ASSESSMENT OF SUBSURFACE HYDROCARBON CONTAMINATION RESULTING FROM MULTIPLE RELEASES AT SIX FORMER BULK FUEL STORAGE AND DISTRIBUTION TERMINALS, AUSTIN, TEXAS: A CASE STUDY

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ABSTRACT

Numerous innovative assessment methods, developed by the petroleum industry, can be used to more fully characterize a site provided the owner/operator, consultant, and regulatory agency recognize the merits of these methods. Although it is relatively easy to employ methods that have been established and accepted by the regulatory agencies, these methods often do not provide a complete nor accurate assessment of the problem.

Exploration geochemical methods developed and utilized by the petroleum industry can be invaluable in environmental site characterizations. Environmental companies or consultants do not use many of these methods because they are not required by the EPA and are not recommended by regulatory agencies. In addition, these methods are unfamiliar to environmental scientists and most regulatory agencies. The "rule of thumb" methods of site characterization (randomly placed monitoring wells, EPA method analyses for target compounds, etc.) are rarely adequate to fully delineate and explain the nature and distribution of the subsurface contamination.

The Austin, Texas case study demonstrates how a phased assessment approach can be used to accurately define the petroleum contamination in a study area. Various unconventional (standard petroleum industry, but non-EPA) methods and techniques, including forensic geochemistry, were used to delineate the areal and vertical extent of subsurface contamination. The relationships between vapor, sorbed (residual), dissolved and free (NAPL) phase contamination and the merits of analyzing (and resolving the distribution of) all four phases are mandatory for an accurate site characterization.

More than 400 boreholes, monitoring wells, and temporary monitoring wells were installed on the six former storage and distribution terminals and pipeline properties, and adjacent private and public properties in the East Austin area prior to this study. Despite this large number of sampling points, the testing performed by the oil companies' consultants was incomplete and inadequate for defining the true degree and extent of off-site contamination. The assessments performed by these consultants included standard regulatory methodologies (borehole drilling, monitoring well installation, EPA method BTEX and TPH laboratory analyses, etc.) in an attempt to characterize individual properties. The migration of contaminants off the terminal properties, however, was unresolved and unreported.

The scope of work for this study included the documentation of historical hydrocarbon releases, the collection of soil vapor, soil core and groundwater samples, and analyses of these samples obtained in close proximity and down-gradient to the terminal/pipeline properties. Geochemical analytical methods were used to determine the different types of products released and the distribution of these petroleum products (contaminants) in vadose zone soils and groundwater. The data collected during this study were integrated with all available data collected by industry consultants contracted by the oil companies. All data were quality controlled and confirmed using different analytical methods.

Subsurface petroleum contamination beneath the oil companies' undeveloped properties, private properties, and City of Austin park is present as vapor phase and sorbed (residual) phase in the vadose or unsaturated zone soils, and as liquid (NAPL), dissolved and sorbed phase in the saturated zone or groundwater aquifer. The sources of the vapor, soil and groundwater contamination were multiple releases on the oil companies' terminal and pipeline properties. Contamination resulting from these releases have coalesced in soils and groundwater and subsequently migrated off-site onto public and private properties. Based upon the results of the work performed, it is obvious that the oil companies were unable to assess the off-site migration of petroleum contaminants from the terminal and pipeline properties using conventional "rule of thumb" random drilling techniques.

Soil vapor, soil and groundwater isoconcentration maps, and geologic cross sections were constructed using the data collected during this study. These products and forensic geochemistry techniques were used to delineate and demonstrate the areal and vertical extent of petroleum hydrocarbon impact to private and public properties located down-gradient of the six former fuel storage and distribution terminals and product pipeline properties in the East Austin area of Austin, Texas.

INTRODUCTION

Environmental scientists (companies or consultants) perform most environmental assessment and remediation activities in accordance with regulatory agency guidelines. Many regulatory agencies, however, are untrained or uninterested in trying a new approach that does not have current widespread acceptance by the public (Rowley et al., 1998). As a result, most assessments performed are not very effective in delineating the true areal and vertical extent of the subsurface contamination present in soils and groundwater. Unfortunately, companies and consultants continue to install "randomly placed" monitoring wells at contaminated sites without gaining a true understanding of the degree and extent of the problem. An inadequate assessment of a site, generally results in either no remedial action, since a significant part of the contamination has been overlooked, or the installation of an expensive, inefficient remediation system that is not suited to the site conditions and contaminants present.

Numerous innovative assessment methods, developed by the petroleum industry, can be used to more fully characterize a site provided the owner/operator, consultant, and regulatory agency recognize the merits of these methods. Although it is relatively easy to employ methods that have been established and accepted by the regulatory agencies, these methods often do not provide a complete nor accurate assessment of the problem.

Exploration geochemical methods developed and utilized by the petroleum industry can be invaluable in environmental site characterizations. Environmental companies or consultants do not use many of these methods because they are not required by the EPA and are not recommended by regulatory agencies. In addition, these methods are unfamiliar to environmental scientists and most regulatory agencies. The "rule of thumb" methods of site characterization (randomly placed monitoring wells, EPA method analyses for target compounds, etc.) are rarely adequate to fully delineate and explain the nature and distribution of the subsurface contamination.

Additional information that must be integrated with analytical data to better characterize a site includes historical data, as well as subsurface geology and hydrogeology. To understand the nature and extent of the contamination, it is necessary to understand what products were stored/dispensed on and in the vicinity of a site, where potential source areas were located over time, and along what geological/hydrogeological pathways released products migrated. The subsurface strata through which contaminants migrate are not isotropic and homogeneous, and definitely not "layer cake" in nature. It is mandatory that the subsurface stratigraphy be properly assessed and mapped in order to understand the distribution and migration of hydrocarbon contaminants. The effectiveness of a remedial action plan and remediation system is directly dependent on the thoroughness and accuracy of the site characterization, especially with regard to subsurface stratigraphy.

The Austin, Texas case study demonstrates: 1) various unconventional (standard petroleum industry, but non-EPA) methods and techniques used to delineate the areal and vertical extent of subsurface contamination, 2) the importance of understanding and accurately mapping subsurface geology and hydrogeology in the study area, 3) the merits of compiling and integrating the historical information for the various facilities (where releases occurred), 4) the importance of forensic geochemistry, and 5) the relationships between vapor, sorbed (residual), dissolved and free (NAPL) phase contamination and the merits of analyzing (and resolving the distribution of) all four phases.

BACKGROUND

Six former bulk fuel storage and distribution terminals and various petroleum product pipelines associated with those terminals were operated by six major oil companies for over 40 years in the East Austin area of Austin, Texas. Residential and commercial properties, and a City of Austin park (Figure 1) border the former terminals and undeveloped pipeline properties. Although various environmental site assessments and limited remediation activities were conducted on the terminal properties by consultants contracted by the owners/operators of the terminals, these activities were not adequate to properly detect or prevent offsite migration of contaminants.

Assessment reports, corrective action plans, and quarterly groundwater monitoring reports were submitted to the Texas Water Commission (TWC) beginning in 1987. In 1992, the TWC required that owners/operators of the terminals and pipelines report all historic petroleum product releases, assess their respective properties and determine whether off-site migration of petroleum products had occurred. The reports prepared by industry consultants and submitted to the TWC and the Texas Natural Resource Conservation Commission (TNRCC), formerly the TWC, included a limited number of minor releases (dated post-1987) but failed to report the existence of any off-site migration of petroleum products. The petroleum product contamination reported by the oil companies' consultants in the study area was attributed to a few minor releases. More than 400 boreholes, monitoring wells, and temporary monitoring wells were installed on the six storage and distribution terminals and pipeline properties, and adjacent private and public properties between 1987 and 1992. Despite this large number of sampling points, the testing performed was incomplete and inadequate for defining the true degree and extent of off-site The assessments performed by the industry consultants used standard regulatory contamination. methodologies (borehole drilling, monitoring well installation, EPA method BTEX and TPH laboratory analyses, etc.) in an attempt to characterize individual properties. The migration of contaminants off the terminal properties, however, was unresolved and unreported.

HISTORICAL INFORMATION – TERMINAL/PIPELINE OPERATIONS

For the purposes of this case study, the former terminal and pipeline properties have been labeled counterclockwise from A through G (Figure 1). Limited historical information for the six terminal properties and pipelines were discussed in reports submitted to the TNRCC, prepared by the oil companies' consultants. A more detailed summary of this historical information is included in a summary report submitted to the TNRCC, prepared by Exploration Technologies, Inc. (January 1994).

Construction dates for the six terminals ranged from 1948 to 1962. Refined petroleum fuel products to the six terminals were delivered through product pipelines that ran northwest along Airport Boulevard to one of three pipeline manifolds located on terminal properties C, E and F. The Company C and Company E manifolds provided refined petroleum products to the three oldest terminals that contained approximately 60% of the total storage capacity of the six terminals (346,572 barrels). Refined petroleum fuels were distributed from the pipeline manifolds to above ground storage tanks via separate product distribution lines. The total storage capacity of the above ground tanks was approximately 576,000 barrels.

The Company E and Company C pipeline manifolds supplied jet fuel to a former U.S. Air Force Base until 1971 via a pipeline on the Company C undeveloped property. This pipeline ran southeast across the Company C undeveloped property (Figure 1) and then southwest and southeast along Shady Lane and Airport Boulevard to the former U.S. Air Force Base. Company A also began supplying jet fuel to the Air Force Base in 1971 when they purchased the pipeline/manifold facilities. Other refined petroleum

fuels stored and distributed by the six terminals included regular and premium leaded and unleaded gasoline, kerosene and diesel.

The majority of refined fuel products delivered to the six terminals via pipelines over a 40 year period of operation exited the six terminals via the truck loading racks. Products were distributed from the above ground storage tanks by product distribution lines via pump manifolds to the truck loading racks, all of which appear to be major sources of unreported releases. The product distribution lines were located underground as late as 1986 at Terminal C, and appear to have been sources of undetected (and unreported) releases either at flange connections or from holes in the distribution lines (caused by corrosion). Loading racks. In addition, after the refined fuel products were separated from water in the USTs, the waters, containing dissolved phase hydrocarbons, were pumped into the berm areas around the storage tanks and allowed to seep into the subsurface soils.

It should be noted that the oil companies' consultants focused on those loses that occurred after 1987, when the State of Texas began enforcing environmental regulations regarding refined petroleum products. The largest volumes of liquid product (NAPL) found off-site appear to be related to releases that occurred prior to 1987. A major jet fuel release that occurred in 1971 accounted for the majority of NAPL found off-site.

Subsurface assessments indicated vapor, soil and/or groundwater contamination in the vicinity of the loading racks on all six terminals. The loss of gasoline fuels containing both lead and methyl tertiary butyl ether (MTBE) indicates both relatively early and late subsurface releases, since lead usage peaked in the 1970's and MTBE was not in general usage until 1985. The presence of MTBE over the majority of the study area, and the commingling with older jet fuel product(s) in many areas indicates that releases from the terminal properties continued after 1985, when MTBE became a common gasoline additive.

Results of the initial study performed for the City of Austin, including information obtained from the oil company reports, was submitted to the TNRCC in a comprehensive summary report (Summary of Subsurface Petroleum Product Contamination, East Austin Bulk Storage Terminal Area, Austin, Texas, January 1994).

STUDY AREA

General

The study area is located in a portion of east Austin consisting of residential, industrial, commercial, and City of Austin (Govalle Park) properties. The area is bounded by a residential area on the north, Airport Boulevard on the west, Bolm Road on the south, and an unnamed tributary to Boggy Creek and residential properties on the east (Figure 1). Austin is located within the Blackland Prairie physiographic province of central Texas. The topography slopes gently to the southeast and has an average elevation of 455 feet above sea level. Boggy Creek, a tributary to the Colorado River located approximately one mile to the south, is the most prominent drainage feature in the area. The climate of the Austin area is humid subtropical with average precipitation of 32 inches per year (Garner and Young, 1976).

Geology

Austin (central Travis County), Texas is located on formations of Upper Cretaceous and Lower Tertiary age which gently dip to the southeast into the Gulf of Mexico Basin. The study area is situated on Pleistocene terrace deposits of the Colorado River. The Pleistocene terrace deposits are underlain by (in descending order) the Navarro and Taylor Groups, Austin Chalk, Eagle Ford Group, Buda Limestone, Del Rio Clay, Georgetown Formation and numerous Cretaceous Formations of the Fredericksburg Group. The Edwards Formation, included in the Fredericksburg Group, is a major groundwater aquifer in the west Austin area. The Pleistocene terrace deposits increase in grain size, porosity, and permeability with depth and consist of (in descending order) clays, silty clays, silts, and sands which are graveliferous in some areas. The Pleistocene terraces range in thickness from less than 10 feet to over 60 feet in the Austin area. The study area is situated on the Pleistocene First Street Terrace (Urbanec, 1963).

The majority of the site-specific lithologic data was compiled from borehole and monitoring well logs. The Pleistocene First Street Terrace in the study area ranges in thickness from 24-32 feet. Subsurface lithologies in descending order include clays, silty clays, clayey silts, silts and sands with occasional gravel, and show a general increase in grain size, porosity and permeability with depth. The First Street Terrace is underlain by the Cretaceous Taylor Formation.

Interpretation of lithologies described in the monitoring well and boring logs allowed for a regional areal depiction of the First Street Terrace aquifer beneath the study area. An understanding of the threedimensional stratigraphic framework of the First Street Terrace is essential to understanding the migration pathways of subsurface contamination in the unsaturated and saturated zones. The vertical relationships of the lithologies encountered in the First Street Terrace are illustrated in cross section A-A' (Figure 2). The location of the cross section is shown on Figure 3.

A wide variation in the depth to sand and other overlying lithologic units exists over the study area. The sand is at relatively shallow (4-10 feet) or intermediate depths (10-14 feet) beneath most of the terminal properties. A contour map showing the depth to the top of the first massive sand is included as Figure 3. East and south of Shady Lane, the sand is generally encountered at depths in excess of 18 feet. In areas where the sand is present at depth, the sand is generally overlain, in ascending order, by silts, clayey silts and silty clays (Figure 2). A trend of relatively thick silt and clayey silt immediately overlies the sand in the central part of the private properties and Govalle Park east and south of Shady Lane.

Hydrology

The Pleistocene terrace deposits and Edwards Formation are the two principal groundwater aquifers in the study area. The City of Austin public water supply is derived primarily from the lakes of the Colorado River and the fresh water zone of the Edwards Formation. In the East Austin area, the Edwards Formation is not considered a source of potable water or suitable for industrial use due to its high salinity. The water contained in the Pleistocene terrace deposits, from depths of 10 to 15 feet below the ground surface, is used for irrigation purposes (Texas Department of Water Resources, June 1983). Unfortunately, the groundwater in the study area is no longer suitable for irrigation due to the petroleum hydrocarbon contamination detected during this study. The Pleistocene terrace aquifer is unconfined in the study area. The potentiometric surface map (Figure 4), constructed using data obtained during June-September 1994, indicates the direction of groundwater flow beneath the off-site properties is generally to the southeast, toward the Colorado River.

INVESTIGATIVE METHODS

The scope of work for this study included the documentation of historical hydrocarbon releases, the collection of soil vapor, soil core and groundwater samples, and analyses of these samples obtained in close proximity and down-gradient to the terminal/pipeline properties. All data were integrated with public data collected by the oil companies' consultants and reported to the TNRCC (*Summary of Subsurface Petroleum Product Contamination, East Austin Bulk Storage Terminal Area, Austin, Texas, January 1994*). The soil vapor surveys (542 sample sites) performed in Govalle Park, on the undeveloped property, and private properties were used to locate 91 borings and 13 monitoring wells. The drilling and installation of these borings and monitoring wells were necessary to confirm the areal extent of contamination delineated using the soil vapor data, and to determine the vertical extent and degree of hydrocarbon contamination in soils and groundwater. Various geochemical analytical methods were used to determine the different types of products released and the distribution of these petroleum products (contaminants) in vadose zone soils and groundwater.

An initial investigation of the Bulk Fuel Storage and Distribution Terminal area was commenced in 1993 at the request of the City of Austin (COA). The goal was to determine if Govalle Park (owned by the COA) was impacted by petroleum hydrocarbon releases on the terminal and/or pipeline properties located up-gradient. Data provided by the oil companies' consultants, and included in the TNRCC files, were examined and interpreted. These data and the historical information available indicated it was highly probable that releases on the terminal/pipeline properties over several decades had caused widespread contamination in the area. The areal and vertical extent of the contamination was determined using a well planned, organized assessment consisting of several phases. Various geochemical methods were used to confirm the presence, and delineate the morphology of off-site hydrocarbon contamination resulting from releases on the various terminal and pipeline properties.

Soil Vapor Survey

A soil vapor survey was performed over the City of Austin park (Govalle Park) and adjacent private properties, down-gradient of the terminal/pipeline properties. When utilized properly, a soil vapor survey is an excellent screening technique to delineate the areal (horizontal) extent of subsurface contamination (Marrin, 1988; Jones and Agostino, 1998). Soil vapor samples were collected at a total of 542 sites in the study area to determine the possible presence and areal extent of petroleum product constituents contained in near surface soils and/or groundwater. The survey was conducted south and east of the six terminal/pipeline properties on a staggered sampling grid containing approximately 50 foot centers. The survey grid was adjusted slightly to avoid natural hazards such as major roadways, utility lines, buildings and concrete surfaces. The sites at which the soil vapor samples were collected are shown on Figure 5.

At each sampling location, a manually operated pounder bar was used to advance a 1/2 inch diameter hole into the soil to a depth of 12 feet. Immediately following the removal of the pounder bar, a specially designed soil vapor sampling probe was inserted into each pre-driven sampling hole for collection of a soil vapor sample. In some instances, samples were collected at depths shallower than 12 feet due to soil conditions or the presence of shallow groundwater. Based upon results of the initial soil vapor survey and existing borehole and monitoring well data, an additional 158 soil vapor samples were collected in close proximity to the groundwater aquifer (depths of 16-18 feet) using a truck mounted direct-push collection system. Data obtained from the direct-push vapor survey were integrated with the hand-probe soil vapor data (12 foot samples collected at 384 sites).

An evacuated 125 cc septum top glass bottle was attached to the probe and utilized to collect a soil vapor sample at each location. An additional 60 cc's of soil vapor were extracted from the soil and added to the

bottle in order to create a positive pressure within the bottle, and provide an adequate volume of sample for analysis. The septum was sealed with a silicone rubber sealant to avoid leakage of the vapors and to help preserve the integrity of the sample.

The pounder bars, manual sample collection probes, and the direct-push sampler were decontaminated between each sample site using a detergent and distilled water rinse. A "blank" sample of ambient air was collected through the probes at each sample location for possible analysis to ensure that no hydrocarbon constituent carry-over occurred.

Although soil vapor measurements are commonly utilized for screening purposes, it is important to properly quantify individual hydrocarbon and biogenic gas constituents. Most portable field screening instruments measure total volatile organic constituents (VOCs) and are not capable of accurately quantifying individual soil vapor compounds. In addition, studies by Robbins et al. (1990) have shown that data obtained from portable total organic vapor detection instruments can be misleading since these instruments are influenced by many factors. Although more time-consuming and more costly, detailed soil vapor analyses, where individual constituents are identified, are invaluable in properly characterizing the areal extent of subsurface contamination. All soil vapor samples, therefore, were analyzed in a laboratory under strict QA/QC procedures.

Two flame ionization detector (FID) gas chromatographs were used to independently determine C1-C4 (methane, ethane, propane, and butanes), and C5+ (pentane-xylenes+) hydrocarbon concentrations, in order to characterize and quantify the hydrocarbon constituents present. Light hydrocarbon analyses (C1-C4) measure the lightest, most volatile constituents present in gasolines, diesels, jet fuels and other petroleum products. Methane, ethane, propane and butanes are present in varying concentrations in most refined petroleum products. These light hydrocarbon compounds tend to volatilize and dissipate rapidly with time and/or distance from the point(s) at which petroleum constituents are introduced into the subsurface environment. These light gases are often sustained by solubility enhancements associated with the presence of liquid product. Light hydrocarbon analyses allow for the identification and differentiation of natural gas, biogenic methane, gasoline, diesel and other refined petroleum products.

C5+ (pentane-xylenes+) hydrocarbon analyses yield a quantitative measure of the concentration, by volume, of petroleum product vapors present in near surface soils. C5+ hydrocarbons dissipate more slowly than lighter fraction (C1-C4) compounds. Due to the large number of individual compounds present in gasolines, diesels, jet fuels, etc., the results of C5+ analyses are often grouped and reported according to the relative boiling points of selected hydrocarbon compounds. For this study, analytical laboratory results were quantified and summed for the following groups of hydrocarbon compounds: pentane to benzene, benzene to toluene, toluene to xylene, and xylenes+. Laboratory results of C1-C4 and C5+ hydrocarbons were measured in parts per million by volume (ppmv).

Carbon dioxide is generated by the biodegradation of petroleum products (gasoline, diesel, kerosene, etc.), oils, greases, solvents and other organic materials contained in the subsurface environment. Aerobic bacteria utilize the oxygen present in subsurface soils and groundwater to consume organic material, such as hydrocarbons, to produce carbon dioxide. These biochemical reactions are quite common in soils containing petroleum products since such products are excellent food sources for bacteria. Carbon dioxide (CO_2) concentrations were determined using a gas chromatograph equipped with a thermal conductivity detector (TCD). These data when used in tandem with organic vapor analyses (C1-C4 and C5+) are very useful in defining the areal extent of hydrocarbon contaminants in the subsurface environment. Carbon dioxide concentrations were measured in percent by volume.

Soil vapor constituent concentrations were posted and contoured to display the areal extent of petroleum hydrocarbon and biogenic gas vapors in subsurface soils. These contoured "plume" maps were used to

illustrate the areal extent of the subsurface contamination, and to determine the locations of borings and monitoring wells.

Direct-Push Borings

Ninety-one (91) borings were advanced to groundwater and soil core samples (2-foot lengths) were collected continuously from the ground surface to total depth using a direct-push sampling system. All two-foot composite soil core samples were analyzed for BTEX and TPH concentrations using proprietary screening instruments (Hager and Jones, 1990; Smith, Agostino and Jones, 1992). The borings were located based upon the results of the soil vapor surveys.

The drilling of borings was necessary to confirm the morphology of the soil vapor constituent plumes, to define the vertical extent of hydrocarbon constituents, and to determine the depth to groundwater at various locations in the study area. Each two-foot soil core was logged on-site by a geologist. The collection, logging and analysis of continuous soil core samples are mandatory to determine the subsurface stratigraphy, and to fully characterize the subsurface contamination in vadose zone soils. The vertical distribution of hydrocarbon contaminants must be understood to properly delineate source areas, determine migration pathways and formulate a remedial action plan.

Groundwater samples were also collected from borings through a slotted wellpoint attached to the drillstring, or PVC slotted casing temporarily inserted into the boreholes. This methodology has been extensively utilized by many environmental consultants, and is believed to yield a more representative groundwater sample (and therefore, true contaminant levels) than those obtained from monitoring wells, at a given point in the aquifer (Chiang et al., 1995).

Monitoring Well Completions

Thirteen monitoring wells were drilled and completed using a rotary drill rig with 12 inch O.D. hollow stem augers. Locations of monitoring wells were determined using borehole and soil vapor data. The wells were completed at total depths of between 23 and 29 feet. Each well was developed to ensure a fresh fluid sample was obtained from the aquifer. After the wells were allowed to recharge, disposable bailers were used to collect fluid (groundwater/NAPL) samples from each well. The locations of borings and monitoring wells, drilled and installed during this study, are shown on Figure 1.

Twelve of the monitoring wells installed contained NAPL. Several of these wells were installed within 50 to 100 feet of wells installed by the TWC and oil company consultants, that contained only moderate levels of dissolved phase contaminants. No NAPL was found in these randomly placed wells since they were installed outside of the narrow channels (preferential migration pathways) along which the liquid contaminants migrated. Without the aid of the soil vapor surveys, these narrow preferential pathways were overlooked. The previous assessments, therefore, were incomplete and inadequate in fully characterizing the geology, stratigraphy, and contamination in the study area. The well installed during this study that did not encounter NAPL was intentionally located a long distance down-gradient to serve as a permanent "background" sampling station.

Laboratory Analyses

Soil Vapors

Soil vapor samples were analyzed for C1-C4 (methane, ethane, propane and butanes) and C5+ (pentanexylenes+) hydrocarbons and carbon dioxide (CO_2). Laboratory results of hydrocarbon analyses were quantified in parts per million by volume (ppmv), and carbon dioxide concentrations in percent by volume.

EPA Method Analyses - Soils and Groundwater

Benzene, toluene, ethylbenzene and xylenes (BTEX) analyses of soils and groundwater were performed in accordance with EPA Method 8020/5030 and EPA Method 8020/602, respectively. Total petroleum hydrocarbons (TPH) analyses of soils and groundwater were performed in accordance with EPA Method 418.1.

GC/MS analyses were also run on selected samples to confirm the presence and concentrations of MTBE (EPA Method 8240 modified). Total lead analyses were performed on selected groundwater samples obtained from monitoring wells in accordance with EPA Method 7420.

Vapor Headspace Analyses - Groundwater Samples

In addition to analyzing each groundwater sample in accordance with EPA methodology, the vapor headspace of each water sample collected from borings and monitoring wells was analyzed for dissolved C1-C4 (methane, ethane, propane and butanes) and C5+ (gasoline range) hydrocarbons by standard headspace methods. The headspace was introduced into each sample bottle by displacing 10 ml of water with nitrogen prior to analysis. Vapor headspace chromatograms were also analyzed and utilized to confirm the presence of MTBE.

Miscellaneous Analyses - Product "Fingerprinting"

Several different analytical methods can be used to "fingerprint" soil, water, and liquid product (NAPL) samples to determine the specific petroleum product type(s) responsible for the contamination. Some methods are more rigorous and definitive than others. Standard EPA method BTEX and TPH analyses yield concentrations of specific compounds contained in petroleum products but, unfortunately do not allow for the identification or differentiation of specific product types. Various "fingerprinting" techniques were utilized throughout the assessment phase of this study.

Synchronous Fluorescence

Synchronous fluorescence analyses were performed on soil core samples obtained from the 91 borings (and 16 additional bore holes/monitoring wells drilled by oil company consultants), as well as on selected fluid samples. These analyses provide an estimate of the molecular weight range of extractable aromatic hydrocarbons contained in petroleum products. A spectrometer with an ultraviolet (UV) light source is

used to analyze samples extracted into a hexane solvent. When UV light is projected through the sample, the absorption and excitation of various aromatic hydrocarbon compounds occurs. The excitation of aromatic compounds (benzene, polynuclear aromatic hydrocarbons or PAHs, etc.) causes the emission of the light at different wavelengths depending upon the range of compounds present. As shown by the product standards included in Figure 6, this technique is an excellent tool for analyzing and "fingerprinting" petroleum compounds such as gasoline, diesel, kerosene, jet fuel, crude oil, etc., and is widely used by the petroleum industry (Pharr et al., 1992; Gray et al., 1993).

Fluorescence analyses were used to screen soil samples and identify types of petroleum products present in subsurface sediments within impacted (plume) areas. Fluorograms generated (for each 2-foot soil core interval) are very effective in illustrating product types and the vertical distribution of the contamination at a given location (Figures 6 and 7).

Modified EPA Method 8015 (8015M)

Soil, groundwater and liquid product (NAPL) samples were analyzed using EPA Method 8015M (for total fuels hydrocarbons). Samples were extracted into carbon disulfide (CS_2) and analyzed by FID gas chromatography for C5+ hydrocarbons (ranging from C5-C20) to characterize ("fingerprint") and determine concentrations of hydrocarbon compounds present. This well established analytical method was used to compare and confirm the results of the synchronous fluorescence analyses and to help select samples for HRCGC analyses.

High Resolution Capillary Gas Chromatography

High resolution capillary gas chromatography (GC) is an excellent technique for "fingerprinting" various types of refined and crude petroleum products (Bruce and Schmidt, 1994; Zemo et al., 1995). This technique is more rigorous, more expensive, and more definitive than synchronous fluorescence or method 8015M. Based upon these other methods, selected soil, groundwater and liquid product (NAPL) samples were analyzed using high resolution capillary gas chromatography, a modification of ASTM method D-3328. This method utilizes a methylene chloride solvent to extract various molecular weight hydrocarbons from the sample. The extract is analyzed on a capillary column using a flame ionization detector (FID) to identify and characterize hydrocarbon compounds, and define product types (gasoline, diesel, jet fuel, kerosene, solvents, etc.).

RESULTS

Soil Vapors

Laboratory results of soil vapor samples collected down-gradient of the six terminal properties indicate elevated concentrations of carbon dioxide (CO₂) and methane over a significant portion of the survey area. CO_2 concentrations in excess of 14 percent and methane in excess of 10 percent are present south and east of the terminal properties in residential areas and Govalle Park. The biodegradation of hydrocarbons by both aerobic and anaerobic bacteria in the subsurface environment can occur within very close proximity, and thus yield elevated concentrations of both carbon dioxide and methane in areas containing hydrocarbon contaminants (Hayman et al., 1988; Jones and Agostino, 1998). The excellent correlation of elevated C5+ (pentane-xylenes+) hydrocarbon concentrations with elevated CO_2 and

methane concentrations indicates the biogenic gases are the result of degradation of petroleum hydrocarbons in specific regions of the study area. Regional CO₂, methane, and C5+ concentrations plume maps are included as Figures 8, 9 and 10, respectively. Three contaminant lobes that coalesce in the vicinity of Govalle Park and surrounding private properties make up the various constituent plumes. These plume maps confirm that hydrocarbon contaminants originated on the terminals and product pipeline properties, traversed the Company C undeveloped property and migrated beneath COA and private properties. Migration pathways within the contaminant plumes are controlled by silt and sand channels contained in the Pleistocene sediments. These well-defined pathways are between 50 and 150 feet wide, linear in shape, and separated by areas of background concentrations of hydrocarbon and biogenic gases.

The distribution of ethane, propane and normal-butane concentrations exhibit similar contaminant plumes (not included in this paper) containing slightly more limited areal extents. Although the constituent plumes are located in the same general areas as those addressed above, these compounds are highly volatile and do not remain in the subsurface environment over as long a period of time as the C5+ compounds. Despite their lower magnitudes, these more volatile hydrocarbon compounds clearly exhibit contaminant distributions similar to the C5+ plume map, further confirming the petrogenic nature and source of the off-site contamination. The high CO_2 , methane and C5+ vapor concentrations, coupled with moderate concentrations of light hydrocarbon compounds (ethane, propane and butanes) adjacent to the terminal properties, pipelines, residential areas and Govalle Park, confirm there have been releases of petroleum hydrocarbons in the area over a long period of time.

A natural gas pipeline leak was detected along Shady Lane, west of the Terminal A property. The soil vapor results in this area indicated a typical natural gas signature (where methane > ethane > propane > iso-butane, etc). Methane concentrations in excess of 60 percent and ethane in excess of 3 percent (and other light gases) confirmed this linear anomaly as natural gas. Carbon dioxide anomalies, having a limited areal extent, are present in other portions of the study area. These anomalies are interpreted as resulting from the biodegradation of organic material(s) other than petroleum hydrocarbons, since no significant concentrations of C1-C4 or C5+ hydrocarbons are present in these areas.

Soil vapor surveys, conducted using relatively dense sampling grids, were necessary to delineate the areal extent of subsurface contamination, and especially the narrow migration pathways controlled by the subsurface geology (channels), along which contaminants moved beneath private properties and Govalle Park. These narrow migration pathways were not recognized nor defined during the "random" drilling of boreholes and monitoring wells on private properties and Govalle Park, prior to this assessment. Plume maps constructed using the soil vapor data were used to optimally locate borings and monitoring wells in the study area with virtually 100 percent accuracy.

Soils

Soil core samples, collected during direct-push boring operations, were analyzed using various screening and accepted oil industry analytical techniques to determine the degree of impact and specific petroleum products responsible for the impact. Each composite two-foot soil sample was initially analyzed (screened) using a derivative ultra-violet spectrometer for BTEX compounds and a fixed wavelength infrared spectrometer for total petroleum hydrocarbons (Hager and Jones, 1990; Smith, Agostino and Jones, 1992). In addition, synchronous fluorescence and EPA method 8015M analyses were performed on all soil core samples. These analyses are more definitive in determining the source(s) and products responsible for the impact, and in most cases less expensive than EPA method BTEX and TPH analyses.

BTEX and TPH screening analyses were used to determine the soils having the highest contaminant levels. These samples were then analyzed for BTEX and TPH using EPA methodology in order to comply with standard regulatory practices. The TPH screening analyses were also used to construct TPH concentration "slice" maps (Figure 11) for various depth intervals using the continuous soil screening data. These slice maps show the areal and vertical distribution of heavier molecular weight hydrocarbon contaminants, and the cones of dispersion in vadose zone soils associated with various petroleum product releases on the terminals and pipeline properties

EPA method BTEX and TPH analyses were performed on selected samples collected from both borings and monitoring wells. These data were integrated with data collected by consultants for the terminal and pipeline owners/operators. Figures 12 and 13 are isoconcentration maps of total BTEX and TPH (total petroleum hydrocarbons) concentrations in vadose zone soils beneath private properties, Govalle Park, and the terminals and product pipeline (undeveloped) properties. These maps include larger areas (includes terminal properties) than the soil vapor maps and provide the links between impacted soils on COA (Govalle Park) and private properties, and the terminal and pipeline properties located up-gradient. It is apparent from these maps that contaminants in subsurface soils are the result of multiple releases of hydrocarbons on the terminal and pipeline properties.

Lithologic information from borings confirms that sand and/or silt sediments control the migration of the petroleum hydrocarbons. The locations of the sand and silt channels, in general, are defined by the soil vapor, BTEX and TPH plume maps. The petroleum contaminants, located using various geochemical methods, are analogous to dyes that stain the sediments, thus outlining the geological pathways. The narrow migration pathways (channels) are best defined on the soil vapor maps (Figures 8, 9 and 10) due to a larger number (higher density) of sample locations. These narrow pathways were not defined by the random drilling performed by industry consultants prior to this study.

Groundwater

Dissolved phase contaminant plume maps, including benzene, total BTEX, TPH, and MTBE concentrations, containing data collected during the third quarter 1994 were constructed. The total BTEX, TPH and MTBE plume maps are included as Figures 14, 15 and 16, respectively. The dissolved phase groundwater data used to construct these maps were collected from direct-push borings and monitoring wells drilled for the COA, and monitoring wells on the terminal properties (data collected by oil company consultants) during a scheduled quarterly monitoring event. This data set (196 groundwater analyses) is the most comprehensive assembled in the study area.

The benzene and total BTEX isoconcentrations maps are very similar in geometry and areal extent. The major total BTEX plume (Figure 14) extends from Terminal B south across terminals C, D, and E, and undeveloped (pipeline) properties, and south of Shady Lane across private properties and Govalle Park. A smaller plume of elevated BTEX concentrations is located on and south of the Terminal A property. The Terminal F property also shows significant BTEX contamination that extends eastward across private properties into Govalle Park and south of the intersection of Airport Boulevard and Bolm Road.

The TPH plume (Figure 15) has a similar geometry to the benzene and BTEX plumes. Large portions of the terminal/pipeline properties, private properties, and Govalle Park exceed 1 ppm, the TNRCC action level for this area during the time the initial assessments were conducted. Both the total BTEX and TPH plumes clearly indicate off-site migration of petroleum hydrocarbon contaminants from the terminal and pipeline properties.

Methyl tertiary butyl ether (MTBE), the most common oxygenate additive in gasoline, is more soluble (48,000 mg/L) in groundwater than other petroleum hydrocarbon compounds. It does not sorb to aquifer material and is more mobile than other BTEX compounds. Evidence indicates that MTBE moves as rapidly in groundwater as a conservative tracer, and undergoes only dispersive attenuation (Barker et al., 1990; Squillace et al., 1996). Due to its extremely high solubility and mobility, the MTBE plume (Figure 16) exhibits the greatest areal extent of the dissolved phase contaminants. Although there is no established TNRCC action level or target cleanup goal for MTBE at the present time, the EPA has established a Health Advisory Level of 40 ppb as the limit considered safe for drinking water. Other regulatory authorities, such as the State of Maine (50 ppb action level), consider MTBE a health hazard (Klan and Carpenter, 1994). The state of California has recently outlawed (1999) the future use of MTBE in gasoline.

The MTBE plume is the most extensive in areal extent and indicates that releases MTBE occurred on all the terminals and some pipeline properties over time. The MTBE plume confirms that releases on the terminal and pipeline properties have impacted Govalle Park and private properties located down-gradient (south-southeast), at least as far as the baseball field located south of Boggy Creek (Figure 16).

C5+ vapor headspace concentrations (Figure 17) were measured, plotted and mapped for all groundwater samples collected by Exploration Technologies, Inc. between June and September 1995. The headspace analyses have a higher sensitivity for volatile hydrocarbons present in groundwater than EPA BTEX and TPH, and provide an independent and alternate data set for quantifying hydrocarbon components. The C5+ vapor headspace concentrations map shows a contaminant plume similar in morphology to the BTEX and TPH plumes, and indicates that groundwater is impacted over a larger areal extent than indicated by the BTEX and TPH maps (Figures 14 and 15). Note that this plume was not mapped on the terminal properties, since the oil company wells located on the terminal properties were not available for sampling.

A positive link between the terminal/pipeline properties (contamination sources) and Govalle Park and private properties is clearly established by these extensive data sets. Fingerprinting of the samples obtained on the Company C undeveloped property provides additional proof of the links to the terminal and pipeline properties.

Petroleum Product Identification

Synchronous fluorescence and CS2 extraction/C5+ analyses (method 8015M) were performed on all soil, groundwater and product (NAPL) samples collected from borings and monitoring wells. These petroleum industry analytical methods are relatively inexpensive (compared to EPA analyses) and quite definitive in distinguishing specific petroleum products. Figure 6 shows synchronous fluorescence results of soil cores obtained from direct-push boring PUBH-23. The figure includes fluorograms (signatures) of soil core samples (2 foot lengths) collected continuously from 0-2 feet down to the total depth of the boring (18-20 feet). The fluorograms graphically demonstrate that the subsurface contamination begins at a depth of approximately 6-8 feet, and the signature indicates the contaminants are a mixture of diesel and gasoline. This diesel and gasoline signature continues to a depth of 12-14 feet. At 14-16 feet, petroleum contamination is virtually absent, as shown by the fluorograms. At a depth of 16-18 feet, petroleum contamination is again apparent, however, the signature indicates the product type is gasoline. This typical example (also see Figure 7) illustrates how the subsurface contamination in the study area varies with depth, and demonstrates the need for continuous sampling in borings and monitoring wells. It also shows that the contamination is the result of multiple product releases (that is often the case) that are present in distinct zones at various depths.

Based upon the results of the fluorescence and CS2 extraction/C5+ analyses, selected product samples were analyzed using high resolution capillary gas chromatography (HRCGC). Product samples from boring PU-38, between the Company E and Company C pipeline manifolds, boring PU-62 at the south property line of the Company C undeveloped property, and borings PU-116 and PU-107 on private properties were identified as jet fuel using HRCGC. Jet fuel was also identified at numerous locations in Govalle Park and on private properties (Figure 18). In addition to jet fuel several other product types were identified including gasoline (both leaded and unleaded), kerosene, MTBE, solvents, a heavy lubricant, and mixtures of these products. Figure 18 shows HRCGC chromatograms of some of the various products identified and the locations (borings and monitoring wells) at which these products were obtained. The various types of petroleum products identified from liquid products (NAPL) were found and identified in soil and groundwater samples collected in the study area. All fingerprinting results (not included in this paper due to space limitations) are included in the comprehensive report prepared by Exploration Technologies, Inc. and submitted to the TNRCC (*Environmental Investigation of Subsurface Hydrocarbon Contamination, East Austin Storage and Distribution Terminals Area, Austin, Texas, November 28, 1995*)

CONCLUSIONS

Several different assessment and analytical techniques were used to determine the areal and vertical extent of petroleum product contamination in subsurface soils and groundwater in the East Austin area. The data collected for the COA were integrated with all available data collected by industry consultants contracted by the oil companies. All data were quality controlled and confirmed using different analytical methods.

Subsurface petroleum contamination beneath the undeveloped properties, private properties, and COA property (Govalle Park) is present as vapor phase and sorbed (residual) phase in the vadose or unsaturated zone soils, and as liquid (NAPL), dissolved and sorbed phase in the saturated zone or groundwater aquifer. The sources of the vapor, soil and groundwater contamination were multiple releases on the oil companies' terminal and pipeline properties. Contamination resulting from these releases have coalesced in soils and groundwater and subsequently migrated off-site onto public and private properties. Based upon the results of the work performed, it is obvious that the oil companies were unable to assess the off-site migration of petroleum contaminants from the terminal and pipeline properties using conventional "rule of thumb" random drilling techniques.

Soil vapor, soil and groundwater isoconcentration maps, geologic cross sections and product analyses were used to delineate and demonstrate the areal and vertical extent of petroleum hydrocarbon impact to private and public properties located down-gradient of the six former fuel storage and distribution terminals and product pipeline properties in the East Austin area of Austin, Texas. Results of the assessment study are summarized as follows:

- Elevated soil vapor concentrations present in near surface soils are the result of petroleum product contamination in subsurface soils and groundwater.
- Various refined petroleum products have impacted subsurface soils, extending from the ground surface to groundwater in many areas. These soils containing sorbed (residual) phase hydrocarbons are the major source of dissolved phase contamination in the aquifer.
- The groundwater aquifer in the East Austin area has been impacted by multiple releases of refined petroleum products, as exhibited by liquid phase (NAPL) hydrocarbons on the groundwater in several areas, as well as the elevated concentrations of dissolved phase benzene, total BTEX, MTBE and TPH.
- The groundwater flow in the area is generally to the south-southeast, down-gradient of the six former storage and distribution terminals and pipeline properties.
- The MTBE (most soluble compound present in refined petroleum products) plume is the largest in areal extent (over 3000 feet). This plume extends over 1800 feet down-gradient (south-southeast) of the terminal and pipeline properties across Boggy Creek.
- Analytical results of soil, groundwater and liquid product (NAPL) samples, using synchronous fluorescence, EPA method 8015M and high resolution capillary gas chromatography, indicate the petroleum products responsible for the contamination are gasoline, kerosene, jet fuel, diesel, solvents, and a heavy lubricant. These are essentially all the products handled or stored on the terminal and pipeline properties.
- The age of the petroleum products impacting Govalle Park and private properties, in some cases, are in excess of twenty years, based upon high resolution capillary GC analyses and historical data.

- In most impacted portions of the study area, mixtures of different petroleum products have been identified, indicating multiple releases of hydrocarbon products for over 40 years.
- The majority of the NAPL found in the off-site (down-gradient) wells was weathered (aged) jet fuel. Loses of jet fuel were not reported by the oil company consultants, primarily because such loses occurred prior to 1987.
- The sources of the three major coalescing contaminant plumes are the six former fuel storage and distribution terminals and associated pipelines owned and operated by companies B, C, D, E, F and A.
- Remediation of soils and groundwater beneath the public and private properties in the East Austin area, if in fact possible, will require a long period of time due to the nature of the relatively low porosity and low permeability soils. This remediation can only be achieved if all properties are treated simultaneously, including the oil companies' properties (contaminants sources), since the main sources of the contamination must be eliminated if the cleanup is to be successful.

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FIGURES

- FIGURE 1. LOCATION MAP OF STUDY AREA SHOWING THE SIX FORMER BULK STORAGE AND DISTRIBUTION TERMINALS/PIPELINE PROPERTIES (A-F) AND SURROUNDING CITY OF AUSTIN PARK (GOVALLE PARK), RESIDENTIAL AND COMMERCIAL PROPERTIES. BOREHOLE AND MONITORING WELL LOCATIONS ARE ALSO SHOWN.
- FIGURE 2. CROSS SECTION A-A' SHOWING STRATIGRAPHIC SEQUENCE ENCOUNTERED IN THE FIRST STREET TERRACE.
- FIGURE 3. CONTOUR MAP OF DEPTH TO THE TOP OF THE MASSIVE SAND IN THE STUDY AREA.
- FIGURE 4. POTENTIOMETRIC SURFACE MAP OF THE FIRST STREET TERRACE AQUIFER, DOWN-GRADIENT OF THE TERMINAL/PIPELINE PROPERTIES, USING DATA COLLECTED JUNE-SEPTEMBER 1994.
- FIGURE 5. THE SITES AT WHICH SOIL VAPOR SAMPLES WERE COLLECTED ARE SHOWN BY DOTS.
- FIGURE 6. (A) FLUOROGRAMS SHOWING PRODUCT TYPES IDENTIFIED IN SOILS FROM THE GROUND SURFACE (0 FEET) AND 20 FEET IN BORING PUBH-23. (B) BAR GRAPH SHOWING THE FLUORESCENCE DATA FOR VARIOUS WAVELENGTH WINDOWS (IN NM). (C) STANDARD FLUORESCENCE SIGNATURES FOR GASOLINE, DIESEL, CRUDE OIL AND JET FUEL.
- FIGURE 7. CROSS SECTION B-B' SHOWING FLUOROGRAMS FOR EACH TWO-FOOT SOIL CORE SAMPLE COLLECTED AND ANALYZED IN VARIOUS BORINGS. NOTE THE VARIATIONS IN INTENSITY AND CONTAMINANT TYPE IN INDIVIDUAL BORINGS AS WELL AS ALONG THE SECTION. DIFFERENT PRODUCT TYPES ARE COLOR CODED IN ACCORDANCE WITH THE LEGEND AT THE LOWER RIGHT.
- FIGURE 8. COLOR CONTOUR MAP OF CARBON DIOXIDE SOIL VAPOR PLUME.
- FIGURE 9. COLOR CONTOUR MAP OF METHANE SOIL VAPOR PLUME.
- FIGURE 10. COLOR CONTOUR MAP OF C5+ (PENTANE-XYLENES+) SOIL VAPOR PLUME.
- FIGURE 11. TPH SCREENING ANALYSES "SLICE" MAPS SHOWING THE AREAL EXTENT OF TPH CONCENTRATIONS AT VARIOUS DEPTH INTERVALS (SLICES) BELOW THE GROUND SURFACE.
- FIGURE 12. COLOR CONTOUR PLUME MAP OF TOTAL BTEX CONCENTRATIONS (EPA METHOD ANALYSES) IN SOILS.
- FIGURE 13. COLOR CONTOUR PLUME MAP OF TPH CONCENTRATIONS (EPA METHOD ANALYSES) IN SOILS.
- FIGURE 14. COLOR CONTOUR PLUME MAP OF TOTAL BTEX CONCENTRATIONS (EPA METHOD ANALYSES) IN GROUNDWATER.
- FIGURE 15. COLOR CONTOUR PLUME MAP OF TPH CONCENTRATIONS (EPA METHOD ANALYSES) IN GROUNDWATER.
- FIGURE 16. COLOR CONTOUR PLUME MAP OF MTBE CONCENTRATIONS (EPA METHOD ANALYSES) IN GROUNDWATER.
- FIGURE 17. COLOR CONTOUR PLUME MAP OF C5+ GROUNDWATER HEADSPACE CONCENTRATIONS.
- FIGURE 18. MAP OF STUDY AREA SHOWING PRODUCT TYPES IDENTIFIED IN FLUID (NAPL AND GROUNDWATER) SAMPLES COLLECTED FROM BORINGS AND MONITORING WELLS USING HIGH RESOLUTION CAPILLARY GAS CHROMATOGRAPHY. PRODUCT TYPES ARE COLOR CODED IN ACCORDANCE WITH THE LEGEND AT THE LOWER RIGHT. HIGH RESOLUTION CAPILLARY GC CHROMATOGRAM SIGNATURES ARE SHOWN FOR EACH BORING AND MONITORING WELL SAMPLE ANALYZED.





































