LAB, NEPHELOMETRIC TURBIDITY UNITS, NTU
URANIUM, NATURAL, DISSOLVED, UG/L
URANIUM, NATURAL, TOTAL (PC/L AS U)
VANADIUM, DISSOLVED (UG/L AS V)
VINYL CHLORIDE, TOTAL, UG/L
XYLENE, TOTAL, UG/L
ZINC, DISSOLVED (UG/L AS ZN)
ZINC, TOTAL (UG/L AS ZN)

Appendix X - Carbon isotope ratios by depth

FIGURE 15 $^{13}C/^{12}C$ STABLE ISOTOPE RATIOS IN GROUNDWATER BY DEPTH IN THE COUNTIES OF INTEREST.

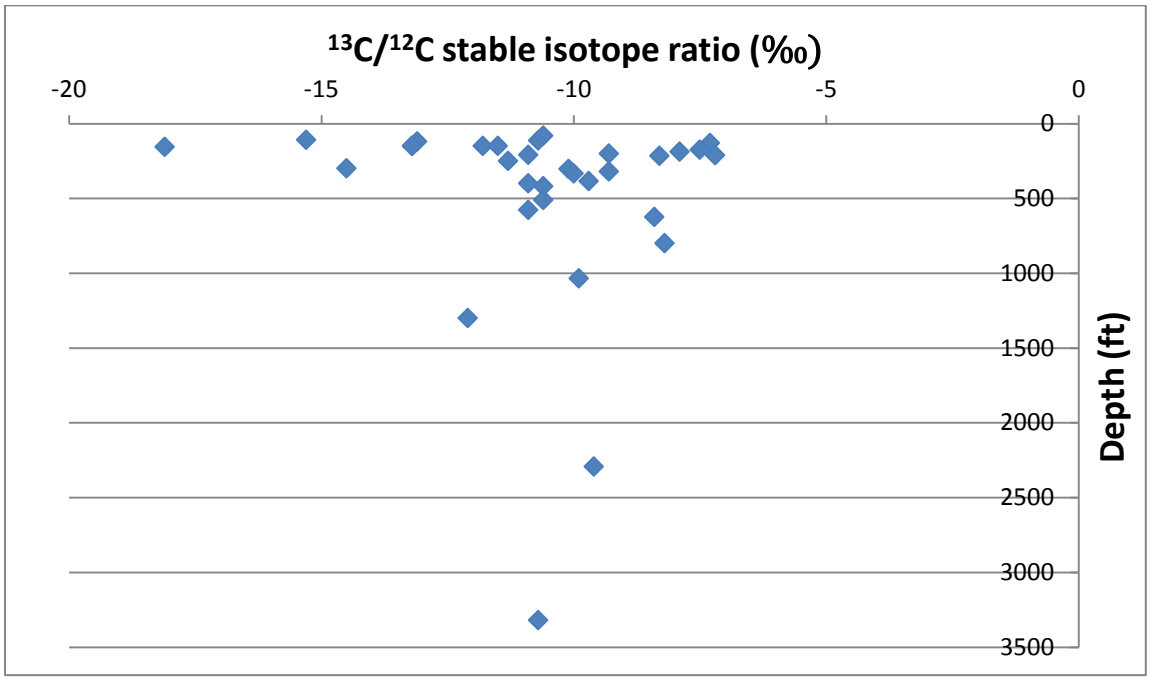


FIGURE 16 COUNTIES WHERE $^{13}C/^{12}C$ STABLE ISOTOPE RATIO DATA FOR GROUNDWATER OR CORE SAMPLES ARE AVAILABLE.

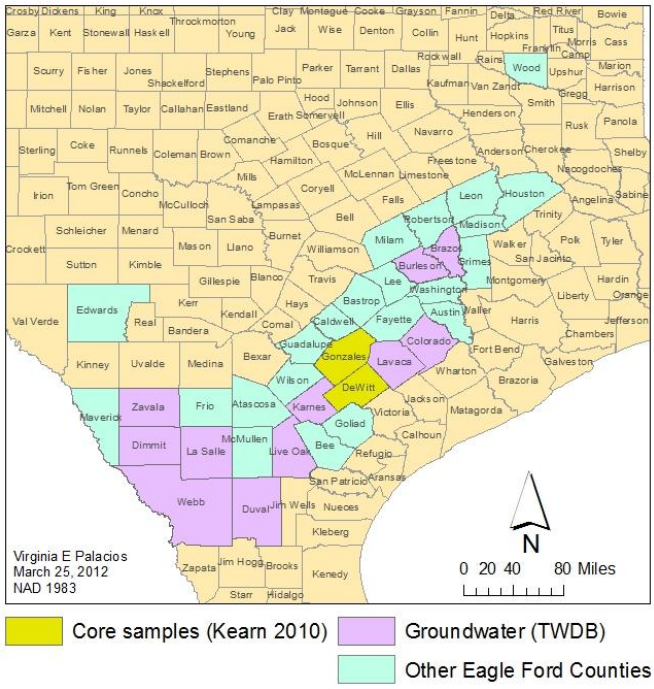


TABLE 23 CARBON ISOTOPE RANGES FOR GROUNDWATER IN THE COUNTIES OF INTEREST.

County	Number of samples	$^{13}C/^{12}C$
Brazos	1	-10.1
Burleson	1	-14.5
Colorado	2	-11.3 to -7.9
Dimmit	2	-18.1 to -12.1
Duval	4	-13.2 to -8.2
Karnes	2	-10.6 to -7.2
La Salle	1	-9.6
Lavaca	6	-13.1 to -7.3
Live Oak	4	-10.9 to -8.3
Webb	1	-10.7
Zavala	2	-11.8 to -9.9
Total	**26**	

FIGURE 17 DISTRIBUTION OF CARBON ISOTOPE RANGES FOUND IN GROUNDWATER IN EAGLE FORD SHALE COUNTIES.

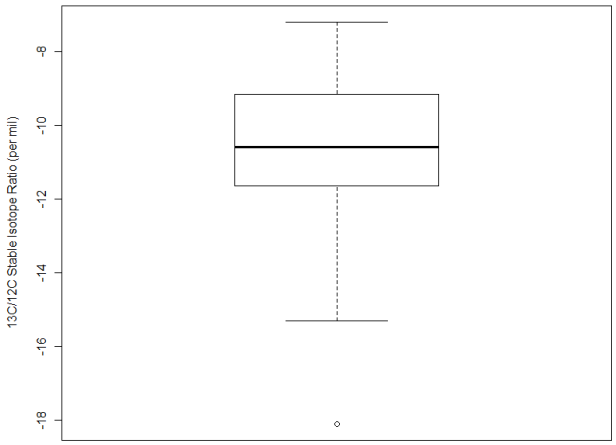


FIGURE 18 NUMBER, PERCENT OF TOTAL WATER WELLS, AND GROUNDWATER TESTING NEEDS FOR GAS HYDROCARBONS WITH IN EAGLE FORD SHALE COUNTIES. TESTING CODES: A = AS NEEDED, R = RECOMMENDED, T = TESTING NEEDED

County	Total wells	Total organic carbon			$^{13}C/^{12}C$		
Bastrop	791	13	1.6%	T			T
Bee	631	1	0.2%	T			T
Brazos	687			T	1	0.1%	T
Burleson	847			T	1	0.1%	T
Colorado	574	11	1.9%	T	2	0.3%	T
Dimmit	527			T	2	0.4%	T
Duval	683	1	0.1%	T	4	0.6%	T
Edwards	604		0.0%	T	3	0.5%	T
Fayette	863	12	1.4%	T			T
Goliad	507	1	0.2%	T	5	1.0%	T
Karnes	410			T	2	0.5%	T
La Salle	362			T	1	0.3%	T
Lavaca	386			T	6	1.6%	T
Live Oak	540	5	0.9%	T	5	0.9%	T
Webb	339	9	2.7%	T	1	0.3%	T
Zavala	748			T	2	0.3%	T

Appendix XI – Salts

Produced water comparison with groundwater

TABLE 24 WOOD COUNTY T-TEST RESULTS FOR PRODUCED WATER COMPARED TO GROUNDWATER; ALL CONCENTRATIONS MEASURED IN MG/L, EXCEPT FOR PH. [35]

Parameter	Mean of the differences	p-value	t	df	Lower 95% CI	Upper 95% CI
pH	-0.3834286	0.1175	-1.6063	34	-0.8685358	0.1016787
Bicarbonate	225.9209	3.86E-12	10.7383	32	183.0664	268.7754
Calcium	1978.569	0	24.5712	33	1814.742	2142.396
Chloride	52614.51	0	46.3473	34	50307.46	54921.56
Magnesium	444.2947	0	24.845	33	407.9122	480.6772
Sodium	31611.01	0	52.758	32	30390.54	32831.47
Sulfate	-7.293103	0.1655	-1.4241	28	-17.783536	3.197329
Total Dissolved Solids	86411.64	0	43.3803	32	82354.16	90469.12

TABLE 25 WOOD COUNTY SUMMARY STATISTICS. WW = PRODUCED WATER, GW = GROUNDWATER; ALL CONCENTRATIONS MEASURED IN MG/L, EXCEPT FOR PH.[36]

Parameter	n	Mean	Min.	1st Qu.	Median	3rd Qu.	Max
WW pH	35	7.096	6.4	7.025	7.15	7.25	7.45
GW pH	55	7.472	4.22	6.525	7.91	8.47	8.89
WW Bicarbonate	35	414.7	137	366.5	430	459	570
GW Bicarbonate	53	176.63	24.41	125.69	170.85	218.44	452.75
WW Calcium	35	1990	1156	1631	1894	2432	2761
GW Calcium	54	10.14	0.76	1.975	3.425	8.23	61
WW Chloride	35	52651	26562	52497	54285	55156	60965
GW Chloride	55	34.142	1	8.055	14.3	38.4	285
WW Magnesium	35	445.5	205	399	415	518	638
GW Magnesium	53	2.066	0.2	0.5	1	1.4	11.8
WW Sodium	34	31665	13590	31356	32110	32802	35963
GW Sodium	53	82.19	2.09	36.8	81	106	344
WW Sulfate	29	17.28	3	12	17	22	48
GW Sulfate	54	23.36	1	10.22	18.3	34.85	95
WW TDS	35	86702	43435	86487	89366	90671	100321
GW TDS	52	266.3	56	204.8	251.5	308.5	887

[35] For p-values of zero, the p-value returned in the statistical software used, "R," is "<2.2e-16" which is coded as "***" and indicates a p-value of 0.

TABLE 26 ALL EAGLE FORD SHALE COUNTIES: T-TEST RESULTS FOR PRODUCED WATER COMPARED TO GROUNDWATER. TDS = TOTAL DISSOLVED SOLIDS; ALL CONCENTRATIONS MEASURED IN MG/L, EXCEPT FOR PH.

Parameter	Mean of the differences	p-value	t	df	Lower 95% CI	Upper 95% CI
pH	-0.220177	0	2827	1524	-0.2693818	-0.1709723
Bicarbonate	536.3342	0	26.6662	1583	496.8834	575.7849
Calcium	2355.311	0	16.8098	1593	2080.48	2630.142
Chloride	26434.53	0	28.7776	1591	24632.77	28236.28
Magnesium	305.6848	0	16.9282	1570	270.2651	341.1045
Sodium	14162.53	0	32.3223	1562	13303.07	15021.98
Sulfate	202.6485	1.62E-09	6.0823	1121	137.2767	268.0203
TDS	44018.91	0	29.5107	1569	41093.12	46944.7
Potassium	147.9325	7.27E-08	5.6843	141	96.48327	199.3818

TABLE 27 ALL COUNTIES IN THE EAGLE FORD SHALE REGION: SUMMARY STATISTICS. WW = PRODUCED WATER, GW = GROUNDWATER. ALL CONCENTRATIONS MEASURED IN MG/L, EXCEPT FOR PH.

Parameter	n	Mean	Min	1st Qu.	Median	3rd Qu.	Max
WW pH	1555	7.254	5	6.65	7.4	7.9	8.9
GW pH	2827	7.459	4.14	7	7.37	7.96	9.86
WW Bicarbonate	2881	898.2	3	344.5	701	1185.5	4731
GW Bicarbonate	2864	333.4	0	214.8	290.4	366.1	2374.8
WW Calcium	1600	2412.3	1	37	189.5	1521.2	40992
GW Calcium	2877	55.96	0.1	6.84	40.7	83	909
WW Chloride	1605	26751	490	3589	11876	32517	245367
GW Chloride	2869	187.6	1	30.7	75.3	194	9579
WW Magnesium	1577	317.8	1	17	51	338	17205
GW Magnesium	2876	12.501	0	1.518	6.55	15.1	327
WW Sodium	1589	14398	148	2725	7357	18061	123775
GW Sodium	2835	213.3	1.1	51.6	119	248	7230
WW Sulfate	1128	336.3	1	13	43	210	14100
GW Sulfate	2868	117.4	0	18.68	46.5	109	2830
WW TDS	1603	45032	1033	7568	21275	54148	398024
GW TDS	1543	795.6	36	333	538	909	17606
WW Potassium	143	155.6	2	10	15	138.5	1635
GW Potassium	2832	6.37	0	2.498	4.64	7.482	134

Salts data availability

TABLE 28 NUMBER, PERCENT OF TOTAL WATER WELLS, AND GROUNDWATER TESTING NEEDS FOR SALTS FOUND IN PRODUCED WATER IN ATASCOSA, AUSTIN, BASTROP, BEE, AND BRAZOS COUNTIES. TESTING CODES: A = AS NEEDED, R = RECOMMENDED, T = TESTING NEEDED

County	Atascosa			Austin			Bastrop			Bee			Brazos		
Total wells	1117			321			791			631			687		
TDS	180	16%	A	67	21%	A	84	11%	A	43	7%	A	72	10%	A
Chloride	182	16%	A	68	21%	A	84	11%	A	43	7%	A	72	10%	A
Sodium	180	16%	A	68	21%	A	84	11%	A	44	7%	A	73	11%	A
Sulfate	182	16%	A	68	21%	A	84	11%	A	43	7%	A	72	10%	A
Calcium	182	16%	A	68	21%	A	84	11%	A	44	7%	A	73	11%	A
Magnesium	182	16%	A	68	21%	A	84	11%	A	44	7%	A	73	11%	A
Bicarbonate	182	16%	A	67	21%	A	84	11%	A	44	7%	A	73	11%	A
Potassium	176	16%	A	68	21%	A	84	11%	A	42	7%	A	73	11%	A

TABLE 29 NUMBER, PERCENT OF TOTAL WATER WELLS, AND GROUNDWATER TESTING NEEDS FOR SALTS FOUND IN PRODUCED WATER IN BURLESON, CALDWELL, COLORADO, DEWITT, AND DIMMIT COUNTIES. TESTING CODES: A = AS NEEDED, R = RECOMMENDED, T = TESTING NEEDED

County	Burleson			Caldwell			Colorado			De Witt			Dimmit		
Total wells	847			599			574			513			527		
TDS	85	10%	A	25	4%	T	104	18%	A	40	8%	A	97	18%	A
Chloride	85	10%	A	25	4%	T	105	18%	A	40	8%	A	99	19%	A
Sodium	85	10%	A	25	4%	T	104	18%	A	40	8%	A	98	19%	A
Sulfate	85	10%	A	25	4%	T	105	18%	A	40	8%	A	99	19%	A
Calcium	85	10%	A	25	4%	T	105	18%	A	40	8%	A	100	19%	A
Magnesium	85	10%	A	25	4%	T	105	18%	A	40	8%	A	100	19%	A
Bicarbonate	85	10%	A	25	4%	T	105	18%	A	40	8%	A	99	19%	A
Potassium	85	10%	A	24	4%	T	104	18%	A	40	8%	A	98	19%	A

TABLE 30 NUMBER, PERCENT OF TOTAL WATER WELLS, AND GROUNDWATER TESTING NEEDS FOR SALTS FOUND IN PRODUCED WATER IN DUVAL, EDWARDS, FAYETTE, FRIO, AND GOLIAD COUNTIES. TESTING CODES: A = AS NEEDED, R = RECOMMENDED, T = TESTING NEEDED

County	Duval			Edwards			Fayette			Frio			Goliad		
Total wells	683			604			863			756			507		
TDS	129	19%	A	75	12%	A	60	7%	A	140	19%	A	42	8%	A
Chloride	129	19%	A	79	105%	A	60	7%	A	143	19%	A	42	8%	A
Sodium	129	19%	A	75	95%	A	60	7%	A	140	19%	A	42	8%	A
Sulfate	129	19%	A	79	105%	A	60	7%	A	143	19%	A	42	8%	A
Calcium	129	19%	A	79	100%	A	60	7%	A	143	19%	A	42	8%	A
Magnesium	129	19%	A	79	100%	A	60	7%	A	143	19%	A	42	8%	A
Bicarbonate	129	19%	A	76	96%	A	60	7%	A	142	19%	A	42	8%	A
Potassium	129	19%	A	79	104%	A	60	7%	A	140	19%	A	42	8%	A

TABLE 31 NUMBER, PERCENT OF TOTAL WATER WELLS, AND GROUNDWATER TESTING NEEDS FOR SALTS FOUND IN PRODUCED WATER IN GONZALES, GRIMES, GUADALUPE, HOUSTON, KARNES COUNTIES. TESTING CODES: A = AS NEEDED, R = RECOMMENDED, T = TESTING NEEDED

County	Gonzales			Grimes			Guadalupe			Houston			Karnes		
Total wells	582			357			638			400			410		
TDS	277	48%	A	40	11%	A	18	3%	T	81	20%	A	43	10%	A
Chloride	277	48%	A	41	11%	A	18	3%	T	82	21%	A	43	10%	A
Sodium	277	48%	A	40	11%	A	18	3%	T	81	20%	A	43	10%	A
Sulfate	277	48%	A	41	11%	A	18	3%	T	82	21%	A	43	10%	A
Calcium	277	48%	A	41	11%	A	18	3%	T	82	21%	A	43	10%	A
Magnesium	277	48%	A	41	11%	A	18	3%	T	82	21%	A	43	10%	A
Bicarbonate	277	48%	A	41	11%	A	18	3%	T	82	21%	A	43	10%	A
Potassium	277	48%	A	41	11%	A	17	3%	T	82	21%	A	41	10%	A

TABLE 32 NUMBER, PERCENT OF TOTAL WATER WELLS, AND GROUNDWATER TESTING NEEDS FOR SALTS FOUND IN PRODUCED WATER IN LA SALLE, LAVACA, LEE, LEON, AND LIVE OAK COUNTIES. TESTING CODES: A = AS NEEDED, R = RECOMMENDED, T = TESTING NEEDED

County	La Salle			Lavaca			Lee			Leon			Live Oak		
Total wells	362			386			399			323			540		
TDS	84	23%	A	96	25%	A	65	16%	A	73	23%	A	65	12%	A
Chloride	85	23%	A	97	25%	A	73	18%	A	73	23%	A	65	12%	A
Sodium	84	23%	A	96	25%	A	66	17%	A	75	23%	A	65	12%	A
Sulfate	85	23%	A	97	25%	A	73	18%	A	73	23%	A	65	12%	A
Calcium	85	23%	A	97	25%	A	74	19%	A	75	23%	A	65	12%	A
Magnesium	85	23%	A	97	25%	A	74	19%	A	75	23%	A	65	12%	A

Bicarbonate	85	23%	A	97	25%	A	71	18%	A	75	23%	A	65	12%	A
Potassium	83	23%	A	97	25%	A	66	17%	A	74	23%	A	65	12%	A

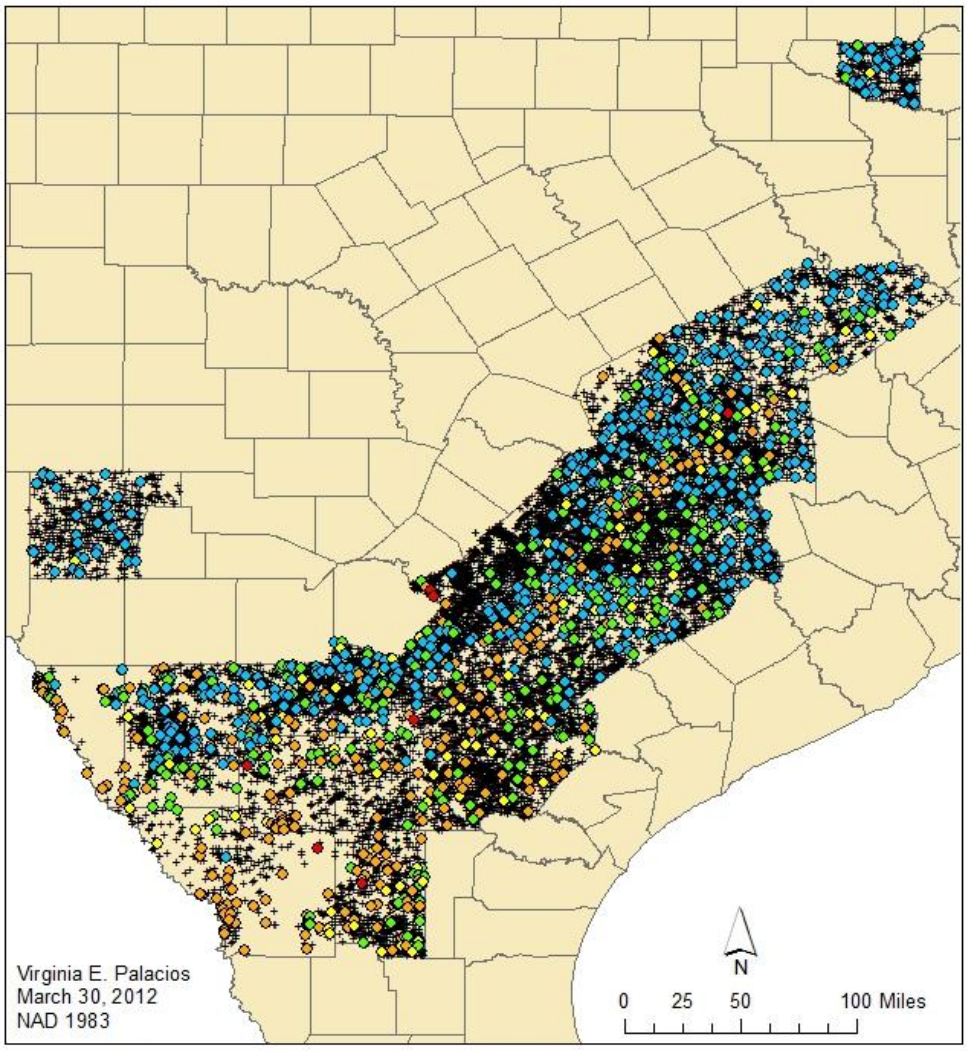
TABLE 33 NUMBER, PERCENT OF TOTAL WATER WELLS, AND GROUNDWATER TESTING NEEDS FOR SALTS FOUND IN PRODUCED WATER IN MADISON, MAVERICK, MCMULLEN, MILAM, AND ROBERTSON COUNTIES. TESTING CODES: A = AS NEEDED, R = RECOMMENDED, T = TESTING NEEDED

County	**Madison**			**Maverick**			**McMullen**			**Milam**			**Robertson**		
Total wells	365			92			184			314			824		
TDS	36	10%	R	64	70%	A	47	26%	A	70	22%	A	95	12%	A
Chloride	37	10%	R	66	72%	A	47	26%	A	78	25%	A	96	12%	A
Sodium	37	10%	R	64	70%	A	47	26%	A	71	23%	A	96	12%	A
Sulfate	37	10%	R	65	71%	A	48	26%	A	78	25%	A	96	12%	A
Calcium	37	10%	R	66	72%	A	48	26%	A	79	25%	A	97	12%	A
Magnesium	37	10%	R	66	72%	A	48	26%	A	79	25%	A	97	12%	A
Bicarbonate	37	10%	R	66	72%	A	48	26%	A	78	25%	A	97	12%	A
Potassium	37	10%	R	65	71%	A	48	26%	A	71	23%	A	96	12%	A

TABLE 34 NUMBER, PERCENT OF TOTAL WATER WELLS, AND GROUNDWATER TESTING NEEDS FOR SALTS FOUND IN PRODUCED WATER IN WASHINGTON, WEBB, WILSON, WOOD, AND ZAVALA COUNTIES. TESTING CODES: A = AS NEEDED, R = RECOMMENDED, T = TESTING NEEDED

County	**Washington**			**Webb**			**Wilson**			**Wood**			**Zavala**		
Total wells	478			339			512			442			748		
TDS	37	8%	R	126	37%	A	95	19%	A	52	12%	A	114	15%	A
Chloride	38	8%	A	127	37%	A	100	20%	A	55	12%	A	115	15%	A
Sodium	37	8%	R	127	37%	A	97	19%	A	53	12%	A	114	15%	A
Sulfate	38	8%	A	127	37%	A	100	20%	A	54	12%	A	115	15%	A
Calcium	38	8%	A	127	37%	A	100	20%	A	54	12%	A	115	15%	A
Magnesium	38	8%	A	127	37%	A	100	20%	A	53	12%	A	115	15%	A
Bicarbonate	38	8%	A	126	37%	A	98	19%	A	54	12%	A	115	15%	A
Potassium	38	8%	A	127	37%	A	96	19%	A	53	12%	A	114	15%	A

FIGURE 19 TOTAL DISSOLVED SOLIDS (TDS) CONCENTRATIONS IN THE EAGLE FORD SHALE REGION.



Regulated salts data availability

TABLE 35 NUMBER, PERCENT OF TOTAL WATER WELLS, AND GROUNDWATER TESTING NEEDS FOR SALTS WITH PRIMARY DRINKING WATER STANDARDS IN EAGLE FORD SHALE COUNTIES. TESTING CODES: A = AS NEEDED, R = RECOMMENDED, T = TESTING NEEDED

	Total wells	Bromide			Nitrate			Selenium		
Atascosa	1117	168	15%	A	41	4%	A	174	16%	A
Austin	321	67	21%	A	13	4%	T	67	21%	A
Bastrop	791	62	8%	A	15	2%	T	78	10%	A
Bee	631	40	6%	A	13	2%	T	42	7%	A
Brazos	687	62	9%	A	15	2%	T	72	10%	A
Burleson	847	70	8%	A	22	3%	T	76	9%	A
Caldwell	599	13	2%	T	4	1%	T	17	3%	T
Colorado	574	87	15%	A	22	4%	T	95	17%	A
De Witt	513	38	7%	A	10	2%	T	39	8%	A
Dimmit	527	103	20%	A	35	7%	R	104	20%	A
Duval	683	139	20%	A	17	2%	T	141	21%	A
Edwards	604	66	11%	A	15	2%	T	66	11%	A
Fayette	863	45	5%	A	18	2%	T	56	6%	A
Frio	756	130	17%	A	39	5%	A	137	18%	A
Goliad	507	41	8%	A	15	3%	T	42	8%	A
Gonzales	582	197	34%	A	14	2%	T	207	36%	A
Grimes	357	39	11%	A	17	5%	T	40	11%	A
Guadalupe	638	14	2%	T	3	0%	T	17	3%	T
Houston	400	66	17%	A	17	4%	T	79	20%	A
Karnes	410	37	9%	R	11	3%	T	40	10%	A
La Salle	362	72	20%	A	19	5%	T	88	24%	A
Lavaca	386	95	25%	A	19	5%	T	95	25%	A
Lee	399	50	13%	A	15	4%	T	55	14%	A
Leon	323	56	17%	A	20	6%	T	72	22%	A
Live Oak	540	72	13%	A	26	5%	R	75	14%	A
Madison	365	28	8%	R	9	2%	T	34	9%	R
Maverick	92	8	9%	T	56	61%	A	36	39%	R
McMullen	184	35	19%	R	13	7%	T	43	23%	A
Milam	314	52	17%	A	17	5%	T	53	17%	A
Robertson	824	75	9%	A	14	2%	T	83	10%	A
Washington	478	42	9%	A	19	4%	T	42	9%	A
Webb	339	114	34%	A	37	11%	R	119	35%	A
Wilson	512	92	18%	A	23	4%	T	93	18%	A
Wood	442	33	7%	R	20	5%	T	52	12%	A
Zavala	748	104	14%	A	22	3%	T	114	15%	A

Appendix XII – Metals: number of samples

TABLE 36 NUMBER, PERCENT OF TOTAL WATER WELLS, AND GROUNDWATER TESTING NEEDS FOR METALS IN ATASCOSA, AUSTIN, BASTROP, BEE, AND BRAZOS COUNTIES. A = AS NEEDED, R = RECOMMENDED, T = TESTING NEEDED

	Atascosa			Austin			Bastrop			Bee			Brazos		
Total wells	1117			321			791			631			687		
Aluminum	167	15%	A	54	17%	A	60	8%	A	30	5%	R	66	10%	A
Antimony	139	12%	A	53	17%	A	56	7%	A	28	4%	R	60	9%	A
Arsenic	179	16%	A	67	21%	A	78	10%	A	42	7%	A	74	11%	A
Barium	179	16%	A	67	21%	A	80	10%	A	42	7%	A	75	11%	A
Beryllium	139	12%	A	54	17%	A	56	7%	A	29	5%	R	60	9%	A
Boron	229	21%	A	75	23%	A	106	13%	A	34	5%	R	118	17%	A
Cadmium	174	16%	A	54	17%	A	76	10%	A	30	5%	R	69	10%	A
Chromium	174	16%	A	54	17%	A	67	8%	A	30	5%	R	69	10%	A
Cobalt	140	13%	A	54	17%	A	56	7%	A	29	5%	R	60	9%	A
Copper	179	16%	A	67	21%	A	78	10%	A	43	7%	A	74	11%	A
Iron	204	18%	A	71	22%	A	146	18%	A	44	7%	A	75	11%	A
Lead	179	16%	A	67	21%	A	69	9%	A	42	7%	A	74	11%	A
Manganese	180	16%	A	67	21%	A	81	10%	A	44	7%	A	74	11%	A
Mercury	60	5%	A	26	8%	R	33	4%	R	17	3%	T	21	3%	T
Molybdenum	167	15%	A	54	17%	A	58	7%	A	35	6%	R	66	10%	A
Nickel	86	8%	A	27	8%	R	28	4%	R	21	3%	T	41	6%	A
Phosphorus	60	5%	A	13	4%	T	29	4%	R	1	0%	T	14	2%	T
Silver	60	5%	A	26	8%	R	24	3%	T	17	3%	T	20	3%	T
Strontium	139	12%	A	54	17%	A	56	7%	A	29	5%	R	60	9%	A

TABLE 37 NUMBER, PERCENT OF TOTAL WATER WELLS, AND GROUNDWATER TESTING NEEDS FOR METALS IN COUNTIES. A = AS NEEDED, R = RECOMMENDED, T = TESTING NEEDED

	Burleson			Caldwell			Colorado			De Witt			Dimmit		
Total wells	847			599			574			513			527		
Aluminum	76	9%	A	13	2%	T	78	14%	A	28	5%	R	104	20%	A
Antimony	69	91%	A	13	2%	T	78	14%	A	28	5%	R	67	13%	A
Arsenic	81	117%	A	17	3%	T	94	16%	A	39	5%	A	104	20%	A
Barium	81	100%	A	17	3%	T	98	17%	A	39	5%	A	104	20%	A
Beryllium	69	85%	A	13	2%	T	78	14%	A	28	5%	R	69	13%	A
Boron	137	199%	A	36	6%	R	135	24%	A	49	5%	A	125	24%	A
Cadmium	73	53%	A	17	3%	T	74	13%	A	29	5%	R	97	18%	A
Chromium	73	100%	A	17	3%	T	68	12%	A	29	5%	R	97	18%	A
Cobalt	69	95%	A	13	2%	T	78	14%	A	28	5%	R	69	13%	A
Copper	81	117%	A	17	3%	T	94	16%	A	39	5%	A	104	20%	A

Iron	87	107%	A	45	8%	A	104	18%	A	61	5%	A	105	20%	A
Lead	81	93%	A	17	3%	T	88	15%	A	39	5%	A	104	20%	A
Manganese	81	100%	A	17	3%	T	91	16%	A	39	5%	A	104	20%	A
Mercury	20	25%	T	7	1%	T	35	6%	R	16	5%	T	51	10%	A
Molybdenum	76	380%	A	13	2%	T	78	14%	A	28	5%	R	104	20%	A
Nickel	55	72%	A	8	1%	T	39	7%	A	18	5%	T	40	8%	A
Phosphorus	23	42%	T	14	2%	T	6	1%	T		5%	T	26	5%	R
Silver	20	26%	T	7	1%	T	29	5%	R	16	5%	T	51	10%	A
Strontium	64	320%	A	13	2%	T	78	14%	A	28	5%	R	69	13%	A

TABLE 38 NUMBER, PERCENT OF TOTAL WATER WELLS, AND GROUNDWATER TESTING NEEDS FOR METALS IN COUNTIES. A = AS NEEDED, R = RECOMMENDED, T = TESTING NEEDED

	Duval			**Edwards**			**Fayette**			**Frio**			**Goliad**		
Total wells	683			604			863			756			507		
Aluminum	128	19%	A	64	11%	A	42	5%	A	130	17%	A	30	6%	R
Antimony	124	18%	A	63	10%	A	40	5%	A	106	14%	A	28	6%	R
Arsenic	141	21%	A	75	12%	A	56	6%	A	141	19%	A	42	8%	A
Barium	141	21%	A	75	12%	A	61	7%	A	144	19%	A	42	8%	A
Beryllium	124	18%	A	63	10%	A	40	5%	A	106	14%	A	28	6%	R
Boron	147	22%	A	69	11%	A	62	7%	A	181	24%	A	31	6%	R
Cadmium	115	17%	A	66	11%	A	50	6%	A	137	18%	A	32	6%	R
Chromium	115	17%	A	66	11%	A	42	5%	A	137	18%	A	32	6%	R
Cobalt	124	18%	A	63	10%	A	40	5%	A	106	14%	A	28	6%	R
Copper	141	21%	A	75	12%	A	57	7%	A	141	19%	A	42	8%	A
Iron	151	22%	A	79	13%	A	56	6%	A	172	23%	A	42	8%	A
Lead	141	21%	A	75	12%	A	48	6%	A	141	19%	A	42	8%	A
Manganese	141	21%	A	75	12%	A	48	6%	A	141	19%	A	42	8%	A
Mercury	51	7%	A	12	2%	T	21	2%	T	52	7%	A	18	4%	T
Molybdenum	135	20%	A	63	10%	A	42	5%	A	130	17%	A	42	8%	A
Nickel	50	7%	A	38	6%	A	27	3%	R	63	8%	A	17	3%	T
Phosphorus	10	1%	T	29	5%	R	6	1%	T	54	7%	A	4	1%	T
Silver	51	7%	A	12	2%	T	13	2%	T	52	7%	A	18	4%	T
Strontium	124	18%	A	63	10%	A	40	5%	A	106	14%	A	28	6%	R

TABLE 39 NUMBER, PERCENT OF TOTAL WATER WELLS, AND GROUNDWATER TESTING NEEDS FOR METALS IN COUNTIES. A = AS NEEDED, R = RECOMMENDED, T = TESTING NEEDED

	Gonzales			**Grimes**			**Guadalupe**			**Houston**			**Karnes**		
Total wells	582			357			638			400			410		
Aluminum	193	33%	A	24	7%	T	14	2%	T	66	17%	A	31	8%	R
Antimony	192	33%	A	24	7%	T	14	2%	T	63	16%	A	27	7%	R

Arsenic	209	36%	A	40	11%	A	17	3%	T	82	21%	A	40	10%	A
Barium	209	36%	A	41	11%	A	17	3%	T	82	21%	A	40	10%	A
Beryllium	192	33%	A	24	7%	T	14	2%	T	64	16%	A	27	7%	R
Boron	293	50%	A	48	13%	A	30	5%	R	68	17%	A	81	20%	A
Cadmium	206	35%	A	33	9%	R	17	3%	T	79	20%	A	32	8%	R
Chromium	206	35%	A	33	9%	R	17	3%	T	79	20%	A	32	8%	R
Cobalt	192	33%	A	24	7%	T	14	2%	T	64	16%	A	27	7%	R
Copper	209	36%	A	40	11%	A	17	3%	T	82	21%	A	40	10%	A
Iron	252	43%	A	42	12%	A	57	9%	A	83	21%	A	41	10%	A
Lead	209	36%	A	40	11%	A	17	3%	T	82	21%	A	40	10%	A
Manganese	217	37%	A	40	11%	A	17	3%	T	82	21%	A	40	10%	A
Mercury	29	5%	R	18	5%	T	5	1%	T	26	7%	R	16	4%	T
Molybdenum	193	33%	A	24	7%	T	14	2%	T	66	17%	A	37	9%	R
Nickel	152	26%	A	19	5%	T	10	2%	T	43	11%	A	18	4%	T
Phosphorus	116	20%	A	2	1%	T	5	1%	T	32	8%	R	5	1%	T
Silver	27	5%	R	18	5%	T	5	1%	T	20	5%	T	16	4%	T
Strontium	192	33%	A	24	7%	T	14	2%	T	64	16%	A	27	7%	R

TABLE 40 NUMBER, PERCENT OF TOTAL WATER WELLS, AND GROUNDWATER TESTING NEEDS FOR METALS IN COUNTIES. A = AS NEEDED, R = RECOMMENDED, T = TESTING NEEDED

	La Salle			**Lavaca**			**Lee**			**Leon**			**Live Oak**		
Total wells	362			386			399			323			540		
Aluminum	75	21%	A	78	20%	A	55	14%	A	58	18%	A	54	10%	A
Antimony	70	19%	A	78	20%	A	49	12%	A	54	17%	A	49	9%	A
Arsenic	89	25%	A	95	25%	A	57	14%	A	73	23%	A	75	14%	A
Barium	89	25%	A	95	25%	A	57	14%	A	73	23%	A	75	14%	A
Beryllium	70	19%	A	78	20%	A	49	12%	A	54	17%	A	49	9%	A
Boron	116	32%	A	91	24%	A	129	32%	A	56	17%	A	72	13%	A
Cadmium	88	24%	A	76	20%	A	55	14%	A	72	22%	A	62	11%	A
Chromium	88	24%	A	76	20%	A	55	14%	A	72	22%	A	62	11%	A
Cobalt	69	19%	A	78	20%	A	49	12%	A	54	17%	A	49	9%	A
Copper	89	25%	A	95	25%	A	57	14%	A	73	23%	A	75	14%	A
Iron	117	32%	A	98	25%	A	100	25%	A	97	30%	A	80	15%	A
Lead	90	25%	A	95	25%	A	57	14%	A	73	23%	A	75	14%	A
Manganese	89	25%	A	95	25%	A	68	17%	A	74	23%	A	76	14%	A
Mercury	28	8%	R	37	10%	R	13	3%	T	26	8%	R	36	7%	R
Molybdenum	74	20%	A	78	20%	A	55	14%	A	56	17%	A	54	10%	A
Nickel	54	15%	A	38	10%	A	34	9%	R	40	12%	A	24	4%	T
Phosphorus	33	9%	R	1	0%	T	22	6%	T	29	9%	R		0%	T
Silver	28	8%	R	37	10%	R	13	3%	T	25	8%	T	36	7%	R
Strontium	69	19%	A	78	20%	A	49	12%	A	54	17%	A	49	9%	A

TABLE 41 NUMBER, PERCENT OF TOTAL WATER WELLS, AND GROUNDWATER TESTING NEEDS FOR METALS IN COUNTIES. A = AS NEEDED, R = RECOMMENDED, T = TESTING NEEDED

	Madison			Maverick			McMullen			Milam			Robertson		
Total wells	365			92			184			314			824		
Aluminum	28	8%	R	34	37%	R	32	17%	R	52	17%	A	83	10%	A
Antimony	28	8%	R	7	8%	T	32	17%	R	52	17%	A	72	9%	A
Arsenic	37	10%	R	35	38%	R	45	24%	A	53	17%	A	85	10%	A
Barium	37	10%	R	36	39%	R	45	24%	A	53	17%	A	85	10%	A
Beryllium	28	8%	R	7	8%	T	32	17%	R	52	17%	A	72	9%	A
Boron	33	9%	R	17	18%	T	48	26%	A	80	25%	A	182	22%	A
Cadmium	34	9%	R	35	38%	R	41	22%	A	53	17%	A	78	9%	A
Chromium	34	9%	R	35	38%	R	41	22%	A	52	17%	A	78	9%	A
Cobalt	28	8%	R	7	8%	T	32	17%	R	52	17%	A	72	9%	A
Copper	37	10%	R	36	39%	R	45	24%	A	53	17%	A	85	10%	A
Iron	41	11%	A	40	43%	A	62	34%	A	88	28%	A	160	19%	A
Lead	37	10%	R	36	39%	R	45	24%	A	53	17%	A	85	10%	A
Manganese	37	10%	R	36	39%	R	45	24%	A	65	21%	A	96	12%	A
Mercury	10	3%	T	29	32%	R	14	8%	T	14	4%	T	30	4%	R
Molybdenum	28	8%	R	34	37%	R	32	17%	R	52	17%	A	83	10%	A
Nickel	20	5%	T	7	8%	T	25	14%	T	30	10%	R	36	4%	R
Phosphorus	13	4%	T	5	5%	T	12	7%	T	25	8%	T	14	2%	T
Silver	5	1%	T	29	32%	R	14	8%	T	14	4%	T	30	4%	R
Strontium	28	8%	R	7	8%	T	32	17%	R	50	16%	A	72	9%	A

TABLE 42 NUMBER, PERCENT OF TOTAL WATER WELLS, AND GROUNDWATER TESTING NEEDS FOR METALS IN COUNTIES. A = AS NEEDED, R = RECOMMENDED, T = TESTING NEEDED

	Washington			Webb			Wilson			Wood			Zavala		
Total wells	478			339			512			442			748		
Aluminum	24	5%	T	106	31%	A	90	18%	A	51	12%	A	104	14%	A
Antimony	24	5%	T	77	23%	A	73	14%	A	33	7%	R	92	12%	A
Arsenic	42	9%	A	120	35%	A	96	19%	A	54	12%	A	114	15%	A
Barium	42	9%	A	117	35%	A	96	19%	A	55	12%	A	114	15%	A
Beryllium	24	5%	T	77	23%	A	73	14%	A	35	8%	R	92	12%	A
Boron	41	9%	A	105	31%	A	131	26%	A	52	12%	A	153	20%	A
Cadmium	33	7%	R	102	30%	A	93	18%	A	49	11%	A	110	15%	A
Chromium	33	7%	R	103	30%	A	93	18%	A	51	12%	A	110	15%	A
Cobalt	24	5%	T	77	23%	A	73	14%	A	33	7%	R	92	12%	A
Copper	42	9%	A	118	35%	A	96	19%	A	54	12%	A	114	15%	A
Iron	62	13%	A	117	35%	A	96	19%	A	134	30%	A	121	16%	A

Lead	42	9%	A	117	35%	A	96	19%	A	52	12%	A	114	15%	A
Manganese	44	9%	A	114	34%	A	96	19%	A	56	13%	A	114	15%	A
Mercury	21	4%	T	47	14%	A	37	7%	R	25	6%	T	49	7%	A
Molybdenum	24	5%	T	107	32%	A	90	18%	A	49	11%	A	104	14%	A
Nickel	18	4%	T	63	19%	A	38	7%	A	21	5%	T	39	5%	A
Phosphorus		0%	T	27	8%	R	33	6%	R	18	4%	T	48	6%	A
Silver	21	4%	T	47	14%	A	37	7%	R	28	6%	R	49	7%	A
Strontium	24	5%	T	77	23%	A	73	14%	A	33	7%	R	92	12%	A

Appendix XIII – Radionuclides: number of samples

TABLE 43 NUMBER OF RADIONUCLIDE SAMPLES AVAILABLE IN THE TWDB GROUNDWATER DATABASE FOR EACH COUNTY.

County	Total Wells	Radium-226 and Radium-228	Radon 222	Uranium	Thorium	Potassium-40
Atascosa	1117	20		25		
Austin	321	13		13		
Bastrop	791			13		
Bee	631	5	1	5	1	1
Brazos	687	6		8		
Burleson	847	3		8		
Caldwell	599			3		
Colorado	574	20		22		
De Witt	513	6		5		
Dimmit	527	9		16		
Duval	683	38	4	39	4	4
Edwards	604	9		14		
Fayette	863	4		6		
Frio	756	17		21		
Goliad	507	6	1	8	2	2
Gonzales	582	2		12		
Grimes	357	2		2		
Guadalupe	638			2		
Houston	400	3		11		
Karnes	410	9	4	6	3	3
La Salle	362	2		9		
Lavaca	386	20		20		
Lee	399			7		
Leon	323	1		8		
Live Oak	540	14	3	13	3	3
Madison	365	1		4		
Maverick	92	11				
McMullen	184			3		
Milam	314	1		11		
Robertson	824	18		26		
Washington	478	3		3		
Webb	339	21	13	25	16	16
Wilson	512	3	1	17		
Wood	442			9		
Zavala	748	14		27		
Grand Total	18715	281	27	421		

TABLE 44 NUMBER, PERCENT OF TOTAL WATER WELLS, AND GROUNDWATER TESTING NEEDS FOR RADIONUCLIDE PARTICLE EMISSIONS IN EAGLE FORD SHALE COUNTIES. A = AS NEEDED, R = RECOMMENDED, T = TESTING NEEDED

County	Total Wells	Alpha			Beta		
Atascosa	1117	41	4%	A	40	4%	A
Austin	321	26	8%	R	13	4%	T
Bastrop	791	21	3%	T	13	2%	T
Bee	631	16	3%	T	12	2%	T
Brazos	687	21	3%	T	15	2%	T
Burleson	847	20	2%	T	17	2%	T
Caldwell	599	4	1%	T	4	1%	T
Colorado	574	38	7%	A	9	2%	T
De Witt	513	17	3%	T	12	2%	T
Dimmit	527	36	7%	R	33	6%	R
Duval	683	66	10%	A	18	3%	T
Edwards	604	26	4%	R	12	2%	T
Fayette	863	20	2%	T	18	2%	T
Frio	756	34	4%	R	34	4%	R
Goliad	507	17	3%	T	12	2%	T
Gonzales	582	18	3%	T	15	3%	T
Grimes	357	18	5%	T	16	4%	T
Guadalupe	638	3	0%	T	3	0%	T
Houston	400	21	5%	T	18	5%	T
Karnes	410	18	4%	T	13	3%	T
La Salle	362	19	5%	T	19	5%	T
Lavaca	386	38	10%	A	18	5%	T
Lee	399	8	2%	T	8	2%	T
Leon	323	20	6%	T	19	6%	T
Live Oak	540	38	7%	A	23	4%	T
Madison	365	10	3%	T	9	2%	T
Maverick	92	28	30%	R	28	30%	R
McMullen	184	13	7%	T	13	7%	T
Milam	314	3	1%	T	3	1%	T
Robertson	824	40	5%	A	22	3%	T
Washington	478	21	4%	T	18	4%	T
Webb	339	25	7%	T	22	6%	T
Wilson	512	24	5%	T	26	5%	R
Wood	442	18	4%	T	19	4%	T
Zavala	748	28	4%	R	22	3%	T
Grand Total	18715	814	4%	A	596	3%	A

Appendix XIV – PAH samples

TABLE 45 NUMBER AND PERCENT OF SAMPLES OUT OF THE TOTAL NUMBER OF WATER WELLS IN EACH COUNTY FOR PAH CONCENTRATIONS IN GROUNDWATER.

	Atascosa	Bastrop	Colorado	Dimmit	Fayette	Karnes	La Salle	Wilson	Zavala
Total wells	1117	791	574	527	863	410	362	512	748
Percent	0.6%	0.4%	0.2%	4.7%	0.3%	0.2%	1.4%	0.2%	0.4%
Acenaphthene	7	3	1	25	3	1	5	1	3
Acenaphthylene	7	3	1	25	3	1	5	1	3
Anthracene	7	3	1	25	3	1	5	1	3
Benzo(a) anthracene	7	3	1	25	3	1	5	1	3
Benzo-(a)-pyrene	7	3	1	25	3	1	5	1	3
Benzo(b)fluoranthene	7	3	1	25	3	1	5	1	3
Benzo(ghi)perylene	7	3	1	25	3	1	5	1	3
Benzo(k)fluoranthene	7	3	1	25	3	1	5	1	3
Chrysene	7	3	1	25	3	1	5	1	3
Dibenzo (a,h) anthracene	7			25		1	5	1	3
Fluoranthene	7	3	1	25	3	1	5	1	3
Fluorene	7	3	1	25	3	1	5	1	3
Indeno (1,2,3-cd) pyrene	7	3	1	25	3	1	5	1	3
Naphthalene	7	3	1	25	3	1	5	1	3
Phenanthrene	7	3	1	25	3	1	5	1	3
Pyrene	7	3	1	25	3	1	5	1	3