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# Visual Methods for Geochemical Screening of Possible Impacts to Groundwater by Oilfield Brines

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#### **ABSTRACT**

The primary components of oilfield brines (sodium and chloride) occur in groundwater naturally and from other contaminant sources. Therefore, sodium and chloride content alone are not reliable indicators of possible low-level oilfield brine impacts. Graphical methods used to evaluated chemical characteristics facilitate comparison of groups of samples (e.g., groundwater and brine) based on relative proportions of multiple ions.

A recent investigation in Texas used histograms, Piper plots, and Stiff diagrams, to visually compare major ion content of well water with suspected brine impacts to produced water from a nearby oilfield, and to regional groundwater chemistry from a published database. Graphical comparison showed allegedly impacted well water to be geochemically distinct from oilfield brine, and similar to regional groundwater quality.

To demonstrate a complimentary approach, the data from the Texas study were reanalyzed using cluster analysis, which combines multivariate statistics with simple graphics to aid interpretation of the similarities among multiple variables. Samples are clustered with similarity expressed as a simple percentage displayed on a single dendrogram plot, facilitating visual discernment of similarities or differences among multiple samples without the need to compare numerous individual plots. Reanalysis of the Texas data provide an additional line of evidence to support the conclusion that well water chemistry is not the result of anthropogenic brine impacts.

## INTRODUCTION

Deep formation brines, which are co-produced with oil and gas, represent a major potential source of saline impacts to fresh groundwater. The potential for brine impacts are more acute in mature production areas due to the sheer volume of brine produced (often exceeding the volume of produced oil many times over) and historical field practices of reinjection of brine, use of unlined pits and improper plugging and abandonment of wells (1). Due to slow groundwater flow rates, it may take many years for a release of oilfield brine to manifest itself as a gradual increase in the salinity of well water, and determination of whether a low level salinity increase is due to natural occurrence, oilfield brine, or other anthropogenic sources of salinity can be a challenge.

The primary dissolved components of oilfield brines, sodium and chloride, are present in virtually all groundwater to some extent, due to the interaction of the water with the soil and rock matrices through which it flows. Contact with geologic materials such as evaporite minerals can result in groundwater with naturally high concentrations of total dissolved solids (TDS) including chloride among other ions, especially in arid and semi-arid regions. Anthropogenic sources of

salinity in groundwater may also include sea-water intrusion, concentration of salts in surface water and soil via evaporation with subsequent infiltration, agricultural effluents, landfill leachates and road salting (1,2).

Some of these latter sources can be ruled out by common sense on the grounds of geography, land use and contact pathways in specific situations. However, identifying the source of salinity impacts, especially at low levels, poses a difficult problem that has received attention in several recent studies (1,2,3,4,5). As a general rule, the issue of salinity is evaluated using a combination of graphical, statistical, and/or modeling techniques, in conjunction with an evaluation of local hydrogeology. Qualitative and quantitative methods are used to develop a conceptual model of the chemical evolution of groundwater as it migrates through the aquifer system. Waters of interest are compared using the tools listed above, creating a 'lines of evidence' approach to identify the source of dissolved ions.

Hem (6) describes a number of graphical techniques for presentation of geochemical data that can be helpful in identifying sources of salinity in groundwater. The simplest of these techniques, bivariate plots of sodium/chloride ratios, (oilfield brines are less than 0.60 and brines formed by dissolution of halite are greater than 0.63, by weight), may work well for distinguishing salinity sources at relatively high concentrations in simple systems. However, identification of low-level salinity impacts to groundwater with more complicated chemistry typically requires evaluation of the relative proportions of major ions and less commonly analyzed minor constituents such as boron, bromide, iodide, and lithium, among others (1,2,4).

As noted by Davis et al. (4), the evaluation of minor constituents is promising as relatively small differences in the concentration of a minor constituent such as bromide can result in significant differences in Cl/Br ratios. However, as the authors acknowledge, analysis of bromide, for example, is not common in groundwater studies, and historical data for minor or trace ions, even when it is available, may be unreliable due to analytical challenges. Additionally, acquisition of sufficient new analytical data to enable reliable statistical evaluation may be impractical or cost-prohibitive.

This paper provides a brief synopsis of some simple graphical methods available for evaluating possible low-level impacts from saline sources, and it describes an example of their use in evaluating a suspected incidence of brine contamination in south Texas. Piper trilinear plots, Stiff diagrams, and histograms were used to compare the major ion chemistry of allegedly impacted well water with oilfield brine, water flood source water, and regional water quality from a water quality database published by the Texas Water Development Board (TWDB) (7, 8). This study clearly demonstrated that the salinity in the allegedly impacted wells was within the range of regional water quality and was not due to a brine impact. Subsequently, the data were reevaluated using multivariate cluster analysis, which confirmed the chemical dissimilarity of allegedly impacted groundwater to oilfield brine, and its similarity to background groundwater chemistry.

#### **DESCRIPTION OF METHODS**

Methods for analysis of salinity data can be roughly grouped into graphical methods and statistical comparisons. The basis for most graphical methods is the comparison and correlation of different ratios of dissolved constituents. Three purely graphical methods, histograms, Stiff diagrams, and Piper trilinear plots, are most commonly used to visually display distinctive composition signatures and relationships. Cluster analysis combines statistical and graphical

methods to provide an alternative or complimentary approach. Commercially available software products facilitate the conversion of data from spreadsheets or databases to graphical images using all of these methods.

#### **Graphical Methods**

Histograms provide perhaps the simplest tool for quickly illustrating the ratios of two or more ions (e.g., sodium and chloride). Since oilfield brines may be distinguished from brines derived from solution of evaporite deposits based on Na/Cl ratios, bivariate histograms of sodium and chloride may be useful in relatively simple situations. However, as the number of variables increases, histograms are of limited value in illustrating relationships between samples.

Stiff diagrams and Piper trilinear plots facilitate visual comparison of samples based on six variables. Most commonly, concentrations of the cations calcium, magnesium and sodium plus potassium, and the anions sulfate, chloride, and carbonate plus bicarbonate are plotted. Examples of a histogram, a Stiff diagram and a Piper plot comparing two waters are shown on Figure 1.

Stiff diagrams graphically illustrate the relative abundance of major ions, creating polygons with distinctive shapes. Cation and anion concentrations are first converted from mg/L to milliequivalents per liter (meq/L) to account for differences in the charge of different ions, and are then plotted on horizontal axes, with cations to the left of the zero point and anions to the right. Most commonly, sodium and potassium are plotted across from chloride, calcium is plotted opposite carbonate and bicarbonate, and magnesium is plotted opposite sulfate. This arrangement reflects potential or expected mineralogical sources of each of these dissolved ions in groundwater. The points are then connected to form a polygon, the size and shape of which visually indicate the total ionic concentration and the relative importance of the individual ionic species.

Piper Diagrams consist of two triangular ("trilinear") plots representing cations and anions, and a third diamond-shaped plot onto which the relative cation and anion concentrations are projected. Relative concentrations of the individual cations and anions in meq/L are expressed as percentages of the total cations or total anions (e.g., calcium, divided by the total of calcium, magnesium, and sodium plus potassium). The points are then plotted on the central diamond-shaped field by projection along lines parallel to the axes of the central field. The intersection of these projections represents the composition of the water with respect to the combination of ions shown. The circles plotted in the central field have radii proportional to the dissolved solids concentration of each water sample.

When combined with geographic information, histograms, Stiff and Piper diagrams can be displayed on a map or cross-section to illustrate spatial trends in the data across a region. Piper diagrams can illustrate temporal changes in water quality when multiple samples from the same location are plotted on the same diagram. Piper and Stiff diagrams are useful in identifying characteristic ratios of ions from various water sources, even when absolute concentrations of ions are dilute. If a fresh water has been impacted from a brine, the relative proportions of major ions would resemble those observed in the saline source.

### **Cluster Analysis**

Cluster analysis is a standard multivariate statistical approach that reduces the complexity associated with interpreting the similarities among a large number of variables (multiple "variates") such as major and minor ions and or trace elements, for a set of samples (9,10). The

analysis reduces the data and the samples are clustered based on similarity expressed as a simple percentage. Dendrogram plots permit easy visual discernment of similarities or differences among the samples. While this approach is similar to the more standard methods described above in that it relies on a graphical representation of the data, it has the inherent advantage of being able to incorporate a much larger set of data without increasing the complexity of the visual presentation or interpretation.

The method compares the normalized ion composition of each water sample to all other water samples in the data set to identify those samples that are most similar and most dissimilar, and then group or "cluster" the samples based on their relative similarity. It is particularly valuable for evaluation of groundwater impacts because of the high data density that is associated with typical datasets, both in terms of the number of samples collected and the number of constituents analyzed for each sample. The objective is to condense the dataset into a single graphical representation that clearly displays relationships between samples and can be easily interpreted to determine potential brine impacts.

In principle, cluster analysis is simply a hierarchical classification method, similar to taxonomic analysis used for categorizing biological species. Like phylogenetic taxonomy, the results of the cluster analysis are presented in a graphical "dendrogram" in which the height of the branch linking each sample pair or cluster indicates their relative degree of similarity, i.e., pairs or groups linked by a very low branch height share a very similar composition, while pairs linked by a very high branch are very different. In the case of the example dendrogram shown on Figure 2, progressing upward results in larger clusters that include a larger portion of the sample set, but with decreasing similarity between these individual samples.

The similarities between individual samples are calculated using standard statistical methods, in which the "distance" (or similarity) between sample pairs is defined (typically as Euclidian distance for a set of variables common to each sample) and rules to determine how this distance is used to "link" together groups are followed. There are a number of permutations of this approach, but in general, the analysis follows an algorithm where there is no *a priori* knowledge of how the samples are grouped, or even the number of groups that might be expected. Rather, a distance matrix is generated based on the number of samples collected, and the linkage method will cluster based on either nearest neighbor or further neighbor calculations where samples are clustered in a step-wise manner based on the relative values in the matrix. The process continues to compare the distance between individual members in clusters with remaining ungrouped samples, making increasingly larger clusters until all samples are part of the same group. Raw data for each of these samples can be used, or the data can be standardized based on mean values in cases where different constituents have significantly different concentration ranges.

For groundwater data, cluster analysis is most applicable for inorganic ions, similar to the manner in which Piper or Stiff diagrams are employed. However, the number of variables can also be increased to include other constituents which may be useful in determining the source of a suspected salinity impact, and data can be normalized to correct for possible dilution effects. As a consequence, this analysis can compare data from various locations that have been collected at different time intervals, such that there may be no need to conduct additional sampling if an existing dataset is available.

#### **EXAMPLE FROM SOUTH TEXAS**

#### Overview

The graphical methods described above were utilized as part of a study conducted in 2002 to evaluate suspected oilfield brine impacts to private water wells located in an oil-producing area in south Texas. Results of major ion analyses from four "landowner wells" were compared to samples of brine from the oil-producing formation using histograms, Piper plots and Stiff diagrams. In addition, the landowner well water chemistry was compared to regional water quality from a database published by the Texas Water Development Board (TWDB) (7). It is important to note that the study used the graphical methods in the context of a detailed evaluation of the regional hydrogeology, which due to space considerations is not discussed in detail in this paper.

Subsequently, the same data were re-analyzed using cluster analysis, which was conducted specifically as a demonstration of the method for this paper. This exercise confirmed the results of the prior study in a manner that greatly simplified the visual interpretation.

#### Hydrogeologic Setting and Regional Groundwater Quality

The study area, located in the Interior Gulf Coastal Plain (11) near the Texas-Mexico border, was arbitrarily defined to include land within an approximate 25-mile radius from the allegedly impacted landowner wells. The study area comprises most of Jim Hogg County, and adjacent parts of Star and Zapata Counties. The area is semiarid, with moderate topography, and is sparsely populated with ranching and oil production as the primary land uses. The locations of the landowner wells are shown by red dots on Figure 3, with other water wells in the TWDB database color-coded by the aquifer in which they are reported to be screened.

The area is underlain by Eocene to Pliocene sedimentary deposits that dip and thicken toward the Gulf of Mexico, forming arcuate bands of outcrop that increase with age updip. In the immediate vicinity of the landowner wells, formations exposed at the surface include i) the Miocene-age Catahoula and Frio Formations, comprised of mudstone, claystone, sandstone, tuff, and clay; ii) the Pliocene-age Goliad Formation, composed of clay, sand, sandstone, marl, caliche and conglomerate; and iii) Holocene-age sheet sand and stabilized dune deposits. Many of the units exposed within the study area are groundwater-bearing units at depth. The stratigraphic and hydrogeologic units beneath the region are shown on Figure 4. The Eocene-age Jackson Group is also an oil producing formation in the area, and includes the Colorado Sand, from which the brine sample was obtained, and the overlying Pettus sand, from which naturally saline (TDS >10,000 mg/L) source water for the oilfield water-flood operations was derived.

As described in several studies (12, 13, 14, 15), groundwater in the counties along the Rio Grande in south Texas is characterized by high dissolved solids content, consisting mainly of sodium, chloride and sulfate. The mineral content of the groundwater reflects the mineralogy of the rocks forming the aquifers and underlying the recharge areas, as well as the low recharge rates characteristic of the semiarid climate. Dissolved solids content of groundwater in the study area generally exceeds 1,000 mg/L and frequently is greater than 3,000 mg/L. Groundwater in the region often fails to meet Texas Department of Health (TDH) secondary drinking water standards for both chloride and sulfate (i.e., 300 mg/L for both ions), and the high TDS content limits its use for irrigation.

The area also has a large number of oilfields, making determination of "background" salinity concentrations problematic. The background salinity problem is further complicated by the fact that groundwater in the study area is produced from several different geologic formations, in wells ranging in depth from less than 50 ft to more than 1000 ft, and to a large degree, water chemistry appears to be independent of well location, depth, or screened formation. Therefore, it is difficult to know with certainty whether the salinity of any particular well may be influenced by oilfield activities.

#### **Database for Study and Sources**

Available data from published and unpublished sources were compiled in a database prepared for the study. Groundwater samples from each of the four landowner wells were collected by the landowner and analyzed by the Texas Agricultural Extension Service. Locations are shown by red dots on Figure 3. The depths, productive intervals, and construction details of the four landowner wells were not provided.

Geochemical data for produced water from production wells and water-flood source water wells in the oilfield were provided by a former producer. The "produced" water is separated from oil produced from the Colorado Sand, while the "source" water is from the overlying Pettus Sand. Both sands are members of the Eocene-age Jackson Group, which is also one of the aquifers screened in wells updip of the study area.

Regional groundwater quality data were obtained from the TWDB, and historical information was available for three municipal water supply wells in Hebbronville (16), located in northern Jim Hogg county. The TWDB (7,8) maintains a publicly-available groundwater database with information on over 130,000 wells in the State of Texas. The database includes location, depth, well type, formation, geographic coordinates and water quality parameters. The TWDB database has sufficient data to construct Stiff and Piper diagrams for most major groundwater formations in Texas, providing information on background concentrations in various locations. The State of Texas also provides geo-coded aerial photographs and topographic maps that can be accessed free of charge and used to plot both the location of wells and their chemical composition. Additionally, the Geological Atlas of Texas, which illustrates major geologic formations in Texas, is available in geo-coded electronic format for a small fee (17). Research conducted for this paper did not identify similar databases in other oil-producing states, such that Texas may be unique in having access to this type of resource.

Geochemical data for a total of 59 wells in Jim Hogg, Starr, and Zapata counties were extracted from the 2002 version of TWDB database (7). Each well is identified by a seven-digit location code assigned by the TWDB. Wells in the database with available latitude and longitude information are shown on Figure 3. The color of the dots indicates the formation in which individual wells are reportedly screened. Note that the "Gulf Coast Aquifer System" includes the Catahoula, Oakville, and Goliad aquifer sands (Figure 4); therefore, that the water chemistry of wells designated as Catahoula, Oakville, or Goliad may be indistinguishable that of water from wells designated as "undifferentiated Gulf Coast Aquifer."

The major ion chemistry of each water sample was entered into the project database, along with information such as the source formation of the water and geographic coordinates of the well. Summary statistics were determined for the major ions (sodium plus potassium, chloride, calcium, magnesium, sulfate, and bicarbonate plus carbonate) for the landowner wells,

the groundwater from other area formations, and the produced and water-flood source water. Histograms, Stiff diagrams and Piper plots for all individual wells and for the average compositions of the various waters (i.e., landowner wells, groundwater by aquifer, produced and source waters).

#### **Results of Graphical Water Quality Comparisons**

As a first comparison method, a series of histograms illustrating the major ion content of the landowner wells and the wells from the regional database were prepared. Histograms presented on Figure 5 compare the average composition of the landowner wells to average compositions for groundwater from the various aquifers in the region. These histograms demonstrate that the water quality of the landowner wells falls within the range of that observed regionally. Note that in all of the waters, sodium and chloride are the dominant ions, sulfate and bicarbonate are of secondary importance, and there is very little calcium and almost no magnesium by comparison. In general, most of the groundwater in the area can be classified as sodium-chloride to sodium-mixed-anion water.

Figure 1 compares the relative proportions of major ions in the landowner wells versus the produced water and water flood source water using a histogram, Stiff diagram, and Piper diagrams, based on average composition. (Note that the concentrations are plotted against a logarithmic scale). Again, sodium and chloride predominate in both the groundwater and the brine samples. However, the histogram clearly shows the relative importance of calcium and magnesium in the produced water, compared to the landowner wells. Comparison of the Stiff diagrams also illustrates the dominance of chloride compared to other ions in the brine samples compared to the landowner wells. The ratio of sodium to chloride (in meg/L) is close to 1 for the oilfield water, producing a nearly symmetrical Stiff diagram, and close to 2 for the landowner wells, producing a pronounced asymmetry. The ratio of sodium/chloride (in mg/L) is 0.6 for the produced water and water-flood source water, while in the landowner wells, on average, it is more than twice that, 1.3. The Piper diagram also illustrates that while sodium is by far the predominant cation in both waters, the carbonate and sulfate content of the landowner wells is appreciable, while in the brine they are negligible. (Note that both the Stiff and Piper diagrams sum sodium and potassium, and in some cases, potassium was not analyzed; however, when potassium was analyzed it represented a very small fraction of the total. Similarly, carbonate and bicarbonate are summed, and carbonate (when analyzed) represented a small fraction of the total).

To further assess whether the landowner wells were impacted by oil production activities in the vicinity, water quality data from the landowner wells was compared to that from water wells in the surrounding area. As noted above, well depths and the formations screened vary significantly within the area. Stiff diagrams representing the average composition for each aquifer are displayed on Figure 6, which also shows the number of wells in each aquifer used to compute the average.

Statistical evaluation of the data had indicated that as a general trend, as total chloride content and dissolved solids increase, ratios of sodium to chloride decrease (i.e., chloride becomes more predominant compared to sodium). However, the landowner wells varied from this trend, in that they were relatively enriched in sodium versus chloride compared to other wells in the database with similar chloride content. The Stiff diagrams demonstrate this point visually by the relative asymmetry of the diagrams for the landowner wells compared to the diagrams for the other aquifers with comparable high sodium content.

Stiff and Piper diagrams for each individual well in the database were also prepared for the study, but are not reproduced here for the sake of brevity. For display purposes, the wells were grouped by aquifer and then arbitrarily subdivided into smaller subsets of wells based on total salinity and or geography (e.g., high and low-salinity (greater or less than 70 meq/l Cl) Catahoula formation wells, north and west or south of the landowner wells) in order to facilitate visual comparison. A single example, Figure 7, compares the landowner wells to low-salinity Catahoula Formation wells and shows the greatest similarity. Since these wells were geographically closest to the landowner wells, the similarity was not surprising.

The study concluded that compared to the produced and source water samples, the water from the landowner wells was found to have a relatively high sodium to chloride ratio, and to be relatively enriched in sulfate and relatively depleted in calcium. Compared with other water wells within the study area, water samples collected from the landowner wells were found to have concentrations of anions and cations that are well within the range observed for wells in Jim Hogg, Starr, and Zapata counties, both in terms of concentration and relative proportions. Compared to the data set as a whole, the landowner wells exhibited higher mean concentrations of sodium, bicarbonate, and sulfate, and lower mean concentration of chloride. Therefore, the landowner wells actually showed less indication of possible oilfield brine impacts than other wells in the study area with comparable chloride content.

To a large extent, the graphical techniques for displaying and visually comparing the data from numerous wells were the key elements in making this case. However, it was necessary to produce and compare a large number of individual plots. As an alternative approach, the data were recently re-evaluated using cluster analysis, which facilitated visual comparison by plotting the results on a single page.

#### **Example of Cluster Analysis Applied to South Texas Study**

The cluster analysis approach was applied to the same dataset of groundwater samples and produced water samples described above. The objective was to test the method's ability to validate the conclusions reached on the basis of the more familiar methods used in the prior study, and to illustrate the conclusions in a more readily observable manner. Cluster analysis is well-suited for comparing the ionic fingerprint of each sample and for determining whether the groundwater samples are influenced by produced water even at low levels because it removes the effects of dilution.

The analysis was conducted using standard methods for multivariate analysis of groundwater (9,10) using the statistical software Minitab<sup>TM</sup> (Release 13.1). To run the analysis, the distance matrix was generated and evaluated using squared Euclidian distances and the complete linkage method. The option to standardize variables (by subtracting the mean value for a variable and then dividing by the standard deviation) was also selected. This standard data adjustment serves to normalize the constituents for concentration, thereby correcting for dilution effects, and to reduce the bias introduced by one or more dominant constituents (i.e., chloride which has a large concentration range). Data from samples collected from the same formation were averaged, and the produced water and water-flood source water samples were also averaged to generate a single data point to represent oilfield brine.

The results of the statistical cluster analysis on the entire database are summarized on Figure 2. As shown, the ionic content of all groundwater samples is very distinct from that of the oilfield brine (produced water and water-flood source water), with the relative similarity (as

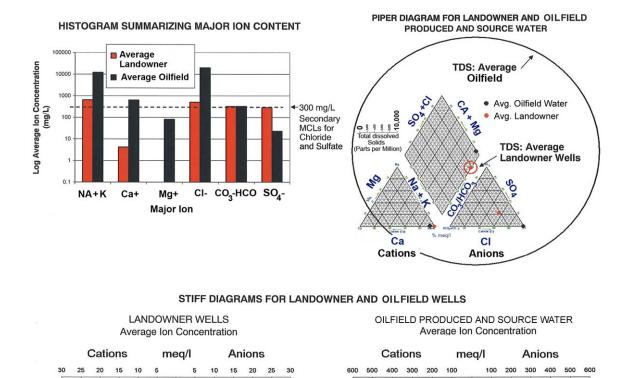
shown on the y-axis) approaching 0%. All groundwater samples cluster into a group with a minimum 58% similarity rating, indicating that all groundwater samples share a relatively similar ionic composition, which is very different from that of the produced water. Regardless of the aquifer from which they were collected, the groundwater samples were all more similar to each other than they were to the produced water sample. Significantly, the chemistry of the landowner wells matches very closely with the low salinity water wells screened in the Catahoula formation, which also showed the best visual match by the Stiff and Piper diagrams.

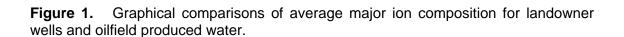
In conclusion, cluster analysis provides an additional line of evidence for evaluating alleged or suspected low-level brine impacts to water wells. It is of particular value because the analysis can be conducted without making any assumptions about existing relationships between individual groundwater samples or with produced water. Therefore, it provided an independent assessment technique that condensed a large and complicated dataset in such a way that interpretation is facilitated by comparing all of the wells on a single plot. Cluster analysis would be best used as a corroborative tool in conjunction with, rather than in lieu of, the other graphical methods, which directly represent the water chemistry, as opposed to just the statistical similarity among the samples. Furthermore, all of these methods should be used in the context of a good understanding of local and regional hydrogeology and groundwater geochemistry.

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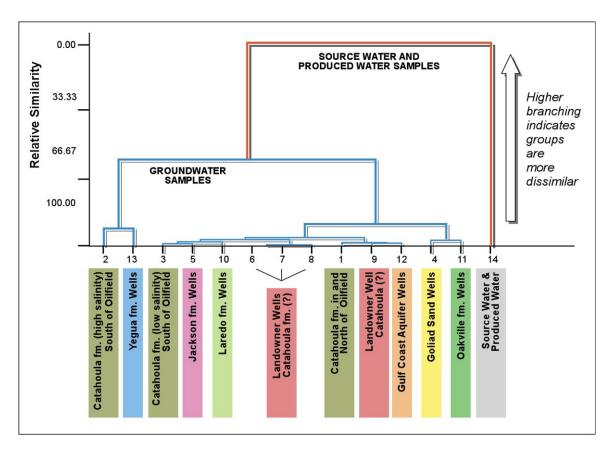
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Mg SO4

нсоз+соз



**Figure 2.** Cluster analysis of inorganic ions in landowner wells compared to study area groundwater and produced water, based on averaged concentrations by aquifer.

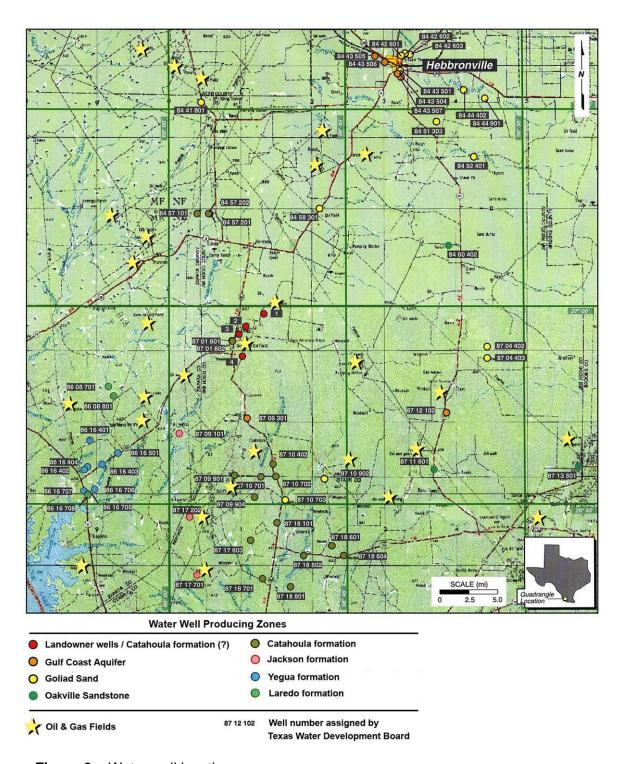
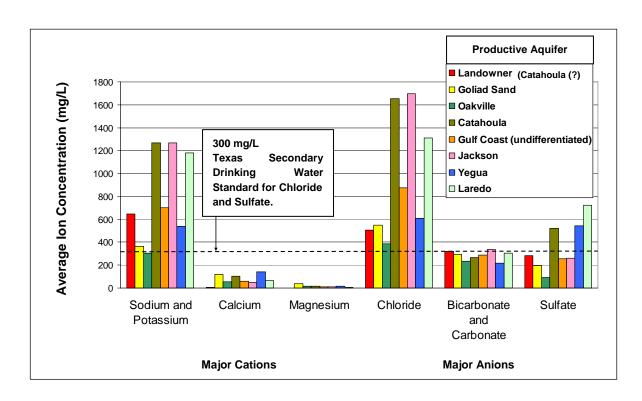


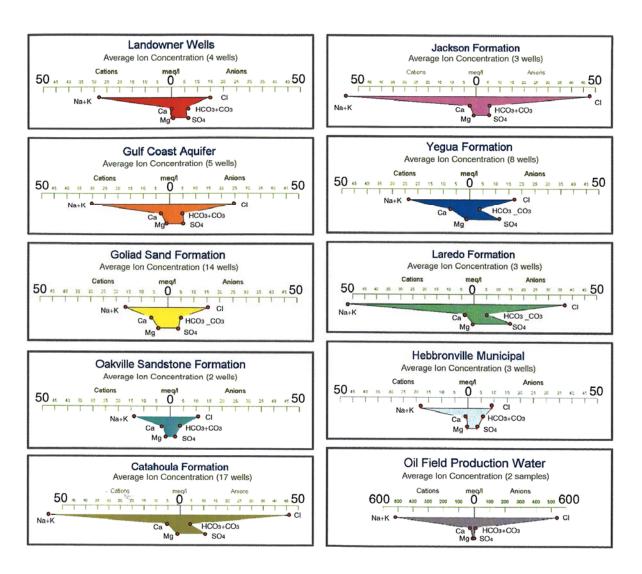
Figure 3. Water well location map.

Series	Local Stratigraphic/Hydrogeologic Unit			Lithology	
Pliocene	stem	stem		Formation Sand	Sand, silt, and clay
	Coastal Lowlands Aquifer System (Gulf Coast Aquifer)	Fleming Formation		Clay, silt, and sand	
Miocene			kville dstone Catahoula	a Sandstone or Tuff	Sand, silt, and clay
	ŏ	Anahuac Formation		Clay, silt, and sand	
Oligocene				Frio Formation	Sand, silt, and clay
J		Frio Clay		Vicksburg Formation	
	Confining Unit	Jackson Group	Whitsett Formation		Clay and silt
			Manning Clay		
			Wellborn Sandstone		
			Caddell Formation		
Eocene	Coastal Uplands Aquifer System	Claiborne Group	Yegua Formation		Sand, silt, and clay
			Laredo Formation		Clay, silt, and sand
			El Pico Clay		Sand, silt, and clay
			Bigford Formation		Clay, silt, and sand
		0		Carrizo Sand	Sand, silt, and clay

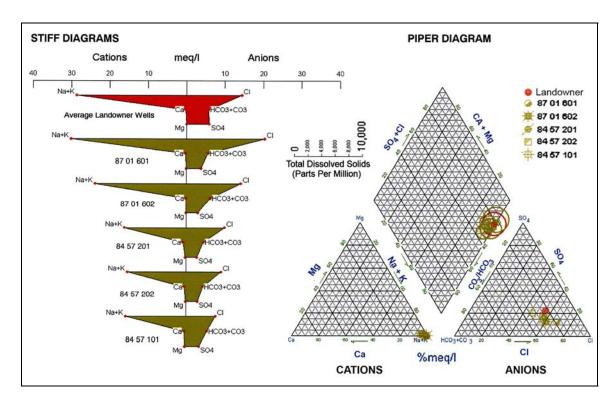
Figure 4. Hydrostratigraphic units underlying Jim Hogg County, Texas (12).



**Figure 5.** Major ion composition of study area well water, concentrations averaged by aquifer.



**Figure 6.** Stiff diagrams comparing average major ion composition for landowner wells and study area wells grouped by aquifer.



**Figure 7.** Comparison of ionic composition of landowner wells to low-salinity (Na and Cl meq/l) Catahoula formation wells.