

Oil and Gas Seepage in the Southern Gulf of Mexico: Regional Studies of Oil Generation, Charge and Source

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Abstract

This paper is an overview of TDI-Brooks' surface geochemical exploration (SGE) coring programs conducted for Pemex Exploración y Producción (PEP) in 1998, 2000 and 2001. These studies, consisting of approximately 900 cores, represent the first major SGE coring studies undertaken in the southern Gulf. The program successfully identified many areas of widespread and active oil seepage. Satellite radar imagery provided by the NPA Group was also undertaken over most of the Mexican Gulf, which further confirmed the presence of numerous and widespread naturally occurring oil seeps. This body of data supports the conclusion that the Cenozoic strata of the continental shelf and deeper waters of the Mexican part of the Gulf contain petroleum reserves that could potentially match those found to date in U.S. waters [i.e., 78 BBOE, of which 12 BBOE (15%) are in deep water (Pettingill and Weimer, 2001)]. The analogy between the proven resources of the U.S. Gulf and the undrilled potential of the Mexican areas is rooted in their shared geological history, similar petroleum systems, and petroleum seepages, as documented here.

Introduction

Like many Tertiary Delta systems worldwide, studies of macroseepage of oil and gas into seafloor sediments in the Gulf of Mexico provide important information on oil generation, charge, source and quality ahead of the drillbit (Cole et al., 2001). Since the early 1980s the northern Gulf of Mexico has been extensively studied in various consortium and private surface geochemical exploration (SGE) coring programs by two of us (JMB and BBB). Results from the nearly 10,000 SGE cores acquired over this period in the northern Gulf have had major impact on deep water exploration by delineating source, maturity and charge risk. In the northern Gulf, strategically placed cores based on regional 2-D and 3-D seismic data have a high percentage yield of "live" oil (often 5% to >10% of cores). Active oil generation on the northern Gulf margin facilitated by salt tectonics that produce conduits for leakage to the seafloor allows SGE programs to obtain oil in many areas on the seafloor that, when analyzed, aids in the understanding of petroleum systems.

Surface Geochemical Exploration (SGE) Studies

SGE studies in the Gulf of Mexico can be used at two levels. Most early studies were used to define the regional distribution of oil, condensate and gas seepage on the continental margin to

high-grade areas and prospects by defining areas of active oil migration and charge using routine gas and high molecular weight hydrocarbon screening methods. In the northern Gulf over the last twenty years, these programs have had a major impact on deep-water exploration in the Gulf by delineating areas of active oil migration to the seafloor (Fisher et al., 2007). This active migration acts to charge reservoirs in the same geological system. On a secondary level, SGE studies can be used to define the distribution of oil families and maturities. We have found considerable macroseepage of 'live' oil into seafloor sediments of the northern and southern Gulf all the way from the shelf/slope break to abyssal depths. Using biological marker distributions, different oil families and oil maturities which relate to oil quality can be mapped along the Gulf continental margin. Detailed biological marker (aliphatic and aromatic hydrocarbons) and stable isotope analysis of the macroseeps and bitumen-rich samples allow direct comparison to GeoMark's regional oil and seep database (www.RFDbase.com) in the Gulf using identical analytical techniques. These programs provide important new information on oil families, maturities and oil quality in undrilled regions of the Gulf margin.

Satellite Imagery

As part of this study, NPA Group acquired synthetic aperture radar (SAR) images of the majority of the offshore Mexican Gulf margin as outlined in **Figure 1**. This area represents what is expected to be the most prolific areas of the Mexican Gulf coast. SAR is a useful tool to capture regional oil seepage events on the ocean surface. Utilizing C-band radar, SAR can image the ocean surface both day and night and the microwaves it transmits and receives are not impeded by cloud cover or rain storms. SAR images depict the backscatter from the ocean surface. The Bragg scattering is dampened by oil slicks on the surface, causing the slicks to appear dark (Macklin, 1992). As an example of this, **Figure 2** show the SAR image from this study of a surface slick in ~3,200 meters of water, recently confirmed with underwater photography to be associated with massive tar layers on the seafloor (MacDonald et al., 2004).

Complete and duplicate SAR coverage was obtained in the area outlined in red in **Figure 1**. The SAR images were rectified, georeferenced and evaluated, and surface oil slicks from all images were manually traced and converted to shapefiles for each separate image. **Figure 1** depicts the first and second order natural surface slicks interpreted by the NPA Group. These are the slicks mostly likely to originate from seepage based on slick dimension, shape, edge, retention and orientation with respect of oceanographic conditions, temporal repetition, etc. It is apparent that the greatest concentration of slicks corresponds to areas underlain by allochthonous salt. There is a strong correlation in many areas between the slick areas and the oil and gas hits from the SGE coring. This correlation is predictable from our understanding of the highly efficient migration pathways around and above the salt.

Fewer and smaller slicks were seen in the Mexican Ridges trend where hydrocarbon migration is dependent on deep-seated faulting. The greater degree of biodegradation in piston core oil samples found in this area suggests that seepage to the seafloor is less copious. A first order surface slick is noted at the northeastern edge of the Yucatán carbonate platform ("?" in **Figure 1**). This area has heretofore been thought to contain only immature source rocks because of the low geothermal gradients associated with the thick Mesozoic carbonates and the relatively thin cover of Tertiary clastics as observed on seismic lines at the edge of the Grijalva Fan. This site is also quite far from the thermogenic gas localities on the platform to the east that could potentially be related to localized heating from the Chicxulub K/T asteroid/comet impact (Rosenfeld, 2003). This Yucatan slick occurrence warrants further study.

Selection of Sites and Core Acquisition

Loading by thick Tertiary through Recent clastic sediments derived from mountain building west and south of the Gulf has generated oil and gas in the Mesozoic to Paleogene source rocks. Expulsion and movement of the hydrocarbons requires effective hydrocarbon migration pathways that are most likely related to the movement of salt and the presence of deep cutting faults observed on Pemex seismic data lines that conduct migrating hydrocarbons into adjacent and overlying strata.

The Jurassic through Paleogene source units occur in a relatively thin sequence that immediately overlies either salt or, in its absence, post-salt oceanic crust. Salt movement in response to uneven loading by later sedimentation caused salt bodies to break through the overlying source rocks. The extrusion of the salt, both laterally and vertically, facilitated the migration of oil and gas out of the deeply buried source units and into shallower reservoirs, and to the seafloor. These relationships are shown in **Figure 3**; which is a geological interpretation of the Delta de Rio Bravo area of the northern Mexican Gulf coast derived from seismic data.

The goal of an SGE program is to core the shallow seafloor over the deep cutting faults to obtain samples of potential oil and gas fluids moving up the faults. In areas such as the Delta del Río Bravo and southern Gulf of Campeche, much of the faulting observed in Pemex seismic data lines is associated with salt movement. Where salt is absent because of the post-salt rifting; i.e. the Lankahuasa or Mexican Ridges Provides area of this study, deep rooted faults are interpreted as the principal hydrocarbon migration pathways in both the extensional and compressional regions.

Six (6)-meter, 900-kilo piston coring was used to acquire the cores for this study. The core sites were selected based mostly on 2-D seismic data available from PEP. Seismic data lines were examined to determine whether a relatively simple migration pathway could be inferred between the potential source rocks and the seafloor. Preference was given where features exist at, or near the seafloor, such as faults, domes, possible vent buildups and shallow sediment "wipe-out" zones.

An important consideration was whether the seafloor features identified on the seismic data sections could actually be detected and confirmed while at sea with the Chirp subbottom profiler. Prior to core acquisition, one kilometer Chirp subbottom profiles were run over each core site to collect acoustic graphical data of the first ~50 meters of seabed. The purpose of this effort is to pinpoint interesting features that may be related to seepage, obtain the best core location and information of sub-bottom structure, and determine bottom hardness for each site. **Figure 4** shows two examples where the Chirp subbottom transect across each site was used to move the core target to a more favorable location that produced an enhanced seepage hit.

Seep Hits

A comprehensive suite of geochemical analyses was provided on each core. The cores were analyzed for free-hydrocarbon gas, the higher molecular weight, migrated hydrocarbons as determined by total scanning fluorescence and capillary gas chromatography (Brooks et al., 1983 and 1986). Three sections per core were analyzed. In all, 2,666 screening analyses were conducted on the ~900 cores. Samples containing significantly elevated levels of methane through butane concentrations were analyzed for carbon stable isotopes of these gases. Detailed biological marker analysis was performed by GeoMark Research on cores containing significant amounts of seepage. This is an identical analytical protocol used on thousands of cores from the northern Gulf of Mexico (Cole et al., 2001; Fisher et al., 2007).

Cole et al. (2001), who analyzed a sample suite of >2,000 cores from the central and eastern deep water northern Gulf, classified seepage hits based on total scanning fluorescence (TSF) and the unresolved complex mixture (UCM) from the GC-FID analysis as follows:

Macroseeps: TSF > 1 million units and UCM >300 ppm

High Confidence Anomalies: TSF >500,000 units and UCM > 200 ppm

Low Confidence Anomalies: TSF>300,000 units and UCM> 100 ppm

These authors considered that for the central portion of northern Gulf, TSF <300,000 units and UCM < 100 ppm could be considered background – i.e., related to high levels of recent organic matter (ROM) contamination originating from modern autochthonous organic matter and from outflow of the Mississippi River. This classification is consistent with a somewhat similar classification scheme of Abrams and Segall (2001). However, in the southern Gulf the ROM background is less, and we considered background to be TSF <50,000 units and UCM < 20 ppm. **Figure 5** shows a crossplot of all the PEMEX data using a similar classification scheme as Cole et al. (2001). These oil seepage hits along with those thermogenic gas seepage hits are also shown on the map in **Figure 1**. Thermogenic gas in the cores is indicated by methane values > ~ 10 times background, ethane/ethene ratios > ~ 2, and the presence of heavier than biogenic carbon isotopes.

Based on these data set of 2,666 analyses, 84 and 178 of the samples, or about one or two percent of the cores, had TSF intensities over 100,000 and 50,000 units, respectively, and UCM concentrations greater than ~20 ppm. However, if we remove from consideration the large number of samples in water depths less an 200 meters for direct comparison to our northern Gulf core data base -- which was mostly acquired in water depths >500 meters -- the deep water hit rates increases to near 12 percent (147 of 1258 samples). In the northern Gulf, hit rates (i.e., level of seepage) on the shelf are at least an order of magnitude less than on the continental slope. The Mexican Gulf deep water hit rates are similar to or higher than those obtained in our 1990's SGE coring programs in the northwestern Gulf, where coring locations were based on 2-D seismic data. Hit rates increase when core sites are selected based on 3-D seismic data, which are now generally available throughout the northern Gulf.

The high rate of success in deep water compared with the low rate of success in shallow water is significant. As an example in *Delta del Rio Bravo*, 50 sites were sampled in water depths greater than 200 meters and 41 sites in less than 200 meters. The deeper water sites had a success rate of 54% (using a TSF intensity of 50,000 units as a hit threshold), while the shallow water sites were successful only 7% of the time. Most of the shallow water samples were in water depths less than 100 meters and the shallowest successful site was at a water depth of 116 meters.

The following sections of this paper highlight select findings from two individual portions of the study area.

Delta del Rio Bravo

Figure 6 shows that an excellent petroleum system is active in water depths > 200 meters in the Delta del Rio Bravo area -- 54% of sampled locations showed positive indications for oil and/or gas. The shelf area, in water depths < 200 meters, also displays evidence for an active petroleum system (7% positive for oil and/or gas), in spite of geological constraints on shallow

migration and operational difficulties (i.e., hard and sometimes sandy bottom) in sampling this environment.

Excellent results were obtained in the ultra deep water (>2,000 meters) of Delta del Río Bravo in the Perdido Foldbelt area. Site selection from seismic was generally straightforward due to the availability of very good seismic data. The deep migration pathways follow salt keels, salt canopies and deep seated faults, while the shallower migration pathways are concentrated near fold axes.

The presence of axial fracturing typical of folded brittle rock is not expected in the recently consolidated Cenozoic deep water, predominantly argillaceous strata. It is our opinion that excess pressures generated by thick hydrocarbon columns in the folds intermittently exceed the capacity of the seals and allow oil to escape to the seafloor. The minimal effect of biodegradation in these samples indicates that this migration is relatively rapid. The ductile seals can probably retain sufficient hydrocarbon column in these anticlines for the area to be considered for future exploration objectives.

A second cluster of positive sites in Delta del Rio Bravo occurs in water depths between 500 and 1,000 meters on the continental slope, where active salt tectonics prevails and allochthonous salt is very close to the seafloor. Hydrocarbons can migrate efficiently behind and around the active salt from the deep source rocks almost to the seafloor. The salt movement also created shallow faults that permit the oil and gas to reach the seafloor as illustrated, in **Figure 7**. Although the deeper migration is predicted to be very efficient, these oils are more biodegraded than those noted in the previous paragraph, indicating slower release to the seafloor (Wenger et al., 2002).

An example of a positive oil show, this time in relatively shallow water near the shelf edge of Delta del Bravo, is shown in **Figure 8**. In this case, allochthonous salt is very close to the surface and provided the migration pathway.

Lankahuasa

A second example of active oil generation and migration into shallow sediments was observed in the Lankahuasa area, where cores were acquired between 19° and 21°N. Hydrocarbons were found in 9% of the sites deeper than 200 meters. The deep water portion of Lankahuasa is in the compressional part of the Mexican Ridges Province (**Figure 1**). Therefore, the deep water positive localities are situated along thrust faults that cut upward towards the seafloor from a deep subhorizontal decollement. This can be inferred in **Figure 9**. There is no salt in this part of the Gulf of Mexico, and these active thrust faults provide the obvious deep hydrocarbon migration pathways. Oil samples from deep water Lankahuasa show moderate biodegradation, indicating fairly active seepage. The possible presence of gas hydrates is suggested by the presence of Bottom Simulating Reflectors (BSRs), as seen in **Figure 9**. These are visible on other seismic lines in the area, and always occurs in the crestal position of hanging wall anticlines. This seems to confirm that widespread gas seepage and the crystallization of hydrates occur at the structural highs (rather than more widespread BSRs produced by biogenic methane elsewhere in the Gulf).

Biological Markers

The collection of cores with significant seepage allowed for the correlation of seafloor oil seeps to produced oils from the greater Gulf of Mexico. The analysis and classification of surface seep

oil samples to oils obtained from major producing regions permits extension of known petroleum systems to the more sparsely drilled Mexican shelf and deepwater areas. GeoMark Research analyzed one hundred and fifteen (115) of the seep samples and compared them to (a) seventy-one (71) crude oils provided by PEMEX and (b) oils of GeoMark's Greater Gulf of Mexico Study, consisting of nearly 1000 oils (Zumberge et al., 1997, 2005; Holguin et al., 2002). The locations of the PEP oil and seeps analyzed in this study are shown in **Figure 10**.

The biomarker and isotope data on the oils and seeps were analyzed by multivariate statistical techniques to distinguish both source rock depositional environments and genetically related oil families. Principal component analysis (PCA) and cluster analysis are two statistical approaches used for the compositional classification of oils (Zumberge et al., 2005; Peters et al., 2007). Many of the seep samples analyzed contained sufficient thermally generated biomarkers (migrated crude oil) to measure with confidence many of the key ratios used in constructing the various K-Nearest Neighbors (KNN) models. Interference by immature terpane and sterane biomarkers from Recent organic matter and severe bacterial degradation limits the ability to classify many seep samples with the precision that normal oil samples can be classified.

Figure 11 presents a map that shows the major oil families defined from the Mexican oil data set, and the families to which the offshore seeps have been assigned. The "heritage" of nomenclature for the classification of Mexican oils and seeps (Zumberge *et al.*, 1997) has been preserved in the symbols used on the map. Most of the seep samples classify as Family SE2, equivalent to Mexican oil Family 1 (Cam/TamA) and Family 3 (TS), which implies an Upper Jurassic (probably Tithonian) carbonate-rich source or a combination of closely related sources. Oils in this family also occur in the deep offshore US Gulf, where they contribute to important oil accumulations (Cole *et al.*, 2001). For example, the northern Gulf deep water fields of Mars, Europa, Fuji and Gunnison are this type of high-sulfur oil.

There are also other oil source types identified from the seep biological marker results. For example, a number of the seep oils in the Rio Bravo area contain relatively significant amounts of the Tertiary biomarker oleanane. Two samples can be favorably compared to Rio Bravo oil Family Tert A/B (**Figure 11**). These seeps were generated from Tertiary paralic/deltaic shales containing abundant land plant detritus, suggesting more of a gas prone source than an oil prone source. Other seeps that apparently contain oleanane have biomarker distributions which suggest a Tertiary marine shale/marl source; these are labeled C2 Tert/OL in **Figure 11**. These Tertiary sources are more oil prone than gas prone and are similar to the source rocks which generated the Isla de Lobos oils. There is evidence in the allochthonous salt region of the Rio Bravo area, based on tricyclic terpane compounds, of mixing of oil seeps from both Mesozoic and Tertiary source rocks. Both paralic/deltaic (gas prone) and distal marine source facies (oil prone) are documented.

Conclusions

Our remote sensing data correlate with SGE piston coring data to show that active seepage to the sea surface occurs regionally throughout the Mexican offshore. The SGE and remote sensing studies confirm the presence of active petroleum systems throughout much of the Mexican continental shelf and slope. This points primarily to a Jurassic carbonate-rich source, although other oil families are present in specific localities. Oil seepage is as common on the Mexican slope as on the prolific northern Gulf slope.

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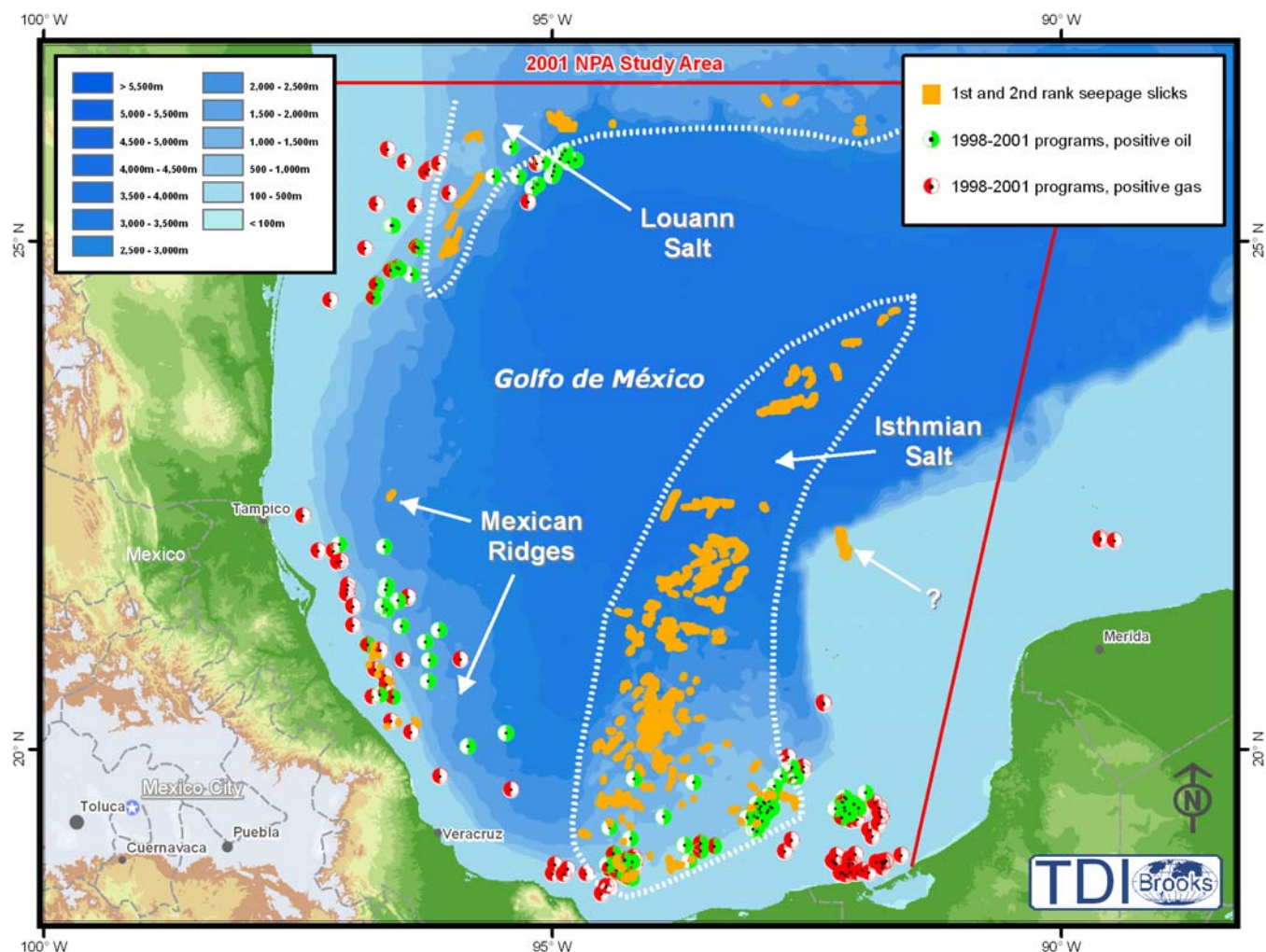


Figure 1. Sea surface natural seepage (slicks) and positive shows in cores. The area of the study covered by SAR remote sensing images is outlined in red.

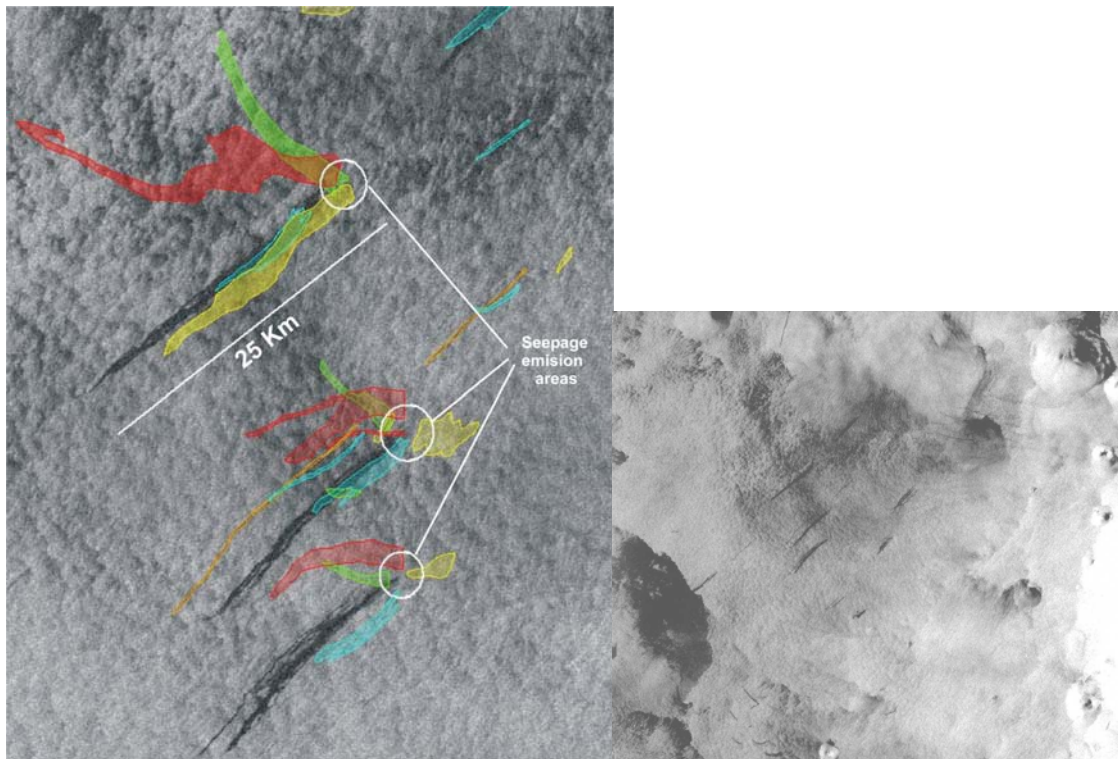


Figure 2. SAR images of an area of the Gulf of Campeche bounded by 21.3° and 22.3°N and 92.7° and 93.7°W in water depths from 2,000 to 3,650 meters. The images is interpreted as active oil seepage to the seafloor.

NW

SE

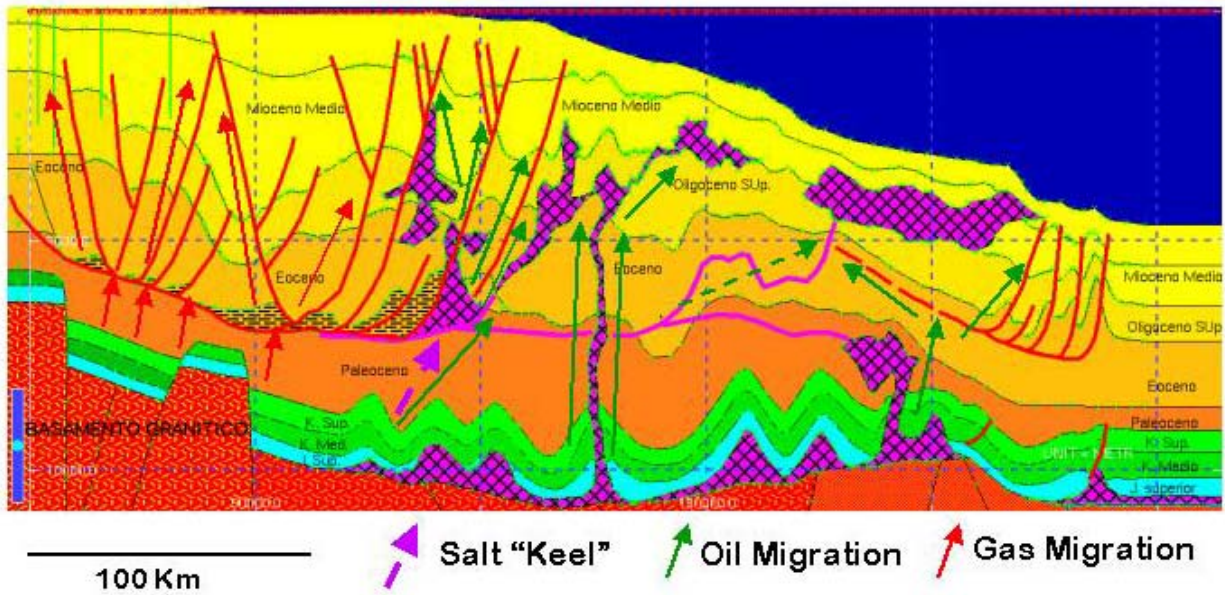


Figure 3. Schematic of the geological interpretation of Delta del Rio Bravo area.

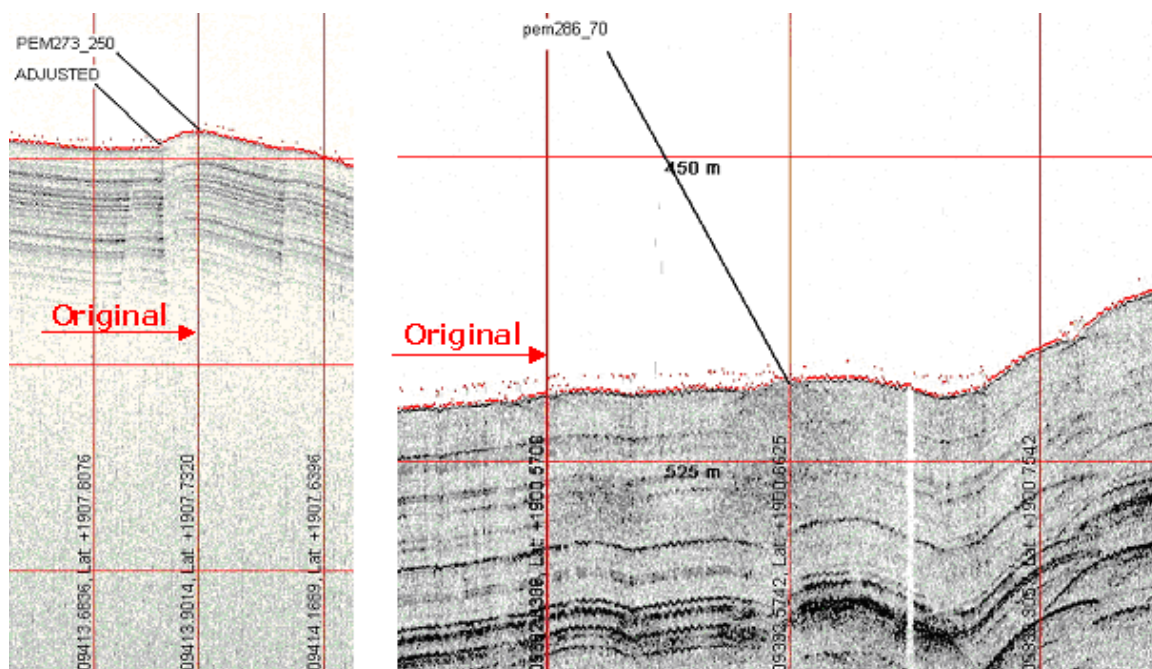


Figure 4. Chirp subbottom profiles across two core sites where the Chirp record was used to move the core site to a more favorable target. On the left panel at Site PEP273, the location was moved to an fault identified by the Chirp record. On the right panel (Site PEP 266) the core was moved to a wipe-out acoustical section. In both of these examples, seepage hits were obtained in the relocated core site based on the Chirp subbottom transect across the core site.

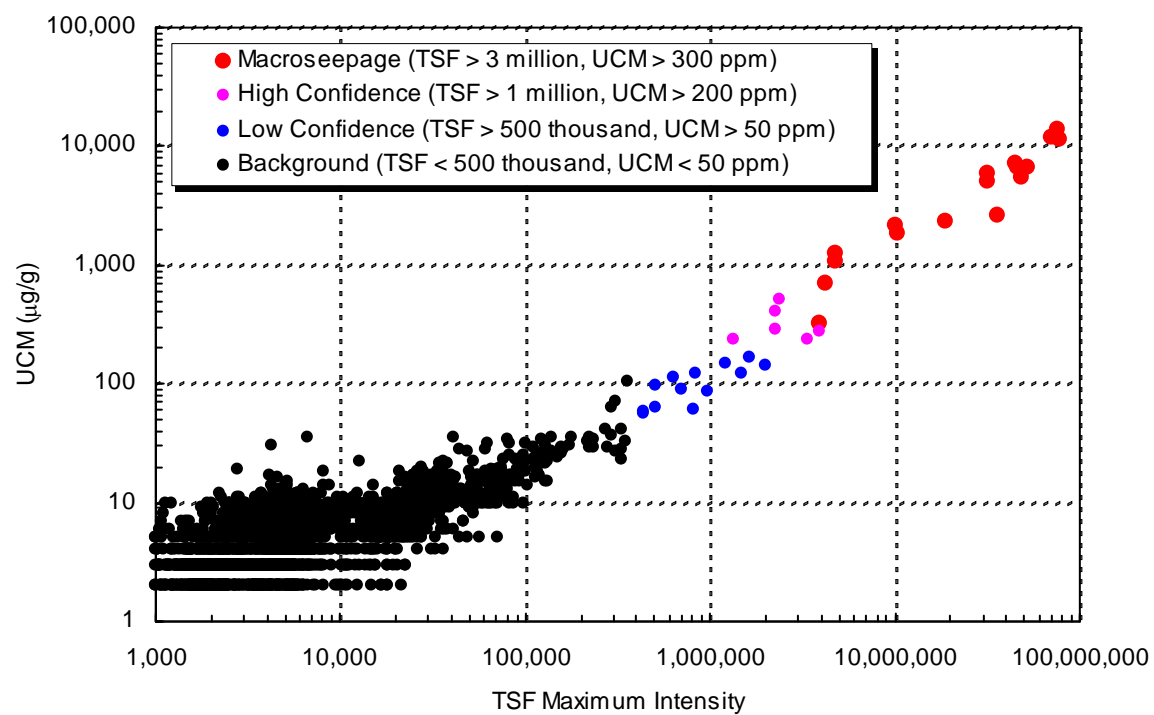


Figure 5. Crossplot of total scanning fluorescence (TSF) and UCM content from gas chromatography on the ~900 cores from the southern Gulf.

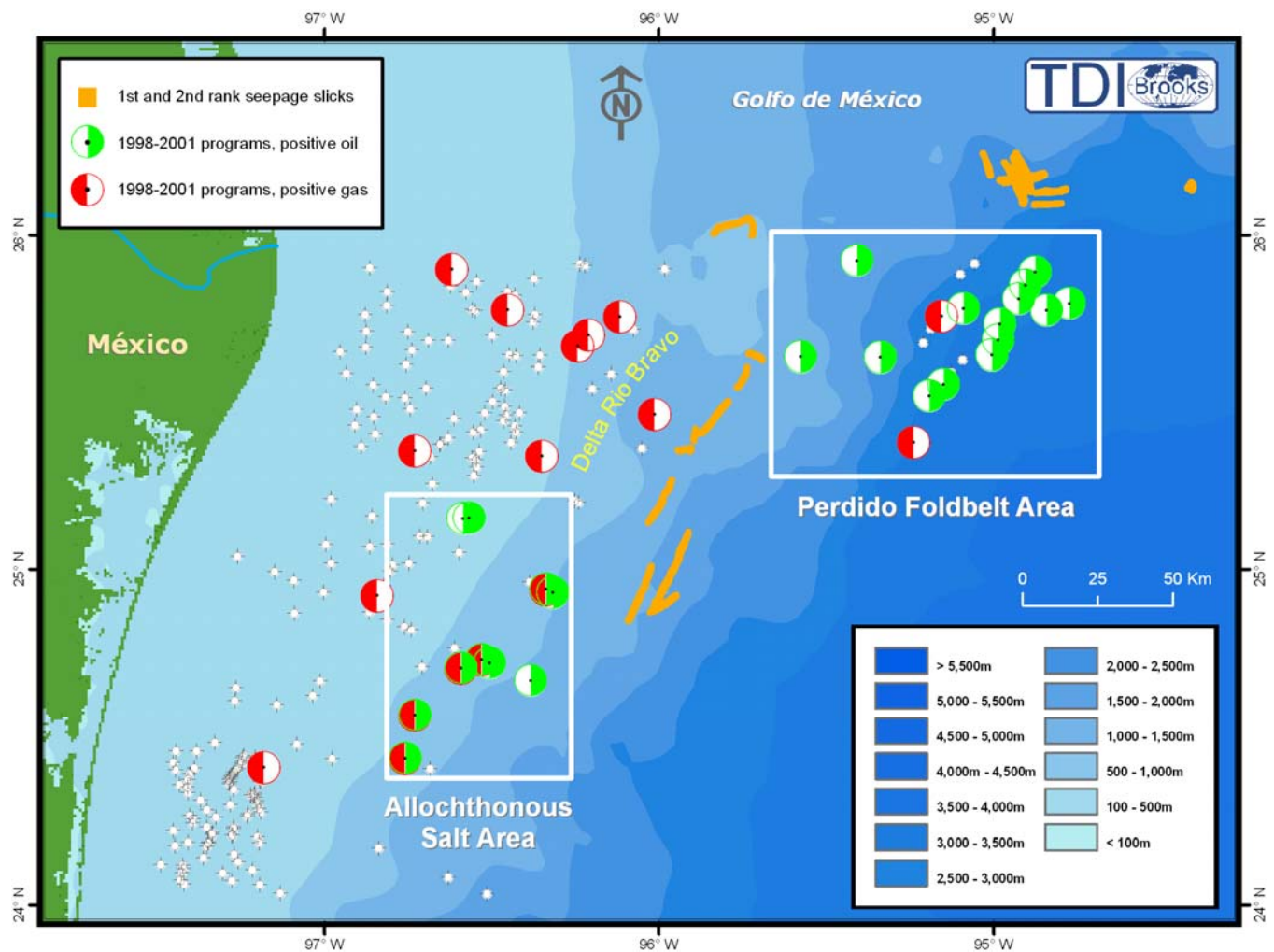


Figure 6. Location of oil and gas hits in the Delta de Rio Bravo area offshore northern Mexico. Gas and oil hits are identified by red or green shading in the circles. Sites without seepage hits are shown in white. Locations of observed SAR remotely sensed slicks are also shown for this area.

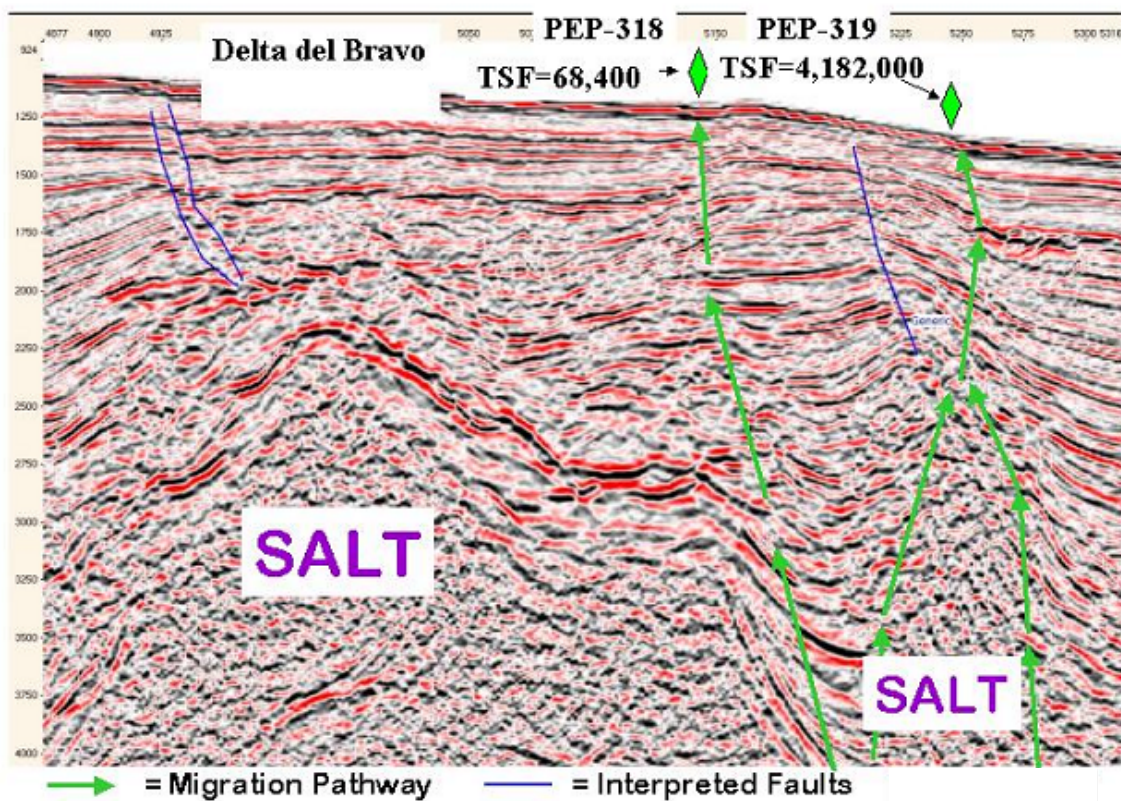


Figure 7. 2-D seismic data line showing near-surface geology at core sites PEP318 and PEP319 in Delta del Rio Bravo area. The arrows show potential migration pathways for oil seepage observed in the two cores along this seismic section.

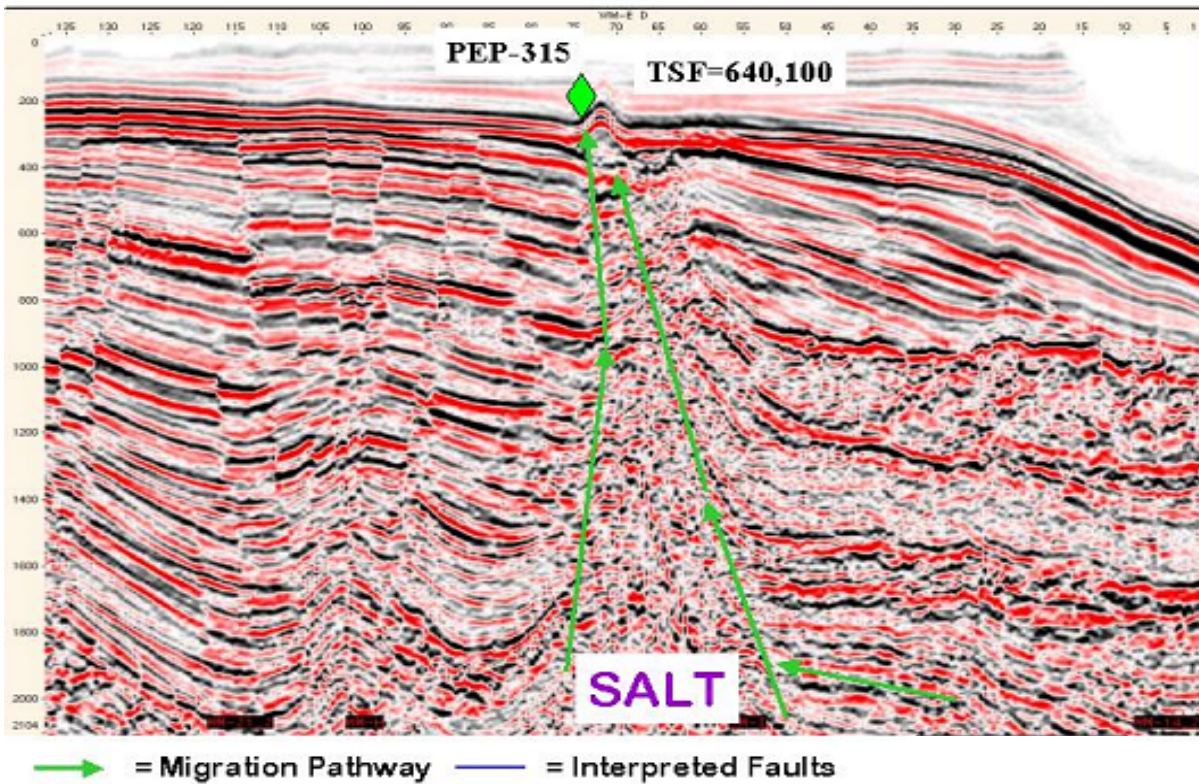


Figure 8. 2-D seismic data line showing near-surface geology at core site PEP315 in Delta del Rio Bravo area. The core at this site had a macroseepage oil hit associated with a seabottom mound associated with subsurface diapir.

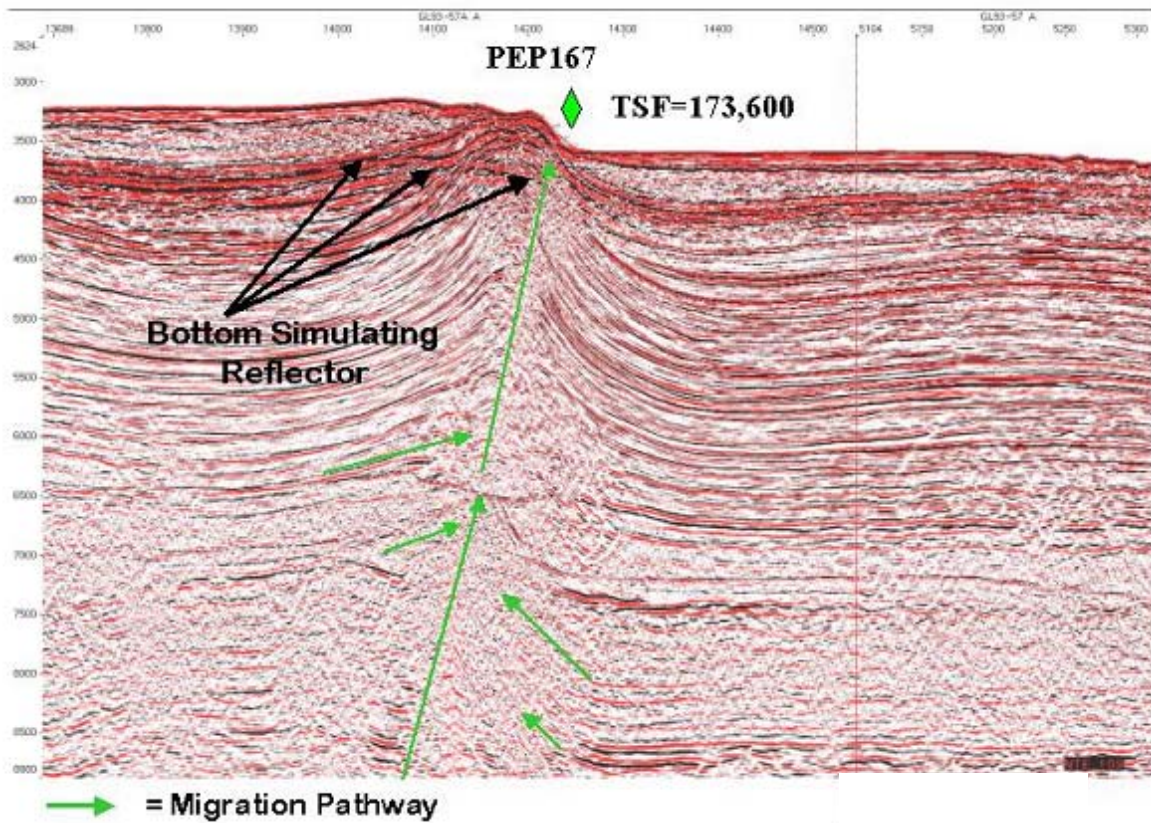


Figure 9. 2-D seismic data line showing near-surface geology at core site PEP167 in the Lankahuasa study area. Arrows show bottom simulating reflectors and potential migration pathways. This core site had oil seepage with TSF levels of 173,600 units.

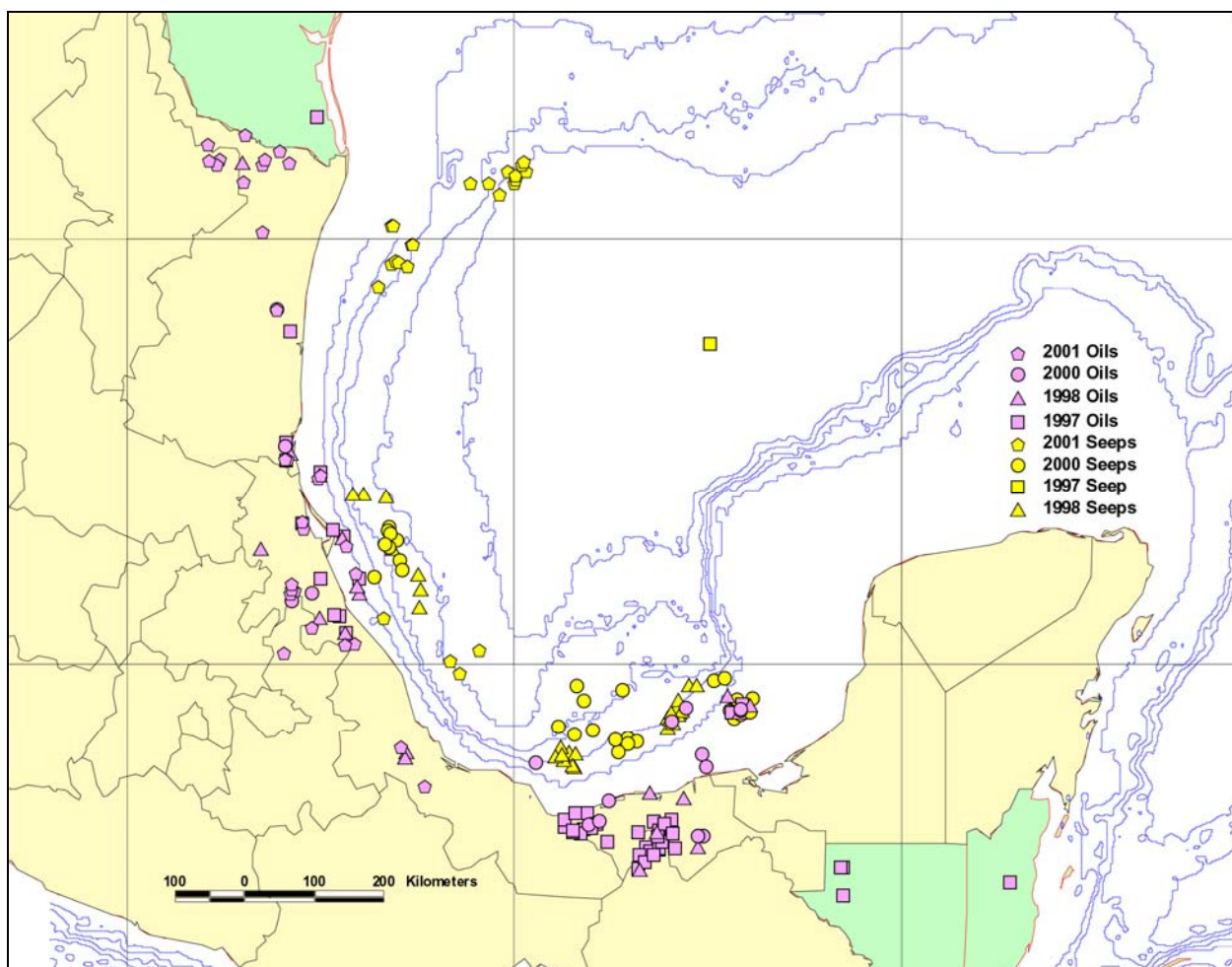


Figure 10. Location map of oils and piston core seep samples with biological marker analyses.

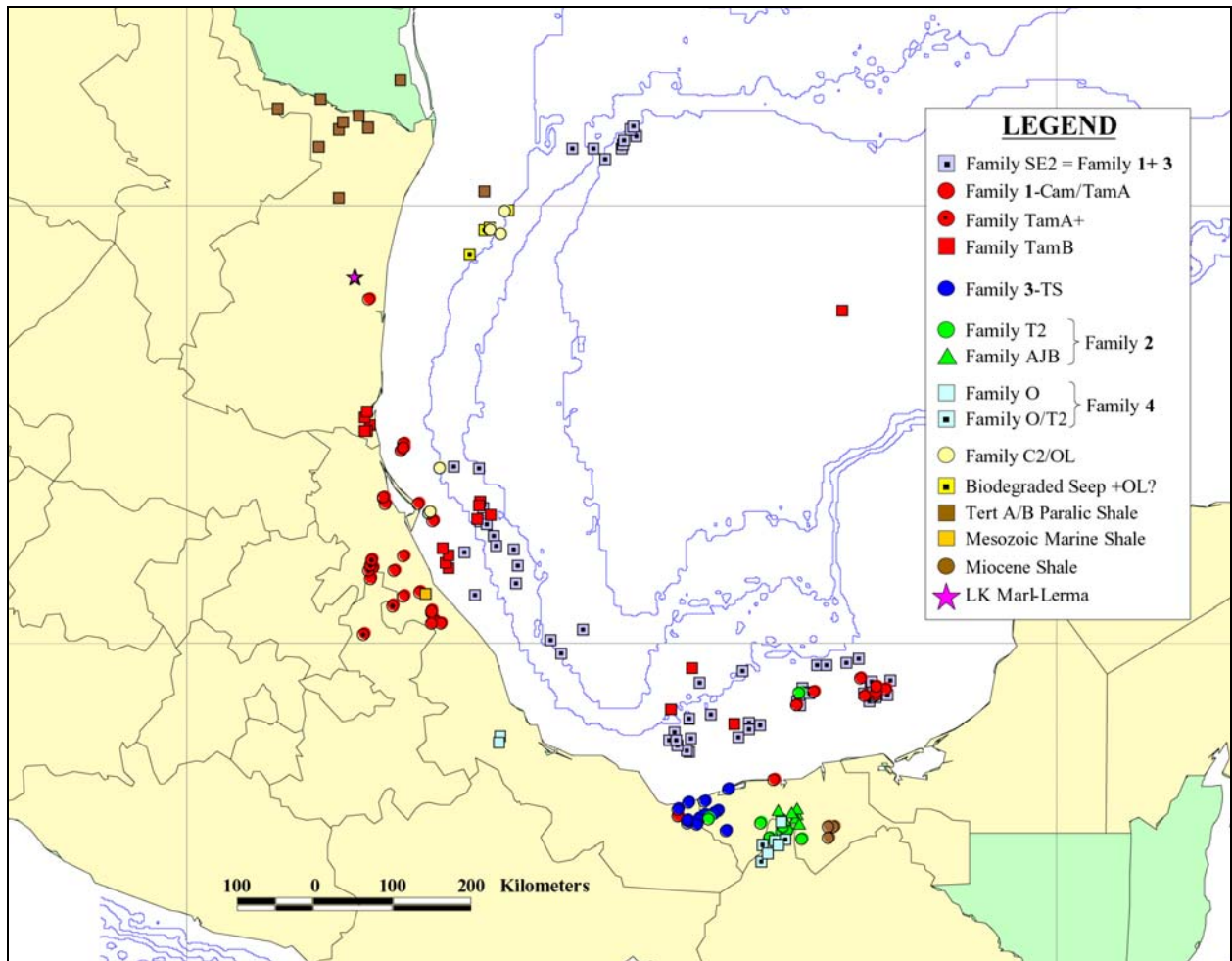


Figure 11. Oil family distribution map by on biological marker analyses.