

## **ASSESSMENT OF NEAR SURFACE PETROLEUM PRODUCT CONTAMINATION PETROCHEMICAL COMPLEX (PCC) AND SURROUNDING AREAS**

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### **ABSTRACT**

All environmental assessments have one main objective, to define the horizontal and vertical distribution of subsurface contamination. Most assessments begin with the installation of water wells to determine the impact and gradient of the groundwater. This ignores the vadose zone impact, which is the avenue for product to reach the groundwater. Typically, 95% of any lost petroleum remains in the vadose zone, with less than 5% dissolved in the groundwater (Wilson and Brown, 1989). Extensive experience gathered over many years has demonstrated that petroleum products can migrate in the vadose zone as well as on the groundwater, with the vadose zone migration having little to no regard for the groundwater gradient. This paper will provide an example, where the product migrated in the vadose zone, nearly perpendicular to the groundwater gradient.

This case study conducted over a very large Petrochemical complex (PCC) demonstrates how a phased assessment approach, starting with measuring the soil gas hydrocarbon vapors derived from the lost product can be used to much more accurately define petroleum contamination and the complex subsurface geological pathways that control the migration and distribution of these petroleum products in the earth. The more volatile components (methane, ethane, propane, butanes and C<sub>5</sub>+) naturally contained within the lost product provide more definitive results than the more soluble components, such as benzene/BTEX. An additional advantage for using soil gas vapors is the reduced cost over monitor wells, allowing for much higher density sampling grids. In this case, 4072 soil gas samples were placed on a 50 ft. (15m) regional grid, with final infill (1109 sites) varying down to as close as 10 ft. (3m) in order to properly place and design recovery trenches during the remediation phase.

Using the soil gas component maps as a guide, 104 borings/monitor wells were installed and sampled on 2 foot intervals to determine the vertical contaminate distribution in the subsurface. Eighty-two (82) of these monitor wells had significant concentrations of contaminants, with 63 having up to 2 feet of liquid hydrocarbons on the ground water. Sediment core samples were analyzed on two foot intervals using multiple analysis techniques (synchronous fluorescence, in addition to BTEX and TPH), for mapping vertically distributed products. Geological coring logs were used to generate detailed geological cross-sections, and to confirm geological migration pathways, initially defined by the soil gas data.

Free product and groundwater samples were collected and analyzed from the monitor wells on a periodic basis as the free product was purged from the wells. Product thicknesses and groundwater levels were recorded and mapped. All purged free product samples and the impacted groundwater underlying the free product were analyzed for all components, including both C<sub>1</sub>-C<sub>4</sub> soil gases and benzene/BTEX components, illustrating the compositional coherence between the near-surface soil gases, the subsurface free product and the groundwater, validating and confirming the direct association and accuracy of the soil gas plumes for mapping the offsite migration avenues.

This assessment approach, using high density soil gas followed by more accurately placed monitor wells significantly aids the collection of groundwater gradients, migration pathways and barriers to groundwater flow which interrupt and control the movement of product in the subsurface. Pump tests on the wells showed the massive clays on the site limited the wells to no more than a 25 ft. capture radius. When combined with the very narrow oriented soil gas anomalies, the local geological model suggested the shallow sediments were likely dominated by narrow pathways, such as a braided stream environment laid down by the adjacent river that flows northward near the edge of the site.

Semi-continuous sampling on two foot intervals from near-surface to TD provides a more accurate determination of the vertical contaminate distribution, including coordination of soil gas anomalies to massive vadose zone migration pathways. A seven foot deep soil gas data set was used to more accurately determine pathways where interceptor/recovery trenches would be most effective. Using approximately 1109 seven foot deep samples for control, interceptor/recovery trenches, totaling 1600 feet in length, were installed and recovered over 1,300 barrels of hydrocarbon products in less than one year. Contour maps using the braided stream model provide an excellent fit for the localized nature of these vadose zone migration pathways and were used for determining the exact locations for the trenches and the locations within the trenches where product would be more easily recovered.

The PCC complex area surveyed includes an old (inactive) and an active refinery, fuel storage tanks, service stations and even leakage from deep production wells, providing a wide and complex variety of examples where compositional differences in the soil gas data can be directly related to the compositions of the lost products.

Ethylene and propylene found in shallow soil gases are currently believed to be biological degradation products generated in the shallow vadose zone from their saturated counterparts, ethane and propane under low oxygen conditions (Telegina, 1971). This extensive data set confirms their presence in large anomalous concentrations in both the soil gas and in the groundwater in contact with free products. Although their magnitudes are scattered by unknown biological factors, this data clearly shows these two olefins occur in all areas surveyed where anomalous ethane and propane are present. This is true in all contaminated areas, whether from shallow petroleum leakage, or deep production casing leakage.

This paper also provides the very first illustration of the utility for analyzing the compositions of both the free products and the groundwater underlying the free product in the monitor wells. Analysis of benzene in formation water has long been known as a proximity indicator for oil deep production wells (Zarella et al., 1967, Burtell and Jones, 1996). Typically environmental consultants only analyze the benzene in background monitor wells, but not in impacted wells. As shown by this data, analyzing the water from all wells, whether impacted or not, clearly provides a more useful and accurate picture of the contamination over the entire site, including progress made during remediation as product is purged from the wells.

Another concept introduced for environmentalists is the importance of making maximum concentration maps to further insure accurate mapping of the subsurface contaminants that better defines the horizontal extent of contamination. Typically, environmental consultants make maps of contamination measured at specific time intervals controlled by the sampling of the wells. Such maps are useful, but should never be relied on to illustrate the actual site conditions. As a well is developed and sampled, product may suddenly appear that was not present initially. Most significantly, however, if a well is lost, or becomes too damaged to sample, it is usually removed forever from the maps showing the subsurface contamination. If

the assessment is inadequate, then the remediation will extend over a very long time frame (years), with these lost wells left behind as source areas that were never remediated. Maximum maps insure these major source areas are not forgotten during the final evaluation.

Forensic geochemical methods and techniques, including high resolution capillary GC were used to fingerprint and identify the various products. All data were quality controlled and confirmed using a wide variety of analytical methods, including standard EPA methodology for comparison purposes. Synchronous fluorescence graphs illustrating the vertical changes in both magnitudes and compositions of the residual aromatic hydrocarbons found in the boreholes were generated. These work products, along with data tables and high resolution capillary chromatograms for all products are available on request, but are too voluminous to be included in this paper.

## INTRODUCTION

Environmental assessment and remediation activities are nearly always conducted in accordance with regulatory agency guidelines that unfortunately have been set by non-petroleum industry officials or committees. Environmental engineering companies never deviate from these guidelines which were selected with no regard for the complexity of either the geology or contamination. This results in assessments which 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.

Exploration geochemical methods have been developed and utilized by the petroleum industry that can be invaluable in environmental site characterizations. Evidence of leakage associated with reservoirs and environmental contamination, such as refineries, tank farms, pipelines, service stations, etc. (Jones, 1976, Jones and Thune, 1982, Jones and Drozd, 1983, Jones and Burtell, 1994, Jones et al., 1996, Jones, 1997, Jones and Agostino, 1998, Jones and Burtell, 1998, Jones 1998, Jones and Agostino, 1999, Jones et al., 2000, Jones and Agostino, 2001, Jones and Agostino, 2002, Jones et al., 2002, Jones and LeBlanc, 2004 LeBlanc and Jones 2004). These studies have demonstrated the usefulness of natural methane through butanes and pentane plus C<sub>5</sub>+ hydrocarbons for using near-surface seepage to define and map petroleum from all sources, from deep reservoirs to underground storage reservoirs, pipelines, and many other petroleum storage facilities.

Information that must be integrated with analytical data to characterize a site includes historical data in addition to 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 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.

This case study demonstrates various unconventional (standard petroleum industry, but non-EPA) methods and techniques used to delineate the areal and vertical extent of subsurface contamination, such as 1) high density soil gas using components entrained in the petroleum product as indicators, 2) placement of an adequate number of monitor wells using the soil gas as a guide and analyzing both the free product and the water under the product to provide complete coverage of both the contaminated and background areas, 3) analyzing a semi-continuous analysis of vertical cores on no less than two foot centers using multiple methods (in this case Synchronous Fluorescence plus BTEX and TPH) providing data for defining the vertical distribution of the contamination, 4) understanding and accurately mapping subsurface geology and hydrogeology in the study area, 5) using forensic geochemistry to identify residual, dissolved and free (NAPL) phase contamination, 6) generation of maximum concentration maps for both free product and groundwater concentrations and 7) confirmation of olefins (ethylene,

propylene) generated from petroleum products in both the vadose zone and in the impacted groundwater.

## **Statement of the Problem:**

During the paving of a residential street in an area adjacent to a very large petroleum complex, gasoline contamination was detected within three feet of the surface near the intersection of First Street and B Avenue (see Figure-1). In response, the PCC collected and analyzed water samples from 17 water wells located in the neighborhood and installed 4 new monitor wells in the neighborhood and 10 within the PCC complex in order to determine the groundwater gradient and source of the offsite gasoline contamination. The groundwater gradient is marked by arrows on Figure-1, along with the wells sampled; blue dots mark the clean wells and red dots mark the wells containing visual contamination. Three additional wells were installed along with a trench on the PCC property south of main and Avenue B, since this is the closest location on the PCC property to the gasoline found on First Street. Given no obvious up gradient source, the PCC asked ETI for assistance.

After reviewing the situation, it was obvious that a soil gas survey would provide the most effective and cost efficient approach for mapping the pathways to the offsite gasoline source. Once the shallow vadose zone contamination was defined by the soil gas contour maps, boreholes and monitor wells were installed to determine the vertical extent of the contamination and the groundwater impact.

## **Explosive Gases in the Sewers**

In conjunction with the initial soil gas survey, explosive meter measurements were taken in the manholes along the industrial drains crossing the PCC. Explosive levels of combustible gases were detected in these drains. Based on the initial soil gas and explosive meter results, the PCC requested an extension of the soil gas survey into the PCC and other adjacent areas, ultimately providing a total of 4072 four foot deep soil gas measurements, plus 208 gas samples from existing manholes and sewers. Later, during the remediation phase 1109 seven foot deep soil gas measurements were added to better define the exact location for product recovery trenches.

## **Topography and Local Geology:**

Topography in the study area, as shown in Figure-1 slopes gently to the north and northwest, with the terminal and PCC facilities being topographically higher than the residential areas to the north. A slight high along Main Street east of Avenue A could be natural, or may be related to building up the roadway above the swampy areas that previously existed where the neighborhood was built. Highlands to the east and southeast of the city provide approximately 150 m of relief and consist of Oligocene sedimentary rocks capped by basalts. Drainage from the highlands in the vicinity of the PCC facilities would naturally be directed to the northwest and west towards the river which passes by the west side of the PCC complex. Most of the site is on the river floodplain, with the PCC complex being on the eastern edge of this floodplain, thus naturally providing a northwest gradient for the groundwater.

The upper 20 ft (6 m) of sedimentary deposits in the study area consist of fluvial clays, argillaceous clays, silts and sands, gravels, and matrix-supported conglomerates of Quaternary age. Sorting is poor, grain size generally increases with depth, and lithology may vary rapidly vertically and horizontally. The variations are typical of floodplains and deposition by braided streams with narrow channels 10-100 ft (3-30 m) wide likely to be present. Along First Street, a black clay immediately underlies the surface fill under the street. The clay is thicker to the east

and thins to the west. Residents have said the area is built on a filled-in swamp, which probably was a back swamp on the River floodplain. Underlying the black clay there is a gray-green clay that occurs throughout the PCC facility south of Main Street.

Around and south of the PCC complex, a northwest-southeast trend is likely from distal fan deposits derived from the highlands southeast of the PCC. Farther west, lithological trends are likely northeast-southwest, due to floodplain deposits laid down over the past few hundred years. With the study area located along the margin of the floodplain, it is logical for fans and other depositional systems to have entered and modified the margins of the floodplain. Clays, silts, sands, and matrix-supported conglomerates from both the river floodplain and distal fan deposits would be expected to be discontinuous along depositional strike and continuous along depositional dip.

### Hydrology

Ground water is generally encountered at depths of 8-18 ft (2.40-5.50 m) in wells throughout the study area. Water-bearing units are variable, consisting of thin argillaceous silts and sands and matrix-supported gravel. Data obtained from monitor wells and pump tests show that aquifer porosity, permeability, and transmissibility are low. Impermeable clays between the aquifer and the surface, seal the aquifer and cause it to be locally confined. A hydraulic head is apparent since static ground water levels in monitor wells are several feet higher than the depths at which water is first encountered during drilling.

### Methodology: Soil Gases

Soil gas samples were collected on an approximate 50 ft. (15m) grid over the PCC property and in the neighborhood. Location maps for the four and seven foot deep soil gas data are shown on Plate-1a and Plate-1b, respectively. At each sampling location, a 0.5 inch (13 mm) diameter rod with a slide hammer was driven into the soil to a depth of 4 or 7 ft (120 – 213 cm). Once the pounder bar was at the required depth, it was extracted from the soil and immediately replaced with a 0.5 inch (13 mm) diameter vapor sampling probe. In instances where hard layers or shallow ground water were encountered and prevented sample collection at the desired depth, samples were taken at depths less than 4 feet. An evacuated 125 cc septum top glass bottle was attached to the probe and filled with a soil gas sample. An additional 30 cc of soil gas were extracted from the soil through the probe and added to each bottle to create a positive pressure within the bottle and provide an adequate volume of sample for geochemical analyses. Vapor collection probes were decontaminated between each sample by injecting Alconox detergent and distilled water through the probe, rinsing with distilled water, and then purging with compressed air. Blank (reference) samples of ambient air were collected through the probe at approximately ten percent of the sampling sites to ensure no cross-contamination between samples occurred.

Soil gas samples were sent to Exploration Technologies, Inc.'s Houston, Texas laboratory and analyzed by flame ionization detector (FID) gas chromatography to determine C<sub>1</sub>-C<sub>4</sub> (methane, ethane, ethylene, propane, propylene and iso and normal butanes) and C<sub>5</sub>+ (gasoline range) hydrocarbons concentrations. Methane, ethane, propane, and butanes occur in varying concentrations in many petroleum products, and allow for the identification and differentiation of natural gas, biogenic methane, gasoline, and other refined petroleum products. Light hydrocarbon analyses (C<sub>1</sub>-C<sub>4</sub>) measure the lightest, most volatile constituents, which tend to dissipate rapidly with time and/or distance from point(s) of introduction into the subsurface.

C<sub>5</sub>+ hydrocarbons are a quantitative measure of gasoline range vapors in near-surface soils and dissipate more slowly than lighter C<sub>1</sub>-C<sub>4</sub> compounds. Because large numbers of hydrocarbon compounds are present in gasoline and other heavier petroleum products, C<sub>5</sub>+ analyses are grouped for reporting purposes according to the relative boiling points of the various compounds: pentane-benzene, benzene-toluene, toluene-xylene, and xylenes+. Laboratory results of all hydrocarbon compounds analyzed are given in parts per million in Table-1a and Table-1b for the four foot and seven foot data, respectively (data Tables available on request). Posted contour maps for the four foot soil gas data are included as Plates-(2 through 9) for all components.

### **Methodology: Borehole Drilling, Analysis and Monitor Well Installation**

A total of 106 bore holes were drilled with a truck-mounted, Mayhew-1000 drilling rig equipped with 10.25 inch (26 cm) OD hollow-stem augers. Split-spoon core barrels pushed in advance of the augers provided continuous core samples from which the sediments were gathered and described. A composite soil sample was collected from each 2 ft (60 cm) cored interval, starting below the concrete/asphalt surface. Samples were placed in 4 oz (120 cc) jars sealed with Teflon-lined lids and immediately placed on ice. ETI analyzed the soil samples from each well for BTEX (benzene, toluene, ethylbenzene and xylenes) and TPH (total petroleum hydrocarbons) concentrations using ETI's proprietary screening instruments located on site at the terminal. The samples were subsequently shipped to ETI's Houston laboratory for U.S. Environmental Protection Agency (EPA) method laboratory analyses. Split-spoon core barrels were cleaned between each 2 ft core with Alconox and water followed by a distilled water rinse to eliminate the possibility of cross-contamination between samples.

Soil samples collected from the cores were analyzed in the field for BTEX and TPH using ETI's proprietary B-TEX 9000™ and TPH418S™ field screening instruments. The B-TEX 9000™ derivative ultra-violet spectrometer heats a 10 gram soil sample, driving off the volatile hydrocarbons, and then senses the unique molecular absorption of ultra-violet radiation characteristic of aromatic hydrocarbons.

Samples were screened for TPH by dissolving non-volatile hydrocarbons from the soils in Freon and analyzing the solution with a fixed wavelength infrared spectrometer to measure the amount of hydrocarbons in solution. The procedure is similar to the EPA Method 418.1 used for total petroleum hydrocarbon analyses, except the extraction procedure is faster.

Screened soil samples with the highest BTEX and TPH concentrations were analyzed by ETI in Houston using EPA methodology. BTEX analyses of soils were performed in accordance with EPA Method 8020/5030. The analyses included purge and trap and chromatographic separation of various compounds and measuring the quantity of gasoline range (aromatic) hydrocarbons. Results are calculated as micrograms/kilogram or parts per billion (ppb).

TPH analyses of soils were performed in accordance with EPA Method 418.1, which measures the quantity of heavier molecular weight hydrocarbons in petroleum products. TPH results are calculated as milligrams/kilogram or parts per million (ppm).

EPA method laboratory analyses of soil core samples were consistent with and confirmed the field screening results. Total BTEX concentrations in excess of the TWC allowable limit of 30 ppm generally coincided with monitor wells having TPH concentrations in excess of the TWC regulatory limit of 100 ppm.



The highest concentrations of BTEX and TPH occurred at depths of 4-10 feet in each monitor well, indicating extensive vadose zone contamination, consistent with contaminant zones observed during drilling operations. High levels of BTEX and TPH also occurred in water-saturated soils.

### **Analysis of Borehole Soils using Synchronous Fluorescence**

Synchronous fluorescence analyses were performed on soil core samples collected during drilling operations to directly measure aromatic hydrocarbon compounds in gasoline, diesel, kerosene, and other petroleum products. See Agostino, P.N., R.J. LeBlanc, Jr., V.T. Jones, III, 2002, for details on methodology and calibration on Synchronous Fluorescence. These additional analyses provided additional information on the type of petroleum products present in the near-surface sediments within the contaminated areas, indicating heavier molecular weight petroleum products that were possibly derived from releases of crude oil, fuel oils, and diesel products refined and/or stored on the PCC facilities over an extended time frame.

The synchronous fluorescence indicated the soil contamination was the result of liquid hydrocarbons present in multiple layers within the vadose zone and the underlying ground water. Dissolved phase hydrocarbons present in the ground water likely results from various petroleum product spills and/or leaks on the PCC facilities.

Although synchronous fluorescence can highlight anomalous areas and show the general range of hydrocarbon compounds present, it cannot identify specific products. It provides a vertical distribution of types of products contained in the soil core samples from each monitor well, and is used to select samples for detailed analyses by more expensive, high resolution capillary gas chromatography.

### **Ground Water Assessment, Monitor Well Completions**

A total of 104 ground water monitor wells were installed to establish the ground water gradient and serve as permanent ground water sampling locations. Location for all monitor wells are shown on Plate-1c.

Monitor wells were completed at depths of 14-24 ft (4.27-7.32 m), and contain 10 or 15 ft (3.05 or 4.57 m) sections of 4 inch (10 cm) diameter 0.10 or 0.20 inch (2.54 or 5.08 mm) schedule 40 PVC slotted screen. Each well has 5-10 ft (1.52-3.05 m) of slotted screen below and a minimum of 5 ft of slotted screen above the water-saturated zone. The annular space in each well is filled with silica sand from total depth to approximately 2 ft (60 cm) above the top of the slotted screen. Bentonite powder seals the annulus to approximately 2-3 ft (60-90 cm) below the ground surface, with the remaining annular space having a concrete/bentonite mix. Each well has a flush-mounted steel manhole installed at the ground surface with a removable steel cover marked "Monitor Well".

### **Monitor Well Water Level Measurements, Product Recovery and Groundwater Sample Collection**

Static ground water levels in all monitor wells were periodically measured using an ORS interface probe. Water levels are subtracted from the casing elevation of the respective monitor

wells to determine ground water elevations. Free product is bailed and removed from the well. Several casing volumes of water were bailed from each well, prior to sampling, to remove all suspended sediment and ensure that a fresh ground water sample was obtained from the aquifer. After the wells were allowed to recharge, a disposable bailer was used to collect three water samples from wells not containing liquid hydrocarbons. Two 40 ml VOA vials were overfilled to obtain an inverted meniscus, sealed with a Teflon-lined septum, and checked to ensure that no headspace was present in the vials. These primary and backup samples were used for EPA method BTEX analyses. A third water sample was collected in a one liter glass jar, sealed with a Teflon-lined lid, and utilized for EPA method TPH analysis. Samples were immediately placed on ice following collection and shipped to ETI's Houston laboratory for analysis.

Water samples were also collected from the oil-water separator effluent, streams, and river in the study area and analyzed for BTEX and TPH.

Ground water elevations were corrected for the thickness of liquid hydrocarbons in those wells containing free product and used to construct potentiometric surface maps. The ground water gradient in the study area is generally to the north and northwest. Groundwater elevation and product thickness data is listed in Table-2 and available on request.

Benzene, toluene, ethylbenzene and xylenes (BTEX) analyses of ground water samples were performed in accordance with EPA Method 8020/602 which includes purge and trap and chromatographic separation of various compounds. EPA BTEX results are included in Table-3, and is available on request. The method measures the quantity of gasoline range (aromatic) hydrocarbons in the samples, with the results given in micrograms/liter (ppb). Total petroleum hydrocarbons (TPH) analyses of ground water samples were performed in accordance with EPA Method 418.1 to measure the quantity of heavier fraction hydrocarbons in petroleum products. TPH results are given in milligrams/liter (ppm).

#### **Analyses of Recovered Free Products for C<sub>1</sub>-C<sub>4</sub> and C<sub>5</sub>+ Gases**

Product samples collected from monitor wells were analyzed for light C<sub>1</sub>-C<sub>4</sub> and C<sub>5</sub>+ gases, in addition to high resolution capillary GC to better calibrate and correlate the gases analyzed from the soil gas survey. Product headspace data is included in Table-4 (available on request). Although comparison is somewhat hampered by the lower density of the monitor wells as compared to the soil gas samples, compositional variations and magnitude variations exhibit obvious changes that show the soil gases are linked to the recovered products.

#### **Dissolved Gas Analyses from Monitor Wells**

Water samples were also collected below floating product in monitor wells containing liquid phase hydrocarbons. Although larger concentrations of dissolved gases are present in waters collected below product, the objective is to locate the product(s) and compare relative component concentrations that can provide a significant improvement to mapping the distribution of the lost products and for distinguishing individual products. These water samples were analyzed for methane through butanes, C<sub>5</sub>+ and for BTEX using EPA methodology. Headspace groundwater data for EPA BTEX is in Table-3 and methane through butanes and C<sub>5</sub>+ data are included in Table-5.

## Results and Discussion:

### Delineation of Shallow Migration Pathways Using Soil Gas Methodology

Soil gas data is presented in three formats; posted contour maps Plates-(2 through 9), composite contour maps Figures-(2a through 2h) and color dot maps Figures-(3a through 3h) in order to define both the vadose zone migration pathways and the compositions of the associated subsurface petroleum products. Magnitudes for all components vary from background (methane < 2.00 ppmv and ethane plus < 0.030 ppmv) to percent levels. Although methane (Plate-2, Figure-2a) appears to be very extensive, with over seven percent of the methane concentrations exceeding 200,000 ppmv (20%); contours suggest the presence and outline of many narrow migration pathways. A comparison with the heavier ethane plus components Plates-(2 through 9) and Figures-(2a through 2h) shows a high degree of correlation, indicating a positive association with petroleum based contaminants, regardless of whether the methane is deep thermogenic or shallow biogenic. The brown dots in Figure-3a marking methane/ethane ratios greater than 100 suggests most of the methane is likely biogenic gas generated from shallow petroleum contamination, with the exception of the area near the deep production wells where red and yellow dots mark sites having methane/ethane ratios below 100, indicative of mixing with mature, deep source methane from a reservoir.

The largest cluster of soil gas anomalies cover most of the PCC Complex, which contains product storage tanks, loading terminals and an active refinery. The second largest cluster is obviously associated with the service station and inactive refinery in the southeastern corner of the survey area. The third much smaller cluster located west of Avenue A in the northwest corner of the survey area is unique in both aerial extent and composition due to the presence of larger ethane and propane magnitudes associated with casing leakage of deep source reservoir gases from the four production wells.

Ethane, propane and butane, which are not of biogenic origin also provide a way to distinguish not only deep thermal gases, but also leakage associated with petroleum fuels and other refinery based products (Jones and Drozd, 1983, Jones and Agostino, 1998). Deep thermal gas sources almost always have ethane > propane > butanes, whereas refined products such as gasoline have an inverse relationship where butanes > propane > ethane (Agostino, LeBlanc and Jones, 2002). End members for demonstrating these differences between deep thermal gases versus a gasoline type fuel are clearly defined by comparing the largest magnitude ethane from the plume surrounding the four production wells (site 1597) with the largest magnitude n-butane from the anomalies found in the PCC office building parking lot (site 31). Their concentrations in ppmv at these two sites are:

#### Casing Leakage

| Site No. | Methane | Ethane | Propane | n-Butane |
|----------|---------|--------|---------|----------|
| 1597     | 480,841 | 29,839 | 9,160   | 1,429    |

#### PCC Office Parking Lot

|    |         |     |     |        |
|----|---------|-----|-----|--------|
| 31 | 383,090 | 375 | 991 | 59,930 |
|----|---------|-----|-----|--------|

As shown by Figures-(3b through 3h), the concentration of ethane and/or propane relative to the butanes further defines and confirms the differences between natural (deep production) and refined fuel and/or refinery products. Site 31, has the distinction of having the largest magnitude n-butane, yet also, has the second largest magnitude C<sub>5</sub>+ of 44,894 ppmv. This site located in

the PCC parking lot north of the main office building was selected for the first monitor wells (MW-101 and MW-102) installed, and flowed gasoline onto the surface when drilled, confirming the presence of northward migration of gasoline in the vadose zone at the edge of the PCC property. As shown by Figures-(2b through 2h), with the exception of a few sites along First Street, all n-butane and C<sub>5</sub>+ concentrations greater than 10,000 ppmv occur within the PCC complex, or near the service stations. These two components also clearly define two major offsite migration pathways which connect the PCC complex to First Street within the residential area. The easternmost plume shows the gasoline contamination extends south, under the office building towards a group of four gasoline storage tanks, suggesting a likely source. This link is strongly reinforced by the propane contour maps (see Plate-4, Figure-2c), which also focuses on this gasoline storage tank area. It is significant to note that site 31 has the largest magnitude propane value (991 ppmv) outside of the deep mature gases migrating upwards from the deep production wells. Such a large propane concentration located under the parking lot in front of the PCC office building suggests this area is acting as a secondary source for the gasoline recovered near the First Street and B Street intersection.

A second plume of n-butane and C<sub>5</sub>+ gases lies further west, exiting the PCC complex near the intersection of Main and A Streets. This more extensive plume extends back into the PCC refinery, indicating likely sourcing from both the refinery and the storage tanks south of the office building. The lack of propane and dominance of n-butane and C<sub>5</sub>+ hydrocarbons in the updip portion of this second plume suggests the sourcing from the active refinery likely includes a more weathered (or volatilized) gasoline along with heavier refinery based products as the main C<sub>5</sub>+ components in this plume.

Soil vapor component concentrations depend on the volatility of the hydrocarbons within the fuel contaminate present and the degree of weathering of the hydrocarbons. With the exception of diffusion, light hydrocarbon vapors do not migrate laterally away from their liquid fuel source(s). Experience has shown the dissolved gases in liquid fuels migrate with the liquid fuel and are maintained, somewhat as a buffer like water vapor is maintained by liquid water, as the contaminant migrates through the earth. These volatile hydrocarbons migrate vertically in the vadose zone, disappearing rapidly without recharge from a fuel source. Thus, the presence of significant concentrations of ethane, propane and butanes in the shallow (four foot deep) soil gas vapors cannot be maintained without a source.

The volatility of propane makes it particularly noteworthy as a trace gas indicator due to its presence in both deep natural gases and as a trace component in gasoline. As shown by Plate-4 and Figure-2c, the largest propane contours (red, orange and yellow, above 25 ppmv) are focused within small areas, outlining three major areas of concern, the PCC complex, the larger service station and the four deep Cretaceous production wells.

Propane contours over the PCC complex indicate the gasoline on First Street was sourced mainly from the storage tanks rather than from the refinery. The service stations exhibit fairly large magnitude plumes which are mostly confined to the service station, with little contribution from the old refinery, and with essentially no offsite migration, and finally, the east-west plume that extends along Third Street appears to originate from the deep production well casing leakage area. This association with production gases rather than fuel products is confirmed by the relative concentrations of ethane > propane > n-butane along the Third Street plume.

Although some of these vapor migration pathways are likely following geologically defined permeability channels in the shallow subsurface, there is also a possibility for product to migrate along man-made permeability channels. All the soil gas maps Figures-(2a through 2h) and

Figures-(3a through 3h) contain anomalies that follow streets in the adjacent residential area (First Street, Third Street, Main Street) and in the PCC complex. There is bias in contours due to the samples being confined to the streets, in addition to the fact, the conduits in the streets for water, sewers, and pipelines can preferentially carry the contaminants laterally along these manmade permeability channels. Water and power line conduits can also provide migration away from the streets into the residences. The sewer manholes along First Street and the adjoining streets were sampled as part of the initial soil gas survey. Gasoline type vapors detected in the sewer manholes were consistent with the subsurface plumes located by the regional soil gas survey and monitor wells, making the sewers a danger to the local residents, even though they did not appear to be the main migration conduits for the gasoline liquids.

Within the PCC complex, industrial drains that connect storage tank farms and other areas to the separator appear to be sources of long-time hydrocarbon leakage. Petroleum products apparently continue to leak from the drains because all constituents (C<sub>1</sub>-C<sub>5</sub>+) have anomalous concentrations along the drainage trends. In addition, pluvial drains in the PCC facility are also very likely sources of contamination. Spills in areas not served by industrial drains wash into the pluvial drains during rains, and leaks in the drains release contaminants into the subsurface. In storage tank areas where the industrial drains are built up under the tank valves, leaks from the tanks cannot get into the industrial drains unless the surface of the spilled product is above the level of the industrial drain under the valves (approximately 18 inches [45 cm]). In a storage tank failure the lost product would likely enter the pluvial drains rather than the industrial drains.

In addition to providing transverse migration orientation pathways perpendicular to the groundwater gradient, the n-butane and C<sub>5</sub>+ contour maps both suggest the presence of a migration barrier in the direction of the downdip groundwater gradient. Subsequent borehole data discussed in the next section suggests the possibility of a clay barrier occurring parallel to the western edge of the termination line shown by these two contour maps. In addition, observation of water levels in the monitor wells further indicated some hydrologic variations confirming this possibility.

The presence of fairly large magnitude ethylene and propylene occur in association with the main three anomaly clusters in the PCC complex, the service station and old refinery and with the deep production casing leakage. The similarity of the ethylene and propylene contours with ethane and propane suggest a likely relationship between these saturate and olefin gases. Soil gas concentrations for selected samples from all three anomalous areas are very large, as shown below in ppmv:

#### **PCC Complex**

| Site No. | Ethane | Propane | Ethylene | Propylene |
|----------|--------|---------|----------|-----------|
| 29       | 728    | 284     | 128      | 56        |
| 31       | 375    | 991     | 60       | 68        |
| 121      | 854    | 310     | 51       | 35        |
| 123      | 25     | 0.24    | 260      | 1         |

#### **Production Well Casing Leakage**

|      |        |       |     |    |
|------|--------|-------|-----|----|
| 3801 | 19,550 | 786   | 42  | 26 |
| 1590 | 19,764 | 7,780 | 191 | 4  |

#### **Service Station and old refinery**

|      |     |     |     |    |
|------|-----|-----|-----|----|
| 1069 | 320 | 319 | 41  | 67 |
| 3192 | 129 | 11  | 306 | 2  |

With only a few exceptions, the saturate hydrocarbons are nearly always larger than the olefins, supporting the possibility the olefins are derived biologically from their saturate counterparts. In any case, whatever the relationship, these are very large concentrations for ethylene and propylene in shallow soil gas samples. Soil gas surveys conducted by ETI over the past 40 years have always found these two olefins to be present in similar relative concentrations to their respective saturate components. This environmental survey is unique in finding such large magnitudes in the shallow vapors, perhaps due to the very large concentrations and time that this contamination has been present in the shallow clay sediments. This will become even more interesting when we examine the headspace groundwater samples collected from the monitor wells, where similar concentrations will be found in groundwater in contact with contaminated sediments and free product. In both cases, soil gas or headspace groundwater, all the larger anomalous concentrations are associated with the product contamination. No such large anomalous values are found in the background areas.

### **Assessment of Vertical Extent of Sediment Contamination**

Although the geochemical soil gas survey can establish the horizontal extent of the contaminate plumes in the shallow vadose zone, along with some compositional distinctions, it cannot determine the depth of the subsurface contamination. This can only be done by drilling and analyzing boreholes for determining the vertical extent of the contamination, using the soil gas maps as a guide for placement.

As noted, 106 boreholes were drilled and sampled vertically on two foot intervals to determine the vertical distribution of the contamination and the depth to ground water. Lithologic descriptions of all soil samples were recorded, and each cored interval was described. Geological cross sections were generated to show the lithology's encountered and the discontinuous nature of the stratigraphic units, which consisted of fluvial clays, argillaceous clays, silts and sands, gravels, and matrix-supported conglomerates of Quaternary age. Sorting was poor with grain size increasing with depth. Lithology varied rapidly, both vertically and horizontally, with variations typical of floodplains and braided streams with channels ranging from 10-100 ft (3-30 m) in width.

Within the lower 6 ft (180 cm) of the unsaturated zone, which ranges from depths of 6-14 ft [1.8-4.25 m], two lithology trends were noted and mapped using the silt-clay ratio as shown by Figure-04. Around and south of the PCC complex, a northwest-southeast trend is related to probable distal fan deposits derived from the highlands southeast of the terminal. Farther west, in the PCC, lithological trends are northeast-southwest and likely related to River floodplain deposits laid down over the last few hundred years. Due to the location of the study area along the margin of the River floodplain, it appears logical for fans and other depositional systems to enter and modify the margins of the floodplain. Clays, silts, sands, and matrix-supported conglomerates in both the River floodplain and distal fan deposits are expected to be discontinuous along depositional strike and continuous along depositional dip.

In areas with more sand and silt, the saturated zone should be closer to the surface, since the water can easily rise in permeable zones. Depth to the saturated zone, or the thickness of the vadose zone, is inversely related to the permeability of the sediments which is controlled by increasing grain size. Coarse grain size as interpreted from vadose zone thickness was used to make an isopach maps of the vadose zone. (Figure-5). This map correlates fairly well with the

transverse migration pathways defined by the n-butane and C<sub>5</sub>+ contour maps, confirming possible migration pathways within the upper vadose zone.

During the collection and logging of soil samples, it was observed that the majority of petroleum product contamination was present at depths of 4-10 feet. Liquid hydrocarbons were present in shallow gray-green clay and silty clay sediments derived from the bore holes. The hydrocarbons trapped in these low porosity and permeability vadose zone sediments would likely be severely restricted from migrating offsite, whereas these more porous and permeable (silty) zones, which could also contain groundwater would more easily transmit the liquid contaminants needed to support the soil gas vapor plumes.

A product thickness map shown in Figure-6 provides a map of the subsurface contamination, which varies from greater than 2 ft. down to detection. As shown, the thickest product was found in the refinery and near the sales terminal loading racks, providing a possible source area in the refinery for the larger western C<sub>5</sub>+ plume. A map of product thickness made from only monitor wells is inadequate for determining the source of the gasoline, due to their limited coverage area, which was the cause for the investigation. Although propane and n-butane soil gas data (Figure-2ah) have pinpointed a source area and migration pathway for the offsite gasoline migration, product thickness alone is inadequate for showing the free product is the source for the soil gas vapors. To do this the free product must be analyzed for the same components that are measured in the soil gas survey.

## **Hydrologic Results**

Data collected from monitor wells indicated that the ground water gradient dips to the north and northwest as expected, however, different water levels noted in the aquifer suggested the presence of three distinct aquifers bounded by permeability barriers. Erosion and deposition by the River when it occupied these three separate positions on the floodplain could account for the presence of three separate aquifers. Permeability barriers between the aquifers, as shown by Figure-7 would likely act as erosional surfaces sealed by impermeable floodplain deposits or clay drapes.

The most obvious of these permeability barrier occurs immediately west of monitor wells MW-109 and 119, conforming very well with the transverse termination of the soil gas plumes shown by the n-C<sub>4</sub> and C<sub>5</sub>+ contour maps Plates-(2a through 2h). Soil vapor concentrations are significantly lower west of the barrier, where the monitor wells have higher proportions of clay (Figure-4 and Figure-5), providing support for the lack of soil gas, or product migration to the west of this barrier.

Hydrographs of the monitor wells provided additional evidence for the presence of these three aquifers. Water levels in all of the monitor wells generally rise and fall together in response to seasonal fluctuations in rainfall. Each aquifer, however, has a hydrograph different from the others, with all the monitor wells in one aquifer having virtually the same hydrograph (Figure-7). Evaluations of the hydrographs since the inception of pumping in trench 3 and changes in dissolved hydrocarbons in water samples from the monitor wells taken after the pumping started, strongly support the presence of three aquifers.

No apparent migration of water or contaminants between the three aquifers was ever observed. Migration between aquifers might occur along man-made fairways or where permeable strata in adjacent aquifers are coincidentally juxtaposed. Each aquifer will likely require its own cleanup

effort, and extraction of contaminants from one aquifer will probably not extract contaminants from adjacent aquifers.

### **Headspace analysis of C<sub>1</sub>-C<sub>4</sub> and C<sub>5</sub>+ Gases in the Free Product Recovered from Monitor Wells**

Figure-8 and Figure-9 illustrate the distribution of the C<sub>5</sub>+ versus the propane contained within the recovered free product from the monitor wells. Again, as expected, excellent correlations are noted between the soil gas vapor and the lost product. Products containing the highest ethane, propane, and butanes concentrations are present in the plume located under the PCC office building; products with larger C<sub>5</sub>+ concentrations are present in the active refinery area. These results are consistent with the soil gas data which indicate the plume under the PCC office building is predominantly gasoline and the plumes within the PCC contain heavier petroleum product(s).

### **Dissolved Gas Analyses from Monitor Wells**

As noted earlier, water samples were also collected below floating product in monitor wells containing liquid phase hydrocarbons during the remediation phase whenever the wells were purged of product and water. Typically, on environmental surveys benzene/BTEX are collected and measured only on background wells that have not been impacted by free product. A map using only background data is shown on Figure-10. This map outlines the product contaminated area shown by the product thickness in Figure-6, but provides no information about the contaminants within the impacted area. This is typically what is done on environmental surveys, but does not provide adequate information. Significantly more information can be obtained by collecting a water sample from all wells, including water samples lying under and in contact with the free product, as shown by Figure-11. Since gasoline always contains more BTEX than most other petroleum products, this map specifically focuses on the main area contaminated by gasoline. Note that the BTEX in the groundwater underlying the free product bears a striking correlation to the soil gas propane map (Plate-4, Figure-2c). With this addition we have two independent variables found in gasoline, propane as the vapor above the product, and BTEX as the dissolved phase below the product confirming one another.

In addition to BTEX, this approach provides very useful information for all components, whether soluble or not. As expected, the propane in the underlying groundwater (Figure-12) shows an even better correlation with the BTEX in the water than with the soil gas propane. High propane concentrations are apparent in the vicinity of the PCC office building and high C<sub>5</sub>+ concentrations occur both under the PCC office building and adjacent to the industrial drains in the PCC. Note how well the C<sub>5</sub>+ in Figure-13 correlates with the free product thickness in Figure-4, whereas BTEX and propane independently confirm one another, in addition to defining the areas where gasoline occurs within the free product. The dissolved headspace gases in the groundwater provide a completely independent data set for confirming and even better defining the free product contamination and possible sources in the refinery and storage terminal, including progress made during remediation as product is purged from the wells.

Figures-(14a through 14h) show the contour maps for all the main components. Clearly, analyzing the groundwater from all monitor wells, whether impacted by free product or not, provides a more useful and accurate picture of the contamination over the entire site. As with the soil gases, it is again interesting to note the presence of very large olefins (ethylene and



propylene) in the groundwater within the more contaminated areas. The close fit of the contours for ethane and propane with respect to these two olefins suggests some sort of genetic relationship between these saturate and olefin components. The presence of these olefins in both the soil gas above, and the groundwater below product contaminated areas suggests they are likely generated independently within the vadose zone and the underlying groundwater. Since the olefins do not occur in the background uncontaminated areas, they are clearly related to the presence of the free product contamination.

### **Ethylene and Propylene Associations with Ethane and Propane**

In order to view the relationship of ethane/ethylene and propane/propylene a series of bar-graphs have been generated for selected monitor wells and included as Figure-15. Contour maps for ethylene and propylene have been placed in the center portion of this figure, with bar graph plots of ethane/ethylene and propane/propylene placed to the left and right of the contour maps, respectively. Cross sections consisting of three wells each have been generated for easy comparison (oriented from west to east for profiles 1 to 6 and from north to south for profiles 7 and 8) with the headspace groundwater contour maps of these two olefin contour maps. Relative locations for each of the selected monitor wells profiles are shown on the contour maps for easy reference.

As shown in Figure-15, MW-102 located just south of Main Street on the office building parking lot is striking by comparison to all the other wells, having the very largest ethylene values observed in the entire data set. This unique well, with ethylene actually exceeding ethane in concentration lies within the heart of the PCC contamination. This unique relationship occurred on most of the samplings, reverting to the typical behavior shown by the other wells only on the final two samplings, where ethane exceeded ethylene in magnitude. MW-102 also had the largest propylene values found in the groundwater under free product, but did always have more propane than propylene. In contrast MW-101 had a more constant relationship where both ethane and propane were always larger. With the exception of MW-102, all the other wells suggest a dependent relationship controlling the generation and relationship of these olefins to their saturate analogs. In all cases the monitor wells having the largest olefins directly correlate with the largest ethane and propane concentrations measured, both in the groundwater and in the soil gases.

Product thickness and dates sampled started on 8/28/1992 and continued until 4/8/1994 as listed in Table-2. The maximum thickness was approximately 2 feet, as shown in Figure-4. The collection and analysis of water under product was started in January 1993 and was continued only through December of 1993. A comparison of the sampling dates for water under product (Table-5) versus product thickness (Table-2) shows that in most cases these monitor wells were purged numerous times between their analyses for water under product, so the measurements are not sequential. They are, however, in correct time order. Each sampling date is unique and is dependent on the recharge of both free product and groundwater in each well after it had been purged. By following this process, each well sample is essentially a new sample containing free product and groundwater that has recharged from the adjacent aquifer/sediment.

A comparison of product thickness (Table-2) with the component magnitude variations shows no obvious relationship to variations in product thickness in any of these wells. With the exception of MW-102, similar variations are noted for all the wells, with ethane and propane always being larger than ethylene and propylene, again suggesting these olefins are likely generated from their respective saturate components. The scatter between the saturate and olefin ratios suggests a microbiological relationship that strongly depends on the local

environmental conditions, which would be effected by purging the wells of water and free product. Oxygen levels would likely be increased by this process, interrupting the biological community.

These two olefins do not occur at such large concentrations in any of the background sites, but only where there are large magnitude ethane and propane present in close proximity. To our knowledge, this is the first and only time that these olefins have ever been collected and measured in groundwater under free product.

Although MW-102 is initially unique in having a negative ethane/ethylene ratio, all the other wells that contained free product, such as 121, 122, 123, 139, 140, 147, 149, 153, 174, 175, 181, 182, 198 and 199 all contained anomalous olefins on every sampling date with positive ratios. As shown by Figures-(14a through 14h), the olefin contour maps have similar distributions as ethane and propane, see Figures-(12a through 12h), both of which map the free product contamination. It also appears significant to note that the more restricted aerial extent of the two olefins maps more closely aligns with the main free product distributions. Product in the vadose zone will have the largest effect on the soil gas concentrations while liquid (floating product) or dissolved phase hydrocarbons in the ground water will have the largest effect on the dissolved gases. Maps of both sets of data provide the best representation of contaminated areas, and ensures that no contaminated areas are omitted.

Contour maps comparing the ethane, propane, ethylene and propylene soil gases found over the deep production well casing leaks, the PCC Complex and the service station/old refinery are included as Figures-(16a through 16d), Figures-(17 through 17d) and Figures-(18a through 18d), respectively. In spite of their magnitudes being scattered by unknown biological factors, this data clearly shows that these two olefins occur in all areas surveyed where anomalous ethane and propane soil gases are present. This is true in all contaminated areas, whether from refined products, or from deep production casing leakage.

A comparison of the ethane, propane, ethylene and propylene concentrations in monitor wells MW-101 and MW-102 with the adjacent soil gases located near these wells in ppmv are listed below.

| MW Well | Ethane | Propane | Ethylene | Propylene |
|---------|--------|---------|----------|-----------|
| 101     | 131    | 61      | 24       | 28        |
| 102     | 755    | 91      | 321      | 53        |

| Soil Gas | Ethane | Propane | Ethylene | Propylene |
|----------|--------|---------|----------|-----------|
| 29       | 728    | 284     | 128      | 56        |
| 31       | 375    | 991     | 60       | 68        |

While there is some scatter in the saturate/olefin ratios, there does appear to be a definite association between the olefins and saturates. In addition, they are present in fairly significant concentrations in both the soil gas and in the underlying water in the monitor wells, as shown by this data located in the PCC parking lot. Although the variability is likely caused by some unknown environmental conditions, such as oxygen and nutrients needed for microbiological activity, the active wells are consistently the same, suggesting local environmental conditions are important for allowing the reactions to occur, provided that adequate concentrations of ethane and/or propane are also present as a food source.

As this data shows, measuring the relative amounts of dissolved gases in the groundwater under product provides much more useful than just mapping product thickness, since these hydrocarbon components can distinguish and identify individual products along with their distribution within the free product and the adjacent groundwater.

### **Maximum Concentration Maps for Headspace waters**

Another concept introduced for environmentalists is the importance of making maximum concentration maps to further insure accurate mapping of the subsurface contaminant. Typically, environmental consultants make maps of contamination measured at specific time intervals controlled by the sampling of the wells. Such time dependent maps are useful, but should never be relied on to illustrate the actual site conditions. As a well is developed and sampled, product may suddenly appear that was not present initially. Most significantly, however, if a well is lost, or it becomes too damaged to sample, it is usually removed forever from the maps showing the subsurface contamination. If the assessment is inadequate, then the remediation will likely extend over a very long time frame (years), with these lost wells left behind as source areas that were never remediated. Maximum maps insure that these major source areas are not forgotten during the final evaluation. Composite maximum concentration maps for all components are included in Figures-(19a through 19h). These max maps provide a much more reliable way to evaluate the entire site. Again, note the excellent correlation with the soil gas and water headspace maps.

### **Remediation Trenches Confirmed by close-spaced 7 foot deep Soil Gases**

This assessment approach, using high density soil gas followed by more accurately placed monitor wells significantly aids the collection of groundwater gradients, migration pathways and barriers to groundwater flow that interrupt and control the movement of product in the subsurface. Pump tests on the wells showed the massive clays on the site limited the wells to no more than a 25 ft. capture radius. When combined with the very narrow oriented soil gas anomalies, the local geological model suggested that the shallow sediments were likely dominated by narrow pathways, such as a braded stream environment laid down by the adjacent river that flows northward near the edge of the site. In order to determine the exact locations and length for the remediation trenches a very close-spaced 7 foot deep soil gas data set was collected and contoured to fit a potential braded stream environment, as shown by Figure-20.

### **Abatement and Containment Measures**

Petroleum products were periodically recovered from all the monitor wells along with purge tests to determine the potential usefulness for using the monitor wells for remediation. Pump tests on the wells showed the massive clays on the site limited the wells to no more than a 25 ft. capture radius. When combined with the very narrow oriented soil gas anomalies, further reinforced by the closed spaced 7 foot deep soil gas data, suggested the local geological model is controlled by shallow sediments dominated by narrow pathways, such as a braded stream environment laid down by the adjacent river that flows northward near the edge of the site. On this basis three recovery trenches were installed to recover contaminants and prevent further migration. Trench 1 immediately north of the PCC office building and trench 2 along the northern edge of the PCC parking lot (Figure-2) were placed to intercept any product south of the PCC parking lot

migrating northward toward the adjacent residential area. Trench 3 along First Street was placed to recover any product that has migrated into the neighborhood, preventing additional product migration to the north beyond this trench.

The trench 1 hydrocarbon recovery system consists of three four-inch diameter monitor wells and one four-inch diameter recovery well. It is 30 meters long (98 feet) and 4.5 meters (14.75 feet) deep. The recovery well recovers floating liquid hydrocarbon product (LHC) using a pneumatic pump operated manually. It was placed in operation on February 9, 1993 and recovered 221 barrels of LHC by August 31, 1993. The LHC is directed to an oil/water separator in the PCC refinery. Trench 2, which is 210 meters long (690 feet) and contains four-inch monitor wells and three eight-inch diameter recovery wells. It was constructed to also recovery product and to prevent offsite migration from the PCC property. Trench 2 was operated over the same time frame as Trench 1 and recovered 806 barrels of LHC. Together these two trenches recovered 1,016 barrels within the first six months of operation.

Trench 3 was constructed along the south side of First Street to prevent any additional product from entering the residential area. It is 310 meters long (1017 feet) and 4.5 meters deep (14.75 feet) and has five four-inch monitor wells and four eight-inch diameter recovery wells. It was placed in operation on July 28, 1993 and has recovered 53 barrels of LHC and 117,436 barrels of water. Recovery volumes of LHC for each of the recovery wells appears to be directly related to the cumulative thickness of the more porous hydrocarbon contaminated silty clay or silt above the aquifer. The contaminated vadose zone in the vicinity of RW-4001 is composed of a plastic clay causing this well to have produced the smallest volume of the four recovery wells.

A series of product thickness contour maps are shown in Figure-21, illustrating the initial conditions on 01/13/1993 (Figure-21b) and extending to 08/05/1995 (Figure-21h). In addition to these time series maps, Figure-21a shows the maximum product thickness found within each well, regardless of the time series. The maximum product thickness map in Figure-21a correlates best with the maximum water headspace methane (Figure-19a) and the C<sub>5</sub>+ (Figure-19e) contour maps. Propane (Figure-19c) provides the most compact maps defining the location of the main gasoline product contamination. Product thickness on a time sampling series can be misleading because the limited number of monitor wells, as restricted by cost considerations, are never going to be in exactly the most optimum positions for product recovery. As shown by these product thickness maps, product can most unexpectedly appear within wells that had previously been declared as clean.

The maximum product thickness map in Figure-21a also provides a better estimate of where the product was initially located on the site and is the best map to use to show the effectiveness of the remediation trenches in achieving the last product thickness map in Figure-21h, which demonstrates the success of this approach for cleaning up a LHC contaminated site.

## Summary

- 1) A high density soil gas survey (4072 sites placed on a 50 ft grid) was used to identify and map the horizontal extent of petroleum product contaminant plumes and serve as the basis for locating monitor wells and trenches. Extended regional grids and closely spaced detailed sampling as needed based on the interpretation of all data. The soil gas data show the contaminated area to be very large. Contaminant plumes may be following braided stream type channels northward into the neighborhood.
- 2) Installed borings and monitor wells in those areas containing high concentrations of hydrocarbon contaminants. These wells, coupled with the soil gas data, confirmed the gasoline along First Street originated from a major contaminant plume in the shallow clays under the PCC office complex. Other contaminant plumes detected by the soil gas survey south and west of the PCC have been confirmed by monitor wells. Continued sampling of monitor wells was essential to mapping the depth and extent of contamination of the ground water in the study area.
- 3) Contamination from the PCC facilities accumulated in the vicinity of the PCC offices and parking lot and the shop complex west of the offices. Contaminants from these accumulations crossed Main Street into the residential area. High soil vapor concentrations along segments of the industrial drains adjacent in the PCC indicate a history of leaks from these drains. Contaminants from leaks in the drains entered higher permeability pathways in the subsurface and migrated down the hydraulic gradient and depositional dip toward the north and northeast to the PCC parking lot and the adjacent residential area. Suggested the integrity of the drains should be checked and repaired.
- 4) Pluvial drains are also likely sources of contamination. Hydrocarbons spilled on the surface at the storage terminal and throughout the PCC facility are most likely washed into the drains and subsequently leaked into the subsurface. As with the industrial drains, products migrate downward to strata with higher permeability and then northward along permeability pathways corresponding to the old River braided channels.
- 5) A pumping test was conducted south of the laboratory using monitor wells MW-120, MW-121, and MW-122. The area of influence (area affected by the pumping well) for each well was approximately 20-25 feet, indicating that the water bearing strata have low porosity, permeability, and transmissibility.
- 6) Data collected from 92 monitor wells indicated the ground water gradient is to the north and northwest. Different water levels found in four sub-areas suggest the aquifer should be interpreted as having four distinct aquifers bounded by permeability barriers. A fifth aquifer may occur in the west with monitor wells MW-191 and MW-192 each being in separate aquifers. With only two wells to define one aquifer or differentiate between two aquifers, this data is inconclusive. Erosion and deposition by the River when it occupied four separate positions on the floodplain is interpreted to account for the presence of four separate aquifers. Permeability barriers between the aquifers, (Figures 11 through 14), are likely erosional surfaces sealed by impermeable floodplain deposits or clay drapes.
- 7) The most obvious permeability barrier occurs immediately west of monitor wells MW-109 and 119, appearing on all the soil gas maps, particularly C<sub>1</sub>, n-C<sub>4</sub> and C<sub>5</sub>+ (Plates 2, 5 and 6). Soil vapor concentrations are significantly lower west of the barrier, and monitor wells have higher proportions of clay, indicating a correlation.

8) Hydrographs of the monitor wells provided additional evidence for the presence of four aquifers. Water levels in all of the monitor wells generally rise and fall together in response to seasonal fluctuations in rainfall. Each aquifer, however, has a hydrograph different from the others, with all the monitor wells in one aquifer having virtually the same hydrograph. Preliminary evaluations of the hydrographs since the inception of pumping in trench 3 and changes in dissolved hydrocarbons in water samples from the monitor wells taken after the pumping started, strongly support the presence of four aquifers and track the progress of the remediation effort.

9) Installed pilot trenches in the PCC parking lot (trenches' 1 and 3) and along First Street (trench 2) to confirm hydrocarbon contamination along the fill/clay interface and utility conduits. All trenches showed that the primary migration pathways are within the gray-green clay at depths of approximately 4-10 ft.

10) Based on the data and the maps, trenches were determined to be the most efficient method for recovering the product contaminating the soils and ground water in most portions of the study area. Individual trenches oriented perpendicular to the permeability trends, and, therefore, perpendicular to the trends of the contaminant plumes, could intersect several permeability trends, enabling PCC to recover product from several different contaminant zones simultaneously. Trenches 1, 3, and 2 (Figure-1) are currently extracting product from the PCC parking lot and First Street. Trenches (1 and 3) in the PCC parking lot will intercept product migrating northward from the terminal and PCC facilities into the adjacent residential area. Trench 2 in the neighborhood along First Street was necessary to recover product currently in the soils and ground water of the neighborhood.

Although methane and ethane Figures-(2a and 2b) confirm the migration plumes outlined by propane, n-butane and C<sub>5</sub>+, they also exhibit independent plumes that extend eastward along Third Street from the area containing the four deep production wells. The presence of propane with essentially no n-butane and C<sub>5</sub>+ suggests this Third Street plume is sourced mainly by gases derived from casing and/or production line leaks. The relative concentrations of ethane > propane > n-butane in these soil gas plumes confirms deep source rather than refinery source, indicating the Third Street gases are independent and not related to the First Street refinery sourced anomalies. Methane is also very large and could be made up of both deep Cretaceous gases and biogenic methane generated from near-surface contamination.

Large concentration soil gas anomalies occur to the east over the service stations, which lie adjacent to an old inactive refinery. These anomalies near the service station are dominated by propane, n-butane and C<sub>5</sub>+ on the service station property, all of which have degraded gasoline type signatures where (butanes > propane > ethane). Anomalies lying just south of the service stations contain more moderate propane, n-butane and C<sub>5</sub>+, but significantly larger methane and ethane suggesting older, more aged products derived from the old inactive refinery.

Based on all these correlations, one can conclude that the soil gas sample analyses (C<sub>1</sub>-C<sub>4</sub> and C<sub>5</sub>+), accurately represent the products present in the subsurface. The vapors collected and analyzed in a shallow four foot soil gas survey potentially detect all subsurface contaminants, regardless of whether hydrocarbon products are contained within the vadose zone or floating on the ground water. Vadose zone contamination will obviously dominate shallow soil gas data, making it impossible to accurately assess the presence of liquid phase or dissolved phase

contaminants in the ground water without drilling, however, monitor well installations and the subsequent collection of samples from these wells can not only supplement the soil gas data, and establish the nature vertical extent of the subsurface contamination, but can link and confirm compositional associations that significantly improve the assessment and insure the potential for cleaning up and even closing the site, something that is almost never accomplished.

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