PROJECT SUMMARY

Hydrologic-Hydrochemical Characterization of Texas Gulf Coast Saline Formations Used for Deep-Well Injection of Chemical Wastes

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ABSTRACT

This research program was conducted to investigate fluid migration potential, direction and velocities in the regional hydrologic environment of the Texas Gulf Coast Tertiary formations in the context of deep-well injection of hazardous chemical wastes. The study has focussed on the Frio Formation as it is the target of a very large waste injection volume as well as due to availability of a large database of formation pressures and water chemistry in the Frio.

Pressure data gathered from drillstem tests and bottomhole pressure measurements in onshore oil and gas wells were used in evaluating pressure regimes. Pressure-depth profiles and potentiometric surfaces were constructed from the pressure data and these reflect existence of three hydrologic regimes: a shallow fresh to moderately saline water section in the upper 3-4 thousand feet, an underlying 4-5 thousand feet thick essentialy saline hydrostatic section, and a deeper overpressured section with moderate to high salinities. The complexity of the hydrologic environment is enhanced due to extensive depressurization in the 4,000 to 8,000 ft depth interval. This presumably results from the estimated production of over 10 billion barrels of oil equivalent and associated brines from this interval alone in the past 50 years. Hydrologic analysis indicates that transition to geopressured sediments in some areas of the Gulf Coast is encounterd as shallow as 6,000 feet.

Due to variability in thickness and pressure regimes, a composite potentiometric surface of the entire Frio can not be constructed to determine 'natural' flow gradients or 'natural' points of discharge. Present conditions are already quite altered from original ones. Potentiometric surfaces representing discrete depth intervals were mapped for evaluating regional flow trends. Average formation porosity and permeability values were obtained from published data. These values and the flow gradients determined from potentiometric surfaces were used to compute linear fluid flow velocities ranging from 0.01 ft/year to 105 ft/year in the lateral direction.

Potential for vertical fluid migration was identified from equivalent environmental hydraulic heads. The presence of widespread pockets of depressured formations significantly affects the direction and value of fluid gradients, in as much as these depressured oil and gas fields carry the risk of becoming sinks for the injected chemical wastes. Any subsequent pathway to sources of fresh water will be determined by the capacity of faults and fractures to act as conduits for flow, and/or the presence of abandoned wells to facilitate such flow.

Published water chemistry data was supplemented by field sampling of waters from thirty-two oil fields. Active recharge of Frio by continental waters is not occurring. All waters sampled appear in isotopic equilibrium with the rock matrix. The chemical composition of brines from the northern section indicates that salt dome dissolution is the primary reaction controlling water chemistry in this region. Brines from the deeper geopressured section may be leaking into the hydrostatic section of the central and southern Gulf Coast Frio. This leakage does not appear to extend all the way up to the fresh to moderately saline section.

An offshoot of the current research is the evidence of microbial degradation of organic material shallower than approximately 7,000 ft. The lack of organic acids and the alteration of Frio oils from these zones suggests biodegradation. This has useful implication for degradation of injected chemical wastes and needs to be further investigated.

A detailed analysis of the localized hydrodynamics in Victoria County, Texas, as a sample case study shows the applicability of the developed techniques to injection facility siting and monitoring process, where depressurization was observed on a local, county-size scale.

This project summary was developed by the Bureau of Economic Geology, the University of Texas at Austin, and the complete project report is available separately (see Project Report ordering information at the end).

INTRODUCTION

Liquid wastes generated by chemical and manufacturing industries have been disposed of by deep-well injection into Gulf Coast Tertiary formations for nearly thirty five years. The popularity of this method is reflected in the ever increasing volumes estimated at about 6 billion gallons per year in the mid 1980's in

Texas. These practices are regulated by federal and state agencies concerned with preventing contamination of ground water resources. Figure 1 shows the active waste injection sites along the Texas Gulf Coast.

The injection of large volumes of liquid chemical wastes in the permeable Tertiary sediments along the Texas Gulf Coast raises concern about the hydrologic and geochemical interaction with formation fluids. A description of this interaction requires first the characterization of formation fluid hydrology and hydrochemistry, and then the evaluation of superposition of injected fluids onto the existing system. This study has dealt with the first part, namely describing the hydrologic regimes existing in the Tertiary formations, the potential for fluid movement, and the chemistry of formation waters. The chemical processes controlling interaction of injected chemical wastes with the insitu fluids and formation rocks are being investigated by the Bureau of Economic Geology under a separate cooperative agreement with the EPA.

Potential for fluid migration in the subsurface is controlled by formation hydrologic properties (permeability and porosity) of the sedimentary formations, existence of a flow gradient and pathways for flow. The methodology described in this study facilitates determination of flow gradients and velocities. This can be integrated with regional geologic information about flow paths such as depositional facies, faults and fractures for compiling a geohydrologic flow model. The hydrochemical information from this report can be used for hedrogeologic interpretation and for analyzing chemical interaction and degradation processes.

PROCEDURE

The main focus of this research is the description of Texas Gulf Coast Frio hydrologic and hydrochemical environment using formation fluid pressures and water chemistry. The formation pressures used to construct pressure-depth profiles and potentiometric surfaces are taken from drillstem tests (DSTs) and bottomhole pressure measurements in oil and gas wells. Nearly 17,400 pressure values in Frio were gleaned from a large commercial database after careful screening. Figure 2 plots these pressures versus depths and was the starting point in identifying the different hydrologic regimes. Reliability of DST data was verified by plotting histograms of initial and final shut-in test pressures and by evaluating their convergence ratio. These pressures were further separated by test depths in 2,000 ft thick intervals, with the objective of segregating the shallow hydropressured section from the deeper saline hydrostatic and overpressured sections. Additionally, brine chemistry data were used to confirm the delineation of different regimes. Fluid pressures were converted to equivalent fresh water and brine heads for constructing potentiometric surfaces. Selection of which fluid gradient to use for conversion to hydraulic heads was based on analysis of water salinity data. A surface contouring package CPS-1 was utilized for making the potentiometric contours. Data in each horizontal depth slice were carefully screened to cull abnormally high and low values and were selected from similar time intervals (usually 10 years) to minimize their dated nature.

Potential for vertical fluid migration was analyzed by constructing residual brine-equivalent potential surfaces. This involved subtracting the potentiometric surface of one (shallower) depth interval from the other (deeper) depth interval.

The hydrochemistry effort consisted of evaluating nearly 850 Frio analyses from previously published reports. These mostly contained major cation and anion data. Thirty-two additional oil field waters were sampled by the Bureau of Economic Geology. These were analyzed for major and minor ions, isotopes, organic acids, and organic composition of oils. Samples were collected from depths between 3,000 and 10,000 feet for a good representation of normal as well as potentially biodegraded oils. Various plots were generated to determine correlation between chemistry, origin and migration patterns of these waters. Figure 3 provides an overview of the range of salinity values encounterd along the Gulf Coast Frio. For ease of handling the large pressure and chemistry data, the study area was divided into three regions: A, B, and C; corresponding to north, central and south Gulf Coast.

RESULTS

Pressure-depth profiles generated separately and integrated for different regions and different well types in the Gulf Coast reflect the complexity of regional pressure regimes. Two major hydrologic regimes are evident on Figure 2: a brine hydrostatic regime (with a slope of 0.465 psi/ft) which extends to depths of 10,000-11,000 ft, and, a geopressured regime (with a slope approaching 0.9 psi/ft) which extends as shallow as ~7,000 ft and is shallower than previously recognized. The hydrostatic regime represents a hydrologic zone of potentially active ground-water circulation. The geopressured regime represents a zone of restricted circulation. Chemical wastes are injected into the hydrostatic section. Also evident are the large areas of depressurization correlatable to hydrocarbon producing fields. Potentiometric surfaces for Frio slices are quite flat in the shallow fresh to moderately saline sections above 4,000 ft depth. But the deeper saline sections in the 4,000-8,000 ft interval contain widespread sub sea level potential contours indicating depressured hydrologic conditions. These result in horizontal flow gradients significantly steeper than those in the shallow sections. Still deeper sections are dominated by highly positive potentiometric contours due to the transition into geopressured sediments. Residual surfaces constructed to assess vertical flow potential also reconfirm the tendency of flow to be directed toward depressured sections, with the flow gradient being a function of the degree of depressurization in a slice. No regional flow into shallow fresh aquifers is observed.

Analysis of Frio water chemistry shows a gradual shift from Na-Cl water in the north and north central region to a Na-Ca-Cl character in the south central and a Na-Ca-Cl-SO_4 water in the south. Chlorides increase with depth in the north Frio, in the salt domes region. This correlation is variable in the south region and is reversed in San Patricio and Nueces Counties, which may be tied to the transition to geopressured conditions. Sulfate concentrations are generally low. Sodium concentrations mostly increase linearly with chloride except for the south. Calcium versus chloride is variable and may be linked to cation exchange in clays. Similarly, relatively high magnesium values may be either derived from clay reactions or dolomitization. A plot of bromide versus chloride breaks up in two trends; one is increasing Br with Cl, and the other is constant Br with increasing Cl (Figure 4). Plotting Cl/Br ratio versus Cl, and Na/Cl ratio versus Cl similarly shows separation of two populations. The Cl/Br and Na/Cl ratios for the low Br waters indicate halite dissolution in the Houston Embayment salt dome region. Source of the high Br in the central and southern region suggests upward leakage of deeper waters.

Total field titrated alkalinity provides a qualitative estimate of the organic acids in deep formation waters. Two trends are observed in the total alkalinity versus organic alkalinity correlation; increasing organic acid concentartion with total alkalinity, and almost zero organic alkalinity for a limited total alkalinity value in some samples. In the first trend, nearly 50% of the total alkalinity is attributable to organic acids.

This suggests existence of a decarboxylation reaction. For the second trend, absence of organic acids for total alkalinity values less than 800 mg/l suggests biodegradation. These waters were collected from depths shallower than 7,000 ft.

Gas chromatographic analyses of eleven oil samples were performed to test for evidence of biodegradation. Normal paraffins (NC) and isoprenoids (IP) appear to dominate the composition of these oils. Paraffins between C5 and C13 are most susceptible to biodegradation. The ratio of NC17 to IP19 as reflected in the loss of NC17 peak in comparison to the IP19 peak is another indicator of biodegradation. This phenomenon is observed in the sample in Figure 5a, which shows a loss of nearly all organic compounds. The oil sample of Figure 5b in comparison is not biodegraded. Five out of the eleven oil samples indicate varying degree of biodegradation. All degraded oils were collected from depths shallower than 7,000 ft.

An insitu pH of 5-6 was estimated for the oil-field water sampled. A linear trend of higher pH for increasing alkalinities was observed. Degassing of CO_2 does not appear to cause significant loss of inorganic alkalinity. Isotope composition of hydrogen (δ^2H) versus oxygen ($\delta^{18}O$) for Frio waters shows a general trend of isotropic enrichment for $\delta^{18}O$ away from the meteoric water line (Figure 6). Increasing $\delta^{18}O$ but constant δ^2H values with depth and isotopic equilibration of Frio waters with formation clays is observed in field sampled brines and other available data. Recently recharged meteoric waters (light $\delta^{18}O$ values) were not found.

DISCUSSION

The Frio pressure-depth profiles indicate hydrostatic and subhydrostatic conditions in sediments above 10,000 ft. This coexists with overpressures observed as shallow as 6,000 ft. Large scale depressurization is linked to hydrocarbon production. This variability of pressure regimes is also reflected on the potentiometric surfaces which tend to be flat in the shallow sections and show steeper gradients in the deeper sections. Because of this depressurization, injected wastes may be constrained from migrating upward into fresh-water aquifers but may migrate toward the depressured oil and gas fields. Overpressured and hydrostatic conditions exist at same depth range and suggest hydrologic discontinuity in the form of compartmentalization. This may be advantageous in locating future waste injection facilities.

County scale potentiometric surface map (Figure 7) show the general coincidence of depressurization and oil fields. The county scale is considered an appropriate scale to map the depressurization; the county area is large enough for sufficient data coverage, but small enough to map perturbations of the potentiometric surface. Such maps should be integrated with structure maps locating faults and salt domes, as well as with maps of oil and gas fields, and with deep-well/abandoned-well maps. These integrated maps would be valuable in evaluating permeability pathways and direction for potential fluid flow for injection facility siting decisions.

The geochemical environment in the 4,000-7,000 ft Frio depth range used for deep-well injection has implication for the long-term confinement, migration and degradation of these chemical wastes. This environment is typically slightly acidic (pH 5-6), saline (Cl range from 20,000 to above 60,000 ppm), reducing (presence of NH_4), warm (less than 80^{o}C), and biologically active (evidence of microbial degradation of oils). The varying salinities can affect the degree of mixing of injected wastes with formation brines. Degradation of wastes through hydrolysis proceeds favorably under high or low pHs. The slightly acidic pH of formation waters does not enhance reaction rates. Biodegradation of wastes will occur faster than abiotic reactions in the relatively shallow moderately warm (70-80^{o}C) hydrostatic section. But, significantly higher temperatures are required to accelerate abiotic processes such as hydrolysis. Presence of microorganisms at temperatures above 80^{o}C (deeper horizons) is not expected. Presence and relative activities of aerobic and anaerobic bacteria associated with chemical degradation needs further study.

Active recharge of continental waters is not occurring in the Frio. All sampled waters appear in isotopic equilibrium with the rock matrix. Total dissolved solids are also much higher than in the underlying Wilcox Formation, where deeper penetration of meteoric waters is observed. Although evidence from organic acids and biodegraded oils suggests deep circulation of meteoric waters for transport of bacteria, such an active circulation is not supported by chemical data. The presence of Br-rich brines in the hydrostatic sections of central and south Gulf Coast suggests upward leakage of fluids from the undercompacted geopressured section. Constant Br values in Houston Embayment region indicate the importance of halite dissolution and reflect lack of upward fluid leakage there. This contradicts the general concept that growth faults and salt domes in this region are pathways for upward migration of deeper brines. The processes of salt dissolution and fluid leakage suggest an active rather than a stagnant hydrologic environment in the Frio, in the context of geologic time. However, natural flow rates are probably slow enough to have no impact on the confinement of injected wastes.

CONCLUSIONS

The use of bottomhole pressures and water chemistry data in conjunction with regional structure and geology is an appropriate technique for hydrologic-hydrochemical characterization of Gulf Coast saline formations being used for deep-well disposal of chemical wastes. Flow gradients in the Frio Formation calculated from potentiometric surfaces and available pemeability values were used to determine horizontal linear velocities ranging from 0.01 to 105 ft/year. The depressurization in and around oil and gas fields seems to overwhelm the natural conditions. Natural hydrologic conditions may be better delineated through hydrochemical data. Upward migration of water in the hydrostatic section is presently constrained by the depressurization and density differential between shallow fresh to moderately saline aquifers and the deeper saline aquifers. Decisions on injection facility siting should be evaluated in the context of local hydrologic conditions which can be better described with county-scale maps.

Hydrochemical data suggest that the Frio is not being actively recharged in geologic time scale by continental meteoric waters. Brines from the deeper geopressured section may be leaking up into the hydrostatic section of the Frio in the central and southern regions. Vertical leakage does not appear to be occurring in the northern region, where salt dome dissolution is the dominant geochemical process. The presence of degraded hydrocarbons suggests microbial reactions which can prove useful in chemical waste degradation.

FUTURE RESEARCH DIRECTIONS

Detailed investigation of depressurization from oil and gas production is needed to determine whether injected wastes can migrate to producing or depleted and abandoned fields. Field studies and pilot projects to monitor waste/formation reactions and possible biodegradation of chemical wastes can prove very useful.

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Jerry Thornhill is the EPA Project Officer (see below)

The complete report, entitled "Regional Hydrologic-Hydrochemical Characterization of Saline Formations in the Texas Gulf Coast that are Used for Deep-Well Injection of Chemical Wastes," (order No. ________________) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

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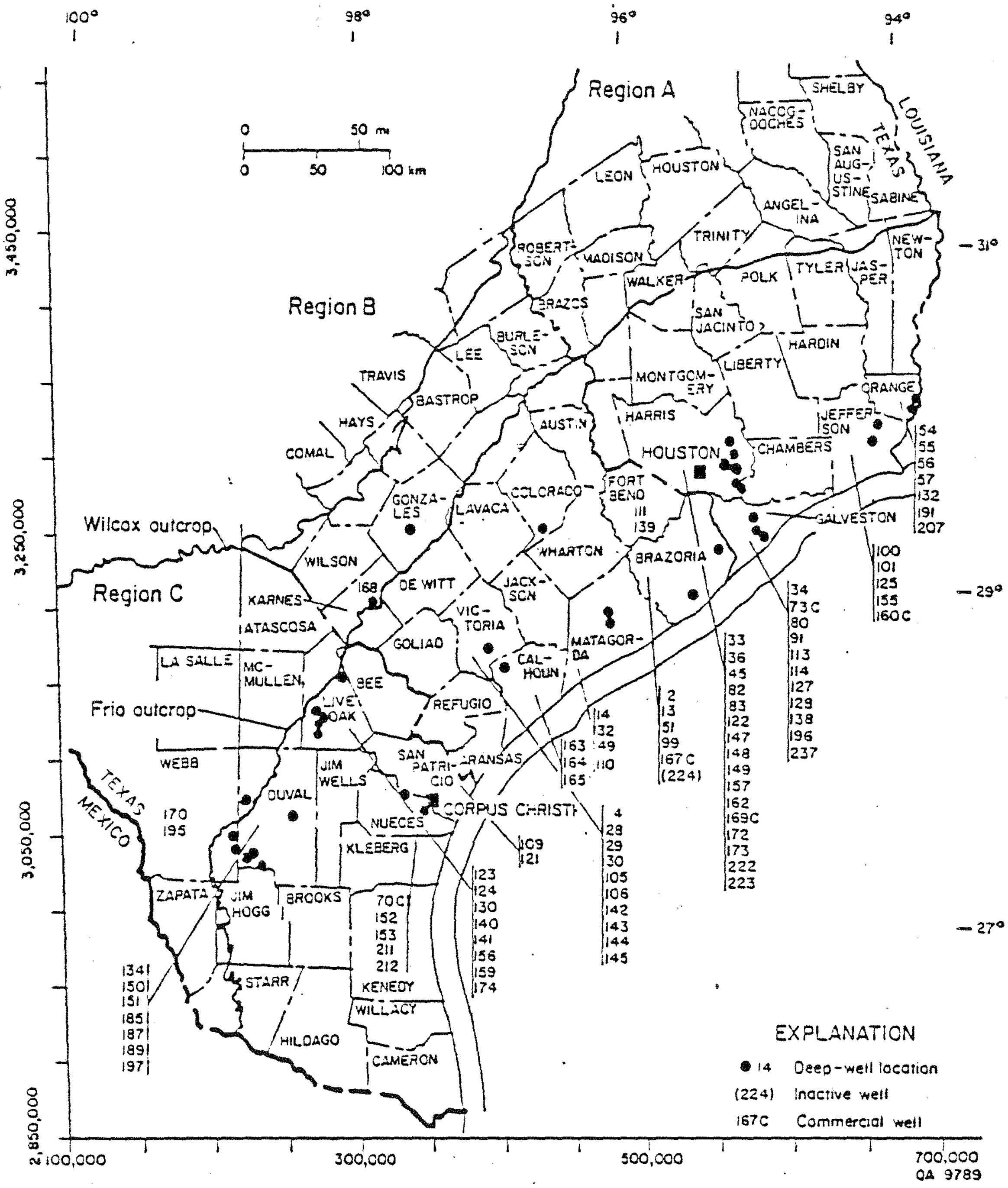

Figure 1. County map with deep-well injection locations, Texas Gulf Coast.

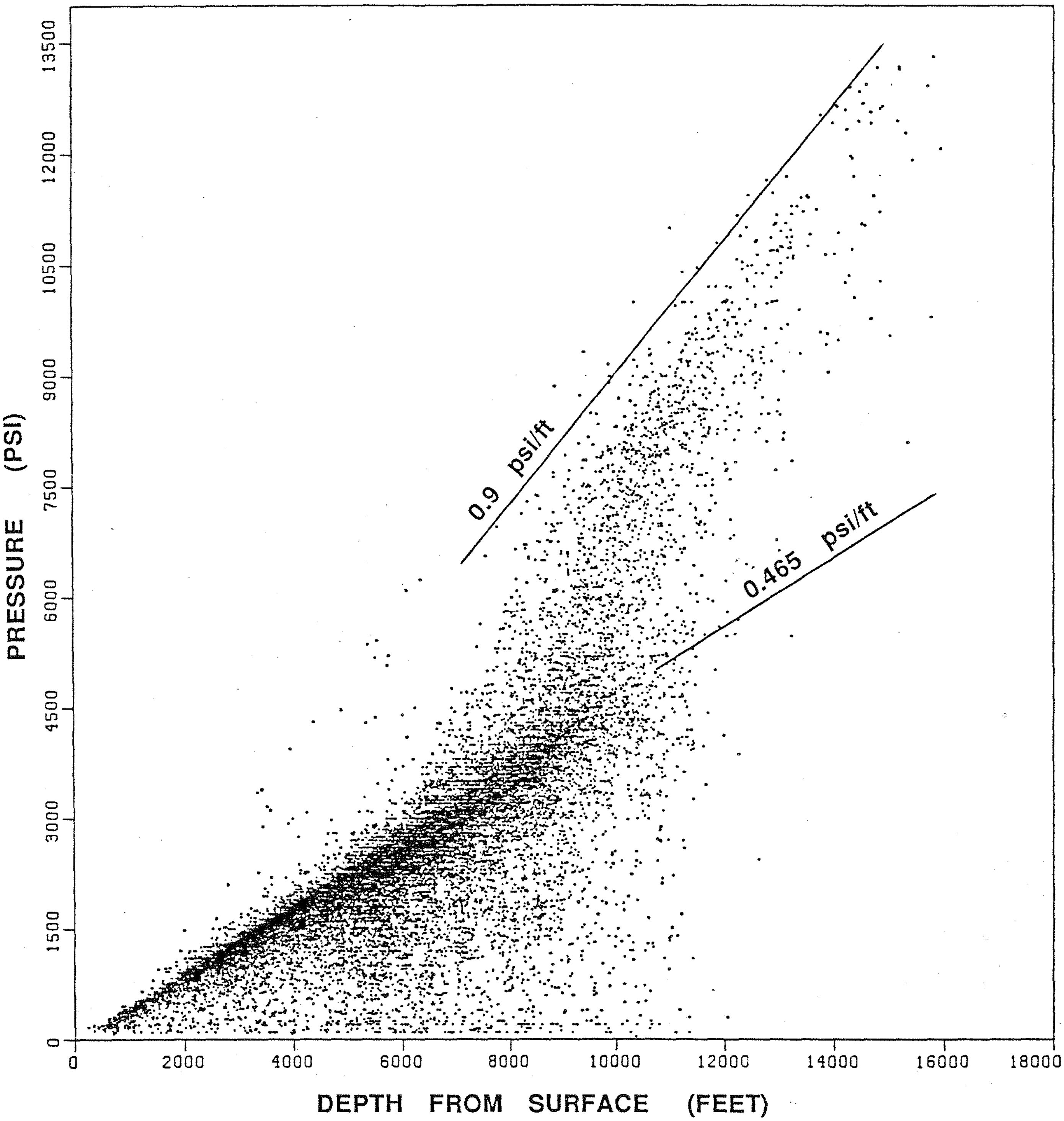

Figure 2. Pressure-depth diagram for Frio Formation; regions A, B, and C data. 17,411 pressure measurements used in this figure.

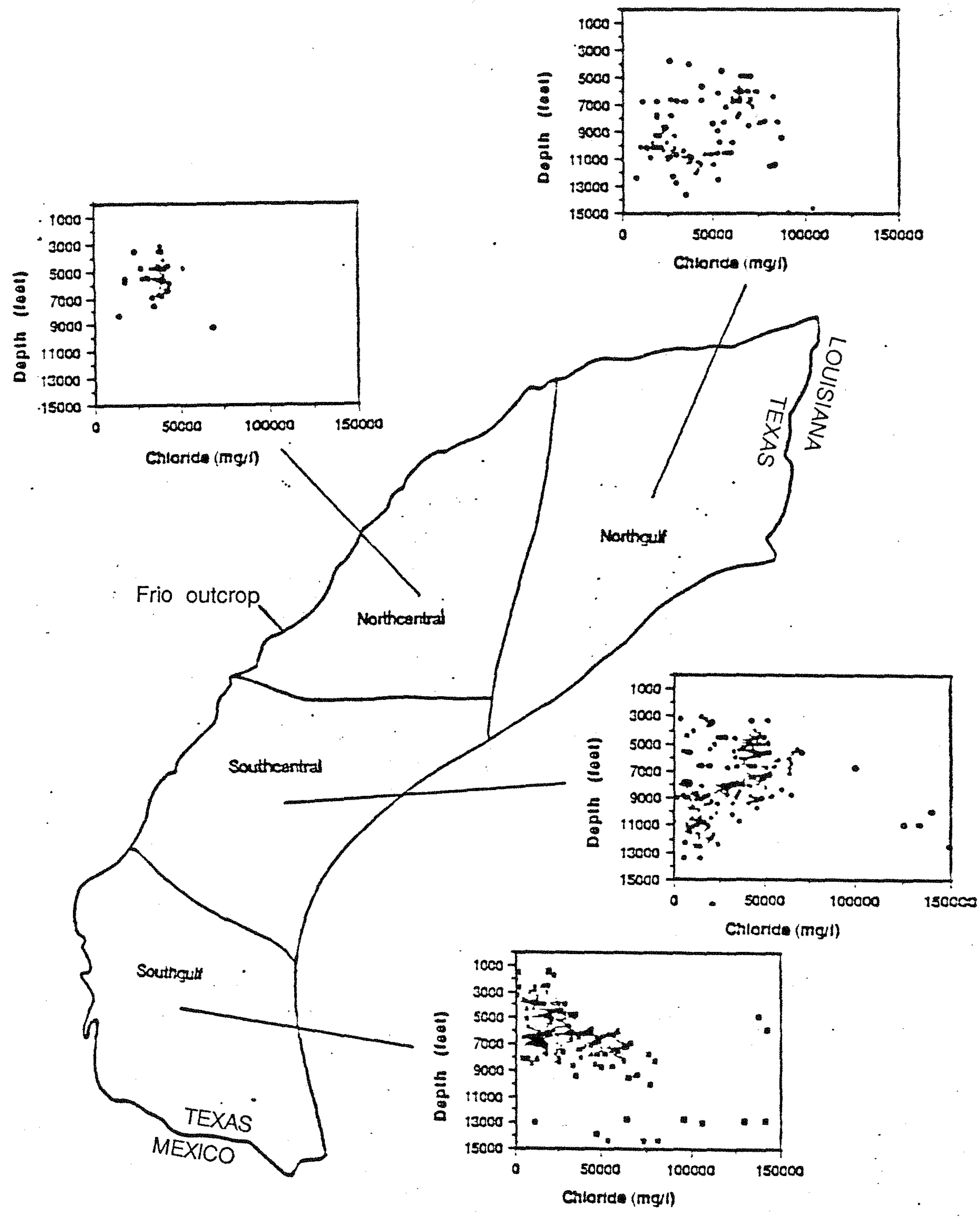

Figure 3. Chloride distribution for the Frio Formation for various depths from Northgulf, Northcentral, Southcentral and Southgulf regions. Chemical compositions in mg/l.

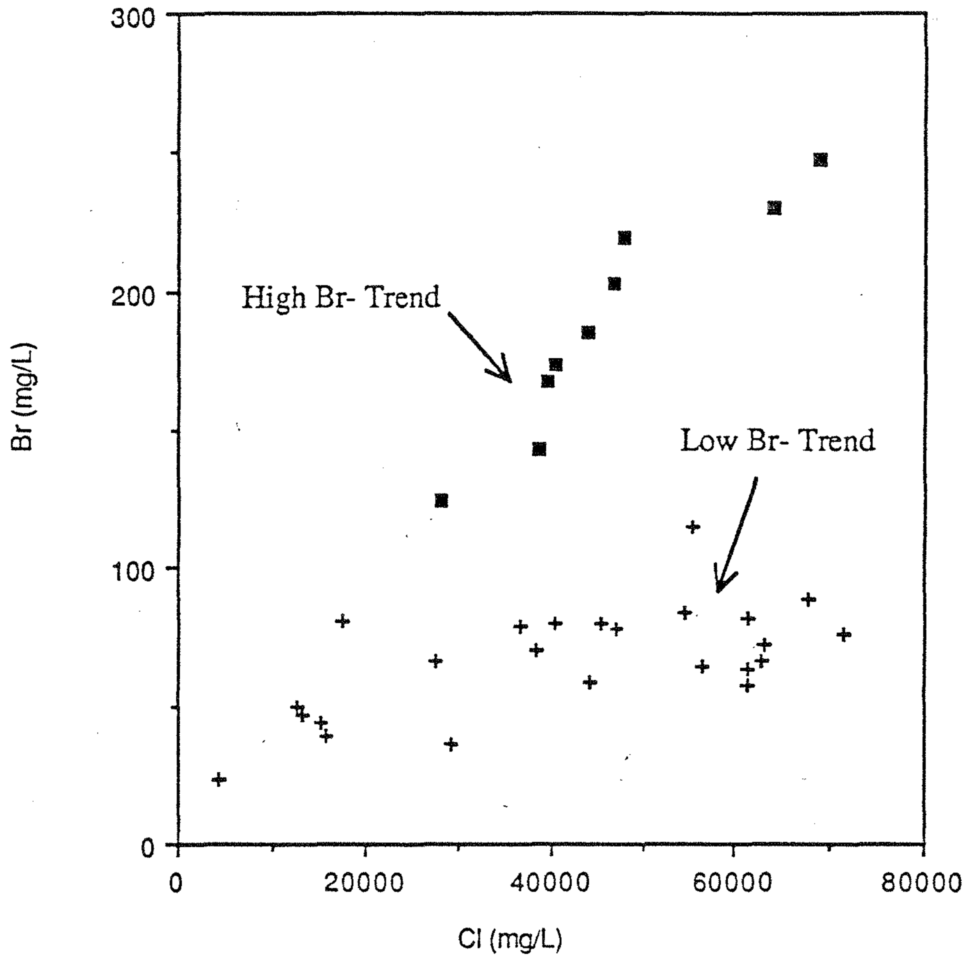

Figure 4. Plot of bromide versus chloride from brines collected for this study for Frio Formation. Note two different populations of data. High Br trend from central and south Texas regions suggests leakage of brine from deeper geopressured sediments. The low Br trend from northern Houston embayment region results from halite dissolution.

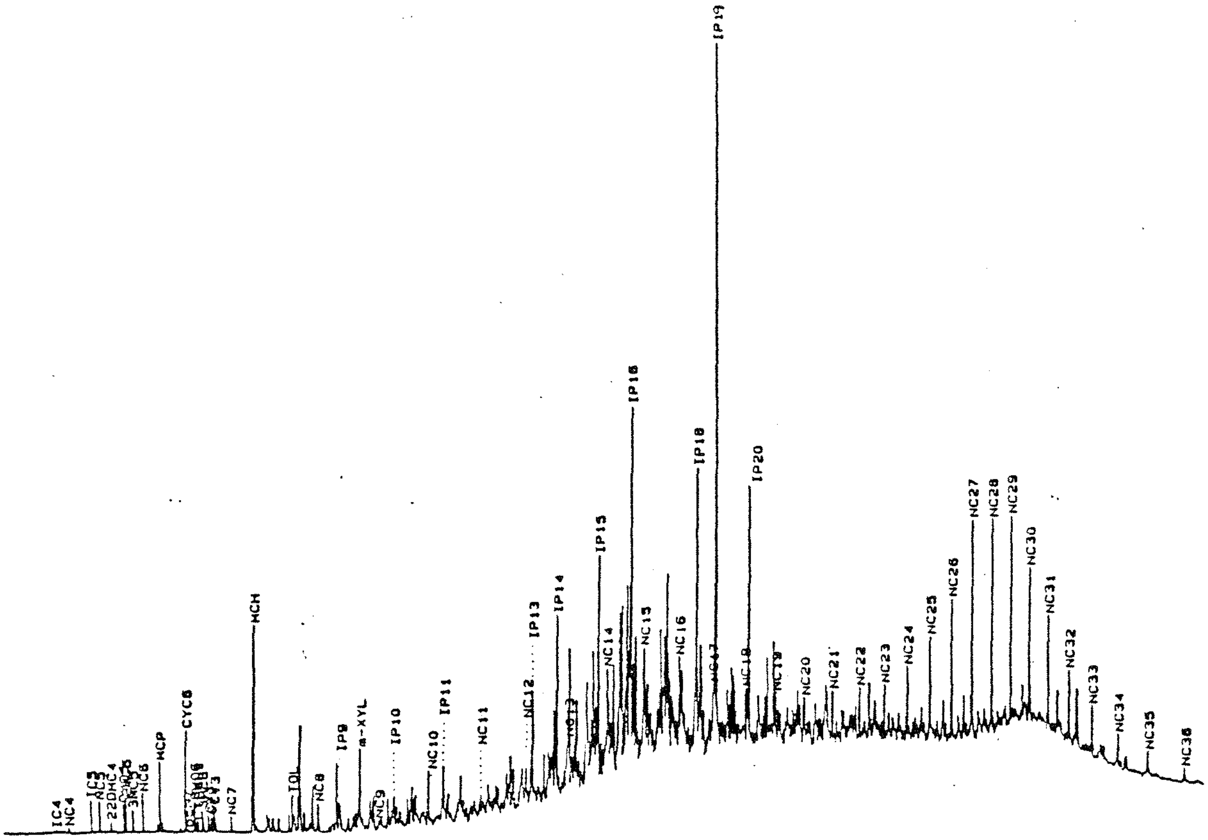

Figure 5a. Gas chromatograph trace of whole oil sample TBEG-34. Sample appears to be degraded. Sample depth is 6,244 ft.

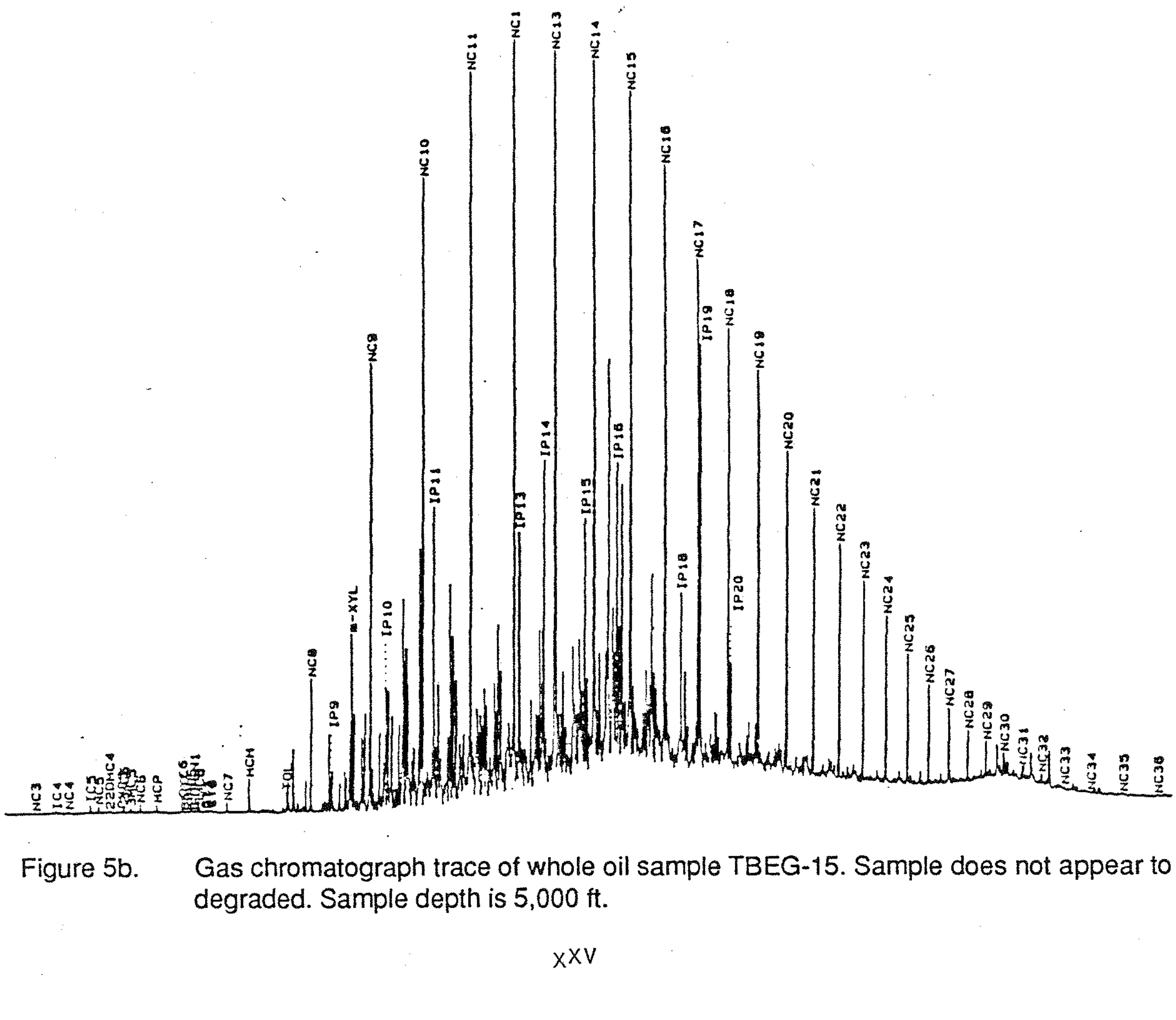

Figure 5b. Gas chromatograph trace of whole oil sample TBEG-15. Sample does not appear to be degraded. Sample depth is 5,000 ft.

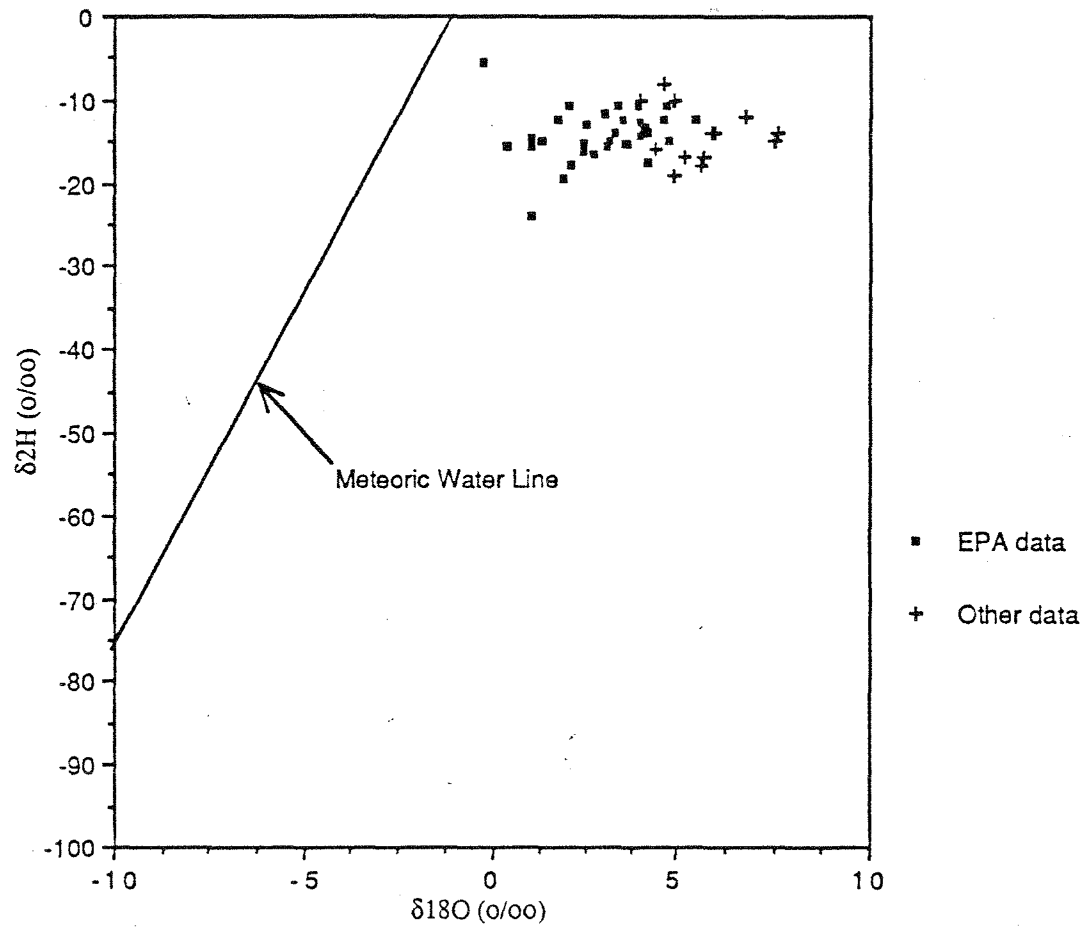

Figure 6. Hydrogen versus oxygen isotopic composition of Frio waters collected for this study. Global meteoric water line from Craig (1961).

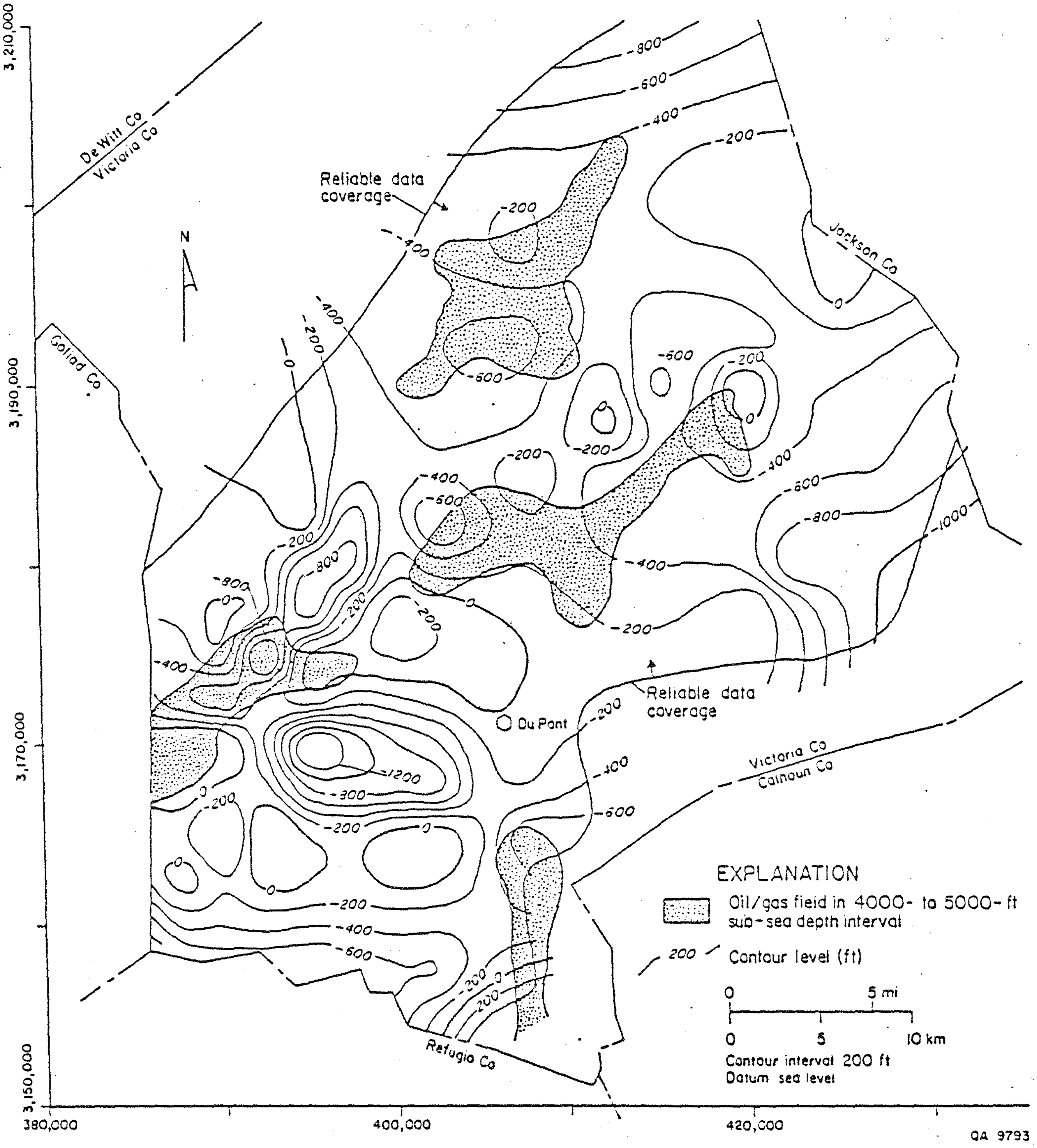

Figure 7. Potentiometric surface, 4,000-4,900-ft slice, Victoria County, Frio and Catahoula, all classes, 1945-1984 data. Includes formation pressure at Du Pont injection facility. Equivalent brine heads.