

DRAFT FINAL REPORT
BACKGROUND HYDROCARBON
VAPOR CONCENTRATION STUDY
FOR UNDERGROUND FUEL STORAGE TANKS

U.S. EPA CONTRACT NO. 68-03-3409

February 29, 1988

Prepared for:

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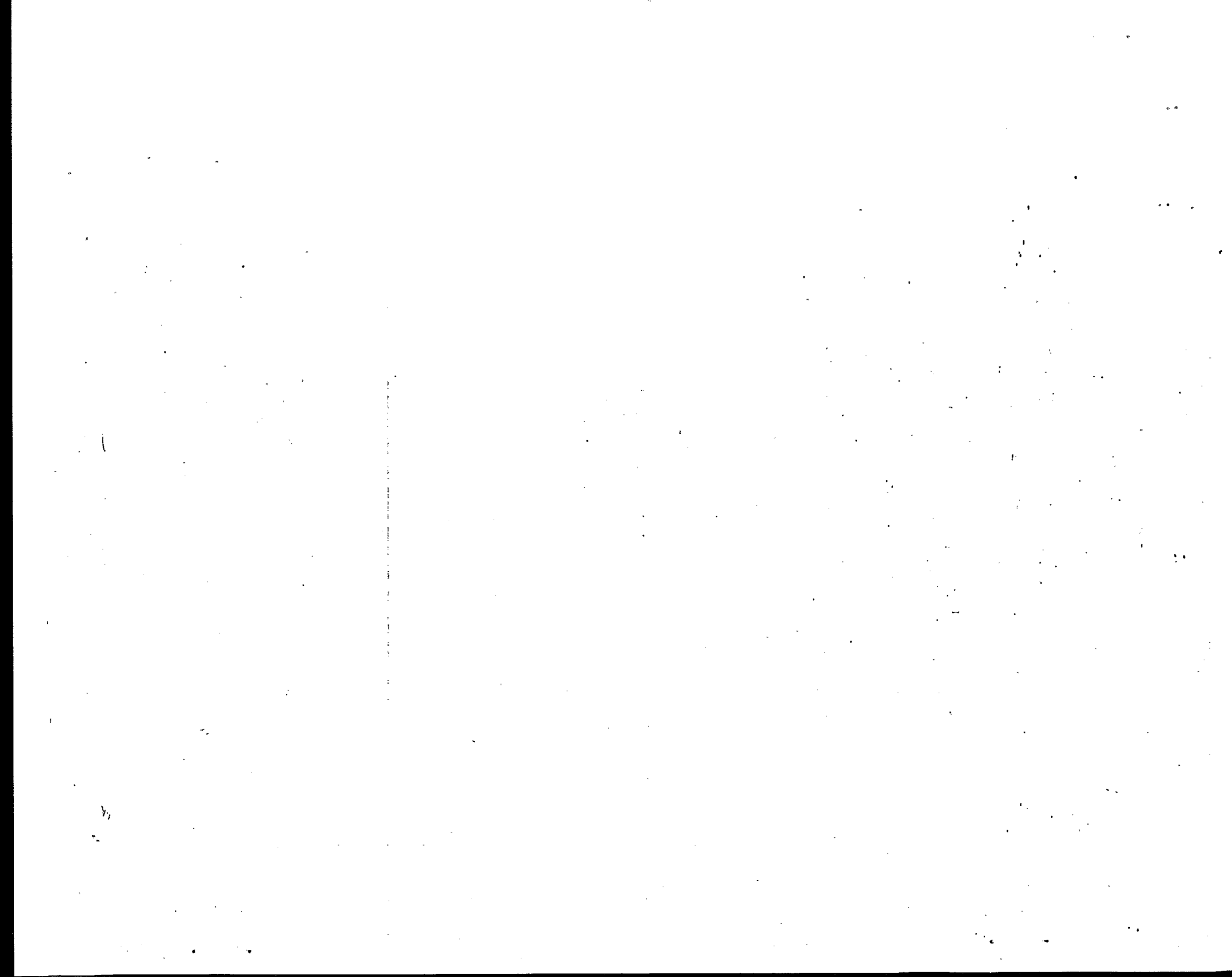
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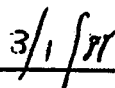


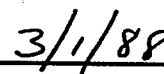
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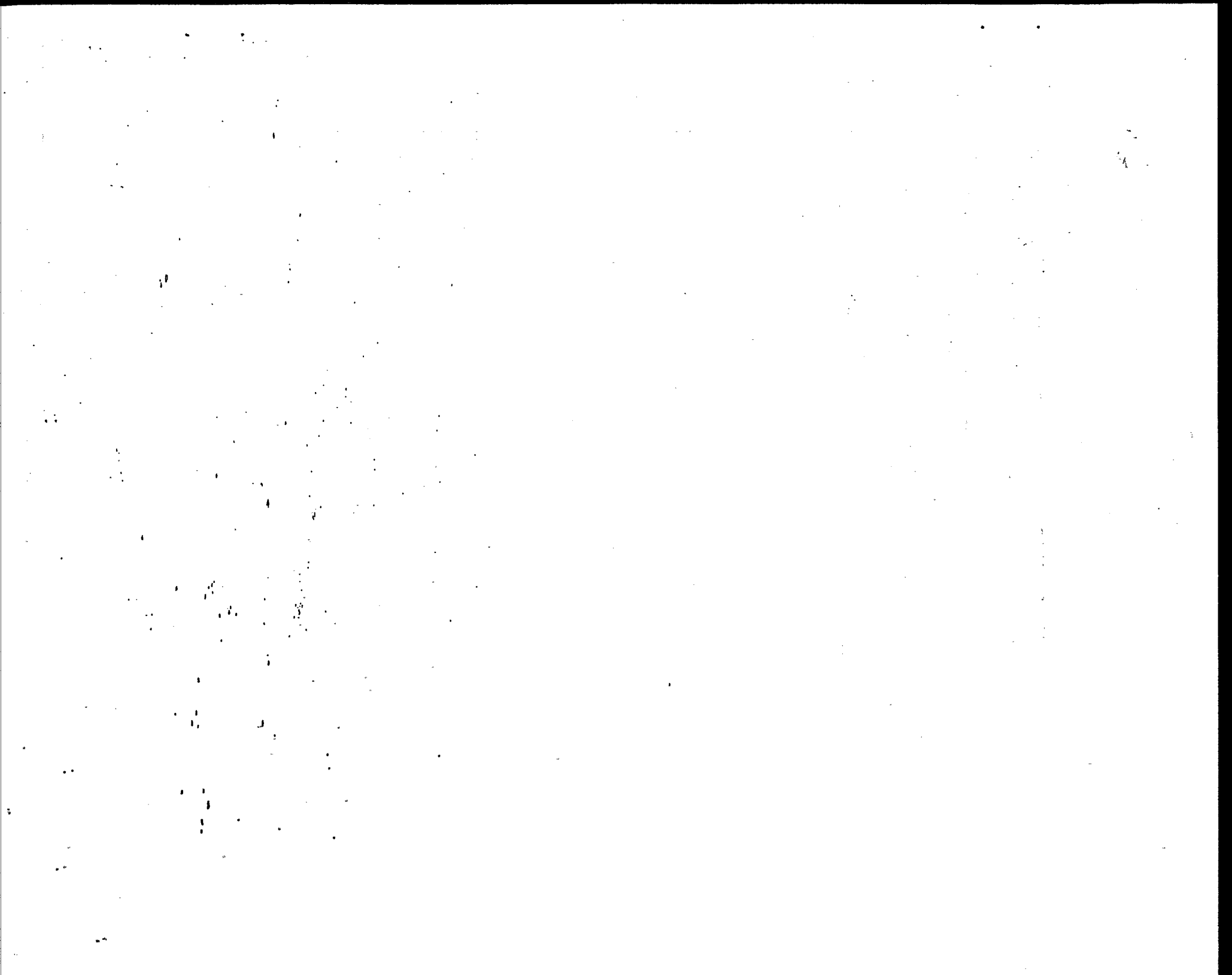


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1.0 EXECUTIVE SUMMARY

The Environmental Monitoring Systems Laboratory (EMSL) of the USEPA awarded Contract No: 68-03-3409 to Camp, Dresser and McKee (CDM) to conduct a study to determine the background hydrocarbon concentrations in soil vapor in the backfill of representative underground fuel storage tank (UST) sites across the country. CDM designated Geoscience Consultants, Ltd. (GCL) to select sampling sites, prepare sampling strategies, review data collection, analyze the data and prepare a final report. Field data on clean UST sites were collected from September 14 to December 13, 1987. Data on UST sites with documented releases were obtained from Tracer Research Corporation files.

Since no database for soil vapor information at non-contaminated underground storage tank sites was known to exist, a field sampling program was undertaken to establish a baseline data set of hydrocarbon vapor concentrations. Data were collected from 27 gasoline service stations selected as non-contaminated sites in three diverse geographic regions: Central Texas (Austin, Texas); areas surrounding Long Island Sound (Suffolk County, New York; Providence, Rhode Island; Storrs, Connecticut); and Southern California (San Diego, California). The three regions were selected for their active underground storage tank regulatory programs, as well as their differences in geology, hydrology and climate. The non-contaminated database consists of 279 soil vapor samples from 25 service stations. At the other two stations, observed or suspected leaks prevented their data from being used in the non-contaminated database.

At each location, soil was sampled at varying distances and depths from UST appurtenances (such as submersible pumps, vents and product flow lines) to determine if a particular pattern of hydrocarbon concentration existed. Samples were collected by driving a hollow steel probe into the ground, and evacuating 5 to 10 liters of soil vapors with a vacuum pump. Volatile hydrocarbon species were identified and quantified at the site

by utilizing gas chromatograph/flame ionization detection (GC/FID) equipment. Ten to fifteen samples were collected and analyzed at each site.

Hydrocarbon vapor concentrations from the non-contaminated sites range from detection limit levels of 0.02 micrograms per liter (ug/l) to maximum values of 870,000 ug/l of methane, 110,000 ug/l of benzene, 160,000 ug/l of toluene, 25,000 ug/l of ethylbenzene, and 110,000 ug/l of xylenes. The maximum concentration of total hydrocarbons (less methane) is 1,000,000 ug/l. Determination of total hydrocarbon concentrations exclude methane peaks in order to elevate the compounds most representative of gasoline. Additionally, subtraction of the methane peaks precludes the inclusion of methane concentrations caused by naturally-occurring organic decomposition.

The statistical distribution of total hydrocarbons (less methane) indicates that a majority of the concentration values are in the lower concentration ranges. The relative frequency distribution shows 53.2 percent of the samples below 1,500 ug/l (500 ppm by volume) and 93.1 percent below 100,000 ug/l (27,000 ppm by volume). The median is 800 ug/l and the mean is 23,300 ug/l.

Contaminated site data were obtained from Tracer Research Corporation's historical records. The contaminated site data consists of 60 soil vapor samples taken from nine sites having known contamination from a petroleum fuel leak or spill. These sites were all active gasoline service stations or fueling facilities. The contaminated site data also shows much variability. The statistical distribution of total hydrocarbons (less methane) shows a majority of sample values to be in the lower concentration ranges. The relative frequency distribution shows 35 percent of the samples below 1,500 ug/l (500 ppm by volume) and 66.7 percent below 100,000 ug/l (27,000 ppm by volume). The median is 9,000 ug/l and the mean is 160,000 ug/l.

Although much variability exists in both the non-contaminated and contaminated site data, significant differences can be seen between the two distributions. A ten-fold difference exists between the means and the medians of each data set. This ten-fold difference also exists between the numbers of samples with concentrations above 10,000 ug/l (3,000 ppmv) for the two data sets. For example, 29.6 percent of the non-contaminated samples occurred in the range of 10,000 ug/l to 100,000 ug/l while 33.3 percent of the contaminated samples concentrations occurred in the range of 100,000 ug/l to 1,000,000 ug/l.

Statistical data patterns associated with site location and sample depth were delineated using non-parametric statistical methods. Statistically significant differences were found to exist between the total hydrocarbon (less methane) vapor concentrations among the five locations studied for steel tank systems, whereas these differences were not significant for fiberglass tank systems. Statistically significant differences also occurred between the total hydrocarbon (less methane) vapor concentrations among the sample depths of 2, 6 and 10 feet for both steel and fiberglass tank systems. Higher concentrations were found at the lower depths.

A fresh spill at one station in Austin provided an opportunity to add butane to the list of analytes under study. The butane concentration in 15 soil gas samples taken during the first four days after the spill occurred ranged from 530 ug/l to 300,000 ug/l. Butane was also sampled at sites in Storrs, Connecticut and Providence, Rhode Island both of which had no evidence of recent leaks or spills. At these two sites, butane concentrations in 65 soil gas samples ranged from the minimum detection limit of 0.02 ug/l to 930 ug/l. The large difference between the butane concentrations at the fresh spill site in Austin and the non-contaminated sites in Connecticut and Rhode Island suggests that butane may be a good indicator of a fresh spill or leak.

Because there are no standard procedures for calculating and reporting total hydrocarbon concentration data, GCL evaluated different calculation

methods. It was determined that the best approximation of total hydrocarbon (less methane) concentrations, based on available calibration data, was achieved using an average response factor calculated from the daily response factors of benzene, toluene, ethylbenzene and ortho-xylene.

2.0 PURPOSE OF STUDY

Proposed Federal regulations to monitor ground water contamination around underground storage tank (UST) systems require the development of effective external and internal leak detection methods. Soil gas sampling is an external detection method which could prove useful in determining whether an underground storage tank is leaking.

In order to determine the effectiveness of soil gas surveys in leak detection, a study was designed with the following goals:

- Collection of soil gas data from sites where the tank system was tested and found to be tight, providing background soil gas data, and
- Comparison of these background data to soil gas data from sites known to be contaminated by spills or leaks in order to identify a data pattern which may be indicative of a leaking system.

To fulfill these goals, soil gas surveys were performed at 27 active gasoline service stations in three diverse geographic regions. Hydrocarbon vapor concentrations in the backfill surrounding the underground storage tanks were sampled and analyzed.

The term "soil gas" refers to vapors found in the interstitial area between particles of sand or gravel (pores). "Soil gas" and "soil vapor" are used interchangeably in this report. These vapors, often loaded with hydrocarbons when a underground storage tank is leaking, escape into the gravel or sand which is used to surround the tank during installation. This surrounding tank medium is called "backfill". Typically pea gravel is used for backfill around fiberglass tanks, and sand around steel tanks. An overview of a typical UST arrangement is shown in Figure 2-1.

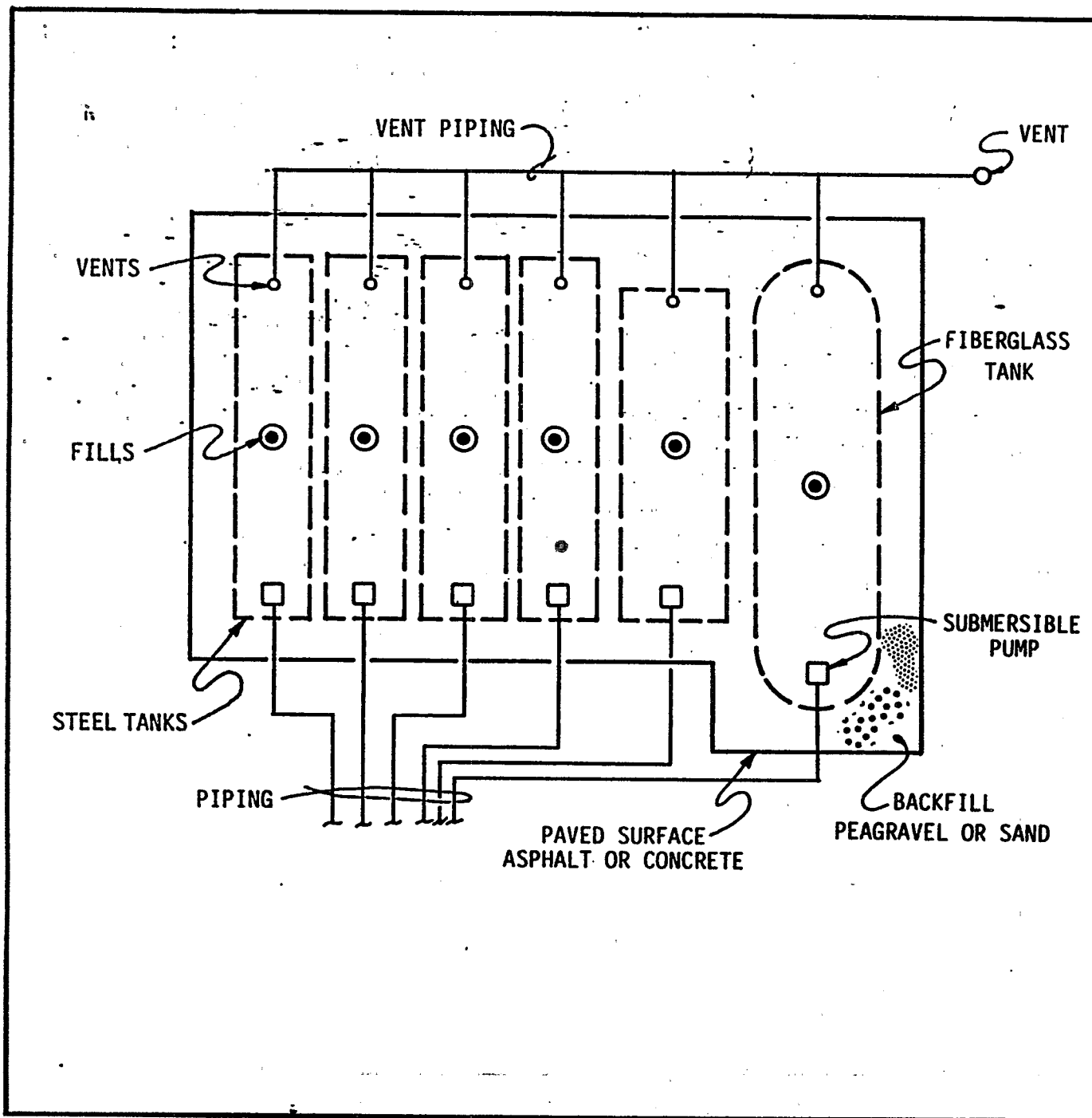


FIGURE 2-1
TYPICAL UST ARRANGEMENT

3.0 SITE SELECTION

3.1 LOCATIONS

Soil-gas surveys were conducted at the following locations:

- Austin, Texas
- San Diego, California
- Long Island Sound area
 - Suffolk County, New York
 - Providence, Rhode Island
 - Storrs, Connecticut

Austin, San Diego and Suffolk County, New York were originally selected as the locations for the study because they were recognized as having exemplary local underground storage tank regulatory programs, and they represented different geographical situations. Stations in Providence and Storrs were added to provide a broader data base from the Long Island Sound area, and to interact with the underground storage tank evaluation program at the University of Connecticut.

Active regulatory programs were desired in order to assure that accurate information would be available for the stations to be studied. Since a major purpose of the study was to determine background soil vapor levels at clean, well-managed stations, it was necessary to determine if leaks or spills had previously occurred at the stations being tested. Records at Austin, San Diego and Suffolk County were carefully reviewed and all available information was obtained concerning the specific stations to be studied.

Different geographical locations were desired for the study in order to eliminate possible data bias that could occur if sampling were done at one location. The selected locations represent a wide range of temperature, humidity, geology and topography. Although soil gas samples were taken primarily from the backfill areas of the tanks, the surrounding geology and climatic conditions can affect the concentration of vapors existing in the backfill material.

3.2 SERVICE STATIONS

Three oil companies cooperated in the study by offering several of their service stations as candidates for field testing. Twenty-seven stations were selected which represent a variety of tank ages, tank materials, products stored, and backfill materials. The stations were selected according to the following screening criteria:

- The stations were to be clean, well-managed businesses with no major environmental problems.
- Existing tanks were required to meet the appropriate operation specifications.
- The tanks must have been in the ground and operational for at least 6 months prior to the site sampling.
- The stations were required to have relatively large total throughputs of product since beginning operation and relatively large throughputs on a monthly basis.
- The stations were required to have good inventory control.

Twenty-seven service stations with ten to fifteen sample points at each station were selected, providing a broad data base with a variety of tanks, backfills and field conditions. There were a total of 100 underground storage tanks involved in this study, of which 63 were made of steel and 37 of fiberglass. Tank installation dates ranged from 1940 to 1984 for steel tanks, and 1978 to 1984 for fiberglass tanks. A listing of all of the tanks is shown in Appendix A.

4.0 GEOLOGY, HYDROLOGY AND CLIMATE

This section briefly describes the geologic, hydrologic and climatic characteristics which may effect hydrocarbon soil gas concentrations within the three study regions.

4.1 AUSTIN, TEXAS

4.1.1 Geology and Hydrology

Bedrock in the Austin area consists dominantly of limestones, marls, and shales, all of Cretaceous age. Terrace deposits and alluvium locally overlie the bedrock units in the present valley of the Colorado River and on terraces representing older Quaternary drainage levels.

Station sites AU-2, AU-4, AU-5, and AU-6 all lie in outcrop areas of the Upper Cretaceous Austin Group, which consists of chalk, limestone and marly limestone. A very thin (less than 5 feet) cover of sand and gravel terrace deposits may be present at site AU-4. Site AU-5 lies within 100 feet of a fault which exposes Cretaceous clay at the land surface on the side of the fault opposite the station.

Sites AU-1 and AU-7 are located in areas of alluvial sand and gravel comprising terrace deposits, but these deposits are probably less than 10 feet thick at both sites. The alluvium is underlain by Lower Cretaceous clay of the Del Rio Formation, a pyritic, gypsiferous and calcareous shale unit which may represent a barrier to ground water or soil gas movement.

Site AU-3 lies within a small exposure of altered volcanic tuff of Cretaceous age, in an area consisting dominantly of Austin Group limestones. A very thin cover of terrace deposits similar to those at AU-4 may also be present at AU-3. As at site AU-5, a Cretaceous clay unit crops out within 100 feet of the AU-3 site, on the opposite side of a fault passing near the station.

The Edwards aquifer underlying the Austin area is contained within limestones of Cretaceous age. Depth to water in the Edwards aquifer is

highly dependent on topography, ranging from the land surface in river valleys to over 250 feet below it in upland areas.

Elevation of the water table varies by as much as 50 feet over time, depending on recharge and pumpage. Local zones of perched water occur above the Edwards aquifer in areas where impermeable lithologic units are present. Ground water was encountered at a depth of 7 feet at sites AU-4 and AU-6, at a depth of 9 feet at site AU-7, and at a depth of 10 feet at site AU-5.

4.1.2 Climate

The climate of Austin, Texas is humid subtropical with an average rainfall of 20 to 40 inches per year which is evenly distributed throughout the year. During the first sampling period, September 28 through October 2, the weather was partly cloudy to clear with temperatures ranging from 62°F to 92°F. The barometric pressure during this period ranged from 29.49 inches Hg to 30.09 inches Hg. The second sampling period was October 26 to October 30. The same weather patterns were seen with temperatures ranging from 70°F to 96°F and barometric pressures ranging from 29.84 inches Hg to 30.12 inches Hg. Appendix B contains a summary of the actual field conditions.

4.2 LONG ISLAND SOUND AREA, NEW YORK, RHODE ISLAND AND CONNECTICUT

4.2.1 Geology and Hydrology - Long Island, New York

Long Island consists dominantly of glacial till and outwash deposits representing a terminal moraine formed during the Quaternary Period. Cretaceous and Tertiary rocks crop out locally in western Suffolk County, but are not areally significant. All station sites examined for this project are located in areas of glacial till.

Ground water on Long Island is contained within the glacial till and local alluvial deposits of reworked glacial material. Depth to water varies from about 10 to 100 feet on the Island. At site NY-2, ground

water is about 22 feet below the surface. At all other Long Island sites, ground water is between 60 and 90 feet below the surface.

4.2.2 Geology and Hydrology - Providence, Rhode Island

In the Providence area, Quaternary glacial deposits of varying thickness overlie bedrock of Cambrian and Precambrian age. As on Long Island, ground water is found at depths up to about 50 feet in the Rhode Island glacial deposits. Ground-water conditions are not well known in many areas because most public water supply is derived from surface sources. The depth to water at the station sites is not known.

4.2.3 Geology and Hydrology - Storrs, Connecticut

In the Storrs area, Quaternary glacial deposits of varying thickness, up to about 100 feet, overlie crystalline and metamorphic bedrock of Cambrian and Ordovician age. Limited quantities of ground water are found in the glacial fill, but water supply wells generally tap more extensive reserves in fractures of the Paleozoic rocks. Depth to water at the Connecticut station sites is 10 feet.

4.2.4 Climate

The three Long Island Sound locations included in the study have similar climatic conditions which are influenced by the continental and oceanic weather systems. The average rainfall for these locations is from 40 to 60 inches per year. During the sampling period, September 22 to September 25 in Suffolk County, the temperature ranged from 61°F to 75°F with the barometric pressure ranging from 29.70 inches Hg to 29.94 inches Hg. During the sampling visit to Storrs, Connecticut from November 11 to November 13, the temperatures ranged from 29°F to 51°F with snow and rain occurring on November 11 and November 12. The barometric pressure during this time ranged from 29.65 inches Hg to 29.99 inches Hg. The sampling visit to Rhode Island during the period of December 9 to December 11 experienced one day of rain, December 11, with temperatures ranging from 40°F to 58°F and the barometric pressure ranging from 29.32 inches Hg to 29.83 inches Hg. Appendix B contains a summary of actual field conditions at the time of sampling. Appendix C contains general weather

data for the Long Island Sound area for the months of September, October, November and December 1987.

4.3 SAN DIEGO REGION, CALIFORNIA

4.3.1 Geology and Hydrology

The San Diego area of southern California contains two distinct physiographic sections, a coastal plain section and a mountain-valley section. The coastal plain section consists of Tertiary marine sediments, in many parts of which wave-cut terraces are apparent, and through which alluvial valleys have been cut between inland watersheds and the sea. The mountain-valley section includes alluvium-filled valleys dissecting mountain ranges which are comprised of a wide variety of volcanic, sedimentary, and igneous rocks.

Station sites SD-1, SD-4, and SD-6 are located in Quaternary coastal sediments overlain by a thin veneer of Recent alluvium. All three of these sites are at elevations within a few feet above sea level. Water was encountered 7 feet below the land surface at site SD-1 and 12 feet below the land surface at site SD-6. Ground water probably exists at a shallow depth at site SD-4, but was not encountered during the study.

Stations SD-3 and SD-7 are on a terrace of Tertiary sediments elevated about 200 feet above sea level, and are located about 3 to 5 miles inland from the sea. Depth to water at stations SD-3 and SD-7 is not known.

Sites SD-2 and SD-9 are located in valleys near the eastern margin of the coastal plain section. At these locations alluvium of unknown but probably shallow depth overlies volcanic or metamorphic bedrock. Ground water was encountered at a depth of 8 feet at site SD-2. Depth to water at site SD-9 is unknown.

Sites SD-5 and SD-8 are in a broad valley within the mountain-valley physiographic section. These sites are located on the residuum produced by in-situ weathering of underlying volcanic bedrock. Based on

information from wells in the vicinity, depth to water at sites SD-5 and SD-8 is probably between 10 and 25 feet.

4.3.2 Climate

The coastal location of San Diego, California tempers the climate of this city. Rainfall in San Diego ranges from 10 inches to 20 inches per year, with 85% of this precipitation occurring during the months of November through March. During the sampling period, September 15 through September 24, the temperature ranged from 70°F to 86°F with one day of slight rain (September 22). The barometric pressure during the sampling period ranged from 29.90 inches Hg to 30.10 inches Hg. Appendix B contains a summary of actual field conditions at the time of sampling. Appendix C contains general weather data for the San Diego area for the months of September, October, November and December 1987.

5.0 FIELD METHODS

The field investigation consisted of on-site sampling and analysis of soil gas at a total of 27 service stations in the three regional areas. Tracer Research Corporation (TRC) performed the soil-gas sampling and the on-site analysis of the samples. TRC also performed on-site analysis of backfill samples for each site to determine soil moisture content. Geoscience Consultants, Ltd. (GCL) was responsible for overall sampling strategy and data quality assurance.

The field work began on September 14, 1987 in San Diego, California and was completed on December 13, 1987 in Rhode Island. The field schedule was as follows:

San Diego, CA	9 Stations	Sept 14 - 24, 1987
Suffolk County, NY	5 Stations	Sept 21 - 25, 1987
Austin, TX	4 Stations	Sept 28 - Oct 2, 1987
	3 Stations	Oct 26 - Oct 30, 1987
Storrs, CT	2 Stations	Nov 10 - 13, 1987
Providence, RI	4 Stations	December 10 - 13, 1987

5.1 SAMPLING STRATEGY

The sampling strategy was designed to determine the range and spatial distribution of hydrocarbons within the backfill of the underground storage tanks. The sampling points were very close to the tanks because excavation and backfill typically extended only one to three feet laterally from the edges of the tanks.

Soil-gas samples were collected only from the backfill areas of the tank excavations. The specific sample sites were located at varying distances from tank fill ports, pump chambers, and product and vent piping, all of which can be sources of leaks. A typical sampling grid consisted of four or five sample holes with samples collected at depths of 2, 6, and 10 feet in each hole. Typically, ten to fifteen samples were collected at each service station. The locations of the sample points are identified on the site maps of the stations in Appendix D.

Soil samples to determine moisture content of the backfill material were taken from fifty percent of the sample points. These samples were analyzed on-site by JRC personnel utilizing a portable oven and balance. Two soil samples were collected at each station by GCL personnel. These samples were sent to an independent certified laboratory, Professional Service Industries, Inc., for the determination of moisture content and particle size distribution (sieve analysis). The results of these analyses are included in Appendix E.

Some additional sampling other than for soil gas was performed at 5 stations where some unusual conditions existed. This consisted of: 1) vapor sampling from U-Tube monitoring systems at Stations #4 and #6 in Suffolk County, New York, and 2) water sampling from shallow ground water at Stations #1 and #2 in Storrs, Connecticut, and Station #6 in Austin, Texas.

5.2 SAMPLING METHODS

Soil-gas samples were collected by driving a hollow probe into the ground to an appropriate depth and evacuating a small amount of soil gas (five to ten liters) using a vacuum pump. A hydraulic hammer was used to assist in driving probes past cobbles and through unusually hard soil.

Probes consisted of 7-foot lengths of 3/4-inch diameter steel pipe which were fitted with a detachable drive point. The above ground end of the sampling probe was fitted with a steel reducer, a silicone rubber tube and polyethylene tubing leading to the vacuum pump. Samples were collected in a syringe during evacuation by inserting the syringe needle into the silicone rubber evacuation line and drawing a sample from the gas stream.

A split spoon device was used to collect soil samples of backfill material utilizing the probe holes that were used to collect the soil gas samples. The soil samples were stored in sealed plastic bags prior to analysis.

Promptly upon completion of the sampling program at each site, all holes made in the concrete or asphalt apron were patched to restore the integrity of the apron.

5.3 ANALYTICAL PROCEDURES

Tracer Research Corporation used a mobile field laboratory which was equipped with gas chromatographs and computing integrators. A flame ionization detector (FID) was used to measure methane, butane, isopentane, benzene, toluene, ethylbenzene, xylenes and total hydrocarbons. The methane concentrations measured in the soil gas represent a total of C₁ to C₅ compounds since it was difficult to identify individual peaks within this range. In instances when butane and isopentane concentrations were reported, a variation in the temperature program in the gas chromatograph was used to help clarify these peaks. However, some interference in peaks was still observed.

Typically, three samples were analyzed from each sampling point and operator judgement was used in the field to determine which of the various results could be considered as reliable. Mean values were calculated in the field based upon experienced operator judgement and these averages were considered to be representative of the actual soil gas concentration at the individual sample locations. This type of field judgement is generally used in soil gas surveys because of the variability of the soil gas analysis technique and the skill required to achieve reproducible results. Means derived in this manner were used in this study in order to provide data that is comparable to existing soil gas data and to data that can be expected to be obtained in future soil gas surveys. The actual values of each analysis, which may be useful in further statistical analyses, are provided in Appendix F.

6.0 QUALITY ASSURANCE AND QUALITY CONTROL

The quality assurance/quality control (QA/QC) goals and procedures for this project are described in the "Quality Assurance Project Plan for Background Vapor Value Study" (QAPP) dated August, 1987 (Appendix G). The majority of the goals for accuracy, completeness and validity of data, as listed in the QAPP, were attained during field sampling and analysis. Because some of the project activities were modified, during the course of the field work, to reflect goals slightly different from those anticipated in the original Work Plan, certain corresponding modifications were necessary in the QA/QC procedures.

Additionally, a few field procedures were modified because those outlined in the QAPP proved unworkable. These modifications to field methods were discussed with project personnel and approved by the GCL QA Officer at the time of the QA Field Audit, which was performed at two sites in San Diego, California on September 17, 1987. All modifications to the original QAPP are discussed in Sections 6.1 through 6.12 of this report.

6.1 QA OBJECTIVES FOR MEASUREMENT DATA (QAPP SECTION 3.1)

6.1.1 Gas Chromatograph Analyses

The gas chromatograph (GC) was calibrated daily by measuring the instrumental area count for each analyte against the known concentration of that analyte in a standard gas mixture. The gases, which were traceable to those of the U.S. National Bureau of Standard, were obtained from Scott Specialty Gases. The calibration procedure is described in Section 6.4 of this report.

Because calibration was performed directly from the BTEX gas standard, the independent accuracy check against another standard was not feasible. Accuracy checks during the field day were performed against the same gas standard used for initial calibration. These accuracy checks, generally two or three per field day, were performed at the discretion of the analyst. They were consistently performed more frequently than the goal of once per 20 analyses which was stated in Section 3.4 of the QAPP. Area counts for all calibration runs and

accuracy checks are tabulated in Appendix H. All response factors (RF's) determined by the accuracy checks were within $\pm 30\%$ of those established at the beginning of the field day, so no recalibrations during any field day were required. RF's used for each day's work are also listed in Appendix H.

In order to assess analytical precision, all analyses performed for this project were done in triplicate, by injecting three separate aliquots of the sample into the GC. In a few cases, where one of the injections clearly produced anomalous results, additional injections were made as necessary to yield three valid analytical runs. For each set of three analyses for each component at each sample point, Tracer determined a mean value which is presented in Appendix D, and a standard deviation, which is presented with the three analytical values in Appendix F. The standard deviation exceeded 25% of the mean value in 58 out of the 950 triplicate analyses in which all three results exceeded the detection limit, or 6.1% of such analyses. This surpassed the goal, stated in the QAPP, that the standard deviation should exceed 25% of the mean in no more than 15% of the triplicate analyses. At most points where the standard deviation was more than 25% of the mean concentration determined at a point, the analyte was present at a relatively low concentration, in which case analytical error is normally expected to be a greater percent of the concentration than for samples in which a greater quantity of the analyte is present.

At sites where low total hydrocarbon and methane concentrations were encountered, the detection limits for analytes of interest were normally less than 0.10 ug/l, and in many cases were less than 0.05 ug/l, the goal stated in the QAPP. As anticipated, detection limits for all analytes were much higher in locations where high hydrocarbon concentrations were encountered. Detection limits for all non-detected compounds are reported in the accompanying data sets.

6.1.2 Soil Moisture Content Analyses

Due to sampling and analytical problems encountered in the field, Tracer reported fewer soil moisture analytical results than were anticipated in the QAPP. Sample splits, and in some locations the majority of soil samples, were sealed in air-tight containers and submitted by GCL to Professional Service Industries, Inc. (PSI) in Albuquerque, New Mexico for moisture content analysis. PSI submitted results for 42 soil samples, and Tracer submitted results for 26 samples. Because of inconsistent sample identification, particularly in New York and Rhode Island, it was not always possible to identify which Tracer samples were in fact splits of PSI samples.

Table 6-1 lists and compares all soil moisture replicate analyses identified in a review of the Tracer and PSI data. In most cases, the laboratory values agree well with those obtained in the field, but significant discrepancies exist for the data at sites AU-2 and SD-2. There is good internal consistency among the values reported for replicate samples which were both sent to the PSI lab.

6.2 SAMPLING PROCEDURES (QAPP SECTION 3.2)

Soil gas sampling was performed as described in the QAPP. At the request of EPA EMSL, sample points were confined to the area of the backfill immediately adjacent to the USTs at each site, and in a few cases to soil just outside the backfill. There were generally no more than 6 sample points per site, and samples were normally taken from 3 depths at each point.

A total of 78 soil samples, mostly backfill material, were analyzed for moisture content. The samples were not uniformly distributed among the sites because of difficulties encountered in obtaining soil samples at some locations and the realization that moisture content was of little utility in others, such as sites where the backfill material consisted of pea gravel. The values reported in this document represent only samples that were properly packaged, transported and analyzed.

TABLE 6-1

RESULTS OF REPLICATE ANALYSES FOR SOIL MOISTURE
CONTENT

(ALL ANALYTICAL VALUES IN PERCENT BY WEIGHT)

<u>SITE</u>	<u>TRACER SAMPLE NUMBER</u>	<u>PSI SAMPLE NUMBER</u>	<u>TRACER ANALYTICAL VALUE</u>	<u>PSI ANALYTICAL VALUE</u>	<u>REMARKS</u>
AU-1	8709291807	8709301819 8709301825	14.7	13 11	Erroneous date on samples delivered to PSI. Two replicates to PSI.
AU-2	8709300935	8709300940 8709300946	12.4	4 3	Two replicates to PSI.
SD-2	8709161636	8709161637	11.3	20	
NY-2	NY2-SG4-10	8709231230	10.0	7	
NY-4	NY4-SG4-10	8709241545 8709241600	5.0	3 5	Correlation uncertain. Two replicates to PSI.
NY-5	NY5-SG4-10	8709251310	6.9	8	Correlation uncertain.
NY-6	NY6-SG2-10	8709251800 8709251830	5.7	5 6	Two replicates to PSI.

6.3 SAMPLE CUSTODY (QAPP SECTION 3.3)

Chain-of custody procedures described in the QAPP were followed for all soil samples sent to PSI for moisture content or sieve analysis. Chain-of-custody forms for these samples are on file at the GCL office in Albuquerque.

6.4 CALIBRATION PROCEDURES AND FREQUENCY

(QAPP SECTION 3.4)

The GC was calibrated daily, using gas standards obtained from Scott Specialty Gases. These standards are traceable to those of the U.S. National Bureau of Standards. Two separate three-point calibration curves were established, as described in Section 3.4 of the QAPP, one for methane (hydrocarbons C_1 - C_5) and one for the aromatic hydrocarbons C_6 - C_9 . However, the curve used to quantify hydrocarbons C_6 - C_9 was established using the BTEX gas standard rather than an aqueous standard. It was found that this procedure yielded accurate and replicable results, while the aqueous standard produced a response factor (RF) that did not accurately quantify the gaseous BTEX standard. Additional calibration and accuracy checks were made periodically during each field day, and RF's were then revised as necessary. Recalculation of RF's during the field day was not found to be necessary at any site. Area counts and response factors as reported by Tracer are shown in Appendix H.

Isopentane was not originally included among the compounds to be specifically isolated under the original Work Plan and QAPP. However, GCL and Tracer were subsequently requested by the EPA to attempt a determination of isopentane concentrations at selected locations. Since no standard for isopentane had been provided in the field, isopentane values were determined after field work was complete by reanalyzing the chromatograms to identify the isopentane peak. A response factor (RF) for isopentane was defined by comparison with the known RF for benzene, a gas which had been included among the standards available in the field.

To assure the cleanliness of sampling equipment, syringe blanks and system blanks (air samples) were taken and analyzed each morning and periodically during the day, as provided in the QAPP.

6.5 ANALYTICAL PROCEDURES (QAPP SECTION 3.5)

Analytical Procedures are described in Section 5.3 of this report. All soil gas analyses for benzene, toluene, ethylbenzene and xylenes (BTEX) and for total hydrocarbons were performed by Tracer personnel in accordance with the procedures described in Section 3.5 and Appendix B of the QAPP, except for the treatment of samples yielding total hydrocarbon values greater than 500 ug/l. Experience during the first day of field work indicated that reducing the injection size for such samples, as proposed in the QAPP, resulted in obscuration of the chromatogram peaks for hydrocarbons C₆-C₉ (gasoline constituents), while not significantly improving the accuracy of methane measurements. Since the use of smaller injection sizes resulted in a great loss of data, the practice was discontinued.

6.6 DATA REDUCTION, VALIDATION AND REPORTING (QAPP SECTION 3.6)

Data presented to GCL by Tracer were recorded and analyzed as described in Section 3.6 of the QAPP. The results of the analyses performed are described elsewhere in this report.

Some extreme values ("outliers") identified in the original data recorded on site were discarded from the data set by Tracer because the on-site chemist, based on his field experience, believed them not to be representative of actual hydrocarbon concentrations in the sample analyzed (see Section 6.10 of this report). Consequently, GCL has made no attempt to identify or explain the few outliers remaining in the data set, which would require excessive time and yield little information.

The data presented in this report have been subjected to Tracer's internal review process, and have been spot-checked for accuracy by GCL personnel. Although a few minor errors were detected and corrected

during the GCL review, and a few others undoubtedly remain in the large data set, GCL is confident that such errors represent a very minor portion of the total body of data.

6.7- INTERNAL QUALITY CONTROL CHECKS (QAPP SECTION 3.7)

GC calibration procedures and frequency were described in Section 6.4 of this report. As a standard part of Tracer's analytical procedure, daily "blanks" consisting of pure nitrogen, of air, and of air drawn through a soil gas probe and adapter ("system blank") were analyzed. These blanks were repeated as necessary during the field day, and specifically after any event which was suspected may affect analytical results.

Soil gas samples at each point were analyzed in triplicate, as described in Section 6.1.1. of this report, and duplicate soil samples for moisture content analysis were taken at selected points, as described in Section 6.1.2. Replicability of results was within the goals established by the QAPP.

6.8 PERFORMANCE AND SYSTEM AUDITS (QAPP SECTION 3.8)

A field system audit and evaluation of operational procedures was performed in San Diego on September 17, 1987 by the GCL QA Officer. Minor modifications to field sampling and analytical procedures were discussed with project field personnel and approved by the QA Officer at that time. A letter report describing the results of the field audit was submitted to CDM FPC on September 18, 1987, and is included in Appendix I of this report.

6.9 PREVENTIVE MAINTENANCE (QAPP SECTION 3.9)

All equipment was maintained in operable condition during the field work. Spare parts and new equipment were obtained as necessary to complete field work in a timely manner.

6.10 ASSESSMENT OF DATA PRECISION, ACCURACY AND COMPLETENESS (QAPP SECTION 3.10)

The data presented in this report are complete in the sense that all values believed to represent valid analyses have been included. Gas chromatographic analysis as a procedure is subject to interpretation by the GC operator, who must evaluate each run, on the basis of his experience, to determine its validity. Volume of sample injection, concentrations of the analytes of interest, and possible residual effects of previous sample runs must be considered by the operator in deciding whether to accept the concentrations indicated for any given sample injection. Concentration values which were clearly in error were rejected by the GC operator in the field, and are not included in the data set. Some other values which appear to be "outliers" inconsistent with the rest of the data set have been included in the tabulated analytical results (Appendix F), but were not used in determining the mean values of the triplicate analyses reported in Appendix D. In some of these cases, the outlying values were excluded by Tracer in calculation of the mean concentration, but were included in calculation of the standard deviation. GCL and Tracer have attempted to indicate such points where such operator judgment was exercised. These undoubtedly represent far less than 1% of the total data set.

During the course of the project, Tracer was asked to recalculate the total hydrocarbon concentrations to show them relative to the BTEX total, rather than as benzene. Consequently, the mean values used in the data analysis (Section 11.0) for total hydrocarbons (less methane) differ from the means of the values shown in Appendix F (individual GC-FID injections). The standard deviations for the total hydrocarbon data were calculated on the basis of the values reported "as benzene", and consequently should not be applied directly to the total hydrocarbons (less methane) data calculated from average daily response factors for BTEX.

Concentration values reported in micrograms per liter for analytes of interest in this report are normally given to two significant figures if greater than 10 ug/l, and to one significant figure if less than 10 ug/l. As illustrated by the standard deviations presented with this data set, and based on Tracer's experience in soil gas analyses, instrumental precision does not normally justify greater precision in the reporting of results.

Further information regarding analytical accuracy, precision and replicability was presented in Section 6.1 of this report.

6.11 CORRECTIVE ACTIONS (QAPP SECTION 3.11)

During the field system audit, the requirements for proper chain-of-custody procedures were explained to some site personnel who were not fully aware of them. Samples previously taken for soil moisture content analysis had been properly handled, but the QA Officer felt that additional explanation was necessary to prevent the possibility of future problems.

No other corrective actions were found to be necessary during field work. Problems with Tracer's handling procedure of the soil moisture samples were discovered too late to be remedied by GCL personnel.

6.12 QUALITY ASSURANCE REPORTS TO MANAGEMENT (QAPP SECTION 3.12)

Monthly quality assurance reports were submitted during the course of the project, as described in Section 3.12 of the QAPP.

7.0 REPORTING METHODS

One of the problems encountered in this study concerned the calculation and reporting of the total hydrocarbon concentration data. Different practices in calculating and reporting these data were discovered within the environmental industry and among those who collect and analyze soil gas data. For example, some leak detection devices were found to report total hydrocarbons in parts per million by volume (ppmv) "as hexane", and others in ppmv "as butane" (Radian). Additionally, laboratories using gas chromatograph, flame ionization detection (GC/FID) equipment to analyze soil gas, report total hydrocarbon concentrations in micrograms per liter (Tracer). The method of determining total hydrocarbon concentration values using a GC/FID also vary. A GC/FID must use a response factor based on the calibration of a known gas to determine the concentration of an unknown gas. This calibration gas, or "gas standard" may be benzene, toluene, or some other hydrocarbon compound.

Because of these variations, GCL evaluated different calculation methods to determine the most appropriate method for reporting total hydrocarbon concentrations. In this method evaluation, both the calculations and their accuracy were examined. Since these data may be used in developing threshold limits between non-contaminated and contaminated sites, they must be comparable to soil gas data determined by different methods.

The evaluation consisted of two parts:

- Calculation of total hydrocarbon concentrations in micrograms per liter from the calibration of the GC/FID, reported both "as benzene" and according to an average response factor, and
- Calculation of total hydrocarbon concentrations in parts per million.

7.1 DETERMINATION OF TOTAL HYDROCARBON CONCENTRATIONS IN MICROGRAMS PER LITER

The field investigation phase of this study required that soil gas samples be collected and analyzed at non-contaminated sites. These samples were analyzed on-site using a portable Gas Chromatograph with a

flame ionization detector (GC/FID). The results of these analyses yield concentration values in micrograms per liter. Section 7.1.1 contains a brief discussion on the function of a GC/FID and the procedure used to calculate the total hydrocarbon concentrations from the GC/FID in the field. This procedure uses benzene as the calibration gas. Section 7.1.2 discusses a more accurate method used to calculate total hydrocarbon concentrations in micrograms per liter using data from all the calibration gases.

7.1.1 Gas Chromatograph and Flame Ionization Detector Operation

A gas chromatograph is (GC) an analytical instrument that can be used to separate volatile organic compounds for analysis (EPA Methods 8000). A GC equipped with a flame ionization detector (FID) can be used to generate a chromatogram that consists of peaks corresponding to different compounds. The complete analytical system used in the field investigation of this study consisted of a chromatographic packed column containing Alltech OV101, a hydrogen flame ionization detector, an integrator-recorder, calibration gases and glass syringes (Tracer).

Calibration gases were used to generate a chromatogram that formed a base-line or standard of peaks in the chromatogram. Response factors, defined as the ratio of the mass of each gas standard to the integrated area of the peak produced by that mass, were determined for each gas standard. Individual hydrocarbon compounds in the soil gas samples were identified by a comparison of sample chromatograms to the standard chromatogram. Concentrations of individual compounds were calculated from the response factors for the corresponding gas standard.

Concentrations of individual compounds were determined in micrograms per liter. This is based on the principal of operation of the flame ionization detector in which pyrolysis of organic compounds produces ionic intermediate compounds that can carry an electric current. The resulting current flows through the flame, and the ions are collected and measured. The current responds linearly to the mass of carbon in the

sample, and consequently, response factors and concentrations are measured in mass units (Tracer).

The calibration gas standards used were methane, benzene, toluene, ethylbenzene, and ortho-xylene. Concentrations of each of these compounds in each sample were calculated directly using the corresponding calibration gas response factor and the sample injection size. However, concentrations for total hydrocarbons (less methane) were required to be approximated.

7.1.2 Calculation of Total Hydrocarbons as Benzene

During the field investigation, total hydrocarbon (less methane) concentrations were approximated by using the response factor for benzene to compute the concentrations. During the data analysis, it was discovered that this approximation yielded a low estimate of total hydrocarbons (less methane) concentrations. This discovery was made by a comparison of the combined concentrations of benzene, toluene, ethylbenzene and xylenes (BTEX) to the total hydrocarbon concentration (less methane). This comparison shown in Appendix J, indicates that the concentration of BTEX was greater than the concentration of total hydrocarbons (less methane) in 30 percent of the samples.

A possible cause for the discrepancy between the concentrations of total hydrocarbons (less methane) and BTEX could have been an erroneous interpretation of the chromatogram peaks. However, a re-examination of the chromatograms showed that no interpretation errors had occurred.

The discrepancy was determined to be the result of using the benzene response factors for the approximation of total hydrocarbon (less methane) concentrations. By an examination of the response factors for all of the gas standards (Appendix D), it was found that the benzene response factor was usually lower when compared to response factors for toluene, ethylbenzene and ortho-xylene. In theory, response factors for similar hydrocarbon compounds should be similar. However, in practice, response factors vary because of chemical and instrument effects.

Because of the discrepancies between the total hydrocarbon (less methane) concentrations and the combined BTEX concentrations, a better approximation of total hydrocarbon (less methane) concentrations was needed. This was considered important because these values obtained from non-contaminated sites may affect the development of threshold limits to be used to distinguish between contaminated and non-contaminated sites.

7.1.3 Calculation of Total Hydrocarbon Concentrations

Using Average Response Factors

The total hydrocarbon concentration in a soil gas sample is actually the summation of all the hydrocarbon compounds that can be detected from the GC/FID analysis. To accurately determine this concentration would require that a gas standard be analyzed in the GC/FID for every compound that existed in the soil gas. This comprehensive type of analysis was considered impractical since an enormous amount of GC/FID calibration work would have been necessary to quantitatively analyze all the peaks in the soil gas samples.

The best approximation, based on the available calibration data, was to determine total hydrocarbons (less methane) using the average of the response factors for all the calibration gases (less methane). Therefore, total hydrocarbon (less methane) concentrations were calculated from an average of the daily response factors for benzene, toluene, ethylbenzene and ortho-xylene.

This approximation resulted in new total hydrocarbon (less methane) concentrations that were generally higher. A comparison of total hydrocarbon (less methane) concentrations calculated from average BTEX response factors and "as benzene" is shown below.

<u>TOTAL HYDROCARBON (LESS METHANE) CONCENTRATIONS</u>	<u>PERCENTAGE OF SAMPLES</u>
As Benzene > As BTEX Average	8.6%
As Benzene = As BTEX Average	15.1%
As Benzene < As BTEX Average	76.3%

In the case where the new values (as BTEX average) were greater than the old values (as benzene), these new values ranged from 7% to about 100% higher. A comparison of the old values and new values for each sample is provided in Appendix J.

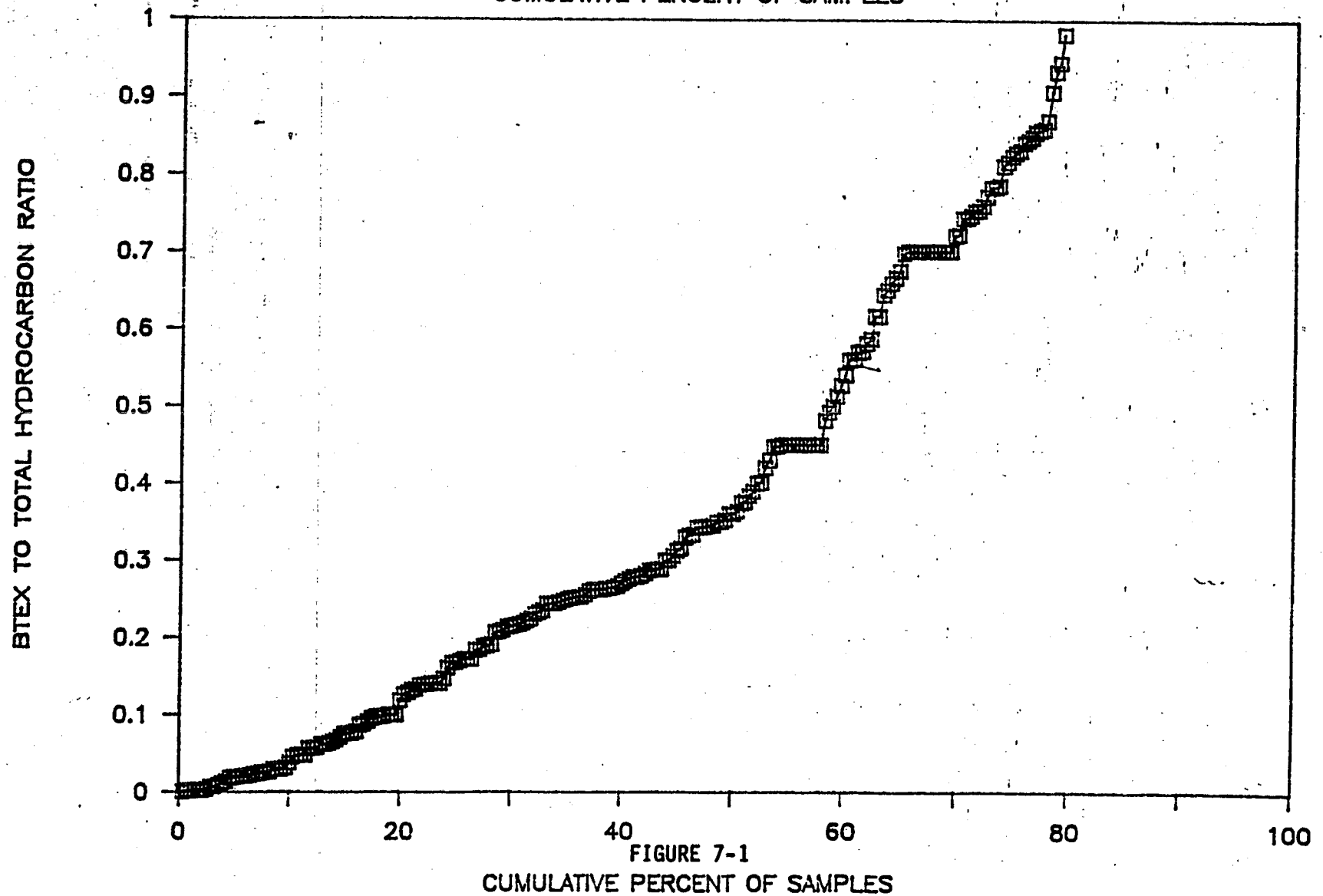
The new concentrations also result in values that are larger than the combined BTEX concentrations which indicates a more reasonable approximation of total hydrocarbon concentration. A comparison of the BTEX and the new total hydrocarbon (less methane) concentrations are shown in Appendix J.

The calculation of total hydrocarbon (less methane) concentrations using the average BTEX response factors, was found to be a better approximation than when using only benzene, because it accounted for variations in the response factors. However, it is understood that some error still exists in this method because several peaks in the chromatograms and their corresponding compounds were not identified and quantified.

To better understand the extent that compounds other than BTEX are contained in total hydrocarbons, a comparison of the combined BTEX concentrations to total hydrocarbons (less methane) concentrations (calculated from average BTEX response factors) was made. These results are shown in Figure 7-1. The tabular data used to generate this figure is included in Appendix J. The percentage of samples where the BTEX concentrations were less than 50 percent of total hydrocarbons (less methane) was about 59 percent of the total samples. This means that in about 59 percent of the samples, compounds other than BTEX make up the majority of the total hydrocarbon concentrations.

The result that compounds other than BTEX make up the majority of the total hydrocarbon concentration in most of the samples is not surprising when the composition of gasoline is considered. A typical gasoline contains several hundred hydrocarbon compounds, each falling into one of four chemical groups: paraffins, olefins, naphthenes or aromatics (NM EID). The aromatics, which includes BTEX, are considered most important

RATIO OF BTEX TO TOTAL HYDROCARBONS VS CUMULATIVE PERCENT OF SAMPLES



because they are relatively soluble in water, and therefore, present a risk of ground-water contamination. Table 7-1 shows a list of major components of an API PS-6 Gasoline, some of which can be expected to be present in soil gas. These compounds represent C₄ to C₁₀ molecules (API-1985).

Some selected sample chromatograms from Suffolk County, NY, San Diego, CA and Austin, TX were qualitatively analyzed for a wide range of compounds where BTEX was found to represent less than 10 percent of the total hydrocarbon concentration. These qualitative analyses identified some additional compounds: methane, butane, isopentane, 2-methylhexane, iso-octane, and octane. These chromatograms are shown in Appendix J.

7.2 DETERMINATION OF TOTAL HYDROCARBON CONCENTRATIONS IN PARTS PER MILLION

The concentration of extremely dilute solutions are expressed in parts per million (ppm). Typically, liquid solutions are expressed in parts per million by weight (ppmw) and gaseous solutions are expressed in parts per million by volume (ppmv). (Himmelblau)

Parts per million by volume (ppmv) is a measurement unit that is commonly used in the environmental industry for reporting air pollutant concentrations (Wark and Warner). Many leak detection systems report hydrocarbon contamination in soil gas in ppmv (Radian). Therefore, parts per million by volume was considered appropriate rather than parts per million by weight.

Ppmv is defined as:

$$1 \text{ ppmv} = \frac{1 \text{ volume of gaseous pollutant}}{10^6 \text{ volumes of pollutant \& air}} \quad \text{Equation 1}$$

TABLE 7-1

MAJOR COMPONENTS OF API PS-6 GASOLINE

<u>COMPOUND</u>	<u>PERCENT WEIGHT</u>
2-Methylbutane	8.72
M-Xylene	5.66
2,2,4-Trimethylpentane	5.22
Toluene	4.73
2-Methylpentane	3.93
N-Butane	3.83
1,2,4-Trimethylbenzene	3.26
N-Pentane	3.11
2,3,4-Trimethylpentane	2.99
2,3,3-Trimethylpentane	2.85
3-methylpentane	2.36
O-Xylene	2.27
Ethylbenzene	2.00
Benzene	1.94
P-Xylene	1.72
2,3-Dimethylbutane	1.66
N-Hexane	1.58
1-Methyl, 3-Ethylbenzene	1.54
1-Methyl, 4-Ethylbenzene	1.54
3-Methylhexane	1.30

The data in micrograms per liter can be converted to ppmv by the following equation:

$$\text{ppmv} = \frac{\text{ug}}{1} \times \frac{RT}{P \cdot (\text{Mol Wt})} \quad \text{Equation 2}$$

where: ppmv = Parts Per Million by Volume
 ug/l = Micrograms Per Liter
 R = Gas Constant = $0.08205 \frac{\text{atm liter}}{\text{gmole} \cdot ^\circ\text{K}}$
 P = Pressure in Atmosphere
 T = Temperature in $^\circ\text{K}$
 Mol Wt = Molecular Weight of Hydrocarbon

This equation was derived from the ideal gas equation:

$$PV = nRT$$

where: P = Pressure
 T = Temperature
 V = Volume
 n = Moles
 R = Gas Constant
 Equation 3

The derivation is shown in Appendix J (Wark and Warner).

The temperature and pressure used in these calculations represented the ambient conditions measured in the field at each site.

The assumption of an ideal gas was justified by examining a mean compressibility factor. The mean compressibility factor is a factor that is introduced into the ideal gas equation to account for non-ideal or real gas relationships. Therefore, the ideal gas equation becomes:

$$PV = Z_m nRT \quad \text{Equation 4}$$

where: Z_m = mean compressibility factor

If calculations can show that Z_m is approximately equal to one for the soil gas mixtures, then the assumption that the soil gas samples in this study can be approximated to an ideal gas is valid one. (Himmelblau)

Two cases were examined in testing this assumption. Because the complete composition of soil gas is not known, Case 1 assumed soil gas contains 80% air and Case 2 assumed soil gas contains 20% air. The mean compressibility factor was determined to be 0.99 for Case 1 and 0.85 for Case 2. Therefore, the ideal gas assumption introduces about 1 to 15 percent error in calculating hydrocarbon concentrations in soil gas. This small deviation (1 to 15%) from the ideal gas assumption is reasonable since the pressure conditions are low, and the hydrocarbons in the mixture are similar in their chemical nature.

The conversion calculations from micrograms per liter to ppmv were made for each sample and each compound within that sample. The molecular weight of each compound was used in the conversion calculation. However, for total hydrocarbons (less methane), an average molecular weight was used. This average molecular weight was based on the average of the BTEX concentrations at each sample.

To compute total hydrocarbons (with methane), the methane concentration was converted to ppmv and then added to total hydrocarbons (less methane) in ppmv. In these calculations, the detection limits were divided by 2 to approximate the actual concentration. A sample calculation is shown in Appendix J.

The average of the BTEX concentrations was used to compute the average molecular weight of each sample since BTEX concentrations were known at all sample points. It is recognized that some error is introduced by using only BTEX concentrations. However, this is considered to be the best approximation possible from the available data. Reporting hydrocarbon concentrations in parts per million may be useful for some purposes. However, reporting them in micrograms per liter provides more accurate values based on fewer assumptions.

8.0 RESULTS

8.1 SOIL GAS DATA

The maximum soil gas concentration values determined in this study are presented in Table 8-1 for the sites in Austin, Table 8-2, for the sites in the Long Island Sound area and Table 8-3 for those in the San Diego area.

Average hydrocarbon vapor concentration data and site maps for all 27 gasoline service stations are presented in Appendix D. The average hydrocarbon vapor concentration data, in most cases represent mean values for each set of three gas chromatograph/flame ionization detection (GC/FID) analyses for each sample. These data are presented in two formats: 1) concentration values listed by sample number and depth, and 2) concentration values listed by depth and sample number. In the second format, computed average concentrations for all samples at each depth are shown. Additionally, each site map contains an average total hydrocarbon concentration computed from concentrations at each depth within each hole. In computing these average concentrations, the concentrations reported at detection limits were divided by two to approximate the actual concentration.

A pipeline was accidentally punctured during the investigations at Station #6 in Austin, Texas. Data were collected during four consecutive days at this station to study soil gas migration under dynamic conditions. These data are also included in Appendix D.

Data in Appendix D presented both in microgram per liter and parts per million by volume.

8.2 CONTAMINATED SITE DATA

Soil gas surveys were previously conducted at a number of UST sites in which product spills were known to have occurred. Data from 27 sites were examined as candidates. Of these sites, 8 were selected as being appropriate for comparison purposes because site maps were available and contamination was known to exist. Data collected from Austin Station #6

TABLE 8-1

MAXIMUM CONCENTRATIONS AT AUSTIN, TEXAS

(All concentration values in micrograms per liter)

	METHANE C ₁ -C ₃ (AS METHANE)	BENZENE	TOLUENE	ETHYLBENZENE	XYLENES	TOTAL HYDRO- CARBONS (LESS METHANE)	TANK TIGHTNESS TEST RESULTS
Station 1	790,000	7,400	5,300	<310	2,300	21,000	Tight
Station 2	210,000	16,000	17,000	160	21,000	63,000	Tight
Station 3	120,000	3,300	1,700	<63	410	5,700	NR
Station 4	870,000	97,000	85,000	<680	83,000	210,000	NR
Station 5	1,500,000	24,000	26,000	25,000	8,200	1,100,000	Tight
Station 6							
10/27/87	710,000	110,000	90,000	<220	<240	960,000	
10/28/87	8,600	27,000	83,000	<250	70,000	790,000	
10/29/87	13,000	<250	<280	<270	<260	690,000	
10/30/87	4,800	53,000	1,600	<20	<31	290,000	
Station 7	59,000	<42	<48	<50	<58	55,000	Tight

Notations:

NAZ = Not Analyzed.

NR = No records available showing tank tightness results.

Notes:

- (1) Total hydrocarbons are reported less methane to reflect a profile of compounds similar to gasoline, and to exclude products of naturally occurring degradation.
- (2) Total hydrocarbons are calculated from average response factors for Benzene, Toluene, Ethylbenzene and Orthoxylene.
- (3) <310 means the compound was analyzed but not detected within this detection limit. The detection limit varies according to sample injection size and compound.
- (4) Spill occurred at 9:00 AM on 10/27/87. These data were collected after the spill.
- (5) At stations where C₄/C₅ are not analyzed, the methane concentration represents C₁-C₅ peaks.
- (6) Tight means petrolium test results were < 0.05 gallons per hour.

TABLE 8-2:

MAXIMUM CONCENTRATIONS LONG ISLAND SOUND COASTAL AREA

(All concentration values in micrograms per liter)

	METHANE (C ₁ -C ₅) (AS METHANE)	BENZENE	TOLUENE	ETHYLBENZENE	XYLENES	TOTAL HYDRO- CARBONS (LESS METHANE)	TANK TIGHTNESS TEST RESULTS
Station 1	<40	2,700	11,000	12,000	10,000	270,000	NR
Station 2	140	<29	420	130	<41	2,100	Tight
Station 4	<24	3,700	1,000	<37	<42	69,000	NR
Station 5	4	2,300	13,000	2,900	91	110,000	NR
Station 6	15	<.6	55	<.7	<.8	1,500	NR
Station 1	25,000	<10	840	<6	<8	3,700	Leak
Station 2	11,000	<8	<8	<7	2,300	49,000	NR
Station 1	8	<.1	110	130	110	590	NR
Station 2	72	23	230	<.1	130	1,400	Tight
Station 3	9	<.08	0.8	<.1	<.2	0.3	NR
Station 4	2,800	670	1,400	400	840	24,000	Leak

Notations:

NAZ = Not Analyzed.

NR = No records available showing tank tightness results.

Notes:

- (1) Total hydrocarbons are reported less methane to reflect a profile of compounds similar to gasoline, and to exclude products of naturally occurring degradation.
- (2) <310 means the compound was analyzed but not detected within this detection limit. The detection limit varies according to sample injection size and compound.
- (3) Total hydrocarbons are calculated from the average response factors for benzene, toluene, ethylbenzene and ortho xylene.
- (4) At stations where C₄/C₅ are not analyzed, the methane concentration represents C₁-C₅.
- (5) Tight means tightness test results were <0.05 gallons per hour.

TABLE 8-3
MAXIMUM CONCENTRATIONS AT SAN DIEGO, CALIFORNIA

(All concentration values in micrograms per liter)

	<u>METHANE</u> <u>(C₁-C₅)</u> <u>(AS METHANE)</u>	<u>BENZENE</u>	<u>TOLUENE</u>	<u>ETHYLBENZENE</u>	<u>XYLENES</u>	<u>TOTAL HYDRO-</u> <u>CARBONS</u> <u>(LESS METHANE)</u>	<u>TANK TIGHTNESS</u> <u>TEST RESULTS</u>
Station 1	48,000	<89	11,000	<120	4,900	31,000	Leak
Station 2	110,000	<89	11,000	<120	5,100	77,000	Tight
Station 3	22	<.1	17	<.05	.8	62	Leak
Station 4	420,000	<90	17,000	<.1	1,800	110,000	Tight
Station 5	55,000	<86	2,600	<.1	1,600	7,700	Tight
Station 6	33,000	<83	23,000	<.1	10,000	58,000	Tight
Station 7	390,000	<90	31,000	<.1	8,800	210,000	Tight
Station 8	21,000	<81	22,000	<.1	8,600	120,000	Tight
Station 9	280,000	<98	32,000	<.1	8,200	110,000	NR

Notations:

NAZ = Not Analyzed.

NR = No records available showing tank tightness results.

Notes:

- (1) Total hydrocarbons are reported less methane to reflect a profile of compounds similar to gasoline, and to exclude products of naturally occurring degradation.
- (2) Total hydrocarbons are calculated from the average response factors for benzene, toluene, ethylbenzene and ortho-xylene.
- (3) <310 means the compound was analyzed but not detected within this detection limit. The detection limit varies according to sample injection size and compound.
- (4) At stations where C₄/C₅ are not analyzed, the methane concentration represents C₁-C₅ peaks.
- (5) Tight means tightness test results were <0.05 gallons per hour.

was included as Site 9 since data from this station represents a fresh spill.

Table 8-4 gives a brief description of these sites and Table 8-5 presents the maximum concentration data for them. These sites include active service stations or fueling facilities. Site maps and data are presented in Appendix K. Specific sample locations at these sites were selected for use in the contaminated site database because of their close proximity to the tanks or contamination source. It was desirable to use sampling points close to the tanks so that the data would be comparable to the clean site data collected from the tank backfill areas under this study. A summary of the soil gas data is included in Appendix K. Total hydrocarbon values are reported less methane, and "as benzene".

8.3 EXPANDED AUSTIN STUDY

A four-day study was conducted at Austin Station #6 to take advantage of a spill that occurred when a product line was punctured during the field investigations. Soil gas samples were taken from the same holes each day and the results are included in Appendix D. Figure 8-1 shows the concentration of total hydrocarbons for each of the four days at 2-foot and 6-foot depths, and Figure 8-2 shows the corresponding concentrations of C4-C6 components.

This intensified study provided the following basic information:

- Total hydrocarbon concentrations increased initially to >100,000 ug/l near the spill site and higher concentrations migrated into the entire backfill area.
- Total hydrocarbon concentrations decreased after peaking one day after the spill.
- High concentrations of C4-C6 components were found to parallel the total hydrocarbon concentrations.
- Since high concentrations of C4-C6 components were not usually encountered in the field sampling at clean stations, it may be

TABLE 8-4

DESCRIPTION OF CONTAMINATED SITES

- Site 1** New Service Station. Tanks were tested tight, but found floating product in ground water. Ground-water depth = 8'.
- Site 2** Active Service Station.
- Site 3** Active Service Station. Floating product in ground water. Ground-water depth = 15' - 20'.
- Site 4** Active Fueling Facility. Pipeline leak. No ground-water contamination. Ground-water depth = >20'.
- Site 5** Active Fueling Facility. Ground-water depth = 12'.
- Site 6** Active Service Station. No ground-water contamination. Ground-water depth = 15'.
- Site 7** Active Fueling Facility.
- Site 8** Active Service Station. Floating product on ground water. Ground-water depth = 25' - 35'.
- Site 9** Active Service Station (Austin #6). Spill resulting from product like puncture.

Note: These sites were selected from Tracer Research Corporation files to develop database of hydrocarbon vapor concentrations for sites with known hydrocarbon contaminated.

TABLE 8-5

MAXIMUM CONCENTRATIONS AT CONTAMINATED SITES

(All concentration values in micrograms per liter)

	METHANE C ₁ -C ₃ (AS METHANE)	BENZENE	TOLUENE	ETHYLBENZENE	XYLENES	TOTAL HYDRO- CARBONS (LESS METHANE)	TANK TIGHTNESS TEST RESULTS
Station 1	1,200,000	100,000	68,000	61,000	NAZ	2,200,000	
Station 2	NAZ	<10	1,200	120	140	19,000	
Station 3	NAZ	NAZ	31,000	NAZ	NAZ	400,000	
Station 4	NAZ	780	620	50	<4.5	15,000	
Station 5	NAZ	28,000	11,000	<850	<800	280,000	
Station 6	NAZ	<230	4,000	<58	<61	210,000	
Station 7	NAZ	<55	1,700	<80	<80	9,500	
Station 8	100,000	60,000	40,000	NAZ	NAZ	800,000	

Notations:

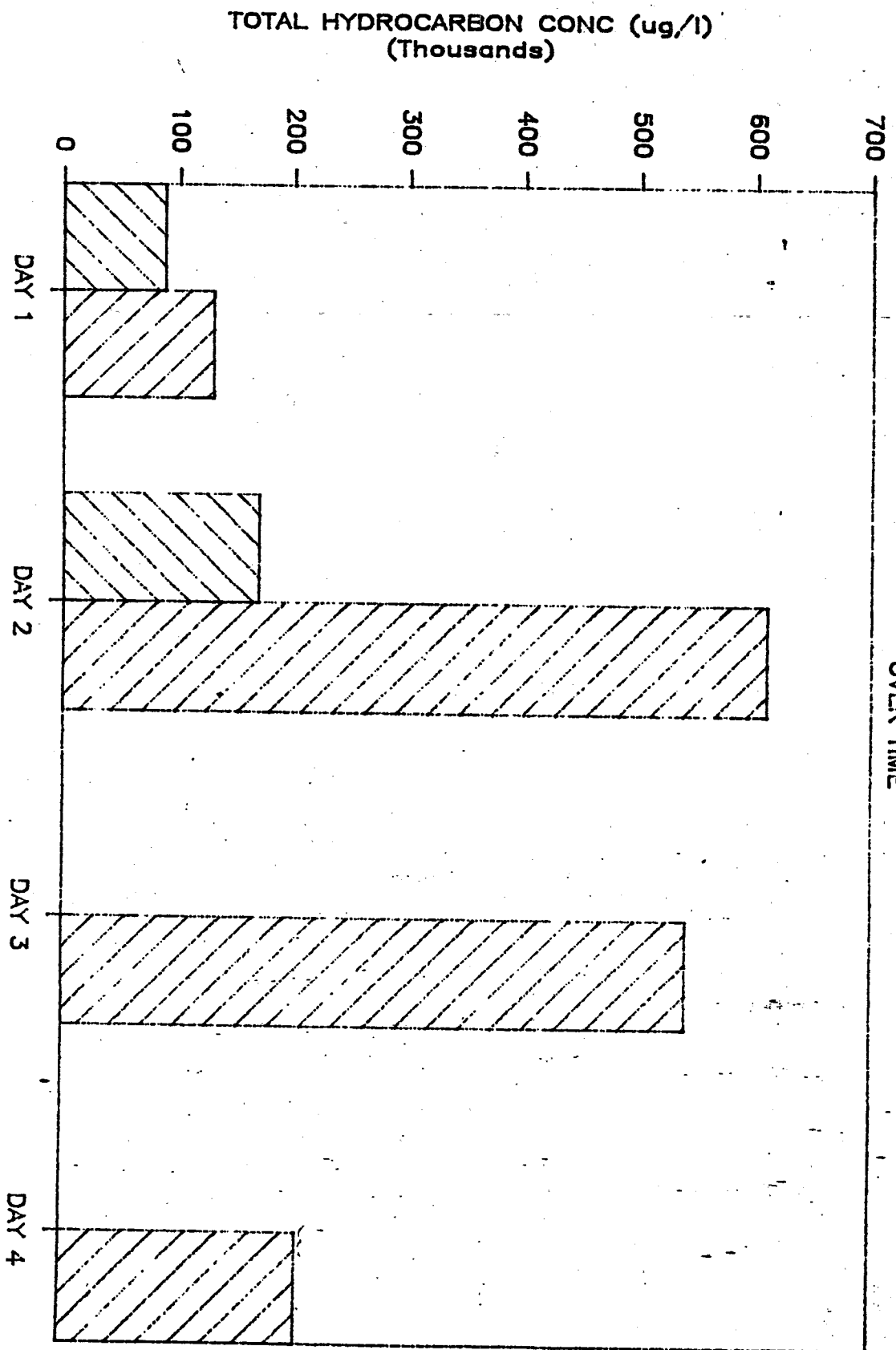
NAZ = Not Analyzed

* = Ethylbenzene/Xylene concentration value

Notes:

- (1) Total hydrocarbons are reported less methane to reflect a profile of compounds similar to gasoline, and to exclude products of naturally occurring degradation.
- (2) Total hydrocarbon values are calculated from the average response factor for benzene, toluene, ethylbenzene and ortho-xylene.

AUSTIN 6 MEDIAN TOTAL HYDROCARBON DATA OVER TIME



2' DEPTH
6' DEPTH

FIGURE 8-1

AUSTIN 6 MEDIAN C4-C6 HYDROCARBON DATA

OVER TIME

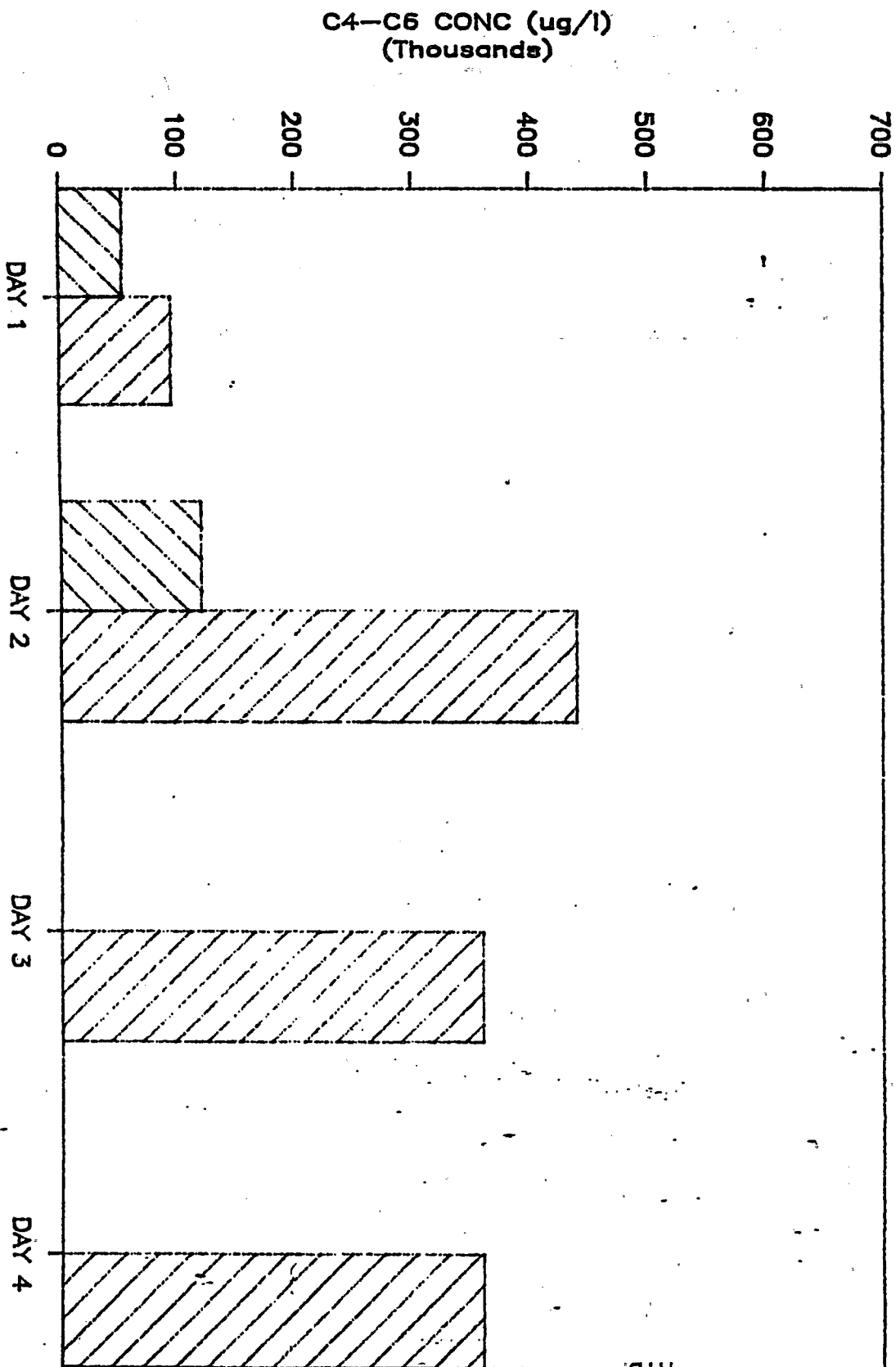


FIGURE 8-2

possible to use C4-C6 concentrations, as compared to those of total hydrocarbons, to detect fresh leaking conditions. More study is required to confirm this preliminary indication.

8.4 CHARACTERIZATION OF BACKFILL MATERIAL

Soil moisture and particle size of the backfill materials impacts hydrocarbon vapor concentrations because of liquid/vapor partitioning and porosity effects. Consequently, soil moistures and sieve analyses were performed on soil samples collected from the backfill of the non-contaminated sites. A summary of the results of these sample analyses are presented in Table 8-6. Laboratory analyses are included in Appendix E.

Backfill soil material at steel tank installations included fine, medium and silty sands while the backfill at fiberglass tank installations were of fine gravel, gravelly sand and coarse sand mixed with gravel. Moisture contents were higher in the sands than in the gravels and the porosities of the sands were less than those of the gravels.

Because gravel is more porous and less moist, hydrocarbons will likely move more quickly through gravel backfill than through sand. Also, moisture will tend to inhibit the movement of hydrocarbons and will absorb hydrocarbons through liquid/vapor partitioning.

8.4 U-TUBE SAMPLING

Leak detection methods are classified into four groups: Volumetric, Nonvolumetric, Inventory Control, and Leak Effects methods (EPA). Methods within the Leak Effects classification are those that identify leaks by examining the environmental effects of the leak. Those methods usually require the installation of monitor wells and chemical analysis.

Since soil gas contamination is an environmental effect that can result from a leaking UST system, then soil gas sampling, as performed in the field investigation of this study, would be classified as a Leak Effects method.

Another method for monitoring leaks within the Leak Effects classification utilizes a U-Tube device. The U-Tube consists of a four-inch diameter, schedule 40, PVC pipe installed as shown in Figure 8-3.

TABLE 8-6

MOISTURE RANGES OF SOIL AND BACKFILL SAMPLES

(Values in percent by weight. Moisture content analyzed by PSI, Albuquerque, NM)

LOCATION/STATION	TANK TYPE	MOISTURE CONTENT			SIEVE ANALYSIS RESULTS
		SAND	GRAVEL	NATIVE SOIL	
AUSTIN, TEXAS					
AU1	Steel	11-13	-	10	Silty sand
AU2	Steel	3-4	-	11	-
AU3	FRP	-	6	79 *	Sandy gravel
AU4	FRP	-	5	-	Gravelly sand
AU5	Steel	4-13	-	-	Medium sand
AU6	FRP	-	1-15	-	Fine gravel
AU7	FRP	-	-	-	-
STORRS, CONNECTICUT					
CONN1	Steel	-	-	-	-
CONN2	Steel	-	-	-	-
PROVIDENCE, RHODE ISLAND					
RI1	Steel	15	-	-	Fine sand
RI2	Steel	10	-	-	Medium sand with silt
RI3	Steel	4	-	-	Fine sand
RI4	Steel	4	-	-	Medium to fine sand
SUFFOLK COUNTY, NEW YORK					
NY1	FRP	-	-	-	-
NY2	Steel	-	-	-	-
NY4	FRP	-	-	-	-
NY5	Steel	8	-	-	-
NY6	FRP	5-6	-	3-6	Fine sand
SAN DIEGO COUNTY, CA					
SD1	Steel	-	-	-	-
SD2	Steel	13-20	-	-	Fine sand with silt
SD3	FRP	-	-	-	-
SD4	Steel	15-17	-	-	Fine sand with silt
SD5	FRP	-	1	-	-
SD6	FRP	-	1	11	Crs sand with gravel
SD7	Steel	7-9	-	-	Medium sand with silt
SD8	Steel	6-7	-	-	Medium sand with silt
SD9	Steel	3-10	-	-	Silty sand

NOTE: All Sieve Analysis results from backfill samples.

** Native Soil Sample taken from saturated zone in bottom of monitor well.

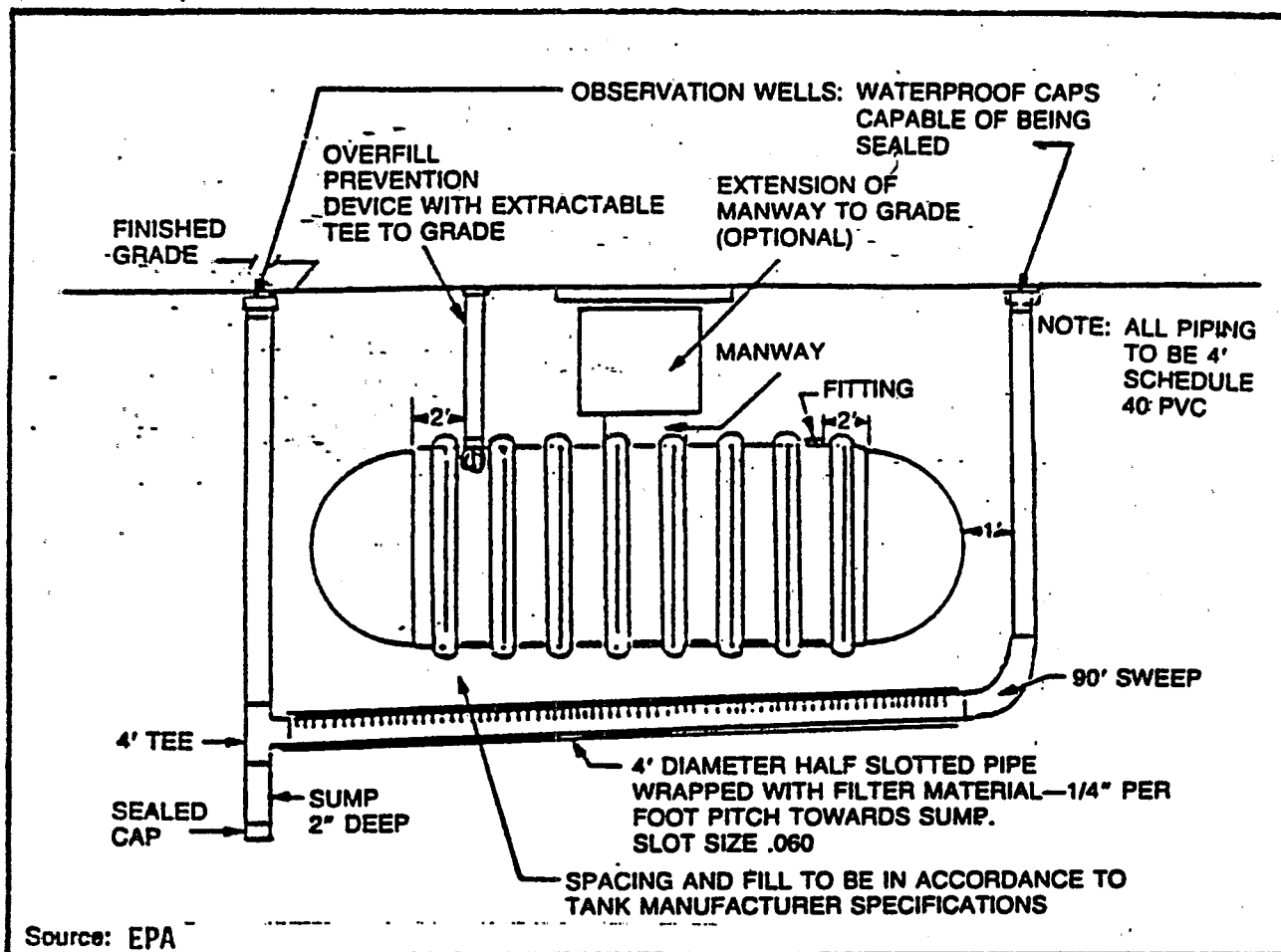


FIGURE 8-3
U-TUBE LEAK DETECTION SYSTEM

These tubes were installed under each tank within the backfill material at Stations #4 and #6 in Suffolk County, New York.

A comprehensive comparison of leak detection methods was not within the scope of this project. However, two stations with U-Tubes were included in the study in order to make a comparison of hydrocarbon vapor concentrations from U-Tubes versus hydrocarbon vapor concentrations in soil gas.

The method of collecting soil gas samples from the backfill areas was presented in Section 5.2. Briefly, soil gas samples were collected by inserting a hollow probe into the backfill and evacuating a soil gas sample using a vacuum pump. Vapor samples from the U-Tubes were also collected by inserting a hollow probe to the desired depth in the U-Tube and evacuating a sample using a vacuum pump. Samples were collected near the bottom of the U-Tubes to minimize the effects of dilution from the outside air.

Since vapor samples from the U-Tubes were collected near the bottom of the U-Tubes, these data were compared to soil gas samples collected from the backfill at the 10-foot depth. The U-Tube samples and soil gas samples (at 10 feet) are shown in Table 8-7.

At Station #4 in Suffolk County, New York, the U-Tube sample contained 90,000 micrograms per liter of total hydrocarbons (less methane) while the soil gas samples ranged from 42,000 to 69,000 micrograms per liter of total hydrocarbons (less methane). Benzene and toluene were found in both the U-Tube and soil gas samples while methane, ethylbenzene and the xylenes were not found at detection limits for either the U-Tubes or soil gas samples.

At Station #6 in Suffolk County, New York, the U-Tube sample contained 47 micrograms per liter of total hydrocarbons (less methane) while the soil gas sample contained 1,500 micrograms per liter of total hydrocarbons

TABLE 8-7

**U-TUBE VAPOR SAMPLES
SUFFOLK COUNTY, NEW YORK**

(Micrograms Per Liter)

	<u>METHANE</u> <u>(C₁-C₅)</u>	<u>BENZENE</u>	<u>TOLUENE</u>	<u>ETHYLBENZENE</u>	<u>XYLENES</u>	<u>TOTAL HYDRO- CARBONS</u> <u>(LESS METHANE)</u>	<u>TANK TIGHTNESS</u> <u>TEST RESULTS</u>
<u>Station #4</u>							
U-Tube-11'	<24	2800	850	<37	<42	90,000	
SG1-10'	<24	730	120	<37	<42	42,000	
SG2-10'	<24	980	300	<37	<42	42,000	
SG3-10'	<24	3300	1000	<37	<42	69,000	
SG4-10'	<24	1800	930	<37	<42	58,000	
<u>Station #8</u>							
U-Tube-14'	<0.02	<0.03	2	<0.04	<0.04	47	
SG2-10'	<0.4	<0.6	55	<0.7	<0.8	1500	

Notations:

NAZ = Not Analyzed.

NR = No records available showing tank tightness results.

Notes:

- (1) Total hydrocarbons are calculated from the average response factors for BTX.
- (2) <24 indicates that the concentration is less than the detection limit of 24 micrograms per liter.

(less methane). Only toluene was identified in both the U-Tube and soil gas samples.

These results indicate that the composition of hydrocarbon vapors found in U-Tubes are similar to the vapors found in soil gas. However, the magnitude of the vapor concentrations may differ. These conclusions are preliminary since more sample data is required to accurately delineate these differences.

8.6. GROUND WATER SAMPLING

Shallow ground water was encountered at several locations which prevented soil gas samples from being taken at the 10-foot levels. In these cases, samples of the ground water were taken and analyzed by the GC/FID using the same procedures as were used for the soil gas. These results are shown in Table 8-8.

TABLE 8-8

HYDROCARBON CONCENTRATIONS FROM
GROUNDWATER SAMPLES

STATION	SAMPLE NUMBER	DATE	DEPTH (FT)	METHANE	BUTANE	ISOPENTANE	BENZENE	TOLUENE	ETHYL-BENZENE	XYLENES	TOTAL HYDROCARBO
AUG	MW/H2O	10/29	7.	4000	5700.	NA	77000.	150000.	<140.	80000.	380000.
AUG	MW/H2O/P	10/29	8.	5400	5000.	NA	52000.	130000.	<140.	110000.	410000.
AUG	MW/H2O	10/30	8.	6700	8900.	NA	50000.	16000.	<49.	<79.	100000.
AUG	MW/H2O/S	10/29	8.	6600	6200.	NA	71000.	18000.	<140.	110000.	480000.
AUG	MW/H2O	10/29	9.	4200	4900.	NA	67000.	120000.	<140.	51000.	290000.
AUG	SG4/H2O	10/28	10.	2100	4300.	NA	27000.	83000.	<25.	70000.	200000.
AUG	SG5/H2O	10/28	10.	4700	2400.	NA	5600.	10000.	<12.	12000.	37000.
AUG	SG2/H2O	10/28	10.	1800	2100.	NA	5600.	15000.	<49.	17000.	42000.
AUG	MW/H2O	10/29	11.	9300	5700.	NA	67000.	160000.	<140.	93000.	400000.
AUG	MW/H2O/P	10/29	11.	10000	1000.	NA	7300.	15000.	<140.	17000.	53000.
AUG	MW/H2O/S	10/29	11.	13000	690.	NA	7500.	15000.	<140.	<130.	36000.
AUG	MW/H2O	10/30	11.	4200	2400.	NA	4500.	1300.	<49.	<79.	18000.
AUG	MW/H2O	10/28	NA	8600	8500.	NA	10000.	25000.	<250.	21000.	86000.
COHH1	GW-04	11/12	10.	62	<7.	<6	<6.	<8.	<4.	<8.	<7.
COHH2	GW-04	11/13	6.	18	<4.	<4	<6.	<6.	<7.	<10.	<6.
COHH2	GW-03	11/13	10.	18	<4.	<4	<6.	<6.	<8.	<10.	<6.
COHH2	GW-05	11/13	10.	4400	1700.	<6	<30.	-31.	<37.	48000.	240000.

Notes:

- (1) Total hydrocarbons are less methane, as benzene.
- (2) NA refers to Not Analyzed.
- (3) Samples noted as MW/H₂O/P indicate values immediately after pumping.
- (4) Samples noted as MW/H₂O/S indicate values gathered 1.5 hours after pumping.
- (5) GW refers to Ground-water samples.
- (6) Values less than detection limits are indicated by "<".

9.0 UST REGULATIONS

9.1 AUSTIN, TEXAS

Underground storage tanks at existing facilities in Austin must have a permit to operate and are required to be tested or monitored for leaks on a regular basis. If tank testing is conducted, a precision tank test, as defined in the NFPA National Fires Codes, Section 329, is performed on each tank according to the following schedule:

Tank Age
(As of 6/18/85)

Test Frequency

0 to 5 years

0

6 to 10 years

Within 12 months of 6/18/85 and then every 2 years until over 10 years old.

over 10 years

Annually, beginning within 12 months of 6/18/85.

The Department of Environmental Protection (DEP) assumed the underground tank responsibility from the fire department on January 14, 1987. At the present time, the DEP has approved seven tests for tank tightness testing: Petro-tite (Kent-Moore), Hunter, Horner, Acutest, Massney, Tanty-Tech, and Tank Auditor. Companies who perform these tests are registered by the DEP.

Monitoring wells may be used as an alternative to precision tank testing for leak detection of underground storage tanks. For existing facilities, leak detection monitoring by surface geophysical methods such as ground penetrating radar, electromagnetic induction, resistivity, magnetometers, and X-ray fluorescence or by tracer analysis may be permitted only by approval from the DEP.

9.2 SUFFOLK COUNTY, NEW YORK

Suffolk County began regulating underground storage tanks in 1980 when a law was passed stating that all new tank installations except underground petroleum tanks had to be double-walled with leak detection between the walls. The law further stated that all tanks had to be replaced with

double-walled tanks by 1990. Underground petroleum tanks could remain single-walled up to 1985 in critical aquifer recharge areas at which time they had to be replaced with double-walled tanks with leak detection between walls. The main aquifer recharge area is inland and encompasses 75% of the island. The coastal areas do not affect the recharge of the aquifer and tanks in this area can remain single-walled with external leak detection.

Testing of underground storage tanks is performed by county licensed testing companies. Tests are performed every two years on older tanks and every 5 years on newer tanks (since 1975). The only test recognized by the county is the Petro-Tite Tank Tester (formerly Kent-Moore) system.

9.3 SAN DIEGO, CALIFORNIA

California state law regarding the monitoring and testing of underground storage tanks allows for implementation of these regulations to be carried out at the local level. Counties implement the regulations through the issuance of permits to underground storage tank owners. A city may, by ordinance, assume such responsibilities within its boundaries.

All owners of existing underground storage tanks are required to implement a visual monitoring or alternative monitoring system. Visual monitoring should be used as the principal leak detection monitoring method, where feasible. When visual monitoring is not possible, an alternative method should be implemented. The alternative methods are:

- **Underground Storage Tank Testing,**
- **Vapor or Other Vadose Zone Monitoring and Ground Water Monitoring with Soil Sampling,**
- **Vadose Zone Monitoring, Soil Sampling, and Underground Storage Tank Testing,**
- **Ground Water and Soil Testing,**
- **Inventory Reconciliation, Underground Storage Tank Testing, and Pipeline Leak Detectors,**

- Inventory Reconciliation, Underground Storage Tank Testing, Pipeline Leak Detectors, Vadose Zone, or Ground Water Monitoring and Soil Testing,
- Underground Storage Tank Gauging and Testing, and
- Interim Monitoring.

Most tank owners select the first alternative - underground storage tank testing method. In the past, initial testing was required on all tanks within 12 months but subsequent testing on non-leaking tanks less than 10 years old was authorized to be done in 30 months rather than annually. Following the expiration of the 30 month period, all underground storage tanks operating under the option will require annual testing. The specific test is not designated, but it must comply with the NFPA National Fire Codes, Section 329.

10.0 TANK TIGHTNESS TESTING RECORDS

Tank tightness test records were available for most of the study sites. Two commercially available systems were used to test the tanks - the Petro-Tite Tester (formerly Kent-Moore) and the Hunter Leak Lokater. The Petro-Tite Tester has been a recognized standard for accurate tank testing within the industry for many years. This system works on the principle of applying a hydraulic pressure head to the tank by an externally connected, graduated standpipe which is filled with product to approximately four feet above ground level. Product level in the standpipe is monitored for rise and fall and measured amounts of product are added or removed. Readings are taken every fifteen minutes for six hours.

The Hunter Leak Lokater measures tank leakage by sensing weight changes in a sensor which is suspended in the liquid of the tank. Changes in weight are transmitted to a recorder that registers these changes as leaks in or out. The only station in this study to use the Hunter Leak Lokater was RI-4.

The manufacturers of the Petro-Tite Tank Tester and the Hunter Leak Lokater both report that these systems can detect leaks as low as 0.05 gallons per hour (gph) in tanks and pipes. The accuracy of these tests is currently being examined in other EPA-related studies. Both tests do not have the capability of detecting spills.

Some records of tank tightness tests were obtained from the oil companies who owned the various sites. In addition, San Diego County provided test results for several of the San Diego sites (SD-1 and SD-3 through SD-7). A government agency provided tightness data for Conn-1. All records which were obtained are included in Appendix L. These records have been modified to protect the confidentiality of the site locations and operators.

Table 10-1 presents the Tank Tightness Test Results of the study sites. Tanks with absolute leak rates of less than 0.05 gph are labeled "TIGHT".

TABLE 10-1

TANK TIGHTNESS TEST
RESULTS

<u>SITE/STATION</u>	<u>TANK MATERIAL</u>	<u>NUMBER OF TANKS</u>	<u>TANK INSTALLATION DATE</u>	<u>DATE OF TEST</u>	<u>TEST RESULTS</u>
AU-1	Steel	3	1961	4/9/86	TIGHT
	FRP	1	1981	4/9/86	TIGHT
AU-2	Steel	3	1973	5/1/86	TIGHT
AU-3	FRP	4	1984	NT	
AU-4	FRP	4	1981	NT ¹	
AU-5	Steel	3	1984	4/15/86	TIGHT
AU-6	FRP	4	1984	NT ²	
AU-7	FRP	4	1984	NT	
NY-1	FRP	3	1982	T	
NY-2	Steel	6	1968	12/30/85	TIGHT
NY-4	FRP	3	1980	NT	
NY-5	Steel	3	1972	NA	NA
NY-6	FRP	3	1980	NT	

FRP = Fiberglass Reinforced Plastic

NA = Not Available

NT = Tank Tightness Tests Not Required

¹ 1980-1987 maintenance records indicate station had several small spills in dispensing areas, and possibly some pipeline spills.

² Spill occurred from product line during testing. Corrective action was taken.

TABLE 10-1 (CONTINUED)

TANK TIGHTNESS TEST
RESULTS

<u>SITE/STATION</u>	<u>TANK MATERIAL</u>	<u>NUMBER OF TANKS</u>	<u>TANK INSTALLATION DATE</u>	<u>DATE OF TEST</u>	<u>TEST RESULTS</u>
RI-1	Steel	3	1973	NA	NA
RI-2	Steel	3	1976	9/25/87	TIGHT
RI-3	Steel	6	1965	NA	NA
RI-4	Steel	1	1966	1/22/86 (Hunter)	LEAK ¹
	Steel	1	1966	1/22/86 (Hunter)	TIGHT
	Steel	1	1966	1/22/86 (Hunter)	LEAK ²
	Steel	1	1966	1/22/86 (Hunter)	TIGHT
	Steel	1	1966	1/22/86 (Hunter)	TIGHT
	FRP	1	1984	1/22/86 (Hunter)	TIGHT
CONN-1	Steel	1	1984	1/22/87	TIGHT
	Steel	1	1966	1/21/87	TIGHT
	Steel	1	1978	1/21/87	TIGHT
	Steel	1	1966	1/21/87	LEAK ³
	Steel	1	1966	1/21/87	TIGHT
CONN-2	Steel	1	1985	NA	NA ⁴
	Steel	2	1940	NA	NA

FRP = Fiberglass Reinforced Plastic

NA = Not Available

- ¹ Failed tightness test on 1/22/86 due to a leak in system line. No records on further testing.
- ² Failed tightness test on 1/22/86. No records on further testing.
- ³ Failed tightness test on 1/21/87 due to leak in suction piping under pump. Tank has been out of service since 1/87.
- ⁴ H₂O was discovered in super unleaded tank in 1/85. Tank was excavated and replaced with new steel tank.

TABLE 10-1 (CONCLUDED)

**TANK TIGHTNESS TEST
RESULTS**

<u>SITE/STATION</u>	<u>TANK MATERIAL</u>	<u>NUMBER OF TANKS</u>	<u>TANK INSTALLATION DATE</u>	<u>DATE OF TEST</u>	<u>TEST RESULTS</u>
SD-1	Steel	2	1971	11/11/86	TIGHT
	Steel	1	1971	11/21/86	TIGHT ¹
	FRP	1	1978	11/21/86	TIGHT ²
SD-2	Steel	3	1972	6/17/87	TIGHT
SD-3	FRP	2	1982	12/10/86	TIGHT
	FRP	1	1982	12/22/86	TIGHT ³
SD-4	Steel	4	1965	11/5/86	TIGHT
SD-5	FRP	3	1983	5/7/86	TIGHT
SD-6	FRP	3	1983	5/18/87	TIGHT
SD-7	Steel	1	1972	4/16/86	TIGHT
	Steel	1	1965	4/16/86	TIGHT
	Steel	1	1965	4/17/86	TIGHT
SD-8	Steel	4	1965	1/21/86	TIGHT
SD-9	Steel	3	1967	NA	NA

FRP = Fiberglass Reinforced Plastic

NA = Not Available

¹ Failed tightness test on 11/11/86 due to a leak in diesel vent line. Retested on 11/21/86 and passed.

² Failed tightness test on 11/11/86 due to tank leak of -0.5 gph. Retested on 11/21/86 and passed.

³ Failed tightness test on 12/10/86 due to leak in the vapor line. Retested on 12/22/86 and passed.

Tanks with leak rates greater than 0.05 gph are labeled "LEAK" and an explanation of the leak and the surrounding circumstances is provided in the accompanying footnote. Several sites had no available records or had not been tested due to recent tank installations and are labeled "NA" and "NT", respectively, in the table.

There are a total of 100 underground storage tanks at the 27 gasoline stations that were studied. Of this total, 63 tanks are fabricated from steel and were installed between 1940 and 1984. The remaining 37 are made of fiberglass reinforced plastic (FRP) and were installed between 1978 and 1984.

Of the 63 steel tanks, 42 were determined tight in recent tests. Three steel tanks, two from RI-4 and one from CONN-1, were found to be leaking. No further records are available to indicate repair and/or subsequent testing of these tanks. No tank tightness test records are available on the remaining 18 steel tanks.

Tank tightness tests were conducted on 12 of the FRP tanks; all tested tight. Tests on the remaining 25 were not required by the regulating government agency due to the relatively new age of the tanks.

Seven gas stations had histories of leaks: AU-4 & 6; RI-4; CONN-1 & 2; and SD-1 & 3. Maintenance records from AU-4 for the period of 1980 to 1987 indicate that numerous surface spills occurred from vandalized split hoses and dispensers. Records also exist of low or slow flow which might indicate pipeline leaks. AU-4 was removed from the database as a clean site because of its history of high maintenance and its unusually high soil gas concentrations. AU-6 was also removed from the database because of a known spill that occurred from a product line break. The five other stations remained in the database as background data because the soil gas concentrations were not excessive.

11.0 DATA ANALYSIS

Geoscience Consultants, Ltd. investigated hydrocarbon vapor concentrations in the backfill of underground storage tanks (UST) in two phases: a field investigation phase and a data analysis phase.

Since no database for soil gas information in non-contaminated UST sites was known to exist, it was necessary to conduct field investigations to establish a baseline of hydrocarbon vapor concentrations. Data were collected from twenty-seven gasoline service stations selected as non-contaminated sites. Selection criteria (Section 3.0) were used to develop a data set which included a variety of tank ages, tank materials, stored products and backfill materials. The underground storage tanks selected were believed to be non-leaking, or "tight." UST systems were considered to be tight if:

- Tightness testing within the previous two years indicated the system to be without leaks, or
- In cases where test records were not available, the environmental and maintenance personnel of the oil company had no knowledge of contamination due to leakage at the site.

Two stations sampled (Stations #6 and #4 in Austin, Texas) were determined to be inappropriate as non-contaminated sites, and their data were not included in the data set. Station #6 had a fresh gasoline spill from a product line puncture that occurred during the field investigation. Station #4 had a history of frequent product line and dispenser problems, according to maintenance records, and no test records were available.

The non-contaminated site data, therefore, consisted of 279 soil gas samples taken from twenty-five service stations.

Contaminated site data were obtained from Tracer Research Corporation historical records. The contaminated site data was selected from sixty soil gas samples taken from nine sites having known contamination from a petroleum fuel leak or spill. These sites were all active gasoline service stations or fueling facilities.

The strategy for data analysis was determined by the fact that no usable data for non-contaminated sites were known to exist. Therefore, analyses were employed which could delineate patterns in the data, if they existed, and which could prove useful in establishing contamination thresholds.

Data analysis was broken down into three parts:

- Analysis of total hydrocarbon concentrations ("less methane" and "including methane") in soil gas at non-contaminated sites with the objective of establishing a descriptive statistical baseline.
- Comparison of the non-contaminated site baseline information to data from sites where petroleum fuel contamination was known to exist. This comparison examined the appropriateness of establishing an upper limit for total hydrocarbon (less methane) vapor concentrations at non-contaminated sites that could provide a "threshold" concentration value between non-contaminated and contaminated sites.
- Non-parametric statistical testing of each data set (non-contaminated and contaminated) in order to substantiate observed differences and identify significant trends among total hydrocarbon vapor concentrations, sample depth, location, backfill materials, tank age and tank material.

Analyses focused on concentrations of total hydrocarbons (less methane) in soil gas, as the presence of total hydrocarbons is indicative of contamination from a petroleum leak or spill. Methane was excluded from the reported concentrations in order to present a profile of compounds similar to that of gasoline, and to exclude methane concentrations which may have been present due to naturally-occurring decomposition of organic matter.

The use of total hydrocarbon concentrations in soil gas as a contamination index is consistent with current EPA ground water and soil monitoring proposals. An analysis of total hydrocarbon data (including methane) is presented (Section 11.2) to show how these data are

distributed as compared to total hydrocarbon concentrations (less methane). This comparison may be useful in evaluating total hydrocarbon concentrations from leak detection devices which include methane.

Accuracy in the data analysis was essential because the results may be used to provide direction for future leak detection methods. Towards this goal, the soil gas data were reported in micrograms per liter (ug/l) because this provided a better approximation of the total hydrocarbon vapor concentrations than parts per million by volume (ppmv) (Section 7.0). Also, three gas chromatograph/flame ionization detection (GC/FID) analyses were generally performed on each sample, and the arithmetic mean of the usable samples, as judged by the GC/FID operator, was used in the analyses. The replicability of analytical results were within 25 percent of the average concentration value for each sample.

11.1 EMPIRICAL DISTRIBUTION OF TOTAL HYDROCARBON CONCENTRATIONS (LESS METHANE) FOR NON-CONTAMINATED SITES

An empirical distribution of the total hydrocarbon (less methane) vapor concentrations in soil gas surrounding non-contaminated UST systems is useful for two reasons:

- It shows what concentrations can be considered as "background" concentrations in a UST system, and
- The distribution can be compared to similar concentration distributions from contaminated sites.

Even at sites with no known contamination, a level of total hydrocarbon vapor concentrations is present resulting from surface spills or small undetected leaks of petroleum fuels. These concentrations are defined as the total hydrocarbon background level of the soil gas at the site.

The best way to describe the distribution of total hydrocarbon concentration data is by using the relative frequency distribution.

The relative frequency distribution is obtained by grouping the data into

concentration classes and determining the proportion of samples in each of the classes. This distribution for total hydrocarbon (less methane) concentrations is shown in Table 11-1 in micrograms per liter (ug/l) and in Table 11-2 in parts per million by volume (ppmv).

The classes in these distributions were chosen to show the overall distribution of samples, as well as the percentage of samples below 1500 ug/l (approximately 500 ppmv). The 1500 ug/l concentration class was chosen because proposed EPA regulations concerning leaking UST systems have considered 500 ppmv as a possible threshold value to differentiate non-contaminated from contaminated sites. The relative frequency distribution shows that 53.2 percent of the samples were below 1500 ug/l. The overall distribution shows that 93.1 percent of the samples were less than 100,000 ug/l.

There are nineteen samples (6.8 percent of the total) that have average concentration values greater than 100,000 ug/l. Site and sample data were examined to explore causes for these high values. Table 11-3 shows the site and sample location of the data points. The nineteen samples came from seven service stations studied. Tightness test results showed the UST systems at four of these stations to be tight, while no test records were available for the other three.

A possible source for the high total hydrocarbon (less methane) concentrations at the seven sites is from surface spills. Interviews with the participating oil companies revealed that underground fuel storage tanks are occasionally overfilled by the transporter. Since there is no system for monitoring these surface spills, the frequency of this event is unknown.

Another possible source for the high concentrations could be related to the age of the tanks. Six of the stations contained steel tanks installed between the years 1965 and 1971. One station contained a

TABLE 11-1

**DISTRIBUTION OF NON-CONTAMINATED SITE DATA
FOR TOTAL HYDROCARBONS LESS METHANE**

<u>CONCENTRATION RANGES (Micrograms Per Liter)</u>	<u>NUMBER OF SAMPLES</u>	<u>RELATIVE FREQUENCY DISTRIBUTION (%)</u>	<u>CUMULATIVE RELATIVE FREQUENCY (%) DISTRIBUTION</u>
Not Detected	65	23.2	23.2
< 1500	84	30.0	53.2
1501 - 5000	17	6.0	59.2
5000 - 10,000	12	4.3	63.5
10,000 - 50,000	56	20.0	83.5
50,000 - 100,000	27	9.6	93.1
100,000 - 270,000	18	6.4	99.5
1,100,000	1	.5	100.0
	<u>280</u>	<u>100</u>	

Mean 23,300
Median 800
Upper
Quartile 33,000

TABLE 11-2

**DISTRIBUTION OF NON-CONTAMINATED SITE DATA
FOR TOTAL HYDROCARBONS LESS METHANE**

(Parts Per Million by Volume)

(ppm) CONCENTRATION RANGES (Micrograms Per Liter)	NUMBER OF SAMPLES	RELATIVE FREQUENCY DISTRIBUTION (%)	CUMULATIVE RELATIVE FREQUENCY (%) DISTRIBUTION
Not Detected	65	23.2	23.2
< 500	88	31.4	54.6
501 - 1,350	14	5.0	59.6
1,351 - 2,700	11	3.9	63.5
2,701 - 13,500	57	20.4	83.9
13,501 - 27,000	27	9.6	93.5
27,001 - 72,900	17	6.1	99.6
> 72,900	1	.4	100.0
	<u>280</u>	<u>100.0</u>	

Mean 7,200
Median 220
Upper
Quartile 9,200

TABLE 11-3

**TOTAL HYDROCARBON CONCENTRATIONS LESS METHANE
GREATER THAN 100,000 MICROGRAMS PER LITER**

<u>STATION</u>	<u>TANK AGE AND MATERIAL</u>	<u>PETROTITE TEST RESULTS</u>	<u>SAMPLE NUMBER-DEPTH</u>	<u>TOTAL HYDROCARBONS CONCENTRATION LESS METHANE (Micrograms Per Liter)</u>
<u>Austin, Tx</u>				
Station #5	1971-Steel	Tight	SG1 - 2	150,000
			SG1 - 6	110,000
			SG1 -10	1,100,000
			SG2 - 6	120,000
			SG3 - 2	190,000
			SG4 - 2	140,000
<u>Suffolk County, NY</u>				
Station #1 (1)	1 9 8 2 Fiberglass	NR	SG2 - 2	170,000
			SG2 - 6	210,000
Station #5	1972-Steel	NR	SG2 - 8	270,000
			SG4 - 10	110,000
<u>San Diego, CA</u>				
Station #4	1965-Steel	Tight	SG4 - 2	110,000
Station #7 (1)	1965-Steel	Tight	SG1 -10	120,000
			SG2 - 2	120,000
			SG2 - 6	130,000
			SG2 -10	210,000
Station #8 (2)	1965-Steel	Tight	SG2 -10	110,000
			SG3 -10	104,000
			SG4 -10	120,000
Station #9 (1)	1967-Steel	NR	SG2 - 6	110,000

NOTES: (1) SG2 is located near a tank fill cap.
(2) Station #8 is an inactive service station.

fiber-glass tank installed in 1982. The possibility of undetected leaks could be greater in older tanks.

11.2 EMPIRICAL DISTRIBUTION OF TOTAL HYDROCARBON CONCENTRATIONS (INCLUDING METHANE) OF NON-CONTAMINATED SITES

It may be useful to report total hydrocarbons as "including methane" for two reasons:

- Methane can also occur by the natural decomposition of petroleum fuel in soil, and
- Some UST leak detection methods are based on detection equipment that is sensitive to any hydrocarbon compound. Therefore, these detection devices will detect the presence of methane in soil gas in addition to other hydrocarbon compounds.

The empirical distribution of average total hydrocarbon vapor concentrations (including methane) is compared to the distribution of average total hydrocarbon vapor concentrations (less methane) in micrograms per liter in Table 11-4, and in parts per million by volume in Table 11-5.

The distribution of total hydrocarbons including methane are similar to total hydrocarbons less methane in two class ranges: 5,001 - 10,000 ug/l and 50,001 - 100,000 ug/l. However, differences exist in the other class ranges. These differences can best be shown by summarizing the distributions into two classes as follows:

CONCENTRATION RANGES (Micrograms Per Liter)	RELATIVE FREQUENCY PERCENT	
	<u>Less Methane</u>	<u>Including Methane</u>
≤ 100,000	93.2	73.8
> 100,000	6.8	26.2
	<u>100.0</u>	<u>100.0</u>

TABLE 11-4

COMPARISON OF TOTAL HYDROCARBONS INCLUDING
METHANE AND LESS METHANE AT NON-CONTAMINATED SITES

(Micrograms Per Liter)

CONCENTRATION RANGES (Micrograms Per Liter)	RELATIVE FREQUENCY DISTRIBUTION (PERCENT)	
	<u>Less Methane</u>	<u>Including Methane</u>
< 5,000 *	59.2	48.9
5,001 - 10,000	4.3	4.3
10,001 - 50,000	20.0	11.0
50,001 - 100,000	9.6	9.6
100,001 - 400,000	6.4	21.8
400,000 - 1,000,000	-	3.9
1,100,000	0.5	-
1,250,000	-	.5
	<u>100.0</u>	<u>100.0</u>

* Includes non-detected values.

TABLE 11-5 :

COMPARISON OF TOTAL HYDROCARBONS INCLUDING
METHANE AND LESS METHANE AND LESS METHANE AT
NON-CONTAMINATED SITES

(Parts Per Million by Volume)

CONCENTRATION RANGES (Micrograms Per Liter)	RELATIVE FREQUENCY DISTRIBUTION (PERCENT)	
	<u>Less Methane</u>	<u>Including Methane</u>
< 500 *	54.6	45
501 - 1,350	5.0	2.1
1,351 - 2,700	3.9	2.5
2,701 - 13,500	20.4	8.9
13,501 - 27,000	9.6	5.0
27,001 - 72,900	6.1	11.1
72,901 - 250,000	0.4	15.0
250,001 - 600,000	-	6.4
> 600,000	-	4.0
	<u>100.0</u>	<u>100.0</u>

* Include non-detected values.

The effect of including methane in the total hydrocarbon concentration is to lower the percentage of samples with concentrations equal to or less than 100,000ug/l (or 30,000 ppmv) by 21 percent. This effect was expected since the soil gas data showed high concentrations of methane at many of the sites. This was probably due to naturally-occurring methane as well as methane which occurs from the decomposition of hydrocarbon compounds.

11.3 COMPARISON OF TOTAL HYDROCARBON CONCENTRATIONS FOR NON-CONTAMINATED SITE AND CONTAMINATED SITE DATA SETS

The data distribution in Section 11.1 has shown that a wide range of background hydrocarbon vapor concentrations exist in the soil gas in backfill at non-contaminated UST sites. These concentrations ranged from the lower detection limits of 0.02 micrograms per liter (ug/l) to 1,100,000 ug/l for total hydrocarbons (less methane). Although much variability exists in these data, a comparison of these data to data from known contaminated sites is required to determine if background vapor concentrations differ from vapor concentrations at sites with known contamination. If statistically significant differences exist between these data distributions, then the results of this comparison could be useful to UST regulators, service station owners and others who must interpret soil gas data to determine if contamination exists at a UST site.

An evaluation of these differences could also determine the appropriateness of establishing a threshold concentration for total hydrocarbons (less methane). Statistical testing was performed (Section 11.4) to determine if observed differences concluded from the descriptive statistics are significant differences.

In order for the data sets to be comparable, the data in each set must be collected in a similar fashion. Since the contaminated site data set was obtained from historical records, data for this set were selectively chosen to be consistent with the samples taken at non-contaminated sites during the field investigation.

The sampling strategy for non-contaminated sites, as outlined in the Field Methods (Section 5.0) was to collect samples from the backfill of the tanks and at depths of 2, 6 and 10 feet. Although samples at contaminated sites were usually not in backfill, data were chosen that were within approximately 50 feet of the USTs, and at 2, 6, and 10-foot depths. The method of sampling was similar for both data sets since soil gas samples were collected by Tracer Research Corporation (TRC) using similar procedures.

In this comparison, total hydrocarbons are reported "less methane" and in micrograms per liter for both data sets. The total hydrocarbon (less methane) concentrations in the non-contaminated data set were calculated from average response factors for benzene, toluene, ethylbenzene and xylenes (BTEX). However, in the contaminated data set, total hydrocarbon concentrations (less methane) were calculated from the response factor for benzene. Therefore, contaminated site data could be as much as 50 to 100 percent higher if it were reported on the basis of an average BTEX response factor. A comparison of calculation methods and their effects on total hydrocarbon concentrations was presented in Section 7.0.

The sample size for the non-contaminated data set was 279 samples from 25 sites. The sample size for the contaminated data set was 60 samples from 9 sites.

The descriptive statistics used to compare the non-contaminated and contaminated data sets were: mean, median, upper quartile and the relative frequency distribution percentages. These statistics are useful because they show the distribution of each data set and these distributions can be compared even though the sample sizes in each data set are different. The descriptive statistics for the non-contaminated sites were shown in Table 11-1 and those for the contaminant sites are shown in Table 11-6. A comparison of these descriptive statistics are shown in Table 11-7 in micrograms per liter for total hydrocarbons (less methane). The relative frequency distribution for the non-contaminated

TABLE 11-6

DISTRIBUTION OF CONTAMINATED SITE DATA FOR TOTAL
HYDROCARBONS LESS METHANE

<u>CONCENTRATION RANGES (MICROGRAMS PER LITER)</u>	<u>NUMBER OF SAMPLES</u>	<u>RELATIVE FREQUENCY DISTRIBUTION</u>	<u>CUMULATIVE RELATIVE FREQUENCY DISTRIBUTION</u>
Not Detected	2	3.3%	3.3%
< 1500	19	31.7%	35.0%
1501 - 5000	6	10.0%	45.0%
5000 - 10,000	5	8.3%	53.3%
10,000 - 50,000	7	10.0%	65.0%
50,000 - 100,000	1	1.7%	66.7%
100,000 - 270,000	6	10.0%	76.7%
270,000 - 1,100,000	13	21.7%	98.4%
>1,000,000	1	1.7%	100.0%
		<u>100.0%</u>	<u>100.0</u>

Mean	160,000
Median	9,000
Upper Quartile	22,000

TABLE 11-7

COMPARISON OF NON-CONTAMINATED AND CONTAMINATED
SITE DATA DISTRIBUTIONS FOR
HYDROCARBONS LESS METHANE

CONCENTRATION RANGES (MICROGRAMS PER LITER)	RELATIVE FREQUENCY PERCENT CONTAMINATED	RELATIVE FREQUENCY PERCENT NON-CONTAMINATED
Not Detected	3.3	23.2
< 1500	31.7	30.0
1501 - 5000	10.0	6.0
5001 - 10,000	10.0	4.3
10,001 - 50,000	10.0	20.0
50,001 - 100,000	1.7	9.6
100,001 - 270,000	10.0	6.4
270,001 - 1,100,000	21.6	0.4
2,200,000	1.7	0.0
	<u>100.0</u>	<u>100.0</u>
Mean	160,000	23,300
Median	9,000	800
Upper Quartile	220,000	33,000

site data was shown in Figure 11-1 and that for the contaminated site data is shown in Figure 11-2.

The relative frequency distributions show much variability in both data sets. Nine concentration ranges were selected to show this variability.

An evaluation of the means and medians gives additional information about these data sets. The mean is an arithmetic average that is computed by summing the concentration values and dividing by the total number of samples. The median is defined as the middle value after the samples have been arranged in order of magnitude (Hoel 1967).

In both data sets, the medians are much lower than the means. These differences show that both data distributions are skewed to the right with a majority of samples in the lower concentration ranges. The high mean values show the effect of a few high concentration values that exist in both data distributions.

Although similarities exist in the distribution of these data sets, some differences can also be seen. An order of magnitude difference exists between the mean of each data set, and between the medians of each data set. This suggests that although similarities exist in how these data sets are skewed, that an order of magnitude difference exists for much of the data.

The order of magnitude can best be seen in the concentration ranges above 10,000 ug/l. The relative frequency percentages from Table 11-7 are summarized below for concentrations above 10,000 ug/l, or about 3000 parts per million by volume.

CONCENTRATION RANGES (Micrograms Per Liter)	RELATIVE FREQUENCY PERCENT	
	<u>Non-Contaminated</u>	<u>Contaminated</u>
10,000 - 100,000	29.6	13.4
100,000 - 2,200,000	<u>6.9</u>	<u>33.3</u>
	36.5	46.7

NON-CONTAMINATED SITE DATA DISTRIBUTION

TOTAL HYDROCARBONS LESS METHANE

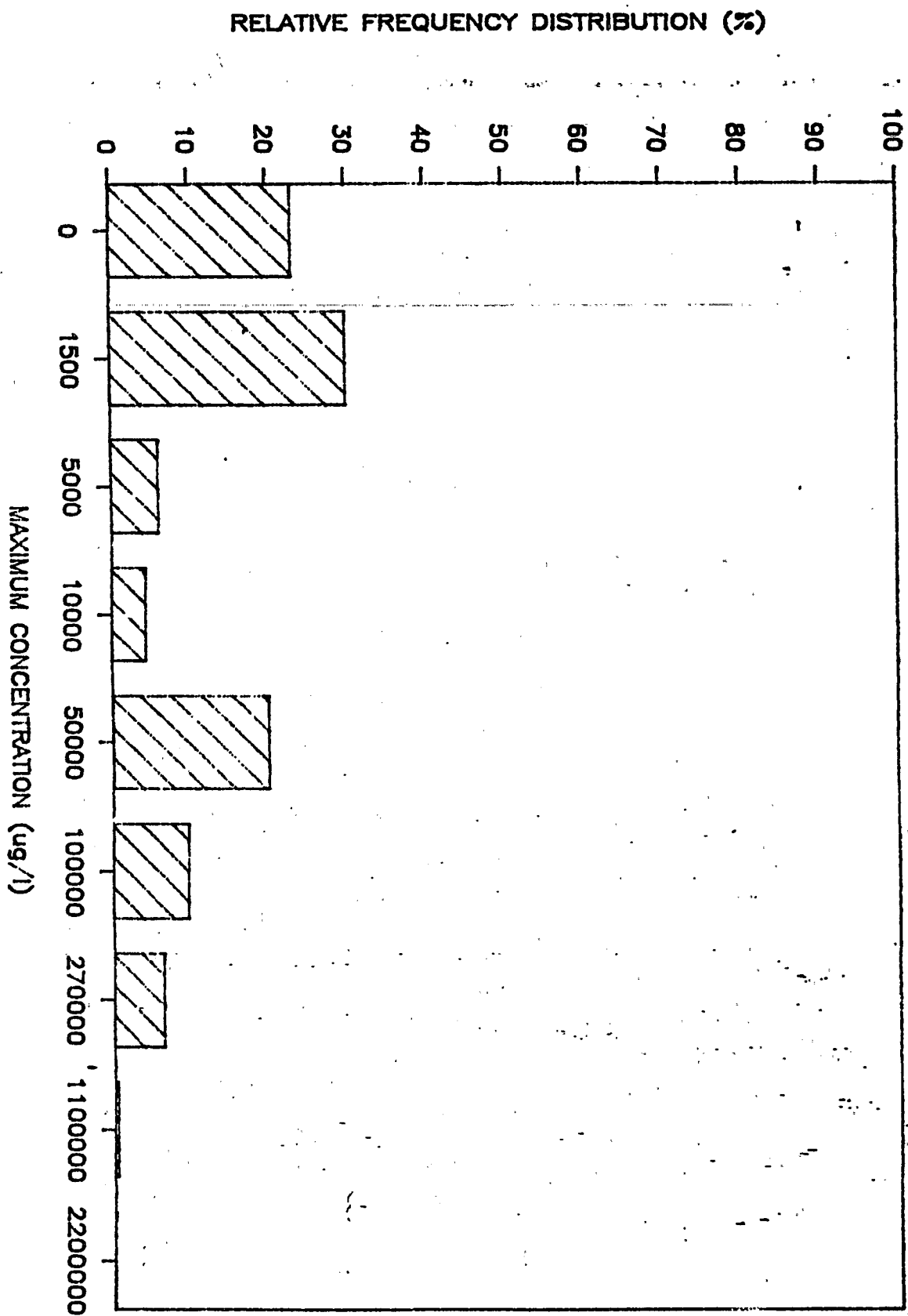


FIGURE 11-1

CONTAMINATED SITE DATA DISTRIBUTION

TOTAL HYDROCARBONS LESS METHANE

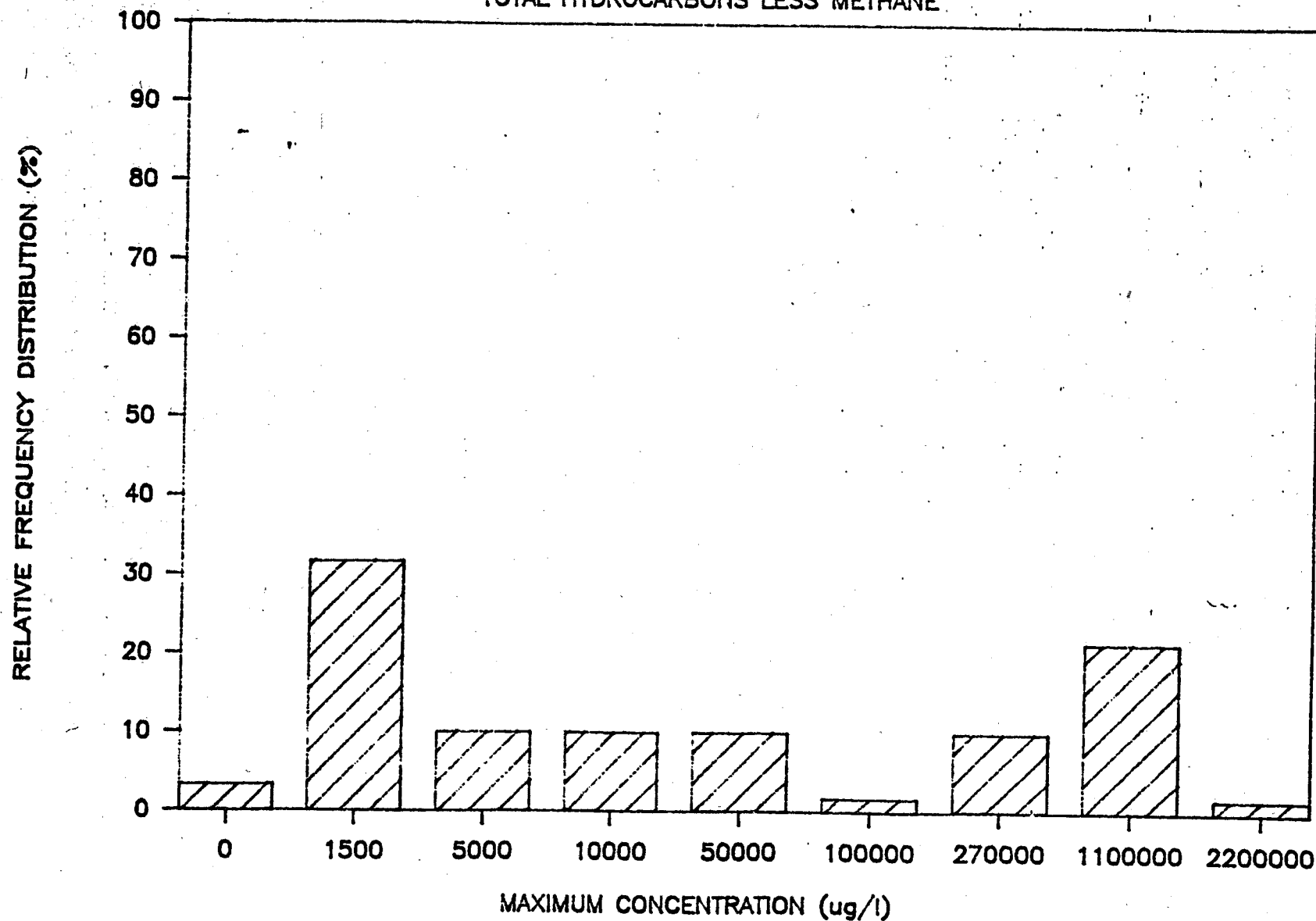


FIGURE 11-2

Most of the non-contaminated samples occur in the 10,000 to 100,000 ug/l range, while most of the contaminated samples occur above 100,000 ug/l.

The order of magnitude difference between the data sets can also be seen by comparing the upper quartiles of each data set. The definition of upper quartile is that 75% of the samples occur below the upper quartile (Hoel 1967).

The upper quartile for the non-contaminated and contaminated data sets are 33,000 ug/l and 220,000 ug/l, respectively.

The observed conclusions from these descriptive statistics is that both data sets contain much variability and both are skewed to the right. An order of magnitude difference exists between the data sets for concentrations above 10,000 ug/l. Statistical testing in Section 11.4 confirms the significance of these differences between the data sets.

11.4 NON-PARAMETRIC STATISTICAL TESTING

The purpose of statistical methods is to describe data quantitatively, and to draw inferences for decision-making (Kilpatrick 1987). The descriptive statistics have been examined in the previous sections, and these described the means, medians, upper quartiles and relative frequency distributions for the data sets.

In this section, statistical methods are employed to determine what inferences can be made about the non-contaminated site and contaminated site data sets.

The statistical testing in this data analysis served two purposes:

- The testing determined the significance of the observed statistical differences between the data sets (non-contaminated and contaminated) noted in the descriptive statistics, and
- The testing delineated data patterns that existed among such parameters as location of site, depth of sample, tank material, tank age and backfill material.

The types of statistical tests chosen were dictated by the characteristics of the data set distributions. These distributions, as described previously, did not appear to correspond to any known statistical distribution such as a Normal distribution. Non-parametric statistical methods were used since these methods did not require that the sample data correspond to a known statistical distribution (Harval).

These statistical methods also introduce the element of probability as related to the drawing of conclusions. Probability was considered important in developing conclusions about these data sets because these data sets do not contain complete information about the entire data set of underground storage tanks that exist. Therefore, a probability must be attached to any conclusions made about the data sets. A discussion of the risks associated with statistical testing, and how these risks were controlled is given in Section 11.4.1.

11.4.1 The Risks Associated with Hypothesis Testing

There is always the possibility of making an incorrect decision when testing a hypothesis. This is because inferences about a particular distribution are based upon random samples from that distribution. A statistical hypothesis is simply an assumption or statement, which may or may not be true, concerning one or more populations.

There are two types of error or risk associated with the testing of any hypothesis. Type 1 error is the probability of rejecting a true null hypothesis, while Type 2 error is the probability of rejecting a true alternative hypothesis. A null hypothesis indicates that no differences exist between distributions. An alternate hypothesis indicates that differences do exist between distributions.

Type 1 error is usually controlled by setting the significance level of the test to a small value. This significance level, designated as "p", numerically describes the probability that a particular hypothesis is true. Typically this value is set at 0.05. This corresponds to a

confidence level (probability) of 95 percent. The significance level becomes a specification of the Type 1 error rate of probability.

Type 2 error is usually controlled by taking a properly-sized sample. This study did not consider the control of Type 2 error as a criteria for determining sample size. However, when large discrepancies exist between the information contained in the samples and the specification of the null hypothesis with respect to the samples, then the Type 2 error will generally be small.

When testing more than one hypothesis, the Type 1 error rate must be controlled. A simple example will demonstrate what happens to the Type 1 error rate when testing several hypotheses.

Suppose that each of 10 independent hypotheses are to be tested at a significance level of 0.05. If the null hypothesis is true in all 10 cases, the probability of detecting this is only 0.60. Therefore, the Type 1 error rate is 0.40, which is totally unacceptable. One way to control the Type 1 error rate when testing several hypotheses is to test each hypothesis at a reduced significance level. A good conservative procedure for determining the significance level in a multiple testing situation is the Bonferroni procedure. This procedure is described below.

If an overall Type 1 error rate of 0.05 is to be attained, the significance level for each hypothesis tested is computed by dividing 0.05 by the number of hypotheses to be tested.

In the example above, the significance level of each hypothesis should be:

$$0.05 / 10 = 0.005$$

Thus, if each hypothesis is tested at a Type 1 error rate of 0.005, then an overall Type 1 error rate of 0.05 will be maintained.

There were 16 statistical tests performed in this study. Therefore, in order to maintain an overall Type 1 error rate of 0.05 for this study, each hypothesis was be tested at a Type 1 error rate of 0.003.

11.4.2 Comparison of Non-Contaminated Site and Contaminated Site Data Distributions

The descriptive statistics showed some similarities in how the non-contaminated and contaminated site data were distributed. The distribution of both data sets were skewed to the right with a majority of samples in the lower concentration ranges. However, an order of magnitude difference existed in the data above 10,000 ug/l. This difference was seen by a comparison of the means, medians and upper quartiles of each data set. In this section of the report, a non-parametric test is used to compare these data sets. This test will determine if the distributions of these data sets are significantly different.

The non-parametric test used for this comparison is the Two-Sample Wilcoxon Rank Sum Procedure (Siegel 1956). This test is designed to determine if two independent samples are from different distributions. Since the sample values within each data set contain much variability, the question is whether the differences observed between the data sets signify genuine differences in distributions or whether they represent differences that can be expected between two random samples from the same distribution.

The Wilcoxon technique tests the null hypothesis that two independent samples come from identical distributions. This is called a null hypothesis because it assumes that there is no difference between distributions. If the outcome of the test rejects the null hypothesis (that is, $p < 0.003$), then it can be concluded that the samples came from two different distributions.

This test was computed using a computer software package called Statgraph. Results of the test are included in Appendix M. In most

cases, the data used in this test represent the mean of three GC-FID injections for each sample. The concentrations at non-detection levels were approximated by dividing the detection limit in half.

The outcome of this test is show below.

<u>DISTRIBUTION</u>	<u>SAMPLE SIZE</u>	<u>AVERAGE RANK</u>	<u>LEVEL OF SIGNIFICANCE</u>
Non Contaminated	279	160	0.00008
Contaminated	60	215	

This test result shows that there is a significant difference ($p < 0.003$) between the distributions of the non-contaminated and contaminated site data. This test result confirms that the distributions of non-contaminated and contaminated data, as shown in Table 11-7, actually represent two different distributions.

11.4.3 Non-Parametric Testing for Data Patterns Within the Non-Contaminated Data

Non-parametric techniques can be used to identify patterns in the non-contaminated data set if they exist. The results of non-parametric testing can be used to draw inferences about the data.

The purpose of this testing was to examine the effects that different parameters had on the data. These parameters included site location sample depth, tank material, tank age and backfill material. The testing was designed so that independent effects from each parameter could be seen. However, insufficient data were available to delineate the individual effect of tank material, tank age and backfill material.

The determination of insufficient data was made from observations about the data at a time when further data could not be collected (i.e., the field investigation had been completed). Two observations were made:

- All the fiberglass tanks used pea gravel backfill and corresponded to newer tank ages (1978 to 1984), and
- All the steel tanks used sand backfill and corresponded to older tank ages (1940 to 1984).

The data could not be separated to distinguish between tank materials, tank age and backfill material. In this analysis, these three parameters are combined and referred to as either a steel tank system or a fiberglass tank system. The presentation of test results are organized according to the parameters of location, sample depth and steel or fiberglass tank systems. Test results that involve fiberglass tank systems are only shown for the locations of Austin, Texas, Suffolk County, New York and San Diego, California since no fiberglass tank systems were sampled in Providence, Rhode Island or Storrs, Connecticut.

11.4.3.1 Location

The first parameter examined was site location. The Kruskal-Wallis One-Way Analysis of Variance by Ranks (Siegel 1956) was chosen to test the null hypothesis that samples from different locations come from the same distribution.

This testing was again accomplished by the use of the Statgraph computer software package. In order to test only for the effect of location, the data set was broken down into subsets corresponding to sample depth and the combined group of tank material, tank age and backfill material. The above breakdown yields six subsets as follows:

- fiberglass tank systems at sample depths of 2, 6 and 10 feet and
- steel tank systems at sample depths of 2, 6 and 10 feet.

The mean concentrations for each sample were used as data. The concentrations below detection limits were set to positive values at the detection limits to represent the worst case for concentrations at these sample points.

The results of these tests are shown in Table 11-8 for the steel tank systems and Table 11-9 for the fiberglass tank systems, and are also included in Appendix M.

The subsets consisting of steel tank systems at 2, 6 and 10 foot sample depths show significance at $p < 0.003$. The interpretation of these results is that the null hypothesis, which states that these subset samples are from the same distribution set, must be rejected. It is concluded that significant differences do exist among the total hydrocarbon (less methane) vapor concentrations from the five locations studied for steel tank systems. The differences were significant at all three sample depths (2, 6 and 10 feet).

The average rank is an indication of how these concentrations were ranked. The total hydrocarbon concentrations in Austin, Texas and San Diego, California were greater than in Providence, Rhode Island, Suffolk County, New York and Storrs, Connecticut.

The subsets consisting of fiberglass tank systems at each of the 2, 6 and 10 foot sample depths do not show significance ($p > 0.003$) at any of the sample depths. The interpretation is that the null hypothesis, which states that these subset samples are from the same distribution, is accepted. It is concluded that no significant differences exist among the total hydrocarbons (less methane) vapor concentrations from the three locations studied for fiberglass tank systems. This conclusion can also be seen by examining the average ranks. The value of these ranks are similar within each sample depth subset.

11.4.3.2 Sample Depth

The second parameter examined was sample depth. The analysis was designed to determine if differences existed among samples taken at different depths. This analysis is based on the assumption that samples taken from different depths within a hole are related, and the tests determine if data at different sample depths have been drawn from the same distribution.

TABLE 11-8

RESULTS OF KRUSKAL-WALLIS TESTS FOR LOCATIONS
WITH STEEL TANK SYSTEMS USING NON-CONTAMINATED DATA

<u>STEEL TANK SYSTEMS</u>	<u>LOCATION</u>	<u>SAMPLE SIZE</u>	<u>AVERAGE RANK</u>	<u>SIGNIFICANCE LEVEL</u>
Sample Depth = 2 Foot	Austin, TX	14	51	0.000003
	San Diego, CA	29	49	
	Providence, RI	14	30	
	Suffolk County, NY	8	20	
	Storrs, CT	10	15	
Sample Depth = 6 Foot	San Diego, CA	28	48	0.00002
	Austin, TX	13	43	
	Suffolk County, NY	6	28	
	Providence, RI	15	22	
	Storrs, CT	9	17	
Sample Depth = 10 Foot	San Diego, CA	17	33	0.0006
	Austin, TX	11	27	
	Suffolk County, NY	5	18	
	Providence, RI	11	14	
	Storrs, CT	3	7	

TABLE 11-9

RESULTS OF KRUSKAL-WALLIS TESTS FOR LOCATIONS
WITH FIBERGLASS TANK SYSTEMS USING NON-CONTAMINATED DATA

<u>FIBERGLASS TANK SYSTEMS</u>	<u>LOCATION</u>	<u>SAMPLE SIZE</u>	<u>AVERAGE RANK</u>	<u>SIGNIFICANCE LEVEL</u>
Sample Depth = 2 Foot	Suffolk County, NY	10	21	0.06
	Austin, TX	9	20	
	San Diego, CA	14	12	
Sample Depth = 6 Foot	Suffolk County, NY	11	18	0.4
	Austin, TX	8	14	
	San Diego, CA	11	14	
Sample Depth = 10 Foot	San Diego, CA	8	13	0.5
	Suffolk County, NY	9	12	
	Austin, TX	5	9	

Two non-parametric tests were chosen. These were the Page L Test for Ordered Alternatives based on Friedman Rank Sums, and the Wilcoxon Matched-Pairs Signed-Ranks Test (Siegel 1956).

The Page L Test was chosen to test the null hypothesis that data at different sample depths have been drawn from the same distribution. If differences do exist, this test also reveals how these data are ordered. Specifically, this test will determine if one of the following trends exist for total hydrocarbon (less methane) vapor concentrations taken from non-contaminated sites:

$$2' < 6' = 10'$$

$$2' = 6' < 10'$$

$$2' < 6' < 10'$$

$$2' = 10' < 6'$$

If test results show a level of significance ($p < 0.003$) then the null hypothesis is rejected and one of these conditions exist.

In cases where these test results showed a level of significance for a particular data subset, the Wilcoxon Matched-Pairs Signed-Ranks Test was employed to further test the following hypotheses for total hydrocarbon (less methane) vapor concentrations at non-contaminated sites:

$$2' < 6'$$

$$6' < 10'$$

$$2' < 10'$$

A separate calculation was required to test for each of these conditions.

The benefits in using the Wilcoxon Test as a supplement to the Page L test are not only to determine exactly how the data at different depths are ordered, but also to utilize more data from the non-contaminated data

set. There were service stations in San Diego and Austin in which shallow perched water zones were encountered that precluded taking samples at 10 feet. Therefore, soil gas samples were only collected at 2 and 6 foot depths. By using the Wilcoxon Test, these data could also be utilized. The computations for both techniques (Page L and Wilcoxon) were done by hand, under the direction of a qualified statistician and are shown in Appendix M.

The results of the Page L Tests and the Wilcoxon Tests are shown in Tables 11-10 and 11-11, respectively. Calculations for these tests are included in Appendix M. These test results show variations in significance levels at individual locations in both the steel and fiberglass tank systems. A summary of the significant test results is given below.

- 1) Two significant test results were shown from the Page L Test for the overall data. The significant differences were among total hydrocarbon (less methane) vapor concentrations at the different sample depths (2, 6 and 10 feet) for both steel and fiberglass tank systems. The overall test represents data that are combined from the different locations.
- 2) Significant test results were also shown from the Page L Test for individual locations. There were significant differences among total hydrocarbon (less methane) vapor concentrations at the different sample depths (2, 6 and 10 feet) for steel tank systems in San Diego, CA and for fiberglass tank systems in San Diego, CA and Suffolk County, NY.
- 3) One significant test result was shown from the Wilcoxon Test for San Diego, CA. The significant difference was shown in the test of 2' < 6'. Therefore, total hydrocarbon (less methane) concentrations are greater at 6 feet than at 2 feet for the steel tank system in San Diego, California.

The variations in significance at the different locations could be due to two factors: 1) The differences in the locations, such as geology, hydrology, backfill material, etc., and 2) insufficient data to detect significant differences using the statistical methods.

TABLE 11-10

RESULTS OF PAGE L TEST FOR DIFFERENCES
IN DATA ACCORDING TO SAMPLE DEPTH

<u>STEEL TANK SYSTEMS</u>	<u>LOCATION</u>	<u>SAMPLE SIZE</u>	<u>SIGNIFICANCE LEVEL</u>
	Austin, TX	11	< 0.05
	Suffolk Co, NY	3	> 0.05
	San Diego, CA	15	< 0.001
	Providence, RI	5	> 0.05
	Overall	34	< 0.0002
<u>FIBERGLASS TANK SYSTEMS</u>			
	Austin, TX	6	< 0.05
	Suffolk Co, NY	7	< 0.001
	San Diego, CA	8	< 0.001
	Overall	21	< 0.0002

TABLE 11-11

RESULTS OF WILCOXON TESTS FOR DIFFERENCES
IN DATA ACCORDING TO SAMPLE DEPTH

<u>STEEL TANK SYSTEMS</u>	<u>LOCATION</u>	<u>TEST</u>	<u>SAMPLE SIZE</u>	<u>SIGNIFICANCE LEVEL</u>
	San Diego, CA	2'<6'	24	<0.001
	San Diego, CA	6'<10'	16	0.004
	San Diego, CA	2'<10'	11	0.0012

Unfortunately, the paired-sample Wilcoxon test is not as sensitive as the Page L test for detecting significant differences. This is due to the nature of the null distribution of the paired-sample Wilcoxon test for small samples. Thus, even though the Page L test may have detected significant differences in total hydrocarbon concentrations between the three sample depths, the paired-sample Wilcoxon may not uncover the nature of these differences. Also, the Wilcoxon could only be applied in cases where the sample size was greater than nine samples.

Each of the paired-sample Wilcoxon tests were tested at individual significance levels of 0.0015. This was derived by dividing 0.003 by two, since two independent test cases ($2' < 6'$ and $6' < 10'$) were performed.

11.4.3.3 Conclusions from Non-Parametric Tests

Within the Non-Contaminated Data

The data patterns associated with site location and sample depth were delineated by the use of Kruskal-Wallis, Page L and Wilcoxon non-parametric statistical methods. The Kruskal-Wallis method, used to delineate patterns according to location, revealed that significant differences in total hydrocarbon (less methane) vapor concentrations among the five locations studied for steel tank systems. The differences were significant at all three sample depths (2, 6 and 10 feet). There were no significant differences between the total hydrocarbon (less methane) vapor concentrations at the three locations studied for fiberglass tank systems.

The Page L method, used to delineate patterns according to sample depths, revealed that significant differences exist between the total hydrocarbon (less methane) vapor concentrations among the different sample depths (2, 6 and 10 feet) for both steel and fiberglass tank systems.

The results of these tests indicate that data from steel tank systems at different locations and sample depths represent significantly different

data distributions. Also, data from fiberglass tank systems from all locations, but at different sample depths represent significantly different distributions.

The means, medians, lower and upper quartiles are shown in Table 11-12 for the steel tank systems and Table 11-13 for the fiberglass tank systems for total hydrocarbon (less methane) vapor concentrations in micrograms per liter.

The difference in total hydrocarbon (less methane) vapor concentrations at different sample depths can be seen in these tables. The steel tank systems in Austin, TX, San Diego, CA and Suffolk County, NY show increasing concentrations with depths in the means, medians, and lower and upper quartiles. The differences in concentrations at the different locations can also be seen.

11.5 RESULTS AND CONCLUSIONS OF DATA ANALYSIS

The distribution of total hydrocarbon (less methane) vapor concentrations was skewed to the right with a majority of samples in the lower concentration ranges. The relative frequency distribution showed 53.2 percent of the samples below 1,500 ug/l and 93.1 percent below 100,000 ug/l. The median was 800 ug/l and the mean was 23,300 ug/l. The difference between the mean and the median is because of a few high concentration values.

The distribution of total hydrocarbon (including methane) vapor concentrations showed that 21 percent more samples existed above 100,000 ug/l as compared to total hydrocarbons (less methane). High concentrations of methane were seen at many of the sites. These concentrations are probably due to decomposition of the background hydrocarbons as well as naturally occurring methane.

Although much variability existed in both the non-contaminated and contaminated data, significant differences could be seen between the two distributions. Both distributions were skewed to the right with a

TABLE 11-12 :

DESCRIPTIVE STATISTICS FOR TOTAL HYDROCARBON
LESS METHANE CONCENTRATIONS IN STEEL TANK
SYSTEMS AT DIFFERENT LOCATIONS AND SAMPLE DEPTHS

(Micrograms Per Liter)

	SAMPLE DEPTH		
	2 Foot	6 Foot	10 Foot
Austin, TX			
Mean	41000	24000	120000
Median	15000	16500	12000
Lower Quartile	570	380	160
Upper Quartile	36000	35000	36000
Providence, RI			
Mean	1700	1200	1300
Median	1	0.3	0.1
Lower Quartile	Detection Limit	Detection Limit	Detection Limit
Upper Quartile	0.1	450	350
San Diego, CA			
Mean	30000	44000	72000
Median	27000	41000	71000
Lower Quartile	5100	2400	39000
Upper Quartile	37000	70000	104000
Storrs, CT			
Mean	270	5300	1.0
Median	Detection Limit	0.3	0.06
Lower Quartile	Detection Limit	Detection Limit	Detection Limit
Upper Quartile	1.0	11.0	3.0
Suffolk County, NY			
Mean	5300	16000	27000
Median	1.6	1100	110
Lower Quartile	Detection Limit	Detection Limit	Detection Limit
Upper Quartile	2100	39000	36000

TABLE 11-13 :

DESCRIPTIVE STATISTICS FOR TOTAL HYDROCARBON
LESS METHANE CONCENTRATIONS IN FIBERGLASS TANK
SYSTEMS AT DIFFERENT DEPTHS

(Micrograms Per Liter)

	SAMPLE DEPTH		
	<u>2 FOOT</u>	<u>6 FOOT</u>	<u>10 FOOT</u>
Mean	16142.9	21689.1	49132.7
Median	28	780	5850
Lower Quartile	.1	2	27
Upper Quartile	21000	38500	58000

majority of samples in the lower concentration ranges. However, an order of magnitude difference existed between the mean of each data set, and between the median of each data set. The order of magnitude was best seen in concentrations above 10,000 ug/l. Of the non-contaminated samples, 29.6 percent occurred in the range of 10,000 to 100,000 ug/l while 33.3 percent of the contaminated samples occurred in the range above 100,000 ug/l.

12.0 CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER STUDY

12.1 CONCLUSIONS

The following conclusions are derived from the results of this study:

- Underground storage tank sites evaluated in this study where total hydrocarbon (less methane) concentrations in soil vapor exceeded 100,000 ug/l (27,000 ppmv) were generally considered contaminated, whereas sites that exhibited vapor values less than 100,000 ug/l typically had not had a release and were considered non-contaminated. This apparent threshold value of 100,000 ug/l (27,000 ppmv) of total hydrocarbon (less methane) vapors may be used to help differentiate between non-contaminated and contaminated sites.
- Calculation of total hydrocarbon values "as BTEX" based on the average of the response factors for benzene, toluene, ethylbenzene and ortho-xylene provides a more accurate representation than when calculated "as benzene".
- Because of the regional variability of the data collected in this study, any soil vapor concentration limits that are to be utilized to differentiate between contaminated and non-contaminated sites may best be established on a regional or local basis.
- Soil gas techniques can effectively be used to evaluate the backfill areas of underground gasoline storage tanks to determine if significant leaks exist, especially if appropriate regional or local threshold levels are established.
- Limited analysis of butane vapor concentrations indicates that butane analysis may be useful in detecting recent leaks or spills.

12.2 RECOMMENDATIONS FOR FURTHER STUDY

Analysis of the data collected in this study revealed several areas where additional study would be useful in developing a more complete understanding of the occurrence and characteristics of soil gas at both clean and contaminated underground gasoline storage tank sites.

Recommendations for further study are:

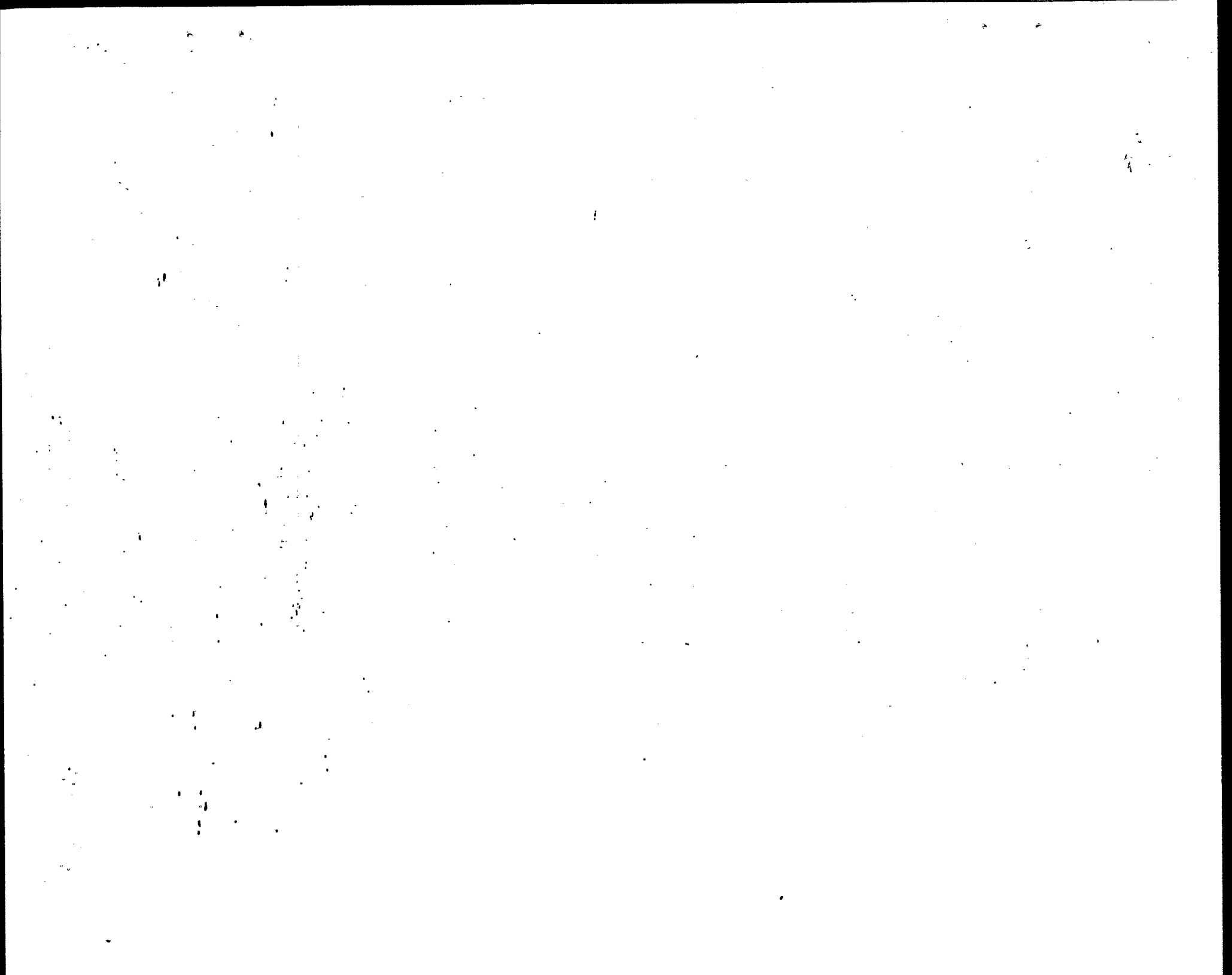
- Develop a standardized method for reporting soil gas concentrations in the backfill areas of underground storage tanks. This can be done by a more thorough analysis of soil gas in each of the three geographical areas used in this study. The objectives would be to measure the concentrations, develop

simplified calculations to be used in reporting the concentration values and determine the appropriate assumptions and approximations.

- Determine the minimum amount of data required to decide if a site is contaminated by a leak. The objectives would be to determine the required number and locations of sampling points, the number of samples above a specified threshold limit that would be acceptable, and whether butane concentrations can be used to distinguish between a leak and a spill.
- Determine the effects of geology, backfill material, tank age and tank material on soil gas concentrations. A sufficient amount of data was not collected in this study to determine the effects of these parameters.
- Examine the dispersion and decomposition of contamination by additional sampling at Austin #6, taking advantage of the recent documented spill.
- Determine the effects of a leaking pipeline on an underground storage tank system as compared to the effects of only a leaking tank.

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