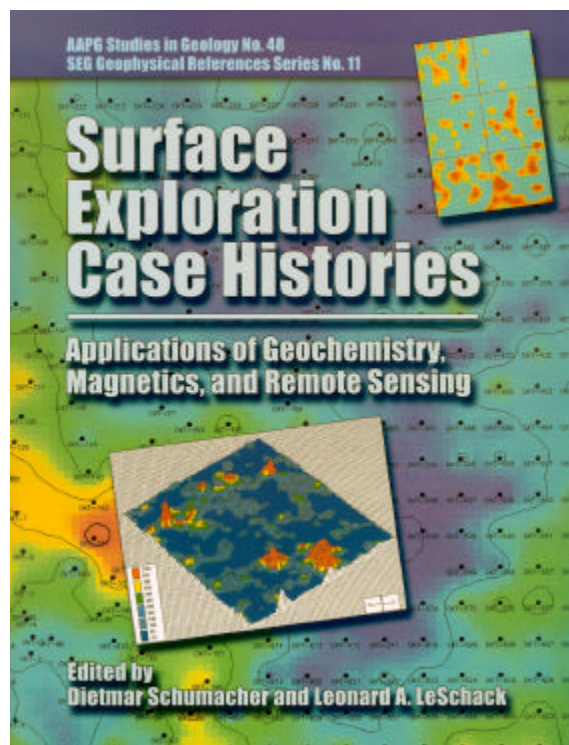


Assessment of Subsurface Hydrocarbon Contamination Resulting from Multiple Releases at Six Former Bulk-fuel Storage and Distribution Terminals, Austin, Texas: A Case Study

Patrick N. Agostino, Victor T. Jones, III, and Rufus J. LeBlanc Jr.



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ABSTRACT

Exploration geochemical methods developed and used by the petroleum industry can be invaluable for environmental site characterizations. Many of these methods are not used because they are unfamiliar to environmental scientists and to most regulatory agencies. The rule-of-thumb methods of site characterization (randomly placed monitoring wells, EPA method analyses for target compounds, and the like) are rarely adequate to fully delineate and explain the nature and distribution of subsurface contamination.

The Austin, Texas, case study demonstrates how a phased assessment approach can be used to accurately define petroleum contamination in a study area. Various unconventional methods and techniques (standard for the petroleum industry, but not for the EPA), including forensic geochemistry, were used to better delineate the areal and vertical extents of subsurface contamination.

Prior to this study, more than 400 boreholes, monitoring wells, and temporary monitoring wells were installed on six former storage and distribution terminals and pipeline properties and adjacent private and public properties in the east Austin area. The assessments performed included standard regulatory methodologies (borehole drilling, monitoring-well installation, EPA method BTEX and TPH laboratory analyses, and the like), with the goal of characterizing individual properties. The migration of contaminants off the terminal properties, however, was unresolved and unreported.

The scope of work for this study included documentation of historical hydrocarbon releases; collection of soil-vapor, soil-core, and groundwater samples; and analyses of these sam-

ples obtained in close proximity to and down-gradient of the terminal and 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 previously collected.

Geologic cross sections and soil-vapor, soil, and groundwater isoconcentration maps were constructed using the data collected during this study. The maps and sections and forensic geochemistry techniques were used to delineate and demonstrate the areal and vertical extents of petroleum hydrocarbon impact on 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.

The sources of the vapor, soil, and groundwater contamination were multiple releases on the terminal and pipeline properties, based on historical records and assessment data. Contamination resulting from these releases has reached groundwater and subsequently has migrated off-site onto public and private properties. Based on the results of the work performed, it is obvious that the use of soil-vapor studies and other geochemical methods was essential to economically assess off-site migration of petroleum contaminants from the terminal and pipeline properties.

INTRODUCTION

Exploration geochemical methods developed and used by the petroleum industry can be invaluable in environmental site characterizations. Environmental companies and consultants do not use many of these methods because the methods are unfamiliar to environmental scientists and to most regulatory agencies. The rule-of-thumb methods of site characterization (randomly placed monitoring wells, EPA method analyses for target compounds, and the like) are rarely adequate for fully delineating and explaining the nature and distribution of subsurface contamination.

Additional information that must be integrated with analytical data to better characterize a site includes historical data and subsurface geology and hydrogeology. To understand the nature and extent of the contamination, it is necessary to understand what products were stored and dispensed on and in the vicinity of a site, where potential source areas were located over time, and what geologic and hydrogeologic pathways the released products migrated along. 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 for investigators to understand the distribution and migration of hydrocarbon contaminants. The effectiveness of a remedial action plan and remediation system depends directly on the thoroughness and accuracy of the site characterization, especially with regard to subsurface stratigraphy.

The Austin, Texas, case study demonstrates (1) the effectiveness of unconventional methods and techniques (standard to the petroleum industry, but not to the EPA)

for delineating the areal and vertical extents of subsurface contamination; (2) the importance of understanding and accurately mapping the subsurface geology and hydrogeology in the study area; (3) the merits of compiling and integrating the historical information for the various facilities; (4) the importance of forensic geochemistry; and (5) the relationship among 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 more than 40 years in the east Austin area of Austin, Texas, U.S.A. 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, these activities were not adequate to properly detect or prevent off-site 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 and operators of the terminals and pipelines report all historical 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 Nat-

ural Resource Conservation Commission (TNRCC) included a limited number of minor releases (dated post-1987). More than 400 boreholes, monitoring wells, and temporary monitoring wells were installed on the six storage and distribution terminals and pipeline properties and adja-

cent private and public properties between 1987 and 1992. Despite this large number of sampling points, the testing performed down-gradient of the terminal and pipeline properties was incomplete and inadequate for defining the true degree and extent of off-site contamination.

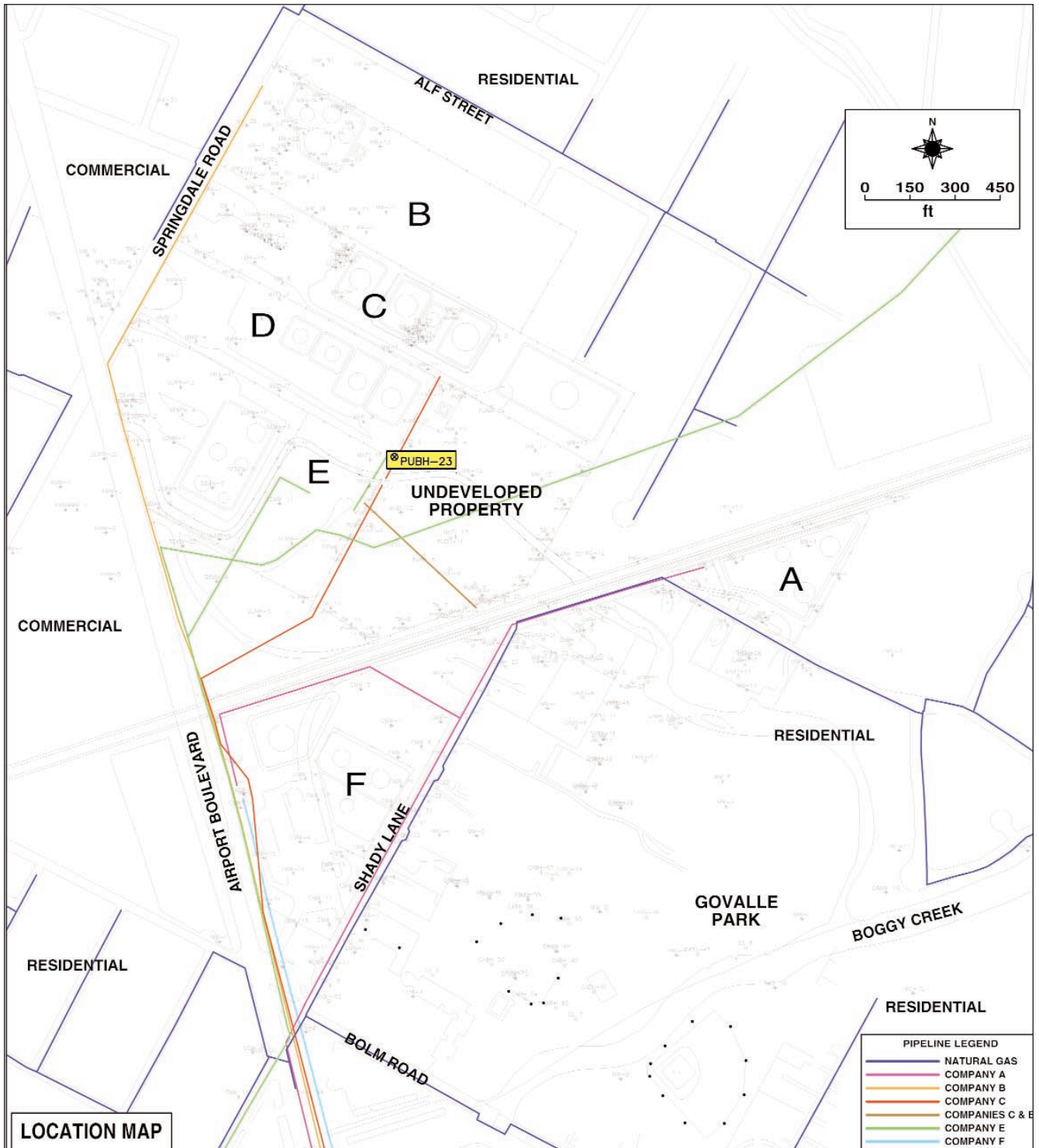


FIGURE 1. Location map of study area, showing the six former bulk storage and distribution terminals and pipeline properties (A-F) and surrounding city of Austin park (Govalle Park) and residential and commercial properties. The locations of pipelines, boreholes, and monitoring wells are also shown.

HISTORICAL INFORMATION— TERMINAL AND PIPELINE OPERATIONS

For the purposes of this case study, the former terminal and pipeline properties have been labeled counterclockwise from A through F (Figure 1). Limited historical information for the six terminal properties and pipelines was 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 (Figure 1) 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, which contained approximately 60% (346,572 bbl) of the total storage capacity of the six terminals. Refined petroleum fuels were distributed from the pipeline manifolds to aboveground storage tanks via separate product distribution lines. The total storage capacity of the aboveground tanks on the six terminals was approximately 576,000 bbl.

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 to supply jet fuel to the Air Force base in 1971 when the company purchased the pipeline and manifold facilities. Other refined petroleum fuels stored and distributed by the six terminals included regular and premium leaded and unleaded gasoline, kerosene, and diesel. No crude-oil products were ever transported to or stored on any of the six terminals.

The majority of refined fuel products delivered to the six terminals via pipelines during a 40-year period of operation exited the six terminals via truck-loading racks. Products were distributed from the aboveground 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, based on the data compiled during this study. The product distribution lines were located underground as late as 1986 at Terminal C, and they 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-rack drains emptied into underground storage tanks (USTs) in the vicinity of the six loading racks. In addition,

after the refined fuel products were separated from water in the USTs, the water, which contained dissolved-phase hydrocarbons, was pumped into the berm areas around the storage tanks and allowed to seep into subsurface soils.

It should be noted that the oil companies' consultants focused on those losses that occurred after 1987, when the state of Texas began to enforce 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, based on the product types identified in subsurface soils and groundwater.

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, because lead usage peaked in the 1970s 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 indicate 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 companies' reports, were submitted to the TNRCC in a comprehensive summary report (Exploration Technologies, Inc., 1994).

STUDY AREA

General

The study area is located in a part of east Austin consisting of residential, industrial, commercial, and city (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 in the Blackland Prairie physiographic province of central Texas. The topography slopes gently to the southeast and has an average elevation of 455 ft (137 m) above sea level. Boggy Creek, a tributary to the Colorado River (the primary drainage feature in the Austin area), located approximately 1 mi (1.6 km) to the south, is the prominent drainage feature in the study area. The climate of the Austin area is humid-subtropical, with an average precipitation of 32 in. (82 cm) per year (Garner and Young, 1976).

Geology

Austin, in central Travis County, Texas, is located on formations of Late Cretaceous and early Tertiary age that 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, in descending order, by the Navarro and Taylor Groups, Austin Chalk, Eagle Ford Group, Buda Limestone, Del Rio Clay, Georgetown Limestone, and numerous Cretaceous formations of the Fredericksburg Group. The Edwards Limestone, 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 that are graveliferous in some areas. The Pleistocene terraces range in thickness from less than 10 ft (3 m) to more than 60 ft (18 m) 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 is 24–32 ft (7–9.6 m) thick. 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.

An understanding of the areal and vertical stratigraphic framework of the First Street Terrace is essential to understanding the migration pathways of subsurface contamination in the unsaturated (vadose) and saturated zones. Relatively narrow, silt-filled channel deposits are present in the shallow subsurface soils (Figure 2). These silt-filled channels contain relatively young sediments that were deposited after the initial erosion of the First Street Terrace. The channels trend northwest to southeast across the terminal and pipeline and undeveloped properties and extend into Govalle Park and adjacent residential areas.

The depth to sand and other overlying lithologic units varies widely over the study area. The sand is at relatively shallow (4–10 ft, or 1.3–3 m) or intermediate depths (10–14 ft, or 3–4.2 m) beneath most of the terminal properties. East and south of Shady Lane, the sand is

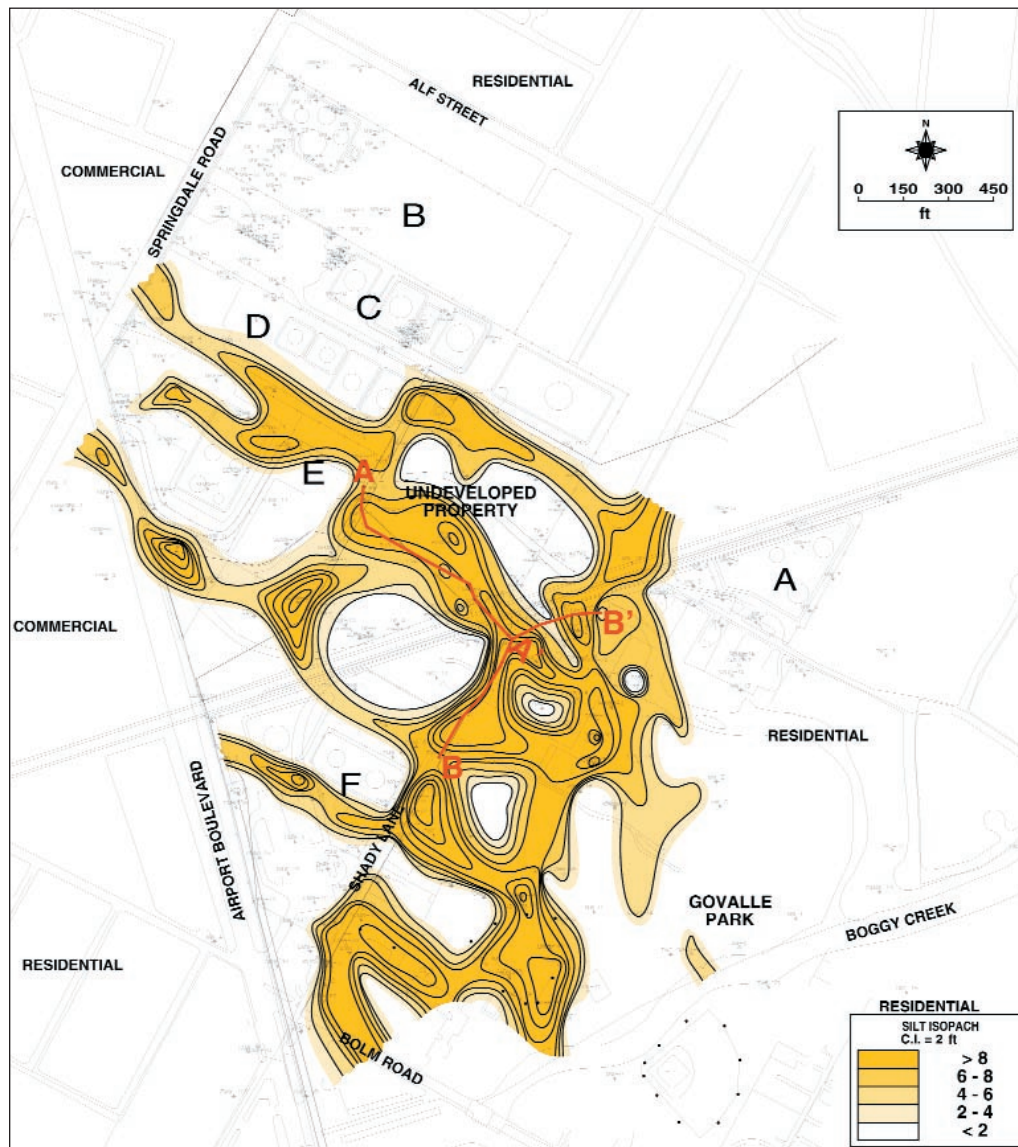


FIGURE 2. Silt isopach map constructed using soil-core data collected in the study area. Note the relatively narrow linear channels in which silt sediments were deposited.

generally encountered at depths in excess of 18 ft (5.4 m). In areas where sand is present at depth, it is generally overlain, in ascending order, by silts, clayey silts, and silty clays. The vertical relationships of the lithologies encountered in the First Street Terrace are illustrated in cross section A-A' (Figure 3). The location of the cross section is shown in Figure 2.

The relatively narrow silt channels present in vadose-zone soils (Figure 2) were primary pathways along which hydrocarbon contaminants migrated off the terminal properties toward Govalle Park and residential properties. These contaminants also migrated vertically down to groundwater, thus impacting the aquifer in the study area. The contaminants that impacted the groundwater continued to migrate off-site (down-gradient) because of the regional south-southeast groundwater gradient present in the study area.

Hydrology

The Pleistocene terrace deposits and Edwards Limestone are the two principal groundwater aquifers in the study area. The city of Austin's public water supply is derived primarily from the lakes of the Colorado River and the freshwater zone of the Edwards Limestone. In the east Austin area, the Edwards Limestone is not considered to be a source of potable water and is not suitable for industrial use because of its high salinity. The water contained

in the Pleistocene terrace deposits, from depths of 10 to 15 ft (3 to 4.5 m) 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 because of 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 through September 1994, indicates that the dominant groundwater flow direction beneath the off-site properties is to the southeast, toward the Colorado River.

INVESTIGATIVE METHODS

The scope of work for this study included documentation of historical hydrocarbon releases; collection of soil-vapor, soil-core, and groundwater samples; and analyses of these samples obtained in close proximity to and down-gradient of the terminal and pipeline properties. All data were integrated with public data collected by the oil companies' consultants and reported to the TNRCC (Exploration Technologies, Inc., 1994). The soil-vapor surveys (542 sample sites) performed in Govalle Park, on the undeveloped property, and on private properties were used to locate 91 borings and 13 monitoring wells. The drilling and installation of these borings and monitoring

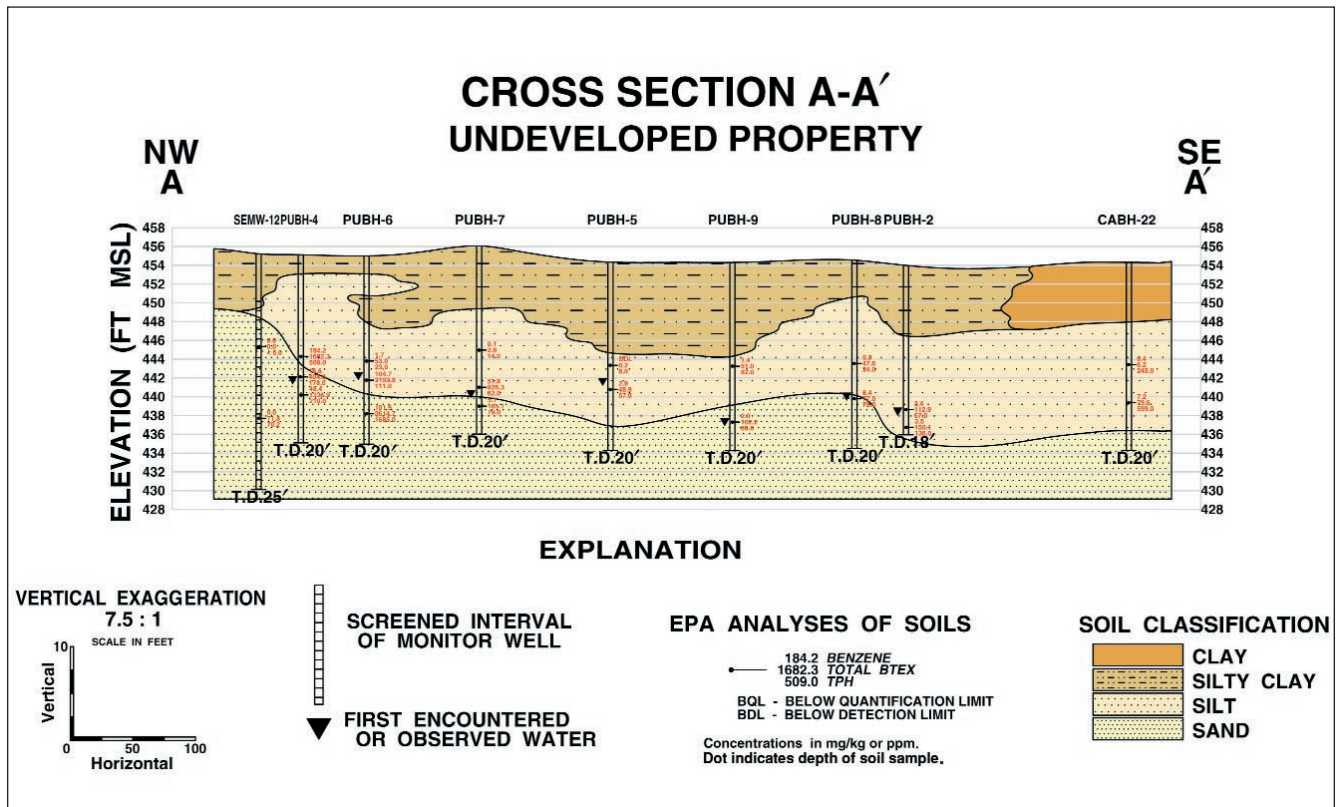


FIGURE 3. Cross section A-A', showing the stratigraphy of the First Street Terrace.

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

and concentrations of these petroleum products (contaminants) in vadose-zone soils and groundwater.

An initial investigation of the bulk-fuel storage and distribution terminal area was begun in 1993 at the request of the city of Austin (COA). The goal was to determine if Govalle Park (owned by the city) was impacted by

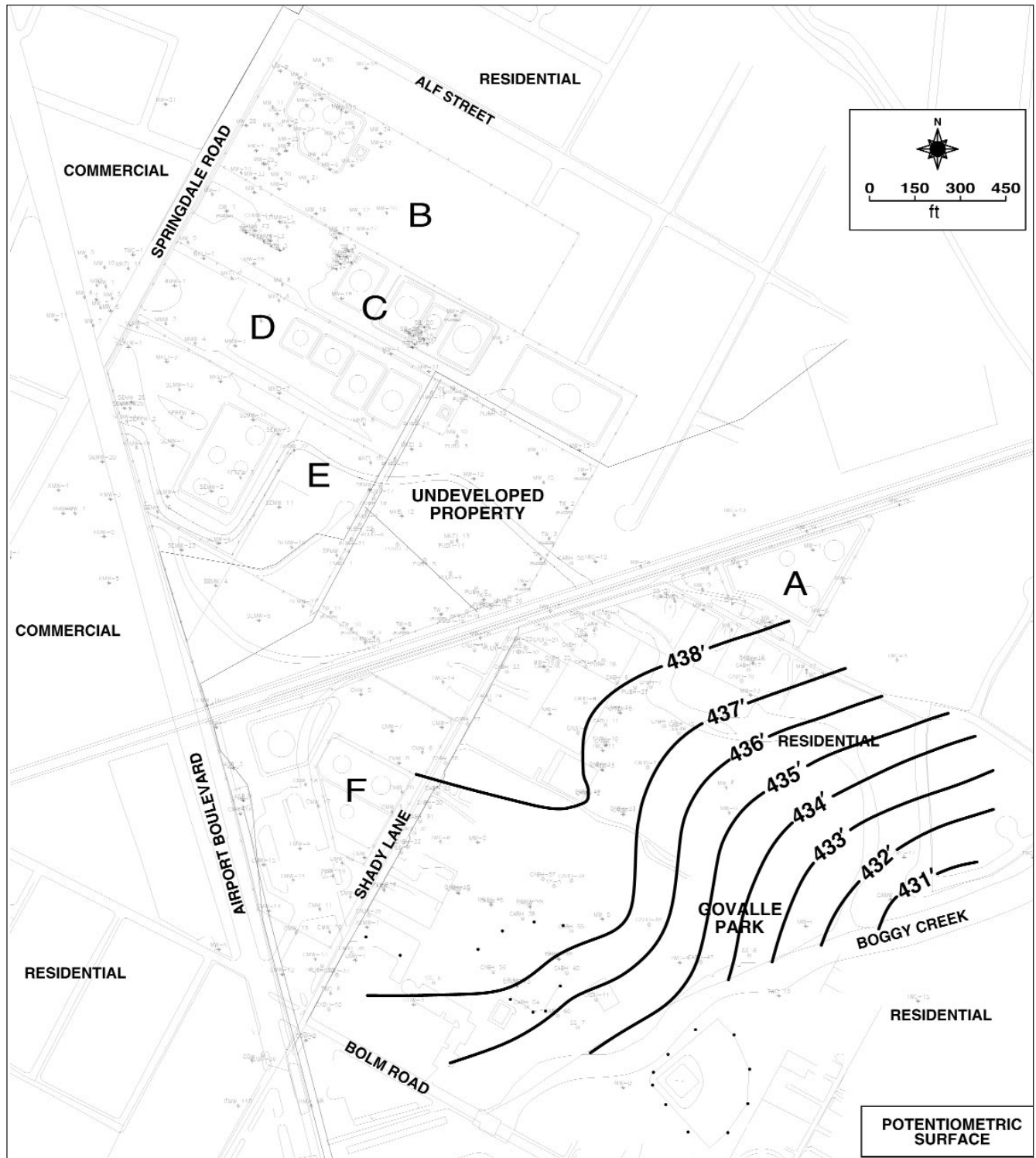


FIGURE 4. Potentiometric surface map of the First Street Terrace aquifer, down-gradient of the terminal and pipeline properties, using data collected in June through September 1994.

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 that it was highly probable that releases on the terminal and pipeline properties during 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 Surveys

An initial soil-vapor survey was performed over city-owned Govalle Park and adjacent private properties down-gradient of the terminal and pipeline properties. When used properly, a soil-vapor survey is an excellent screening technique for delineating the areal (horizontal) extent of subsurface contamination (Marrin, 1988; Jones and Agostino, 1998). Soil-vapor samples were collected at 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 and pipeline properties on a staggered sampling grid containing approximately 50-ft (15-m) 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 in Figure 5.

At each sampling location, a manually operated pounder bar was used to advance a 0.5-in.- (1.3-cm-) diameter hole into the soil to a depth of 12 ft (3.6 m). Immediately after removal of the pounder bar, a specially designed soil-vapor sampling probe was inserted into each predriven sampling hole for collection of a soil-vapor sample. In some instances, samples were collected at depths shallower than 12 ft because of soil conditions or the presence of shallow groundwater. Based on 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 (at depths of 16–18 ft, or 4.8–5.4 m), 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-ft [3.6-m] samples collected at 384 sites). The soil-vapor concentration maps include all data collected using both hand-probe and direct-push methods.

An evacuated 125-cm³ septum-top glass bottle was attached to the probe and used to collect a soil-vapor sample at each location. An additional 60 cm³ of soil

vapor was extracted from the soil and added to the bottle to create a positive pressure within the bottle and to 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 direct-push sampler were decontaminated between each of the sample sites, using a rinse of detergent and distilled water. 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 used 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. (1990a, b) have shown that data obtained from portable total organic vapor-detection instruments can be misleading because those instruments are influenced by many factors. Although more time-consuming and more costly, detailed soil-vapor analyses, in which individual constituents are identified and quantified under laboratory conditions, are invaluable for properly characterizing the areal extent of subsurface contamination. All soil-vapor samples, therefore, were analyzed in ETI's central laboratory.

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.

Direct-push Borings

Results of the soil-vapor surveys were used to determine 91 locations at which soil cores were collected. At these locations, borings were advanced to groundwater, and soil-core samples (in 2-ft, or 0.6-m, lengths) were collected continuously from the ground surface to total depth, using a direct-push sampling system. Composite soil samples from each core were analyzed for concentrations of benzene, toluene, ethylbenzene, and xylenes (BTEX) and total petroleum hydrocarbons (TPH), using proprietary screening instruments (Hager and Jones, 1990; Smith et al., 1992).

The borings were drilled 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. A geologist logged each 2-ft soil core on-site. The logging results were used to determine the subsurface stratigraphy and to fully characterize the subsurface contamination in vadose-zone soils. The vertical distribution of

hydrocarbon contaminants was used to delineate source areas and to determine migration pathways.

Groundwater samples were also collected from borings, through a slotted well point attached to the drill string or through PVC slotted casing temporarily inserted into the boreholes. Other groundwater samples were derived from conventional monitoring wells.

Completion of Monitoring Wells

Thirteen monitoring wells were drilled and completed using a rotary-drill rig with hollow-stem augers of 11-in. outside diameter. Locations of monitoring wells were determined using borehole and soil-vapor data. The wells were completed at total depths of 23 to 29 ft (7 to 8.7 m).

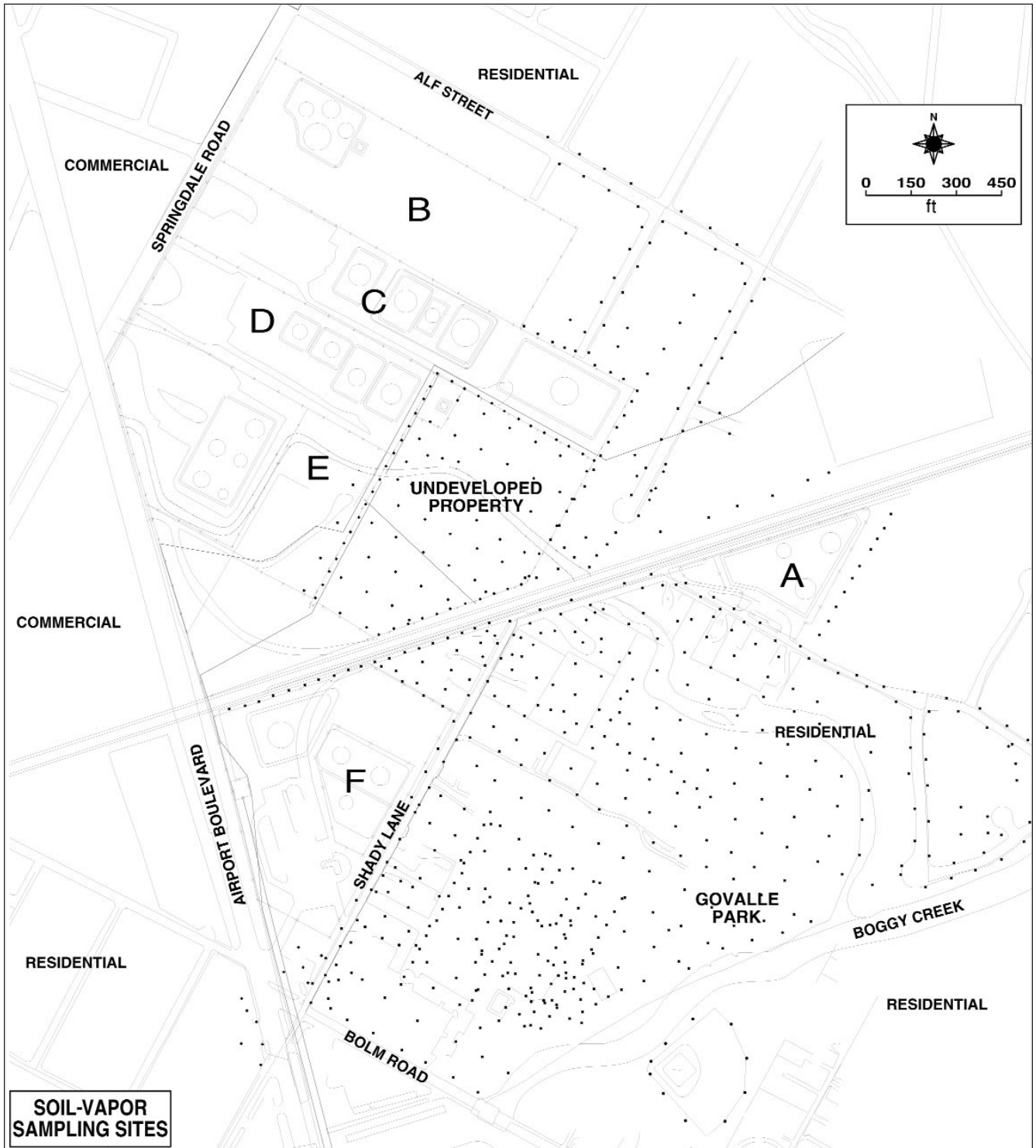


FIGURE 5. The sites at which soil-vapor samples were collected, indicated by dots.

Each well was developed to ensure that 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 ft (15 to 30 m) of preexisting wells that contained only moderate levels of dissolved-phase contaminants. No NAPL was found in the preexisting wells, because they were located outside the narrow channels (preferential migration pathways) along which the liquid contaminants migrated. The only 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₊ (pentane–xylenes+) hydrocarbons and for carbon dioxide (CO₂). Laboratory results of hydrocarbon analyses were quantified in parts per million by volume (ppmv), and carbon dioxide concentrations in percent by volume.

Two flame-ionization-detector (FID) gas chromatographs were used to independently determine the 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 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.

Pentane–xylenes+ (C₅₊) hydrocarbon analyses yield a quantitative measure of the concentrations, by volume, of petroleum-product vapors present in near-surface soils. C₅₊ hydrocarbons dissipate more slowly than lighter-fraction (C₁–C₄) compounds. Because of the large number of individual compounds present in gasolines, diesels, jet fuels, and the like, 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 use 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, because such products are excellent food sources for bacteria. Carbon dioxide (CO₂) concentrations were determined using a gas chromatograph equipped with a thermal-conductivity detector (TCD). These data, 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.

EPA Method Analyses— Soils and Groundwater

BTEX analyses of soils and groundwater were performed in accordance with EPA method 8020/5030 and EPA method 8020/602, respectively. TPH analyses of soils and groundwater were performed in accordance with EPA method 418.1.

Preliminary MTBE analyses of groundwater samples were performed in accordance with EPA method 8020/602. Gas chromatography/mass spectrometry (GC/MS) analyses were also run on several 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, using standard headspace methods. The headspace was introduced into each sample bottle by displacing 10 ml of water with nitrogen, prior to analysis. Results of these analyses were quantified in parts per million by volume (ppmv). Vapor headspace chromatograms were also analyzed and used as an alternate method to confirm the presence of MTBE.

Miscellaneous Analyses— Product Fingerprinting

Several 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. Fingerprinting techniques used in this study will be summarized below.

Synchronous fluorescence.—Synchronous fluorescence analyses were performed on soil-core samples obtained from the 91 borings (and 16 additional boreholes and 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 occur. The excitation of aromatic compounds (e.g., benzene and polynuclear aromatic hydrocarbons, or PAHs) causes the light to be emitted at different wavelengths, depending on the range of compounds present. As shown by the product standards included in Figure 6, this technique is an inexpensive tool for analyzing and fingerprinting petroleum compounds such as gasoline, diesel, kerosene, jet fuel, and crude oil, 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-ft (0.6-m) soil-core interval are shown in Figure 6 to illustrate product type distributions in boring PUBH-23, and in Figure 7 in various other borings. The results are discussed in more detail below.

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 (CS₂) and analyzed by FID gas chromatography for C₅₊ hydrocarbons (C₅–C₂₀) to characterize (fingerprint) and determine the 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 high-resolution capillary gas chromatography analyses.

High-resolution capillary gas chromatography.—High-resolution capillary gas chromatography (HRCGC) 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 on these other methods, selected soil, groundwater, and liq-

uid product (NAPL) samples were analyzed using high-resolution capillary gas chromatography, a modification of ASTM method D-3328. Soil and groundwater samples are prepared by using a methylene chloride solvent to extract various molecular-weight hydrocarbons from the matrix. Liquid product samples do not require an extraction procedure. The extract or liquid product is analyzed on a capillary column using a flame ionization detector (FID) to identify and characterize hydrocarbon compounds and to define product types (gasoline, diesel, jet fuel, kerosene, solvents, and the like).

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 part of the survey area. Concentrations of CO₂ in excess of 14% and methane in excess of 10% are present south and east of the terminal properties, in residential areas and in Govalle Park. The biodegradation of hydrocarbons by both aerobic and anaerobic bacteria in the subsurface environment can occur within very close proximity, and thus can 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 CO₂ and methane concentrations indicates that the biogenic gases are the result of degradation of petroleum hydrocarbons in specific regions of the study area. Regional CO₂, methane, and C₅₊ concentration plume maps are included as Figures 8, 9, and 10, respectively. Three contaminant lobes exist between the terminals and undeveloped properties and Govalle Park and surrounding private properties. The plume maps indicate that hydrocarbon contaminants originated on the terminals and product pipeline properties, traversed the Company C undeveloped property, and migrated beneath city and private properties. Migration pathways for the contaminant plumes are controlled by silt-filled channels contained in the Pleistocene sediments. These well-defined pathways are 50 to 150 ft (15 to 45 m) wide, linear in shape, and separated by areas of background concentrations of hydrocarbon and biogenic gases.

The distributions of ethane, propane, and normal butane are similar to that of C₅₊ but are slightly more limited in areal extent. 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 CO₂, methane, and C₅₊ vapor concentrations, coupled with moderate con-

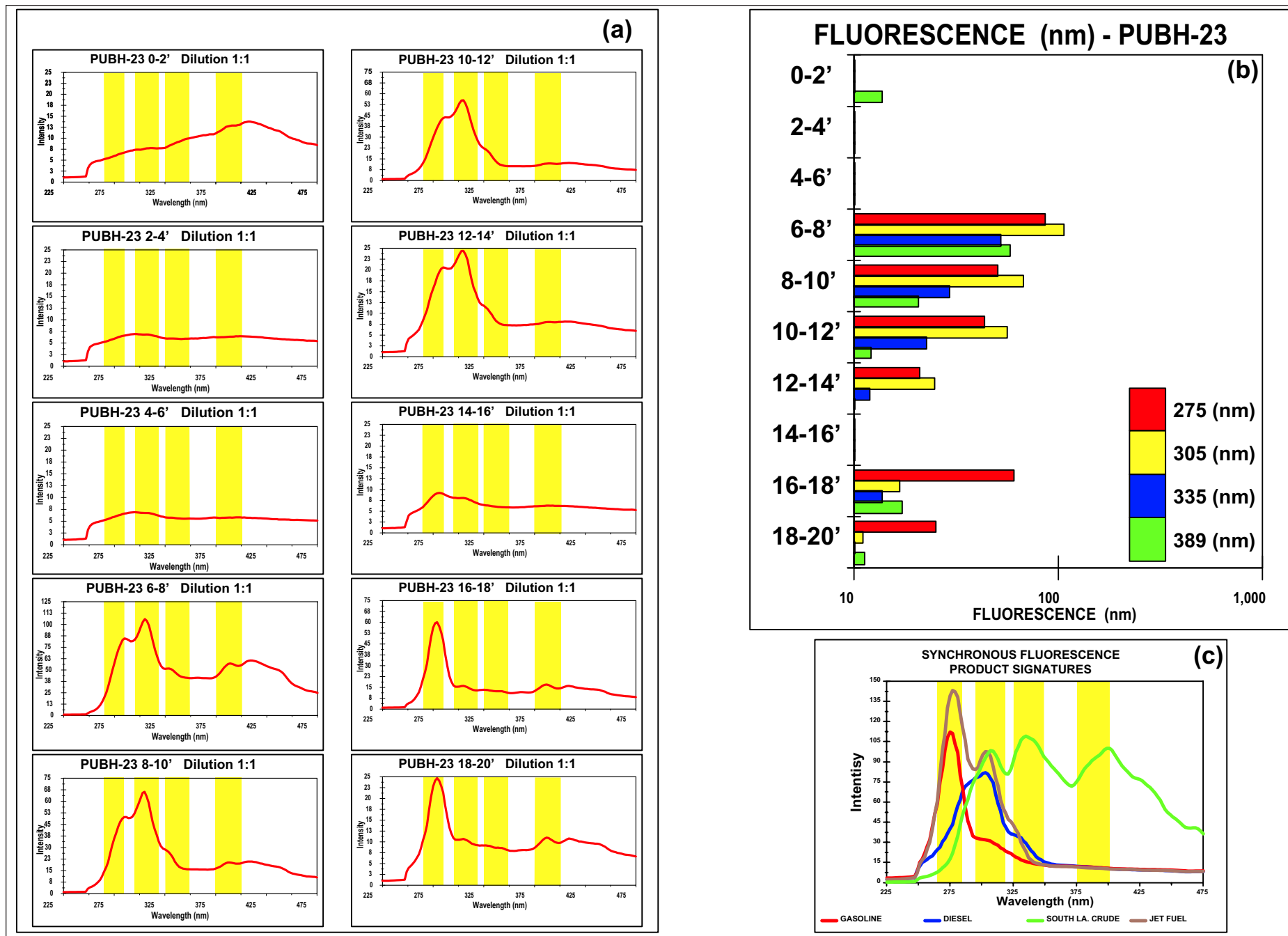


FIGURE 6. (a) Fluorograms showing product types identified in soils from the ground surface to -20 ft (6 m) in boring PUBH-23. (b) Bar graph showing the fluorescence data for various wavelength windows (in nm). (c) Standard fluorescence signatures for gasoline, diesel, crude oil, and jet fuel.

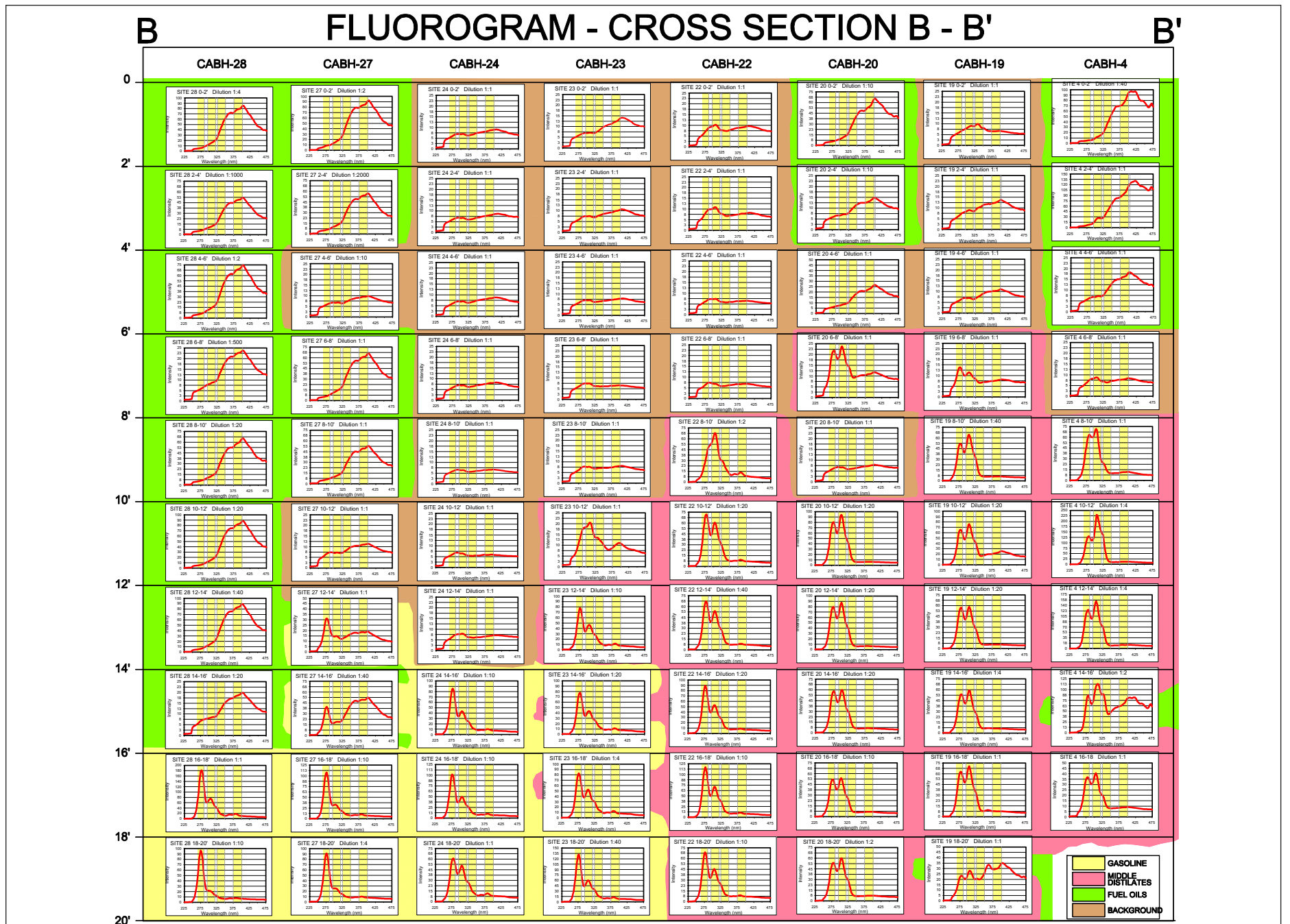


FIGURE 7. Cross-section B-B' showing fluorograms for each 2 ft (0.6 m) soil core sample collected and analyzed in various borings. Note variations in intensity and contaminant type in individual borings and along the line of section. Different product types are color-coded in accordance with the legend at the lower right.

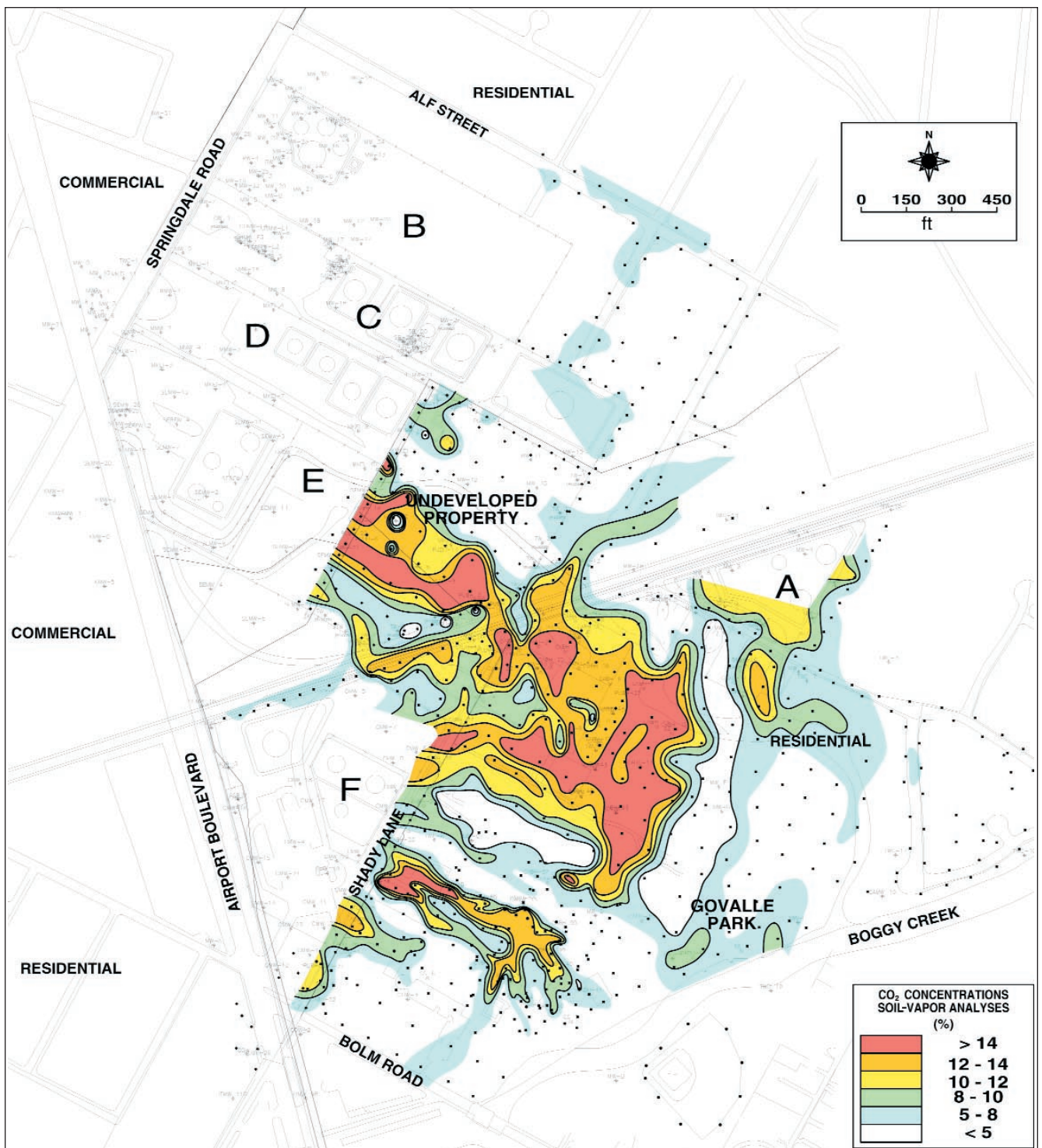


FIGURE 8. Color contour map of CO₂ soil-vapor plume.

centrations of light-hydrocarbon compounds (ethane, propane, and butanes) adjacent to the terminal properties, pipelines, residential areas, and Govalle Park, confirm that there have been releases of petroleum hydrocarbons to the area from the terminal properties.

A natural-gas pipeline leak was detected along Shady Lane, west of the Terminal A property. The soil-vapor re-

sults in this area indicated a typical natural-gas signature (where methane > ethane > propane > isobutane, and so forth). Methane concentrations in excess of 60% and ethane in excess of 3% (and other light gases) confirmed this linear anomaly as natural gas. Carbon dioxide anomalies having a limited areal extent are present in other parts of the study area. These anomalies are interpreted as

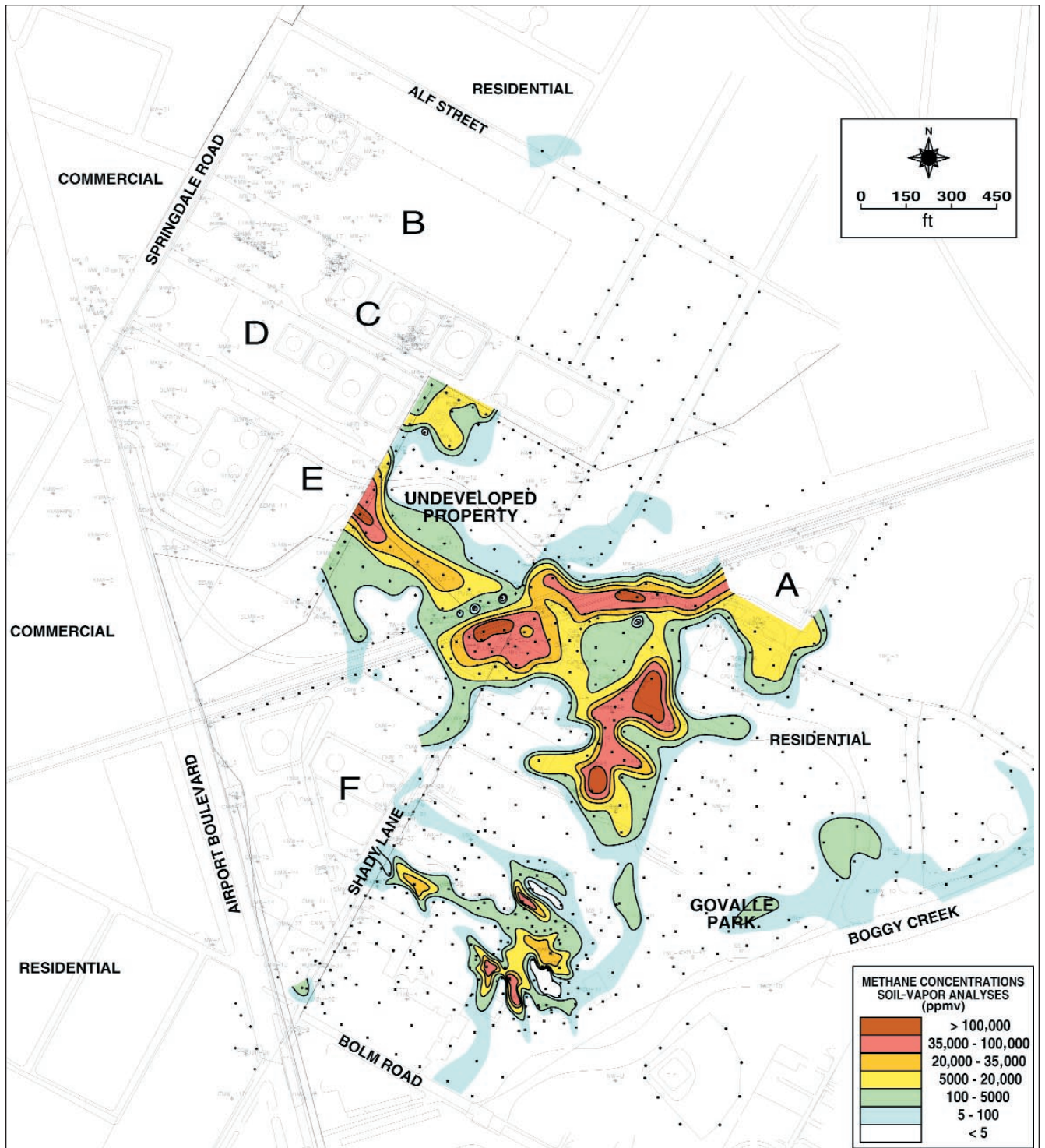


FIGURE 9. Color contour map of methane soil-vapor plume.

resulting from the biodegradation of organic material(s) other than petroleum hydrocarbons, because no significant concentrations of C_1 – C_4 or C_{5+} 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 mi-

gration pathways controlled by the subsurface geology (channels) along which contaminants moved beneath private properties and Govalle Park. Plume maps constructed using the soil-vapor data were used to optimally locate borings and monitoring wells in the study area, with virtually 100% 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 to identify specific petroleum products responsible for the impact. Each composite 2-ft soil sample was analyzed initially (screened) using a derivative ultraviolet spectrometer for BTEX compounds and a fixed-wavelength infrared spectrometer for total petroleum hydrocarbons (Hager and Jones, 1990; Smith et al., 1992). In addition, synchronous fluorescence and EPA method 8015M analyses were performed on all soil-core samples. These analyses can be definitive in determining the source(s) and products responsible for the impact.

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 both from borings and monitoring wells. These data were integrated with data collected by consultants for the terminal and pipeline owners and operators. Figures 12 and 13 are isoconcentration maps of total BTEX and TPH concentrations (EPA method 418.1 results) in vadose-zone soils beneath private properties, Govalle Park, and the terminals and product pipeline (undeveloped) properties. These isoconcentration maps include larger areas (including the terminal properties) than do 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 releases of hydrocarbons from multiple locations on the terminal and pipeline properties.

Lithologic information from borings confirms that silt sediments (channels) control the migration of the petroleum hydrocarbons off the terminal and pipeline properties. The locations of the silt channels in general are defined by the soil-vapor, BTEX, and TPH plume maps and are consistent with the silt isopach map (Figure 2). The petroleum contaminants, located using various geochemical methods, are analogous to dyes that stain the sediments, thus outlining the geologic pathways. The narrow migration pathways (channels) are best defined on the soil-vapor maps (Figures 8, 9, and 10) because of the larger number (higher density) of sample locations. These nar-

row pathways were not defined by the random drilling performed by other consultants prior to this study.

Groundwater

Dissolved-phase contaminant plume maps were constructed, including total BTEX, TPH, and MTBE concentrations, containing data collected during the third quarter of 1994. The total BTEX, TPH, and MTBE plume maps are included here 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 from 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 one assembled in the study area.

The major total BTEX plume (Figure 14) extends south from Terminal B 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 geometry similar to that of the BTEX plume. Large portions of the terminal and pipeline properties, private properties, and Govalle Park exceed 1000 µg/L (or 1 ppm), which was 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). Because of 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 µg/L (or 40 ppb) as the limit considered safe for drinking water. Other regulatory authorities, such as the state of Maine (which has a 50-µg/L action level), consider MTBE to be a health hazard (Klan and Carpenter, 1994). In 1999, California outlawed the future use of MTBE in gasoline.

The MTBE plume is the most extensive in areal extent, and indicates that releases of MTBE occurred over

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

Vapor headspace concentrations of C₅₊ (Figure 17) were measured, plotted, and mapped for all groundwater samples collected by Exploration Technologies, Inc., between June and September 1995. The headspace analyses

provide an independent and alternate data set for quantifying volatile hydrocarbon components present in groundwater. The C₅₊ vapor headspace concentrations map (in ppmv) 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, because the monitoring wells on these properties were not available for sampling.

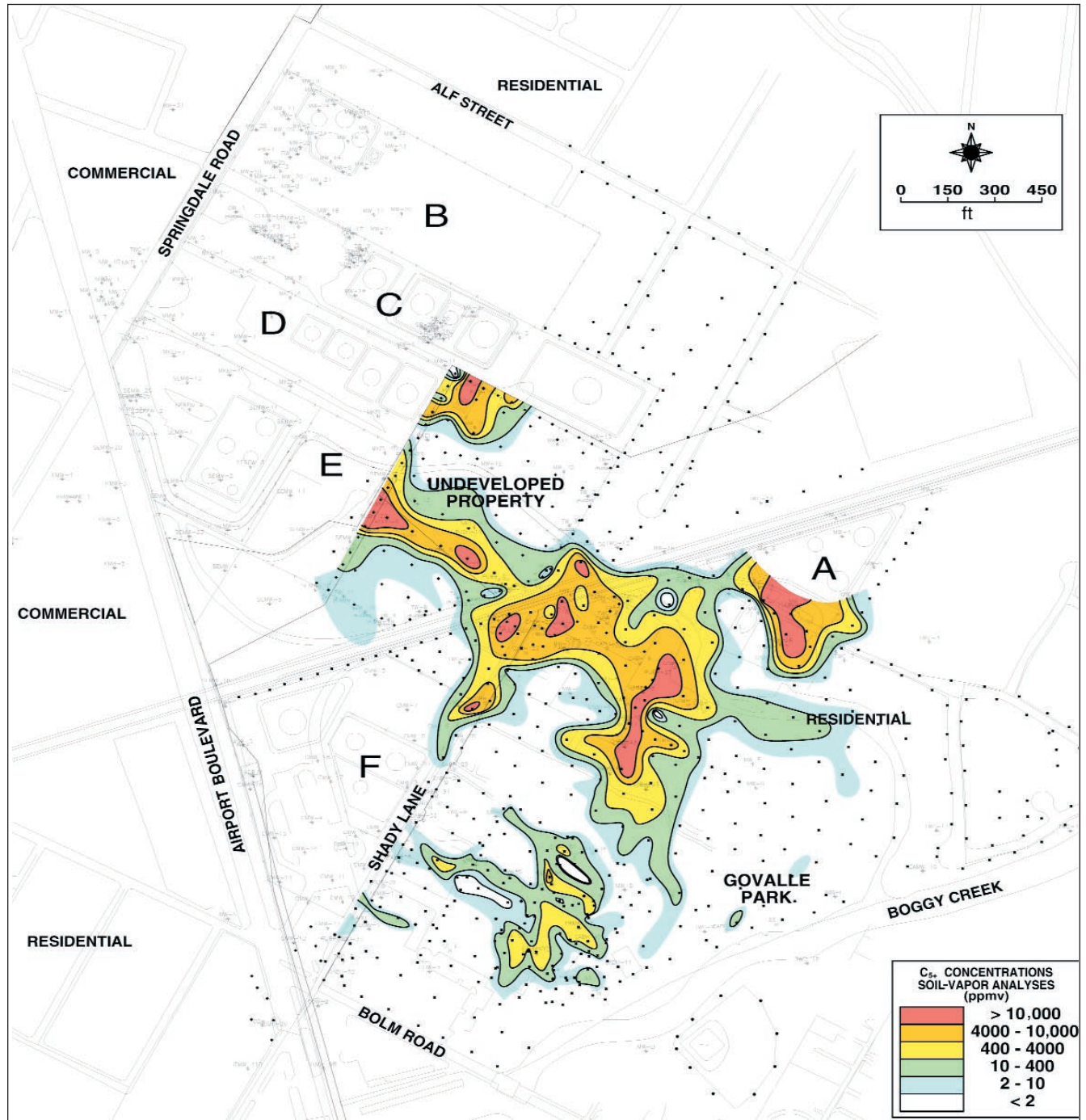


FIGURE 10. Color contour map of C₅₊ (pentane-xylenes+) soil-vapor plume.

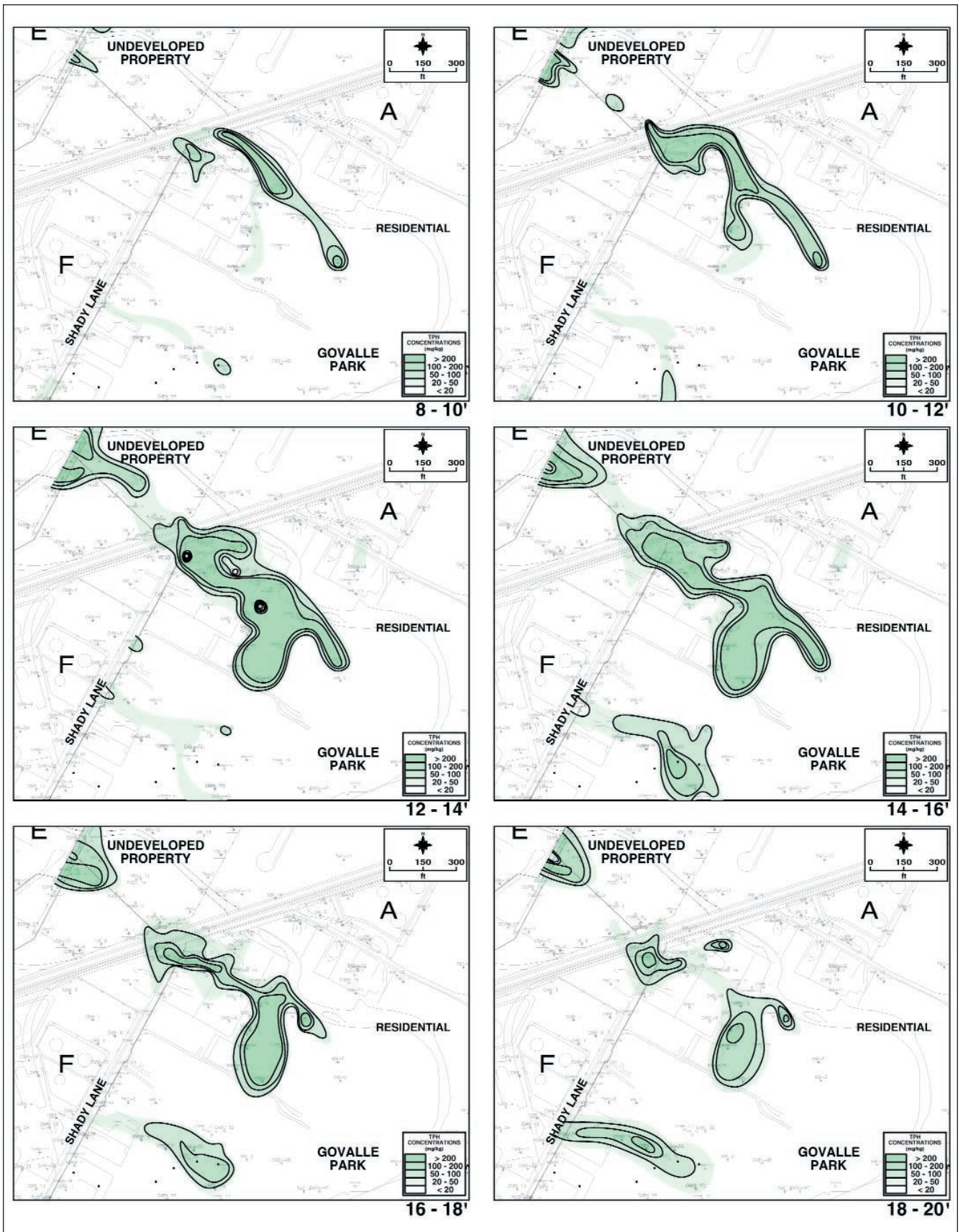


FIGURE 11. TPH screening analyses “slice” maps, showing the areal extent of TPH concentrations at various depth intervals (slices) over the interval 8 ft to 20 ft (2.4 m to 3 m) below the ground surface.

These extensive data sets clearly establish a positive link between the terminal and pipeline properties (contamination sources) and Govalle Park and private properties. 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

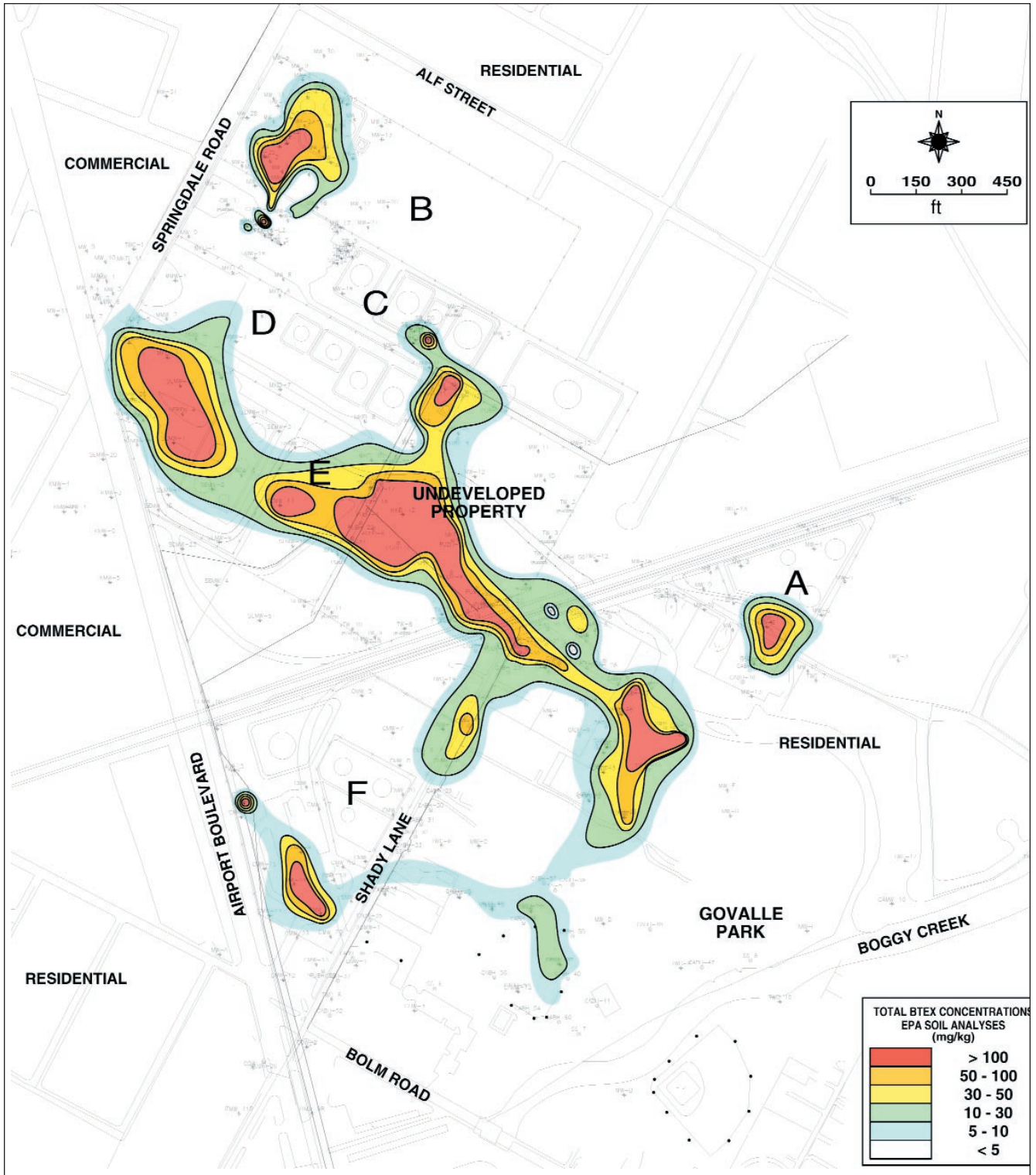


FIGURE 12. Color contour plume map of total BTEX concentrations (EPA method analyses) in soils.

analytical methods are relatively inexpensive (compared with EPA analyses) and are quite definitive in distinguishing specific petroleum products. Figure 6 shows synchronous fluorescence results of soil cores obtained from direct-push boring PUBH-23 (highlighted in Figure 1), located on the western boundary of the undeveloped property. The figure includes fluorograms (signatures) of

soil-core samples (2-ft [0.6-m] lengths) collected continuously, from 0–2 ft deep, down to the total depth of the boring (18–20 ft [5.4–6 m]). The fluorograms graphically demonstrate that subsurface contamination begins at a depth of approximately 6–8 ft (1.8–2.4 m), and the signatures indicate that the contaminants are mixtures of diesel and gasoline. These signatures continue to a depth of 12–14

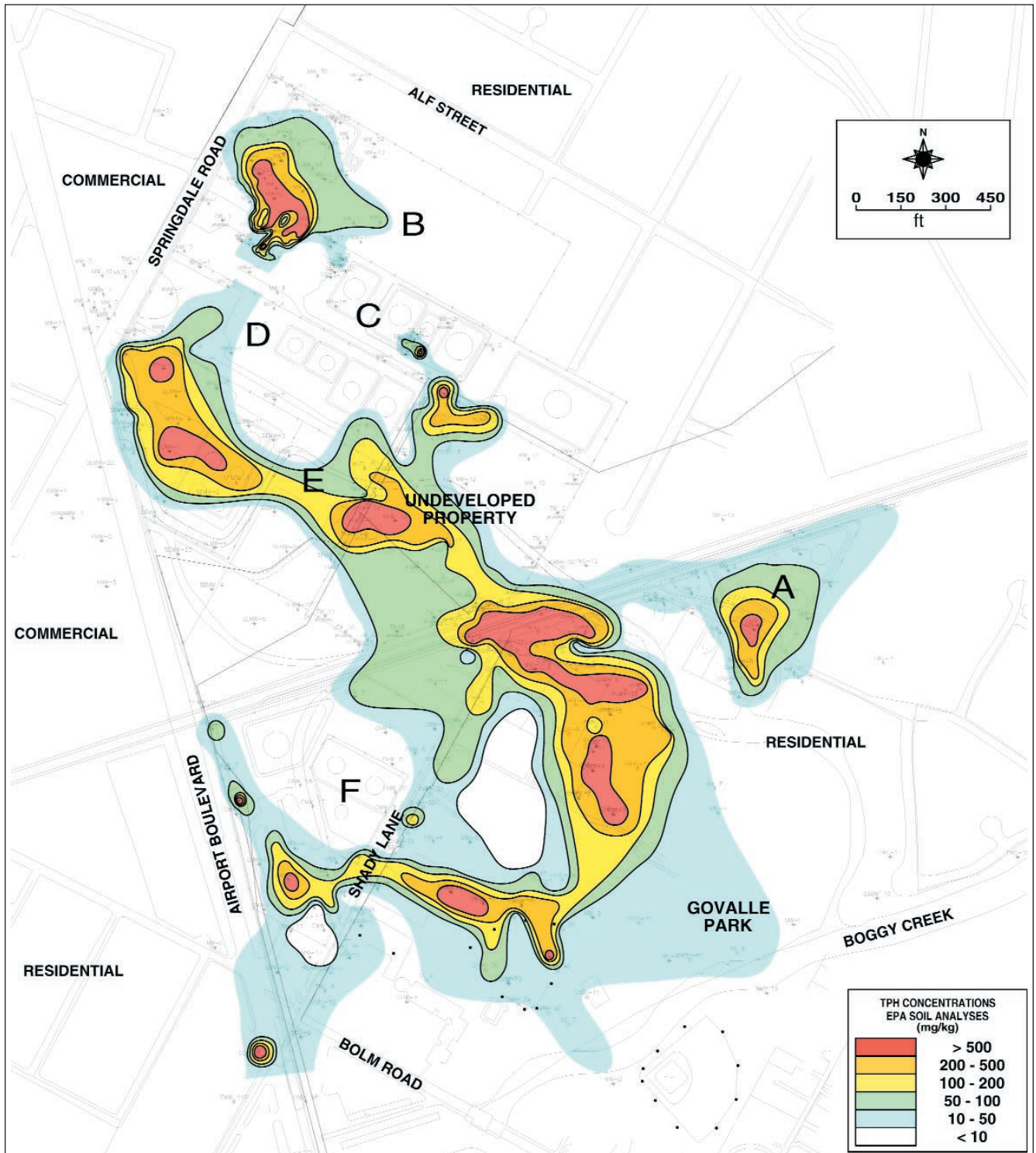


FIGURE 13. Color contour plume map of TPH concentrations (EPA method analyses) in soils.

ft (3.6–4.2 m). At 14–16 ft (4.2–4.8 m), petroleum contamination is virtually absent, as shown by the fluorograms. At a depth of 16–18 ft (4.8–5.4 m), petroleum contamination is again apparent, but the signature indicates that the product type is gasoline.

Cross section B-B' (Figure 7) shows synchronous fluo-

rescence signatures for various direct-push borings located down-gradient of the terminal and pipeline properties. The location of this cross section is shown in Figure 2. This figure illustrates how the subsurface contamination and contaminant type(s) vary with depth and location in the study area. Both Figures 6 and 7 demonstrate that the

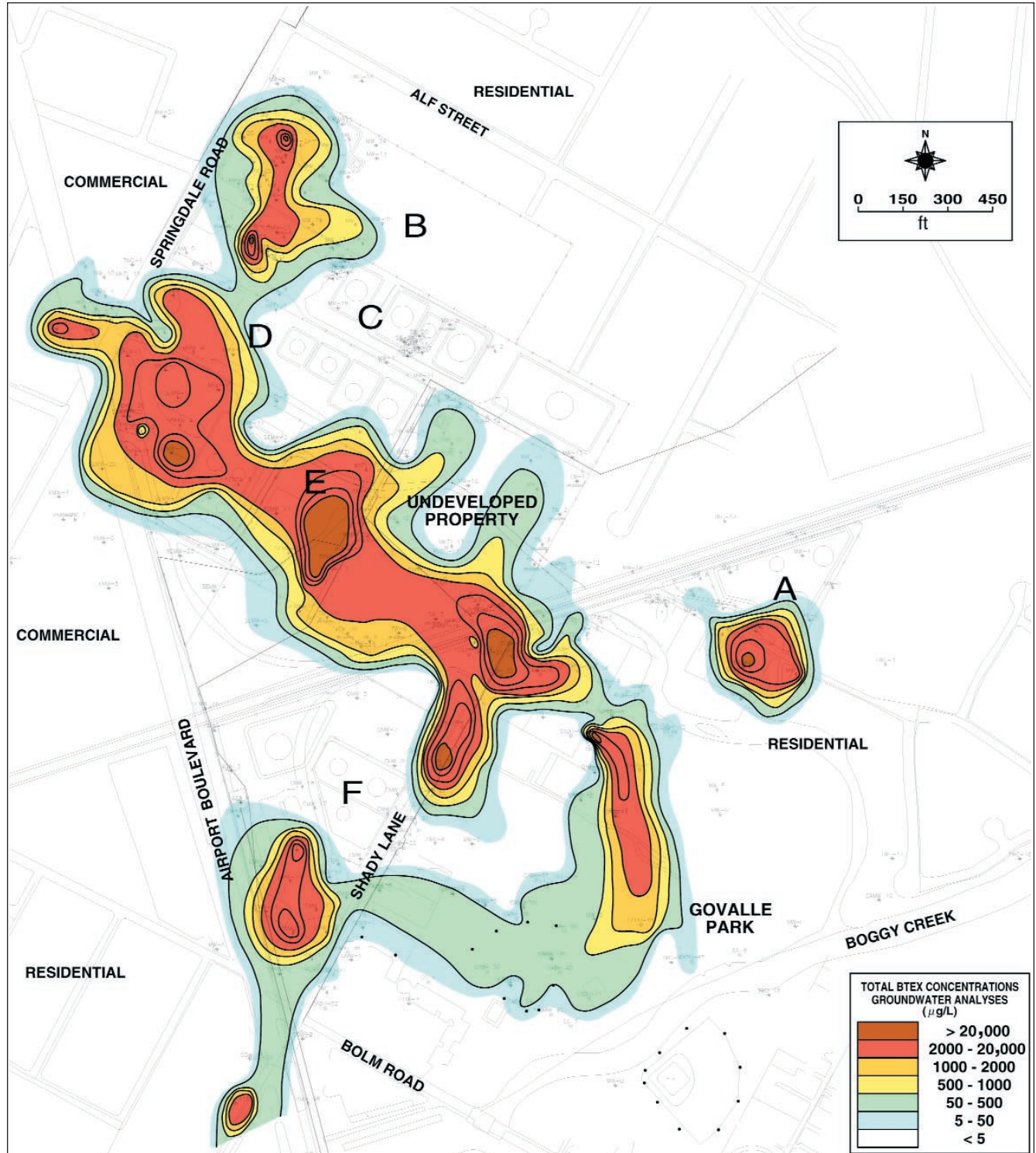


FIGURE 14. Color contour plume map of total BTEX concentrations (EPA method analyses) in groundwater.

contamination in the Austin study area is the result of multiple product releases present in distinct zones at various depths.

Based on the results of the fluorescence and CS₂ extraction/C₅₊ analyses, selected product samples were analyzed using high-resolution capillary gas chromatography (HRCGC). Product samples obtained (using a direct-push

sampling system) from site PUBH-23, between the Company E and Company C pipeline manifolds, site PUBH-16 at the south property line of the Company C undeveloped property, and sites PUBH-30 and PUBH-28 on private properties, were identified as jet fuel. Jet fuel was also identified at numerous locations in Govalle Park and on private properties (Figure 18). In addition to jet fuel, sev-

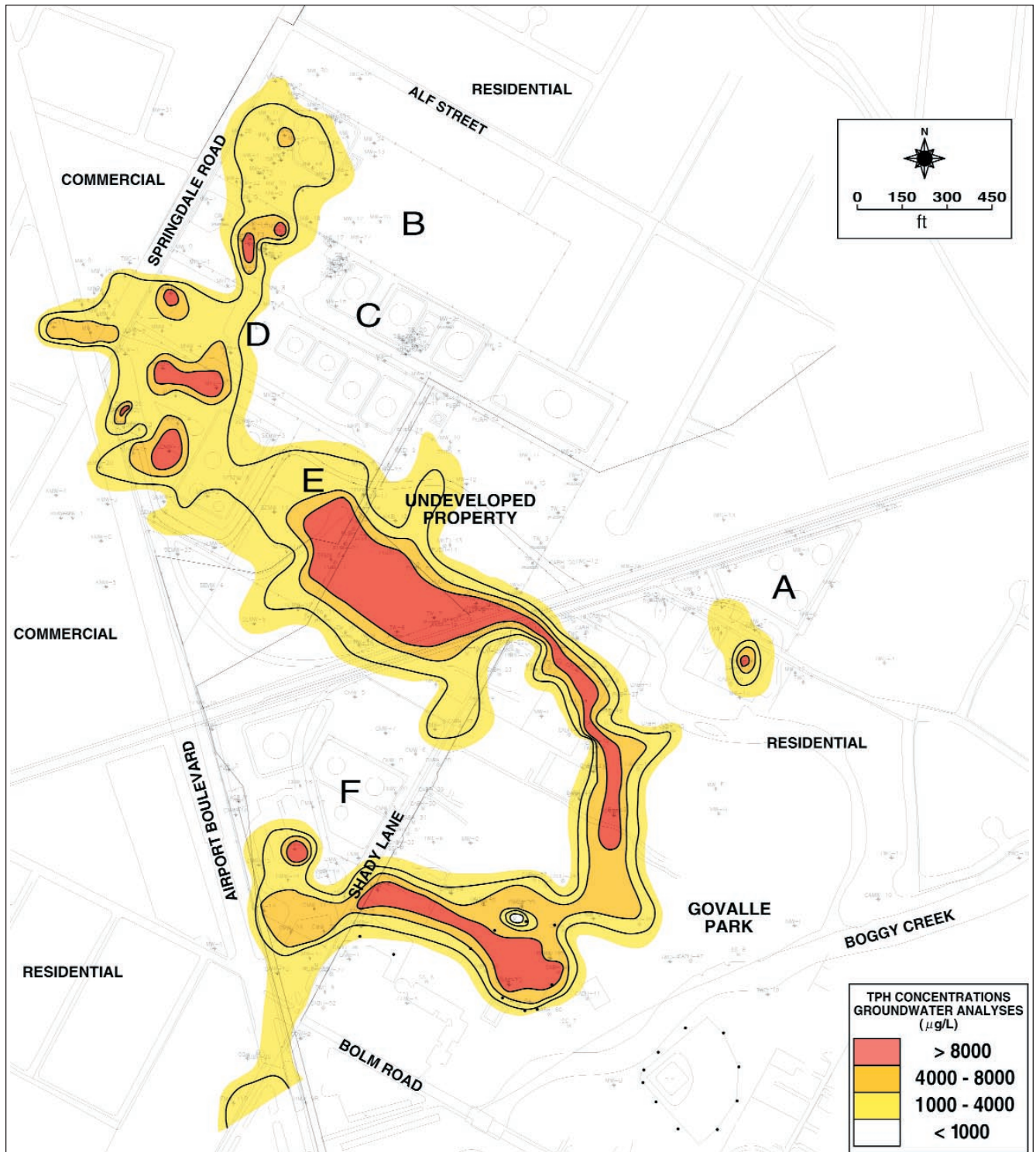


FIGURE 15. Color contour plume map of TPH concentrations (EPA method analyses) in groundwater.

eral other product types were identified, including gasoline (both leaded and unleaded), kerosene, MTBE, solvents, a heavy lubricant, and mixtures of those products.

Figure 18 shows HRCGC chromatograms of various petroleum products identified, and the locations (borings and monitoring wells) where those products were obtained. The petroleum-product types identified from liq-

uid product (NAPL) samples were also found and identified in soil and groundwater samples collected in the study area. All fingerprinting results (excluded from this paper because of space limitations) are included in the comprehensive report prepared by Exploration Technologies, Inc., and submitted to the TNRC (Exploration Technologies, Inc., 1995).

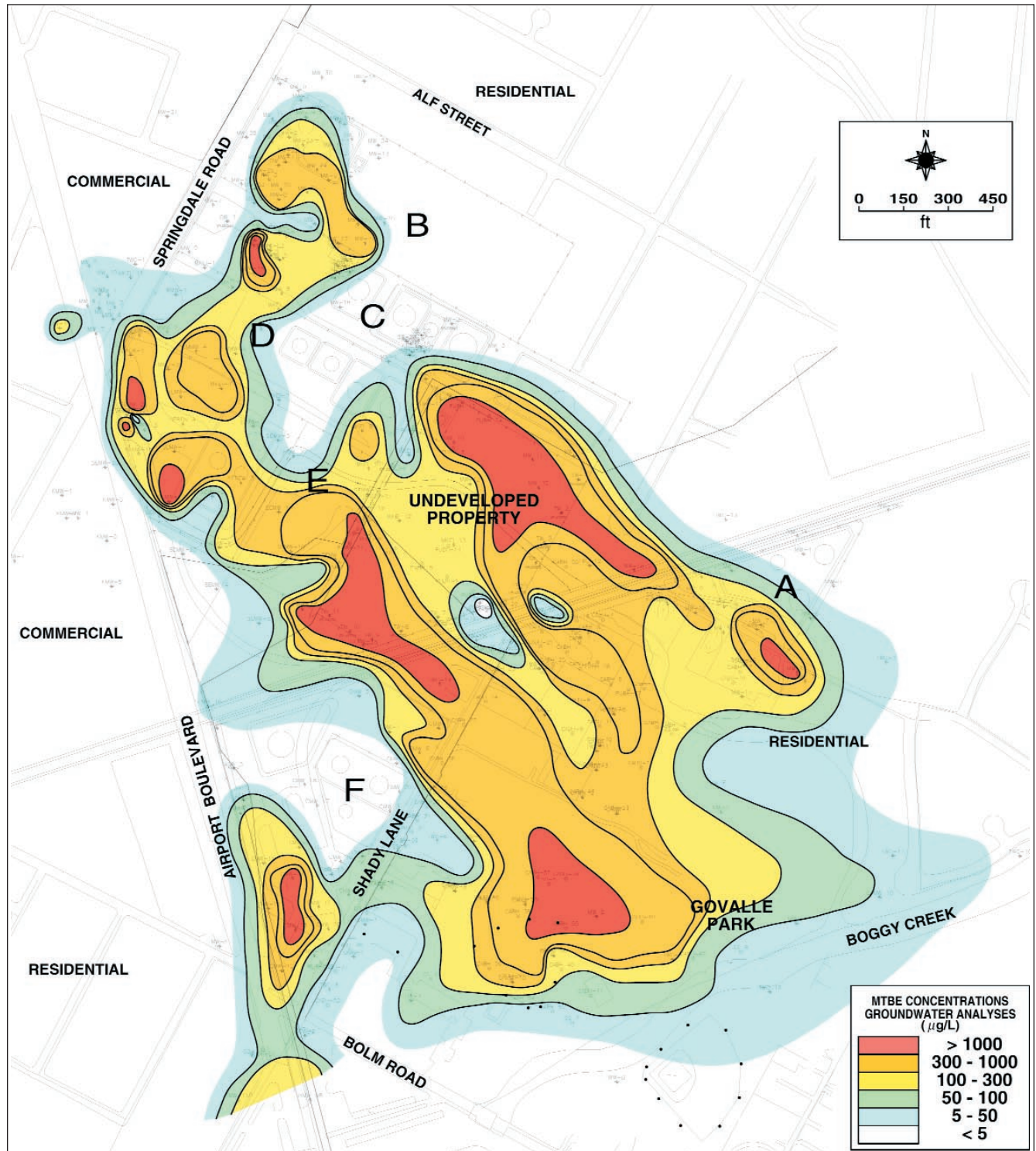


FIGURE 16. Color contour plume map of MTBE concentrations (EPA method analyses) in groundwater.

CONCLUSIONS

Several 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 city of Austin (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

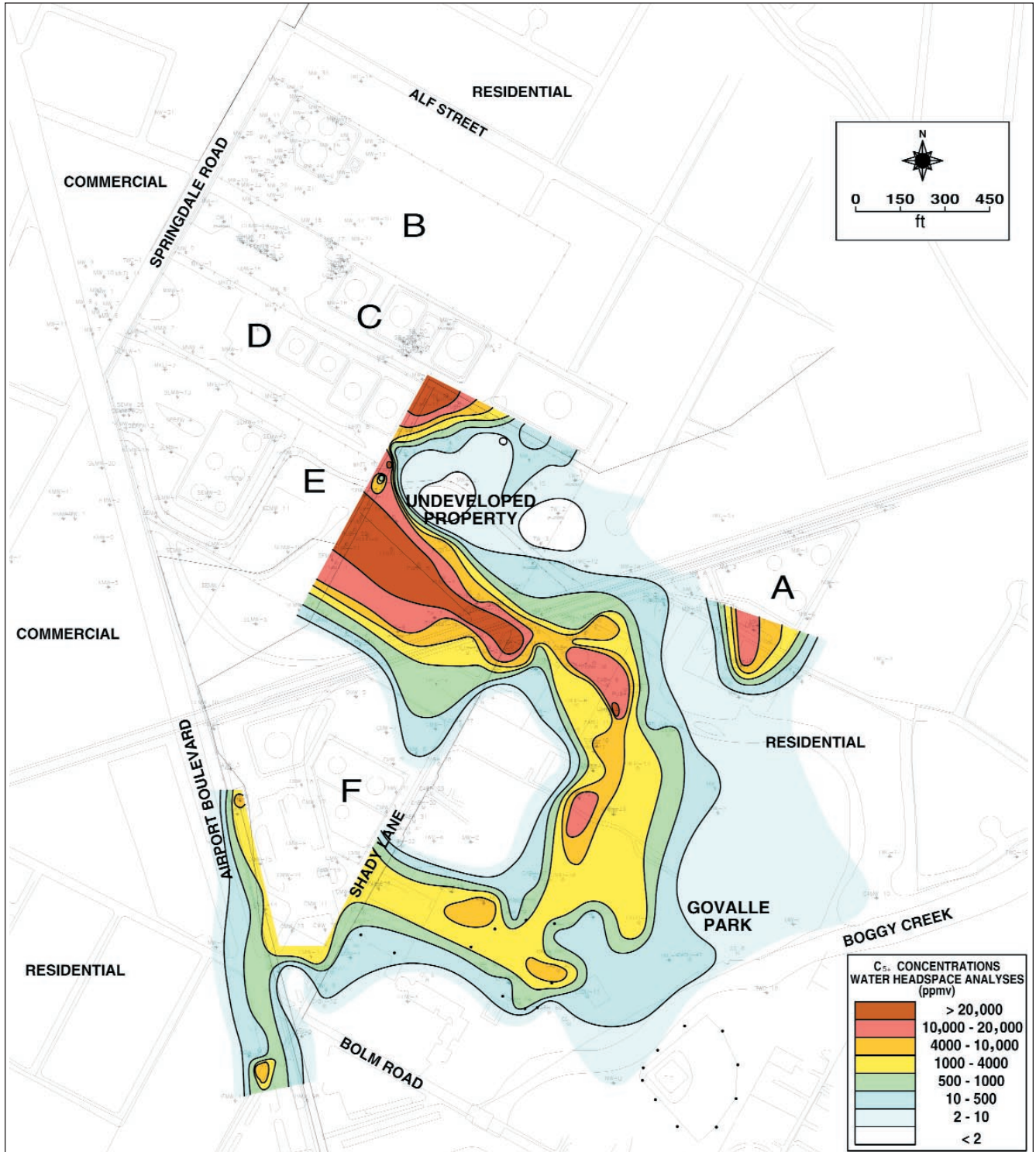


FIGURE 17. Color contour plume map of C₅+ groundwater headspace concentrations.

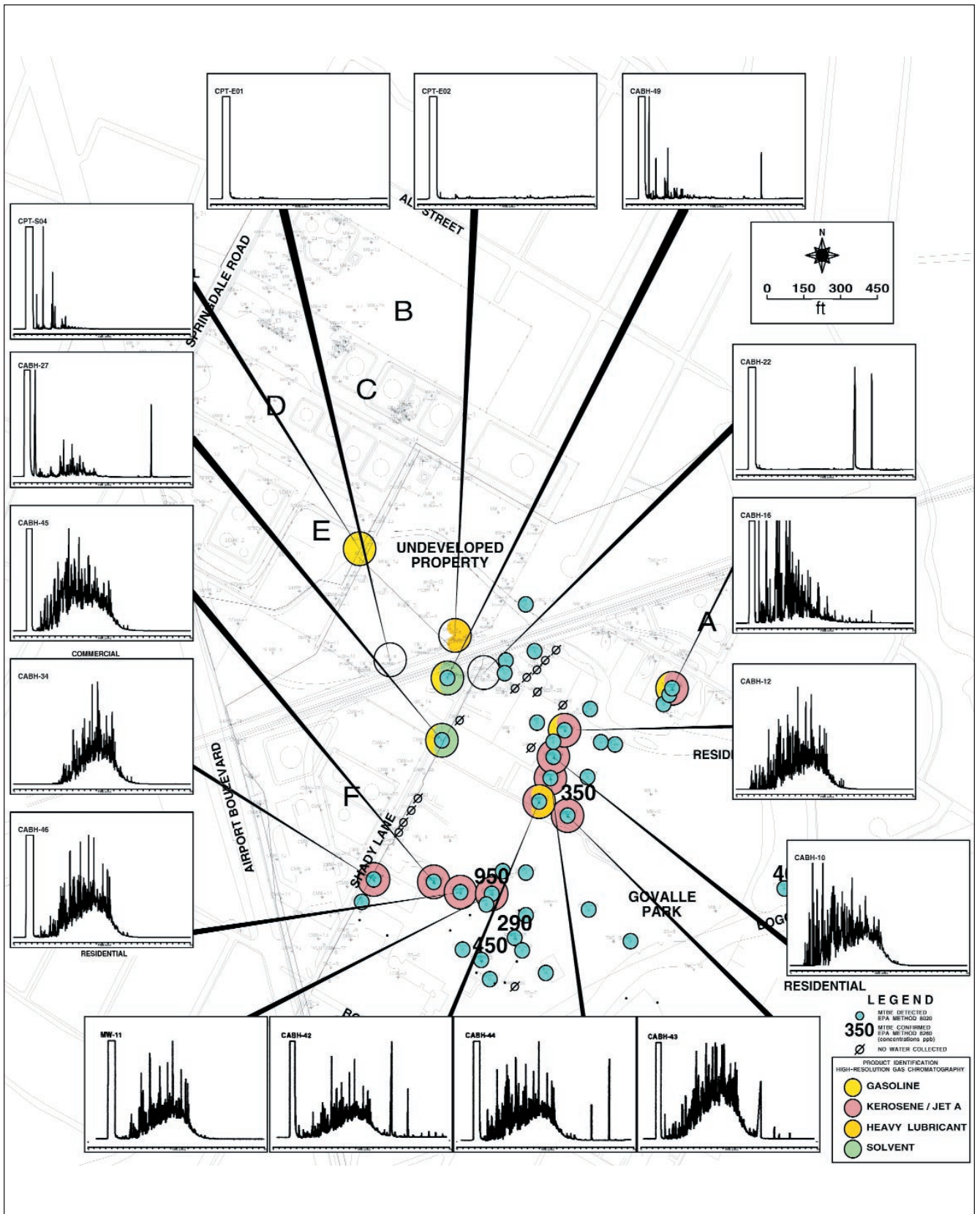


FIGURE 18. Map of study area, showing product types identified in fluid (NAPL and groundwater) samples collected from borings and monitoring wells using high-resolution capillary gas chromatography. Product types are color-coded in accordance with the legend at lower right. High-resolution capillary GC chromatogram signatures are shown for each boring and monitoring-well sample analyzed.

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 has coalesced in soils and groundwater and subsequently has migrated off-site onto public and private properties.

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 the impact of petroleum hydrocarbons on private and public properties 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 the groundwater in many areas. These soils containing sorbed- (residual-) phase hydrocarbons are and will continue to be 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, and by the elevated concentrations of dissolved-phase 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 plume (the most soluble compound present in refined petroleum products) is the largest in areal extent, measuring more than 3000 ft (900 m) in length from northwest to southeast. This plume extends more than 1800 ft (540 m) 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 that the petroleum products responsible for the contamination are gasoline, kerosene, jet fuel, diesel, solvents, and a heavy lubricant. These are essentially all the products that were handled or stored on the terminal and pipeline properties.

The ages of the petroleum products impacting Govalle Park and private properties, in some cases, exceed 20 years, based on high-resolution capillary GC analyses and historical data.

In most of the impacted parts of the study area, mixtures of different petroleum products have been identified, indicating that there have been multiple releases of hydrocarbon products.

The majority of the NAPL found in the off-site (down-gradient) wells was weathered (aged) jet fuel. Oil-company consultants did not report losses of jet fuel, primarily because such losses 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.

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