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Article

Hydrogeological Characterization and Statistical Analysis for Ogallala Aquifer in the Southern High Plains Region, USA

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Abstract: The purposes of this study are to analyze the groundwater quality of Ogallala Aquifer and evaluate the hydrological characteristics in the southern High Plains region of the Permian Basin, Texas. Levels of chloride, fluoride, nitrate, pH, selenium, and total dissolved solids (TDS) were analyzed through the years 1990-2016. A total of 133 wells were collected from the Texas Water Development Board (TWDB) which is an open database by the US government. Statistical analysis was utilized to evaluate the groundwater quality and propose trends. The average levels of the contaminants were compared to their respective Maximum Contaminant Levels (MCL) by the Environmental Protection Agency (EPA). Potential human health risks that each contaminant possesses were described. Possible sources of each contaminant were discussed with oil/gas activities, agricultural practices, and other human actions impact its conditions. This research provides important information for groundwater quality of Ogallala aquifer and contributes on understanding the response to development in the Permian Basin, Texas.

Keywords: Ogallala aquifer; Groundwater quality; Statistical analysis; High plains region; Permian Basin; Texas

1. Introduction

Water is one of the most vital natural resources that is present on Earth. The Ogallala aquifer (also known as the High Plains Aquifer) is the largest freshwater aquifer in the world, so it is crucial that it is kept sustainable for life. The Ogallala aquifer is increasingly susceptible to contamination with the presence of oil field activity. Irrigation and the use of fertilizers is very common in the High Plains. The water quality of the Ogallala aquifer is often sufficient for irrigation purposes, but in most places, not for drinking water standards set by the U.S. Environmental Protection Agency (EPA) for parameters like chloride, fluoride, and total dissolved solids (TDS) [1].

The Ogallala is an unconfined aquifer that has seen drastic changes in its properties throughout the years due to agricultural processes and other uses [2]. Hornbeck and Keskin [3] mentioned that center pivot irrigation technology greatly improved through the 1950s. This new technology was manufactured and distributed at a large scale, which led to a five-fold groundwater withdrawal rate from 1949 to 1974. The US Geological Survey (USGS) [4,5] conducted a study that measured water levels from 1950s to 2015 based off 3,164 wells and showed the Ogallala Aquifer demonstrating an average declination of the water level of 234 feet throughout Texas. Based off 7,524 wells from 2013 to 2015, there was a decline in the water level with an average of 33 feet throughout Texas. Since predevelopment to 2015, the saturated thickness declined from 10 to more than 50 feet throughout Texas [4, 5]. The declines in water level, saturated thickness, and recoverable water throughout Texas is very alarming and action to combat this is imperative.

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The Permian Basin in Texas is well known throughout the world for producing some of the largest amounts of oil and gas. The exploration for oil in the Permian Basin has been occurring for approximately a century. Unconventional drilling methods such as horizontal drilling, hydraulic fracturing, and other advanced technologies, have greatly increased oil production in the past decade [6]. Hydraulic fracturing alone has had a 10-fold increase from 2000 to 2015 in the United States [7]. The population of the Permian Basin is continuously growing, with a total of 2,061,422 residents in 2018 [8]. From 2013 to 2018, the population grew 3.3%, which added 65,942 residents and expects another 2.3% increase by 2023.

There are many environmental concerns for the Permian Basin, Texas, especially when oil and gas activity is so prevalent [9,10]. Also, the continuous increase in population and agriculture are causes for concern [11]. Some contaminants can be found naturally in bodies of water, but the biggest causes of contamination are anthropogenic, such as agriculture, littering, and industrialization [10]. Epstein [9] mentioned that many reserve pits are known to leak and when groundwater and sources for drinking water are contaminated with pollutants such as arsenic, benzene, chromium, lead, and other metals. These pits can overflow from heavy rain and flooding too [11-13]. The failure of casing and cementing technologies, although a very low possibility, can cause contamination of groundwater as well. Old pipes in the public water system can corrode over time, which leads to an increase in contaminants like copper and lead. Agriculture is one of major industries in the Southern High Plains region that plays a pivotal role for the economy. Robertson & Sharp [14] conducted a study highlighting how synthetic and natural (manure-based) fertilizers were the primary anthropogenic culprits for groundwater contamination, specifically nitrates. Synthetic fertilizers have been commonly used since the 1950s, becoming the primary choice of fertilizer. Total commercial fertilizer use greatly increased until approximately the 1980s, where it has fluctuated since then due to supply and demand [15].

In the past decade, hydraulic fracturing has become a beneficial technique in extracting oil and gas from reservoir rocks that have very low permeability and porosity [16-18]. Hydraulic fracturing is the process of creating fractures by injecting fluids, mostly composed of water, sand, and chemicals, in reservoir rocks that lack porosity and permeability [16]. Jasechko & Perrone [7] conducted a study that demonstrated how hydraulic fracturing wells in a proximity of approximately 1-3 kilometers of domestic groundwater wells can impact groundwater contamination. It was also shown that conventional oil and gas wells were in a proximity to water wells and posed a risk of contaminating groundwater. Oil refineries, like the one in in Big Spring, Texas in Howard County for example, can also prove hazardous not only to water quality, but also air and soil. These refineries can be a substantial cause of the release of toxic compounds such as BTEX (benzene, toluene, ethylbenzene, and xylene) [19]. Water discharge from these refineries is under strict regulations from the Safe Water Drinking Act (SWDA) and Clean Water Act (CWA); however, contamination from previous discharge can remain in water bodies [19,20].

With all these concerns and facts stated, the objective of this study was to assess the hydrochemical characteristic and groundwater quality of the Ogallala Aquifer in the southern High Plain region, Texas. Since the petroleum and agriculture industries are such a vital portion of the economy in this region and groundwater resources are so crucial, it is important to determine the quality of groundwater here. The contaminants of chloride, fluoride, nitrate, and TDS along with pH, were analyzed from approximately 1990 to 2016 to determine if groundwater was safe to consume for the populations of their respective counties. With this data, an evaluation of the impact from energy development and agricultural practices was made to determine the effect on groundwater resources in the study area. This research provides important information for groundwater resource management and contributes on understanding groundwater's response to energy and agriculture development in the Permian Basin and Southern High Plains.

2. Study Area

The study area consists of the southern-most portion of the high plains located in the Permian Basin, in West Texas, USA. There are ten counties that the study area is comprised of: Borden, Cochran, Dawson, Gaines, Garza, Glasscock, Howard, Lynn, Terry, and Yoakum (Figure 1). These counties combined produce an area of 9,350.1 square miles. Most of the study area is of a rural environment and slightly populated. The population of the study area is generally increasing as a whole in the Permian Basin of Texas by a range of 0.6% to 22.6% from 2010 to 2019 [21,22]. The Ogallala aquifer provides more water in the state of Texas than any other aquifer. Precipitation is uncommon with an average rainfall for all 10 counties ranging from around 18-21 inches per year [23]. In the eastern side of the study area, there is a large increase in closed drainage depressions compared to the western side, which can fill with water after precipitation [24,25]. The year 2007 had its greatest amount of precipitation with ~28 inches of rain, while the greatest average temperature occurred in 2016 being ~64 °F. Most of this precipitation occurred between the months of May and June, while March, July, and September contributed but to a lesser degree (Figure 2).

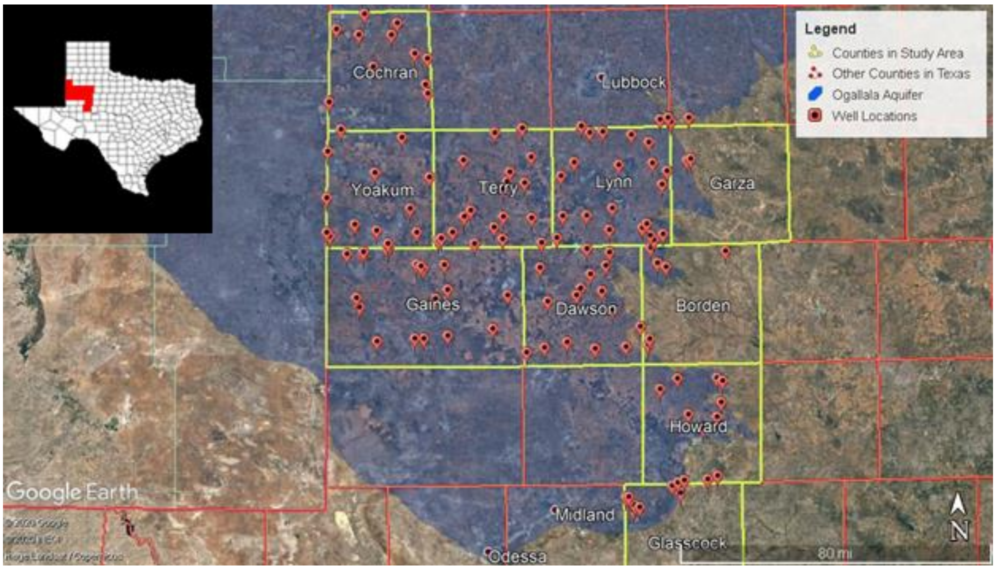

Figure 1. Location of groundwater wells in the study area with the underlying Ogallala Aquifer.

The study area experienced Ogallala sediment deposits during the Tertiary Period from the erosion of the southern Rocky Mountains and continuous tectonic activity occurring into the late Tertiary [24]. The Ogallala Formation has a thickness from 0 to approximately 800 feet with an average saturated thickness of 95 feet [26]. The Ogallala was deposited as an alluvial outwash from the Rocky Mountains with the thickest sediments being closest to the mountains and get finer further from the mountains. The sediments in the aquifer consist of fluvial sand, gravel, clay, silt, eolian sand, and silt. Throughout most of the Ogallala Aquifer area, withdrawal of water has exceeded the recharge rate. Water levels have declined in an excess of 300 feet in the last 50 to 60 years. The use of groundwater from the Ogallala is mainly dominated by agriculture, as ~95% of the groundwater is used for such. The remaining ~5% of groundwater use includes livestock production, oil and gas production, manufacturing, and wholesale and retail trade.

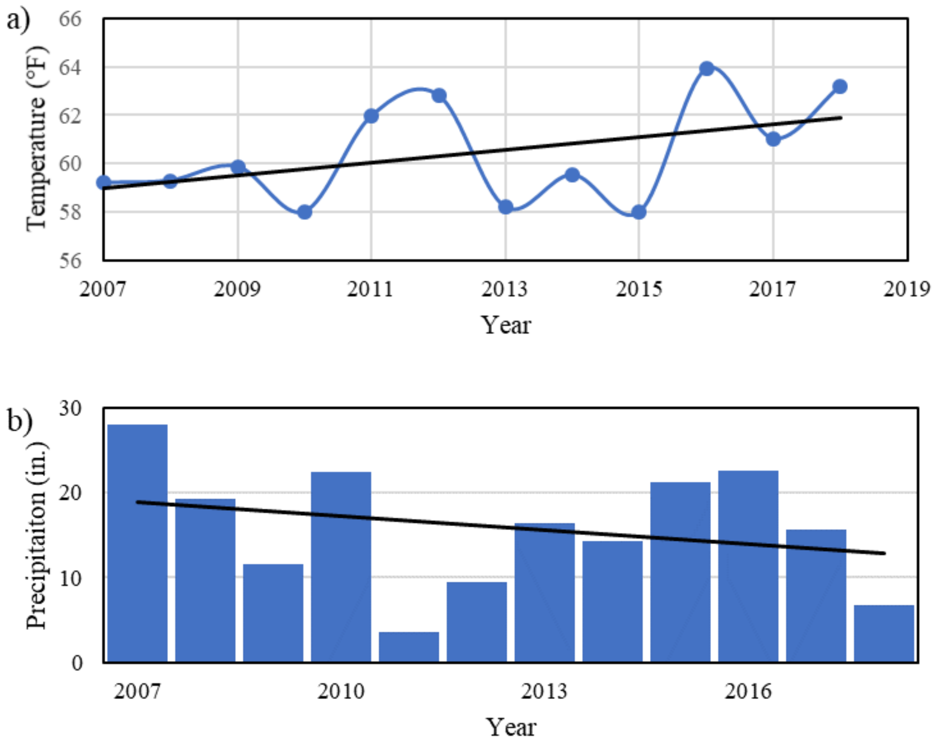

Figure 2. (a) Annual average temperature and (b) annual total precipitation in Lamesa, TX reported by the US Climate Data.

3. Data and Methods

The data for groundwater quality was collected for all 10 counties through the Texas Water Development Board (TWDB) - Groundwater Database (GWDB) in the water quality by county database. The water quality by county database can display information on every county in Texas, the aquifers that underlie each county, and the coordinates of the water wells that were drilled and tested in each county. All parameters can be acquired from this database and are able to be filtered out manually if one does not want or need certain contaminants. This database also provided state well numbers, aquifer codes, parameter codes, reliability, well depths, dates of wells tested, and other information. The data collected in this study was brought into Excel and rearranged to utilize and interpret the data more easily. A total of 133 wells were analyzed with the most recent data, starting from the 1990 to 2016. The years selected in this study were based on data availability, with most data being given every 4 years, but some data was also available in between too. Average depths of these wells were calculated for each county, along with the contaminant parameters: chloride, fluoride, nitrate, pH, selenium, and TDS. These contaminants were analyzed, which displayed the average values for each parameter to its respective year in each county.

The averages of each parameter were further assessed where changes in groundwater levels throughout time were made evident, compared to their respective maximum contaminant level (MCL). The MCL was provided from the EPA due to the Safe Water Drinking Act (SWDA) which was established in 1974. With these line graphs, interpretations were made for counties that had exceeded their MCL for each parameter and what counties did not. Each county was then displayed with every parameter and visualized a range of values, making it possible to see the maximum and minimum values, the 25th and 75th percentiles, and the medians. This data presented the statistical values of groundwater quality for each county. This included the actual minimum and maximum values of each parameter throughout the years (not just the averages), the standard deviation, and

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range. Standard deviation was calculated using the sample standard deviation method, since not every well in each county was analyzed.

Table 1. Summary of groundwater well data used in the study area (depth unit: feet below land surface).

County	Well ID	Latitude	Longitude	Depth
Borden County	2827602	32.56861	-101.66	113
	2827509	32.54695	-101.667	135
	2812402	32.83098	-101.585	70
	2812105	32.84556	-101.623	55
	2806801	32.88583	-101.324	70
	2804401	32.95056	-101.596	60
	2803901	32.90116	-101.652	145
	2803604	32.94667	-101.652	60
	2803601	32.92956	-101.637	57
Cochran County	2540502	33.44222	-103.0517	n/a
	2524304	33.70972	-103.0203	210
	2436105	33.4725	-102.6186	240
	2428104	33.60056	-102.62	220
	2427903	33.505	-102.6283	210
	2427201	33.61944	-102.6756	n/a
	2426402	33.57167	-102.8575	350
	2418601	33.68806	-102.7783	238
	2418308	33.73139	-102.7522	228
	2417503	33.68889	-102.9214	170
	2409901	33.765	-102.897	193
Dawson County	2827201	32.61417	-101.7008	150
	2826902	32.54083	-101.7639	160
	2825902	32.53528	-101.8983	140
	2818504	32.67639	-101.8206	n/a
	2818101	32.745	-101.8664	125
	2817115	32.73167	-101.9767	150
	2809804	32.75694	-101.9581	190
	2809601	32.80806	-101.915	154
	2802801	32.88667	-101.8311	101
	2801801	32.90056	-101.9294	80
	2732702	32.54111	-102.1178	65
	2732601	32.56028	-102.0197	127
	2731803	32.52444	-102.1953	155
	2724101	32.70972	-102.1022	100
	2715302	32.83361	-102.1339	175
	2708503	32.94194	-102.06	100
	2707606	32.92472	-102.1264	117

County	Well ID	Latitude	Longitude	Depth
Glasscock County	4403406	31.94056	-101.74	53
	4403404	31.95222	-101.712	35
	4403102	31.95972	-101.733	90
	4402312	31.99028	-101.771	128
	4402309	31.99083	-101.759	140
	4402301	31.9775	-101.756	155
	2862419	32.06306	-101.373	200
	2861615	32.05111	-101.416	306
	2860902	32.00222	-101.534	90
	2860811	32.04083	-101.546	250
	2860807	32.02944	-101.571	n/a
	2859607	32.08083	-101.647	n/a
Howard County	2853206	32.23833	-101.4342	150
	2846712	32.27889	-101.3722	67
	2846401	32.33222	-101.3531	75
	2845701	32.29	-101.4967	84
	2838701	32.41083	-101.3458	120
	2838401	32.42194	-101.3706	100
	2836702	32.38472	-101.6181	30
	2836601	32.42194	-101.542	136
Lynn County	2803303	32.98917	-101.6669	60
	2803201	32.97472	-101.6869	50
	2802207	32.96889	-101.8303	80
	2464904	33.02139	-102.0328	70
	2456601	33.16778	-102.0389	82
	2358504	33.04806	-101.8164	75
	2357803	33.02222	-101.9289	80
	2352502	33.18139	-101.5756	80
	2351301	33.21111	-101.6383	80
	2350602	33.20556	-101.7858	90
	2349103	33.21639	-101.9806	100
	2344104	33.37056	-101.6017	90
	2343901	33.28722	-101.6531	n/a
	2343407	33.31583	-101.7289	124
	2342403	33.32806	-101.8539	n/a
	2341603	33.325	-101.9108	145
	2341205	33.34917	-101.9478	171

	2810101	32.83861	-101.8478	160
Gaines County	2717511	32.6925	-102.919	211
	2717212	32.72639	-102.933	188
	2712909	32.75528	-102.536	n/a
	2712201	32.84611	-102.55	150
	2711605	32.83278	-102.641	116
	2711320	32.84167	-102.651	n/a
	2711206	32.84861	-102.67	159
	2706512	32.93889	-102.296	160
	2705527	32.9225	-102.418	160
	2704518	32.93667	-102.575	155
	2704505	32.94278	-102.563	168
	2702908	32.91472	-102.791	190
	2702811	32.90056	-102.795	180
	2702507	32.92444	-102.795	165
	2701910	32.89389	-102.902	180
	2722303	32.73361	-102.276	110
	2701908	32.88222	-102.902	250
	2701706	32.88667	-102.974	262
	2608522	32.95111	-103.049	300
Garza County	2353703	33.37583	-101.476	n/a
	2353108	33.22	-101.487	100
	2353107	33.225	-101.471	135
	2344206	33.36111	-101.554	n/a
	2336806	33.37667	-101.5669	218
	2352703	33.1325	-101.5975	155
Terry County	2704310	32.965	-102.5133	n/a
	2462903	33.02056	-102.292	n/a
	2462202	33.1225	-102.2931	165
	2461704	33.02194	-102.4622	186
	2461703	33.01944	-102.4675	165
	2461503	33.04417	-102.4336	150
	2455802	33.14333	-102.1981	n/a
	2455202	33.2375	-102.1683	50
	2454907	33.14861	-102.2739	150
	2454609	33.18333	-102.262	152
	2453103	33.22778	-102.4645	154
	2446501	33.32722	-102.3264	150
	2706208	32.98194	-102.3325	160
	2463802	33.01528	-102.1689	243
	2447206	33.34361	-102.2056	n/a
	2447101	33.34056	-102.2108	n/a
Yoakum County	2703204	32.96472	-102.6692	175
	2701212	32.99111	-102.9558	230
	2701201	32.99	-102.9425	222
	2608205	32.96528	-103.062	260
	2564201	33.09167	-103.0617	n/a
	2556503	33.18333	-103.0533	180
	2548803	33.26139	-103.0575	60
	2459502	33.05195	-102.6981	126
	2458504	33.04083	-102.815	300
	2457304	33.11278	-102.8886	n/a
	2452703	33.16639	-102.6128	n/a
	2450406	33.18361	-102.8514	195
	2450404	33.18056	-102.8567	196
	2443402	33.31195	-102.7328	145
	2441101	33.34195	-102.9995	200
	2702105	32.97194	-102.8442	187
	2701210	32.99445	-102.9392	261

4. Results and Discussion

All groundwater data was acquired from the Texas Water Development Board (TWDB) - Groundwater Database (GWDB) which is an open database provided by the US government. We collected all historically available data in our study area from TWDB - GWDB and checked the location of their wells spanning the years 1990-2016. However, some levels of pollutants were not able to be acquired for every year as they were only provided for some. Most data for the pollutants were consistently provided every four years starting at 1990. All ten counties had data for their pollutants in 2016 except for Borden, Glasscock, and Howard, which had their latest data recorded in 2012. For this reason, we finalized the total 133 wells to evaluate the groundwater quality and analyze the hydrological characteristics throughout the study area.

4.1. Chloride

Chloride is a naturally and anthropogenically occurring anion that is mostly known for being combined with sodium to form halite or salt. Chloride is commonly found in oil field brines and evaporites, which are common constituents in the Permian formations underlying parts of the Ogallala [27-29]. This anion can often be found in marine shales from seawater as chloride gets trapped during the time of its deposition [27]. In semi-arid regions such as the study area, the soils are not fully leached which allows an accumulation of solutes. Then when the land gets irrigated the rates of leaching increase which in turn, increase the buildup of solutes in groundwater, such as chloride. There are plenty of agricultural practices in the study area to support this claim, with an example from Terry County, shows an overview of the substantial amount of crop circles where irrigation occurs (Figure 3). Freeman [30] went on to confirm that halite contamination in shallow groundwater systems is impacted by road salts and the dissolution of natural halite invading aquifers, but discharge from water softening systems in houses affects groundwater.

Figure 3. Crop circles in Terry County, Texas (image from Google Earth).

The MCL for chloride is 250 mg/l [20]. This elevated level of chloride tends to cause a salty taste in drinking water. If chloride concentrations reach 350 mg/l, the groundwater becomes unacceptable for industrial use as high concentrations can cause corrosion in pipes. With these levels of concentrations in mind, oil field brines typically consist of chloride concentrations of 50,000 mg/l [28]. The chloride ion is also an electrolyte that can be found in all fluids of the body [30,31]. Its job is to maintain an acid/base balance, regulate fluids going in and out of cells, and transmit nerve impulses. The most common mineral that chloride is found in is halite; however, other minerals like sylvite, carnallite, kainite, and sodalite also contain chloride. Chloride can be combined with other ions to form compounds that make products such as salt, dry-cleaning agents, plastics, dyes, and synthetic rubbers [30].

In this study, only the counties of Cochran, Dawson, Gaines, Garza, Howard, and Yoakum fell within the MCL safe zone for chloride in 2012 and 2016 (Figure 4). The study showed chloride concentrations in the Southern High Plains. Many of the chloride concentrations resulted in being below the MCL of 250 mg/l; however, there was a concentration that was approximately 10 times that value. The Northern High Plains was less susceptible to high concentrations of chloride while the Southern High Plains resulted in most concentrations exceeding the MCL [28,29]. Another study

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done by Reedy et al. [32] showed concentrations of chloride having a median of 31.3 mg/l, with a maximum value reaching 13,898 mg/l. These high values in the Southern High Plains could be a result from the wells being at shallower depths. Influence from the underlying formations, upward hydraulic gradient that is intensified by pumping, and oilfield activity can lead to high amounts of chloride contamination of the Ogallala in the study area.

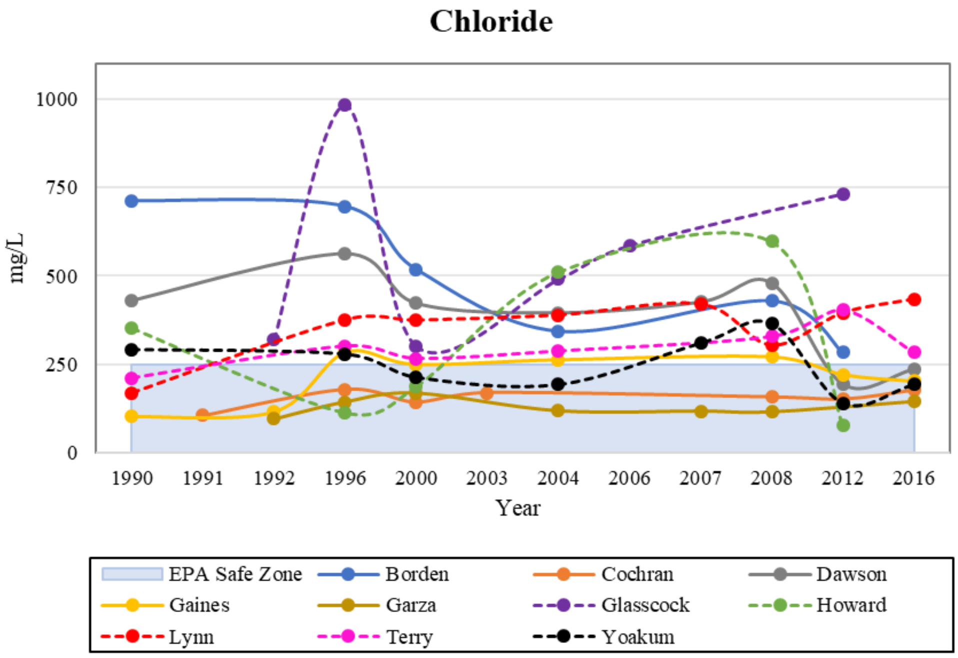

Figure 4. Historical analyses of Chloride levels with EPA safe zone in the study area.

4.2. Fluoride

Fluoride is an inorganic, naturally and anthropogenically occurring ion that is found along the natural surface and in groundwater [33]. It can be naturally found in volcanic rocks and Precambrian rocks, where there are said to be significant concentrations [34]. Other secondary sources of fluoride can be found from the pollution of industries, such as ceramics and the burning of coal, and agricultural practices, specifically the use of phosphatic fertilizers. Fluoride can originate from the dissolution of fluorite, fluoropatite, and certain silicates. Mukherjee & Singh [35] confirmed this path of fluoride contamination as the dissolution of fluorapatite was observed by Pseudomonas fluorescens for gaining nutrients contributed to fluoride in the environment. The chemical formula for fluoride is one fluorine atom that has a negative charge, F^-, making it an anion. The molecular weight of fluoride is 18.998 grams per mole (g/mol), making it slightly greater in mass than water [36]. Fluoride's MCL is 4 mg/l [20]. The MCL was created to have a limit for undesirable cosmetic, aesthetic, and technical effects.

Fluoride can have beneficial effects when taken in moderation such as improving dental health and bone mineralization [29,33]. However, when there has been a prolonged exposure or intake to high levels of fluoride, it can cause dental and skeletal fluorosis. It can also cause liver, kidney damage, brain damage, problems with growth, harm to the central nervous system, and reduction in intelligence. Drinking water is the primary pathway for intake and exposure of elevated levels of fluoride [34]. The movement of fluoride in groundwater is not fully understood but the displacement of fluoride ions by hydroxyl ions is a common consensus [35].

The measurements for fluoride in our study area have generally exceeded their MCL. Previous studies showed an increase in concentrations in fluoride in the Southern High Plains [28,32,37]. The average median value of fluoride was 2.4 mg/l while the maximum value was 9.8 mg/l, more than twice its MCL. Hudak [28] observed a maximum value of fluoride resulting in approximately 4 times

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greater its MCL in the semiarid environment of the High Plains region. According to the data compiled in this study, fluoride's MCL was only exceeded in the counties of Garza, Lynn, and Terry (Figure 5). This could result in high concentrations of fluoride in the shallow groundwater environments if these are the conditions present. Fluoride mobility in soil to water is impacted by adsorption and leaching processes, which thrive in a semiarid to arid environment with alkaline soils.

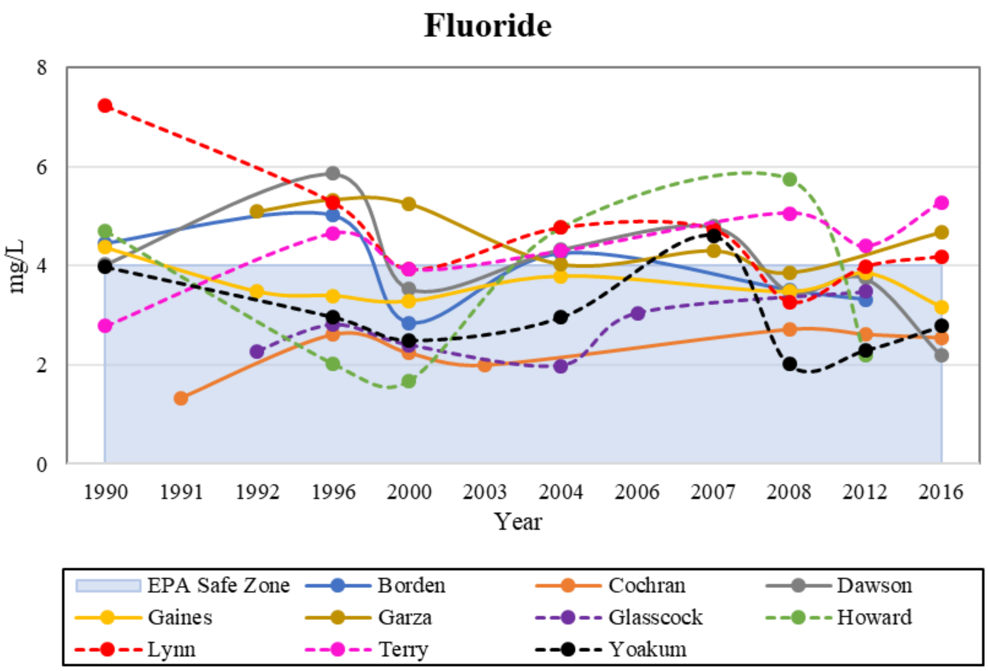

Figure 5. Historical analyses of Fluoride levels with EPA safe zone in the study area.

4.3. Nitrate

Nitrate is an inorganic, naturally and anthropogenically occurring compound that is common throughout the world and vital for life. The nitrogen atom carries a formal charge of -1 and has a molecular weight of 62.005 grams per mol (g/mol), making it approximately 3 times greater in mass than water, as its molecular weight is 18.015 g/mol. The MCL for nitrate is 10 mg/l [20]. Nitrate is used extensively in fertilizers, which seems to be the main source of nitrate contamination throughout the world. This compound moves very easily when it has entered the groundwater, as it does not absorb nor precipitate on solids of the aquifer [38,39]. If these crops are grown in a soil enriched with fertilizers, a mechanism is created for nitrates to infiltrate the groundwater. A prime example of a potential mechanism are the center pivot irrigation systems, which move in circles spraying water on crops (Figure 6). Nitrate plays a pivotal role in the nitrogen cycle. Ammonium is produced from a process called fixation, which can occur in nitrogen fixation through atmospheric processes, industrial fixation such as combustion processes, and biological fixation. This compound can then be oxidized through a process called nitrification to produce nitrite or be consumed by organisms. Once nitrate is produced, it can either be assimilated by plants or denitrified by certain bacteria which is then released back into the atmosphere.

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Figure 6. A traditional center pivot irrigation system spraying crops in the study area (image from Google Earth).

Texas is ranked in the top five states in the US for total crop exports, with over 194,000 farms covering approximately 77% of the land in 2000s [22,28]. There are six possible sources of nitrate in the arid environments of west Texas: 1) sewage waste from septic tanks/fields, 2) atmospheric deposition of reactive nitrogen, 3) movement of mineralized nitrogen, 4) microbial fixation, 5) accumulation of nitrate in desert soils, and 6) anthropogenic fertilizers. With these potential sources of nitrate contamination, anthropogenic fertilizers are the main culprit due to its wide-spread use and seasonal repetition [14]. The possibility of sewage waste being the main source of nitrate contamination can be ruled out because heavily populated areas, such as Dallas and Houston, would experience the most sewage waste yet do not have significant groundwater-nitrate problems when compared to the study area. In this study, every county consistently exceeded the MCL for nitrate except in 2016 where Dawson, Garza, Lynn, and Terry Counties fell below the MCL (Figure 7). It is important to note that almost all counties began to trend downward past 2008, with the exception of Borden County. Howard County experienced a very high spike in 2004, which could be due to an increase in precipitation that year as the average water level was closer to the surface than the couple years before and after 2004. Due to an increase in precipitation, pollutants on the surface have a stronger mechanism to infiltrate the ground. Further up-to-date data in the study area would present more accurate trends of how the levels of contaminants are changing in the study area.

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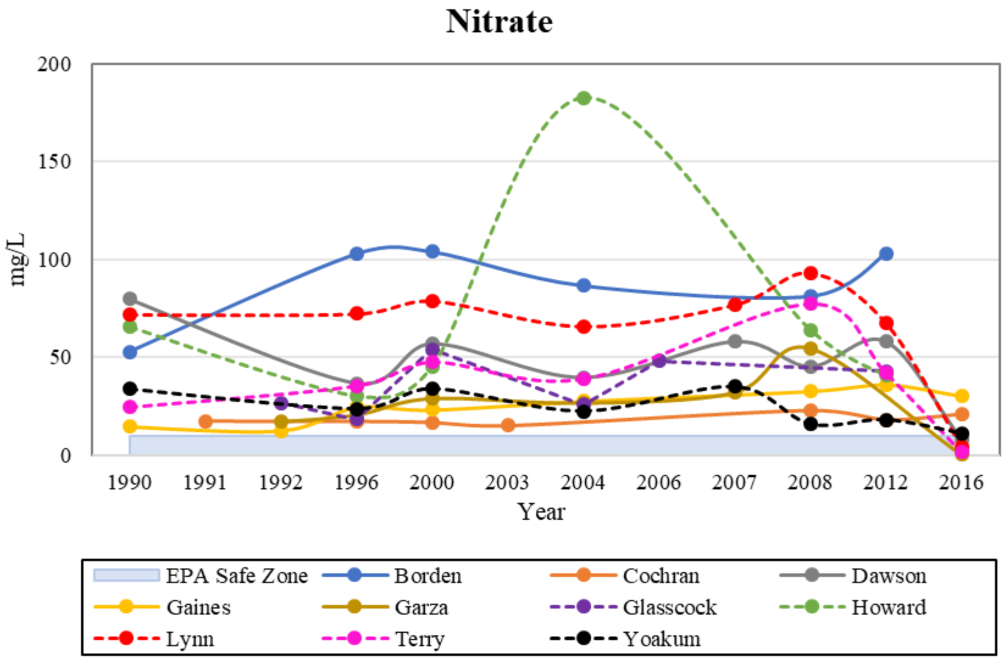

Figure 7. Historical analyses of Nitrate levels with EPA safe zone in the study area.

4.4. pH

pH is a measure on how acidic or basic a water solution is. It is measured by way of a scale that ranges from 0 to 14, with 0 being most acidic, 7 being neutral, and 14 being most basic. It measures how many hydrogen or hydroxide ions are in water. If there are more hydrogen ions, then the water is more acidic, whereas if there are more hydroxide ions, then the water is more basic. Metals become more soluble in water with a low pH, making it more toxic to life. , The MCL for pH is from 6.5 to 8.5 [40]. Drinking water with a low pH generates a bitter, metallic taste and corrosion occurs. Drinking water with a high pH will have a soda-like taste and a slippery feel.

The acidity of water can be a result from atmospheric deposition such as acid rain, surrounding rock, and wastewater discharge. Appleyard et al. [41] stated how the acidity of soil and groundwater can increase if the aquifer is of sandy composition with no carbonate content to serve as an acid buffer. This same study showed soils that were less than 2 meters from the surface experienced little pH change, which could be due to organic matter and biological activity that would sustain pH levels. When depths became greater than 2 meters, pH levels started to become more acidic. Low pH values can be a result from mine wastes, geologic units that are acid-bearing, power plants, coal pile runoff, industrial effluents, landfills, animal feeding facilities, oxidation and reduction processes, and draining of floodplains or wetlands [40]. High pH values can be a result from industrial discharge, basic geologic units, asphalt production, agricultural lime, oil and gas brines, landfills, cement and soap manufacturing, and limestone roads [40]. Based on all concerns, pH quality in our study area was nonexistent as all counties fell within the pH legal limit set by the EPA of 6.5 to 8.5 standard units (SU) (Figure 8).

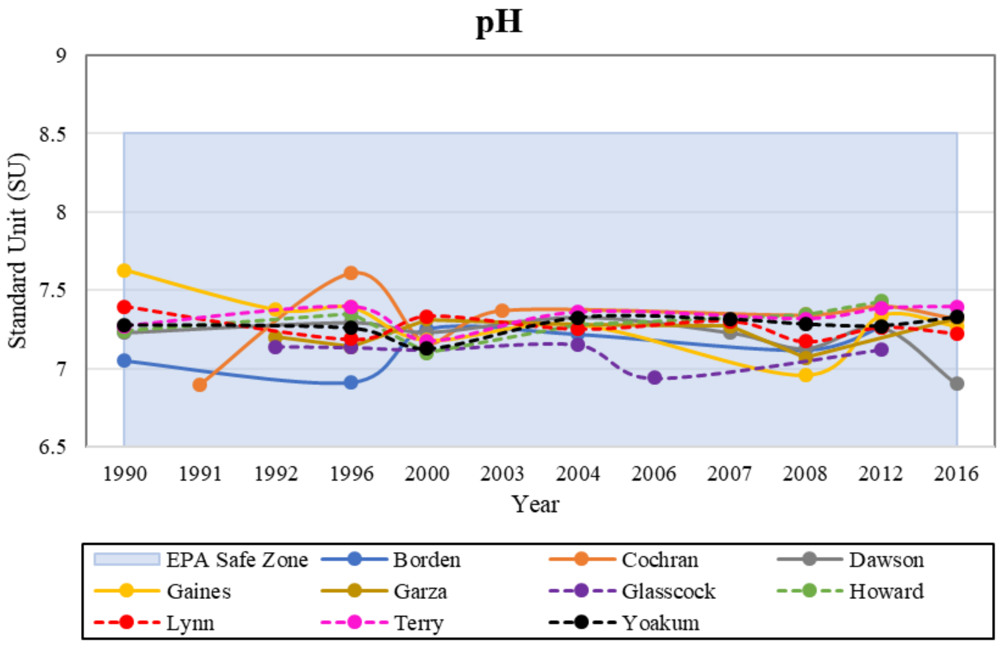

Figure 8. Historical analyses of pH levels with EPA safe zone in the study area.

4.5. Selenium

Selenium is a naturally occurring substance found in the Earth's crust that is essential for life; however, when taken in high concentrations it can be toxic. Selenium can also be anthropogenically produced, as it can form as a byproduct from the mining of sulfide ores. The density of selenium is 4.819 g/cm^3 which is also about 4 times greater than water. Selenium can be most commonly found in 4 different oxidation states: selenide (-2), elemental state (0), selenite (+4), and selenate (+6), with selenide having the least mobility and selenate having the greatest [37,42]. Arid environments that typically see high concentrations of gypsum and soluble salts like magnesium sulfate and thenardite, allow easy access for selenate to be fused with these minerals. Mills et al. [42] also stated how an increase of nitrate can lead to an increase in mobility of selenium in shallow groundwater aquifers, like the Ogallala.

Potential sources that cause inflated selenium concentrations are the leaching of marine shales, irrigation water and fertilizers, and discharge from oil refineries and mines. Oil refineries, such as the one located in Howard County for example (Figure 9), can be potential sources for selenium contamination [43]. Although these refineries are under strict regulations from the SWDA and CWA when it comes to how they discharge water, contamination can still remain in water bodies due to previous discharges before these Acts were enacted [19]. Soluble salts resulted in being the dominant source of selenium contamination and the selenium in gypsum had very little impact on contributing to the concentrations in groundwater. There is a weak relationship between selenium concentrations on the surface or in the unsaturated zone and selenium in groundwater. Organic matter is a major factor in high selenium concentrations and distribution [44].

Figure 9. Oil Refinery in Howard County, Texas (image from Google).

Selenium is a key component in the electronics and glass industry. It is used as a pigment in the production of plastics, rubber, paint, enamels, and ink. Pharmaceuticals, anti-dandruff shampoo, and fungicides are other products that require selenium. Selenium can also be used as a feed additive for poultry, livestock, and pesticides. Selenium's MCL is 50 µg/l [20]. The possible human effects of exceeding these levels are hair or fingernail loss, numbness in fingers or toes, and circulatory problems. The recommended intake of selenium is 55 µg/day with 400 µg/day being the upper limit. The most common symptoms for selenium toxicity observed were diarrhea, fatigue, hair loss, joint pain, nail discoloration or brittleness, nausea, and headache [45,46]. Previous research reported generally higher selenium concentrations in the Southern High Plains [11,16,37]. Our study also indicated that the greatest selenium concentration was approximately 5 times higher than its MCL. Figure 10 represents selenium levels and all counties succeeded in staying below the MCL of 50 mg/L, except for Borden, Dawson, and Glasscock during the observation periods.

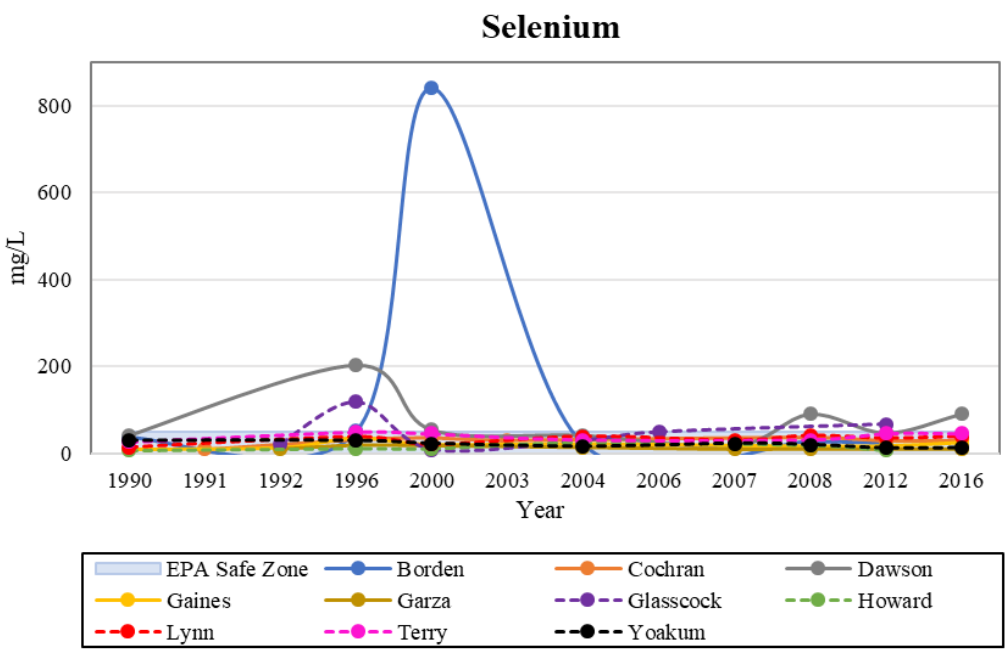

Figure 10. Historical analyses of Selenium levels with EPA safe zone in the study area.

4.6. Total Dissolved Solid (TDS)

TDS is not only an indicator of salinity but a measurement of all the dissolved inorganic and organic substances in water. The MCL for TDS is 500 mg/l [47]. If the groundwater has a concentration above this MCL, one can expect a higher hardness, colored water, staining, and a salty taste. Freshwater has a TDS concentration range from 0-1,000 mg/l, this would include rainwater, surface water, and diluted groundwater. When TDS concentrations range from 1,000-10,000 mg/l, it is categorized as brackish water, which includes groundwater and coastal marshes. TDS concentrations that range from 10,000-100,000 mg/l is considered saline water, which includes sea water and groundwater. Anything over 100,000 mg/l is considered brine water, which is observed in deep basin brines and saline lakes. Potential sources that directly impact TDS concentrations include industrial discharges, sewage, fertilizers, road runoff, and soil erosion [11,19,47]. Not only is it pivotal to stray away from substantially elevated TDS concentrations but it is also desirable to not have excessively low concentrations, as it will not contain the desired amount of necessary nutrients.

Potential sources of elevated TDS concentrations in the study area include mineral fertilizers and underlying bedrock units, such as the Dockum Aquifer and Permian evaporates [48]. The Dockum Aquifer has TDS concentrations ranging from 1-35,000 mg/l in the study area [25]. Other possible sources of salinity being from brine pits from old oil and gas wells, and the upward mobilization of oil and gas from wells that were not properly plugged [49]. The increase in solutes is due to evaporation and the occasional flushing of salts by irrigation water is one of the primary mechanisms of elevated salt concentrations in shallow groundwater [11,48]. The Southern High Plains seems to be of greater concern than the Northern High Plains as 84% of observations exceeded the brackish water limit of 10,000 mg/L. A saline plume exists along the northeastern margin of the Southern High Plains which could result in elevated concentrations around the plume [49]. We also observed that the groundwater quality diminished in the shallow observations compared to deeper observations, which gives reason to believe that the source of contamination is primarily coming from the surface rather than deep in the subsurface. A MCL of 500 mg/L was set for TDS and all counties failed to fall below that limit (Figure 11).

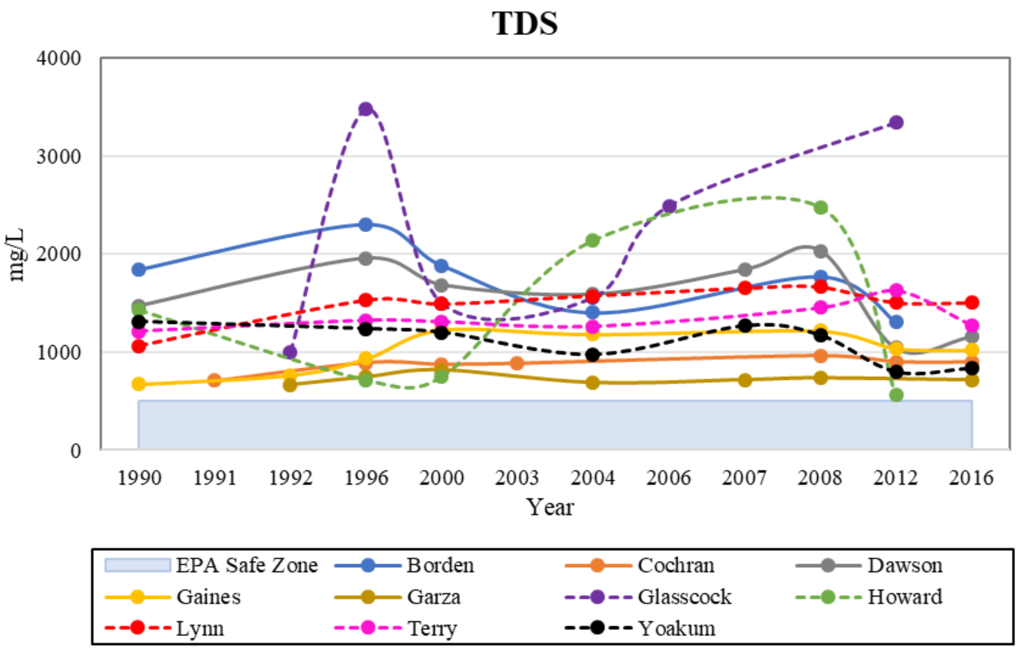

Figure 11. Historical analyses of TDS levels with EPA safe zone in the study area.

4.7. Hydrogeological Characterization

Box and whisker plots were compiled together, which highlighted each pollutant and the spread of the values for all counties in this study more efficiently. The data were used to form these box and whisker plots, which showed the minimum and maximum values, the 25th and 75th percentiles, and median. By creating these box and whisker plots, it becomes more efficient to visualize which counties have greater values of pollution versus other counties (Figure 12). Statistical mean values were also calculated for each parameter in their respective counties to further reinforce the understanding of the data (Tables 2).

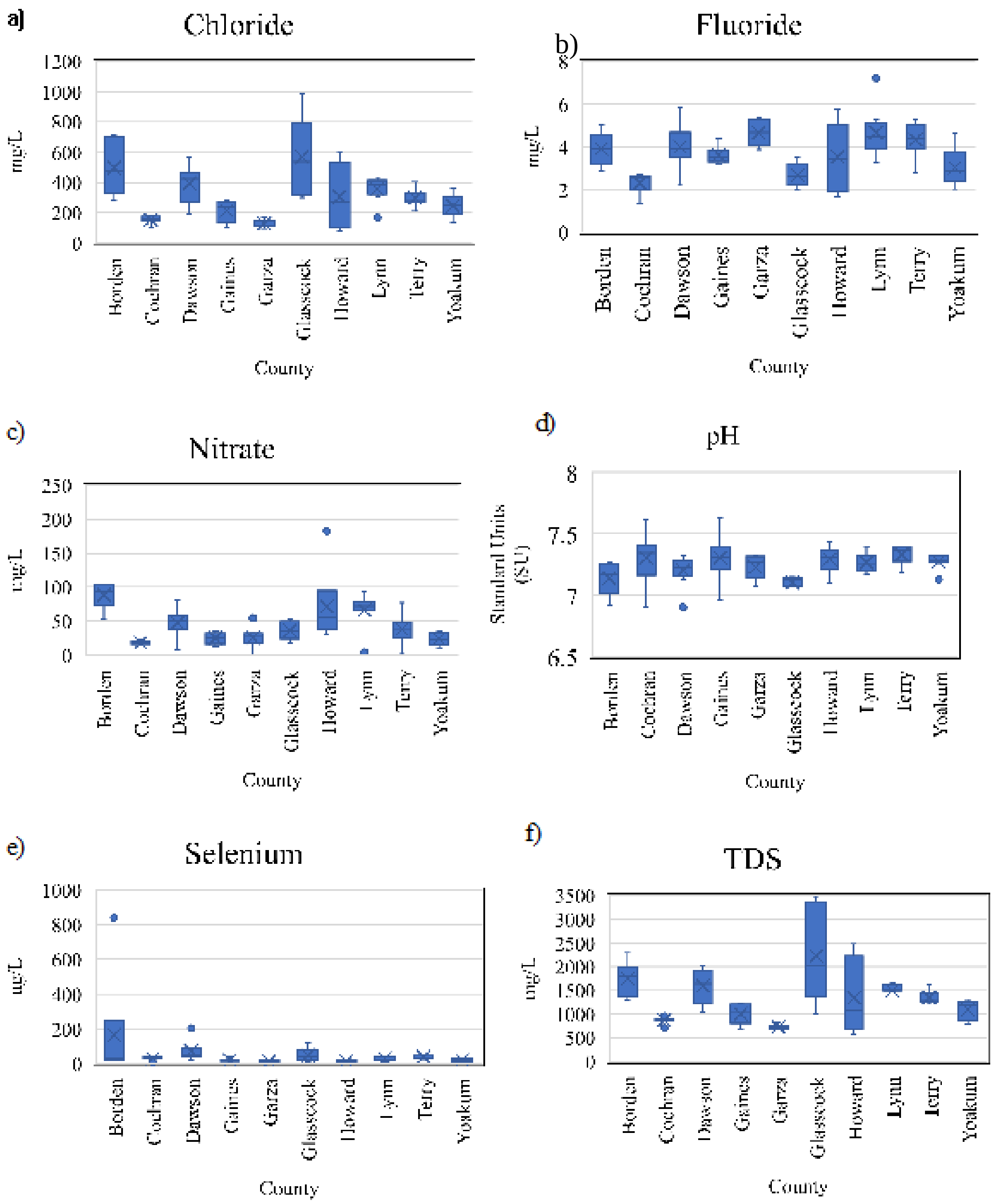

Figure 12. Box and whisker plots of (a) chloride, (b) fluoride, (c) nitrate, (d) pH, (e) selenium, and (f) TDS parameters recorded compared to their respective county.

In order to further understand the relationship between depth and groundwater quality, correlations between these two parameters were graphed to determine if the source of contamination was from the surface or underlying formations (Figure 13). The groundwater data for each county, as the latest data were from 2012, were used because it was the most recent data available. Garza County was not able to be used for this portion of the study due to no known depth for the wells. A linear regression line was also calculated and graphed to determine whether the data in this study would follow suit. The data collected in our study area has a decreasing linear regression for all parameters excluding pH, which suggests that contamination is coming from the surface rather than the underlying formations. Groundwater contamination should be worse in shallower wells compared to deeper wells due to human impact that occurs at the surface [11,16]. Consequently, deep aquifers should present lower levels of pollution. This relationship shows that deep aquifers are expected to present lower levels of contamination.

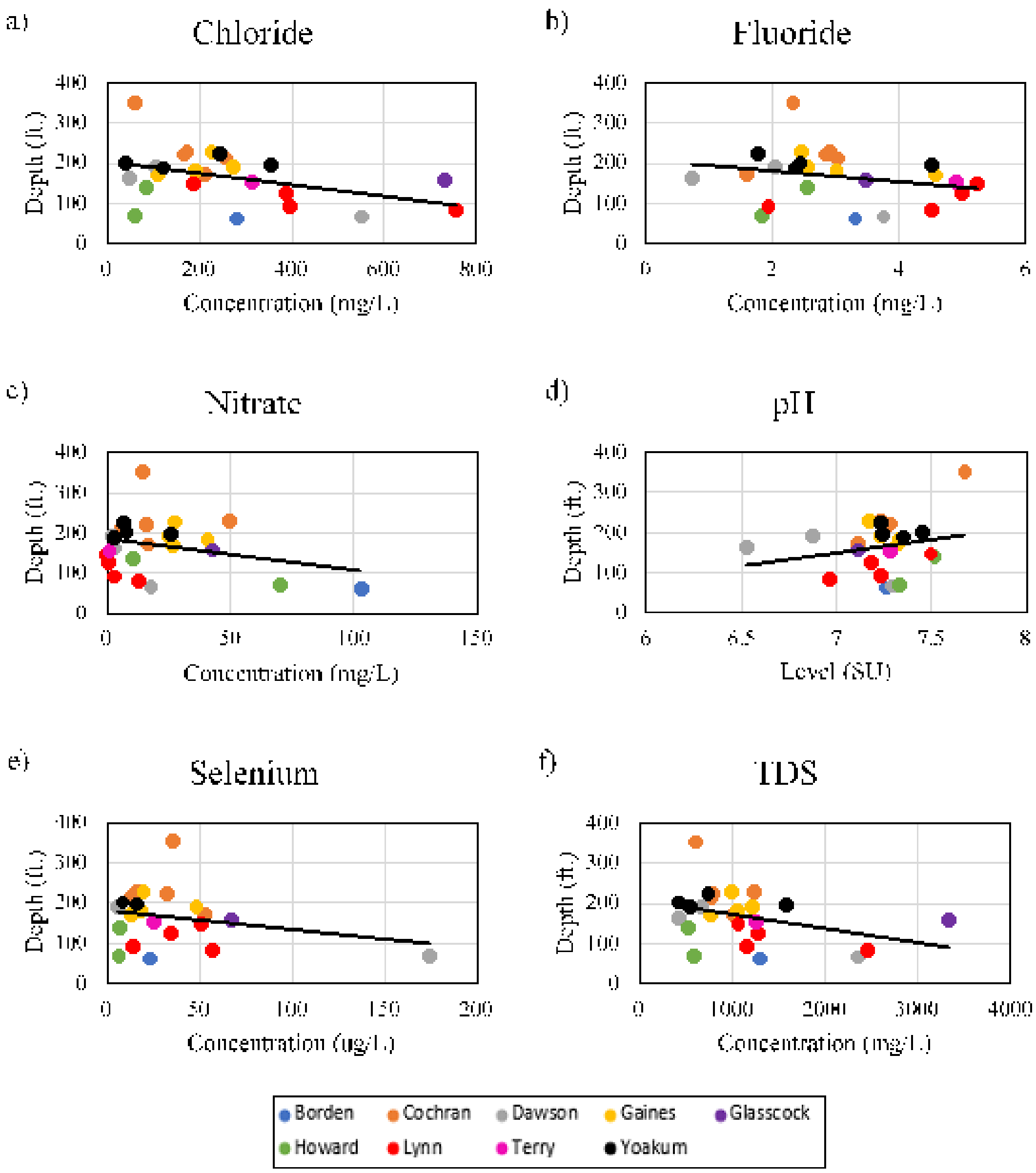

Figure 13. The latest data available of (a) chloride, (b) fluoride, (c) nitrate, (d) pH, (e) selenium, and (f) TDS values versus well depth for each county excluding Garza County.

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Table 2. Statistical mean of groundwater quality parameters in all counties of the study area.

	Borden	Cochran	Dawson	Gaines	Garza	Glasscock	Howard	Lynn	Terry	Yoakum
Chloride (mg/L)	497.7	153.8	393.6	213.4	128.4	568.8	305.5	357.5	297.3	247.5
Fluoride (mg/L)	3.9	2.3	4.0	3.6	4.7	2.7	3.5	4.7	4.4	3.0
Nitrate (mg/L)	88.4	18.3	48.0	25.2	25.9	36.0	71.5	66.4	38.2	24.3
pH (SU)	7.2	7.3	7.2	7.3	7.2	7.1	7.3	7.3	7.3	7.3
Selenium (ug/L)	167.0	29.8	73.7	20.5	13.7	49.6	13.6	32.6	39.9	20.9
TDS (mg/L)	1749.7	873.2	1597.0	1006.1	725.9	2228.0	1346.4	1497.1	1351.8	1099.1

5. Conclusions

This study analyzed the groundwater quality of Ogallala aquifer in the southern High Plain region of the Permian Basin, Texas from 1990 to 2016. The study area experienced high concentrations of groundwater contamination for most parameters, except for pH where most counties were within the contaminants' respective MCL. According to the standards set by the EPA, groundwater would be considered overall unsafe to drink in most counties, without some sort of filtration, when analyzing the final year of data for each county. Regarding the main culprits behind the high levels of groundwater contamination, human activities are either moderately or mostly to blame. This does not rule out the fact that there are some naturally occurring reasons as to why there are elevated levels of groundwater contamination.

Statistical methods were proven to be helpful in analyzing datasets with information of different sizes. Borden and Dawson counties experienced the overall highest amounts of groundwater pollutants. Pollutants such as chloride, fluoride, and TDS trended downward toward more recent years and natural events like precipitation can be a contributing factor for this escalation. The significance of this research highlights the elevated concentrations of groundwater contamination in the Southern High Plains region. Historical data in each county presents trends of groundwater contamination and possible reasons for some years exhibiting higher concentrations than others. This study focuses on anthropogenic and naturally occurring sources for each of the parameters, whether it be oil/gas activity, agricultural practices, or underlying bedrock that is hydraulically connected to the Ogallala, for example. Therefore, this research can provide significant information for the management of water resources in the High Plain region and the response to development in the Permian Basin, Texas.

Author Contributions: D.H. collected detailed information on the groundwater, calculated the environmental and groundwater changes, and analyzed the results with conclusions. J.H. designed the structure, developed the arguments, and contributed for the overall paper. All authors reviewed and approved of the final manuscript.

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