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Near-Surface Gas Mapping Studies of Salt Geologic Features at Weeks Island and Other Sites

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NEAR-SURFACE GAS MAPPING STUDIES OF SALT GEOLOGIC FEATURES AT WEEKS ISLAND AND OTHER SITES

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ABSTRACT

Field sampling and rapid gas analysis techniques were used to survey **near-surface soil gases** for **geotechnical** diagnostic purposes at the **Weeks Island** Strategic Petroleum Reserve **(SPR)** site and other **salt dome** locations in southern Louisiana. This report presents the complete data, results and interpretations obtained during 1995. Weeks Island 1994 gas survey results are also briefly summarized; this earlier study did not find a definitive correlation between sinkhole #1 and soil gases. During 1995, several hundred soil gas samples were obtained and analyzed in the field by gas chromatography, for profiling low concentrations and gas anomalies at ppm to percent levels. The target gases included **hydrogen**, **methane**, ethane and ethylene. To supplement the field data, additional gas samples were collected at various site locations for laboratory analysis of target gases at ppb levels. Gases in the near-surface soil originate predominantly from the oil, from petrogenic sources within the salt, or from surface microbial activity. Surveys were conducted across two Weeks Island **sinkholes**, several mapped **anomalous zones** in the salt, and over the SPR repository site and its perimeter. Samples were also taken at other south Louisiana salt dome locations for comparative purposes. Notable results from these studies are that elevated levels of hydrogen and methane (1) were positively associated with anomalous gassy or shear zones in the salt dome(s) and (2) are also associated with suspected salt fracture (dilatant) zones over the edges of the SPR repository. Significantly elevated areas of hydrogen, methane, plus some ethane, were found over anomalous shear zones in the salt, particularly in a location over high pressure gas pockets in the salt, identified in the mine prior to SPR operations. Limited stable isotope ratio analyses, **SIRA**, were also conducted and determined that methane samples were of petrogenic origin, not biogenic. We postulate that the near-surface gas mapping techniques and results are useful for locating anomalous, gassy zones and other structural features in salt domes at Strategic Petroleum Reserve sites and, possibly, for other salt mine sites.

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1. INTRODUCTION AND BACKGROUND

Sandia National Laboratories was authorized by the Department of Energy Strategic Petroleum Reserve Project Management Office, DOE SPRPMO, to conduct near-surface gas-mapping investigations at the Weeks Island SPR and several other related salt dome sites. Geochemical gas mapping studies were intended to assist and supplement overall geotechnical diagnostic investigations of the significance of a sinkhole on the storage integrity of the Weeks Island SPR facility.[1] The total sinkhole diagnostic program, including geochemical, assorted geophysical, drilling and inspection procedures is described in detail elsewhere,[1] along with the preliminary results and interpretations for such studies. Louisiana State University, Institute of Environmental Studies, LSU IES, personnel conducted the field and laboratory geotechnical and analytical work to support these gas mapping investigations, under contract to, and with participation from Sandia.

Gas mapping studies were conducted over two separate time periods for several distinct, but related purposes. The first period studies were conducted at the Weeks Island SPR site in May through July of 1994. The second period studies were conducted predominantly in April through July of 1995, at Weeks Island and other southern Louisiana salt dome locations. The primary focus of this document is to describe and report complete data, results and interpretations obtained from the second period, 1995 gas mapping studies. Most of the detail and results from these studies are presented in Appendices 1 (methane studies, 1994) and 2 (1995 studies) of this document. These appendices are data reports from Louisiana State University, submitted to Sandia, and have not been not previously published. The main body of this document provides a brief summary of this overall gas mapping effort plus supplemental details, discussions, and recent methane stable isotope ratio analysis data not included in the LSU IES data reports.

1.1. Weeks Island 1994 Gas Mapping Study

During the first period study, in 1994, we conducted a gas mapping survey in the vicinity of sinkhole #1 and other nearby areas at the Weeks Island SPR site. Our intent [2,3a] was to adapt the LSU IES gas mapping technique and equipment, described in detail in the Procedure section of Appendix 2, as a specific sinkhole diagnostic tool. This technique has been used successfully in limited applications for geochemical oil exploration.[4-7] The major purposes of this geotechnical effort were to clearly detect and diagnostically evaluate the sinkhole and possible subsurface fractures or other significant geologic features in the near vicinity of the SPR site. This study was based on a gas survey of hydrogen and methane gas concentrations, from baseline or background levels to anomalous, high concentrations due to geological or other causes.

In brief, this 1994 evaluation did not find a direct hydrogen gas-release pathway from the SPR oil to the immediate vicinity of, or in the sinkhole. The available hydrogen gas results were non-conclusive as a sinkhole diagnostic tool. These results were not successful in distinguishing the original or any incipient sinkholes. However, other high hydrogen concentration results away from the immediate sinkhole vicinity lead to some thought provoking, but non-definitive clues for possible detection of salt anomalies below. Most of the results and interpretations from this study (through August 1994) are documented separately.[1, 3a,b] These results are briefly summarized in the Results section, herein.

Additional 1994 Weeks Island gas mapping data were analyzed and interpreted by LSU IES personnel, then reported [8] to Sandia several months after most other preliminary diagnostic results [1] had been transmitted to DOE SPRPMO. This later data report [8] indicated that high localized concentrations of methane, but not hydrogen, were found directly in sinkhole #1 and at its edges. Appreciable methane levels were also found along several other sampling transects at Weeks Island. These results are presented in full in Appendix 1 and summarized in the Results section of this document. There is a credible possibility that the high methane levels in the sinkhole and elsewhere correspond to surface expressions of geological or petrogenic methane released from disturbed salt, from either below the sinkhole or along anomalous zones in the salt. Multiple investigators have found a good correlation between high methane levels in salt samples and salt *mine* blowouts, particularly in salt areas dubbed anomalous or anomalous shear zones.[9-14] These other studies were conducted in domal salt, particularly in southern Louisiana.

1.2. 1995 Gas Mapping Studies

Based on the initial, 1994 methane results, we conducted a continuation and modest expansion of the near-surface gas mapping survey at the Weeks Island SPR site. The continuation was intended to satisfactorily conclude this geotechnical diagnostic study with *defensible* interpretations, to substantiate and confirm the existing database for both methane and hydrogen, and to extend it to other relevant gases possibly released from the crude oil. The specific purposes for these second period, 1995 evaluations were to:

(1) use near-surface gas survey techniques to diagnostically profile low concentrations of selected components (hydrogen, methane, other light hydrocarbons) across two Weeks Island sinkholes (sinkhole #1 and sinkhole #2, discovered in February 1995);
(2) to survey several mapped anomalous zones in the salt dome; and,
(3) to survey over several mine edges of the SPR petroleum repository.

The target gases can originate in the repository oil, in the rock salt itself or, possibly from microbial activity on hydrocarbon gases or other organic materials. Near-surface gas surveys are presumed to provide good indicators of any gas transport through suspected salt fracture (dilatant) zones over the edges of the SPR repository. Specific salt features problematic to salt dome mining or other use that may be detectable by near-surface gas mapping are anomalous zones and otherwise gassy zones, including underground pressurized gas pockets or inclusions in the salt.

During 1995, gas mapping was also extended, to a limited extent, to an "*alternate*" salt dome in southern Louisiana. The purpose of this extension was to help confirm interpretations related to gas releases from anomalous salt zones at Weeks Island. This alternate salt dome (*not specifically identified nor described due to confidentiality requests*) was selected for gas mapping evaluation because it is geologically very similar to the Weeks Island dome. The alternate dome has well defined shear or anomalous zones, areas of suspected gassy salt inclusions, several sinkholes, and mining activity; however, it has no petroleum storage. We presumed that additional, alternate salt dome data could help confirm our postulate: that petrogenic-origin methane released from gas-bearing (gas source or conduit) salt anomalous zones can be tracked or mapped on a "microscopic" scale, i.e., meters to tens of meters, by near-surface gas surveying. This data and postulate were to be compared with earlier "macroscopic" scale (hundreds of meters) gassy oil results from a separate study at other SPR sites.[15] In the earlier study, gas intrusion, suspected of originating from anomalous salt zones, was to be correlated with the gassy oil content in several SPR caverns. These "macroscopic" scale correlations were not conclusive.[15]

2. SUPPLEMENTAL EXPERIMENTAL DETAILS

In brief, the LSU IES gas mapping technique uses a tubular probe and a field-portable gas chromatograph to analyze for near-surface concentrations of relevant gases. The detection instrument uses two fully functional, microchip gas chromatographic columns, operated simultaneously; one column was optimized for detection of hydrogen and helium, the other column for methane. The field instrument had a detection sensitivity down to about the 1-10 ppm level. In a large fraction of the samples, however, methane (and all heavier hydrocarbon gases) concentrations were below the detection limits of the portable gas chromatograph. Therefore, supplemental gas samples were also obtained in the field, contained within 50 ml. gas sample bottles, then transported to Louisiana State University and analyzed on a more sensitive laboratory gas chromatograph. The laboratory instruments allowed the samples to be analyzed for methane, ethane, ethylene, propane, propylene, and other C4-C6 hydrocarbons at sensitivities of 10's of ppb.

For the first, 1994, sampling period study at Weeks Island, full details are documented in reference 3b and include relevant site geology, sampling transect locations (Figure 2 of 3b; Figure 6 in Appendix 1), gas sampling procedures and equipment, chromatographic analyses, and data processing. Supplemental details on interpretations of the gas chromatograms for methane and other gases found in the soil gas samples, plus headspace gas samples over a SPR crude oil sample are provided in Appendix 1. Appendix 1 is the LSU IES data report "Weeks Island Soil Gas Survey: Data Supplement and Final Observations," October 26, 1994, by K. Carney.

Similarly, most experimental details for the second,1995 sampling period are contained in Appendix 2 of this document. Appendix 2 is the LSU IES report "Final Report: Near-Surface Gas Mapping at the Weeks Island Strategic Petroleum Reserve and Other Salt Dome Locations, Phase III," January 31, 1996, by K. Carney. The following sections focus on supplemental details not included in Appendix 2.

2.1. Sampling Locations

A comprehensive description of the Weeks Island site geology, including surface soil cover, underlying sediments, and salt dome detail, are contained in the "Weeks Island Geology" section in Appendix 2. Figure 1 (from Appendix 2), following, shows the Weeks Island shear zones, i.e., the zones of mapped or postulated anomalous salt, as well as the sampling transects used in 1995. The four main sampling transect locations are described in the "Extent of Survey" section in Appendix 2. Sampling transect WK shown in Figure 1 intentionally followed the "power line swath" (a mowed grass pathway). It is shown somewhat west of its actual location; subsidence marker W 138, shown east of the power line, is actually on the power line swath, at approximately the 240 - 250 m point on transect WK. Also, the eastern end of transect WK crossed Snyder Rd. near subsidence marker W 135, not W 134 as shown in Figure 1. Transect WL, over the eastern edge of the lower SPR mine level, was purposely located over a previously detected [16, 17] (mine subsurface) alignment of significant gas blowouts or gas inclusions in or above the salt mine, along the boundary of Shear Zone D.[18] Locations of Transects WK and WL plus the gas blowouts, particularly for the eastern edge of the lower mine level, are illustrated in Figure 2,[16, 17] following. Our main test objective for the transect WL location was an attempt to detect possible near-surface traces of petrogenic-origin gas from the mapped or other gas inclusions.

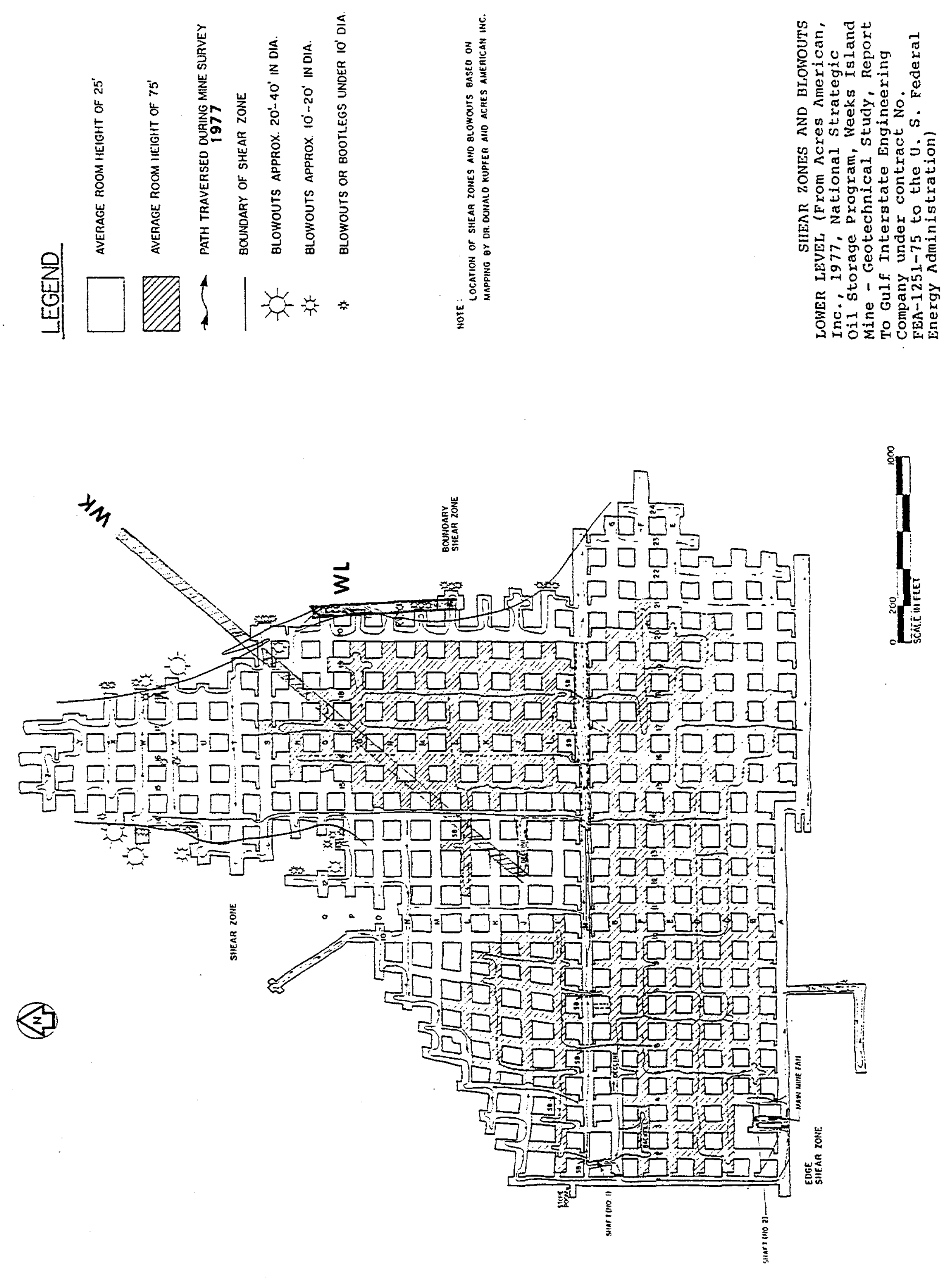

Figure 2. Shear Zones and Blowouts - Weeks Island Lower Level [16, 17]
(with overlays of transects WK and WL indicated)

For purposes of comparison with Weeks Island SPR suspected blowout/inclusion gases, we attempted to obtain samples of gas trapped in salt pockets or inclusions from the Morton Salt mine on Weeks Island. The 1200 ft. level of the Morton Salt mine is a location with known gassy salt (termed "crackle" or "popcorn" salt) associated with salt blowouts. Such "crackle" gas samples could provide us with an analyzed composition "fingerprint" to help identify or confirm the origin of analyzed soil gases from transects WK or WL. Unfortunately, the 1200 ft. level at the Morton Salt mine had been abandoned and was not accessible.[19] As a substitute, gassy salt samples were obtained for analyses from the nearby Cote Blanche salt mine in southern Louisiana.

Three sampling transects, AA, AB and AC (A = alternate), were also established for limited gas surveying purposes at the "alternate" salt dome location. There is a near linear alignment of multiple sinkholes at this dome. Sampling transect AA started both in (the bottom of) and at the edge of the end (northern most) sinkhole. Transect AB paralleled the western edge of all the sinkholes. Transect AC was basically perpendicular to the line of the multiple sinkholes and about 30 m south of the southern most sinkhole.

2.2. Gas Sampling and Analyses

LSU IES personnel incorporated several improvements in their gas sampling equipment and procedures prior to the start of the 1995 studies. A most notable improvement was the incorporation of a new gas sampling device or container. This container consists of a stainless steel gas cylinder with multiple valves, a sampling septum, a vacuum gage, and a hand pump for evacuating the cylinder prior to sampling. The sampling cylinder was connected to the in-ground sampling probe by a flexible tube. This gas sampling equipment is illustrated in Figure 2 in Appendix 2. The evacuated sampling vessel draws about 150 ml of gas out of the emplaced sampling tube. Multiple gas aliquots can be taken from the sampling vessel by syringe, and the sample aliquot then carried back to the gas chromatograph, or injected into gas sample bottles for future laboratory analyses. The gas chromatograph did not have to be carried over frequently rough terrain to the sampling sites. Compared to the 1994 techniques, this sampling technique provided a considerable savings in both time and labor, quite important since several hundred gas samples were taken and analyzed in the field. The total LSU IES sampling procedure, equipment, and associated details are described in Appendix 2.

Approximately 10 gas samples with high methane concentration were collected for stable isotope ratio analysis, SIRA. These samples were shipped to a subcontractor analytical laboratory, Krueger/Geochron Laboratories, for analyses. Stable isotope ratios for hydrogen (δ D/H, in units of parts per thousand) and carbon ($\delta\ ^{13}C/^{12}C$) in methane can help to distinguish between petrogenic and biogenic methane sources although perhaps not between modern and ancient biogenic methane.[20,21] Figure 3, included in the Summary Results and Discussion section of this document, illustrates various genetic classifications of methane based on measured δ D and $\delta\ ^{13}C$ ratios.[20,21]

3. SUMMARY RESULTS AND DISCUSSION

Gases detected in the near-surface soil can originate primarily from within the stored crude oil at the Weeks Island SPR, from petrogenic sources or anomalies within the salt formation (including trapped petroleum or other organic contaminants), from sub-surface anaerobic microbial degradation of hydrocarbon vapors and from near-surface microbial activity (aerobic and anaerobic) on organic materials. Hydrogen was initially presumed to provide the primary indicator for gas leakage pathways in these gas mapping studies. The hydrogen is primarily oil-source specific. It can originate directly in the oil, produced from anaerobic degradation of hydrocarbons. Hydrogen can also be produced from anaerobic degradation of methane [22] or other hydrocarbons released from the salt. Other chemical mechanisms that could generate hydrogen are insignificant by comparison.

Methane also served as a major survey indicator for these studies although data interpretations were made more difficult due to possible generation by near-surface microbial degradation reactions. Methane and other hydrocarbon gases found in the soil, including ethane, ethylene, propane, propylene, and their concentration ratios, provided the primary means to evaluate origin of the hydrocarbon gases, either petrogenic or biogenic. Limited stable isotope ratio analyses, SIRA, were also used to distinguish petrogenic-origin methane from biogenic-origin gas.

Localized near-surface regions of high gas concentration (anomalies) could indicate enhanced gas leakage pathways from the oil to the surface via subsurface fractures (in the salt dome or overlying sediment), zones of higher permeability, and/or zones of geologic structure possibly associated with fracture development processes. Gases migrate to the surface either dissolved in, or in a miscible phase with the groundwater or brine that wets or saturates most of the sediments and soil above the salt dome. The gas permeabilities are relative to the liquid, wetting-phase permeabilities; both permeabilities are also a function of saturation.[23] The gases would be released from solution in the near-surface soil.

In this study, elevated levels of both hydrogen and methane are associated with anomalous zones in the salt dome and with suspected salt fracture zones, particularly over the outer edges of the mined SPR repository. Salt microfractured pathways for gas or solution transport can occur due to shear failure isovolumetrically. This shear failure may predominate in or near the mapped shear zones in the salt. Dilatancy will dominate in the salt disturbed rock zone that develops around the underground excavations.[23]

3.1. Weeks Island 1994 Overview

Results from the first period, 1994, gas mapping survey did not indicate a direct, hydrogen-release pathway from the SPR oil to the immediate vicinity of, or in, the sinkhole. However, we did find several regions of enhanced hydrogen concentration in the vicinity of the sinkhole and nearby SPR site areas that point to the repository as the source of the gas seeps. These hydrogen gas survey data are illustrated in Figure 6, in Appendix 1.

Near the end of the 1994 field work, high localized concentrations of methane gas were detected in the center of sinkhole #1 and in the sinkhole (soil) edges. The supplemental methane gas work and results are described and included as Appendix 1. High methane and hydrogen concentrations were also measured near or on the northern edge of subsurface, anomalous Shear Zone E, south and east of the sinkhole. Refer to Figures 6 and 7 in Appendix 1. Shear Zone E was originally proposed [18] or based on a possibly coincidental alignment of gas pockets found in the salt mine during previous mining activities. No other hydrocarbon gases were detected in the 1994 gas surveys, due primarily to instrumentation limitations. No simple, defensible interpretation for the sinkhole high-methane findings can be offered based on the available data.

We also found several regions of elevated hydrogen and methane concentrations in the vicinity of the sinkhole and nearby SPR site areas (in Figures 6 and 7, Appendix 1). Correlation of any of the high gas zones directly with the sinkhole is difficult except to the extent that they apparently correspond well to one or more of the notable seismic features detected by assorted geophysical techniques [1] and/or surface indications of subsurface geologic anomalies. Locations of other, potentially incipient sinkhole areas were not detected nor proven by the gas geochemical technique. Our initial goal to use near-surface gas mapping as a specific sinkhole diagnostic tool was not successful.

Observed patterns of the hydrogen and methane gas seeps (in Figures 6 and 7, Appendix 1), in conjunction with or in comparison to the geophysical diagnostic evaluations [1] at Weeks Island tentatively suggested a structural control associated with fracture development processes. Fracture permeability may be associated within and near the edges of any of the mapped geologic anomalous zones, particularly gassy, anomalous features in salt shear zones. However, the 1994 gas mapping data for hydrogen and methane were not adequate to provide firm or defensible conclusions on ties to the existing sinkhole nor to resolve other diagnostic uncertainties remaining in this geochemical investigation.

3.2. 1995 Results

Full details, data and discussion of the gas mapping studies conducted in 1995 at Weeks Island and nearby salt domes are contained in the Louisiana State University Final Report, included as Appendix 2. This Final Report is an update of a previous summary paper [24] presented at the Solution Mining Research Institute (SMRI) Fall Meeting, San Antonio, Texas, in October 1995. The final report includes all data (available through January 1996) in both tabular and graphical format. The last portion of data, on methane stable isotope ratio analysis results, was received from a subcontractor several months after the Final Report was submitted. Therefore, the SIRA results and interpretations are included in the following sections.

3.2.1. Weeks Island Overview

We conducted a very limited amount of gas sampling both in and in the near-vicinity of sinkhole #1 in April 1995. This sampling was an attempt to recheck or extend the methane (high concentration) results obtained in 1994; refer to Appendix 1. Unfortunately, the sinkhole vicinity was being prepared for preliminary freeze wall drilling and construction at this time. This ground disturbance could have had a significant impact on near-surface gas concentrations. No detectable levels of methane in or near sinkhole #1 were found nor are reported in Appendix 2.

Notable results of the 1995 near-surface gas mapping survey at Weeks Island suggest two significant findings. First, there appears to be a correlation of high soil gas concentrations with anomalous salt zones and associated subsurface features. Second, there is an apparent correlation of soil gas anomalies with mine edge effects resulting from possible increased salt dilatancy.

The most significant feature in the soil gas trend on transect WK (refer to Figure 1) was a very large spike in both hydrogen and methane concentrations at sample location WK 250 m. Soil gas at this location also included significant amounts of ethane and propane, but no ethylene. Following methane, ethylene is the most prominent indicator of biogenic activity in soil gas.[25] There are no unsaturated hydrocarbons such as ethylene and propylene contained in the SPR crude oil. Stable isotope ratio analysis results, described below, indicate that the methane in sample WK 250 m was definitely of petrogenic origin. It seems likely, therefore, that the soil gas at WK 250 is related to a high permeability pathway from a subsurface source. It can be speculated that the pathway may be associated with Shear Zone D (refer to Figure 1). This gas concentration anomaly could have a source in the anomalous, gassy salt of Shear Zone D or could result from trapped or occluded gas pockets in the salt, as shown in Figure 2, previously. The gas could also originate from the SPR repository oil in the lower mine level. The obtained gas data cannot define the specific source. The gases may emanate from multiple sources, but are then conducted through a common fracture pattern in their upward migration.

We found evidence for the effect of the mine structure, i.e., microfracturing (dilatancy) in the salt near the mine perimeter, on gas concentrations at 3 separate locations at Weeks Island:

(1) along the northern sections of transects WK and WL, which lie in similar orientation to the perimeter of the lower mine level;
(2) at area W2, adjacent to sinkhole #2 on the northwestern perimeter of the upper mine, at various locations near the mine perimeter; and,
(3) on transect WM, along the eastern perimeter of the upper mine.

At area W2, gas concentrations of hydrogen and methane, especially, showed strong evidence of higher concentrations in samples associated with the upper-level SPR mine edge, particularly with the mine edge near sinkhole #2. Few of the samples were clearly outboard of the mine perimeter at this location, so the composition of the soil gas further beyond the perimeter remains unknown. Microfracture orientation, soil (gas and fluid) permeability, and possibly horizontal fluid flow could channel the gases a notable distance away from the mine edge. The effect of mine boundary position and associated dilatancy is clearly visible in the hydrogen concentration profile along transect WM. Here, gas samples outside the mine perimeter had higher concentrations than those directly above the mine edge and above the mine proper.

3.2.2. Stable Isotope Ratio Analysis Results

The methane stable isotope ratio analysis, SIRA, results from two of the ten submitted gas samples were received from Kreuger/Geochron Laboratory about nine months after submittal. The delay was presumably due to technique refinements caused by concerns of the potential explosibility (from methane and oxygen concentrations) of the samples. Because of the lengthy time delay, many of the submitted samples were lost due to leakage from the sample bottles. Fortunately, the available results were quite conclusive, indicating both samples, one from Weeks Island and one from the alternate salt dome, were of petrogenic origin. The available data are plotted on Figure 3, [20, 21] following.

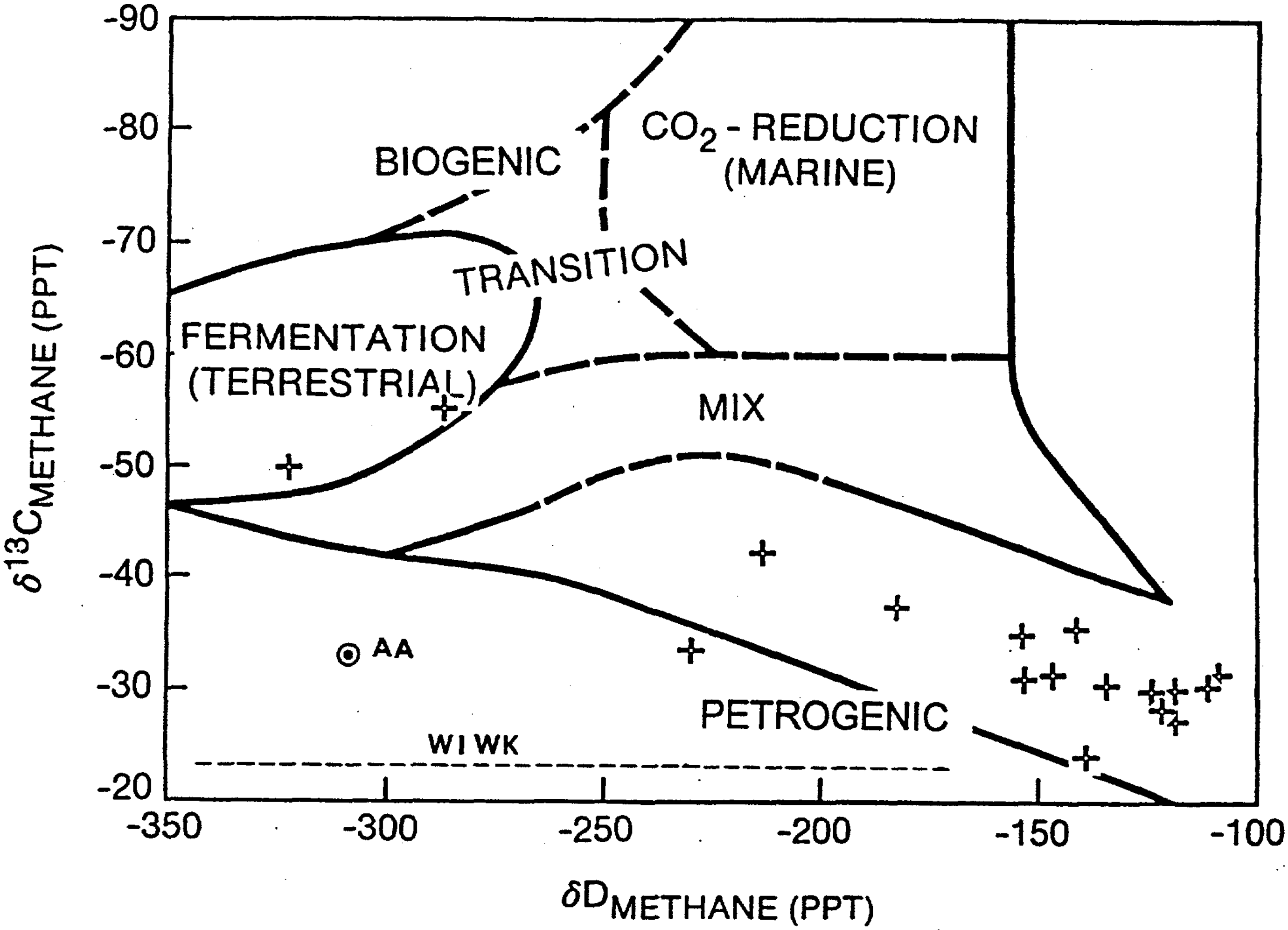

Figure 3. Genetic Classification of Methane using δ D and δ ^{13}C Stable Isotope Ratios [20,21] with 1995 Weeks Island (WI) and Alternate Dome (AA) Results

Note: The ✣ data points in Figure 3 are from methane from multiple SPR gassy oil samples,[21] not from this gas mapping study. Based on these data, Giles [21] interpreted the gassy oil gas samples to be clearly petrogenic, not biogenic in origin.

The Weeks Island gas sample was obtained at the 250 m position on transect WK, over the SPR lower mine, near the edge of anomalous salt Shear Zone D, and possibly over areas of gas blowouts or inclusions detected during previous mining activities. This zone of blowouts or inclusions is illustrated in Figure 2, [16,17] earlier. The methane $\delta\ ^{13}C/^{12}C$ value, -22.7 parts per thousand, is plotted in Figure 3 as a dashed line, "WI WK 250 m", not a point, since no δ D/H results were reported. The $\delta\ ^{13}C$ data falls within the "petrogenic" genetic classification zone on this figure.[20,21]

This data strongly supports our presumption that the WK 250 m gas is petrogenic in origin, not biogenic. It could originate from the stored petroleum or, more likely from gas pockets or inclusions in the salt, slowly released through microfractured zones in the salt.

The alternate salt dome methane sample was obtained from the bottom of the northern-most sinkhole, on transect AA at 0 m. The SIRA results for this sample, both $\delta\ ^{13}C$ and δ D values, are plotted in Figure 3 as point AA. Point AA is definitely within the petrogenic zone.

3.2.3. Alternate Salt Dome Results

High, localized concentrations of both hydrogen and methane were detected in and at the edge of the northern-most sinkhole, near the origin of transect AA. This finding presumably indicates a pathway from a gassy salt anomalous zone below. The methane SIRA results at this location support the non-biogenic origin of this gas sample. These results also suggest and support the likelihood that the anomalies seen at the alternate dome location reflect the alignment of a zone of gassy salt proposed by Whitney Autin, LSU IES, on the basis of the topography of the area. This postulate is described in Appendix 2.

Elevated methane and hydrogen concentrations were also found at several points along transect AB, paralleling the (western edge) line of multiple sinkholes. Because of the orientation of this transect, no conclusions could be drawn beyond the inference that the transect crossed a possibly anomalous area. There was a distinct hydrogen maximum at the 30 meter point of transect AC. Methane results were, unfortunately, not available. This point, AC 30 m, was 30 m directly south of the southern-most sinkhole. It coincided with a small topographic break and could be another surface expression of a suspected gassy salt zone below. Further, more detailed gas mapping sampling and analyses at this alternate dome would be required to obtain more definitive conclusions. Only the correlation between a suspected subsurface feature and anomalous soil gas readings can be asserted.

3.3. Overall Conclusions

Results of the 1995 near-surface gas mapping study at the Weeks Island SPR site suggest a significant relationship between anomalies in soil gas concentrations and subsurface features in the salt dome. The gas mapping techniques and equipment used, and interpretations of data obtained during this Sandia-Louisiana State University team effort were effective in elucidating anomalous salt zones and dilatant zones associated with the mine edges.

The surface expression of an anomalous salt zone, Shear Zone D (shown in Figure 1 in Appendix 2), was tentatively identified on the basis of the soil gas profiles of hydrogen and methane. The gases may derive from occluded gas pockets in anomalous salt associated with this shear zone, as shown in Figure 2. The possibility also exists that hydrocarbons from the lower mine level of the SPR reservoir may be permeating through anomalous salt associated with the eastern portion of the SPR mine perimeter. A sample of methane obtained from transect WK, at the 250 m location, near where the transect crosses the edge of Shear Zone D, was tested by SIRA and was definitely of petrogenic origin, although its specific source could not be determined. At the alternate salt dome location investigated, we found a similar correlation between anomalously high soil gas measurements and a suspected subsurface zone of gassy salt.

Gas survey results at multiple locations at Weeks Island have also suggested that dilatancy associated with salt mine edges leads to anomalously high concentrations of hydrogen and possibly methane as well. Gas concentrations were higher either over the perimeter or just outboard of the mine perimeter. However, the limited size and scope of the 1995 sampling effort has left unanswered important questions about the specific source and transport of the anomalous gases, especially with respect to the effect of the mine structure.

During the 1994 gas mapping evaluations at Weeks Island (as described in Appendix 1), the observed patterns of the hydrogen and methane gas seeps, particularly, also tentatively suggested a similar structural control associated with fracture development processes. High methane levels were detected over or near subsurface anomalous Shear Zone E, south of the southern edge of the SPR mine; refer to Figure 1, in Appendix 2. Fracture permeability may be associated within and near the edges of any of the mapped geologic anomalous zones, particularly gassy, anomalous features in salt shear zones. The 1995 gas surveys results and interpretations above, from both Weeks Island and the alternate salt dome, both build on and reinforce the tentative 1994 findings and postulates.

The extended 1995 analyses of C2+ hydrocarbons, plus the limited methane SIRA results from both Weeks Island and the alternate salt dome site, have been quite useful for distinguishing different types of soil gas anomalies. These results were specifically useful for distinguishing near-surface biogenic anomalies from more important subsurface, petrogenic-related anomalies.

Near-surface gas mapping, as used in this study, can be a very useful tool for elucidating subsurface structure and for site characterizations, particularly when combined with other geological and geophysical evaluations. The apparent correlation found between near-surface soil gas results and dilatancy or enhanced permeability zones at and near the mine perimeter may provide a means for early detection of stress/strain effects on the mine. This correlation was relevant at the Weeks Island SPR site and is quite possibly pertinent at other salt dome locations. Admittedly, the data and interpretations from the 1994 and 1995 gas surveys were certainly not comprehensive nor fully conclusive on their own. However, they demonstrate that near-surface soil gas surveys can provide complementary geotechnical information that is both valuable and easily obtainable for investigations of salt dome structures. These near-surface gas mapping studies were less expensive, quicker, and simpler than other geotechnical techniques used for the overall Weeks Island SPR diagnostic evaluation.[1] Additional gas mapping studies may potentially yield distinct cost-benefit advantages in appropriate situations at other salt mine or cavern sites.

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Appendix 1

(1994)

**Weeks Island Soil Gas Survey:
Data Supplement and Final Observations**

Report submitted to Sandia National Laboratories
by

Kenneth Carney
Louisiana State University
Institute of Environmental Studies
October 26, 1994

Weeks Island Soil Gas Survey: Data Supplement and Final Observations

submitted to:
Martin A. Molecke
Sandia National Laboratories

by
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Institute for Environmental Studies
October 26, 1994

This is a supplement to the July 1994 report on the soil gas survey performed at the Weeks Island Strategic Petroleum Reserve site by the Institute for Environmental Studies (LSU) in May and June 1994 [1]. This supplement includes details of the oil headspace chromatography results and interpretation of methane concentrations found at the site.

SUMMARY

Previously, the distributions of free hydrogen concentrations in the soil gas were presented. Those results were obtained with a portable μGC equipped with a 5Å molecular sieve PLOT column. The μGC was also equipped with a 25cm micropacked HayeSep A column. Both columns used nanoliter scale thermal conductivity detectors; so to optimize detection of hydrogen in the soil gas, nitrogen was used as the carrier gas for the MolSieve column. Thus, while the MolSieve column could conceivably be used to determine methane, sensitivity for methane was traded off for hydrogen sensitivity. Helium was used as the carrier for the HayeSep column and so that column was used for methane determinations.

The sampling program, described in the preceding report involved inserting a stainless steel probe to a depth of approximately 4 feet and withrawing a sample of the soil gas. The soil gas sample was immediately analyzed with the portable micro GC to determine concentrations of prinicpally hydrogen and methane but also possibly constituents as well. The rapid sampling and analysis technique provided the opportunity to quickly obtain a substantial amount of data over a wide area for a reasonable cost.

BACKGROUND

Previous uses of this technique were geared toward identifying accumulations of natural petroleum accumulations at depths greater than 5000 feet on the basis of vapor, notably hydrogen, seeps into the surface soil gas. Such seeps, over the course of time, result in a steady state flux of material from the resevoir to the surface. The concentrations in the soil gas then are related to the flux of material from depth. The existence of such seeps have been documented by other workers[2]. A number of near-surface phenomena may affect soil gas concentrations– soil permeability, changes in atmospheric pressure, subsurface biological activity and changes in water content just to name a few. Because of its high mobility, even through otherwise impermeable barriers, hydrogen was thought to be capable of indicating the locations of deep petroleum accumulations. The other components of the vapor seeps (hydrocarbons) were much more likely to be sufficiently impeded that the steady state concentrations in the near surface soil gas are below the detection limits of easily portable instrumentation.

Whether the source of the hydrogen is the reservoir itself or whether the hydrogen is a secondary product of the hydrocarbon vapor seeps associated with the reservoir is still uncertain. Hydrogen production can clearly be associated with the reductive decomposition of organic contamination (e.g., petroleum hydrocarbons) [3]. Simultaneously however, with the generation of any appreciably amount of hydrogen, however, is the generation of large amounts of methane. Thus methane concentrations approximately one thousand times higher than the corresponding hydrogen concentrations can be expected in the vicinity of methanogenic decomposition of organic material. If the reduction were relatively deep, then the much higher permeation of hydrogen through the soil would serve to enhance the concentration of hydrogen relative to methane. With respect to near surface soil gas concentrations then, the results would be similar if the hydrogen source were the reservoir itself or a secondary source such as the reductive (probably biological) decomposition of the hydrocarbon vapors at a lesser, though still substantial, depth. In less strongly reducing zones, the reduction of sulfate, nitrate and ferric ions can produce hydrogen but on a much smaller scale. Because these ions are relatively common in the near surface soil this could account for a significant background level of free soil gas hydrogen in general. On this basis, previously, we had used extremely high methane levels to eliminate localized near surface generation of hydrogen.

Whether the hydrogen is generated at depth or is the result of anoxic decomposition of hydrocarbons as they seep to the surface is not important with respect to deep reservoirs. The important question is whether or not large systematic variations in concentrations are discernible over a given area. Within the constraints of variability in soil types and soil structure, a correlation between near surface hydrogen anomalies and deep petroleum deposits has been observed [2]. The biggest concerns in using near surface hydrogen are (a) generation of hydrogen by electrochemical or biochemical reduction of near surface deposits of detritus or other organic wastes, (b) reaction of hydrogen in with the oxidation potential (either biological or electrochemical) in the near surface soil and (c) variance associated with the soil structure near the surface.

The situation at the Weeks Island storage facility, however, the situation is different from our previous exploration oriented work. The storage facility is not deep in the geological sense. Further, the sinkhole represents a possibly direct channel from a strongly reducing zone. This reduced zone may or may not be contaminated with petroleum hydrocarbons. In a case of relatively direct channeling from a reduced, methanogenic zone to the surface, the lowering of the methane flux relative to hydrogen by differential permeation rates would be less pronounced. Consequently, whereas a source of hydrogen in a deep methanogenic zone could give rise to elevated hydrogen levels without insignificantly elevated methane levels, a similar source located nearer the surface could still show strongly enhanced methane levels. Consequently, our previous practice of eliminating large methane sources as unrelated to the target source (the storage facility in this case, geological oil deposits in the previous case) may be inappropriate for this project.

A further difference relevant to the soil gas survey was that the Weeks Island gas field provides a second source for light hydrocarbons and associated hydrogen. The contribution of that source to the background levels found in the area sampled is not clear. In absolute values, the background levels for hydrogen in the area of the storage facility are much higher at Weeks Island than we have seen in the past (≈350 ppmv at Weeks Island vs. <50 ppmv in southern Mississippi).

RESULTS

Details of the procedure were given in the July 1994 report and will not be repeated here. One of the basic premises of the soil gas work undertaken was that the soil gas concentrations of petroleum light hydrocarbons would track somewhat the composition of the source oil in the SPR storage facility.

SPR Oil Headspace Chromatograms

The following two chromatographs (Figures 1 and 2) show the distribution of components in sample of SPR oil taken from the resevoir in May 1994. Dilution of the headspace sample by a factor of 50 before analysis reduced the size of all peaks in constant proportion. This prevented overloading of the system while maintaining the relative concentrations of the various components. The chromatogram in Figure 1 shows resolution of hydrogen and helium from oxygen and the organic components in the sample with a 10 meter MolSieve 5Å column. Of the organic components in the headspace only isobutane elutes from the MolSieve column during the chromatographic run. Isobutane elutes anomalously early from this column due to a unique combination of vapor pressure and structure comparedwith the other organic compounds in the sample. The elution order is the same for the 2 meter column used in the early stages of the project, but with that column hydrogen and helium were not completely resolved.

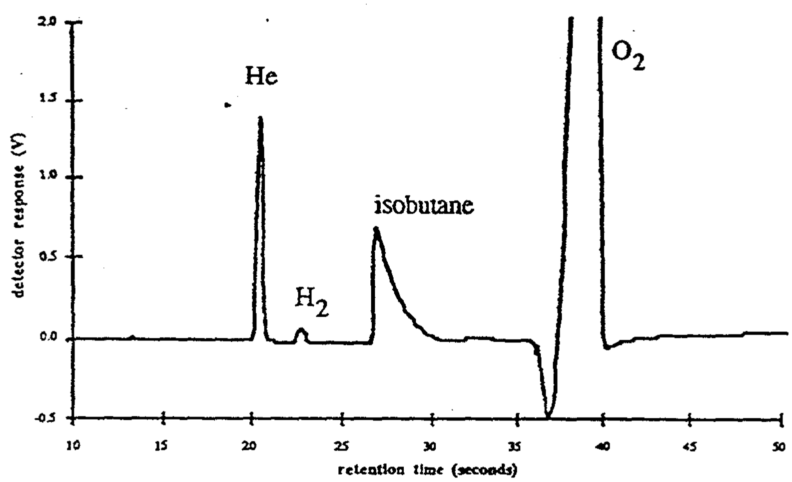


Figure 1. MolSieve 5Å chromatogram for headspace of SPR oil stored at Weeks Island. (10m x 0.32mm i.d. PLOT column @ 40°C)

The HayeSep A column, installed in the micro GC as "Channel B" provided a more complete picture of the volatile organic components in the oil (Figure 2). The HayeSep column separated the organic components from methane through butane in approximately 60 seconds. The so-called permanent gasses– hydrogen, helium, oxygen, nitrogen– comprise an unresolved composite peak eluting before methane. Using helium rather than nitrogen as the carrier gas for the HayeSep A column enhanced sensitivity for the organic components, providing detection limits in the low parts-per-million (ppmv) range for soil gas samples.

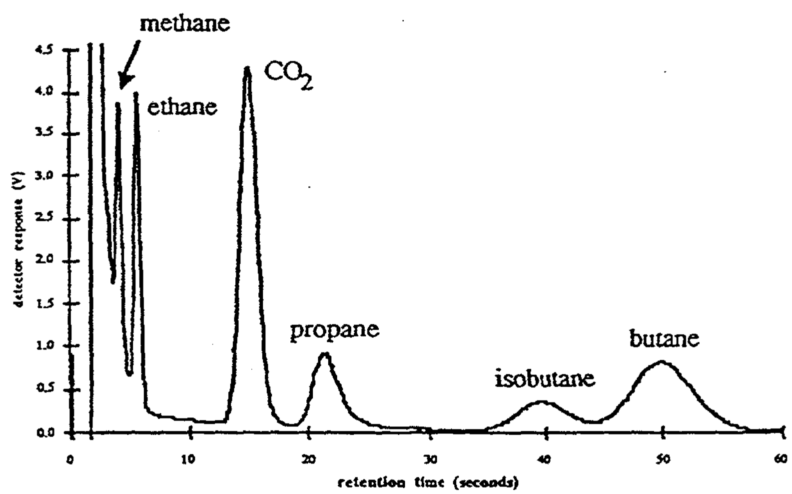


Figure 2. HayeSep A chromatogram for headspace of SPR oil stored at Weeks Island. (25 cm micropacked column @ 100°C)

Soil Gas Chromatograms

Three different types of chromatograms were seen over the area of Weeks Island. For samples located off the edge of the salt dome, hydrogen levels were generally high, higher than most locations near the sinkhole, while methane levels remained low. At the sinkhole, hydrogen levels were very low while methane levels were very high. The third type, simultaneously elevated hydrogen and methane levels, was not observed in this data set.

Locations off of the salt dome

The relatively large 1.5 V hydrogen peak coupled with an insignificant methane peak exemplified in Figure 3 was, based on our previous experience, typical for locations in the vicinity of deep oil resevoirs. In retrospect, that such profiles should be seen off the edge of the salt dome, near the Weeks Island field was not surprising. The chromatogram in Figure 3A was obtained from a 2 meter PLOT column, and so hydrogen and helium coeluted. When soil gas from this area was analyzed at a later date with a 10 meter column, resolved peak areas for helium were less than 10% of the areas for hydrogen. Thus, based on the peak shapes from the 10 meter column and those later results, hydrogen predominated over helium in these samples. Methane was the second component eluted from the HayeSep A column. The low methane concentration illustrated in Figure 3B was typical of areas located over the edge of the dome.

Locations near the sinkhole

Soil gas samples taken at the sinkhole, on the other hand, contained large concentrations of methane and lower concentrations of hydrogen. The chromatogram in Figure 4A shows the hydrogen peak and a partially resolved helium peak, demonstrating the resolution provided by the 2 meter MolSieve column used for the bulk of this project. The smaller of the pair is helium. It is not clear that the helium peak in the chromatogram accurately represents helium in the sample; subsequent analyses from the Weeks Island site indicated that the helium possibly resulted from an instrument malfunction. While hydrogen concentrations at the sinkhole locations were only about 10% of the concentrations at the off dome locations, methane concentrations in the sinkhole were among the highest in the area. The chromatogram in Figure 4B is typical of the results from soil gas in the sinkhole (which had been filled with sand) and immediately outside the perimeter of the hole. Significantly no detectable ethane was found, even though methane concentrations were very high. In Figure 4B ethane would elute as a clearly distinct peak very shortly after methane.

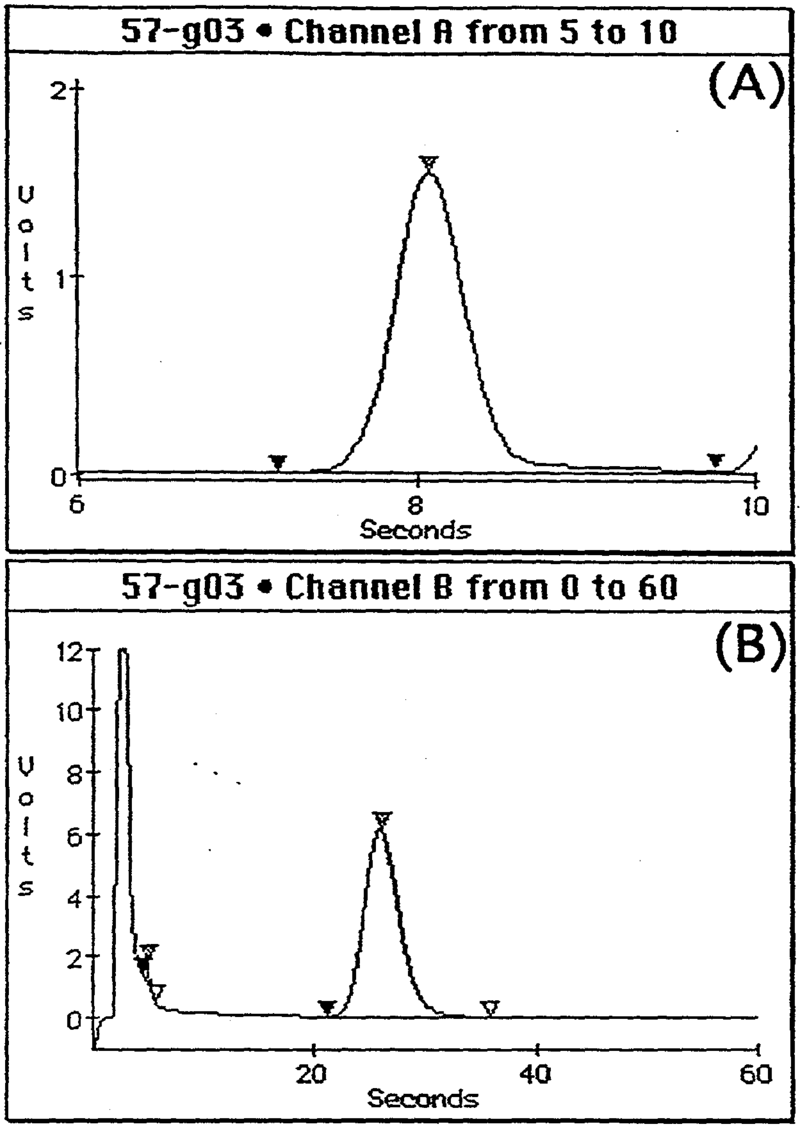
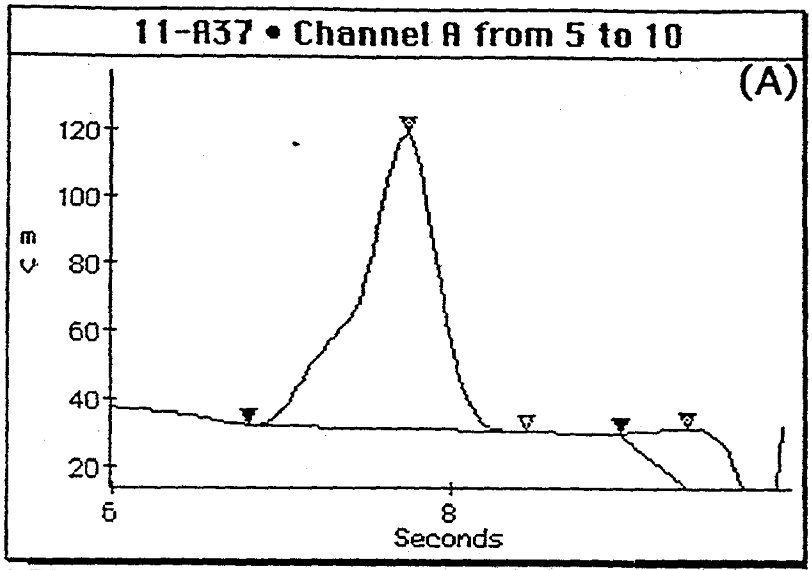


Figure 3: Typical chromatogram of soil gas from a sample location off of the salt dome. (A) hydrogen peak on MolSieve 5A (B) air, methane and CO_2 peaks on HayeSep A. Spatial patterns in soil gas concentrations.



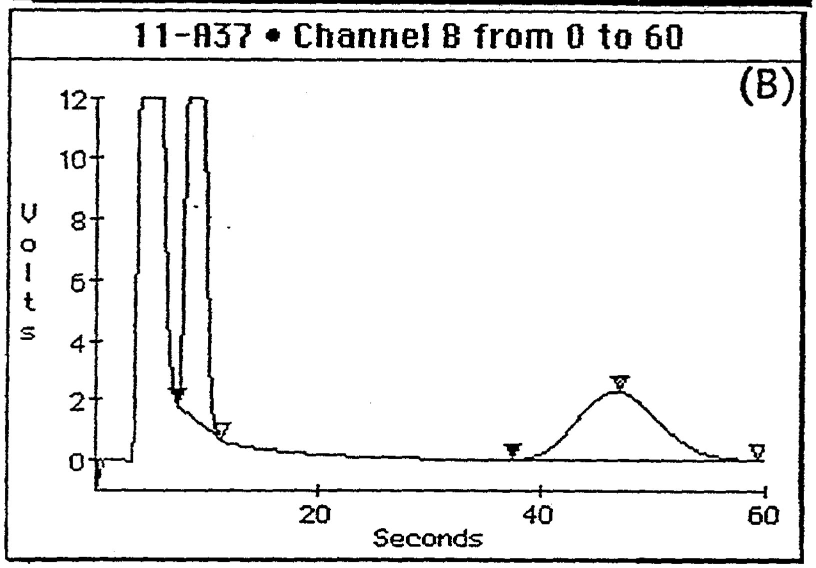


Figure 4. Chromatogram of soil gas from a sample location next to the sinkhole at Weeks Island. (A) hydrogen peak on MolSieve 5Å (B) air, methane and CO_2 peaks on HayeSep A.

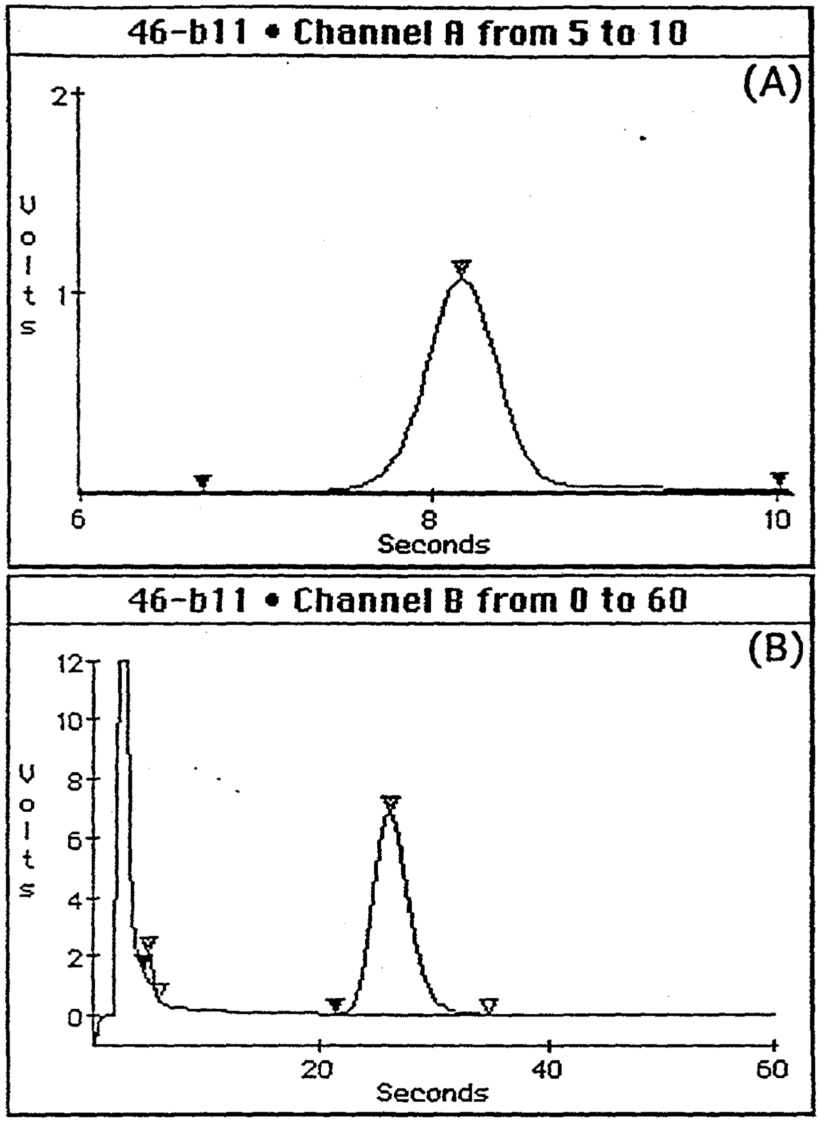


Figure 5. Chromatogram of soil gas from a sample location next to Advanced Materials Rd. (A) hydrogen peak on MolSieve 5Å (B) air, methane and CO_2 peaks on HayeSep A.

Other locations near the storage facility

As mentioned above, hydrogen concentrations were lowest at the sinkhole. At distances further removed from the sinkhole hydrogen levels were higher. Most notably, high levels were observed on transect B along Advanced Materials Road, on the southern end of transect D, on the southern end of transect C and around the pipeline south of Fill Hole Road. Hydrogen concentrations at these points were considerably higher than at point near the sinkhole, but they were not as high as concentrations off the edge of the salt dome. Nevertheless the areas of higher hydrogen concentrations near the storage facility shared the off-dome characteristic of high hydrogen concentrations paired with low methane concentrations.

Directional trends in soil gas profiles.

Regions of lower hydrogen concentrations ran roughly east-west along transects F, F' and A north of Morton Road (Figure 6). These areas extended at least as far east as transect D, but did not extend as far west as transect B. A similar pattern was not seen south of transect A, an area basically south of the surface lineation associated with Shear zone E. South of this lineation hyrogen levels were generally high (levels 4,5) and did not exhibit a directionally oriented pattern other than a possible general decrease in hydrogen levels closer to the sinkhole.

Data for methane concentrations were much more sparse than the hydrogen data (Figure 7). Trends in methane concentrations, however, seemed to support a hypothesis that transect B and points south of transect A approximated a background reading for the area near the storage facility. High methane levels were found at the sinkhole itself and in a cluster on transect D immediately north of Morton Rd. Samples at transect H, located near the storage facility fill holes, consistently showed low methane levels even though hydrogen levels were high. A few samples on transects F and F' and on transect D at the lineation showed elevated methane levels, but they were sparsely located and did not constitute "clusters" of methane highs. Unfortunately the absence of methane data for large portions of transects A and C left considerable uncertainty about the areal distribution of methane concentrations at the site. As with the high methane levels at the sinkhole, high methane concentrations at the various point throughout the area were unaccompanied by similarly high ethane concentrations.

Hydrogen Distribution in Soil Gas at Weeks Island May-June 1994

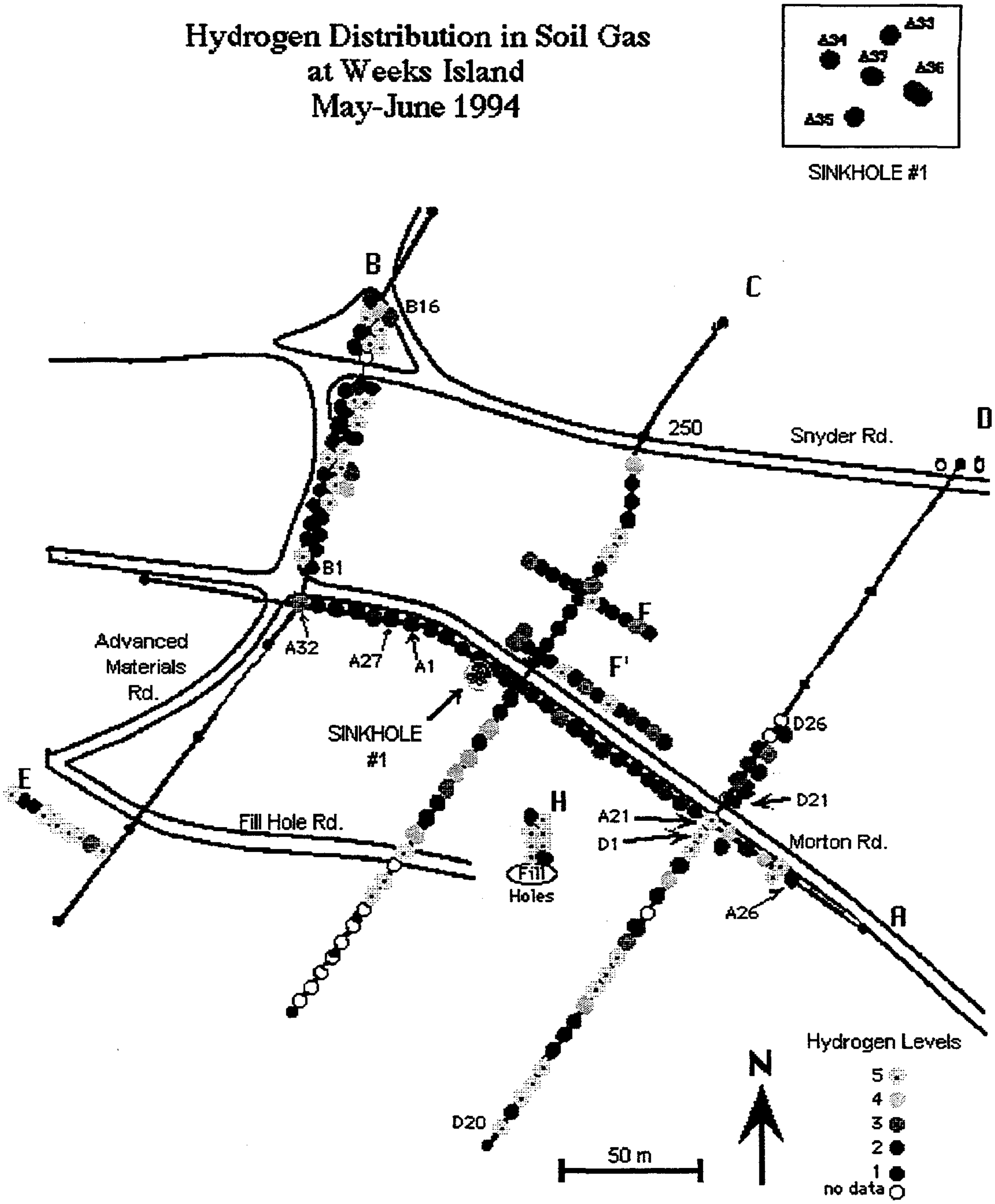


Figure 6. Distribution of soil gas hydrogen concentrations over an area adjacent to the SPR facility

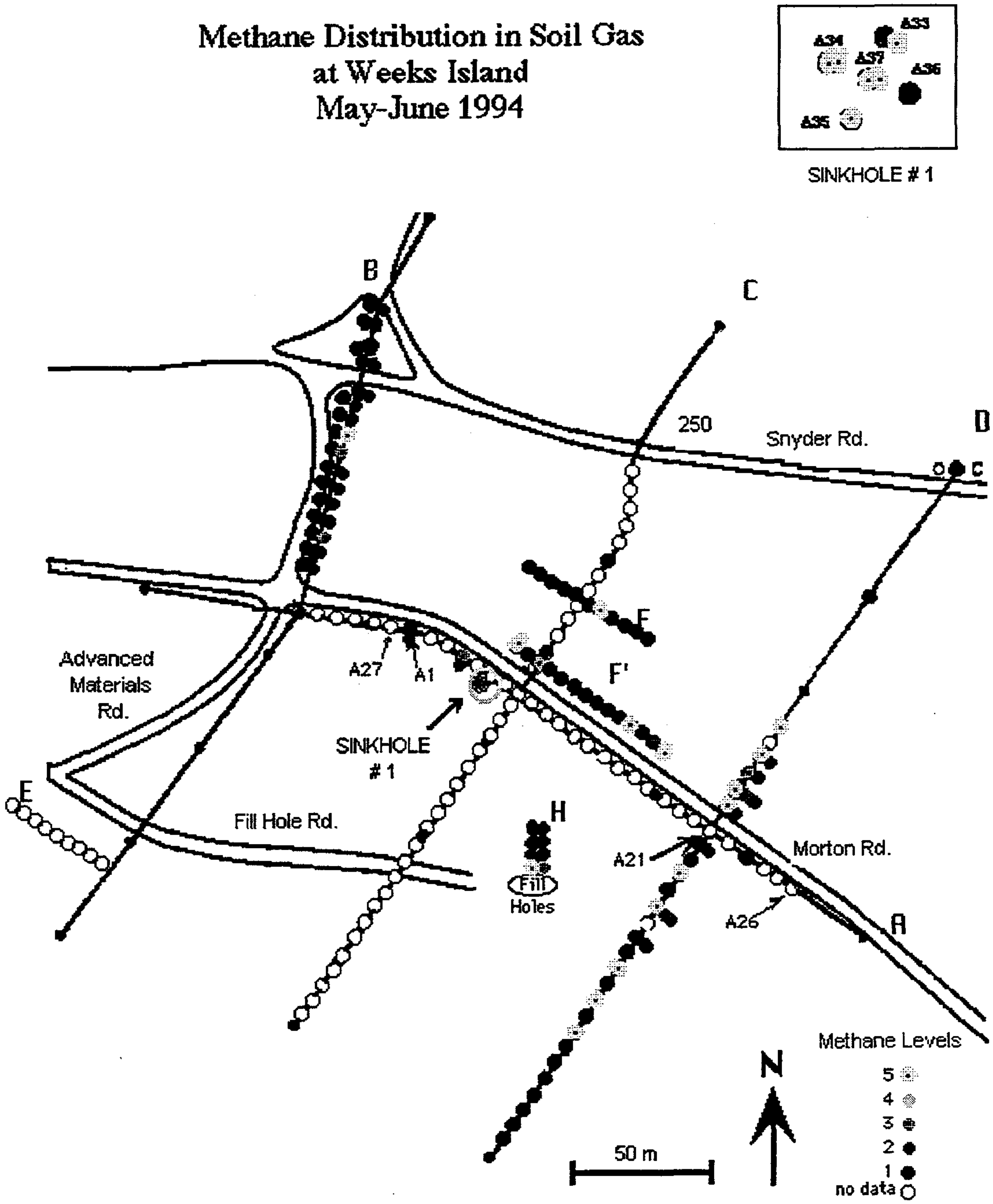


Figure 7. Distribution of soil gas methane concentrations over an area adjacent to the SPR facility

CONCLUSIONS

- Many places in the SPR area showed the same type of result as the background area, albeit with lower H2 levels. It's possible that this indicates a general trend down as one moves away from the Weeks island field and over the top of the dome. The sampling plan, however, was not intended to describe a trend linking off-dome concentrations with concentrations at the storage facility. The results suggest a connection between the sinkhole and shear zone E and the distribution of soil gas concentrations for hydrogen and methane. The layout of sample points, however, leaves large areas of uncertainty as to the specific orientation and strength of those connections. There is clearly a strong connection between the sinkhole and elevated methane concentrations.

The methane concentrations are probably not the result of direct leakage from the storage reservoir. If a vapor seep directly from the reservoir were the source of the methane, then methane concentrations as high as were seen at the sinkhole would have been accompanied by at least detectable amounts of ethane. Also a detectable elevation in helium concentration could be expected. As shown by Figure 2, headspace helium concentrations were much larger than hydrogen concentrations. Consequently, the permeation rates of helium and hydrogen being roughly the same, one would expect substantial elevations of helium relative to hydrogen if seepage from the reservoir were the direct source of the hydrogen.

As discussed by Lovely *et al.* [3] and summarized above, the leakage of hydrocarbons into the groundwater zone can lead to methanogenesis and consequent hydrogen elevation. Thus the methane and hydrogen elevations would indirectly point to areas where hydrocarbons may be leaking from the storage facility. As a direct indicator of leakage from the reservoir, helium concentrations provide a highly desirable factor. The portable instrumentation used by LSU in this study has been upgraded and is now capable of resolving helium and detecting it at concentrations down to 1ppmv. Alternatively subsequent soil gas surveys could be performed, at much greater cost, with instrumentation capable of detecting low parts-per-billion levels of the higher hydrocarbons (e.g., propane, butane) that may be more direct indicators of leakage from the reservoir. Accurately locating the source would still require a large number of sample locations and, as with the hydrogen measurements, background levels from the Weeks Island production area would interfere with the interpretation.

Less attractively, the methane and hydrogen source may be reduction of organic matter overlying an intact salt barrier. Thus no SPR hydrocarbons would be feeding the methane source and the soil gas profiles obtained with respect to methane and hydrogen will monitor only surface fracturing of the overlying soil. Monitoring for helium as a direct indicator would still be feasible as helium concentrations in the oil headspace are high (Figure 1) and background levels of helium in the near surface soil gas are demonstrably low. Hydrogen and methane monitoring alone could still be useful as an indicator of the general stability of the site as changes in the soil fracturing pattern reflect changes in the salt dome structure.

With regard to the Weeks Island gas field, the distribution of hydrogen concentrations is consistent with our previous interpretations in Mississippi. Namely that producing oil and gas fields result in elevated hydrogen concentrations in the near surface soil gas.

Recommendations

Any subsequent high resolution monitoring of soil gas composition should focus on filling in gaps in the current mapping of soil gas distributions. Oblique transects connecting the original set, A through H, should be planned to fill in the map. The new transects should also be geared to obtaining an accurate radial profile of soil gas composition as one moves away from the sinkhole. The question of background levels is less critical if one accepts the hypothesis that transects B, H and the southern end of transect D represent background for the SPR area. An additional set of data would be desirable to verify that hydrogen levels continuously increased as one approached the productive fields on the edge of the salt dome.

Any subsequent monitoring should also use the upgraded instrumentation to monitor helium as well as hydrogen, methane and ethane concentrations. Helium has no near surface or biogenic source at Weeks Island and so one could reliably attribute elevated helium concentrations to deep sources. Furthermore, the SPR oil has been shown to offgas substantial amounts of helium which would provide a direct tracer to defects in the storage reservoir.

1. "Weeks Island Soil Gas Survey: Preliminary Observations", Report to Sandia National Laboratories, July 1994.

2. D.T. Ghahremani; "Significance of Radon/Hydrocarbon Seeps in Petroleum Exploration", Sixth Thematic Conference on Remote Sensing for Exploration Geology; Houston, Texas; May 16-19, 1988.

3. D.R. Lovely, F.H. Chapelle, J.C. Woodward; "Use of Dissolved H_2 Concentrations to Determine Distribution of Microbially Catalyzed Redox Reactions in Anoxic Groundwater"; Environ. Sci. & Technol., 28(7), 1205-10 (1994).

Appendix 2

(1995)

Final Report:
Near-Surface Gas Mapping at the Weeks Island Strategic Petroleum Reserve And Other Salt Dome locations, Phase III

Report submitted to Sandia National Laboratories
by

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January 31, 1996

FINAL REPORT: NEAR-SURFACE GAS MAPPING AT THE WEEKS ISLAND STRATEGIC PETROLEUM RESERVE AND OTHER SALT DOME LOCATIONS, PHASE III

ABSTRACT

Field sampling and rapid gas analysis techniques were developed to survey near-surface soil gases– including hydrogen, methane, ethylene and ethane– for geotechnical diagnostic purposes at the Weeks Island Strategic Petroleum Reserve (SPR) site and at other salt dome locations in south Louisiana. Phase III was a follow-up to an earlier survey at Weeks Island in 1994 (Phase I and Phase II). The 1994 survey focused principally on a sinkhole discovered at Weeks Island in 1992[1]. Several hundred soil gas samples were obtained and analyzed in the field by gas chromatography for profiling low concentrations of the target gases at ppmv to percent levels. Surveys were conducted across two sinkholes, mapped anomalous zones in the salt, and the Weeks Island SPR repository. Samples were taken at other south Louisiana salt dome locations as well. To supplement field data, soil gas samples were collected at various locations for laboratory analysis of target gases at ppbv levels and for stable isotope ratio analysis (SIRA) of the methane in the soil gas. Gases in the near-surface soil can originate from the oil, from within the salt, or from surface microbial activity. Methane SIRA were intended to aid in distinguishing between biogenic and petrogenic methane; but, unfortunately, samples collected during the summer of 1995 had not been analyzed at the end of the project period. Given the extensive delay between sample collection and analysis, it is unlikely that useful information will be obtained from the SIRA samples.

The relative concentrations of various light hydrocarbons in near-surface soil gas provided the means for distinguishing between general background composition for the area and localized anomalies. Elevated levels of hydrogen and methane were associated with anomalous zones in the salt dome and with suspected salt fracture (dilatant) zones, particularly over the edges of the SPR repository. For sample showing elevated concentrations thought to be correlated with dilatant zones, the hydrocarbon profiles for concentration anomalies showed no clear difference from the profiles associated with background areas. Significantly elevated ethane concentrations were found repeatedly in the vicinity of one anomalous salt zone (Shear Zone D). This location was unique in showing not only an elevated ethane concentration, but also a total absence of detectable C2-C4 alkenes. The results were interpreted as representing a surface expression of a shear feature in the salt that had been identified in the mine prior to SPR operations.

INTRODUCTION

The purpose of this study was to use near-surface gas survey techniques at the Weeks Island Strategic Petroleum Reserve (SPR) site to diagnostically profile low concentrations of selected components (hydrogen, methane, other hydrocarbons) across two sinkholes, mapped anomalous zones in the salt dome and the SPR petroleum repository. This near-surface gas mapping study was initiated to benefit and support the Weeks Island Strategic Petroleum Reserve site sinkhole diagnostic and risk abatement programs, conducted for the Department of Energy Strategic Petroleum Reserve Project Management Office[1,2]. This is the third phase of the soil gas work at Weeks Island. Phases I and II[3], conducted in 1994, were a feasibility demonstration and a small survey of areas at Weeks Island near the location of a sinkhole discovered in 1992 near Morton Road. The results of that survey indicated elevated hydrogen levels consistent with suspected subsurface geology related to the formation of the sinkhole. During the 1995 survey (Phase III), operations involved in mitigating the geotechnical risks associated with water intrusion during removal of oil stored at the Weeks Island facility (i.e., brine injection and freeze wall construction) hindered access to much of the previously surveyed area. As a result relatively few samples were taken for direct comparison with the results from Phases I and II. The majority of samples in Phase III focused on an area adjacent to a second sinkhole discovered in 1994, areas above the mine perimeters, and areas associated with anomalous salt. The areas chosen in the Phase III survey were designed to complement and confirm interpretations from Phases I and II. The methodologies and results from this study (Phases I, II, III) could also possibly have wider applicability to other salt dome and mine sites.

Near-surface gases can originate from the stored repository crude oil, from gases in the rock salt or, possibly from surface microbial activity. Near-surface soil gas surveys are assumed to provide good indicators of gas transport through suspected salt fracture (dilatant) zones over the edges of the SPR repository. Further, high concentrations of hydrogen and methane, predominantly, can be useful indicators of other features in salt domes, and may be applicable to other SPR sites, salt mines or cavern storage sites. Among the features problematic to salt dome utilization are anomalous zones and otherwise gassy zones (i.e., underground pressurized gas pockets) in the salt.

We used the near-surface gas survey techniques over known or suspected geologic features at Weeks Island to evaluate potential relationships between near-surface soil gas composition and geologic salt features. Available data tend to support the relationships between near-surface soil gas composition and geologic structures in the salt.

The results of the present survey at Weeks Island suggest a significant relationship between anomalies in surface soil gas concentrations and subsurface features such as anomalous zones in the salt and dilatant zones associated with the mine structures at Weeks Island. The surface expression of an anomalous salt zone, Shear Zone D, has been tentatively identified on the basis of soil gas profiles. The results also repeatedly suggested that dilatancy associated with the mines may correlate with anomalously high concentrations of hydrogen and possibly methane. The limited size and scope of the sampling design left unanswered important questions about the source and transport of the anomalous gas, especially with respect to the effect of the mine structure. The extended hydrocarbon analysis of the C2+ hydrocarbons was useful for distinguishing different types of soil gas anomalies, specifically for distinguishing near-surface biogenic anomalies from more important subsurface related anomalies.

BACKGROUND

The use of near-surface geochemical surveys has experienced a revival recently for oil exploration and geological investigations. The advent of accurate, portable, and reliable analytical instrumentation has provided field geologists and mineral prospectors with the means to effectively obtain *in situ* chemical analyses in a field setting. The availability of on-site analysis allows one to perform a geochemical survey over wide areas with sufficient spatial resolution and replication to address the inherent heterogeneity of surface soil environments. Near-surface soil gas measurements have been used successfully for locating oil reservoirs[4] , fault zones[5] and have been correlated with seismic events.[6] This technique is appreciably less expensive, quicker and simpler than traditional geophysical techniques, yielding a distinct advantage in appropriate situations.

Historically, detection of visible hydrocarbon seeps has been one of the most successful oil exploration techniques ever used. It has been observed that detection of visible seeps has been, over the life of the industry, the preeminent oil exploration technology[7]. The availability of sensitive chemical analysis has extended the detection from visible macroseeps to ever smaller quantities, undetectable with the unaided eye. Investigators thus may derive information about variations in subsurface structure and composition by locating anomalous concentrations of target analytes in the near-surface soil. Because some components are present in the near-surface soil gas due to material flux from deeper sources, information gained by a near-surface soil gas survey may pertain to depths well below those at which the sample was taken. This is true whether the phenomenon is the presence of an oil reservoir, a structural feature or a temporal feature such intermittent fault movement.[8,9]

The fundamental premise of using near-surface soil gas surveys to elucidate deeper structures and sources rests on the concept that the target analyte concentrations in the near-surface gas are affected by the strength of the source and by the rate of conduction to the surface. Gases emanating from a subsurface source will follow the highest permeability pathway to the surface. High permeability pathways will generally be along fault or shear planes or through material having enhanced permeability relative to neighboring material in the same stratum. Enhanced permeability may arise from composition anomalies or, possibly, stress induced dilatancy. The material thus rising to the surface passes *through* the soil surface and into the atmosphere. A steady state concentration in the near-surface soil gas then represents the net flux into and out of the near-surface soil. Any increase in the flux *into* the near-surface such as by an anomalously strong source or an anomalously permeable pathway leads to an increase in soil gas concentrations, given a constant rate of removal from the near-surface soil gas. The removal from the near-surface soil gas of upward migrating hydrocarbons may be by either loss to the atmosphere or loss to some other sink (e.g., adsorption, chemical or biological degradation).

Advantages/Problems of Near-Surface Geochemistry

The principal advantages of near-surface soil gas surveys are low cost and short analysis times compared with other geophysical techniques. Wide areas can be screened economically without extensive preparation of the landscape as is required by soil boring or drilling operations. In a soil gas survey, the concentrations of selected compounds are measured in the interstitial soil atmosphere at depths of less than 25 feet—typically 3 to 6 feet . This eliminates the need for analyte extraction methods, reduces the need to bring solvents and other equipment to the survey site, and maintains an extremely high level of portability.

The difficulties in interpreting the results of soil gas surveys stem principally from the heterogeneous structure of the soil and from interactions between the soil gas and the atmosphere. The heterogeneity of the soil can lead to high variations in measured concentrations from point to point within the soil, even though the points may be in very similar position with respect to the variable being probed (e.g., location of a fault or oil reservoir). This high variability may necessitate the running of a larger number of replicates than one would initially expect. Typically the scale of heterogeneity in soil structure—i.e., the precision with which survey data can locate a significant anomaly— is on the order of a few feet within a given soil type. As one moves from one soil type to another, however, analyte concentrations may change as soil permeability, moisture, organic content and biological activity change. Biological activity is of particular concern when the analytes are compounds such as hydrogen, methane and carbon dioxide that are involved in biological cycles and may be generated or consumed in the near-surface soil. These factors must be considered when evaluating the results of the survey data.

The second confounding factor in using gas survey data derives from interactions between the soil gas and the atmosphere. Displacement of interstitial gas by rainwater or by sudden changes in barometric pressure can alter soil gas concentrations. In the case of reactive compounds such as hydrogen potential chemical reactions with atmospheric constituents, which are generally more highly oxidized than soil constituents, present an additional source of uncertainty. Any weather phenomena that affect soil porosity can change the relative transport of deep sourced gases into and out of the near-surface soil will alter absolute concentrations. Examples are prolonged periods of wet or dry weather and prolonged periods of hot or cold weather. Atmospheric factors can also affect the biological cycles mentioned above. Increasing the sampling depth reduces the effect of atmospheric conditions. For example, diurnal variations in measured concentrations caused by temperature and pressure changes over the course of a day are eliminated by sampling at depths greater than four feet. The cost and time of sampling increase dramatically with depth, however, and sampling at greater depths often means sacrificing the areal resolution of the survey. Sampling depths of approximately 5 to 6 feet are generally easy to accomplish without much difficulty and represent a good compromise between high sample throughput and minimal interference due to surface phenomena.

Near-surface soil gas results require careful interpretation when comparing data from different soil regimes and time periods. Most temporal and climatic variations can be compensated by collecting replicate samples at various times and weather conditions. Soil type variations, however, are not so easily eliminated and extreme care must be exercised when generalizing results across grossly different soil types and conditions At Weeks Island, the survey covered no more than four different soil regimes.

Weeks Island Geology

Weeks Island, one of the Five Islands salt dome chain on the south central Louisiana coast, comprises uplifted late Wisconsinian Peoria Loess covering alluvial deposits of the Prairie Complex. The geology of Weeks Island has been described in detail previously[10] and will only be summarized here. Topographic features of Weeks island were formed by diapiric uplift, sediment reworking, drainage network development, and localized subsidence. The "Devil's Backbone", a generally north-south ridge underlain by loess covered sandy deposits, occupies the highest part of the island at elevations up to 52 meters. Shear Zone D (see Figure 1) has been mapped in association with this ridge[11,12]. A sinkhole that developed in approximately 1992, is near the projected alignment of Shear Zone E[11]. The sinkhole overlies the southern edge of the SPR mine, where the upper and lower mine level edges are coincident.

Surficial sediment at Weeks Island represents sediment of the late Pleistocene Prairie Complex and sediment veneers that cover the Prairie Complex.[13,14] In and around the Five Islands, surficial sediments of the Prairie Complex consist of ancestral Mississippi River fluvial deposits. Surface veneers include Peoria Loess, a basal loess mixing zone, overwash colluvium, gully fill sediment, and Holocene marsh deposits. Peoria Loess is a brownish silt loam with a friable consistency, becoming slightly plastic or sticky when wet. Perched water occurs at or near the base of the unit where loess is underlain by clayey sediment. The surface soil covering most of Weeks Island is a Memphis Silt Loam (Typic Hapludalf) with moderate blocky structure and clay films on peds. The maximum loess thickness cored by Autin et al.[10] was 380 cm. The Peoria Loess mixing zone has a modal thickness of approximately 50 cm and is normally a brown to yellow silt loam to sandy loam with weak blocky structure and friable to sticky consistency. Overwash colluvium can reach approximately 150 cm thickness and is a gray to brown silt loam. Gully fills are gray brown silt loam to loamy sand. Holocene marsh sediment at Weeks Island is a very dark gray to black silty clay loam to mucky clay with fibric to hemic reed, grass and wood fragments.

Several Shear zones have been tentatively mapped in the salt stock at Weeks Island.[15] These areas are interpreted to represent the interface of individual salt spines moving differentially during the upward migration of the salt stock.[16] Internally, these areas are characterized by intense folding and banding of the salt and the inclusion of foreign sedimentary material as well as brine, oil and gas. This naturally reduces the physical homogeneity of the salt stock and could be expected to provide multiple higher permeability pathways for the escape of entrained gas. In room and pillar mines, such as those at Weeks Islands, Shear zones are associated with "blowouts" where pockets of salt break out during routine blasting. Figure 1 shows the location of the various Shear zones, labeled A-E, identified or suspected at Weeks Island.[11]

Mining operations have been ongoing at Weeks Island for many years. The two mine levels at approximately -535 feet and -735 feet were filled, beginning in 1980, with crude oil as part of the Strategic Petroleum Reserve Program. In 1992 a sinkhole was discovered above the southern edge boundary of the upper (535 foot) mine level, as shown in Figure 1. In 1995 a second, smaller, sinkhole was discovered above the northwestern perimeter of the upper mine level, also as shown in Figure 1.

EXTENT OF SURVEY

Between April and July 1995, four areas at Weeks Island were surveyed by near-surface soil gas analysis for hydrogen, methane, ethylene, ethane, 1-propene and propane. Approximately 30 samples were taken from a nearby island having very similar geology and mining activity. This alternate location established a point of comparison for soil gas composition in the absence of any possible contribution from stored SPR oil. Multiple other areas were also surveyed at Weeks Island in 1994; results of the 1994 survey have been documented previously[2,3]. Approximately 270 samples were analyzed on site for hydrogen and methane on 10 days over the period between April and July. Additionally, almost 130 samples were collected for laboratory analysis of C1 to C6 hydrocarbons. Though the number of samples seems large, the density of samples in the survey is actually rather low. The survey covered a fairly large area, with four major differences in important factors that can affect soil gas concentrations: location with respect to anomalous zones, location with respect to mine perimeters, surficial soil type, and natural temporal variations in absolute gas concentrations. Thus the data are spread thin and, while significant trends can be identified and strong hypotheses made about the origin of the soil gas anomalies, drawing specific, definitive conclusions about gas sources and subsurface geology and engineered structures may be premature.

Two of the surveyed areas were transects near Shear Zones A and D (WK and WL, Figure 1). A third transect was oriented above the eastern perimeter of the upper mine (WM). Sample points on transects were generally 10 meters apart. Finally, an area near the location of the second sinkhole (W2) was briefly surveyed. A fifth location (northeast of Figure 1) was occasionally sampled as a background region removed from the SPR facility and salt mining activities. This background location was topographically similar to the area above Shear Zone A but was located near the northeastern edge of the dome near the intersection of Snyder Rd and LA Hwy 83.

The first sampling transect (WK) was outside the perimeter of the upper mine for its entire 700 meter length. Transect WK crossed the lower (735 foot) mine boundary at approximately 400 meters from the transect origin (at its southwestern end, 0 meters) on the crown of the Devil's Backbone ridge. Oriented normally to Shear Zone A, transect WK crossed over the mapped boundary of the shear zone near the intersection of Shear Zones A and D. The transect ended (northeastern end) at its intersection with Snyder Road, as shown in Figure 1). The mapped boundaries of the shear zones represent their estimated locations in the salt[11] and, while the surface expressions should lie somewhat above the feature, the mapped boundaries may not exactly coincide with the surface location of associated anomalies.

Transect WL was located above the eastern perimeter of the lower mine within the mapped boundary of Shear Zone D. The salt at the lower mine level beneath this transect was known to contain pressurized gas pockets and to be subject to multiple blowouts[17]. The transect ran generally north-south, in a grassy area east of and parallel to Snyder Road, for 280 meters (Figure 1).

The third transect, WM, followed the upper mine perimeter from Snyder Road northward for a distance of 380 meters. The location was fairly well removed from any known accumulations of gassy salt or previously mapped shear zones. Transect WM crossed a set of three deep, east-west, ravines. At several points along this transect additional samples were taken at points inboard and outboard of the mine perimeter, but on the same landscape position with respect to the ravines, to explore the effect of the mine perimeter (i.e., presumed dilatancy) on the soil gas readings.

The final location surveyed on Weeks Island during this period, area W2, was above the northwest perimeter of the upper mine near the location of the second sinkhole (see Figures 1 and 6). A short transect ran from monument UL62 northward for 50 meters. Additional sample locations were distributed around an area encompassing monuments UL62 through UL56. These locations included points inboard and outboard of the upper mine perimeter. Samples were also taken from the sand fill in the sinkhole, which was about 5 m in diameter by 3 m deep, and from the native soil at the edges of the sinkhole.

Three transects on the nearby island crossed above zones of gassy salt that had been detected by horizontal borehole drilling in the mine below.[18] Surface topographic features suggested that gassy zones in the salt formed a more or less continuous band between the identified zones of gassy salt in the mine. The inference of a continuous gassy zone was based on surface features alone; no independent confirmation of this was available. Two of these three "Alternate" transects– transects AA and AC– crossed above the suspected feature at roughly right angles to its suspected alignment . Transect AB connected the ends of transects AA and AC near the feature. Transect AA was thought to cross the feature at the transect origin (0m, see Appendix C), based on the surface topography and the known locations of gassy zones in the salt. Transect AC was thought to cross the feature about 30m from the transect origin. A sinkhole had formed near the point AA was thought to cross the feature; samples were taken from the bottom of the sinkhole. Samples taken from sinkholes at the alternate location differed from those taken at the Weeks Island sinkholes in that the former were taken from the natural soil at the bottom of the sinkhole while the latter were taken from the upper level of the sand that was used to fill the sinkhole.

PROCEDURE

Soil Gas Sample Collection

The soil gas sampling device (Figure 2) consisted of a 150 ml stainless steel cylinder with a vacuum gauge and a 500ml hand operated sample pump capable of evacuating the cylinder to 26" Hg vacuum (660 mm Hg). A ball valve isolated sample cylinder from the sampling probe until the sample was taken. The sampling probe was a 1.8 m (6 foot) long, 0.63 cm (1/4 inch) o.d. stainless steel tube, fitted with a Quick-Connect™ valve body (Swagelok).

At each sample location a 90 cm (3 feet), 1.3 cm (1/2 inch) diameter pilot hole was drilled with a power drill or similar device. The sampling probe, fitted with a removable drive tip, was then inserted into the pilot hole, pressed to a total depth of 170 cm (5.5 feet), and attached to the sampling device with the Quick-Connect fitting and 60 cm (2 feet) of 0.3 cm ($\frac{1}{8}$ inch) PTFE tubing. The sample cylinder was then evacuated and after withdrawing the probe 5 cm (2 inches) to dislodge the drive tip, the ball valve was opened, allowing soil gas to flow into the tube. The amount of sample in the cylinder was indicated by the pressure rise in the cylinder.

After the soil gas sample had been collected in the sample holding cylinder, a 5 ml portion was removed from the holding cylinder with a gas tight syringe and analyzed immediately (<2 minute holding time) with a portable gas chromatograph (GC).[19] The on-site analysis targeted helium, hydrogen and methane. In many samples however, helium and methane concentrations were below the detection limits of the portable GC. For a number of samples, an additional 50 ml portion of sample was removed to sample bottles for hydrocarbon analysis with a more sensitive laboratory GC housed at the Institute for Environmental Studies (IES), Louisiana State University . In the laboratory, samples were analyzed for methane, ethylene, ethane, 1-propene, propane and other C4-C6 hydrocarbons at low ppbv levels. Except for small amounts of butane, no C4 or higher hydrocarbons were detected in the soil gas at Weeks Island. Also, at several locations approximately 100 ml of sample was retained for stable isotope ratio analysis (SIRA) of samples containing significant quantities of methane (>2500 ppmv). SIRA samples were sent to Krueger/Geochron Laboratories (Cambridge, MA). Stable isotope ratios for hydrogen and carbon in methane can help to distinguish between petrogenic and biogenic methane sources as described by Whiticar *et al.*[20]

Often the soil porosity was low enough that the cylinder pressure recovered only slowly. If the recovery time exceeded two minutes, the sample tube was pulled up from the soil until the vacuum released. This resulted taking a fraction of the sample from the churned soil at the bottom of the pilot hole. Method evaluations performed at a test site in Baton Rouge suggested that while this step affected the results to a small degree, the difference was small compared to variations between replicate analyses at the same location. Also, the soil over compared survey areas tended to have similar recovery rates so relative concentrations within an area were unaffected by variations in sampling procedure

Gas Chromatography

The on-site chromatography was simultaneously performed on two different columns— a 0.32 mm i.d. x 10m 5Å molecular sieve PLOT column (MS5Å) using nitrogen carrier gas and a 0.32mm i.d. x 10m PoraPLOT Q column using helium carrier gas. Both columns used a microliter scale thermal conductivity detector (µTCD). Column temperatures were 50°C and 100°C, respectively. The MS5Å column was used to analyze helium, neon, and hydrogen with detection limits below 10 ppmv. Furthermore, the MS5Å column could determine methane in less than two minutes, though because nitrogen was used as the carrier gas the detection limit was over 100 ppmv. The PoraPLOT Q column with helium carrier gas could detect methane, CO_2, and water at concentrations as low as 10 ppmv. Detection limits of the M200 were one to two orders of magnitude too high for analyzing the C2 to C6 hydrocarbons, although an LSU developed concentrator that lowers detection limits to the low ppbv range became available after the field work for this project was completed.

Because of the high detection limits for the field method, extended hydrocarbon analysis for the C2 to C6 hydrocarbons was performed in the IES analytical laboratories by GC-FID. A 30m J&W DS-Q column (similar to PoraPLOT Q) was installed into a Hewlett-Packard HP5890 GC. Temperature programmed gas chromatography was used to analyze C1 to C6 hydrocarbons at concentrations down to approximately 50 ppbv. Samples were taken from the sample cylinder in the field and placed into amber 100ml sample bottles that had been oven conditioned at 140°C for 24 hours, sealed with Teflon lined silicone septa and evacuated to 26" Hg vacuum. Fifty milliliter volumes of soil gas sample were placed in each sample bottle so that the pressure in the bottles was subambient. Standards were similarly prepared in the field at concentrations of 1 ppm each for C1-C6 n-alkanes and C2-C6 1-alkenes. Ambient air samples were similarly taken. Samples were analyzed for hydrocarbons within one week of collection. At analysis time, 50 ml of ultra high purity air was added to the bottle and the resulting pressure indicated the extent of leakage in the bottle. Few of the samples showed signs of leakage over the one week holding period.

Stable Isotope Ratio Analysis

Samples that contained high methane concentrations (determined by the on site analysis) were collected for SIR analysis and sent to Krueger/Geochron Laboratories for determination of H/D and C^{12}/C^{13} ratios. The analysis involved condensing the hydrocarbons (principally methane) at liquid nitrogen temperatures from the air matrix followed by controlled oxidation to CO_2 and H_2O. Mass Spectral analysis of the resulting CO_2 and H_2O then provides the stable isotope ratios. Relatively high oxygen concentrations in the soil gas samples caused concern at the isotope laboratory about possible explosion hazards on condensation, leading to considerable delays in obtaining the SIRA results.

Salt Gas Analysis

Attempts were made to obtain fresh samples of gassy salt from the nearby Morton mine at Weeks Island for comparison of salt-trapped gas composition with analyzed near-surface gas compositions. Unfortunately, the 1200 foot Morton mining level, where gassy salt and gassy outbursts had been encountered previously, has been abandoned. No access to this level was available and no gas samples could be obtained. Samples were obtained from five locations in a nearby mine at another salt dome island. Three of the sample locations were near recent blowouts and one was from a vein of anomalous salt. A fifth sample was run of the mine salt. Each of these five samples were analyzed by dissolving 10g of salt with 30ml of distilled water in a closed 40 ml vial. The dissolution of the salt released entrained gases into the 10ml headspace, which was then analyzed by GC-FID in the same manner as the soil gas samples. The gas composition in salt from the adjacent dome was presumed to be reasonably comparable to that in Weeks Island salt and to contain the same components in roughly similar ratios.

RESULTS

The soil gas survey provided two types of information about the soil gas, concentrations of the target analytes as a function of location and the analyte profiles (relative concentrations) at a particular locations. The bulk of the data, obtained with the portable GC, pertained to the trends in hydrogen and methane concentrations across the landscape of the island. The extended hydrocarbon analyses of the samples returned to the laboratory provided the lower detection limits necessary to determine soil gas concentrations of not only methane, but also ethane, ethylene, propane and 1-propene. Appendix A provides an extensive tabulation of all results from this study for both the on-site determinations of hydrogen and of the laboratory results the normal alkanes, including methane. A leak in the microchip sample injector in one of the chromatographs compromised the quality of the on-site methane data. Consequently, all methane data referenced in this report were obtained with the laboratory analyses.

Hydrogen and Methane trends

Hydrogen concentrations in the soil gas closely paralleled methane concentrations through the entire survey. Transect WK hydrogen and methane trends, shown in Figure 3 exemplify the correlation between hydrogen and methane results. Because of the above mentioned instrumental problem, the more complete set of methane data came from the extended hydrocarbon analysis performed in the LSU Institute for Environmental Studies laboratories. Only the laboratory results for methane are presented. The relatively small number of samples returned to the laboratory, however, limited the spatial resolution in the methane data. Consequently, some uncertainty remains about the specific sources of the observed trends.

The most significant feature in the soil gas trend on transect WK is the very large spike in hydrogen and methane concentrations at approximately 250 meters (sample location WK250). This feature was observed on successive trips in May, June and July. The peak methane level for the data shown in Figure 3b was approximately 2000 ppmv, though methane levels at this location were sometimes as high as 2%. The high methane concentration at WK250 was consistently the highest value along the transect. The 250 meter point was unique in having no detectable ethylene and 1-propene in the soil gas. On different surveys of the transect, the precise location of the concentration maximum varied by ±10 meters, with 10 meters being the spatial resolution used in this survey. Occasionally, the loci of the hydrogen and methane concentration maxima differed by 10 meters.

A second feature on transect WK was a small but noticeable drop in hydrogen levels (unfortunately, corresponding methane levels were not available) as the transect crossed the 400 meter mark, approximately where the transect crossed above the mine perimeter. In May, hydrogen readings at the 400 meter point were 10 times higher than the average readings at 650 meters. The northern extreme of transect WK (positions beyond 550 m, including positions above the mapped location of Shear Zone A) consistently yielded the lowest readings along the transect for both hydrogen and methane. The southern extreme of WK, from 0 to 100 meters, sometimes had elevated hydrogen levels along with slightly elevated methane levels. While the hydrogen levels at this southern end on one occasion were nearly as high as at WK250, methane concentrations, though somewhat elevated, did not approach similarly high levels. Further, the soil gas in the 0-100m segment of transect WK contained approximately equal concentrations of ethane and ethylene when these C2 compounds were detected, suggesting that at least some biological or chemical action was involved in the presence of the hydrocarbons in the soil gas.[21]

Transect WL was slightly analogous to a northern segment of transect WK. Located above the mapped location of Shear Zone D and over the perimeter of the lower SPR mine, transect WL corresponds to points at approximately 400 meters on transect WK. The comparability of the two locations is limited by the location of transect WL in a transitional area where the soil is changing from brown to gray due to a wetter soil moisture regime.[10] Like the sampling points just south of WK400, methane concentrations on transect WL were consistently higher than those at the northern extreme of transect WK (points beyond 500 m). Though methane concentrations vary along transect WL, as shown in Figure 4a, even the lowest methane concentration measured along transect WL was more than three times higher than the corresponding value at the northern extreme of transect WK. More representative of the transect as a whole, however, were the samples at the 180 meter point on transect WL which were almost an order of magnitude higher than those at the northern end of transect WK. A high methane reading at the 140 meter point was near a drainage ditch crossing Snyder Rd and so is the most likely of any sample from the survey to contain large amounts of near-surface biogenic methane. This point had a methane concentration near that measured at WK 250, approximately 1%. Importantly, methane was the only hydrocarbon detected in the soil gas at WL 140 while during the same time frame the soil gas at WK 250 also contained ethane at roughly 5 ppmv. Again, significant ethane concentrations at WK 250 were not accompanied by detectable ethylene concentrations. This marks an important difference between the suspected biogenic methane at WL 140 and suspected petrogenic soil hydrocarbons at WK250. Hydrogen concentrations along the WL transect, shown in Figure 4b, weakly paralleled methane concentrations, but were not as elevated with respect to the northern extreme of transect WK as methane; the median hydrogen concentration from transect WL was 2 to 3 times higher than the corresponding value from the northern end of transect WK.

Transect WM ran north-south above the eastern perimeter of the upper SPR mine and was considerably further from Shear Zone D than was transect WK. Transect WM crossed a portion of the Devil's Backbone ridge that is in the process of being dissected by gully erosion. The gullies trend east-west and cut almost normally across the transect. Absolute concentrations of all gases were low during the time period that this transect was surveyed (see Appendix A, p. A-7). The soil had been relatively dry for several weeks prior to sampling and the porosity of the predominantly sandy surface soil is high; this undoubtedly led to greater atmospheric exchange and, presumably, to consequently low soil gas concentrations. During this period the absolute concentrations of target analytes were also significantly lower at other, previously surveyed locations (cf. transect WL June and July). Because of the generally low concentrations in the soil gas during this period, many of the samples showed no detectable concentrations of the target hydrocarbon analytes. Thus the hydrocarbon profile, other than methane concentration, was unavailable for any of the locations on transect WM. The number of locations for which hydrocarbon samples were taken during this time was small, 4 for transect WL and 6 for transect WM. In Figure 5a, the data from the transect have been separated with respect to the sample location relative to the mine perimeter. Sample points were classified as IN or OUT if they were clearly inboard or outboard of the mine perimeter; otherwise they were classified as being above the mine perimeter and labeled as EDGE. Inboard and outboard samples taken at the same distance along the transect came from the same landscape position. The data are again unfortunately sparse; but where inboard and outboard results can be compared, the outboard methane concentrations were consistently higher. The corresponding hydrogen concentrations show a similar tendency toward higher values for outboard measurements (Figure 5b). Additionally, the hydrogen concentrations oscillate with position along the transect, roughly reflecting the topography of the transect, but with clearly higher concentrations in the first 50 meters. The hydrogen data may reflect methane trends as they do at the other Weeks Island locations, but the methane results are simply too few to draw definitive conclusions.

The final surveyed area at Weeks Island, area W2, was on the northwest perimeter of the upper mine boundary near the site of a sinkhole (Sinkhole #2) discovered in early 1995 (Figure 6). Samples were distributed widely over this area, and were focused principally on various sections of the mine perimeter. Table I summarizes the gas concentration results from area W2. A 50 meter transect running north from monument UL62 and crossing over the mine boundary near the sinkhole showed the highest hydrogen concentrations in the area as the transect crossed the mine perimeter (sample M62N20). Elevated hydrogen was also found, to a lesser extent, 30 meters further north (M62N50). Elevated hydrogen was found in soil gas samples above the mine perimeter at 2 other points in the area. Only one of eight samples taken inboard of the mine perimeter showed elevated hydrogen concentrations, whereas 4 of 5 samples taken above the perimeter showed elevated hydrogen. The only substantially elevated methane concentration was in the soil gas sample taken near monument UL60. Samples taken 15-20 meters north of UL60, and also a sample from 50 meters north of UL62 showed very slightly elevated methane concentrations. Only two samples contained detectable higher hydrocarbons (C2+) at low ppbv levels and they both contained ethane and ethylene at equal concentrations. Samples taken at the edge of the sinkhole contained low concentrations of both hydrogen and methane.

Hydrocarbon Profiles

Three distinct hydrocarbon patterns were found at Weeks Island, in addition to the hydrogen and methane concentration results discussed so far. Figure 7 shows typical chromatographic traces for two of the hydrocarbon profiles along with a 1 ppmv calibration standard. The calibration standard contains the C1-C4 alkanes (methane through butane) and the corresponding 1-alkenes (e.g., ethylene, 1-propene, etc.) at 1 ppmv each. The standard components elute in pairs with the 1-alkene immediately preceding the corresponding alkane. The chromatogram of the soil gas from the background area typifies the hydrocarbon profile found at most locations where C2+ hydrocarbons were detected on Weeks Island, including a location from the 1994 survey (transect WB, Appendix A-2). Ethane and ethylene were present in approximately equal amounts as were propane and 1-propene. The same appears to be true for butane and 1-butene as well, though concentrations near method detection limits made such a determination difficult. The 1:1 ratio was presumed to be typical of near-surface soil gas hydrocarbons associated with deep natural sources; similar profiles were found in the soil gas at a location in Baton Rouge that was associated with a producing oil reservoir.

The hydrocarbon profile of soil gas samples taken from the 250 meter point on transect WK, on the other hand, showed a pronounced absence of alkenes, even when ethane concentrations approached 5ppm. The "high ethane/no ethylene" profile was found repeatedly at WK250 but nowhere else on Weeks Island except for a single occurrence at WK70 in June. A subsequent analysis at WK70 in July did not distinguish that point from the typical Weeks Island profile. According to Vermoesen *et al.*, ethylene is the most prominent biogenic hydrocarbon– after methane– in soil gas, and is present in very small quantities relative to methane.[21] Alkane/Alkene ratios greater than one have been considered strong indicators that the gas is at least partly derived from petroleum sources.[22] Thus, the preponderance of alkanes over alkenes in the hydrocarbon profile argues against a near-surface biogenic source for these hydrocarbons. The third type of profile, thought to suggest near-surface biogenic origin, contained high methane concentrations (over 2000 ppmv), but no detectable higher hydrocarbons above 50 ppbv. Figure 8 shows a comparison of typical high methane samples from transects WK and WL. Samples from transect WL showed no ethane or propane even when methane concentrations approached those found at WK250.

Stable Isotope Ratios

Stable isotope ratio analysis of the soil gas hydrocarbons was intended to confirm the source of hydrocarbons in the near-surface soil gas as petrogenic or biogenic. Unfortunately, the SIR samples that had been collected and sent for analysis as early as July 1995 had not been analyzed by the end of the project period. Delays were attributed to concerns by the laboratory that high concentrations of oxygen in the samples (10-20%) could lead to potentially explosive conditions during sample preparation. At this point, any SIRA results from the samples collected in 1995 would be suspect given the long delay between sample collection and analysis.

Gas Composition in Mine Salt

The gas chromatograms of samples taken from the nearby mine were not integrated as they were intended only for qualitative comparison with the Weeks Island soil gas profiles. The salt samples were taken from a nearby salt mine and, though they were not taken from a Weeks Island mine, they were presumed to be somewhat similar to Weeks salt. The chromatograms are presented in Appendix B, Figures B-1 through B-6. Even without integrating peak areas, it is apparent that salt from the blowout areas contains significantly more methane than the normal, non-gassy salt from the mine. Furthermore, the salt from near the largest of the three blowouts (blowout 3) contains the largest amount of methane. The sample of "anomalous" salt also contained significantly higher concentrations of methane than the normal salt. Expanded views of the chromatograms of gas from the anomalous salt sample (Figure 9a) and from one of the blowout locations (Figure 9b) show traces of ethylene, though at a concentrations much lower than ethane. All of the gas extracted from the mine salt except for the sample from blowout location 3 showed traces of ethylene. Any ethylene in the sample from the blowout 3 location would have been obscured by the extremely large methane peak, so it's possible that all of the gassy salt samples from the mine salt contained traces of ethylene.

DISCUSSION

The results from the present soil gas survey at Weeks Island can be divided into two main findings. First, there appears to be a correlation of soil gas anomalies with anomalous salt zones and associated subsurface features. Second, there is an apparent correlation of soil gas anomalies with possible increased dilatancy related to mine structures.

Hydrocarbon Anomaly Near Shear zone D

The most dramatic result from this gas survey was the occurrence of methane and hydrogen concentration spikes at the 250 meter point of transect WK. The soil gas at that point also included significant amounts of saturated hydrocarbons, namely ethane propane. An area along transect WL, located near a drainage ditch, had similarly high concentrations of methane that was likely to be of near-surface biogenic origin. Chromatographic analysis of the soil gas from the two locations showed that while the suspected biogenic methane was the only hydrocarbon in the sample, the soil gas from transect WK also contained ppmv levels of ethane and propane. This clearly distinguishes the two locations and strongly suggests that the methane at WK250 is not of near-surface biogenic origin. Further, the absence of unsaturated hydrocarbons (e.g., ethylene) also suggests that the source is not biogenic. In fact, the composition was more suggestive of a direct headspace sample of unweathered oil (see Figure 10).

The absence of alkenes in the soil gas also differentiates the soil gas at WK250 from all other samples taken at Weeks Island. Firm conclusions would require further investigation, but current results suggest several possibilities. It seems highly likely that the soil gas at WK250 is related to a high permeability pathway from a subsurface source. The pathway may be associated with Shear Zone D though this is slightly more speculative with only a single transect across the area. Coincidence with a topographic break thought to be related to Shear Zone D, however, introduces the possibility that the gas anomaly could have a source in the anomalous salt of Shear Zone D. Alternatively, the source could also be an oil or gas pocket in the salt not associated with Shear Zone D, or from the SPR repository oil . An important possibility regarding gas sources is that the gases may emanate from multiple sources, but are then conducted through a common fracture pattern in their upward migration. For example, the methane and hydrocarbons could emanate from gas pockets in the salt while the hydrogen permeates through the salt barrier from the SPR repository oil or is generated by the mixing of meteoric water into deep zones with ferrous mineral constituents (FeO). It should be noted that at this point, source attributions are only hypotheses; and the survey data to date cannot be considered conclusive with respect to the source of the detected gas.

If the source of the hydrocarbons found in the soil gas at WK250 is occluded gas in the anomalous salt of Shear Zone D, a question remains as to why no ethylene was found in the soil gas, even in samples containing the highest concentrations of ethane. Presumably, gas occluded in the Weeks dome salt would be similar to the salt from the mine on the nearby island and would contain some ethylene. Given the low concentrations of ethylene found in the salt gas, it is certainly possible that ethylene concentrations in the salt gas are too low to result in detectable ethylene concentrations at the surface. On the other hand, one might expect at least a trace of ethylene in samples containing over 40 ppmv ethane (sample #197, Appendix A). Given the tendency of anomalous salt toward higher permeability, the possibility that the gases are emanating directly from the SPR reservoir through the anomalous salt zone can not be ruled out.

Results from Alternate Salt Dome

The thirty samples taken from the alternate salt dome– transects AA, AB and AC– provided supportive evidence for the conclusions drawn from the Weeks Island data. Contamination of the soil gas samples during transit made the extended hydrocarbon analysis data from these transects unusable, although the methane data were unaffected. Methane concentrations near the origin of transect AA (AA0) showed significant elevations compared with points further removed from the suspected zone of gassy salt. Hydrogen concentrations generally paralleled methane concentrations; although hydrogen concentrations tended to have more variability and the concentration differences between points near the feature and points further from the feature were not as dramatic. By far the highest methane concentration was in the sinkhole near the origin of transect AA (Appendix C-1). The hydrogen concentration in the sinkhole soil was elevated as well, though the highest hydrogen concentration measured on the transect was associated with the high methane concentration at the 5m point (AA5). The results from a repeat survey (Appendix C-2) of transect AA were not so straightforward, although the maximum hydrogen and methane concentrations were still within 15m of the transect AA origin.

Elevated methane and hydrogen concentrations were found on transect AB; but, because of the orientation of the transect, no conclusions could be drawn beyond the inference that the transect crossed a possibly anomalous area. Methane results were not available for transect AC, but the hydrogen analyses showed a distinct maximum at the 30 meter point (AA30). This coincided with a small topographic break which could be a surface expression of the suspected gassy salt feature.

The absence of both SIRA results and, particularly, extended hydrocarbon analyses leaves the origin of the soil gas anomalies on transects AA, AB and AC undetermined. The elevated methane concentrations could have arisen from biogenic methane production or from gas in the salt below. Detection of ethylene in these samples would have greatly strengthened the case for attributing SPR oil as the source of the hydrocarbons at WK250 on Weeks Island. Without the complementary laboratory analyses, however, only the correlation between a suspected subsurface feature and anomalous soil gas readings can be asserted.

Effect of mine structure

Evidence for the effect of the mine structure (e.g., dilatancy or microfracturing in the salt near the mine perimeter) on soil gas concentrations can be found at three separate locations around the island. First is the area encompassed by the northern section of transects WK and WL which lie in similar orientation to the perimeter of the lower mine level. The second location, area W2, is adjacent to the sinkhole on the northwestern perimeter of the upper mine where 20 samples were obtained at various locations near the mine perimeter. Finally, data from transect WM, along the eastern perimeter of the upper mine, allowed comparison of sample locations with similar landscape positions but different positions with respect to the mine perimeter.

The hydrogen profile across the 400 meter position of transect WK showed a significant break, with hydrogen concentrations at the northern extreme (>550m) of the transect being approximately an order of magnitude less than concentrations at positions just south of the 400 meter position (Figure 3a). WK400 was near the point that the transect crosses over the lower mine boundary, but also near the mapped location of an intersection of Shear Zones A and D. The differences between points north and south of WK400 may reflect a weak effect of the mine dilatancy or an anomaly related to the intersection of the shear zones A and D. Hydrogen concentrations from transect WL, which lies in similar relationship to the mine boundary, compare similarly with the northern extreme of transect WK although the difference was not as large. Fewer methane results were available, but the comparison seems to hold for methane as well. Comparisons between the northern extreme of transect WK and transect WL should be taken cautiously, however, as the concentrations are low, the number of data points is small and, most importantly, they are situated near a boundary between differing soil types. The effect of soil type on gas concentrations can not be ruled out in accounting for the higher concentrations at WL compared with the northern extreme of transect WK.

Soil type difference was not a significant factor in the results from survey area W2. All samples from area W2 were from brown silty loess soils on landscape ridges adjacent to a ravine. The soil gas concentrations of hydrogen, especially, and methane showed strong evidence of higher concentrations in samples associated with the upper-level SPR mine edge, and particularly with the edge near sinkhole #2. Few of the samples were clearly outboard of the mine perimeter at this location so the composition of the soil gas further beyond the perimeter remains unknown. Further, there is no reason to expect that the surface soil gas expression of a dilatancy effect would show up as a spike directly above the subsurface feature itself. Microfracture orientation and soil permeability may channel the gas a notable distance away from the mine edge. That the presentation of these data may make that implication may be simply a coincidence or the result of a relatively small data set. Additional transects from inboard to outboard of the mine perimeter boundary could show a pattern that correlates to dilatancy structures formed along the mine perimeter. Unfortunately, the limited scope of this soil-gas survey program did not allow for collecting the additional samples needed to provide a more definitive data set.

Aspects of the soil-gas survey along transect WM were designed to further investigate the effects of mine boundaries on soil gas concentrations. The effect of landscape position is clearly visible in the hydrogen profile of this transect (Figure 5), which was cut by several ravines; concentration highs in the profile generally relate to higher landscape positions. Inboard and/or outboard samples were taken at points where the inboard, outboard, and edge samples could be taken from the same landscape position. On examining the results presented in Figures 5a and 5b two relationships become evident. First, landscape position and position with respect to the mine boundary affects the concentration of both hydrogen and, seemingly, methane. When similar landscape positions are compared– such as at 45 meters, 120 meters, 180 meters, and 210 meters on transect WM– the samples outside the mine perimeter have higher concentrations than those above the mine edge and above the mine proper. Here again is preliminary evidence that the presence of the mine boundary and associated dilatancy affects the soil gas results. This could be the same effect as seen in the 0-100 meter section of transect WK; although those data are confounded by the presence of a gravel and dirt road near the transect. Also, the samples from the first 100m of transect WK are somewhat further outboard of the mine perimeter than are the samples from transect WM. The evidence would be more convincing with supporting results from longer transects, analogous to transect WK, running from slightly inboard of the mine boundary to a point beyond the lower mine boundary. This would presumably include a surface expression of Shear Zone D similar to WK250. Again, the limited scope of this soil-gas survey program did not allow for collecting the additional samples needed to provide a more definitive data set.

The second relationship, again accounting for landscape differences, is the general decrease in concentrations with position along the transect. If dilatancy is a contributor to increased soil gas concentrations of the target analytes, then one may ask if the higher concentrations in this area represent significantly increased risk of subsidence. The results from area W2, scant though they are, suggest that the soil gas anomalies may be of greater magnitude on the mine boundary near the sinkhole. A causal relationship between microsubsidence and soil gas anomalies is certainly suggested by the work of Wassman[23] on stress/strain and subsidence over caverns in bedded salt in the Netherlands. Thus the portion of transect WM with the most elevated readings warrants additional investigation, if a more definitive proof of the relationship between soil gas results and microsubsidence is desired.

CONCLUSIONS

The results of the current near-surface soil gas survey of Weeks Island suggest a significant relationship between anomalies in surface soil gas concentrations and subsurface features such as anomalous zones in the salt and dilatant zones associated with the mine edge structures at Weeks Island. The surface expression of an anomalous salt zone, Shear Zone D, has been tentatively identified on the basis of soil gas profiles. The source of the hydrocarbons in the soil gas at WK250 is uncertain. The gas may derive from occluded gas in anomalous salt associated with Shear Zone D; however, the possibility exists that hydrocarbons from the SPR reservoir may be permeating through the anomalous salt associated with the eastern portion of the SPR mine perimeter.

The results also have repeatedly suggested that dilatancy associated with the mines leads to anomalously high concentrations of hydrogen and possibly methane as well. The limited size and scope of the sampling design has left unanswered important questions about the specific source and transport of the anomalous gases, especially with respect to the effect of the mine structure. The extended hydrocarbon analysis of the C2+ hydrocarbons has been useful for distinguishing different types of soil gas anomalies, specifically for distinguishing near-surface biogenic anomalies from more important subsurface related anomalies.

In conjunction with other geological interpretations the apparent correlation between near-surface soil gas results and dilatancy effects at the mine perimeters may provide a means for early detection of stress/strain effects on the mine relevant at Weeks Island and possibly at other locations. Near-surface gas mapping technique can be very useful tool for elucidating subsurface structure and for site characterizations. While the data from this small survey are certainly not comprehensive or fully conclusive on their own, they demonstrate that a soil gas survey can provide complementary information that is both valuable and easily obtainable to investigations of salt dome structures. This technique is appreciably less expensive, quicker, and simpler than traditional geophysical diagnostic techniques, potentially yielding a distinct cost-benefit advantage in appropriate situations.

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TABLE I. Area W2 results summary.

Position	IN/OUT	hydrogen*	methane*	comment
from Sinkhole				
3 m N		nd	—	
7 m N		nd	1.8	
3 m S		nd	1.3	
7 m S		nd	1.7	
from UL62				
3 m N	IN	1	—	
10. m N	IN	39	—	
20 m N	EDGE	434	—	highest reading in area
20 m N	EDGE	285	—	
30 m N	OUT	5	—	
40 m N	OUT	32	—	
50 m N	OUT	162	3.2	near a corner
from UL61				
1 m N	IN	2	2.3	
15 m N	IN	5	1.2	
from UL60				
1 m N	IN	6	6.5	near a corner
15 m N	EDGE	100	3.2	near a corner
25 m NW	OUT	nd	2.6	near a corner
from UL 57				
1 m N	IN	150	—	
15 m N	IN	6	1.5	
25 m NW	EDGE	245	—	
from UL 56				
1 m SE	IN	11		near a corner

* Values are chromatographic peak areas. To convert to ppmv, multiply by 0.7 for hydrogen and by 1 for methane.

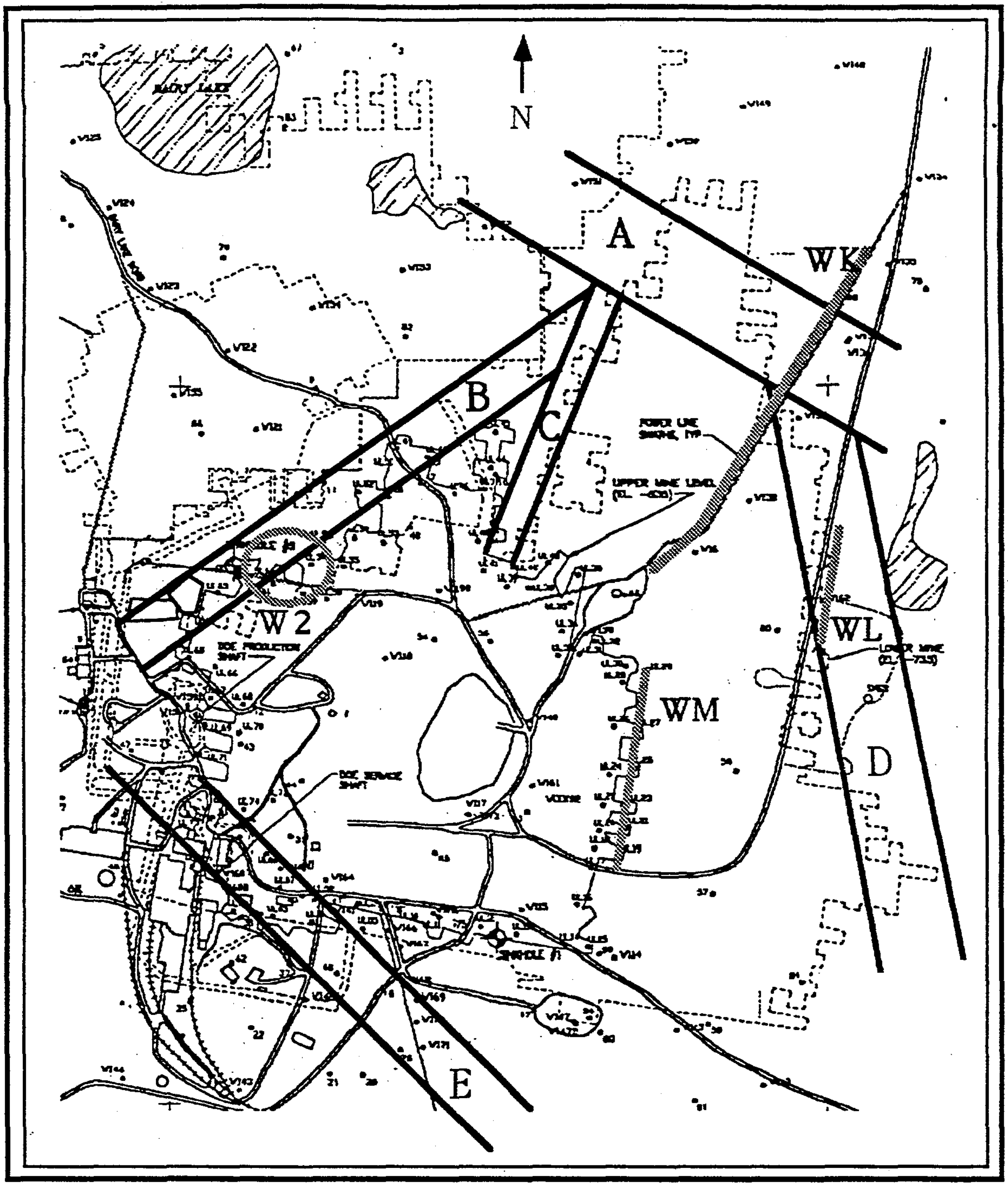


Figure 1. Map of Weeks Island showing mapped shear zones and sampling transects (after ref. 8).

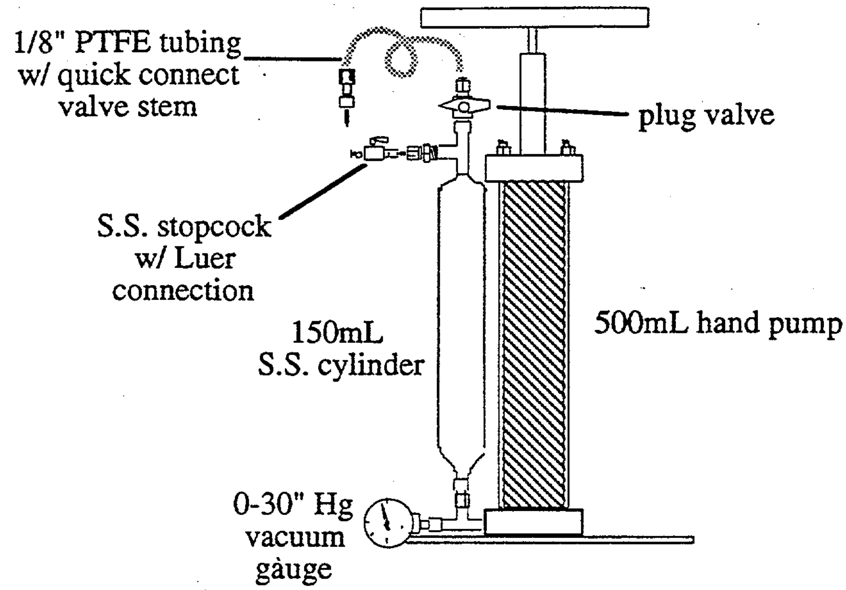
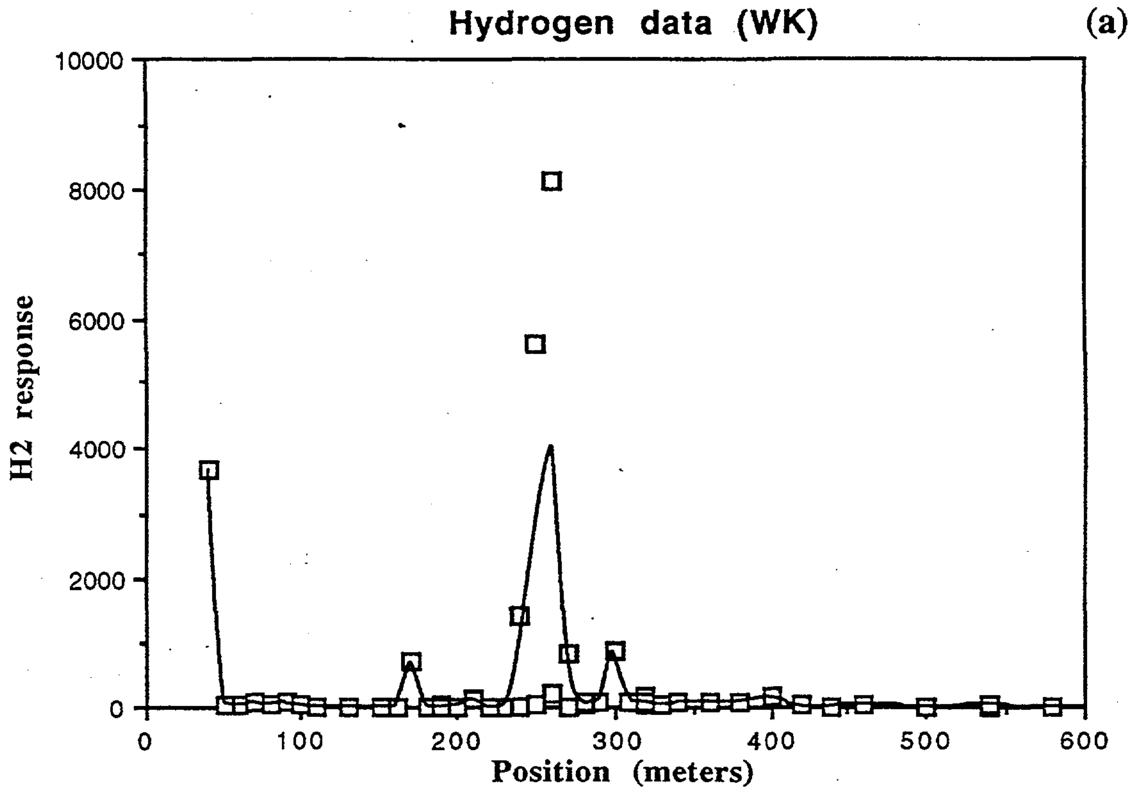


Figure 2. Diagram of portable soil gas sampler.



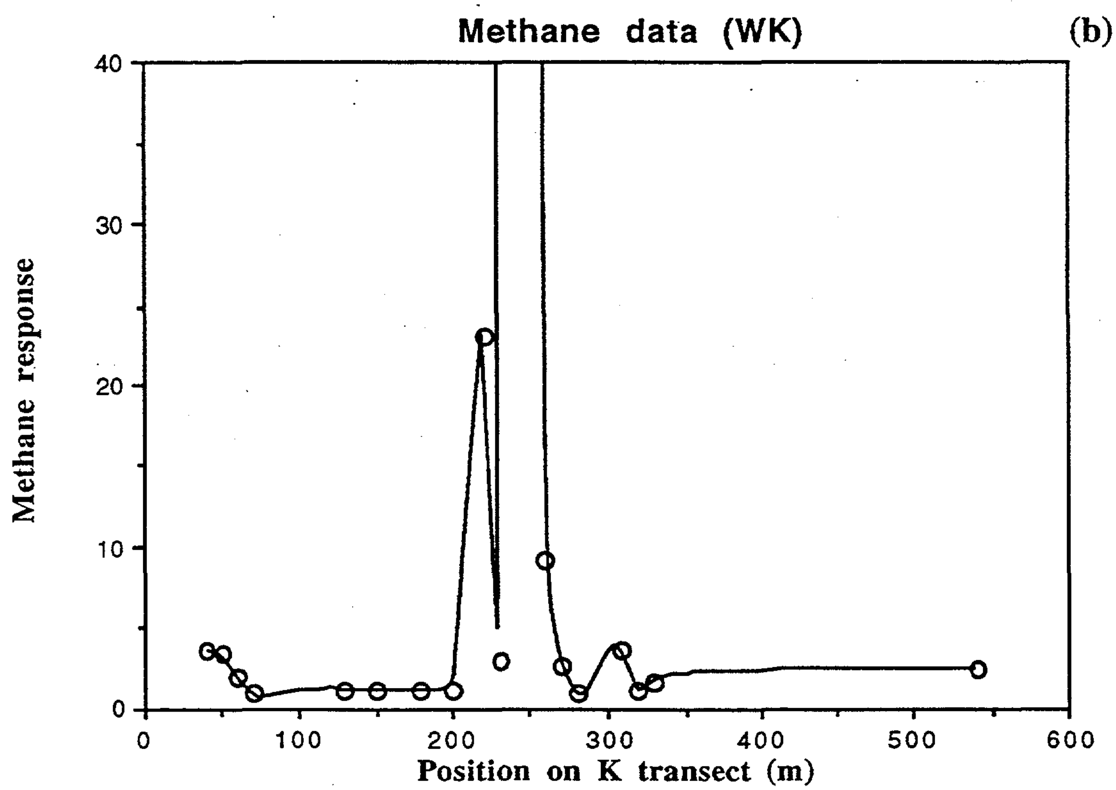


Figure 3. Profile of hydrogen (a) and methane (b) concentrations across transect WK. To convert chromatographic response to ppmv, multiply by 0.7 for H_2 and by 1.0 for methane

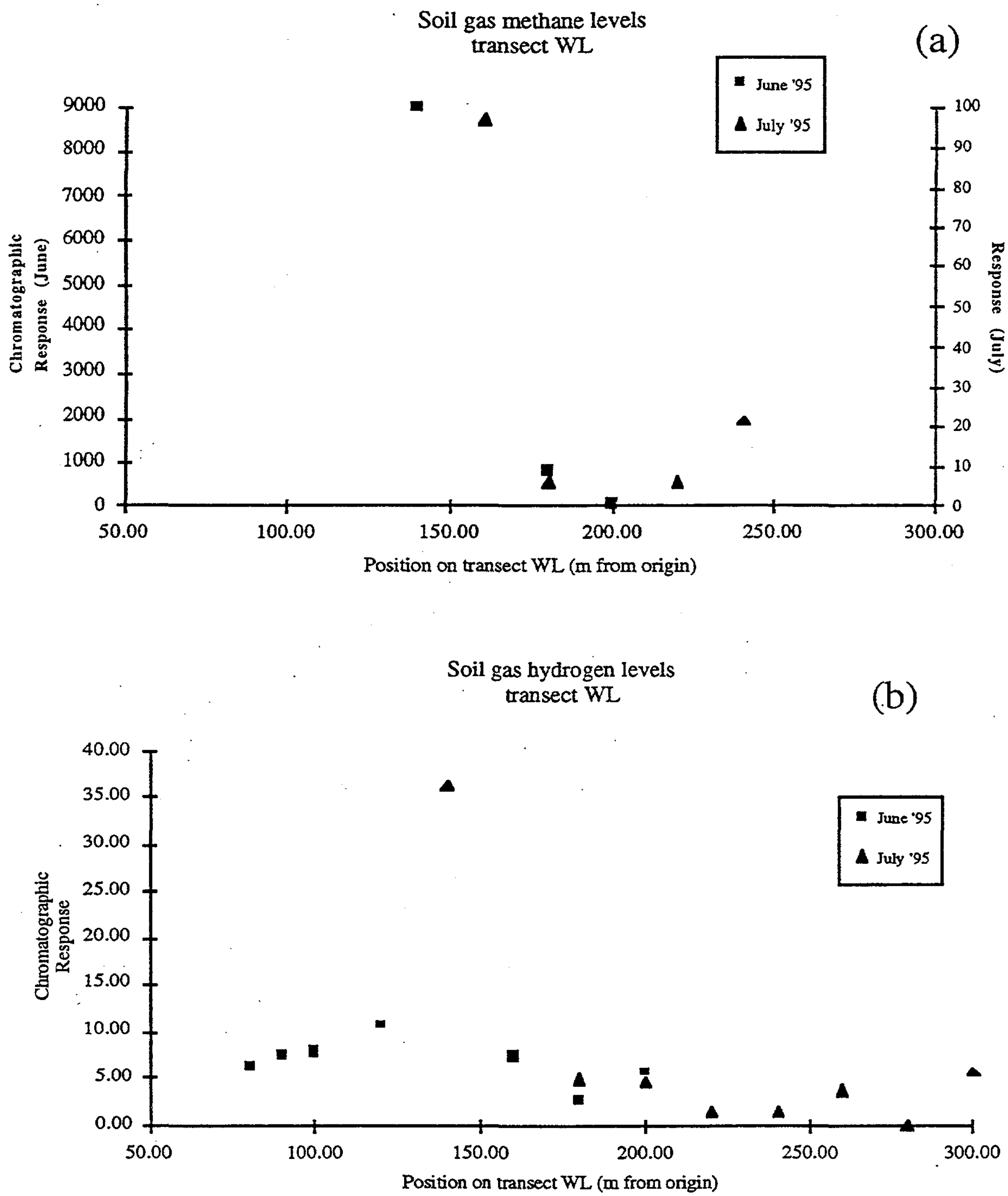
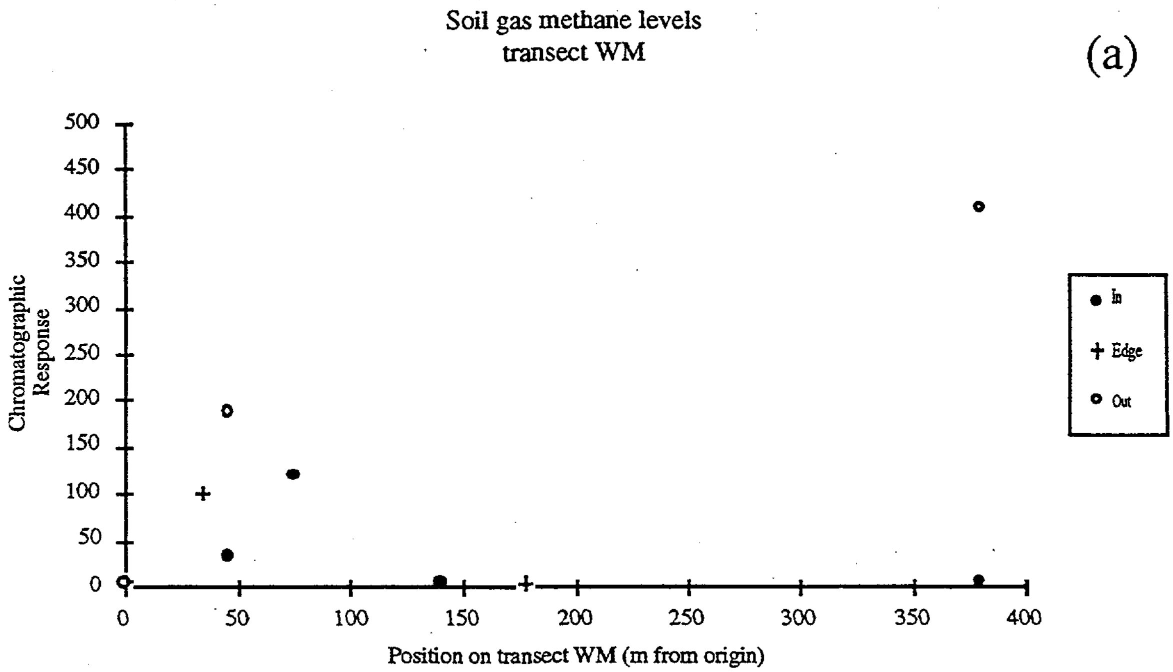


Figure 4. Profile of methane (a) and hydrogen (b) across transect WL. To convert chromatographic response to ppmv, multiply by 0.7 for H_2 and by 1.0 for methane



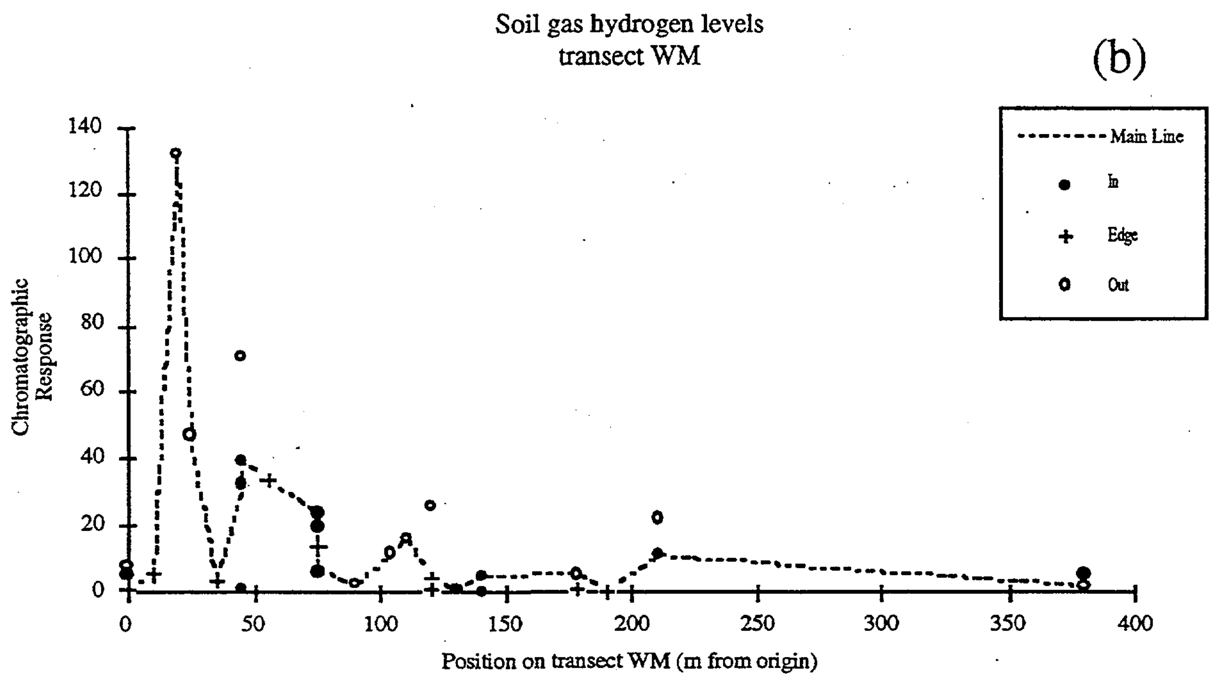


Figure 5. Profile of methane (a) and hydrogen (b) across transect WM. To convert chromatographic response to ppmv, multiply by 0.7 for H_2 and by 1.0 for methane

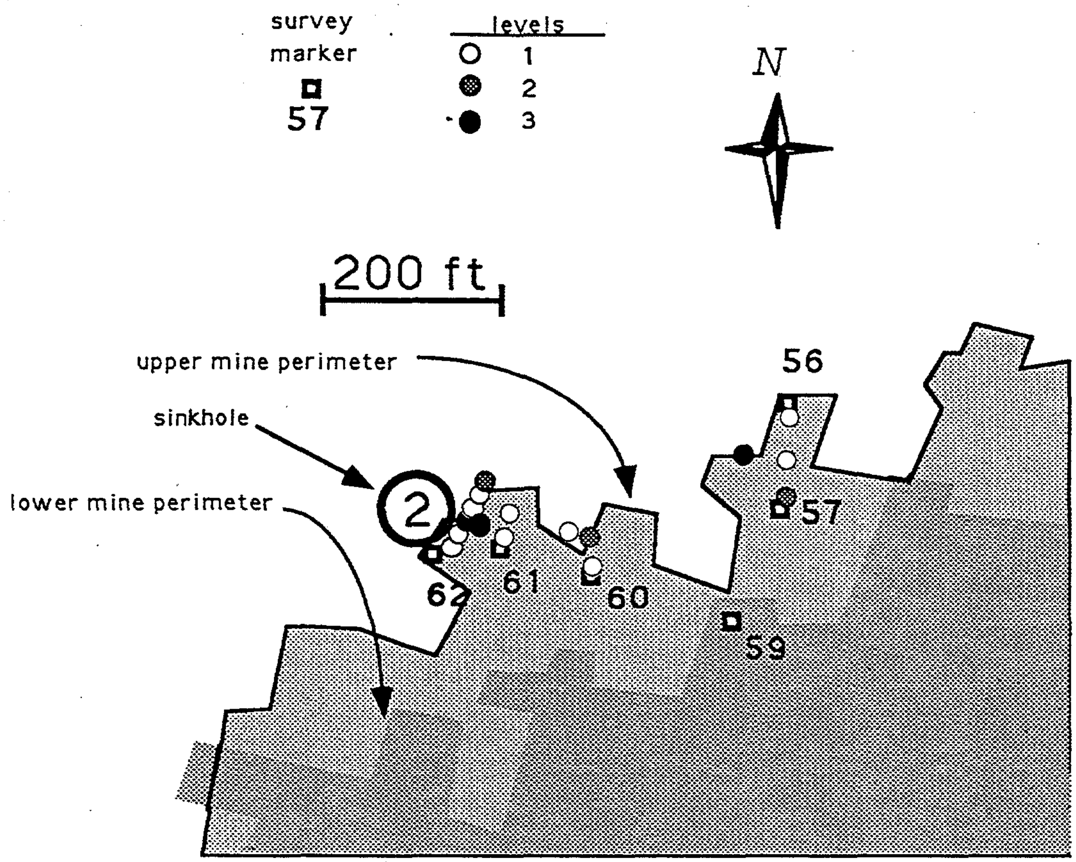


Figure 6. Distribution of hydrogen anomalies across area W2 near sinkhole #2.

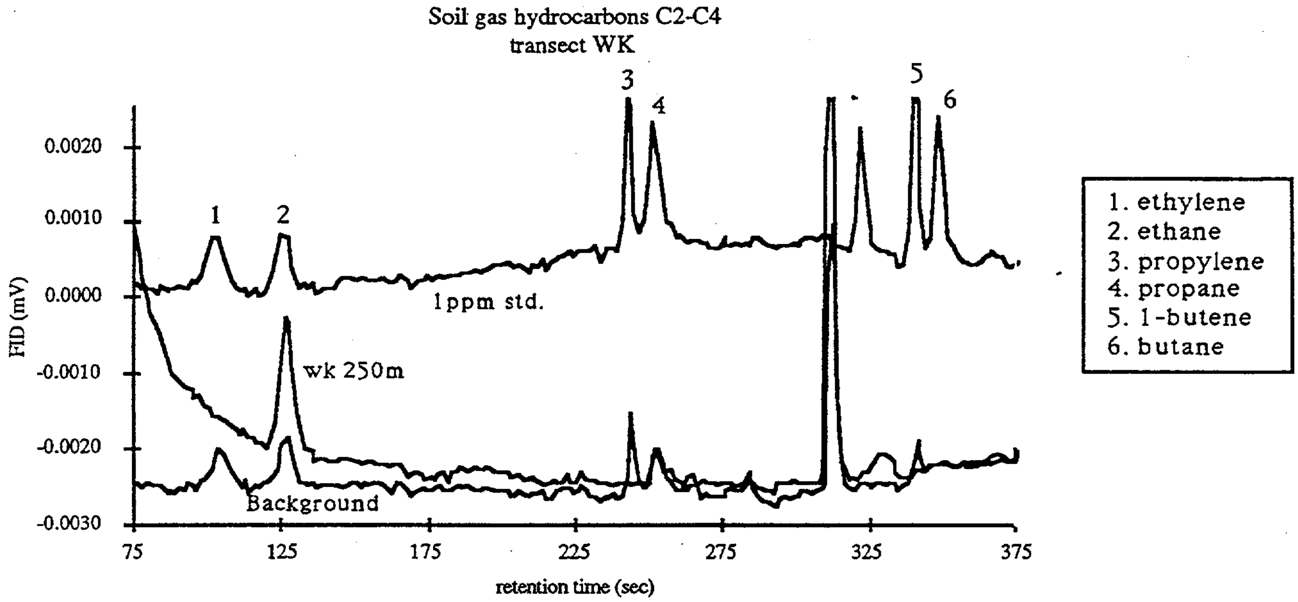


Figure 7. Chromatographic traces showing hydrocarbon profile for two different locations at Weeks Island. Methane (not shown) elutes at 60 seconds (cf. Figure 8).

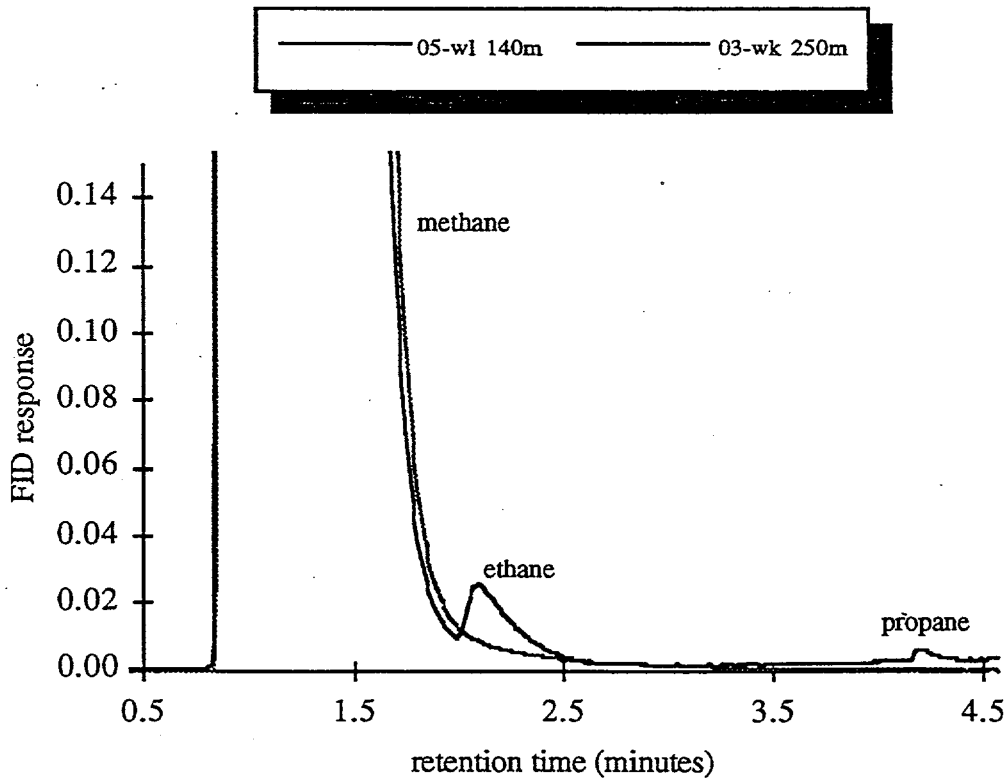


Figure 8. Comparison of high methane samples from transect WL (presumed biogenic) and from transect WK.

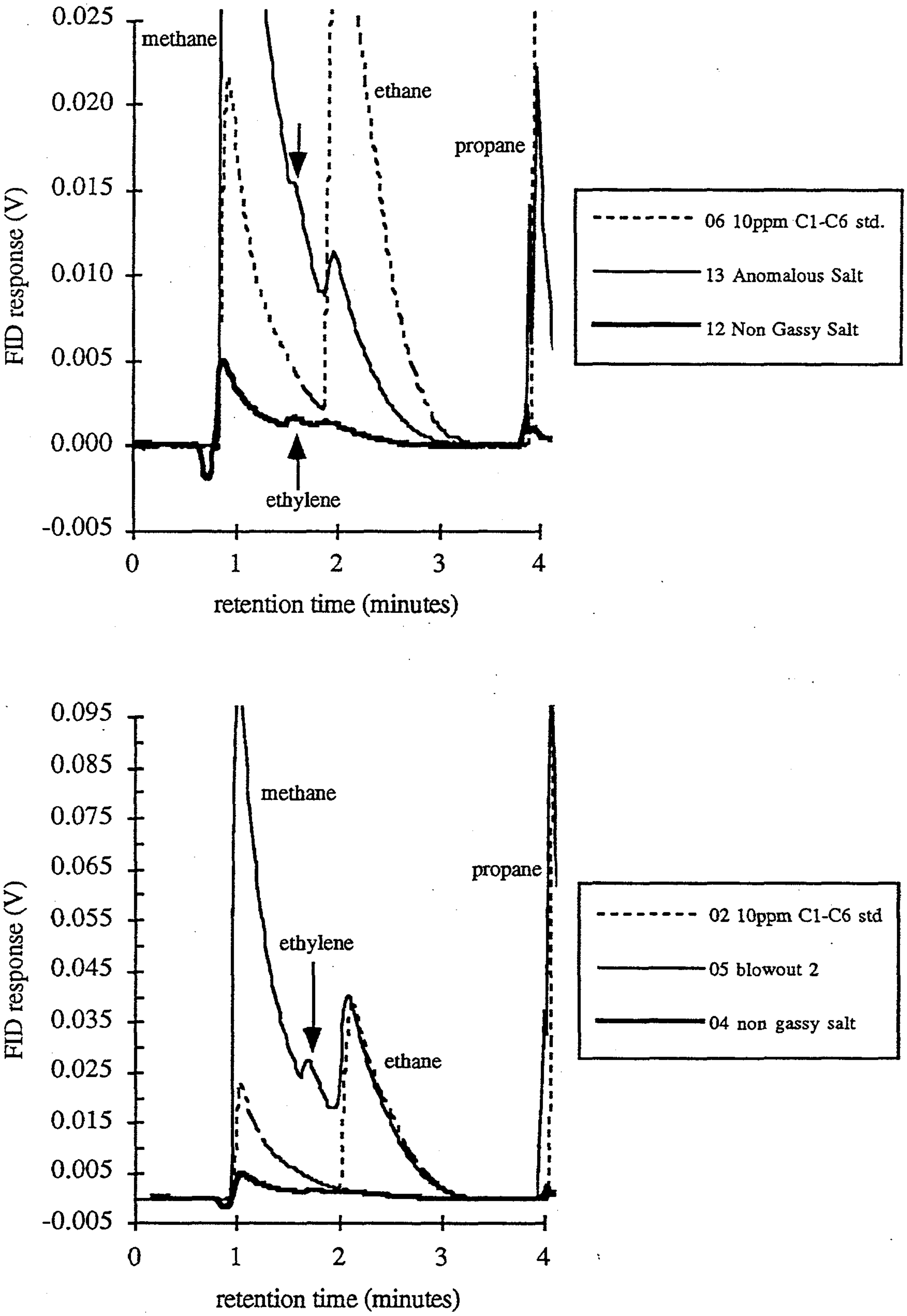


Figure 9. Evidence of ethylene in salt samples from a mine near Weeks Island.

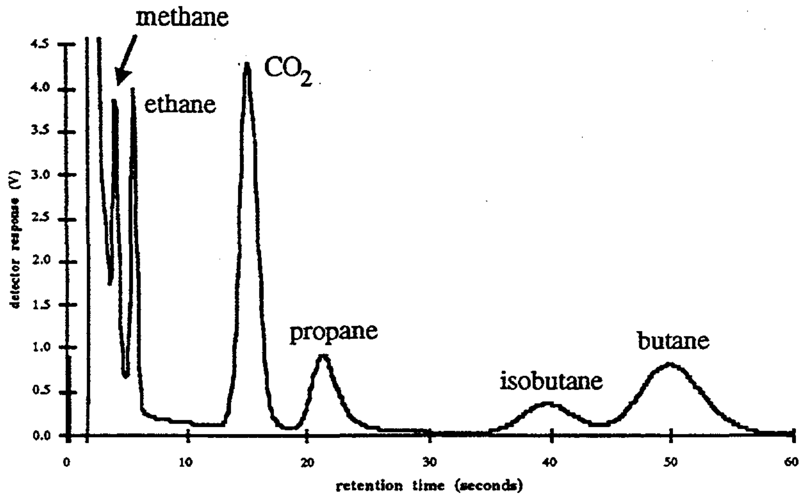


Figure 10. Chromatogram of headspace above an oil sample taken from the SPR facility at Weeks Island, LA. Note the absence of ethylene and 1-propene. (M200 GC, Isothermal at 100°C, HayeSep A column)

APPENDIX A

NEAR SURFACE SOIL GAS DATA, WEEKS ISLAND, LA
MAY-JULY, 1995

May 15, 1995. Weeks Island

position (m from transect origin)	transect	sample #	hydrogen (ppmv)	laboratory run #	methane (ppmv)
100	WK	43	2.28		no methane analyses for May 15
110	WK	44	0.21		
110	WK	45	0.07		
130	WK	46	0.11		
150	WK	47	0.16		
170	WK	48	49.85		
190	WK	49	3.21		
190	WK	50	0.37		
210	WK	51	9.31		
220	WK	52	0.36		
230	WK	53	0.66		
240	WK	55	99.78		
250	WK	54	3.27		
260	WK	57	568.82		
270	WK	58	60.13		
280	WK	59	3.24		
300	WK	60	62.62		
320	WK	61	2.64		
320	WK	62	10.17		
340	WK	63	4.38		
360	WK	64	6.38		
380	WK	65	6.29		
400	WK	66	10.31		
420	WK	67	1.49		
440	WK	68	0.99		
460	WK	69	3.88		
500	WK	70	0.38		
540	WK	71	2.39		
580	WK	72	0.34		
620	WK	73	0.05		
660	WK	74	0.06		
700	WK	75	0.27		

May 16, 1995. Weeks Island

position (m from transect origin)	transect	sample #	hydrogen (ppmv)	laboratory run #	methane (ppmv)	ethane (ppmv)	ethylene (ppmv)	propane (ppmv)
40	WK	77	785	11	7.0	1.3	1.5	0.9
50	WK	76	5	10	6.4	n.d.	n.d.	
60	WK	78	7	12	5.0	n.d.	n.d.	0.5
70	WK	79	15	16	3.9	n.d.	n.d.	n.d.
80	WK	80	5					
90	WK	81	13					
110	WK	82	1					
130	WK	83	1	17	4.4	n.d.	n.d.	n.d.
150	WK	84	1	18	4.2	n.d.	n.d.	n.d.
160	WK	85	3					
160	WK	86	1					
180	WK	87	0	19	4.2	n.d.	n.d.	n.d.
190	WK	88	0					
200	WK	89	1	21	4.3	n.d.	n.d.	n.d.
210	WK	90	28					
220	WK	91	1	22	27.4	n.d.	n.d.	n.d.
230	WK	92	3	23	5.1	n.d.	n.d.	n.d.
240	WK	93	0					
250	WK	94	1196	24	2291.5	4.7	n.d.	0.9
260	WK	95	41	25	9.5	n.d.	n.d.	n.d.
270	WK	96	2	26	5.9	n.d.	n.d.	n.d.
280	WK	98	14	27	4.2	n.d.	n.d.	n.d.
290	WK	99	15					
310	WK	100	19	20	5.8	n.d.	n.d.	n.d.
320	WK	101	21	28	4.3	n.d.	n.d.	n.d.
330	WK	102	8	29	4.7	n.d.	n.d.	n.d.
540	WK	103	4	30	5.3	n.d.	n.d.	0.4
540	WK	104	7					
control site 1		105	516	31	7.1	1.8	2.4	1.2
control site 1		106	597					
control site 3		107	12					
control site 5		108	12					
30m from sinkhole #1	WA	109	3					
30m from sinkhole #1	WA	110	1					
140	WB	111	10	38	4.9	n.d.	n.d.	n.d.
140	WB	112	276	39	6.9	1.4	1.5	1.2

May 17, 1995. Weeks Island, Sinkhole #2.

position (m from transect origin)	transect	sample #	hydrogen (ppmv)	laboratory run #	methane (ppmv)	ethane (ppmv)	ethylene (ppmv)	propane (ppmv)
Sinkhole 2								
North 3		113	0					
North 7		114	3	44	1.9	n.d	n.d	n.d
South 3		115	4	45	1.3	n.d	n.d	n.d
South 7		116	1	46	1.7	n.d	n.d	n.d
Marker 62								
North 50		117	114	53	3.2	1.1	1.5	n.d
North 40		118	22					
North 30		119	4					
North 20		120	304					
North 10		121	28					
North 3		122	1					
North 20		123	199					
Marker 61								
N.W. 1		124	1	47	2.3	n.d	n.d	n.d
North 15		125	4	48	1.2	n.d	n.d	n.d
Marker 57								
North 1		127	105					
North 16		128	4	49	1.5	n.d	n.d	n.d
North 32		130	171					
Marker 56								
S.E. 1		129	8					
Marker 60								
North 1		131	4	50	6.5	n.d	n.d	n.d
North 15		132	70	51	3.2	n.d	n.d	n.d
N.W. 25		133	0	52	2.7	n.d	n.d	0.3

June 22, 1995. Weeks Island.

position (m from transect origin)	transect	sample #	hydrogen (ppmv)	laboratory run #	methane (ppmv)	ethane (ppmv)	ethylene (ppmv)	propane (ppmv)
650	WK	188	0	04	13.7	n.d.	n.d.	n.d.
650	WK	189	0					
650	WK	190	1					
300	WK	191	7					
300	WK	192	2					
300	WK	193	5					
280	WK	194	22					
270	WK	195	8					
260	WK	196	13					
250	WK	197	6	03	8638.9	98.1	n.d.	n.d.
240	WK	198	1					
230	WK	199	9					
250	WK	200	6					
250	WK	201	35					
70	WK	202	39	08	5822.0	21.1	n.d.	n.d.
60	WK	203	4	09	19.4	n.d.	n.d.	n.d.
60	WK	204	8					
50	WK	205	29	10	19.3	n.d.	n.d.	n.d.
30	WK	206	48					
40	WK	207	117	11	21.8	n.d.	n.d.	n.d.
30	WK	208	0					
20	WK			12	22.9	n.d.	n.d.	n.d.
80.00	WL	209	4					
90.00	WL	210	5					
100.00	WL	211	6					
120.00	WL	212	8					
140.00	WL	213	64	05	8975.3	n.d.	n.d.	n.d.
160.00	WL	214	5					
180.00	WL	215	2	13	836.6	n.d.	n.d.	n.d.
200.00	WL	216	4	14	38.3	n.d.	n.d.	n.d.

July 17-18, 1995. Weeks Island.

position (m from transect origin)	transect	sample #	hydrogen (ppm)	laboratory run #	methane (ppm)	ethane	ethylene	propane
0	WM	217	0.78	05	7.0	n.d.	n.d.	n.d.
10	WM	220	3.54					
20	WM	221	92.31					
25	WM	222	33.03					
35	WM	223	2.42	08	101.3	n.d.	n.d.	n.d.
45	WM	224	22.62	09	30.6	n.d.	n.d.	n.d.
45	WM	229	27.43					
55	WM	227	23.74					
75	WM	228	16.70	12	8327.2	n.d.	n.d.	n.d.
75	WM	230	4.25					
75	WM	231	4.49					
90	WM	234	1.51					
104	WM	235	8.10					
110	WM	239	11.28					
120	WM	236	2.87					
130	WM	240	0.33					
140	WM	241	3.27	05	5.8	n.d.	n.d.	n.d.
178	WM	243	3.79					
190	WM	246	0.08					
210	WM	247	7.63					
380	WM	249	1.47	08	406.6	n.d.	n.d.	n.d.
140	WL	256	25.36					
160	WL	255	78.25	11	96.9	n.d.	n.d.	n.d.
180	WL	254	3.44	12	5.9	n.d.	n.d.	n.d.
200	WL	252	3.27					
220	WL	253	1.10	13	6.0	n.d.	n.d.	n.d.
240	WL	257	1.16	14	21.6	n.d.	n.d.	n.d.
260	WL	258	2.67					
280	WL	277	0.00					
300	WL	278	4.12					

July 17-18, 1995. Weeks Island.

The following three tables categorize data from transect WM by position relative to perimeter of upper mine. ON transect data are also presented in the transect WM table. OFF transect data are presented only in these three tables. OFF transect notation is followed by position relative to transect WM (e.g., E10 is 10m east of transect WM).

Off Mine (m from origin of WM)	On/Off transect	sample #	hydrogen (ppm)	laboratory run #	methane (ppm)	ethane	ethylene	propane
0	Off E10	218	5.75	06	3.9	n.d.	n.d.	n.d.
20	On	221	92.31					
25	On	222	33.03					
45	Off E10	225	49.43	10	188.6	n.d.	n.d.	n.d.
90	On	234	1.51					
104	On	235	8.10					
110	On	239	11.28					
120	Off E18	238	17.93					
178	On	243	3.79					
210	Off E25	248	15.62					
380	On	249	1.47	08	406.6	n.d.	n.d.	n.d.

On Mine (m from origin of WM)	On/Off transect	sample #	hydrogen (ppm)	laboratory run #	methane (ppm)	ethane	ethylene	propane
0	Off W30	219	3.66	07	5.8	n.d.	n.d.	n.d.
45	On	224	22.62	09	30.6	n.d.	n.d.	n.d.
45	Off W18	226	0.51	11	35.3	n.d.	n.d.	n.d.
45	On	229	27.43					
75	On	228	16.70	12	8327.2	n.d.	n.d.	n.d.
75	Off W2	230	4.25					
75	On	231	4.49					
75	Off W17	233	13.79	04	120.9	n.d.	n.d.	n.d.
130	On	240	0.33					
140	On	241	3.27	05	5.8	n.d.	n.d.	n.d.
140	Off W20	242	0.20	06	3.0	n.d.	n.d.	n.d.
210	On	247	7.63					
380	Off W25	250	3.70	09	6.5	n.d.	n.d.	n.d.
Monument UL32	see note	251	0.39	10	33.7	n.d.	n.d.	n.d.
note: monument UL32 is approximately 300m WNW of WM380.								

Mine Edge (m from origin of WM)	On/Off transect	sample #	hydrogen (ppm)	laboratory run #	methane (ppm)	ethane	ethylene	propane
0	On	217	0.78	05	7.0	n.d.	n.d.	n.d.
10	On	220	3.54					
35	On	223	2.42	08	101.3	n.d.	n.d.	n.d.
55	On	227	23.74					
75	Off E10	232	9.42	03	2993.6	n.d.	n.d.	n.d.
120	On	236	2.87					
120	Off W10	237	0.64					
178	Off W14	244	1.03	07	3.8	n.d.	n.d.	n.d.
178	Off W13	245	0.48					
190	On	246	0.08					

July 19, 1995. Weeks Island

position (m from transect origin)	transect	sample #	hydrogen (ppmv)	laboratory run #	methane (ppmv)	ethane (ppmv)	ethylene (ppmv)	propane (ppmv)
10	WK	276	1	13	16.3	n.d.	n.d.	n.d.
20	WK	275	1	12	12.9	n.d.	n.d.	n.d.
30	WK	274	17	10	14.1	n.d.	n.d.	n.d.
40	WK	273	35	09	17.5	1.4	1.5	n.d.
50	WK	272	16	08	19.5	n.d.	n.d.	n.d.
60	WK	271	25	07	15.7	1.7	1.5	2.2
70	WK	270	70	06	13.7	n.d.	n.d.	n.d.
80	WK	269	2	05	14.2	n.d.	n.d.	n.d.
90	WK	268	10	04	13.5	n.d.	n.d.	n.d.
100	WK	267	5	03	13.8	n.d.	n.d.	n.d.
250	WK	263	68	11	9035.3	223.8	n.d.	28.9
260	WK	264	3					
280	WK	265	10					
300	WK	266	4					
650	WK	259	1					
650	WK	260	1					
650	WK	261	1					
650	WK	262	2					
650	WK	279	0					
650	WK	280	1					

APPENDIX B

CHROMATOGRAMS OF GAS EXTRACTED FROM SALT SAMPLES TAKEN IN DOMAL SALT MINE NEAR WEEKS ISLAND, LA, NOVEMBER 1996

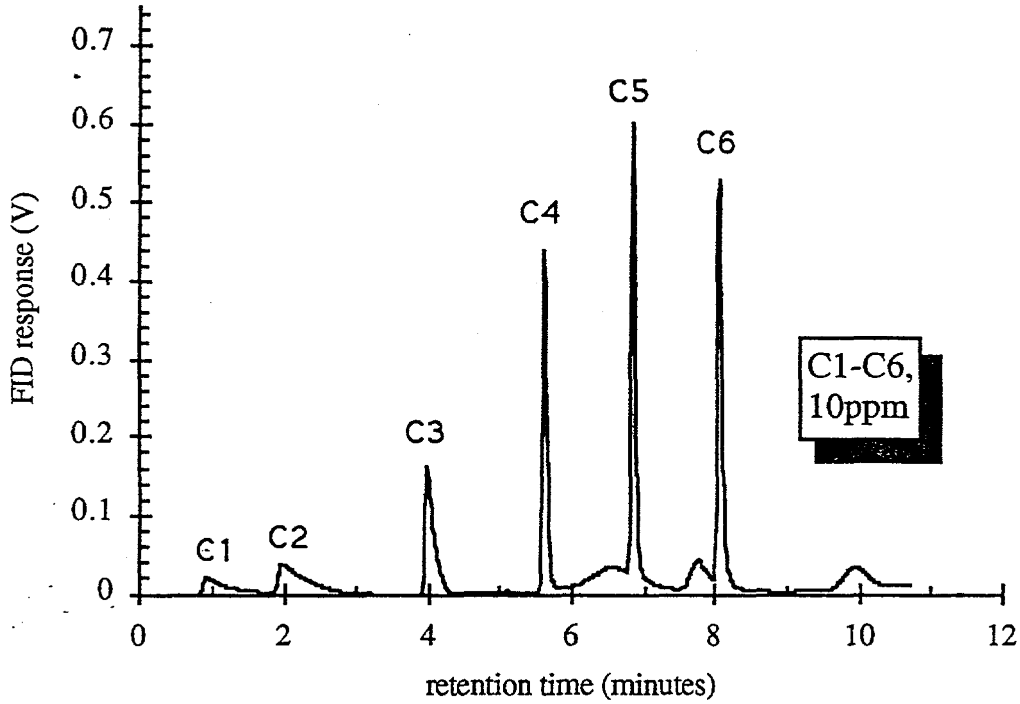


Figure B-1. 10 ppm by volume n-alkanes reference sample (methane through hexane).

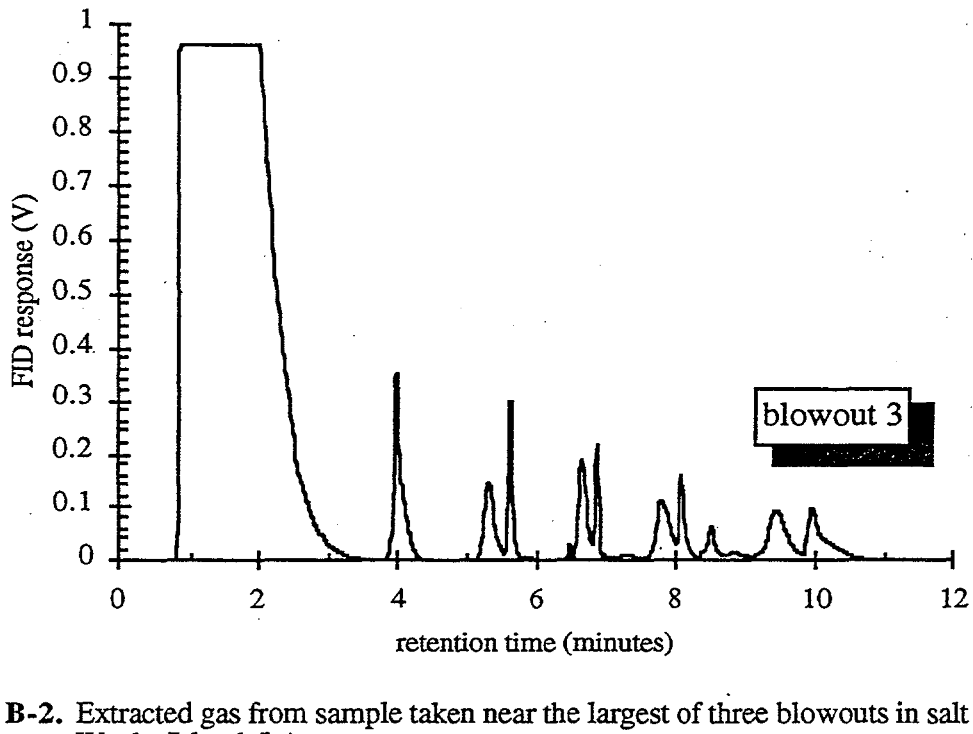


Figure B-2. Extracted gas from sample taken near the largest of three blowouts in salt mine near Weeks Island, LA.

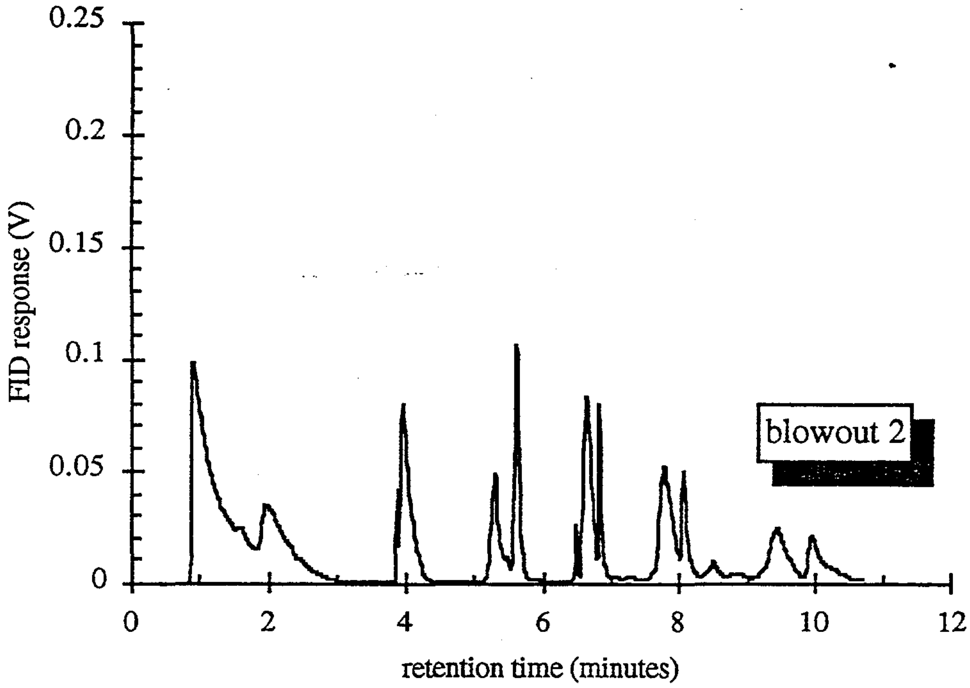


Figure B-3. Extracted gas from salt taken near a moderate blowout location in salt mine near Weeks Island, LA..

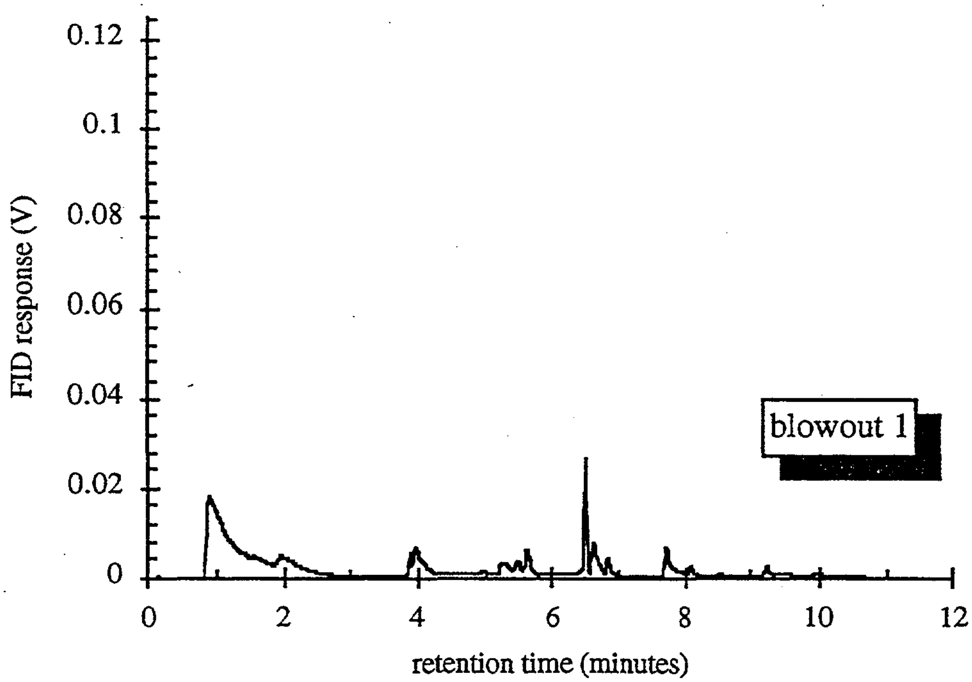


Figure B-4. Extracted gas from salt sample taken near a blowout location in salt mine near Weeks Island, LA..

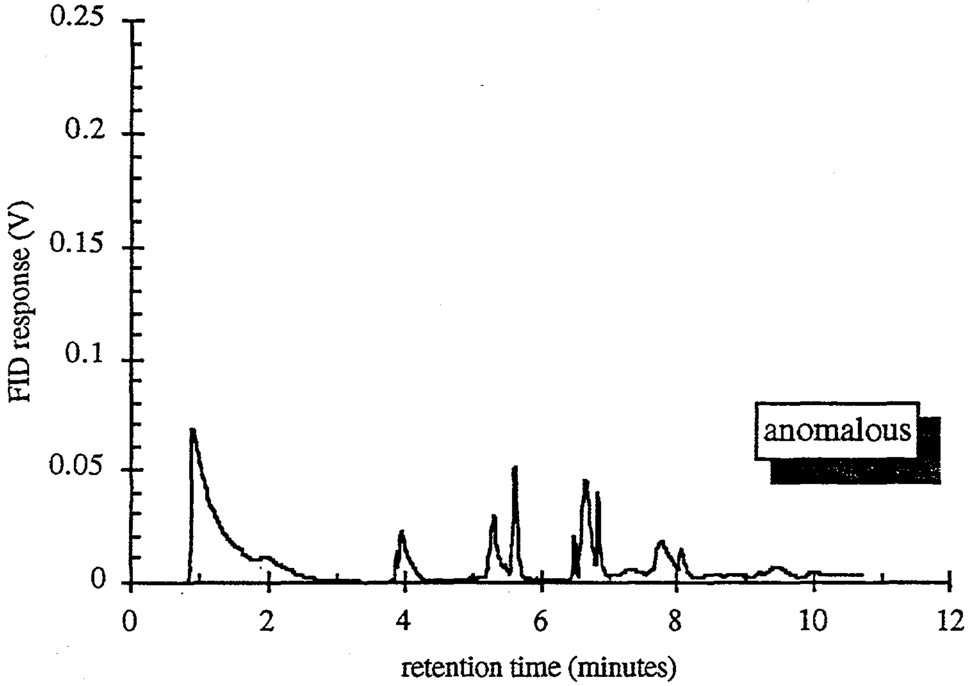


Figure B-5. Extracted gas from sample of anomalous salt taken from mine near Weeks Island, LA.

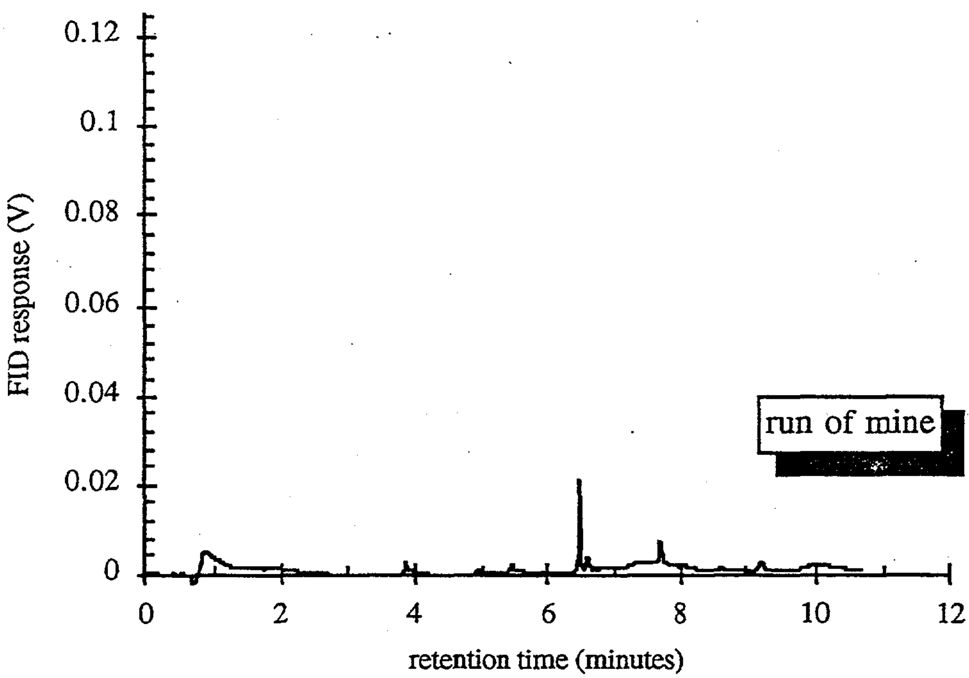


Figure B-6. Extracted gas from sample of normal salt taken from mine near Weeks Island, LA..

APPENDIX C

NEAR SURFACE SOIL GAS DATA, ALTERNATE SALT DOME SITE, SOUTH LOUISIANA
JUNE, 1995

June 20, 1995. Alternate Salt Dome Site.

position (m from transect origin)	transect	sample #	hydrogen (ppmv)	laboratory run #	methane (ppmv)	ethane (ppmv)	ethylene (ppmv)	propane (ppmv)
172	AA	134	7	19	14.4	extended hydrocarbon samples for June 20 were contaminated in transit.		
162	AA	135	14	21	11.7			
0	AA	136	42	22	15.1			
-2	AA	137	68	23	10280.0			
5	AA	138	1395	24	3492.8			
20	AA	139	16	25	168.3			
42	AA	140	12	26	42.7			
52	AA	141	49	31	24.3			
62	AA	142	5	32	16.1			
72	AA	143	78	42	18.3			
82	AA	144	4	33	15.4			
102	AA	145	4	34	13.8			
122	AA	146	17	35	18.5			
162	AA	147	13	36	17.4			
142	AA	148	26	37	15.8			

June 21, 1995. Alternate Salt Dome Site.

position (m from transect origin)	transect	sample #	hydrogen (ppmv)	laboratory run #	methane (ppmv)	ethane (ppmv)	ethylene (ppmv)	propane (ppmv)
72	AA	149	14.99					
62	AA	150	8.62	01	18.0	extended hydrocarbon samples for June 21 contaminated during transit		
52	AA	151	44.60	02	17.5			
52	AA	152	4.50					
42	AA	153	335.06	03	17.9			
42	AA	154	17.23					
35	AA	155	3.68	04	16.3			
35	AA	156	78.30					
25	AA	157	6.62	06	15.8			
15	AA	158	3.47	07	455.6			
15	AA	159	25.61					
10	AA	160	10.78	08	12.7			
5	AA	161	16.44	09	11.5			
5	AA	162	12.90					
0	AA	163	1393.28	10	13.4			
0	AA	164	65.23	11	13.7			
0	AA	165	35.57					
0	AA	166	4.33					
-2	AA	167	79.93					
10	AB	168	6.36					
10	AB	169	10.75					
20	AB	170	617.81		7102.0			
30	AB	171	8.94					
40	AB	172	0.00					
50	AB	173	9.55					
60	AB	174	2.47		26.9			
70	AB	175	113.76					
70	AB	176	20.90					
10	AC	180	12.64					
20	AC	181	160.93					
20	AC	182	20.72					
30	AC	183	1674.58					
30	AC	184	5176.76					
40	AC	185	32.99					
50	AC	186	12.31					
60	AC	187	2.02					

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