CASE STUDIES OF ANAEROBIC METHANE GENERATION AT A VARIETY OF HYDROCARBON FUEL CONTAMINATED SITES

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Recent studies and publications by the U. S. Air Force Center for Environmental Excellence indicate that anaerobic biodegradation processes dominate the natural "intrinsic" remediation of contaminated aquifers (Wiedemeier et al., 1995; Newell et al., 1995). Methanogenesis (39%) and sulfate reduction (29%) are estimated to account for approximately 68% of anaerobic degradation. The majority of previous studies have focused on dissolved phase contaminants, oxygen, nitrate, iron (II), sulfate and methane in groundwater, components which can vary spatially in an aquifer depending upon heterogeneous pathways and groundwater recharge. These studies have utilized data obtained mainly from monitor wells. The temporal changes caused by re-aeration, and the low density of monitor wells installed on most sites often significantly limit the spatial information.

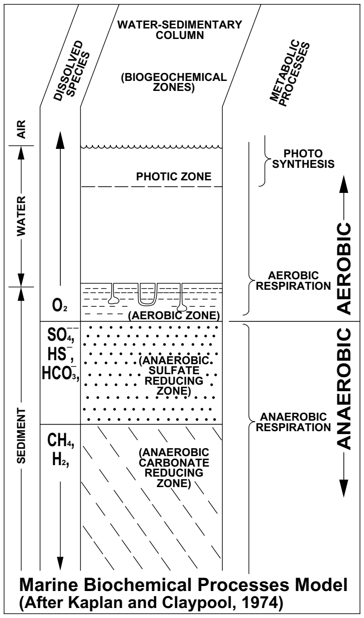
Extensive data collected by Exploration Technologies, Inc. (ETI) over the past several years have included dissolved gases (in groundwater) and soil gas from vadose zone soils. Results from actual field studies show that methane is generated in extremely high concentrations in aquifers as well as vadose zone soils. Methane vapor concentrations generated within the vadose zone are often within the percent range, and correlate directly with non-aqueous phase liquid (NAPL) contaminant plumes. Vadose zone methane in most cases provides the best estimate of the physical location of the most highly contaminated sediments. Although carbon dioxide is generated by the aerobic biodegradation of organic materials (and must be used with some caution), a concentrated buildup of carbon dioxide can also be used to identify a concentrated petroleum source in the subsurface. Indigenous bacteria that generate carbon dioxide under aerobic conditions and methane under anaerobic conditions are ubiquitous and occur at almost every site (Marrin, 1987b; Vance, 1993; Chapelle et al., 1996). The various case studies cited prove that aerobic and anaerobic biodegradation of hydrocarbon contaminants produce high concentrations of carbon dioxide and methane; these compounds are commonly the largest magnitude constituents present in the soil gas and dissolved gas mixtures.

The average concentration of carbon dioxide in ambient air is only 0.03 percent. Biodegradation of typical soil organic matter generally yields soil gas values between 0.2 to 3-5 percent (%). Higher concentrations of carbon dioxide measured in various soil vapor samples collected in the vicinity of subsurface petroleum contamination yields values as high as 5 to 30 percent, an indication that biodegradation is significantly enhanced within the area surveyed. Methane in ambient air ranges from 1.5 to 2 ppm by volume. Soil gas values where there is no pollution or deep petrogenic gas migration, generally range from 0.5 to 1 ppm, suggesting that normal soils act as a sink for atmospheric methane. Since biogenic methane is generated under anaerobic conditions, it is usually generated deeper in the subsurface sediments than carbon dioxide and appears to correlate very well with the location of liquid product (NAPL). As with carbon dioxide, the longer the pollution is present in the subsurface environment, the higher are the methane soil gas levels.

Numerous site assessment examples where these two biogenic gases were generated in association with different fuel releases (gasoline, jet fuel, kerosene, diesel, crude oil and propane cooking fuel) are illustrated by various component plume maps. Carbon dioxide commonly defines the shallow contamination and outer edges of the plumes, while methane defines the limits of the highly contaminated vadose zone sediments and/or groundwater. Assessments performed on sites containing different lithologies and fuel type releases are documented and demonstrate that hydrocarbon product type, coupled with the duration that the product has been in the subsurface environment, greatly affects the concentrations and types of biogenic gases generated. Both carbon dioxide and methane can also be measured with reasonable accuracy in the field using infrared detectors, and are highly recommended for field screening during an assessment.

Biogenic methane and carbon dioxide data, when measured in tandem with specific organic vapor components are very useful in defining the horizontal extent of hydrocarbon contaminants in the subsurface environment. The presence or absence of specific petroleum related hydrocarbons aids in interpretation and confirms the relationship of the biogenic gases to their appropriate sources. These two biogenic gases generally can be used for mapping the distribution of contaminated soils; even when the contamination is very old and the lighter hydrocarbon volatiles are nearly absent.

I. INTRODUCTION

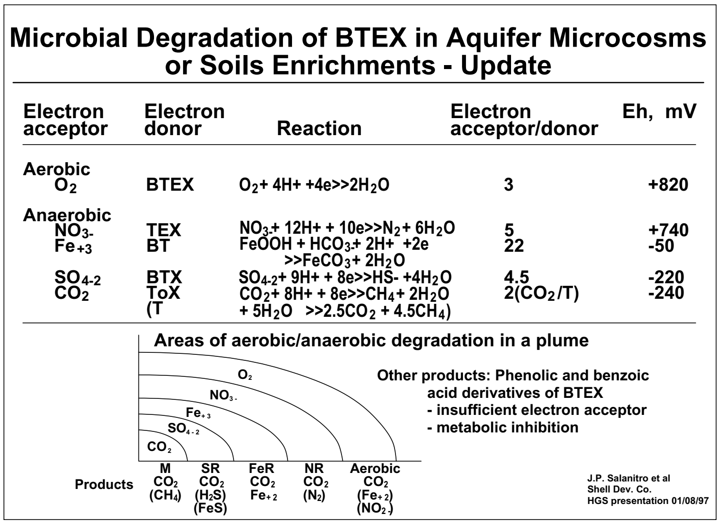


Marine Biochemical Processes Model (After Kaplan and Claypool, 1974)

Figure 1

Recent studies and publications by the U. S. Air Force Center for Environmental Excellence indicate that anaerobic biodegradation processes dominate the natural "intrinsic" remediation of contaminated aquifers (Wiedemeier et al.,1995; Newell et al., 1995). Methanogenesis (39%) and sulfate reduction (29%) are estimated to account for approximately 68% of anaerobic degradation. A marine sedimentary depositional model, first proposed by Claypool and Kaplan (1974) has an application in environmental science for explaining "intrinsic" bioremediation. This model, (Figure 1) was originally proposed to explain the biogeochemical processes that occur in a marine sedimentary environment. The biogeochemical processes associated with this model, which apply to the degradation of refined petroleum products, are explained in detail by Kaplan (1992), and supported by numerous studies (Anderson et al., 1983; MacDonald et al., 1989; Thompson, 1996). Typical reactions that occur are shown in Figure 2 (Salanitro, 1997). Some debate continues regarding whether anaerobic methane is generated from degradation of hydrocarbon contaminant sources, or from reducing conditions associated with the biodegradation cell creating the right conditions for methanogenesis of natural organic matter (Lundegard et al., 1997). ETI's examples provide empirical evidence that methane is generated in direct response to the presence of subsurface hydrocarbon contamination. Any organic matter, whether natural or anthropogenic, will generate methane under the appropriate reducing conditions. Studies performed over oil seeps in the Gulf of Mexico have shown that both petrogenic and biogenic methane isotopes are stimulated by reducing conditions provided by the hydrocarbon contamination (Anderson et al., 1983). The examples presented in this paper will show that methane plumes are generated in direct association with petroleum contamination. The clear association of carbon dioxide and methane from the same soil gas sample sites suggests that there must be some local oxygen sources within reasonable proximity to the contamination. Generation of both biogenic gases probably occurs within micro-pores, a process that may be quite complex.

Extensive data collected by Exploration Technologies, Inc. (ETI) over the past several years have included dissolved gases (in groundwater) and soil gas from vadose zone soils. Results from actual field studies show that methane occurs in extremely high concentrations in both vadose zone soils and aquifers. Methane concentrations found within the vadose zone are often within the percent range, and appear to correlate directly with liquid product contaminant plumes. Case studies demonstrate that vadose zone methane usually provides the best estimate of the physical location of the most highly contaminated sediments. Although carbon dioxide is generated by the aerobic biodegradation of organic materials (and must be used with some caution in mapping subsurface contamination), a concentrated buildup of carbon dioxide in soil gas often identifies a source of petroleum contamination in the subsurface. Indigenous bacteria that generate carbon dioxide under aerobic conditions and methane (under anaerobic conditions) are ubiquitous and occur at almost every site (Marrin, 1987b; Vance, 1993; Chapelle et al., 1996). The various case studies cited prove that aerobic and anaerobic biodegradation of numerous types of petroleum based contaminants produce high concentrations of carbon dioxide and methane. These biogenic gases are commonly the largest magnitude constituents present in the soil gas and/or dissolved gas mixtures.



Microbial Degradation of BTEX in Aquifer Microcosms or Soils Enrichments - Update

Electron acceptor	Electron donor	Reaction	Electron acceptor/donor	Eh, mV
Aerobic				
O_2	BTEX	O_2+ 4H+ +4e>>2H_2O	3	+820
Anaerobic				
NO_{3-}	TEX	NO_{3-}+ 12H+ + 10e>>N_2+ 6H_2O	5	+740
Fe_{+3}	BT	FeOOH + HCO_{3-}+ 2H+ +2e >>$FeCO_3$+ 2H_2O	22	-50
SO_{4-2}	BTX	SO_{4-2}+ 9H+ + 8e>>HS- +4H_2O	4.5	-220
CO_2	ToX (T	CO_2+ 8H+ + 8e>>CH_4+ 2H_2O + 5H_2O >>2.5CO_2 + 4.5CH_4)	2(CO_2/T)	-240

Other products: Phenolic and benzoic acid derivatives of BTEX
- insufficient electron acceptor
- metabolic inhibition

J.P. Salanitro et al
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HGS presentation 01/08/97

Figure 2

Surface geochemistry is the oldest method used for determining the presence of unrefined petroleum products, both at the surface and in the subsurface: Teplitz and Rogers (1932), Link (1952), Jones (1979), Janezic (1979), Mousseau and Williams (1979), Weismann (1980), Drozd et al. (1981), Williams et al. (1981), Jones and Thune (1982), Jones and Drozd (1983), Jones (1983), Richers (1984), Price and Heatherington (1984), Matthews et al. (1984), Jones and Burtell (1996), Jones et al. (in press). Extensive research has proven that light gases (methane, ethane, propane, and butanes) present in near surface seeps, measured directly over various producing fields, could be related directly to the type of hydrocarbons (oil versus gas) within the producing reservoir based upon the compositions of these gases (Jones and Drozd, 1983). These types of measurements can be utilized in frontier basins to predict the oil versus gas potential in advance of drilling. Similar soil gas geochemical methods have been recently utilized by environmental scientists: Baehr (1984), Bond et al. (1982), Lappala et al. (1983), Eklund et al. (1985), Kerfoot et al. (1986), Marrin (1987a, 1987b), Mohsen et al. (1983), Spittler, et al. (1985), Robins et al. (1990a, 1990b, 1995). The case studies cited show that the application of this exploration technology to environmental assessments offers a significant improvement in defining the horizontal and vertical extent of the liquid product (NAPL) sources, and the associated sorbed and dissolved phase contamination.

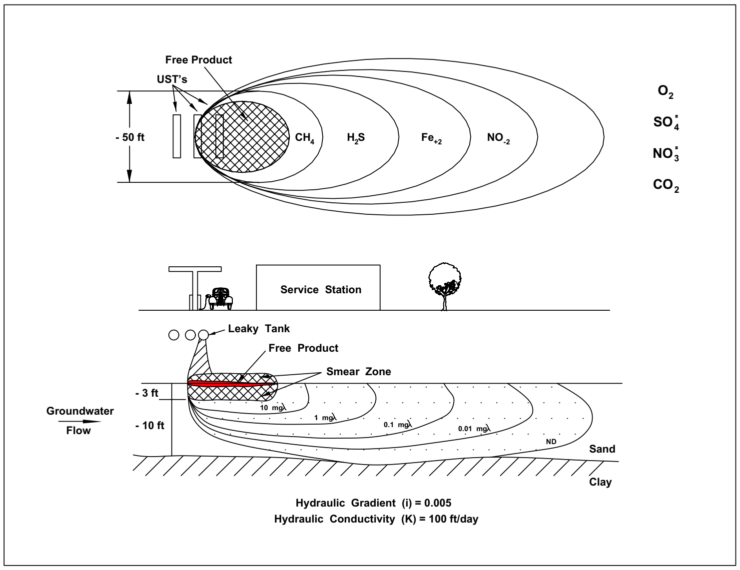


Figure 3

Figure 3 shows a simplified model that is commonly used to represent a typical plume (containing only one core) in the "intrinsic" bioremediation discussion. This model, however, is almost never adequate for describing and interpreting actual field conditions. Noted experts in the field of remediation have pointed out that the physical heterogeneity of the subsurface environment makes contaminant pathways extremely difficult to detect (Ward, 1996). These natural heterogeneities make it impossible to interpolate between sampling points in characterizing the subsurface, and can significantly reduce the effectiveness of remediation systems. Contaminant removal from inaccessible regions is controlled by diffusion rather than by groundwater flow, often adding decades to the cleanup process. Cherry (1996) has proposed a fringe and core model to point out that site assessments conducted using only monitor wells generally defines only the fringe, which is then commonly interpreted to represent the plume as a whole. This neglects the presence of individual cores, which are actually the source of the groundwater fringe. Due to the sparseness of control points, monitor well networks only rarely encounter these liquid product "cores" (Cherry, 1996). Soil vapor measurements are, therefore, often more effective than monitor wells in characterizing the entire plume because each individual core has a biodegradation halo. In addition, the majority of most contaminant plumes begin, and remain within the vadose zone as residual (or sorbed) phase contamination (Valkenburg, 1994).

II. LIGHT (C1-C4) AND GASOLINE RANGE (C5+) SOIL GASES

Although refined products, such as gasoline, are typically thought of as containing only C5 to C12 hydrocarbons, as reported by Johnson et al. (1988), fresh gasoline contains significant levels of butanes in addition to trace levels of propane and ethane. As early as 1975, oil industry scientists used the light gas composition of gasoline (butane dominance) to recognize interference from shallow gasoline contamination when conducting soil gas surveys in exploration areas. Analyses of both fresh and weathered samples indicate gasoline (and other refined products) contains very significant levels of the very light alkanes (ethane, propane, iso-butane and normal-butane). In contrast to typical soil gas seepage detected over deep oil and gas reservoirs, concentrations of these light gases in refined products (such as gasoline) are found in inverse order, such that normal-butane > iso-butane > propane > ethane.

These light hydrocarbons (methane, ethane, propane and butanes) are the most volatile constituents present in gasoline, and other petroleum products. In addition to providing excellent tracers, these light hydrocarbon compounds also tend to dissipate more rapidly with time and/or distance from the point(s) at which petroleum constituents are introduced into the subsurface environment. Light hydrocarbon analyses thus provide very useful information for the identification and differentiation of natural gas, biogenic gas, gasoline, and many other refined petroleum products.

Empirical evidence also demonstrates that almost all refined products (such as gasoline, kerosene, diesel, fuel oils and lube oils) have distinctive component signatures with respect to heavier fraction hydrocarbons (pentane-xylenes+). Since the relative yield of light gases decreases significantly with heavier molecular weight petroleum products, such as kerosene or diesel, detection and recognition of these heavier products requires an analysis of the C5+ (pentane-xylenes+), gasoline range volatile constituents. These C5+ analyses can be used to generate "fingerprints" much like high resolution capillary gas chromatographs, but without the detail of the much more expensive method. In addition, they can be used for a first approximation in determining the type of product present, and the relative weathering of individual samples.

Light (C1-C4) and gasoline range (C5+) hydrocarbon analyses yield a quantitative measure of the actual concentrations, by volume, of petroleum product type vapors present in subsurface soils. However, they do not represent, nor allow a prediction of the volume of the residual (sorbed), liquid (NAPL or free phase), nor dissolved phase hydrocarbon concentrations at depth. Although C5+ (gasoline range) hydrocarbons dissipate more slowly than lighter fraction (C1-C4) compounds, both tend to remain in higher concentrations in soils containing liquid products because of a buffering effect generated by the liquid product. The concentrations of volatile components establish an equilibrium in both the vapor and dissolved state that is dependent not only on their vapor pressures and water solubility, but also on their relative solubility in the gasoline, or other free product mixtures. Thus the solubility of each gas in the liquid product mixture exerts significant control over the equilibrium saturation in the vapor or dissolved phase.

III. BIOGENIC GASES

When conducting soil gas surveys and subsequently mapping the subsurface pollution, it is very important to note and measure biogenic gases. Bacteria that attack hydrocarbons generate carbon dioxide under aerobic conditions and methane under anaerobic conditions. Not only do bacterial activities occur, but percent levels of carbon dioxide and methane are often generated. These biogenic gases are often the largest magnitude components in the entire soil gas mixture. In general, the longer the pollution is present in the subsurface environment, the higher are these biogenic gas levels. Both carbon dioxide and methane can be field screened (measured) with reasonable accuracy in the field using infrared detectors. All screening results, however, should be supported by more rigorous laboratory analyses performed under stringent QA/QC procedures.

Although carbon dioxide is generated by the biodegradation of all types of organic materials and must be used with caution in soil gas investigations, the presence of a concentrated petroleum source such as gasoline, diesel, kerosene, etc., causes a concentrated buildup of carbon dioxide in the subsurface. The average concentration of carbon dioxide in ambient air is only 0.03 percent. Biodegradation of typical soil organic matter generally yields carbon dioxide concentrations between 0.2 to 3-5 percent. Higher concentrations of carbon dioxide measured in various soil vapor samples collected in the vicinity of subsurface petroleum contamination yields values as high as 5 to 30 percent, an indication that biodegradation is significantly enhanced within the area of the contaminant plume.

Ambient air methane ranges from 1.5 to 2 ppm by volume. Methane concentrations generally range from 0.5 to 1 ppm in areas where there is no pollution or deep gas migration, suggesting that normal soils act as a sink for atmospheric methane. Since biogenic methane is generated under anaerobic conditions, it is usually generated deeper in subsurface sediments than is carbon dioxide and appears to correlate mainly with the location of free (liquid) product. As with carbon dioxide, the longer that the pollution is present in the subsurface environment, the higher are the methane soil gas levels. Petroleum contaminated sites often exhibit biogenic methane concentrations ranging from several thousand parts per million (ppm) to percent levels. For example, JP4 jet fuel under the Miami Airport generated methane levels as high as 60 percent (Hayman et al., 1988).

Biogenic methane and carbon dioxide data, when used in tandem with specific organic vapor components (C1-C4 and C5+), are very useful in defining the horizontal (areal) extent of hydrocarbon contaminants in the subsurface environment. The presence or absence of specific petroleum related hydrocarbons aids in interpretation and confirms the relationship of the biogenic gases to their appropriate sources. These two biogenic gases generally can be used for mapping the distribution of contaminated soils, even when the contamination is very old and the lighter hydrocarbon volatiles are nearly absent.

IV. CASE STUDIES

All of the case studies discussed in this paper included the collection and analysis of multiple hydrocarbon components, such as the C1-C4 (methane through butane light gases) and C5+ (pentane-xylenes+) gasoline range constituents. Most of these case studies also involved soil and groundwater analyses for BTEX and TPH from borings and/or monitor wells. Whenever possible, high resolution capillary gas chromatography was utilized to analyze liquid samples (free product or water) for direct comparison with available product samples. Unfortunately, addressing a large variety of fuels and different ages of product contamination is beyond the scope of this paper. The case studies presented will focus on the biological gases, methane and carbon dioxide, and plume maps for these gases as well as the butanes (mainly for gasoline) and the C5+ gasoline range components (for heavier fuel products) will be shown and compared.

Following the sewer explosions in Guadalajara, Mexico (1992), ETI conducted several site assessments over a variety of petroleum production storage and transportation facilities. Six of the twelve case studies presented were chosen from surveys conducted in Guadalajara because these surveys were conducted in a geological area where the soils are not conducive to natural generation of biogenic methane. Most of the contamination lies within volcanic tuff deposits made up of compacted angular volcanic fragments of varying grain size, which generally increase in size with depth. Below two meters, the tuff deposits contain coarse sand to gravel sized particles. The sediments are poorly sorted and contain pumice, volcanic glass, feldspar, mica and quartz grains of varying size; these tuff deposits overlie fractured basaltic rocks. Near-surface soils are also the result of erosion of these various volcanic rocks and debris. In these six examples it is highly likely that anaerobic methane would not be generated in the absence of hydrocarbon contamination. This is supported by the fact that despite the collection and analysis of approximately 2000 regional soil gas samples in Guadalajara, localized methane anomalies (plumes) do not occur in background areas where sediments and/or groundwater are not affected by hydrocarbon contamination.

Case One – Guadalajara Service Station
Gasoline, Pre-Existing Leak

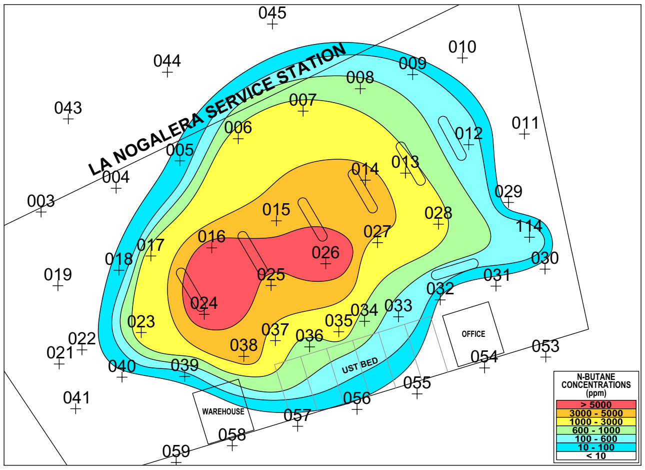


Figure 4

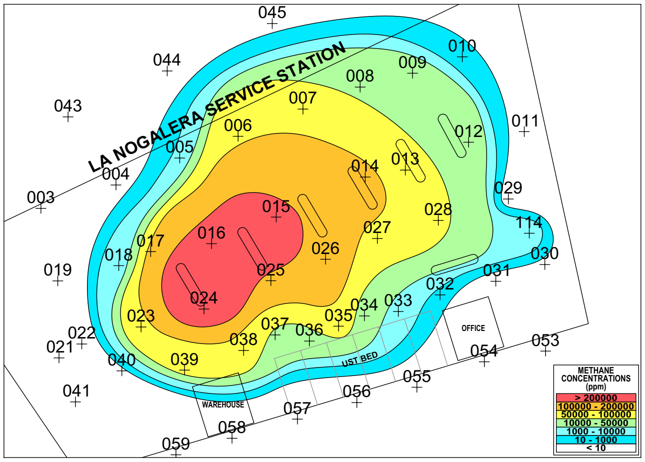


Figure 5

Normal-butane and methane plume maps (Figures 4 and 5, respectively), constructed using data collected on a service station in Guadalajara illustrates a simple case where a leaking dispenser line release resulted in a plume of gasoline in the vicinity of the leak. Soil gas samples were collected at a uniform depth of four feet with ETI's manually operated soil gas sampling probe. Methane concentrations up to 200,000 ppm (20%) were detected near the source of the leak. It is important to note that the methane concentrations (and contours) correlate very well with the normal-butane (a major vapor phase component of gasoline) concentrations. In this case, as shown by the plume maps, the contamination was confined to the service station property.

Case Two – Guadalajara Service Station
Gasoline/Diesel, Pre-Existing Leak

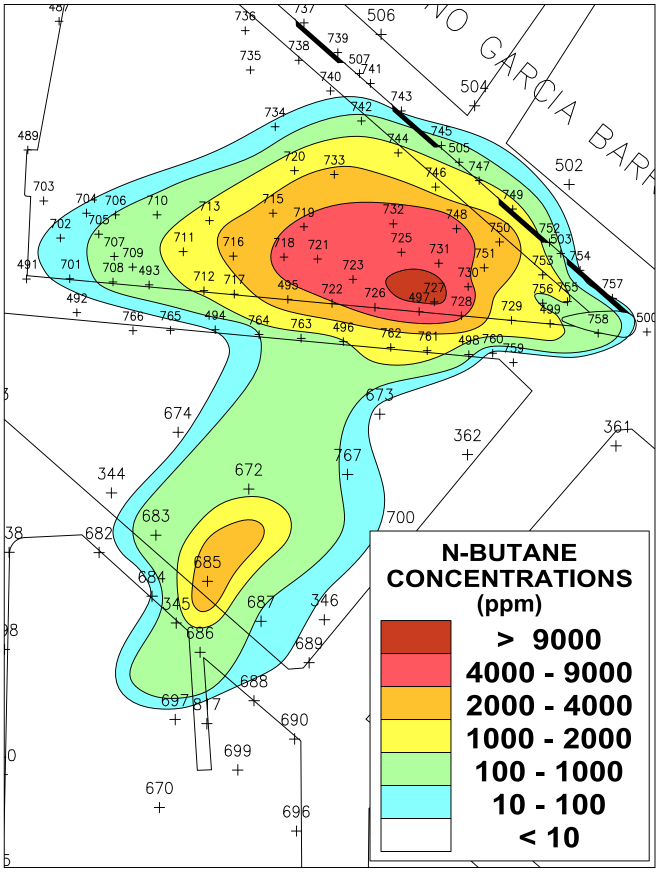


Figure 6

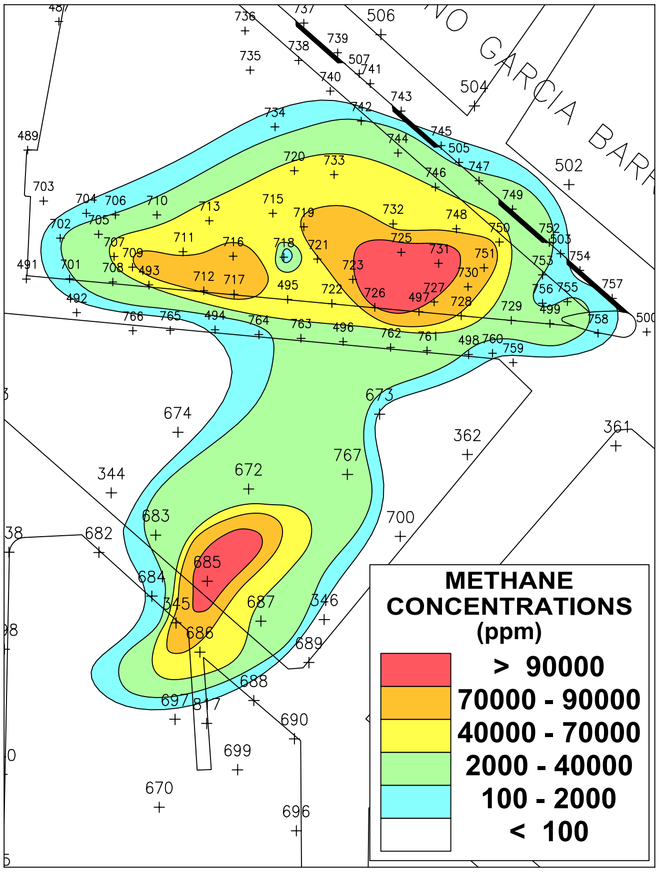


Figure 7

In another area of Guadalajara, more than one year after the explosions, liquid hydrocarbons were observed entering a 10-meter deep trench/canal along a street during the installation of a large diameter sewer conduit. A regional soil vapor survey was conducted in the area to determine the source(s) of the liquid hydrocarbons (gasoline and diesel) and the migration pathway(s). The location and geometry of the contaminant plume is well defined by normal-butane (Figure 6). In this case, both the methane (Figure 7) and carbon dioxide (Figure 8) plumes show a clear association with the normal-butane plume and define the subsurface contamination. The normal-butane and methane plume maps are coincident and delineate the location(s) of residual soil and groundwater contamination. The carbon dioxide plume (Figure 8), however, has a larger areal extent than the methane and normal-butane plumes. The outer edges of this carbon dioxide plume form a halo around the main area of residual contamination where oxidizing conditions appear to be dominant. Two active migration pathways, that extend from the residual portion of the plume southward toward the trench, are only apparent on the carbon dioxide plume map. It is highly probable that oxidizing conditions are dominant along these highly oxygenated (highly porous and permeable) active pathways, thus allowing for the generation of predominantly carbon dioxide. Liquid product was observed entering the trench at the two locations where the carbon dioxide plume "extensions" or "fingers" intersect the trench (Figure 8).

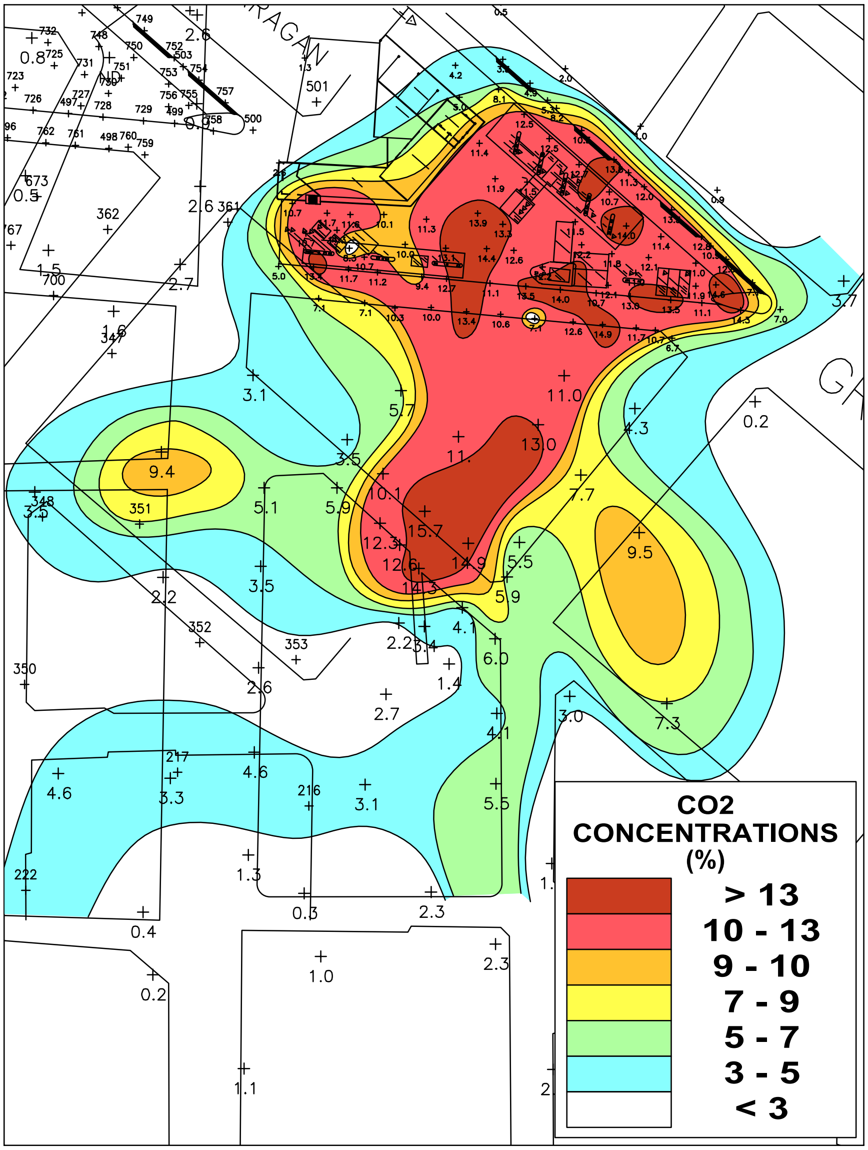


Figure 8

Based upon the hydrocarbon constituents quantified and mapped, it was determined that both diesel and gasoline had been released at this service station, which is north and upgradient of the trench. Ten monitor wells were installed using the plume maps as a drilling guide. These wells confirmed the groundwater gradient and migration pathway of the contamination. High resolution capillary gas chromatography results of soil vapor samples, and soil and groundwater samples obtained from the trench and monitor wells confirmed that the hydrocarbons entering the trench included a gasoline/diesel mix that originated at the service station. In this case the leak had definitely existed for a considerable period of time; methane concentrations approaching 90,000 ppm (9%) were detected.

Case Three- Guadalajara Service Station
Gasoline, Recent Leak

Liquid product (gasoline) was discovered in a sewer adjacent to a service station in Guadalajara. A monitor well drilled in the street adjacent to the sewer was also found to contain liquid phase gasoline. A soil gas survey was conducted in the vicinity of the sewer and service station using ETI's manually operated four-foot sampling probe. Soil vapor analytical results (and the resulting plume maps) indicate the location and areal extent of the contaminant plume; the main free product (NAPL) plume is clearly defined by normal-butane (Figure 9). The well containing the free product is located within the plume, however, it is not located near the leak (which occurred at a dispenser island). The offsite migration of contaminants to the northwest onto the adjacent property caused minimal impact to the adjacent sewer. Methane (Figure 10) has a similar distribution to normal-butane, and aids in the interpretation of the extent and migration pathways associated with the contaminant plume. The largest methane concentration of 25,000 ppm (2.5%) occurs at site 47 (near the dispenser island leak, where contamination has existed for a long period of time), while much more modest levels 4,000 – 15,000 ppm (0.4% - 1.5%) are present over an area where gasoline has appeared to migrate offsite more recently. These lower methane concentrations suggest areas of relatively recent migration of gasoline (involving a shorter biodegradation time). This interpretation, however, should be used with caution, since other site conditions could affect the levels of methane generation.

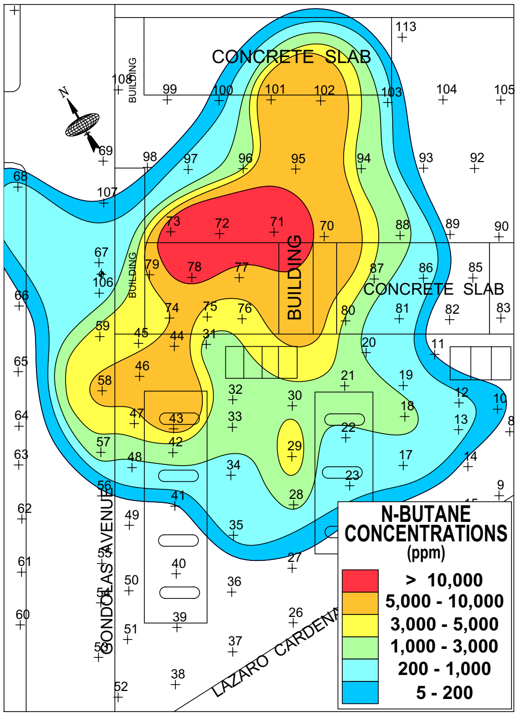


Figure 9

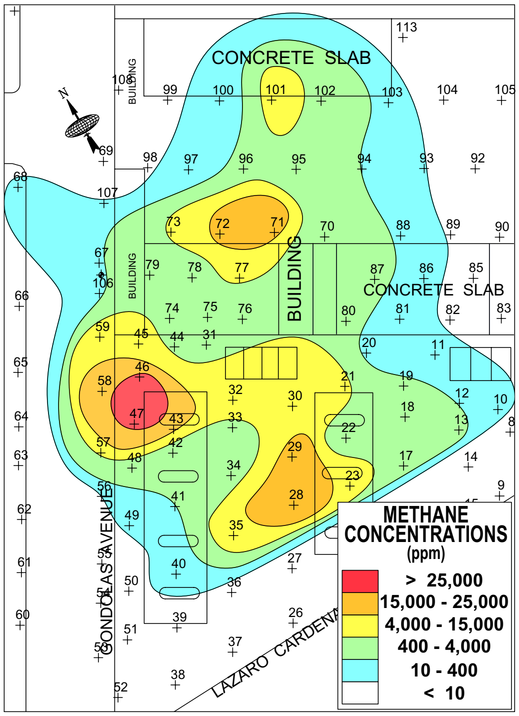


Figure 10

Case Four – Guadalajara Pipeline Leak
Gasoline, Survey 14 Days After Leak

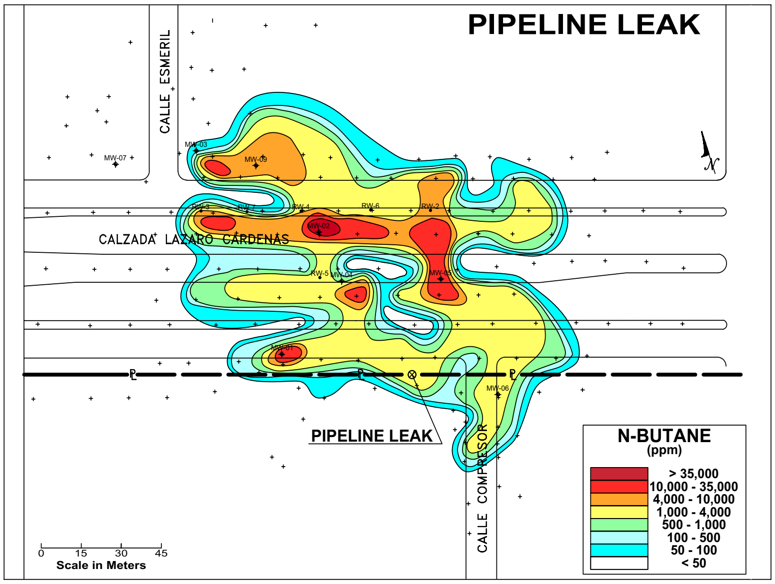


Figure 11

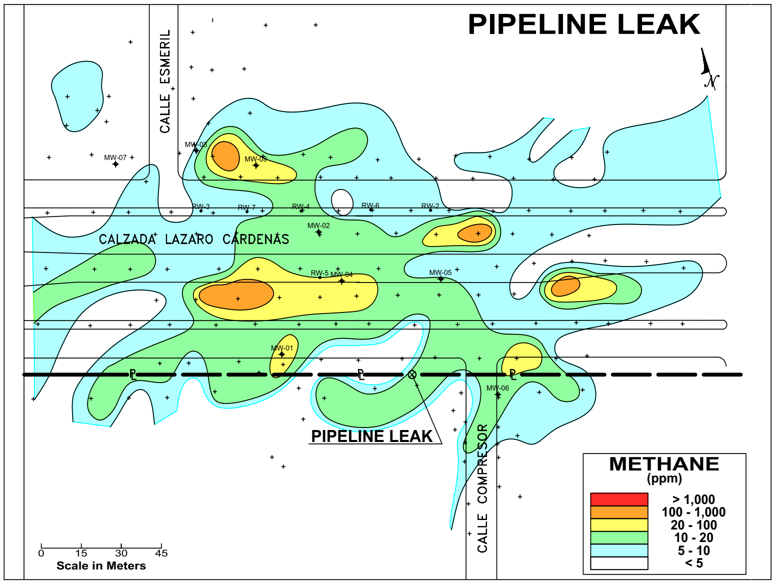


Figure 12

An excellent opportunity to investigate the time required for gasoline contamination to generate anaerobic methane was provided by a release from a liquid petroleum product pipeline in a residential area of Guadalajara. The release was detected during pressure testing of the pipeline following the sewer explosions in 1992. Although the location of the release (hole in the pipeline) was determined, the volume and product type(s) released were unknown. ETI's task included determining the areal and vertical extent of contamination resulting from the release and the type of product or products lost. It was mandatory that the assessment and remediation of the contamination be performed quickly and efficiently since the residents in the area had been evacuated from their homes. The residents would not be allowed to return to the area until the local government officials were certain that there was no threat to their health and safety.

A soil vapor survey was conducted using ETI's manually operated four-foot probes along the pipeline, and on a uniform sampling grid throughout the adjacent residential area. All vapor samples were analyzed for light C1-C4 and C5+ (pentane-xylenes+) hydrocarbons. The results of the soil vapor analyses were used to construct hydrocarbon component plume maps that exhibited the areal extent of the contamination. The soil vapor plume maps were used to determine the placement of boreholes/monitor wells, which were necessary to determine the vertical extent of the contamination.

Hydrocarbon constituent plume maps were constructed to illustrate the areal extent of subsurface contamination in soils and groundwater. The normal-butane (a major volatile component of gasoline) soil vapor plume map (Figure 11) was extremely diagnostic in delineating the extent of the contamination, since a gasoline product was released from the pipeline. Boreholes were drilled and sampled, using the soil vapor plume maps as a guide, to determine the vertical extent of the contamination. Integration of the soil vapor and borehole data allowed for a three dimensional interpretation of the subsurface contamination. Monitor wells were installed in the most strategic locations within the plume boundaries, and converted to recovery wells (for NAPL, dissolved and vapor phase contaminants) during the remediation phase of the project. Due to a systematic and efficient approach to the problem, the soils and groundwater in the area were remediated to specified cleanup levels four months after installation of the remediation systems (six months after the commencement of the assessment). Of particular interest is the methane plume map (Figure 12); methane levels associated with the high normal-butane concentrations are generally less than 1000 ppm (0.1%). In this case, the gasoline contamination had occurred only 14 days before the assessment was conducted, therefore, anaerobic degradation (and the formation of biogenic methane) was in its early stages.

Case Five – Three Service Stations, Austin Chalk Gasoline, Pre-Existing Leak (Four Years Old)

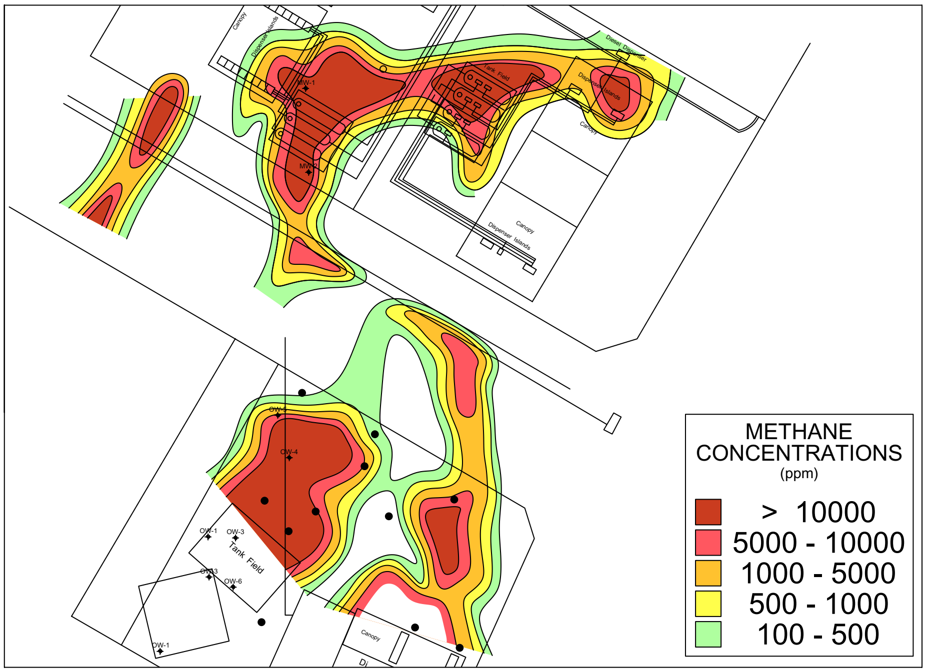


Figure 13

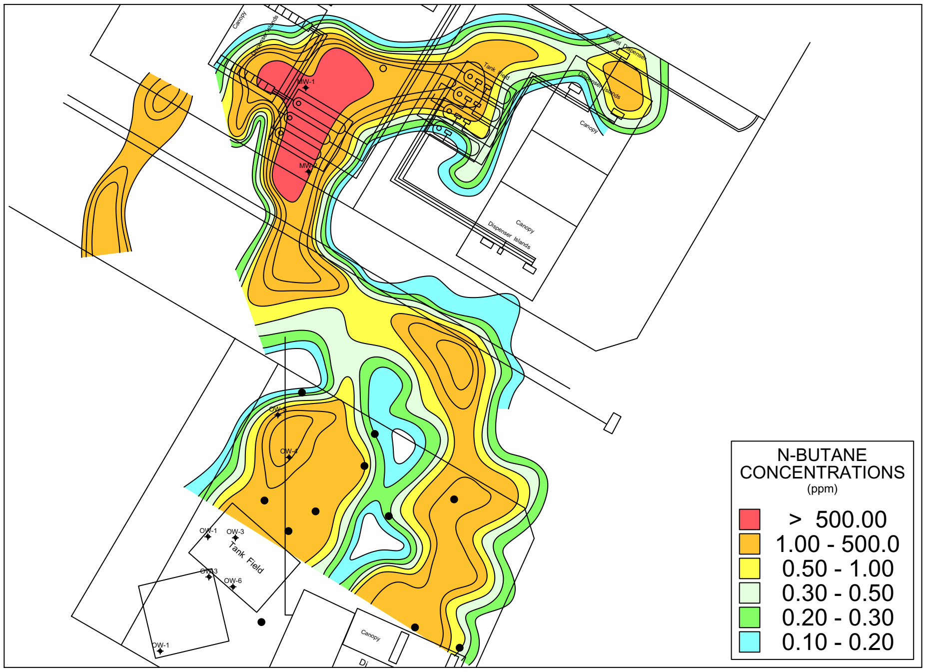


Figure 14

This case study involves the soil gas assessment of three gasoline stations at a busy intersection in a major Texas city. Four to seven feet of soil overlies the Austin Chalk, an unconformable surface that provided the lower boundary for the contamination; no groundwater was present in this interval. The surface is nearly completely covered by concrete, which provides a cap. Gasoline had entered the underground telephone conduits four years before ETI's soil gas assessment was conducted. In this area, no significant amount of liquid product (NAPL) was trapped onsite because there is effectively no available near-surface reservoir, except for fractures in the top of the chalk. Methane and normal-butane plume maps constructed using data collected in the area show good correlation (Figures 13 and 14, respectively). Due to the lack of NAPL and the length of time (four years) since the release had occurred, the normal-butane concentrations were relatively low (500 ppm) resulting from volatilization and/or biodegradation. The methane concentrations, however, approached 10,000 ppm (1%), despite the low residual levels of contamination. It is also important to note that the methane plume boundaries are similar to the normal-butane plume boundaries. Despite the shallow depth of the soils (4 to 7 feet) and the confinement provided by the concrete cover, the biogenic methane generated did not spread out and fill all the available space under the concrete cover. It is probable that methane oxidizers consume any methane that migrates to the outer edges of the plume, thereby keeping the biogenic gases confined to the plume geometry defined and controlled by the subsurface contaminants.

Case Six – Natural Condensate Gas Processing Plant
Condensate/Crude Oil, Pre-Existing Leak

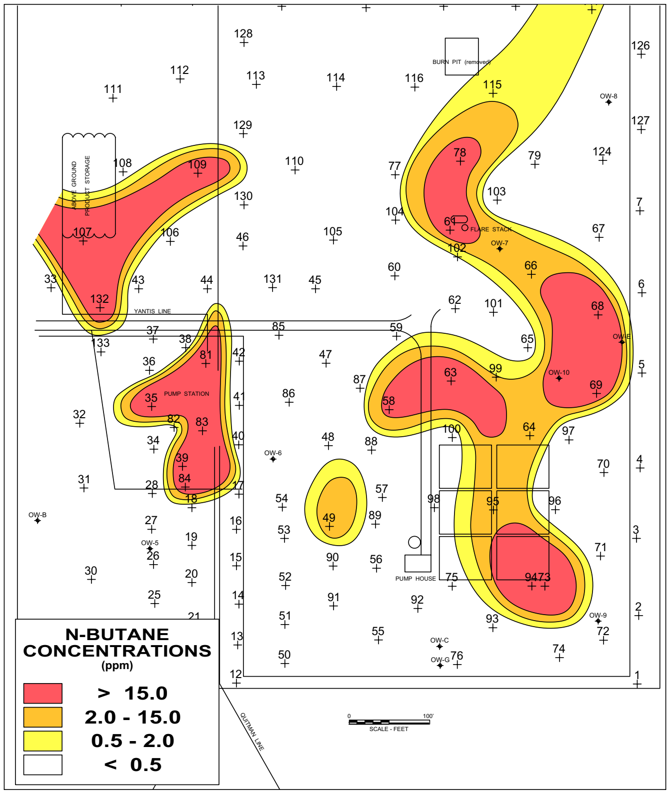


Figure 15

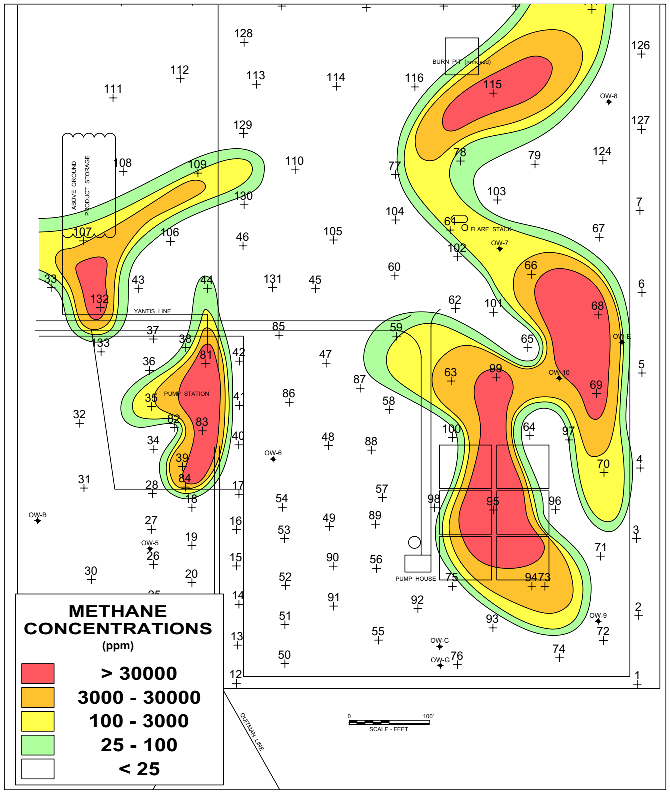


Figure 16

Non-aqueous phase liquids (NAPL) were encountered in one of several observations/monitor wells drilled on a gas processing facility. It was suspected by facility personal that a product pipeline entering the property was leaking. ETI conducted a soil vapor survey on the facility in the vicinity of the pipelines and monitor well where the NAPL had been encountered on the groundwater. A sampling grid containing 100-foot centers was initially utilized, and later increased to 50-foot centers in areas where more detail was required.

The normal-butane map (Figure 15) clearly shows that the contamination was not limited to the area surrounding the monitor well containing the NAPL. Five distinct contaminant plumes were delineated on the facility. A comparison of liquid product sample chromatograms with soil vapor sample chromatograms indicated that several releases of at least three distinct products (two condensates and a crude oil) had occurred at the facility over time. Hydrocarbon component ratios and various chromatographic signature analyses were used to determine which product was lost in each area of the property. A very good correlation exists between the methane plume map (Figure 16) and the normal-butane plume map (Figure 15) which defines the subsurface liquid product contamination.

Case Seven – Product Pipeline
Benzene – Hexane Mix, Pre-Existing Leak

This study involved the soil vapor assessment of contamination resulting from leakage from a product pipeline carrying an unusual product mix of benzene in a hexane matrix. The methane plume map (Figure 17) correlates well with the benzene plume map shown in Figure 18. However, the methane levels are fairly modest (less than 10,000 ppm, 1%) even though the leak had existed for some time before the survey was conducted.

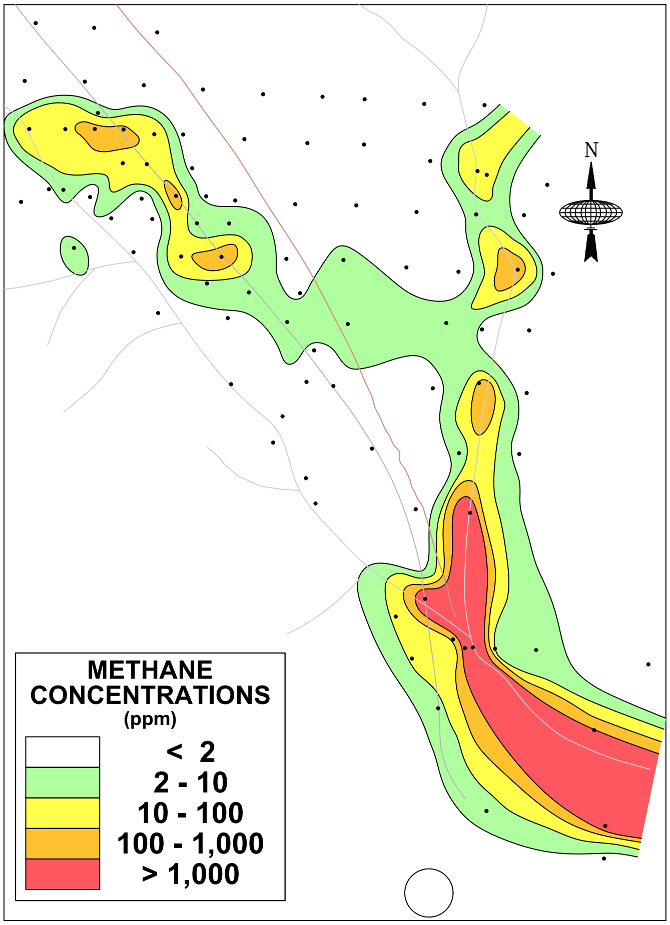


Figure 17

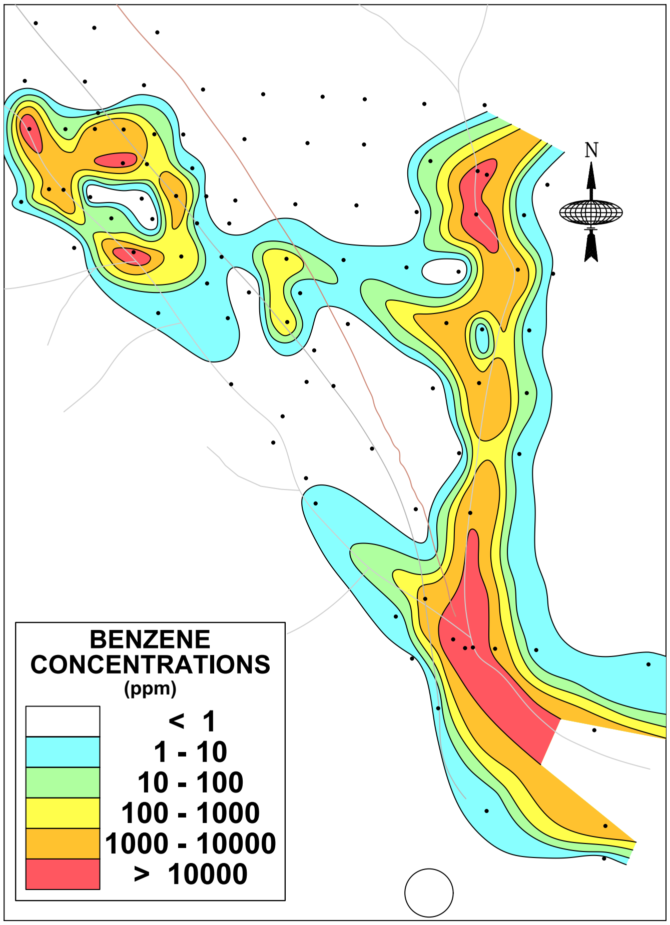


Figure 18

Case Eight – Gulf Coast Refinery
Gasoline/Diesel, Pre-Existing Leak

This case study involves a soil gas assessment conducted over a refinery located on a Gulf of Mexico beach. The dominant lithology beneath the site is sand, and the groundwater is approximately four feet below the surface. Methane, carbon dioxide and C5+ hydrocarbon plume maps (Figures 19, 20, and 21, respectively) were constructed using results from samples collected with manually operated four-foot soil vapor hand probes. Samples were collected in the vicinity of the loading racks where both gasoline and diesel contamination were known to exist for an extended period of time. High resolution capillary gas chromatography results (Figure 22) confirm areas of predominantly diesel and gasoline/diesel contamination. Lead analyses and high resolution capillary gas chromatography analyses were performed on actual products stored on-site at the time the survey was conducted. The analyses confirmed that the NAPL encountered in monitor wells (Figure 22), and soil vapor signatures of contaminants present in the subsurface were not current formulation fuel products. The contamination was the result of relatively old releases of refined petroleum products. Beneath this site, methane and carbon dioxide concentrations reached levels as high as 200,000 ppm (20%) and 18%, respectively, indicating biodegradation processes had occurred over a long period of time.

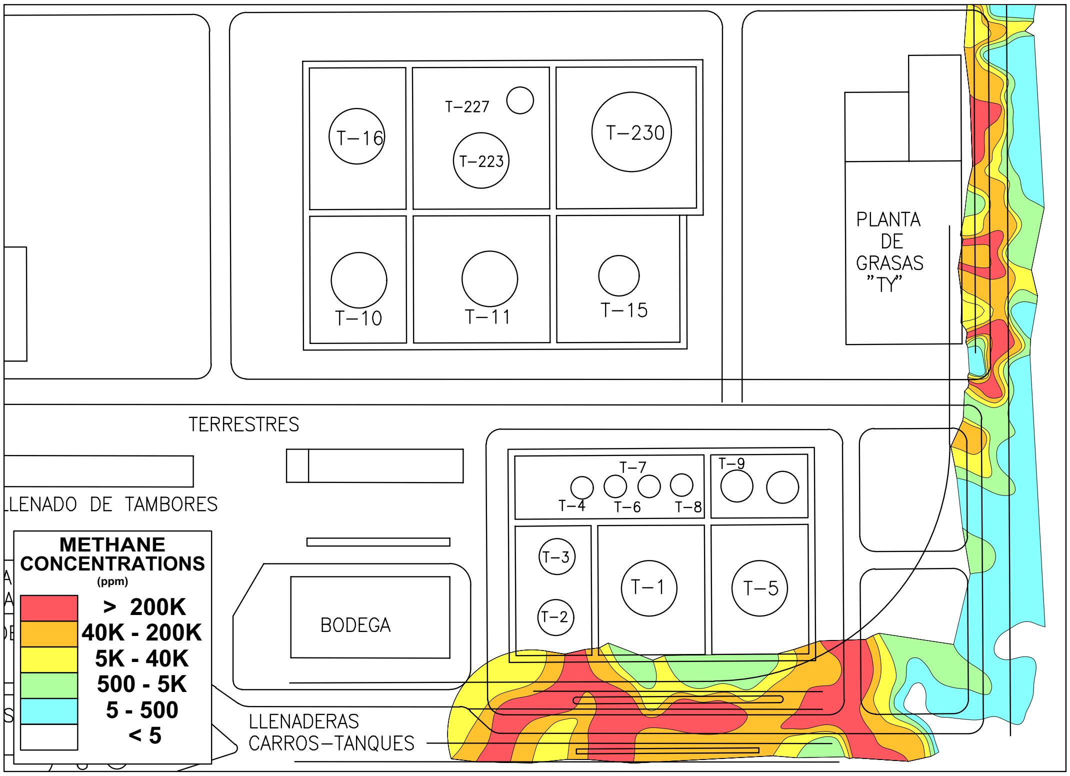


Figure 19

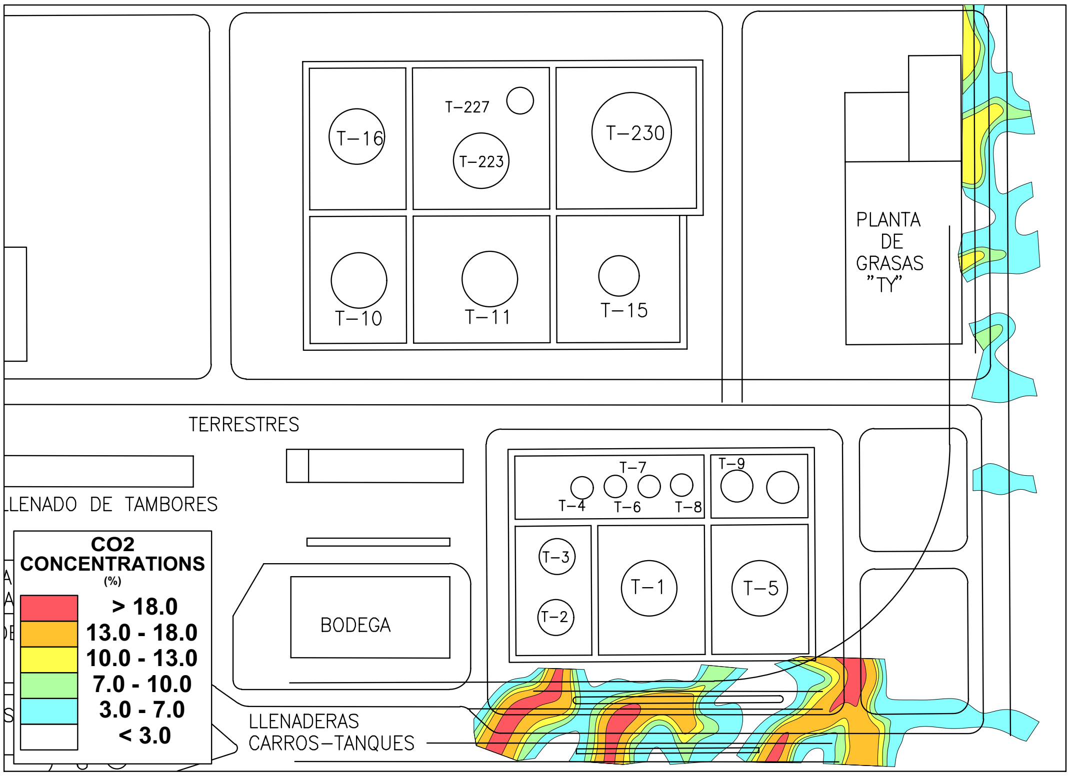


Figure 20

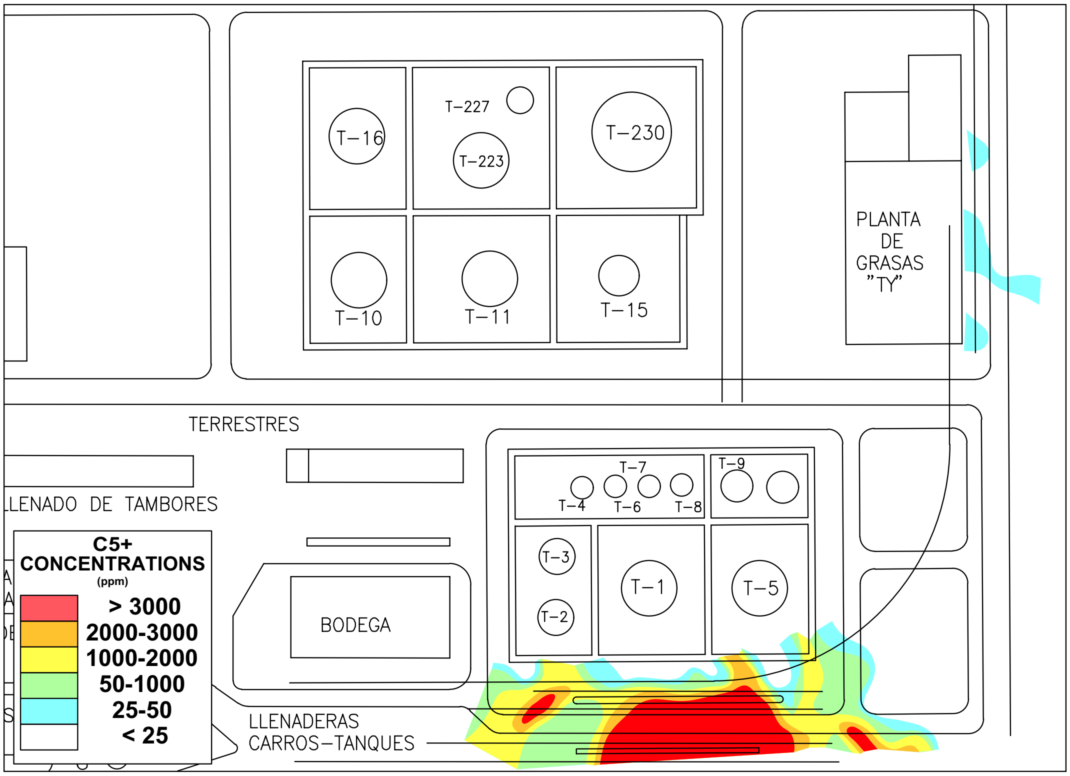


Figure 21

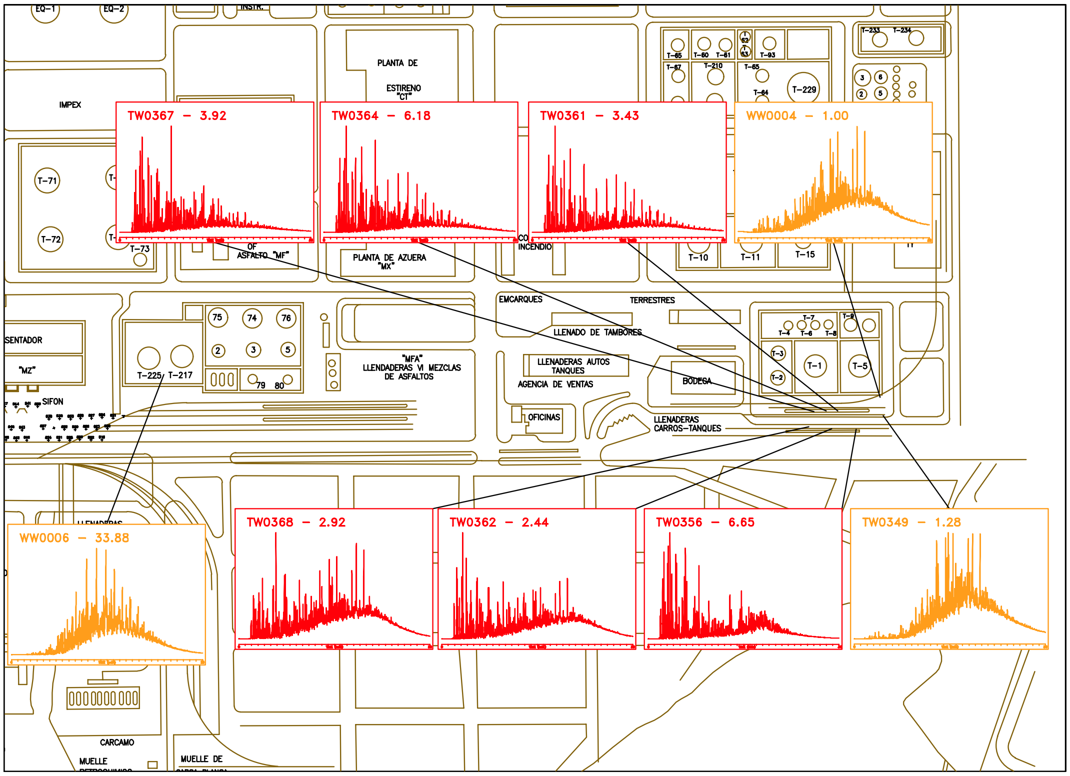


Figure 22

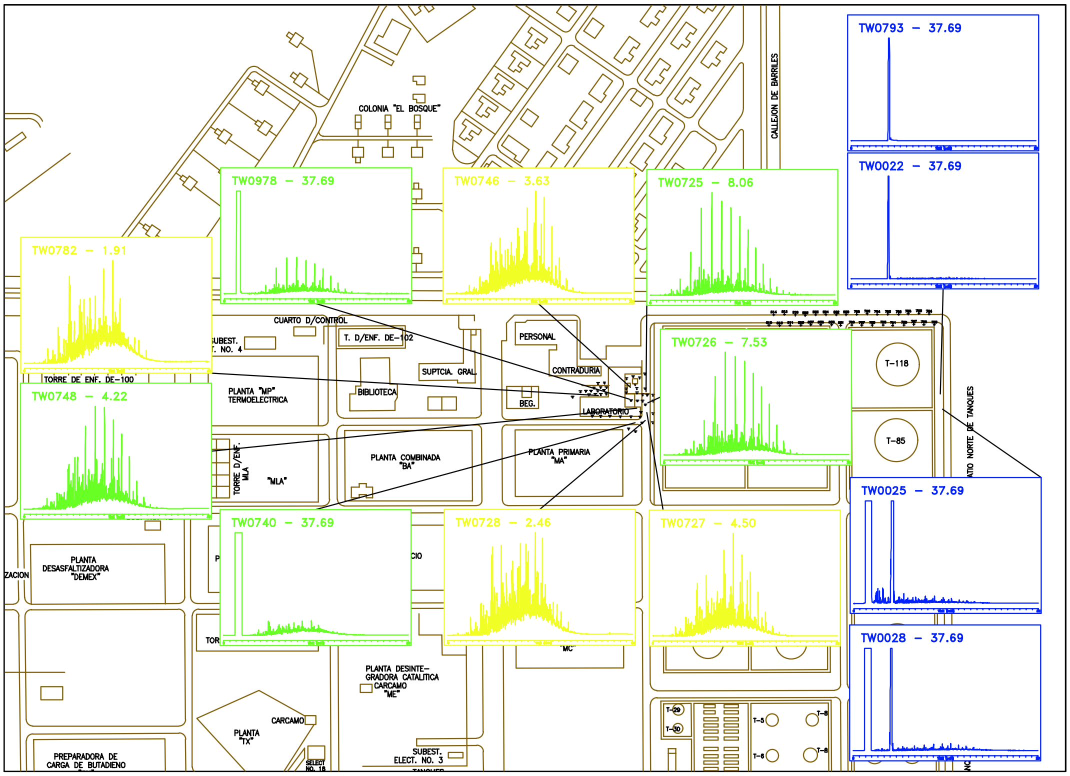


Figure 23

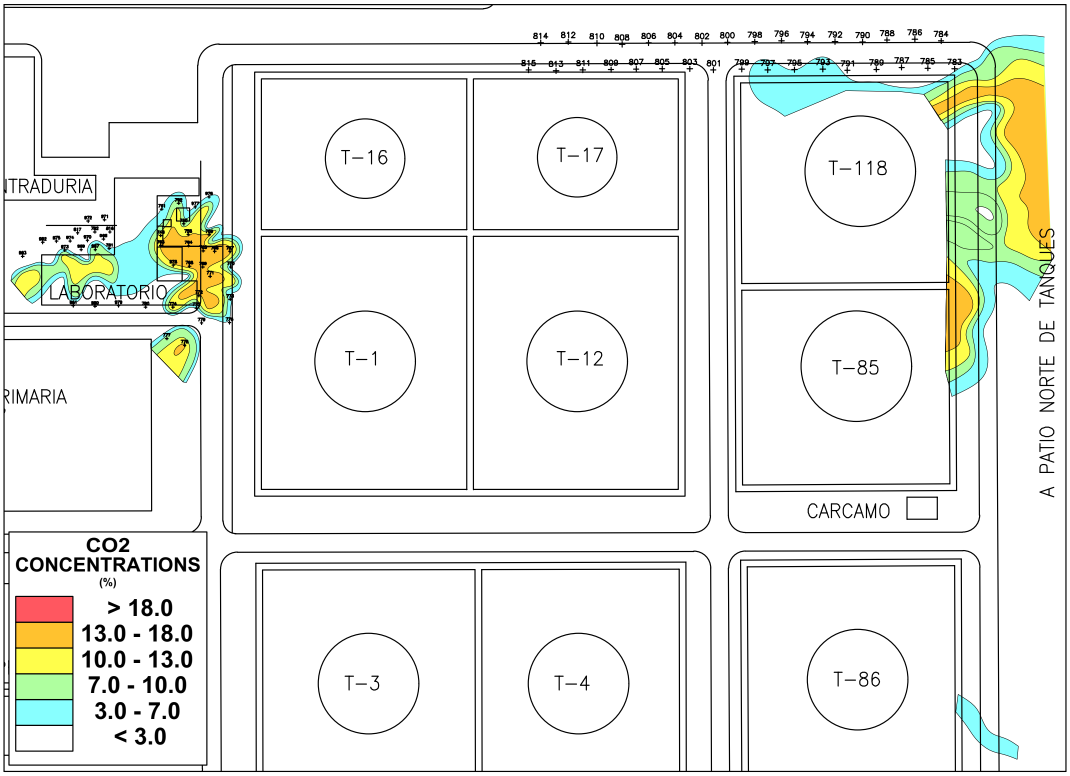


Figure 24

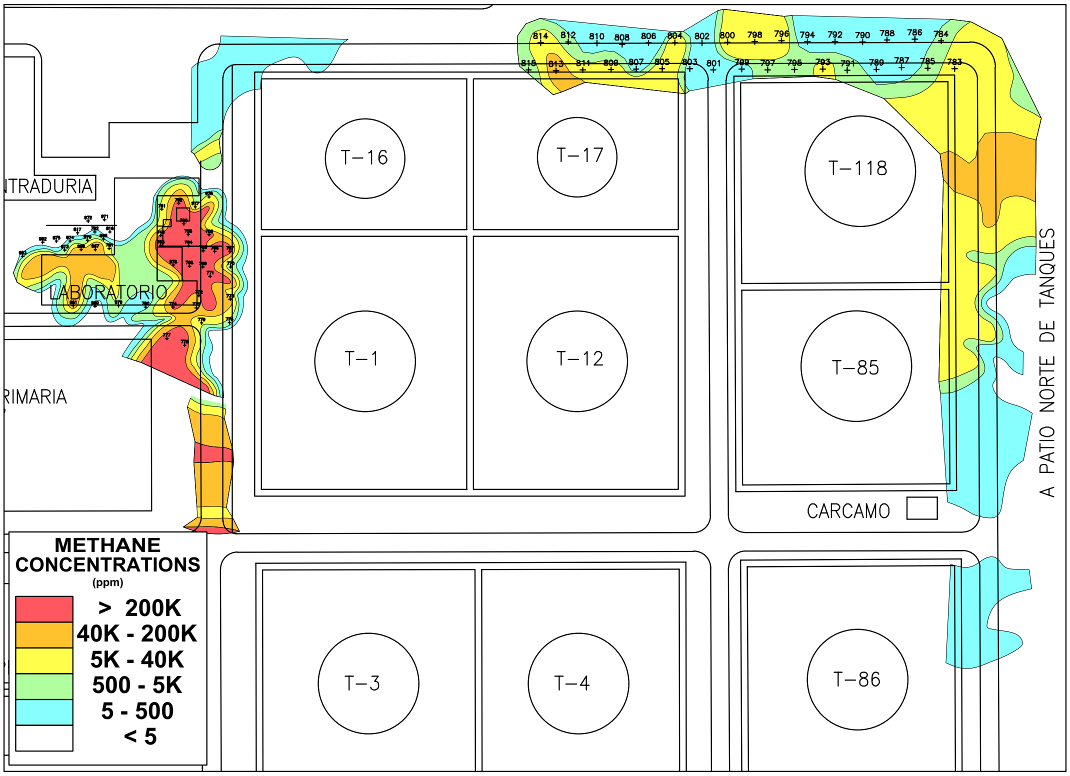


Figure 25

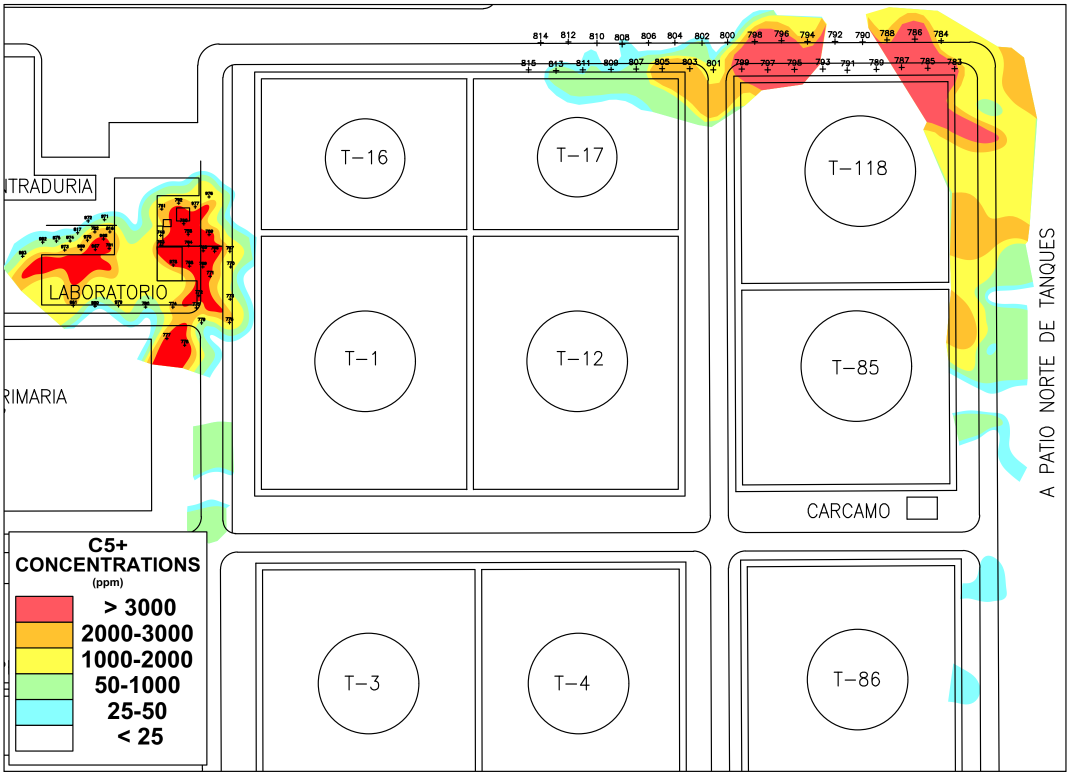


Figure 26

Case Nine – Gulf Coast Refinery
Kerosene/Para-Xylene, Pre-Existing Leak

Another example from the same refinery (discussed above) provides some contrast in that different product types were lost in different areas. Two additional plumes mapped using the soil vapor data were related to two different product pipeline leaks: kerosene under the basement of a laboratory, and para-xylene near the eastern boundary of the refinery. High resolution capillary gas chromatography results (Figure 23) identified these two products. The locations of these two separate plumes were delineated using the soil vapor results. The association of the carbon dioxide (Figure 24) and methane (Figure 25) plumes with the C5+ hydrocarbons plume (Figure 26) is obvious. Methane and carbon dioxide concentrations are as high as 200,000 ppm (20%) and 18%, respectively within the kerosene plume, but are considerably lower in the para-xylene release area. The abundant amounts of normal alkanes in the kerosene favor biological reactions, leading to high concentrations of these biogenic gases. Fuel products, such as para-xylene appear to produce less favorable environments for the biodegradation by anaerobic and aerobic bacteria.

Case Ten – Guadalajara Railroad Facility
Diesel, Pre-Existing Leak (At Least Eighteen Years)

A plume consisting entirely of railroad diesel fuel was mapped using data obtained from a near surface soil vapor survey. In this case, diesel product was entering a subway station through the walls of a tunnel. At the time of this investigation, the diesel had been accumulating in the subway for over 18 years. Two sumps had been installed to collect and extract the product from the underground station. The continuing source of the diesel product was undetermined. State and federal agencies in Mexico contracted ETI to determine the source and migration pathway(s) of the hydrocarbon contaminants (diesel) entering the subway station and adjacent residential area.

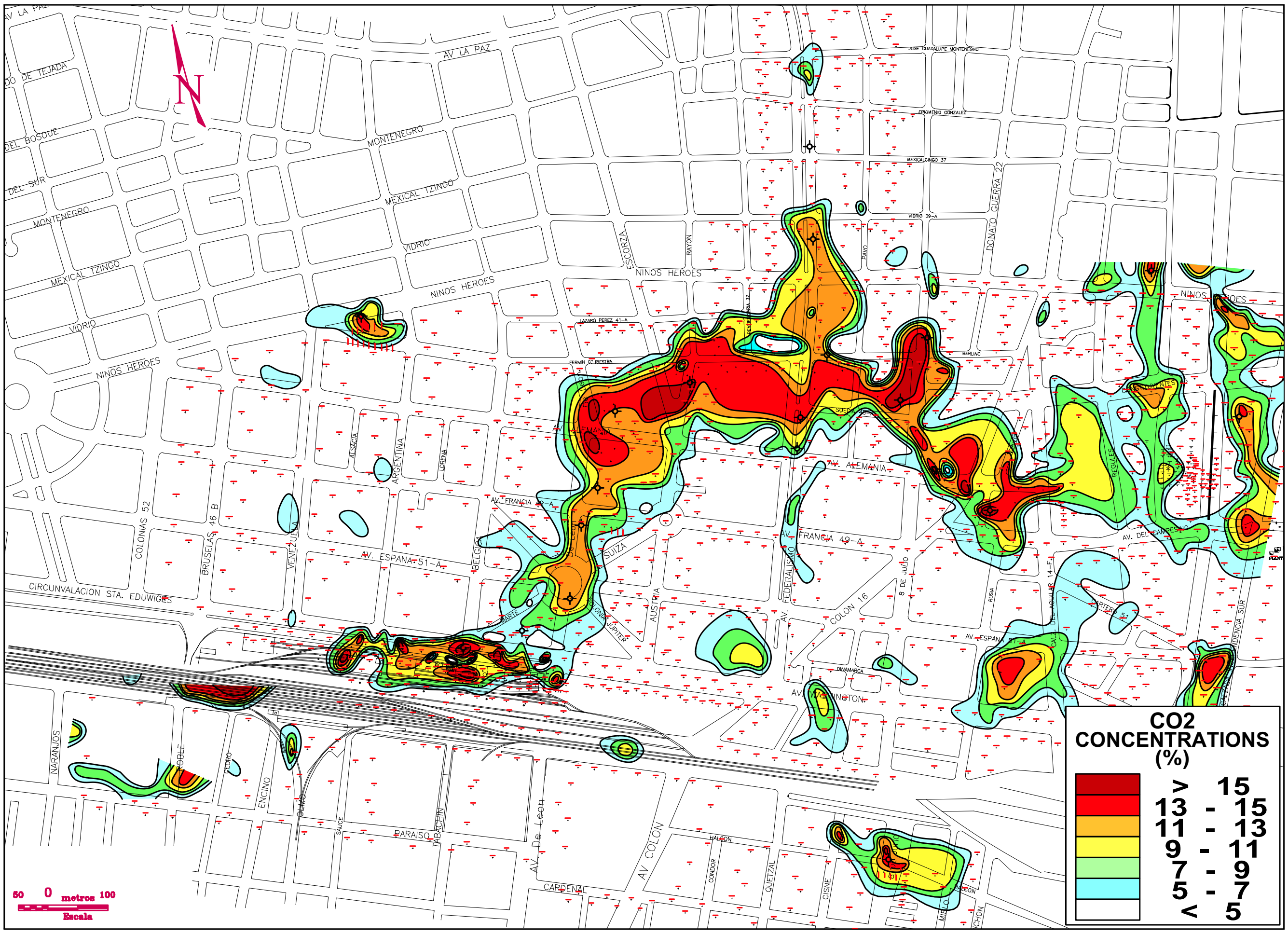


Figure 27

A regional soil vapor survey, using ETI's seven-foot manually operated probe, was conducted throughout the residential area and in the vicinity of the subway to determine the source and migration pathway(s) of the liquid diesel product. Soil vapor samples were collected on a regional grid spacing containing 30 meter spacing, with closer spaced detailed sampling performed along the subway and in areas containing underground sewer, water and electrical conduits.

The primary source of the diesel contamination was determined to be a railroad maintenance facility, which had been active for approximately 40 years. Soil vapor plume maps (Figures 27, 28, and 29) show the horizontal extent and migration pathways of diesel products lost at the railroad facility located southwest of the subway station. The soil vapor plume patterns are consistent with the reported ground water gradient in the area, which is to the northeast. Liquid product samples were collected from the subway station sumps, and from active and inactive facilities that store and dispense petroleum products in the area. High resolution capillary gas chromatography analyses were used to fingerprint the liquid product samples obtained from monitor wells on the railroad facility and diesel samples collected from the subway sumps. These analyses indicated that the products were derived from the same parent diesel product released at the railroad maintenance facility.

Although diesel does not contain significant light vapors, the C5+ plume map (Figure 29) does provide accurate information on the location of the diesel plume. The methane plume map (Figure 28) is nearly identical in form to the C5+ plume, suggesting that methane is generated in very close proximity to the liquid product, where highly reducing conditions exist. In contrast, carbon dioxide (Figure 27) forms a very broad plume, and provides information for detection and delineation of the entire diesel plume.

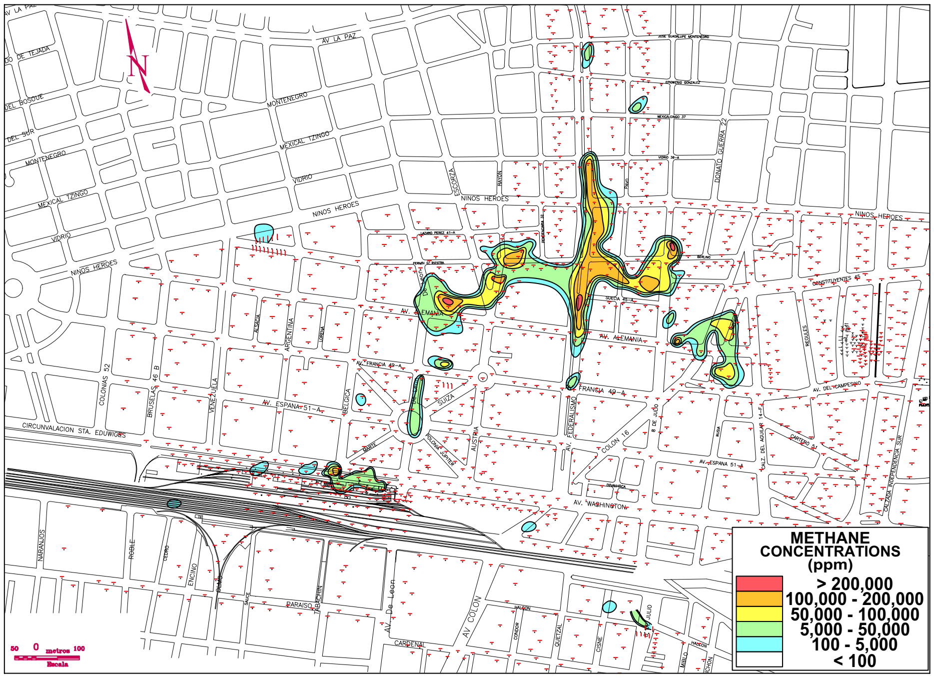


Figure 28

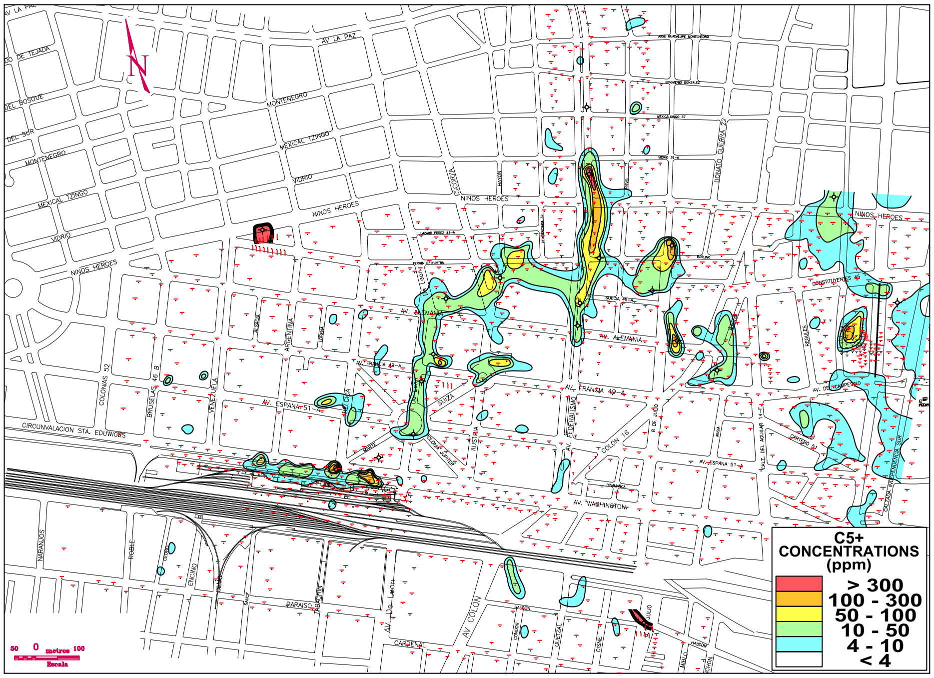


Figure 29

Case Eleven, Guadalajara LNG Manifold
Cook-stove Propane, Pre-Existing Leak

A detailed soil vapor survey was conducted on a sampling grid containing 5 to 10 meter spacing in the vicinity of a propane, butane and ethane soil vapor anomaly, detected during the above regional survey. The ratios of propane, butanes, ethane and other trace gases composing this anomaly indicated the probable source of contamination was leakage of LNG (liquid natural gas) utilized throughout Mexico by residences and businesses. Interpretation of the soil vapor data indicated that the source of the subsurface contamination was located in the garden area of a Social Services Building Complex. The supervisor of the complex had no knowledge of underground gas lines on the property. During excavation and gas monitoring operations, active and abandoned lines and valves were discovered in the garden area of the complex. A box containing corroded valves and distribution lines were found at the location containing the highest concentrations of propane (Figure 30) and butanes. The exact location of the underground LNG ("cook-stove" gas) source was determined by the detailed soil vapor survey, and a vapor extraction system was installed in the garden area to extract the potentially explosive gases.

This case study provides an excellent example of the concentrations and relative locations of biogenic methane (Figure 31) and carbon dioxide (Figure 32) associated with a unique fuel product, that consists mainly of propane (and butanes) with a small complement of other light hydrocarbon gases. Analytical laboratory results of the "cook-stove" propane and associated gases are shown in tabular form in Figure 33. The biodegradation cells associated with the propane contamination is unique, since this contamination occurs in soils made up of volcanic tuff. The tuff deposits are very low in organic carbon, making it less likely that the biogenic gases are being generated from the degradation of natural organic material. The highest methane (Figure 31) and carbon dioxide (Figure 32) concentrations form halos around the edges of the highest propane concentrations. The carbon dioxide occurs where oxygen is more plentiful. The slightly lower methane concentrations (10,000 ppm, 1%) observed within the main propane anomaly might be the result of dilution associated with the leaking propane fuel.

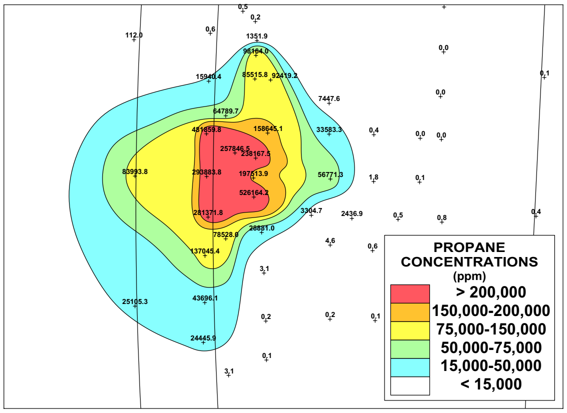


Figure 30

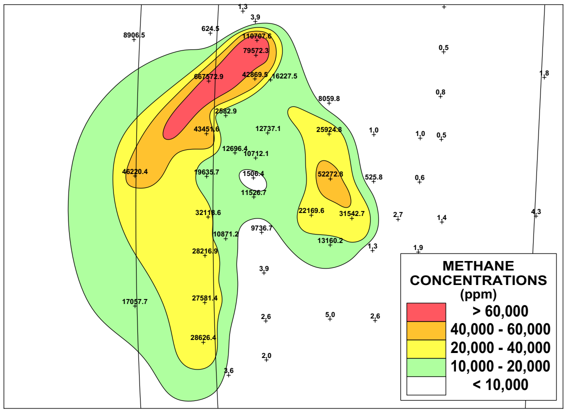


Figure 31

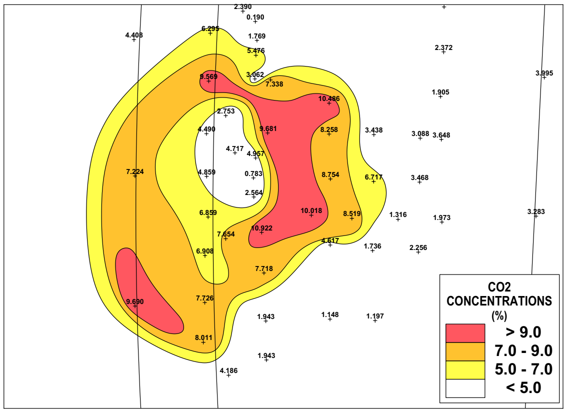


Figure 32

TYPICAL SOIL GAS ANALYSIS - PROPANE GAS LINE
VOLATILE ORGANIC HYDROCARBONS ANALYSIS (ppm) & CO2 (%)

Site No.	Methane	Ethane	Propane	I-Butane	N-Butane	C5 +	CO2
1477	667572.9	3213.54	15940.38	81727.57	32.35	192.2	9.569
1478	43451.6	11749.09	481859.80	103974.68	241492.82	580.8	4.490
1479	19635.7	3701.84	293883.77	81655.11	176975.95	289.4	4.859
1480	32118.6	7836.02	281371.78	61105.60	189685.68	201.6	6.859
1481	28216.9	2654.06	137045.43	35149.18	83354.19	48.2	6.908
1482	27581.4	552.22	43696.10	9593.74	17515.49	40.5	7.726
1483	28626.4	321.24	24445.88	8158.59	2852.96	35.4	8.011
1484	9.8	2.25	292.99	63.99	191.97	8.2	0.450
1485	1.3	0.12	0.53	0.11	0.88	2.1	2.390
1486	3.9	0.05	0.16	0.11	0.15	3.2	0.190
1487	110707.6	442.37	1351.94	14827.23	109.62	14.8	1.769
1488	79572.3	2436.77	98163.95	23138.12	42698.70	203.7	5.476
1489	42869.5	1838.68	85515.82	17369.74	28054.31	66.9	3.062
1490	16227.5	1782.55	92419.15	22201.31	49020.75	231.2	7.338
1491	12696.4	3229.87	257846.48	68389.72	147997.97	247.6	4.717
1492	12737.1	1911.58	158645.09	38068.14	93040.35	116.0	9.681
1493	10712.1	3816.71	238167.47	38312.62	97837.99	635.5	4.957
1494	1506.4	245.18	197513.85	101978.43	275211.61	593.7	0.783
1495	11526.7	4298.88	526164.16	125281.49	285344.56	360.4	2.564
1496	9736.7	318.22	28880.98	10463.23	37464.13	44.8	10.922
1497	3.9	0.35	3.13	1.65	1.36	5.2	7.718
1498	2.6	0.11	0.15	0.04	0.36	3.2	1.943
1499	2.0	0.12	0.05	0.02	0.05	4.4	1.943
1500	5.0	0.36	0.21	0.05	0.10	9.3	1.148
1501	2.6	0.15	0.10	0.03	0.07	3.4	1.197
1502	13160.2	2.42	4.59	2.70	2.60	7.4	4.617
1503	52272.8	608.33	56771.33	19227.50	40075.86	100.4	8.754
1504	3.8	0.45	3.54	0.89	4.57	5.2	1.988
1505	8.7	1.13	0.90	0.49	1.75	3.0	0.881
1506	624.5	2.69	0.62	1.47	0.02	3.6	6.295
1507	0.5	0.04	0.02	0.02	0.02	1.8	2.813
1508	0.5	0.04	0.02	0.02	0.02	1.8	2.372
1509	0.8	0.09	0.04	0.02	0.04	1.9	1.905
1510	8059.8	187.06	7447.60	2358.30	4025.60	22.0	10.486
1511	25924.8	689.92	33583.30	11736.60	19253.90	31.4	8.258
1512	1.0	0.16	0.40	0.07	0.34	3.7	3.438
1513	1.0	0.07	0.04	0.01	0.04	1.5	3.088
1514	0.5	0.05	0.01	0.01	0.02	2.2	3.648
1515	525.8	4.00	1.77	0.27	0.82	4.0	6.717
1516	0.6	0.05	0.11	0.03	0.09	2.5	3.468
1517	22169.6	74.30	3304.70	2118.40	2451.10	7.1	10.018
1518	31542.7	139.30	2436.90	4476.90	835.18	11.7	8.519
1519	2.7	0.41	0.47	0.11	0.27	3.9	1.316
1520	1.4	0.11	0.77	0.22	0.31	4.0	1.973
1521	1.3	0.23	0.55	0.15	0.29	3.2	1.736
1522	1.9	0.42	0.19	0.01	0.13	1.6	2.256
1523	1.6	0.35	0.26	0.04	0.12	2.9	3.548
1524	2.0	0.26	0.12	0.01	0.07	1.5	14.725
1525	0.8	0.03	0.07	0.03	0.06	1.5	8.352
1526	4.5	0.35	0.21	0.03	0.15	1.6	4.484
1527	3.1	0.39	1.53	0.24	0.61	2.5	4.243
1528	9.7	0.49	0.20	0.06	0.10	3.5	0.199
GAS SAMPLE	***4697.4***	***43736.70***	***476303.50***	***46354.60***	***82306.00***	***116.3***	***ND***

Figure 33

Case Twelve – Tank Farm Storage Complex
Gasoline/Diesel/Jet Fuel, Pre-Existing Leak (25 Years)

The final case study addressed in this paper involves an area containing six tank farm storage and distribution terminals. ETI was contracted by city officials to conduct a site assessment to determine the extent of any offsite migration of refined petroleum products (originating at the terminals) that might have occurred down gradient onto residential and public park properties. ETI's 12-foot manual sampling probe was used to collect soil vapor samples on a grid containing approximately 350 sampling sites. As in the previous case studies, the carbon dioxide plume map (Figure 34) shows the largest areal extent, while the methane plume (Figure 35) shows a more focused areal extent. Both plumes correlate well with the C5+ hydrocarbon plume (Figure 36) which is a direct result of the petroleum contaminants present in subsurface soils and groundwater. C5+ concentrations clearly show a good correlation with methane concentrations, which exceed 100,000 ppm (10%). The largest carbon dioxide concentrations are in excess of 14%, and clearly encompass the C5+ and methane anomalies (plume maps).

To further confirm the areal extent of the contaminant plumes, and to delineate the vertical extent, over 90 direct-push borings were continuously sampled from surface to ground water (approximately 20 feet depth) using the soil gas plume maps as a guide. Thirteen (13) monitor wells were subsequently installed using the soil vapor and borehole data. Twelve of these 13 wells were found to contain NAPL. Liquid product samples were analyzed using high resolution capillary gas chromatography to determine the product types released at the terminals over a 40-year period. The products released included several formulations of gasoline, diesel and jet fuel. Groundwater samples analyzed for C5+ hydrocarbons (using the same GC method used for the soil gas samples), benzene (Method 8020/602) and MTBE (by GC and confirmed by GCMS) are shown in Figures 37, 38 and 39, respectively.

A good correlation exists between carbon dioxide, methane and C5+ hydrocarbon vapors from the vadose zone soils. The groundwater contaminant plume (Figures 38 and 39) confirms the usefulness of measuring vapor phase biological gases. The very narrow plume (less than 50 feet wide) in the lower portion of the maps should be noted. Liquid product was obtained from four monitor wells installed along this very narrow migration pathway identified by mapping the soil vapor data. These wells could never be properly located by random drilling. The state regulatory agency had installed 17 wells within this general area (one within 50 feet of one of the main plumes) without encountering any NAPL (free product).

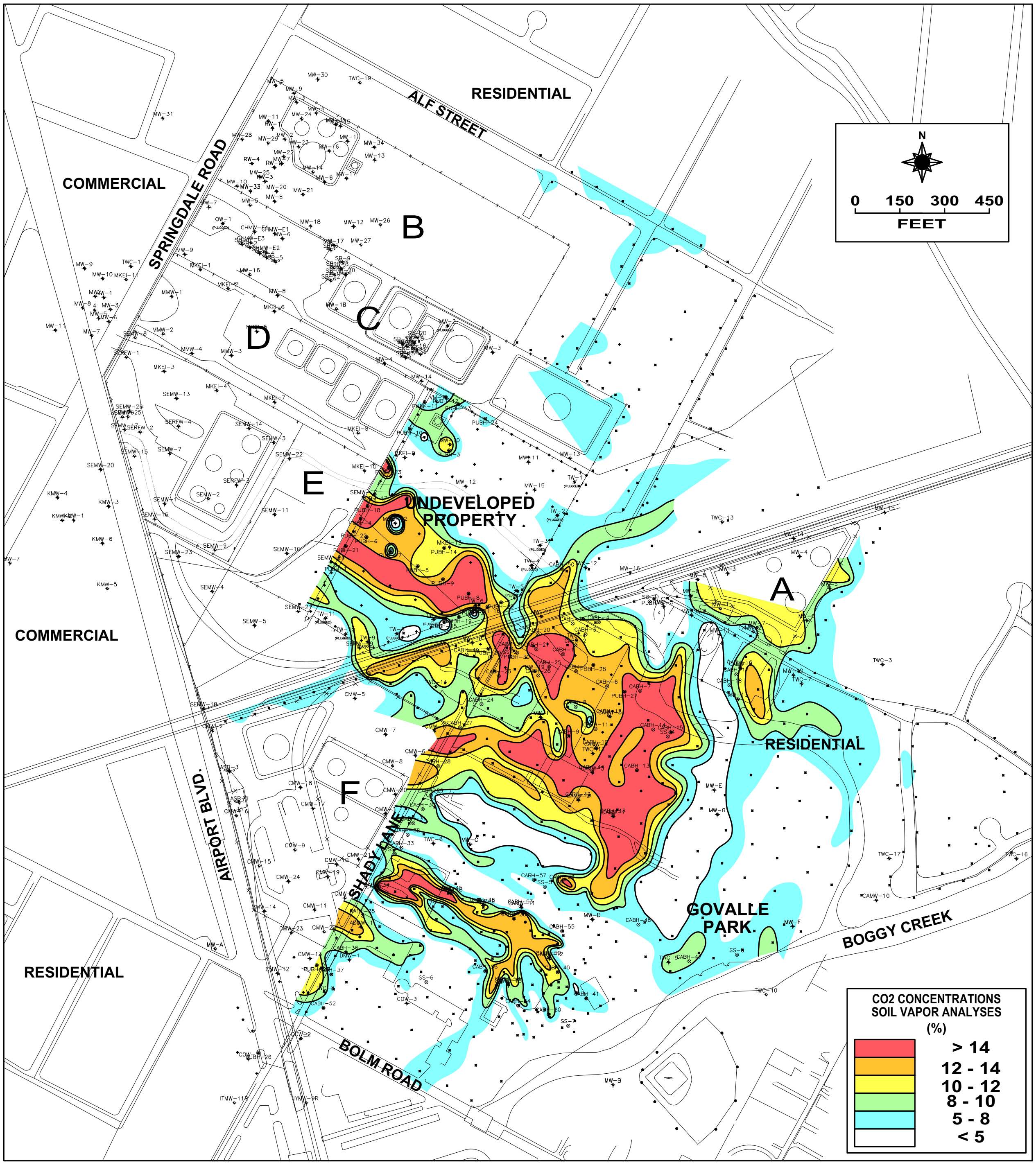
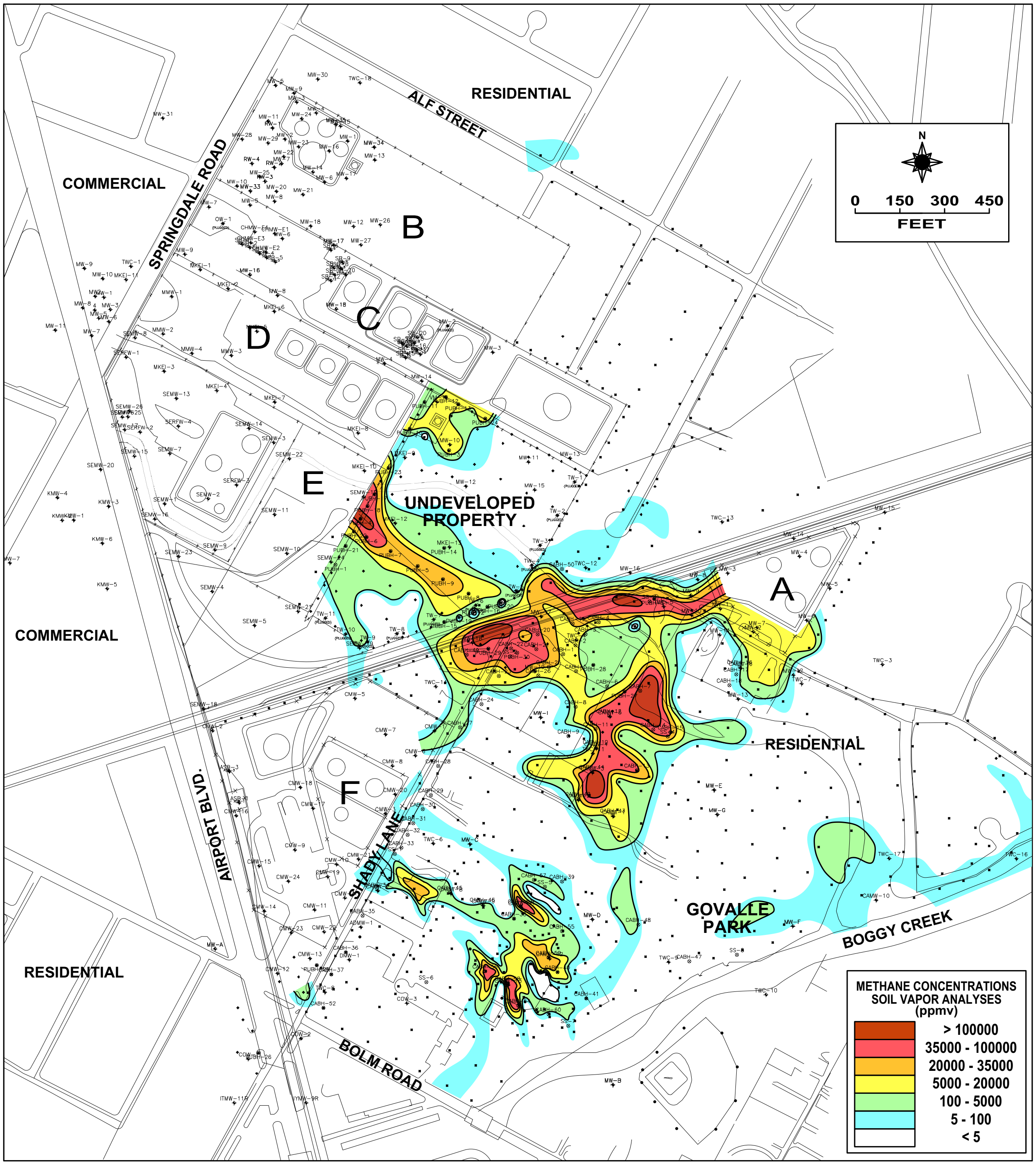

RESIDENTIAL
ALF STREET
COMMERCIAL
SPRINGDALE ROAD
B
C
D
E
UNDEVELOPED PROPERTY
A
COMMERCIAL
RESIDENTIAL
F
AIRPORT BLVD.
SHADY LANE
GOVALLE PARK
BOGGY CREEK
RESIDENTIAL
BOLM ROAD
N
0 150 300 450
FEET
CO2 CONCENTRATIONS
SOIL VAPOR ANALYSES
(%)
> 14
12 - 14
10 - 12
8 - 10
5 - 8
< 5

Figure 34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COMMERCIAL
SPRINGDALE ROAD
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E
UNDEVELOPED PROPERTY
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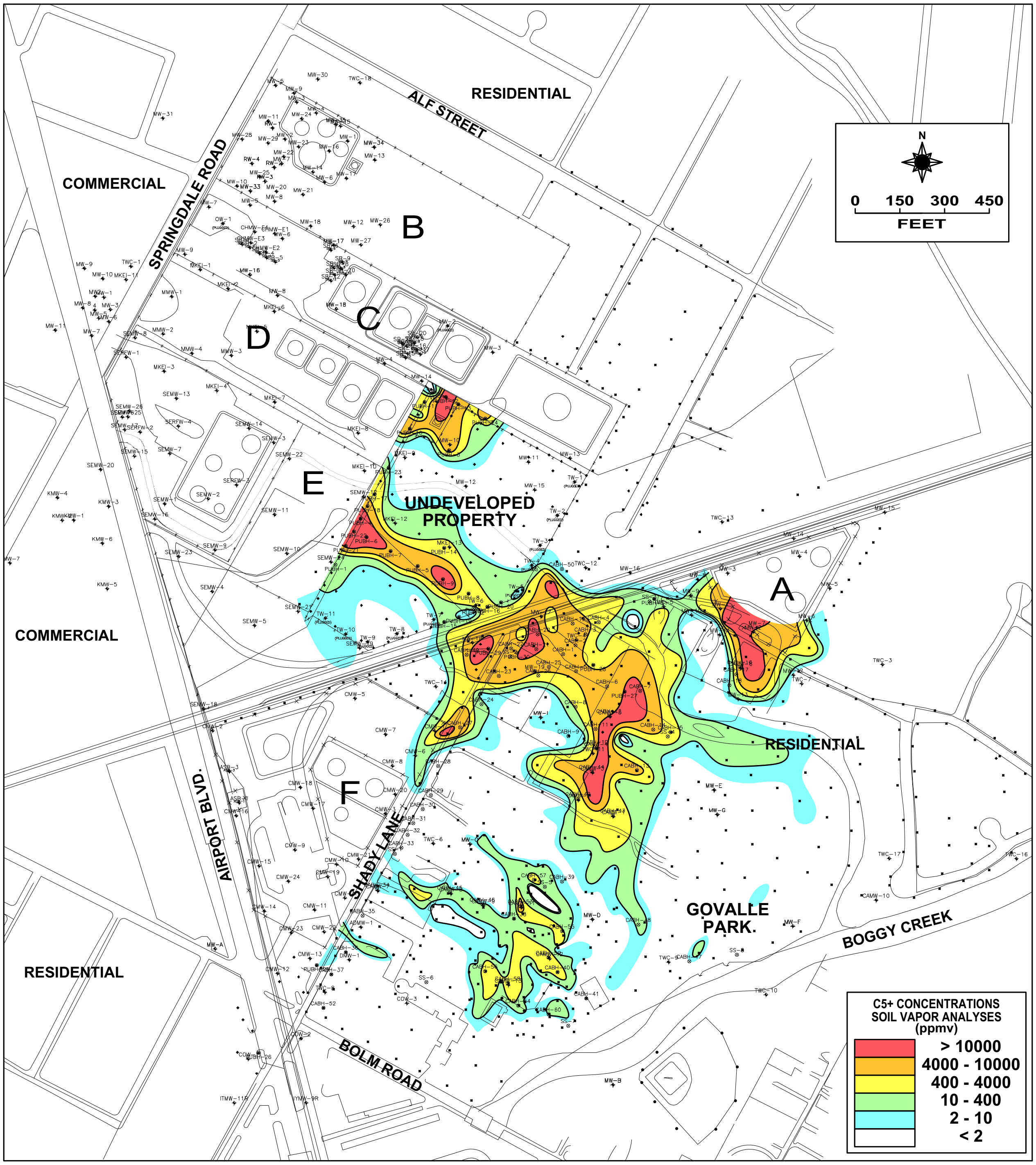
COMMERCIAL
RESIDENTIAL
F
AIRPORT BLVD.
SHADY LANE
GOVALLE PARK
BOGGY CREEK
RESIDENTIAL
BOLM ROAD
N
0 150 300 450
FEET
METHANE CONCENTRATIONS
SOIL VAPOR ANALYSES
(ppmv)
> 100000
35000 - 100000
20000 - 35000
5000 - 20000
100 - 5000
5 - 100
< 5

Figure 35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SPRINGDALE ROAD
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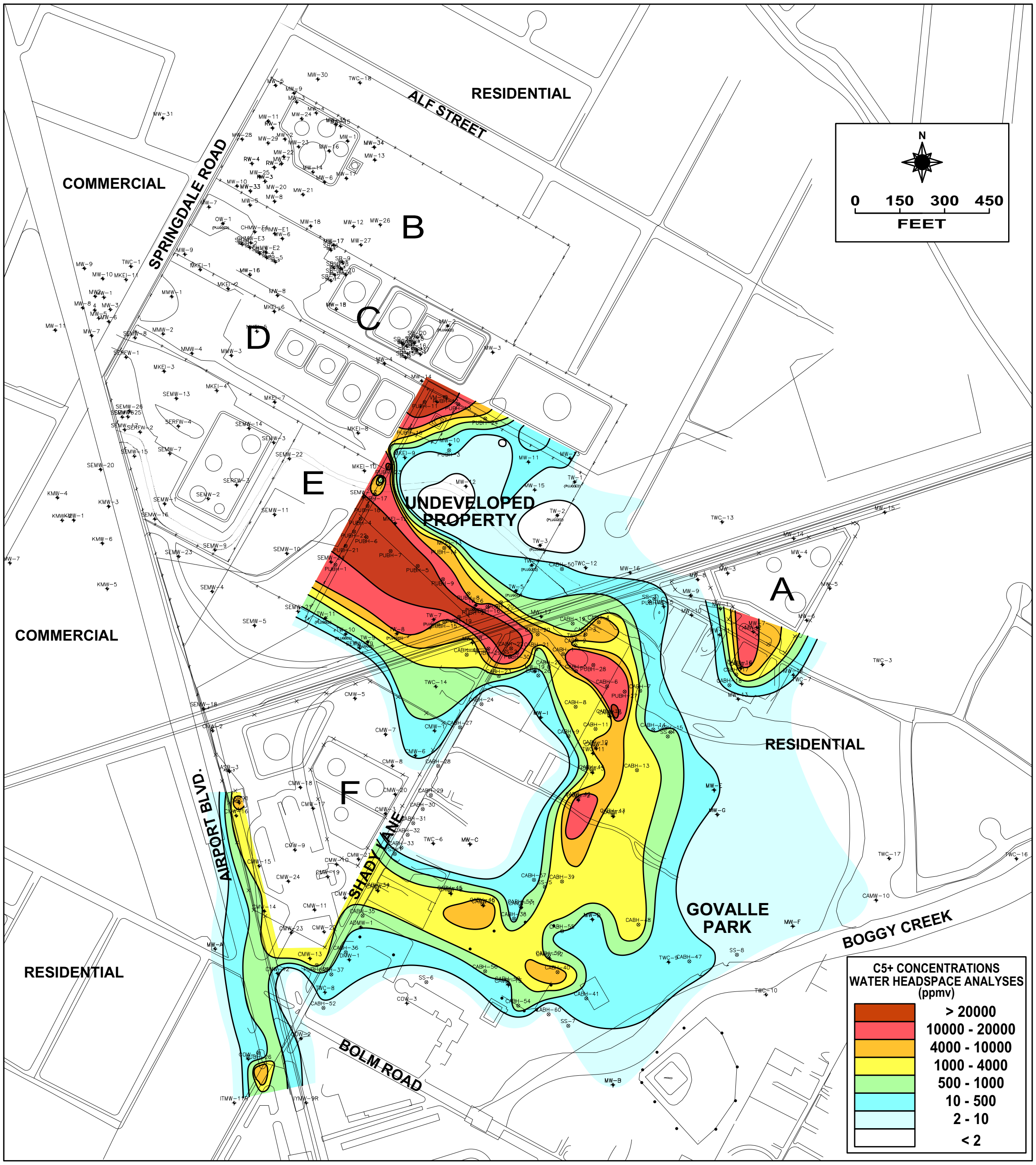
UNDEVELOPED PROPERTY
A
COMMERCIAL
RESIDENTIAL
F
AIRPORT BLVD.
SHADY LANE
GOVALLE PARK.
BOGGY CREEK
RESIDENTIAL
BOLM ROAD
N
0 150 300 450
FEET
C5+ CONCENTRATIONS SOIL VAPOR ANALYSES (ppmv)
> 10000
4000 - 10000
400 - 4000
10 - 400
2 - 10
< 2

Figure 36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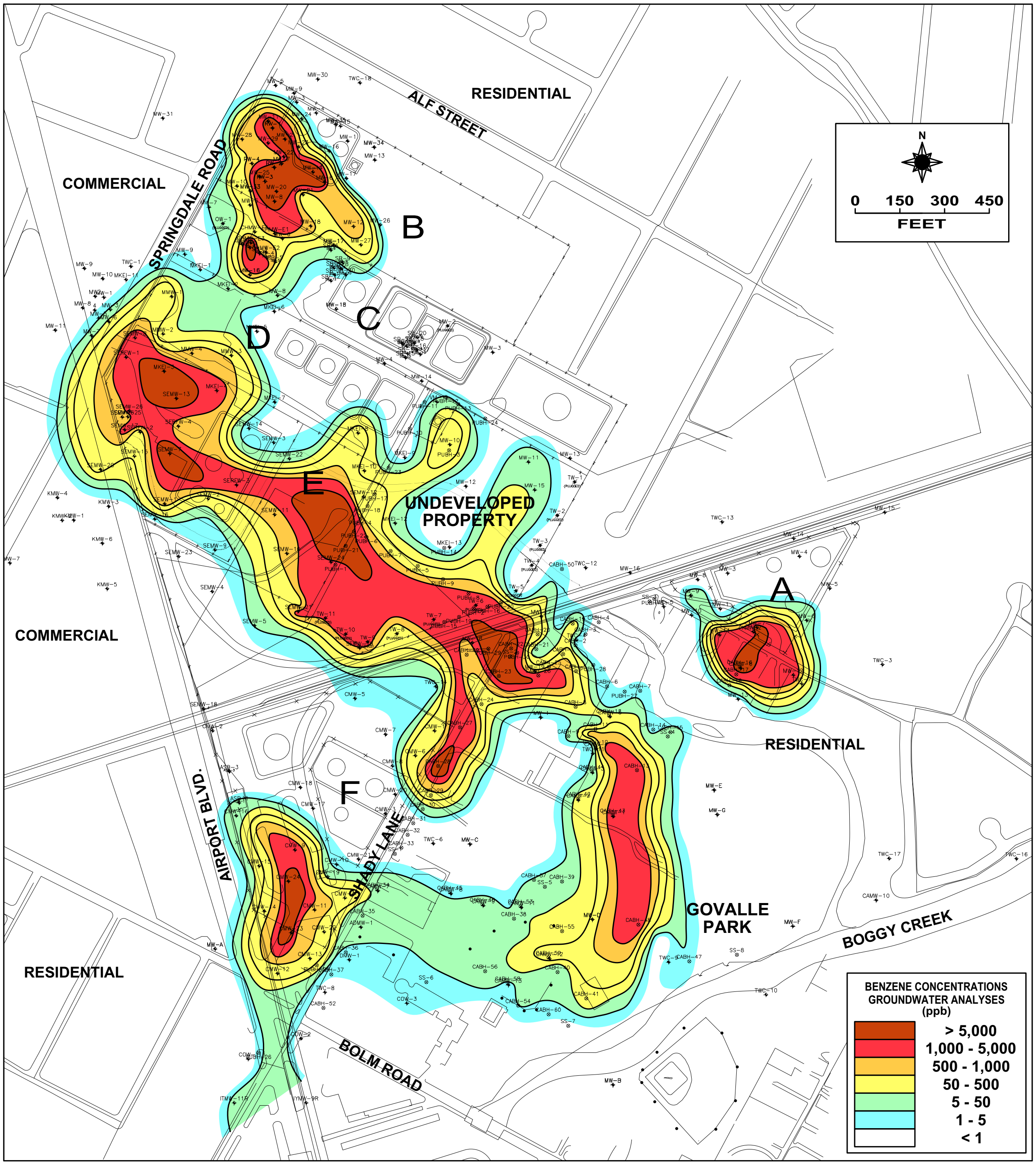
A
COMMERCIAL
RESIDENTIAL
F
AIRPORT BLVD.
SHADY LANE
GOVALLE PARK
BOGGY CREEK
RESIDENTIAL
BOLM ROAD
N
0 150 300 450
FEET
C5+ CONCENTRATIONS
WATER HEADSPACE ANALYSES
(ppmv)
> 20000
10000 - 20000
4000 - 10000
1000 - 4000
500 - 1000
10 - 500
2 - 10
< 2

Figure 37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UNDEVELOPED PROPERTY
A
COMMERCIAL
RESIDENTIAL
F
AIRPORT BLVD.
SHADY LANE
GOVALLE PARK
BOGGY CREEK
RESIDENTIAL
BOLM ROAD
N
0 150 300 450
FEET
BENZENE CONCENTRATIONS
GROUNDWATER ANALYSES
(ppb)
> 5,000
1,000 - 5,000
500 - 1,000
50 - 500
5 - 50
1 - 5
< 1

Figure 38

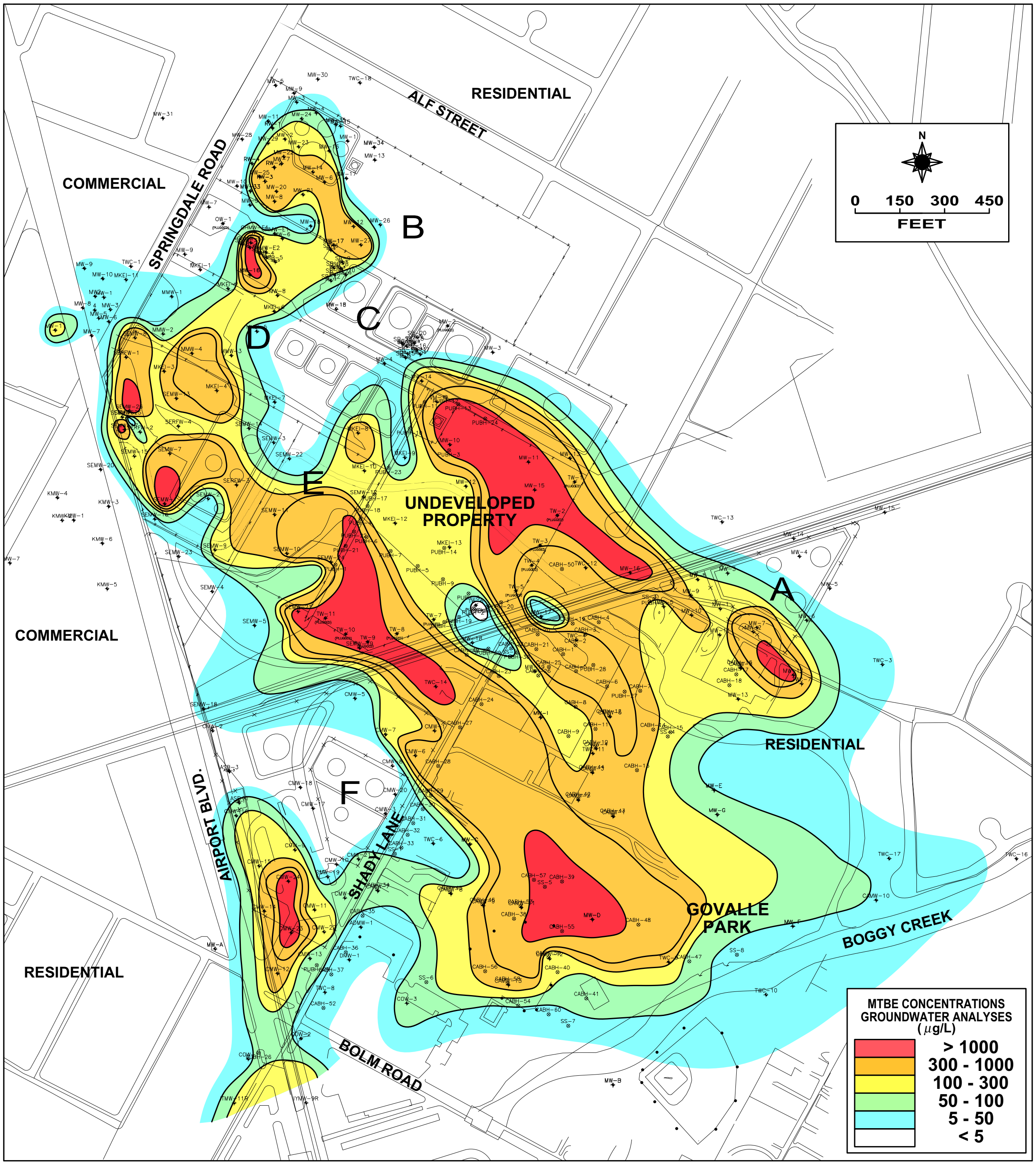
RESIDENTIAL
ALF STREET
COMMERCIAL
SPRINGDALE ROAD
N
0 150 300 450
FEET
B
C
D
E
A
F
UNDEVELOPED PROPERTY
COMMERCIAL
RESIDENTIAL
AIRPORT BLVD.
SHADY LANE
GOVALLE PARK
BOGGY CREEK
BOLM ROAD
RESIDENTIAL
MTBE CONCENTRATIONS
GROUNDWATER ANALYSES
(µg/L)
> 1000
300 - 1000
100 - 300
50 - 100
5 - 50
< 5

Figure 39

V. ORGANIC VAPOR DETECTOR INSTRUMENTS

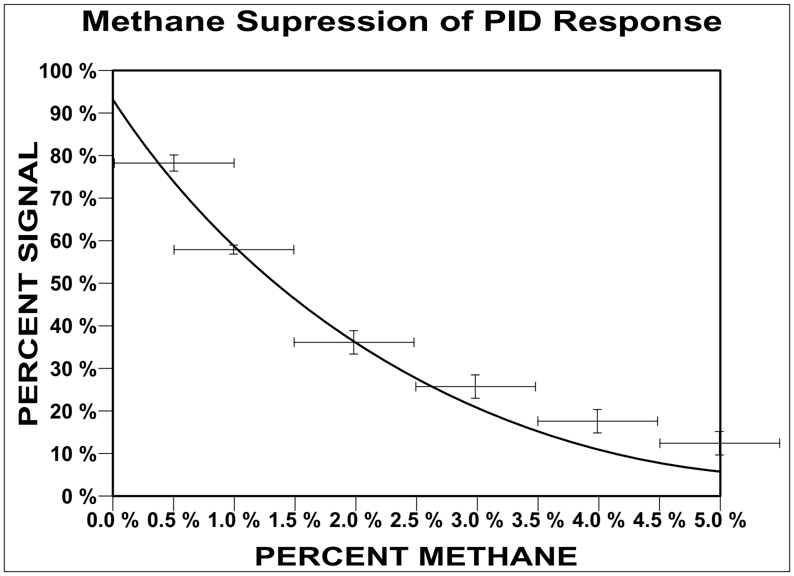

Figure 40

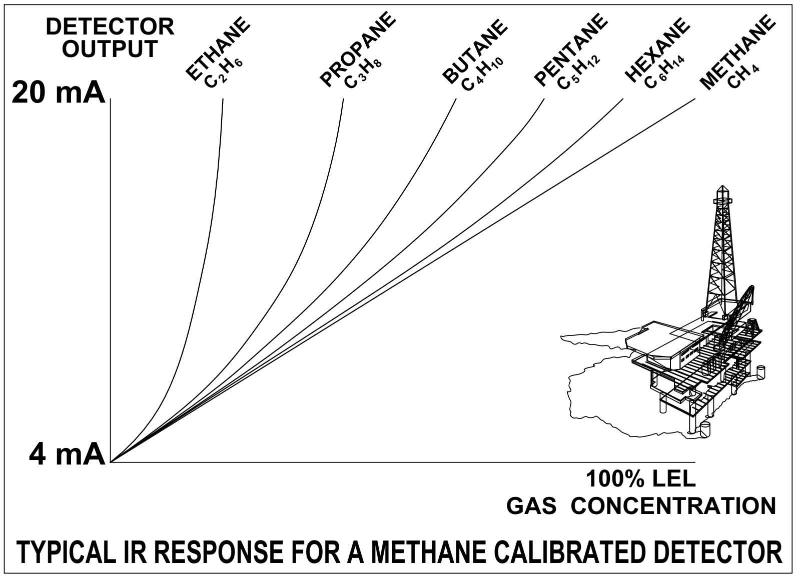

Figure 41

Given the utility of soil gas surveys, it is unfortunate that many environmental scientists have a low opinion of the technology. This problem has been addressed in considerable detail by Nyquist et al. (1990) and Robbins et al. (1990a, 1990b) who have found that a large number of the reported failures in the application of this technology are caused by the use of organic vapor detection instruments which do not yield a correct response under most site conditions. The response of total organic detector instruments is significantly affected by moderate to high concentrations of biogenic methane and carbon dioxide. The reduction in response of a PID detector in the presence of anomalous methane (50,000 ppm, or 5%) can be 95% (Figure 40). Although the PID does not detect methane, the methane absorbs energy and reduces the sensitivity of the detector. Infrared detectors (Figure 41), however, shows a good response to methane and other natural gas and/or gasoline type mixtures down to levels around 1000 ppm (0.1%). Heavier molecular weight hydrocarbons also produce a positive response, which make infrared detectors very useful for field screening samples. The infrared instruments are also capable of measuring carbon dioxide.

VI. SOIL GAS SURVEYS

Soil gas surveys are excellent assessment tools for defining the areal (horizontal) extent of subsurface contamination, when used properly, as demonstrated by the case studies addressed above. The main reason some soil gas surveys fail to delineate the areal extent of contamination is the surveys are not performed properly. Many surveys are performed similar to groundwater monitoring events where three volumes of vapors are removed from the probe hole prior to collecting a sample. The objective should be to collect and measure the equilibrated vapors present in the subsurface soils. In nature, equilibrium is established between various vapors (methane, carbon dioxide, C5+ hydrocarbons) and the subsurface petroleum product responsible for the contamination. This equilibrium is in delicate balance (particularly in low-permeability clays) and is easily disturbed.

Soil gas anomalies occur in “hydrocarbon spots” defined by geologic depositional features, and as such, are naturally discontinuous (Jones and Burtell, 1996). This limitation can be overcome by high-density sampling, coupled with a proper understanding of the geological environment. A 15-meter grid spacing (distance between sampling locations) is generally recommended, although on some sites a 3-meter grid may be required. Soil vapors are derived from residual (sorbed) phase, free phase (NAPL) and dissolved phase hydrocarbons present in the subsurface environment. Obviously residual phase contaminants (in soils) contribute more to the hydrocarbon soil gas levels measured than dissolved or liquid phase contaminants. This is a result of the sorbed phase contaminants being present at shallower depths, closer to the depths at which the samples are collected. These differences, however, can be addressed during interpretation of the data, provided adequate sampling (high density, multiple depth samples, etc.) has been performed.

The importance of spacing cannot be overemphasized, both for soil gas samples and monitor wells. The objectives of soil gas and monitor well investigations are to provide the true horizontal and vertical extent of the contaminated areas. Monitor wells are no substitute for soil gas surveys unless they are plentiful and closely spaced. In addition, the borehole/monitor well must be sampled continuously from the surface down to groundwater. The above options are not practical for monitor wells because they are not cost-effective. Soil gas surveys, followed by selected borings (sampled continuously), followed by monitor well installations can collectively and successfully accomplish the desired objectives at a reasonable cost.

VII. DISSOLVED GAS SAMPLES

Contrary to popular belief, surface geochemical sampling does not have to be confined to soil vapors located entirely above the water table. Equivalent results can be obtained by measuring the gases dissolved in shallow perched groundwater zones or aquifers, which are always in dynamic equilibrium with the surrounding environment. If anomalous gases are contained in the pore space of subsurface soils, then these same gases will generally be dissolved in the subsurface waters.

Gas magnitudes in the free pore space and dissolved in the associated waters will be different, however, they will both be very close to zero in background areas, and show sufficient contrast from background, whenever they are in close proximity to contamination. In areas of very shallow ground water the best sample is generally obtained from analyzing the dissolved gases in the subsurface water sample. If sufficient contrast with background is observed, it is possible to mix samples obtained from different media (soil vapors and dissolved gases in water) in a near surface geochemical reconnaissance survey.

IX. CONCLUSIONS

A soil gas survey is an accurate method for quickly and inexpensively measuring the presence and horizontal extent of contamination resulting from a large variety of hydrocarbon products such as gasoline, jet fuel, diesel and chlorinated solvents. The recognition and analysis of biogenic methane and carbon dioxide gases significantly increases the effectiveness of soil gas technology, particularly for the less volatile products, such as diesel and kerosene. Both methane and carbon dioxide can be measured (screened) with reasonable accuracy in the field with very little interference using infrared detectors. Extreme caution must be exercised when using PID detectors since these instruments are sensitive to, and interfered with by nearly everything (methane, carbon dioxide, moisture content, etc.), generally resulting in erratic and erroneous results.

Carbon dioxide is generated at the top, edges, and possibly the bottom of the contaminant mass where oxygen dominates. Methane requires strict anaerobic conditions, and is obviously generated in close proximity to the free product “cores”, where oxygen has been scavenged. If samples are collected on a high enough density, every contaminated “core” becomes a biodegradation center that can be individually mapped using the assessment data. Our data show that anaerobic methane is generated in significant concentrations in those areas containing petroleum product contamination. Data from regional environmental studies conducted by ETI verify that biogenic methane is not generated in background areas, located adjacent to those areas containing moderate to high levels of hydrocarbon contamination.

It should be noted that soil gases indicate the presence of contamination, but do not directly reflect the actual concentrations of residual or dissolved phase contaminants, or the thickness of the NAPL in the subsurface. Additional samples/data must always be gathered from direct-push borings and monitor wells to determine the true horizontal and vertical extent of any subsurface contamination. Because the horizontal extent of subsurface contamination is controlled by geologic factors, a geochemical survey plume map should never be considered to provide an exact picture of any or all contaminated layers; the plume map is often a composite of the subsurface contamination at all levels. Samples should be collected at multiple depths and on a high-density grid in order to fully evaluate the horizontal and vertical extent of the contamination within a study area. An understanding of the subsurface geology will also help one appreciate the complexity of the problem (contamination) and allow for a sound interpretation.

Soil gas surveys are cost-effective, time-efficient, and have the advantage of being non-disruptive to normal business operations. ETI's soil gas sampling probes can be used in congested areas, within a refinery or gas plant, where no other equipment can easily be deployed. Because of the lower cost and time involved in conducting a soil gas survey, a greater number of locations can be sampled, greatly increasing the potential for more accurate mapping of the horizontal and vertical extent of the contamination. Using the soil gas data, monitor wells can be placed within the most contaminated areas, thus significantly improving the assessment data. This approach will allow for a more thorough remedial action plan and shorten the time required for cleanup.

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