

TECHNICAL REPORT

NON-AQUEOUS PHASE LIQUID (NAPL)
SOURCE STUDY AT
DEFENSE SUPPLY CENTER PHILADELPHIA
PHILADELPHIA, PENNSYLVANIA

Prepared For



Prepared By



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MARCH 1998

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GLOSSARY OF ENVIRONMENTAL TERMS

ACCURACY - The degree of agreement between a measured value and a true or expected value.

ACUTE TOXICITY - Toxic symptoms that develop shortly after exposure, usually within 24 hours.

ADSORPTION - The assimilation of gas, vapor, or dissolved matter by the surface of a solid.

ADSORPTION COEFFICIENT (K_{oc}) - A parameter describing the tendency of a chemical to be adsorbed; largely independent of soil or sediment properties.

ADVECTION - The process by which solutes are transported with and at the same rate as moving ground water.

ALCOHOLS - Organic compounds containing a hydroxyl (OH) group, e.g., methyl alcohol or methanol.

ALIPHATIC - Carbon atoms linked in a chain-like formation; includes alkanes and alkenes.

ALIPHATIC HYDROCARBONS - Refers to hydrocarbon molecules whose carbon atoms are arranged only in chains, as distinguished from those whose carbon atoms are in rings; includes normal and branched-chain alkanes.

ALKANE -

(1) normal-alkane (n-alkane or paraffin)

saturated hydrocarbons which have an unbranched structure.

(2) isoalkane (branched alkane or isoparaffin)

differs from n-alkanes in the presence of one or more points of branching within the chain.

(3) cycloalkane (naphthene)

Saturated hydrocarbons composed of one or more rings.

ALKENE - Aliphatic hydrocarbons with the general formula C_nH_{2n} which contain a double bond, a characteristic chemists have termed unsaturation. Olefins are present in living organisms but are rare in natural crude oils. They are readily produced in refinery cracking processes and are important in the petrochemical industry.

ALKYL GROUP - Denotes an acyclic saturated hydrocarbon radical, general formula C_nH_{2n+1} (sometimes abbreviated in chemical structures by the symbol R-). This term is commonly used to denote an aliphatic hydrocarbon moiety which is bonded at a specific point in a chemical structure e.g., the alkyl side-chain in steranes.

GLOSSARY OF ENVIRONMENTAL TERMS (CONTINUED)

ANTHROPOGENIC - Relating To, or influenced by the impact of humankind on nature.

API GRAVITY - The standard American Petroleum Institute method for specifying the density of crude petroleum. The formula used to calculate API gravity is:

$$^{\circ}\text{API} = 141.5$$

$$(131.5 \times \text{specific gravity at } 60^{\circ}\text{F})$$

? Low gravity (heavy oil) $<20^{\circ}\text{ API}$

? Medium gravity $27^{\circ}\text{ API}+$

? High gravity (light oil) $>35^{\circ}\text{ API}$

AQUIFER - A formation, group of formations, or part of a formation that contains sufficient saturated permeable material to yield economical quantities of water to wells and springs.

AQUITARD - A geologic formation, group of formations, or part of a formation through which virtually no water moves.

AROMATIC HYDROCARBONS - A class of unsaturated cyclic organic compounds containing one or more ring structures or cyclic groups with very stable bonds through the substitution of a hydrogen atom for an element or compound.

ARTESIAN WELL - A well deriving its water from a confined aquifer in which the water level stands above the ground surface; synonymous with flowing artesian well.

ASPHALT/ASPHALTICS - Dark brown, viscous liquid or low-melting solid that contains asphaltenes and resins, is soluble in carbon disulfide and insoluble in n-heptane. Asphaltenes occur as tiny colloidal particles dispersed in the oil, and are commonly isolated in the laboratory by precipitation in pentane (see below). The higher the proportion of asphaltene, the harder the residual asphalt.

ASPHALTENES - Constitute a general class of aromatic-type substances which are defined on the basis of their solubility: Asphaltenes are soluble in carbon disulfide and insoluble in light alkanes such as n-pentane and n-heptane. Asphaltene molecules carry a core of stacked flat sheets of condensed (fused) aromatic rings linked at their edges by chains of aliphatic and/or naphthenic-aromatic ring systems. The condensed aromatic sheets contain NSO atoms and probably vanadium and nickel complexes.

ATTENUATION - Reducing or removing constituents in the ground water by the sum of all physical, chemical, and biological events acting upon the ground water.

BARRIER BOUNDARY - An aquifer system boundary represented by a rock mass that is not a source of water.

GLOSSARY OF ENVIRONMENTAL TERMS (Continued)

BEDROCK - A general term for rock, usually solid, that underlies soil or other unconsolidated material.

BENZENE - A common liquid hydrocarbon in petroleum, formula C_6H_6 : the simplest of the aromatic series.

BIODEGRADATION - The breakdown of chemical constituents through the biological processes of naturally occurring organisms.

BIOLOGICAL MARKER (BIOMARKER) - Compounds found in petroleum or rock extracts which possess a carbon skeleton that indicates an unambiguous link with a natural product. The most common biomarkers in petroleum include isoprenoids, triterpanes and steranes.

BIOLOGICAL TRANSFORMATION - Structural alteration of a chemical by an organism. In regard to fuel, it refers primarily to the decomposition of organic compounds by microorganisms. Also, biodegradation when taken to full mineralization.

BOREHOLE GEOPHYSICS - The general field of geophysics developed around the lowering of various probes into a well.

BRANCHED CHAIN - The alkanes are classified as "branched chain" when more than two carbon atoms are linked to at least one carbon atom.

CHEMICAL ACTIVITY - The molal concentration of an ion multiplied by a factor known as the activity coefficient.

CHRONIC TOXICITY - Toxic symptoms that develop after repeated low-level exposure. Often effects are not immediately apparent.

CLASTIC - Pertaining to a rock or sediment composed principally of broken fragments that are derived from pre-existing rocks or minerals and that have been transported some distance from their places of origin.

CLAY - A plastic, soft, variously colored earth, commonly a hydrous silicate of alumina, formed by the decomposition of feldspar and other aluminum silicates.

COEFFICIENT OF STORAGE - The volume of water an aquifer releases from or takes into storage per unit surface area of the aquifer per unit change in head.

COLLOID - Extremely small solid particles, 0.0001 to 1 micron in size, which will not settle out of a solution; intermediate between a true dissolved particle and a suspended solid which will settle out of solution.

GLOSSARY OF ENVIRONMENTAL TERMS (Continued)

CONE OF DEPRESSION - A depression in the ground-water table or potentiometric surface that has the shape of an inverted cone and develops around a well from which water is being withdrawn. It defines the area of influence of a well.

CONFIDENCE LEVEL (Confidence Limit is 95 percent) - A level of data reliability achieved by setting a percent confidence limit. A 95 percent confidence limit is the limit of the range of analytical values within which a single analysis will be included 95 percent of the time.

CONFINED AQUIFER - A formation in which the ground water is isolated from the atmosphere at the point of discharge by impermeable geologic formations; confined ground water is generally subject to pressure greater than atmospheric.

CONFINING BED - A body of material of low hydraulic conductivity that is stratigraphically adjacent to one or more aquifers. It may lie above or below the aquifer.

CHROMATOGRAMS - Record of detector response (intensity vs. time) during gas chromatography. Individual hydrocarbons appear as peaks above a baseline, and may be identified and quantified.

CHROMATOGRAPHY - A technique for separating components in a mixture based on their physical or chemical properties.

CONDENSATE - A product of condensation known sometimes as distillate; contains hydrocarbons in the C₄ to C₁₀ range. Condensates occur in gas reservoirs of great depth and high pressure, are normally in vapor phase, but condense as reservoir pressure is reduced by production gas. Petroleum geochemists commonly use this term to refer to liquid hydrocarbons which are dominantly gas and light oil.

CRACKING - A process whereby larger hydrocarbon molecules are broken down into smaller hydrocarbon molecules. Catalytic cracking is a refinery process which breaks down the molecules through the use of a catalyst which speeds up the reaction. The term is also used to refer to the thermal decomposition of petroleum in the reservoir.

CRUDE OIL - Unrefined oil, usually with gas in solution, as found in accumulations in the subsurface.

CYCLIC - Refers to those compounds having ring structure:

- (1) Homocyclic - only carbon atoms in the ring.
- (2) Heterocyclic - one or more of the ring atoms are elements other than carbon, e.g., sulfur.

CYCLOALKANES (NAPHTHENES) - A saturated, closed-ring hydrocarbon series.

GLOSSARY OF ENVIRONMENTAL TERMS (Continued)

DEASPHALTING - Refinery or lab procedure for precipitating asphaltenes out of complex hydrocarbon mixture (e.g., a crude oil) by adding pentane, hexane, etc. The same process may occur naturally when methane and other gases move into crude oil reservoirs.

DIESEL - Refined petroleum distillate boiling in the approximate range of 230 to 300 degrees Centigrade. Diesel contains mainly hydrocarbons of 13 to 20 carbon atoms and is commonly used as an additive in oil-based drilling muds.

DISSOLVED PRODUCT - The water-soluble fuel components; namely, benzene, toluene, and xylene.

DNAPL - Acronym for dense, nonaqueous-phase liquids.

DOWNGRADIENT WELL - A well that has been installed hydraulically downgradient of the site and is capable of detecting the migration of contaminants from a regulated unit. Regulations require the installation of three or more downgradient wells depending on the site-specific hydrogeological conditions and potential zones of contaminant migration.

DRAINAGE DIVIDE - A boundary line along a topographically high area which separates two adjacent drainage basins.

DRAWDOWN - The distance between the static water level and the surface of the cone of depression.

DRY GAS - Natural gas as it comes from the well is classified in the field as dry gas, lean gas, or wet gas, according to the amount of liquid vapors it contains. A dry gas contains less than 0.1 gallon gas liquid vapor per 1000 cubic feet, and a wet gas 0.3 or more. Geochemically, dry gas is defined as follows:

- (a) Reservoir gas: methane greater than 97% of total hydrocarbons.
- (b) Cuttings gas: methane greater than 75% (sometimes 50%) of the total hydrocarbons.

DURATION CURVE - A graph showing the percentage of time that the given flows of a stream will be equaled or exceeded. It is based upon a statistical study of historic stream-flow records.

DYNAMIC EQUILIBRIUM - A condition in which the amount of recharge to an aquifer equals the amount of natural discharge.

EFFECTIVE POROSITY - The amount of interconnected pore space through which fluids can pass, expressed as a percent of bulk volume. Part of the total porosity will be occupied by static fluid being held to the mineral surface by surface tension, so effective porosity will be less than total porosity.

GLOSSARY OF ENVIRONMENTAL TERMS (Continued)

ENVIRONMENTAL FATE What happens to a chemical once it is released or escapes into the environment.

FLASHPOINT - The lowest temperature at which a combustible liquid will give off a flammable vapor which can be ignited and will burn momentarily.

FORMATION - A mappable unit of consolidated material and unconsolidated material characterized by a degree of lithologic homogeneity.

FREE PRODUCT - Fuel product accumulated on top of the ground water that is recoverable by well withdrawal methods. Free product is often mobile.

GAMMA-GAMMA RADIATION LOG - A borehole log in which a source of gamma radiation, as well as a detector are lowered into the borehole. This log measures bulk density of the formation and fluids.

GAS CHROMATOGRAPHY (Gas-Liquid Chromatography) - A form of chromatography where the moving phase is a gas (helium, hydrogen, etc.) and the stationary phase is generally a solid coated with a liquid in a coiled tube (column) through which the gas flows. Used to analyze complex mixtures for their individual components.

GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) - A tandem analytical instrument in which a gas chromatograph is coupled to a mass spectrometer. As compounds elute from the gas chromatographic column, they are fragmented and ionized in the mass spectrometer. Different compounds have characteristic fragmentation patterns, which are used in their identification. This is one of the main analytical tool for the characterization of biological markers.

GASOLINE - Automotive gasoline is a generic term used to describe volatile petroleum fuels used primarily in internal combustion engines. In general it is the fraction of petroleum boiling between 30 and 180C. Hydrocarbons in the gasoline boiling range range from C4 to C10.

GASOLINE-RANGE HYDROCARBONS - General term for the light hydrocarbons; often used synonymously with C4-C7, but could also include portions of C8-C10 range. These compounds can occur in mature source rocks.

GEOSTATISTICS - (a) Statistics as applied to geology; the application of statistical methods or the collection of statistical data for use in geology. (b) Statistical techniques developed for mine evaluation by the French school of G. Matheron

GLACIAL DRIFT - A general term for unconsolidated sediment transported by glaciers and deposited directly on land or in the sea.

GLOSSARY OF ENVIRONMENTAL TERMS (CONTINUED)

GLACIOFLUVIAL - Pertaining to the melt-water streams flowing from wasting glacier ice and especially to the deposits and landforms produced by such streams.

GRADED - An engineering term pertaining to a soil or an unconsolidated sediment consisting of particles of several or many sizes or having a uniform or equitable distribution of particles from coarse to fine.

GRAVEL PACK (ARTIFICIAL FILTER PACK) - (See also Filter Pack). A term used to describe gravel or other permeable filter material placed in the annular space around a well intake to prevent the movement of finer material into the well casing, to stabilize the formation, and to increase the ability of the well to yield water.

GROUND-WATER TABLE - The surface between the zone of saturation and the zone of aeration; the surface of an unconfined aquifer.

HETEROGENEOUS - Pertaining to a substance having different characteristics in different locations. Synonymous for nonuniform.

HOMOGENEOUS - Exhibiting a uniform or similar nature.

HOMOLOG - A member of a series of organic chemical compounds of uniform chemical type. A homologous series shows a regular gradation in physical properties, whereby the molecule of each member of the series differs from the preceding one by a definite constant group of atoms.

HYDROCARBON - Organic chemicals such as benzene or toluene that contain atoms of carbon or hydrogen.

HYDROGENATION - Chemical combination of hydrogen with unsaturated compounds, reducing oxygen and sulfur content and converting chemically reactive, unstable hydrocarbons into stable hydrocarbons.

HYDRAULIC CONDUCTIVITY - A coefficient of proportionality describing the rate at which water can move through a permeable medium. The density and kinematic viscosity of the water must be considered in determining hydraulic conductivity.

HYDRAULIC DIFFUSIVITY - A property of an aquifer or confining bed defined as the ratio of the transmissivity to the storativity.

HYDRAULIC GRADIENT - The change in total head with a change in distance in a given direction. The direction is that which yields a maximum rate of decrease in head.

HYDROCHEMICAL FACIES - Bodies of water with separate but distinct chemical compositions contained in an aquifer.

GLOSSARY OF ENVIRONMENTAL TERMS (Continued)

HYDRODYNAMIC DISPERSION - The process by which ground water containing a solute is diluted with uncontaminated ground water as it moves through an aquifer.

HYDROGEOLOGIC - Those factors that deal with subsurface waters and related geologic aspects of surface waters.

HYDROLYSIS - A chemical-transformation process in which an organic molecule reacts with water to form a new carbon-oxygen bond while cleaving a carbon-x bond from the original molecule.

HYDROPHOBIC - The tendency not to dissolve in water.

HYDROSPHERE - All waters of the Earth, as distinguished from the rocks (lithosphere), living things (biosphere), and the air (atmosphere).

ISOMERIZATION - The term is commonly used to describe the apparent interconversion of two hydrocarbons which differ in their orientation about a single carbon atom.

ISOPRENOIDS - A series of acyclic compounds composed of one or more "isoprene units". They are commonly derived from plant and bacterial precursors and are regarded as biological markers. Geochemically, the most important isoprenoids are the saturated hydrocarbons phytane and pristane.

ISOTOPES - Elements which have the same atomic number but differing atomic weights, and the same chemical properties (e.g., C12,C13,C14). Relative abundance of isotopes is given by isotopic ratios expressed in parts per thousand relative to a standard expressed as Delta (d) values. Carbon and sulfur isotopes are useful in oil-oil and oil-source rock correlation.

KEROGEN - The insoluble organic matter preserved in sedimentary rocks. It is derived from the breakdown of plant and bacterial remains and yields hydrocarbons on natural burial or laboratory pyrolysis. Three types (identified as I, II and III) are commonly defined based on optical properties and elemental composition.

KINEMATIC VISCOSITY - The ratio of dynamic viscosity to mass density. It is obtained by dividing dynamic viscosity by the fluid density. Units of kinematic viscosity are square meters per second.

GLOSSARY OF ENVIRONMENTAL TERMS (Continued)

KRIGING - A weighted moving average interpolation (extrapolation) method which minimizes the estimated variance of a predicted point (node) with the weighted average of its neighbors. The weighting factors and the variance are calculated using a variogram model which describes the differences versus distance for pairs of samples in the input dataset. Determining an optimal variogram model is the important first step in producing a defensible kriged estimate. With other software, the burden of fitting the variogram is left to the user. In EVS, this task is automated with an expert system.

LAW OF MASS ACTION - The law stating that for a reversible chemical reaction, the rate of reaction is proportional to the concentrations of the reaction.

LEAKY CONFINING LAYERS - A low permeability layer that can transmit water at sufficient rates to furnish some recharge to a well pumping from an underlying aquifer. Also called aquitard.

LIGHT HYDROCARBONS - Hydrocarbons which are gaseous and near gaseous at normal temperatures and pressures. They range from methane (C1) to octane (C8), including aromatic compounds, normal, iso-, and cyclic alkanes.

LIQUID CHROMATOGRAPHY (LIQUID-SOLID CHROMATOGRAPHY)

A form of chromatography where the moving phase is a liquid and the stationary phase a solid. Used to fractionate an oil or extract into saturated hydrocarbons, aromatic hydrocarbons and heterocompounds.

LNAPL - Acronym for light, nonaqueous-phase liquids.

MASS SPECTROMETRY - An analytical method for identifying and measuring hydrocarbon compositions. Compounds introduced into a mass spectrometer at high vacuum are fragmented, ionized and ratios of mass to charge are measured. These ratios are related to the chemical structure of the parent compound.

MICROGRAM (μg) - One-thousandth part of a milligram (mg); one-millionth part of a gram; one-billionth part of a kilogram.

MISCIBLE - Materials that are soluble in water and are typically mobile in the subsurface.

NAPHTHA - The word is usually applied to a narrow-boiling fraction of petroleum with volatility somewhere between that of gasoline and kerosene (approx. C7-C10).

NAPHTHALENE - An aromatic hydrocarbon consisting of two fused benzene rings.

GLOSSARY OF ENVIRONMENTAL TERMS (CONTINUED)

NATURAL GAS - Gaseous petroleum; consists of the lighter paraffins, of which the most abundant is methane. The natural gas of commerce, as delivered to the pipelines, usually ranges between 900 and 1200 BTU per 1000 cubic feet and has the following general composition:

Methane (CH₄) 72.3 percent

Ethane (C₂H₆) 14.4 percent

Carbon dioxide (CO₂) 0.5 percent

Nitrogen (N₂) 12.8 percent

NEUTRON LOG - A borehole log obtained by lowering a radioactive element, which is a source of neutrons, and a neutron detector into the well. The neutron log measures the amount of water present; hence, the porosity of the formation.

NONEQUILIBRIUM TYPE CURVE - A plot of logarithmic paper of the well function $W(u)$ as a function of u .

NONGRADED - An engineering term pertaining to a soil or an unconsolidated sediment consisting of particles of essentially the same size.

OBSERVATION WELL - A well drilled in a selected location for the purpose of observing parameters such as water levels and pressure changes.

OCTANOL/WATER PARTITION COEFFICIENT - The ratio of a chemical concentration in an octanol phase to its concentration in water in a two phase octanol/water system. K_{ow} .

ORGANIC - A carbon-containing compound.

OUTWASH - Stratified sand and gravel removed or washed out from a glacier by melt-water streams and deposited in front of or beyond the end moraine or the margin of an active glacier. The coarser material is deposited nearer to the ice.

OVERBURDEN - The loose soil, silt, sand, gravel, or other unconsolidated material overlying bedrock, either transported or formed in place; regolith.

OXIDATION - The combining of an element with oxygen.

PARAFFIN - See alkane (normal).

PARTIAL PENETRATION - When the intake portion of the well is less than the full thickness of the aquifer.

n-PENTANE (C₅H₁₂) - A normal alkane hydrocarbon (paraffin) with a continuous chain five carbon atoms long.

GLOSSARY OF ENVIRONMENTAL TERMS (Continued)

PERMEABILITY - The property or capacity of a porous rock, sediment, or soil for transmitting a fluid; it is a measure of the relative ease of fluid flow under unequal pressure.

PIEZOMETERS - Generally a small diameter, non-pumping well used to measure the elevation of the water table or potentiometric surface.

PURGE (wells) - Pumping out well water to remove drilling debris or impurities; also conducted to bring fresh ground water up into the casing for sample collection. The latter is a means of collecting a representative water sample from the aquifer being investigated.

PURGEABLE ORGANIC - An organic chemical with a high vapor pressure that can be removed from water by bubbling a nonreactive gas, such as helium, in the water.

PETROLEUM - That naturally occurring mixture of dominantly hydrocarbon substances liquid, gas, or solid that constitutes the commercial crude oil, natural gas and natural asphalt of the petroleum industry." (Hedberg, 1964).

pH - Measure of alkalinity or acidity of a solution; the log of the reciprocal of the hydrogen ion activity i.e., water with a hydrogen ion activity of 10^{-7} , has a pH = 7. Acidity, pH < 7. Alkalinity, pH > 7.

PHENANTHRENE - Aromatic hydrocarbon consisting of three fused benzene rings; an isomer of anthracene.

PHYTANE - A common isoprenoid hydrocarbon containing 20 carbon atoms. Phytane is not found in living organisms but is usually present in sediments and crude oils.

PHYTOPLANKTON - Unicellular photosynthetic organisms that live in marine or lake waters. They include algae, diatoms and dinoflagellates.

PRISTANE - A common isoprenoid hydrocarbon containing 19 carbon atoms. In contrast to phytane, pristane is found both in living organisms and in sediments and crude oils.

PRISTANE/PHYTANE RATIO - The ratio of the relative abundance of the isoprenoids pristane and phytane. The ratio is characteristic of organic facies and depositional environment; values less than 1.0 are often associated with carbonate source rocks and oils while values greater than 4.0 are typical of terrigenous organic matter.

PYROLYSIS (Destructive distillation) - The decomposition of coal, wood, petroleum or other organic matter by heating in the absence of air.

RADIAL FLOW - The flow of water in an aquifer toward a vertically oriented well.

GLOSSARY OF ENVIRONMENTAL TERMS (Continued)

RADIUS OF INFLUENCE (CONE OF DEPRESSION) - The radial distance from the center of a well under pumping conditions to the point where there is no lowering of the water table or potentiometric surface.

RECHARGE - The addition of water to the zone of saturation; also, the amount of water added.

RECHARGE AREA - An area in which there are downward components of hydraulic head in the aquifer. Infiltration moves downward into the deeper parts of an aquifer in a recharge area.

RECHARGE BOUNDARY - An aquifer system boundary that adds water to the aquifer. Streams and lakes are typical recharge boundaries.

RECOVERY - The rise in water level in a pumping well and nearby observation wells after ground-water pumping has ceased.

REDOX - A chemical reaction in which an atom or molecule loses electrons to another atom or molecule. Also called oxidation-reduction. oxidation is the loss of electrons reduction is the gain in electrons.

REMEDIAL ACTION - Action taken to correct a problem such as fuel contamination of soil and groundwater.

REPRESENTATIVE SAMPLE - A sample that is assumed not to be significantly different than the population of samples available. In fuel leak investigations, samples are often selected to be representative of the worst case situation.

SATURATED HYDROCARBONS - A saturated hydrocarbon is one in which the valences of all the carbon atoms is satisfied by single bonds.

SATURATE FRACTION - The fraction of crude oils and sediment extracts which contain normal, branched and cyclic alkanes, isolated during liquid chromatography.

SPECIFIC CAPACITY - An expression of the productivity of a well, obtained by dividing the rate of discharge of water from the well by the drawdown of the water level in the well. Specific capacity should be described on the basis of the number of hours of pumping prior to the time the drawdown measurement is made. It will generally decrease with time as the drawdown increases.

SPECIFIC GRAVITY - The weight of a particular volume of any substance compared to the weight of an equal volume of water at a reference temperature.

SPECIFIC RETENTION - The ratio of the volume of water that a given body of rock or soil will hold against the pull of gravity to the volume of the body itself. It is usually expressed as a percentage.

GLOSSARY OF ENVIRONMENTAL TERMS (Continued)

SPECIFIC YIELD - The ratio of the volume of water that a given mass of saturated rock or soil will yield by gravity to the volume of that mass. This ratio is stated as a percentage.

SPLIT-SPOON SAMPLER - A hollow, tubular sampling device driven by a 140-pound weight below the drill stem to retrieve samples of the formation.

SPONTANEOUS POTENTIAL LOG - A borehole log made by measuring the natural electrical potential which develops between the formation and the borehole fluids.

STAGNATION POINT - A place in a ground-water flow field where the ground water is not moving. The magnitude of vectors of hydraulic head at the point are equal but opposite in direction.

STATIC WATER LEVEL - The distance measured from the established ground surface to the water surface in a well neither being pumped nor under the influence of pumping nor flowing under artesian pressure.

STATIC WATER LEVEL - The level of water in a well that is not being affected by withdrawal of ground water.

STORAGE, SPECIFIC - The amount of water released from or taken into storage per unit volume of a porous medium per unit change in head.

TILL - Predominantly unsorted and unstratified drift, generally unconsolidated, deposited directly by and underneath a glacier without subsequent reworking by meltwater, and consisting of a heterogeneous mixture of clay, silt, sand, gravel, and boulders ranging widely in size and shape.

TOLUENE (METHYL BENZENE) - Aromatic hydrocarbon consisting of a benzene ring with a methyl group.

TORTUOSITY - Sinuosity of the actual flow path in porous medium; it is the ratio of the length of the flow path divided by the length of the sample.

TOTAL DISSOLVED SOLIDS, TDS - A term that expresses the quantity of dissolved material in a sample of water, either the residue of evaporation, dried at 356 degrees F (180 degrees C), or, for many waters that contain more than about 1,000 mg/l, the sum of the chemical constituents.

TOXICITY - The harmful effect produced by exposure to a substance.

TRANSMISSIVITY - The rate at which water of a prevailing density and viscosity is transmitted through a unit width of an aquifer or confining bed under a unit hydraulic gradient. It is a function of properties of the liquid, the porous media, and the thickness of the porous media.

GLOSSARY OF ENVIRONMENTAL TERMS (Continued)

UCM - Abbreviation for "Unresolved Complex Mixture", it refers to the part of the saturate or aromatic hydrocarbon fraction of extractable organic matter which is not resolved into peaks during gas chromatography. Also informally known as the hump, it becomes accentuated in biodegraded oils.

UNCONFINED AQUIFER - An aquifer where the water table is exposed to the atmosphere through openings in the overlying materials.

UNSATURATED ZONE - The zone between the land surface and the water table. It includes the root zone, intermediate zone, and capillary fringe. The pore spaces contain water at less than atmospheric pressure, as well as, air and other gases. Saturated bodies, such as perched ground water, may exist in the unsaturated zone.

VADOSE ZONE - The unsaturated zone containing water under pressure less than that of the atmosphere, including soil water, intermediate vadose water, and capillary water. This zone is limited above by the land surface and below by the surface of the zone of saturation (i.e., the water table)..

VISCOSITY OF OIL - The ability to flow. Measured in arbitrary units by the time required for a specified volume of oil to flow through a hole (Saybolt seconds) or a capillary tube (centipoises) of definite size under controlled temperature conditions.

WATER-WASHING - A non-thermal alteration process affecting oils in reservoirs; waters flowing through the reservoir carry away the more soluble hydrocarbons (chiefly the aromatics benzene and toluene, and the light paraffinic hydrocarbons).

WAX - Commonly refers to the solid n-alkane (paraffin) hydrocarbon fraction recovered from petroleum. The term wax is commonly used to refer to n-alkanes in petroleum containing greater than 25 carbon atoms; hence an oil enriched in these components would be termed "waxy" (not to be confused with the term paraffinic, which refers to an abundance of n-alkanes in petroleum without any implied carbon number preference).

WELL, FULLY PENETRATING - A well drilled to the bottom of an aquifer, constructed in such a way that it withdraws water from the entire thickness of the aquifer.

WELL SCREEN - A filtering device used to keep sediment from entering a water well.

WELL YIELD - The volume of water discharged from a well in gallons per minute or cubic meters per day.

XENOBIOTIC - A substance foreign to the indigenous life in a system. A contaminant.

LIST OF ACRONYMS

ACF	Advanced chemical fingerprinting
API	American Petroleum Institute
ARCO	Atlantic Richfield Company
ARMOS	Areal Multiphase Organic Simulator
AST	Above-ground storage tank
ASTM	American Society of Testing and Materials
BIP	Biphenyl
BLS	Below land surface
BRAC	Base Realignment and Closure
BTEX	Benzene, toluene, ethylbenzene, and xylenes
CCC	Civilian Conservation Corps
CERFA	Community Environmental Response Facilitation Act
CHP	Central Heating Plant
CSL	Chemical Systems Laboratory
CO ₂	Carbon dioxide
DBCRC	Defense Base Closure and Realignment Commission
DDT	dichloro-diphenyl-trichloroethane
DLA	Defense Logistics Agency
DHA	Detailed hydrocarbon analysis
DMDEL	Dimethyldiethyl lead
DNAPL	Dense non-aqueous phase liquid
DO	Dissolved oxygen
DoD	Department of Defense
DRO	Diesel-range organics
DPSC	Defense Personnel Support Center
DSCP	Defense Supply Center Philadelphia
EDB	Ethylene dibromide
EDC	Ethylene dichloride
EPA	United States Environmental Protection Agency
ES&T	Environmental Science and Technology
EVS	Environmental Visualization System
F&B	Friedman & Bruya, Inc.
FE ⁺³	Ferric iron
FIA	Fluorescent Indicator Adsorption

LIST OF ACRONYMS (Continued)

GC/ECD	Gas chromatography with electron capture detection
GC/FID	Gas chromatography with flame ionization detector
GC/MS	Gas chromatography/mass spectrometry
GC/MS/SIM	Gas chromatography with mass spectrometry in selected ion monitoring mode
gpm	gallons per minute
GRO	Gasoline-range organics
HFS	Hydrocarbon fuel scan
IBP	Initial boiling point
IP	Isopentane
IRM	Instrumental reference material
IST	Integrated Science & Technology, Inc.
MCH	Methylcyclohexane
MSL	Mean sea level
M/BE	Methyl-tertiary butyl ether
MTEL	Methyltetraethyl lead
NAPL	Non-aqueous phase liquid
NGVD	National Geodetic Vertical Datum
NIR	Near infrared analysis
NO ₃	Nitrate
NOAA	National Oceanics and Atmospheric Administration
O ₂	Oxygen
OQMG	Office of the Quartermaster General
PADEP	Pennsylvania Department of Environmental Protection
PAH	Polynuclear aromatic hydrocarbon
Pb	Lead
PC	Principal component
PCA	Principal component analysis
PGW	Philadelphia Gas Works
Ph	Phytane
PID	Photoionization detector
ppmv	Parts per million, volume
Pr	Pristane
PRR	Pennsylvania Railroad
QC	Quality control

LIST OF ACRONYMS (Continued)

SHC	Saturated hydrocarbon compounds
SIM	Selected ion mode
SO ₄ ⁻²	Sulfate
SOP	Standard operating procedure
TBP	True boiling point
TEL	Tetraethyl lead
TMB	Trimethyl benzene
TMEL	Tetramethylethyl lead
TML	Tetramethyl lead
TPH	Total petroleum hydrocarbon
TPH-DRO	Diesel-range TPH
TPH-GRO	Gasoline-range TPH
USACE	United States Army Corps of Engineers
UCM	Unresolved complex mixture
UST	Underground storage tank
VOC	Volatile Organic Compound

EXECUTIVE SUMMARY

The Defense Supply Center Philadelphia (DSCP), formerly known as the Defense Personnel Support Center (DPSC), which is located in southeast Philadelphia, Pennsylvania, is scheduled for closure in 1999 under the Base Realignment and Closure Act of 1993. During the course of pre-site closure environmental assessments, environmental consulting firms working under contract with the U.S. Army Corps of Engineers discovered a plume of light non-aqueous phase liquid (NAPL) hydrocarbon on the surficial groundwater table under the DSCP facility. The DSCP and its consultants contend that the source of contamination was not on the DSCP itself but rather that it was a nearby refinery located west of the DSCP. Sun Company, Inc. (Sun), currently owns and operates the refinery. DSCP has asserted that the plume is made up of a light refinery naphtha characterized as JP-4, a substance that DSCP claims to have never used at the facility, but a substance that the refinery produced.

Like the DSCP, Sun has retained environmental consultants who have studied the plume extensively and analyzed possible sources. Their comprehensive and integrated evaluation included reviewing the results of all available soil and groundwater data from locations on or proximate to the DSCP, the refinery, the area between them (a CSX, formerly Conrail and Pennsylvania, railroad right of way), and other adjoining locations. These data include the results of sampling performed by the DSCP, by Sun, and by governmental agencies. Sun also considered the geology of the region and the site, the hydrogeology, the morphology of the plume, and available information about possible NAPL sources at the DSCP, the refinery, and elsewhere in the area. In addition, Sun also incorporated historical information about the composition and use of JP-4 and other hydrocarbon products, such as naphtha and gas condensate, that merit consideration as possible contributors to the plume into the body of data being evaluated. Sun's consultants employed standard statistical and modeling techniques and computer software in their work.

Based on its extensive analysis, Sun flatly disagrees with the DSCP's conclusion as to the nature and source of the plume beneath the DSCP. The preponderance of the available data does not support the DSCP's position that the refinery is the source of the DSCP plume. Rather, the data strongly

points toward a conclusion that the plume originated at the DSCP itself. Five factors bear on the inquiry into where the plume originated, all of which indicate that the DSCP rather than the refinery was the source:

1. **The Direction of Groundwater Flow:** Groundwater currently flows south under the DSCP with a westerly component that is strongest in the western aspect of DSCP. This current flow direction has persisted throughout the history of the study area. The refinery lies to the west of the DSCP. Thus, the refinery is downgradient from the DSCP and, therefore, cannot be the source of the plume. Also, extensive groundwater pumping, which has occurred for many years at the refinery, would have enhanced the pre-existing westerly flow component. This historical pumping, therefore, further supports the conclusion that the refinery was not the source of the plume. Moreover, a groundwater divide beneath the DSCP, as well as infiltration into the 26th Street sewer, separates the groundwater beneath the refinery from the groundwater beneath most of the DSCP, including the area where most of the plume is located.
2. **The Absence of Evidence of a Migration Pathway:** The DSCP has contended that the plume migrated from the refinery to the DSCP beneath 26th Street and the CSX railroad property that lies between them. If this were the case, substantial residual hydrocarbon unquestionably would exist in the soil and smear zone beneath 26th Street and the CSX property that served as the supposed pathway. However, the available soil inspection and analytical data show no zone between the DSCP and the refinery with hydrocarbon concentrations that would suggest that NAPL migrated through it. This is true, both at the level of the current water table and at the elevation of the water table, when it was at its historical low point, when the release and migration allegedly occurred according to DSCP's hypothesis. Analysis of the travel time that would have been required for the plume to migrate from the refinery to the DSCP revealed that it would have been impossible for the plume to have migrated from the refinery during the time window hypothesized by the DSCP. Moreover, analysis revealed that it would have been impossible to create the plume beneath DSCP even if migration from the refinery began in 1870.
3. **The Morphology of the Plume:** The shape and configuration of the plume indicate that the DSCP was its source. The plume is thickest near its center, below the southern portion of the DSCP, and it thins in all directions toward its edges. It also contains discrete thickness centroids that are characteristic of source areas. The shape, thickness, and distribution are also consistent with the groundwater divide beneath the DSCP and the general direction of groundwater flow. Further, weathering analyses clearly show that the freshest or least weathered aspect of the plume is where it is thickest, becoming progressively more weathered toward the refinery. The most weathered portion of the plume is at its edges. This also indicates that DSCP is the source of its own plume.

4. **The Chemical Character of the NAPL:** The material in the plume is not JP-4 and is not a light refinery naphtha. It is primarily gasoline and naphtha or naphtha-like products. Its composition is different from a small separate plume under part of the refinery, which is comprised of a mixture of gasoline, diesel fuel, kerosene-range products, and lubricating oil. Examination of other potential sources also shows that products such as those in the NAPL plume were used during DSCP operations.
5. **DSCP Source Analysis:** Potential sources other than the refinery exist in the study area, both on and off the DSCP site. An analysis of these potential sources and the history of the DSCP site revealed that DSCP used a large quantity of petroleum fuels, naphtha, and naphtha-like products during its operation. DSCP's investigations of these potential sources were woefully inadequate to ascertain the type, quantity, and release pathways from these sources. Considering the four previous factors that point to DSCP and not the refinery, these additional hydrocarbon sources on and off the DSCP site must be the source of the NAPL plume.

The following discussions summarize the scientific evidence that support the above-stated conclusions on the five questions relevant to the search for the source of the DSCP plume.

GROUNDWATER FLOW DIRECTION

Sun evaluated the direction of groundwater flow in the study area from the perspective of NAPL transport. This evaluation used both historical and current data on a regional and a local scale; it also used data generated by governmental agencies in addition to the data generated by Sun and the DSCP. The evaluation also considered current and historical anthropogenic effects on the direction of groundwater flow in the study area.

Since the water table generally is a subdued replica of topography, the pre-development topographies of the Sun and DSCP properties, as well as depositional and erosional processes that acted on the area in geologic time, were examined. This examination showed that topography on the two sites resulted from deposition and erosion that occurred in the drainage basins of the Delaware and Schuylkill Rivers. Before development, a ridge oriented northeast to southwest across the DSCP property was the highest point on the two properties. The flanks of this ridge sloped to the south-southwest and south-southeast. As such, this ridge served as a topographic divide between the two rivers. The presence of this topographic divide then, strongly implies a groundwater divide in the same area.

Historical regional water-table maps prepared by the United States Geologic Survey, as well as water-table maps that have been prepared using site-specific data, do indeed show that a groundwater divide exists on the DSCP site in the vicinity of the former topographic high. According to these maps, groundwater flows south-southwest on the western side of the divide and south-southeast on the eastern side of the divide. This groundwater flow pattern would profoundly affect the migration of NAPL that was released on either of the subject properties that comprise the study area. Clearly, NAPL released on the western side of the divide would migrate south-southwest, and NAPL released on the eastern side of the divide would migrate south-southeast. If NAPL had been released on the refinery, it would have migrated to the south-southwest toward the Schuylkill River and not toward the DSCP property.

Groundwater pumping can also affect groundwater flow, and thus NAPL transport, on a local or regional basis. As the area surrounding the study area was developed, a portion of the water requirements was satisfied by groundwater pumping. The historical record shows that extensive, long-term pumping occurred at the Philadelphia Navy Yard, which is approximately 1.2 miles south-southeast of the subject site. The pumping from the deep, semi-confined aquifer at the Navy Yard and drought conditions that occurred from the 1940s to the 1960s depressed the regional water table approximately 10-ft. However, groundwater flow direction in the study area was not influenced by this Navy Yard pumping. In addition to the Navy Yard pumping, pumping for water supply and NAPL recovery occurred from the water-table aquifer at the refinery. Early refinery records show that pumping began at the refinery as early as the late 1800s; it continues to the present. This pumping depressed the water table around the pumping centers, which induced groundwater flow toward these areas. The induced groundwater flow would have been greatest on the refinery property because the pumping centers were located there. This anthropogenic activity would have caused released NAPL to flow west toward the pumping centers. Thus, pumping on the refinery would have augmented the natural groundwater gradient component toward the west.

Other anthropogenic activities and features can also affect the direction of groundwater flow. In the early to mid-1960s, a sanitary sewer with a storm-water by-pass to handle excess runoff during large precipitation events was installed beneath 26th Street adjacent to the refinery's eastern boundary and between the refinery and DSCP. Logs of geotechnical borings installed prior to sewer construction

do not mention hydrocarbon odors or the presence of NAPL. Since the installation of the sewer required extensive tunneling, the presence of hydrocarbon in the soil samples from these borings would have been noted. During the sewer construction proper, groundwater pumping was required to lower the water table over a large portion of the construction project because the sewer was installed beneath the water table. These groundwater withdrawals caused a modification to the normal flow regime. A trough in the water table was created along the length of the construction project, which enhanced the westward groundwater flow to the sewer on the western portion of DSCP and induced flow from the eastern side of the refinery to the east toward the trough. After it was constructed, leakage into the sewer lowered the water table along this trough thereby inhibiting potential migration of NAPL between the two properties.

The sewer currently receives and has historically received a substantial amount of groundwater drainage. Based on recent potentiometric-surface maps of the area, groundwater drainage to the sewer is most prevalent in the area of 26th Street east of the Sun #2 Tankfarm. Because it drains groundwater in this area, the trough created during construction dewatering persists in the water table along this portion of the sewer. In summary, the construction and continued operation of the 26th Street sewer would have impeded any theoretical migration of NAPL between Sun and DSCP since the mid-1960s. The presence of the sewer, in combination with the recovery wells operating along the eastern border of the refinery, will continue to inhibit migration of NAPL between the two properties and will, in fact, augment the natural flow from the DSCP to the west.

NAPL MIGRATION PATHWAY

Sun evaluated the distribution of hydrocarbon in the subsurface, especially with respect to any occurrence of hydrocarbon in the area between the refinery and the DSCP property to determine if NAPL might have migrated through the area. The data used to make this evaluation consisted of all available soil-residual hydrocarbon analyses, all available soil screening data, and all available NAPL distribution data from monitoring well gauging. These data were analyzed, and observed hydrocarbon concentrations were compared to residual saturations via conceptual analyses and numerical modeling. Although DSCP hypothesized that the plume migrated through the alleged pathway beneath 26th Street and the CSX property, there is no evidence that such a pathway ever existed.

Malcolm Pirnie prepared the, "NAPL Plume Study Final Report," in 1997. It was tasked specifically to conduct a "definitive investigation" of the NAPL plume under the DSCP site. There were several noticeable inconsistencies and omissions in the report. The most striking omission is related to the alleged pathway. The report included a significant amount of discussion about the observation of "oil soaked" soil in boring B of the Schuylkill Expressway geotechnical borings; but it made no mention of several other borings (borings A and C through J) near and in the alleged pathway in which no mention of contamination was observed. The report also incorrectly identifies pre-construction borings from the 26th Street sewer construction as containing NAPL. In fact, NAPL or petroleum contamination was not identified in any of the pre-construction 26th Street borings.

In the conceptual theoretical analysis, estimated soil-residual hydrocarbon saturation and corresponding concentrations that would have had to have existed if the NAPL in the DSCP plume had migrated through the area were calculated and compared with observed total petroleum hydrocarbon concentrations. This theoretical comparison is based on three of the primary physical characteristics of immiscible multi-phase fluid transport: first, adequate NAPL must be present to exceed the residual capacity of the soil through which migration is occurring; second, a continuous NAPL wetted zone must exist; and third, an adequate NAPL head must be present to provide the energy to "push" the NAPL along. Analysis of the available soil analytical data shows that there is no zone between the properties where hydrocarbon concentrations suggest that NAPL migrated through it. The analyses were carried out both at the current water-table elevation and at the elevation of the water table when it was at its historical low point. Further, if the zone where the residual saturation of the soils had been exceeded existed, NAPL would have accumulated in the monitor wells installed in that area. None of the wells in the center of the alleged pathway contain NAPL.

Sun also evaluated the rate of NAPL travel in the subsurface as it related to the development of the plume beneath the DSCP. This issue is particularly germane because DSCP has hypothesized that migration from the refinery occurred in a 12- to 14-year window from about 1950 to 1964. Making extremely conservative assumptions about hypothetical releases at the refinery and applying established and peer-reviewed time-transport factors applied to the subsurface in the area between

the two properties, Sun estimated the time it would have taken for a release on the refinery to migrate to the DSCP site. The results of this analysis showed the plume could not have migrated from the refinery within the alleged timeframe.

Numerical modeling was the third approach used to evaluate the NAPL distribution on and between the two properties. The ARMOS multi-phase transport code was used in this application. Input values for the model were based on the physical characteristics of NAPL and observations from soil borings installed across the study area as part of the many investigations that have been carried out to date. In addition to these, data from soil borings installed in the course of various private and governmental construction projects were also used. Numerous release areas, configurations, and migration scenarios were used to evaluate the potential for NAPL migration from the refinery to the DSCP property. In each scenario, the subsurface conditions as described by the available geologic data were used as inputs to the model. These efforts showed that a release on the Sun property could not have migrated onto the DSCP property and created a plume with the morphology and configuration of the plume that exists today, regardless of the release volume, NAPL migration rate, and water-table fluctuation.

The modeling results also confirmed the results of the residual-saturation analysis discussed above, as well as the NAPL plume morphology results described below. The results of all the scenarios simulated through modeling showed that a very significant residual-hydrocarbon fraction would exist if a plume had migrated through the interval between the two properties and that this residual fraction would have translated to very high total petroleum hydrocarbon concentrations. The soil analytical data shows that no significant residual fraction exists. Further, the modeling results demonstrate that had migration occurred through the interval between the two properties, the wells in the path would contain measurable NAPL today. Again, none exists. The simulations also show that, even with a very large and highly conductive pathway and with multiple releases over the 127-year operational history of the refinery, the DSCP plume could not be replicated.

In conclusion, analyses using three independent approaches, each with different theoretical and analytical bases show that large quantities of NAPL did not migrate through the interval between the Sun refinery and the DSCP property. If migration of more than 1,000,000 gallons occurred through this "pathway" as DSCP alleges, significant volumes of NAPL manifested as residual hydrocarbon,

concentrations in soil, or NAPL on the water table unquestionably would remain in it. This is entirely consistent with the conclusions presented elsewhere in this report relative to the direction of groundwater flow, NAPL plume morphology, and the chemical character of the NAPL plume.

NAPL PLUME MORPHOLOGY

Sun also examined the orientation, configuration, distribution, and thickness of the NAPL plume beneath DSCP. The data used in this analysis and evaluation were generated during synoptic gauging events that occurred on the two properties and surrounding areas. The results of these evaluations showed that individual, unconnected, and isolated plumes of NAPL exist beneath each of the properties. The presence of separate plumes is consistent with the analysis disproving the existence of a pathway, the differences observed in chemical character of the NAPL, and the groundwater flow direction.

The morphologies of the separate plumes in the study area also indicate that the plume beneath the DSCP originated on the DSCP itself. At the time of the synoptic gauging events, active NAPL recovery was being carried out on the refinery, and had been for some time. In contrast, no active recovery had occurred on the DSCP property. While the plume on the Sun property is relatively small and thin, the plume on the DSCP property is larger and thicker. The thickest aspect of the plume on the DSCP property is near its center in the southern part of the property. From this point, the plume thins in all directions, and a zone with no NAPL completely surrounds the plume. Given the physics of immiscible phase transport, the thickest aspect of an NAPL plume would be expected to be nearest the source in the absence of active recovery. The morphology analysis also shows several very distinct thickness centroids, which strongly indicate overlying sources. Thus, the morphology of the NAPL plume beneath the DSCP property is consistent with a source or sources on the DSCP property. The source or sources would occur near the thickest aspect of the plume, as opposed to a source on the refinery property. Also, recovery well pumping on the refinery over the years would have had little effect on the plume's current morphology and configuration.

The morphology of the plume is also consistent with the presence of the groundwater divide and a localized east to west component of groundwater flow, as discussed above. That is, the elliptical plume is oriented northeast to southwest, and its center is in the south-central aspect of the DSCP

site. The plume also thins in a non-linear pattern over a large distance interval to the south, which is also consistent with the regional groundwater flow direction. This morphology is consistent with NAPL migration to the east and to the west on either side of the divide. The weathering patterns observed in the chemical analysis also support this observation relative to morphology. The freshest aspect of the plume, which would be found nearest to its source, coincides with the thickest portion of the plume. The NAPL within the plume becomes progressively more weathered toward the refinery and to the south, farther from the thickest portions of the plume on DSCP. This indicates a greater age for the NAPL on the plume's periphery nearest the refinery. Thus, the morphology of the plume beneath the DSCP demonstrates that its source is within the DSCP site.

CHEMICAL CHARACTER OF NAPL

Sun used data generated by DSCP, as well as its own data, to evaluate the physical and chemical character of the NAPL in the study area. The analyses carried out by Sun included chemical analyses of NAPL, soil, and water samples for petroleum hydrocarbons, polynuclear aromatic hydrocarbon compounds, substituted polynuclear aromatic hydrocarbon compounds, organic lead, additives, and pesticides. Following the analyses, the generated data were evaluated using advanced chemical fingerprinting techniques to evaluate the character of the NAPL on the two properties.

This phase of the evaluation showed that the NAPL beneath the Sun property, both at the depth of the current water table and at the depth of the water table when it was at its historic low point (circa 1950s), is distinctly different from that beneath the DSCP property. The NAPL beneath the refinery consists of a mixture of hydrocarbon products including gasoline, diesel fuel, kerosene-range products, and lubricating oil. In contrast, the NAPL beneath the DSCP property is a mixture of primarily gasoline and naphtha, or naphtha-like products. Sun's analyses and evaluations conclusively showed that the NAPL beneath the DSCP site is not a light refinery naphtha and it is not JP-4, as DSCP contends. Thus, the chemical evidence demonstrates that the NAPL on the DSCP property is not related to either the current, distinct NAPL beneath the refinery or residual NAPL in the saturated zone beneath the refinery.

DSCP SOURCE ANALYSIS

Finally, DSCP contends that it never used products similar to those found in the NAPL plume beneath it, reasoning that only the refinery could be the source. Sun identified other potential source areas both on and off the DSCP site. A number of potential hydrocarbon source areas do exist on DSCP and immediately to its south. DSCP's physical evaluation of these source areas with respect to their possible contribution to the NAPL plume was inadequate. DSCP's fact-finding investigation was also inadequate. In addition to storing petroleum products in both underground and aboveground storage tanks, DSCP reportedly discharged petroleum to sectional clay-tile sewer drains causing back ups. It is imperative that a more complete fact-finding investigation and a more thorough physical evaluation be undertaken before these likely sources of the NAPL are ruled out.

SUMMARY

Sun's comprehensive integrated evaluation and analysis of NAPL in the subsurface in the vicinity of its refinery and the adjacent DSCP facility shows that the refinery could not be the source of the NAPL beneath DSCP. This evaluation and analysis incorporated available information on geology, hydrogeology, chemistry, microbiology, transport and fate, and site history, as well as mathematical modeling, into an examination of the occurrence and behavior of NAPL in the subsurface beneath the two properties. The chemical makeup of the NAPL plume, flow direction, soil-residual hydrocarbon concentrations, and modeling of groundwater flow and fate and transport independently demonstrate that the NAPL beneath the Sun refinery is not related to that on the DSCP site. When viewed collectively, these independent conclusions support each other, and when integrated, they provide convincing proof that the NAPL plume on the DSCP property could not be related to hydrocarbons that originated on the Sun refinery.

1. INTRODUCTION

Sun Company, Inc. (Sun), and the Defense Logistics Agency (DLA), the Federal entity responsible for the Defense Supply Center Philadelphia (DSCP), formerly known as the Defense Personnel Support Center (DPSC) in Philadelphia, Pennsylvania (Figure 1-1 and Plate 1-1), are in dispute regarding the source of light non-aqueous phase liquid petroleum hydrocarbon (NAPL) on the water table beneath the DSCP facility and property to the south. The dispute stems from DLA's allegation that the hydrocarbon originated on the refinery property, migrated beneath 26th Street, beneath a CSX railroad right-of-way, and onto the DSCP property. DLA has apparently based this conclusion solely on the proximity of the refinery to the plume and on the known, distinct, and isolated plumes beneath the refinery. Based on compelling evidence developed through comprehensive and integrated analysis of available data generated by State and Federal agencies, DSCP, and Sun, Sun has concluded not only that the refinery is not the source of the NAPL, but also that the source of NAPL is or was on the DSCP property. This conclusion is based on the geology and hydrogeology of the subsurface beneath the study area, the physics of immiscible phase transport and fate in the subsurface, the chemistry of the subject NAPL, historical information regarding product use and disposal on the DSCP facility, and known and suspected releases of similar materials on DSCP. Summaries of the specific facts that support these conclusions include the following:

- The direction of groundwater flow and thus, the transport direction for any hydrocarbon (i.e., separate phase or dissolved phase) introduced into the subsurface environment in the vicinity of the study area is from the north-northeast to the south-southwest (i.e., from DSCP toward Sun). This flow direction currently exists, and substantial evidence indicates that it existed throughout the history of the study area.
- Available subsurface hydrocarbon concentration data and the distribution of NAPL in the study area demonstrate that there is no continuous free- or residual-phase hydrocarbon to support DSCP's allegation that a pathway connects the refinery's #1 Tankfarm with the DSCP plume. If migration from the refinery occurred as alleged, the physics of NAPL flow dictate that substantial residual material would still be present in the pathway. Further, the

geology of the alleged pathway does not support a conclusion that there was ever a generalized pathway or a preferential pathway.

- The morphology of the NAPL plume beneath the DSCP property is totally consistent with one that originated on the DSCP property (i.e., thickest at its center) and is inconsistent with one presumed to have originated on the refinery and migrated onto the DSCP property. Even considering the NAPL recovery operations of other plumes that were carried out on the refinery property over the years, the plume morphology is consistent with a source on the DSCP property and is inconsistent with a refinery source.
- The NAPL beneath the DSCP property is not a light refinery naphtha, characteristic of JP-4, as DSCP contends. The NAPL in the plume is primarily a mixture of gasoline and naphtha or naphtha-like products. The chemical makeup of the NAPL beneath the DSCP property is clearly dissimilar to that beneath the refinery both at the elevation of the current water table and at the elevation of the water table in the time frame that DSCP alleges the NAPL migration occurred (i.e., circa 1952 to 1964).
- DSCP stored and used considerable quantities of petroleum products of the type in the plume over its life. DSCP has had documented and suspected releases of fuel to the subsurface, as well as intentional disposal of petroleum into sectional clay sewer pipes directly above the NAPL plume. Considering this evidence, the narrow scope of DSCP's fact-finding investigations, and its physical investigations of likely source areas, potential sources on DSCP cannot be ruled out.

Hard data and theoretical considerations, which are presented in the ensuing sections of this document, support each of these summary statements and conclusions. This document is organized as follows:

- History and use of the study area
- Theoretical Considerations, including hydrogeology, the physics of NAPL transport, NAPL fate, and petroleum hydrocarbon chemistry
- Groundwater flow direction
- NAPL pathway analysis
- NAPL plume morphology
- NAPL chemistry
- Historical NAPL source analysis
- Summary and conclusions

The conclusions drawn in this document are comprehensive, integrated, and mutually supportive. The evaluations and analyses carried out and presented in this document are based on a database

that includes all the published data Sun has obtained relative to the region and study area, as well as field data generated by Sun and DSCP to supplement the original database. Because processes in the physical world are highly interactive, this document presents evaluations and analyses that were carried out by integrating Sun's and DSCP's histories, the geology, the hydrology, the chemistry, and the microbiology of the subsurface in the vicinity of the study area, rather than by examining disjointed facts from discrete disciplines in an isolated manner. Appendix A lists the references used to prepare this integrated evaluation.

1.1 BACKGROUND

Before the southern aspect of Philadelphia was developed, the land was heavily forested and dissected by numerous tributaries to the Schuylkill and Delaware Rivers. During the early phases of development of the area surrounding the current Sun and DSCP properties in the 1800s, the land was converted from forests and fallow fields to farms. As development continued into the 1900s, industrial operations encroached on and ultimately displaced the farms. This evolution toward more industrialized land use continued to the point that today the area west of 26th Street to the Schuylkill River is occupied primarily by petroleum refining and storage operations and the area east of 26th Street is occupied by the DSCP facility, other commercial, industrial, and transportation facilities, and residential communities.

In the mid-1860s, Atlantic Petroleum Storage Company (Atlantic) first developed the site where the Sun refinery is currently situated as a petroleum-handling operation. In 1870, Atlantic formed a refining division and initiated crude oil-refining operations. This aspect of the study area has been dedicated to this type of land use ever since, and refining and finished-product storage continue there today.

In 1917, following the acquisition of an 87-acre parcel of farmland by the Federal government, construction began on the DSCP facility, which was intended to replace the former Schuylkill arsenal, which was located nearby. The facility was developed to manufacture, store, and distribute goods and supplies to support the U.S. military. Its functions included printing, vehicle and locomotive repair, woolen fabric treatment and cleaning, painting, chemical laboratory operations, and fuel dispensing and storage. It was owned and operated by the Federal government because it

was a part of the Department of the Army, more specifically the Quartermaster Corps. Heightened periods of activity at the facility occurred during World War I, World War II, the Korean Conflict, the Vietnam Conflict, and Operation Desert Storm. In 1995, as part of the Base Realignment and Closure (BRAC) process, the DSCP facility was scheduled for closure in 1999.

The Federal legislation that set forth the BRAC process requires that any site slated for closure be evaluated in detail and that any environmental impact that posed a threat to human health or the environment be addressed to mitigate that threat before the site is vacated. Numerous environmental investigations have been carried out over the past several years at the DSCP site. In the course of these investigations, NAPL was found floating on the surficial water table beneath the site of one of DSCP's vehicle-fueling operations, which had been used since about 1940. DSCP concluded that the NAPL on the water table beneath their site was a light refinery naphtha (characteristic of jet petroleum, JP-4) and that it must have originated on the Sun refinery property and migrated onto the DSCP site because DSCP claims to have never handled this type of product.

To respond to these allegations, Sun initiated its own series of historical information gathering efforts, data evaluations, and field investigations. These included collecting historical information on the processes and practices at DSCP and the refinery, evaluating the data gathered and reported by DSCP, and generating new empirical data. Sun retained Integrated Science & Technology, Inc. (IST), to conduct its study. Arthur D. Little was retained to perform analytical chemistry and fingerprinting work. Sun's conclusions, which are reflected in this document, are based on the work of IST and Arthur D. Little.

Sun drew two conclusions as a result of this study. First, it concluded that the material beneath the DSCP site is not a light refinery naphtha and it is not JP-4. It is primarily gasoline and naphtha or naphtha-like products. Sun also concluded that the refinery is not the source of the NAPL beneath the DSCP property due to the stratigraphy of the subsurface in the area as well as the patterns of groundwater flow and thus, NAPL transport patterns.

1.2 STATEMENT OF PURPOSE

The primary purpose of the investigations carried out in the study area and the evaluation of the data generated from them was to determine if the NAPL plume beneath the DSCP property could

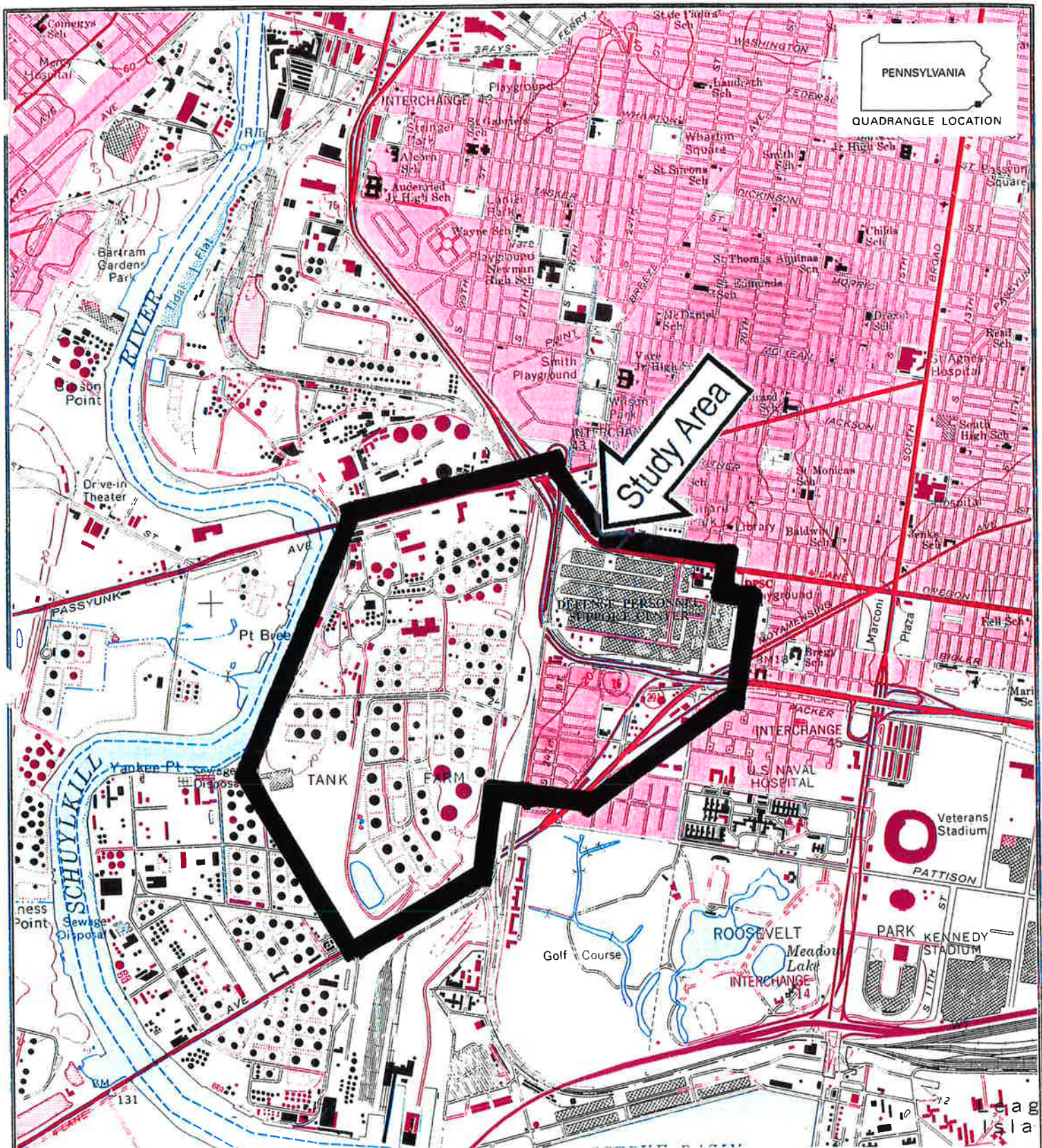
have originated from the Sun refinery and, if not, what other sources on and off the DSCP might exist. This report presents the results of the intensive and exhaustive evaluation Sun has carried out to discern the character of the subsurface beneath the study area and how this character may have influenced the behavior of NAPL. The direct purpose of the investigations was to ascertain the source of NAPL beneath the DSCP property, to evaluate the mechanisms through which the NAPL might have migrated from its source, and to evaluate the extent to which fate mechanisms might have affected its location and character as a function of time.

1.3 OBJECTIVES

The following are the primary objectives of the data-gathering and evaluation efforts described in the ensuing sections of this document:

- To determine both the current and historical groundwater flow in the study area
- To determine whether a pathway ever existed through which NAPL released on the refinery could have migrated to the DSCP
- To determine if the morphology of the NAPL plume beneath the DSCP property is consistent with a source to the northwest
- To determine if the material in the DSCP NAPL plume is a light refinery naphtha characteristic of JP-4, whether the chemical characteristics of the material in the plume are consistent with material that may be in the subsurface between DSCP and the refinery or with material in the subsurface beneath the refinery, and whether the material is consistent with any products that DSCP may have used
- To examine and evaluate potential NAPL sources on and off the DSCP property that might have contributed to the plume.

The ensuing sections of this document contain the results of historical and field data collection efforts, the results of analysis of the data gathered, integration of the data, and the conclusions drawn from the analyses carried out.



MAP SOURCE:
U.S.G.S. TOPOGRAPHIC QUAD (7.5 Min)
PHILADELPHIA, PA.-N.J., 1967 (REVISED 1994)

INTEGRATED
SCIENCE &
TECHNOLOGY, INC.

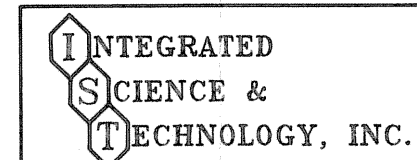
Site Vicinity Map

Scale: 1" = 2000'



STUDY AREA
Philadelphia, PA

FIGURE
1-1



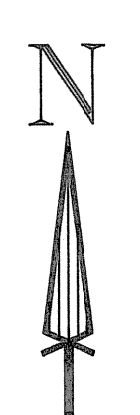
0 400 800
SCALE IN FEET

THIS MAP WAS COMPILED FROM BASE DRAWINGS
AND/OR SKETCHES SUPPLIED BY OTHERS.
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BASE MAP RELATED INFORMATION CONTAINED HEREIN.



SUN PHILADELPHIA
REFINERY

DEFENSE SUPPLY
CENTER PHILADELPHIA
(DSCP)



2. HISTORY

The study area has been industrialized for well over 100 years. Over that period, while there have been operational changes, both aspects of the study area maintained the same basic manufacturing objectives: DSCP manufactured and warehoused clothing, printed documents, maintained and painted vehicles, performed laboratory testing, warehoused food, and otherwise supported the Department of Defense (DoD) mission; and the refinery refined, blended and stored petroleum products. Examining the histories of these two manufacturing sites allows a better perspective of the activities that were carried out there that may have bearing on the NAPL in the subsurface beneath the two sites.

The remainder of this section includes discussions of the development of the DSCP and Sun sites, a summary of the activities that were carried out on the sites over the years of operation, and a summary of the environmental-quality assessment activities that have been carried out on each of the sites over the years.

2.1 DSCP FACILITY

2.1.1 Site Development

Historical documentation indicates that the DSCP vicinity was uncultivated and consisted of pastures in the late 18th century. By 1810, three farmstead complexes had been established; these fronted the Penrose Avenue. The collective property was divided and used as farmsteads until 1831, when Stephen Girard acquired it. Following his death in 1831, he left his extensive property, including the property occupied by the DSCP, in trust to the Mayor, aldermen, and citizens of Philadelphia. Although this property was originally undeveloped farmland, the City of Philadelphia slowly encroached and absorbed it. In 1918, the U.S. Federal Government leased a 60.6-acre tract of this property at the corner of 21st Street and Oregon Avenue from the City of Philadelphia to construct the U.S. Army Quartermaster's Department facility. This facility ultimately became the DSCP (Hunter Research 1994).

The facility assumed responsibility for many of the activities that had been conducted at the former Schuylkill Arsenal. Throughout its operational history, the facility's primary mission was to act as a manufacturing, warehousing, textile research, and distribution center for clothing and equipment to support the U.S. DoD, and to a lesser extent the Civilian Conservation Corps. The facility also coordinated the subcontracted private manufacture of clothing and inspected this clothing. Although operational activities evolved throughout the operational life of the facility, its primary mission changed little until recently.

In 1918, five warehouse buildings (M-1 through M-5) were constructed at the site. A series of administrative buildings and associated support structures were constructed east of the warehouses, and each warehouse had railroad tracks leading into the structures. During World War I, the warehouses served as storage for goods to be packed and shipped to the war zone; they also stored clothing, such as underwear, shoes, stocking, etc. (Hunter Research 1994). Figure 2-1 shows the configuration of the site in 1922 (Sanborn 1922). This configuration includes the original five warehouses. In addition to the warehouses, various support structures, such as the gasoline pump house, laboratory, printing shop, maintenance shop, and, most noticeably the railroad spurs that served the individual warehouses, are included on this figure.

On 25 September 1923, the United States acquired the original parcels of property that had been leased from the City of Philadelphia by eminent domain; subsequently, between 1928 and 1944, the United States government acquired additional parcels of property (PRC 1994). After World War I the clothing factory from the Schuylkill Arsenal was moved to the Intermediate Depot in 1921 and 1922. Limited production of special sized officers' uniforms began in 1918; full production was reached by 1926 and 1927. In 1927 the new facility was officially designated the U.S. Army Quartermaster Depot. Production, however, was scaled back to special items from 1928 until 1933; uniform manufacturing ultimately ceased at the facility in 1942.

After the outbreak of the war in 1939, and the anticipation of uniform and equipment needs after the Selective Service Act was passed in 1940, the facility expanded to include the area to 20th Street to the east (the former John Hannaker farmstead). At that time, the site became known as the Philadelphia Depot. The facility expanded with the addition of several new buildings to manufacture and house military goods and material; other additions included buildings to house new

heating facilities and administrative offices. During this construction, the rail lines were relocated to the south and west of the site. Figure 2-2 shows the facility's configuration after the addition of the property to the east at the 20th Street; it also shows the additional facilities on the site. Table 2-1 summarizes the Depot Construction between 1940 and 1942 (Haggard 1956).

The Depot provided work for 8,728 employees at the end of World War II in September 1945. The factory ceased operations for the month of September 1945. After it reopened in October, it focused on cloth reclamation and producing special-size clothing. Relatively little new construction took place after World War II. By June 1950, when the Korean Conflict started, the number of employees had been reduced to 3,438. Reserve parachutes and women's clothing were made at the factory during this war. The Korean Conflict brought a rush order for the delivery of 250,000 winter jackets to be produced in 30 days. The Depot served in the role of manufacturer, coordinator of subcontracted private manufacture, inspector and shipping agent of emergency clothes.

The facility continued its primary mission, providing manufacturing and warehousing support for the Vietnam Conflict and Operation Desert Storm. In 1965, the Defense Clothing and Textile Supply Center (formerly the Quartermaster Depot) combined with the Defense Subsistence Center and the defense Medical Supply Center to form what is now DSCP. Until the closure of the clothing factory in 1994, manufacturing was also part of the installation's mission (PRC 1994).

The post-1942 site configuration is presented in Figure 2-2. This figure is a composite of historical structures (crosshatched symbols) and the recent structures present in 1992. Various new construction activities have occurred at the facility over time, and some buildings have been replaced or demolished. The following list summarizes the buildings, which were replaced with the construction of Buildings 6 and 8 in 1942 and 1940, respectively:

- Building 5: Former Clothing and Tent Factory (demolished in 1991)
- Building 6: Administration Building
- Building 7: Motor Transportation Shop
- Building 8: Pump House
- Building 9: Water Tank (fire protection)
- Building 11: Guard House (front gate)
- Building 16: Greenhouse

- Building 21: Laboratory
- Building 25: Tunnel House
- Building 27: Electric Switch House
- Building 31: Garage
- Building 32: Garage

The following buildings were demolished in 1942 when buildings 13 and 9 were constructed:

- Building 12: Garage
- Building 13: Garage
- Building 14: Utilities
- Building 15: Plumbing Shop
- Building 17: Scale House
- Building 18: Garage
- Building 19: Paint Shop
- Building 22: Utilities Office
- Building 30: Guard House, South Gate
- Building 35: Blacksmith and Tinsmith Shop
- Building 36: Oil Shed
- Building 40: Gasoline and Oil Station (with underground storage tanks [USTs])

2.1.2 Site Activities and Operational History

Operational activities at the site obviously have evolved since the beginning in 1918, but its primary mission has remained the same throughout the history of the site. The following are seven of the functions that were performed at the DSCP related to its manufacture and storage of clothing:

1. Sponging and mothciding of cloth
2. Manufacturing
3. Warehousing
4. Modifying and altering garments
5. Operating as a pilot production unit for short-notice production
6. Serving as a “yardstick” for costs of materials, labor, and overhead for outside clothing manufacture contractors
7. Conducting textile research and quality control

Table 2-2 summarizes the activities that were carried out in the buildings on the site.

1941 was a significant and very active year at the DSCP to meet the demands of the Army and the Allies of World War II. Using wool as the primary textile for the clothing presented significant challenges. These challenges included shrinkage, water proofing, and protection from insect vermin. Similarly, shrinkage was a also major concern for cotton fabrics. Broad and intense research was

necessary to improve the quality of the textiles. Extensive experimentation at DSCP was carried out to determine suitable substitutes to fill possible scarcities and to modernize army clothing and textile equipment to more efficiently meet the demands of the war effort. Also, the effects of field use and care were evaluated by using experimental subjects to test and use the equipment and clothing. Field concerns, such as mildew treatment, waterproofing of equipment and clothes, and treating the cloth for insects, also required research to select the optimal processes. The laboratory at DSCP played a very large role in the research necessary to address field problems and to improve the quality of the material for the troops (Haggard 1956).

With the entry of the U.S. into World War II, DSCP could not manufacture all the clothing and textile equipment necessary for the war effort even after significant expansion of its workforce and 24-hr/d operation. The DSCP facility then took on added responsibilities for preparing specifications and quality-control processes that would enable the U.S. Government to purchase materials from private concerns (Haggard 1956). The laboratory played a large role in the necessary quality assurance and quality control to assure private suppliers met the government specifications.

One material that the facility used to protect the cloth against insect and moth infestation was DDT. Although DDT was discovered in 1874, it became a very important resource for the military during World War II. As the war was beginning, lice that carried the organism responsible for Typhus were becoming a major problem, and the power of DDT to control that problem was quickly recognized and became an important facet of the war effort. Since DDT is relatively insoluble in water, it was necessary to find a solvent in which this new compound could be solubilized for application. For the clothing industry, the solvent could not produce a residue, and it needed to dry rapidly. West and Campbell (1952) document that DDT was applied to clothing in a manner similar to that employed in the dry cleaning process. That is, the insecticide was solubilized in "white solvent," a naphtha, and the cloth was treated by dipping or impregnation. Although many solvents were tested, those that were most efficient apparently were all naphthas, including Stoddard solvent and aromatic naphthas. Solvent application of DDT was the method of choice because it left no residue and the DDT remained active through five to seven washings. In contrast, DDT applied as a water emulsion did leave a residue, and it was effective for only one or two washings.

In 1956, John V. Haggard prepared a monograph, "Manufacture of Clothing 1945 - 1953." This monograph focused on the Philadelphia DSCP. The Haggard document (1956) also discusses solvent application of DDT to bulk cloth to prevent moth damage. There is strong evidence to suggest that the solvent used in this operation was naphtha. A Military Specification, "Insecticide - Ingredient; Solvent for DDT" 51-I-14, 15 June 1946 specifies a "solvent... free from rancid, objectionable odor." It also specifies the distillation range for the solvent: "the initial boiling point of the solvent shall be not be less than 550 degrees F and the end point shall be not more than 710 degrees F." The solvency power for DDT was specified at solubilization of 20 grams of DDT in 50 ml of solvent. The Haggard Report (1956), which was referenced in DSCP's Cultural Resources Survey (Hunter 1994), also states that extensive DDT application was conducted at DSCP from at least the 1940s until the 1950s, when the monograph was written. Guthrie (1960) indicates that naphtha was the solvent of choice to solubilize and apply DDT in the 1940s and 1950s.

Another of the major operations in the manufacture of clothing at the DSCP facility was sponging and mothciding. In the sponging process, virgin cloth (especially wool) was pre-shrunk so that finished clothing maintained its size. A sponging plant was established at the Depot in 1921 as an element of the Manufacturing Division in Building M-5. In 1921 the sponging plant consisted of two wetting tanks, two loop-drying machines, two, 25 cylinder dryers and two rolling and measuring machines. In the following 2 years, two rotary laundry machines were installed to steam and finish serge cloth (Haggard 1956). In 1935 the plant was expanded, and during the fall of 1941, a newer sponging plant was established within two bays of the newly constructed Building 9. The process and chemicals used in the sponging process changed over the years. However, based on photographs (Philadelphia Quartermaster 1944) and descriptions (Haggard 1956), the following general processes were employed:

- Textiles and fabrics were "dipped" or conveyed through wetting (water) tanks to preshrink the fabric.
- Prior to combining the DDT application process with the wetting process, a second "dipping" in a DDT/solvent solution was performed. This process allowed the fabric to be impregnated with DDT. In this process, the formulation was most likely 3 percent DDT in 97 percent solvent to achieve a final DDT residual in the cloth of 0.2 to 0.7 percent (DSCP 1961). This process then would have consumed large solvent volumes, presumably naphtha, which would have needed to be disposed.

- Fabric was then conveyed through dryers it was rolled onto bolts and stored.

Nonetheless, the older plant in Building M-5 remained in operation giving additional capacity. In 1947, the application of DDT was found to be effective in either an aqueous emulsion or a solvent solution. There were still problems, however, in using an aqueous solution because it was shown to alter the shade of the fabric during the finishing processes. In 1950, the issues with the emulsion were resolved and impregnation of DDT with the sponging operation began at the Depot. Alterations to the sponging facility were completed to include those process changes.

Haggard (1956) also states that moth infestation in the storage of textiles and fabrics was a major problem at DSCP and that applying naphthalene flakes proved both ineffective and expensive. As a result of a 1946 research program, DDT application was mandated. In this process, DDT, in concentrations that ranged from 2 to 5 percent was used, and according to the Haggard report "only deodorized kerosene [a naphtha] should be used as a solvent." In this process, the ends of all rolls of cloth, as well as the "warehouse itself" were sprayed with DDT. In 1949, naphthalene application was completely discontinued in lieu of 5 percent DDT application. Areas used to store woolen cloth and garments were given aerosol DDT treatments every 2 weeks from 1 April to 31 October and every 10 weeks from 1 November to 31 March. In this process, "aerosol treatment would be accomplished with a "Tifa" fogging machine using airplane spray to apply 20 percent DDT" (Haggard 1956). As noted in a 1950 Office of the Quartermaster General (OQMG) warning, the "insecticide" contained a petroleum solvent (naphtha); the warning also stated that the vaporized material would sink to the floor and become an "explosive mixture" (Haggard 1956). During 1950, a water emulsion was prepared for DDT application, but it was rejected because of the higher cost than the petroleum solvent formulation. In the 1950s, sponging and DDT-based mothciding operations were continued with new equipment and facility improvements that reduced the explosion hazard. In the 1960s, a solution of DDT, chlordane, and tetrachloroethene was developed for sponge application to the cloth.

The day-to-day operation of the DSCP also required the use of many other materials, some of which were petroleum products. One such material was heating oil. The primary heat source for DSCP was the central heating plant (CHP) in Building 8. The CHP provided heat for offices, laboratories, manufacturing, warehouses, and any occupied space. Boilers No. 3 and 4 were installed in 1940;

Boiler No. 5 was installed in 1976. The heating system was a steam distribution system. The components of the system included:

- Economizer
- Low-temperature feed-water heater tank
- High-temperature feed-water heater tank
- Condensate water tank
- Two water-softening tanks
- Three compressed-air tanks
- Potable water-storage tanks
- Emission stack
- 550-gallon waste-oil tank

Boilers 3 and 4 were stationary with rated steam capacities of 100,000-lb/hr at 180 psi and 435 degrees F. Only one of these boilers was routinely used; the other was used as a standby. Boiler No. 5 was a low capacity boiler rated at 30,000-lb/hr and was used during low demand in the summer. The steam was supplied to domestic heaters, to presses and former sponging operations. All three were capable of using either No. 6 fuel oil or gas. The gas-distribution system is depicted on Figure 2-2.

No. 6 fuel oil was stored at the southwest corner of DSCP next to Building 18. The fuel-oil reserve was stored in two, 200,000-gallon, steel aboveground storage tanks (ASTs) next to Building 18. Five, 25,000-gallon steel tanks were adjacent to Building 18 to warm the fuel oil so it could be pumped through a 4-in underground pipe to the boilers. An area with storage facilities for paint and pesticide mixing was located next to Building 18; east of the area where heating oil was stored. There was a gas station next to Building 28 that had USTs for diesel and gasoline (leaded and unleaded).

Building 30 housed a locomotive repair shop waste-oil tank and a steam-cleaning area. The building also contained a large paint booth.

On the eastern side of this facility, Building 9 contained sponging equipment and dryers for the cloth and clothing. Buildings 9 and 13 housed activities such as pre-shrinking, sponging, cutting, assembling, dry cleaning, pressing, and storage. Gas odors were identified in Building 13. DSCP's own Environmental Baseline Survey Report noted that as early as 1952 and 1953, vapors from

petroleum solvents, gasoline or heavy ends from natural gas were a problem in the basements in buildings 9 and 13. The DSCP was discharging petroleum solvents (i.e. naphtha) into drains from which they were escaping into the soil. This practice was so prevalent and the disposed volumes so large it caused backups in the drains requiring safety inspections and corrective measures (Chemical Systems Laboratory 1982). Gas odors were also reportedly detected in the steam tunnel connecting Buildings 12, 13, and 14.

In 1981, an audit team identified another former gasoline station, which was removed when Building 9 was constructed. The site is generally referred to as the former Bash Street Gasoline Station. The former gasoline station at Bash Street was found to have five tanks with a total capacity of 10,500 gallons. The status of the tanks has never been resolved.

The laboratories (wet chemistry and physical testing), as well as the printing and photocopying operations, were housed in Buildings 15 and Building 12. The laboratory in Building 15 performed research quality-control tests on a number of different materials procured by DLA. The analyses included tensile strength, water repellency, reaction to ultra-violet light, and reaction of DDT treated material to numerous washings and dry cleaning. The laboratory also conducted wet-chemistry, mass spectroscopy, and atomic adsorption sample analyses for different customers throughout the DoD.

The number and size of known petroleum product storage tanks on the property is presented in Table 2-3. Although the quantity of oil and petroleum products shipped to the site are not well documented in the DSCP environmental reports, DSCP was clearly a large user of petroleum products throughout the site's history.

In addition to tank storage of petroleum products numerous other historical sources were referenced in previous DSCP reports, such as the hazardous materials and waste storage area by Fort Indiantown Gap Maintenance Division at Building 44. Vehicle and locomotive maintenance was also performed in Building 30. Substantial railroad transport, loading, and unloading activities, including heating-oil and gasoline deliveries by remote fill manifolds located on rail sidings, also occurred on the site, as evidenced on the historical DSCP site plans.

2.1.3 DSCP Site Assessment Activities

The physical investigations into petroleum product contamination at the DSCP site have been almost exclusively at UST and AST locations. Because of that focus, the number and location of soil borings and groundwater monitoring wells are essentially limited to those areas with tanks. The large-scale and diverse operation at DSCP, however, suggests usage of petroleum beyond the areas studied by DSCP.

In 1988, the U.S. Army Corps of Engineers (USACE), Baltimore District, conducted a Fuel Contamination Study. This study was performed in January 1988 near the southwest corner of the facility to evaluate the extent of diesel contamination resulting from a leak in the piping between a diesel UST and the fuel dispenser at the Building 28 Gasoline Station. This leak was discovered in September 1987. Soil impacted with hydrocarbons was also found during the investigation; the maximum total petroleum hydrocarbon (TPH) concentration was 18,673 mg/kg. NAPL, at a thickness of approximately 2.2-ft, was observed on the water table both upgradient and downgradient from Building 28. The report of this investigation concluded that petroleum contamination had spread laterally along two clayey soil layers at depths of 3- and 7-ft below land surface (BLS).

Environmental Science and Technology, Inc. (ES&T), prepared the "Engineering Report for the Defense Personnel Support Center, Prepared for the DPSC, November 1991." This investigation was also conducted in the vicinity of Building 28. Seven soil borings were installed during the investigation, all of which were later converted to monitoring wells. Soil samples were analyzed for benzene, toluene, ethylbenzene, and xylenes (BTEX) and TPH. The highest total BTEX concentration was reported to be 1,060,300 µg/kg, and the highest TPH concentration was 17,100 µg/kg. Petroleum contaminated soils were identified in the depth interval from 0- to 10-ft BLS; were absent in the interval 14- to 16-ft; and were "widespread below 16-ft" (Kemron/Versar 1995). NAPL was observed in six of the seven monitoring wells.

In October 1992, USACE, Baltimore District, performed another investigation; the purpose of this investigation was to characterize the area of a proposed building in the vicinity of the eastern portion of Buildings 1, 2, and 3. The results of this investigation are detailed in, "Site

Characterization Report for the New ADP/Admin Building, DPSC, Philadelphia, Pennsylvania.” During this investigation, NAPL was encountered in one of the two monitoring wells that were installed. MW-1 exhibited NAPL and TPH in groundwater up to 1,500 mg/L. TPH levels of 2,100 mg/kg were detected in soil boring SB-5 at a depth interval from 5- to 9-ft BLS. The conclusion of the study stated that the soil concentrations were not believed to be associated with the NAPL at MW-1.

Versar, American Construction Services, and Wu Associates performed an investigation from 1993 to 1995. This investigation entailed the closure or replacement of USTs (Table 2-3). Soil sampling and analyses for petroleum hydrocarbon constituents were performed during the program. The analytical results from the tank-closure activities were reported in the Versar Phase I RI/FS in 1995. Concentrations of petroleum in soil samples were obtained during the tank removals at the USTs, Building 28, Building 8, Oregon Avenue tanks and Building 8 waste-oil tank. Closure samples were primarily collected at 14-ft BLS with the highest gasoline-range TPH (TPH-GRO) result (8,100 mg/kg) under Tank 1001 and the highest lead concentration (170 mg/L) in GS004 (26-in BLS) .

Since the DSCP was recommended by the Defense Base Closure and Realignment Commission (DBCRC) in 1993 for closure and realignment, the investigations have purported to change their focus to address criteria for documentation and cleanup required by CERCLA and the Community Environmental Response Facilitation Act (CERFA).

Also in 1994, PRC conducted a baseline investigation, the results of which are detailed in “Final Environmental Baseline Survey Report.” This report was prepared for the DLA and the USACE in Huntsville, Alabama. The document presented historical information of past practices on the DSCP site. In the document, PRC identified past problems with petroleum solvent vapors due to past discharging into drains, which resulted in soil contamination. The potential for contamination from natural gas heavy ends was also identified as a potential source.

Kemron Environmental Services and Versar Inc. prepared the “Final Phase I Remedial Investigation/Feasibility Study Report, Defense Personnel Support Center, Philadelphia, Pennsylvania,” in 1995. The report concluded that the data acquired during the site investigation did not support the hypothesis that the #1 Tankfarm in the South Yard of the refinery was the

source of the NAPL plume on the DSCP site. Furthermore, the wells installed on the CSX property on the western portion of the DSCP did not exhibit NAPL. Finally, the groundwater flow direction was identified as north to south.

Figure 6-2 of the Kemron/Versar report indicates a south-southwest component to groundwater flow in the southwestern aspect of DSCP. The report goes on to make the following conclusions:

“Free product releases and dissolved phase contaminants in the shallow portion of the unconfined aquifer originating in the northeastern part of the refinery south yard would be expected to migrate in a southerly direction, towards the Pollock Street/Packer Avenue sewer lines. Since groundwater flow at [DSCP] is primarily north to south, for the massive free product plume to have originated from the south, other transport mechanisms needed to be evaluated. At this point, attention was directed towards a major sewer line located just to the south of [DSCP].”

Even before issuing its final report, Kemron/Versar said in meetings held with DSCP, the Philadelphia District USACE, and the Pennsylvania Department of Environmental Protection (PADEP) in January and March 1995, as reflected in minutes prepared by Versar, that there was no geometric tie between the refinery and the DSCP. It recommended that they try to develop a chemical connection to the refinery. The basis for DSCP's initial reason for suspecting the refinery and dismissing sources on its own facility is also suggested. The minutes of the 18 January 1995 meeting refer to an estimated plume size of 10,000,000 million gallons of product and say, “based solely on the volume, this finding suggests that [DSCP] and most of the surrounding properties could not have caused a plume of this size and that a major off-site source is responsible for the plume.” These very same minutes indicate that the DSCP had no evidence to blame the refinery. This pre-disposition to find a link to the refinery on the assumption that DSCP could not have used sufficient petroleum to beget the NAPL plume appears to have driven DSCP's approach to this day.

Malcolm Pirnie and Louis Berger & Associates, Inc., conducted an investigation in 1996. The “Draft Final Phase II Expanded Site investigation Report,” documents the results of this investigation. The results indicated that areas such as the Bulk Storage Facility had lead and diesel-range TPH (TPH-DRO) concentrations that exceeded Pennsylvania regulations. Soil samples from other areas of concern did not exhibit concentrations in exceedence of the PADEP criteria. Reference to clean-up standards, which later supports decisions not to conduct additional tests, is

repeated many times in this and in Malcolm Pirnie's final report as a basis for concluding that a studied potential source is not a source.

Malcolm Pirnie also prepared the, "NAPL Plume Study Final Report," in 1997. Malcolm Pirnie was tasked specifically to conduct a "definitive investigation" of the NAPL plume under the DSCP site. The report concluded that the NAPL plume is light refinery naphtha characteristic of JP-4 that originated on the Sun property. This report also resurrected the notion of a pathway from the #1 Tankfarm on the Sun South Yard under 26th Street and under Schuylkill Expressway to the DSCP site. There were several noticeable inconsistencies and omissions in the report. The most striking omission is related to the alleged pathway. The report included a significant amount of discussion about the observation of "oil soaked" soil in boring B of the Schuylkill Expressway geotechnical borings; but it made no mention of several other borings (borings A and C through J) near and in the alleged pathway where no evidence of contamination was observed. The report also incorrectly identifies pre-construction borings from the 26th Street sewer construction as containing NAPL. In fact, NAPL or petroleum contamination was not identified in any of the pre-construction 26th Street borings.

2.2 SUN REFINERY

2.2.1 Site Development

In about 1870, the Atlantic Petroleum Storage Company (Atlantic) constructed an oil refinery adjacent to the Schuylkill River in an area known as Point Breeze in the southern part of Philadelphia, Pennsylvania. Soon after the refinery was constructed, the company became part of the Standard Oil Company Trust. It remained part of it until 1911, when the Trust was dissolved. After 1911, the company was once again known as the Atlantic Refining Company. Among the changes in the company during the War and the post-war years was acquisition of additional production and distribution (i.e. pipeline) capabilities.

The refinery produced a variety of refined petroleum products using a number of processes over its history. In the 1960s, a major renovation was completed and refining was moved to the South Yard and some storage was moved to the North Yard. In 1985, the refinery was sold by the Atlantic

Richfield Company (ARCO) to the Atlantic Refining Company, which was subsequently acquired by Sun.

Generally, the northern portion of the South Yard (referred to as Tankfarm #1) has stored finished products. The southern portion (Tankfarm #2) has primarily stored intermediate products for blending operations. The tank configurations, as they currently exist, are very similar to that documented back to 1932. Refinery drawings in 1932 identify tanks along 26th Street that are essentially the same today. Figure 2-3 presents the existing tank configuration based on refinery drawings; however, tanks have been added since 1932, including the following:

- | | |
|--------------------------------|---------------|
| • Tanks 172, 177, 119, and 121 | Unknown |
| • Tank 190 | 1945 |
| • Tanks 128 and 129 | 1971 and 1972 |

Historical aerial photographs for 1945, 1959, and 1975 are presented in Figures 2-4 to 2-6. These photographs exhibit the study area with the portion of the Sun property near 26th Street and the entire DSCP site. The general tank configuration on the Sun refinery near 26th Street for those respective dates is similar with the above exceptions to the configuration on the site today. The contents of the tanks obviously have changed over that time period. Other notable events in the development of the site include the construction of the Schuylkill Expressway in 1953 and the 26th Street sewer between 1962 and 1967.

2.2.2 Refinery Site Activities

This discussion focuses on Sun's environmental activity for addressing separate plumes near the alleged pathway. The following discussion focuses on the activities in the #1 Tankfarm of the South Yard. It also includes discussion the construction of the Schuylkill Expressway, the 26th Street Sewer, and the Pollock Street sewer, which, are adjacent to the Sun site. The #1 Tankfarm in the South Yard is west of and upgradient from the alleged plume migration "pathway" to the DSCP. Further discussion of the activities at the refinery (in terms of production) is not included because those do not exist near the alleged pathway.

During construction of the 26th Street sewer, vapor concentrations and petroleum infiltration to the sewer occurred. However, pre-construction borings that were installed in 1962 along 26th Street

adjacent to the refinery reported no evidence of petroleum. During construction, dewatering of the area occurred since the sewer was below the water table. This pulled petroleum hydrocarbon into the area. There was an explosion and loss of life. The 1964 construction logs are the first sign of NAPL seepage into the sewer. Since that time, vapors in the sewer have been a continuing challenge and are being controlled with vapor-control measures on the sewer.

2.2.3 Refinery Site-Assessment Activities

The effort to identify and remediate petroleum releases on the Sun property dates back to the early 1930s. During the operation of the South Yard, recovery wells have been installed and operated over various time periods. Approximately 30 recovery wells have been installed since 1932 in the study area. Recovery wells were installed in the South Yard and along the 26th Street sewer during three periods. The wells along Hartranft Street and the southern portion of the tankfarm were installed in 1932. Wells along 26th Street and west of the DSCP, except well 10 near Tank 85 at the northern portion of the yard, were generally installed between 1965 and 1967. A more recent series of wells along 26th Street were installed in the 1970s and 1980s.

Site investigations have been conducted at the refinery for a number of years. The first occurrence of vapors or NAPL in the 26th Street sewer in 1962 resulted in investigation of the seepage and product recovery in 10 wells near the sewer. Another occurrence of seepage into the sewer was identified in 1979. In 1980 ARCO installed surface-mounted blowers to evacuate vapors from the 26th Street sewer. In 1984, ARCO discovered product in a well near the 26th Street sewer again. Sun instituted a comprehensive oil-recovery project covering the entire refinery in 1993.

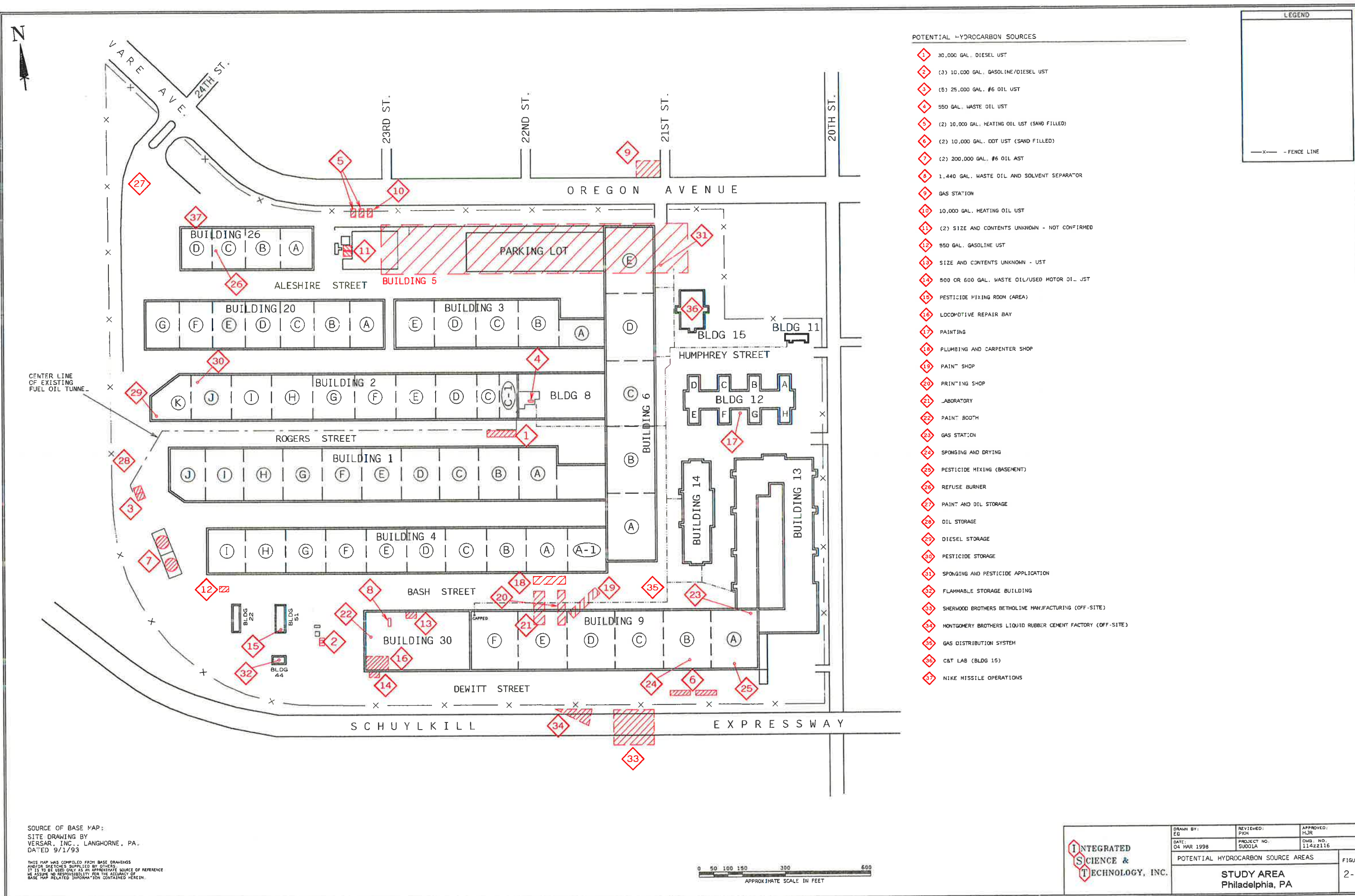
Several investigations occurred in 1988. Engineering Enterprises, Inc., completed a 26th Street Pilot Remedial Recovery Investigation at the refinery. The investigation included the installation of two monitoring wells. Product recovery tests were also performed to evaluate the potential for increased pumping in the area of an apparent breach in the sewer near Tank 42 and 83. This activity reduced the vapor concentrations in the 26th Street sewer. In that same year, GES completed the well evaluation at the South Yard of the refinery. The conclusions of the report indicate an increase in product in the vicinity of RW-1 (specifically in well 60). Two apparent new or recurring NAPL

occurrences were observed: 0.12-ft and 0.19- to 2.32-ft of apparent thickness. Bail-down tests were conducted to evaluate the "true" product thickness.

Also in 1988, GES performed a Perimeter Environmental Assessment. A total of 76 monitoring wells (North, South and West Yards) were installed as part of this investigation. NAPL was observed in 23 of these wells. Bail-down tests were conducted in 18 of these wells. Groundwater samples were collected from the remaining wells that did not exhibit NAPL. Distinct, isolated, and separate plumes were identified in this assessment. In addition to evaluating the presence and character of the petroleum contamination (NAPL and dissolved phase), the thrust of the investigation was to determine static water (and NAPL) level elevations with respect to the 26th Street sewer main.

In 1992, GES performed another investigation. The results of this investigation are summarized in, "Groundwater Assessment Phase I Report: Field Verification of Refinery Monitoring Wells." The report identified 23 monitoring wells that were no longer locatable. (Eighteen of the wells were previously located in the South Yard.). The report recommended replacement wells and additional wells to provide necessary site coverage.

More recently, Handex continues remedial system monitoring and performance reporting for all three yards (including the South Yard). Recovery along the 26th Street sewer is limited by the groundwater flow rates with the exception of RW #401, which has pumping rates in the range of 1 to 4 gallons per minute (gpm). The other wells pump at 1 gpm or less.



POTENTIAL HYDROCARBON SOURCES

- 1 30,000 GAL. DIESEL UST
- 2 (3) 10,000 GAL. GASOLINE/DIESEL UST
- 3 (5) 25,000 GAL. #6 OIL UST
- 4 550 GAL. WASTE OIL UST
- 5 (2) 10,000 GAL. HEATING OIL UST (SAND FILLED)
- 6 (2) 10,000 GAL. DOT UST (SAND FILLED)
- 7 (2) 200,000 GAL. #6 OIL AST
- 8 1,440 GAL. WASTE OIL AND SOLVENT SEPARATOR
- 9 GAS STATION
- 10 10,000 GAL. HEATING OIL UST
- 11 (2) SIZE AND CONTENTS UNKNOWN - NOT CONFIRMED
- 12 550 GAL. GASOLINE UST
- 13 SIZE AND CONTENTS UNKNOWN - UST
- 14 500 OR 600 GAL. WASTE OIL/USED MOTOR OIL UST
- 15 PESTICIDE MIXING ROOM (AREA)
- 16 LOCOMOTIVE REPAIR BAY
- 17 PAINTING
- 18 PLUMBING AND CARPENTER SHOP
- 19 PAINT SHOP
- 20 PRINTING SHOP
- 21 LABORATORY
- 22 PAINT BOOTH
- 23 GAS STATION
- 24 SPONGING AND DRYING
- 25 PESTICIDE MIXING (BASEMENT)
- 26 REFUSE BURNER
- 27 PAINT AND OIL STORAGE
- 28 OIL STORAGE
- 29 DIESEL STORAGE
- 30 PESTICIDE STORAGE
- 31 SPONGING AND PESTICIDE APPLICATION
- 32 FLAMMABLE STORAGE BUILDING
- 33 SHERWOOD BROTHERS BETHOLINE MANUFACTURING (OFF-SITE)
- 34 MONTGOMERY BROTHERS LIQUID RUBBER CEMENT FACTORY (OFF-SITE)
- 35 GAS DISTRIBUTION SYSTEM
- 36 C&T LAB (BLDG 15)
- 37 NIKE MISSILE OPERATIONS

LEGEND

—X— FENCE LINE

SOURCE OF BASE MAP:
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0 50 100 150 300 600
APPROXIMATE SCALE IN FEET

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	DATE: 04 MAR 1998	PROJECT NO. SU00LA	DWG. NO. 11422116
	POTENTIAL HYDROCARBON SOURCE AREAS		
STUDY AREA Philadelphia, PA			FIGURE 2-2



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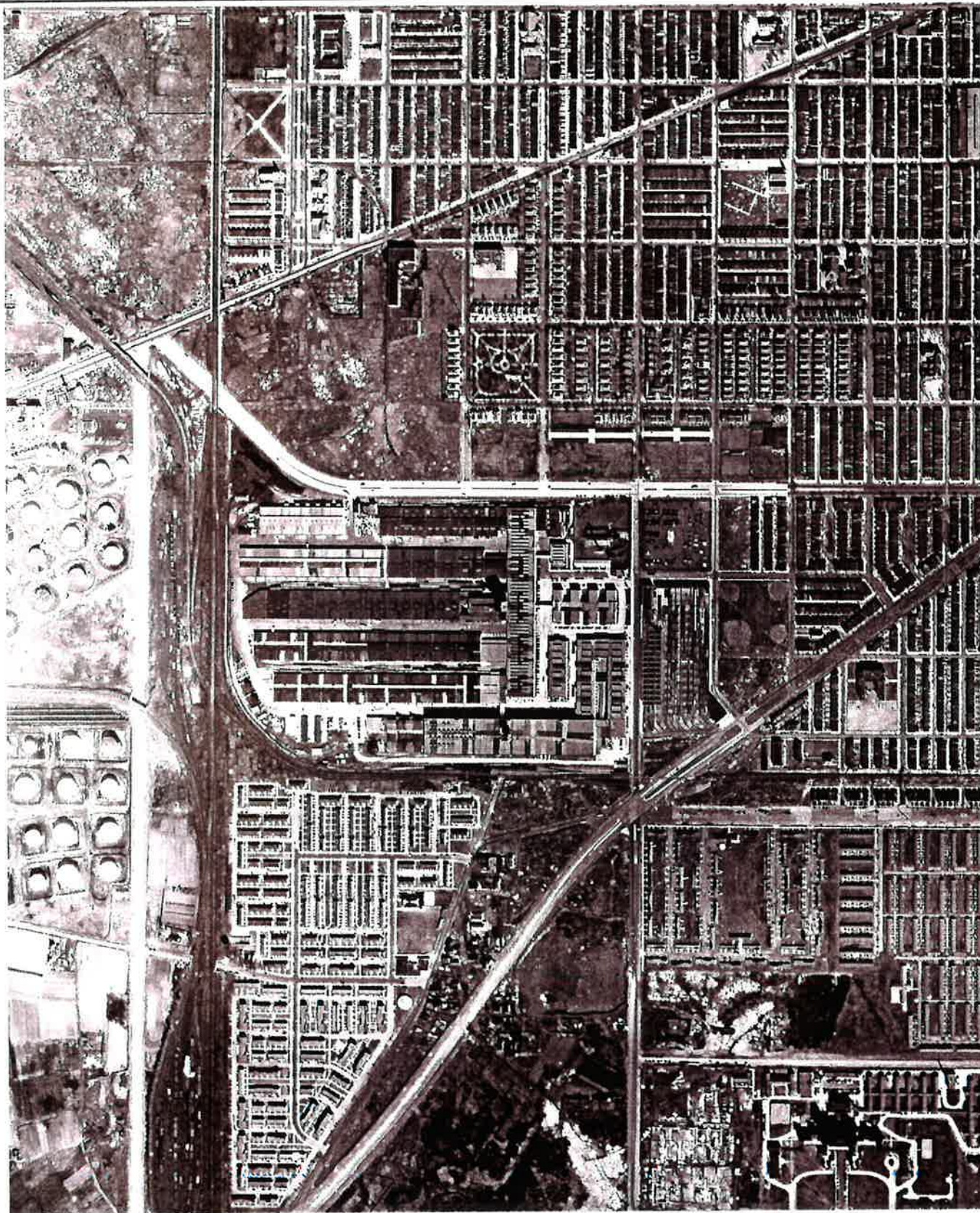
DRAWN BY:
REVIEWED:
APPROVED:

DATE: September 1997
PROJECT NO. SU001E
DWG. NO. S01LBLOC

TANK DESIGNATIONS

SUN REFINERY - SOUTH YARD
SUN COMPANY, INC. (R&M)
PHILADELPHIA, PENNSYLVANIA

FIGURE
2-3



Aerial View of Study Area
March 13, 1945

Scale: 1" = 800'



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STUDY AREA
Philadelphia, PA

FIGURE
2-4



INTTEGRATED
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Aerial View of Study Area
 April 5, 1959

Scale: 1" = 800'



STUDY AREA
 Philadelphia, PA

FIGURE
 2-5



Aerial View of Study Area
March 11, 1975

Scale: 1" = 800'



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STUDY AREA
Philadelphia, PA

FIGURE
2-6

TABLE 2-1
Philadelphia Depot Construction, 1940-1942

BUILDING NUMBER	FUNCTION	REMARKS
6	inspection	
7	dispatcher's office	demolished 1945
8	boiler house	
9	warehouse/sponging	
10	oil boiler house	demolished 1947
11	main guard house	
12	administration	
13	manufacturing plant	
14	cafeteria	
15	laboratory	
16	materials aging	
17	scale house	
18	fuel oil pump house	
19	day fuel tanks	modern 130 - 134
M-20	warehouse	
21	fuel storage tanks	modern 135 - 136; upgraded 1984
22	utilities warehouse	modern paint shop
23	incinerator	demolished
25	garage	demolished 1975
M-26	warehouse	
28	gasoline/oil station	
29	flagstaff	
30	motor transport	
31	sentry box	replaced 1960
32	sentry box	replaced 1994
33	sentry box	replaced 1990 by Bldg. 39
34 - 42	sentry boxes	demolished
43	greenhouse	demolished
44	oil storage	modern hazardous storage
45	doghouse	demolished
46	receiving office	replaced 1984 by hazardous storage
47	dispensary	demolished
48A	office	demolished
48B	office	demolished 1947
	foot bridges	modern 137 - 139

NOTE: Hunter Research. 1994.

TABLE 2-2
1996 Structures at DPSC

BUILDING NUMBER	SQUARE FT	YEAR BUILT	STORIES	STRUCTURE	DESCRIPTION 1996 USE
1	227,637	1918	1	Warehouse	
2	198,905	1918	1	Warehouse	
3	104,362	1918	1	Warehouse	
4	213,119	1918	1	Warehouse	
6	342,984	1942	2	Administration	
8	72,869	1940	12	Heating Plant	Central heating boiler plant, public works office, water storage tanks, training classrooms, loading dock
9	864,000	1942	4 + Basement	Warehouse	Office space, clothing factory's sponging plant, warehouse
11	8,475	1942	2 + Basement	Administration	Base security office
12	196,162	1942	3 + Basement	Administration	Office space, printing shop
13	370,311	1942	2 + Basement	Textile Plant	Clothing factory
14	104,005	1942	2 + Basement	Community Facilities	Cafeteria, auditorium, bowling alley, convenience store
15	37,481	1942	2 + Basement	Testing Lab	Testing laboratory
16	306	1942	1	Material Aging Facility	Room for fire testing of fabrics
17	86	1942	1	Scale House	
18	1,118	1942	1	Pump Station	Pump house for no. 6 fuel oil
20	135,742	1940	1	Warehouse	Health club, equipment storage
22	3,172	1941	1	Paint Shop	Masonry paint shop
26	77,473	1940	1	Warehouse	Vehicle maintenance facility, DRMO storage
28	462	1942	1	Gas Station	
30	71,420	1942	1	Motor Repair Shop	
31	232	1960	1	Sentry Station	
32	54	1942	1	Sentry Station	
36	96	1966	1	Shelter	
37	16	1970	1	Sentry Station	
40	16	1972	1	Sentry Station	
42	96	1973	1	Shelter	
44	1,500	1942	1	Flammable Storage	
46	900	1984	1	Haz. Mat. Storage	
49	520	1971	1	Switch House	
50	140	1971	1	Gas Metering Station	
51	4,000	1975	1	Pest Control Shop	USDA laboratory, motor vehicle pools safety classroom

NOTE: Reference CH2M-Hill 1996

TABLE 2-3
Summary of DSPC Storage Tanks

TANK #	BRAC TANK #	CAPACITY (gal)	CONTENTS	LOCATION	1996 USE	DATE INSTALLED	TANK CONDITION	CONTAMINATION	COMMENTS
UST's 001 - 005	7 - 11	25,000 each	No. 6 Fuel Oil	Bldg 18 tankfarm (between Bldg 18 and AST's)	Active	Jan 1942	Cleaned and precision-tested in Fall 1994 - tested tight	Several releases of fuel oil near Bldg 18 have been documented	In operation from 1942 to present. Tanks encased in concrete. Connected in two ASTs and pump house (Bldg 18). Supplies fuel to Bldg 8 boiler as backup power supply
006	4	10,000	Unleaded Gas	South of Bldg 28 (gas station). Top of each tank is 3-ft BGS.	Removed May 1994	1942 Jan 1971	All in good condition	Removed 20 yd ³ of contaminated soil. Additional soil left in place. Removed 50 yd ³	In operation from 1971 to 1994. Used for on-site automotive consumption; replaced with one 2,000 gallon and one 4,000 gallon tank (ASTs No. 004A and 005A, respectively)
007	5	10,000	Diesel Fuel	South of Bldg 28 (gas station). Top of each tank is 3-ft BGS.	Removed May 1994	1942 Jan 1971	All tanks and piping tightness tested in 1988 - no leaks		
008	6	10,000	Diesel Fuel	South of Bldg 28 (gas station). Top of each tank is 3-ft BGS.	Removed May 1994	1942 Jan 1971	Leak in Tank 008. Fuel line discovered and repaired October 1987		
9	17	30,000	Diesel and No 2 Fuel Oil	Rogers Street between Buildings 1 and 8. Top of tank is 3-ft BGS	Removed February 1995	Jan 1971 Jan 1973 Early 1970s	Intact, no evidence of leaking from tank or piping	No VOC or TPH contamination observed beneath the tank	In operation from 1973 to 1993. Supplied fuel to Bldg 8 standby emergency diesel generators. Out of service for 10 years
010	18	550	Waste Oil (Used Motor Oil)	Courtyard of Bldg 8 (center of site)	Removed May 1994	Jan 1973	Intact, no holes or evidence of leakage in tanks or piping during removal	Minor release beneath tank (TPH - 1,200 ppm). No contaminated soil found during tank removal	Exact contents of the tank are unknown. In operation from 1973 to 1992. Waste-oil tank for two standby emergency diesel generators in Bldg 8.

3. RELEVANT HYDROGEOLOGIC, AND GEOLOGIC CHARACTERISTICS AND SCIENTIFIC PRINCIPLES

To thoroughly examine the source, distribution, and behavior of NAPL in the subsurface of the study area, it is necessary to understand the physical character of the subsurface as well as a number of fundamental theoretical concepts. The ensuing discussions in this section contain a detailed presentation of the regional and local geology and hydrogeology of the area; a detailed presentation of the principals of NAPL behavior, transport, and fate in the environment; and some basic background on the genesis and chemistry of petroleum products. These tools will be used throughout the remainder of this document.

3.1 HYDROGEOLOGY

3.1.1 Regional Hydrogeology

The study area is situated in the area of south Philadelphia, Pennsylvania, near the confluence of the Delaware and Schuylkill Rivers. It lies within the Coastal Plain Physiographic Province. Industrial facilities and multi-family residences are the primary land uses in the vicinity of this area investigation. The topography in this locale is relatively flat; and surface elevations range from just above sea level to 25-ft in elevation. All elevations are given relative to the National Geodetic Vertical Datum (NGVD) of 1929.

Figure 3-1, which shows the area of this investigation on the Philadelphia, PA - NJ Quadrangle, United States Geologic Survey (USGS) 1967, Revised 1994, indicates two low ridges in the study area. The 20-ft contour line that outlines the shape of these ridges is highlighted in the figure. The orientation of the first ridge is northeast to southeast along and parallel to the Schuylkill River, which lies to the west of the Sun property. Geologic logs of borings in the area of this ridge indicate that it is composed of terrace deposits with various amounts of fill. Surface drainage on the western side of this elevated area enters the Schuylkill River, and drainage along the east side of this feature flows east then south. The second low ridge trends northeast to southwest. It passes near the center of the northern boundary of

the DSCP facility and then continues southwesterly along a path to the east of 26th Street. This topographic feature also represents a surface-drainage divide. Runoff on the western side of this divide flows west and then south toward the Schuylkill River. Surface drainage originating on the eastern side of the feature flows east and south toward the Navy Yard and the Delaware River. To a large degree manmade drainage controls have altered the directions of runoff movement across the study area, but in areas where no controls are present the overall directions of flow, as controlled by the two ridges, appear to be maintained.

The area of this investigation lies on a narrow strip of unconsolidated sediments within the Coastal Plain Physiographic Province. Fenneman (1937) describes this province as being a gently sloping plain underlain by Cretaceous or younger sediments that have not been subjected to substantial deformation. In this area, these sediments extend inward to the west from the shore of the Atlantic Ocean in New Jersey to the fall line in Pennsylvania. The Fall Line is a seaward facing escarpment that marks a geologic unconformity where more recent sedimentary strata of the Coastal Plain contacts the Paleozoic and older metamorphic and igneous crystalline rocks of the Piedmont Physiographic Province.

Both consolidated and unconsolidated sediments can occur in the Coastal Plain Physiographic Province. In this area of Pennsylvania, however, only unconsolidated clastic sediments of Cretaceous or younger age crop out or occur in the subsurface. Overall, the Coastal Plain geologic units dip toward the sea, but the angle of this inclination is generally steeper than the slope of the land surface. This orientation commonly results in the most recent of the exposed Coastal Plain sediments occupying a thin belt along the coast. Farther inland, older sediments crop out in successive bands. In the study area, however, erosion and deposition along the major streams that traverse this portion of the Coastal Plain have altered this pattern. The Delaware River and its tributaries have modified the study area in more recent times by both removing sediments of Coastal Plain origin and causing the aggradation of alluvium. The resulting areas of erosion and deposition have significantly altered the surface and subsurface geology of this area.

Figure 3-2 is a generalized stratigraphic column showing the relationship of geologic units in the southern Philadelphia area. The uppermost geologic unit cropping out in the study area is Quaternary Alluvium. This unit consists of flood plain and channel deposits ranging from 0- to 78-ft thick. Deposited in the last 10,000 years, these clastic deposits are exposed at the surface in a limited number

of topographic highs in the study area. Made up of silts, muds, and fine sands (Greenman et al. 1961), this geologic unit is overlain by fill in most of the area of this investigation. In places, this fill material can approach a thickness of as much as 40-ft, but this maximum thickness is observed almost exclusively in areas underlying some of the railroad tracks in the vicinity of the site. An increased thickness of fill material apparently representing an ancient stream channel is also identified in borings drilled along the southeastern side of the DSCP property and Philadelphia Housing Authority property (Malcolm Pirnie 1997a). However, in most of the region studied, this material rarely exceeds 10-ft in thickness. Neither the fill material or the recent alluvium are used as sources of groundwater. Groundwater is normally not found in these units except for some instances where perched conditions exist as coarse sediments overlie fine-grained stratum.

The Pleistocene Age Trenton Formation unconformably underlies the Quaternary Alluvium. The Trenton is a gray and brown sand and gravel with minor amounts of silt and clay (Greenman et al. 1961). This geologic unit crops out in a thin band along the Delaware River, and the width of its outcrop area reaches its maximum in the general vicinity of the site. Underlying almost all of the study area, this formation represents the primary unit in the unconfined aquifer system. The thickness of the Trenton Formation ranges from 0- to 80-ft, but it is generally about 20- to 25-ft. The highly variable grain-size distribution causes the hydraulic properties of this unit to vary widely. Yields between 1 gpm and 1,370 gpm have been observed in wells tapping the Trenton Formation (Paulachok 1991). However, water-quality considerations, primarily with respect to dissolved inorganics, require that, in most cases, wells tapping this unit not be used as sources of drinking water. According to Paulachok (1991), the median concentration of dissolved solids is 700 mg/L in wells tapping the Trenton. Dissolved iron and dissolved manganese median values in the unit are 7.6 mg/L and 1.4-mg/L, respectively. Locally dissolved organic compounds may also occur in the unconfined Trenton aquifer (Paulachok 1991).

The Miocene Bridgeton Formation may lie beneath the Trenton in limited areas of this investigation. If it is present at all, this unit is probably confined to the topographically higher portions of the site. Where this geologic unit occurs, the contact between the Bridgeton and the Trenton formations is unconformable. The Bridgeton is comprised of poorly sorted sand and gravel with a thickness of 10-ft or less. Distinguishing this unit from the overlying Pleistocene sediments is difficult because it has a

similar lithology. If present, the Bridgeton Formation is included with the Trenton in the unconfined aquifer system (Paulachok 1991).

Mesozoic sediments underlie the Cenozoic sediments described above. These Mesozoic sediments were deposited during the Cretaceous Period. The uppermost of these is the Upper Clay unit (Paulachok 1991). This unit corresponds to the Upper Cretaceous Magothy Formation of Greenman et al. (1961). The Upper Clay is described as a variegated clay that is silty, sandy, or gravelly in places. The thickness of this unit is between 0- and 35-ft in the Philadelphia area, and the Upper Clay only occurs in areas near the Delaware River. This clay is less widespread in the subsurface than other Cretaceous Clays, and it is discontinuous and relatively thin over most of the study area. When present, the Upper Clay unit acts as a localized semi-confining bed between the unconfined aquifer and the Upper Sand (Paulachok 1991). If the clay is absent, the Upper Sand is included in the unconfined aquifer system. Due to the thin nature of this clay in the study area, any semi-confined conditions in the underlying Upper Sand appear to be isolated and of little areal extent.

The Upper Cretaceous Old Bridge Sand Member of the Raritan Formation described by Greenman (1961) is equivalent to the Upper Sand unit of Paulachok 1991. This sand underlies the Upper Clay, when this fine-grained unit is present, and underlies the Cenozoic sediments when the clay is absent. The Upper Sand is a medium- to fine-grained sand that has some mica and gravel. This unit occupies channels in the surface of the Middle Clay (Paulachok 1991), and its thickness ranges from 0- to 50-ft. In areas that are near the Delaware River, the Upper Sand unit is generally overlain by a relatively thin Upper Clay unit. In this geologic configuration, the Upper Sand may be a semi-confined or unconfined aquifer. In other areas, where the Upper Clay is thin or absent, the Upper Sand is hydraulically connected to the overlying aquifers, and it and the overlying sediments combine to form an unconfined aquifer. This second condition is more prevalent in the area of the site.

Beneath the Upper Sand Unit is a stratum referred to by both Greenman (1961) and Paulachok (1991) as the Middle Clay. The Middle Clay is described as a red, white, and variegated clay that may be sandy in some places. The thickness of this unit is between 0- to 60-ft, but it is more widespread in the subsurface than the Upper Clay. According to Paulachok (1991), this unit forms an extensive

semi-confining bed in the Philadelphia area. A sand, the Middle Sand Unit, may underlie this clay. This sand represents channel deposits in the deeper Lower Clay Unit. When both the Middle Clay and the Middle Sand are present, they form an isolated semi-confined aquifer. If the Middle Sand is absent, then the Middle Clay and Lower Clay are in contact, and jointly they form the semi-confining bed for the Lower Sand or Farrington Sand artesian aquifer.

The Middle Sand Unit is a fine- to coarse-grained sand with some clay that varies in thickness between 0- and 40-ft (Paulachok 1991). Greenman (1961) refers to this geologic unit as the Sayerville Sand Member of the Raritan Formation. In the southern Philadelphia area, the Middle Sand Unit is usually within 1.5 miles or less of the Delaware River. Where it occurs, the Middle Sand occupies channels in the surface of the Lower Clay. The average thickness of this unit is generally less than 20-ft, and in most areas, it is overlain by the Middle Clay. When located between the Middle and Lower Clay, the Middle Sand forms a separate semi-confined aquifer. Few wells derive all of their water from the Middle Sand; for this reason, only limited data is available about this aquifer. Well yields in the Middle Sand Unit are, however, large to very large, and withdrawal rates of over 900 gpm have been reported. The mean discharge of wells open to this unit is 355 gpm (Paulachok 1991). Based on analytical data from the small number of wells extracting groundwater from this unit, the quality of water in this aquifer is similar to that of the underlying Lower Sand with total dissolved solids in the range of 500 mg/L (Paulachok 1991).

Underlying the Middle Sand Unit is the Lower Clay. The Lower Clay Unit is composed of red and variegated stiff clay, which may be up to 120-ft thick in some areas. This geologic unit forms an extensive semi-confining bed in the coastal plain sediments south of Philadelphia. Where it is present, the Lower Clay Unit represents an aquitard that results in semi-confined conditions occurring in the underlying Lower Sand.

The oldest strata of Cretaceous age that is present in the subsurface in the site area is the Lower Sand Unit. The Lower Sand corresponds to the Farrington Sand Member of the Raritan Formation as described by Greenman (1961). This geologic unit is described as a medium- to fine-grained sand that grades downward into a coarse-grained sand with fine gravel. Underlying the Lower Sand are either Paleozoic or older crystalline bedrock or residual soils that have resulted from weathering of these consolidated rocks (saprolite). The Lower Sand ranges in thickness from almost nothing near

the fall line to 90-ft in the area of the Delaware River. This unit forms a semi-confined aquifer that is the principal source of groundwater in the Philadelphia area. Wells open to the Lower Sand yield from 3.3 to 1,350 gpm; the average yield is 360 gpm (Paulachok 1991). The median concentration of dissolved solids in wells tapping this aquifer is 510 mg/L. Median concentrations of dissolved iron and dissolved manganese are 18 mg/L and 1.4 mg/L, respectively, in groundwater from the Lower Sand.

Underlying the Lower Sand is the Wissahickon Formation. This formation consists primarily of schist that is thought to be of late Proterozoic and early Paleozoic age. It is believed that this geologic unit was formed when a thick accumulation of sediments metamorphosed into dense foliated rock (Paulachok 1991). The Wissahickon Formation outcrops in the Piedmont Physiographic Province north of the study area, and in the area of its outcrop, it is an important aquifer for domestic water supplies. Because the Coastal Plain sediments overlying the Wissahickon generally produce copious amounts of groundwater, few wells in the study area are open to this formation.

3.1.2 Site-Specific Geology

The site-specific geology is based on boring logs prepared during numerous investigations in the study area. These investigations were conducted over a period of more than 10 years. In addition to subsurface data collected by IST, other site-specific information has been gleaned from soil borings described by the following sources:

1. Malcolm Pirnie
2. Dames and Moore
3. GES
4. Delaware River Port Authority
5. Philadelphia City Government
6. Fluor Daniel GTI
7. Army Corps of Engineers
8. ENSR
9. R. E. Wright and Associates
10. M and R Soil Investigations
11. Kemron/Versar
12. Handex

Over 400 boring logs were examined and input to a geologic database covering the area of the site. These logs are included as Appendix B. Plate 3-1 shows the locations of most of these borings on a site plan; the boring identification numbers are also shown on this plate. From the database, geologic cross sections showing subsurface conditions on both the DSCP property and the Sun Refinery were prepared. Figure 3-3 shows the locations of these cross sections in plan view, and they are provided in this section as Figures 3-4 through Figure 3-12. Three cross sections, A-A', B-B', and C-C', (Figures 3-4 to 3-6) are oriented from west to east, and these figures show the subsurface of Sun and DSCP. Cross section A-A' is the southernmost of these, and cross sections B-B' and C-C' are located approximately 250-ft and 700-ft north, respectively, of A-A'. The remaining six cross sections (D-D', E-E', F-F', G-G', H-H', and I-I') are oriented north to south, and they are ordered from east to west showing the subsurface on only one of the two properties (Figures 3-4 through 3-9).

The stratigraphic contacts shown on the cross sections are based on a geostatistical analysis of data from all of the 429 borings associated with the site. This was done to decrease the potential variability in the identification of geologic contacts that could result from the numerous geologists describing the same strata. This technique provides a better overall representation of the subsurface of the study area. The statistical algorithm used for this analysis involves kriging, which assumes all data points within a specified distance are related, but gives more weight to closer data points (Davis 1973). For this reason, the logs of borings may not exactly match the stratigraphic contacts depicted in these figures, but because the borings included in each individual section are the closest data points used in the kriging analysis, correlation between boring logs and the cross sections should be very close.

In addition to the cross sections, two figures (Figures 3-13 and 3-14) three dimensionally depict the subsurface of both sites as wedge cuts along a northeast-to-southwest and a northwest-to-southeast transect. The locations of these two wedge cuts in plan view are also shown on Figure 3-3. These wedge-cut figures aid in the visualization of the portion of the subsurface geology in the study area through which Malcolm Pirnie alleges the NAPL plume migrated.

Almost the entire upper surface of the study area is covered with fill material composed of compacted soil and debris. Across the site, the fill ranges in thickness from 1- or 2-ft to over 20-ft.

The thickest areas of fill are under railroads and in an old channel along the southeastern border of DSCP. In borings in the study area, the fill is recognized as un-stratified clays, sands, and gravels containing construction debris, asphalt, and ash. Isolated zones of perched water can occur over compacted clays and silts in the fill material.

In the area of this investigation, the Quaternary Alluvium, a gray, brown, or green sandy silt and sandy, micaceous clay with occasional sand and gravel lenses, underlies the fill material. This geologic unit ranges in thickness from 0- to over 20-ft within the study area. Occasional zones of perched water can also occur over sections of fine-grained sediments in this unit. The upper surface of the Quaternary Alluvium shows signs of erosion primarily in the northern half of the study area just east of 26th Street, and a more pronounced lowering of the upper surface of the Quaternary Alluvium is seen along the southeastern aspect of DSCP. The lower surface is more uniform and inclines generally to the west and south. The thickest sequence of this unit is beneath the north central area of the refinery. Since most of the anthropogenic modifications to the site topography involved placing fill material, the upper surface of this unit should reasonably represent the pre-construction lay of the land in the site area.

The Trenton Formation underlies the Quaternary Alluvium over almost the entire study area. This geologic unit is a gray-to-brown, poorly sorted sand with considerable sub-angular to rounded gravel. Since this deposit is poorly sorted, Owens and Minard (1979) postulated that it may represent reworked moraines. Their paleocurrent study indicated that sediments of the Trenton Formation were deposited along a northeast to southwest flow path. In the site area this parallels the existing flow direction of the Delaware River. The thickness of the Trenton Formation ranges from very thin to absent in the southeast corner of DSCP to a maximum of over 40-ft. The thickest sequence occurs in the south central aspect of the Sun property. A possible channel in the upper surface of the Trenton trends north to south along the eastern edge of the DSCP property. Figure 3-15 is an isopach map of the Trenton Sand that shows the thickness of this formation on a plan view of the study area. As shown in this figure, areas of increased thickness for the Trenton Sand are in the southwestern portion of the study area, near the center of the southern boundary of the refinery, and along an arc extending from the northwestern aspect of the refinery to 26th Street and then curving back to the southwest in the southern half of the Sun property. The upper surface of

the Trenton slopes generally to the south, and this surface is roughly convex in an east-west orientation; the crest occurring near the center of the DSCP property.

Over most of the site, this unit represents the uppermost stratum of the unconfined aquifer. The hydraulics of this unit vary greatly, but in many cases it is a prolific aquifer and hydraulic conductivities can be greater than 500-ft/d. However, the Trenton unit is not used extensively as a groundwater source because of problems with water quality.

Beneath the Trenton Formation, the Upper Clay may occur in the area of this investigation. This geologic unit is a gray to gray-green, sandy clay or sandy silt that may in some cases be mottled orange and brown. It is generally plastic and can be identified on geophysical logs by an increase in the emission of gamma radiation. The presence of increased zones of gamma emissions was used to both confirm and infer the subsurface location of the Upper Clay in many of the borings drilled in association with investigations in the Sun and DSCP study area. This unit, which is traceable in the subsurface, may be younger than Cretaceous in age. However, for purposes of this study the layer of fine-grained sediments will be assigned to the Upper Clay of Cretaceous age. Within the study area, this clay is present in most of the subsurface at a thickness of over 0.5-ft. The thickness of this unit is generally between 0- and 10-ft, but the unit may exceed 30-ft in some areas. Figure 3-16 is an isopach map of this clay. As can be seen on this figure, the stratum is not completely continuous across the site. The Upper Clay unit thins under the southern portion of the Sun refinery and may be totally absent south of the DSCP property. When present in sufficient thickness, however, the clay may result in localized semi-confined conditions in the underlying sand. This sand is believed to represent the Old Bridge Sand Member of the Raritan Formation. Hydraulic separation of the Trenton and Old Bridge is, however, not achieved with respect to the overall site.

The cross sections provided in this section (Figures 3-4 through 3-12) indicate that the upper surface of this clay unit is highly variable. In an east-west orientation, this surface generally slopes toward a shallow depression in the area of 26th Street and into the channel feature near the southeast border of DSCP. Along the cross sections with a north-south orientation, a shallow depression near the Pollock Street is observed, but the overall slope of this stratum is to the south.

The Old Bridge Sand is the lowest coarse-grained unit in the unconfined aquifer. It is positioned below the Upper Clay unit over a large portion of the site. When the Upper Clay is absent, the Old Bridge Sand directly underlies the Trenton Formation. In boring logs from the study area, the Old Bridge Sand is described as a gray to dark brown generally fine- to medium-grained sand with small amounts of silt and clay. The exact stratigraphic relationship of this sand is unknown, and the unit may represent sediments deposited earlier in geologic time than the Old Bridge Formation. In this report, however, it will be assigned to the Upper Cretaceous. In this position, the unit may be correlated with the Upper Sand Unit of the Raritan Formation (Paulachok 1991). This sand stratum appears to reach its greatest thickness in the center of the Sun refinery, where it appears to fill a north-south trending channel in the underlying Middle/Lower Clay Unit and achieves a thickness of over 25-ft thick. Over the rest of the area of this investigation, the unit is much thinner and ranges in thickness from 1- or 2-ft to approximately 15-ft. Over most of the site this unit is hydraulically connected to the Trenton Formation, but where the overlying fine-grained Upper Clay unit is thick, semi-confined conditions may exist. The semi-confined conditions, however, extend over only small localized areas. Because most wells open to the Old Bridge are also open to the Trenton, little is known about the specific hydraulic characteristics of this unit.

Underlying the Old Bridge Sand is the Middle/Lower Clay. In the study area, this unit is described as a red to white sometimes variegated stiff clay. Based on the available boring logs and gamma emissions detected in geophysical logs, this clay exists under almost the entire study area. Observed thicknesses of the clay unit over the study area are between 5- and 25-ft. The greatest thickness appears to occur along the southern half of the eastern boundary of the DSCP property and along most of the western boundary of the refinery. On the geologic cross sections included in this section (Figures 3-4 to 3-12), a well-entrenched channel partially cutting the clay trends roughly north to south around 1,000-ft west of 26th Street. The Upper Clay Unit is considered an aquitard that semi-confines the underlying Lower or Farrington Sand causing artesian conditions to occur in this stratum.

The oldest Coastal Plain Formation in the study area is the Farrington Sand. Few borings installed during the many site investigations penetrated this unit. When the Farrington was encountered, it was described as a reddish-brown, coarse sand with rounded gravel and few fine-grained sediments.

The Farrington is a semi-confined aquifer, and it is the primary source of groundwater supplies in the vicinity of Philadelphia. Wells open to the Farrington Sand produce substantial amounts of water. Withdrawal rates from the Farrington, however, peaked in the 1950s and have since declined.

The Wissahickon Formation underlies the Coastal Plain sediments in the study area. This geologic unit was also encountered in only a few borings. In logs from these borings, it was described as a dark gray mica schist. In the study area, the Wissahickon is not important as a source of groundwater. To the north of the site along the Fall Line, the Wissahickon is, however, a significant groundwater source.

Local erosional and depositional features are visible on the geologic cross sections and wedge cuts included in this portion of the report (Figures 3-4 to 3-14). The locations of these features can also be delineated from the isopach maps referenced above. Two sizable channels are noted to occur in the study area. One of these trends from north to south. It underlies the center of the refinery property about 1,000-ft west of 26th Street. This channel is apparently cut into the Middle/Lower Clay unit. Filling of this channel in subsequent geologic time has caused increases in thickness in the Old Bridge Sand and Upper Clay in this area of the subsurface. Evidence of this channel essentially disappears during deposition of the Trenton Formation. Terraces resulting in a decreased thickness of the Old Bridge and Upper Clay flank both sides of this channel. Based on elevations in the former channel, for the most part, flow was from north to south.

The second channel feature is found near the southeastern corner of the DSCP property. Because only a few borings have been completed south and east of DSCP, the orientation of this channel is not possible to totally discern. This channel also cuts into the upper surface of the Middle/Lower Clay, and based on the shape of the strata in this channel, some degree of erosion occurred in this area up until recent times. All formations deposited subsequently to the Middle/Lower Clay are found in the channel. However, the reduced thicknesses of these stratigraphic units in this area and the configuration of their upper surface indicate that some degree of erosion continued to occur in this area until the Quaternary. Approximately 25-ft of fill was recently used to level the area of this channel so that the land in this part of the site could be used as a park.

An area where all of the subsurface units occur (with the exception of the Middle/Lower Clay) at slightly higher in elevations divides these two channels. The crest of this low ridge occurs near the center of the DSCP property, and the feature trends generally north to south. The ridge is best defined by the upper surface of the Quaternary Alluvium, but the Trenton Formation, the Upper Clay and the Old Bridge Sand also occur at slightly higher elevations in this area of the site.

All three of the erosional or depositional features discussed above appear to conform to likely directions of surface-water flow during the geologic past. Owens and Minard (1979) conducted paleocurrent studies in the Coastal Plain of New Jersey and Pennsylvania. Their studies indicated that almost all deposition of sediment during the Cenozoic Epoch occurred more or less parallel to the flow direction of the Delaware River. In the study area, this flow direction would be to the southwest.

3.1.3 Site-Specific Hydrogeology

The vadose zone in the study area occurs primarily in the Quaternary Alluvium and in the overlying fill. Both geologic units are composed of predominantly fine-grained material. Due to the compacted fine-grained nature of the fill and the large amount of paving in the general area of this study, local recharge is inhibited.

The uppermost saturated unit in the site area is referred to in this report as the unconfined aquifer. Over most of the study area, the upper surface of the water table occurs in the Trenton Formation. However, it may extend into the recent alluvium in a few areas where former channels or erosion have resulted in a lower surface of the Trenton. In the majority of the study area, unconfined conditions extend down into the Upper Clay and the Old Bridge Sand units. In isolated areas where the Upper Clay unit is relatively thick, portions of the Old Bridge Sand may be semi-confined.

Groundwater generally flows south in the unconfined aquifer. A potentiometric-surface map that was generated from gauging data collected in November 1997 is included as Figure 3-17. This figure shows the current groundwater-flow regime. As shown on this figure the overall southerly flow pattern in the area of 26th Street and the nearby NAPL recovery wells is altered as groundwater is removed from the unconfined aquifer by these anthropogenic features. However, Figure 3-17 also shows that the effects of groundwater withdrawal only influence flow directions in the areas

near the sewer and extraction wells. In the other areas of this investigation, farther to the east and west of 26th Street, flow to the south appears to predominate. Groundwater flow on the western side of the refinery is shown on Figure 3-17 to have a component of westerly flow, especially in the southern half of the property.

Prior to the recent investigations in the study area, little information relating to aquifer characteristics at the site were available. To better define the hydraulic properties of the unconfined aquifer at the site, IST conducted a series of aquifer tests. The results of this testing are described below.

3.1.3.1 Refinery Aquifer Characterization

Rising-head aquifer testing was conducted in the unconfined aquifer beneath the refinery during August 1997. The tests were analyzed using the procedure developed by Bouwer and Rice (1976) and refined by Bouwer (1989). The Bouwer and Rice method was designed to measure aquifer hydraulic conductivity in the immediate vicinity of a well (production, monitoring, or test wells). The tested wells can be partially penetrating and partially screened, perforated, or otherwise open. This test method can be conducted by quickly withdrawing a volume of water, or “slug,” from the well and measuring the subsequent rate of rise in the water level. Data for analysis by the Bouwer and Rice method can also be based on a falling water level after adding a “slug” of water or an object that displaces groundwater to a well. The change of the groundwater level in the well with time is then measured as the water level recovers to its starting position. The method can be used for unconfined, confined, or semi-confined aquifers. Anomalies (“double straight line effect”) are sometimes observed in the measured rate of rise of the water level in the well. These are attributed to drainage of a gravel pack or developed zone around the well following lowering of the water level. The effect of this drainage can be eliminated by ignoring the early data points on the recovery or drawdown curve and using the second straight line portion in the data plot for calculation of hydraulic conductivity. The method is applicable to any diameter and depth of the borehole that is covered by the ranges for which the geometry factor, R_e , has been derived. The smaller the diameter of the hole, however, the more vulnerable the results will be to aquifer heterogeneities and to inaccuracies in estimating effective well diameters.

The results of this testing indicated that hydraulic conductivities in the unconfined aquifer ranged between 0.18- and 617-ft/d. The vast majority of the rising-head aquifer tests, however, indicated a hydraulic conductivity of between 1- and 25-ft/d. The high variability of aquifer-testing results would be anticipated in the poorly sorted Trenton Formation, which makes up most of the unconfined aquifer at the site. During the rising-head aquifer testing, discrete vertical sections of individual monitoring wells were evaluated. However, no pattern of vertical variation in hydraulic conductivity values could be identified. Analyses of the rising-head aquifer test data are provided in Appendix C.

In addition to this rising-head aquifer testing, aquifer evaluation using data developed during standard pumping tests was also performed. The pumping tests were also conducted during August 1997. Groundwater levels in site wells were monitored during the 48-hour period immediately preceding the pumping test. These data were used to evaluate the water table aquifer for evidence of increasing or declining water levels. No significant trend in water-level fluctuations was observed during this pre-test period. During the pumping test, well RW-1 was pumped at an average rate of 225 gpm. Pressure transducers connected to an Insitu, Incorporated Hermit SE2000 data logger and individual recording transducers (Trolls) were used to monitor water-level changes in 14 of the site-monitoring wells. Water levels in these and other site wells were also measured periodically with electronic water-level sensing devices during the test and subsequent recovery period.

As pumping was initiated, water-level measurements were recorded at frequent intervals in the pumping and selected monitoring wells. Both water level and time since pumping started were noted for each manual or automated measurement. Pumping continued at a relatively constant rate for 6.7 days. Minor fluctuations were noted in the discharge rate of well RW-1, primarily during the first 2 hours of the test period. However, the discharge rate varied less than 0.5 percent. The water-level fluctuations measured in the monitoring wells were plotted on semi-logarithmic graph paper as time since pumping began versus the observed drawdown in the monitoring wells. The time drawdown plots and calculation sheets relating to the pumping test analysis are provided in Appendix D.

The semi-logarithmic plots of time versus drawdown were analyzed to determine aquifer characteristics using a method described by Jacob (1963). In this method of pumping test analysis,

the drawdown in observation wells is determined for one log cycle of time. The slope of this line is used to calculate the aquifer characteristic of transmissivity. Since a larger area of the aquifer is evaluated during a pumping test using monitoring wells than in a single well test, values for aquifer characteristics from this type test are more typical of actual conditions. If barrier or recharge boundaries are present in the subsurface, they are also more likely to be detected during aquifer testing that encompasses multiple monitoring wells. Tests of longer duration are, however, beneficial where boundary conditions are suspected. Transmissivities values determined from the pumping test data ranged between 14,581-ft²/d and 8,569-ft²/d. Transmissivity values determined for most of the monitoring wells, however, ranged between 8,000 and 9,000-ft²/d. These values are within the range expected for a poorly sorted sand with moderate gravel, which is the composition of the material in the saturated zone at the site. These transmissivity values also generally correlate to the hydraulic conductivities determined during rising-head test performed at the site.

3.2 NON-AQUEOUS PHASE TRANSPORT AND FATE THEORY

The major element of the dispute between Sun and DSCP is the mechanism by which NAPL might have migrated from the Sun #1 Tankfarm in the northern portion of the south yard of the refinery to the DSCP site. To evaluate the potential for NAPL to migrate from one point to another in the subsurface, the principals of multi-phase transport need to be thoroughly understood. NAPL and groundwater flow are fundamentally equivalent because they are based on traditional Darcian flow. However, from that point, the two processes diverge significantly. To attempt to carry out such an evaluation using solely the principals of groundwater movement in the subsurface is a gross oversimplification that may lead to erroneous conclusions.

This section contains a detailed discussion of the fundamentals of multi-phase transport as they relate to NAPL migration in the study area. It also describes the manner in which NAPL partitions in the environment following a release, the mechanisms that create residual saturations, the methods for estimating residual saturation, the physics and the factors that control immiscible phase migration, and the fate mechanisms that operate on NAPL in the subsurface. This theoretical discussion will serve as the basis for understanding the distribution of NAPL in the subsurface beneath the study area and for the discussion in Sections 5 and 6.

3.2.1 NAPL in the Subsurface

When a xenobiotic or contaminant or any mixture of them, such as a refined petroleum product, enters the environment, they immediately begin to interact with the matrix into which they are released. These interactions change the physical nature of the mixtures released and the concentrations and distribution of the compounds that comprise them. These interactions produce a partitioning of the components into various subsurface environmental compartments, which include vadose zone soils, water in the vadose zone, gaseous atmosphere in the vadose zone, and groundwater (including the capillary fringe). The interactions are loosely termed fate-and-transport processes and are, to a large degree, a function of the physicochemical characteristics of the released compounds and elements and the matrix. Because released compounds and elements interact and partition, and because the compartments into which they partition interact, these must be considered in the assessment and remediation of contaminated sites.

NAPL is in a unique contaminant class and its behavior in the subsurface is unique. It is generally a finished liquid product (as is the case in the study area) or crude oil. As such, a large number of individual constituents comprise it. In aggregate, these constituents give it its physical characteristics, which dictate its behavior in the subsurface. Thus, rather than having the characteristics of and behaving like any single compound, NAPL behaves as a function of the additive and multiplicative effects exerted by each of the constituents that comprise it, as well as the interactions between and among the constituents.

Vapor pressure, solubility, sorption potential, and biodegradability are all fate mechanisms that can act on individual xenobiotics in the subsurface; however, when considering the behavior of a NAPL in the subsurface, perhaps the most important factors are density and specific gravity, viscosity, and interfacial tension. Density is generally defined as the mass per unit volume of a substance at a known temperature. When the density of a standard substance is used as a reference, the parameter becomes specific gravity, which is the density of a given substance as a function of the density of a standard substance at a known temperature. The reference to which most NAPL is compared is water, which has a specific gravity of 1.000. By definition, NAPL has a specific gravity less than 1.000 and will thus float on and spread over the capillary fringe and groundwater table. In contrast, dense, non-aqueous phase liquid (DNAPL) hydrocarbon has a specific gravity greater than 1.000

and thus will sink through the saturated zone until it encounters a confining unit, where it will spread. In both cases, the fluid predominately spreads in the direction of the inclination of the medium on which it has accumulated (i.e., the direction of groundwater flow or the direction of inclination of the confining bed).

Viscosity is another key parameter that controls the migration of NAPL. Viscosity is a measure of the reluctance of a fluid in motion to yield to shear or a measure of a fluid's tendency to resist deformation. More simply, viscosity is the "stickiness" of a fluid or a measure of its tendency to resist flow. In the natural world, fluids with lower viscosities tend to flow more readily and are more mobile than fluids with higher viscosities, which tend to flow more slowly and are less mobile due to the fluid deformation required for flow in porous media. Viscosity also varies inversely as a function of temperature for a given NAPL.

Interfacial tension is another key parameter that controls the migration of two fluids. It is also a constant for any two fluids and is defined as the amount of work that must be performed to separate a unit area of substance i from substance k . Based on this definition, two fluids with a high interfacial tension have a greater tendency to restrict the movement of each other; conversely, two fluids with a low interfacial tension have a greater tendency to enhance the movement with respect to each other.

3.2.2 Immiscible Multi-Phase Fluid Flow Theory

When a NAPL enters the subsurface, it creates a three-phase system comprised of the NAPL itself, the air in the formation, and the water in the formation; the solid soil matrix may, in some instances, be considered a fourth phase. In the vadose or unsaturated zone, the interstitial spaces or pores between the soil particles are filled with air and a small amount of water that surrounds the soil particles before NAPL is introduced. Water in the vadose zone held at the irreducible saturation is termed pendular, and water held above the irreducible saturation is termed funicular. In the capillary fringe and the saturated zone, the pores are filled with water and have an essentially negligible volume of air. Within the capillary fringe, the water is held under a negative pressure, which is reflective of the mechanism that forms the capillary fringe (i.e., suction). At the saturated zone's surface, the water exists under one atmosphere of pressure.

To fully understand and apply the principals of immiscible multi-phase fluid flow, understanding a number of fundamental physical principals is necessary. The first is the coupled concept of interfacial tension and wettability. In this concept, it is assumed that whenever two fluids are present in a porous medium and have different physical characteristics (i.e., density and specific gravity) they will behave as separate phases. Whenever immiscible fluids are present, one fluid is considered the wetting fluid and the other is considered the non-wetting fluid. In a system such as exists in the study area, water in the formation is considered the wetting fluid due to its higher interfacial tension relative to NAPL and the fact that it preceded the NAPL, and introduced NAPL is considered the non-wetting fluid. The interfacial tension is the energy required to allow one fluid to flow over the surface of another, or in other words, the energy that must be exerted to overcome the molecular attraction between the two fluids.

The second physical principal is the concept of capillary pressure. The principal of capillary pressure is germane to the study area because it is fundamental to the understanding of fluid movement through porous media. When two immiscible fluids such as air and water, water and NAPL, or air and NAPL are present in a porous medium, there is a pressure differential at their interface. That is, the pressure exerted at the interface is different in each fluid. If this relationship is described for wetting and non-wetting fluids, it can be expressed by the following equation (Bear 1972):

(Equation 3-1)

$$P_c = P_w - P_{nw}$$

Where: P_c = Capillary Pressure
 P_w = Wetting Fluid Pressure
 P_{nw} = Non-Wetting Fluid Pressure

The third physical principal is the concept of radius of curvature. As stated above, the pressure exerted at the interface between two fluid phases is not equal. This inequality results in a curvature in the interface that is related to capillary pressure according to the following equation:

(Equation 3-2)

$$P_c = \frac{2\sigma}{r'}$$

Where: P_c = Capillary Pressure
 σ = Interfacial Tension
 r' = Radius of Curvature

The degree of curvature is defined as the contact angle, θ . When the contact angle is less than 90 degrees, the fluid is wetting, as defined above. Conversely, when the contact angle is greater than 90 degrees, the fluid is non-wetting. For example, the meniscus that forms at the water-air interface in a small diameter test tube is a manifestation of interfacial tension and the contact angle for a wetting fluid (water).

The fourth physical principal is saturation as it relates to a porous medium. By definition, in the strict chemical sense, saturation is achieved when one medium contains its capacity of another medium. For example, water (the solvent) is saturated when it contains 1,791 mg/L pure benzene (the solute) (Howard 1990). When additional pure benzene is introduced to water that contains this concentration, the additional benzene forms a separate phase. Saturation of porous media can be viewed in much the same way. In a three-phase system (such as sand, water, and air) in a laboratory column, air is displaced and the pores begin to fill when water is added to the system. No water exits the column at this point. As additional water is added, the pores, which have a finite volume, eventually fill, and the water then advances through the column. In this system, water is the non-wetting fluid (air is the wetting fluid), and the wetting front cannot advance beyond a given point until all of the pores at that point have been filled. This ultimately creates a continuous water-wet column. Eventually, all the pores fill, and water begins to exit the column. The medium is then saturated with respect to water. If the column is left open to the atmosphere, water will drain from the column under the influence of gravity (gravity drainage). As the water drains, the continuous water column is broken and the water in the pores retracts and is held under a reduced capillary pressure. At this point, the water, is at its irreducible or residual saturation (S_w). No more water can flow at this point. To remove water held at irreducible saturation, energy in excess of the reduced capillary pressure must be applied. For all intents and purposes, the water is now totally immobile. This process is shown graphically on the left side of Figure 3-18 (Bear 1972).

When another phase is added to the scenario described above, the processes are similar, but are more complex. If the same column of porous media is first filled with water to the point that all of the pores are essentially filled to saturation, the column is water wet, and the water is considered the wetting fluid and the air has been displaced. When this process is carried out via capillary forces alone, the process is termed imbibition. Adding a non-wetting fluid such as naphtha to the column

causes much of the water to be displaced. However, displacement cannot begin until the pressure exerted by the non-wetting fluid exceeds the threshold pressure or bubbling pressure (in crude petroleum reservoir terminology), which is sometimes also called the entry value. Once this pressure (generally in the form of a head) has been achieved, wetting fluid displacement begins. The thickness of the NAPL provides this energy at the DSCP. As the non-wetting fluid is added, it pushes the wetting fluid ahead of itself in the form of a front. This front can only advance if there is a solid and continuous pathway filled with the non-wetting fluid. This continuous pathway exists in the form of interconnected pore throats between soil particles that remain coated with a thin envelope of water, the original wetting fluid. Figure 3-19 illustrates this process. The non-wetting front will continue to advance as long as the pressure or head exerted by the non-wetting fluid exceeds the bubbling pressure at the entry point. When the energy in the non-wetting fluid head falls below the bubbling pressure, the non-wetting NAPL front ceases advancing, and the plume location and morphology become static.

Obviously, in a subsurface system, gravity also affects the movement of the non-wetting fluid as a result of the inclination of the water table. These gravitational forces provide for gravity drainage of some of the non-wetting fluid. However, gravity drainage only reduces the non-wetting fluid saturation in the pathway until the continuous fluid stream is broken. When this occurs, the non-wetting fluid will be at its irreducible saturation. As is the case with the water system described above, the non-wetting fluid is then held under a negative capillary pressure and is immobile. This process is illustrated on the right side of Figure 3-18 (Bear 1972).

The fifth physical principal is the concept of relative permeability. Permeability is the capacity of a porous medium to transmit a fluid independent of fluid properties. However, when two immiscible fluids flow through the same porous medium, the medium transmits the two fluids differentially based on differences between each fluid's properties. This concept, termed relative permeability, is defined as the ratio of the intrinsic or absolute permeability of the fluid at a given saturation ratio to the total intrinsic permeability of the porous medium (Fetter 1993). The wetting fluid and the non-wetting fluid have unique relative permeabilities that govern the degree to which each distributes itself in the porous medium. Therefore, this parameter strongly influences the flow of the multi-phase system through the subsurface.

With these physical principals defined and provided as background, it is now appropriate to initiate a theoretical discussion of the flow and behavior of NAPL in the subsurface.

3.2.2.1 Multi-Phase Fluid Flow in the Vadose Zone

When NAPL is introduced to the subsurface, it immediately begins to migrate vertically due to gravity. The degree of lateral spreading that occurs as the fluid moves downward is a function of the soil's character (i.e., grain size and distribution). On a micro scale, NAPL migration through the vadose zone is, for the most part, a three-phase system consisting of the NAPL, air in the porous medium, and water in the porous medium. Multi-phase flow in the subsurface can be described mathematically by Darcy's Law, as generalized for multi-phase flow (Beckett and Huntley 1998):

(Equation 3-3)

$$q_{pi} = \frac{k_{rp} k_{ij}}{\mu_p} \left| \frac{\delta P_p}{\delta X_j} + \rho_p g \frac{\delta z}{\delta X_j} \right|$$

Where: q_{pi} = Darcy Velocity
 k_{rp} = Relative Permeability Scalar
 k_{ij} = Intrinsic Permeability Tensor of the Soil
 μ_p = Viscosity
 ρ_p = Density
 X_j = Distance
 P_p = Pressure
 g = Gravitational Acceleration
 Z = Elevation

For the released NAPL to continue to migrate through the vadose zone, it must displace the air and the mobile water in the vadose zone and form a continuous NAPL (the non-wetting fluid) wetting front to continue to migrate through the vadose zone. That is, a pathway must be created in the porous medium in which a continuous pathway of pores has been filled with NAPL. Before the introduction of NAPL, the pores were filled with the water or air to their respective saturation levels (S_w and S_a , respectively). Water is present in the vadose zone although this zone is generally considered to be unsaturated. Even in very dry regions, water is present in the form of pendular rings or envelopes around the soil-grains. As the non-wetting fluid (NAPL) front advances and the wetting fluid is displaced, the pores in the pathway fill to the level of non-wetting fluid saturation

(S_{nw}). In any subsurface system, the relationship between these three saturations (water, NAPL, and air) is balanced, as described by the following equation (Essaid et al. 1993):

(Equation 3- 4)

$$1 = S_w + S_{nw} + S_a$$

If the volume of the released NAPL is adequate to fill the pores in a continuous pathway from the point of release to the capillary fringe and the water table, accumulation and spreading begins. If the release volume is not adequate to satisfy the residual saturation throughout the vertical interval to the capillary fringe and the water table, vertical migration terminates within the unsaturated zone, and no NAPL accumulates on the capillary fringe and the water table. This is the reason that it is common to encounter very high concentrations of hydrocarbon in the vadose zone soils beneath release and to find no NAPL on the water table.

As discussed above, when the vadose zone NAPL migration ends, the pores in the continuous pathway in the porous medium are filled to residual saturation (S_{nw}). After input from the source has ceased, gravity causes the mobile NAPL in the pores to drain. However, this drainage does not remove all of the NAPL from the porous medium. A large fraction of the released NAPL (around 20 percent saturation of available pore space), often referred to as the residual hydrocarbon fraction, is held under reduced capillary pressure at its irreducible saturation (Fetter 1993). This fraction then, is immobile and remains as a secondary hydrocarbon source for the underlying groundwater (Reisinger 1995). Because of the strength of the attraction of the NAPL to the porous medium (i.e., interfacial tension) and the reduced pressure under which it is held, the infiltration of precipitation does not mobilize the NAPL, although some solubilization does occur (Fetter 1993). Figures 3-20 and 3-21 (Fetter 1993) show the generalized distribution of a hydrocarbon NAPL such as naphtha in the subsurface, and Figure 3-22 (Eckberg and Sunada 1984) shows the distribution in the vadose zone.

3.2.2.2 Capillary Fringe

The capillary fringe is the interface between the water-bearing zone and the unsaturated zone. As its nomenclature suggests, the capillary fringe contains groundwater from the saturated zone that has “wicked” or risen via capillarity. As such, it is held at or near 100 percent saturation under a reduced pressure or suction. The thickness of the capillary fringe above the water table is a function of the

size of the particles that comprise the porous medium and, thus, the size of the pores in the medium. Bear (1972) shows that the capillary rise ranges from about 2-cm in coarse sand to greater than 200- to 400-cm in clay. Thus, the rise is greater in fine-grained materials and smaller in coarse-grained materials.

The capillary fringe acts as a barrier to continued vertical migration because it has a very high water content, because the NAPL is less dense than water, and because the NAPL is immiscible in water. For many years, it was assumed that the capillary fringe was a smooth and regular surface much like the water table. When NAPL accumulated on it, it was thought that the NAPL formed a distinct layer atop it (Blake and Hall 1987). In this model, it was assumed that the capillary fringe was 100 percent saturated with water. The model further assumed that the NAPL atop the capillary fringe saturated the pores of the medium where it resided and it formed its own capillary fringe.

In 1990, Lenhard and Parker and Farr et al. simultaneously developed models showing that NAPL and water co-exist in pores from the NAPL/water interface to just slightly above the NAPL/air interface and that the surface of this system assumes a rough and irregular surface. They based their models on the multi-phase immiscible fluid transport theory developed in petroleum engineering literature (Brooks and Corey 1966). Their work suggests that the NAPL saturations in this zone are lower than the 100 percent formerly envisioned. In turn, this suggests that the volume and mobility of hydrocarbon in the subsurface are also lower than formerly envisioned, which is consistent with the saturation theory described previously.

3.2.2.3 Immiscible Multi-Phase Fluid Flow on the Capillary Fringe and Water Table

When the volume of a NAPL release is adequate to advance the non-wetting fluid front to the water table, NAPL accumulates in and on the capillary fringe and water table as a separate phase (Figure 3-20). The accumulation rate depends on the leakage rate and the properties of the porous medium through which NAPL must migrate to reach the water table. The accumulated NAPL will migrate laterally on the water table as described in the Darcy equation generalized for multi-phase flow (Equation 3-3). Migration will occur radially in response to the head gradient generated near the center or centroid of the release. Migration will sequentially occur in the direction of the water-table's inclination as the result of gravitational forces (g in Equation 3-3). The degree of water-table

inclination (gradient), the physical character of the NAPL (i.e., viscosity, density, and interfacial tension), the volume and rate of release, and the physical characteristics of the porous medium (i.e., porosity and hydraulic conductivity) control the rate of migration as related in Equation 3-3. As previously discussed, for the NAPL to migrate along the capillary fringe and water-table surface, there must be a head to "push" it. The greater thickness nearest to the source or point of release provides the head or driving energy. It must be at least equal to the bubbling pressure in the formation, otherwise the NAPL (the non-wetting fluid) cannot displace the wetting fluid. When the energy in this head falls below this pressure, migration will cease. Migration can also only continue as long as a continuous non-wetting fluid pathway exists. When either the driving head becomes inadequate or the continuous pathway is broken, migration ceases.

When the driving-head pressure falls below the bubbling pressure or the pathway is broken, migration continues for a short duration until gravity drainage of the pores has been completed. At this point, a layer of essentially immobile NAPL remains on the capillary fringe and water table, and a substantial mass of residual hydrocarbon resides in the saturated and unsaturated aspects of the pathway. The NAPL layer is immobile because, with the exception of the water-table gradient, there is inadequate energy to overcome the bubbling pressure that would allow the residual wetting fluid (i.e., NAPL) to be displaced. Examples of commercial and industrial sites beneath which immobile NAPL plumes have persisted for decades include chemical plants, retail gasoline marketing outlets, manufactured gas plants, airports, and other industrial operations. In many instances, when sampled and analyzed, this aged NAPL has essentially the same physicochemical characteristics as it had when it was released. That is, it has weathered but minimally.

The aforementioned pathway residual NAPL fraction or volume is substantial, and its volume and mass is a function of the irreducible NAPL saturation of the soil (S_{nw}). As described previously, this parameter is the volume of immobile, non-wetting fluid or NAPL that remains after gravity drainage has ceased. This residual NAPL remains in the pathway permanently. It cannot be removed or flushed by infiltrating precipitation or groundwater pumping because the energy in such a head is inadequate to overcome the bubbling pressure required to initiate displacement, because the energy in the head is less than the capillary pressure that is holding the NAPL and because the NAPL non-wetting phase is discontinued.

While the predominant mechanism of NAPL migration is along the inclined water table in the direction of the inclination, groundwater flow is not a totally two-dimensional phenomenon. In most locations, the water table also fluctuates vertically on a seasonal basis as a result of recharge variability. In general, variation in precipitation and thus, recharge causes the vertical fluctuation. That is, the water table rises and reaches its highest elevation during periods of greater precipitation and recharge and falls and reaches its lowest elevation during periods of less precipitation and recharge. In more arid climates, the fluctuation can be very small. Conversely, in areas with more pronounced wet and dry periods, the water table can fluctuate over large vertical intervals. Anthropogenic influences, such as withdrawal, pumping, or periodic flooding, can also produce extreme water-table fluctuations. For example, agrarian regions, particularly those that produce rice using the flood method, can experience water-table fluctuations that exceed 20-ft.

When a layer of NAPL is present on a high and fluctuating water table, the mobile fraction of the NAPL falls as the water table falls. Residual NAPL is left behind at levels of approximately the inducible saturation in the “new” vadose zone created by the receding water table. The interval between the initial NAPL/air interface and the new NAPL/air interface, through which the receding NAPL has passed, is termed the smear zone. If the water table rebounds more rapidly than the NAPL table can rebound as a result of differential interfacial tension, a large portion of the residual NAPL remains submerged and is trapped and immobile. Figure 3-21 (Fetter 1993) is a graphic representation of the formation of a smear zone and provides a relative indication of NAPL and water in it. The residual NAPL volume in the smear zone can be very large (20 percent of available pore space or greater) and varies as a function of the porous medium’s character (i.e., porosity, water content). Testa and Paczkowski (1989) estimated that the residual capacity ranges from 0.03-gal/ft³ for gravel to 0.28-gal/ft³ for silty sand. For example, assuming an area 800-ft by 800-ft by 10-ft, the estimated residual NAPL volume using these relationships would range from 192,000 gallons in gravel to 1,792,000 gallons in silty sand.

3.2.3 NAPL Fate Mechanisms

When any xenobiotic is introduced to the environment, it immediately begins to interact with the media and to partition into various compartments as a function of its physicochemical characteristics. Figures 3-23 and 3-24 show these partitioning patterns and the interactions between them. The manner in which this partitioning occurs is compound-specific as a function of the characteristics of the compound including:

- Aqueous Solubility
- Vapor Pressure
- Diffusivity
- Viscosity
- Density
- Interfacial Tension
- Organic Carbon Partitioning Coefficient
- Henry's Law Coefficient

While partitioning determines the environmental compartments where xenobiotics reside, fate processes govern the final disposition of the xenobiotics. Figure 3-25 graphically depicts these processes. They act on the xenobiotics in the environment to destroy, transform, translocate, or immobilize them. They include:

- Sorption
- Solubilization and Transport
- Volatilization and Transport
- Biodegradation

These processes are discussed as they relate to petroleum hydrocarbons in the ensuing paragraphs.

3.2.3.1 Sorption

While not strictly a fate process because it does not reduce the mass of a xenobiotic, sorption is a physical process that has great bearing on the behavior and partitioning of xenobiotics, particularly when paired with an advancing NAPL front. Sorption is an expression of a constituent's potential to interact with a solid matrix. Interaction between a solute and a porous medium may be either true adsorption through chemical bonding, including both mineral and organic interactions, or it may actually be a partitioning into the organic carbon associated with the solid matrix. These interactions occur in both the vadose zone and the saturated zone. However, mineral interactions

appear to be more important in the low-moisture content vadose zone, particularly when the contaminant is in the vapor state. Organic carbon partitioning appears to be more important in the saturated zone (Chiou et al. 1988). The adsorption and partitioning processes are not abrupt terminal processes; rather, they are equilibrium processes and, therefore, are continuous. In either case, the result is the same—decreased solute mobility and availability for solubilization, volatilization, and other fate processes.

Adsorption potential for soil/water systems in the vadose and saturated zones can be expressed in a number of ways, two of which will be discussed. The first is the organic carbon partitioning coefficient (K_{oc}), which can be expressed as (Lyman et al. 1982): **(Equation 3-5)**

$$K_{oc} = \frac{\mu\text{g adsorbed/g organic carbon}}{\mu\text{g/ml solution}}$$

This expression, which is a linear partition isotherm valid for dilute solute/solvent systems, offers a true representation of partitioning because it is essentially independent of solid matrix properties. It is the ratio of the amount of solute adsorbed per unit weight of organic carbon in the solid matrix to the solute concentration in solution at equilibrium. K_{oc} can be empirically derived and is a direct measure of adsorption potential.

The second expression is the octanol-water partition coefficient. This expression is a direct measure of the partitioning of an organic solute in an octanol (ideal organic compound) water system. It can be measured directly and expressed as (Karickhoff et al. 1985): **(Equation 3-6)**

$$K_{ow} = \frac{C_o}{C_w} = \frac{\phi_w}{\phi_o} = \beta \frac{\gamma_w}{\gamma_o}$$

Where: K_{ow} = Octanol:Water Partitioning Coefficient
 C_o = Solute Concentration in Octanol
 C_i = Solute Concentration in Water
 ϕ_o = Octanol Fugacity Coefficient
 ϕ_w = Water Fugacity Coefficient
 β = Unit Adjustment
 γ_w = Water Activity Coefficient
 γ_o = Octanol Activity Coefficient

It directly relates water solubility, soil adsorption coefficients, and bioconcentration factors for aquatic life. K_{ow} provides a representation of a compound's tendency to partition between an organic phase and an aqueous phase; it can also be used to estimate K_{oc} . Estimation of K_{oc} from K_{ow} is generally done by linear regression analysis using the following expression:

(Equation 3-7)

$$\log K_{oc} = \alpha \log K_{ow} + B$$

Where: α = Data Fitted Coefficient

β = Data Fitted Coefficient

As the preceding discussion shows, sorption does not destroy xenobiotics as a true fate mechanism would; it immobilizes them. Therefore, sorption does not change the mass of a given xenobiotic or mixture. That is, sorption does not change the concentration of naphtha in the soil in a NAPL pathway. It simply alters the partitioning pattern and distribution, as well as the mobility.

3.2.3.2 Solubilization and Transport

Aqueous solubility is one of the more important parameters governing the partitioning, transport, and fate of xenobiotic mixtures and their constituents in the environment. It can be defined as the maximum amount of a mixture or constituent thereof that will dissolve in pure water at a specified temperature. Above this concentration, two phases will exist in the solvent/solute system. Solubility controls the amount of solute that can partition into the aqueous environmental compartment and thus, be transported by it. For pure compounds, the aqueous solubility directly reflects molecular structure and electrochemical characteristics. As such, it is often considered a fundamental physical constant. For organic mixtures, such as naphtha, solubility is a function of the mole fraction of each constituent in the mixture (Burris and MacIntyre 1985). The concentration of an individual compound in a mixture in water at equilibrium with the hydrocarbon mixture can be expressed according to the following equation:

(Equation 3-8)

$$C_i^* = C_i^o X_i \gamma_i$$

Where:

C_i^* = Equilibrium Solute Concentration for Component i in the mixture

C_i^o = Equilibrium Solute Concentration for Component i as Pure Compound

X_i = Mole Fraction of Component i in the Hydrocarbon Mixture

γ_i = Activity Coefficient of Component i in the Hydrocarbon Mixture

As stated above, solubilization of components in a hydrocarbon mixture is an equilibrium process. Hydrocarbon partitioning from a hydrocarbon mixture, such as naphtha, into an aqueous phase appears to follow a source renewal model. This results from other processes occurring as solubilization is taking place (i.e., bulk groundwater flow, volatilization, and sorption).

Solubility is generally expressed in terms of mass per unit volume (mg/L or $\mu\text{g/L}$). Most anthropogenic organic compounds are sparingly soluble in aqueous systems. However, all compounds are at least minimally soluble in water. The solubilities of most organic compounds range from less than 1 mg/L to 100,000 mg/L. The physical parameter that has the greatest effect on aqueous solubility is temperature. However, dissolved solid content, mole fraction, and dissolved organic matter affect aqueous solubility.

In sum, solubilization is the process by which, in the case of NAPL, compounds that are constituents of a mixture partition into or dissolve in groundwater. As such, solubilization alone is a compartmental translocation mechanism. However, because dissolved constituents are transported by groundwater away from a NAPL source area through advection and dispersion, solubilization is a true fate process because it reduces mass within an area of interest. The process is equilibrium based and, as such, depends on the rate of groundwater flow and the solute/solvent diffusion coefficient.

3.2.3.3 Volatilization and Transport

Vapor pressure, another important physicochemical parameter, can be used to estimate a compound's tendency to volatilize and partition into the gaseous state or atmosphere. Strictly defined, the vapor pressure of a compound is the pressure exerted by the vapor at equilibrium with the liquid phase of the compound in a closed system at a given temperature. Vapor pressure is generally expressed in mm of Hg or in atmospheres. Refined petroleum products (and the constituents that comprise them) and many solvents and degreasers, such as naphtha, have relatively high vapor pressures; therefore they are relatively volatile. Vapor pressures for common gasoline constituents typically range from 0.003 to 10.2 atmospheres (2.28 to 7752 mm Hg). Vapor pressure is an important parameter in determining the behavior of contaminants and their constituents in the environment. It indicates a compound's tendency to volatilize from either the aqueous phase, soil,

or parent hydrocarbon mixture. The physical parameters that have the greatest effects on vapor pressure are temperature and the nature of the constituent itself (i.e., critical temperature, critical pressure, and heat of vaporization). For mixtures, the composition of the mixture also has bearing on the vapor pressure according to the following expression:

(Equation 3-9)

$$P_i^* = X_i \gamma_i P_i^o$$

Where:

P_i^*	=	Equilibrium Partial Pressure for Component i
X_i	=	Mole Fraction of Component i in the Hydrocarbon Mixture
γ_i	=	Activity Coefficient of Component i in the Hydrocarbon Mixture
P_i^o	=	Vapor Pressure of Component

The primary mechanisms of vapor transport in the subsurface are gaseous diffusion and isothermal advection. Following a release of volatile NAPL, vapor-phase transport of volatile constituents away from the source will occur, primarily through gaseous diffusion. As such, migration occurs along a concentration gradient. This migration, then, is independent of the groundwater hydraulic gradient and occurs in all directions in the absence of solid matrix heterogeneities and thermal and pressure gradients. Vapor-phase migration will continue indefinitely into the soil atmosphere and outer atmosphere (assuming communication) until the concentration gradient is satisfied or an equilibrium is established.

Diffusive vapor-phase transport is described by Fick's Second Law, which can be expressed mathematically according to the following expression (Jury et al. 1983):

(Equation 3-10)

$$J_{sv} = D_v \frac{\delta C_v}{\delta z}$$

Where: J_{sv}	=	Constituent Vapor Flux
D_v	=	Soil-Gaseous Diffusion Coefficient
C_v	=	Constituent Mass In Vapor Per Volume Of Soil Air
z	=	Distance

While this expression is useful in describing simple, diffusive non-reactive transport, contaminant vapors in the vadose operate in a three-compartment model (Figure 3-24): soil atmosphere, soil water, and the solid matrix. As vapors migrate through the vadose, they interact with and partition

into each of these compartments according to the processes described above. Because the constituents in the vapor phase typically have an affinity for the material in the solid matrix, they partition into it via sorption processes (Chiou et al. 1988). This equilibrium process can be described by the following linear relationship:

(Equation 3-11)

$$C_a = K_d C_l$$

Where: C_a = Constituent Mass Adsorbed Per Mass Of Soil
 K_d = Distribution Coefficient = $K_{oc} f_{oc}$
 C_l = Constituent Mass Dissolved Per Volume Of Solution
 K_{oc} = Organic Carbon Distribution Coefficient
 f_{oc} = Soil Organic Carbon Coefficient

Again, most contaminants are also at least sparingly soluble in water. In examining vapor transport in the vadose, partitioning between the vapor and vadose water phases must be considered. This process can be described mathematically using Henry's Law in the following expression:

(Equation 3-12)

$$C_v = K_H C_l$$

Where: C_v = Constituent mass in vapor per volume soil air
 K_H = Dimensionless Henry's Law coefficient
 C_l = Constituent mass dissolved per volume of solution

These interactions can be combined with the general vapor transport equation to yield the following expression that includes diffusion and partitioning:

(Equation 3-13)

$$\frac{\partial C_T}{\partial t} + r = D_E \frac{\partial^2 C_T}{\partial Z^2} - V_E \frac{\partial C_T}{\partial Z}$$

Where: C_T = Total Concentration
 t = Time
 r = General Reaction Term
 D_E = Effective Diffusion Dispersion Coefficient
 Z = Distance
 V_E = Effective Constituent Convective Velocity

This discussion clearly shows that, as vapors migrate through the vadose zone, they interact with the matrix through which they are being transported. This results in a decrease in velocity of the vapor

front as mass at the leading edge is tied up. Partitioning in the vadose zone renders the soil, as well as the three compartments that comprise it, secondary groundwater contaminant sources. As the contaminants in the vadose react with the vadose atmosphere and infiltrating precipitation, they are transported to the groundwater. Thus the vadose will continue to serve as a groundwater contaminant source until no contamination remains or the vadose contamination is remediated.

Not only does the soil-residual fraction in the vadose serve as a secondary source, but the contaminant vapor plume can also serve as a secondary source. Because vapor transport is a diffusion-dominated process and, therefore, occurs along a concentration gradient, uncontaminated groundwater can be a sink for contaminants in the vadose atmosphere due to solubilization. Upgradient groundwater contamination in an area greater than 100-ft from a contaminant source has been reported to be associated with vapor-phase transport followed by solubilization upgradient (Hinchee and Reisinger 1987).

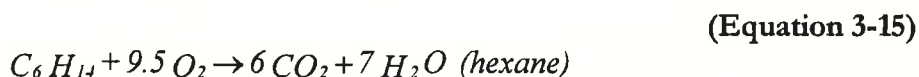
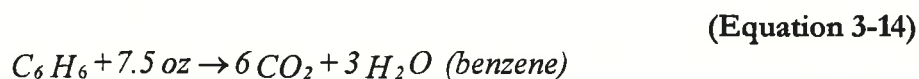
As is the case with solubilization, volatilization alone is not a true fate mechanism because it simply translocates xenobiotics, such as NAPL naphtha, from a source to the vadose-zone atmosphere and ultimately to the atmosphere. However, volatilization will result in a reduction in the soil-residual NAPL concentration.

3.2.3.4 Biodegradation

To this point, the discussion has focused on physical processes that result in partitioning of contaminants in the environment. Contaminants can also be transformed or mineralized as a result of biological activity. Indigenous bacteria that reside in the subsurface carry out these processes, termed biotransformation and biodegradation. These organisms exist in the subsurface in populations that are controlled by the concentrations of essential nutrients, moisture, and oxygen or another appropriate electron acceptor. The rate of biotransformation or biodegradation is controlled by population density, which is, in turn, controlled by concentrations of electron acceptors, essential mineral macro-nutrients, and environmental factors (i.e., pH, water content, temperature). The organisms typically have metabolic pathways that allow them to use specific compounds or classes of compounds as energy sources and as nutrients to support cellular mass increase. Under uncontaminated conditions, the density of the bacterial population that can use the contaminant as an energy source is low. When the contaminant is introduced to the environment,

the density of the heterotrophic population increases to the carrying capacity, where it remains as long as the contaminant concentration and environmental conditions are optimal. The population density decreases as the contaminant concentration decreases. In essence, the bacteria use the contaminant as a source of metabolic energy to support reproduction and increase biomass.

Cellular respiration can be carried out under either aerobic or anerobic conditions. Petroleum hydrocarbons (i.e., aromatic and aliphatic compounds), such as naphtha, typically degrade most rapidly under aerobic conditions. The stoichiometry of aerobic mineralization of aromatic and aliphatic compounds can be expressed as follows for two representative hydrocarbon compounds:



These expressions show that biodegradation is carried to complete mineralization, and thus, total destruction. Thus, biodegradation is truly a fate process that results in a decrease in the mass of xenobiotics in the subsurface.

While the biodegradation of xenobiotics is compound-specific as a function of a compound's stoichiometry, it is not compartment-specific. That is, biodegradation occurs in the vadose zone and the saturated zone as long as adequate water and adequate mineral macro-nutrients (i.e., nitrogen, phosphorus, potassium, trace elements) are present. An essential consideration often overlooked in discussions of biodegradation is bioavailability. It can be defined in general terms as the degree to which a target xenobiotic is available to the indigenous heterotrophs that will ultimately use it as a source of energy and carbon that is necessary to produce cell mass.

Bacteria, the class of biota generally responsible for biodegradation of xenobiotics, reside in the water in the porous medium (Alexander 1961). Thus, the availability of a given xenobiotic is very strongly affected by its aqueous solubility. For a compound to be biodegraded, it must be dissolved in the water where the degrader organisms reside. For this reason (among others), xenobiotics such as polynuclear aromatic hydrocarbon (PAH) compounds with high molecular weight and concomitantly low aqueous solubilities are recalcitrant, or only minimally biodegradable. The concept of bioavailability is particularly germane to mass reduction of an NAPL such as naphtha

through this fate process. Petroleum hydrocarbons are readily biodegradable and are generally considered non-toxic or non-inhibitory to indigenous heterotrophic bacteria. Commonly, strong evidence of petroleum hydrocarbon biodegradation is found even in areas with hydrocarbon concentrations that are near those that suggest irreducible saturation. This is a function of the residence of the bacteria in the soil water, which dictates that the highest hydrocarbon concentration to which the bacteria can be exposed is the respective mole fraction corrected or effective solubility of each compound in the hydrocarbon mixture. Thus, in order for bacteria to reduce the mass of a NAPL plume, a mass transfer of the hydrocarbon constituents in the mixture to the water where the bacteria reside by solubilization must occur before bacteria can utilize the carbon as an energy source.

The necessary transfer of xenobiotic compounds from the NAPL to water for biodegradation and mass removal dictates the weathering patterns of the NAPL and the degree to which the mass in a NAPL plume can be reduced. Hinchee and Reisinger (1987) introduced the concept of differential solubility as it relates to hydrocarbon fate and transport. In this concept, the degree to which compounds are removed from NAPL is a function of their mole fraction corrected solubility. That is, those compounds with very high solubilities (i.e., hydrophilic) transfer from NAPL to water more rapidly and to a larger extent than those with lower solubilities (i.e., hydrophobic). This process causes those compounds that are hydrophilic to be preferentially removed through the solubilization process. The remaining NAPL is less mobile and more recalcitrant. For this reason, as hydrocarbon plumes weather, they become dominated by higher molecular weight compounds. The process also helps explain why it is uncommon to encounter soil through which hydrocarbon has migrated that has no evidence of hydrocarbon.

3.3 CHEMISTRY OF PETROLEUM

This section begins with a discussion of the origin of petroleum (crude oil), providing the basis for understanding the sections that follow. Hydrocarbon chemistry, refining of petroleum, a discussion of fuel types and specifications also are included.

3.3.1 Chemistry of Crude Oil

Crude oil is a degradation product of prehistoric plants and animals buried deep in sediments of swamps, lakes and oceans. Following exposure to high temperature and pressure, these layers of sediment and organic debris formed petroleum-saturated rock over time. It is generally believed that the dominant type of organic matter responsible for the formation of crude oil is derived from phytoplankton (microscopic plants). Accumulation of these organisms, together with their microscopic predators (known as zooplankton) and land vegetation occurred over millions of years.

Bacteria then converted the major biological molecules of the organic matter into simpler forms, particularly amino acids and fatty acids (i.e., biomonomers). Sediment, heated by the earth's geothermal gradient, induce the biomonomers to form a complex organic structure known as kerogen. Under further thermal stress and time, reactions occur which remove oxygen as carbon dioxide and water and transform the kerogen to crude oil. At very high temperature and pressure, the source rock becomes over-mature and crude oil is transformed into hydrocarbon gases. At greater temperatures, most of the crude oil and natural gas are converted to methane. Fluids are mobilized into reservoirs following the formation of oil and gas.

The chemistry of the original organic matter along with the environment, duration, pressure, and heat, dictate the type of crude oil or gas formed. The chemical composition of the resulting oil and gas, and its source rock often can be used to describe the source of the original organic matter, temperature of hydrocarbon generation, and maturity of the oil (Kaplan and Galperin 1996).

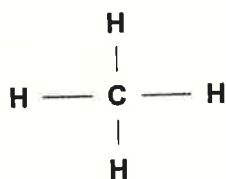
Crude oil is a mixture of many substances, from which various refined petroleum products (such as gasoline, kerosene, naphthas, fuel oils, lubricating oil) and chemicals are extracted and manufactured. These substances are composed mainly of carbon and hydrogen and are, therefore, called hydrocarbons. Other elements including oxygen, sulfur, and nitrogen, as well as trace amounts of phosphorus and some trace metals (vanadium and nickel) may be present in smaller quantities.

3.3.1.1 Hydrocarbon Chemistry

Pure hydrocarbons are compounds containing only hydrogen and carbon. However, we also refer to petroleum compounds that are primarily carbon and hydrogen, but have trace levels of other

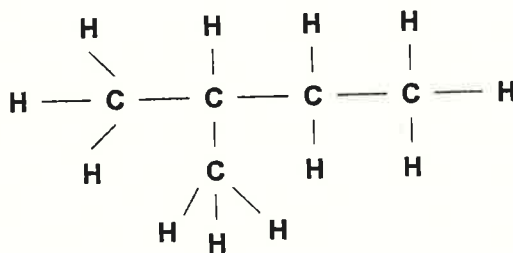
compounds, as hydrocarbons. The simplest hydrocarbon is methane, which consists of one carbon and four hydrogen atoms. Its molecular structure can be presented as CH₄ or:

Methane Structure

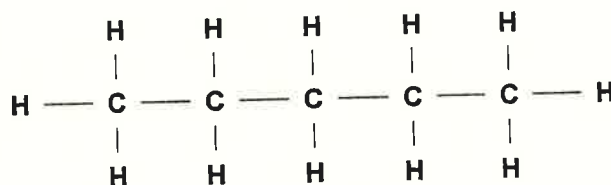


Larger hydrocarbon molecules are composed of two or more carbon atoms joined to one another and to hydrogen atoms. The carbon atoms may form a straight chain (n-alkanes), a branched chain (isoalkanes or isoprenoids), or a ring (cycloalkanes or naphthenes). Each carbon atom must have four chemical bonds as shown below:

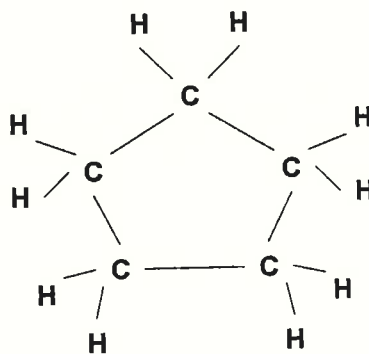
Pentane Structure



Isopentane Structure



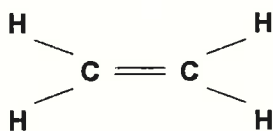
Cyclopentane Structure



When two adjacent carbon atoms are linked by more than one bond (double bond or triple bond), the hydrocarbon is said to be unsaturated. Straight or branched chain hydrocarbons with one or more double bonds are called alkenes or **olefins**, and hydrocarbons with a double bond in a ring are cycloalkenes or cycloolefins. The simplest alkene is ethylene: In terms of geological time, alkenes are less stable than other hydrocarbons and tend to break down to alkanes during formation. Therefore, crude oils and straight run petroleum distillates contain little or no alkenes. Alkenes are formed during thermal and catalytic cracking where larger molecules are broken down into smaller molecules to produce finished products such as gasoline. During the cracking process alkenes or olefins are formed and are found at percent levels in gasolines.

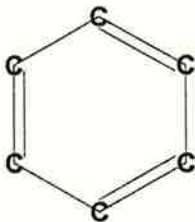
Therefore, the presence of these compounds can be used to differentiate between a cracked product (i.e. gasoline) and a straight-run distillate.

Ethylene Structure

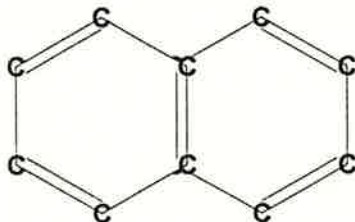


Hydrocarbons that contain a six-membered ring with alternating double bonds are an important group known as monoaromatic hydrocarbons, the simplest of which is benzene. Compounds with multiple aromatic rings comprise another important group of aromatic hydrocarbons called PAH compounds. Naphthalene is an example of a two ring PAH compound.

Benzene Structure



Naphthalene Structure



3.3.1.2 Classes of Compounds

Petroleum contains thousands of hydrocarbons and much fewer non-hydrocarbons with different sizes and structures. The actual number of individual hydrocarbon compounds in crude oil is not known because current analytical procedures are not able to isolate and identify every one of them. The number is estimated to be between 50,000 and 2,000,000 (REF). Compounds are typically grouped in various fashions to accommodate their large numbers, such as:

- chemical structure (e.g., n-decane as a “normal alkane”); or
- number of carbon atoms present (e.g., butane as a “C₄ hydrocarbon”);
- test-specific characteristic (e.g., “diesel range hydrocarbon”).

The following groups typically are used to designate chemical structure:

Paraffins

Paraffins, or alkanes, are the major constituents of crude oil and of most refined products. Paraffins are sometimes called saturated hydrocarbons (or “saturates”) to indicate that the carbon structure is completely saturated with hydrogen molecules and therefore, contains no double bonds. For the discussions that follow, paraffin is used to describe linear or normal (n-alkane) alkanes.

Isoparaffins

Isoparaffins are branched alkanes that are saturated. Isoparaffins are sometimes referred to as isoprenoids and are also a major constituent of crude oil and most refined products. As discussed later, the branched structure of these compounds makes them more resistant to weathering than the linear form. This has important consequences in evaluating the weathering of crude oil and refined products.

Aromatics

Aromatic compounds contain at least one six-carbon ring. The ring structure consists of three alternating double bonds. Higher aromatic compounds (such as naphthalene) contain more than one aromatic ring fused to one another. The ring structure and the arrangement of the double bonds cause these compounds to behave differently from other hydrocarbons.

Naphthenes

Naphthenes are similar to alkanes except that the carbon backbone is cyclical (ringed) and bonds are single, hence they are sometimes called cycloalkanes.

Olefins

Olefins, sometimes called alkenes, are unsaturated hydrocarbons. That is, the carbon structure is not saturated with hydrogen molecules, and that some carbon molecules are double or triply-bonded to each other. Olefins exist at trace levels in crude oils. They are significant because they are produced during certain stages of the oil refining process (e.g., hydrocarbon cracking).

Hetero-Compounds

Hetero-atom compounds also are found at low concentrations in petroleum products. These compounds contain atoms in addition to hydrogen and carbon, and are therefore, not considered pure hydrocarbons. They have a carbon backbone with the substitution of a hetero-atom, such as sulfur, nitrogen, or oxygen. Crude oils are sometimes characterized by the distribution of these hetero-compounds. Dibenzothiophenes, sulfur containing hetero-compounds, are important in the characterization of diesel fuels.

In general, the principal compounds in petroleum are paraffins, naphthenes and aromatic hydrocarbons, with relatively small amounts of asphaltene-type materials. Crudes vary widely, but an average crude may contain 15-60 percent paraffins and isoparaffins, 30 to 60 percent naphthenes, 3 to 30 percent aromatics, and the rest asphaltic material and miscellaneous trace compounds (Guthrie 1960). Most crude oils contain paraffins to approximately $n\text{-C}_{36}$ (36-carbon alkane), although some waxy crude oils can contain alkanes beyond $n\text{-C}_{50}$.

3.3.1.3 Relative Distribution of Compounds

Differences in distribution and abundance of various hydrocarbons are responsible for the unique chemical and physical properties of a crude oil or refined product. These same differences are also used to characterize the petroleum. Because these differences correspond to the source material of the product they can be used to relate unknown petroleum to potential source crudes.

3.3.2 Refining of Petroleum

While modern refining is much more complex than distilling, distillation is the principal method for separating crude oil into what are termed refined products and a key step in the refining process. Distillation at atmospheric pressure separates crude oil into specific fractions based on boiling points of individual compounds. The amount of liquid compounds that are vaporized with heating depends on their individual vapor pressure. In other words, when heated, more of the low boiling compounds will initially vaporize relative to the high boiling compounds. The vapor then condenses to a liquid that contains more of the low boiling compounds. Heating and condensation at controlled temperatures is repeated until the desired separation is achieved (Figure 3-26).

In a typical distillation process, an atmospheric tower is used. The volatile hydrocarbons (i.e., C1 to C4) come off the top of the tower as gases. Liquid gasoline-range compounds (approximately C5 to C12) emit from near the top of the tower at distillation temperatures of 180 to 375 degrees F. Medium boiling compounds (C12 to C17) are collected near the middle of the distillation tower between 350 and 550 degrees F, and are removed as raw kerosene. A third fraction, called light gas oil, is collected near the bottom of the tower. Higher boiling compounds (i.e., greater than C18) collect at the bottom and are called atmospheric residue (Guthrie 1960).

Kerosene and light gas oil are treated to remove odor attributable to sulfur. Straight-run naphtha also is further treated to increase its octane number before it is sold as gasoline. In this process, sulfur is first removed and then the straight-run naphtha is split into two fractions: a light straight-run naphtha (octane rating approximately 80) and a heavy straight-run naphtha (octane rating approximately 35). The heavy straight-run naphtha is then reformed to a product with an octane rating of approximately 95.

The refining process consists of many additional and interrelated steps designed to manufacture products for specific applications. For example, refineries use a cracking process to convert higher molecular weight hydrocarbons into smaller and more volatile compounds because crude oils contain only a portion of hydrocarbons in the gasoline range. Polymerization converts small gaseous alkenes into liquid hydrocarbons. Alkylation transforms small alkenes and isoalkanes into larger isoalkanes with a high octane rating. Combined cracking, polymerization, and alkylation can

result in a gasoline yield representing almost 60 percent of the starting crude oil (Guthrie 1960).

Typical modern refinery processes for gasoline components include:

- Catalytic cracking – sometimes referred to as “cat cracking”, which mixes the product stream with catalysts at high temperatures and breaks larger higher-boiling hydrocarbons into gasoline range product that contain 30 percent aromatics and 20 to 30 percent olefins;
- Hydrocracking – similar to catalytic cracking except hydrogen is added to molecules to facilitate the process, producing a more saturated, stable, gasoline fraction. This process also produces olefins as a secondary product;
- Isomerization - raises gasoline fraction octane number by converting straight chain hydrocarbons into branched isomers;
- Reforming - converts saturated, low octane, hydrocarbons such as methylcyclohexane into higher-octane product containing about 60 percent aromatics such as benzene and toluene;
- Alkylation - reacts gaseous olefin streams with isobutane to produce liquid high octane iso-alkanes.

More advanced processes such as cyclization of paraffins and dehydrogenation of naphthenes to form aromatic hydrocarbons, have also been developed to increase the gasoline octane rating. Modern refinery operation can be shifted to produce almost any fuel-type with specified performance criteria from a single crude feedstock.

3.3.2.1 Product Specifications

Product specifications are important to both the seller (i.e., the refinery) as well as the buyer (i.e., a distributor or an end user). As an example, the refinery strives to ensure that its gasoline is made efficiently and that it meets regulatory requirements and product specifications. The buyer requires that the gasoline is sufficient to power his automobile.

Test methods have been developed to evaluate the performance of petroleum products for specific consumption. These tests typically measure physical parameters (e.g., distillation range, pour point, viscosity, octane rating, etc.). These measurements instill confidence in a buyer that a product will perform as required.

3.3.2.2 Available Product Specifications

Currently, specifications for most generic products are set and published by the American Society of Testing and Materials (ASTM). These publications or standards usually reference appropriate test procedures for product evaluation. Petroleum products are generally manufactured to meet ASTM specifications to facilitate commerce of petroleum products.

Buyers of large product volumes can prepare their own specifications. For example, the US military has its own specifications for gasoline; diesel fuels, and jet fuels which are purchased in large quantities. These specifications may be set due to the need to store chemicals for longer periods of time or to meet specific applications, such as fueling military jet engines.

It is important to note that product specifications have changed over time. Gasoline has undergone a number of formula changes following the change in the design of the internal combustion engine, as well changes in environmental regulations. For example older gasoline were often composed of lower octane grade straight run streams and octane enhanced with tetra ethyl lead (TEL) (Guthrie 1960). Even recently, vapor emission restrictions set forth by the U.S. Environmental Protection Agency (EPA) have caused changes in gasoline specifications.

3.3.2.3 Specifications Versus Analytical Methods

Product specifications also include references to analytical methods. For example, the boiling range for a gasoline is defined by the results of ASTM D86, Standard Method for Distillation of Petroleum Products. These specifications provide control points for reliable production. ASTM 2887 "Boiling Range Distribution of Petroleum Fractions by Gas Chromatography" is a gas chromatography with flame ionization detector (GC/FID) method that separates hydrocarbons by boiling point. It is a rapid analytical tool that requires small volumes of product and may be used to replace conventional distillation methods for control of refining operations and specification testing. The results from the two methods are slightly different. A comparison of the two methods from U.S. military specification MIL-T-5624L for JP-4 fuel is shown in Table 3-1. These results indicate a higher boiling point bias in D2887 relative to ASTM D86.

Boiling point specifications can be used to identify ranges of refined products; however, they do not provide sufficient information to identify individual fuel types that fall within the same range. For example, kerosene, Jet-A, JP-5, and diesel #1 are different products that can all fall within the JP-5 boiling-range specification. Also, specifications were developed to evaluate finished products, and not fugitive products that have been environmentally altered.

Product specification does not have the forensic power of analytical methods that quantify a suite of hydrocarbon compounds. Gas chromatography methods such as GC/FID and GC/MS (mass detector) identify the type and distribution of petroleum related hydrocarbons that are critical to product identification. Reference samples of the suspect product must be analyzed using the same analytical method under the same conditions and compared to the fugitive environmental sample to accurately identify product composition and type. Reliable fingerprinting methods should compare reference and test (suspect) data that are produced with the same analytical methods.

3.3.3. The Chemistry and use of Refined Petroleum Products

As discussed, refined products may be described chemically in a variety of fashions. The following provides chemical compositions and test characteristics for major petroleum product types.

3.3.3.1 Gasoline

Composition

Gasoline is a generic term used to describe petroleum products mainly used in internal combustion engines. It is a complex mixture of hydrocarbon compounds predominantly in the n-C₃ to n-C₁₂ range with boiling points from 105 to 450 °F and a specific gravity of 0.74 g/cm³.

The specific composition of gasoline varies depending on the source of petroleum and refining method. Its composition has changed with changes in automotive engine design and regulatory requirements. During the early 20th Century, oil companies were producing gasoline as a simple distillate from petroleum. Automotive engines, however, were improving rapidly and required a more suitable fuel. A modified engine was developed in the 1910s that ran on kerosene. However, the kerosene engine "knocked", cracking the cylinder head and pistons. This led to the long search for anti-knock agents, culminating in the development of tetraethyl lead.

The sulfur content of the thermally-cracked refinery streams for gasolines was restricted because sulfur in gasoline inhibited the octane-enhancing effect of the alkyl-lead. By the 1930s, the petroleum industry determined that the larger hydrocarbon molecules (such as those in kerosene) had adverse effects on the octane number of gasoline. By the 1940s, catalytic cracking was introduced and gasoline compositions became fairly consistent between brands (Gibbs 1993).

The 1950s marked the beginning of increasing compression ratios, requiring even higher octane fuels. Lead levels were also increased, and some new refining processes, such as hydrocracking, were introduced specifically to provide hydrocarbon components with good lead response and octane number. Minor improvements to gasoline continued to improve yields and octane rating until the 1970s when unleaded fuels and exhaust catalysts were introduced. From 1970 until 1990 gasolines changed slowly as lead was phased out. In 1990 the Clean Air Act started forcing major compositional changes in gasoline (Gibbs 1993).

Over the years, gasoline has contained a number of additives, such as anti-knock agents, lead scavengers, and antioxidants. Among the additives, lead-alkyl antiknocks and lead scavengers are important time markers, and therefore critical for fingerprinting. Leaded gasoline was first marketed in 1923 and until 1960, TEL was used as the only anti-knock agent. Another anti-knock compound, tetramethyl lead (TML), was introduced in 1960. Subsequently, different combinations of these two additives were used. After about 1980, the most common lead additive was TEL, sometimes containing small amounts of TML. In addition, the total amount of lead (as alkyl-lead) added to gasoline has changed with time. A maximum 3.17 grams of lead per gallon of gasoline (g Pb/gal) was recommended in 1926. Lead levels peaked around 1960 at 4.23 g Pb/gal. Government regulations reduced the use of lead and levels after 1960, which gradually decreased to 0.5 g Pb/gal in 1985 and to 0.1 g Pb/gal in 1988. Leaded gasoline was effectively eliminated by the end of 1992.

The lead scavengers, ethylene dibromide (EDB) and ethylene dichloride (EDC), were introduced in 1928 to reduce buildup of lead oxide when using leaded gasoline. The ratio between the two compounds has changed over time. A typical additive stock for automotive gasoline in the 1980s consisted of about 62 percent TEL, 18 percent EDB, 18 percent EDC, and 2 percent of other inactive ingredients (e.g., dyes, antioxidants, petroleum solvent, and stability improvers). TEL is still

used as an anti-knock additive in combination with the lead scavenger EDB in aviation engines. EDC is not used because hydrochloric acid is produced as a combustion by-product.

Oxygenated compounds, such as ethers and alcohols, are increasingly blended into gasolines to maintain a high octane rating and reduce vehicle emissions of carbon monoxide. A common oxygenate, methyl tertiary butyl ether (M/BE), has been blended with gasoline since its first commercial manufacture in 1979 beginning with the east coast in 1982 to the west coast in the late 1980s. The rapid rise in M/BE use beginning in 1992 followed the implementation of a program of winter oxygenated gasoline in thirty-nine metropolitan areas that did not meet minimum air quality standards set forth in the Clean Air Act of 1990. Modern reformulated gasoline contains as much as 15 percent by volume of M/BE. Methanol, ethanol, and tertiary butyl alcohol have all been blended with gasoline.

Advanced Chemical Fingerprinting Characteristics

Modern gasoline is dominated by monoaromatic hydrocarbons, especially benzene; toluene; ethylbenzene; o-, m-, and p-xylene; and C3-alkylbenzenes (Figure 3-27). Benzene, toluene, ethylbenzene, and the three xylenes are well resolved in the GRO analysis of a typical 1990s gasoline. Also present at high concentrations are isopentane and M/BE. The key aromatic components and the C3-alkylbenzenes also dominate the hydrocarbon fingerprint. The PAH analysis targets larger aromatic compounds, beginning at naphthalene (C10). The only PAH compounds present in a typical gasoline are naphthalene and some alkyl-naphthalenes and these are found at relatively low concentrations. Alkylates such as isooctane are the major hydrocarbons in aviation gasoline.

3.3.3.2 Solvents

Solvents refer to the liquid hydrocarbon fractions from crude oil that are used for industrial processes and formulations. Solvents may be used to dissolve, suspend, or transport other process ingredients. Petroleum solvents are attractive because large volumes with relatively high quality are available at low costs. Petroleum solvents are used extensively in the manufacture of paints, printing inks, and adhesives. They are also widely used in industries such as dry cleaning, leather, and pesticide manufacturing and application. The solvent is used to dissolve resins or oils in many

applications. Other applications suspend the ingredients, such as pigments and fillers. The petroleum solvents are also used extensively as cleaners and degreasers.

Solvents are categorized commercially as follows:

- Narrow cut aliphatics
- Special boiling range solvents
- Mineral spirits
- Aromatics
- Kerosene

All of these can also be considered naphthas

Advanced Chemical Fingerprinting Characteristics

The characteristics of a specific solvent depend upon the requirements of its formulation. The fingerprinting characteristics of a specific solvent are formula dependent. Examples of mineral spirits, naphtha, and kerosene composition are given in Figures 3-28, 3-29, and 3-30.

3.3.3.3 Aviation Gasoline

Development of aviation gasolines for spark engines reached a peak during the war years, 1940 to 1945. Invention of the turbine engine slowed development of piston engines and thus, the specifications for aviation gasoline has essentially remained the same since. Aviation gasoline, which requires careful handling to maintain its integrity, is one of the most complex formulations produced by a refinery. The main component of high-grade aviation gasoline is isooctane produced by alkylation, with a small amount of isopentane added for volatility. Catalytic reformat also is added to increase aromatic content. Lower grades (e.g., lower octane ratings) contain straight-run gasoline, which includes varying amounts of paraffins, naphthenes, and aromatics.

3.3.3.3 Jet Fuels

Aircraft turbine engines require fuels with different properties than those of aviation gasoline. In particular, antiknock is not important and a higher energy fuel is needed. In general, two grades of jet fuels are in commercial use today: kerosene and the wide-cut gasoline (JP-4 Figure 3-31). Many commercial jet fuels have compositions similar to kerosene (e.g., Jet A, Figure 3-32; JP-5, Figure 3-33), but they are made under more stringent specifications which call for the decrease of sulfur,

aromatic hydrocarbons and olefins. Other commercial jet fuels are referred to as wide-cut fuels and are usually made by blending kerosene with lower boiling streams (such as straight-run naphtha) to include more volatile hydrocarbons (JP-4, Figure 3-31). Also classified as wide-cut fuels are specialized grades specific to military uses.

Jet fuels consist almost entirely of hydrocarbons, with the exception of trace levels of sulfur compounds and approved additives, such as anti-icing inhibitors. Since they are produced normally by blending straight-run distillate components, they contain virtually no olefins. In fact, olefin content is limited in their specification to prevent fuel gum deposit formation which could impact aircraft performance. Aromatic content is also limited because they do not burn clean, and can cause smokiness and deposits in the engine.

Advanced Chemical Fingerprinting Characteristics

Aviation gasoline, because of its high-octane requirement, is made up of only a few components dominated by isooctane (Figure 3-27a). The GRO analysis is dominated by two peaks: isooctane and toluene (often added to boost octane). Isoalkanes constitute the other peaks. Because of the amount and type of components in aviation gasoline and their low boiling points, other advanced chemical fingerprinting techniques, such as analysis of saturated hydrocarbon compounds (SHCs) and PAH compounds are not useful.

The jet fuels, JP8 (Figure 3-34) and Jet-A (Figure 3-32) all belong to the kerosene family. GRO and SHC chromatograms for these fuel types are dominated by the n-alkanes and will be “hump-shaped” based on the desired boiling point and flammability of the specific fuel.

JP-4 is a wide-cut gasoline fuel. It is generally made by blending kerosene with lower boiling streams, which is apparent from the GRO analysis (Figure 3-31). JP-4 contains benzene, toluene, alkylbenzenes, and isoalkanes from the lower boiling stream; and the n-alkanes nonane, decane, undecane, dodecane, tridecane, tetradecane, and pentadecane from the kerosene distillate. Extensive analysis of fresh and weathered JP-4 products by Arthur D. Little, U.S. Air Force, and other experts, have not detected alkane distributions that extend beyond n-C17 (Roberts and Thomas 1986, Smith et al. 1981, Spicer et al. 1989, Kaplan et al. 1997)). SHC analysis of JP-4 illustrates the kerosene portion of the product, but the presence of the lower boiling stream

component is not readily apparent. The PAH distribution of all of the jet fuels is limited to the low molecular weight compounds, naphthalene and alkyl-naphthalenes.

3.3.3.4 Kerosene

Kerosene became a major petroleum product following the discovery of oil in the mid-1800s. It was initially used for illumination and heat; and while it is less important today, it is still used worldwide.

Kerosene is obtained by fractional distillation of crude oil between approximately 149 degrees C (300 degrees F) and 302 degrees C (575 degrees F). The distillation yield is approximately 5 to 20 percent, depending on the crude source. To decrease smoking potential, higher paraffinic crudes are used as stocks; and naphthenic and aromatic stocks and cracked components are avoided. Kerosene has an approximate specific gravity of 0.81 g/cm³ and is composed of hydrocarbons predominantly in the C9-C16 range (Figure 3-30) (Kaplan 1997).

Advanced Chemical Fingerprinting Characteristics

Kerosene demonstrates the effects of straight-run distillation. For example, GRO analysis of kerosene is dominated by the n-C9 through n-C15 alkanes with smaller amounts of branched alkanes in between, very few aromatics (i.e., alkyl-benzenes) or alkenes (olefins) are present. The SHC fingerprint reveals the same characteristics, but shows that the distillation includes up to n-C17. The PAH distribution is predominately naphthalene and alkyl-naphthalenes with trace amounts of three-ring PAH compounds, such as fluorenes, phenanthrenes, and dibenzothiophenes.

3.3.3.5 Diesel Fuels

Diesel fuel is intended for use in atomizing-type burners, that spray fuel into a combustion chamber where the droplets burn while in suspension. Diesel fuel was originally a straight-run distillation product from crude oil (Figure 3-35). Today, diesel #2, manufactured in the U.S., is a blend of straight-run and catalytically-cracked streams, including straight-run middle distillate, hydrodesulfurized middle distillate, and light catalytically and thermally cracked distillates.

The boiling range of the fuel is approximately 320 to 680 degrees F; and specific gravity is in the range of 0.82 to 0.86 g/cm³ (Guthrie 1960). It consists of hydrocarbons having carbon numbers

predominantly in the range from C9 to C24. It is noteworthy that this fuel has a wide range of PAH compounds, extending from dominant naphthalenes to phenanthrenes (Kaplan et al. 1997).

Diesel #2 often includes sulfur containing aromatics, such as benzothiophenes and dibenzothiophenes, as well as alkylated benzenes. A wide range of additives is often blended in the finished product to assure performance to specification. Diesel #2 is a heavier distillate than diesel #1. Diesel #1 is similar to a blend of kerosene and diesel #2. Diesel #1 is manufactured for use in cold climates because it is less viscous than diesel #2. However, the diesel #2 long-chain hydrocarbons from C16 to C24 aid in engine lubrication, and are therefore, essential for the efficient operation of diesel engines. Diesel #1 is often sold in warmer climates or cities where a local refinery uses its excess kerosene to blend with the more expensive diesel #2.

Advanced Chemical Fingerprinting Characteristics

Diesel fuels demonstrate the basic characteristics of a middle distillation cut. Most contain hydrocarbons from about C9 to C24. The GRO analysis points out the absence of compounds lighter than C8, especially the aromatic compounds benzene, toluene, ethylbenzene and xylene. The SHC chromatogram captures the entire boiling range of this product from C8 through n-C25. Diesel fuels can contain appreciable amounts of a wide range of PAH compounds including naphthalenes, fluorenes, phenanthrenes, benzothiophenes, dibenzothiophenes, and their alkyl-homologues.

3.3.3.6 Heating Oils

Domestic heating oil is also a distillate product. It has an approximate boiling range of 160 degrees C (320 degrees F) to 343 degrees C (650 degrees F). Heating oils contain components from virgin stock of crude distillation; oils manufactured by catalytic cracking of heavier stocks, and thermally cracked process streams. Fuel oils #1 and #2 are distillate fuels with compositions and properties essentially equivalent to diesel fuels #1 and #2.

3.3.3.7 Condensate

Distribution gas is known to contain light/medium range hydrocarbons that condense out in the pipeline during transport. Generally, gas pipelines function like a refinery distillation column.

Heavier hydrocarbons will condense early in the system and the lighter petroleum products will condense farther down the pipeline closer to the end user. The GC/FID distribution of a condensate can range from a straight-run gasoline (n -C₄ through n -C₁₂) to a heavy condensate that has GC/FID characteristics that are similar to a crude oil. These condensate fluids accumulate in low spots in the pipeline, are corrosive, and can cause pipeline failure (Eiceman et al. 1985). Drip-pot systems are located along the gas-distribution system on the DSCP property to collect these hydrocarbon fluids. Little is known about how DSCP managed gas condensates. However, Figure 3-36 contains GRO, GC/FID, and PAH distributions from a mid-range natural gas condensate showing that gas condensates look remarkably like the plume material.

3.3.3.8 Heavier Oils

Because of the method employed in their production, heavy fuel oils fall into two broad classes: distillates and residuals. The distillates consist of distilled products. Residual fuel oils are residues remaining after distillation or cracking of crude oil to produce the middle distillates.

Fuel oils #1 and #2 are distillate fuels with composition and properties essentially equivalent to diesel fuels #1 and #2. Fuel oils #4, #5, and #6 are residuals. Fuel oil #4 is a "light" residual. It is intended for use in burners equipped with devices that atomize oils of higher viscosity than domestic burners can accommodate. Fuel oil #5 is a residual fuel of intermediate viscosity. It may require preheating in some types of equipment for burning under cold climatic conditions. Fuel oil #6, sometimes referred to as "Bunker C", is a high viscosity oil used mostly as a boiler fuel in commercial and industrial heating. It requires preheating in storage tanks to permit pumping and additional preheating at the burner to permit atomization. Bunker C spans the hydrocarbon range from C₉ to C₃₆ and a boiling range of 340 degrees F to 1060 degrees F. In addition, residual oils exhibit a wider range and greater concentrations of PAH compounds than distilled products.

Advanced Chemical Fingerprinting Characteristics

Residual fuel oils generally include hydrocarbons from C₉ through as high as C₃₆. The GRO analysis of Bunker C (#6) illustrates the absence of compounds lighter than C₉. The SHC analysis includes most of the boiling range of this product, the hydrocarbons extending from C₉ through C₄₄. The fingerprint is characterized by a low broad hump, with the normal alkanes from C₂₁

through C40 resolved on top (see Figure 3-37). The large peaks resolved on top of the hump from about 15 to 30 minutes are primarily PAH compounds. These PAH compounds may result from a middle distillate blending with the residuum to lower its viscosity. The PAH distribution is dominated by naphthalenes and phenanthrenes, but it also contains four-, five-, and six-ringed PAH compounds.

3.3.3.9 Lubricating Oils

Lubricating oils are used to reduce friction and wear between moving parts (Figure 3-38). They may also act as carriers for special chemicals and additives such as corrosion inhibitors. Petroleum based lubricating oils are present in the residue boiling above 370 degrees C (698 degrees F) from distillation of both paraffinic and naphthenic crude oils. This residue is further distilled to provide light to heavy stocks. Lubricating oils have a wide variety of applications and include the following:

- Automotive engine oils
- Marine diesel engine oils
- Railway engine oils
- Gas turbine lubricants
- Gas engine oils
- Gear oils
- Automatic transmission fluids
- Hydraulic oils
- Air compressor oils
- Machine tool lubricating oils

Advanced Chemical Fingerprinting Characteristics

Lubricating oils are generally highly refined products. Lubricating oils are generally too high in boiling point distribution to be characterized by GRO. In the SHC analysis, typical lubricating oils exhibit a large 'hump' shape across their specified boiling point range with few resolved peaks. Aromatic content can vary widely in lubricating oils, but is generally from 10 to 30 percent and often does not include most of the PAH compounds.

3.3.3.10 White Mineral Oils

Products classified as white mineral oils are petroleum fractions, from kerosene to lubricating oils, which have been treated to remove reactable hydrocarbons to produce a colorless, odorless, and

non-reactive petroleum product. These properties enhance their widespread application in fields such as cosmetics, plastics, agriculture sprays, food processing, and precision lubricants.

White oils are made from select distillate fractions to produce a finished product with the desired viscosity dependent on the final intended use. Because of the wide variety of uses, there is no single definition of a white mineral oil boiling distribution.

Advanced Chemical Fingerprinting Characteristics

White oils are chemically characterized by their high saturate hydrocarbon content and exceptionally low aromatic hydrocarbon content.

3.3.3.11 Impact of Weathering

Because petroleum and petroleum products are labile mixtures, the composition of a product released into the environment begins to alter almost immediately and continuously to change constantly. This is due to numerous chemical, biological and physical processes, generally referred to as weathering. In this sense, weathering is the aggregate of the fate mechanisms that act on petroleum products when they are introduced to the environment (Kaplan et al. 1996, 1997). Thus, weathering is not, in this application, equivalent to chronological age. Rather, weathering is an indication of the changes that have resulted from the combined action of the fate mechanisms. A detailed description of the fate mechanisms that constitute the weathering process is given in Section 3.2.

The effects of weathering (e.g., ultra-violet degradation, evaporation) and biodegradation (e.g., bacterial consumption) cause compositional changes in the petroleum product. Normal alkanes are very susceptible to biodegradation. Studies of crude oil spills in marine environments have produced weathering data for high molecular weight hydrocarbons. These data include weathering rates for PAH and other compounds.

A gas chromatogram of a severely weathered crude oil demonstrates representative degradation patterns (Figure 3-39). A comparison of chromatograms for fresh and weathered crude oils indicates that low molecular weight hydrocarbons are lost, probably due to evaporation and water washing or solubilization (Figure 3-39). The n-alkanes also are lost through preferential

biodegradation. Remaining at this stage of the weathering process are the prominent branched-chained hydrocarbons (isoprenoids), pristane (Pr) and phytane (Ph). The remaining material is represented as a hump and consists largely of complex polycyclic molecules including biomarkers.

Refined petroleum products generally weather the same way as crude oils (Douglas et al. 1992). Due to a preferential removal of n-alkanes compared to the isoprenoids, the C17/Pristane and C18/Phytane peak ratios, representing adjacent hydrocarbons, tend to decrease with weathering. These ratios are used to indicate weathering. However, when environmental alteration of a middle distillate product is severe, these ratios (and the GC/FID method in total) often does not provide sufficient data for fingerprinting and estimating degradation rates. In such cases, the GC/MS method quantifies numerous hydrocarbon species, producing valuable information for fuel type identification and monitoring of environmental changes.

Among the least affected hydrocarbon components are some substituted aromatic and PAH compounds. In this group, the alkylbenzenes are first to be altered by biodegradation, followed by naphthalene and methylnaphthalenes. Some of the isomers of phenanthrenes and dibenzothiophenes are altered in a uniform manner that may be used for determining relative rates of change (Elmendorf et al. 1994).

Heavy heating oil (Bunker C) represents the distillation residue of a crude oil and contains complex high molecular weight petroleum hydrocarbons such as steranes and triterpanes. Bunker C fuel is differentiated from crude oil by the lack of a lighter, volatile fraction as well as by the presence of the PAH compounds: benzo[b]fluoranthene, benzo[b]fluoranthene, benzo[e]pyrene, and benzo[a]pyrene.

The high-molecular-weight hydrocarbons, steranes and triterpane biomarkers, originate from the polycyclic lipids found in bacteria and plants. Steranes are a class of tetracyclic saturated hydrocarbons derived from sterols. Most common steranes are in the range of C26 to C30 and are detected using the mass quantification (m/z) 217 mass chromatogram. Terpanes form a broad class of complex branched-cyclic alkanes, derived mainly from bacterial cells, and are best monitored using m/z 191 mass chromatograms. Biomarkers represent a large number of different chemical compounds as well as a set of isomers (or enantiomers) because they have unique structures usually

consisting of numerous chiral centers and side chains. These characteristics make them relatively stable and therefore, useful in hydrocarbon source identification.

Among the terpanes, the C₃₀-pentacyclic terpane (hopane) and certain tricyclic terpanes are the most stable. Diasteranes are the most resistant to biodegradation compared to the regular tetracyclic steranes. Most crude oils and Bunker C fuels contain a modified sterane in which one ring, or all three six-carbon rings become aromatized (due to heat exposure) and larger steranes are converted to monoaromatic and triaromatic steranes. These hydrocarbons are highly resistant to degradation.

PAH compounds include a suite of compounds extending from benzene to the six-ringed PAH compounds, including dibenzothiophenes. These PAH compounds may also contain alkyl groups at various carbon positions. The ratios of some of these compounds are very useful in determining the extent of biodegradation.

3.3.4 Analytical Methods to Measure Petroleum

No single analytical method is sufficient to identify the range of petroleum compounds in environmental samples. Furthermore, conventional EPA methods are inappropriate (see Table 3-2) (Douglas and Uhler 1993) to determine potential sources of petroleum contaminants. For these reasons, a combination of analytical procedures based on EPA methods were applied in this investigation, where the character and source of contamination by petroleum-derived material were obscure.

The following sections describe the methods employed during the investigation.

3.3.4.1 Classification Techniques Based on Physical Properties

Early techniques for petroleum classification were based on physical properties. While this approach is still useful, it is limited in its application to environmentally altered products that cannot be directly compared to reference product specifications. Physical properties determined include:

- Density
- Viscosity
- Odor
- Cloud and pour points
- Flash point

Information about the basic physical properties of the product were supplemented by what could be termed “gross level” compositional analyses. These measure more specific composition of petroleum and its refined products. Examples of these analyses include:

- Distribution of paraffinic, naphthenic, aromatic, and residuals content
- Boiling distribution (distillation recovery)
- Sulfur level

Generic classes of petroleum products overlap to some extent (Figure 3-40). Simulated distillation following ASTM method D2887 was also performed on select NAPL samples. Simulated distillation is gas chromatographic analysis that simulates a “true boiling point” (TBP) distillation of a product. During simulated distillation, individual components elute from a GC column in the order of their boiling points, with the GC column acting as a surrogate for the refinery fractional distillation column. The results of the analysis may be used to construct a curve of the mass (or volume) of the material recovered versus temperature (Figure 3-41) (Kaplan et al. 1997).

This analysis is useful in product identification, especially in pure and nearly pure finished products. The simulated distillation curve may be altered by a number of factors, including product degradation, dilution, and mixing. The method correlates boiling points with retention times by using a calibration curve prepared with standards. The calibration mixture covers the complete boiling range of the sample to be analyzed. ASTM Method D2887 has standardized gas chromatographic conditions and determines the true boiling point distribution of components with a final boiling point up to 538 degrees C (1,000 degrees F).

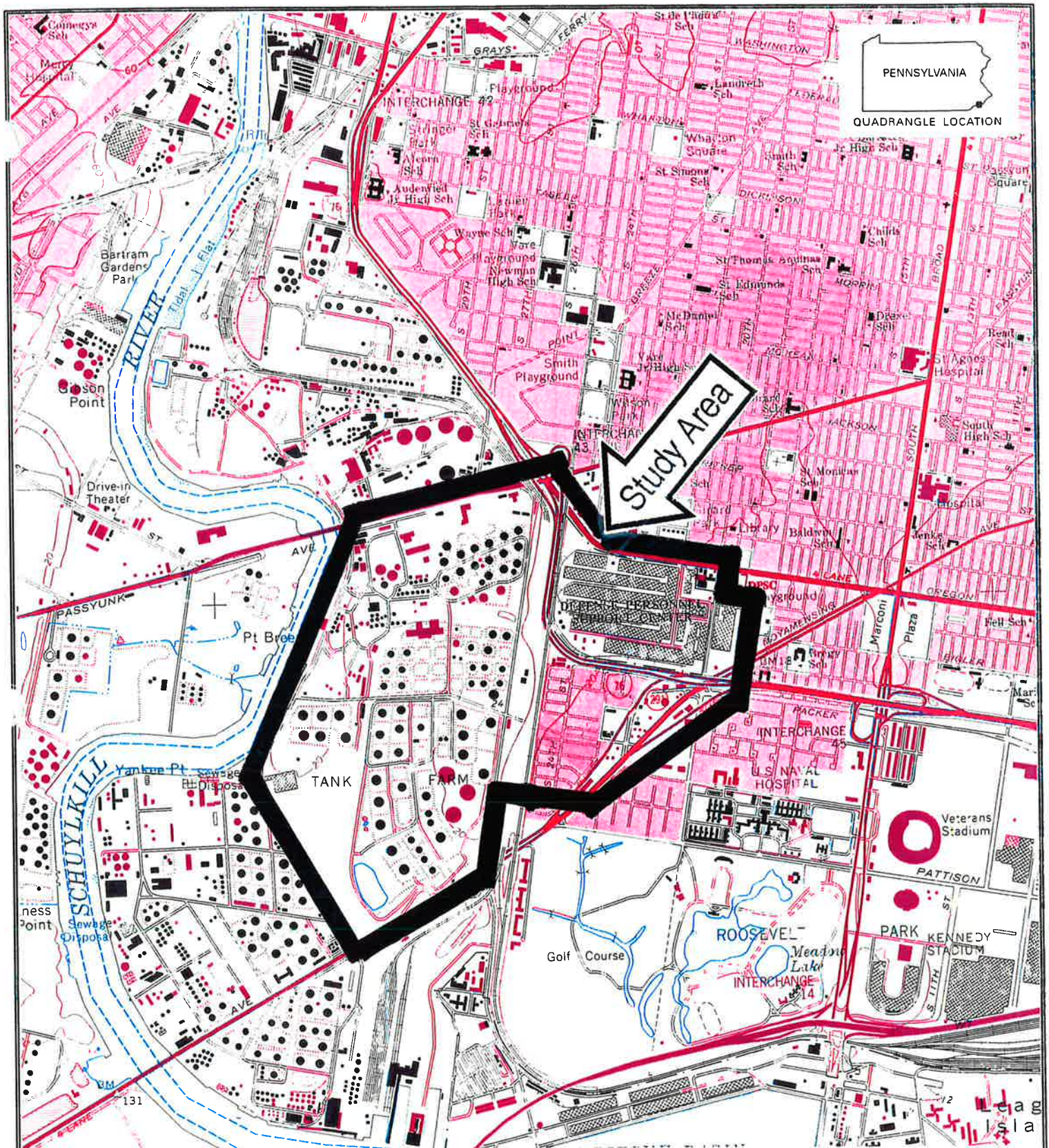
3.3.4.2 Comparison of Sun’s Approach to DSCP Approach

The hydrocarbon fuel scan (HFS) analysis performed by DSCP is the basis for identifying product source in site samples. While DSCP claims to have used a multi-tiered approach to characterize site hydrocarbon contamination, the methods that were employed in their study were lacking in many respects. Critical target compounds, including parent and alkylated PAH compounds, were not analyzed. The analysis of PAH compounds is especially important, as these compounds are relatively stable in petroleum products, and corresponding ratios may provide critical source and

relational information for site samples. Data generated by DSCP are therefore insufficient to draw conclusions regarding the number of plumes or the source of contamination.

The hydrocarbon fingerprinting approach used by Sun makes use of direct comparisons of site samples to reference standards analyzed under the same analytical conditions. As reported by DSCP, source identification relies on the comparison of sample results to military product specification tables. Reference materials were not provided in the DSCP report, therefore, qualitative determinations cannot be validated. Considering the number of times that JP-4 was discussed in the report, it is reasonable to expect at least one JP-4 reference standard in the package. DSCP conclusions are unsupported without analysis of appropriate standards; and standard fingerprinting practices are inappropriate without reliable information.

The accuracy of analytical methods depends greatly on the degree of weathering for the samples. As hydrocarbon products degrade in the environment so do their source signatures; therefore, direct comparisons of chromatographic signatures of degraded samples with those for their corresponding fresh source are not valid. For these reasons use of the HFS GC/FID method for fingerprinting degraded samples is unsubstantiated. The qualitative results for these degraded samples are vague, although they attempt to implicate JP-4 as the product source. These results are by no means conclusive or persuasive. Additional testing using the more reliable GC/MS method should provide data appropriate for source identification of degraded product.



MAP SOURCE:
U.S.G.S. TOPOGRAPHIC QUAD (7.5 Min)
PHILADELPHIA, PA.-N.J., 1967(REVISED 1994)

I NTEGRATED
S CIENCE &
T ECHNOLOGY, INC.

Site Vicinity Map

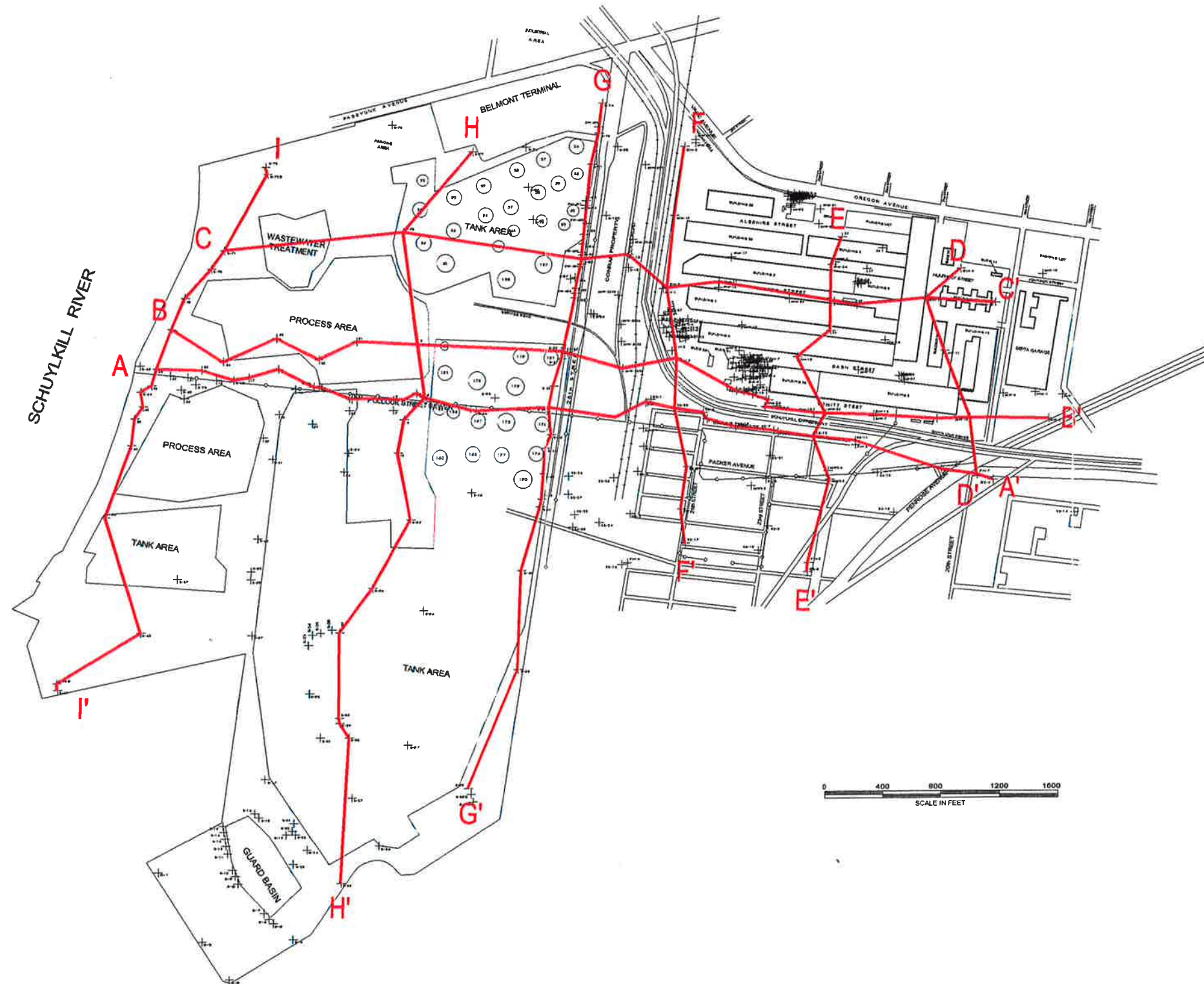
Scale: 1" = 2000'



STUDY AREA
Philadelphia, PA

FIGURE
3-1

SYSTEM	SERIES	GEOHYDROLOGIC UNIT			RANGE OF THICKNESS (ft)	SYMBOL
		Paulachok (1991)	Greenman and others (1961)			
Quaternary	Holocene	Alluvium	Alluvium		0-78	Qal
	Pleistocene	"Trenton gravel" (informal usage)	Cape May Formation		0-80	Qp
			Pensauken Formation		0-80	
Tertiary	Miocene	Bridgeton Formation			0-10	Tb
Cretaceous	Upper Cretaceous	Potomac-Raritan Magothy aquifer system	Upper clay unit	Magothy Formation	0-35	Ku
			Upper sand unit	Upper Clay member	0-35	
			Middle clay unit	Raritan Formation	0-50	Ko
			Middle sand unit		0-60	Km
			Lower clay unit		0-40	Ks
			Lower sand unit		0-61	Kl
				Farrington Sand Member	0-90	Kf
				Crystalline rocks of Glenarm Series (former usage)		Wa
Pre-Cretaceous	Lower Cretaceous	Crystalline rocks, includes Chickies Formation and Wissahickon Formation of Glenarm Group				

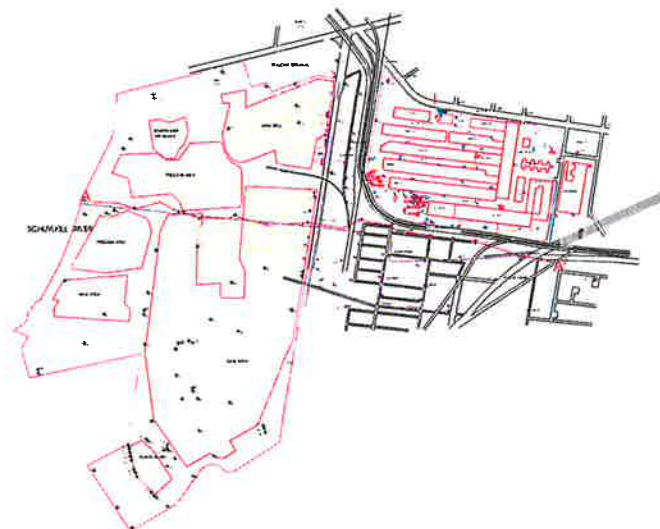
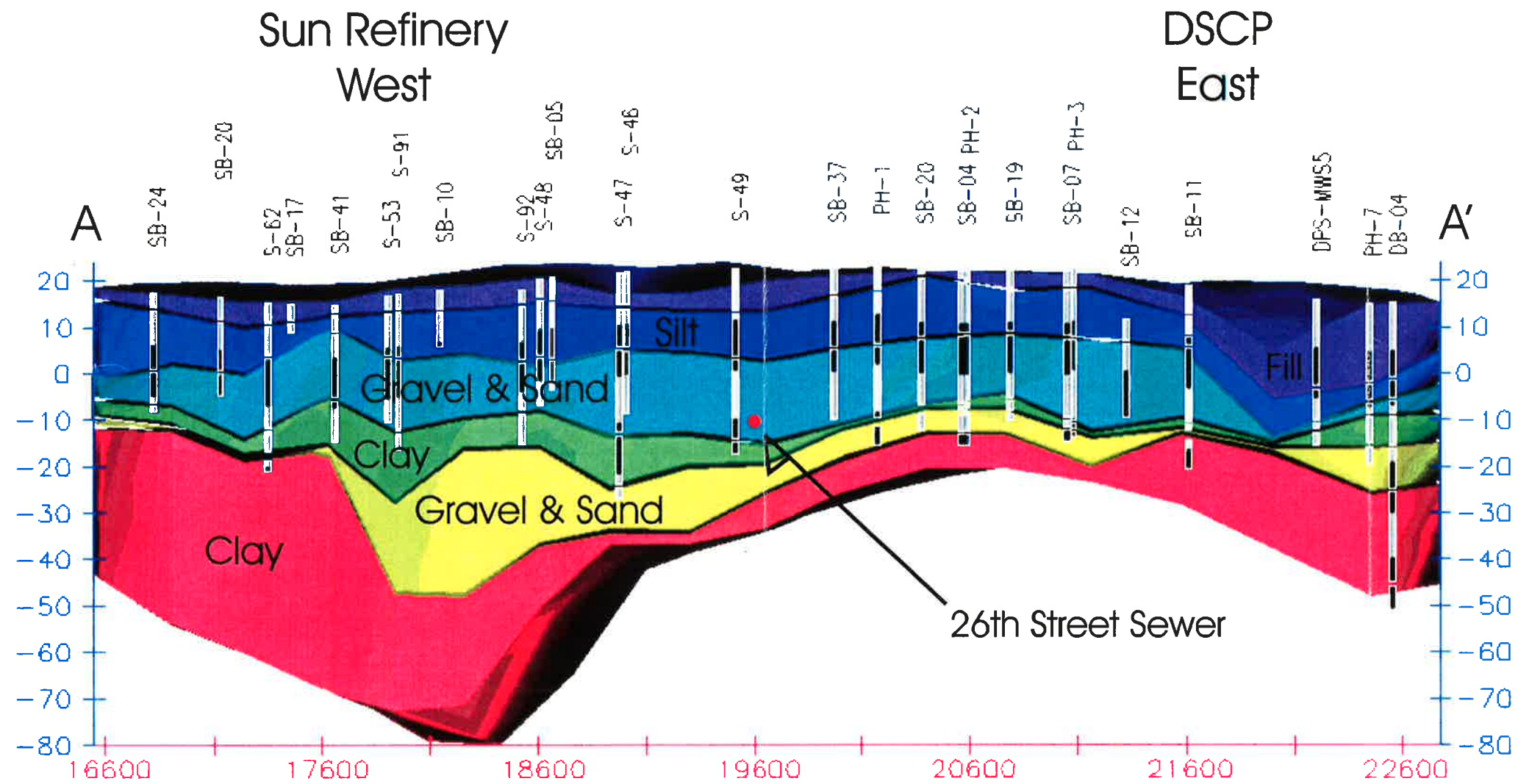


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TECHNOLOGY, INC.

DRAWN BY: CWS	REVIEWED: PKH	APPROVED: HJR
DATE: 19 FEB 1998	PROJECT NO. SU001H	DWG. NO.
Locations of cross sections		
Study Area PHILADELPHIA, PENNSYLVANIA		

FIGURE
3-3



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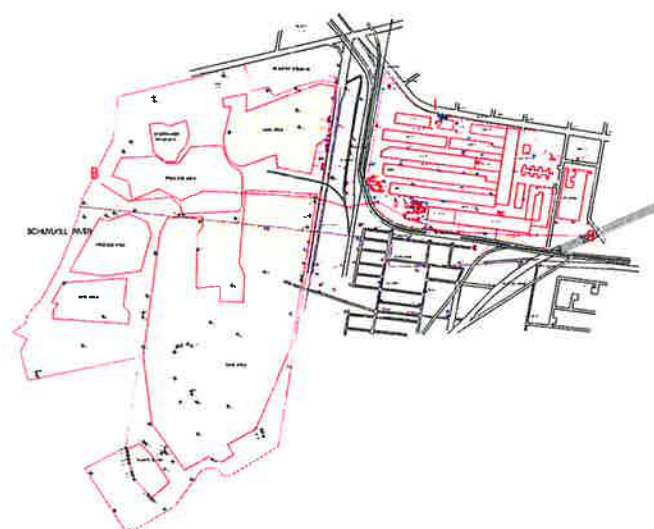
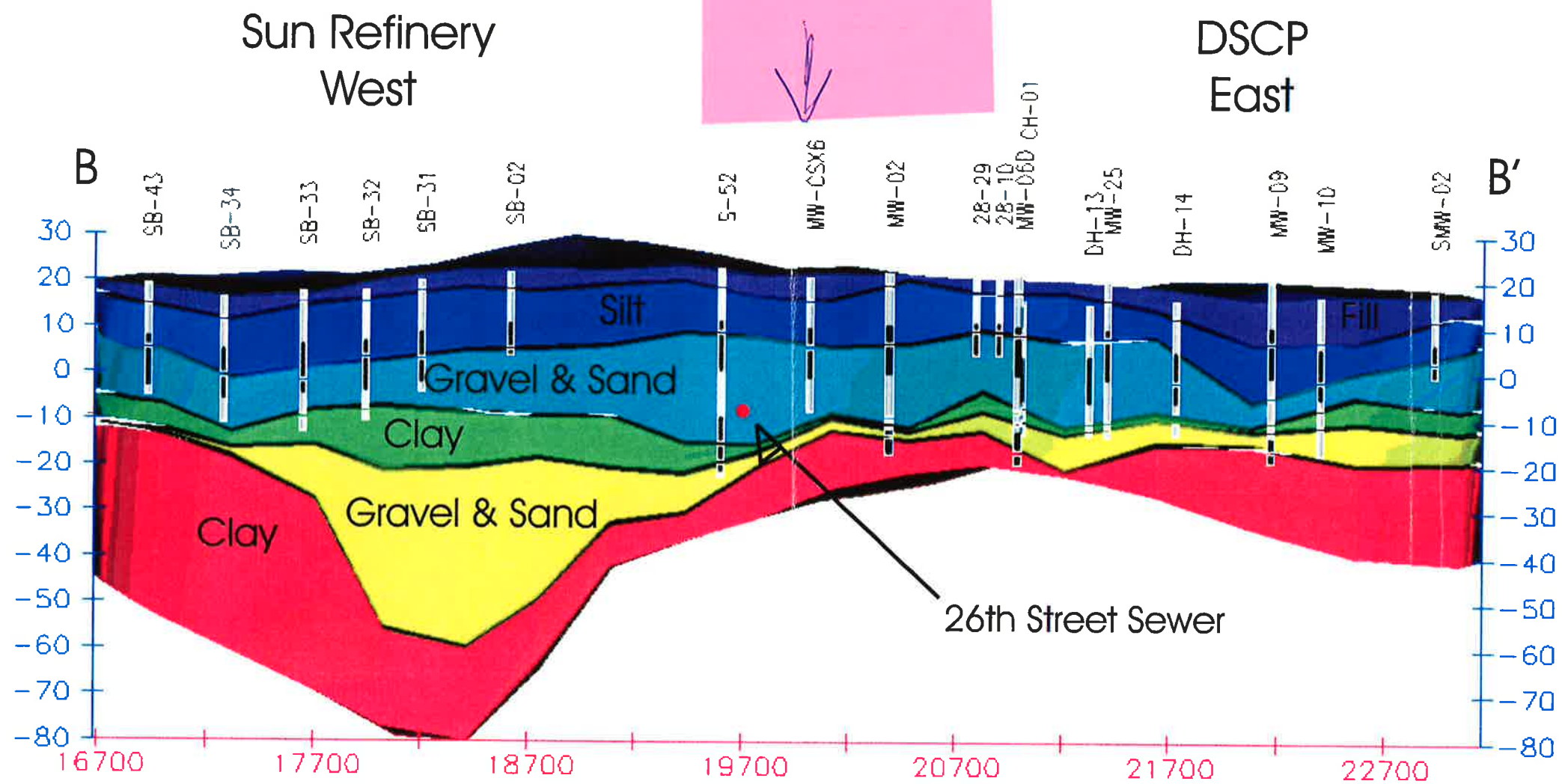
- * Vertical scale in NGVD
- * Horizontal scale in feet
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A-A'
Study Area
PHILADELPHIA, PENNSYLVANIA

FIGURE
3-4



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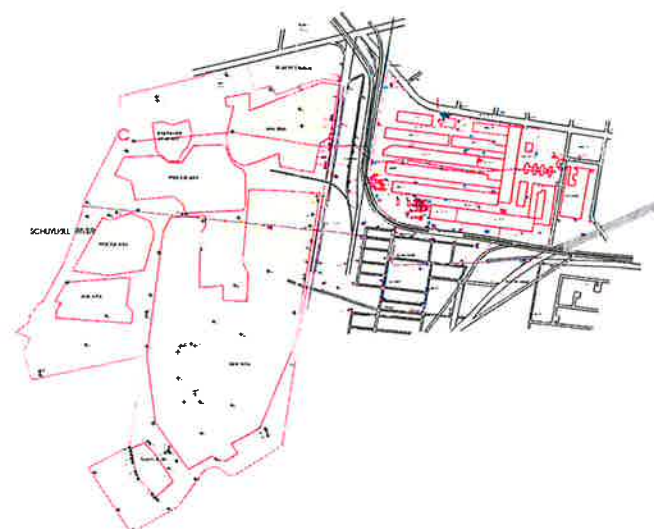
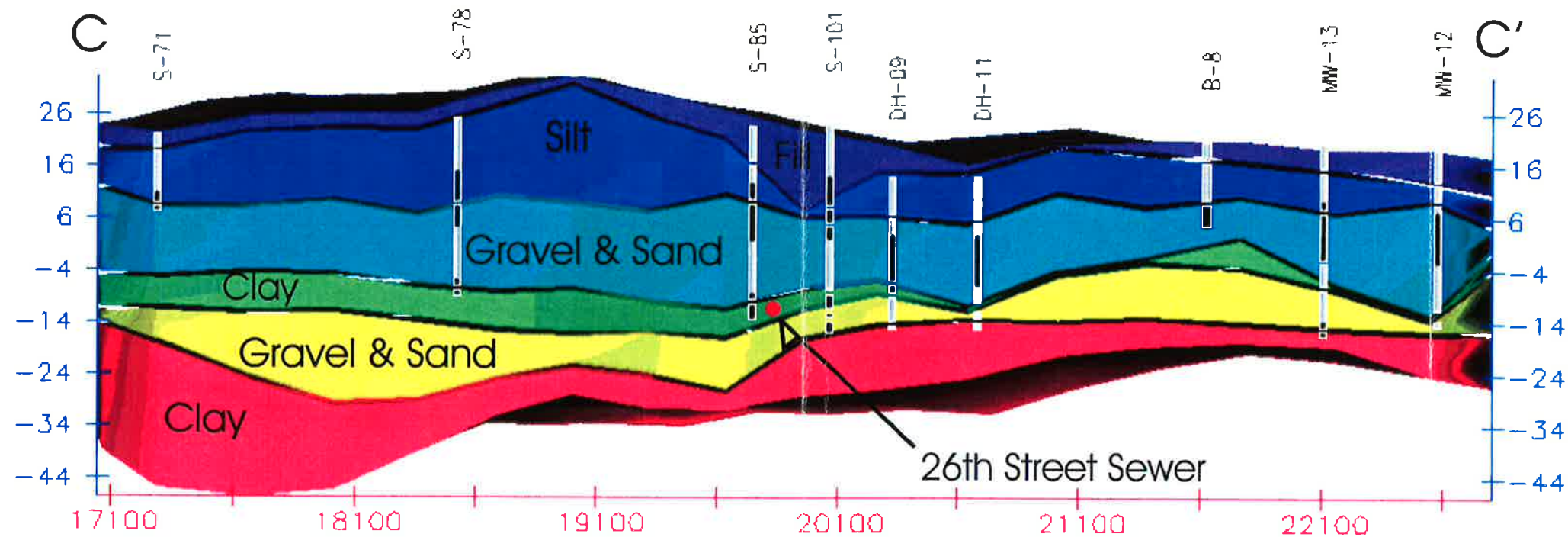
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B-B'
Study Area
PHILADELPHIA, PENNSYLVANIA

FIGURE
3-5

Sun Refinery
West

DSCP
East

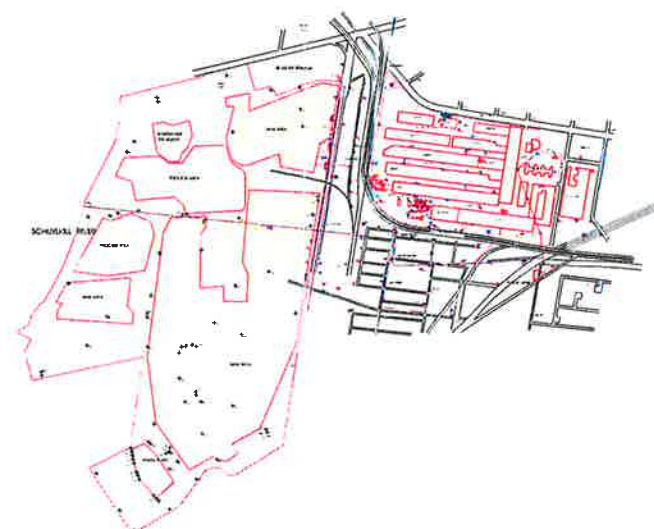
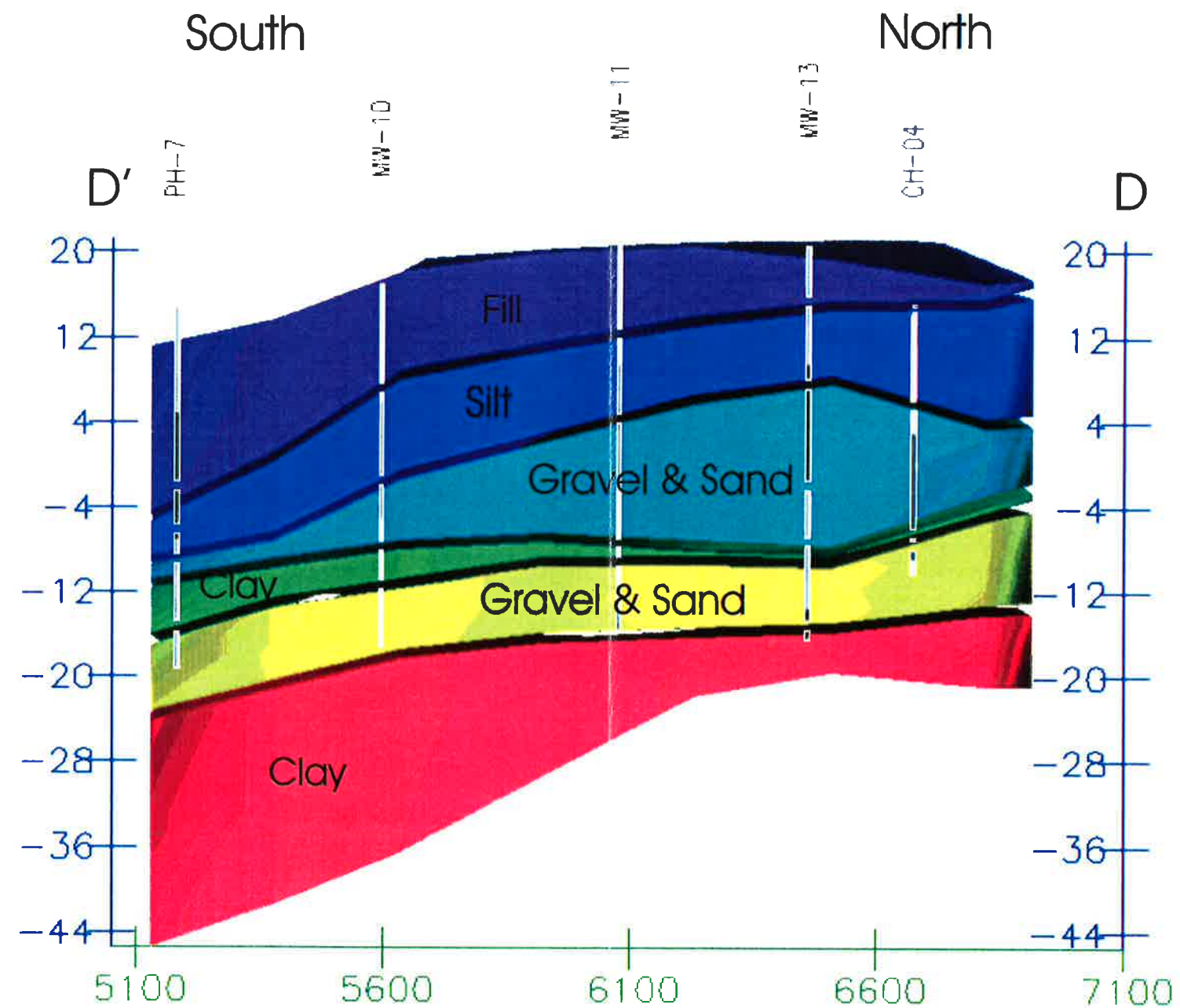


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C-C'		FIGURE 3-6
Study Area PHILADELPHIA, PENNSYLVANIA		

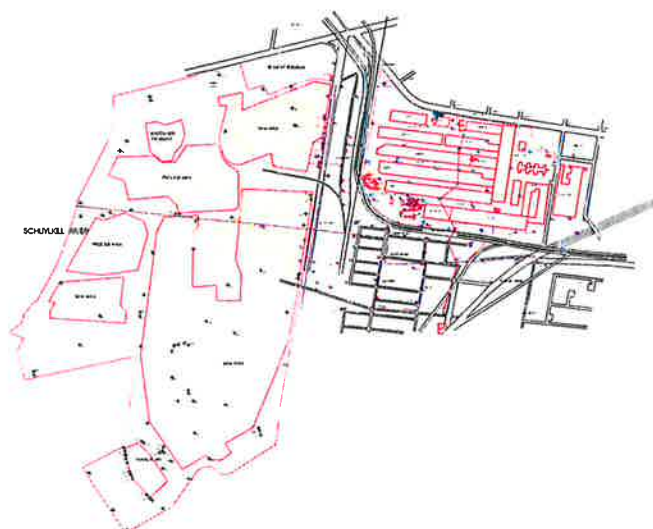
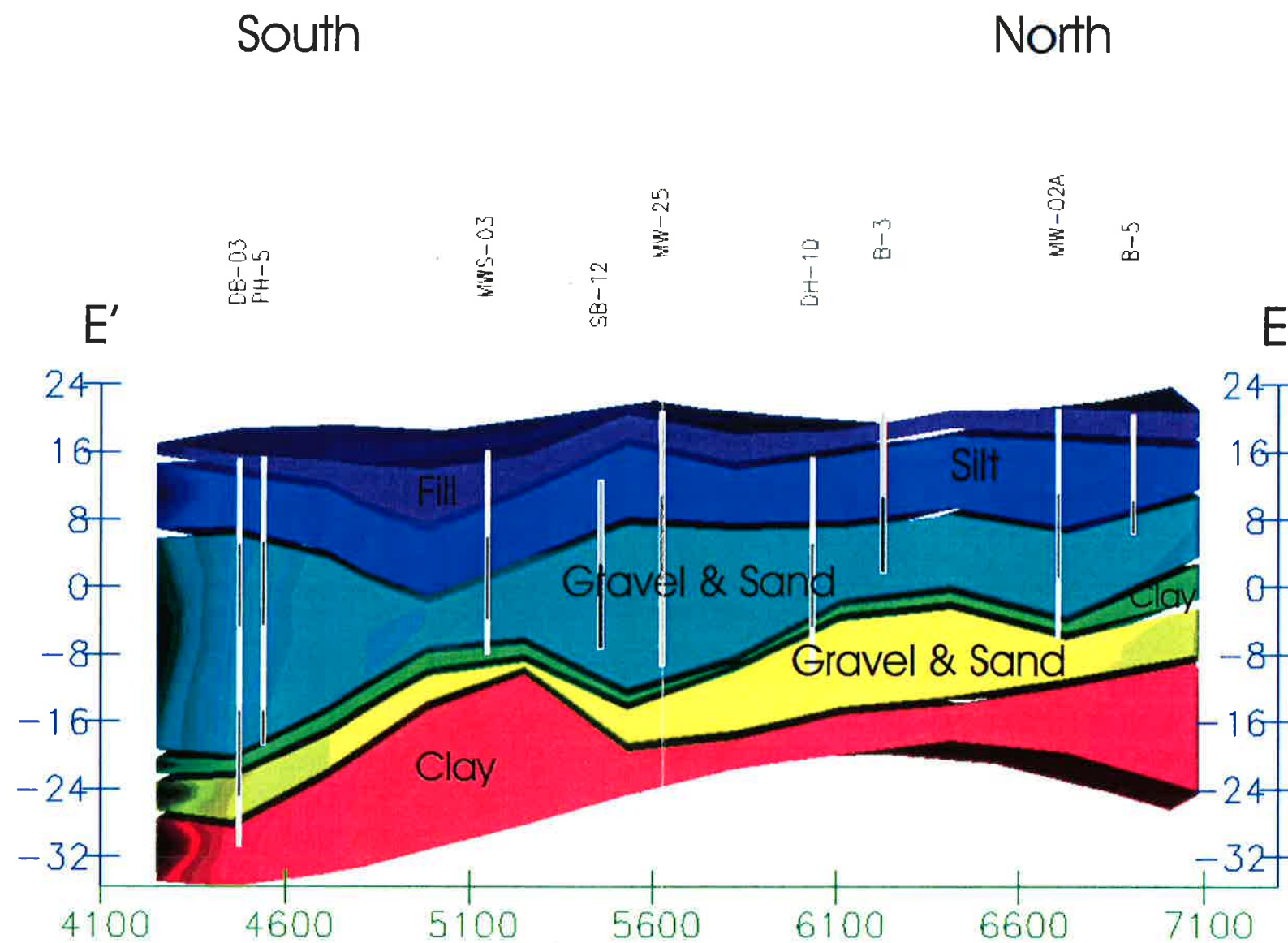


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D-D'		FIGURE 3-7
Study Area PHILADELPHIA, PENNSYLVANIA		

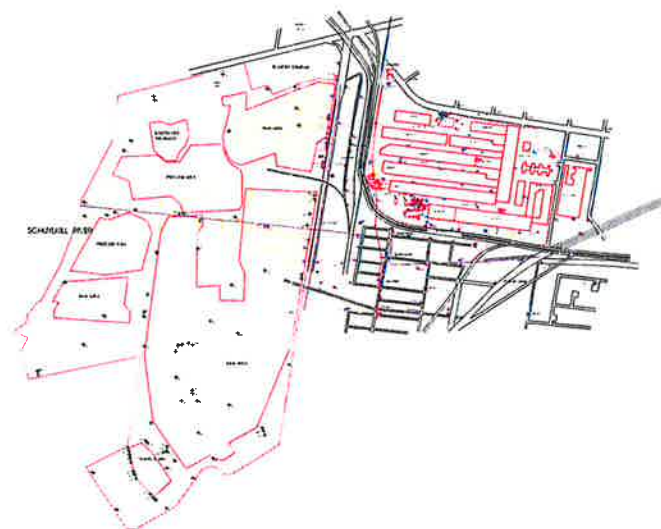
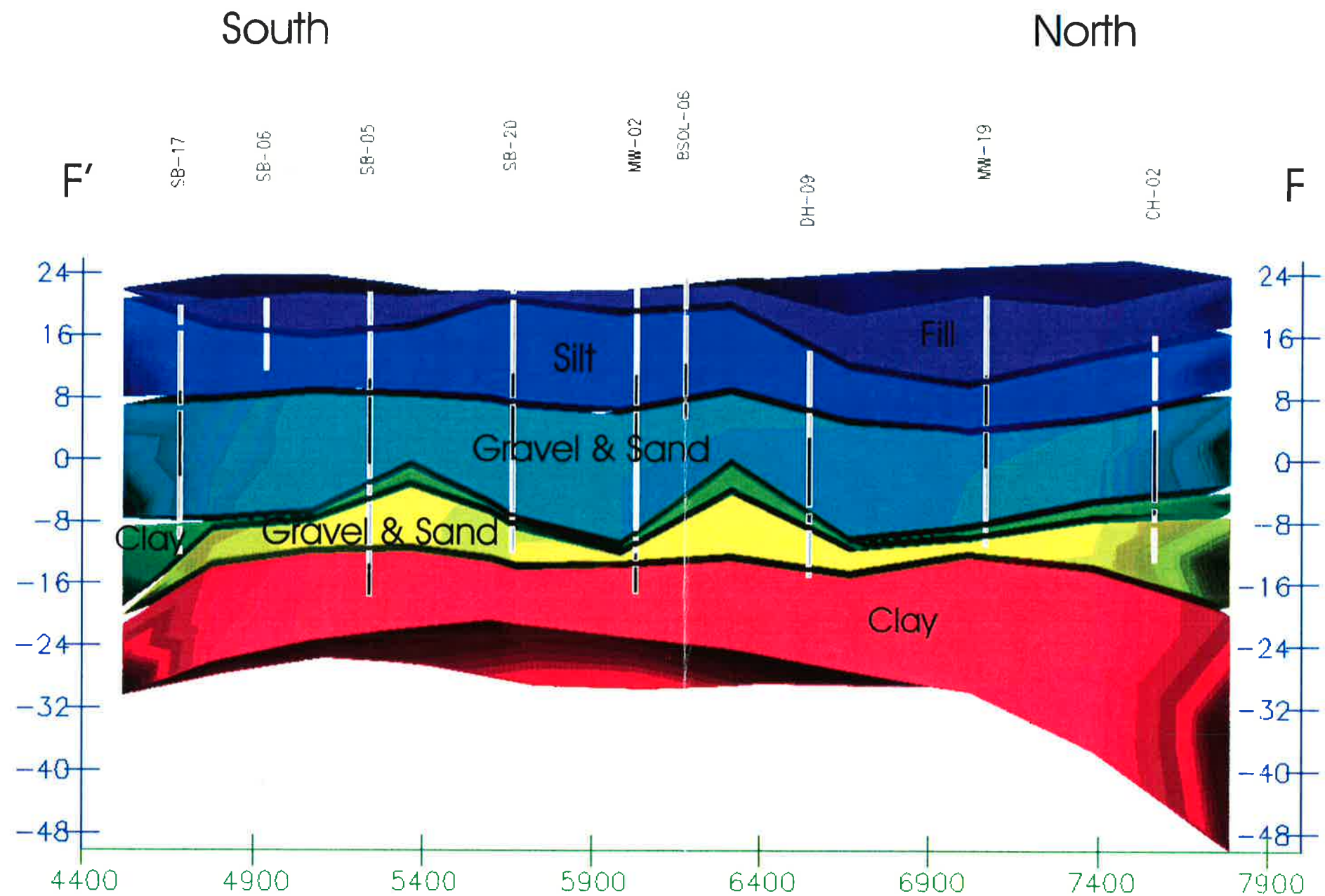


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E-E'		FIGURE
Study Area PHILADELPHIA, PENNSYLVANIA		3-8

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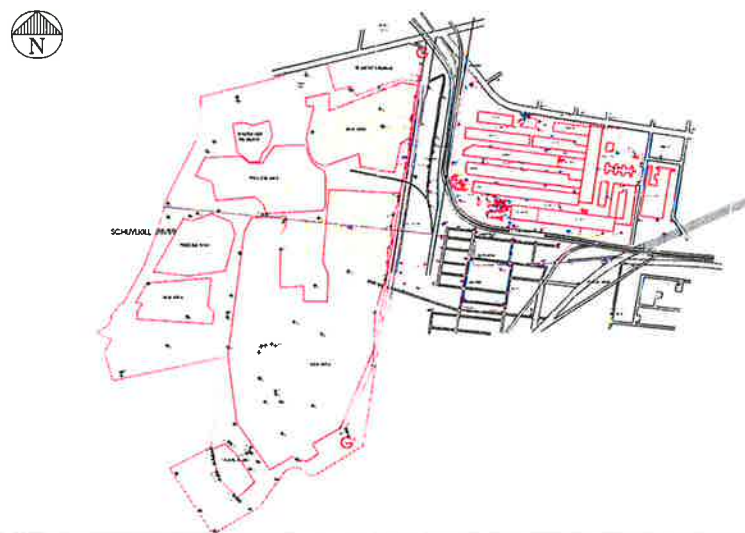
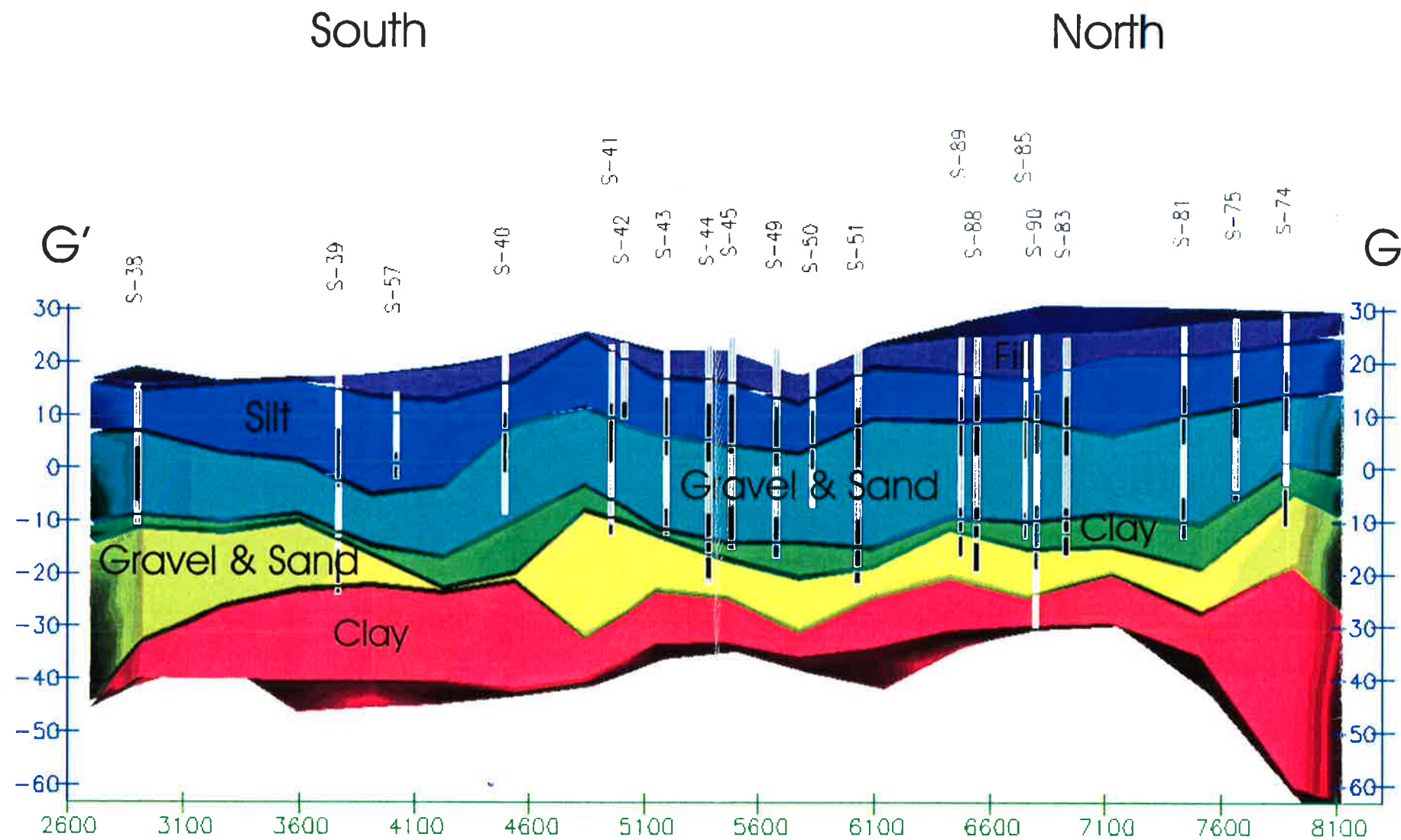


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F-F'		FIGURE
Study Area PHILADELPHIA, PENNSYLVANIA		3-9

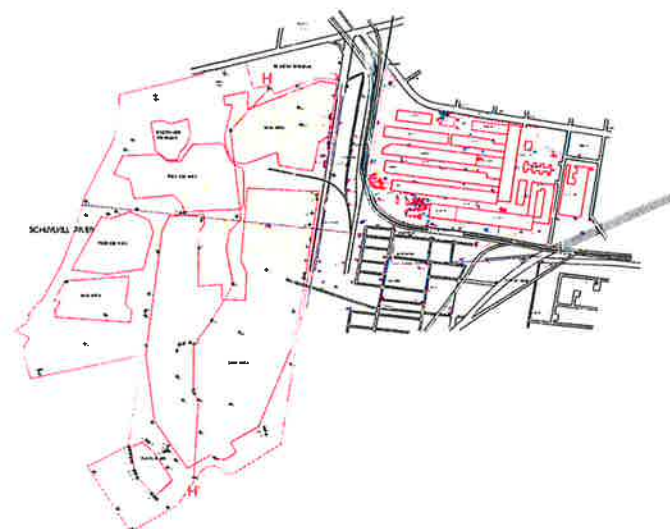
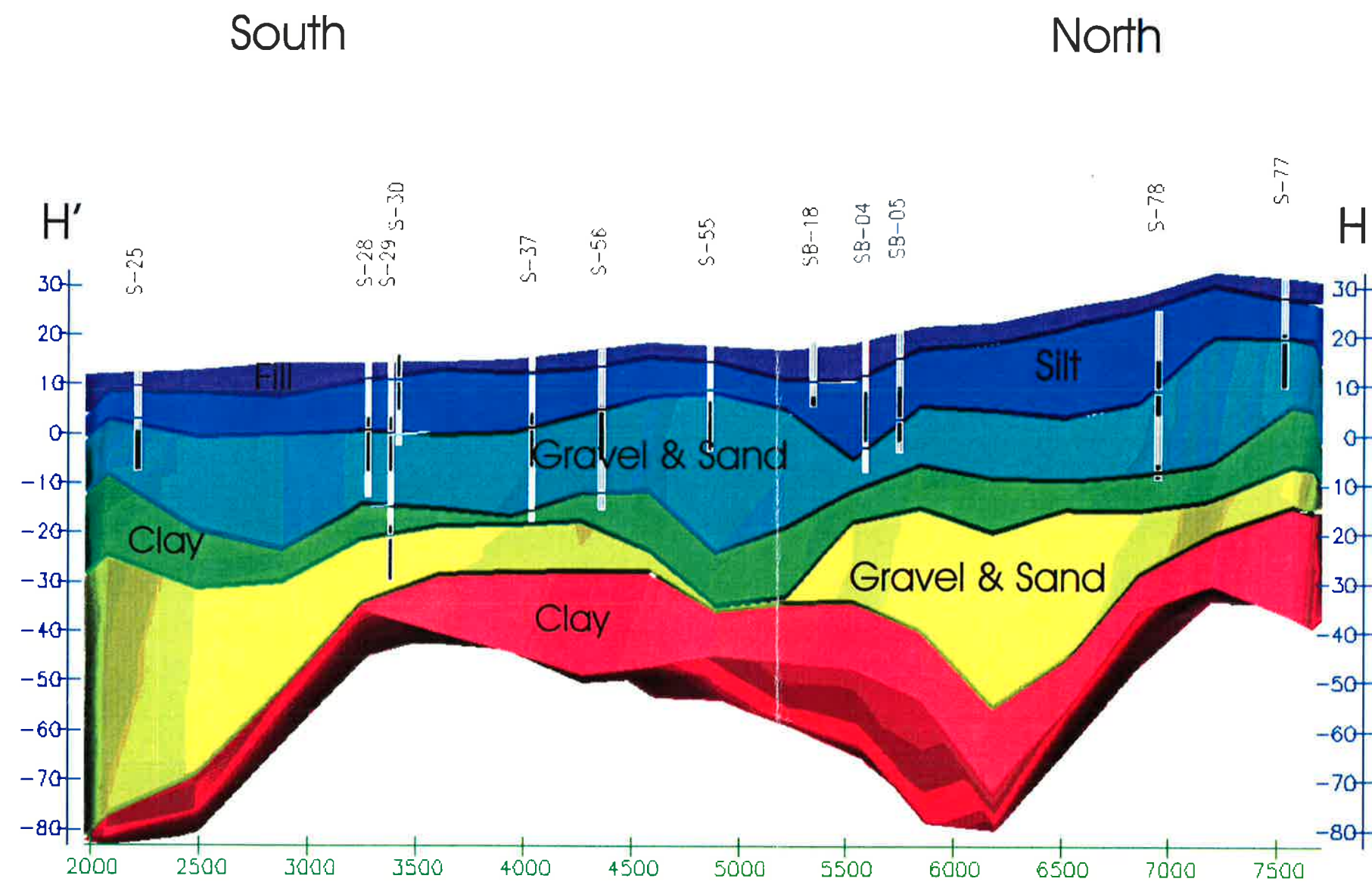


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G-G'		FIGURE 3-10
Study Area PHILADELPHIA, PENNSYLVANIA		

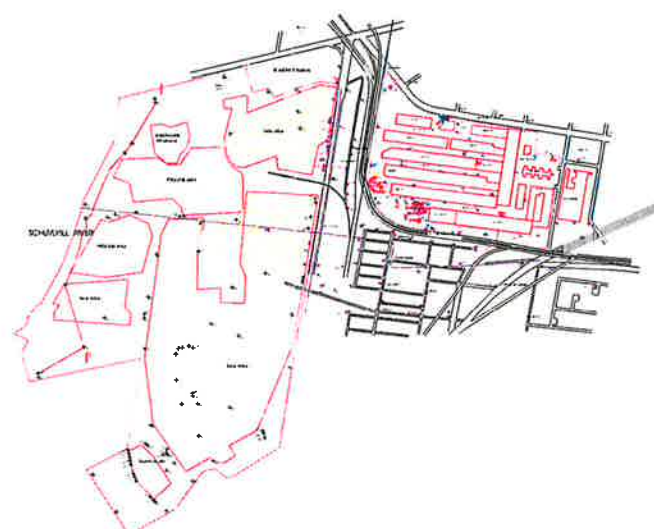
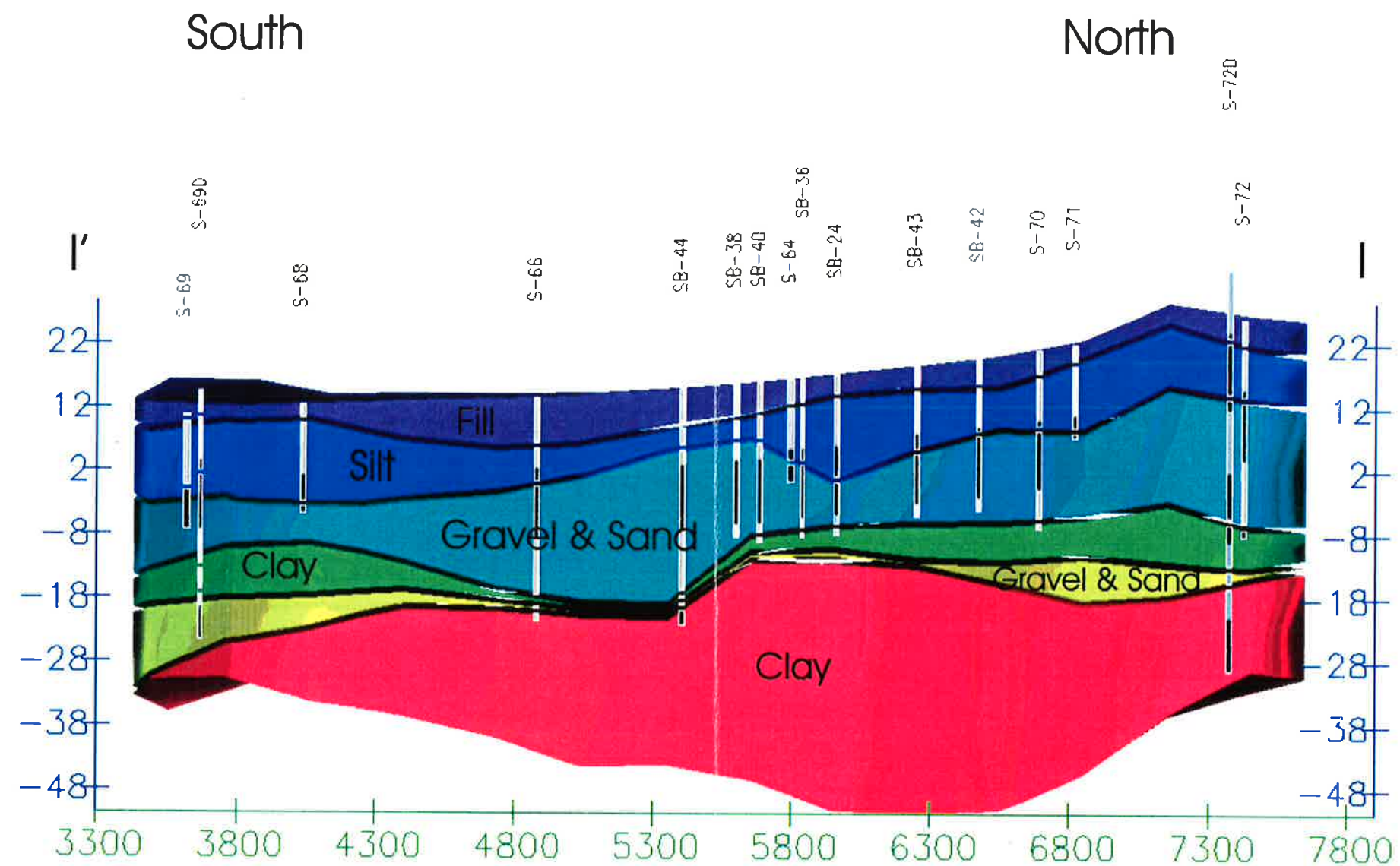


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H-H'		FIGURE 3-11
Study Area PHILADELPHIA, PENNSYLVANIA		



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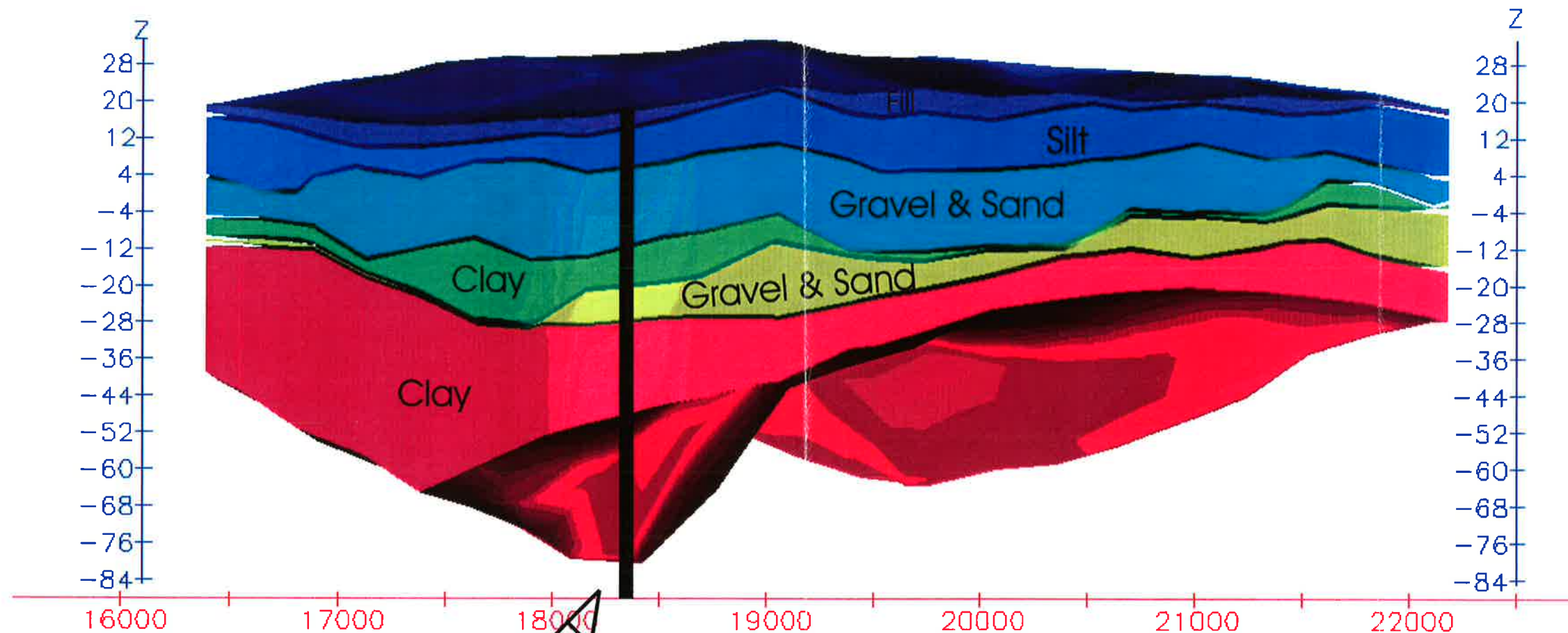
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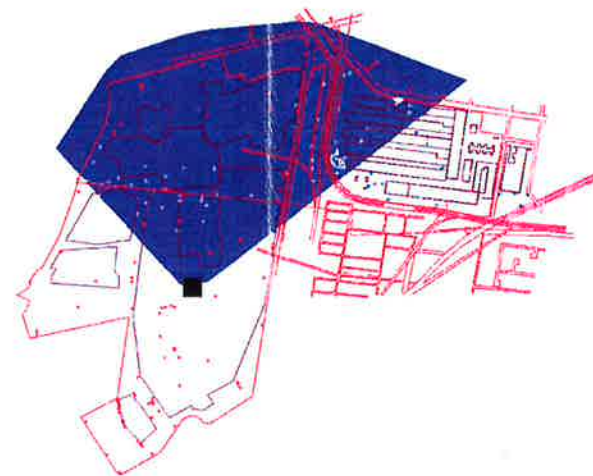
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DATE: 19 FEB 1998	PROJECT NO. SU001H	DWG. NO.
1-1'		FIGURE 3-12
Study Area PHILADELPHIA, PENNSYLVANIA		

Sun Refinery
West

DSPC
East



Signifies corner of wedge



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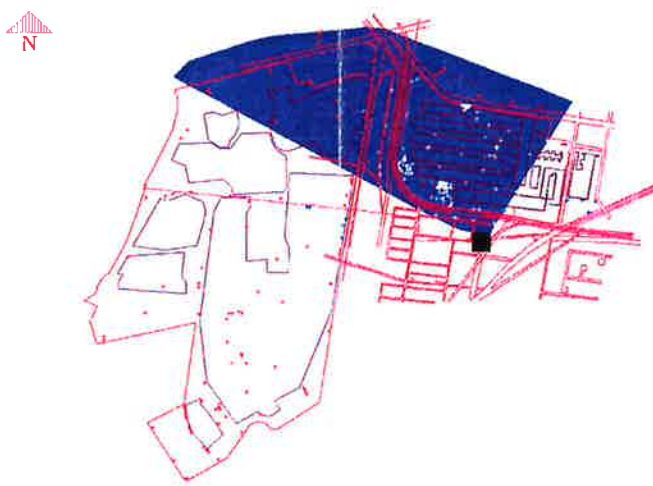
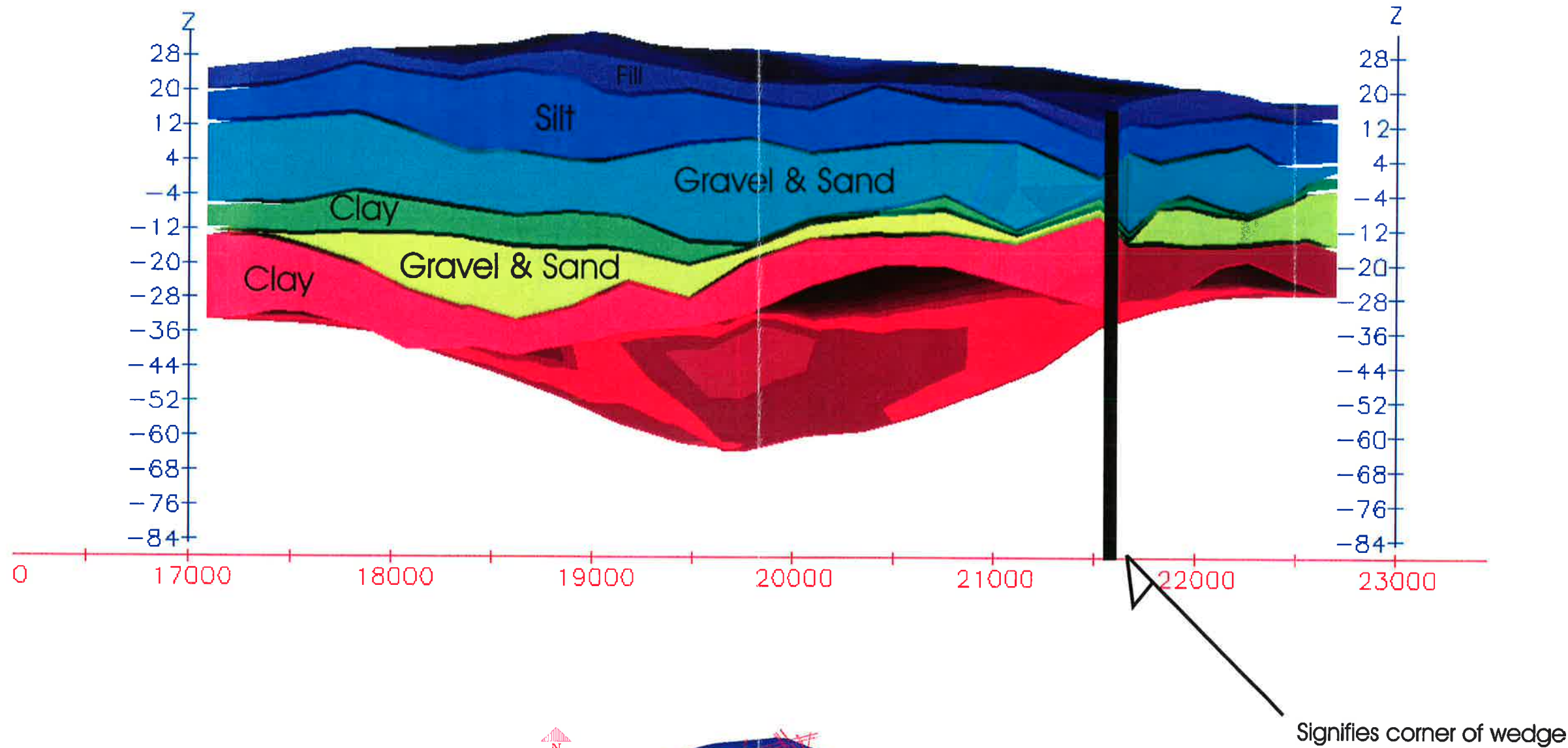
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DATE: 19 FEB 1998	PROJECT NO. SU001H	DWG. NO.
Wedge Cut #1		
Study Area PHILADELPHIA, PENNSYLVANIA		

FIGURE
3-13

Sun Refinery
West

DSPC
East



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Wedge Cut #2		
Study Area PHILADELPHIA, PENNSYLVANIA		
FIGURE 3-14		

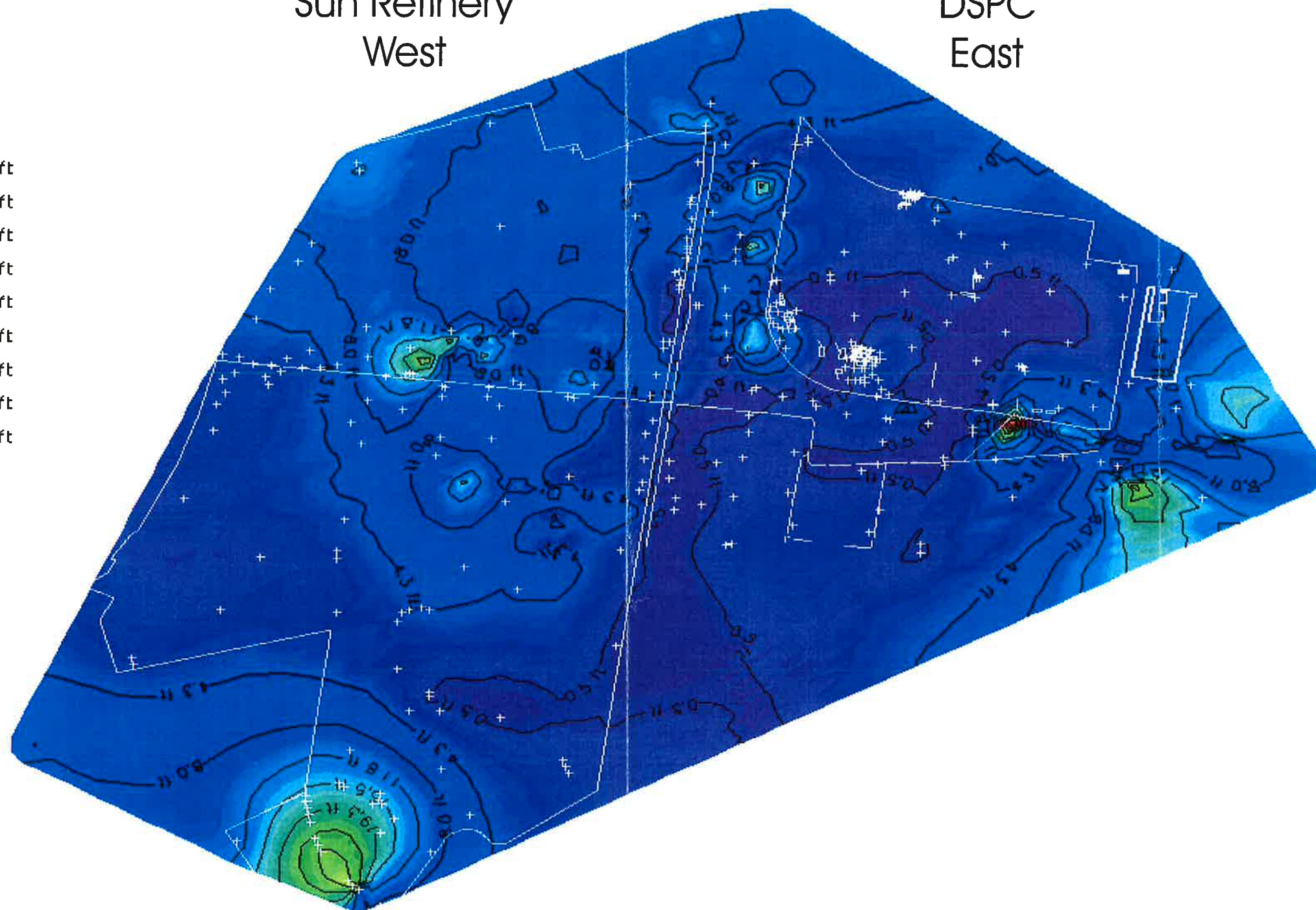


Sun Refinery
West

DSPC
East

Upper Clay Thickness Isopach (ft) Color Scale

38.0 ft
34.8 ft
31.7 ft
28.5 ft
25.3 ft
22.2 ft
19.0 ft
15.8 ft
12.7 ft
9.5 ft
6.3 ft
3.2 ft
0.0 ft



0 870 1740

Scale is in feet
(approximately)

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Upper Clay Thickness Isopach (ft)		FIGURE 3-16
Study Area PHILADELPHIA, PENNSYLVANIA		

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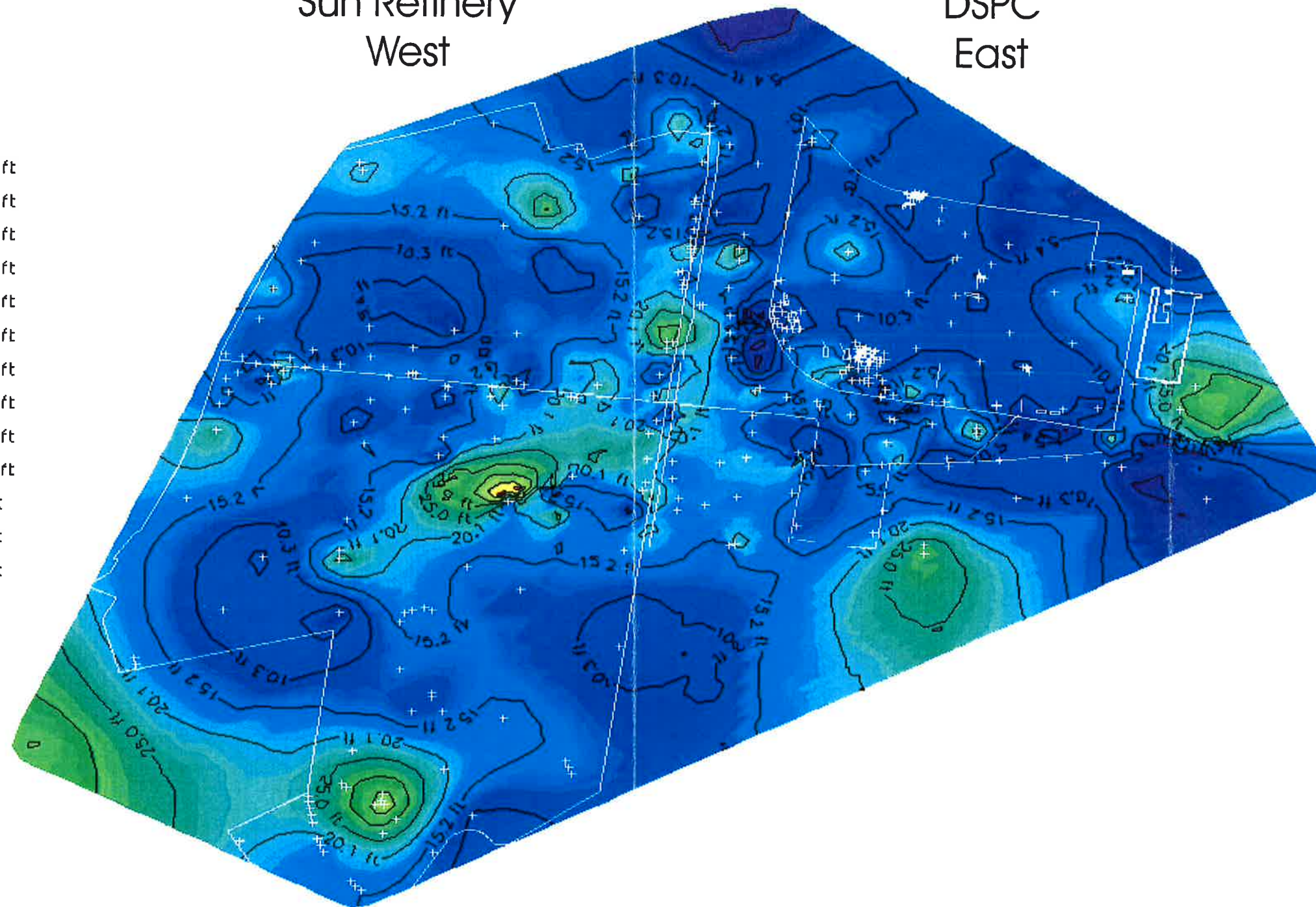


Sun Refinery
West

DSPC
East

Trenton Gravel Thickness Isopach (ft) Color Scale

49.5 ft
45.4 ft
41.3 ft
37.1 ft
33.0 ft
28.9 ft
24.8 ft
20.6 ft
16.5 ft
12.4 ft
8.3 ft
4.1 ft
0.0 ft



0 870 1740

Scale is in feet
(approximately)

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Trenton Gravel Thickness Isopach (ft)		FIGURE 3-15
Study Area PHILADELPHIA, PENNSYLVANIA		

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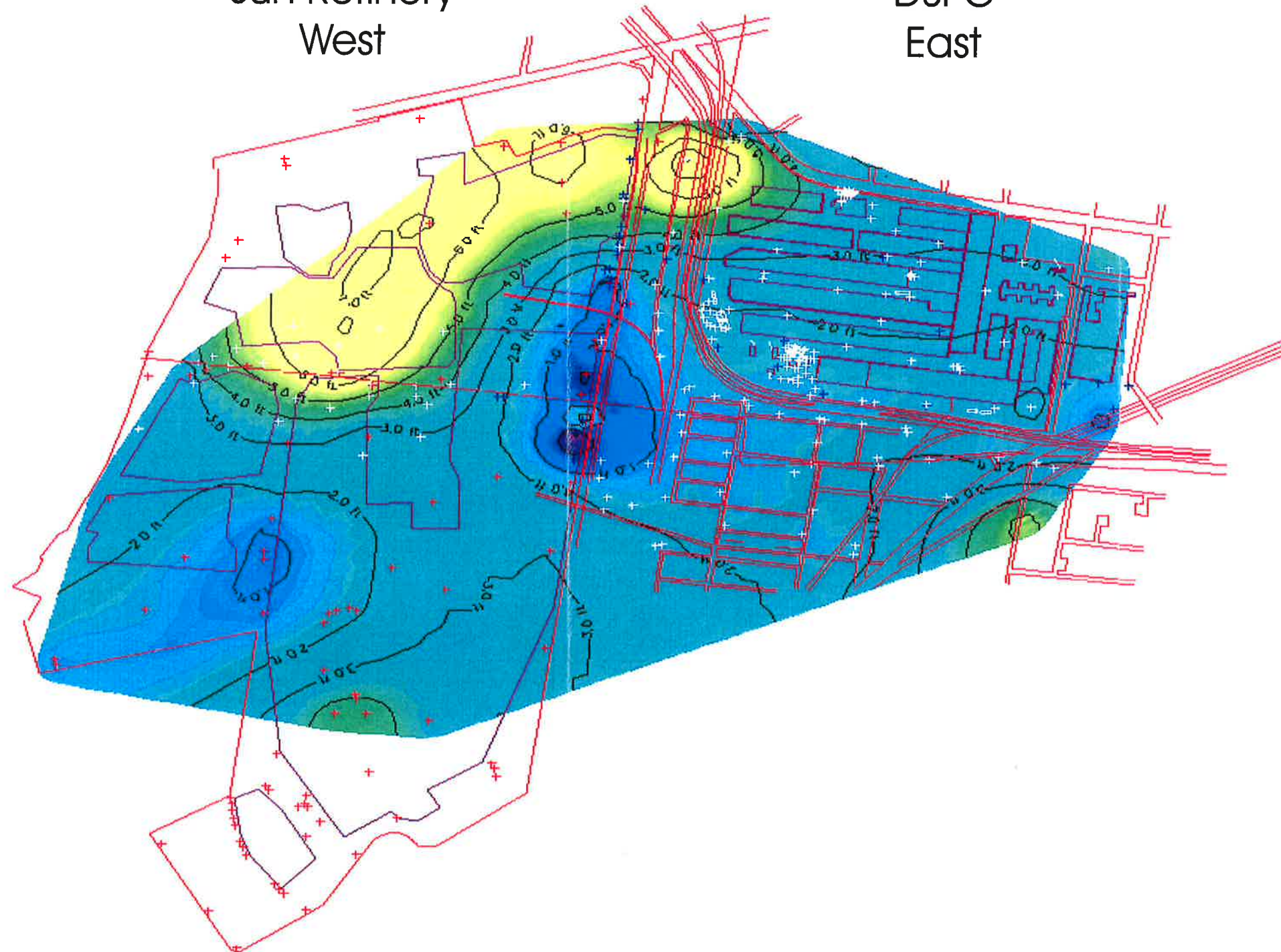


Sun Refinery
West

DSPC
East

GW Elevation (ft) Color Scale

8.1 ft
7.3 ft
6.4 ft
5.6 ft
4.7 ft
3.9 ft
3.0 ft
2.2 ft
1.3 ft
0.5 ft
-0.4 ft
-1.2 ft



0 880 1760

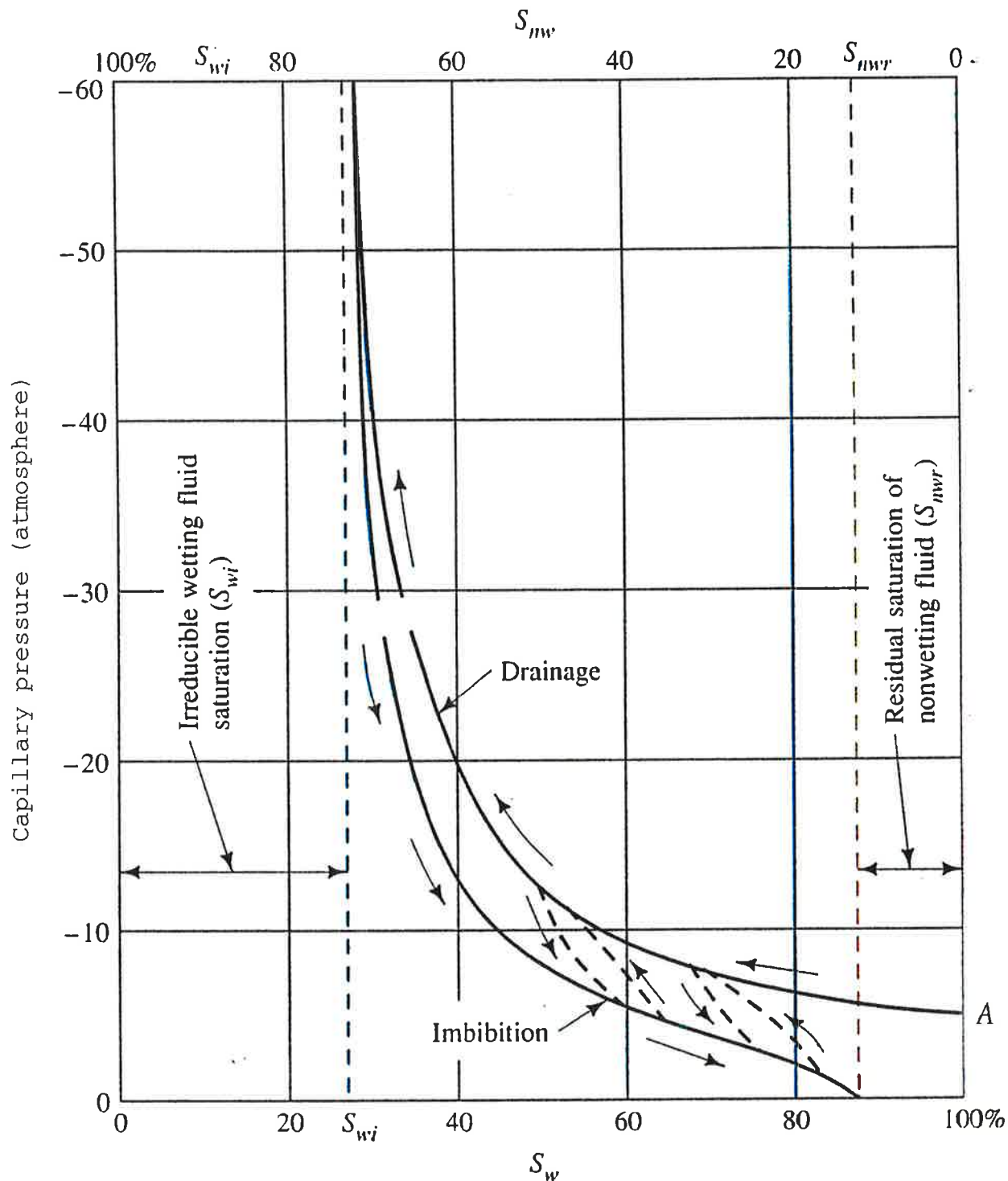
Scale is in feet
(approximately)

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DATE: 19 FEB 1998	PROJECT NO. SU001H	DWG. NO.
GW Elevation Contours 28, July 1997 Study Area PHILADELPHIA, PENNSYLVANIA		

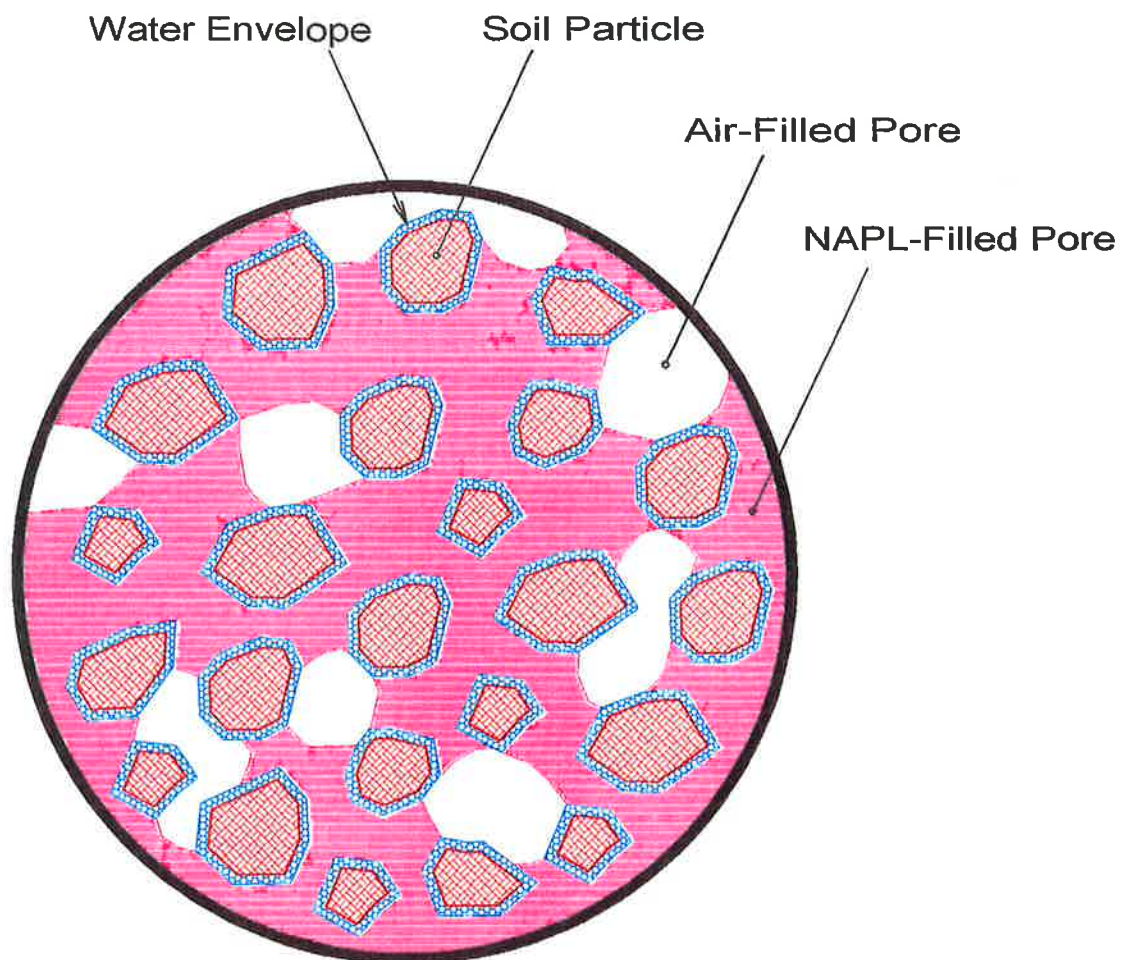
FIGURE
3-17

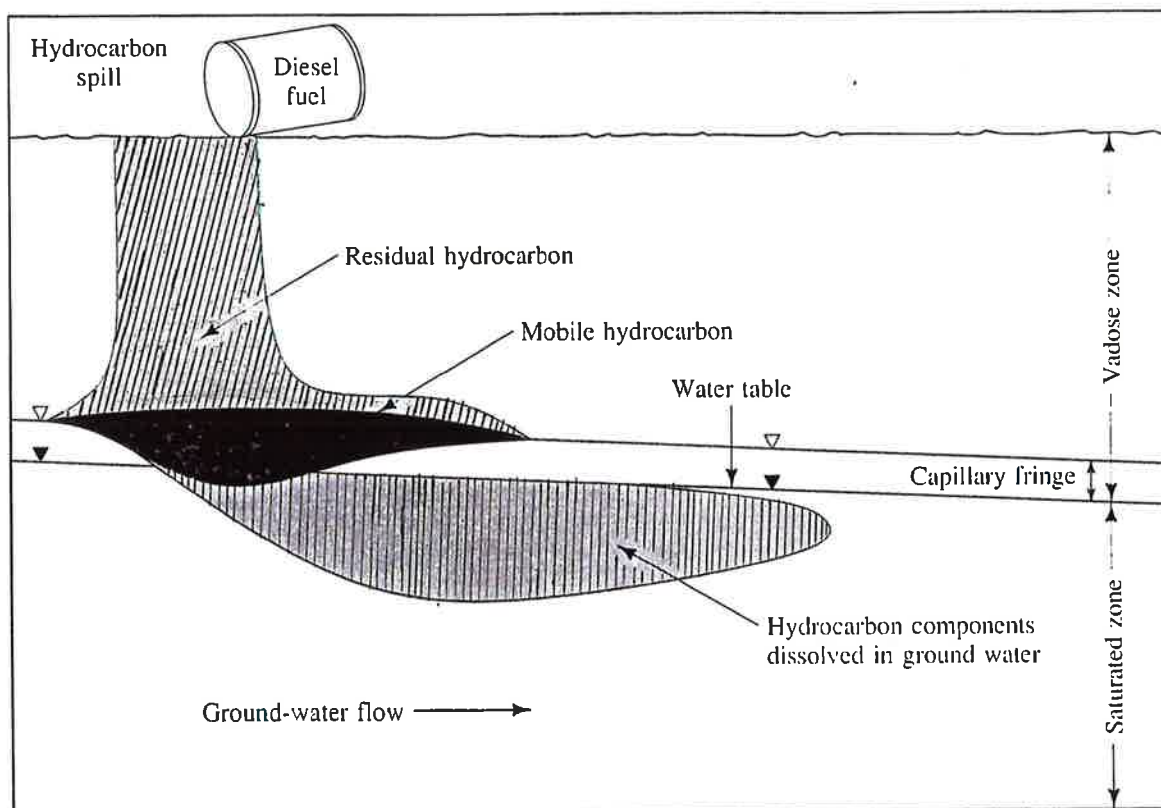
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Typical Capillary Pressure
Wetting Fluid Saturation Curves

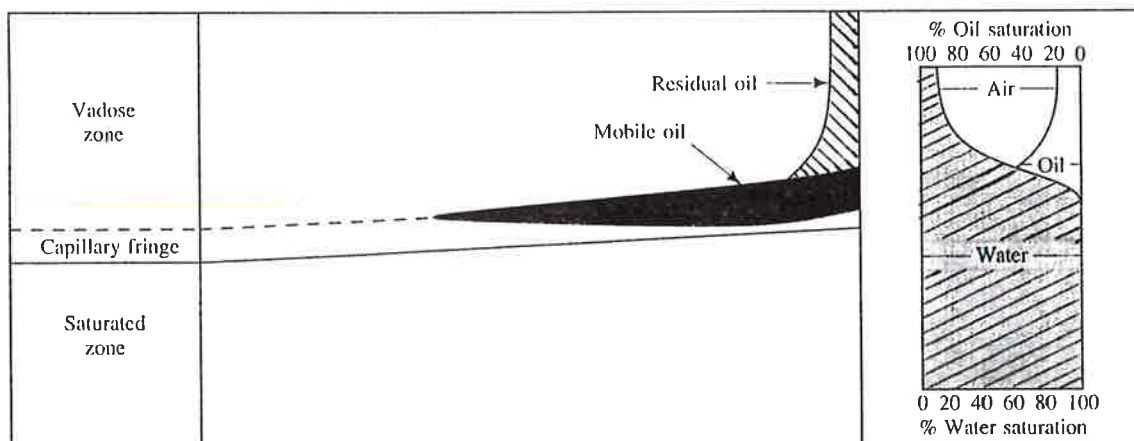
Source: Bear, 1972



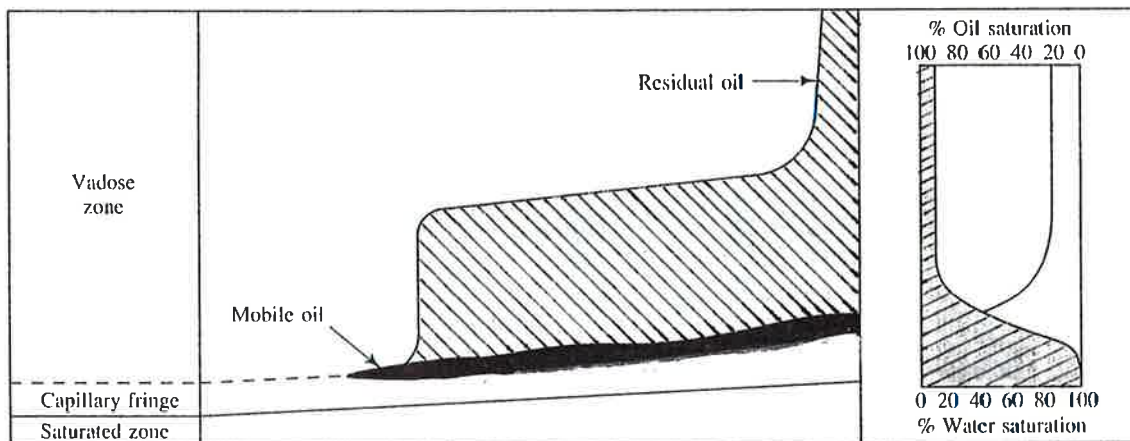


Subsurface distribution of an LNAPL spill.

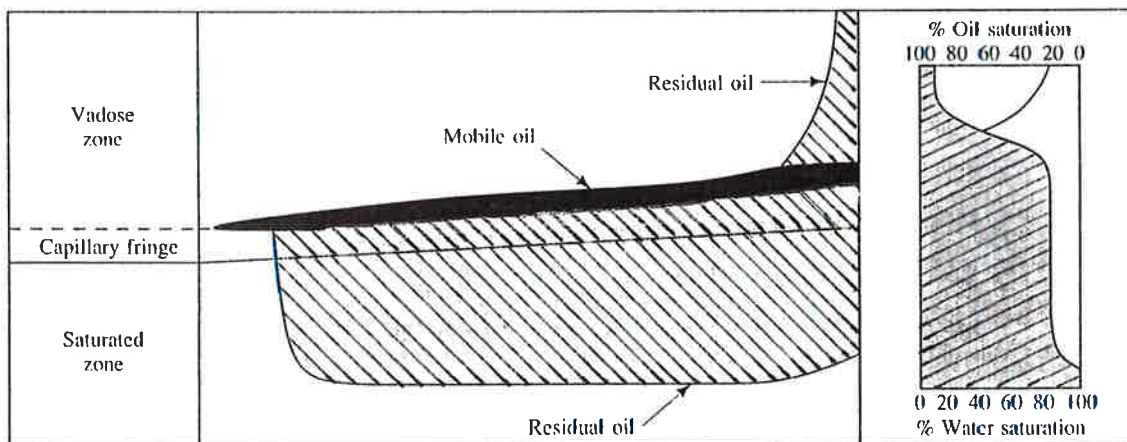
Source: Fetter, 1993



(a)



(b)



(c)

Effect of a falling and then rising water table on the distribution of mobile and residual phases of an LNAPL.

Source: Fetter, 1993

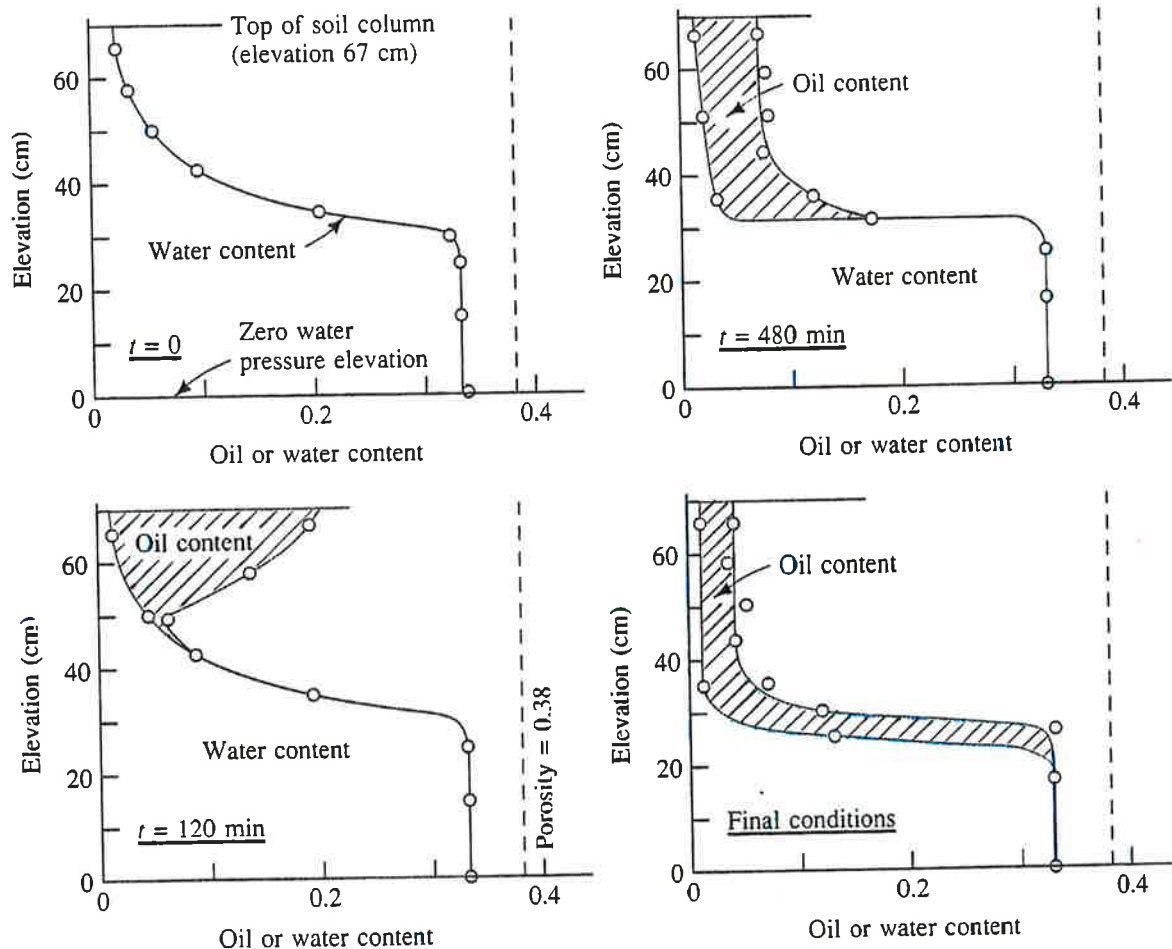
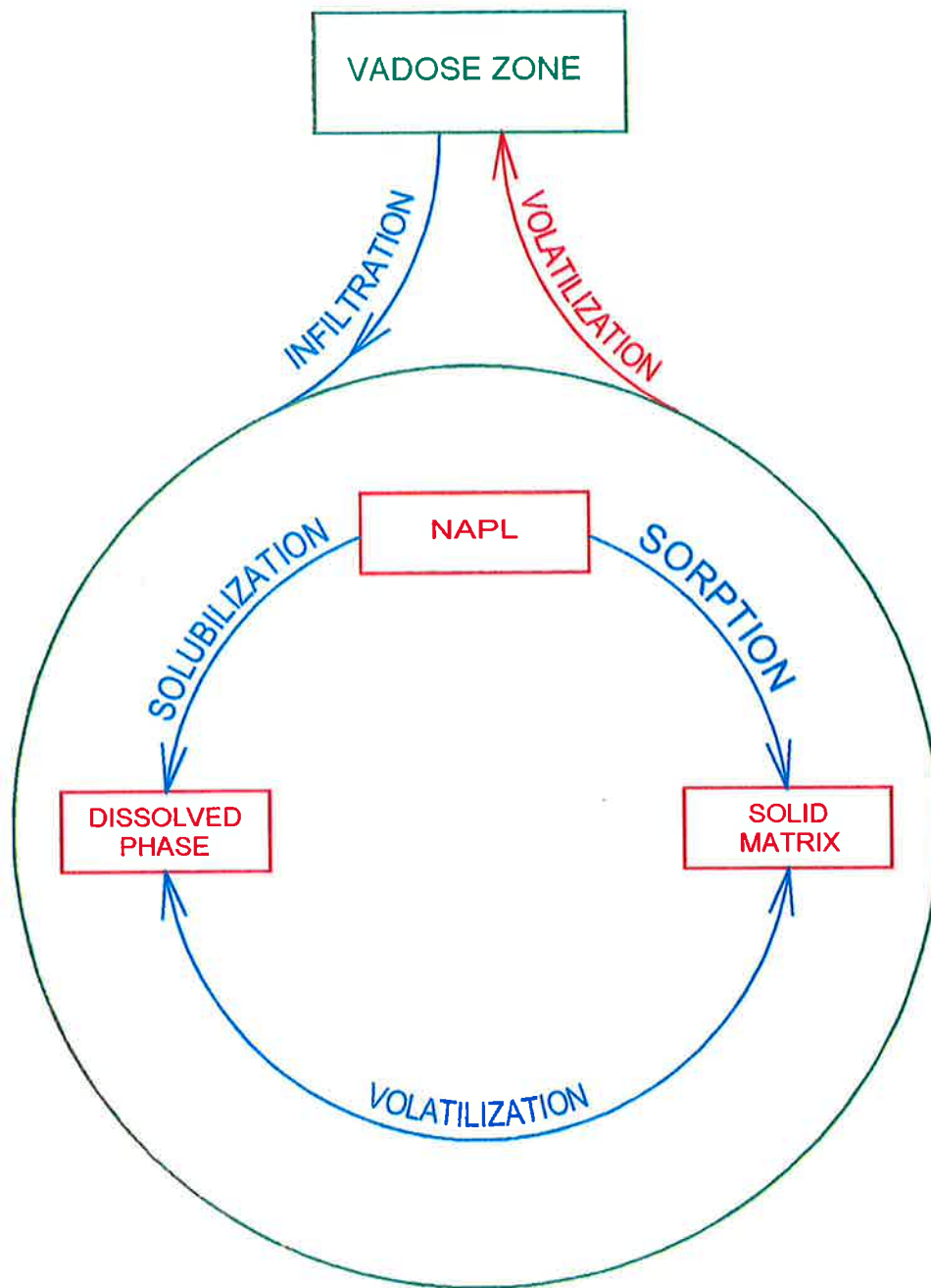
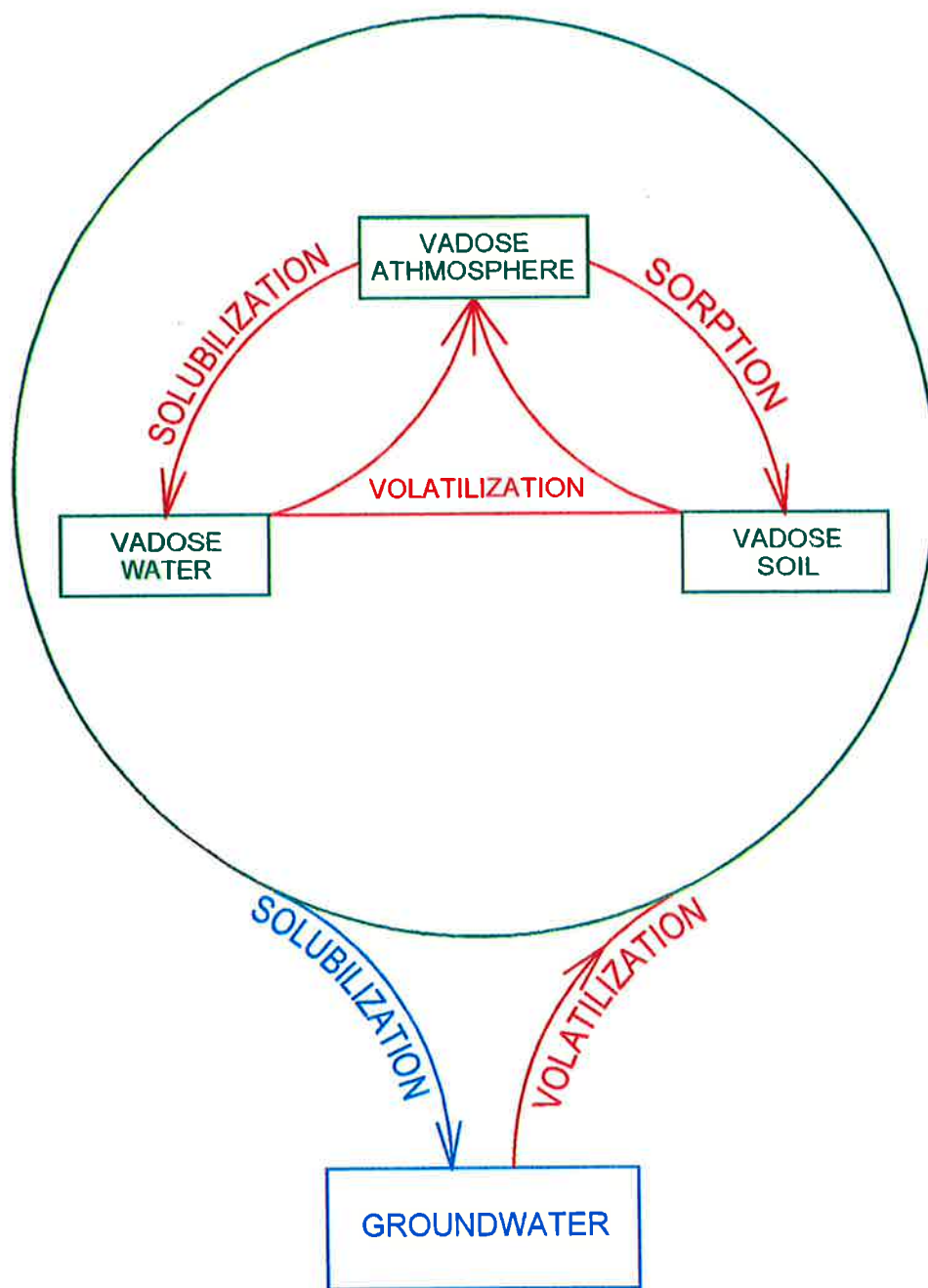


FIGURE Changes in the vertical distribution of oil with time after a slug of oil is added to the top of a column of sand. Oil content and water content are expressed as a fraction of the total volume of the porous media. Source: D. K. Eckberg and D. K. Sunada, *Water Resources Research* 20, no. 12 (1984):1891–97. Copyright by the American Geophysical Union.

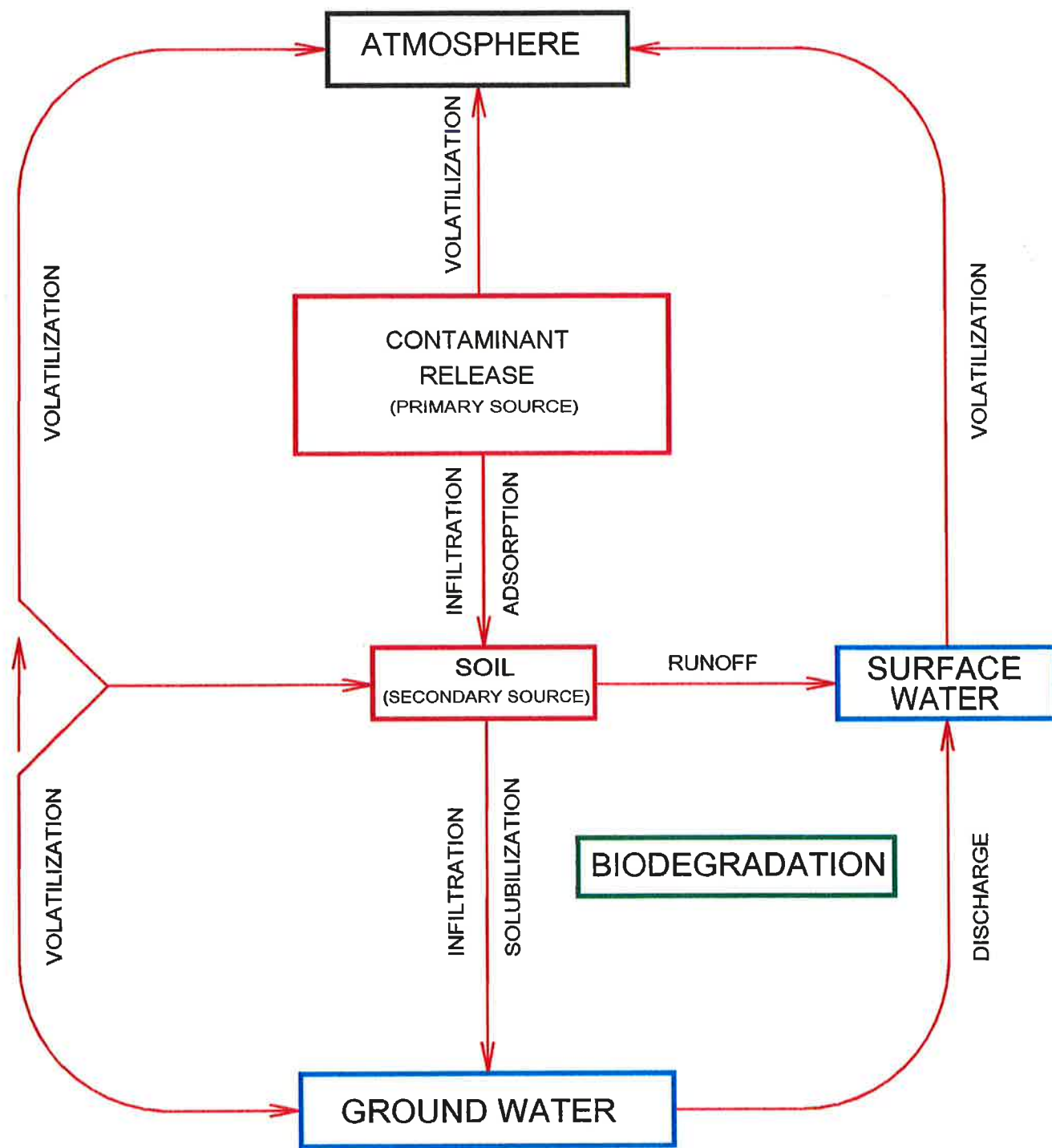
Source: Eckberg and Sunada, 1984.



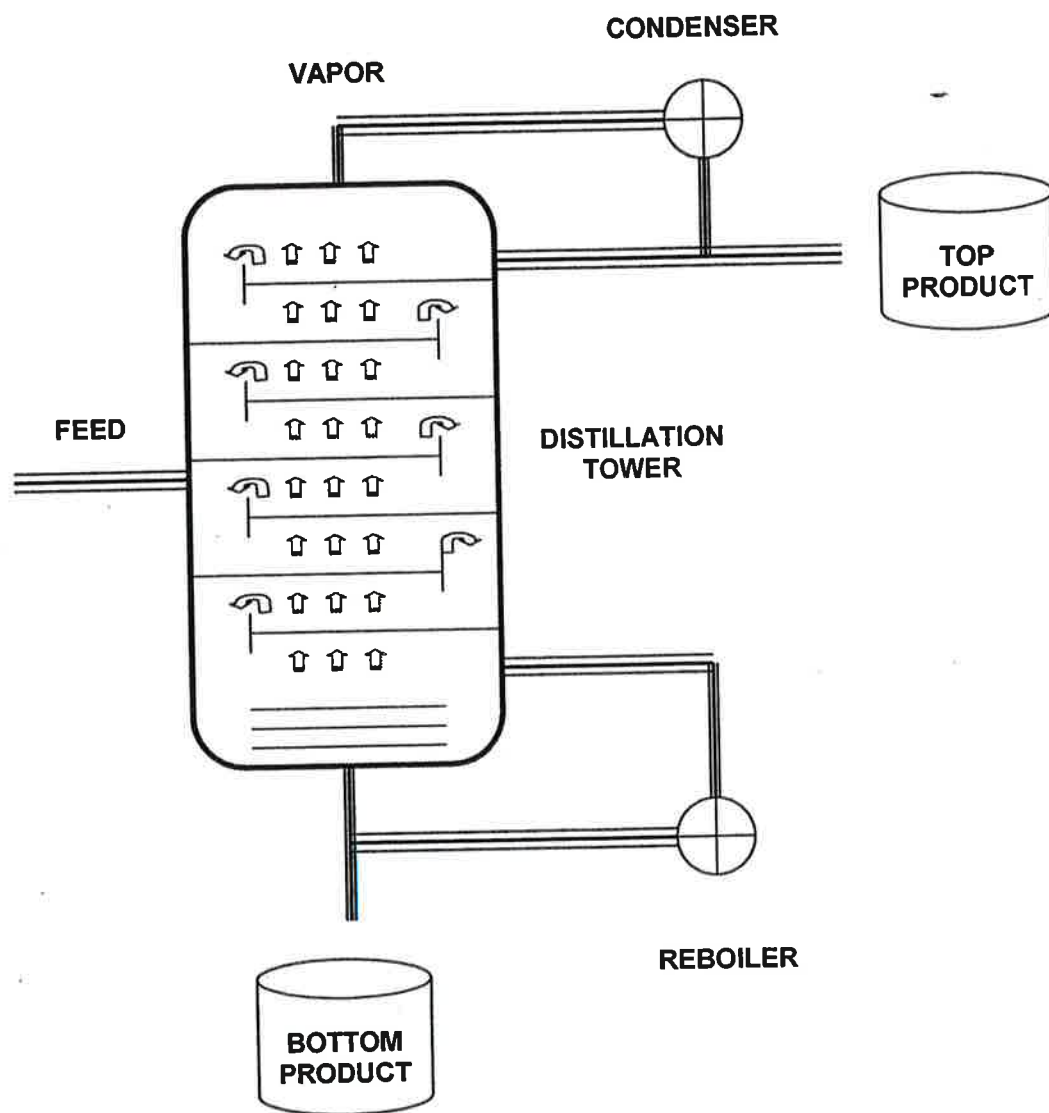
Groundwater Partitioning Model

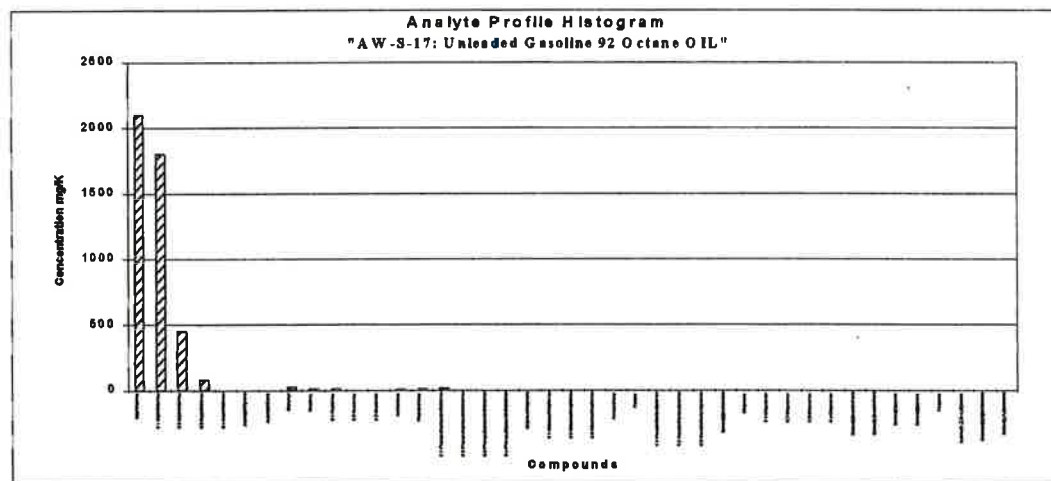
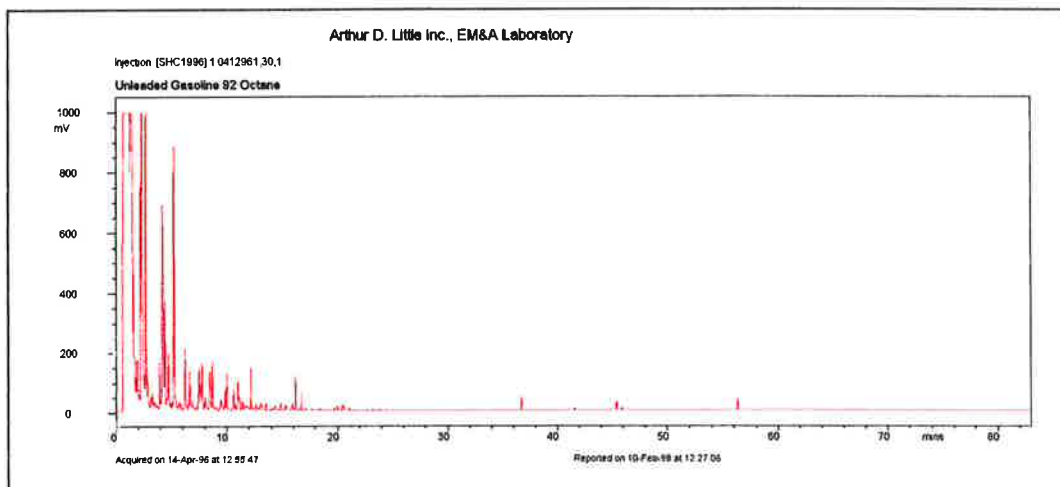
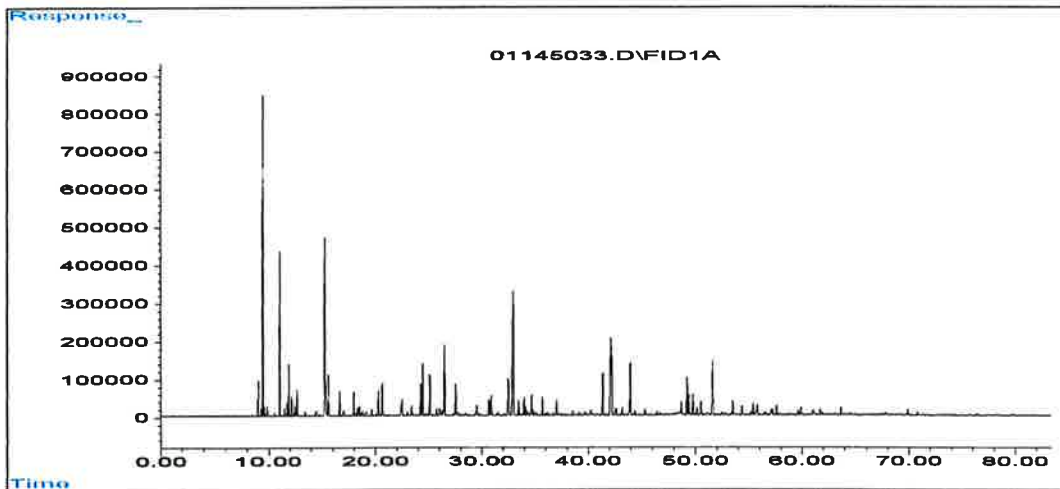


Three Compartment Vadose Partitioning Model

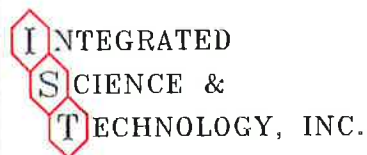
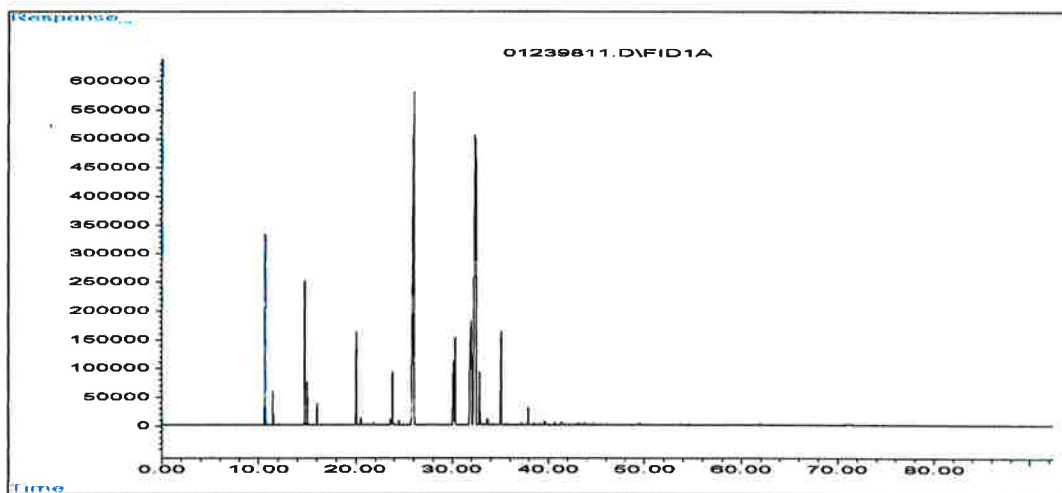


Environmental Partitioning and Fate Model





GRO, SHC 96B0079
PAH: AW-S-17



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EG

DATE:
MARCH 1998

REVIEWED:
PKH

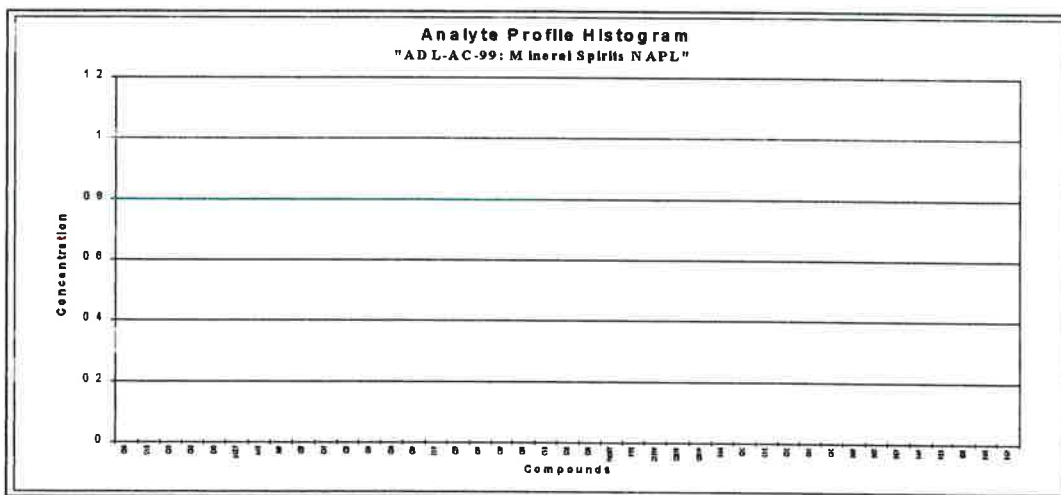
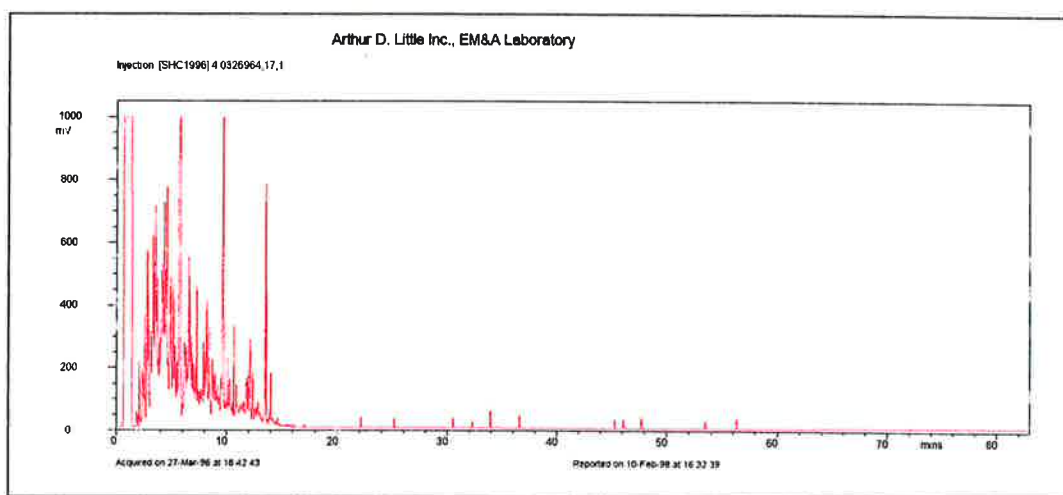
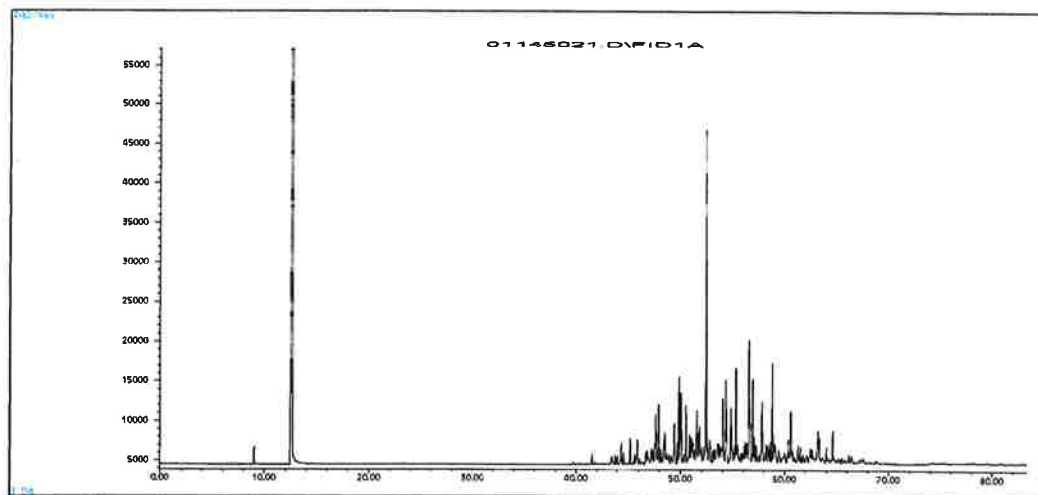
PROJECT NO.
SU001H

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HJR

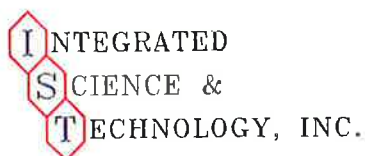
DWG. NO.

**Aviation Gasoline
Advanced Chemical Fingerprinting Characteristics
Study Area, Philadelphia, PA**

FIGURE
3-27a



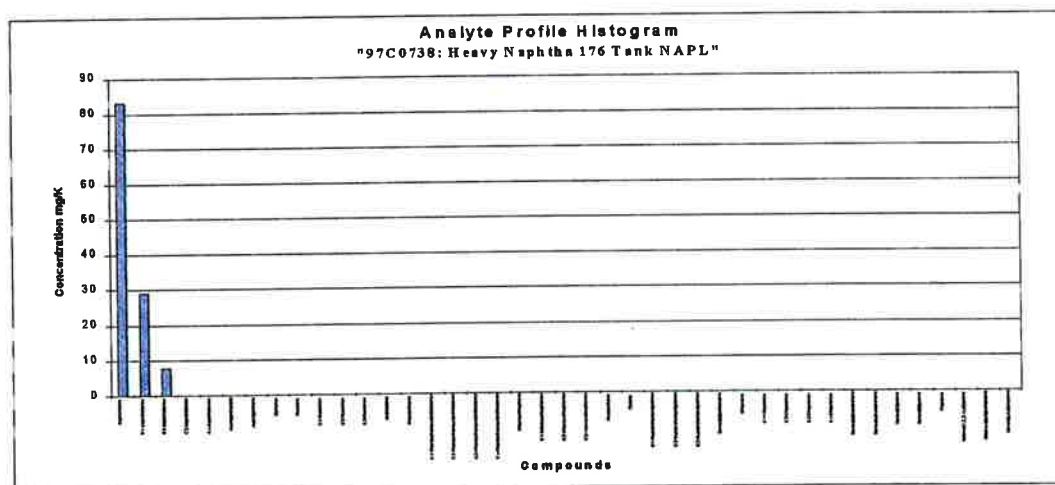
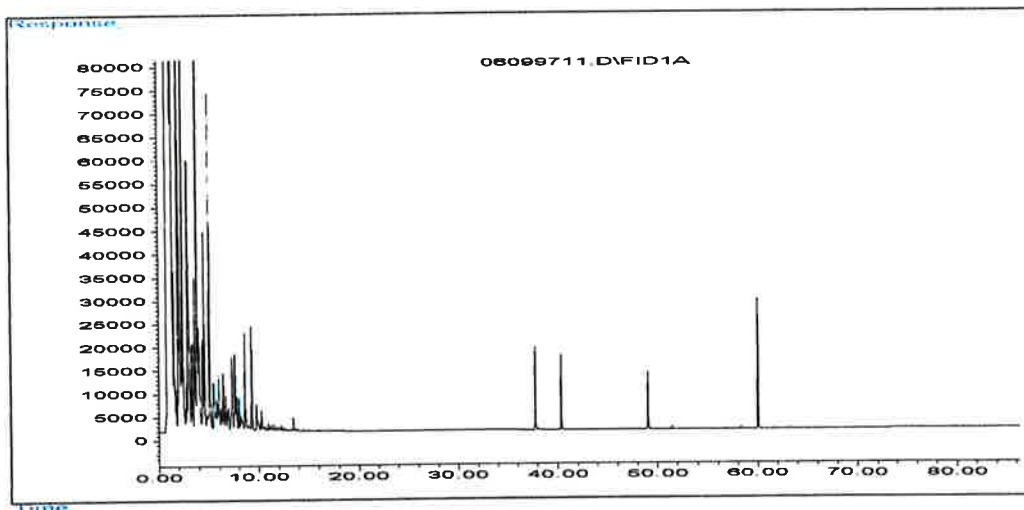
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 SHC: AW-S-74
 PAH: ADL-AC-99



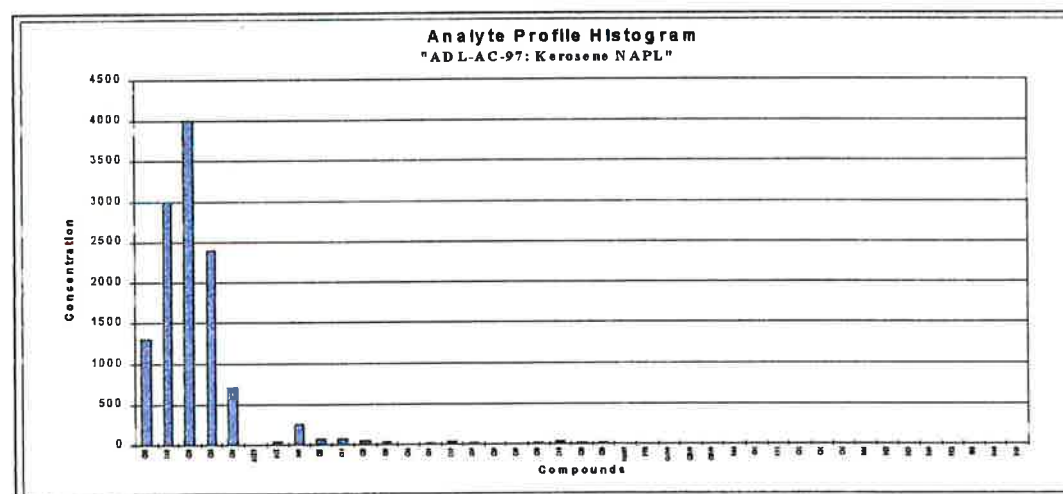
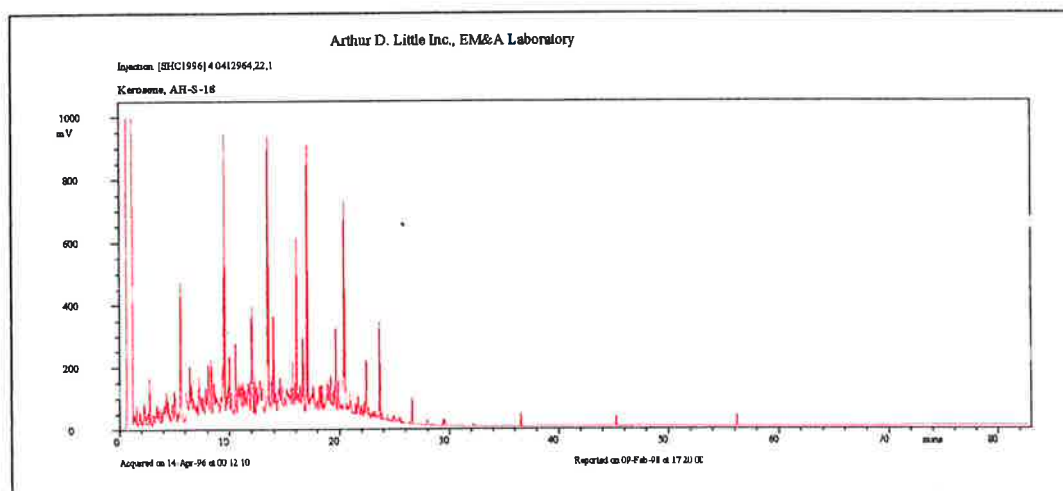
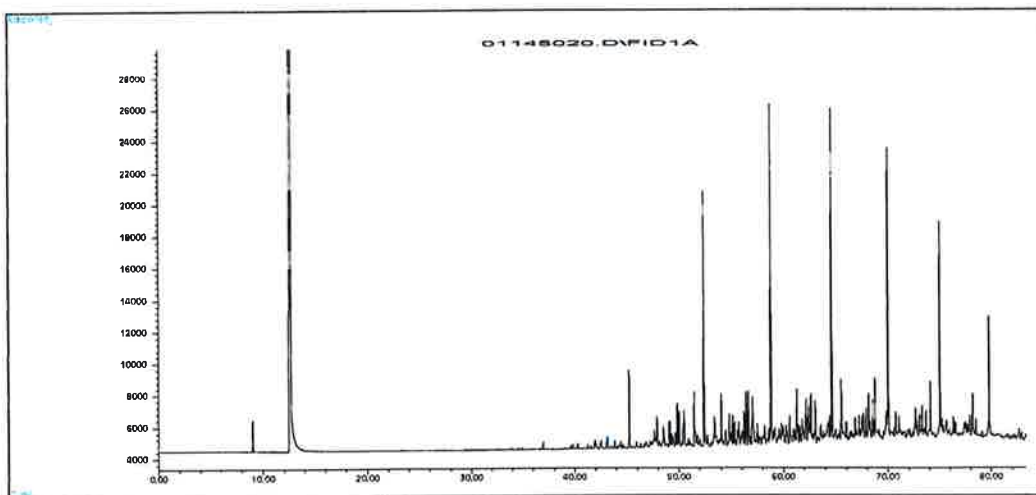
DRAWN BY: EG	REVIEWED: PKH	APPROVED: HJR
DATE: MARCH 1998	PROJECT NO. SU001H	DWG. NO. *****

Mineral Spirits
Advanced Chemical Fingerprinting Characteristics
Study Area, Philadelphia, PA

FIGURE
 3-28



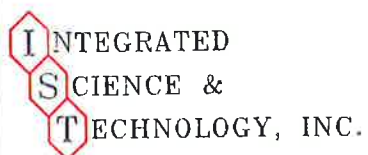
GRO, SHC, PAH: 97C0738



GRO: ADL-AC-97 (Supelco)

SHC: AH-S-18

PAH: ADL-AC-97 (Supelco)



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EG

DATE:
MARCH 1998

REVIEWED:
PKH

PROJECT NO.
SU001H

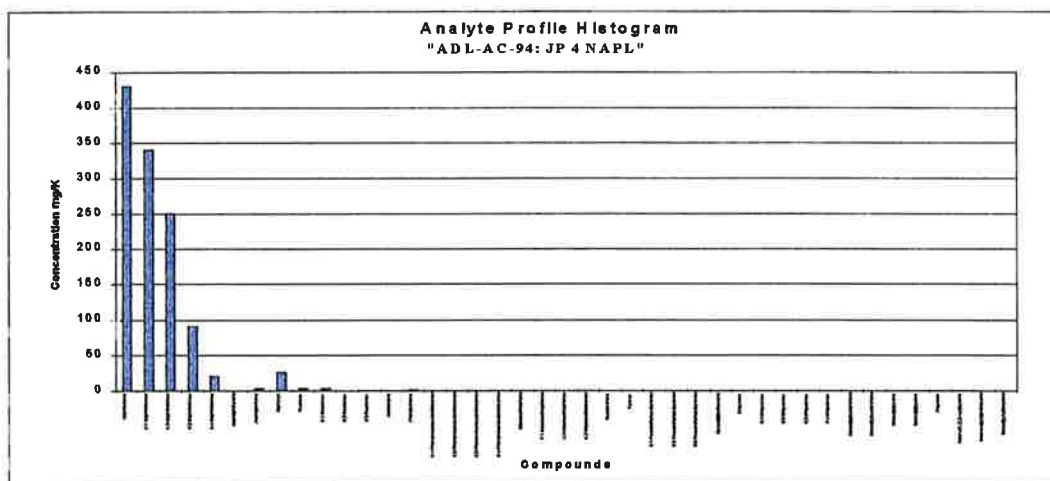
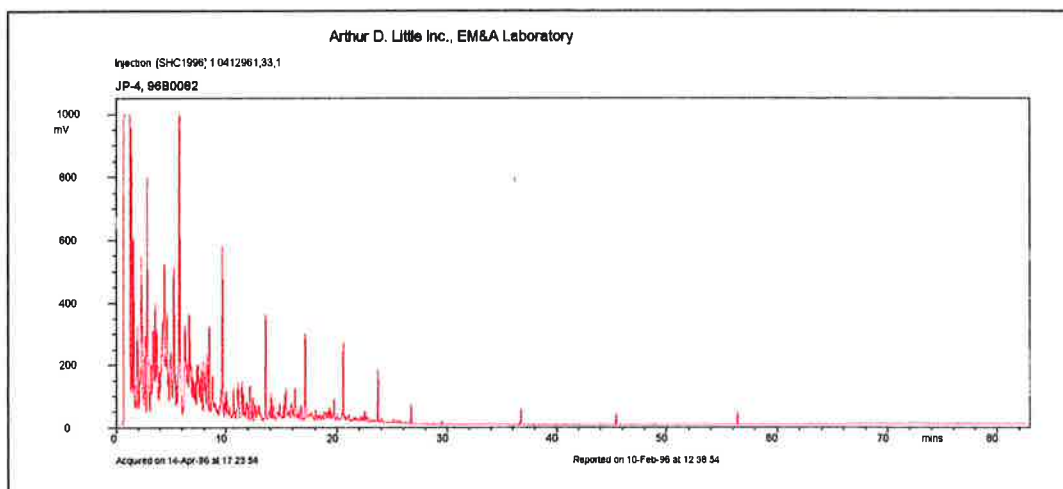
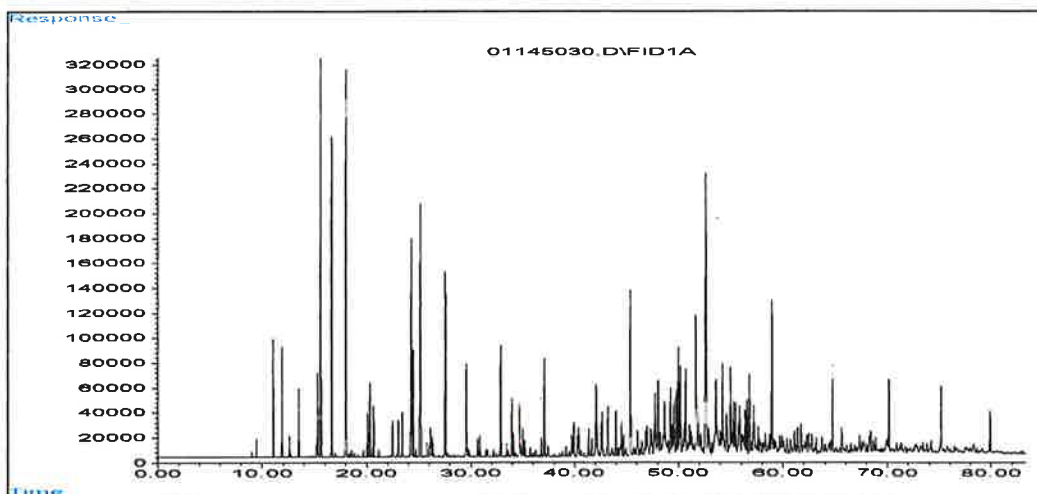
APPROVED:
HJR

DWG. NO.

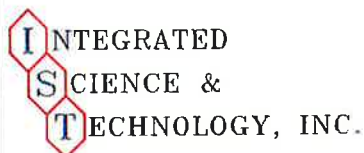
Kerosene
Advanced Chemical Fingerprinting Characteristics
Study Area, Philadelphia, PA

FIGURE

3-30



GRO, SHC: 96B0082
PAH: ADL-AC-94



DRAWN BY:
EG

DATE:
MARCH 1998

REVIEWED:
PKH

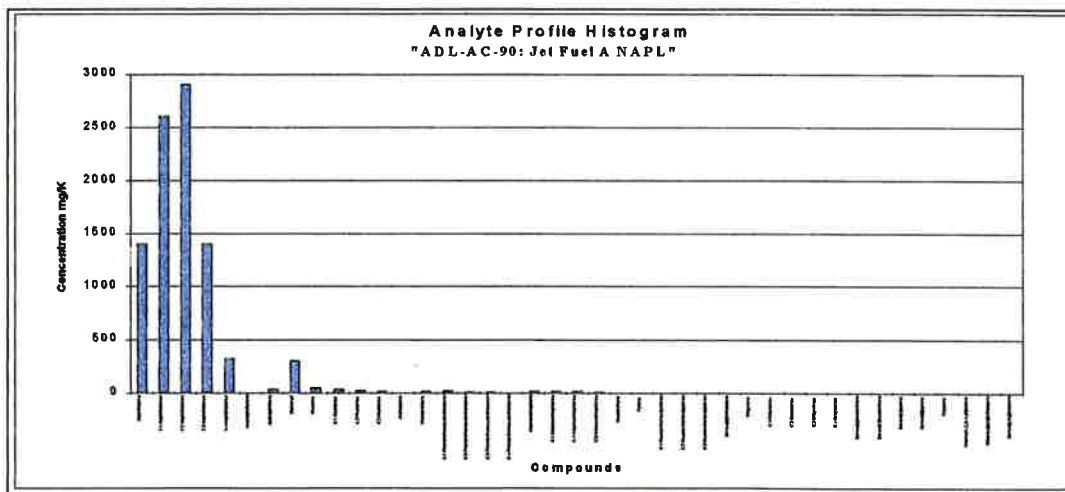
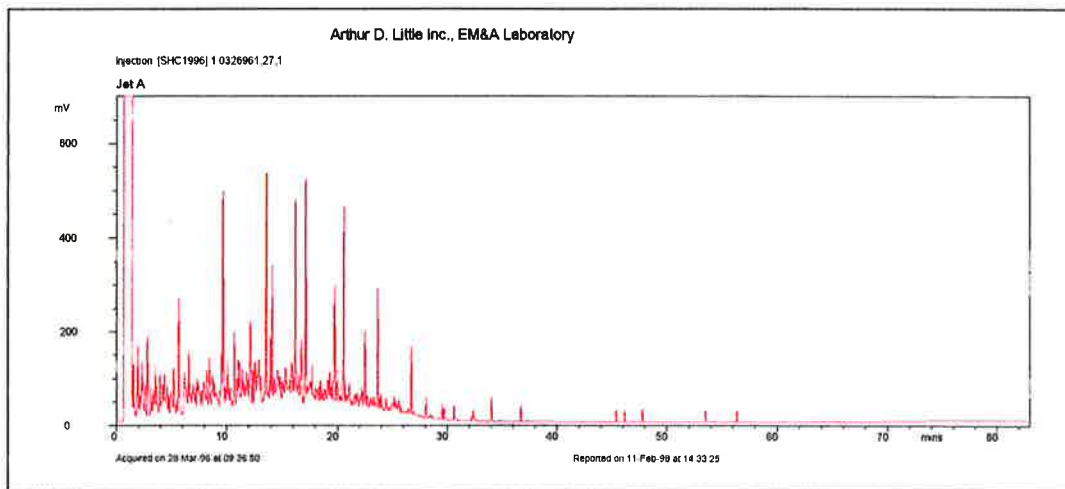
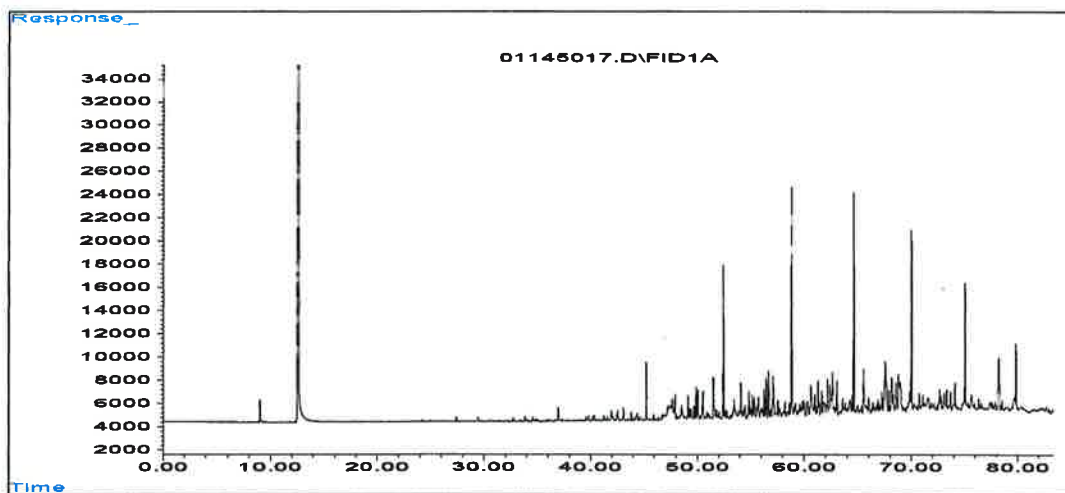
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APPROVED:
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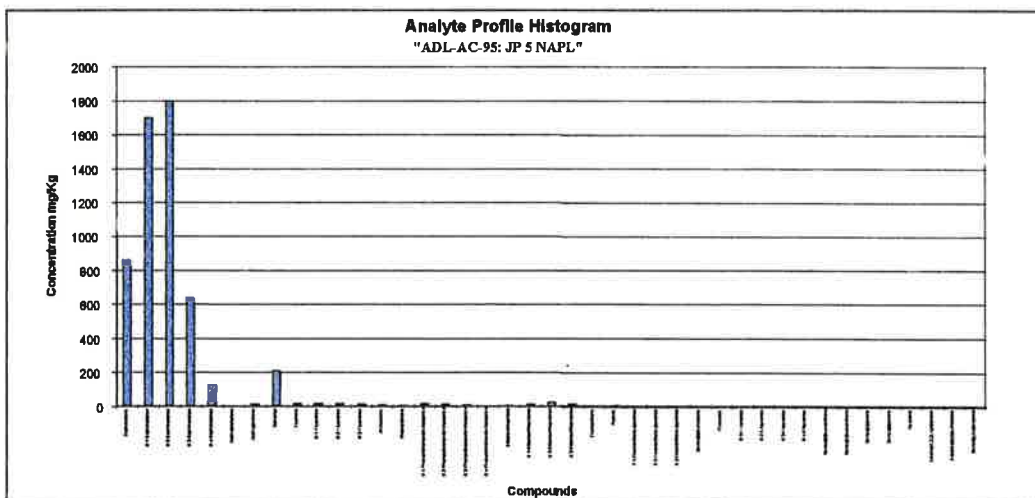
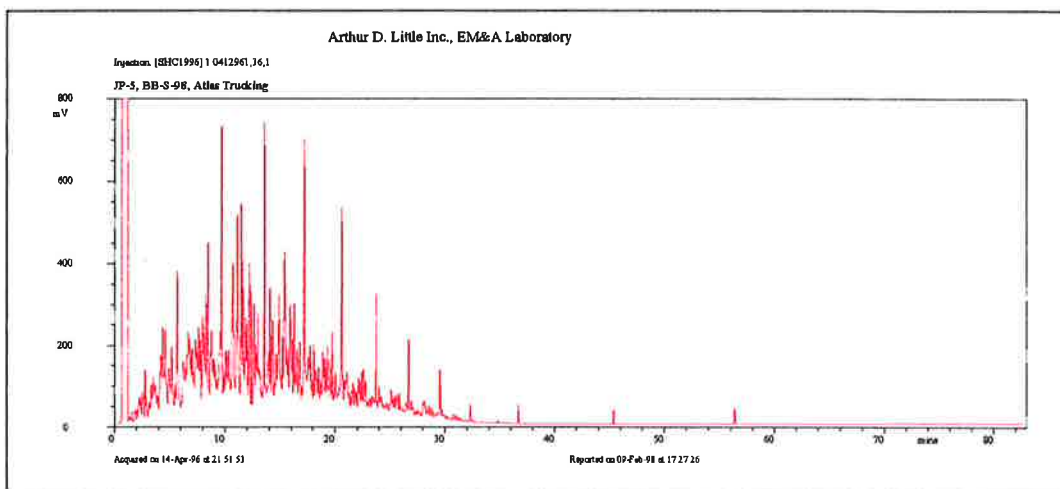
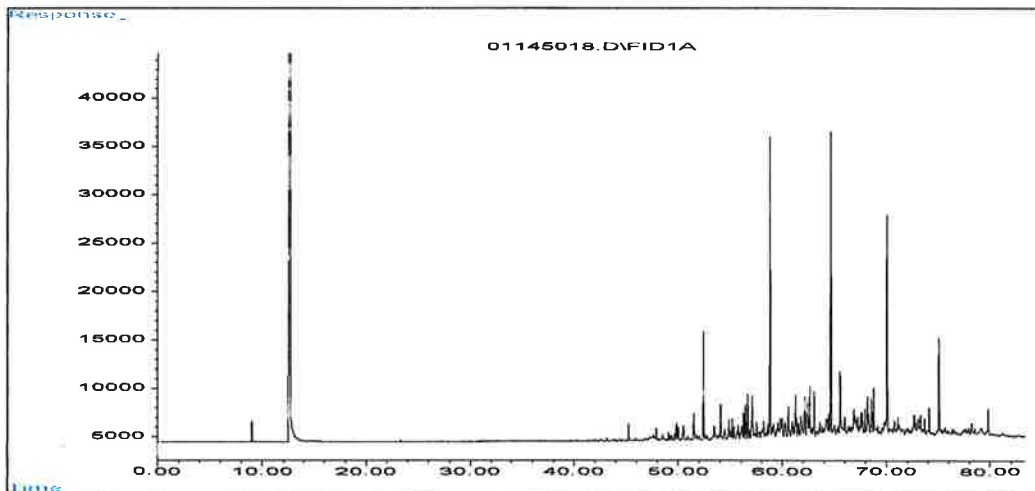
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JP-4
Advanced Chemical Fingerprinting Characteristics
Study Area, Philadelphia, PA

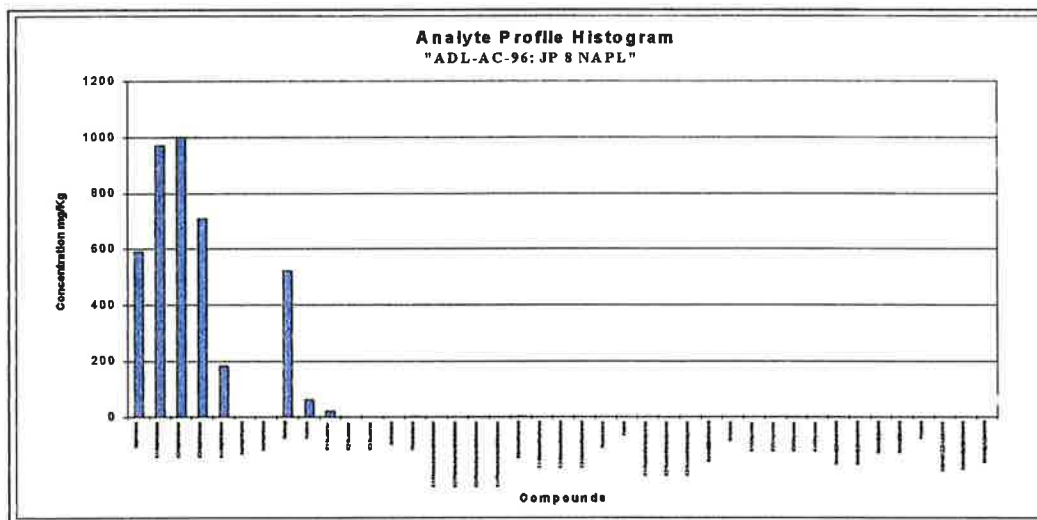
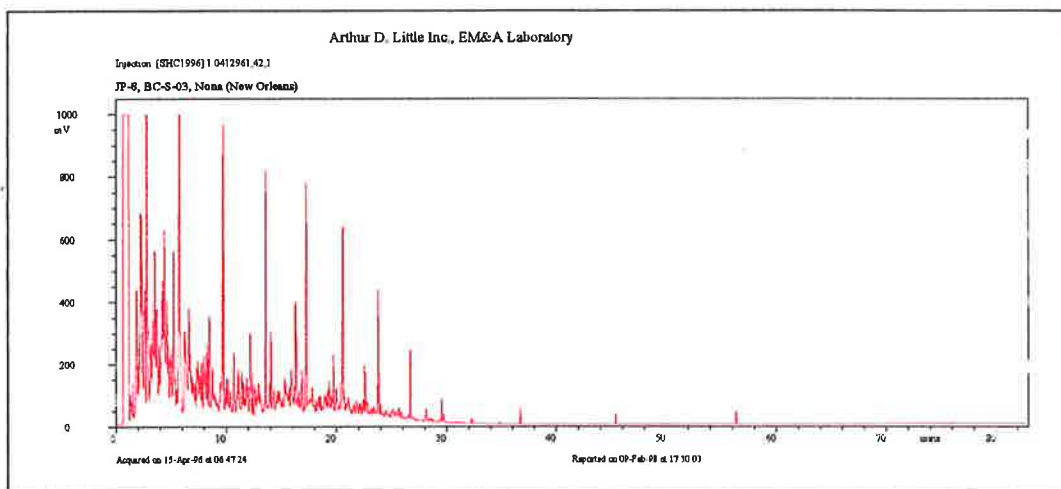
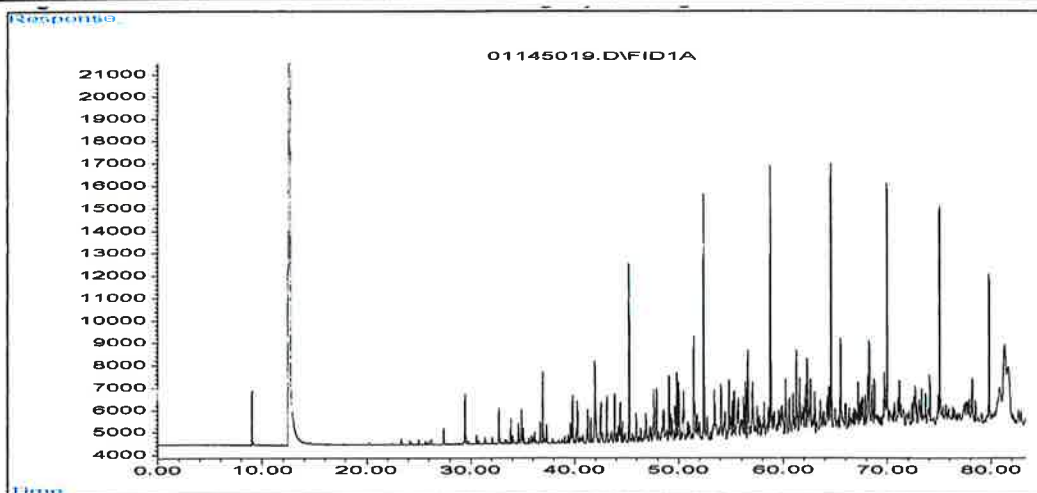
FIGURE
3-31



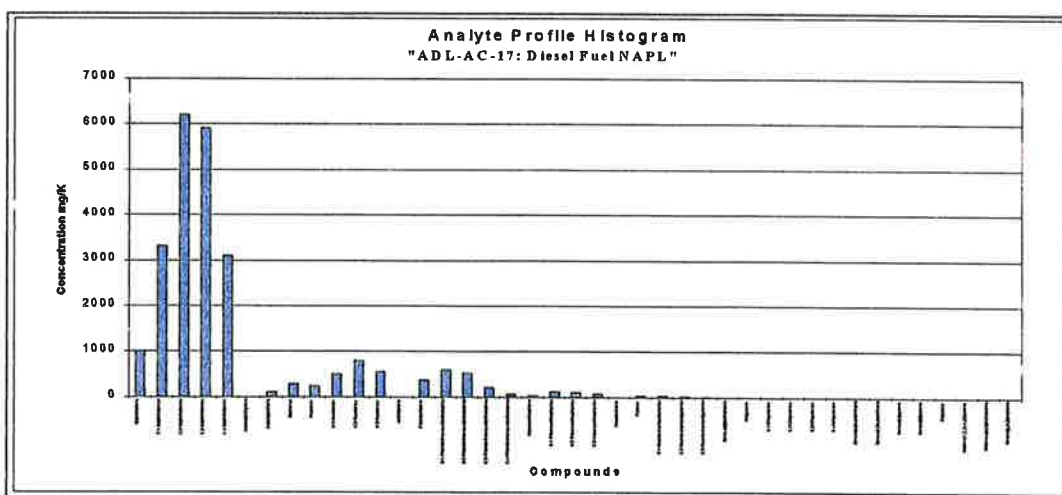
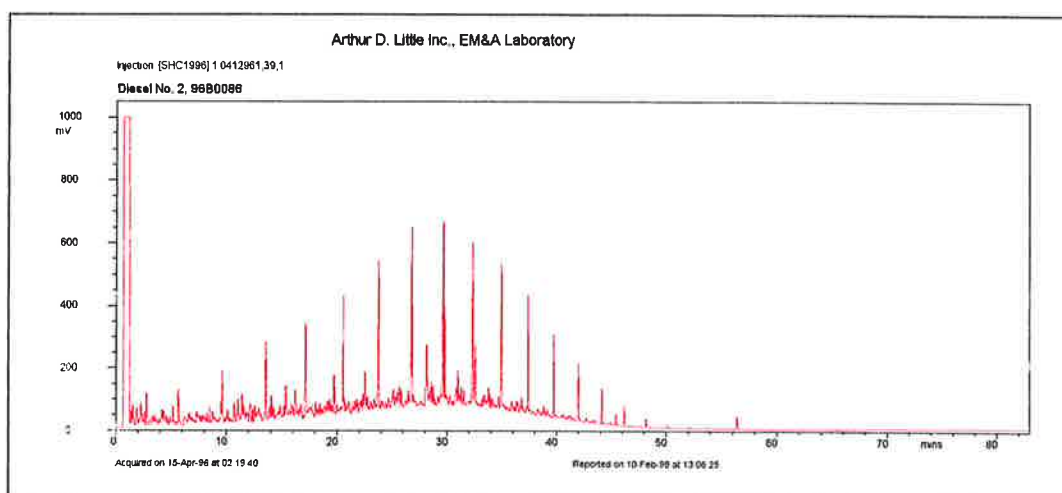
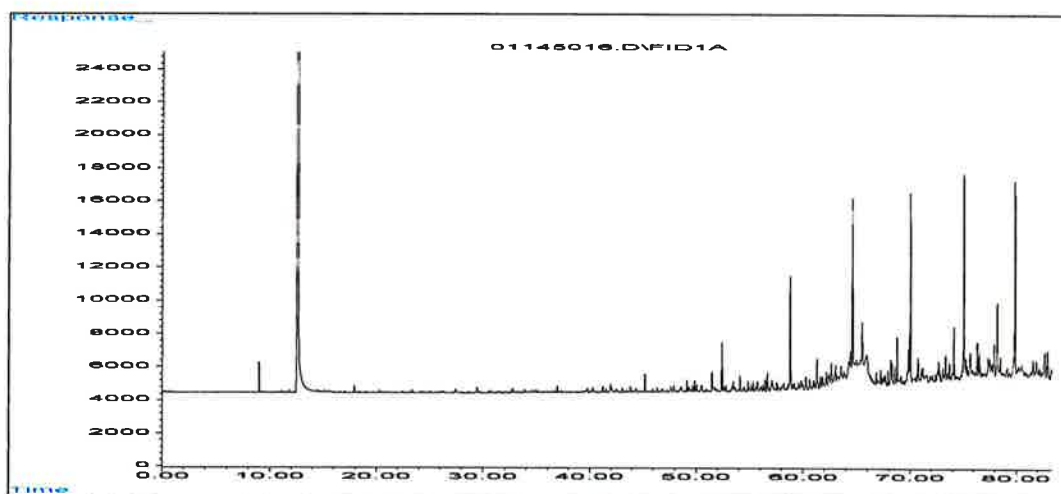
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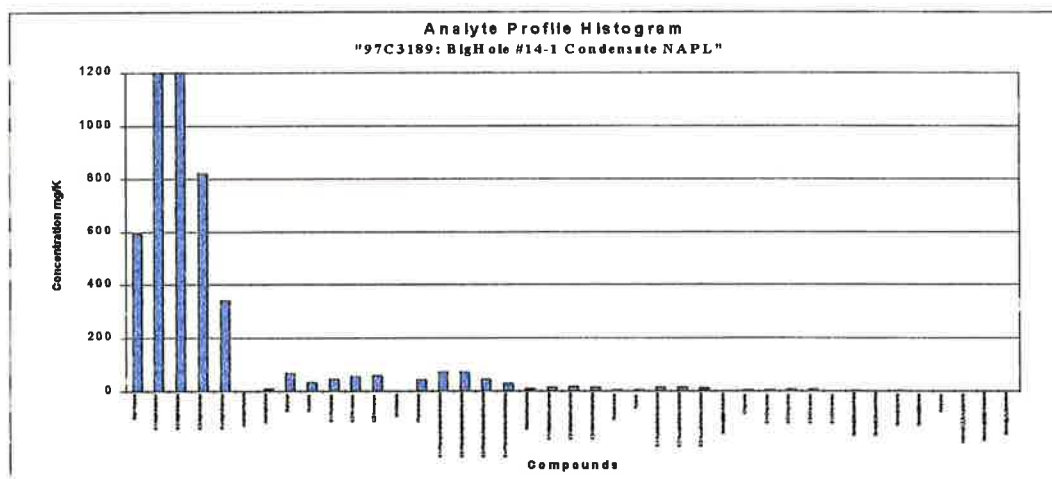
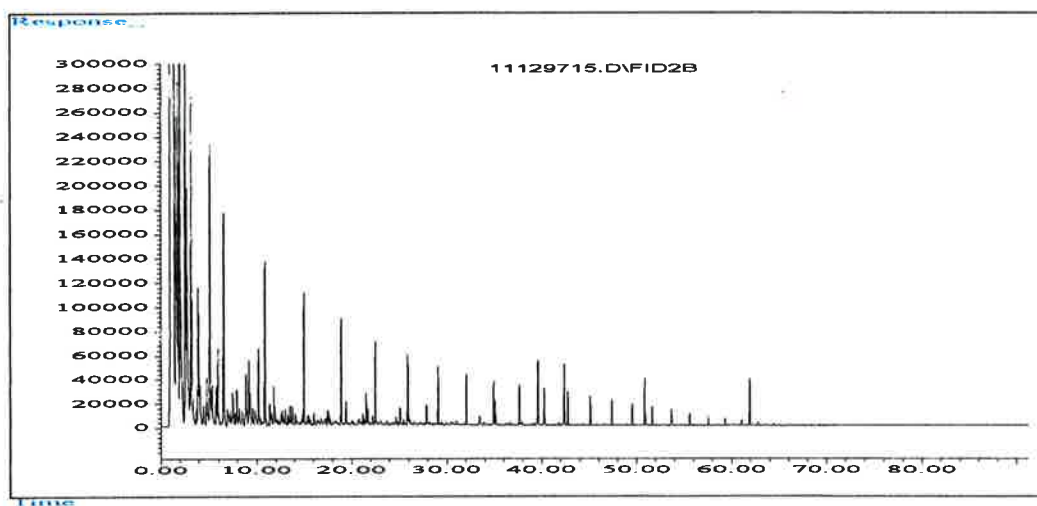
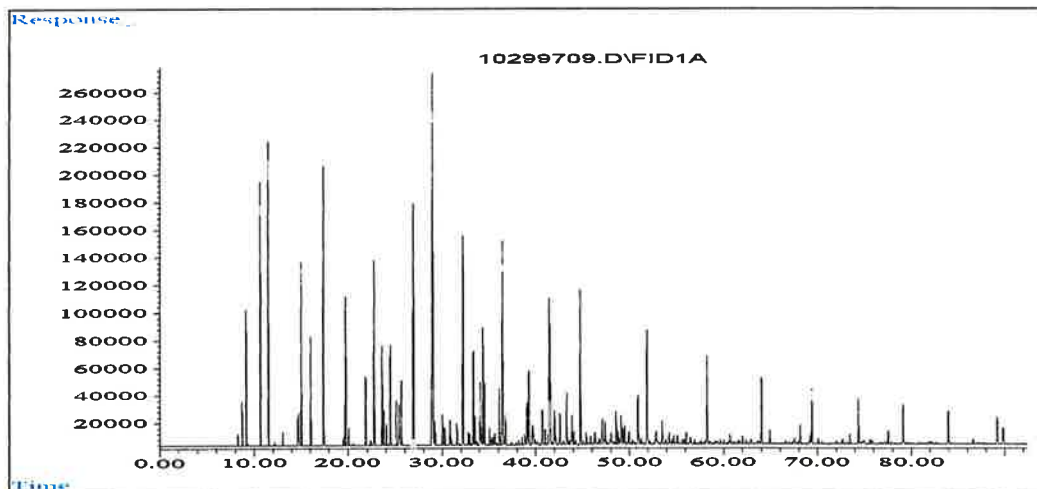
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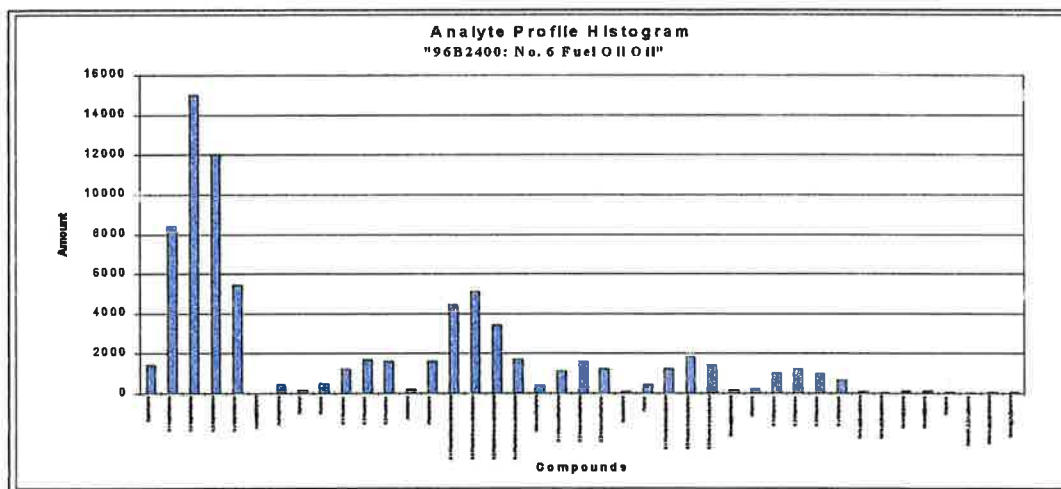
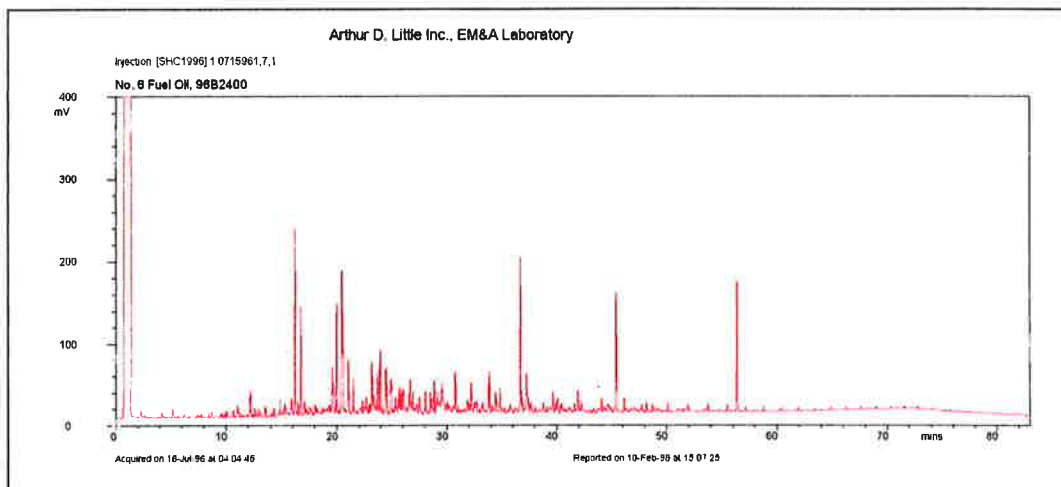
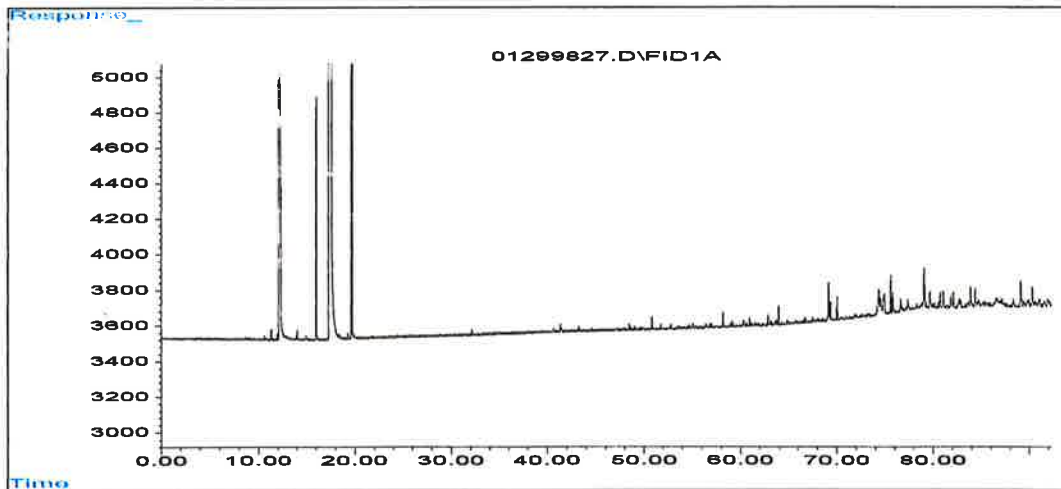
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 SHC: BC-S-03 (NONA)
 PAH: ADL-AC-96 (Supelco)



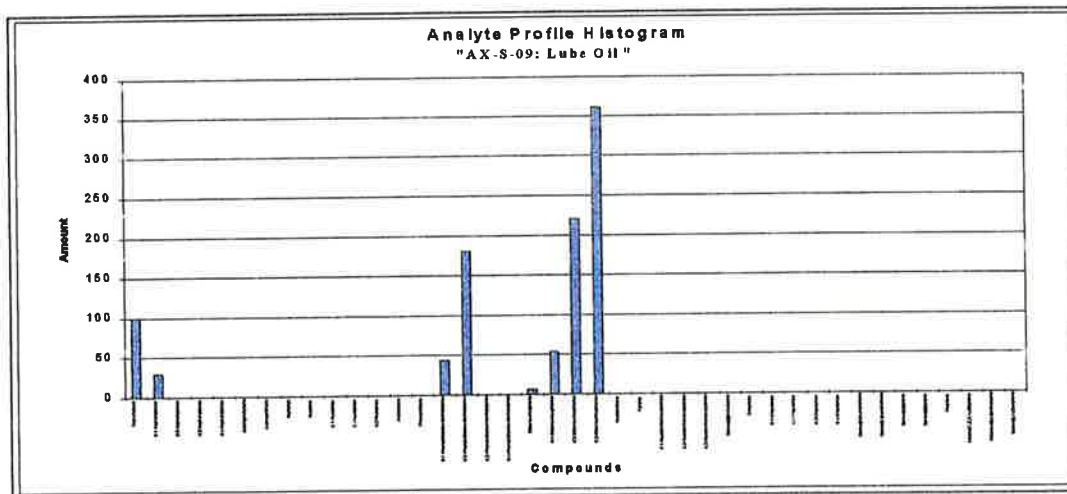
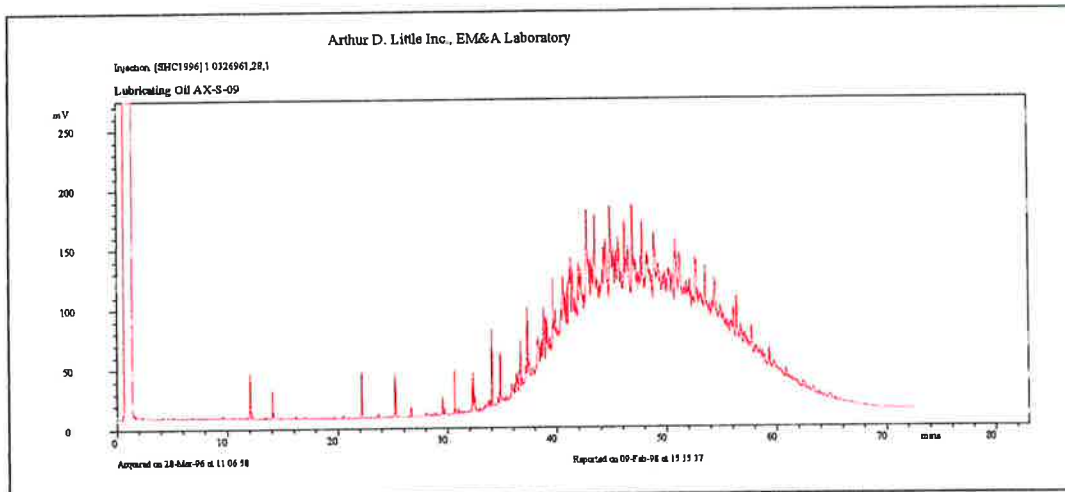
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SHC: 96B0086



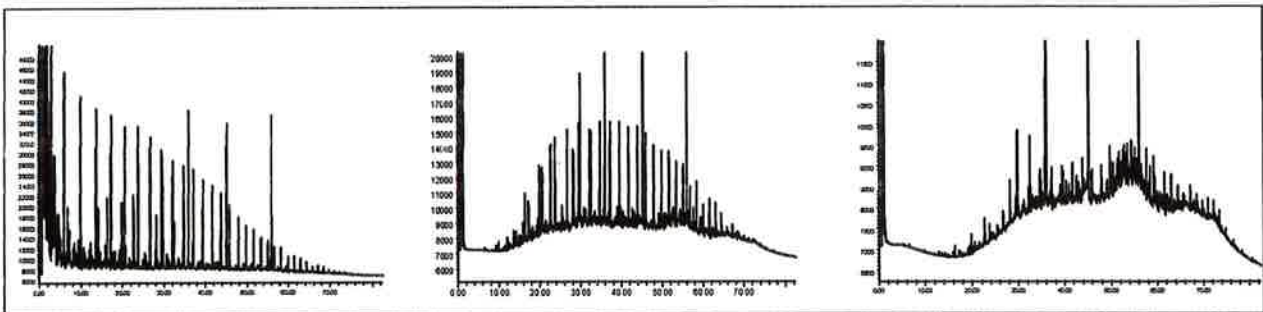
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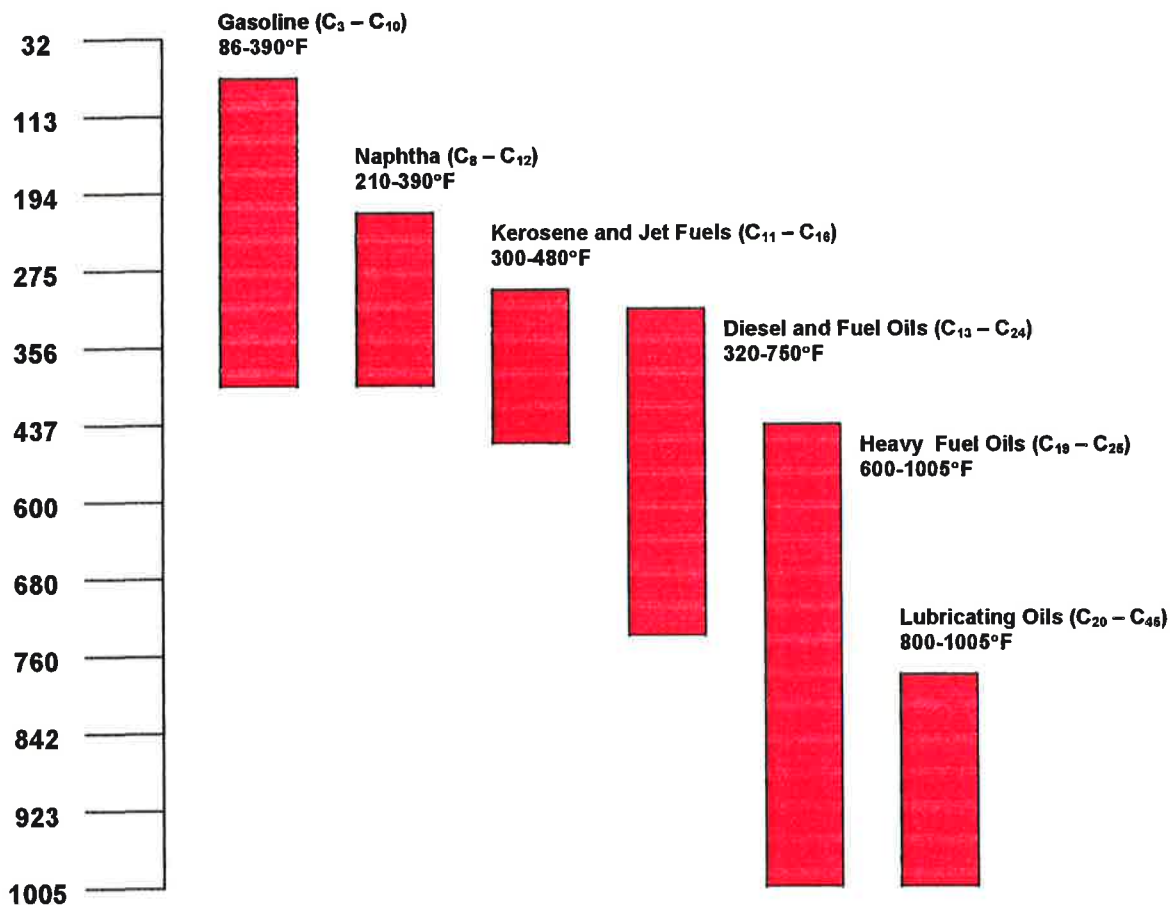
GRO: ADL-AF-58 (RESTEK)
SHC, PAH: 96B2400



GRO: NONE
SHC, PAH: AX-S-09 (SAE10)



Boiling Range (°F)



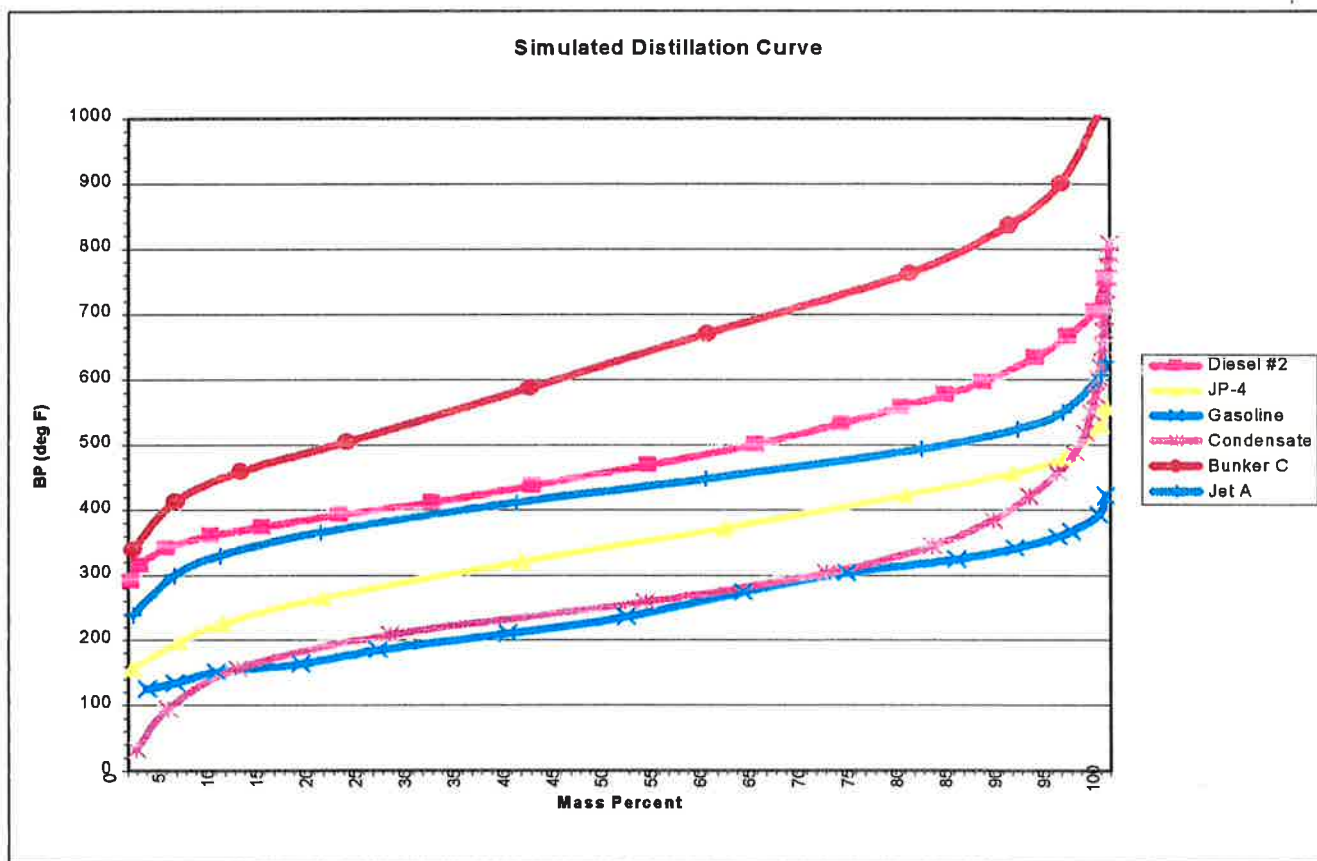


TABLE 3-1
Comparison of ASTM D86 and ASTM D2887 Methods

DISTILLATION PARAMETER	ASTM D86 TEMPERATURE	ASTM D2887 TEMPERATURE
	(degrees C)	(degrees C)
Initial BP	Report	Report
Temp 10 percent Rec (C)	Report	Report
Temp 20 percent Rec (C)	145	130
Temp 50 percent Rec (C)	190	195
Temp 90 percent Rec (C)	245	250
Final BP	270	320

TABLE 3-2
Advanced Chemical Fingerprinting Methods and Application

ANALYSIS	TARGET COMPOUNDS	UTILITY
GRO compounds by GC/FID	Paraffins, Isoparaffins, Aromatics, Naphthenes, Olefins	Light distillate product ID and differentiation
	Gasoline additives (MTBE, EDB, EDC)	Monitoring degree of weathering (evaporation, water washing, biodegradation)
		Determine refining history of gasoline
SHC and TPH by GC/FID	TPHs	Quantification of the concentration of petroleum in soil and water
	C ₈ to C ₄₀ normal and branched alkanes (isoprenoids)	All petroleum contamination – light distillates to asphaltic range organics
		Basic level product ID and differentiation
		Primary weathering (biodegradation) state
		Monitoring biodegradation of crude oils and middle distillates
PAH and heteroatomic aromatic hydrocarbons by GC/MS/SIM		Determine petrogenic vs. biogenic input ratios
	50+ diagnostic target and PAHs series groups	Long-term product and source ID particularly middle distillates and crude oil
	2- to 6-ring PAHs	Long-term weathering
	C ₁ to C ₄ alkyl homologues	Biodegradation indices
		Crude oil vs crude oil or crude oil vs other sources (e.g. coal-derived liquids)
Volatile aromatic hydrocarbons by GC/MS	BTEX	Light distillates (gasolines, kerosene, aviation fuels)
	Alkyl benzene groupings and distribution	Some ability to assess weathering
	Gasoline additives (MTBE)	
Alkyl leads by GC/ECD	Tetraethyl lead and other lead additives	Source differentiation
	Lead scavengers (ethylene dibromide (EDB))	General age dating of gasoline contamination
DDT by GC/ECD	DDT and metabolites	Presence/absence indicates possibility of certain product uses
Properties	Density	Comparison of finished product to specifications
	Simulated distillation	
	Others	Accounting for weathering, used to identify product class-based specification match

4. GROUNDWATER FLOW DIRECTION

4.1 INTRODUCTION

An important element of the dispute between Sun and DSCP is the direction of groundwater flow, and thus, NAPL migration. The current groundwater flow regime in the area of this investigation consist of a major component of flow to the south with some local migration of groundwater toward recovery wells and the sewer near 26th Street. DSCP contends that groundwater beneath the study area flowed from the west to the east at the time of an alleged release, and that it was on this easterly sloping water table that NAPL released in the refinery #1 Tankfarm migrated onto their site. The existing database and integration of geology and hydrogeology data, however, show that groundwater flow today and in the past is primarily from north to south with an east-northeast to the west-southwest trend in the plume's vicinity. There is no evidence to suggest that groundwater ever flowed from west to east. The geology of the site, the presence of a topographic divide on the DSCP property, data from earlier hydrogeologic investigations, and the historical use of groundwater in the area, which tended to strengthen the existence of a westerly component of groundwater flow, provide evidence to support this conclusion.

A series of layers of sediments that are characteristic of coastal plain depositional environments underlie the study area. They range in grain size from very fine silts and clays to very coarse gravels. The available stratigraphic and lithologic information collected during the many subsurface environmental investigations show that through geologic time, the sedimentary units were laid down essentially horizontal by a number of processes and during a number of different geologic events. Over 400 data points have been incorporated into this analysis. The sources used to glean this information include the numerous investigations that have been carried out on each of the sites that comprise the study area, investigations carried out as part of the many construction projects that have been completed on the sites and in the surrounding areas, and those carried out by various governmental agencies.

The geologic record shows that the general study area was dissected by tributaries to the Schuylkill and Delaware Rivers, which are to the west and south of the DSCP site, respectively. In fact,

geologic studies in the general area of this investigation show that the more recent (Quaternary) deposition occurred in paleocurrents that flowed from east-northeast to the west-southwest (Owens and Minard 1979). Furthermore, the lithology confirms the presence of a convex shape to the upper surface of several geologic units in the subsurface of the DSCP property. This convex surface lies in the same general area as a topographic divide, and it may locally influence the groundwater flow direction. The data also show that the grain-size distribution of the sediments beneath the study area vary greatly with an area of finer material in the northern aspect of the Sun #1 tankfield. This finer material would have significantly slowed the rate of ground-water flow and the migration rate of any NAPL that might have been introduced into it. It would also have made it very difficult to recover any NAPL that might have resided in it.

In the vicinity of the study area, groundwater in the most shallow water-bearing unit, the Trenton Gravel Formation, occurs under unconfined or water-table conditions. In the Old Bridge Sand, water occurs under unconfined to semi-confined conditions. This unit is hydraulically connected to the Trenton formation where the clay unit that overlies the Old Bridge is thin, absent, or discontinuous. In isolated areas of small areal extent, semi-confined conditions may exist in this sand unit, when the overlying clay is thicker or less permeable. A more competent clay, the Middle or Lower Clay unit separates the Old Bridge Sand and the Farrington Sand. This clay results in confining conditions in most of the areas where the Farrington underlies the site.

The direction of groundwater flow in the unconfined aquifer is consistent with the observed northeast to southwest orientation of the sediments. Just as there is a ridge evident in the sedimentary record of the DSCP property, there is a corresponding groundwater divide shown on the historical water-table maps (Graham 1946). Water to the east of the divide on DSCP flows south with an easterly flow component, while water to the west of the divide on DSCP flows west-southwest, toward the refinery. This flow regime is consistent with current water-level measurements outside areas of artificial influence, but it differs greatly from that hypothesized by DSCP.

As discussed above, the study area and surrounding environs have been greatly affected by anthropogenic activities. The groundwater elevation beneath the site has also been affected. The average annual water-table fluctuation in the vicinity of the site is about 2-ft. However, extensive

pumping at the Philadelphia Navy Yard from the 1940s to the 1970s and coincident drought conditions in the area that occurred periodically during the same time frame, caused the shallow water table to drop about 10-ft deeper than what would have been considered normal. This lowered water table was only present for a limited portion of this time in the late 1940s and early 1950s. DSCP's consultant, Malcolm Pirnie says that, "no definitive information is available to conclude that groundwater flow directions in the shallow aquifer in the vicinity of [DSCP] were affected by nearby pumping from the lower aquifer." Sun believes, after making a careful and objective analysis of all available data, that the drawdown occurring as a result of Navy Yard pumping and drought conditions simply served to lower the water table regionally. Since this pumping had a regional and not a localized effect, no modifications to the groundwater flow regime in the water table occurred. This area-wide effect would result due to the leaky, discontinuous nature of the semi-confining clay zone overlying the Farrington Sand. Hence, Navy Yard pumping would have no substantive effect on the direction of groundwater flow in the vicinity of the study area.

Groundwater pumping on the refinery property for production water and hydrocarbon recovery is known to have occurred from the unconfined aquifer since the late 1870s and the 1930s, respectively. Unlike groundwater withdrawal from the semi-confined Farrington Sand, centered over 2 miles from the site, this pumping in the immediate study area would have a measurable effect on the local water table. The existing drawdowns and radii of influence around currently pumping wells substantiate this supposition. Similar cones of depression that served to induce groundwater flow toward the points of withdrawal were created around the historical pumping centers. This pumping on the Sun refinery, in aggregate, served to supplement and strengthen the natural westerly component of groundwater flow that is observed on a substantial portion of the study area. No historical evidence exists to indicate groundwater withdrawal from a similar network of pumping wells on the DSCP property. Therefore, any modification of the groundwater flow regime due to localized pumping resulted in flow from DSCP to Sun.

The remainder of this section contains detailed information on the hydrogeology and flow beneath the study area and its immediate vicinity. This additional evaluation supports the conclusions stated above, and shows that until the installation of the 26th Street sewer, groundwater on the Sun property and along the western side of DSCP has flowed primarily south, with a westerly component. Since the installation of the 26th Street sewer in the early 1960s, a trough in the water

table produced first by dewatering during construction and later by leakage into the sewer has both induced flow from the refinery and augmented the natural flow on DSCP toward this anthropogenic feature. The sewer causes the groundwater surface along the western side of the DSCP property and the eastern side of Sun to slope toward it, and then to the south along 26th Street.

4.2 SUN'S ANALYSIS

The ensuing sections (Sections 4.2.1 through 4.2.4) provide the basis for Sun's conclusion that groundwater in the area has always flowed south with a northeast to southwest component. The water table is an undulating surface at which pore water pressure is equal to atmospheric pressure. The position of the water table often follows the general shape of the topography, although water-table relief is not as great as the topographic relief (Fetter 1993). To better understand the migration of NAPL in the study area, the configuration of the water table must be well defined. In addition to its current shape, the configuration of the groundwater surface during several earlier periods must also be defined to the extent possible. These earlier periods include its original configuration before anthropogenic influences, during the period of heavy withdrawal in the 1940s through the early 1960s, and from the 1960s after the installation of the 26th Street sewer to the 1990s when the current site investigations were initiated. To the extent possible, this data should be related to the configuration of the unconfined aquifer. However, groundwater elevation data in the underlying semi-confined aquifer are more extensive in the earlier periods of concern, and this data may be used to supplement the water-table information only when it is available.

4.2.1 The Original Groundwater Configuration

Little actual groundwater elevation data collected prior to the 1940s is available for the area of the site. However, the pre-development water table likely was a subdued representation of the topography of the area. Because the area of this investigation is low lying land, the major modification to the surface during development involved filling areas of lower elevation. With this in mind, a close approximation of the original lay of the land in the study area can be visualized by contouring the top of the Quaternary Alluvium. Figure 4-1 is a shaded contour map of the surface elevation of the upper surface of the alluvium. This surface exhibits an overall slope to the south. As also shown on this figure, an elevated area on the Quaternary alluvium surface occurs in the northeastern aspect of the study area. A less obvious ridge in this geologic unit is also present

starting near the center of the northern boundary of DSCP. This ridge trends to the south across the DSCP property and then turns west and enters the refinery grounds. A ridge with approximately the same location is shown by highlighting the 20-ft contour line on the current topographic map of the area (Figure 4-2). A second smaller ridge along the eastern bank of the Schuylkill River is also shown on this figure. A 1918 survey of the DSCP property further substantiates the pre-development location of a topographic divide in this area. This survey, which is included as Plate 4-1, provides strong evidence of a predevelopment ridge trending roughly northeast to southwest on the DSCP property. The confirmed presence of this topographic high supports the likelihood of a groundwater divide in this area of the site.

This location for a groundwater divide is consistent with other features in the area. The Schuylkill River lies west of the site, approximately 4,000-ft or less from the crest of this ridge. About 1.5 miles south of this suspected divide and approximately 3 miles east of the same area is the Delaware River. The confluence of the two streams is nearly due south of the area under investigation, and because groundwater flow is often a subdued replica of the land surface, an overall southerly direction of groundwater flow would be anticipated. However, the presence of two large streams near the site also implies the existence of a groundwater divide. In such a setting, the water table would probably be represented by a surface sloping down the general direction of topographic incline, in this case to the south, with a less prevalent convex shape trending east to west and cresting near the center of the topographic high, which is, and historically was, on the DSCP property.

Due to the paucity of water-level data collected during the earliest period of interest, the configuration of the pre-development water-table can only be estimated. A pre-development potentiometric surface of the semi-confined aquifer in the southern Philadelphia area was postulated by Sloto (1988). In this theorized groundwater configuration, the potentiometric surface of the Farrington Sand Aquifer shows an indication of an east-west component of groundwater flow near the anticipated divide between the Delaware and Schuylkill Rivers. No actual or theoretical representations of the pre-development water table in the Trenton Sand Aquifer were identified during preparation of this report. However, an overall southern slope of the water table with a convex surface cresting near a topographic high and sloping in the direction of two bounding streams is very consistent with observations made in similar topographic settings.

4.2.2 Period of Heavy Groundwater Withdrawals

The next relevant period of concern is from the 1940s to the early 1960s. During this time frame substantial groundwater was withdrawn from the Coastal Plain aquifers in the vicinity of the site. This is also the time frame during which DSCP alleges that NAPL from the Sun refinery migrated onto their property. Unlike pre-development conditions, more data are available for this time period with respect to groundwater elevations and the flow regime in the unconfined and semi-confined aquifers of the area.

Graham (1946) provides a water-table contour map of the south Philadelphia area based on water level measurements taken in 1944 and 1945 (Figure 4-3). The water-table configuration in the area of the study shows that a groundwater divide occurs east of the Sun refinery. The divide depicted in this figure is just to the east of the center line of the peninsula bounded by the Delaware and the Schuylkill Rivers. This divide turns west and crosses the Sun property south of the DSCP facility, and some indication of both southern and northwestern groundwater flow in the water table on the refinery can be seen in the figure. Figure 4-4 is a potentiometric-surface map of the Farrington (semi-confined) aquifer system prepared from water-level data collected in 1945 (Greenman 1961), the same time period as the water-table configuration shown in Figure 4-3. This figure shows that groundwater in the Farrington (semi-confined aquifer) flows southeast toward the Navy Yard in the study area. At the same time the water table in the study area (Figure 4-3), exhibits no component of southeastern flow. As shown on these two figures prepared from groundwater-level data collected by earlier investigators, drawdown in the Farrington did not induce water-table flow to the southeast in the study area.

Another relevant aspect of Figure 4-3 is that it shows the locations of wells used to develop the water-table map; it also indicates the withdrawal rates of these wells. The map shows two wells on the refinery, and the withdrawal rate of both of these is shown in the legend of the figure to be over 100 gpm. Both wells are shown on the western side of the refinery. Pumping of these wells at the indicated rate would certainly have induced flow in the water-table aquifer to the west in 1945. During August 1997, IST personnel conducted a pumping test at the Sun refinery. Well RW-2 was pumped for 6.7 days at a discharge rate of 225 gpm. During pumping, numerous water-level measurements were made in 14 monitoring wells. As pumpage occurs, the head in the aquifer around the extraction well is lowered (Fetter 1994). Distance drawdown plots of the water-level

data that was collected during the pumping test were prepared. Appendix D contains copies of these distance drawdown plots. These show that drawdown in response to pumping did occur and that it was observed in all directions around the pumping well. The plots also show that between 0.7 and 1.2-ft of drawdown would occur at a distance of 500-ft from the pumping well.

Figure 4-5 shows the locations of groundwater withdrawal points and NAPL recovery wells on the refinery. The use of the wells and the time periods of their installation are also indicated on this figure. Seven wells were used for groundwater supply. These extracted water from the unconfined aquifer. When these wells were operating, similar cones of depression would have developed around them. Data on the operational period and the withdrawal rates for the wells extracting groundwater from the unconfined aquifer are incomplete. However, the locations of these wells clearly show that as cones of depression developed around them, groundwater within the area where DSCP claims that the NAPL plume migrated would have been induced to the northwest or south. The groundwater flow direction and slope of the water table would have been modified. In every instance, the altered direction of the water-table slope is away from the DSCP property.

Water-table contour maps covering later portions of this time period were not identified during the preparation of this report. However, some additional published information relates to the fluctuations of water levels in both the confined and unconfined aquifer. Greenman (1961) provides hydrographs generated from three monitoring wells located at the Navy Yard approximately 2 miles southeast of the study area. These hydrographs show water-level variations in the Trenton Formation, the Sayerville Sand, a geologic unit not identified in borings at Sun or DSCP, and the Farrington Sand. Water-level data in all three aquifers is presented for the time period from around 1945 to 1957. The hydrographs (Figure 4-6) show that the water levels in a monitoring well open to the unconfined aquifer (Trenton Formation) did not vary over 2.5-ft, which is approximately equal to the normal historical fluctuation from 1945 until near the middle of 1950. Considering the minor variation in water levels open to the unconfined aquifer in the monitoring well at the Navy Yard, it is highly unlikely that flow from approximately 2 miles away could have been induced toward the southeast. In addition, the water-table contour map of the unconfined aquifer prepared from 1944 and 1945 data shows no component of southeastern flow in the study area. From the summer of 1950 until June 1953, the water level in the unconfined aquifer rose approximately 12-ft. In the remainder of 1953 and the first half of 1954, the water table returned to

the 1945 to 1950 levels. Between the summer of 1954 and 1955, the water table in both aquifers rapidly declined to levels approximately 12-ft below those of 1945 to 1950. Historical records also indicate that, prior to this time, around 1950, pumping at the Navy Yard began to be reduced (Graham 1952). Since the steepest drop in the water table occurred in 1954 and 1955, after pumping was reduced, it is likely that a regional drought was responsible for this decline. If this were the case, water levels throughout the Philadelphia area would have also declined by a similar amount. No significant change in the flow regime would be expected to occur with the area-wide decline. Based on this information, pumping from the semi-confined aquifer at the Navy Yard did not affect groundwater flow in the shallow unit.

There is another important reason why Malcolm Pirnie's hypothesis of a southeastern flow component is not credible. The NAPL plume on DSCP is actually located more east than south of the known areas of NAPL on the Sun refinery (Figure 4-7). Therefore, if a southeastern flow component were a reality, this could still not explain the plume configuration on the DSCP property. The configuration of the plume under DSCP would require an easterly groundwater-flow direction, not southeast, if it migrated to DSCP from off the site. Malcolm Pirnie does not even hint that historical groundwater flow was from west to east.

4.2.3 Modification of Groundwater Flow in the Immediate Site Vicinity

The next period of interest is from late 1962, when construction of the 26th Street sewer began until the mid-1990s, when widespread environmental investigations began on both of the subject properties. In late 1967, a sanitary sewer was completed along 26th Street. This sewer was also designed with a storm-water by-pass component to handle excess runoff during large precipitation events. The location of this construction extended from approximately 250-ft south of Hartranft Street to the former location of Shunk Street, which is about 200-ft south of Passyunk Avenue. Before undertaking this project, the City of Philadelphia Water Department drilled five geotechnical borings along the path of the proposed sewer. Logs of these geotechnical borings were examined as part of this investigation. The logs contain no mention of hydrocarbon odors or the presence of NAPL. Since extensive tunneling and excavation would be required during installation of the sewer, it is highly likely that the presence of hydrocarbon vapors in the soil samples from these borings would have been noted if they had been detected.

Construction began on the sewer in 1962, and before the tunneling could begin, groundwater pumping was required to lower the water table over a large portion of the construction project. The elevations of the sewer inverts ranged from 10.78- to 8.89-ft below NGVD, which is commonly referred to as sea level. When this is compared to the groundwater elevations at the facility that currently range from 0- to 3-ft above NGVD, a substantial amount of dewatering obviously was required to complete construction of the sewer. The large groundwater withdrawals during this period most certainly modified the normal flow regime. They created a trough in the water table along the length of the proposed sewer, which increased pre-existing westerly flow on the western portion of DSCP and induced flow from the eastern side of the refinery to the east toward this same trough in the water-table surface. After this dewatering began to modify the surface of the unconfined aquifer, NAPL appeared on the groundwater surface in the sewer construction area, and was, in fact, drawn into the excavation. During the remaining period of construction, extensive pumping to lower the water table in the tunnel and to remove NAPL from the working areas was maintained. The lowering of the water table along this trough would have inhibited migration of NAPL between the two properties, if, for the sake of argument, any migration occurred. This is important because the initiation of construction related activities on the 26th Street sewer in mid 1962 represents the disruption of any hypothetical NAPL migration pathway between the two sites.

Appendix F contains copies of the construction specifications for the 26th Street sewer. The sewer is inclined 0.08-ft per 100-ft, and slopes north. The portion of the sewer installed between the DSCP and the Sun refinery was constructed with 48-in vacuum-processed reinforced concrete pipe. A tunnel with at least 6-in of clearance surrounded the concrete pipe. This tunnel annulus was pressure grouted after the 48-in pipe was positioned. Based on this construction design, the grouted tunnel probably extended at least 6-ft above the sewer invert elevations given above. This 6-ft height of the tunnel would still place the entire sewer below the current water table across the study area. Groundwater over most of the site occurs at an elevation of about 3-ft above NGVD. The depth of the sewer below the current water table, excluding areas near pumping centers or other withdrawal points, would then be between 8-ft and 14-ft. With this hydraulic head driving it, small cracks in the concrete and grout would allow a substantial amount of water to enter the sewer.

Infiltration of groundwater to the sewer is occurring, and evidence of the associated lowering of the water table in the vicinity of the sewer can be seen on recent water-table vector plots. Vector plots

with isopotential contour overlays were chosen to depict the groundwater flow direction because they eliminate subjectivity and interpretation, and actually show flow direction. They also contain more detail, and therefore, better show anthropogenic effects such as sewer infiltration. These plots are included as Figures 4-8 through 4-10. These water-table vector plots cover the period from October 1996 until November 1997 and were generated from synoptic gauging data. In almost every instance, flow moves to the sewer and the recovery wells on the Sun property. An overall southward direction of flow is seen on the northern portion of the DSCP property. This changes to southwest toward the sewer in the southern aspect of the property. While on the refinery, flow is predominately southeast. In both instances the groundwater flow reaches the 26th Street sewer and then moves to the south. There is also some indication on several of the maps that the Pollock Street Sewer intercepts groundwater flow in the southern regions of the area of this investigation.

Completed in 1967, the 26th Street sewer receives a substantial amount of groundwater infiltration. Based on the recent potentiometric maps of the area (Figures 4-8 through 4-10) groundwater drainage to the sewer is most prevalent in the area of 26th Street east of the Sun #2 Tankfarm. Because it drains groundwater in this area, the trough created during construction dewatering continues to exist on the surface of the water table along this portion of the sewer (Figures 4-8 through 4-10). This trough, which has been present during both the construction and operation of the sewer, has existed since the middle 1960s, and it forms an impediment to the migration of NAPL between the Sun and DSCP properties. In summary, the construction and continued operation of the 26th Street sewer have impeded any hypothetical migration of NAPL between Sun and DSCP since the middle 1960s.

An additional aspect of the groundwater flow regime that has existed in some form during the 1960s to the present is the operation of recovery wells on the Sun property, especially along 26th Street. Groundwater extraction to control the migration of NAPL has and continues to occur in this area of the site. Table 4-1 summarizes groundwater withdrawal and NAPL recovery operations in the Sun refinery between 1956 and 1989, the period for which information is relatively complete. More detailed records of recovery operations are included in Appendix G. However, Figure 4-5 shows the locations of wells used to recover NAPL on the refinery property that date back to 1932 and production wells that date back to the 1870s. The time periods during which these wells were installed are also indicated on this figure. Only one of the twelve wells along the eastern boundary

of the refinery was installed before 1965, when groundwater flow was altered due to construction dewatering for the 26th Street sewer. This one well, well 10, which was installed in 1951, was south of tankage. After the sewer was completed, leakage into it maintained the modified flow regime from west to east on the eastern side of the refinery, inducing flow toward the post-1969 recovery wells.

The presence of the sewer in combination with the recovery wells operating along the eastern border of the refinery inhibited the potential for the alleged migration of NAPL between the two properties during this period of concern.

4.2.4 Description of Current Groundwater Conditions

The final time frame to be examined is from the middle 1990s to the present. During this time, numerous environmental investigations were conducted on the two properties. A considerable amount of groundwater gauging data was collected during these studies, and a portion of these data are presented as water-table vector maps on Figures 4-8 through 4-10. These figures represent data collected during synoptic gauging events on both properties from October 1996 until November 1997, and they demonstrate that groundwater flow directions have remained essentially unchanged during the entire time frame. The overall directions of flow is to the south. This, however, changes in the vicinity of the 26th Street sewer. Flow on the western side of DSCP is toward the sewer and the recovery wells operating along 26th Street. On the eastern side of the Sun refinery, essentially the same flow pattern exists. That is, groundwater flows east toward the trough in the water table created along 26th street. These water-table contour maps are based on synoptic gauging events where monitoring wells on all of DSCP and along only the eastern edge of the Sun property were utilized for data collection. Figure 4-11 can be used to examine flow on the western portion of the refinery combined with data from one of the synoptic gauging events depicted in Figures 4-8 through 4-10. The water-table contours on Figure 4-11 are the result of gauging data generated during July 1997. This figure shows that the water table on the western side of the refinery slopes primarily to the south with a western component of flow. This figure also shows that groundwater along the eastern side of the refinery and on the west side of DSCP flows toward 26th Street and then south. An eastern component of flow is apparent in the southern area of the eastern side of DSCP; the area where this component of flow becomes identifiable is to the east of the topographic divide discussed in the pre-development water-table configuration.

In summary, the present flow conditions are very similar to those that have prevailed throughout the past. That is, there is an overall southern direction of flow with a component of eastern flow to the east of the topographic divide bisecting the DSCP property and a western component of flow to the west of this same feature. Modifications to the flow regime have resulted from groundwater infiltration to the 26th Street sewer and from the operation of recovery wells in this same general area. The area of NAPL on the DSCP property cannot be explained by this flow regime. In fact, the direction of flow in DPSCs alleged pathway is consistently to the south or southwest. Figure 4-7 shows the locations of NAPL impacts on both properties as isopachs of the apparent hydrocarbon thickness. Areas of impacts on DSCP are more east than south of the NAPL plumes that exist on Sun. The overall flow direction for the entire study area is to the south.

The available data on groundwater flow for the time periods of concern confirms that the plume, as it currently exists, could not have migrated from the Sun property. The overall southern flow of the water-table aquifer in the study area would have precluded migration of NAPL, as described by DSCP. The presence of a topographic divide bisecting DSCP makes it even more unlikely that any groundwater flow from Sun to the DSCP property could have occurred in the past. There has never been a documented flow of groundwater from the Sun Refinery to the DSCP property.



AREA
 TRACT A = 58.813 ACRES
 TRACT B = 1.787 "
 TOTAL = 60.600 "

NOTES
 All Elevations refer to Philadelphia City Datum
 Contour Interval 1'-0"
 Entire property including Tracts A & B located by
 U.S. Government from City of Philadelphia

NO.	DESCRIPTION	STATUS
1	1 Sty. Frame Barn	Demolished
2	1 Sty. Frame Barn	do.
3	3 Sty. Brick Dwelling	do.
4	3 Sty. Brick Dwelling	do.
5	1 Sty. Frame Shed	do.
6	2 Sty. Frame Barn	do.
7	1 Sty. Frame Shed	do.
8	3 Sty. Brick Dwelling	do.

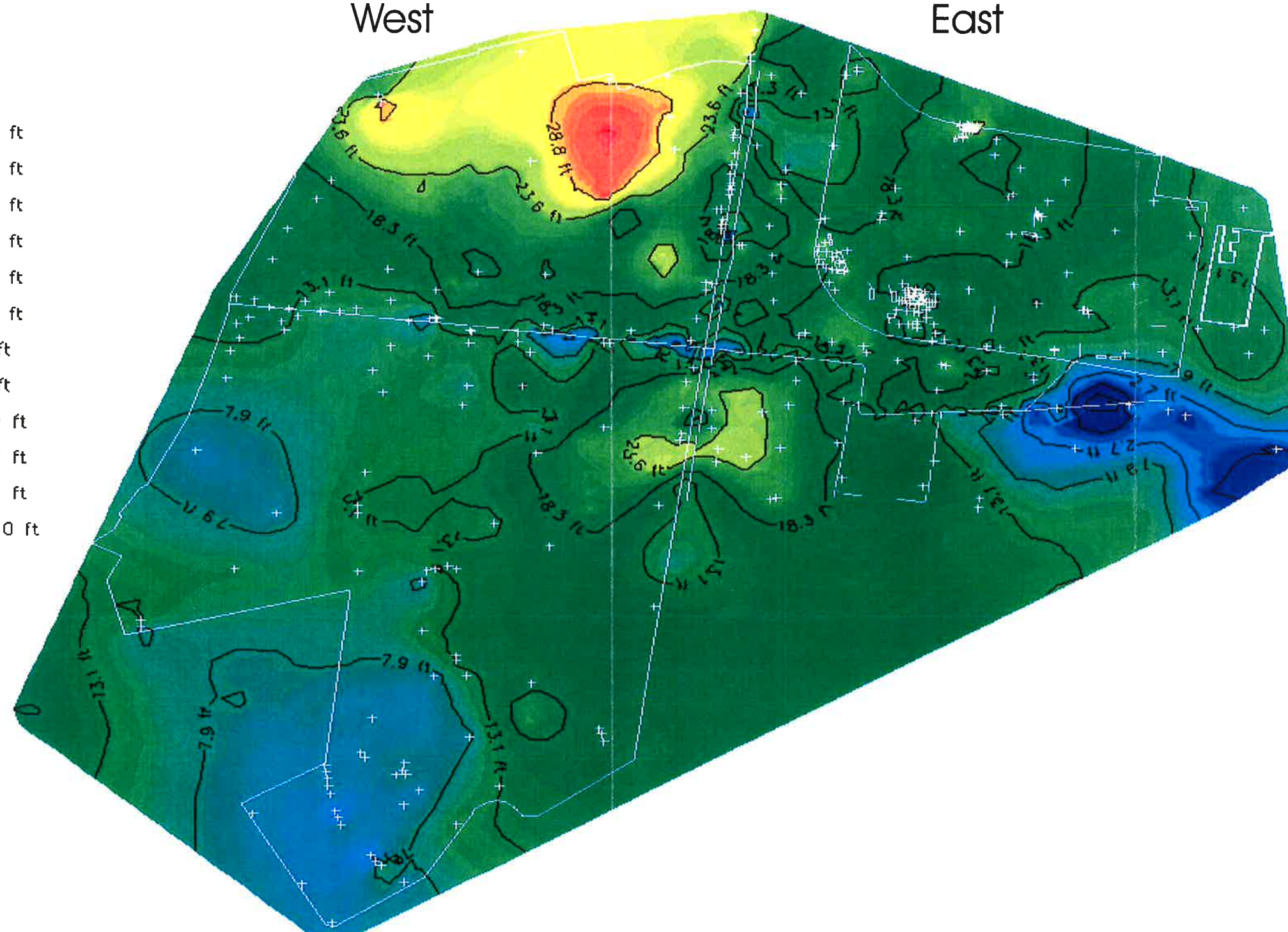
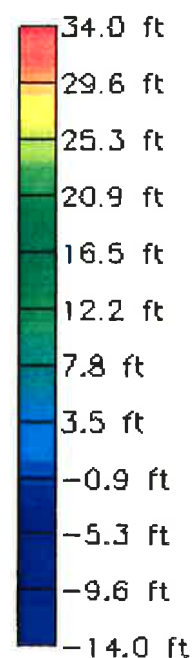
GENERAL QUARTERMASTER INTERIOR DEPOT
PHILADELPHIA, PENNA.
FINAL COMPLETION PLAN
 REAL ESTATE & ORIGINAL TOPOGRAPHICAL MAP
 Constructing Quartermaster E. D. Morden Lt. Col. QMC, NAC
 Officer in Charge M. G. Pomeroy Capt. Eng. RC
 Contractors Wm. Stolle & Sons Corp.
 July 12, 1915 Scale 1" = 100'
 P. D. R. 4: G214-2266



Sun Refinery
West

DSPC
East

Quaternary Alluvium Surface Elevation (ft) Color Scale



0 805 1610

Scale is in feet
(approximately)

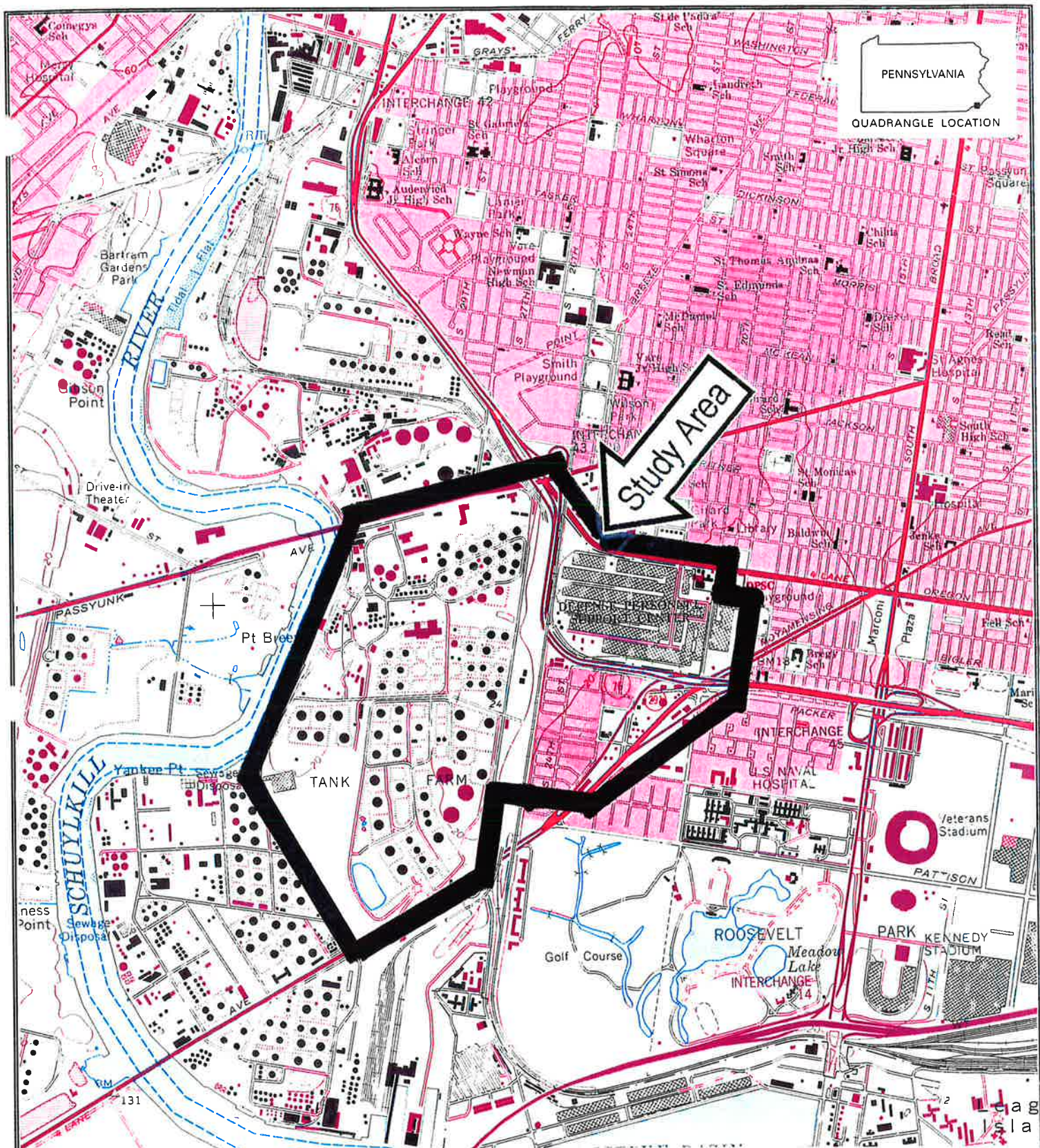
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DATE: 19 FEB 1998	PROJECT NO. SU001H	DWG. NO.

Quaternary Alluvium
Surface Elevation (ft)
Study Area
PHILADELPHIA, PENNSYLVANIA

FIGURE
4-1

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MAP SOURCE:
U.S.G.S. TOPOGRAPHIC QUAD (7.5 Min)
PHILADELPHIA, PA.-N.J., 1967 (REVISED 1994)

Site Vicinity Map

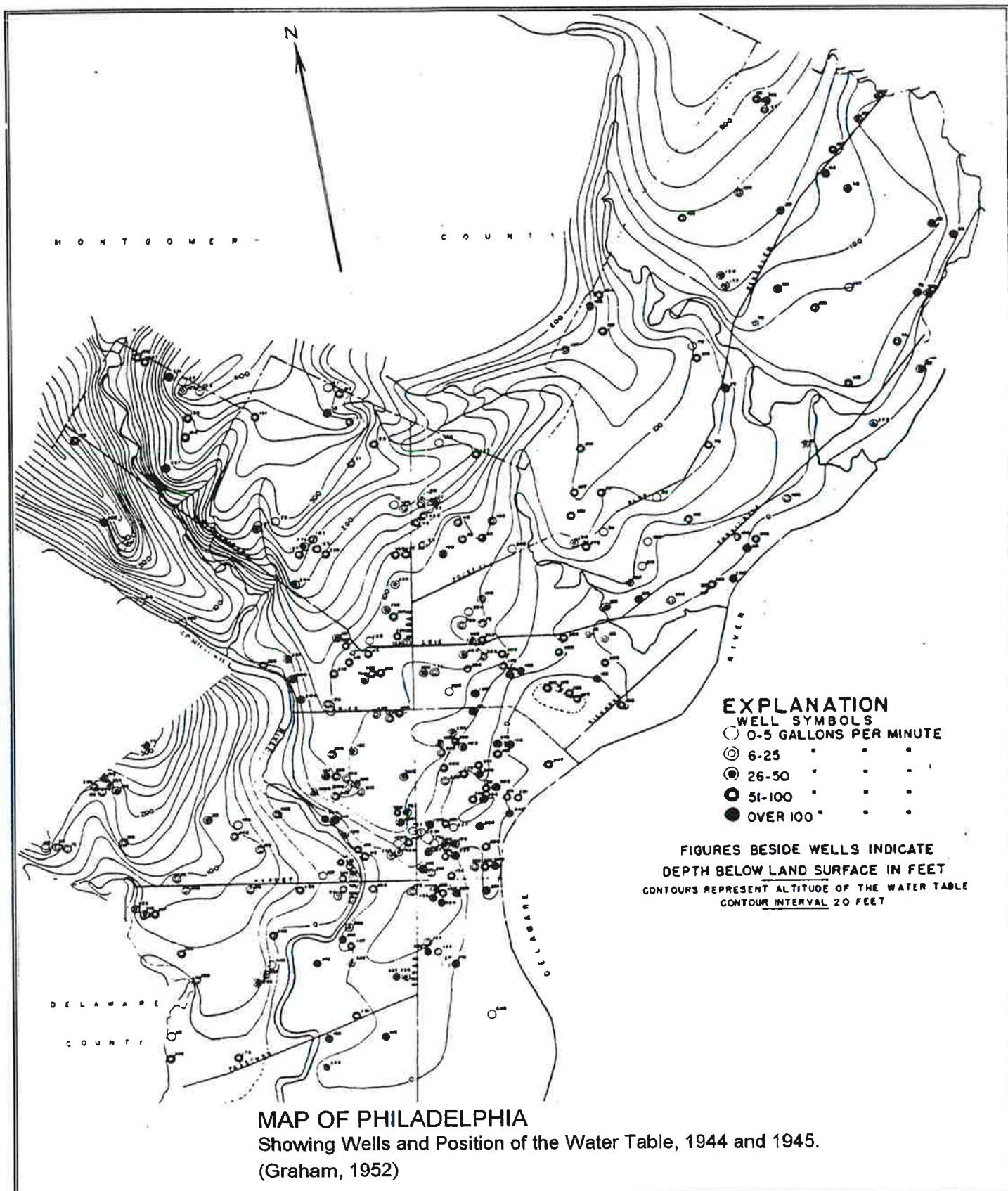
Scale: 1" = 2000'

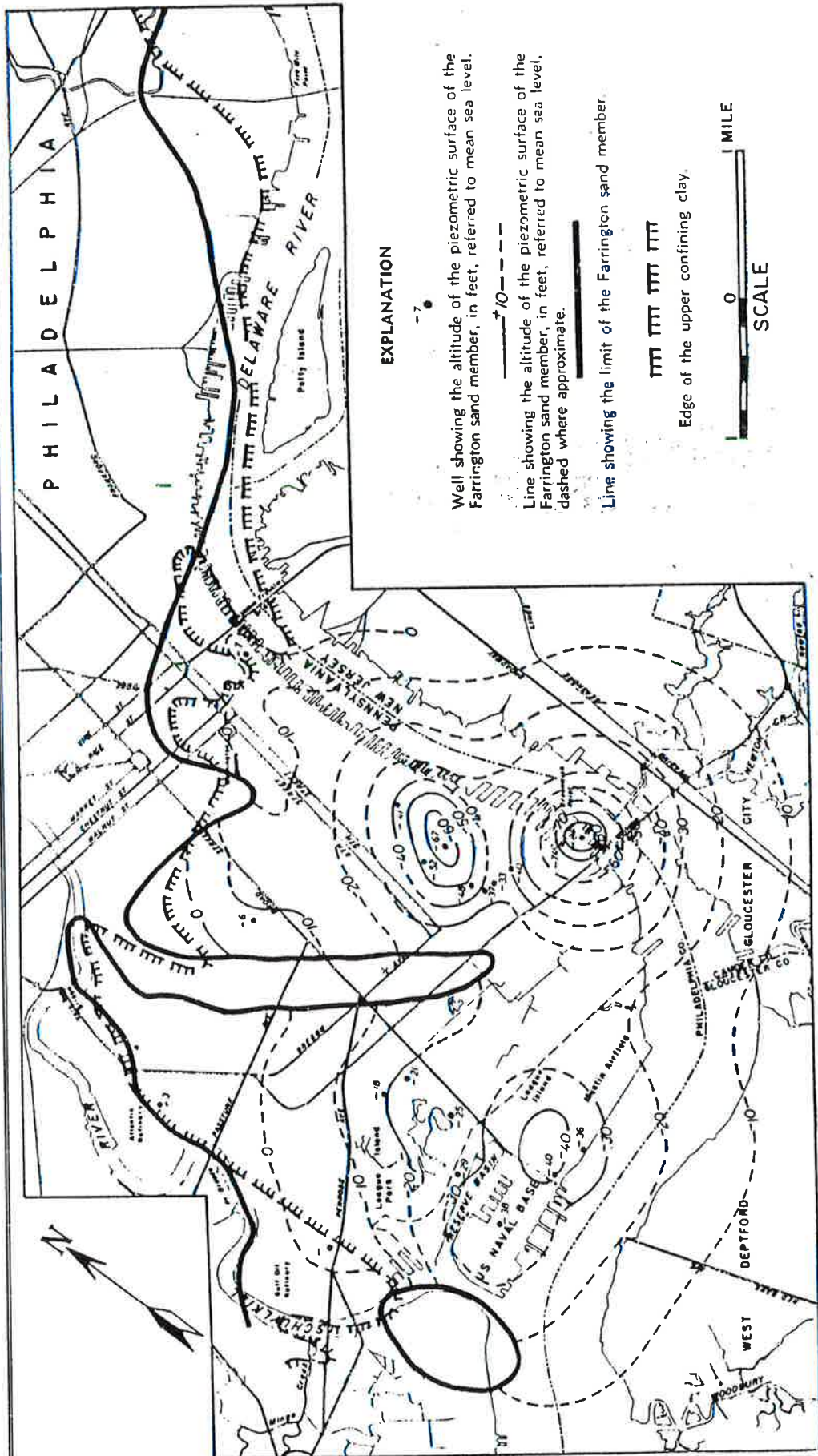


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STUDY AREA
Philadelphia, PA

FIGURE
4-2

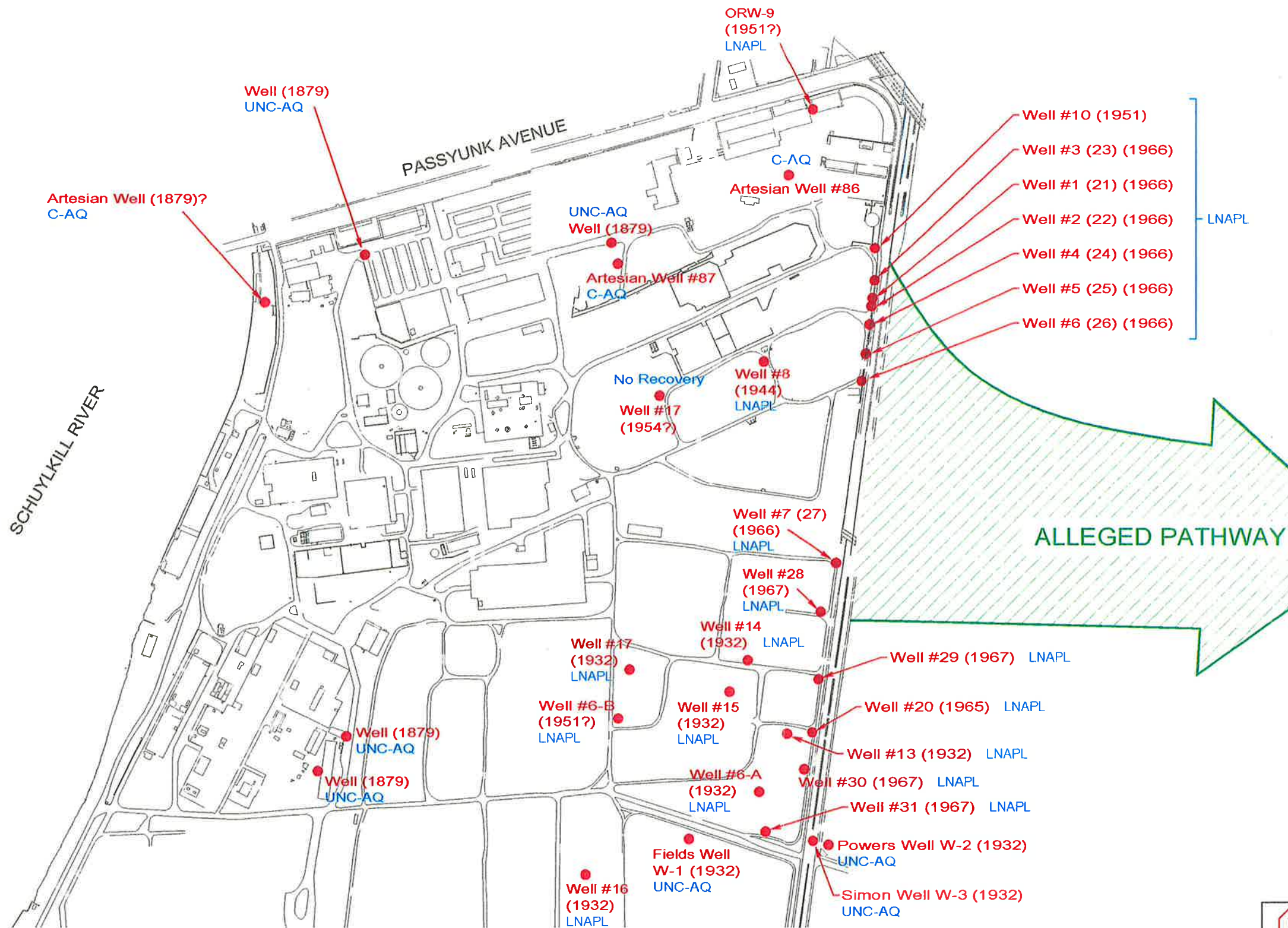




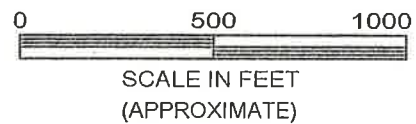
Base from U. S. Geological Survey 7 1/2 minute quadrangle topographic maps.

Map of the Philadelphia area showing a schematic representation of the piezometric surface of the Farrington sand member of the Raritan formation in August 1945.

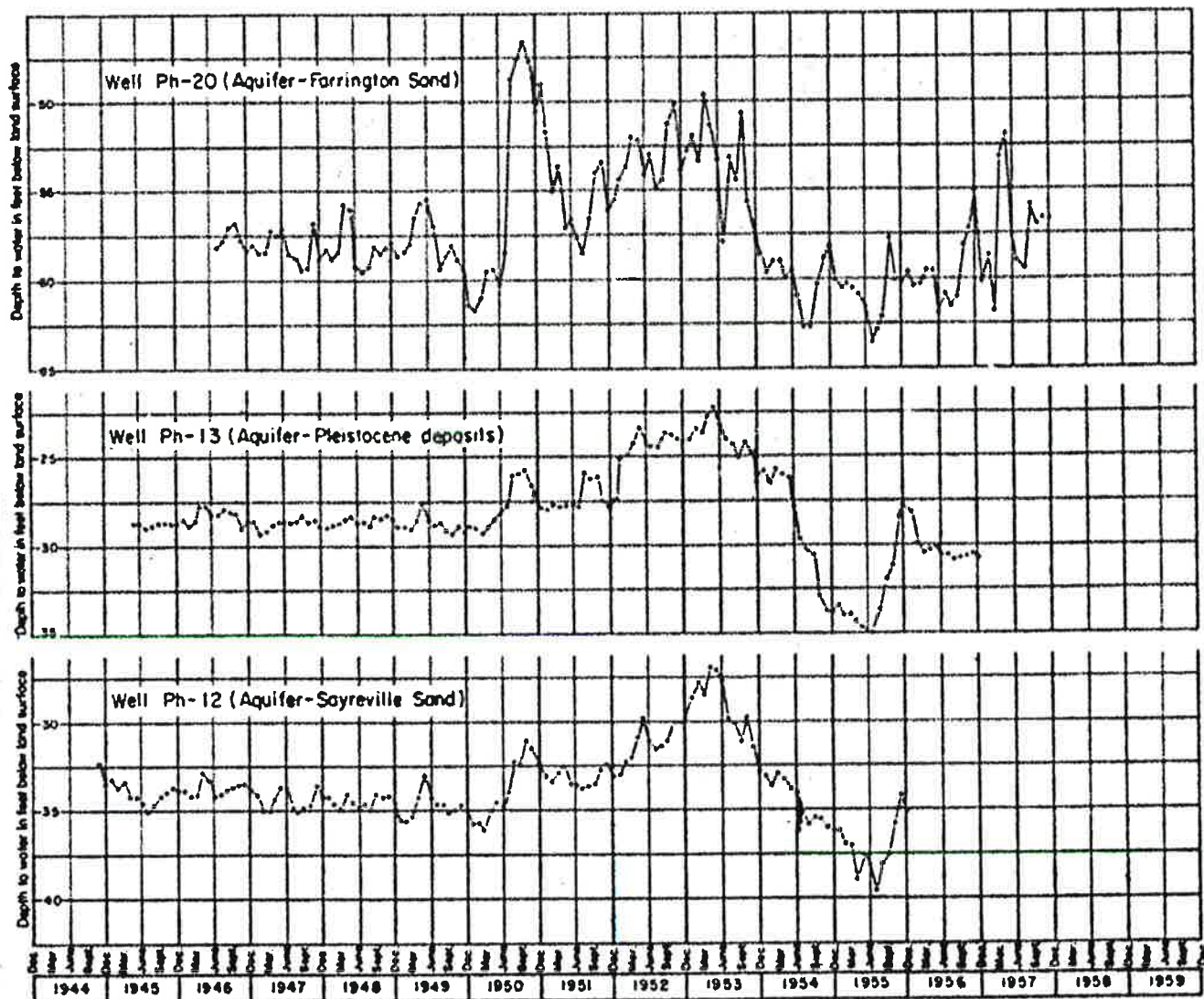
	DRAWN BY: EG		REVIEWED: PKH	APPROVED: HJR
	DATE: 09 FEB 1998		PROJECT NO. SU001H	DWG. NO. 1000



LEGEND	
C-AQ	-Confined Aquifer Well
UNC-AQ	-Unconfined Aquifer Well
LNAPL	-LNAPL Recovery Well



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	REVIEWED: PH	PROJECT NO. SU001H
	APPROVED: HJR	DWG. NO. 11400139
LOCATIONS OF GROUNDWATER WITHDRAWAL POINTS AND NAPL RECOVERY WELLS ON REFINERY		FIGURE 4-5
STUDY AREA, Philadelphia, PA		

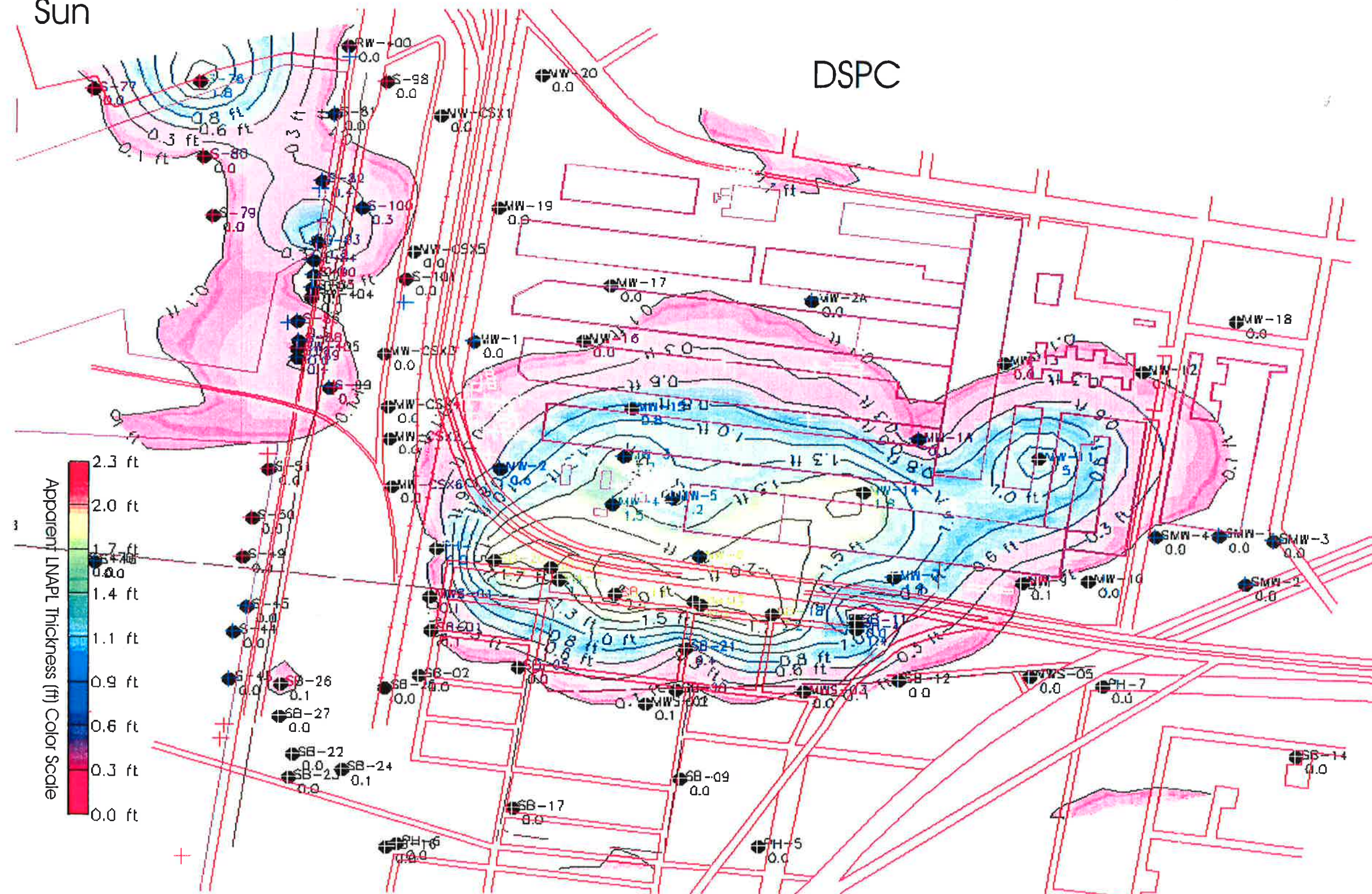


Hydrograph showing the fluctuations of water level in wells at the U.S. Naval Base, Philadelphia, PA (Greenman, 1961)



Sun

DSPC



Apparent LNAPL Thickness (ft) Color Scale

2.3 ft
2.0 ft
1.7 ft
1.4 ft
1.1 ft
0.9 ft
0.6 ft
0.3 ft
0.0 ft

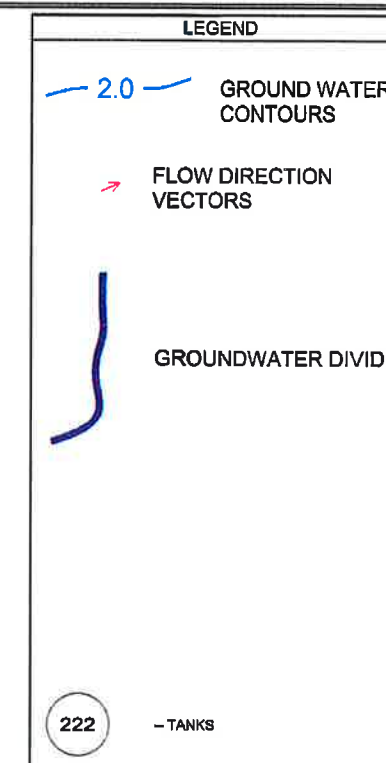
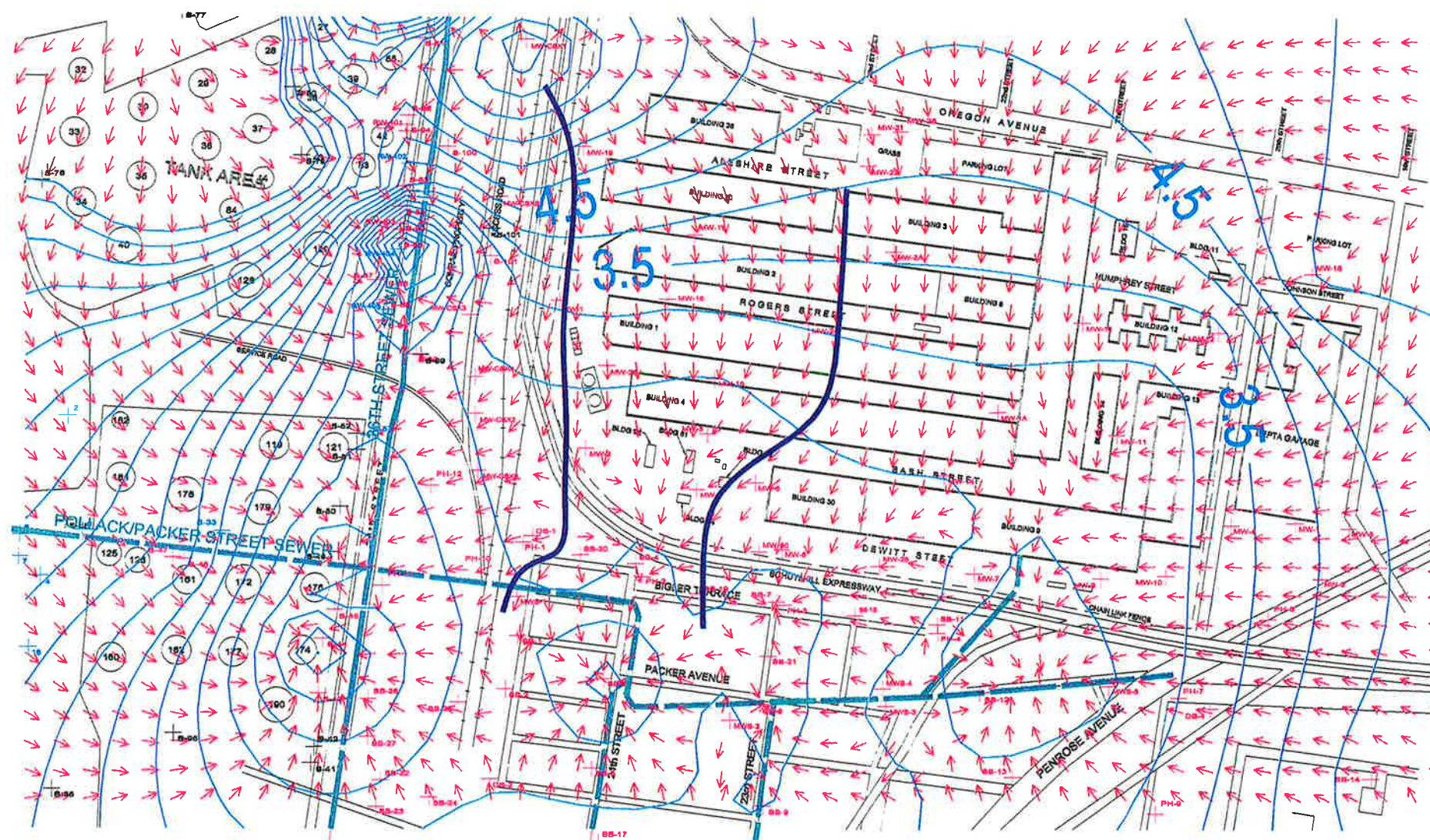
0 400 800

Scale is in feet
(approximately)

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DATE 19 FEB 1998	PROJECT NO SU001H	DWG NO.
Apparent NAPL Thickness (ft) 15, November 1996 Study Area PHILADELPHIA, PENNSYLVANIA		
FIGURE 4-7		

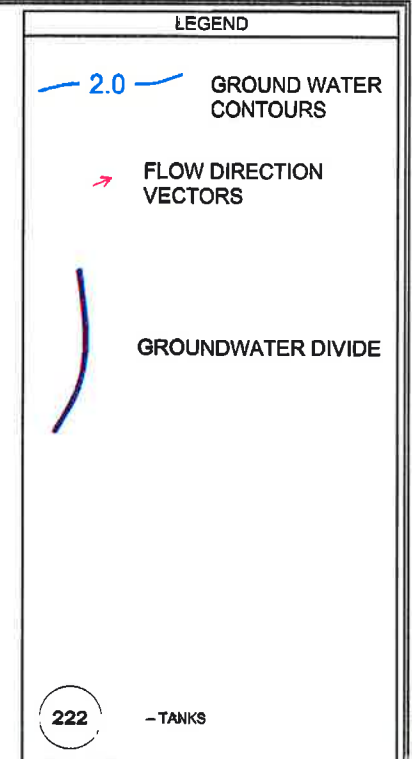
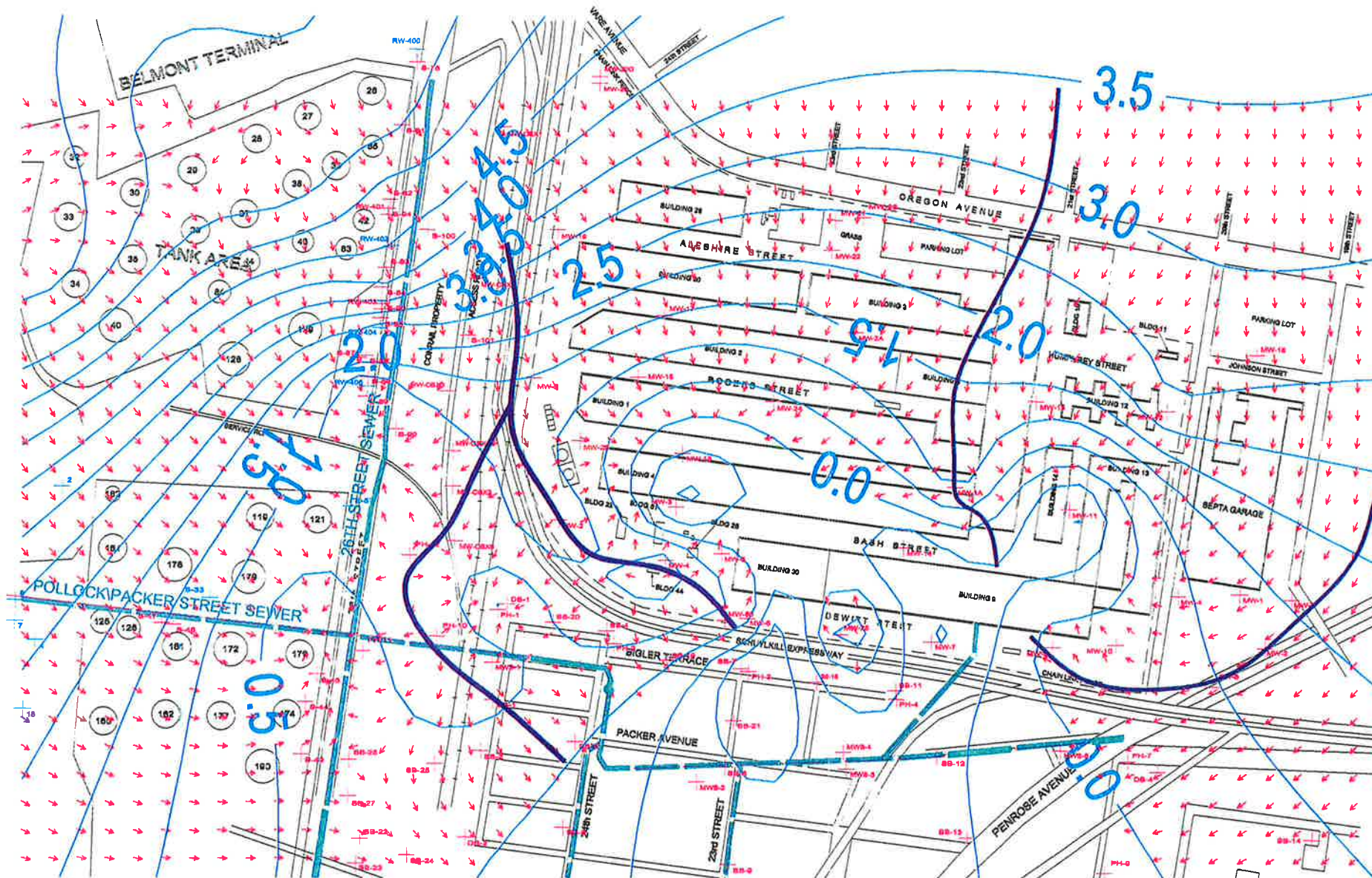
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A horizontal number line with tick marks at 0, 500, and 1000. A shaded bar starts at 0 and ends at 500.

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DATE: 09 FEB 1998	PROJECT NO. SU001H	DWG. NO. SUNHDS
VECTOR ANALYSIS 10/16/96 GROUND WATER ELEVATIONS STUDY AREA PHILADELPHIA, PENNSYLVANIA		FIGURE 4-8

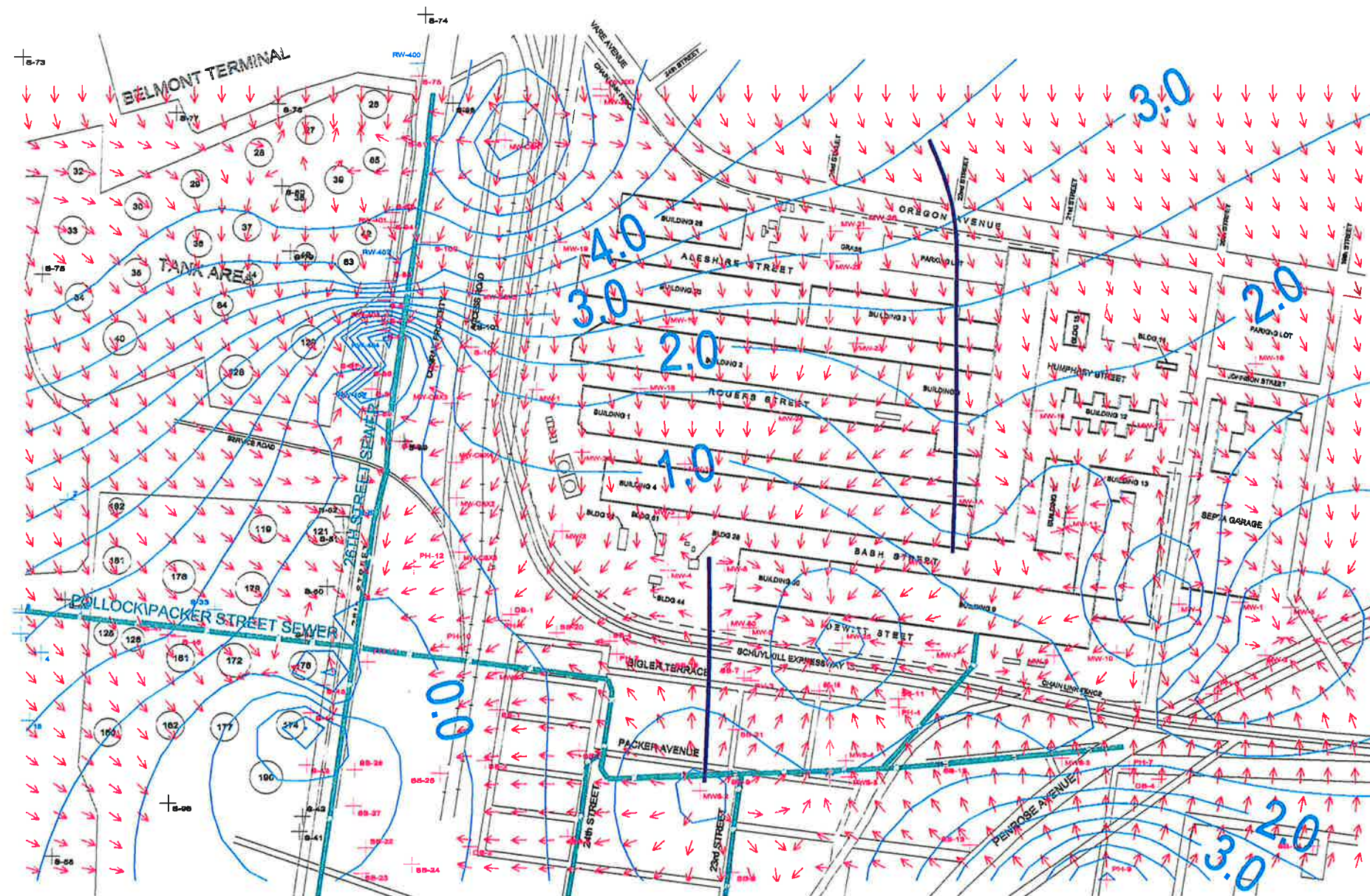


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0 500 1000

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VECTOR ANALYSIS 7/27/97 GROUND WATER ELEVATIONS		FIGURE 4-9
STUDY AREA PHILADELPHIA, PENNSYLVANIA		



LEGEND

2.0 GROUND WATER CONTOURS

FLOW DIRECTION VECTORS

GROUNDWATER DIVIDE

222 - TANKS



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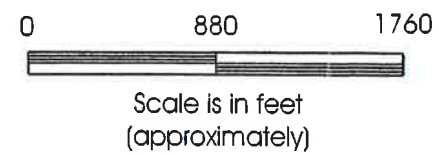
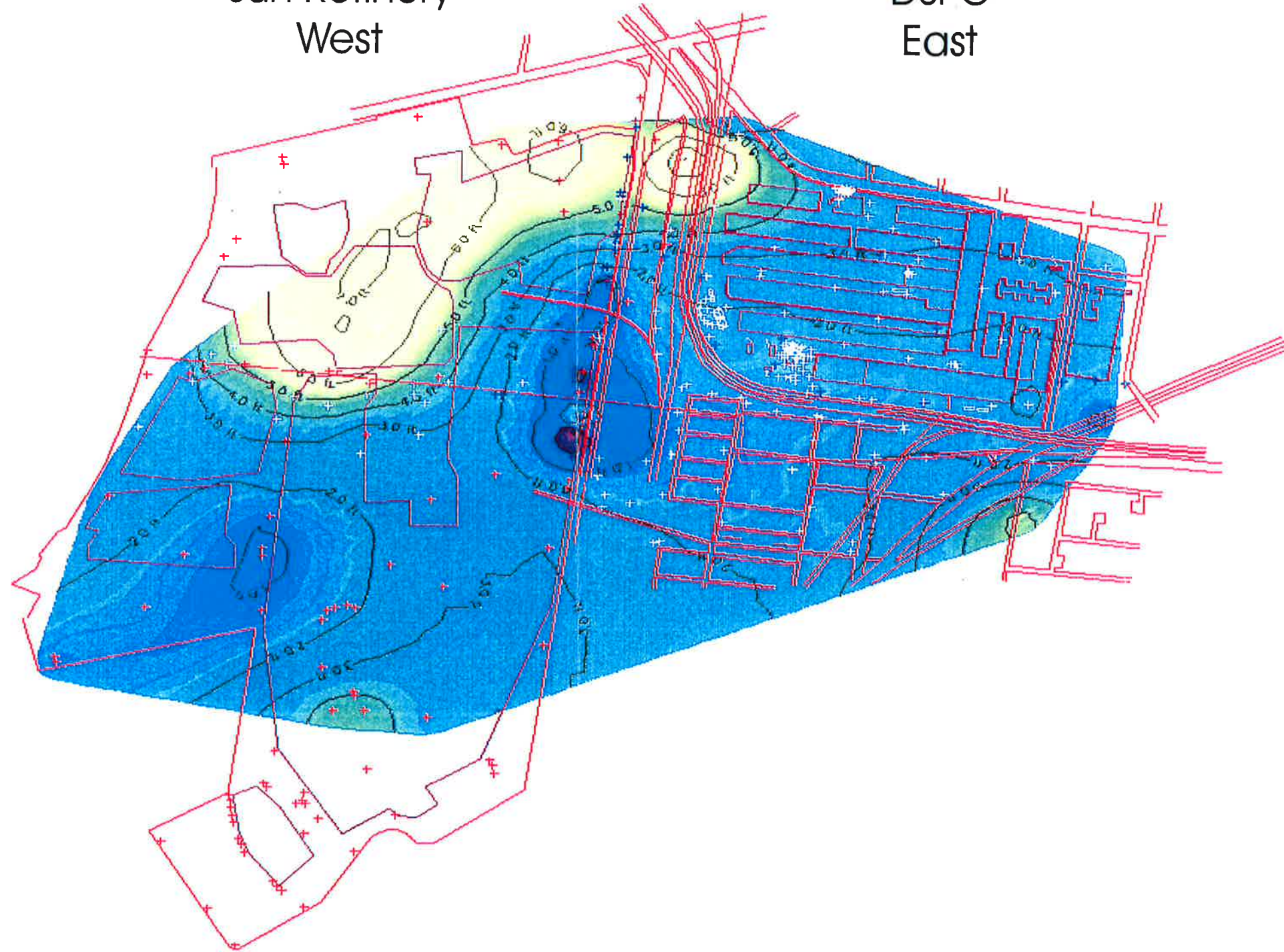
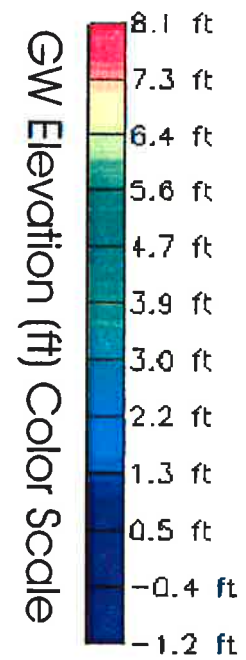


DRAWN BY: EG	REVIEWED: PKH	APPROVED: HJR
DATE: 09 FEB 1998	PROJECT NO. SU001H	DWG. NO. SUNHD1
VECTOR ANALYSIS 11/10/97 GROUND WATER ELEVATIONS		
STUDY AREA PHILADELPHIA, PENNSYLVANIA		
FIGURE 4-10		



Sun Refinery
West

DSPC
East



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DATE 19 FEB 1998	PROJECT NO. SU001H	DWG NO.

GW Elevation Contours
28, July 1997
Study Area
PHILADELPHIA, PENNSYLVANIA

FIGURE
4-11

TABLE 4-1
Groundwater and NAPL Recovery
Sun Refinery
Philadelphia, Pennsylvania

DATE	WELL	OIL PRODUCTION	WATER FLOW RATE	COMMENTS
	#	(gpm)	(gpm)	
1956	16	0.36		#16 producing 4500 bbls/yr to 12/28/56 (0.36 gpm)
	16	0.55		# 16 producing @ 6900 bbls/yr (0.55 gpm)
1965	25	0.09		# 25 produced 97 bbls/mo
	26	0.04		# 26 produced 46 bbls/mo
	8	0.11		# 8 produced 117 bbls/mo
	10	0.00		# 10 produced 0 bbls/mo
	24	0.16		# 24 produced 165 bbls/mo
1966	25	0.06		# 25 produced 65 bbls/mo
	26	0.19		# 26 produced 195 bbls/mo
	8	0.19		# 8 produced 194 bbls/mo
	10	0.01		# 10 produced 11 bbls/mo
	24	1.14		# 24 produced 1175 bbls/mo
1966-1967				recovery wells #1 thru #6 installed
9/66	21	0.85		# 21 produced 0.85BPD @ 63.6 gpm
	27	1.99	6.07	# 27 produced 1.99BPD @ 6.07 gpm
1/67	22	0.01	4.5	# 22 produced 11bbls/mo @ 4.5 gpm
	23	0.004	5.1	# 23 produced 4 bbls/mo @ 5.1 gpm
	21	0.002	4.9	# 21 produced 2.1 bbls/mo @ 4.9 gpm
	25	0.004	5	# 25 produced 3.6 bbls/mo @ 5 gpm
	26	0.004	4	# 26 produced 4 bbls/mo @ 4 gpm
	8	0.35	1.7	# 8 produced 365 bbls/mo @ 1.7 gpm
	9			# 9 well dismantled
	10	0.03	7	# 10 produced 31 bbls/mo @ 7 gpm
	6	0.17		# 6 produced 179 bbls/mo
3/20/68	21	0.00	6	# 21 producing 0 BPD @ 6 gpm
	22	0.00	3.1	# 22 producing 0 BPD @ 3.1 gpm
	23	0.00	4	# 23 0 BPD @ 4 gpm
	24	0.0001	3.1	# 24 producing 0.1 BPD @ 3.1 gpm
	25	0.0006	6.5	# 25 producing 0.6 BPD @ 6.5 gpm
	26	0	4.8	# 26 producing 0 BPD @ 4.8 gpm
9/20/68				# 21- #26 wells are down
1968	27-31			Monthly average for wells 27-31
		0.54	65	Jan- produced 18.43 BPD @ 65 gpm
		0.54	53.6	Feb- 18.55 BPD @ 53.6 gpm
		0.58	71.25	March- 19.8 BPD @ 71.25 gpm
		0.62	74.25	April- 21.15 BPD @ 74.25 gpm
		0.47	75	May-15.95 BPD @ 75 gpm
		0.32	66.75	June- 11.08 BPD @ 66.75 gpm
		0.27	56.5	July- 9.34 BPD @ 56.5 gpm

TABLE 4-1
Groundwater and NAPL Recovery
Sun Refinery
Philadelphia, Pennsylvania

DATE	WELL	OIL PRODUCTION (gpm)	WATER FLOW RATE (gpm)	COMMENTS
1968	27-31	0.41	65.03	Aug- 14.01 BPD @ 65.03 gpm
		0.41	51.74	Sept- 14.16 BPD @ 51.74 gpm
		0.81	69.4	Oct- 27.6 BPD @ 69.4 gpm
		0.83	69.1	Nov- 28.6 BPD @ 69.1 gpm
		0.31	50.7	Dec- 10.6 BPD @ 50.7 gpm
1969	21	0.00	7.5	#21 producing 0 BPD @ 7.5 gpm
	22	0.00	4.3	# 22 producing 0 BPD @ 4.3 gpm
	23 & 24			#23 & # 24 wells down
	25	0.009	2.5	# 25 producing 0.3 BPD @ 2.5 gpm
	26	0.003	10	# 26 producing 0.1 BPD @ 10 gpm
1970	21	0.000	4.55	# 21 producing 0 BPD @ 4.55 gpm
	22	0.000	3.45	# 22 producing 0 BPD @ 3.45 gpm
	23			# 23 down
	24	0.00	2.7	# 24 producing 0 BPD @ 2.7 gpm
	25	0.02	2.2	# 25 producing 0.7 BPD @ 2.2 gpm
	26	0.00	4.65	# 26 producing 0 BPD @ 4.65 gpm
	29	0.11	3.6	# 29 averages 3.6 BPD
	32	0.02		# 32 producing 0.83 BPD
	33	0.06	7.5	# 33 producing 2 BPD @ 7.5 gpm
	34	0.15	12.17	# 34 producing 5.14 BPD @ 12.17 gpm
1971	21	0.00	0.8	# 21 producing 0 BPD @ 0.8 gpm
	22	0.02	2.3	# 22 producing 0.7 BPD @ 2.3 gpm
	23			# 23 down
	24	0.00	0.8	# 24 producing 0 BPD @ 0.8 gpm
	25	0.02	1.7	# 25 producing 0.7 BPD @ 1.7 gpm
	26			# 26 well down
11/16/72				# 8, #10, #21- #25 wells down
	26			# 26 pumping
	6			# 6 pumping to sewer
	27-34			# 27- # 34 wells down
1987?	21-26	0.09	60	# 21- 26 producing 3 BPD @ 60 gpm
doc # 00500	27-34	0.79	10	# 27-34 producing 27 BPD @ 10 gpm
	10	0.04		# 10 producing 1.5 BPD
	8	0.20		# 8 producing 7 BPD
	16			# 16 well down
	6	0.06		# 6 producing 2 BPD
	20			# 20 down
1987	RW-1			WR-1 produced 2564.7 bbls
	PN-1 & PN-2			Pneumatic (2-6") produced 2215.3 bbls
11/4/87	Tank Farm	1.75		Tank farm area producing 60-80 BPD

TABLE 4-1
Groundwater and NAPL Recovery
Sun Refinery
Philadelphia, Pennsylvania

DATE	WELL #	OIL PRODUCTION (gpm)	WATER FLOW RATE (gpm)	COMMENTS
8/25- 12/7/87	RW-1	1.08		RW-1 producing 36.87 BPD
6/21-12/4/87	PN-1 & PN-2	0.84		#PN-1 & PN-2 produced 28.9 BPD
8/87- 3/88	RW-1	0.63		RW-1 produced 646.75 bbls/month
1988	RW-1			RW-1 recovered 10692.03 bbls
	PR-1	0.15	3.6	PR-1 35.78 bbls/week @ 3.6 gpm
	RW-1			WR-1 produced 10679.7 bbls
	PN-1 & PN-2			Pneumatic (2-6") produced 1328 bbls
1989	PR-1	0.32	3.79	PR-1 producing 11 BPD @ 3.79 gpm

5. NAPL PLUME PATHWAY

5.1 INTRODUCTION

A major element of the dispute between Sun and DSCP is the mechanism by which NAPL might have migrated from the Sun #1 Tankfarm to the DSCP property, as hypothesized by DSCP. Sun has examined and analyzed the available geologic, chemical, and hydrogeologic data in the study area, along with the physics of immiscible phase transport, and has carried out a comprehensive fate analysis. Based on this, Sun has concluded that no continuous transport pathway, either geologic or as evidenced by residual saturation, exists between the two sites. Further, Sun has concluded that no such pathway has ever existed.

DSCP contends that migration occurred through a continuous northwest-to-southeast oriented pathway that extends from the refinery #1 Tankfarm, beneath 26th Street, beneath a CSX rail right-of-way, and onto the DSCP property (Figure 5-1). DSCP also contends that hydrocarbon residual in this pathway is all that remains of this hypothesized release that produced an elongated, northeast-to-southwest oriented plume containing an estimated 1,000,000 gallons of NAPL and covering the southern one-third of its site. In this section, Sun will show that there is insufficient evidence of residual hydrocarbon in DSCP's alleged pathway to support DSCP's hypothesis. This is based on application of the basic principles of NAPL fate-and-transport theory, as well as the hydrogeology of the hypothesized pathway.

Before NAPL can migrate through soil, it must displace the air and water that existed in the soil pores before the NAPL was introduced, thereby creating a continuous pathway. The product of NAPL migration is an immobile NAPL fraction held at its irreducible saturation. No amount of groundwater pumping to recover NAPL either in or around the pathway can remove all this NAPL. Natural degradation and weathering also cannot account for a NAPL mass reduction to the point that none exists or is detectable. While substantial dissolution of soluble constituents will occur into groundwater, the mass removal from the residual fraction by this mechanism is negligible. Thus, the absence of NAPL on the water table and the low levels of residual hydrocarbon, which is NAPL

trapped in soil, reflected in the soil analytical data from DSCP's alleged pathway clearly indicate that a major plume never migrated through it. The absence of NAPL, either as floating material on the water table or as product trapped in soil and reflected as TPH concentrations in the soil, scientifically proves that the migration theorized by DSCP never occurred. This section will also confirm, by applying an immiscible multi-phase transport model, that there can be no such pathway from the refinery to DSCP.

However, before explaining Sun's position that there is no pathway, this report will address deficiencies in DSCP's analysis of the "pathway."

5.1.1 DSCP Has Not Established A Pathway

Although DSCP hypothesizes that the plume migrated through a "pathway" beneath 26th Street and the CSX property between the refinery #1 Tankfarm and DSCP, it produces no credible evidence to support the existence of such a pathway. If migration of more than one million gallons had occurred, significant volumes of residual hydrocarbons would unquestionably remain in the pathway. Undisputedly, soil concentrations that are orders of magnitude larger than those detected and reflective of irreducible saturation would be present in such a pathway if one existed. Furthermore, if a plume of the magnitude hypothesized by DSCP had migrated through this area, NAPL would still remain on the water table.

Malcolm Pirnie's foundation to establish the existence of a NAPL plume pathway is extremely weak, biased, and inaccurate. Initially, with the exception of three monitor wells in the alleged pathway (MW-1, CSX-MW3, and CSX-MW4) that reportedly showed NAPL sheening when initially drilled, but no evidence of NAPL since, and one monitor well (S-99), which is at the edge of a Sun plume on the west side of 26th Street and contained NAPL only in the November 1996 gauging event, Malcolm Pirnie's evidence is based on subjective observations of the presence of hydrocarbon contamination noted during well installation. As explained below, the absence of any NAPL on the water table in the hypothesized pathway provides, in itself, strong evidence that the pathway does not exist.

Furthermore, Malcolm Pirnie's report only refers to one instance of historical hydrocarbon contaminated soil in the pathway (boring B from the Schuylkill Expressway construction project).

This alone does not indicate that a pathway between the refinery and the DSCP exists, but Malcolm Pirnie relies heavily on this isolated observation as evidence to establish the presence of the alleged pathway. In fact, entries on other logs for borings installed at the same time in the alleged pathway show absolutely no evidence of hydrocarbon impact to soil. In another instance, borings installed before the 26th Street sewer was constructed also show no evidence of hydrocarbon contamination. This is in direct contradiction to a statement made by Malcolm Pirnie that these 26th Street sewer borings showed that there was contamination in the “pathway” before construction began.

With respect to the Schuylkill Expressway project, Malcolm Pirnie points to boring B for evidence of a pathway. Geotechnical boring B was drilled between December 1952 and February 1953 for positioning the Schuylkill Expressway underpass beneath the, then, Pennsylvania Railroad (PRR) tracks (Figure 5-2). The boring log for boring B (Figure 5-3) describes “oil soaked sand, gravel and clay” between elevations of 11.3-ft above mean sea level (MSL) and 2.7-ft below MSL. The log for Boring A (Figure 5-3), which is approximately 100-ft northwest of boring B and was installed as part of the same effort, does not mention oil, gasoline, or hydrocarbon, even though it lies directly between DSCP and the Sun refinery in the alleged pathway. In fact, none of the remaining eight 25th-Street bridge borings (C through J) mention oil, gasoline, or hydrocarbon, despite the fact that they lie in the middle of the alleged NAPL plume pathway (Figure 5-1). Additionally, borings PB-72, PB-73, and PB-74, which were drilled in the same time frame as the 25th Street bridge borings, do not mention oil, gasoline, or hydrocarbons in their logs (Figures 5-4 and 5-5). These borings were also completed in the alleged pathway (Figure 5-1). Thus, rather than suggesting a “pathway” from the refinery to the DSCP, information from all 13 borings strongly suggests that no such “pathway” exists.

Also, the log for boring B (Figure 5-3) documents “oil soaked” sediments, not JP-4, not naphtha, and not gasoline-soaked sediments. This is worthy of note because the “oil soaked sand” was present in the boring at an elevation of 11.3-ft above MSL, which is over 8-ft above the current groundwater elevation and approximately 11-ft above the water table at the time the boring was drilled. The historical water-table elevation is based on saturated soils described in the log for boring A at an elevation of 0.0-ft. The location of Boring B is 170-ft west of the 200,000-gallon fuel-oil ASTs in the southwest corner of DSCP and over 800-ft southeast of the nearest Sun tank

(Tank 83). Tanks 128 and 129, which are in the vicinity of DSCP's hypothetical refinery source and are several hundred feet closer to boring B, were not built until the early 1970s (Harroun, Inc. 1970), which is after DSCP's alleged refinery release. Therefore, they could not have been the source of this hydrocarbon. Also, as mentioned above, the logs for borings A and PB-73, which lie directly between Sun and boring B, did not indicate the presence of hydrocarbons. This shows that petroleum contamination in this area either was sourced above the water table at DSCP and migrated west on the water table, on a fine-grained unit in the vadose zone, or from above the boring in the railroad yard.

With respect to the 26th Street sewer construction project, Malcolm Pirnie states that, "borings completed in 1963, prior to the 26th Street sewer construction project, and the construction work on the sewer in 1965 indicated extensive presence of petroleum along 26th Street." This statement regarding the pre-construction borings is flatly wrong.

In 1958 and 1961, seven geotechnical soil borings were drilled along 26th Street in preparation for construction of the 26th Street sewer (Figure 5-1). These were installed before construction was initiated. All seven of the boring logs, including three from borings in the alleged NAPL pathway between Sun and DSCP, make no mention of oil, gasoline, or hydrocarbons of any kind (Appendix F). In preparation for construction of the Passyunk Relief Sewer, boring 15 was drilled in 1962, approximately 1,250-ft east of the Schuylkill River in Passyunk Avenue between the Philadelphia Gas Works (PGW) and the Sun refinery. The log for boring 15 (Appendix F) states that the soils just below groundwater at a depth of approximately 34-ft were "saturated with an oily liquid." This shows that logs of borings made during the construction of the sewer would have reflected evidence of petroleum contamination if it in fact existed. Since no impact was noted in soil borings along 26th Street, no such contamination existed before the construction was initiated. It is true that records from construction of the 26th Street sewer reflected petroleum contamination after construction of the sewer began in 1962. De-watering activities, associated with construction of the sewer, necessarily induced flow of hydrocarbons and groundwater into the sewer, as detailed in Section 4. Until the construction of the sewer began in 1962, there is no evidence that hydrocarbons were present in the alleged pathway below 26th Street or the CSX property.

Further evidence that no “pathway” from the refinery exists is gleaned from historical DSCP borings. In 1987, numerous borings were drilled on the DSCP property as part of the Fuel Contamination Study (1988). Several of these borings along the west boundary of DSCP are pertinent to this pathway analysis, specifically CH-2A, CH-3A and DH-9 (Figure 5-1). The log of boring DH-9 (Appendix B) is particularly noteworthy because it lies in the alleged plume pathway. Soil samples collected and laboratory analyzed from depths of 17- to 17.5-ft (above the water table) and 21.7- to 22.2-ft (below the water table) in DH-9 contained no detectable hydrocarbon (less than 40 mg/kg each). The boring log from CH-2A (Appendix B), located on the downgradient edge of the DSCP plume, indicates that NAPL (1/16-in) was floating on the water table. A soil sample from CH-2A, collected from a depth of 21.7-ft (just below the water table), contained TPH concentrations of 18,673 mg/kg, clearly in excess of residual saturation. The analytical data from CH-3A (Appendix B), which is in the extreme northeast corner of DSCP and outside the alleged pathway indicates that soil samples collected from depths between 19.5- and 25.0-ft had TPH concentrations of no more than 192 mg/kg. Samples of the alleged pathway had among the lowest TPH concentrations found in any of the analyses carried out. Further, in its analysis, DSCP only considered those samples that best fit its hypotheses; the others were ignored.

Interestingly, Kemron/Versar in its July 1995 Final Phase I Remedial Investigation/Feasibility Study Report for DSCP concluded that there was no “pathway” from the northern portion of the refinery south yard to the DSCP facility. Kemron/Versar (1995) installed two monitor wells in the CSX right-of-way in February 1995. CSX-MW1 was drilled north of the alleged pathway due east of Tank 85 on the Sun property (Figure 5-1). Maximum PID measurements in this boring were 60 ppmv at a depth of 51-ft BLS (just below the water table). Soil samples, collected from depths of 47- and 49-ft in the same boring were laboratory analyzed to determine the concentration of TPH. The highest measurable TPH concentration detected in the samples was 28 mg/kg, also well below residual saturation. This concentration was detected in a sample collected at a depth of 47-ft. The second boring (CSX-MW2) was drilled in the southern aspect of the alleged pathway due east of Tank 121 in the Sun #2 Tankfarm (Figure 5-1). The maximum PID response in this boring was 400 ppmv at a depth of 47-ft (just below the water table). Soil samples were collected from depths of 45- and 47-ft and were analyzed to determine the concentration of TPH. The highest measurable TPH concentration in the samples (620 mg/kg) was in the sample collected at a depth of 45-ft.

After its study, Kemron/Versar (1995) state on page 13-6 of its report:

“Free product does not appear to have migrated onto the [DSCP] site from a northwest direction following ‘regional groundwater flow patterns’. Although low levels of DRO contaminated media were detected in the northwest corner of [DSCP], no discernible transport pathway for the free product plume was recognizable from the analyses of soil and groundwater samples collected in this area. If the gasoline/diesel plume entered the [DSCP] from the northwest, residual soil concentrations bearing this chemical signature should be evident in the silty, fine grained soils that comprise the aquifer.”

With the exception of the groundwater flow direction, this is consistent with Sun’s position.

Even before Kemron/Versar issued its final report, it recognized that there was inadequate evidence of a “geometric connection” between the refinery and DSCP. At meetings held January and March 1995 with representatives of DSCP, the Philadelphia District of the USACE, and PADEP, Kemron/Versar said in minutes prepared by it that there was no geometric connection that tied the DSCP plume to the refinery. Kemron/Versar suggested development of a chemical connection through dissolved-phase hydrocarbon analysis and fingerprinting. Copies of the minutes from these meetings are included in Appendix H.

After Kemron/Versar rejected the initially hypothesized pathway, it put forth a new hypothesis of a southerly to easterly-to-northerly “pathway.” Initially, Kemron/Versar set out to look for a pathway from the #1 Tankfarm in the south yard of the refinery to DSCP. As explained above, it found insufficient evidence to support this hypothesis. The July 1995 Kemron/Versar Final Phase I Remedial Investigation/Feasibility Study Report stated that, in general, the direction of groundwater flow and, therefore, NAPL transport was to the south. This conclusion is consistent with Sun’s interpretation as detailed in Section 4 of this document, and Figures 6-1 and 6-2 of the Kemron/Versar Report (Appendix I). The hypothesis goes on to state that a release from the refinery migrated south along 26th Street, where it intercepted the Packer Pollack sewer; it was then conveyed to the east, where it pooled and migrated north, upgradient beneath the DSCP site.

The primary factor that must have led to this hypothesis is the southerly direction of groundwater flow and thus, NAPL transport. Sun agrees that releases that may have occurred at the refinery would have migrated south. Utilities, such as sewers and their associated trenches, are potential

preferential pathways. These pathways become even more dominant when the sewer leaks, as many do, especially when they are submerged or partially submerged, as in the Packer Pollack system. However, flow in this system is from east to west and away from DSCP; thus, it would have been impossible for the sewer itself to have conveyed the NAPL to the east. Certainly, the bedding material in the sewer trench could be considered a potential preferential pathway; however, to render the hypothesis valid, the NAPL would need to have been conveyed through the bedding material to the east, or crossgradient, and contrary to the flow direction inside the leaky pipe, in a near perpendicular orientation. In keeping with the hypothesis, the NAPL would have then needed to migrate upgradient some 250- to 450-ft to reach the DSCP property boundary and then an additional 800-ft to reach the northern boundary of the plume. The distance to the thickest aspect of the DSCP plume is 600- to 800-ft from the Packer Pollack sewer system.

Before it could test its new hypothesis, Kemron/Versar was replaced with Malcolm Pirnie. Malcolm Pirnie quickly rejected Kemron/Versar's hypothesis that the NAPL migrated south from the refinery, then west to east along the Packer Pollack sewer, then upgradient from the sewer to DSCP. Malcolm Pirnie concluded that this could not have occurred based on the grade of the sewer and groundwater gradient (Malcolm Pirnie 1997a). Malcolm Pirnie then returned to something close to what Kemron/Versar attempted to establish earlier, but rejected--the existence of a "pathway" from the northerly portion of the refinery to DSCP. As described earlier in this section, the evidence does not support this "pathway."

5.1.2 The Residual Content of Soil and the Lack of NAPL in Monitor Wells Proves There Is No Pathway

As discussed in Section 3.2, whenever NAPL has migrated through a porous medium, it leaves behind a trail of residual product that is held at its irreducible saturation. This results either in NAPL trapped in soil as high TPH concentrations in the soil or in the presence of NAPL in monitor wells installed in the pathway through which NAPL has migrated. The hypothesized DSCP pathway is no exception. However, other than subjective visual observations, there is no indication that a large volume, or for that matter, any significant volume of hydrocarbon passed through the soils in the hypothetical pathway. There is no NAPL in any of the monitor wells in the pathway, and there is no evidence of soil that contains residual hydrocarbon at irreducible saturation.

A secondary line of evidence that significant NAPL has not passed through the hypothetical pathway lies in the concentration of dissolved hydrocarbons in groundwater. Were NAPL present on the water table, or were NAPL present in the soils or in the smear zone, there would be concentrations of dissolved-phase hydrocarbon approaching effective solubility. Results of analysis of groundwater samples collected from the DSCP pathway exhibited little or no evidence of dissolved-phase hydrocarbon. Thus, based on these two lines of evidence, there can be no pathway. The ensuing discussion details the analysis that supports this conclusion.

The ensuing discussion details the results of analysis of the residual hydrocarbon data generated through the various subsurface investigations carried out in DSCP's alleged pathway. Immiscible multiphase transport then, has been used to calculate vadose zone and saturated zone residual NAPL saturation concentrations that would be present in a gravely sand soil such as exists in DSCP's alleged pathway. The calculated vadose zone residual saturation concentration is 9,673 mg/kg as TPH and the calculated saturated zone residual saturation concentration is 23,000 mg/kg TPH. These concentrations, then, are the minimum that would be found in the pathway had NAPL migrated through it, excluding fate processes. None of the pathway samples exceed these thresholds.

As discussed earlier in this section, the 1987 borings drilled on the DSCP property as part of the Fuel Contamination Study (1988) indicate that the residual contamination is much less than would be expected if massive NAPL migration had occurred through the area. The log of boring DH-9 in the alleged plume pathway did not contain detectable hydrocarbons (less than 40 mg/kg each). Boring CH-2A (Appendix B), located on the downgradient edge of the DSCP plume, contains the residual concentrations that would exist in DH-9, if DH-9 were in a "pathway." The log for CH-2A shows that NAPL (1/16-in) was floating on the water table; a soil sample collected from a depth of 21.7-ft in this boring contained a TPH concentration of 18,673 mg/kg, which is near residual saturation and is in the concentration range that indicates residual saturation. The log for CH-3A (Appendix B), which is in the extreme northeast corner of DSCP and well outside the DSCP plume, indicates that soil samples collected from depths between 19.5- and 25.0-ft, which brackets the water table, had TPH concentrations of no more than 192 mg/kg, also well below residual saturation and comparable to the concentration in DH-9, although DH-9 is in the alleged pathway.

Also as discussed earlier, the results from Kemron/Versar's February 1995 drilling activities show that residual concentrations are not what would exist if there was a NAPL "pathway" in this area. CSX-MW1, drilled north of the alleged pathway due east of Tank 85 on the Sun property (Figure 5-1), had maximum PID measurements of 60 ppmv at a depth of 51-ft BLS, well below the current water table and in the depth range of the deepest observed water table. The highest measurable TPH concentration detected in the soils, collected from depths of 47- and 49-ft, was 28 mg/kg. This concentration is well below a concentration that would suggest residual saturation (approximately 10,000 mg/kg). Boring CSX-MW2, drilled in the southern aspect of the alleged pathway, due east of Sun's Tank 121 (Figure 5-1), had a maximum PID reading of 400 ppmv at a depth of 47-ft. This depth is in the range of the historically low water table. The highest measurable TPH concentration detected in soils from this boring (620 mg/kg) was detected in a sample collected at a depth of 45-ft. This concentration is also less the concentration that would reflect residual saturation.

Although DSCP drilled four additional wells in the CSX right-of-way, no samples were collected for laboratory analysis to determine TPH concentrations.

5.1.3 Residual Hydrocarbons in Alleged Pathway

The following discussion describes the method for calculating anticipated residual concentrations. This includes the relationships between oil saturation in the vadose and saturated zones is developed. This relationship is then used to calculate TPH concentrations in the pathway that would exist if significant NAPL migrated through the area. The oil saturation (S_o) was calculated for all the above samples using the following equation from ES&T (1994a, 1994b):

$$S_o = TPH \frac{(1 - \phi) 2.65 \times 10^{-6}}{\rho_o \phi} \quad \text{(Equation 5-1)}$$

where: S_o = oil saturation,
 TPH = Total Petroleum Hydrocarbon concentration (mg/kg),
 ϕ = Porosity,
 ρ_o = Ratio of oil to water density.

The calculated TPH concentrations were compared with the theoretical maximum for the same soil type. Tables 5-1 and 5-2 present the results of these calculations. The maximums range from 5,298 to 44,151 mg/kg. Oil saturation for samples collected from CSX-MW1 and CSX-MW2, which are representative of the alleged pathway soils, was calculated based on observed TPH concentrations to be between 0.02 percent (28 mg/kg TPH) and 0.47 percent (620 mg/kg), respectively. This saturation is far less than the maximum unsaturated zone residual saturation (S_{og}) (7 percent) estimated for a gravelly sand, which is equivalent to approximately 9,673 mg/kg TPH. As stated in Section 3.2, the maximum unsaturated zone residual oil saturation is that oil saturation that would be left in saturated soils after NAPL migration has ceased due to insufficient pressure head and gravity drainage has occurred. For the same soil type, the maximum saturated zone residual-oil saturation (S_{or}) would be 17 percent, which is approximately equivalent to 23,000 mg/kg TPH. The S_{og} and S_{or} were calculated using the following equations from ES&T (1994a.):

(Equation 5-2)

$$S_{og} \approx f_{og} S_m (1 - S_m)$$

$$S_{or} \approx f_{or} (1 - S_m)$$

where: S_{og} = maximum unsaturated zone residual oil saturation
 S_{or} = maximum saturated zone residual oil saturation
 S_m = water saturation at field capacity

where: f_{og} = 0.3 (effect of viscosity)
 f_{or} = 0.3 and
 $S_m = 1 - \phi_e / \phi$

where: ϕ_e = effective porosity, and
 ϕ = total porosity

These TPH concentrations, then, are the minimum that would be found in the pathway had NAPL migrated through it.

5.1.4 Dissolved-Phase Hydrocarbon Concentrations in Alleged Pathway

Additional evidence that refutes DSCP's hypothetical pathway exists in the dissolved hydrocarbon phase. As discussed in Section 3.2, when NAPL is in contact with groundwater, a mass transfer from the NAPL to the groundwater occurs through solubilization. The product of this partitioning

process is formation of a dissolved-hydrocarbon phase. Because smear zones and zones that contain hydrocarbon at or near residual saturation contain trapped NAPL, a high concentration dissolved-phase plume would be expected in a pathway through which NAPL had migrated. Kemron/Versar suggested that this should be the case in a pathway between DSCP and the refinery through which NAPL migrated.

Kemron/Versar (1995) collected groundwater samples in March 1995 and analyzed them to determine dissolved-phase concentrations of TPH-GRO, of TPH-DRO, and of BTEX. Figure 5-6 illustrates the dissolved-phase concentrations of benzene. The benzene concentrations were contoured by Sun using a linear kriging algorithm with no linear drift in Surfer 6.0 (Golden Software 1997). The kriged area consists only of the data domain proper; therefore, the area along the southern boundary of DSCP was not closed. This contour map closely resembles the configuration of the current NAPL plume. The highest benzene concentrations are in MW-6 (37,000 $\mu\text{g/L}$) and MW-3 (32,000 $\mu\text{g/L}$), which are in the thickest aspect of the DSCP NAPL plume. Moving to the west and toward the refinery and the alleged pathway, benzene concentrations steadily decrease from 9,100 $\mu\text{g/L}$ in MW-4, to 1,100 $\mu\text{g/L}$ in MW-2, and finally to 87 $\mu\text{g/L}$ in CSX-MW2 in the middle of the alleged NAPL plume pathway. The other monoaromatic hydrocarbons (toluene, ethylbenzene, and xylenes), which are among the most soluble and mobile of the plume constituents, follow this same pattern. As dissolved-phase plumes migrate, the dissolved solute is transported advectively in the flowing groundwater. Through this process, the solute concentration decreases as a function of distance from the source. That is, the highest concentrations are found nearest the source and the lowest nearest the leading edge. The dissolved-phase plume at DSCP is at its highest concentration on DSCP. It decreases toward the refinery and the alleged pathway. This shows that no pathway exists since high dissolved-phase concentrations would be present in groundwater in a pathway with residual hydrocarbon. The high benzene concentrations in MW-6 and MW-3 indicate the presence of NAPL. For example, most service stations with regular unleaded NAPL on the water table will have a maximum of approximately 15,000 $\mu\text{g/L}$ in monitor wells in close proximity to a NAPL plume (API 1985). Concentrations of up to 24,000 $\mu\text{g/L}$ indicate gasolines with up to 3.2 percent benzene in the gasoline (Bruce et al. 1991). CSX-MW2 is over 400-ft west of the edge of the NAPL plume, which is typical of dissolved-benzene plumes.

The edge of the dissolved plume illustrated in Bruce et al. (1991) is over 300-ft downgradient of the free-product plume.

The dissolved-benzene concentrations in CSX-MW2 do not indicate that a large residual fraction of hydrocarbon is trapped beneath the water table. A residual mass of hydrocarbon would result in dissolved-benzene concentration approaching its effective solubility of about 17,000 µg/L, just as that observed in MW-2, which contained 0.95-ft of NAPL and 1,100 µg/L of dissolved benzene. Analyses of soil samples collected at and below the water table in CSX-MW2 contained no detectable benzene. Low dissolved concentrations of benzene in the alleged NAPL plume pathway indicate that the pathway never existed.

5.1.5 Fate-and-Transport Mechanisms Would Not Have Reduced Residual Hydrocarbon

DSCP has also suggested that the mass and, thus, concentration of hydrocarbon in the soils and smear zone in the alleged pathway have been reduced (in some locations to the point that there is no evidence of hydrocarbon whatsoever) by naturally occurring processes (i.e., solubilization, volatilization, and biodegradation). The ensuing discussion evaluates the potential for these processes to have significantly reduced the hydrocarbon mass in the pathway and quantifies the loss for a 50-year period. This duration represents an upper limit of the time that could have elapsed since DSCP's hypothesized release of the JP-4 at the refinery in the early 1950s. These calculations demonstrate that natural attenuation mechanisms could not have significantly degraded the residual NAPL concentration that would be present in the NAPL pathway alleged by DSCP. In the analyses and calculations discussed below, a 50-year time period was assumed. This time window was selected because it is longer than DSCP's 1950 JP-4 release hypothesis. It is conservative since presumably, migration from the hypothetical release would have ceased in 1964, when the sewer was completed. Further, for the same reasons, the 50-year degradation is appropriate for releases that may have been hypothesized to have occurred before 1950. Even after 50 years, only 15 percent of the initial mass of NAPL (assuming a conservative soil-residual pore fraction of 0.01) would have been lost as the result of aerobic biodegradation, solubilization, and volatilization. Thus, natural fate mechanisms could not have reduced the residual hydrocarbon in the alleged pathway to the point that they exist today if NAPL had migrated through it as DSCP alleged.

5.1.5.1 Volatilization

Mass transfer from a dilute solution or a concentrated NAPL mixture to the overlying soil vapor is referred to as volatilization. For dilute solutions (i.e., dissolved-phase hydrocarbon in ground water) under equilibrium conditions, partitioning of mass between liquid phase and soil-vapor may be described by Henry's Law. Henry's Law describes the relationship between a molar concentration (or mole fraction) in a dilute solution and the equilibrium vapor pressure immediately above the solute/solvent mixture:

(Equation 5-3)

$$P_i = HX_i$$

Where:

P_i = Pressure exerted by component i in vapor phase [atm]

H = Henry's Constant [atm]

X_i = Mole fraction of component i in liquid phase

However, Henry's law does not accurately estimate volatilization from concentrated solutions and free-phase hydrocarbon (i.e., NAPL). This is because, from a molecular perspective, volatilization of a solute from a dilute solution is controlled by the relative affinity of the solute molecules for the surrounding solvent (typically water). However, volatilization from concentrated solutions such as NAPL will be controlled by the relative affinity of the solute for other solute molecules which surround it (Weber and DiGiano 1996). Thus, for concentrated mixtures (i.e., NAPL) under equilibrium conditions, volatilization is best described by Raoult's Law rather than by Henry's Law. Raoult's Law describes the distribution of each component of a mixture as follows:

(Equation 5-4)

$$P_i = X_i P_i^v$$

Where:

P_i = Pressure exerted by component i in vapor phase [atm]

P_i^v = Vapor pressure that would be produced above a pure solution of that component

X_i = Mole fraction of component i in liquid phase

The partial pressure may be converted to a mass using the ideal gas law, which states:

(Equation 5-5)

$$PV = nRT$$

Where:

P = pressure [atm]

V = volume of the vapor [m^3]

n = number of moles = $\frac{\text{mass of compound}}{\text{molecular weight of compound}}$

R = Universal Gas Constant = $8.21 \times 10^{-5} \text{ atm} \cdot \text{m}^3/\text{mol} \cdot \text{K}$

T = Temperature [$\text{K} = ^\circ\text{C} + 273$]

The relationships described above permit the estimation of the initial loss of hydrocarbon mass as a result of volatilization with the assumption that the process is equilibrium based. This approach may be further refined by assuming non-equilibrium conditions as the result of diffusion of vapor-phase hydrocarbon away from the NAPL-vapor interface. This effectively results in a continuous volatilization of hydrocarbon components from the NAPL mixture. At non-equilibrium conditions, assuming no advective transport (i.e., no soil vapor extraction or barometric pumping), the rate of interphase partitioning is then controlled by the rate of diffusive flux from the NAPL to ground surface. Volatilization (or flux) from dilute solutions is often approximated by Fick's second law. Fick's Law was developed in 1855 to describe one-dimensional steady-state diffusion of a component i in response to a spatial concentration gradient dC_i/dy (Weber and DiGiano 1996):

(Equation 5-6)

$$J_{i,y} = -D_{g,i} \frac{dC_i}{dy}$$

Where:

$J_{i,y}$ = diffusive flux in one dimension $\left[\frac{\text{mass}}{\text{L}^2_t} \right]$

$D_{g,i}$ = gaseous diffusion coefficient of compound i $\left[\frac{\text{L}^2}{\text{t}} \right]$

Equation 5-6 assumes one-dimensional transport, which is acceptable because the lateral dimensions of the NAPL plume (approximately 800-ft by 1000-ft; Malcolm Pirnie 1996) are significantly greater than depth of the smear zone BLS (approximately 25-ft). Thus, flux is assumed to occur in the vertical direction above the NAPL. Furthermore, Equation 5-6 assumes that the concentration gradient is constant as a function of time, implying a constant NAPL source (a conservative assumption when calculating the maximum possible mass lost).

However, like Henry's Law, Fick's Law is not directly applicable to diffusion above concentrated mixtures. In the case of concentrated mixtures, such as NAPL, the mole fractions of the representative components will be larger than in dilute solutions such as dissolved-phase hydrocarbon in water. As a result, concentrated mixtures such as NAPL will have a higher total vapor pressure than dilute solutions. Assuming that atmospheric pressure is constant at ground surface, a pressure gradient will thus be present between the NAPL and ground surface. As a result, the contribution of bulk-flow transport may not be ignored when estimating the rate of diffusion from a concentrated solution (Weber and DiGiano 1996). The following equation is used to represent the relative contribution of diffusion and diffusion-induced bulk transport on the total flux, N_i :

(Equation 5-7)

$$N_i = -D_{g,i} \frac{dC_i}{dx} + X_i(N_i + N_j)$$

Where:

N_j = total flux of air (=0 assuming stagnant air in vadose zone)

N_i = total flux of compound i (including transport resulting from both concentration gradient and from bulk – solvent flow)

Assuming that the molar concentration at ground surface (X_L) is effectively zero, substituting $C_i = X_i C_T$, and integrating between the source and ground surface yields the following expression for total diffusion from a concentrated source:

(Equation 5-8)

$$N_i = \frac{-C_T D_{g,i}}{L} \ln(1 - X_o)$$

Where:

$$C_T = \text{total molar concentration} = \frac{n}{V} = \frac{P_T}{RT}$$

L = diffusion distance

$$X_o = \text{mole fraction at NAPL/vapor interface} = \frac{P_v}{P_T}$$

The total mass of component i volatilizing from a NAPL plume may be roughly estimated by multiplying the total flux by the lateral area of the plume (800,000-ft²) and the duration of interest (up to 50 years). Also, the source surface area must be corrected for its presence in a porous media.

Thus, the physical dimensions of the NAPL plume must be multiplied by the estimated mean soil effective porosity (0.25) as follows: (Equation 5-9)

$$M_i = N_i n A t$$

Where:

$M_i(t)$ = total mass of hydrocarbon volatilized from NAPL in time, t [mass]

n = mean effective porosity of soil (correction for total area)

N_i = total flux of hydrocarbon component i $\left[\frac{\text{mass}}{\text{L}^2} \right]$

A = source surface area (i.e., area impacted by NAPL) $[\text{L}^2]$

t = duration [time]

To accurately estimate the total mass of hydrocarbon volatilized from a complex NAPL mixture, such as naphtha, the equations above would need to be solved for each compound in the mixture. This exercise is complicated by the fact that the NAPL mixture of interest contains more than 200 quantifiable components. A simpler and more conservative method of estimating the hydrocarbon mass lost due to volatilization is to calculate an upper bound that represents the maximum mass of hydrocarbon that could volatilize. This estimate is based on published chemical properties for the TPH-GRO compounds, the class of compounds that comprises the most volatile fraction in the NAPL mixture. On average, the TPH-GRO fraction used in these calculations comprises 30.0 percent (on a molar basis) of the NAPL that was sampled from monitoring wells PH-3, MW-5, MW-6, and MW-7 on DSCP. To be conservative, the behavior of the TPH-GRO compounds was extrapolated to the entire NAPL sample (i.e., the rate of flux for the TPH-GRO fraction was multiplied by 3.3 to estimate the total flux from the entire NAPL sample). This approach is conservative because the heavier weight hydrocarbons will actually be less volatile than the compounds that comprise the TPH-GRO fraction. Calculations of total flux over 1 year indicate that approximately 0.3 percent of the total mass of the irreducible hydrocarbon fraction is lost due to volatilization (Table 5-3). Over 50 years, approximately 15 percent of the total mass is lost. As Table 5-3 indicates, volatilization is the most significant mass-removal mechanism for NAPL in the subsurface.

5.1.5.2 Solubilization

Components of a NAPL mixture in contact with groundwater will dissolve in the water as a function of both the solubility and the mole fraction of the respective compounds in the parent mixture. Dissolution of hydrocarbon from the parent NAPL mixture into the water will occur until equilibrium is reached, and each compound attains its saturation concentration in groundwater. This maximum, or saturation, concentration is referred to as the aqueous-phase solubility, or more commonly, the solubility. The solubilities of refined petroleum hydrocarbons in groundwater are limited by the fact that water molecules are highly polar while most hydrocarbon molecules are non-polar. Thus, although aliphatic hydrocarbons make up the majority of the NAPL mixture at the site, the TPH-GRO constituents will dissolve into the water to a relatively greater extent than the heavier weight hydrocarbons.

As stated above, the effective solubility of a compound from a complex mixture is a function of both its pure-phase solubility (measured as the maximum dissolved-phase concentration for water in contact with a pure liquid) and its mole fraction in the parent mixture. Appendix J lists the mean solubilities and relative mole fractions for the majority of TPH-GRO constituents in NAPL samples collected from monitoring wells PH-3, MW-5, MW-6, and MW-7 on DSCP. Solubility constants are referenced from published literature values (CRC Handbook of Chemistry and Physics 1993). Mole fractions have been calculated from the molecular weight and the arithmetic mean mass fraction of each compound in the four NAPL samples. The effective solubility of each compound in water in contact with NAPL is calculated as follows:

(Equation 5-10)

$$S_i = X_i S_{i,o}$$

Where:

S_i = aqueous – phase solubility of compound i from complex mixture

X_i = mole fraction of compound i in parent mixture

$S_{i,o}$ = aqueous – phase solubility of compound i from pure liquid

As with volatilization, the estimated mass of the TPH-GRO fraction that dissolves into the water was multiplied by 3.3 to estimate the total rate of dissolution from the entire NAPL sample. This approach is conservative because the TPH-GRO fraction of the NAPL mixture is also the most soluble. Assuming that the NAPL will dissolve into groundwater entering the upgradient boundary

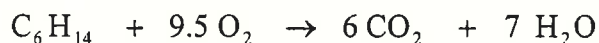
of the impacted zone (measuring 800-ft by 10-ft) and into water infiltrating from ground surface over the impacted zone (800-ft by 1,000-ft), the estimated annual mass of hydrocarbon that could dissolve is approximately 97-lb (44-kg) (Table 5-3). Given a mean laboratory-measured density value of 0.80 g/ml for the NAPL samples from DSCP, this corresponds to approximately 15 gallons (55 L) of NAPL that would be lost as a result of dissolution into groundwater and infiltrating water on an annual basis. Calculations of solubilization over 1 year indicate that less than 0.01 percent of the total mass of the irreducible hydrocarbon fraction is lost. Over 50 years, only 0.12 percent of the total mass is lost through this process.

5.1.5.3 Biodegradation

Natural attenuation of petroleum hydrocarbons in the subsurface includes both biotic and abiotic chemical transformation. Abiotic reactions, such as hydrolysis, are typically less significant than biologically mediated reactions because many hydrocarbons are relatively stable under the environmental conditions found in most aquifers (Borden 1994). As a result, abiotic chemical transformations may be assumed to be negligible in comparison to the other potential hydrocarbon fate mechanisms. Biologically mediated transformations are referred to as biodegradation. Biodegradation is essentially an oxidation-reduction reaction wherein the hydrocarbon is oxidized. Hydrocarbon biodegradation may occur either aerobically or anaerobically. Oxygen (O₂) serves as the terminal electron acceptor during aerobic biodegradation whereas the most common alternative electron acceptors under anaerobic conditions are nitrate (NO₃⁻), ferric iron (Fe⁺³), sulfate (SO₄⁻²), and carbon dioxide (CO₂). Generally, aerobic biodegradation is more thermodynamically favorable (i.e., microorganisms obtain more energy from aerobic reactions) than the anaerobic pathways. Therefore, anaerobic biodegradation will not occur until the available oxygen has been depleted.

Because the hydrocarbon degraders of interest are aerobes, oxygen utilization is a direct measure of hydrocarbon degradation. The relationship between oxygen utilization and hydrocarbon degradation is apparent in the following stoichiometric relationship for the mineralization of hexane.

(Equation 5-11)



In this relationship, 3.5 grams of oxygen are consumed for each gram of hydrocarbon (hexane) mineralized. Hexane is a common representative compound for estimating the mass of

hydrocarbon biodegraded because moderate to lower molecular weight hydrocarbons (C_{10} to C_{24} alkanes and single ring aromatics) are generally degraded more easily than heavier molecular weight hydrocarbon (Borden 1994). Furthermore, on a mass basis, hexane is the eighth most common component of the NAPL TPH-GRO fraction in samples collected from the DSCP property. Therefore, hexane also is also an appropriate site-specific representative compound for evaluating NAPL biodegradation.

In most cases, the availability of the terminal electron acceptor is the rate limiting factor controlling the extent of biodegradation that occurs in a natural system. In addition to the electron acceptor concentration, temperature, pH, and nutrient availability (particularly of nitrogen and phosphorus) may also significantly affect the rate and extent of hydrocarbon biodegradation (Borden 1994, Chappelle 1993). However, because these calculations are intended to estimate the maximum mass loss attributable to biodegradation, it is assumed that these factors (with the exception of the terminal electron acceptor concentration) are sufficient to sustain biodegradation (a conservative assumption when estimating the maximum potential mass lost). Furthermore, reaction kinetics will not be considered a rate limiting condition by assuming that biodegradation of hydrocarbon in the presence of a suitable terminal electron acceptor can be treated as an instantaneous reaction. Thus, the estimated maximum extent of biodegradation will be assumed to be solely a function of the availability of the terminal electron acceptor (i.e., oxygen).

When developing a conceptual model for the degradation of NAPL, it is also necessary to consider the physical conditions under which biodegradation occurs. The indigenous heterotrophic bacteria responsible for biodegradation actually reside in water in the underlying aquifer, in moisture within the soil interstitial spaces, and on the wetted surface of the soil matrix. Furthermore, bacterial metabolism occurs internally within the cell. Thus, substrate (hydrocarbon or other carbon food source) is available only as a dissolved-phase. NAPL can, therefore, only be biologically degraded where the NAPL is in direct contact with the saturated zone or interstitial pore water (i.e., the irreducible water fraction). To be conservative, it is assumed that the rate of dissolution of hydrocarbon from the NAPL will not be a rate limiting step in the biodegradation pathway. Therefore, the primary consideration in estimating the mass of hydrocarbon degraded is the mass of oxygen available to the microorganisms.

For the site-specific scenario of soil-residual hydrocarbon exposed to ground water in the capillary fringe or near the surface of the surficial aquifer, dissolved oxygen (DO) is available from two sources: 1) the groundwater that migrates through the hydrocarbon-impacted zone and 2) in precipitation which infiltrates vertically through the vadose zone to the water table. Vapor-phase oxygen concentrations in impacted soil are typically below 2 percent, and thus are insufficient to support aerobic biodegradation. For both infiltrating water and groundwater, the mass of available dissolved-oxygen will be conservatively assumed to be the solubility of oxygen in fresh water (11.28 mg/L) at 50 degrees F (10 degrees C) and at 1 atmosphere pressure (Metcalf and Eddy 1991). The mass of oxygen available from this latter source may be estimated from the average amount of infiltration per unit surface area. The average total annual infiltration and precipitation rate for Philadelphia, Pennsylvania, is approximately 27.5-in (70-cm) per year and 41.4-in (105-cm) per year, respectively (Leeden et al. 1990, NOAA, Comparative Climatic Data for the United States through 1986). The mass of DO infiltrating per unit (1-m²) of ground surface may be estimated from the following equation:

(Equation 5-12)

$$\text{Mass of oxygen available} = C_{\text{oxygen}} (V_{\text{water}}) = C_{\text{oxygen}} \left(\frac{IAn}{1000} \right)$$

Where:

C_{oxygen} = concentration of dissolved - oxygen [mg/L]

V_{water} = volume of infiltrating water [mL]

I = annual rate of infiltration on water [cm]

A = surface area over which infiltration occurs [cm²]

n = effective porosity of the soil through which infiltration occurs

Assuming an impacted zone in the alleged pathway having the dimensions of 800-ft by 1,000-ft by 10-ft (Figure 5-1), the initial mass of oxygen that is available for biodegradation is 5,634-lb (2,555-kg).

In addition to water initially present, groundwater is assumed to migrate through the impacted zone. Thus, fresh water containing DO would be constantly introduced to the upgradient aspect of the alleged soil-residual hydrocarbon pathway. The maximum mass of DO available from water passing through the impacted zone is 112 kg/yr, assuming that the impacted area has the dimensions of

800-ft (width) by 10-ft (height), as alleged by DSCP (Figure 5-1). This value is estimated from the linear groundwater velocity and the area of the impacted zone. The linear groundwater velocity may be calculated from the hydraulic conductivity of the aquifer, the gradient of the potentiometric surface, and the effective porosity as follows (USGS 1993):

(Equation 5-13)

$$V_{linear} = K \frac{\left(\frac{\partial h}{\partial l} \right)}{n}$$

Where:

V_{linear} = linear groundwater velocity [ft/day]

K = hydraulic conductivity [ft/day]

$\frac{\partial h}{\partial l}$ = hydraulic gradient [ft/ft]

n = porosity (effective) of the soil [unitless]

Given a mean hydraulic conductivity of approximately 30-ft/d, and hydraulic gradient of 0.001, and an assumed effective porosity of 0.25, then the estimated linear groundwater velocity through the alleged NAPL pathway is 0.12-ft/d. Assuming that the pathway is 1,000-ft long (as measured from Sun Tank #42 to DSCP monitoring well MW-1), one pore volume of water will pass through the impacted area approximately every 22 years. DO may also be introduced through infiltration of precipitation. Assuming infiltration of 70-cm/yr (Water Encyclopedia 1993) and a assumed effective porosity of 0.25, an additional 323-lb (146-kg) of DO would be available from infiltration.

In summary, approximately 1,610-lb (730-kg) of hydrocarbon could initially be biodegraded in the first year. This represents 0.04 percent of the initial hydrocarbon mass that would be present in the alleged NAPL pathway. After 50-years, approximately 0.28 percent of the NAPL could have been removed through aerobic biodegradation.

5.1.5.4 Sorption

Sorption is the process by which a molecule in a bulk mixture (gas or liquid) bonds with the solid surface with which it is in contact. Sorption is used to describe both bonding to the solid surface (adsorption) or bonding to the walls of the micropores in the solid (absorption), since it is difficult to differentiate the two processes in the field. From a molecular perspective, sorption results from a variety of attractive forces, including chemical, electrostatic, and physical interactions (Weber and

DiGiano 1996). In the case of NAPL in the subsurface, hydrocarbon molecules in the NAPL mixture will sorb to organic compounds in the surrounding soil matrix (i.e., to naturally occurring organic carbon in the soil). This naturally occurring carbon is often in the form of humic or fulvic acids.

Like other partitioning phenomenon, sorption is an equilibrium process in which a maximum concentration exists for the sorbed molecules on the solid surface. In natural systems, the degree of sorption is limited by the number of bonding sites on the soil matrix. For example, the Langmuir isotherm model assumes that adsorption is ultimately limited by the formation of a monomolecular layer of solute on the solid surface. Although this phenomenon may be significant for very dilute organic solutions, sorption will be a relatively insignificant partitioning mechanism for NAPL hydrocarbon. Furthermore, sorbed hydrocarbon will be detected as part of standard laboratory analytical determinations of soil-residual hydrocarbon concentrations. Thus, sorption will not result in a "loss" of hydrocarbon from soil samples collected within a NAPL pathway. For these reasons, it is assumed that sorption is an insignificant partitioning mechanism for NAPL hydrocarbon and that the majority of sorbed hydrocarbon would be detected with standard laboratory analytical methods.

5.1.5.5 Relative Contribution of NAPL Fate Mechanisms

These calculations demonstrate that natural attenuation mechanisms could not have significantly degraded the residual NAPL concentration that would be present in the NAPL pathway alleged by DSCP. Even after 50 years, only 15 percent of the initial mass of NAPL (assuming a conservative soil-residual pore fraction of 0.01) would have been lost as the result of aerobic biodegradation, solubilization, and volatilization. Given the conservative assumptions used in these calculations, it is likely that this is an upper bound on the rate of natural attenuation occurring in the subsurface. In conclusion, natural fate mechanisms could not have reduced the residual hydrocarbon in the alleged pathway to less than the laboratory analytical detection limits if NAPL had migrated through it as DSCP alleged.

5.2 MODELING VERIFIES SUN'S CONCLUSIONS

Immiscible multi-phase transport modeling of NAPL in the study area was performed using ES&T's Areal Multiphase Organic Simulator (ARMOS) code. For the purposes of this evaluation, the ARMOS modeling was used as a tool to verify Sun's conclusions, reached by analyzing relevant facts. Before initiating the modeling efforts, available data were analyzed, hypotheses were developed and tested, and conclusions were drawn based on the scientific principles discussed above. The modeling was used to test the truth of these conclusions. It was also used to test many different scenarios using even more conservative and implausible input parameters to force, if possible, a release at a hypothetical refinery source to give rise to a NAPL plume on DSCP with approximately the configuration and morphology currently observed. However, none of the scenarios even approached the current configuration and morphology. Thus, the model was also used to ensure that the scientific analysis had not missed potential scenarios that may have led to the conclusion that the DSCP plume was sourced on the refinery. None were found.

The multi-phase modeling of NAPL in the study area was conducted to meet three objectives:

1. Confirming the conclusions developed through the evaluation of site-specific physical and chemical data
2. Attempting to force a hypothetical refinery-sourced plume to migrate to DSCP
3. Ensuring that no potential pathways were overlooked in the physical and chemical analyses.

As discussed above, ARMOS (ES&T 1994a) was the model of choice because of its ability to model multi-phase fluid flow. However, the model has two major drawbacks: it can only model two-dimensional flow, and the number of grid nodes is limited to 2,500. Details concerning the ARMOS model, including the governing equations and the general assumptions used, are presented in Appendix K.

The modeling approach used to address NAPL migration in the study area was essentially traditional. That is, a series of scenarios were developed to investigate the various physical settings and release configurations that could have conceivably allowed NAPL from the refinery to migrate to the DSCP. This approach was attractive because it allowed looking back in time to carry

simulations through DSCP's assumed time window until the present. It also allowed the physical world to be manipulated in order to test implausible sets of circumstances. The ensuing sections of this document discuss the results of these scenarios. Details of these scenarios are given in Appendix K.

5.2.1 Scenario 1

This scenario was run to develop a visualization of a NAPL plume that might develop in a worst-case situation (i.e., from constant long-duration, relatively small-volume releases combined with short-duration, high-volume releases that hypothetically occurred in both tankfarms of the South Yard over the entire 127-year operational history of the refinery). As such, the scenario covers the period from 1870, when refining operations were initiated, to the present. The groundwater flow direction was set from northwest to southeast, which is DSCP's hypothesis with which Sun disagrees. The hydrologic regime included hydrocarbon recovery at various locations on the refinery comparable to known recovery operations, the installation of the 26th Street sewer, leakage into the sewer, and water-table fluctuation. The total volume of NAPL release in this scenario was 84,524,000 gallons, 32,470,680 gallons of which was tied up as residual saturation. Figure 5-7 illustrates the hydraulic conductivity input values for this scenario.

5.2.2 Scenario 2

This scenario was run to develop a visualization of a NAPL plume that might develop from a constant, long-term release from the refinery #1 Tankfarm of a single product such as JP-4. The simulation was run under a hydrogeologic regime as exists in the study area today. The release, which was initiated in 1950 and persisted through a 47-year simulation period until the present, yielded a total released volume of 46,824,800 gallons. At initiation, the groundwater table was 8-ft deeper than the current elevation and near its historical low point. Groundwater was set to flow south, as it does in the study area, under a gradient of 0.001 ft/ft and the aquifer hydraulic conductivity was set at 8.21-ft/d. The simulation was allowed to run under these initial conditions until 1964, when the water table was allowed to rise to its current level over a period of 200 days. In 1965, infiltration into the 26th Street sewer in the vicinity of monitor well S-44 was initiated at a rate of 50 gallons per minute. In 1966, pumping for hydrocarbon recovery along 26th Street adjacent to Sun #1 Tankfarm was inserted at a total rate of 20 gpm. Additional wells along 26th Street adjacent

to the Sun #2 Tankfarm pumping 50 gallons per minute were inserted in 1968. In 1972, all recovery pumping was terminated and the simulation remained in that state until 1994, when #1 Tankfarm pumping was re-initiated at 20 gallons per minute. The simulation was terminated in 1997. Figure 5-7 illustrates the hydraulic conductivity input values for this scenario.

5.2.3 Scenario 3

This scenario was run to develop a visualization of a NAPL plume that might develop from a constant, long-term release from the refinery #1 Tankfarm under a hydrogeologic regime in which groundwater flow is from the northwest to the southeast as hypothesized by DSCP. All other input parameters were identical to those in Scenario 2. This scenario was, however, more conservative than Scenario 2 because the direction of groundwater flow was biased to the southeast, which, as detailed in Section 3.4, is not the case. Figure 5-7 illustrates the hydraulic conductivity input values for this scenario.

5.2.4 Scenario 4

This scenario was run with even more conservative factors that are contrary to real-world data in an effort to determine the physical parameters and leak scenario that would need to come together simultaneously to produce a single-product refinery-sourced, NAPL plume beneath DSCP as hypothesized by DSCP in a configuration and with a morphology like the one that exists today that is separate and distinct from a hypothetical refinery-sourced plume. The primary objective of this scenario was to force formation of the plume as we know it, no matter how implausible the physical setting. Figure 5-8 illustrates the hydraulic conductivity input values for this scenario. The groundwater flow direction was modeled as northwest to southeast. A 47-year duration release beginning in 1950 was simulated from tank 42 at a continuous release rate of 2,880 gallons per day. This release rate yielded an input of 42,048,000 gallons of hydrocarbon over the 47-year simulation. In addition to the release, three hydrocarbon-recovery wells were located on the refinery near the locations of well 8, wells 21 and 22, and wells 25 and 26. Groundwater pumping rates from the three wells were 1.47, 9.40, and 8.35 gpm, respectively, for 20 years; after which time, groundwater extraction was terminated. Hydrocarbon pumping rates were set unreasonably high to ensure that the maximum pumping rate was maintained throughout the 40-year simulation. This provided the greatest potential to remove NAPL from the pathway and create detached plumes, as DSCP has

hypothesized. In addition to the high pumping rates and the large release rate, a 230-ft wide and 30-ft thick gravel conduit, which does not actually exist in the study area, was inserted to ensure that the released NAPL would indeed have a direct conduit to DSCP. The DSCP-hypothesized damming effect of the Packer Avenue sewer was also simulated by setting the hydraulic conductivity of a continuous line of nodes as close as possible to the Packer Avenue sewer to a value that represents near impermeability (i.e., $1.0\text{e-}9\text{-ft/d}$). This sewer was simulated to determine if it could serve as a dam, as put forth in the DSCP NAPL Plume Study Report (Malcolm Pirnie 1997a).

5.2.5 Scenario 5

This scenario was run to develop a visualization of a NAPL plume that might develop from a rapid short-term, high-volume release of a single product, such as a light refinery naphtha characteristic of JP-4, from the refinery #1 Tankfarm under a hydrogeologic regime which simulates the DSCP hypothesized flow to the southeast. In sum, this simulation represents a catastrophic release. It was initiated in 1950 with a 140-day release of 1,500,000 gallons (approximately one-half of the volume of an 85,000-barrel tank). All other parameters and sequences were identical to those applied in Scenario 2. Figure 5-7 illustrates the hydraulic conductivity input values for this scenario.

5.2.6 Scenario 6

This scenario was run to develop a visualization of a NAPL plume that might develop from a multi-source long-term release on the DSCP site. The impetus for this simulation was the results of the plume morphology examination represented in Section 6 in which multiple thickness centroids suggestive of release sources were observed. The four sources in the simulation were placed coincidentally with the centroids. Each was set to leak at a rate of 0.05 gpm (72 gallons per day). All other parameters and sequences were identical to Scenario 2. Figure 5-7 illustrates the hydraulic conductivity input values for this scenario.

5.3 NAPL TRANSPORT MODELING RESULTS

5.3.1 Scenario 1

Results of this simulation are given in Figures 5-9 through 5-11. Each of these depicts NAPL thickness in the form of isothickness contours. Figure 5-9 shows NAPL distribution in 1941, just before the water table began its 8-ft drop. This figure shows that the NAPL was thickest in the vicinity of the release points, and that it thinned in all directions as a function of distance. Further, at this point in the scenario, 575,660 gallons of NAPL were trapped as residual, which is 3.1 percent of the 18,498,000 gallons released. Figure 5-10 shows NAPL distribution in 1961 where the water table reached its maximum depth. Again, the thickest aspect of the plume is nearest the sources or release points. At this point, 49,921,520 gallons had been released and 30,548,320 gallons or 61 percent were tied up in the residual fraction. Figure 5-11 shows NAPL distribution in 1997, the end of the simulation. The maximum eastern migration of the plume is approximately 500-ft into the DSCP western side. NAPL thickness within the CSX property is between 3.5- and 5-ft. The vast bulk of the NAPL plume is confined to the refinery property.

5.3.2 Scenario 2

This scenario was run to visualize the result of a 47-year hypothetical release at the refinery of a single product such as JP-4. It also simulated the hydrogeologic regime as it currently exists. It included water-table fluctuation. Figures 5-12 and 5-13 illustrate the results of the Scenario 2 simulation. Figure 5-13 shows the distribution of NAPL as isothickness contours after 47 years of NAPL release and migration. The NAPL plume shown in the figure shows its greatest thickness (about 15-ft) near the source as would be expected; the NAPL has thinned and spread in the form of a north- to south-oriented ellipse, which is consistent with the southerly direction of groundwater flow. The simulation also shows 8- to 10-ft of NAPL thickness at the edge of the DSCP property. However, the areal extent of the plume is not as large as might have been expected due to residual formation. The results of this simulation show that of the 46,824,800 gallons released, 4,701,180 gallons were tied up in the residual fraction. This plume configuration was generated using a hydrogeologic regime essentially identical to that which would have existed through the past 47 years, and yet it bears no resemblance to the existing NAPL plume beneath DSCP. In fact, at least half of the DSCP site has no NAPL beneath it. This conclusion is consistent with the results of

Sun's direction-of-groundwater-flow analysis and plume-morphology analysis and with the physics of immiscible phase flow.

5.3.3 Scenario 3

This scenario was also run to visualize the result of a single-product, 47-year hypothetical release at the refinery. Figures 5-14 and 5-15 depict the results of the Scenario 3 simulation. Figure 5-14 shows the southeastern flow component, and Figure 5-15 shows the distribution of NAPL as isothickness contours after 47 years of NAPL release and migration. The figure shows a relatively large plume. Further, the easterly-flow component has directed the plume toward CSX and onto the western third of DSCP. The plume is clearly shown to thin from its source as a function of distance. However, the maximum thickness (6.5-ft) occurs nearest the source, as would be expected, and the thickness in the pathway is 2- to 4-ft. This reduced thickness is a function of a decreased leak volume relative to Scenario 2, and the mass loss that occurs as NAPL migrates and the residual fraction is created. Of the 46,824,800 gallons released, 2,386,120 gallons are tied up in the residual fraction. It is striking that the simulated plume morphology is totally unlike the plume beneath DSCP, despite the strong easterly-flow component built into the model. The simulated plume has assumed the configuration anticipated or dictated by immiscible multi-phase flow theory. It is thickest nearest the source and thinner nearest the margins. That is, the thinnest aspect of the plume is nearer the center of the DSCP site, while the actual plume is thickest in this same area. This simulation also clearly shows heavy NAPL accumulation in DSCP's alleged pathway, even after 30 years of pumping for recovery on the refinery, as would be expected. In contrast, no NAPL and no residual hydrocarbon exists in the pathway today. The simulation also shows that the thickness of the NAPL plume decreases from west to east across DSCP, which is not the case for the actual plume, which thins in all directions including toward the west and the refinery. The results of this simulation are consistent with the theoretical material presented in Section 3.2.

5.3.4 Scenario 4

This scenario was run to visualize the result of a single-product, 47-year hypothetical refinery release with even more conservative input. Figures 5-16 and 5-17 illustrate the results of the Scenario 4 simulation. Figure 5-17 shows the distribution of NAPL as isothickness contours after 47 years of release and migration. The figure shows that, even with a very large pipeline-like pathway, a

damming structure, and an extremely high hydraulic conductivity, the DSCP plume could not be duplicated through simulation. Figure 5-17 shows about 2-ft of NAPL in the vicinity of the hypothetical release point and the Packer Avenue sewer. Although, the NAPL plume thickens from the source toward DSCP, over 2-ft of NAPL remains in the pathway. Also note that the plume has a northwest to southeast orientation, which is approximately perpendicular to the DSCP plume orientation. The simulation results also show that of the 46,824,800 gallons released, 1,205,028 gallons are tied up in the unsaturated zone residual fraction.

5.3.5 Scenario 5

This scenario was run to visualize the result of a single-product catastrophic release that occurred on the lowest historical water table. Figures 5-14 and 5-18 depicts the results of the Scenario 5 simulation. Figure 5-18 shows the distribution of NAPL as isothickness contours after 47 years of migration. Figure 5-18 shows that, despite a rapid release of 4,846,292 gallons of NAPL, only small remnants of relatively thin NAPL (i.e., less than 1-ft) exist on the water table. This reflects the 4,690,708-gallon residual fraction (97 percent) that resulted from the 8-ft rise in the water table. In this simulation, little or no NAPL is manifest on the water table, and the plume developed on the DSCP water table. One thin remnant of less than 0.12-ft thickness is found in the western portion of DSCP. This thin plume has no resemblance to the current NAPL plume. Although, the plume appears to be detached from the source area, Figure 5-20 shows that a large amount of residual NAPL resides in the pathway ($0.5\text{-ft}^3/\text{ft}^2$). However, as illustrated above, a very significant residual phase develops. This is consistent with NAPL transport theory, as described in Section 3.2. The simulated water table did not fall after its rise, which is the case for the water table in the study area, and little or no NAPL exists on the simulated water table. For these reasons, the NAPL resides below the water table at irreducible saturation (i.e., approximately 23,000 mg/kg for sand and gravel) in a submerged smear zone. As has been the case for each preceding scenario, a large portion of this residual fraction is in the DSCP alleged pathway. If this simulated pathway were sampled, TPH concentrations near 23,000 mg/kg would be expected.

5.3.6 Scenario 6

As described above, the impetus for this scenario was the results of the morphologic analysis detailed in Section 6. The analysis showed several thickness centroids on the DSCP site. Thus, the

simulation was conducted to determine if a plume with the characteristics of the one on DSCP property could be simulated. Figures 5-14 and 5-19 illustrate the results of the Scenario 6 simulation. Figure 5-19 shows the distribution of NAPL as isothickness contours after 47 years of NAPL release from four source areas identified on DSCP and migration. With the exception of the release points, and the very low release rate per point (0.05 gpm), the inputs for this simulation are identical to Scenario 2. Figure 5-19 also shows that, under this scenario, a plume that nearly perfectly matches the DSCP plume morphology has been simulated. This plume is thickest at its four centroids or release points, and it thins in all directions as a function of distance. It is also striking that unlike any of the other simulations, save the catastrophic release scenario, there is no evidence of NAPL in DSCP's alleged pathway. Because the output from this scenario matches the DSCP plume so closely, and because none of the other scenarios produced simulated plumes that were even remotely similar to the DSCP plume, despite the testing of a variety of scenarios, this model supports a conclusion that the source of the DSCP plume is small long-term releases from multiple sources on DSCP site. The total release volume is 4,899,400 gallons with 1,297,780 gallons being tied up as residual saturation. This leaves 3,601,620 gallons of mobile oil.

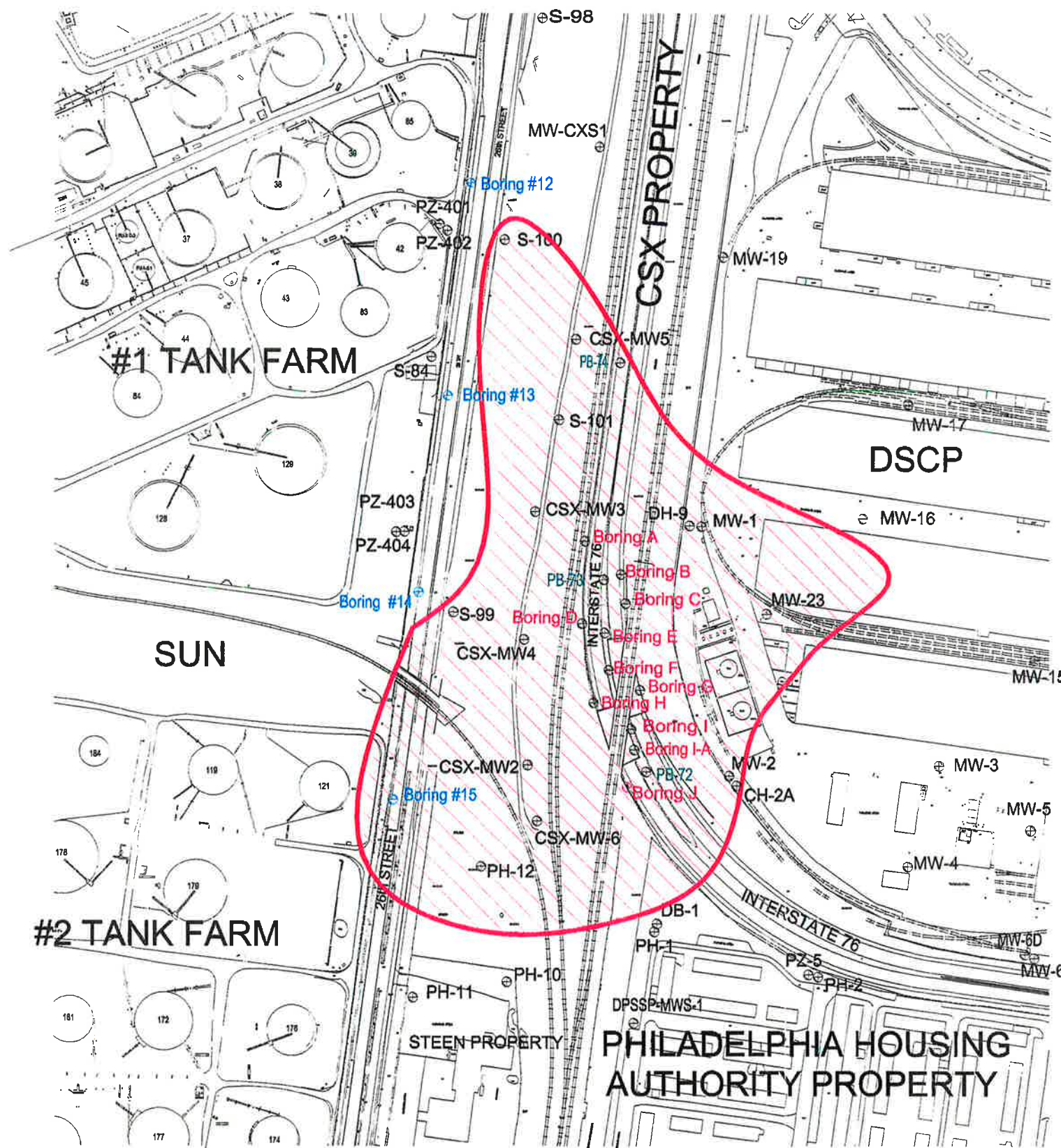
5.4 NAPL TRAVEL TIME

DSCP's hypothetical pathway argument asserts that the product released from the refinery's #1 Tankfarm was JP-4. This hypothesis further asserts that, upon completion of the 26th Street sewer in 1964, migration through the pathway would have ceased. Thus, because the first military specification for JP-4 was issued in about 1950, DSCP's release and migration time window is about 14 years. The analyses and modeling detailed above show that a release from the refinery #1 Tankfarm could not have created the plume beneath DSCP in any time frame.

5.5 CONCLUSIONS FROM OBSERVED DATA AND MODELING

The data and simulations documented in this section demonstrate both independently and collectively that the Sun refinery could not have been the source of the NAPL plume beneath DSCP, despite DSCP's allegations to the contrary. No evidence has been observed either in the empirical data or in the simulations to support DSCP's alleged migration pathway. Little or no NAPL was noted in the borings and monitor wells that have been installed in this alleged pathway. The analytical results that exist also do not reveal the presence of soil-residual hydrocarbon at

concentrations that suggest anticipated residual saturation (i.e., 10,000 and 25,000 mg/kg in the vadose and saturated zones, respectively). These concentrations would be a necessary result after such a large mass of NAPL had migrated through it. In addition to the absence of soil-residual hydrocarbon concentrations in samples collected from the pathway, dissolved-phase concentrations in wells in it do not approach the level that would be expected in the proximity of NAPL, whether floating on the water table or trapped in soil as a residual fraction. The results of ARMOS modeling also support the conclusion that DSCP itself was the source for the plume beneath it. The only modeled simulation that even approached the current configuration of the NAPL plume simulated a plume originating on DSCP. Even with the addition of a large, highly conductive gravel pathway designed to push the NAPL from the Sun refinery to DSCP, a feature that has no analogue at the site, the plume could not migrate to DSCP in anything nearly approximating its current configuration. These factors totally eliminate the possibility of a pathway for NAPL migration beneath 26th Street and the CSX right of way. Thus, the source for the plume beneath DSCP can only be DSCP itself.



LEGEND	
	Alleged DSPC Pathway
	MW-16 Existing Monitor Wells
	PB-74 Schuylkill Expressway Soil Borings (1953)
	Boring A 25th Street Bridge Soil Borings (1953)
	Boring #13 26th Street Sewer Soil Borings (1962)

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0 400 800 1600
SCALE IN FEET

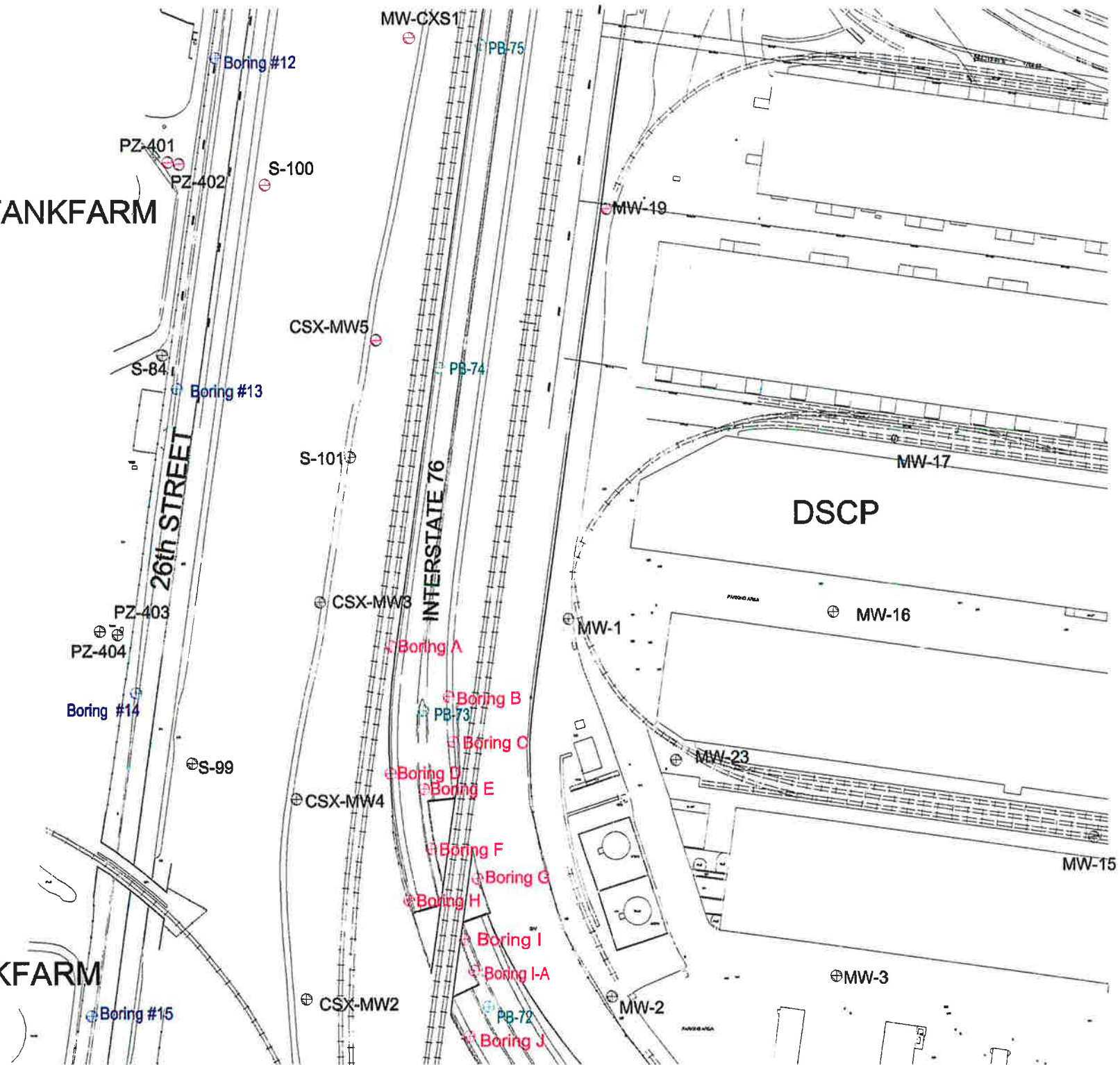
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DRAWN BY: CWS	REVIEWED: PKH	APPROVED: HJR
DATE: 20 FEB 1998	PROJECT NO. SU001H	DWG. NO.
AREA OF THE ALLEGED DSPC PATHWAY		FIGURE
STUDY AREA PHILADELPHIA, PENNSYLVANIA		5-1



SUN #1 TANKFARM

SUN #2 TANKFARM



0 800 1600
SCALE IN FEET

LEGEND

- MW-16 Existing Monitor Wells
- PB-74 Schuylkill Expressway Soil Borings (1953)
- Boring A 25th Street Bridge Soil Borings (1953)
- Boring #13 26th Street Sewer Soil Borings (1962)

THIS MAP WAS COMPILED FROM BASE DRAWINGS AND/OR SKETCHES SUPPLIED BY OTHERS. IT IS TO BE USED ONLY AS AN APPROXIMATE SOURCE OF REFERENCE. WE ASSUME NO RESPONSIBILITY FOR THE ACCURACY OF BASE MAP RELATED INFORMATION CONTAINED HEREIN.

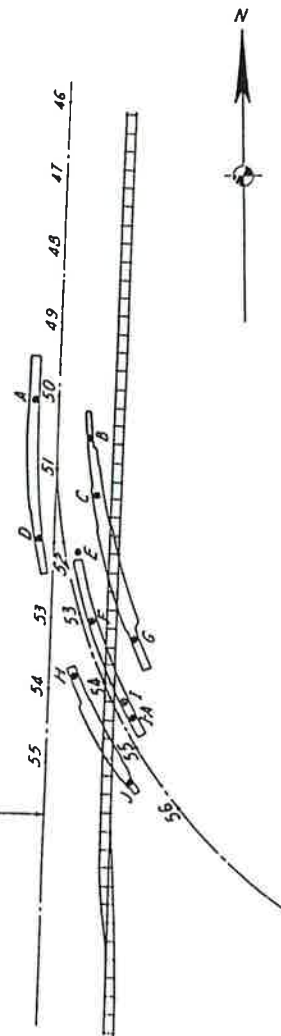
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DATE: 09 FEB 1998	PROJECT NO. SU001H	DWG. NO.
Location of Delaware River Bridge Borings Delaware River Port Authority		FIGURE
STUDY AREA PHILADELPHIA, PENNSYLVANIA		5-2

APPROXIMATE LOCATION OF BORINGS
PRR 25 ST. BRIDGE

BORING NO. STATION OFFSET FROM SURVEY
LINE TANGENT

A	50+10	34' Right
B	50+59	48' Left
C	51+33	58' Left
D	52+00	21' Right
E	52+10	35' Left
F	53+03	57' Left
G	53+25	117' Left
H	53+80	35' Left
I	54+13	108' Left
I-A	54+35	120' Left
J	55+23	119' Left



BORING A

Weight of Hammer 300*	Stratum Elev.	Sample Elev.	Sample No.	Spoon Blows/ft.
Drop of Hammer 20"				
Classification				
Top Soil Sand & Clay	+37.3	32.3	1	12
Brown Clay & Gravel		29.3	2	6
Brown Clay Gravel & Cinders		21.3	3	6
Brown Clay & Vegetation		17.3	4	7
Sand & Clay		12.3	5	32
Sand Gravel Same Clay		7.3	6	91
Gravel		2.3	7	65
Wet Coal	0.0	-1.3	7	65

BORING B

Weight of Hammer 300*	Stratum Elev.	Sample Elev.	Sample No.	Spoon Blows/ft.
Drop of Hammer 20"				
Classification				
Decomposed Mica, Slag, Cinders & Clay Fill	+48.3	47.3	1	14
Cinders, Slag, Clay, Bricks (Fill)	16.3	15.3	2	23
Oil Soaked Sand Loose Clay	11.3	10.3	3	19
Oil Soaked Gravel Clay & Sand	7.3	6.3	4	23
Oil Soaked Sand (Wet)	0.0	-1.7	4	23

NOTE:
Atlantic Refinery Had Oil Process-
ing Plant at one time.

BORING C

Weight of Hammer 300*	Stratum Elev.	Sample Elev.	Sample No.	Spoon Blows/ft.
Drop of Hammer 20"				
Classification				
Decomposed Mica & Boulder Fill	+47.2	46.2	1	9
Cinder Fill	42.2	40.2	2	10
Decomposed Mica Fill	37.2	35.2	3	9
Clay & Cinders	32.2	30.2	4	8
Brown Clay & Sand	17.2	16.2	5	10
Sandy Brown Clay Boulders & Gravel	12.2	11.2	6	30
	7.2	6.2	6	30
	0.0	-2.8		
	-7.8			

BORING D

Weight of Hammer 35*	Stratum Elev.	Sample Elev.	Sample No.	Spoon Blows/ft.
Drop of Hammer 24"				
Classification				
Cinders Bricks Fill Material	+48.4	48.4	1	20
Top Soil Dark Brown Vegetation	18.4	16.4	2	31
Yellow & Gray Clay	15.4	14.4	3	45
Sandy Clay & Gravel	14.4	11.4	4	108
Sand & Gravel Same Clay	8.4	7.4	5	103

NOTE:
Porter Sampler used to take
Boring.

BORING E

Weight of Hammer 300*	Stratum Elev.	Sample Elev.	Sample No.	Spoon Blows/ft.
Drop of Hammer 20"				
Classification				
Sand, Cinders, Clay & Gravel	+31.9	30.9	1	6
Brown Clay Sand & Gravel	26.9	18.9	2	19
Sand Clay (50-50)	18.9	17.9	3	21
Sand & Gravel (50-50)	9.9	7.9	4	20
Sand & Gravel	3.9	2.9	5	22
Wet Sand & Gravel	0.1	-1.1	5	22
Sand & Gravel	-2.1	-2.5	6	46
Cementite with Clay	-3.1			

BORING F

Weight of Hammer 300*	Stratum Elev.	Sample Elev.	Sample No.	Spoon Blows/ft.
Drop of Hammer 20"				
Classification				
Cinder Fill	+34.9	33.9	1	11
Ashes, Clay & Gravel Fill	25.9	22.9	2	122
Brown Clay (Mica Fill)	20.9	18.9	3	18.9
Brown Sandy Clay	17.9	17.9	4	17.9
Coarse Sand & Gravel Some Clay	10.9	11.9	5	11.9
Sand & Gravel Same Red Clay	10.9	10.9	6	11.9
	-1.1	-1.1	7	11

BORING G

Weight of Hammer 35*	Stratum Elev.	Sample Elev.	Sample No.	Spoon Blows/ft.
Drop of Hammer 24"				
Classification				
Cinder Fill	+30.3	29.3	1	5
Brown Clay	17.3	15.3	2	2
Sand, Clay & Gravel	9.3	7.3	3	4
Sand & Small Gravel	3.3	3.0	4	8

NOTE:
Boring Taken with Porter Sampler

BORING H

Weight of Hammer 300*	Stratum Elev.	Sample Elev.	Sample No.	Spoon Blows/ft.
Drop of Hammer 20"				
Classification				
Cinders	45.5	44.5	1	3
Mica, Slag, Clay Cool, Cinders Fill Material	40.5	39.5	2	5
Clay Ashes & Slag	29.5	27.5	3	18
Brown Clay & Sand	17.5	15.5	4	32
Sand, Gravel, Clay	7.5	6.5	5	38
Hardpan Sand & Gravel Some Clay	1.5	-0.5	6	60

BORING I-A

Weight of Hammer 35*	Stratum Elev.	Sample Elev.	Sample No.	Spoon Blows/ft.
Drop of Hammer 24"				
Classification				
Loose Cinders Fill Material	39.1	38.1	1	2
Decomposed Mica & Cinder Fill	33.1	31.1	2	16
Yellow & Brown Clay	18.1	16.1	3	35
Sand, Gravel & Clay	9.1	7.1	4	83

NOTES:
Porter Sampler Driven to Refusal

BORING J

Weight of Hammer 35*	Stratum Elev.	Sample Elev.	Sample No.	Spoon Blows/ft.
Drop of Hammer 24"				
Classification				
Cinder Fill	+47.5	46.5	1	8
Gravel & Red Clay	17.5	15.5	2	27
Brown Sand	10.5	8.5	3	96
Little Gravel & Clay	7.5	5.5	4	156
Sand Clay & Gravel	4.5			

NOTE:
Boring Taken with Porter Sampler



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DATE: 09 FEB 1998	PROJECT NO. SU001H	DWG. NO. *****
BORING LOGS A THROUGH J DELAWARE RIVER BRIDGE		
STUDY AREA Philadelphia, PA		
Figure 5-3		

BORING NO. PB-73

Weight of Hammer 300 ^{lb} Drop of Hammer 20'		Sample Elev	Sample No	Spoon Blow/ft	Moisture content
Classification					
	+340	2261	4		
Cinders		2202	6		
		2263	4		
Clay & cinders	+190	1804	14		
	+160	1305	22		
Brown sand & clay, 90		1806	21		
Fine brown sand & gravel	+60	1307	48		
	20	2208	57		
Fine to coarse brown sand & gravel		2709	41		

BORING NO. PB -72

Weight of Hammer 300 ^{lb} Drop of Hammer 20"	Stratum Elev	Sample Elev	Sample No.	Spcon Glass/Ht	Moisture content
Classification					
Cinders	* 46.3	45.1	1	18	
	* 41.3	40.2	2	15	
Cinders & fill		39.3	3	24	
		30.3	4	34	
		25.5	5	8	
Ground Water	* 19.9	20.3	6	6	
Brown, silty sand	* 17.3	15.3	7	8	
Brown, silty sand, & clay, moist	* 11.3	12.3	8	22	
Coarse sand & gravel	* 6.3	5.3	9	32	
	0.0	0.3	10	41	
		47	11	57	

BORING NO. PB-71

[illegible]

BORING NO. PB-70

Weight of Hammer 300# Drop of Hammer 20	Stratum Elev.	Sample Elev.	Sample No.	Spoon Blows / ft.	Moisture Content
Classification					
Top soil, brown, dry & compact	'21.2	'22.2	1	16	
Fine sandy clay, brown, dry, loose	'16.2	'15.2	2	18	
Fine sand, small to large gravel	'11.2	'10.2	3	62	
	'6.2	'5.2	4	28	
Fine to medium sand & fine to med. gravel		'0.2	5	92	
	-3.8	-4.8	6	53	
Fine to coarse sand & small to large gravel		-9.0	7	56	

BORING NO. PB-69

Weight of Hammer 300* Drop of Hammer 20*	Stream Elev.	Sample Elev.	Sample No.	Soest Blows/H.	Soest Blows/ft.
Classification					
	'172		162	1	12
Cinders, ashes, clay	'162		112	2	11
Cinders, ashes, wood clay	'152		162	3	36
Fine sand, gravel clay	'132		112	4	9
Fine brown sand & clay	'08		138	5	71
Fine to medium sand & gravel	'78		138	6	15
Fine brown sand			138	7	27
Fine brown sand, gravel, clay	'22.8		138	8	22
Fine brown silty sand	'27.8		138	9	10
Brown sand, pea gravel			138	10	22
			138	11	27

BORING NO. PB-68

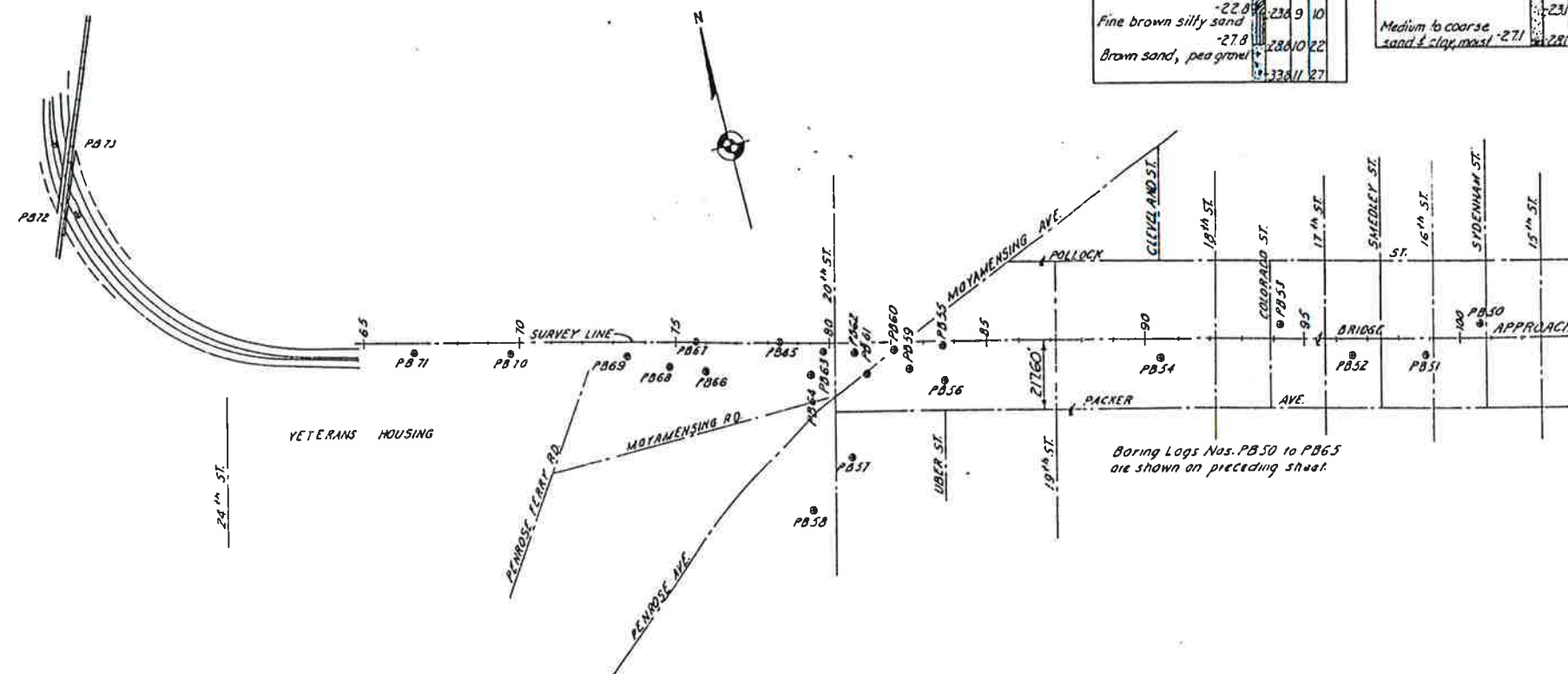
[illegible]

BORING NO. PB-67

Weight of Hammer 300 ^g Drop of Hammer 20"	Stratum Fict.	Sample Elev.	Sample No.	Spec. Weight
Classification				
Top soil; light brown, dry	116.1	115.1	1	17
Broken red brick, wood & ashes; dry, loose	111.1	110.1	2	22
Cinders, brick & ash fill; black, wet & loose	106.1	105.1	3	26
Cinder fill & broken bricks, wet	101.1	100.1	4	23
Cinders, silt, fine sand & large gravel; moist	96.1	95.1	5	8
Sand, gravel & clay; brown moist; medium compact	91.1	90.1	6	43
Medium to coarse sand brown, wet & loose	86.1	85.1	7	22
Fine sand; brown, wet, loose	81.1	80.1	8	26
Coarse sand; brown wet	76.1	75.1	9	17
		70.1	10	11
		65.1	11	42

BORING NO. PB-66

Weight of Hammer 300 ^g Drop of Hammer 20"	Stratum Else	Sample Elev.	Sample No.	Sp. of Bls. Ht.	Moisture Cont.
Classification					
Top Soil & cinders, bricks, ashes; dry	+18.1	+17.1	1	4	
Cinder-brick, osh & wood fill/dry	+13.1	+12.1	2	7	
Clay, mica, brick & cinder fill, brown/dry	+8.1	+7.1	3	18	
Silt, sand & peat, brown, moist, cohesive	+0.0	+2.1	4	39	
Coarse sand & gravel, small to large, moist	-0.3	-2.5	5	43	
Coarse sand, wet	+6.9	-7.9	6	91	
Fine to coarse sand; brown, moist	-11.9	-23.7	7	49	
Fine to medium sand; brown, wet	-16.9	-11.9	8	22	
	-21.9	-21.9	9	24	
		-27.9	10	38	
		-29.1	11	47	



Boring Logs Nos. PB50 to PB6-
are shown on preceding sheet.



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DATE: 09 FEB 1998	PROJECT NO. SU001H	DWG. NO. SEE THE REVISIONS SHEET FOR THIS
BORING LOGS PB-66 THROUGH PB-73 DELAWARE RIVER BRIDGE		Figure 5-4
STUDY AREA Philadelphia, PA		

BORING NO. PB-81

Weight of Hammer 300# Drop of Hammer 10"	Stratum Elev.	Sample Elev.	Sample No.	Spoon Blows/ft.	Moisture Content
Classifications					
	+32.2	+31.2	11		
Cinder fill, black, dry					
	+27.2	+26.2	2	8	
Cinder, clay & gravel fill, dry					
compact	+22.2	+21.2	3	9	
fine silty sand; dark gray, wet	+17.2	+16.2	4	19	
red clay & fine sand					
ry, compact	+12.2	+11.2	5	38	
and gravel & clay; brown					
moist	+7.2	+6.2	6	57	
and gravel boulders & clay					
and gravel & clay, moist	+2.2	+1.2	7	68	

BORING NO. PB-80

Weight of Hammer 300# Drop of Hammer 18"	Stratum Elev.	Sample Elev.	Sample No.	Spoon Blows/ft.	Moisture Content
Classifications					
	+31.0	+30.0	1	0	
Ashes, clay, brick fill, dry, brown & loose					
	+27.0	+26.0	2	8	
Silty clay, brown to gray, moist & cohesive	+24.0	+23.0	3	26	
Sand & clay; brown, moist, cohesive	+16.0	+15.0	4	16	
Sand, gravel & clay; brown, moist	+10.0	+9.0	5	28	
Sand, gravel & boulders	+1.0	+0.0	7	29	

BORING NO. PB-79

Weight of Hammer 300# Drop of Hammer 20"	Stratum Elev.	Sample Elev.	Sample No.	Spoon Blows/ft.	Moisture Content
Classifications					
	+31.1	+30.1	1	17	
Sand & clay fill					
	+26.1	+25.1	2	14	
Clay fill					
Ground Water	+22.1	+21.1	3	22	
Fine, brown sand & clay	+18.1	+17.1	4	39	
Brown sand & gravel	+12.1	+11.1	5	37	
	+5.1	+4.1	6	39	
	+0.1	-0.1	7	26	

BORING NO. PB-78

Weight of Hammer 300# Drop of Hammer 18"	Stratum Elev.	Sample Elev.	Sample No.	Spoon Blows/ft.	Moisture Content
Classifications					
	+31.7	+30.7	1	9	
Cinder fill, black, dry					
	+26.7	+25.7	2	7	
Clay & cinder fill, dry, brown					
Clay; brown, dry & compact	+21.7	+20.7	3	10	
Sand, large gravel & clay	+16.7	+15.7	4	47	
brown, dry & compact	+11.7	+10.7	5	22	
Fine to coarse sand & gravel; moist, loose	+6.7	+5.7	6	57	
Sand; brown, wet & loose	+1.7	+0.7	7	18	

BORING NO. PB-77

Weight of Hammer 300# Drop of Hammer 20"	Stratum Elev.	Sample Elev.	Sample No.	Spoon Blows/ft.	Moisture Content
Classifications					
	+32.5	+31.5	1	10	
Cinder fill, black, dry					
	+27.5	+26.5	2	18	
Silt, fine sand & clay, brown to gray, dry	+22.5	+21.5	3	36	
Fine sand & gravel; brown & moist	+17.5	+16.5	4	54	
Fine to med. sand & gravel	+12.5	+11.5	5	61	
Fine sand & gravel; brown & moist	+6.5	+5.5	6	47	
	+1.5	+0.5	7	18	

BORING NO. PB-76

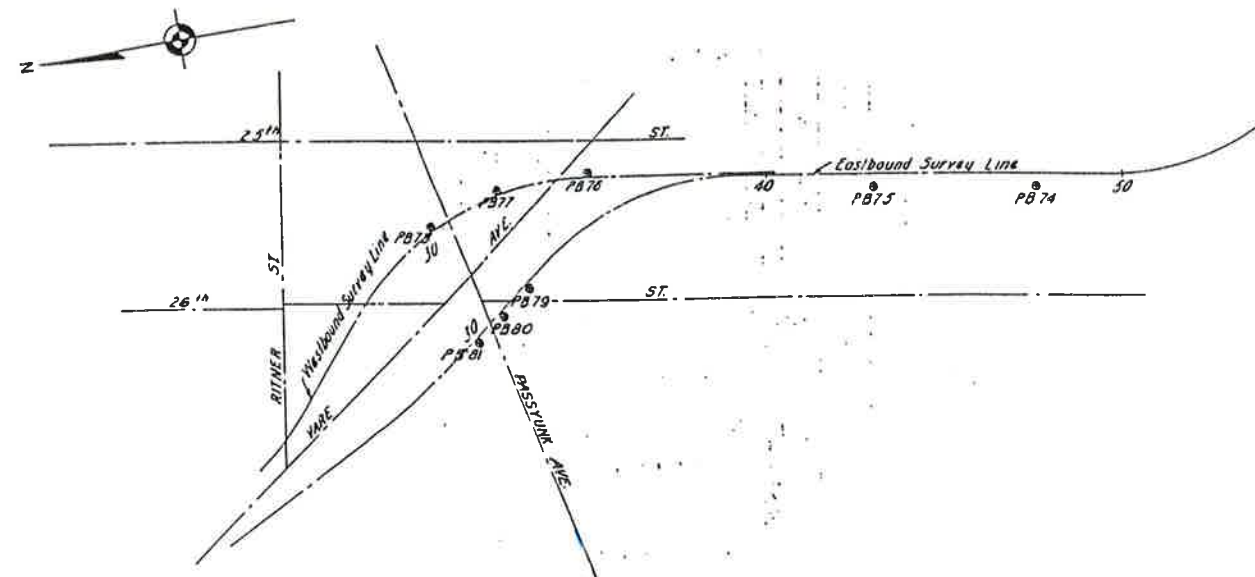
Weight of Hammer 300# Drop of Hammer 20"	Stratum Elev.	Sample Elev.	Sample No.	Spoon Blows/ft.	Moisture Content
Classifications					
	+29.9	+28.9	1	12	
Sand & clay					
	+23.9	+22.9	2	26	
Clay					
	+18.9	+17.9	3	17	
Fine brown sand & clay	+13.9	+12.9	4	18	
Medium sand, gravel	+7.9	+6.9	5	21	
	+2.9	+1.9	6	57	
	-2.1	-3.1	7	49	

BORING NO. PB-75

Weight of Hammer 300# Drop of Hammer 20"	Stratum Elev.	Sample Elev.	Sample No.	Spoon Blows/ft.	Moisture Content
Classifications					
	+43.1	+42.1	1	3	
Cinders & brick					
	+37.1	+36.1	2	8	
	+33.1	+32.1	3	31	
Fine sand & gravel, brown	+28.1	+27.1	4	12	
Clay; light brown, moist, cohesive	+22.1	+21.1	5	15	
	+17.1	+16.1	6	18	
	+12.1	+11.1	7	23	
Fine sandy clay; light brown, moist & cohesive	+7.1	+6.1	8	8	
	+2.1	+1.1	9	39	
Sand, clay & gravel	+0.1	-0.1	10	19	

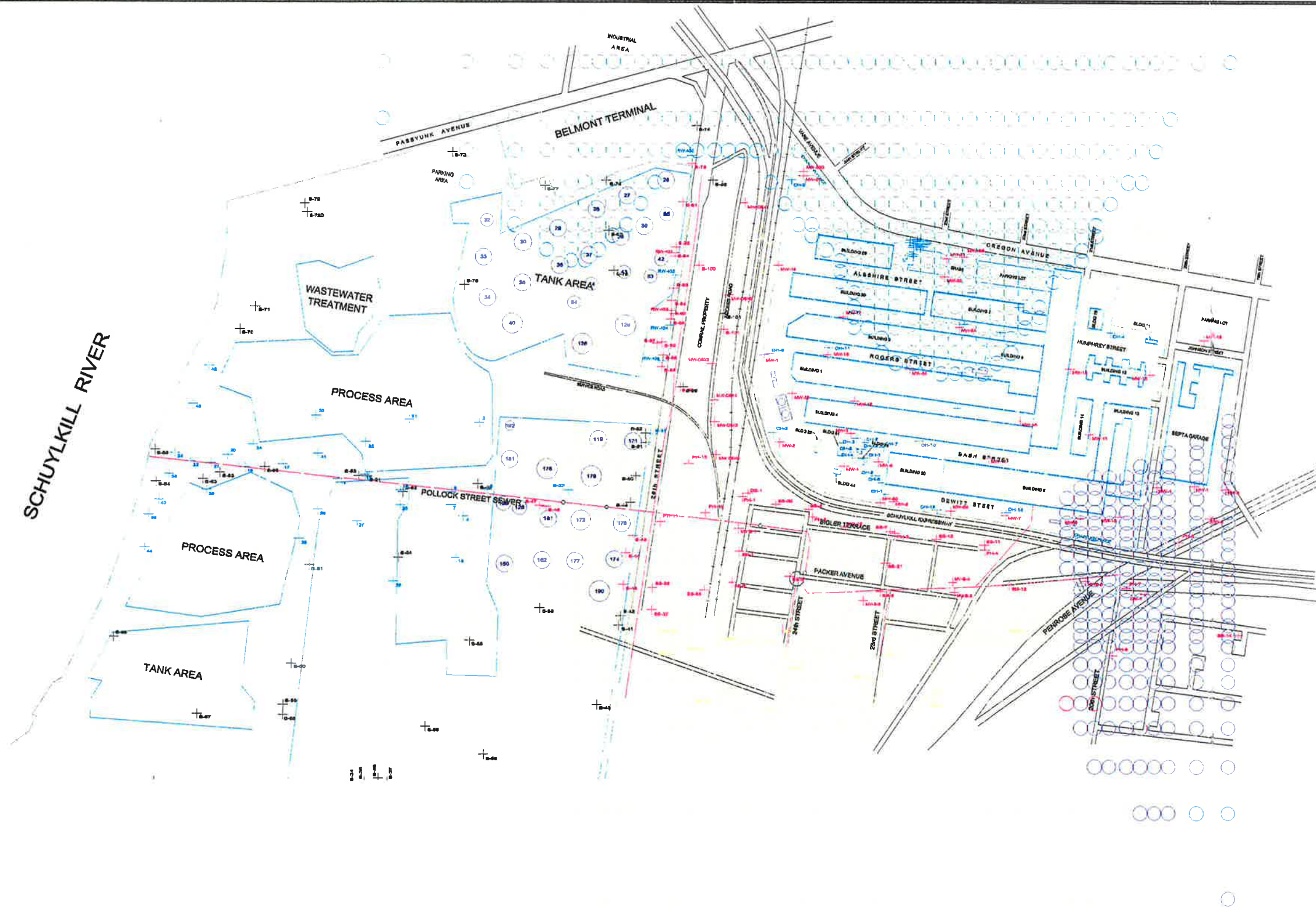
BORING NO. PB-74

Weight of Hammer 300# Drop of Hammer 20"	Stratum Elev.	Sample Elev.	Sample No.	Spoon Blows/ft.	Moisture Content
Classifications					
	+37.7	+36.7	1	14	
Cinders					
	+31.7	+30.7	2	17	
	+27.7	+26.7	3	33	
Medium to fine sand & gravel	+22.7	+21.7	4	7	
Med. to fine sand & gravel, wet, loose	+17.7	+16.7	5	12	
Gray silty clay & gravel, moist	+12.7	+11.7	6	19	
Fine silty sand, light brown, moist, cohesive	+7.7	+6.7	7	51	
Sand, gravel & clay	+2.7	+1.7	8	19	





SCHUYLKILL RIVER



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0 400 800 1200 1600
SCALE IN FEET

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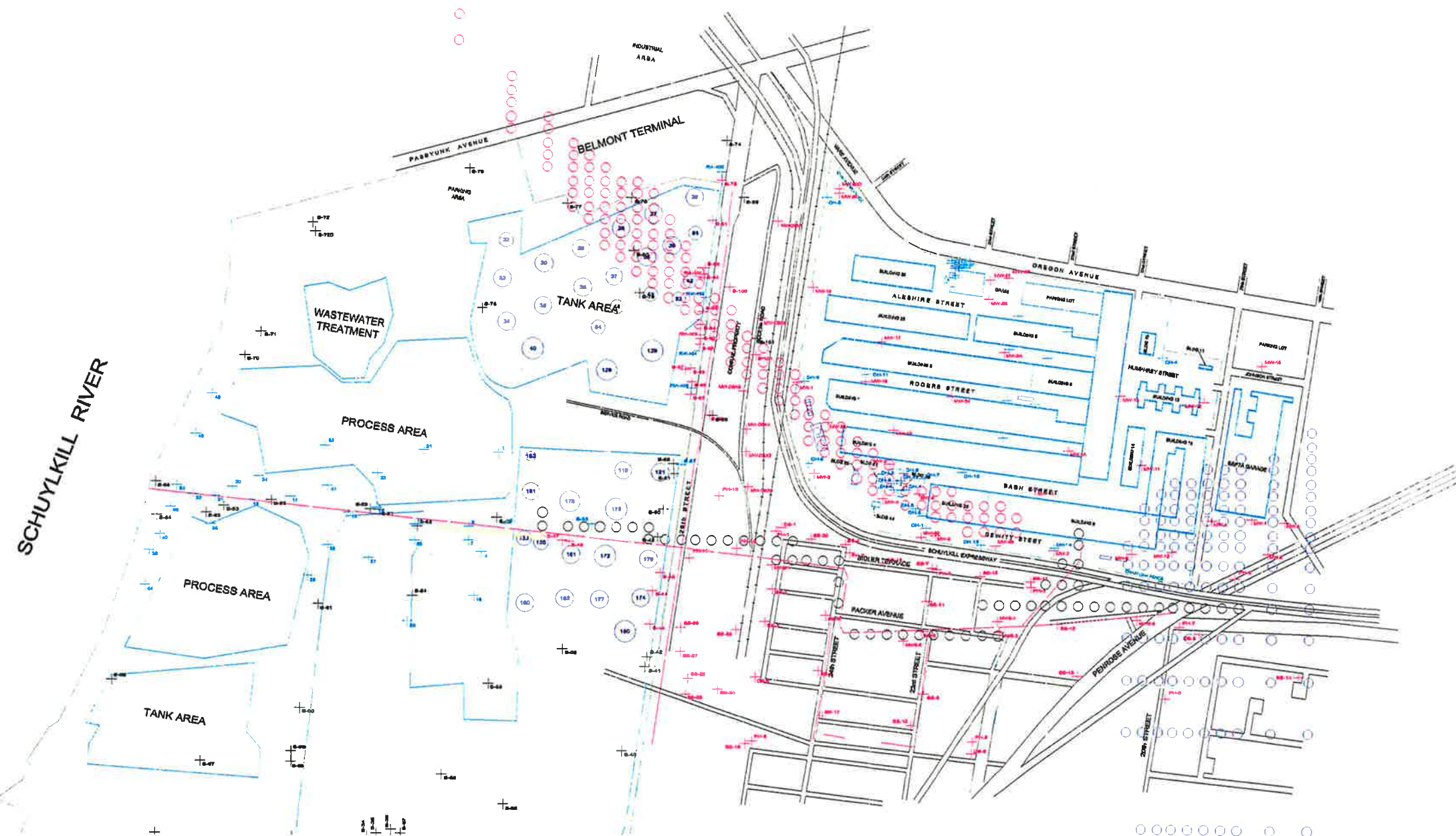
DRAWN BY: CWS	REVIEWED: PKH	APPROVED: HJR
DATE: 20 FEB 1998	PROJECT NO. SU001H	DWG. NO.
MULTIPHASE MODELING INPUT HYDRAULIC CONDUCTIVITY VALUES SCENARIOS #1, 2, 3, 5 & 6 STUDY AREA PHILADELPHIA, PENNSYLVANIA		

FIGURE
5-7



LEGEND

- $k = 450 \text{ ft/day}$
- $k = 8.21 \text{ ft/day}$
- $k = 0.361 \text{ ft/day}$
- $k = 1 \text{ e } -9 \text{ ft/day}$



0 400 800 1200 1800
SCALE IN FEET

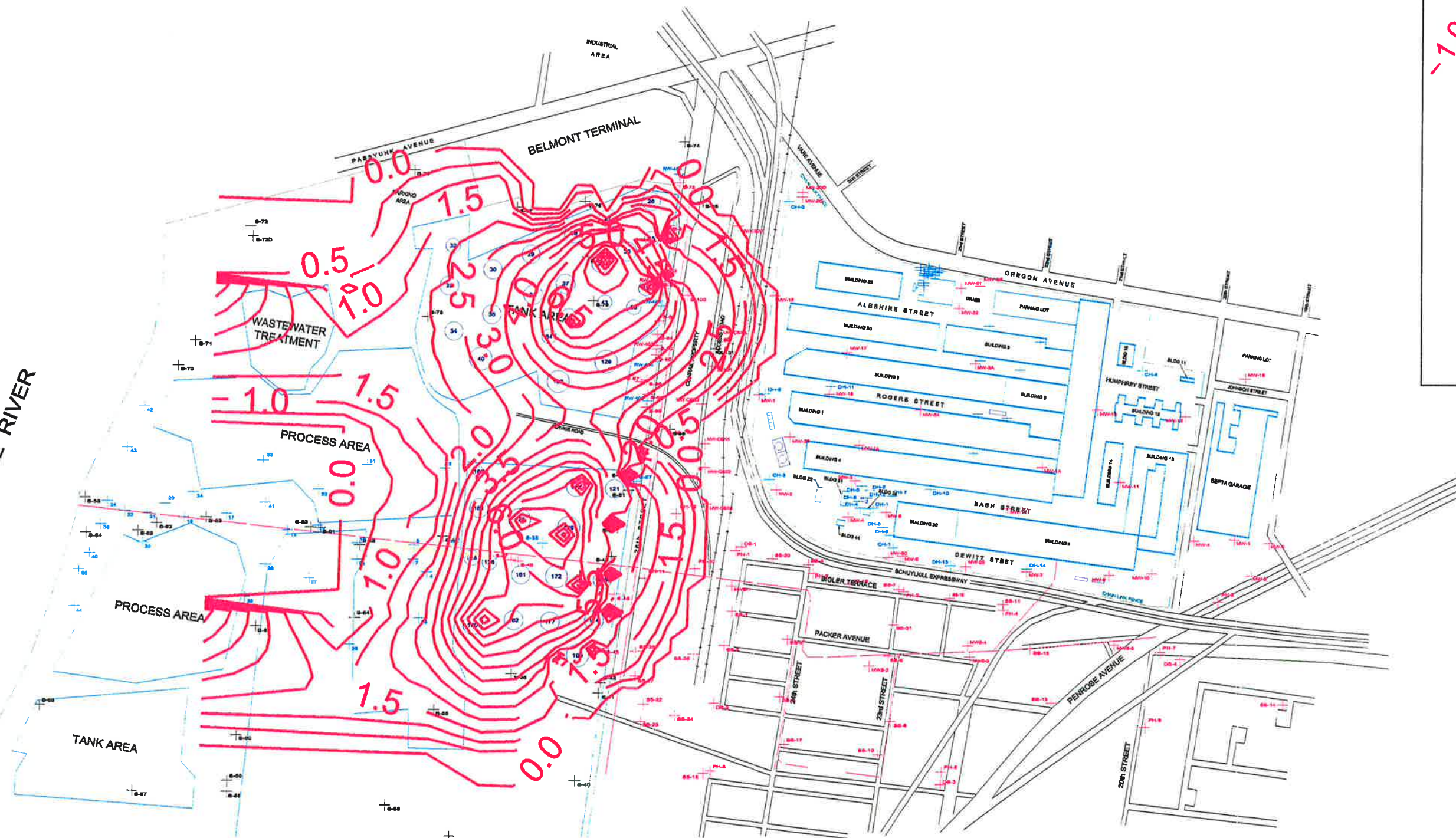
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MULTIPHASE MODELING INPUT HYDRAULIC CONDUCTIVITY VALUES SCENARIO #4 STUDY AREA PHILADELPHIA, PENNSYLVANIA		
FIGURE 5-8		



SCHUYLKILL RIVER



LEGEND

-1.0-
Apparent Hydrocarbon Thickness (ft)

0 400 800 1200 1600
SCALE IN FEET

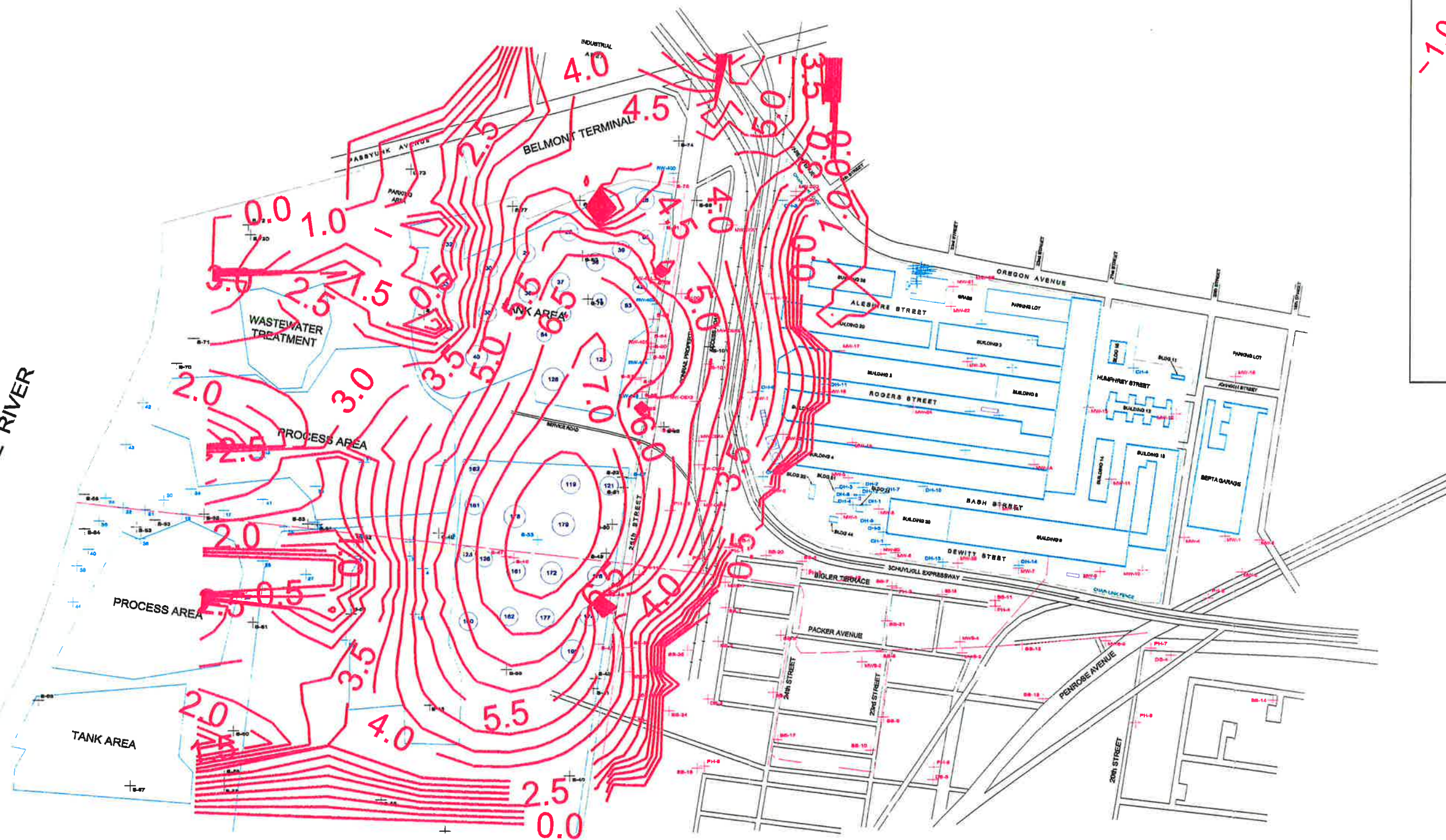
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DATE: 20 FEB 1998	PROJECT NO. SU001H	DWG. NO. SUN1941
MULTIPHASE MODELING RESULTS SCENARIO #1 - AFTER 71 YEARS (1941) CONTINUOUS RELEASE (1870) STUDY AREA PHILADELPHIA, PENNSYLVANIA		
FIGURE 5-9		



SCHUYLKILL RIVER



0 400 800 1200 1600
SCALE IN FEET

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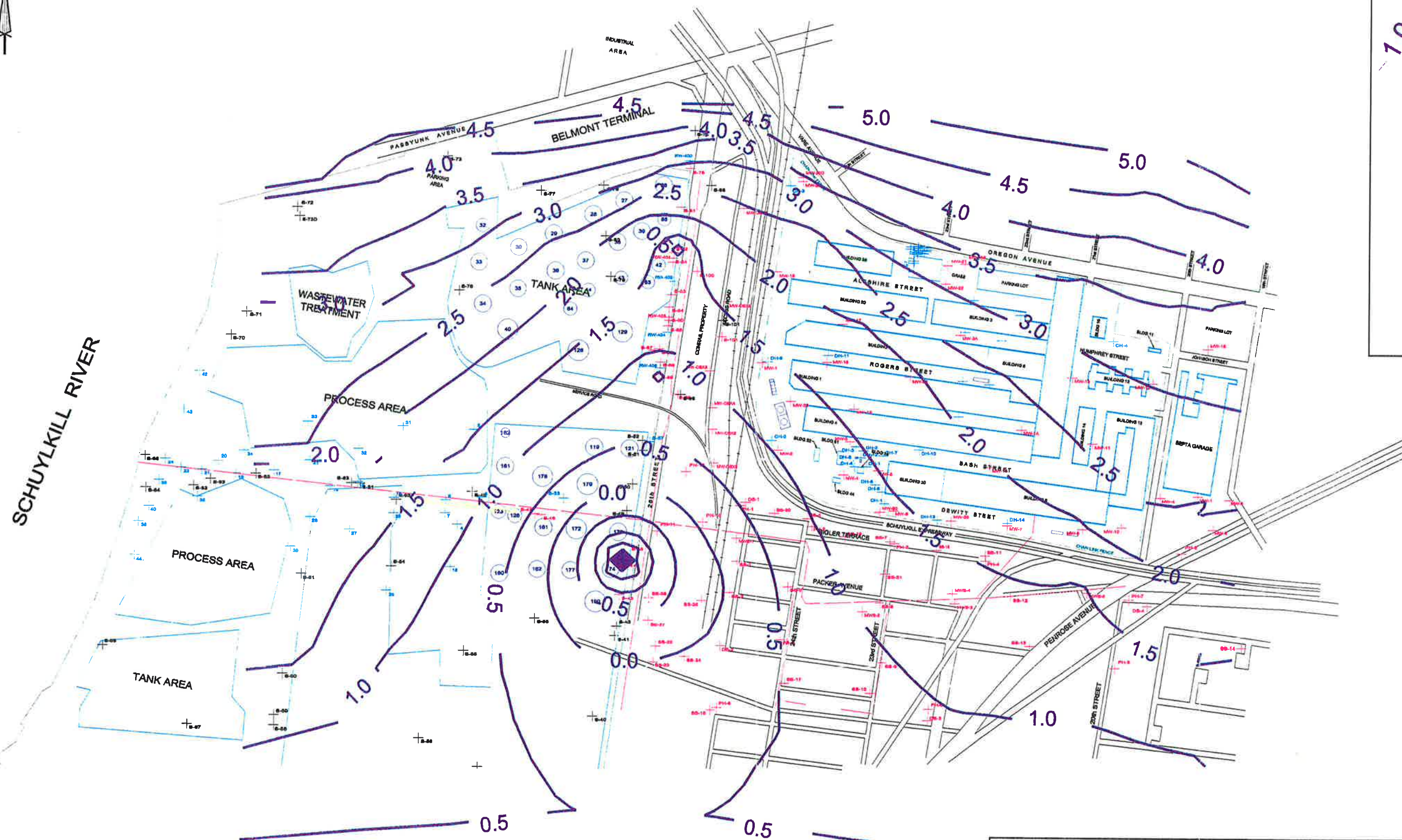
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DATE: 20 FEB 1998	PROJECT NO. SU001H	DWG. NO. SUN1997
MULTIPHASE MODELING RESULTS SCENARIO #1 - AFTER 127 YEARS (1997) CONTINUOUS RELEASE (1870) STUDY AREA PHILADELPHIA, PENNSYLVANIA		
FIGURE 5-11		



LEGEND

1.0
Modeled Ground Water
Elevation (ft)



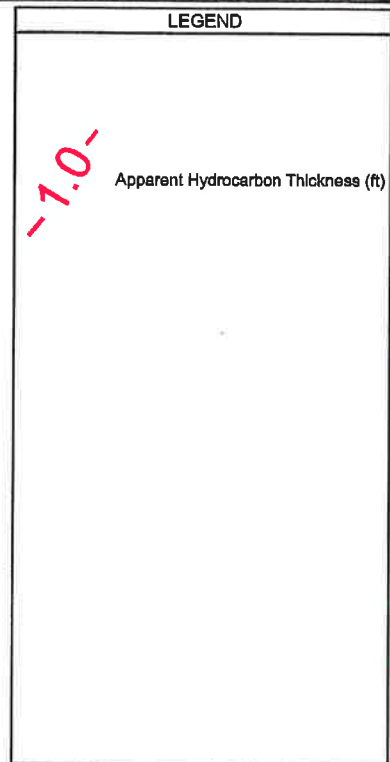
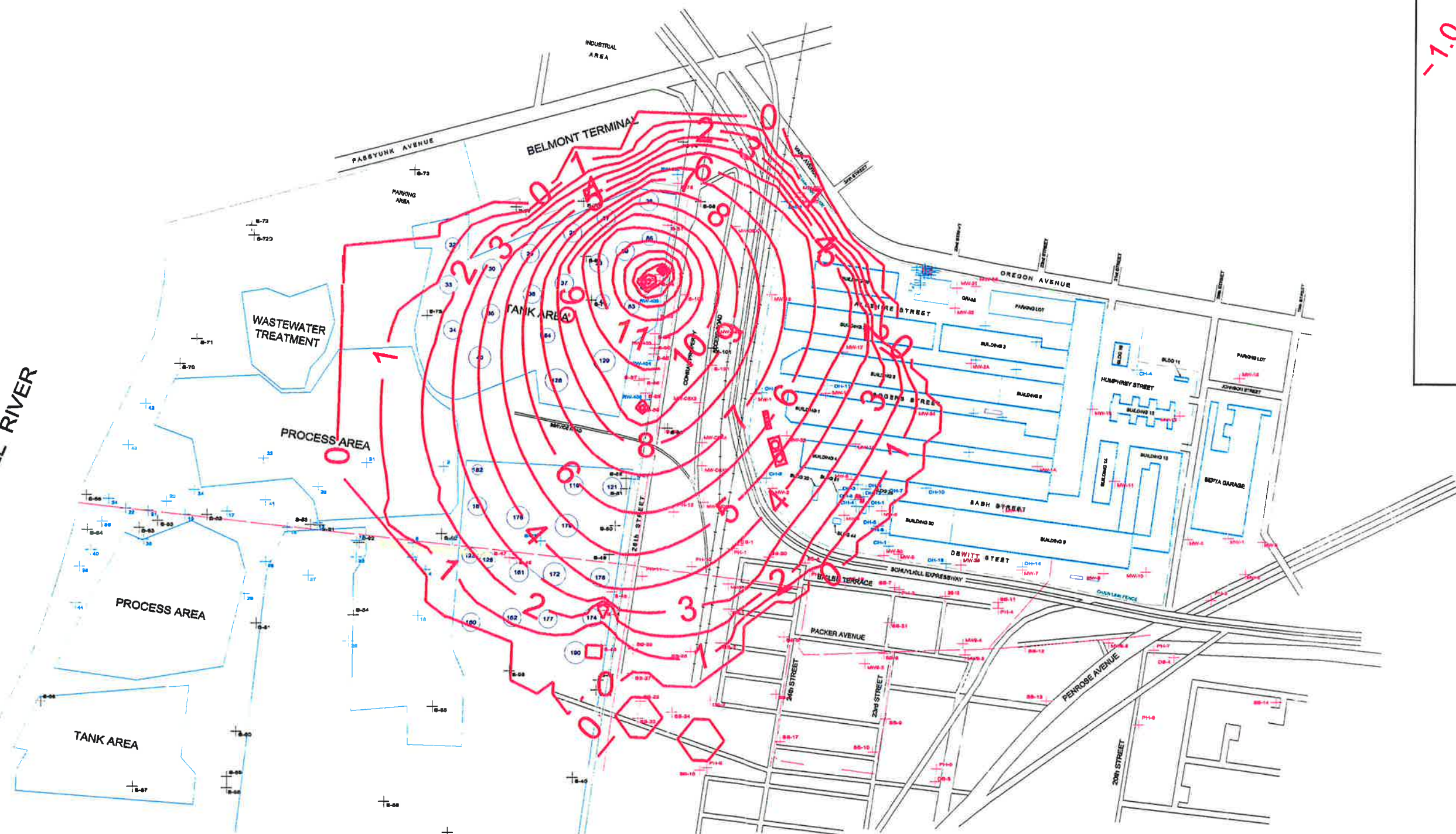
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MULTIPHASE MODELING RESULTS GROUND WATER ELEVATIONS (1997) NORTH TO SOUTH GRADIENT (0.001) STUDY AREA PHILADELPHIA, PENNSYLVANIA		
FIGURE 5-12		



SCHUYLKILL RIVER



0 400 800 1200 1600
SCALE IN FEET

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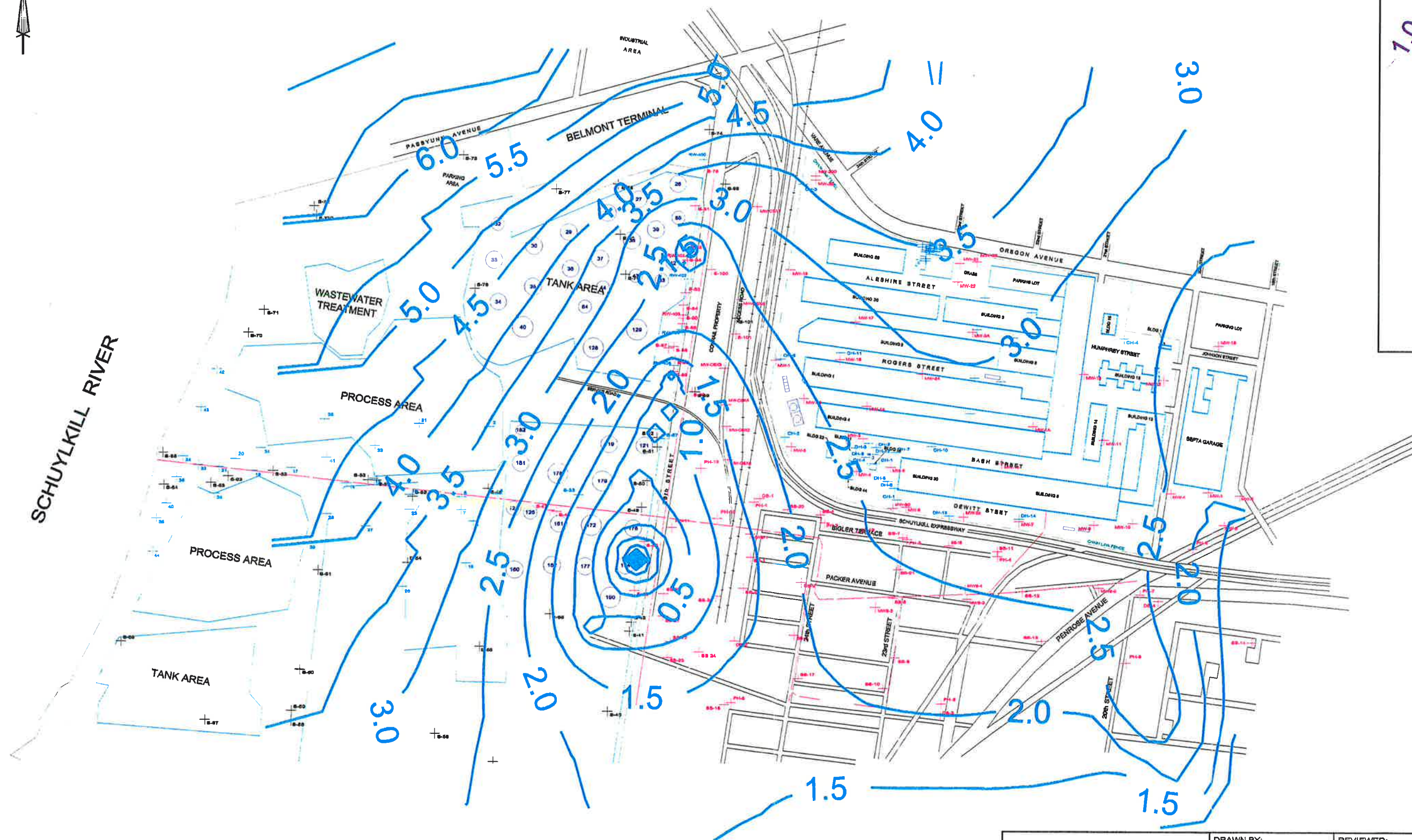
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MULTIPHASE MODELING RESULTS SCENARIO #2 - AFTER 47 YEARS (1997) CONTINUOUS RELEASE (1950) STUDY AREA PHILADELPHIA, PENNSYLVANIA		
FIGURE 5-13		



LEGEND

1.0

Modeled Ground Water
Elevation (ft)

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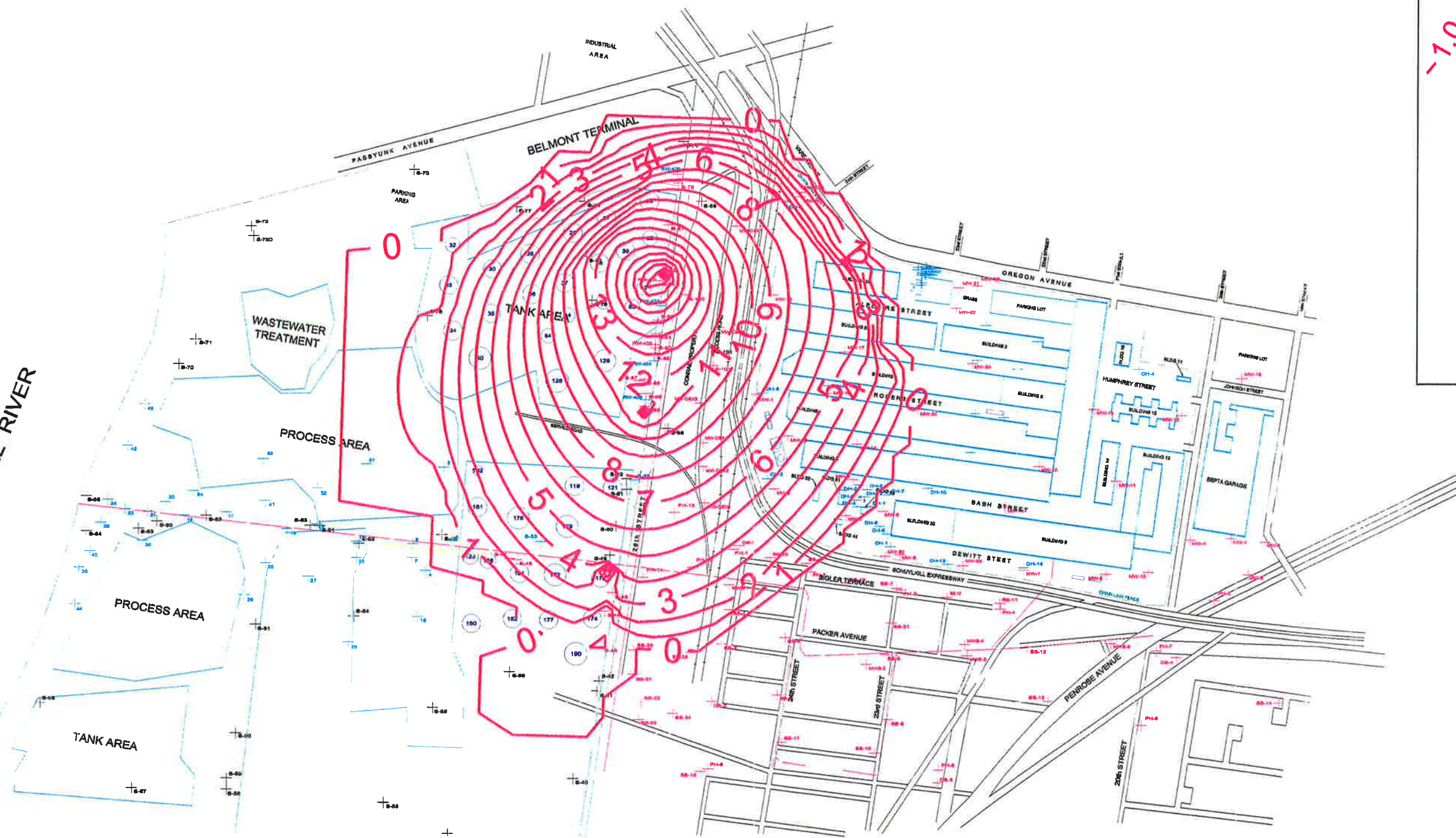
DRAWN BY: CWS	REVIEWED: PKH	APPROVED: HJR
DATE: 20 FEB 1998	PROJECT NO. SU001H	DWG. NO.

MULTIPHASE MODELING RESULTS
GROUND WATER ELEVATIONS (1997)
SCENARIOS #3, 5 & 6 (NW - SE)
STUDY AREA
PHILADELPHIA, PENNSYLVANIA

FIGURE
5-14



SCHUYLKILL RIVER



LEGEND

-1.0-

Apparent Hydrocarbon Thickness (ft)

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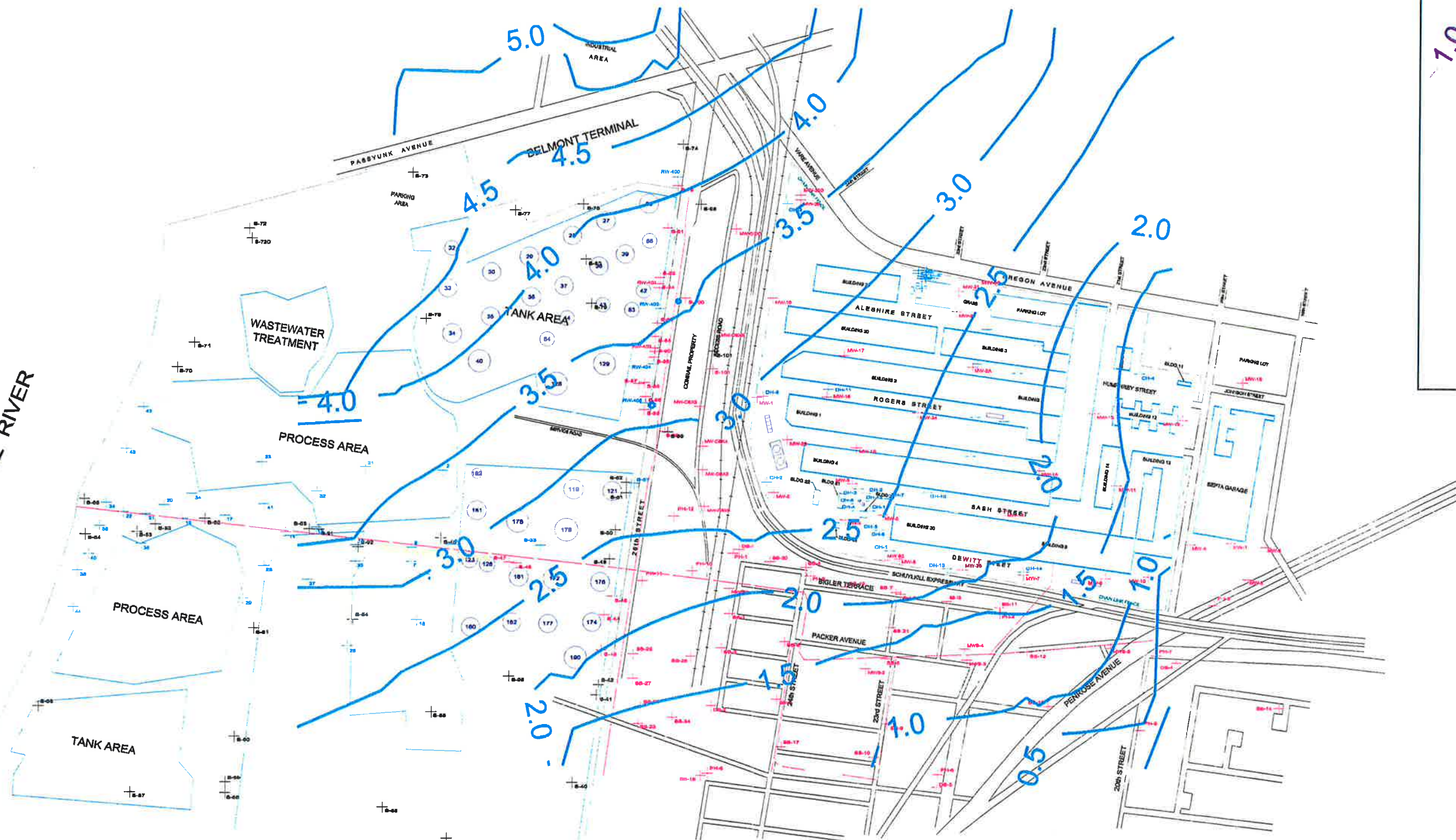
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DATE: 20 FEB 1998	PROJECT NO. SU001H	DWG. NO. SUN202
MULTIPHASE MODELING RESULTS SCENARIO #3 - AFTER 47 YEARS (1997) CONTINUOUS RELEASE (1950) STUDY AREA PHILADELPHIA, PENNSYLVANIA		
FIGURE 5-15		



LEGEND

1.0
Modeled Ground Water
Elevation (ft)

SCHUYLKILL RIVER



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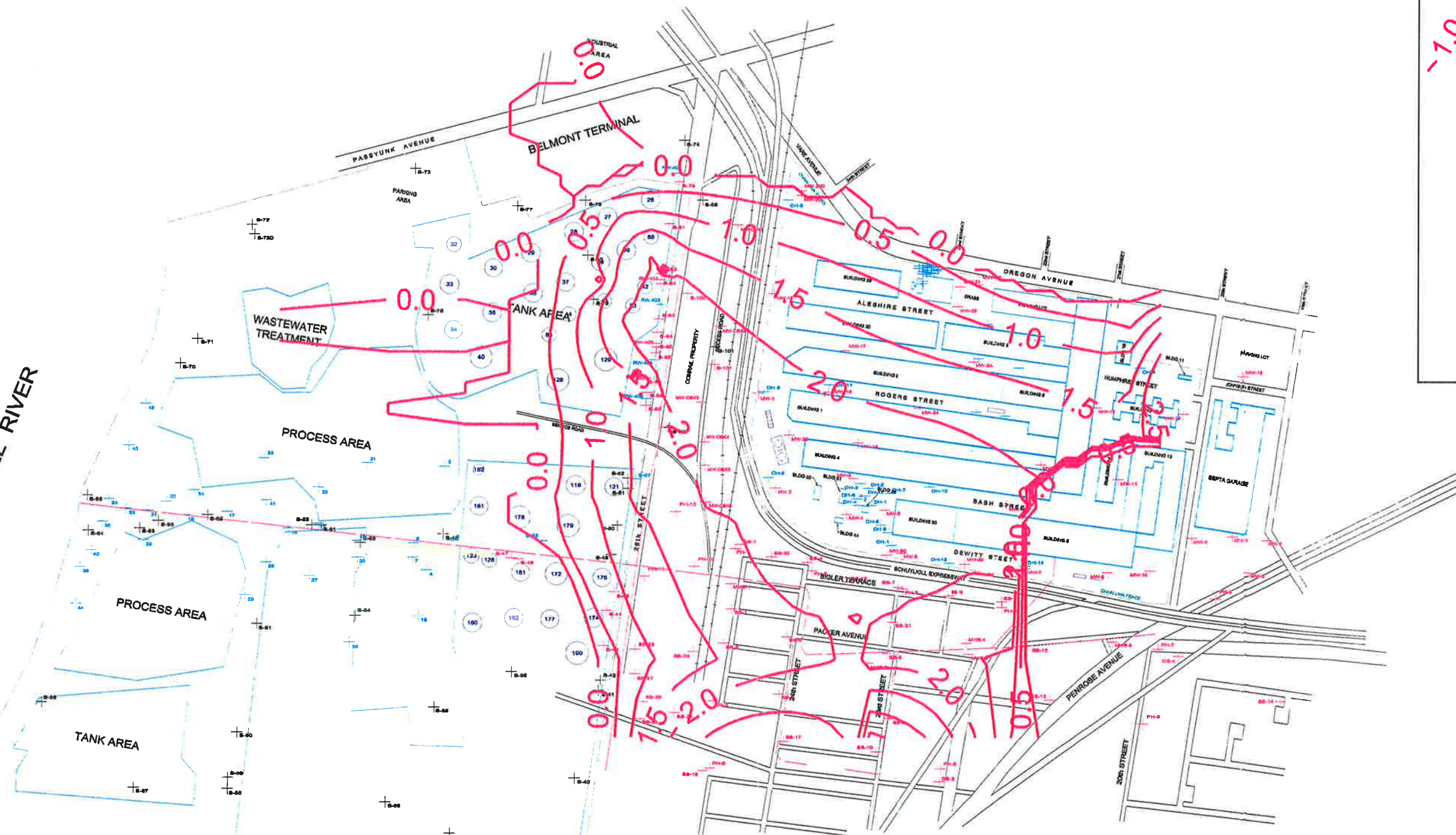
0 400 800 1200 1600
SCALE IN FEET

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MULTIPHASE MODELING RESULTS GROUND WATER ELEVATIONS (1997) SCENARIO #4 (NW - SE) STUDY AREA PHILADELPHIA, PENNSYLVANIA		
FIGURE 5-16		



SCHUYLKILL RIVER



LEGEND

-1.0-

Apparent Hydrocarbon Thickness (ft)



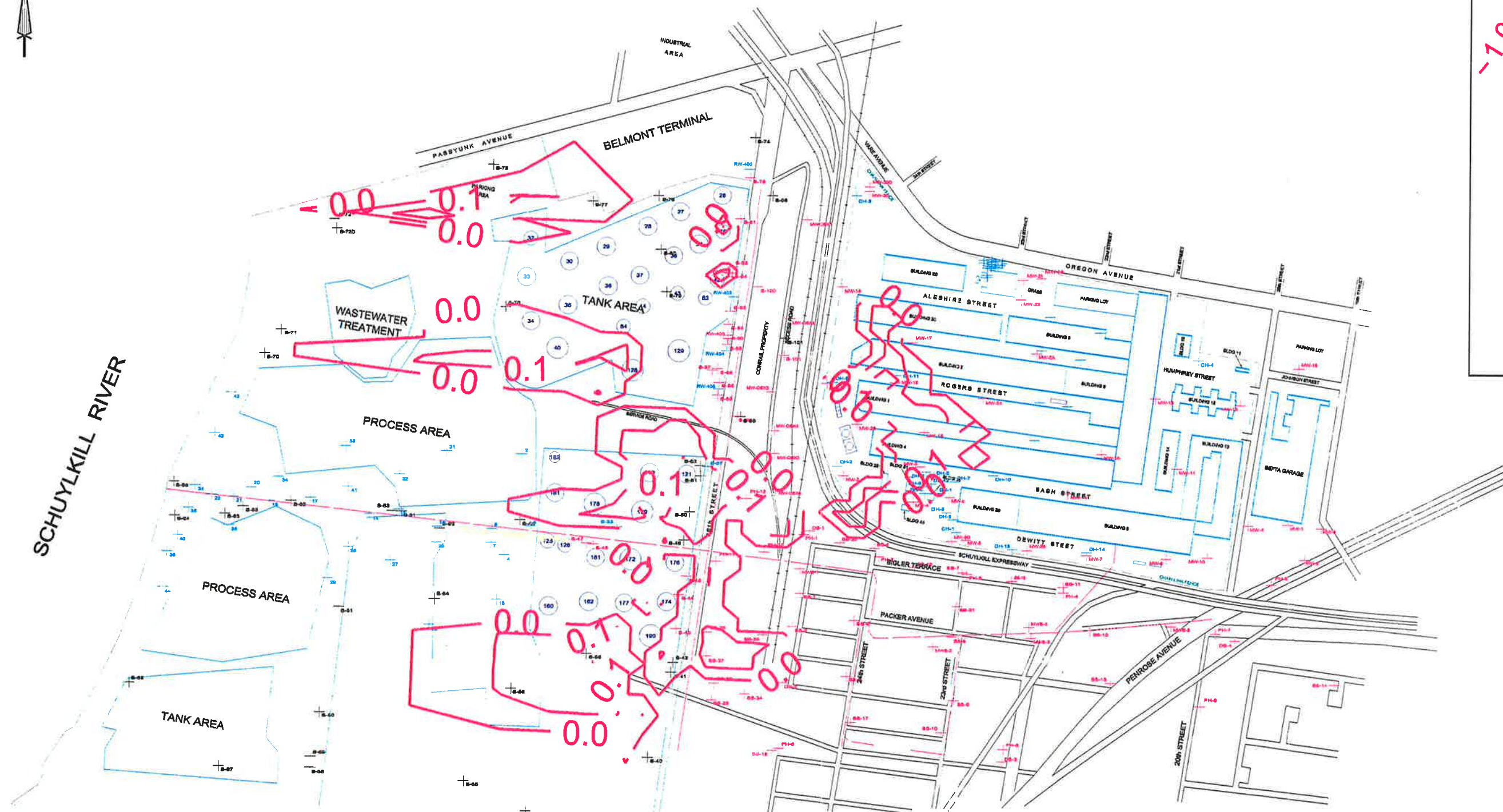
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	MULTIPHASE MODELING RESULTS SCENARIO #4 - AFTER 47 YEARS (1997) CONTINUOUS RELEASE (1950) STUDY AREA PHILADELPHIA, PENNSYLVANIA		
	FIGURE 5-17		



LEGEND

-1.0-
Apparent Hydrocarbon Thickness (ft)



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MULTIPHASE MODELING RESULTS
SCENARIO #5 - AFTER 47 YEARS (1997)
CATASTROPHIC RELEASE (1950)
STUDY AREA
PHILADELPHIA, PENNSYLVANIA

FIGURE
5-18



LEGEND

1.0

Apparent Hydrocarbon Thickness (ft)



0 400 800 1200 1600
SCALE IN FEET

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20 FEB 1998REVIEWED:
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HJRDWG. NO.
SUN210

MULTIPHASE MODELING RESULTS
SCENARIO #6 - AFTER 47 YEARS (1997)
CONTINUOUS RELEASE (DSPC) (1950)
STUDY AREA
PHILADELPHIA, PENNSYLVANIA

FIGURE
5-19



LEGEND

-0.25
Residual NAPL
Volume (ft3/ft2)



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DATE: 20 FEB 1998	PROJECT NO. SU001H	DWG. NO.
MULTIPHASE MODELING RESULTS SCENARIO #5 - AFTER 47 YEARS (1997) RESIDUAL NAPL VOLUME STUDY AREA PHILADELPHIA, PENNSYLVANIA		FIGURE 5-20

TABLE 5-1
Soil Properties

Zone #	1	2	3	4	5	6	7	MW-CSX1 (46-48')	MW-CSX2 (44-46')	MW-CSX2 (46-48')	MW-19 (18-20')
USCS	SW	SP	GP	SM	GW	SM	ML	SP	SP	SP	SP
Description	Gravelly Sand	c-m Sand	Gravel	Sandy Loam	Sandy Gravel	Silty Sand	Clay Silt Loam	Gravelly, c Sand	Gravelly, c Sand	Gravelly, c Sand	Gravelly, c Sand
K_{sw}	28	16	66	3.48	33	2	0.203	16	16	16	16
ϕ	0.31	0.40	0.35	0.41	0.30	0.41	0.32	0.40	0.40	0.40	0.40
S_m	0.484	0.250	0.143	0.390	0.167	0.390	0.378	0.250	0.250	0.250	0.250
α	7.937	6.000	12.186	2.799	8.617	2.121	0.676	6.000	6.000	6.000	6.000
η	2.70	2.68	2.70	1.89	2.70	1.89	1.11	2.68	2.68	2.68	2.68
S_{or}	16%	23%	26%	18%	25%	18%	2%	23%	23%	23%	23%
S_{og}	8%	6%	4%	7%	4%	7%	2%	6%	6%	6%	6%
ϕ_e	0.16	0.30	0.30	0.25	0.25	0.25	0.02	0.30	0.30	0.30	0.30
ρ_b	1.75	1.75	1.75	1.75	1.75	1.75	1.65	1.75	1.75	1.75	1.75
TPH S_{or} (mg/kg)	21,023	45,283	41,776	38,391	32,345	38,391	2699.22	45,283	45,283	45,283	45,283
TPH S_{og} (mg/kg)	10,172	11,270	6,015	14,895	5,434	14,895	2557.16	11,270	11,270	11,270	11,270
Observed TPH								28	620	460	300

$$TPH = \frac{\rho_{ro} \phi S_o}{(1-\phi) 2.65 \times 10^{-6}}$$

TABLE 5-1 (continued)
Soil Properties

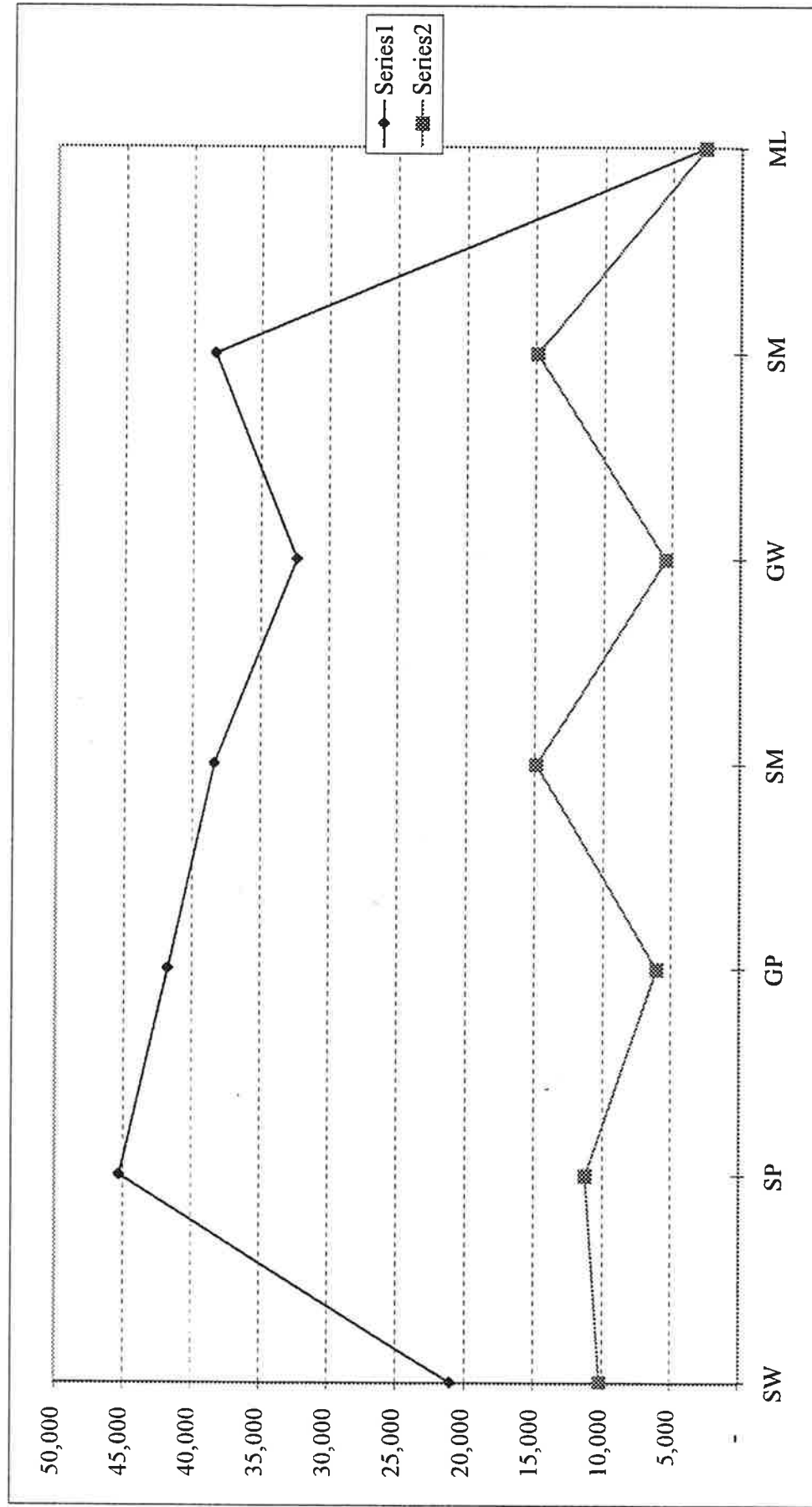


TABLE 5-2
Calculated Residual Saturation and TPH Concentrations (mg/kg)
in DSCP Alleged Pathway Soil Samples

Well # Sample Depth	MW-CSX1 (46-48 ft)	MW-CSX2 (44-46 ft)	MW-CSX2 (46-48 ft)	CH-2A (21.5-21.8 ft)	S-99 (36 ft)
USCS	SW	SW	SW	SW	SP
Description	Gravelly Sand	Gravelly Sand	Gravelly Sand	Gravelly Sand	c-m Sand
ϕ°	0.31	0.31	0.31	0.31	0.40
S_{or}^{*}	0.17	0.17	0.17	0.17	0.23
S_{og}^{*}	0.07	0.07	0.07	0.07	0.06
TPH S_{or} (mg/kg) ⁺	23,010	23,010	23,010	23,010	44,151
TPH S_{og} (mg/kg) ⁺	9,653	9,653	9,653	9,653	10,989
Observed TPH	28	620	460	18,673	8,800
Calculated S_o	0.0002	0.0047	0.0035	0.1412	0.0448

[○] These values are based on data in Table 4-2c from Dames & Moore, 1997.

^{*} Calculated from ES&T (1994a)

⁺ Calculated from ES&T (1994a)

TABLE 5-3
Summary of NAPL Fate Mechanisms
Sun/DPSC Study Area, Philadelphia, Pennsylvania

	English Units			Metric Units			Estimated
	lb	ft ³	gallons	kg	m ³	L	
IRREDUCIBLE LNAPL IN SOIL	3,993,600	80,000	598,400	1,812,278	2,265	2,265,348	% Loss NA
SUMMARY OF MASS LOST in 1 YEAR							
BIODEGRADATION	1610	32.24	241	730	0.91	913	0.04%
SOLUBILIZATION	97	1.94	15	44	0.06	55	0.00%
VOLATILIZATION	11,587	232	1,712	5,267	6.58	6,583	0.29%
TOTAL ESTIMATED MASS LOST	13,293	267	1,967	6,041	7.55	7,551	0.33%
SUMMARY OF MASS LOST in 10 YEARS							
BIODEGRADATION	3074	61.58	461	1,394	1.74	1,743	0.08%
SOLUBILIZATION	969	19	145	440	1	551	0.02%
VOLATILIZATION	115,867	2,325	17,117	52,667	66	65,833	2.91%
TOTAL ESTIMATED MASS LOST	119,910	2,406	17,723	54,501	68	68,127	3.01%
SUMMARY OF MASS LOST in 50 YEARS							
BIODEGRADATION	9,746	195	1,680	5,085	6	6,356	0.28%
SOLUBILIZATION	4,846	97	726	2,202	3	2,753	0.12%
VOLATILIZATION	579,333	11,624	85,583	263,333	329	329,167	14.53%
TOTAL ESTIMATED MASS LOST	593,925	11,916	87,989	270,620	338	338,275	14.93%

6. NAPL PLUME MORPHOLOGY WITHIN THE STUDY AREA

Sun examined and analyzed the distribution of NAPL on the site using the theoretical bases detailed in Section 3.2. This evaluation and analysis included integrating site geology data, site hydrogeology data, the physics of immiscible phase transport, the chemistry of the NAPL beneath the refinery and of that beneath the DSCP site, and the fate and transport of NAPL in the physical setting beneath the site. Sun used this integrated approach, rather than a segmented and discipline-specific approach, to account for the interactions that occur in the natural world. The results of this analysis showed that the data from the various disciplines and analytical approaches support each other. Thus, the conclusions drawn from the analysis are stronger and are better supported than those that might have been developed using a series of independent and isolated analyses. Sun concluded the following from this detailed integrated analysis of the NAPL plume morphology:

- While NAPL has been encountered on both sites, the morphology of the two plumes shows that the two plumes are from different sources.
- The DSCP NAPL plume morphology and configuration are totally consistent with and supportive of the absence of a pathway.
- The DSCP plume morphology and configuration are supportive of the weathering patterns observed in the plume chemistry data.
- The DSCP NAPL plume morphology is totally consistent with a source or sources on the DSCP site.

The focus of this section is evaluating the orientation and morphology of the plume beneath the DSCP site as it relates to source identification and pathway evaluation. As discussed in Section 3.2, the thickest and freshest aspect of a NAPL plume is generally found nearest the source of the NAPL. Sun's analysis and DSCP's own data show that the thickest aspect of the DSCP NAPL plume occurs beneath the southern portion of the DSCP property and that it thins in all directions to its margins away from these centroids or foci.

Sun also performed very detailed analysis and examination of the chemical character of the NAPL beneath both the refinery and the DSCP property using definitive state-of-the-art techniques. Sun examined petroleum hydrocarbons, PAH compounds, substituted PAH compounds, organic lead, additives, and pesticides among others. Following these analyses, the data that were generated were evaluated using advanced chemical fingerprinting techniques to evaluate the NAPL on the two properties. These analyses showed that the NAPL plume beneath the DSCP site is relatively fresh or un-weathered at its thickest point. It also showed that the degree of weathering increases from its thickness centroids to the plume's margins. In light of the physics of immiscible multi-phase fluid transport and hydrocarbon fate in the subsurface environment, this weathering pattern would be expected. As the NAPL plume advances, older and more weathered material is "pushed" ahead of fresh and less weathered material. Thus, because NAPL migrates by displacing previously released material, the NAPL on the leading edge of a plume is thinnest since it has had the greatest opportunity to weather since it was released first. Had the plume originated on the refinery, a fresh to weathered gradient would extend through DSCP's alleged pathway from the refinery to the DSCP. None exists. Rather, the most weathered NAPL occurs in the area beneath the Philadelphia Housing Authority property, which is south-southwest of the DSCP site and around the entire margin of the DSCP plume. This then is consistent with the stratigraphy discussed in Section 3.1 and direction of groundwater flow discussed in Section 4.

The remainder of this section presents the data utilized in this analysis. It details the methods used to carry out the analyses, and contains a detailed presentation of the results of the analyses and the conclusions that were drawn.

6.1 NAPL PLUME ORIENTATION

As described in detail in Section 3.2, when NAPL such as gasoline or naphtha is introduced to the subsurface in a volume adequate to advance its wetting front to the capillary fringe and water table, it accumulates and floats because it is less dense than the water on which it has pooled. This accumulation or piling causes thickening of the NAPL in the area nearest to the source. Very thick accumulations of NAPL result in a thinning of the capillary fringe (sometimes to the point that it is absent) and a depression of the water table because of the mass exerted on the water table (Freeze and Cherry 1979). Detailed graphic data analysis shows that the water table in the thickest aspect of

the DSCP plume has been depressed about 2-ft. This thickening as NAPL accumulates creates a pressure head that drives the migration of the fugitive NAPL if the pressure head is greater than the bubbling pressure or entry pressure. On a water table with no inclination and an isotropic porous medium, NAPL will flow radially, with thinning as a function of distance from the source. For this reason, NAPL can be observed upgradient of its source even at sites where the water-table inclination is steep (Schwille 1988). This process is often deemed pancaking.

Of course, groundwater tables do not exist without some level of inclination. Therefore, as NAPL accumulates on the water table, it will migrate in the direction of the inclination assuming adequate head exists to advance the wetting front. The degree of inclination will exert some control on the migration rate. Migration then results in development of a roughly elliptical plume that is elongated in the direction of the water-table inclination and groundwater flow. Once again, because the head pressure or energy needed to sustain migration is provided by the NAPL accumulation at the source, the plume thickness decreases as a function of distance from the source. Another aspect of plume thinning with distance is the creation of the residual fraction that reduces the volume and mass of the NAPL available for continued migration. For this reason, without a continuing source, NAPL plumes stabilize and cease to migrate.

The morphology and configuration of the NAPL plume beneath the DSCP site is consistent with the theoretical considerations given above and in Section 3.2. As shown in Figures 6-1 through 6-3, the plume on the DSCP site proper exists as a northeast-to-southwest trending ellipse. If the aspect of the plume that has migrated beneath the Philadelphia Housing Authority property is considered, the plume is still elliptical, but the axis has an even stronger southerly orientation. This orientation is consistent with the south-southwest direction of groundwater flow (Section 4) and with the subsurface structure described in Section 3.1. Further, the figures show from two to four thickness centroids, that is, areas of locally maximal thickness. This observation is inconsistent with migration from off the site. If the plume had migrated from a source off the site to the west, it would be thickened from east to west (i.e., from DSCP toward the refinery). The presence of multiple centroids that are spread across the site from east to west provides strong evidence of multiple sources on the DSCP site.

6.2 NAPL PLUME THICKNESS DISTRIBUTION

As discussed above, NAPL plumes generally develop as a result of introduction at a single point, or in the case of multiple sources from multiple points. Regardless of the number of introduction points, each point where adequate NAPL volume has been released to provide for migration to the water table will cause it to accumulate and thicken on the water table at that point. Figures 6-1 through 6-3 are isopachs or thickness maps that show the NAPL thickness in plan view over the expanse of the DSCP site on three separate dates. The dates selected for these plots cover a 2-year time window (1996 to 1997) and they represent the seasonal water-table fluctuation cycle, because data were collected in November and July. The data that were gathered during simultaneous synoptic gauging events are summarized in Tables 6-1 to 6-3. For consistency, the parameter selected for analysis was the uncorrected or apparent NAPL thickness. Uncorrected thickness was selected because it represented actual un-manipulated (i.e., uncorrected) field observation data, and, therefore, was deemed less likely to have been biased through any sort of manipulative correction process.

The analysis was carried out using both manual interpretations of the data as well as computerized geostatistical analysis. Both approaches were used as a quality check to ensure the validity of the geostatistical analysis. For the manual analysis, all available NAPL data were posted on a base map, and isothickness contours were developed. This process was carried out for each of the dates selected. For the geostatistical analysis, all the data for a given date were extracted from the computerized site database, which contains, to the extent they were made available to Sun, all the data generated in all investigations carried out on the DSCP. The data were then imported into the EVS software package and analyzed via kriging, a well-established and commonly used geostatistical tool. In any site characterization, samples and data are collected at various locations. It is never feasible to collect samples and data from each and every location at a site. It is, therefore, necessary to interpolate between the locations where actual data exist. This interpolation can be carried out manually using best professional judgement or with the assistance of a statistical tool such as kriging.

In kriging, subsurface characteristics and structure can be considered mathematically as variables. They are not, however, truly random nor are they completely deterministic. Rather, they are intermediate between the two and are termed regionalized variables. That is, they describe natural

phenomena that have geographic distributions. Unlike random variables, regionalized variables have continuity from point to point, but the changes in the variable are so complex that they cannot be described by any tractable deterministic function. Even when a regionalized variable such as the distribution of NAPL is spatially continuous, it is impossible to know if it is present or absent everywhere on a site. Geostatistical tools such as kriging make it possible to estimate the form of a regionalized variable such as the distribution of NAPL in one, two, or three dimensions.

Kriging, then, is a tool that can be used to geostatistically interpolate between known values thereby estimating values for the intermediate points. The process is carried out by identifying locations where known data values exist (i.e., gauging observations). Values are estimated at points intermediate between known values as a weighted average of the known values. That is, the value at a point where no data exist is based on a small set of nearby known control points. In problems where the data distribution does not actually change, punctual kriging is adequate. However, when the data change along a natural continuum or exhibit drift, universal kriging is preferred. In this process, the drift or the rate of change of a characteristic is taken into consideration in each estimate of the parameter of interest (Davis 1986). The NAPL data from the site were kriged using the universal approach.

The manually generated data and the kriged data (Figures 6.1 through 6.3) show that the DSCP NAPL plume is thickest in the vicinity of Building 30 (a known potential source), the Building 28 gas station (a known source), Buildings 13 and 14, and Building 9 (also known sources). The figures and this data exhibit some variability in thickness distribution in terms of the number of apparent centroids. However, the overall area that consistently exhibits the thickest accumulation of NAPL is coincident over the time period examined. That area is in the south-central aspect of the DSCP site. As the figures show, the thickness decreases in all directions away from the centroids, and at the plume margins, no NAPL occurs. A “halo” of NAPL absence surrounds the entire plume. Importantly, the alleged pathway area has no observed NAPL (Figures 6-1 through 6-3). As discussed in Sections 3.2 and 5, if NAPL had migrated from the refinery through the alleged pathway, NAPL and total petroleum hydrocarbon concentrations suggestive of residual saturation in the pathway would be present. There is no NAPL in the alleged pathway, and the soil-hydrocarbon concentrations are not adequate to support a conclusion that NAPL ever migrated through the area.

Another aspect of the NAPL plume evaluated in this analysis is its orientation. As mentioned previously, the plume is elliptical in shape. The data illustrated on Figures 6.1 through 6.3 show that the orientation of the ellipse, particularly the thickest aspect of it, has a clear northeast-to-southwest orientation. This is consistent with the physics of NAPL flow discussed in Section 3.2 as well as the direction of groundwater flow defined in Section 4.

The plume developed as a result of releases on the DSCP site as a result of historical activities. NAPL accumulated on the water table, thickened, and then migrated on the inclined water table. The northern spread of the NAPL resulted from the very small water-table inclination or gradient (i.e. 0.001-ft/ft) and the radial flow produced by mounding of the NAPL on the water table. Sewer discharges from the laboratory and the remainder of Building 15, as well as natural gas condensate, likely contributed to the northern aspect of the plume. In fact, PRC (1994) reports that "various quantities of hazardous materials and wastes have been stored and disposed of (through the sewer) at the C&T lab." While very little easterly NAPL migration is shown on the figures, what is likely indicated resulted from the mounding effect beneath the sources, as well as the effects of the topographic and groundwater divide that is in the area of the greatest NAPL thickness. NAPL that reached the water table in the vicinity of the divide would have split; some would have flowed east, and some would have flowed west.

6.3 NAPL WEATHERING PATTERN

While weathering patterns in the NAPL will be discussed in detail in Section 7, it is germane to address them as a part of this discussion of morphology because the data support each other. Detailed advanced chemical finger printing analysis of the NAPL data shows that the freshest aspect of the NAPL plume beneath the DSCP site occurs in the vicinity of the thickest NAPL accumulation. The material in the plume becomes substantially more weathered as a function of distance from the thick areas in precisely the same pattern as the thinning occurs. The coincidence of the products of these two distinctly different processes is striking. Thinning of a migrating NAPL plume results from loss through the residual saturation process, which is totally physical. Weathering, on the other hand, is a result of chemical and biological actions as described in Section 3.2 and 3.3.

6.4 EFFECTS OF PUMPING ON PLUME MORPHOLOGY

As discussed in Section 2 and in Section 4, pumping for water supply and hydrocarbon recovery in the unconfined aquifer was carried out at the refinery since the 1930s. Obviously, any pumpage alters the water-table configuration, forming a cone of depression. The extent of this alteration is a function of the formation hydraulic conductivity. The results of the pumping test performed by Sun in August 1997 described in Section 3.1 showed that long-term pumping (i.e., 10 days) at a high rate (i.e., 225 gpm) resulted in drawdown of 0.1-ft approximately 1,200-ft from the pumping well (RW-2). This well is screened in a coarse sand and gravel aspect of the Trenton Formation. In contrast, pumping from the recovery wells along 26th Street is sustained at less than 5 gpm, and the radii of influence are typically less than 50-ft. These wells are obviously screened in a much less conductive aspect of the Trenton Formation or the upper sand.

Examining the DSCP NAPL plume morphology in light of pumping on the refinery shows that the pumping has had no observable effect. Had there been an impact, the plume would have been skewed strongly to the west-northwest of the major pumping centers. It does not. Rather, it is oriented to the south-southwest. Further, had pumping induced plume migration to the west, a pathway would have been created between DSCP and the pumping centers. No such pathway exists. The modeling detailed in Section 5, which included pumping centers on the refinery, supports these conclusions. The results of these simulations showed that pumping had no effect on plume migration. The modeling results also showed that the only mechanism through which the DSCP plume could be duplicated through simulation was by placing source areas at locations of the centroids shown in Figures 6-1 through 6-3. Figure 6-4 compares the actual and simulated plumes. From this comparison, the DSCP plume clearly spread on the DSCP site from the vicinity of the thickness centroids.

Based on the preceding analysis of the DSCP NAPL plume morphology, the following conclusions can be drawn:

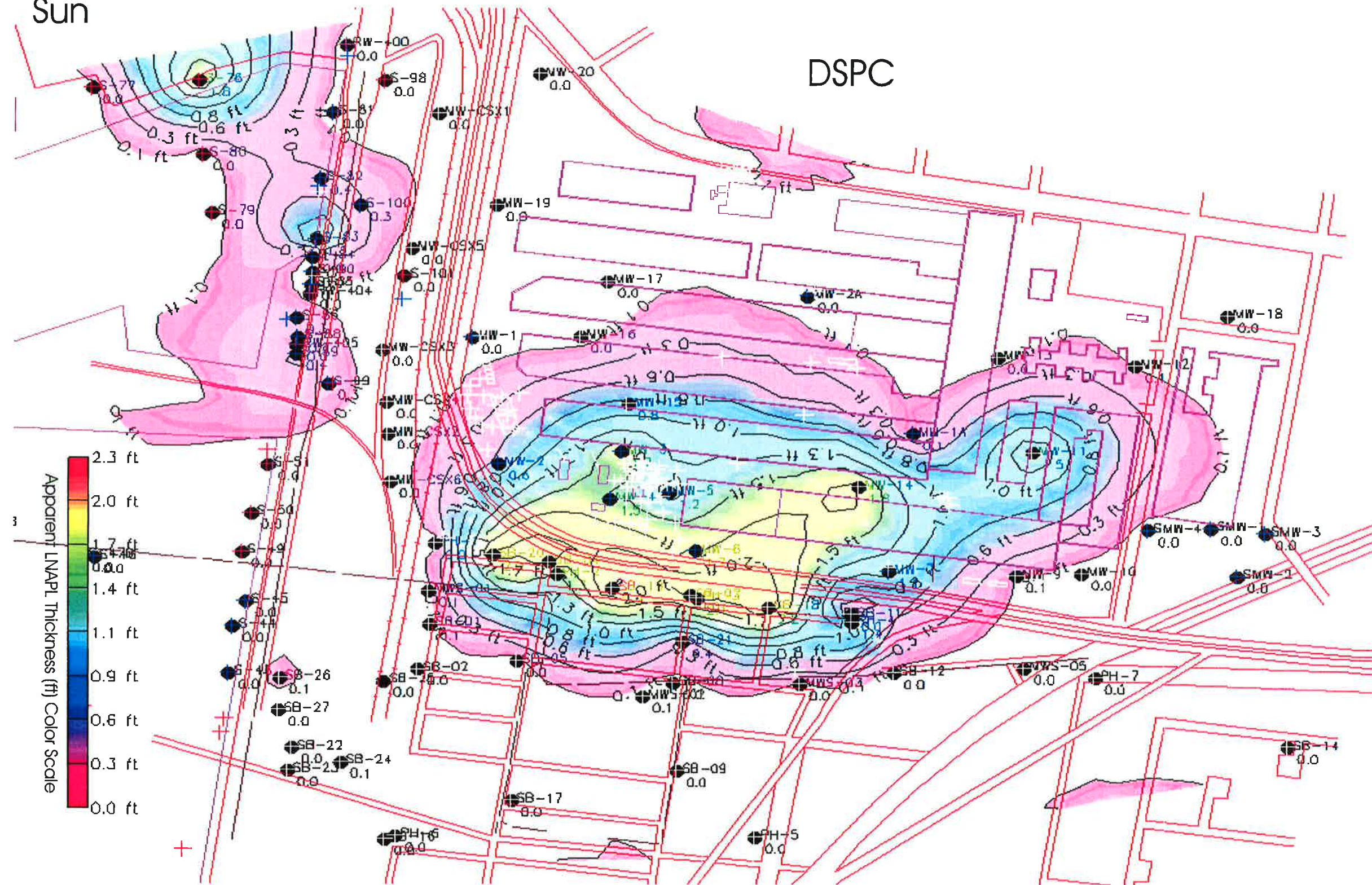
- The plume beneath the DSCP site originated on the DSCP site and migrated away from its sources or points of formation in a predominately south-southwestern direction.
- The plume is thickest nearest the center and its source or sources.

- The plume thins in all directions from the thickness centroids.
- The plume is discontinuous with the alleged CSX pathway
- The plume is less weathered in the thickest aspect and is more weathered as a function of distance from its source.
- The plume morphology is totally consistent, based on immiscible multi-phase fluid transport theory, with one that originated on DSCP property.



Sun

DSPC



Apparent LNAPL Thickness (ft) Color Scale

2.3 ft
2.0 ft
1.7 ft
1.4 ft
1.1 ft
0.9 ft
0.6 ft
0.3 ft
0.0 ft

0 400 800

Scale is in feet
(approximately)

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DRAWN BY: CWS	REVIEWED: PKH	APPROVED: HJR
DATE: 19 FEB 1998	PROJECT NO: SU001H	DWG. NO:

Apparent LNAPL Thickness (ft)
15, November 1996
Study Area
PHILADELPHIA, PENNSYLVANIA

Figure
6-1

THIS MAP WAS COMPILED FROM BASE DRAWINGS
AND/OR SKETCHES SUPPLIED BY OTHERS.
IT IS TO BE USED ONLY AS AN APPROXIMATE SOURCE OF REFERENCE.
WE ASSUME NO RESPONSIBILITY FOR THE ACCURACY OF
BASE MAP RELATED INFORMATION CONTAINED HEREIN.



Sun

DSPC

Apparent LNAPL Thickness (ft) Color Scale

2.1 ft
1.8 ft
1.6 ft
1.3 ft
1.0 ft
0.8 ft
0.5 ft
0.3 ft
0.0 ft

0 400 800

Scale is in feet
(approximately)

INTEGRATED
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DRAWN BY: CWS	REVIEWED: PKH	APPROVED: HJR
DATE: 19 FEB 1998	PROJECT NO: SU001H	DWG. NO.
Apparent NAPL Thickness (ft) 28, July 1997 Study Area PHILADELPHIA, PENNSYLVANIA		

Figure
6-2

THIS MAP WAS COMPILED FROM BASE DRAWINGS
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BASE MAP RELATED INFORMATION CONTAINED HEREIN.



Sun

DSPC

Apparent LNAPL Thickness (ft) Color Scale

2.0 ft
1.8 ft
1.5 ft
1.3 ft
1.0 ft
0.8 ft
0.5 ft
0.3 ft
0.0 ft

0 400 800

Scale is in feet
(approximately)

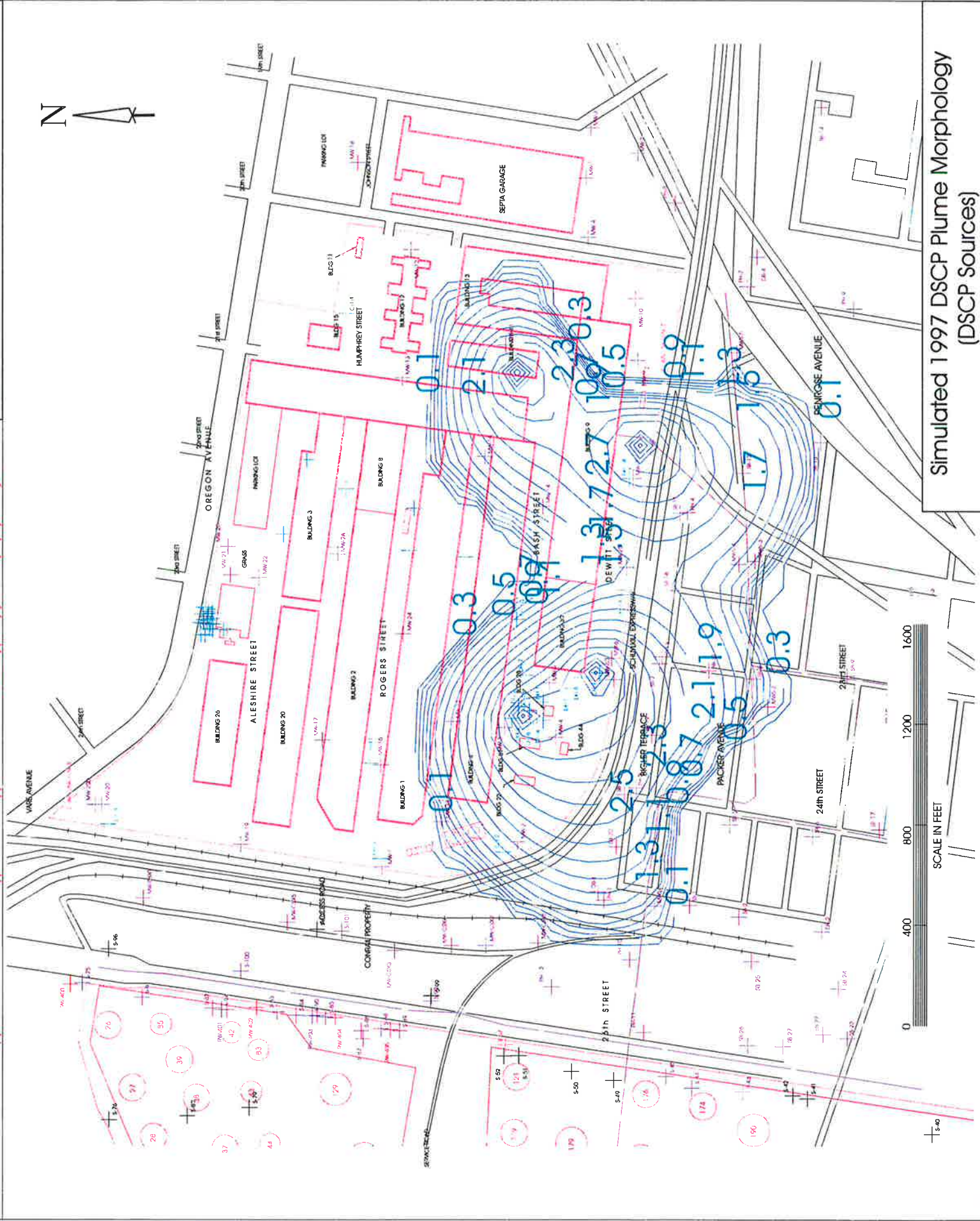
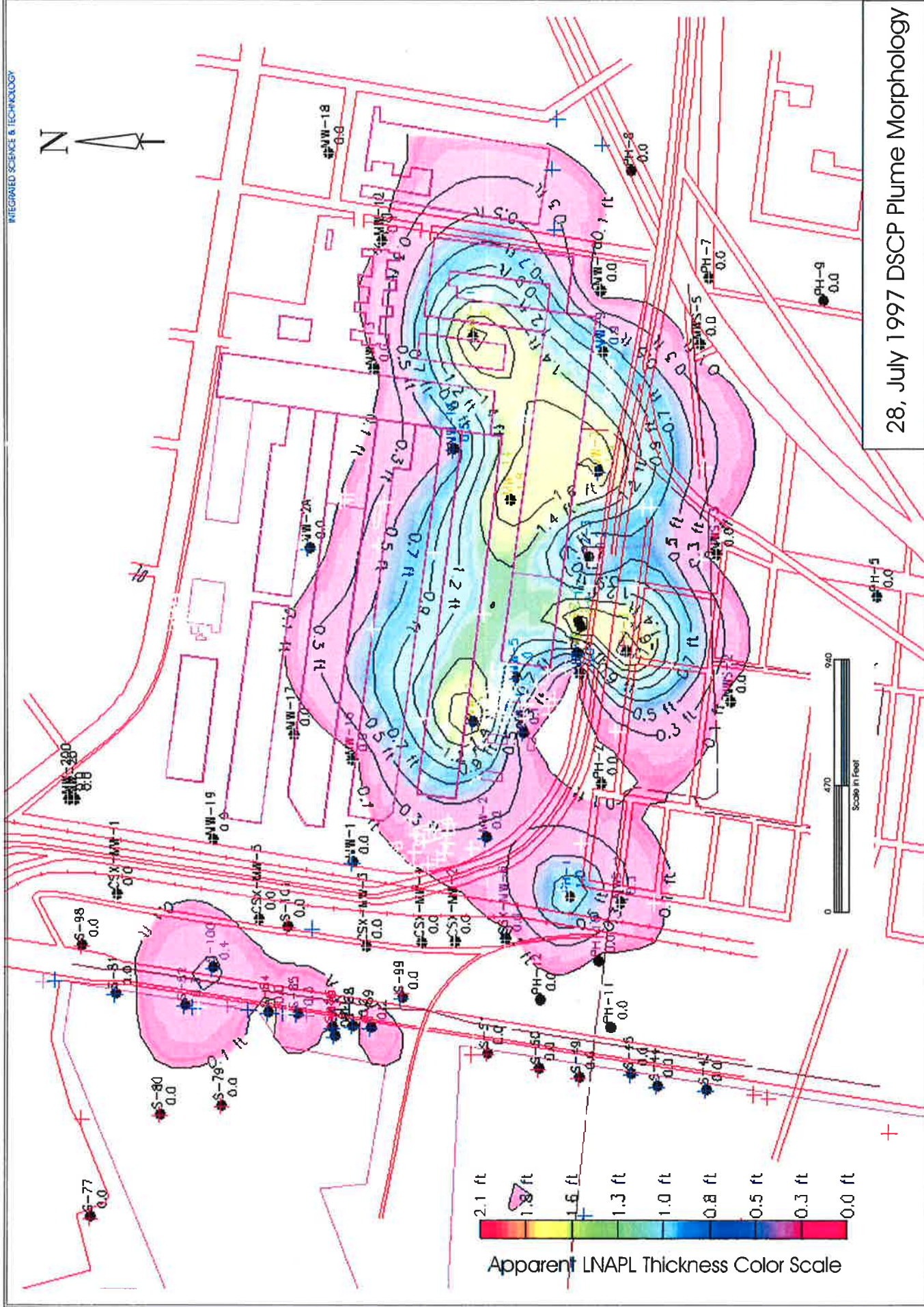
INTEGRATED
SCIENCE &
TECHNOLOGY, INC.

DRAWN BY: CWS	REVIEWED: PKH	APPROVED: HJR
DATE: 19 FEB 1998	PROJECT NO: SU001H	DWG NO:

Apparent LNAPL Thickness (ft)
10, November 1997
Study Area
PHILADELPHIA, PENNSYLVANIA

Figure
6-3

THIS MAP WAS COMPILED FROM BASE DRAWINGS
AND/OR SKETCHES SUPPLIED BY OTHERS.
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BASE MAP RELATED INFORMATION CONTAINED HEREIN.



 INTEGRATED SCIENCE & TECHNOLOGY, INC.	DRAWN BY: CWS	DATE: 3/4/98	Measured vs. Simulated DSCP Plume Morphology	FIGURE 6-4
	REVIEWED: PKH	PROJECT NO. SU001		
	APPROVED: HJR	DWG. NO. 3500000		
Study Area PHILADELPHIA, PENNSYLVANIA				

TABLE 6-1
Groundwater Gauging Data Summary
15 November 1996
DSPC and Sun Refinery
Philadelphia, Pennsylvania

WELL ID	REFERENCE ELEVATION (ft)	DEPTH TO WATER (ft)	GROUNWATER ELEVATION (ft)	DEPTH TO PRODUCT (ft)	APPARENT PRODUCT THICKNESS (ft)
MW-1	20.78	17.92	2.86	17.92	0
MW-2	21.83	20.26	1.57	19.64	0.62
MW-3	20.34	19.59	0.75	17.9	1.69
MW-4	20.6	19.7	0.9	18.21	1.49
MW-5	20.32	19.17	1.15	17.99	1.18
MW-6	21.18	20.42	0.76	18.74	1.68
MW-7	19.3	17.93	1.37	16.79	1.14
MW-1A	21.33	18.83	2.5	18.74	0.09
MW-2A	21.13	17.71	3.42	17.71	0
MW-9	20.08	18.7	1.38	17.8	0.09
MW-10	16.56	14.14	2.42	14.12	0.02
MW-11	20.21	19.19	1.02	17.65	1.54
MW-12	19.54	16.53	3.01	16.45	0.08
MW-13	20.38	17.28	3.1	17.28	0
MW-14	20.27	19.47	0.8	17.65	1.82
MW-15	22.58	20.97	1.61	20.14	0.83
MW-16	20.36	17.42	2.94	17.42	0
MW-17	22.25	18.55	3.7	18.55	0
MW-18	17.93	12.31	5.62	12.31	0
MW-19	23.12	17.96	5.16	17.96	0
MW-20	25.66	19.98	5.68	19.98	0
MW-CSX1	51.32	42.38	8.94	42.38	0
MW-CSX2	46.7	44.66	2.04	44.66	0
S-43	24.22	24.02	0.2	24.02	0
S-44	24.32	25.56	-1.24	25.56	0
S-45	25.55	22.68	2.87	22.68	0
S-46	24.69	21.05	3.64	21.05	0
S-47D	24.34	20.51	3.83	20.51	0
S-48	23.37	18.49	4.88	18.49	0
S-49	24.87	24.63	0.24	24.63	0
S-50	23.46	22.15	1.31	22.14	0.01
S-51	24.76	23.62	1.14	23.62	0
S-76	33.05	27.75	5.3	25.98	1.77
S-77	34.08	28.31	5.77	28.31	0
S-78	32.93	25.65	7.28	25.65	0
S-79	31.46	26.02	5.44	26.02	0
S-80	33.6	27.57	6.03	27.57	0
S-81	28.86	23.14	5.72	23.14	0
S-82	28.3	22.98	5.32	22.58	0.4
S-83	24.4	20.25	4.15	19.06	1.19

TABLE 6-1
Groundwater Gauging Data Summary
15 November 1996
DSPC and Sun Refinery
Philadelphia, Pennsylvania

WELL ID	REFERENCE ELEVATION (ft)	DEPTH TO WATER (ft)	GROUNWATER ELEVATION (ft)	DEPTH TO PRODUCT (ft)	APPARENT PRODUCT THICKNESS (ft)
S-84	23.98	17.81	6.17	17.8	0.01
S-85	26.05	22.3	3.75	22.21	0.09
S-86	28.05	25.48	2.57	25.2	0.28
S-88	25.07	24.15	0.92	23.91	0.24
S-89	26.98	26.52	0.46	26.13	0.39
S-90	25.09	33.4	-8.31	33.4	0
S-98	29.72	24.13	5.59	24.13	0
S-99	25.01	23.74	1.27	23.49	0.25
S-100	27.95	22.73	5.22	22.38	0.35
S-101	50.12	46.62	3.5	46.62	0
RW-400	26.74	31.15	-4.41	31.15	0
RW-404	24.73	29.87	-5.14	29.85	0.02
RW-405	25.1	24.82	0.28	24.8	0.02
SB-01	23.97	22.52	1.45	22.47	0.05
SB-02	23.6	21.59	2.01	21.55	0.04
SB-04	21.72	21.55	0.17	19.45	2.1
SB-05	21.48	20.8	0.68	20.77	0.03
SB-07	21.73	21.85	-0.12	19.82	2.03
SB-08	18.97	17.46	1.51	17.45	0.01
SB-09	17.96	16.03	1.93	16	0.03
SB-11	18.82	16.32	2.5	16.29	0.03
SB-12	12.68	10.3	2.38	10.3	0
SB-14	15.15	10.33	4.82	10.33	0
SB-16	22.24	19.7	2.54	19.7	0
SB-17	19.82	17.6	2.22	17.6	0
SB-18	19.96	19.38	0.58	17.17	2.21
SB-19	22.13	21.65	0.48	19.36	2.29
SB-20	22.1	21.1	1	19.06	2.04
SB-21	20.98	19.22	1.76	18.86	0.36
MWS-01	24.01	22.38	1.63	22.33	0.05
MWS-02	19.97	17.93	2.04	17.88	0.05
MWS-03	16.06	13.61	2.45	13.61	0
MWS-05	15.2	13.11	2.09	13.11	0
MW-CSX3	48.12	45.59	2.53	45.59	0
MW-CSX4	47.15	45.2	1.95	45.2	0
MW-CSX5	49.76	45.07	4.69	45.07	0
MW-CSX6	45.92	44.12	1.8	44.12	0
SMW-1	18.55	16.84	1.71	16.84	0
SMW-2	17.81	16.2	1.61	16.2	0
SMW-3	17.82	16.15	1.67	16.15	0

TABLE 6-1
Groundwater Gauging Data Summary
15 November 1996
DSPC and Sun Refinery
Philadelphia, Pennsylvania

WELL ID	REFERENCE ELEVATION (ft)	DEPTH TO WATER (ft)	GROUNWATER ELEVATION (ft)	DEPTH TO PRODUCT (ft)	APPARENT PRODUCT THICKNESS (ft)
SMW-4	18	14.68	3.32	14.66	0.02
PH-1	23.39	21.53	1.86	21.53	0
PH-2	21.3	20.71	0.59	19.4	1.31
PH-3	22.24	21.82	0.42	19.75	2.07
PH-4	18.25	17.07	1.18	15.66	1.41
PH-5	15.04	12.95	2.09	12.95	0
PH-6	22.04	19.84	2.2	19.84	0
PH-7	14.56	12.75	1.81	12.75	0
SB-22	25.2	24.5	0.7	24.49	0.01
SB-23	24.25	23.65	0.6	23.63	0.02
SB-24	26.55	25.72	0.83	25.66	0.06
SB-25	24.94	25.82	-0.88	25.82	0
SB-26	23.37	24.92	-1.55	24.77	0.15
SB-27	23.46	24.97	-1.51	24.95	0.02

TABLE 6-2
Groundwater Gauging Data Summary
28 July 1997
DSPC and Sun Refinery
Philadelphia, Pennsylvania

WELL ID	REFERENCE ELEVATION (ft)	DEPTH TO WATER (ft)	GROUNWATER ELEVATION (ft)	DEPTH TO PRODUCT (ft)	APPARENT PRODUCT THICKNESS (ft)
S-102	15	12.91	2.09	NT	NT
S-103	15	12.75	2.25	NT	NT
S-111	15	13.39	1.61	NT	NT
S-112	15	13.51	1.49	NT	NT
S-113	15	13.88	1.12	NT	NT
S-114	15	13.89	1.11	NT	NT
S-28	14.5	10.06	4.44	NT	NT
S-31	14	9.54	4.46	NT	NT
S-32	14.5	11.87	2.63	NT	NT
S-37	15.5	13.6	1.9	NT	NT
S-39	18.25	15.1	3.15	NT	NT
S-40	21.25	18.27	2.98	NT	NT
S-41	23.25	21.24	2.01	NT	NT
S-48	20.5	16.18	4.32	NT	NT
S-54	17.25	14.94	2.31	NT	NT
S-55	19	16.57	2.43	NT	NT
S-56	17	14.7	2.3	NT	NT
S-57	14	12.95	1.05	NT	NT
S-60	14.75	13.73	1.02	NT	NT
S-61	15	11.98	3.02	NT	NT
S-63	16.25	14	2.25	NT	NT
S-66	13.5	10.55	2.95	NT	NT
S-68	12.25	10.68	1.57	NT	NT
S-69	10.75	9.59	1.16	NT	NT
S-76	30	23.68	6.32	NT	NT
S-78	26.25	19.15	7.1	NT	NT
S-91	17	10.11	6.89	NT	NT
S-93	16	11.55	4.45	NT	NT
S-95	21.25	18.62	2.63	NT	NT
S-97	15.25	11.82	3.43	NT	NT
MW-1	20.78	18.36	2.42	18.36	0
MW-2	21.83	20.25	1.58	20.05	0.2
MW-3	20.34	20.26	0.08	18.34	1.92
MW-4	20.6	19.05	1.55	18.92	0.13
MW-5	20.32	19.42	0.9	18.45	0.97
MW-6	21.18	20.11	1.07	19.4	0.71
MW-6D	21.45	19.95	1.5	19.95	0
MW-7	19.3	18.99	0.31	17.13	1.86
MW-1A	21.33	19.62	1.71	19.12	0.5
MW-2A	21.13	18.15	2.98	18.15	0

TABLE 6-2
Groundwater Gauging Data Summary
28 July 1997
DSPC and Sun Refinery
Philadelphia, Pennsylvania

WELL ID	REFERENCE ELEVATION (ft)	DEPTH TO WATER (ft)	GROUNWATER ELEVATION (ft)	DEPTH TO PRODUCT (ft)	APPARENT PRODUCT THICKNESS (ft)
MW-9	20.08	19.08	1	18.18	0.9
MW-10	16.56	14.23	2.33	14.23	0
MW-11	20.21	20	0.21	18.06	1.94
MW-12	19.54	17.01	2.53	16.92	0.09
MW-13	20.38	17.72	2.66	17.72	0
MW-14	20.27	19.93	0.34	18.12	1.81
MW-16	20.36	17.9	2.46	17.9	0
MW-17	22.25	19.04	3.21	19.04	0
MW-18	17.93	14.23	3.7	14.23	0
MW-19	23.12	18.15	4.97	18.15	0
MW-20	25.66	20.03	5.63	20.03	0
MW-20D	25.8	23.89	1.91	23.89	0
CSX-MW-1	51.32	43.19	8.13	43.19	0
CSX-MW-2	46.7	45.26	1.44	45.26	0
CSX-MW-3	48.12	46.03	2.09	46.03	0
CSX-MW-4	47.15	45.57	1.58	45.57	0
CSX-MW-5	49.76	45.41	4.35	45.41	0
CSX-MW-6	45.92	44.57	1.35	44.57	0
MWS-1	24.01	23.02	0.99	22.7	0.32
MWS-2	19.97	18.29	1.68	18.29	0
MWS-3	16.06	14.02	2.04	14.02	0
MWS-5	15.2	13.67	1.53	13.67	0
PH-1	23.39	22.71	0.68	21.71	1
PH-2	21.3	19.82	1.48	19.82	0
PH-3	22.24	22.3	-0.06	20.23	2.07
PH-5	15.04	13.4	1.64	13.4	0
PH-7	14.56	12.74	1.82	12.74	0
PH-8	16.06	15.22	0.84	15.22	0
PH-9	15.5	10.12	5.38	10.12	0
PH-10	21.82	20.87	0.95	20.85	0.02
PH-11	21.65	21.32	0.33	21.31	0.01
PH-12	21.51	20.57	0.94	20.56	0.01
S-43	24.22	24.02	0.2	24.02	0
S-44	24.32	25.56	-1.24	25.56	0
S-45	25.55	22.68	2.87	22.68	0
S-49	24.87	24.82	0.05	24.81	0.01
S-50	23.46	23.53	-0.07	23.53	0
S-51	24.76	23.69	1.07	23.69	0
S-77	34.08	28.43	5.65	28.41	0.02
S-78	32.93	25.87	7.06	25.85	0.02

TABLE 6-2
Groundwater Gauging Data Summary
28 July 1997
DSPC and Sun Refinery
Philadelphia, Pennsylvania

WELL ID	REFERENCE ELEVATION (ft)	DEPTH TO WATER (ft)	GROUNWATER ELEVATION (ft)	DEPTH TO PRODUCT (ft)	APPARENT PRODUCT THICKNESS (ft)
S-79	31.46	26.15	5.31	26.15	0
S-80	33.6	27.6	6	27.56	0.04
S-81	28.86	23.3	5.56	23.29	0.01
S-82	28.3	23.41	4.89	23.12	0.29
S-84	23.98	19.77	4.21	19.74	0.03
S-85	26.05	23.36	2.69	23.08	0.28
S-86	28.05	25.91	2.14	25.8	0.11
S-87D	26.88	25.36	1.52	25.35	0.01
S-88	25.07	24.36	0.71	24.35	0.01
S-89	26.98	26.32	0.66	26.09	0.23
S-98	29.72	24.36	5.36	24.36	0
S-99	25.01	23.95	1.06	23.95	0
S-100	27.95	23.24	4.71	22.87	0.37
S-101	50.12	47.18	2.94	47.18	0
PZ-1	21.24	21.1	0.14	19.23	1.87
PZ-2	21.08	20.95	0.13	19.04	1.91
PZ-3	20.23	18.89	1.34	18.65	0.24

Notes: NT = Not taken

TABLE 6-3
Groundwater Gauging Data Summary
10 November 1997
DSCP and Sun Refinery
Philadelphia, Pennsylvania

WELL ID	REFERENCE ELEVATION (ft)	DEPTH TO WATER (ft)	GROUNWATER ELEVATION (ft)	DEPTH TO PRODUCT (ft)	APPARENT PRODUCT THICKNESS (ft)
MW-1	20.78	19.22	1.56	19.22	0
MW-2	21.83	21.88	-0.05	20.93	0.95
MW-3	20.34	21.09	-0.75	19.2	1.89
MW-4	20.6	19.85	0.75	19.85	0
MW-5	20.32	20.53	-0.21	10.26	1.27
MW-6	21.18	20.84	0.34	20.35	0.49
MW-6D	21.45	20.85	0.6	20.85	0
MW-7	19.3	19.96	-0.68	10.04	1.94
MW-1A	21.33	20.7	0.63	18.92	1.78
MW-2A	21.13	18.96	2.18	18.96	0
MW-9	20.08	20.22	-0.11	18.9	1.32
MW-10	16.56	14.98	1.58	14.98	0
MW-11	20.21	20.75	-0.54	18.82	1.93
MW-12	19.54	17.78	1.76	17.7	0.08
MW-13	20.38	18.51	1.87	18.51	0
MW-14	20.27	20.64	-0.37	18.97	1.67
MW-15	22.58	22.19	0.39	21.47	0.72
MW-16	20.36	18.74	1.62	18.74	0
MW-17	22.25	19.95	2.3	19.95	0
MW-19	23.12	18.73	4.39	18.73	0
MW-20	25.66	20.4	5.26	20.4	0
MW-20D	25.8	24.6	1.2	24.6	0
MW-21	20.18	17.01	3.17	17.01	0
MW-22	21.7	18.77	2.93	18.77	0
MW-23	20.72	19.55	1.17	19.55	0
MW-24	20.95	19.61	1.34	19.55	0.06
MW-25	20.36	22.18	-1.8	20.29	1.87
MW-26	20.4	17.13	3.27	17.13	0
CSX-MW-1	51.32	43.59	7.73	43.59	0
CSX-MW-2	46.7	46.12	0.58	46.12	0
CSX-MW-3	48.12	46.88	1.24	46.88	0
CSX-MW-4	47.15	45.43	0.72	45.43	0
CSX-MW-5	49.76	46.13	3.83	46.13	0
CSX-MW-6	45.92	45.45	0.47	45.45	0
MWS-1	24.01	24.04	-0.03	23.55	0.49
MWS-2	19.97	18.24	1.73	18.22	0.02
MWS-3	16.06	15.04	1.02	15.01	0.03
MWS-5	15.2	14.23	0.97	14.23	0
PH-1	23.39	23.35	0.04	22.72	0.83
PH-2	21.3	20.72	0.58	20.72	0

TABLE 6-3
Groundwater Gauging Data Summary
10 November 1997
DSCP and Sun Refinery
Philadelphia, Pennsylvania

WELL ID	REFERENCE ELEVATION (ft)	DEPTH TO WATER (ft)	GROUNWATER ELEVATION (ft)	DEPTH TO PRODUCT (ft)	APPARENT PRODUCT THICKNESS (ft)
PH-3	22.24	23.11	-0.87	21.11	2
PH-5	15.04	14.23	0.81	14.23	0
PH-7	14.56	13.08	1.48	13.08	0
PH-8	16.06	15.98	0.08	15.98	0
PH-9	15.5	9.97	5.53	9.97	0
PH-10	21.82	21.71	0.11	21.71	0
PH-11	21.65	21.97	-0.32	21.97	0
PH-12	21.51	21.37	0.14	21.37	0
PZ-1	24.22	21.92	-0.68	20.12	1.8
PZ-2	24.32	21.86	-0.78	19.98	1.88
PZ-3	25.55	19.78	0.45	19.59	0.19
S-43	24.22	24.02	0.2	24.02	0
S-44	24.32	25.56	-1.24	25.56	0
S-45	25.55	22.68	2.87	22.68	0
S-46	24.69	21.05	3.64	21.05	0
S-47D	24.34	20.51	3.83	20.51	0
S-48	23.37	18.49	4.88	18.49	0
S-49	24.87	24.63	0.24	24.63	0
S-50	23.46	22.15	1.31	22.14	0.01
S-51	24.76	23.62	1.14	23.62	0
S-76	33.05	27.75	5.3	25.98	1.77
S-77	34.08	28.31	5.77	28.31	0
S-78	32.93	25.65	7.28	25.65	0
S-79	31.46	26.02	5.44	26.02	0
S-81	28.86	23.14	5.72	23.14	0
S-82	28.3	22.98	5.32	22.58	0.4
S-83	24.4	20.25	4.15	19.06	1.19
S-84	23.98	17.81	6.17	17.8	0.01
S-85	26.05	22.3	3.75	22.21	0.09
S-86	28.05	25.48	2.57	25.2	0.28
S-88	25.07	24.15	0.92	23.91	0.24
S-89	26.98	26.52	0.46	26.13	0.39
S-98	29.72	24.13	5.59	24.13	0
S-99	25.01	23.74	1.27	23.49	0.25
SMW-1	18.55	16.84	1.71	16.84	0
SMW-2	17.81	16.2	1.61	16.2	0
SMW-3	17.82	16.15	1.67	16.15	0
SMW-4	18	14.68	3.32	14.66	0.02



Stantec

P.6

7-21 "presence of relatively unweathered NAPL at a # of locations beneath PSCP property provides strong evidence of localized sources of contamination"

7-22 - 23 Gas condensate
↳ similar fingerprint

D

Designed by:

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7.1 INTRODUCTION

The NAPL plume beneath the DSCP site has been characterized in multiple investigations over the past decade. The earlier studies commissioned by DSCP, identified the NAPL as a mixture of gasoline and diesel fuel (USACE 1992, Kemron/Versar 1995). In its report of results of the most recent investigation (Malcolm Pirnie 1997), DSCP contends that the material is a light refinery naphtha, characteristic of JP-4, with possibly small amounts of gasoline. DSCP has also concluded that they never used JP-4 (or a similar type product) on its site, and therefore, the source of the contamination is by default the adjacent Sun Refinery. The alleged pathway for NAPL transport is based on the identification of relatively low concentrations of weathered hydrocarbon residues to the west of DSCP on the CSX property. This property is the site of a railroad right of way that routinely transported petroleum products. These “pathway” residues vary in both composition and concentration across the CSX property, and within the underlying smear zones. DSCP contends that these residues represent the “smoking gun” linking the fresh NAPL under DSCP to the #1 Tankfarm in the South Yard of the refinery.

In this section, Sun will show conclusively, that the NAPL is not a light refinery naphtha characteristic of JP-4. The product has been further characterized by Sun’s experts as a mixture of at least two hydrocarbon products, gasoline and a naphtha or naphtha-like product (e.g., gas condensate). As shown in Section 8 of this document, DSCP has historically leaked petroleum products to the environment, and has used naphtha and other naphtha like materials on its property for over 75 years. In addition, Sun will demonstrate that the NAPL plume weathering distribution patterns at the site unambiguously identify DSCP as the source of contamination. Finally, NAPL material located beneath the #1 Tankfarm in the refinery South Yard and its associated smear zones, is clearly distinct from the NAPL underlying DSCP.

7.2 NAPL CHARACTERIZATION

7.2.1 Analytical Methods

Arthur D. Little, Inc., used advanced chemical fingerprinting (ACF) to rigorously characterize the NAPL material in the plume. ACF employs core GC/FID, GC/ECD, and GC/MS analytical methods that are tailored for the characterization of petroleum contaminants (Sauer and Boehm 1991, Douglas et al. 1992, Kaplan et al. 1997, Boehm 1997). The core analyses include a full range of target compounds with the ability to identify chemical differences and similarities within a given sample set. The specific utility of any particular class of compounds to “fingerprint” a sample however depends the following: (1) the ability to resolve products from different geological sources, (2) the relative state of weathering (or aging) of the material, and (3) the presence of specific product additives and refinery process signatures.

The primary analytical approach in ACF involves identifying chemical compounds (or elements) characteristic of each potential source. Examples of target compound classes that have been used in ACF work include volatile organic compounds (VOCs), gasoline-range organics (GRO), PAH compounds and their associated alkyl homologues, source-specific sulfur-heterocyclic hydrocarbons, and normal and isoprenoid alkanes.

The analytical methods used in this study are listed in Table 7-1. Not all samples were analyzed by all methods; however, the processing of the samples available for analysis followed a logical course (Figure 7-1). For example, because GRO analysis is sensitive to light hydrocarbon losses, it was used primarily to analyze NAPL samples and sheen samples where extensive sample extraction and handling was not required. Soil samples require extensive processing, which results in losses of volatile GRO compounds. Therefore, soil GRO was determined to be unreliable; thus, it was not used as a quantitative tool for this report. A discussion of each method follows, including a general description of the procedure, the “target” analytes, and the relevance of the analysis for product characterization and source identification.

Table 7-1: Summary of Analytical Methods

Analysis	Instrument	Target Analytes	Fingerprinting Application
Gasoline Range Organics	GC/FID	Target hydrocarbons $n\text{-C}_3$ to $n\text{-C}_{15}$	GC fingerprint, PIANO distribution, product weathering
Saturated Hydrocarbons (SHC)	GC/FID	Saturated hydrocarbons $n\text{-C}_8$ to $n\text{-C}_{40}$, selected isoalkanes	GC fingerprint, alkane distribution, isoalkane source, and weathering ratios
Polynuclear Aromatic Hydrocarbons (PAH)	GC/MS/SIM	PAH compounds and alkyl homologue groups, selected heterocyclic compounds	PAH distributions, product type analysis, and product weathering ratios
Volatile Aromatic Hydrocarbons	GC/MS	Benzene, toluene, ethylbenzene, xylenes (BTEX)	BTEX ratios, confirmation of GRO results, identification of "unknowns" in gasoline range
Boiling Point Distribution Analysis	GC/FID and Distillation Flask	ASTM Method D86, ASTM Method D2887, and ASTM 2892	Identified boiling point distribution curve of the product for comparison to standard products. Fractionation of NAPL for olefin analysis
Alkyl Leads and EDB	GC/ECD	Target alkyl leads (including TEL) plus EDB	Presence/absence of additives, age estimation of gasoline

GC: Gas Chromatography
FID: Flame Ionization Detection
MS: Mass Spectrometry
SIM: Selected Ion Monitoring
ECD: Electron Capture Detection

EPA protocols, developed to characterize the chemical composition of samples from industrial effluents and solid wastes, were not designed to meet the unique requirements of fingerprinting (Sauer and Boehm 1991). In fact, two of the key markers used in EPA methods (TPH and priority pollutant PAH compounds) are not adequately specific to support fingerprinting (Boehm et al. 1997, Kaplan and Galperin 1996, Douglas and Uhler 1993). Moreover, EPA data-quality requirements are often not stringent enough to ensure sufficiently sensitive or precise data--a critical requirement for determining the identity and amount of contributing contaminant sources--for forensic hydrocarbon studies. Table 7-2, which is included at the end of this section, lists the samples that were analyzed and used for this study

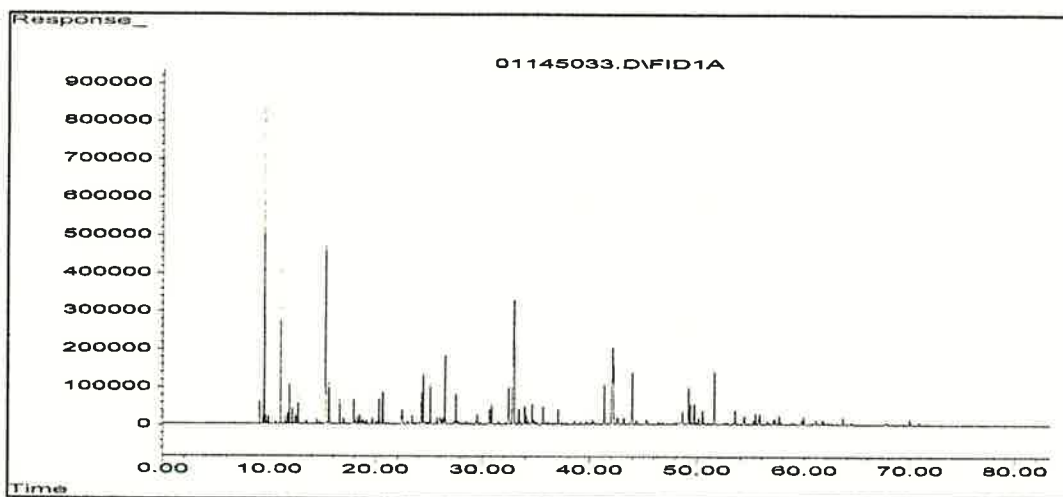
7.2.1.1 Gasoline Range Organics (GRO) by Gas Chromatography/Flame Ionization Detection

Arthur D. Little analyzed NAPL and sheen samples for hydrocarbon compounds ranging from approximately n -C₃ to n -C₁₅ using high resolution capillary column GC/FID. Target analytes included approximately 100 paraffinic, isoparaffinic, aromatic, naphthanic, and olefinic compounds, commonly abbreviated as "PIANO."

Paraffins	-	such as n-hexane and n-heptane
Isoparaffins	-	such as isopentane and 2,2,4-trimethylpentane (isooctane)
Aromatics	-	such as benzene, toluene, and 1,3,5-trimethylbenzene
Naphthenes	-	such as cyclopentane and methylcyclopentane
Olefins	-	such as cis-2-hexene and 1-octene

An example of the GC/FID chromatogram produced by this analysis is shown in Figure 7-2. This analysis quantifies a large number of key hydrocarbon components, providing important data for products with light or low molecular weight constituents such as gasoline, naphthas, jet fuels, mineral spirits, stoddard solvent, kerosene, and the light fraction of diesel oil. Ratios of selected components and PIANO groups can be used quantitatively to further describe the product. For fingerprinting, the analysis can be used to evaluate chemical changes due to refinery processing such as cracking, reforming, and blending. These data can then be used to distinguish between product types as well as between samples of a similar type. The data also provide information concerning the degree of environmental weathering of a product.

Figure 7-2: Gasoline GRO Chromatogram



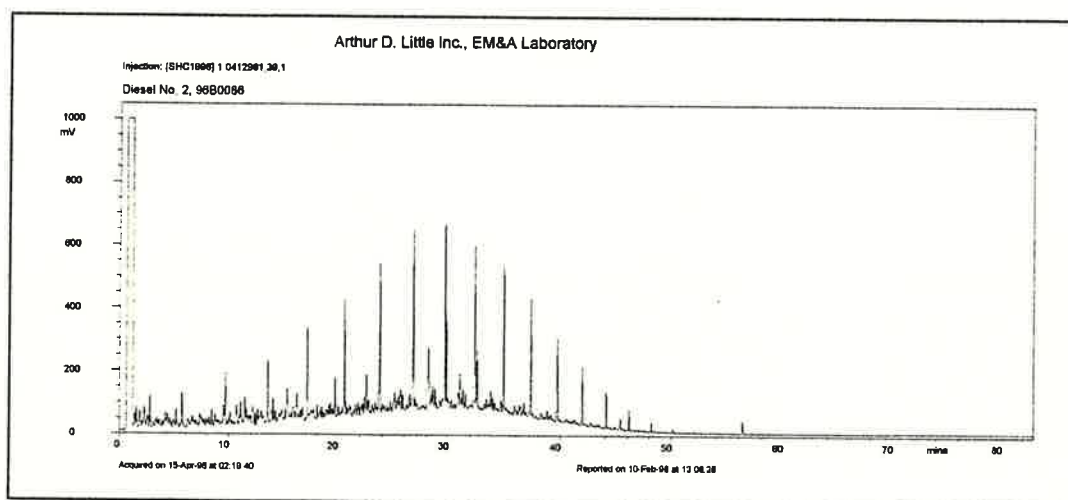
7.2.1.2 Saturated Hydrocarbons (SHC) and Total Petroleum Hydrocarbons by Gas Chromatography/Flame Ionization Detection (GC/FID)

Samples were also analyzed for target saturated hydrocarbons including C₈ to C₄₀ normal alkanes using high resolution capillary GC/FID. Also included in the list of target analytes are selected isoprenoids (i.e., branched alkanes), such as pristane and phytane and TPH. The analysis of saturated hydrocarbons provides compositional information for a product, including concentrations of normal alkanes and total hydrocarbon concentration. Further, because product weathering follows a documented chemical path with compounds weathering at different rates (Kaplan et al. 1996), ratios of select constituents may indicate relative weathering states (e.g., *n*-C₁₇). An example of a diesel chromatogram produced by the analysis is shown in Figure 7-3.

The GC/FID chromatogram provides a chemical picture of the sample that can be used to identify product type, source, and degree of weathering. The degree of weathering will impact the reliability of product identification. Chemical linkages between samples may be inferred by the distribution of resolved hydrocarbons (clearly defined peaks), including normal alkanes (e.g., *n*-C₈, octane) and the retention time of the unresolved complex mixture (UCM). Resolved hydrocarbons are compounds that can be chromatographically distinguished as compared to the UCM, which appears as a chromatographic “hump” and is composed of a variety of components. As product degrades, the resolved compounds are selectively removed and the UCM shape shifts from left to right toward the

higher molecular weight constituents that are more resistant to degradation. The GC/FID chromatogram also provides a visual characterization of the product that can be used for comparison to other samples and reference materials analyzed under similar chromatographic conditions. The utility of the GC/FID analysis decreases as the source hydrocarbon signature degrades.

Figure 7-3 GC/FID Chromatogram of Diesel Fuel



7.2.1.3 Polynuclear Aromatic Hydrocarbons by Gas Chromatography/Mass Spectrometry in the Selected Ion Mode (GC/MS/SIM)

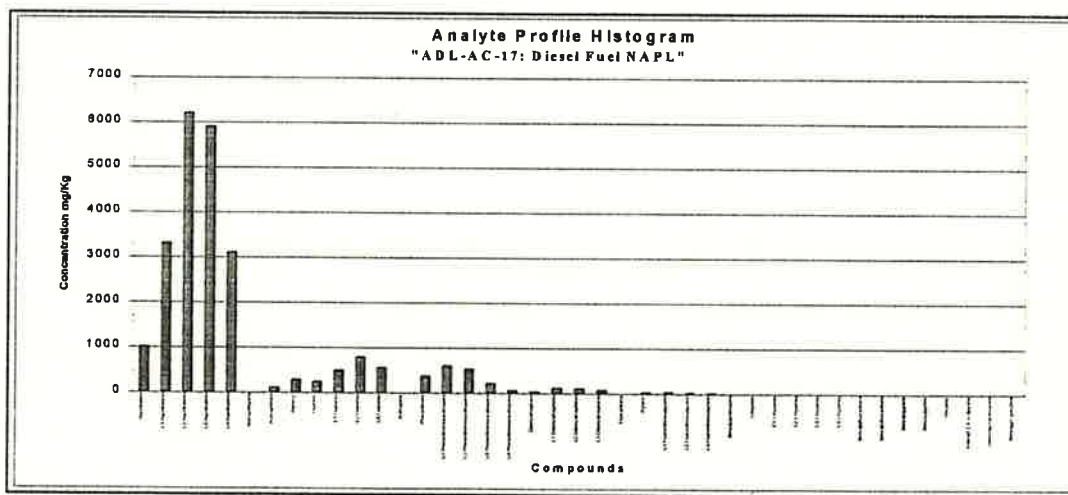
Samples were also analyzed for target PAH compounds, which included two-, three-, four-, five-, and six-ring PAH compounds using GC/MS in the most sensitive and specific selected ion mode (SIM). Also included in the target analyte list for this analysis are alkyl-substituted PAH compounds (e.g., total C₁ naphthalenes, total C₂ naphthalenes) and selected sulfur-containing heterocyclic compounds, such as dibenzothiophene. The instrumentation is configured to provide for the detection of target compounds at trace levels.

The analysis provides compositional PAH data for a product. Here again, because product weathering follows a documented chemical path, ratios of selected PAH compounds can indicate relative weathering states (Elmendorf et al. 1994, Douglas et al. 1996). In the case of the PAH

compounds as a class, compounds exist that degrade at similar rates, making their ratios relatively stable. These ratios may therefore be used as source indicators, even after the product has degraded.

PAH distribution plots (Figure 7-4) provide a visual representation of PAH concentration and relative distribution in the standard products (e.g., naphtha) and the samples. The degradation rates of PAH compounds generally decrease with increasing number of aromatic rings and degree of alkylation (number of attached carbon molecules). For example, naphthalene (a two-ring PAH) is more readily degraded than phenanthrene (a 3-ring PAH); and phenanthrene is more readily degraded than C₄-phenanthrene. When PAH distributions are compared, the concentration data is sometimes normalized in the plot to one of the more degradation-resistant PAH compounds. This allows samples to be compared irrespective of absolute concentration; thus, it can provide information on relative PAH weathering between samples.

Figure 7-4 Diesel Fuel PAH GC/MS Analysis



7.2.1.4 Volatile Aromatic Hydrocarbons and M_tBE by Gas Chromatography/Mass Spectrometry

Selected confirmation samples were analyzed for target volatile aromatic hydrocarbons, including benzene, toluene, ethylbenzene, and xylenes (BTEX), as well as methyl tertiary-butyl ether (M_tBE) using GC/MS. This method has limited use as a fingerprinting tool because of the solubility and volatility of these compounds. In the absence of significant degradation, BTEX concentrations can

provide some diagnostic information. This tool is useful for identifying relative weathering of hydrocarbon releases and areas of suspected sources.

M/BE is an oxygenate added to gasoline because of its anti-knock value. In reformulated gasolines, it is added to replace aromatic compounds. The use of M/BE as a gasoline additive began around 1979, and its levels in various gasolines are relatively well documented. The presence or absence of M/BE as well as its concentration within a product are, therefore, useful as diagnostic parameters of product type (e.g., leaded versus unleaded gasoline). Many of the target compounds for this method are the same as those included in the GRO analysis target analyte list. This provides for qualitative and quantitative comparisons of the analytical results to assist in data validation. Also, since M/BE co-elutes with cyclopentane using the GRO GC/FID methods, selected samples were analyzed to confirm the presence or absence of M/BE in the NAPL samples.

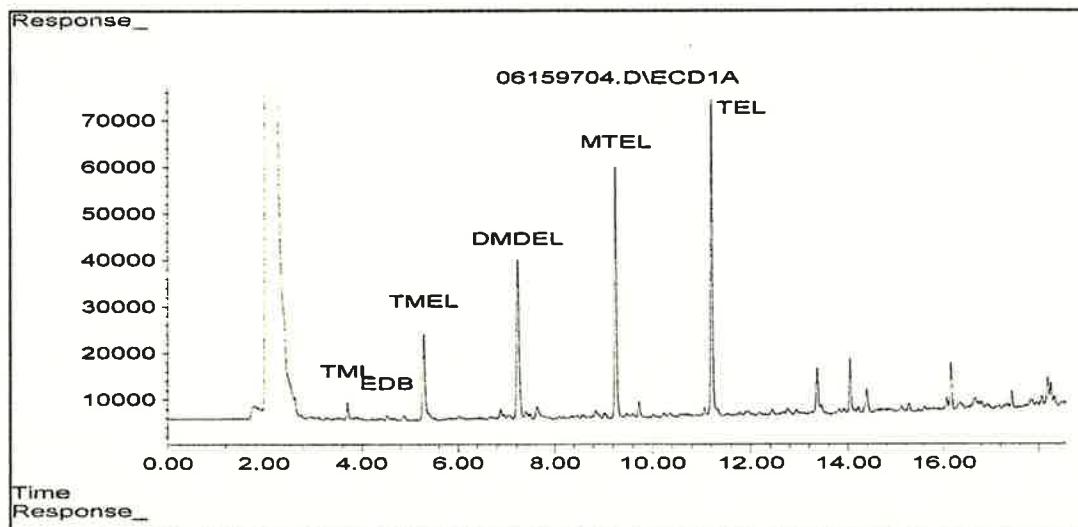
7.2.1.5 Alkyl Leads and Ethylene Dibromide (EDB) by Gas Chromatography/Electron Capture Detection (GC/ECD)

NAPL samples were analyzed for target alkyl-lead compounds and ethylene dibromide (EDB) by GC followed by electron capture detection (GC/ECD). Dual column confirmation was also used to verify the presence of analytes. Figure 7-5 is an example of the chromatogram produced by this analysis. Alkyl-leads were added to gasolines beginning around 1920 as an anti-knock agent to increase gasoline octane rating (Gibbs 1993). Halogenated lead scavengers such as EDB were developed and added at the same time to remove residual lead that would otherwise accumulate in the engine system.

Tetraethyl lead (TEL) was added to gasoline in increasing concentrations up until the late 1960s, when another antiknock agent, tetramethyl lead (TML), was introduced (Kaplan and Galperin 1996). Combinations of these two additives, as well as redistribution reaction mixtures of TEL and TML, were later used (Gibbs 1993). The use of alkylated lead additives began to decline with the introduction of unleaded gasolines in the early 1970s to accommodate the needs of catalytic emission control systems. In the U.S., alkyl-leads were systematically reduced after 1970 (Shelton et al. 1982). These compounds are useful for age dating gasoline inputs (Kaplan et al. 1996).

Target analytes for this method include: TML, EDB, tetramethylethyl lead (TMEL), dimethyldiethyl lead (DMDEL), methyltetraethyl lead (MTEL), and TEL.

Figure 7-5 Gasoline Alkylated Lead Analysis by Electron Capture Detection



7.2.1.6 Boiling Range Distribution Analysis

Boiling point profiles were determined by ASTM Methods D86 "Standard Method for Distillation of Petroleum Products," ASTM Method D2887, "Boiling Range Distribution of Petroleum Fractions by Gas Chromatography," and ASTM Method D2892, "Standard Test Method for Distillation of Crude Petroleum." Petroleum product distillation was also used to isolate specific boiling fractions of the NAPL samples. The isolated fractions were then tested using ASTM Method D1319-93, "Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption (FIA)" for olefins. This was necessary to increase the reliability of the test on samples containing "dark material" such as those from the NAPL plume.

7.2.2 DSCP NAPL Plume Characterization

Figures 7-6 through 7-10 represent the collective GRO, GC/FID, and PAH analysis for a suite of representative samples from the NAPL plume beneath the DSCP facility and from properties to the south and southwest. The representative samples provide a range of sample hydrocarbon distributions across the study area. These figures appear at the end of this section. The complete

data set is provided in Appendix L. In each figure, the GRO chromatogram is at the top (the “a” figure), the GC/FID chromatogram in the center (the “b” figure), and the PAH distribution profile at the bottom (the “c” figure). A description of each sample used in the ensuing analysis follows.

- MW-5 (Figure 7-6) and MW-6 (Figure 7-7) are relatively un-weathered samples from the south central aspect of the DSCP property. The three large peaks in the center of the chromatogram are surrogate and internal standard compounds used to quantify and to monitor data quality.
- MW-7 (Figure 7-8) is a weathered sample from the southeast aspect of the DSCP property.
- SB-20 (Figure 7-9) is a relatively un-weathered sample from a location southwest of DSCP and south of the Schuylkill Expressway.
- SB-27 (Figure 7-10) is a degraded NAPL sample from the extreme southwest aspect of the plume, adjacent to #2 Tankfarm in the refinery South Yard. The large peak on the left side of the chromatogram is the solvent used to isolate small amounts of product from the sample container.

7.2.2.1 GRO Analysis

GRO chromatograms are provided in the referenced figures. A key to the select GRO target compounds identified on the figures is provided in Table 7-3.

The MW-5, MW-6, and SB-20 GRO chromatograms are characterized by a systematic pattern of normal alkane peaks eluting from n -C₃ (propane) to n -C₁₅. This pattern is characteristic of a straight run refinery product such as naphtha or naphtha-like product (i.e., gas condensate). These samples are also representative of samples MW-25, PH-3, SB-4, SB-7, and SB-21. In addition, the abundance and type of light hydrocarbons (e.g., isopentane), olefins, and isooctane are strong indicators of the presence of gasoline in the NAPL.

MW-7 is a more weathered NAPL relative to the samples discussed above in that light-end hydrocarbons and normal alkanes have been lost primarily due to biodegradation. SB-27 (also representative of NAPL samples SB-22, SB-23, and SB-25) is a very weathered sample as evidenced by the loss of light end hydrocarbons and normal alkanes and dominance of methylcyclohexane (MCH), a compound that is resistant to weathering.

Table 7-3: Key to Compounds Identified on GRO Chromatograms

Peak Number	Compound
1	n-Propane
2	Isopentane
3	n-Pentane
4	Cyclopentane
5	2-Methylpentane
6	3-Methylpentane
7	n-Hexane
8	2-Methylpentene-2
9	Methylcyclopentane
10	Benzene
11	Cyclohexane
12	2-Methylhexane
13	3-Methylhexane
14	n-Heptane
15	Methylcyclohexane
16	Toluene
17	2-Methylheptane
18	n-Octane
19	Ethylbenzene
20	m-Xylene
21	p-Xylene
22	o-Xylene
23	n-Nonane
24	1-Methyl-3-Ethylbenzene
25	tert-Butylbenzene
26	n-Decane
27	n-Undecane
28	n-Dodecane
29	n-Tridecane
30	n-Tetradecane
31	n-Pentadecane

In samples SB-25 and SB-27, there appears to be an input of light-end hydrocarbons (i.e., isopentane) into the more degraded product. Isooctane was also detected in samples SB-22, SB-23, SB-25, and SB-27 (Appendix L), which provides further evidence that gasoline is present in these samples.

To evaluate the influence of gasoline in the straight-run product (straight-run products are located closest to the y axis) in the NAPL, a cross-plot comparison of isopentane and MCH was used. Isopentane is a major component of gasoline, added to increase the octane rating. In contrast, MCH concentrations in gasoline (Figure 7-11, gasoline samples are closest to the x axis) are generally low due to its low octane rating (Kaplan and Galperin 1996). Evaluation of the cross plot (Figure 7-12) reveals a clear trend in the NAPL samples closest to the DSCP facility, particularly

those south of the Building 28 gasoline station. In sample SB-20 (Figure 7-12), SB-19 and SB-4, the isopentane concentrations are clearly elevated due to gasoline inputs, indicating a localized source of gasoline contamination.

Olefins are unsaturated hydrocarbons not found or are found in very low concentrations in crude oils or its distilled products (Guthrie). Olefins are created by thermal and catalytic cracking, refinery processes in which long-chain hydrocarbons are broken into smaller ones. Olefins have the desirable effect of raising the octane rating in gasoline; however they also reduce the storage stability of refined products because they can form gums. While some JP-4 fuels are created by cracking, olefins in the finished product have a deleterious effect on jet engines by causing gumming and are thus avoided in jet fuels. The typical olefin concentration in JP-4 is on the order of 1 percent (Beery et al. 1975). JP-4 and its potential relevance to the DSCP plume is discussed in Section 7.2.3.

The GRO target analyte list contains only one isoparaffin, 2,2-dimethylpentane, in the elution range between n-hexane through methylcyclopentane. The remainder of the compounds in this range are olefins, indicators of a cracked product. Evaluation of this chromatographic range then can be used to differentiate between samples. Chromatograms expanded in this range for reference products or standards and a NAPL sample are presented in Figure 7-13. Note that the top figure, which is a JP-4 standard (Figure 7-13a), contains no olefins in this range. For a premium gasoline however, several olefins are detected (Figure 7-13b – four olefins are identified using GRO analysis). These same olefins are detectable in the NAPL at a similar relative abundance (Figure 7-13c – Sample MW-6).

The presence of olefins in this range was observed in a number of the NAPL samples that were analyzed in this study. For comparison, the three olefins found in this range are summed for 15 of the analyzed NAPL samples. The results for the samples and gasoline, naphtha, and JP-4 standards are presented in Figure 7-14. Clearly, olefin inputs in the samples from the plume NAPL material are from gasoline products.

Select NAPL samples with relatively high olefin content were also analyzed by a subcontracted laboratory using ASTM Method D1319, "Standard Testing Method for hydrocarbon Types in

Liquid Petroleum Products by Fluorescence Indicator Adsorption (FIA) for the Analysis of Volume Percent of Olefins, Aromatics, and Saturates in a Petroleum Liquid” for confirmation. The results of the analyses appeared to be biased low, compared to the results obtained by summation of identified olefins by GRO analysis. For example, the FIA analysis indicated an olefin content for PH-3 of 2.5 percent. Analysis of a sample replicate analyzed by GC/FID GRO analysis yielded a higher result. This FIA result was believed to be incorrect based on the GRO data. To address this concern, the NAPL, which was dark in color, was distilled into three fractions, initial boiling point (IBP) to 200°F, 200 to 385°F, and 385 to 550°F, using ASTM D2892, “Standard Test Method For Distillation of Crude Petroleum.” Each of these fractions was tested separately for olefin content. The analysis of the separate fractions resulted in olefin concentrations of 24.5 percent, 13.5 percent, and 6.6 percent, respectively, for a weighted average of 13.6 percent for sample PH-3. These higher olefin concentrations were produced by three separate analytical techniques, FIA, Near Infrared Analysis (NIR), and Detailed Hydrocarbon Analysis (DHA), and document the presence of a substantial amount of gasoline in the sample.

The discrepancy in olefin concentration determined by the analysis of the whole sample and from the distilled sample fractions is a function of the dark color of the NAPL. The ASTM test procedure states, “dark samples sometime require distillation to remove colored components that interfere in reading chromatographic zones (ASTM Method D1319-89, Section 6.1).” A later version of the method (ASTM D1319-93, Section 1.1) states: “Samples containing dark-colored components that interfere in reading the chromatographic bands can not be analyzed.” In other words, analysis of dark colored samples, which the DSCP samples are, is outside the scope of the method. Close agreement of the olefin results by the FIA and NIR analyses of the IBP to 200F sample fractions are all consistent, which leads to the conclusion that FIA analysis of the whole dark colored sample yields erroneous results. This further indicates that olefin concentration in the NAPL has been underestimated in the past and that the amount of gasoline present has been underestimated as well.

While Sun’s results are consistent with results from previous studies that identified gasoline in the DSCP NAPL (CENAB 1988, ESE 1991, USACE 1992, Kemron/Versar 1995), the results are

inconsistent with the most recent DSCP report (Malcolm Pirnie 1997), where Friedman & Bruya, Inc. (F&B) conclude that gasoline represents a minor component of the NAPL.

7.2.2.2 GC/FID Analysis

GC/FID chromatograms are provided in the referenced figures. For the relatively un-weathered NAPL samples (e.g., MW-5 - Figure 7-6b), a representative chromatogram is characterized by the decreasing relative concentration of normal alkane peaks eluting from approximately n -C₇ to approximately n -C₂₀ with the bulk of the material eluting before n -C₁₁. The more weathered samples (e.g., MW-7 - Figure 7-8b) have similar hydrocarbon distributions with differences due to the depletion of the more soluble and volatile compounds and the more labile n -alkanes. Concurrently the more weathered samples display a relative enrichment of the more refractory isoprenoid hydrocarbons such as farnasane, pristane, and phytane. This is clearly evident in samples from the plume fringe, where the NAPL is thinner and subject to greater weathering effects (e.g., SB-12, SB-17, and SB-23 - Appendix L). Although general similarities can be identified (Figure 7-10b), due to the degradation of the GC/FID signature, only general relationships can be derived. Therefore, for the purpose of trying to identify sources of the DSCP plume, this method is of limited utility.

7.2.2.3 PAH Analysis

The NAPL PAH distribution is dominated by naphthalenes and alkylated naphthalenes, with lower concentrations of fluorenes, phenanthrenes, dibenzothiophenes and chrysenes (both parent and alkylated homologues). The elevated parent naphthalene and C1-naphthalenes relative to C2-, C3-, and C4-naphthalenes in the presence of higher molecular weight PAH compounds (phenanthrenes [three-ring PAH] and chrysenes [four-ring PAH]) is an unambiguous indication of at least a two product mixture (e.g., gasoline and naphtha or a naphtha like product, Figure 7-7c).

Straight-run distillation products such as naphthas and gas condensates are characterized by the dominance of the saturated hydrocarbons, particularly a homologous *n*-alkane pattern (Section 3.3), which essentially mimics that which is found in the crude oil stock from which it is derived. The range of the hydrocarbons in sample MW-5, and most of the NAPL samples from beneath DSCP or in the vicinity of DSCP, indicates that the product detected in the *n*-C₇ through *n*-C₂₀ range is comprised primarily of straight run hydrocarbons characteristic of naphtha or a naphtha like product (e.g., natural gas condensate). The presence of gasoline specific light hydrocarbons (e.g., isopentane, isooctane, olefins, naphthalenes, and methylnaphthalenes) is an irrefutable indicator that gasoline is also present in many of the NAPL samples.

7.2.3 The DSCP NAPL Is Not JP-4

The GRO, GC/FID, and PAH data for the NAPL samples do not display the chemical characteristics that would be expected if the product was JP-4 fuel. The NAPL is characterized by substantial amounts of volatile light hydrocarbons (e.g., isopentane and pentane), an extended alkane range (greater than *n*-C₁₆ to *n*-C₁₇) and a PAH and unresolved hydrocarbon distribution that is totally uncharacteristic of JP-4.

JP-4 is a military-grade aviation fuel that is produced to exacting boiling-point distribution standards, especially the upper boiling range (Roberts and Thomas 1986). While the production standard is important as a procurement specification, it is more critically a safety concern. If JP-4 contained significant material outside of the specification, it could cause high performance jet engines to fail, possibly during flight, risking human lives and property. The risk was thus minimized by the

implementation of a requirement by the military that jet fuels meet exacting specifications, as verified by testing, prior to their purchase.

Figure 7-15 is a GRO, GC/FID, and PAH analysis of a fresh JP-4 sample. The JP-4 GRO chromatogram is generally characterized by a bimodal distribution of hydrocarbon peaks eluting from approximately n -C₆ to n -C₈, and n -C₈ through n -C₁₅. The GC/FID chromatogram is characterized by the distribution of decreasing relative concentration of hydrocarbon peaks eluting from approximately n -C₇ to approximately n -C₁₇, with the bulk of the material eluting before n -C₁₁. This is consistent with the military's specification for JP-4 of a final boiling point of 320°C using the gas chromatography method (Exxon 1987). The chromatogram is also consistent JP-4 GC/FID chromatograms published by the U.S. Air Force (Roberts and Thomas 1986) and in other hydrocarbon fingerprinting references documents (e.g., Kaplan et al. 1997, Spicer et al. 1989). The PAH distribution is dominated by the two-ring naphthalenes PAH compounds, followed by trace amounts of biphenyl, fluorene and phenanthrene.

The normal alkane distribution is a characteristic of this JP-4 product. At the Sun refinery, JP-4 was produced as a blend of kerosene stock and a lighter straight-run naphtha stock. The boiling point cutoff for the kerosene stock was 550°F or approximately at n -C₁₆ (S. Coladonato, personal communication). This boiling-point cutoff for JP-4 is consistent with available JP-4 stock sample analyses from the 1960s and 1970s. Moreover, Arthur D. Little has analyzed over twenty-five JP-4 samples from a variety of sources in the U.S. and has not observed an extended alkane distribution beyond n -C₁₆ in any of these samples. JP-4 chromatograms published by the DSCP's hydrocarbon expert F&B and other recognized hydrocarbon experts also do not report the detection of heavy hydrocarbons greater than approximately n -C₁₆ in JP-4 samples (Kaplan et al. 1997, Roberts and Thomas 1986, Spicer et al. 1989, Smith et al. 1981).

F&B's approach to fingerprinting frequently relies on chromatographic techniques and the comparison of unknown samples to reference materials analyzed under similar instrumental conditions. In DSCP's response to Sun's critique, in contrast, F&B state military product specifications (i.e., MIL-5624) as the reference for comparison, although it does not explain this

apparent change in approach, Arthur D. Little does not believe that the DSCP's expert has ever referred to the uncharacteristic extended alkane distributions found in the NAPL in any previous published manuscripts.

The chemical differences between both a fresh and degraded JP-4 and a DSCP NAPL sample are presented in Figure (7-16). The extended alkane distribution beyond n -C₁₆ detected in the DSCP NAPL samples is not characteristic of the JP-4 produced at the Sun Refinery. The JP-4 sample chromatogram contains a pattern of resolved peaks associated with the normal alkanes. The resolved normal alkanes are superimposed over an elevated baseline rise between 8 and 24 minutes, attributable to an un-resolvable complex mixture of hydrocarbons contained in the product (e.g., kerosene). There are significant differences between the DSCP NAPL sample (e.g., MW-5) chromatogram and the JP-4 chromatogram, the most prominent being an extended boiling point range in the DSCP NAPL sample. The analysis of the NAPL sample indicates that the alkane range extends substantially beyond that of the JP-4 fuel sample. In fact, there are traces of detectable material to approximately n -C₃₀, far beyond the upper boiling range limit allowed for JP-4 by military specification or supported by any available JP-4 analytical data. Boiling-range analysis also indicates that up to 10 percent of the NAPL boils higher than 550 degrees F--some boils as high as 700 degrees F.

A second chemical difference between the JP-4 fuel samples and the NAPL (e.g., MW-5) is the absence of any clear unresolved component in the DSCP NAPL sample in the n -C₁₁ to n -C₁₄ alkane boiling range. The absence of an unresolved component is extremely important for the evaluation of aged or weathered hydrocarbon products (Figure 7-16). As seen in the un-weathered JP-4 reference standard (Figure 7-16a), the distribution of hydrocarbons in these standards ends at approximately n -C₁₆ to n -C₁₇. More importantly, these chromatograms demonstrate the change in the pattern due to product aging. As the JP-4 ages, the lighter and more volatile components that comprise the early portion of the chromatogram are lost. Also, degradation effects the normal alkanes faster than the branched cyclic and substituted alkanes that comprise the unresolved mixture and the normal alkanes are lost over time. For JP-4, the result of this process is an apparent rise in the baseline (i.e., the appearance of a "hump") due to the unresolved (and less degradable)

hydrocarbons between 8 and 24 minutes. This is not unexpected considering that JP-4 is a blend of up to 50 percent kerosene that characteristically has a dominant UCM.

The third important chemical difference between JP-4 reference standards and the NAPL (e.g., MW-5) is in the concentrations of light hydrocarbons, as determined through GRO analysis. The JP-4 fuels have substantially less isopentane and pentane than the NAPL (Figure 7-17). This excessive volatility would be a significant problem for JP-4 at high altitudes where light ends of fuels will boil off and reduce the range of the aircraft (U.S. Bureau of Naval Personnel 1965).

Available boiling range data and GC/FID data of Arco JP-4 stock samples from the mid-1960s to early-1970s indicate that the final boiling point of the JP-4 was less than 500°F and the alkane range did not exceed *n*-C₁₇ (Tables 7-4 and 7-5). These samples are representative of the historical refinery JP-4 production formulations during this period. No historical evidence suggests that practices before or after this period would have been any different. The JP-4 has been described as, “a wide cut mixture of heavy naphtha and kerosene with an average 140°F to 460°F boiling range” (Beery et al. 1971). This range is well below the boiling range observed in the NAPL plume material beneath DSCP.

The final chemical difference between JP-4 and the DSCP NAPL is the relative distribution of PAH compounds (Figure 7-18). The primary PAH compounds in JP-4 are naphthalene and alkylated naphthalenes, with trace levels of biphenyl, and fluorene. In contrast, the DSCP NAPL has an extended PAH distribution that is dominated by naphthalenes but also contains substantial three- and four ring PAH distributions as well.

Table 7-4 Historical Boiling Range Data for Refinery Product Samples

Specification	MIL-F-5624A (5/23/61)	JP-4 (2/10/65)	JP-4 Tank 181 (1/71)	JP-4 Tank 178 (1/71)	JP-4 Tank 126 (1/71)	Aero-Jet (2/10/65)	Kero Tank 121 (1/71)	Light Crude Naphtha
IBP °F	NA	143		140	151	293	320	106
5%			180		180		365	
10% °F	250	209	198	205	192	340	376	120
30% °F		248				366	398	
50% °F		277	265	275	274	387	418	153
90% °F		404	428	458	420	474	487	
EP °F	550	490	495	510	482	488	513	330
EP approximate n-alkane limit	n-C ₁₆	n-C ₁₄	n-C ₁₄	n-C ₁₅	n-C ₁₄	n-C ₁₄	n-C ₁₅	n-C ₁₀
API Gravity	40	54.7	54.4	55	59	45.5	42.3	75

Date of specification or data source in parentheses

Table 7-5 Historical GC/FID JP-4 Characterization Data from Sun Refinery

Hydrocarbon Distribution	JP-4 Stock (4/15/68)	JP-4 Stock Tank 125 (8/29/68)	JP-4 Stock (11/21/68)	JP-4 Stock (8/29/68)
Units	Percent	Percent	Percent	Percent
C0 to C6 Hydrocarbons	53	30	34	29
C6 to C8 Hydrocarbons	34	24	39	30
C8 to C10 Hydrocarbons	9	35	26	29
C10 to C13 Hydrocarbons	4	9	0	8
C13 to C17 Hydrocarbons	0	3	0	4

Date of specification or data source in parentheses

7.2.4 Light Refinery Naphtha Issues

DSCP has also claimed that the NAPL is a light refinery naphtha. Table 7-4 contains a typical boiling range distribution of light naphtha from the Sun refinery. The distillation endpoint is far lower than that observed in the NAPL. Figure 7-19 is a GRO chromatogram of a “heavy refinery” naphtha from the Sun Refinery compared to a DSCP NAPL sample from MW-6. Even the heavy refinery naphtha is too light to be the straight run product component of the plume material. These straight run refinery naphthas also cannot explain the substantial concentrations of olefins in these samples.

Table 7-6: Detailed NAPL Characterization Summary PH-3 Sample

Compound Class	Method	Compound Class	Conclusion
Gasoline Range Organics	GC/FID	PIANO Compounds	Gasoline and straight run product
Saturated Hydrocarbons	GC/FID	Alkanes, TPH	Straight run product, not JP-4
Polynuclear Aromatic Hydrocarbons	GC/MS/SIM	PAH, DBTs	Gasoline and straight run product; not JP-4, alkylated naphthalenes present
Boiling Point Ranges	ASTM D86, D2887, D2892	Hydrocarbon Fractions	Light gasoline product mixed with heavier product; boiling range 130-566°F
FIA Analysis	ASTM D1319	Olefins, Aromatics, Saturates	High olefins indicate presence of gasoline
NIR Analysis		Olefins	High olefins indicate presence of gasoline

Based on the extensive chemical differences between the relatively un-weathered NAPL under DSCP and JP-4, and a wealth of reference literature and data describing JP-4 composition, including data published by DSCP's own expert, Sun concludes that the NAPL is not a JP-4 fuel (Table 7-6). Further, the chemical evidence clearly differentiates the hydrocarbon distributions of light and heavy refinery naphthas from the NAPL; both straight-run light naphtha and straight-run heavy naphtha are too light to be related to the heavier NAPL product beneath DSCP.

7.2.5 DSCP Sources of NAPL

The NAPL plume underlying the DSCP property and properties south of the DSCP property is primarily gasoline and naphtha or naphtha-like product. The following list summarizes the hydrocarbon chemistry analyses from the previous section:

- The NAPL is a mixture of at least two products, gasoline and a naphtha or naphtha like product (e.g., natural gas condensate).
- Isopentane, isooctane, TEL, BTEX, and elevated olefin concentrations are conclusive evidence of gasoline inputs. The highest and freshest input of gasoline is in the vicinity of the building 28 gasoline station, the Bash Street gasoline station, Building 30, and in the vicinity of MW-11.
- The n-alkane distribution is evidence of a straight run product that is clearly not JP-4.
- The material is too heavy to be either light or heavy refinery naphtha.
- Both light (MCH) and heavy (e.g., phenanthrene) hydrocarbon NAPL plume weathering contours identify the freshest product in the plume as being directly under the DSCP property (e.g., MW-5), and the most weathered NAPL is located at the plume fringes (e.g., SB-12).
- The presence of abundant concentrations of light hydrocarbons directly beneath the DSCP property suggests a series of localized NAPL sources.

7.2.5.1 DSCP Historical Petroleum Product Use

The presence of relatively un-weathered NAPL at a number of locations directly beneath the DSCP property provides strong evidence of localized sources of contamination. As discussed in Section 8, gasoline, naphtha, solvents, kerosene, and diesel fuel were obviously used in large quantities for over 75 years by DSCP. Sun does not have a complete understanding of the specialty solvents or volumes that were used at the site, particularly during highly active years during World War II, because DSCP has blocked Sun's efforts to identify potential sources. Although DSCP, not Sun, has the responsibility to identify sources on its facility, Sun has discovered evidence that DSCP transported, stored, and handled substantial amounts of naphtha solvent and other solvents for many purposes including use in the application of insecticide to military clothing. One specification of solvent material used for insecticide application is broadly defined in military specification MIL-I-

10502, Amendment-1, 18 January 1954 entitled, "Military Specification Insecticide, DDT, Emulsion Concentrate." This amendment forms a part of Military Specification MIL-I-10502 (QMC) dated 7 September 1950, superseding JCQD No. 1031, 7 June 1945. The primary amendment, as it relates to solvent character, is as follows: "Page 2, paragraph 3.2.3: Delete 'alkylated naphthalenes' and substitute 'aromatic petroleum derivatives' which broadened the specification of the solvent." The distillation range for this product is also defined in this document with an initial boiling point of 300°F (approximately n -C₉) and a final boiling point maximum of 550 °F (approximately n -C₁₆ to n -C₁₇). This boiling range is within the NAPL boiling range; thus, this material must be considered a potential source. Further, the area in which insecticide solvent would have been handled is near one of the NAPL thickness centroids discussed in Section 6.

In addition to this n -C₉ through n -C₁₆ petroleum based solvent, DSCP has acknowledged chronic gasoline releases over the past 50 years (Figure 7-19 - DSCP chromatograms of contaminated soils). As discussed in section 3.3, the gasoline carbon number range extends from propane (n -C₃) to approximately n -C₁₂, and contains substantial amounts of olefins (Gibbs 1993). It is also likely that pre-1960s gasolines had higher concentrations of both olefins and n -alkanes than current gasoline (Gibbs 1993). Olefins were added to gasoline to boost octane ratings of light straight-run naphthas. Gasoline-specific compounds detected in the NAPL also point to localized sources of gasoline contamination in the vicinity of historical DSCP fueling areas. F&B identified gasoline residues and lubricating oils at Building 28 on the DSCP property (Malcolm Pirnie 1997).

In summary, the numerous mixtures of petroleum products used by DSCP for decades can explain the observed hydrocarbon distribution and volume in the NAPL.

7.2.5.2 Natural Gas Condensate

As discussed in Section 8 of this document, DSCP has used large volumes of natural gas and manufactured or "town" gas beginning in 1920s. Distribution gas is known to contain light- or medium-range hydrocarbons that are documented in other similar systems to condense in the pipeline during transport (Bruce and Schmidt 1994, Eicemann et al. 1995). Generally, gas pipelines function like a refinery distillation column. Heavier hydrocarbons condense early in the system, and

the lighter straight-run petroleum products condense farther down the pipeline closer to the end user. These condensate fluids accumulate in low spots in the pipeline, are corrosive, and can cause pipeline failure. Drip pot systems are located along the gas distribution system directly over the DSCP plume on the DSCP property to collect these hydrocarbon fluids.

While the practice of handling natural gas condensate on DSCP is unknown, the gas distribution system is a potential, significant source of the plume. Figures 7-20, 7-21, and 7-22 are comparisons of the GRO, GC/FID, and PAH distributions from a natural gas condensate sample and a sample from MW-5 on the DSCP site. A second condensate GC/FID analysis is presented in Figure 7-23a. A third natural gas condensate from a distribution pipeline is presented in Figure 7-23b. Based on the hydrocarbon distributions in these samples, the chromatograms for the gas condensate references are extremely similar to the NAPL plume material. Based on this chromatographic data, the geographical location of the natural gas distribution lines with respect to plume thickness and plume morphology, the volume of gas that was used by DSCP, and the failure of DSCP to study this potential source by taking soil samples directly under the DSCP drip pots, condensate must be considered as a source of the hydrocarbons observed in the NAPL.

7.2.5.3 Known Product Contamination Above the DSCP Smear Zone

Other evidence that indicates NAPL sources on the DSCP can be found in soil samples that are collected above the NAPL smear zone. Only three soil samples on the DSCP-site were available for this aspect of the study, due to limited access to the DSCP facility. Of the three soil samples analyzed by Arthur D. Little, Inc., one was located at the water table in the vicinity of MW-25 (PZ-3, 19-ft BLS), a second sample was located at a depth of 15-ft in the vicinity of MW-25 (PZ-3, 14 to 15 ft BLS) above current and historical water table elevations, and a third sample was also located near MW-25 at 10 to 12-ft BLS (PZ-2), well above current and historical groundwater levels. PZ-3 at 19-ft was in the NAPL plume; therefore, it reflects the known NAPL contamination signature.

A comparison of GC/FID chromatograms for the two samples located above the water table to the NAPL GC/FID chromatogram shows a remarkable similarity, particularly PZ-3 at 14 to 15-ft. PZ-2 at 10 to 12-ft contains a degraded light hydrocarbon product residue and a second product similar to a lubricating oil (a heavier product than the NAPL), as suggested in the minutes from Versar's

meeting (Appendix H). The lighter product is consistent with samples of weathered NAPL (Figure 7-24a). However, weathering of the critical signature compounds (e.g., n-alkanes) measured using GC/FID techniques prevents unambiguous identification this sample as the source of the NAPL to the groundwater. PZ-2 at 14 to 15-ft, which is substantially less weathered, exhibits GC/FID hydrocarbon distributions that clearly reflect those observed in the NAPL alkane signature (Figure 7-24b). The alkane distributions of the sample from PZ-3 at a depth of 14 to 15-ft are compared to MW-25 (Figure 7-25) NAPL. This one sample represents an extremely close match of a soil sample to the material in the NAPL and strongly indicates a source on DSCP property of the NAPL plume. No soil samples studied on the Sun Refinery or in the alleged "pathway" show such a strong chemical match to the NAPL plume.

In addition, F&B identified a sample near building 28, in TP-05, as a naphtha or a weathered JP-4 (Figure 7-26). This sample was located at 4-ft BLS, well above the smear zone and water table, in an area with over 75 years of petroleum product-handling activities. The locations of these gasoline residues and naphtha or weathered JP-4 products (TP-05) correlate with the freshest area (closest to source) of the NAPL, at MW-5 and downgradient at MW-6. This area is a likely source of contamination to the groundwater where elevated BTEX levels have been detected in the soils by previous investigators (Figure 7-27, ES&E). This area also corresponds to a plume-thickness centroid, as discussed in Section 6.

In summary, three non-smear zone samples from above the water table on the DSCP property provided credible chemical data that suggest that there are sources of the naphtha or naphtha-like NAPL on DSCP's property. As noted above, the DSCP expert also identified a degraded naphtha or JP-4 product in TP-05 at 4-ft BLS. The PZ-2 sample from a depth of 10 to 12-ft BLS has degraded hydrocarbon distributions that are similar to those observed by DSCP in TP-05. Both samples are located above the NAPL plume. In addition to the PZ-2 and PZ-3 data, total BTEX maps prepared by ES&E (Figure 7-27) for the 0 to 10-ft interval show a maximum in the vicinity of MW-6, suggesting a localized source of contamination on the DSCP property. This too is consistent with the plume morphology, as discussed in Section 6.

7.2.5.4 Other Potential Sources of DSCP NAPL

DSCP reported NAPL hydrocarbon distributions in water samples MW-20, and MW-21 (Figure 7-28) that reflect material similar to that observed in the main DSCP NAPL plume. In addition, discussion of these findings was absent in the DSCP report. Examination of aerial photographs of the DSCP site, suggest that the farthest northwest tip of the DSCP property was likely used as a waste disposal site (note dark coloration on photograph near MW-20). DSCP's contractor (ES&E 1991) described the area as follows:

“The northwest corner of the installation is an area of deep (up to 22 feet) fill of questionable quality. Gas emitting from drill holes in that area (CH-3 and CH-3A) had a cesspool-like odor and quickly activated the combustible gas/carbon monoxide detector. Soil samples from the hole contained cinders, ash, wood, coal, pottery, etc., as well as 225 ppm hydrocarbon contamination. The gas from this fill area may be seeping horizontally through the open gravelly, cobbled, sand zone outside the fill area. Drill hole 9, just south of the fill, produced a strong sulphur smell, which also set off the gas detector. Excavation in this area could be hazardous.”

The relatively un-weathered character of the MW-20 sample (Figure 7-28a), and the moderate weathering of the MW-21 sheen sample (Figure 7-28b), suggests that the soil area above MW-20 is a source of NAPL to the groundwater and may reflect historical product dumping activities. Mr. Souser of the USACE in a public meeting (5 January 1995, Appendix H) stated: “the NIKE missile assembly area, formerly in Building 26 (located in the vicinity of MW-20 and MW-21), may be a potential source of the ‘jet lubricating oil’ contamination.” MW-20 is clearly not contiguous with the main plume, which suggests that it is a separate and distinct release.

7.3 THE NAPL HYDROCARBON WEATHERING PATTERNS IN THE PLUME ARE CONSISTENT WITH A DSCP SOURCE

7.3.1 NAPL Hydrocarbon Weathering Patterns

Product weathering patterns are determined based on the relative losses of the more volatile (e.g., butane) and more soluble (e.g., benzene) hydrocarbons. Biodegradation also alters the hydrocarbon signature according to the following continuum (Kaplan and Galperin 1996):

paraffins --> isoparaffins --> naphthenes >= aromatics

For the purposes of this discussion, the physical, chemical, and biological processes that alter the hydrocarbon signatures of petroleum products (Figure 7-29) in the environment will be referred to collectively as “weathering.” As NAPL migrates on the groundwater table, it thins and weathering has a greater impact on the chemical signature due to increased exposed product surface area. The impact of migration on the chemical signature of the NAPL is well documented in sample MW-7, a DSCP plume fringe sample, where light-end hydrocarbon compounds have been lost, probably through volatilization, and the n-alkanes have been biodegraded (Figure 7-8b).

Thick NAPL accumulations, such as those that have accumulated near source areas, have less surface exposure and quickly consume available oxygen, and have less effective area for volatilization and solubilization; therefore, they are subjected to less weathering. Under these circumstances, the NAPL signatures can be preserved for extended time periods. Thus, while a weathering analysis is useful in explaining the location of sources, it does not necessarily explain the age of the plume or the time of the release. In other words, old plumes can be relatively un-weathered close to their sources.

Within a set of NAPL samples containing a similar product, the more recalcitrant compounds (i.e., those more resistant to weathering) become relatively enriched on an oil weight basis due to preferential weathering. For example, MCH is very resistant to weathering in NAPL samples and a generalized plot of its absolute concentration (on an oil weight basis) provides a relative measure of sample weathering within the plume (Figure 7-30, Douglas et al., 1994).

7.3.2 GRO Weathering Distributions

Representative GRO chromatograms from NAPL samples collected in the vicinity of the DSCP and Sun properties are presented in Figures 7-6 through 7-10. All sample chromatograms are presented in Appendix L. Samples collected from directly beneath the DSCP property, such as MW-5 and MW-6 (Figures 7-6 and 7-7), appear relatively un-weathered. This is based on the presence of volatile, low-molecular weight hydrocarbons such as propane, butane, isopentane, and pentane, as well as the relatively water-soluble aromatic constituents such as the BTEX compounds.

MW-6 differs from MW-5 in that it has a higher light hydrocarbon component, which is consistent with localized gasoline inputs from the surface or upper soil column. The alkane distribution has not been significantly altered in the samples suggesting only minor weathering of this sample (Douglas et al. 1994). This finding is consistent with previous studies at this site: “Unweathered naphtha is the dominant material present in the LNAPL collected at locations MW1A, MW2, MW3, MW4, MW5, MW6, MW9, MW11, MW14, MW15, and MW25” (F&B, Malcolm Pirnie 1997).

While the NAPL includes gasoline, this conclusion regarding weathering is consistent with the findings of this study. The lack of GRO hydrocarbon weathering in samples such as MW-6 clearly supports a localized source of these very volatile, soluble, and biodegradable hydrocarbons. The n -C₃ through n -C₁₅ hydrocarbon distribution found in sample MW-6 is clearly similar but not identical in relative distribution to that observed in MW-5, MW-25, PH-3, SB-18, SB-21, SB-20, SB19, and SB-4 (Figure 7-31 and Appendix L).

MW-7, located to the east of MW-6 at the DSCP plume fringe is chromatographically more weathered than the central plume samples (e.g., MW-6). This was implied in the DSCP report: “The extent of the degradation indicates that this material was likely released many years prior to the undegraded naphtha discussed above” (F&B, Malcolm Pirnie 1997), and, “The degraded naphtha is likely from a release that is many years old and the undegraded naphtha from a fairly recent release” (F&B, Malcolm Pirnie 1997).

The conclusions regarding NAPL weathering presented in the Malcolm Pirnie (1997) report are consistent with known NAPL degradation pathways. In their conclusions Malcolm Pirnie states:

“Clearly, there appears to have been at least two releases of naphtha that now make up the LNAPL. One naphtha is highly degraded and is found throughout the [DSCP] facility, as well as to the west and south. The other naphtha is relatively undegraded and is found generally in the southwest portion of the [DSCP] facility” (F&B, Malcolm Pirnie 1997).

While Sun's results indicate that the NAPL is not comprised of naphtha alone, as concluded in the DSCP report, the observed weathering pattern was similar.

As noted above, recalcitrant compounds like MCH become relatively enriched in NAPL (on an oil weight basis) as the more labile compounds are removed by weathering. This fact thus provides for the use of MCH concentration as a measure of relative light hydrocarbon weathering. The concentration of MCH in the NAPL samples is compared in Figure 7-32. These same values are used to generate a concentration plot over the study area (Figure 7-33). This plot shows that the least weathered material (i.e., lowest MCH concentration) is located under DSCP in the vicinity of the Building 28 gasoline station and Building 30 vehicle service area. NAPL weathering increases (i.e., MCH concentrations are higher) from the northeast on the DSCP facility to the southwest intersection of Hartranft and 26th Street. Since the freshest samples are found closest to the source of a release, this data suggests DSCP is the likely source of the NAPL contamination.

7.3.3 GC/FID Weathering Distributions

Product weathering can be evaluated by GC/FID based on the relative losses of the more volatile components (eluting early in the analysis). Water washing also has an effect on the characteristics in that the more soluble components, such as the mono-aromatic compounds, are removed preferentially as a function of their solubility.

In terms of the chromatographic signature, the effects of weathering manifest themselves as a loss of the resolved components beginning with the normal alkanes (Figure 7-29). This is demonstrated by a comparison of NAPL samples MW-6 (un-weathered) and MW-7 (weathered) (Figure 7-7 and 7-8, respectively). The figures show that, the normal alkane pattern has been lost in sample MW-7, indicating that it is more weathered. This weathering trend is also confirmed by the GRO data, as discussed above.

Because the normal alkanes degrade more rapidly than the isoalkanes or isoprenoids (e.g., pristane and phytane, Prince et al. 1994, Douglas et al. 1992), the ratio of these compounds can also be used to evaluate relative weathering state (Miget et al. 1969). For example, in sample MW-5, the ratio of

pristane to the nearest *n*-alkane (*n*-C₁₇) is 1.1, while in MW-7 it is 0.69. This is further evidence that sample MW-7 is more degraded than MW-5. Figure 7-34 is a plot of this weathering ratio for each NAPL and sheen/water sample. The spatial distribution of NAPL weathering based on the *n*-C₁₇/pristane ratio on the DSCP property and south, southwest of the DSCP property is plotted in Figure 7-35.

The *n*-C₁₇/Pristane ratio decreases with increased weathering due to the preferential degradation of the straight-chained alkane (*n*-C₁₇) relative to the branched chain hydrocarbon (pristane). The results of these analyses demonstrate a trend of increased weathering with distance from the centroids that are suggestive of source. The hydrocarbon-weathering pattern indicates that the freshest material is again located in the vicinity of MW-5 (on the DSCP property) or SB-20 just south of the Building 28 gasoline station. These analyses indicate a localized source of hydrocarbon contamination on DSCP property.

7.3.4 PAH Weathering Distributions

The PAH compounds measured in this study include primarily two-, three-, and four-ring compounds. In the NAPL samples, the PAH distribution is influenced primarily by the heavier product or products, but also by the gasoline, naphtha, or solvent present as the secondary product with high naphthalenes. With the exception of naphthalene and C₁-naphthalenes, which are relatively more soluble, PAH compounds generally degrade slowly in NAPL systems. Therefore, as more labile hydrocarbons degrade (e.g., *n*-alkanes), the relative percentage of PAH compounds increases in the NAPL similar to MCH, as discussed in section 7.3.2. A bell-shaped homologous series of PAH compounds indicates a relatively un-weathered PAH pattern (e.g., PAH distributions in fresh diesel fuel Figure 3-35) as shown by Elmendorf et al. (1994) and Douglas et al. 1992). This was observed for the PAH compounds in a majority of NAPL samples

Based on the relative distribution of phenanthrene to its alkylated homologs, little phenanthrene weathering has occurred in the DSCP NAPL samples (Douglas et al. 1994). This mid-range three-ring PAH group (phenanthrene and its alkylated homologs) is a reasonable surrogate for the PAH compounds present in the NAPL. Therefore, as the more labile hydrocarbons in the NAPL are

removed by weathering, the relative concentration of the more recalcitrant phenanthrene will increase, similar to MCH. The contour plot of the percent phenanthrenes (Figure 7-36) in NAPL exhibits a clear weathering trend. This trend is consistent with all of the previous chemical data and shows that weathering increases with distance from DSCP along a line from the southeast to the southwest. This trend is also agrees with the general morphology of the plume as discussed in Section 6 and with the direction of groundwater flow discussed in Section 4.

Results of the weathering analysis using multiple independent chemical tools, show a fresh to weathered continuum from the thick central aspect of the DSCP Plume to the fringes in all directions. This suggests that the source of the material in the DSCP Plume is on the DSCP site, which is also consistent with the plume morphology as discussed in Section 6.

7.4 COMPARISON OF NAPL ON SUN REFINERY AND DSCP PLUME

7.4.1 Introduction

As discussed in Section 7.2 and 7.3, the NAPL plume underlying the DSCP property and properties to the south is a mixture of gasoline and naphtha or naphtha-like products, which shows a clear weathering pattern radiating from the center of the DSCP property. Nonetheless, the DSCP contends that the source of these hydrocarbons must be the Sun Refinery and not DSCP. During the 5 January 1995, Phase I RI/FS Progress/Phase II Scoping Meeting held at the USACE in Philadelphia (Appendix H), Mr. Gaudini of the USACE asked DSCP's expert, Mr. Morganelli of Versar, "whether we had enough evidence to go after Sun as a PRP right now." Mr. Morganelli stated:

"We do not have enough evidence, particularly because there is no good geometric connection of the free product plume to the Sun property. Therefore, we have to develop a chemical connection of the plumes to the Sun property to have sufficient evidence."

In this section, Sun will demonstrate conclusively that there is no chemical fingerprint connection along the pathway alleged by DSCP between #1 Tankfarm in the South Yard of the refinery and DSCP.

7.4.2 Overview of DSCP Hydrocarbon Fuel Scan Approach

The Hydrocarbon Fuel Scan (HFS) technique, a qualitative method used by DSCP's expert F&B, is a full range GC/FID analysis. This technique provides hydrocarbon distribution data from a sample in the form of a chemical picture called a GC/FID chromatogram. This chromatogram is then reviewed by a hydrocarbon fingerprinting specialist and compared to chromatograms of standard hydrocarbon products to identify the hydrocarbon product or product type within the sample. The HFS approach was the primary tool used by F&B to make their qualitative determinations. There is no evidence that quantitative methods were used to identify the product type or the relationships between products. In addition, no reference standard chromatograms were provided to support the qualitative analysis (although requested by Sun).

Based primarily on the HFS data and F&B's qualitative interpretation of DSCP NAPL and soil samples and the CSX hydrocarbon residues, DSCP contends that the NAPL traveled from the #1 Tankfarm to DSCP and that a chemical connection of the DSCP plume to the Sun property has been established. However, several points of quantitative and qualitative evidence, along with the residual saturation analysis given in Section 5 and the morphologic analysis in Section 6, show that the relatively un-weathered NAPL under DSCP is not related to the #1 Tankfarm.

The first fundamental point is simply that if the NAPL had been transported from the #1 Tankfarm to DSCP, then the product would have shown evidence of significant weathering. The fate mechanisms described in Section 5 would have occurred if the NAPL had migrated such a distance along the contended pathway. As described in Section 7.3 these weathering processes result in observable changes in the chemistry of the NAPL (Kaplan et al. 1996). However, these weathering processes are occurring in all directions around the thickest parts of the plume (e.g., MW-5) today, yet the main plume beneath DSCP is relatively un-weathered. These relatively un-weathered samples are also coincident with areas where the historical use of petroleum products similar to those that comprise the NAPL plume was highest (e.g., Building 28 gasoline station, railcar off-loading terminal, Bash Street gas station, Building 30). The lack of weathering under these potential source areas points directly to a localized input, as described in Sections 5 and 6.

DSCP also contends, based solely on HFS analysis, that the low concentrations of hydrocarbon residues detected on the CSX property in the alleged pathway are related to the NAPL transport from the Sun Refinery. Sun has demonstrated in Section 5, that if NAPL had moved through the proposed pathway, soil-residual hydrocarbon concentrations would be in the 10s of thousands of mg/kg and would extend over a large area. The presumed residual concentrations have not been found. DSCP has suggested that the hydrocarbon concentrations in the alleged pathway result from the operation of the fate mechanisms described in Sections 3 and 5. If this had been the case, significant and areally consistent weathering would be expected throughout the DSCP plume. Such weathering does not occur.

Because the pathway theory cannot be supported by the presence of reasonable hydrocarbon residual concentrations, DSCP now contends that the types of hydrocarbons in the pathway are “indicative of light naphtha such as JP-4 or crude oil” (Malcolm Pirnie, 1997). The results of an HFS analysis for a CSX soil sample includes the following qualitative description (most of the soil samples were described in a similar fashion):

“Presence of low boiling compounds, C6-C25, maximum near C6. Patterns displayed are indicative of a light naphtha such as JP-4 or crude oil. Low boiling product appears to have undergone chemical or biological degradation as well as degradation by evaporative processes. Dominant pattern of n-alkanes was not seen for this material” (Table 5.4, Malcolm Pirnie 1997).

It is Sun’s position, and the position of most respected hydrocarbon fingerprinting experts (Kaplan et al. 1996), that it is impossible to provide conclusive chemical linkages using the GC/FID based HFS employed by DSCP’s expert F&B when samples are highly weathered as they are on the CSX property. Table 5-4 “Data Generated for Soil and Groundwater Samples Collected June 1996 Through September 1996, DSCP Philadelphia, PA” (Malcolm Pirnie, 1997) includes F&B’s qualitative interpretation of the CSX hydrocarbon residues.

The common theme of all the CSX analyses performed by F&B is the term indicative. In no case does F&B state that the material on the CSX property is JP-4, diesel, kerosene or even gasoline; it is all described as “indicative of” these products. That is simply because the HFS method, or any

GC/FID method alone has severe limitations for identifying degraded hydrocarbon residues (Boehm et al. 1997, Boehm et al. 1995), such as those identified on the CSX property. Once the hydrocarbon signature is altered, the analyst can no longer reliably identify what the product is, and then, even the qualitative assessment is unsupported and questionable. Qualitative statements on product types like the one quoted above from the Malcolm Pirnie report are particularly suspect because no reference standard was ever provided as a basis for comparison. Malcolm Pirnie's response to Sun's request for the JP-4 reference materials used by F&B to identify the product in the CSX boring samples, referenced the military specification for JP-4. However, a product specification is not an appropriate tool for identification of environmental samples.

Based on the HFS analysis, there is no credible scientific evidence to demonstrate the degraded residues on the CSX property are related to the Sun Refinery or the DSCP NAPL plume. In fact, applying the HFS approach for the purpose of achieving Mr. Morganelli's stated objective of developing, "... a chemical connection of the plumes to the Sun property," is not technically possible, and all qualitative results of degraded residues are simply unsubstantiated guesses.

7.4.3 Sun Advanced Chemical Fingerprinting Approach

To provide chemical linkage data for material in the NAPL plume and smear-zone linkage studies, more rigorous quantitative and statistically based tools must be employed (Boehm et al. 1997). The analytical methods used for the Sun analyses are described in Section 7.2, and provide multiple levels of chemical analyses combined with statistical interpretative tools to identify qualitative relationships based on quantitative data. This substantially reduces analyst bias, and provides a strong, defensible, scientifically based foundation for reaching relevant conclusions.

For fresh products it may be adequate to use the HFS method or similar GC/FID approach for product identification (e.g., such as in DSCP NAPL samples), but, as noted above, once the GC/FID signature is degraded, as it often is in soil samples, the confidence level for source identification and sample linkage is substantially lowered. Figure 7-29 demonstrates the chemical changes that occur to a crude oil during weathering. Crude oil was used as the illustrative example here because it weathers much more slowly than finished products because of its chemical composition and because it demonstrates a much broader range of weathering. Clearly, it would be

impossible to link the degraded product with its source using GC/FID methods alone. However, GC/MS tools have been developed that greatly improve the ability of the analyst to evaluate the source and relative linkages with other samples even in the most weathered samples (Sauer and Boehm 1991, Page et al., 1995, Boehm et al., 1997, Douglas et al. 1996). GC/MS analysis of PAH compounds (Section 7.2.1), supplemented by GRO analyses of NAPL samples combined with the statistically based Principal Component Analysis (PCA) of the large data set generated for this project provides a much higher level of confidence for analyzing weathered oil samples.

PCA is preferred for evaluating large environmental data sets: 1) to minimize analyst bias when defining source relationships in large data sets, 2) to thoroughly explore the data to determine how samples are related and to identify the characteristics that make them similar or different, 3) to simplify large complex data sets to make the detection of relationships and patterns that may have been missed or misinterpreted possible, and 4) to partition samples into related groups or clusters. The real value of Principal Component Analysis is that even if it is not possible to identify the product type within acceptable confidence levels, the relationships between samples can nevertheless be statistically derived.

PCA is a multivariate data analysis technique that is used to capture important chemical information in complex data matrices and transform it into smaller scores and loading matrices that are linear combinations of the original data set. The new scores matrix contains information about "sample patterns" within the data and the relationships between the samples in the data set. The relationships are reflected as clusters of samples on an X:Y plot of the principal component scores. The new loadings matrix reflect the influence each variable has in the sample patterns or clusters. Because these new matrices or principal components (PCs) are created in order of decreasing variance, the first PC accounts for most of the variance in the data, the second PC less, etc. For this study, Sirius for Windows Version 1.2 was used on block/log normalized PAH and GRO data. Block/log normalization is a standard approach for normalizing data from environmental samples and reduces the impact of differences in matrix and concentration.

In summary, PCA can be used to evaluate large complex data sets and reduce the information down to the essential relationships between samples. This approach represents a more comprehensive,

objective, and quantitative analysis of hydrocarbon samples than simply inspecting complex GC/FID chromatograms on a light table. With these ACF tools the following important questions can be objectively evaluated:

- Is the #1 Tankfarm NAPL the source of NAPL in the DSCP plume?
- Are the smear zone soil samples from the Sun Refinery related to the smear zone samples beneath the DSCP plume?
- Is the NAPL in the DSCP plume similar to the NAPL trapped in the smear zones beneath DSCP?

These questions are addressed in detail in the ensuing sections.

7.4.4 Is the #1 Tankfarm NAPL the source of NAPL to the DSCP plume?

The data used to address this question included the results of both GRO and PAH analyses. GRO data was generated from samples where NAPL or sheens of this material were present. GRO analysis was not performed on soil samples due to the anticipated degradation of the compounds that comprise this analytical fraction and losses of light hydrocarbons during sample preparation. All available PAH data was used for the PCA analysis with the exception of C0-, C1-, C2-, and C3-naphthalenes. These were excluded due to the weathering of these compounds in the environment after the initial PCA plots were shown to be dominated by the effects of naphthalene weathering, as shown by Elmendorf et al. (1994) and Douglas et al. (1994). Exclusion of these compounds provided a result that was driven primarily by the compounds that are uniquely different in the samples (i.e., the source-specific and sulfur containing dibenzothiophenes, Page et al. 1995, Page et al. 1997).

Many of the samples used in this analysis were collected in a split sampling effort conducted by the PADEP in January 1997. DSCP's representative, Malcolm Pirnie, received aliquots at the time of collection of the NAPL samples from #1 Tankfarm used in Sun's analysis. DSCP apparently chose not to analyze or report the data despite their stated objective, "to develop a chemical connection of the plumes to the Sun property." Therefore, confirmation analysis of Sun's conclusions by DSCP were not available.

GRO data for the NAPL samples collected from the DSCP plume and the Sun #1 Tankfarm were evaluated by PCA (Table 7-2). The PCA scores (e.g., relative sample relationships) for PC1 and PC2 which represent the sample clusters are presented in Figure 7-37. The PCA loadings (the chemical compounds that drive the sample clusters) that describe why the samples were clustered in a particular orientation are presented in Figure 7-38.

PC1 and PC2 for the GRO analyses account for over 67 percent of the variance in the data set. Three clusters contain additional separations of sample SB-35 (Steen Property) and PZ400 (located near RW-400 in the #1 Tankfarm). Based on the GRO analysis, the #1 Tankfarm samples are clearly not related to the DSCP plume samples. The separation of the #1 Tankfarm from the DSCP plume are based on the enrichment of aromatic hydrocarbons such as xylenes (PX, MX, OX), toluene (Tol) and trimethyl benzenes (TMB) relative to the DSCP plume, which is enriched in isopentane (IP), alkanes, and MCH. Sample S-53 and RW-102, located on the most western aspect of the South Yard are enriched in heavy aromatics and naphthenes, and they are clearly separated from the DSCP plume

Whereas the GRO data represents the lighter components of the NAPL, the semi-volatile PAH data represents the heavier and less labile compounds. PAH data for the NAPL and sheen samples collected from the DSCP, Steen property, Philadelphia Housing Authority property, and Sun #1 Tankfarm were also analyzed using PCA (referred to as DSCP plume samples). More samples were analyzed for PAH analyses because many of the light sheen samples could not be analyzed by GRO which requires whole product. For PAH analyses, the sheen samples were solvent extracted and then were analyzed, providing additional plume data. Again the data was block/log normalized to minimize differences in concentration and analyzed using the Sirius PCA program. The PCA scores for PC1 and PC2 that represent the sample clusters are presented in Figure 7-39. The PCA loadings are presented in Figure 7-40.

The PAH PCA analysis again separates the #1 Tankfarm (blue) from the DSCP plume (red). Samples in the vicinity of MW-25 are enriched in pyrogenic PAH compounds (e.g., fluoranthene, pyrene), and depleted in the crude source specific dibenzothiophenes. In contrast, the majority of the #1 Tankfarm samples (RW-401, RW-402, S-82, S-100) are enriched in the source-specific

dibenzothiophenes (e.g., C2D, Page et al. 1995) and separated from the DSCP plume. The horizontal range of samples within the plume, as depicted in the PCA plots, is driven primarily by weathering (distance) where samples such as RW-D, MW-5, MW-6, and PH3 are shown to be relatively fresh (e.g., enriched in biphenyl [BIP], and C4-naphthalenes [C4N]). This contrasts with the sample from MW-7, which is more degraded. The vertical range within the plume as depicted in the PCA plots reflects different crude sources, suggesting chronic multiple input scenarios or sources. In some cases, however, the NAPL samples are very similar as in MW-6, MW-5, and PH-3, and the degraded samples SB-25, SB-23, and SB-27. These samples were generally geographically related and all of them are from locations on the eastern side of 26th Street. None of them are chemically related to the Sun plume.

In addition to the PCA results, GC/FID chromatograms clearly indicate the presence of relatively un-weathered diesel fuel in #1 Tankfarm samples, which was not detected in any of the DSCP plume samples. In addition to the fact that NAPL weathering, which clearly increases with distance from the center of the fresh NAPL under DSCP, the hydrocarbon distributions found in the tankfarm recovery wells are complex, in some cases highly degraded (e.g., S-89, Figure 7-41), and chemically different (e.g., high diesel and gasoline concentrations, RW-401, Figure 7-42) from the NAPL underlying DSCP. Whereas the NAPL beneath the DSCP is gasoline and a naphtha-naphtha-like product, PAH fingerprint analysis of the product in #1 Tankfarm recovery wells shows it is clearly of different origin (as reflected in the PCA), based on dibenzothiophene concentrations. Soil samples collected at and below the current water table on the Sun refinery identified weathered residues of multiple products from light fuels up to diesel fuel and lubricating oils. These analyses in aggregate show that the NAPL on the current water table beneath DSCP is unrelated to that on the current water table beneath the #1 Tankfarm

7.4.5 Is the NAPL in the smear zone beneath the Sun refinery the same as the NAPL under the DSCP plume?

As described in the preceding section, the NAPL on the Sun property is not the same as the NAPL in the DSCP plume. However, both Sun and DSCP have documented the evidence of a smear zone below the water table. Therefore, a comparison of the smear zone beneath the refinery and DSCP is unwarranted. Because samples from below the water table are typically found in a soil matrix as

trapped residual, they are analyzed as soil samples. PAH data was used in this analysis rather than the GRO analysis, which requires NAPL or sheen products for analysis.

PCA analysis was performed on the PAH data for the soil samples collected from the smear zones beneath DSCP, Steen, and Philadelphia Housing Authority property and beneath the #1 Tankfarm. Four samples were excluded from the data set (samples NR-3, NR-5, and PZ-2 at 10 to 12-ft, PZ-3 at 14 to 15-ft) because they were collected from above the water table on the DSCP property, and, therefore, were outside the smear zone. In addition, these samples were chemically different from the rest of the data set.

The data was block/log normalized to minimize differences in concentration and analyzed using the Sirius PCA program. PC1 and PC2 for the smear zone PAH analyses account for greater than 70 percent of the variance in the data set. The PCA scores for PC1 and PC2, which represent the sample clusters, are presented in Figure 7-43. The PCA loadings that describe why the samples were clustered in a particular orientation are presented in Figure 7-44.

The results of the smear zone PAH PCA clusters the data into three groups. Group 1 is the DSCP plume smear-zone data (red circle); group 2 is the Sun refinery smear-zone data (blue circle); and group 3 is the boring 204 data (blue circle). Group 1 data is enriched in C4-naphthalenes and biphenyl and, to some extent, phenanthrenes and dibenzothiophenes. Group 2 data is enriched chrysenes and pyrogenic (combustion relation) PAH compounds (e.g., pyrene). The results of these analyses clearly show that the products in the smear zones beneath the #1 Tankfarm and DSCP are unrelated. Thus, the NAPL in the smear zone beneath DSCP was not sourced in the #1 Tankfarm.

7.4.6 Is the NAPL in the DSCP Plume Similar to the Smear Zone NAPL Beneath the DSCP Plume?

The samples utilized to answer this question, as identified in Table 7-2, include NAPL and soil samples within the DSCP plume. The results of the PCA scores analysis (sample clusters) are presented in Figure 7-45; the loadings results (chemical drivers) are presented in Figure 7-46. As noted above, the NAPL reflects a wide range of sample clusters. These sample clusters are driven by differences in source crudes (e.g., dibenzothiophenes in PC2, Douglas et al. 1996, Page et al.

1995), combustion products (e.g., fluoranthene/pyrenes in PC2), and to some degree the amount of sample weathering as reflected in PCA 1 where NAPL samples RWD, MW-5, PH-3, and MW-6 are least weathered due to enriched biphenyl (BIP) and C4-naphthalenes,) and NAPL samples SB-12, SB-39, SB-38, SB-23, SB-25, and SB-27 represent some of the most weathered samples in the DSCP plume data set and are enriched in the recalcitrant PAH compounds such as C4-phenanthrenes and fluoranthene/pyrenes.

Three smear zone samples were collected from each RW-G and RW-M boring located on the Philadelphia Housing Authority property, directly south of SB-21. The three RW-G smear zone samples (identified on the plot as GS1, GS2, and GS3) were vertically contiguous and clustered tightly with their associated NAPL sample RW-G (GP1) and two of the nearby smear zone samples from RW-M (MS2 and MS3). The third RW-M smear zone sample clustered more closer to NAPL samples SB-21, SB-20, and SB-37. The Steen property smear zone samples SB-38, SB-37, SB-39, SB-35, and SB-36 were generally vertically contiguous and clustered with NAPL products in the geographical area of the soil borings such as NAPL samples S35, S36, S-37, S-38, and S-39. Based on the PCA analyses, the smear zone samples were highly correlated with NAPL samples from similar geographical areas within the DSCP plume. This is significant because it demonstrates that the soil samples that were contaminated during a low water table are chemically linked to the current DSCP NAPL plume.

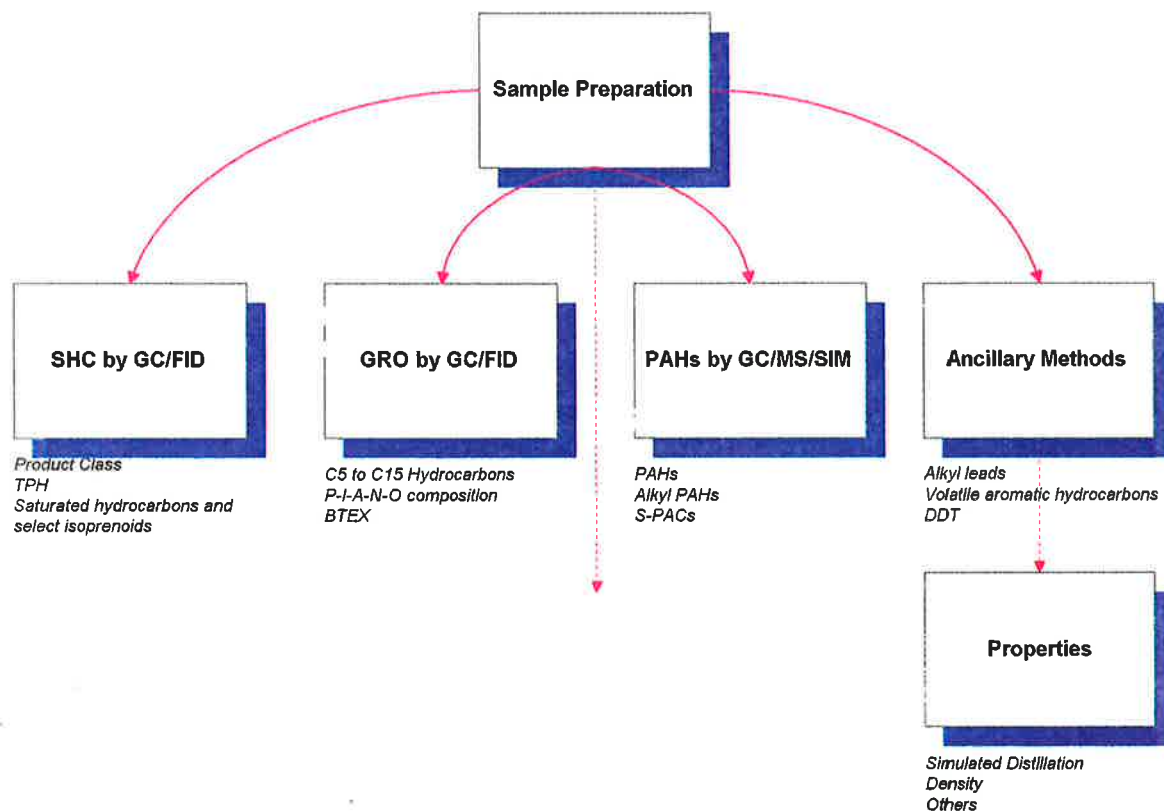


Figure 7-6a: DSCP MW-5 NAPL GRO Analysis

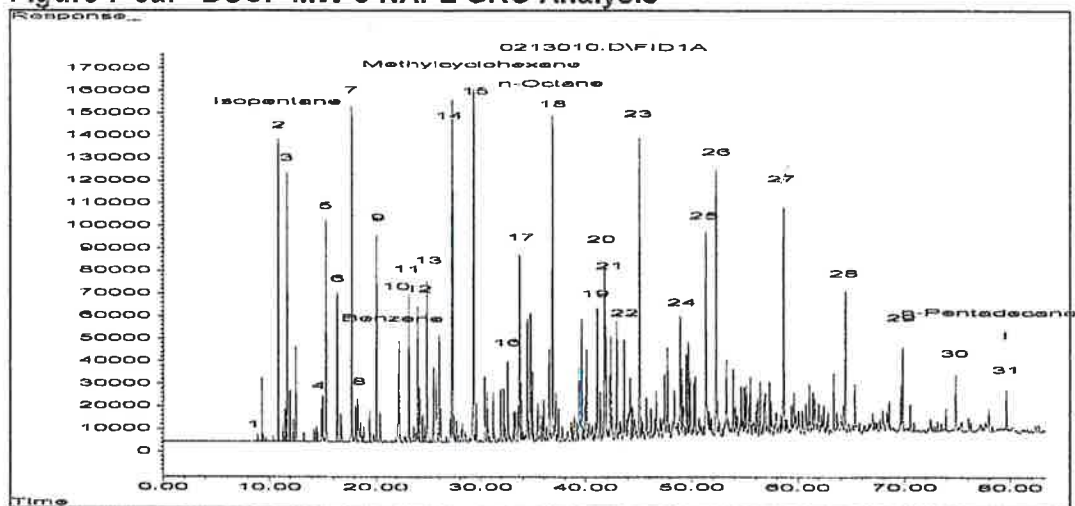


Figure 7-6b: DSCP MW-5 NAPL GC/FID Analysis

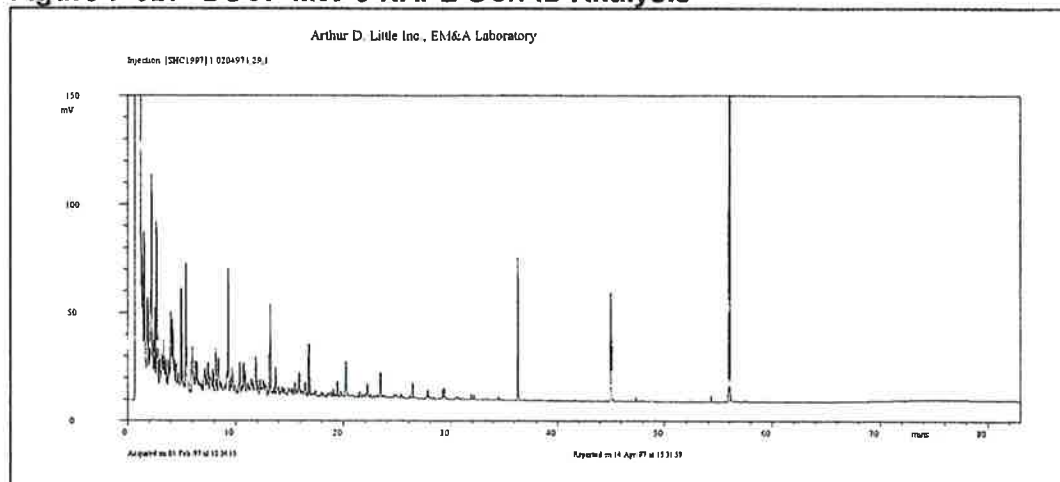


Figure 7-6c: DSCP MW-5 NAPL PAH Analysis

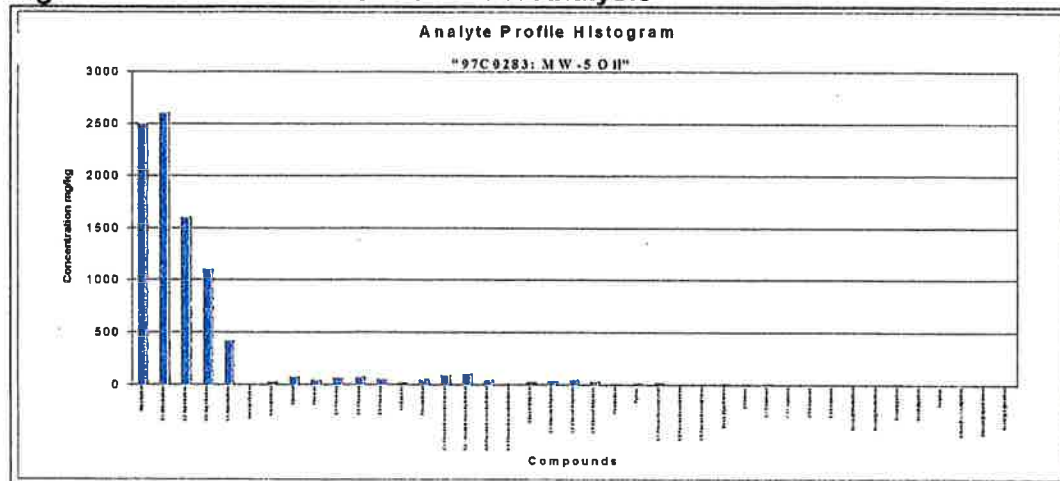


Figure 7-7a: DSCP MW-6 NAPL GRO Analysis

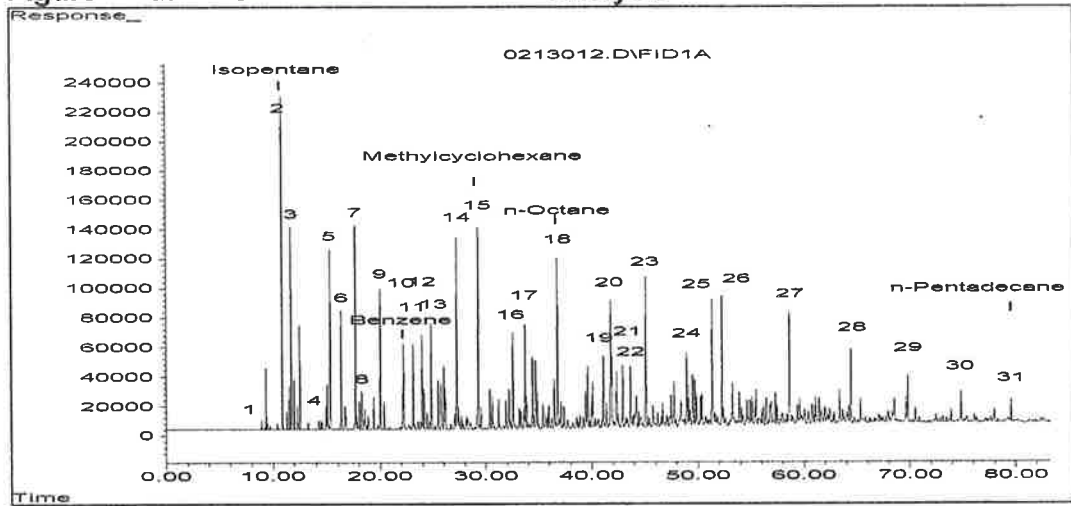


Figure 7-7b: DSCP MW-6 NAPL GC/FID Analysis

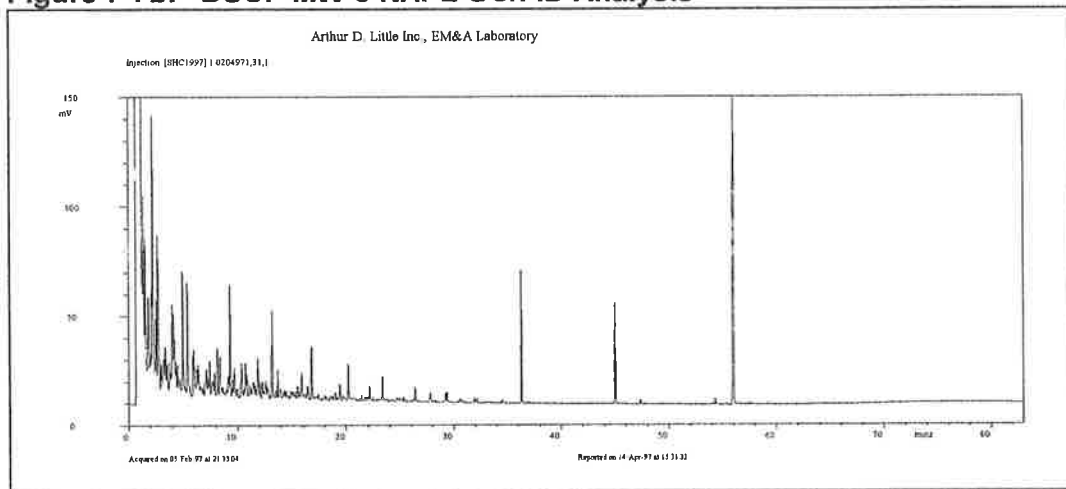


Figure 7-7c: DSCP MW-6 NAPL PAH Analysis

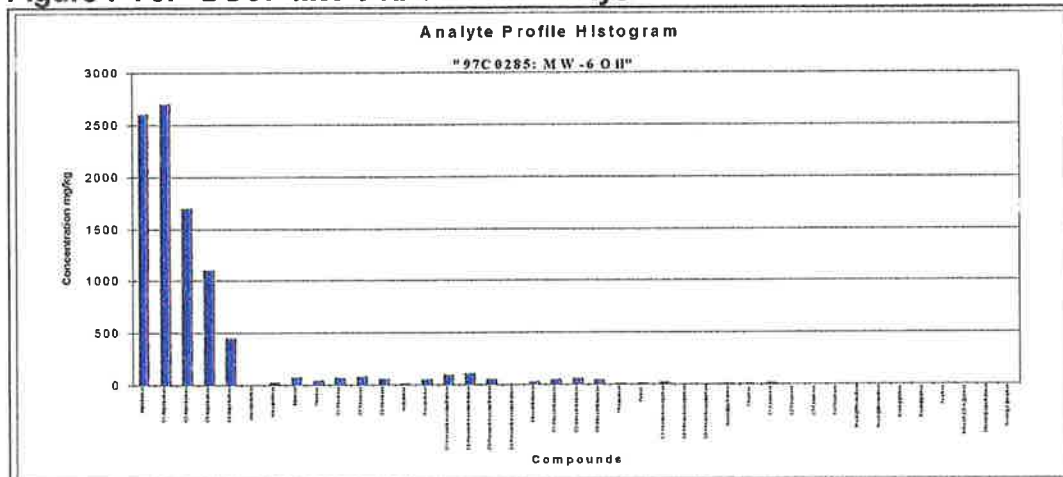


Figure 7-8a: DSCP MW-7 NAPL GRO Analysis

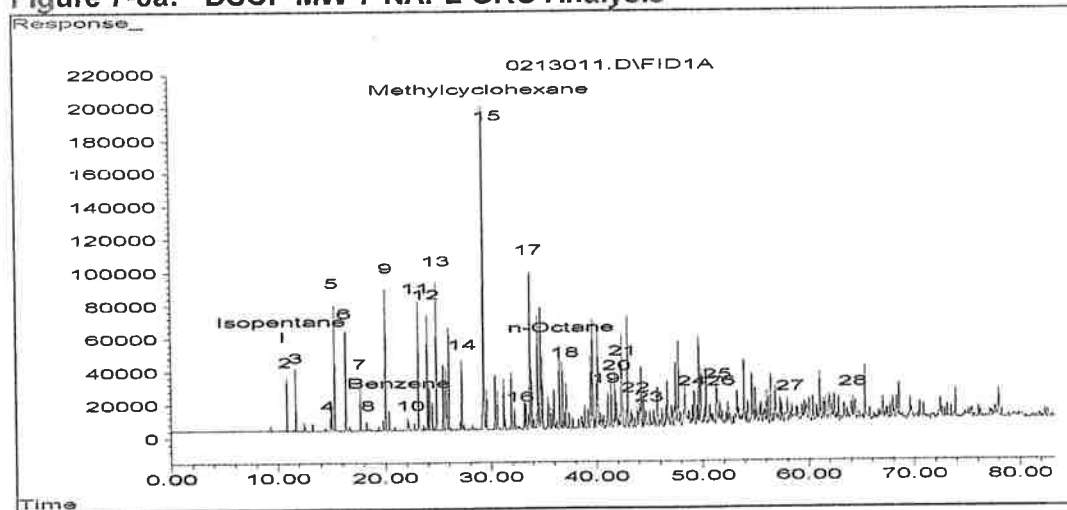


Figure 7-8b: DSCP MW-7 NAPL GC/FID Analysis

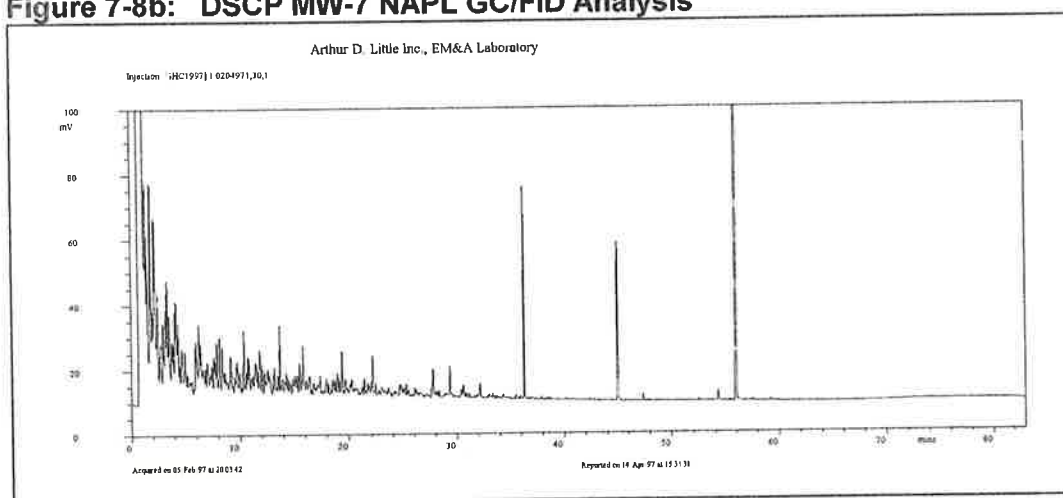
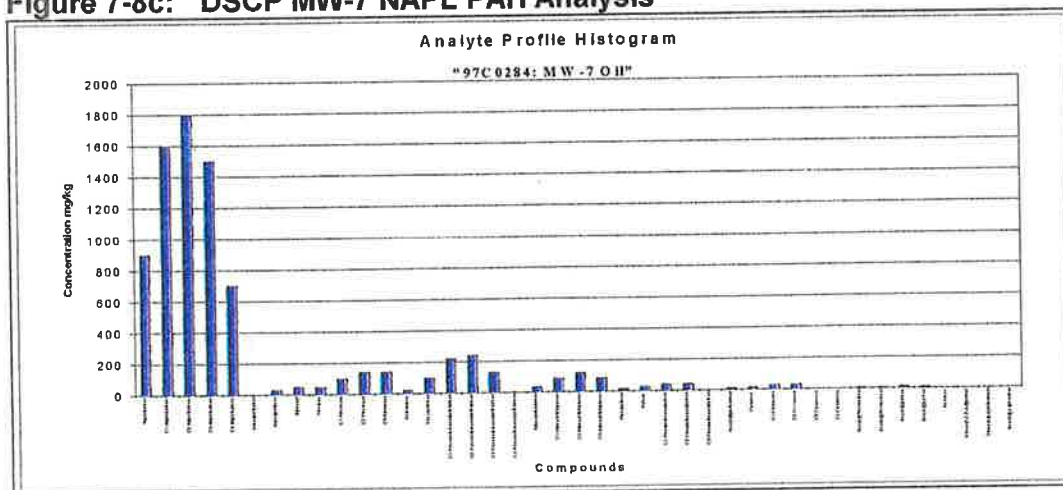
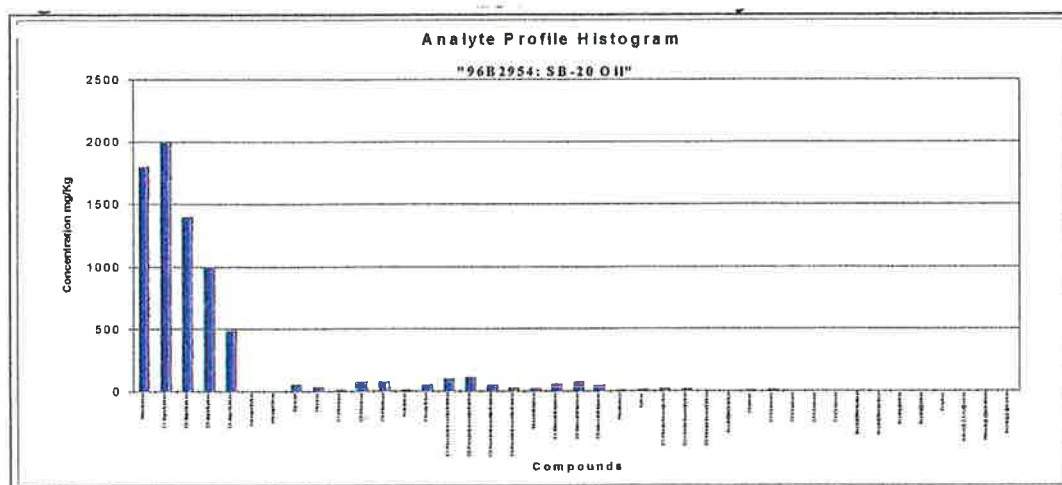
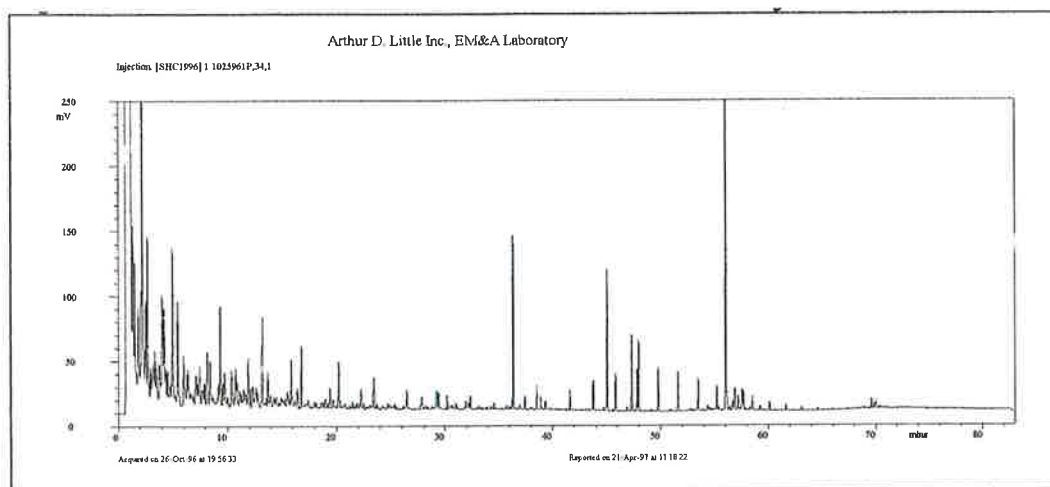
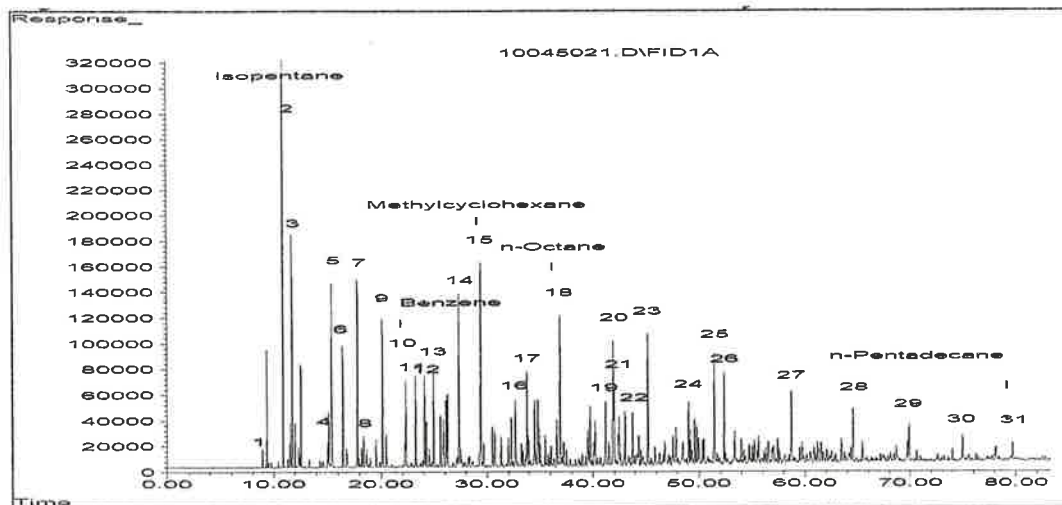
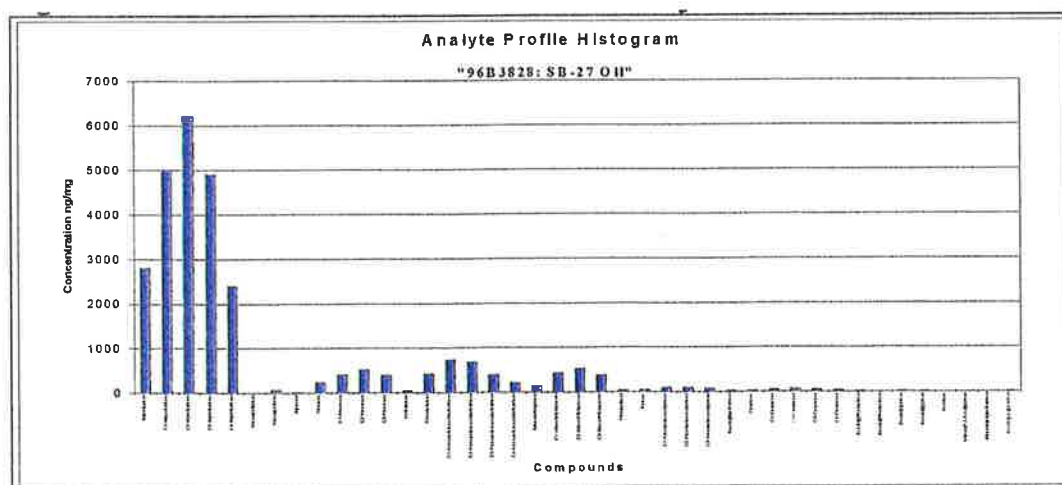
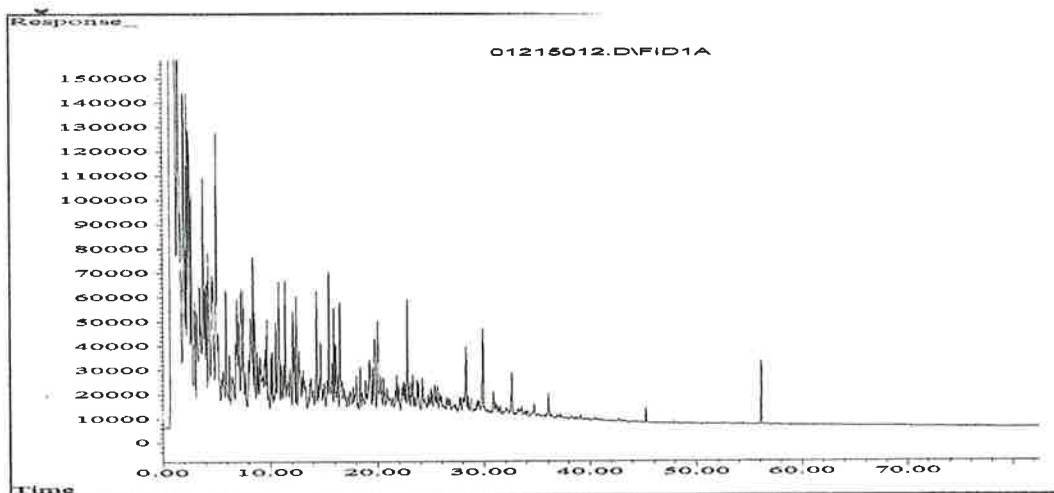
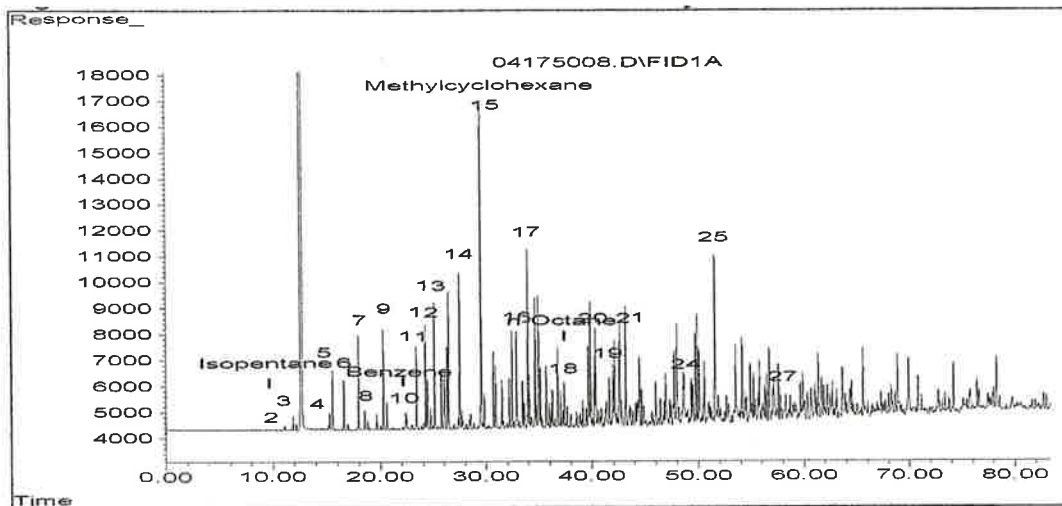


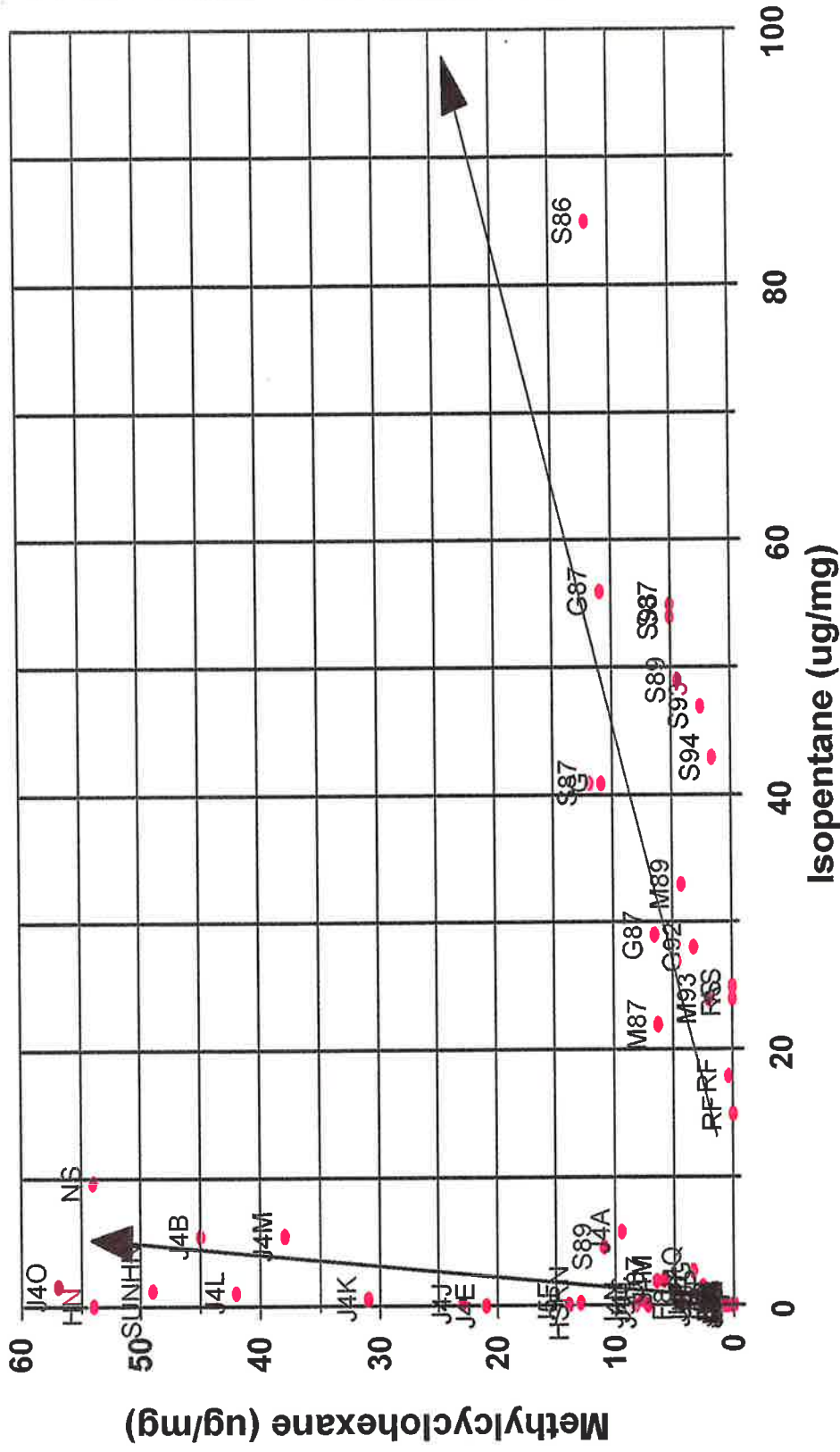
Figure 7-8c: DSCP MW-7 NAPL PAH Analysis



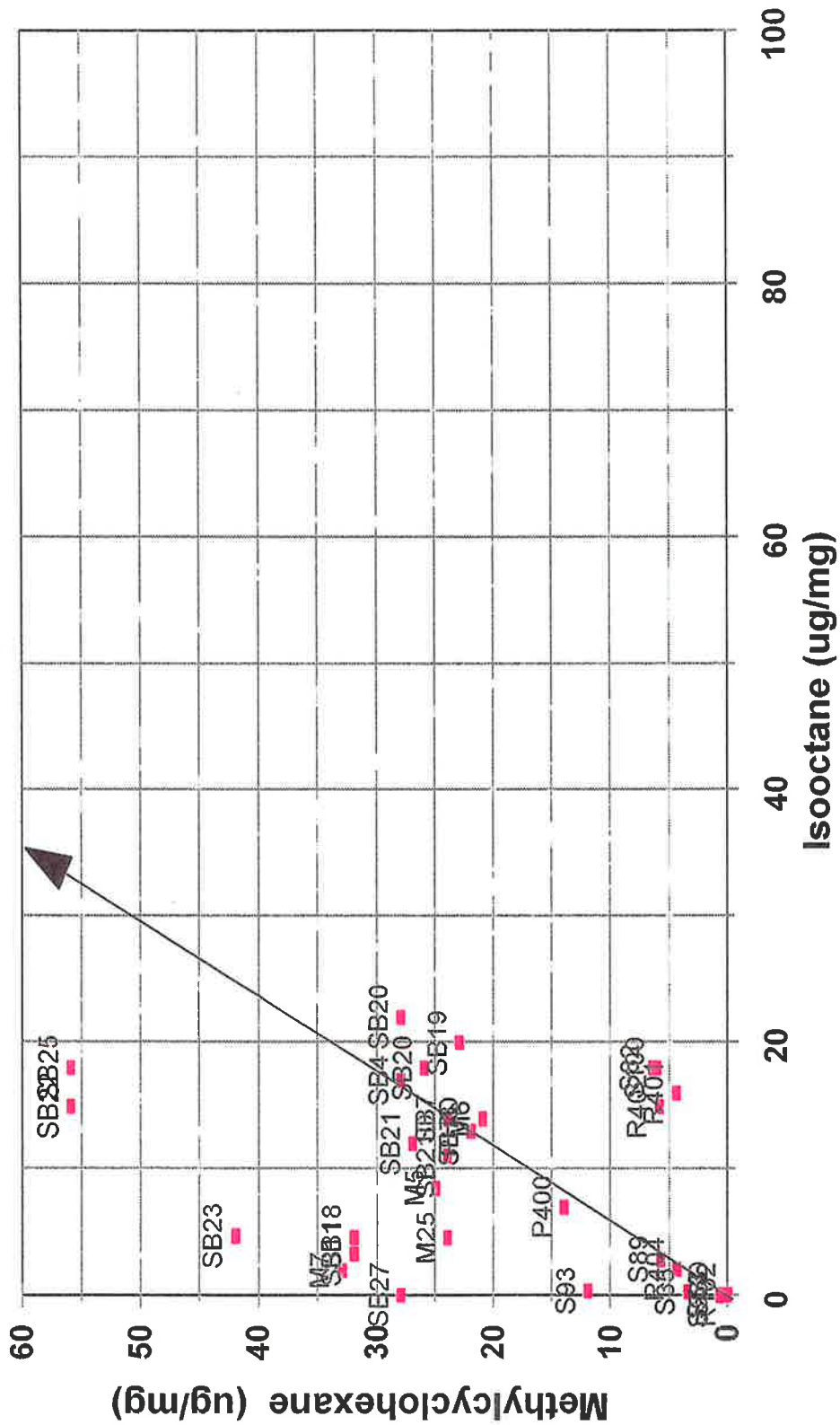




Product MCH Versus Isopentane

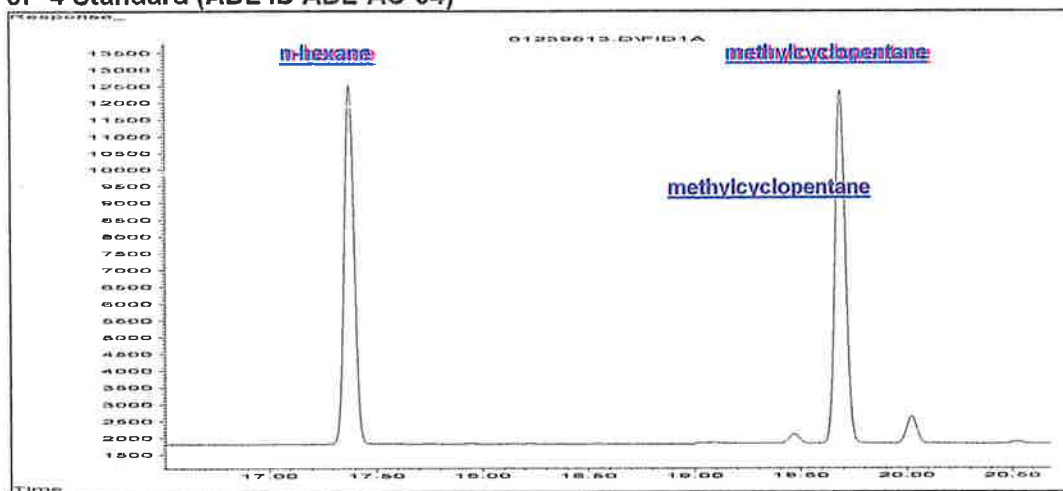


NAPL MCH Versus Isopentane

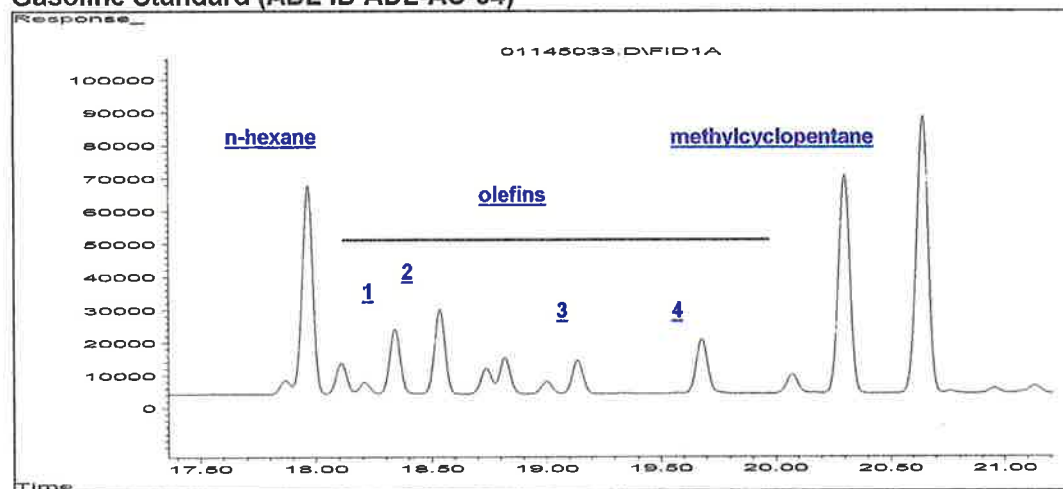


I S T INTEGRATED SCIENCE & TECHNOLOGY, INC.	DRAWN BY: EG	DATE: MARCH 1998	Cross Plot of Isopentane and Methylcyclohexane Concentrations STUDY AREA, Philadelphia, PA FIGURE 7-12
	REVIEWED: PKH	PROJECT NO. SU001H	
	APPROVED: HJR	DWG. NO. -----	

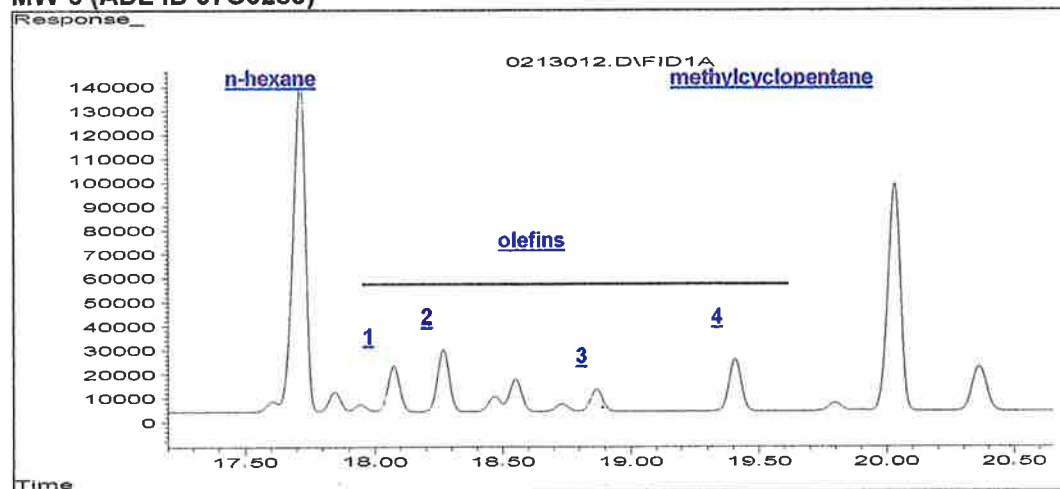
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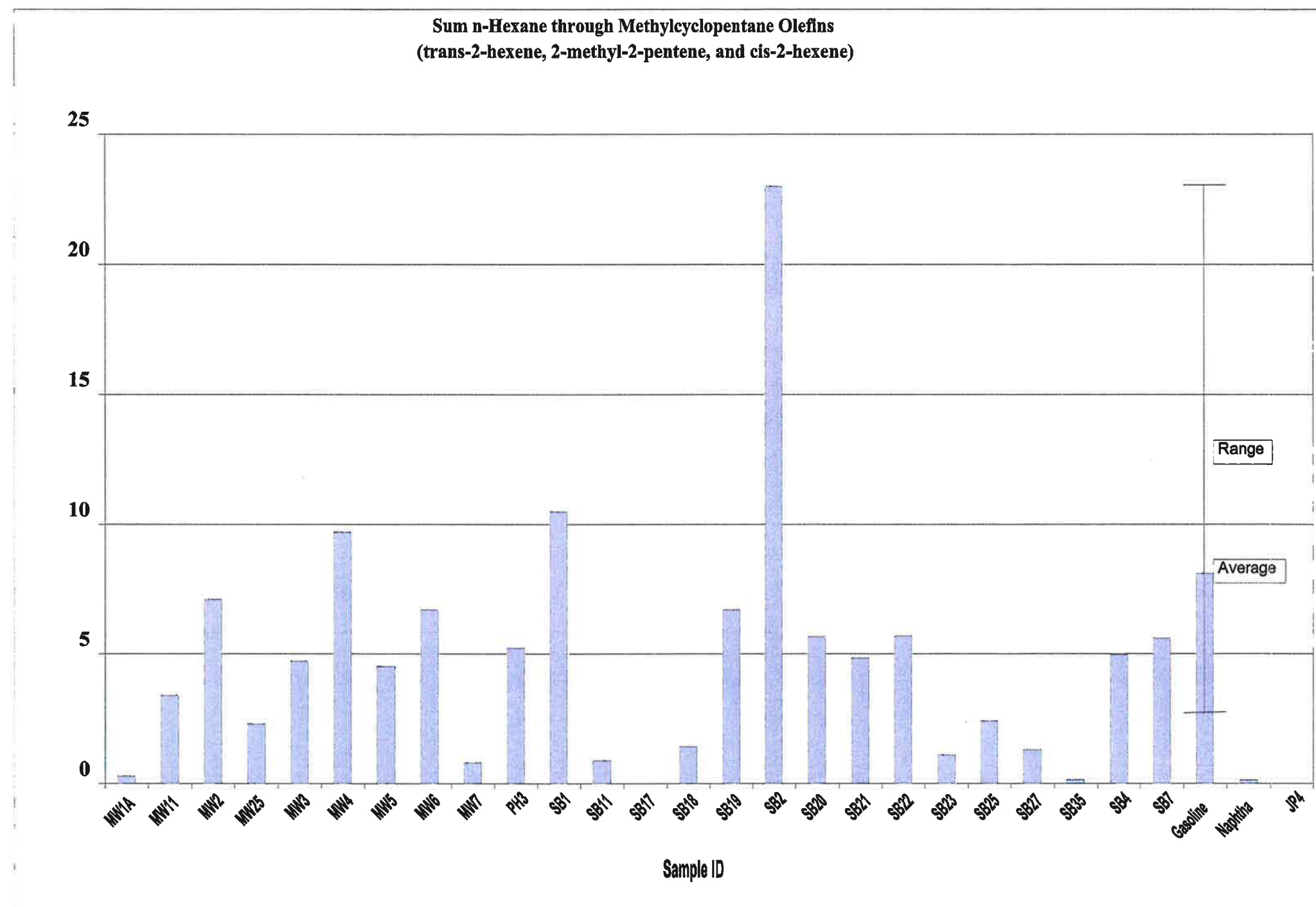


Gasoline Standard (ADL ID ADL-AC-94)



MW-6 (ADL ID 97C0285)

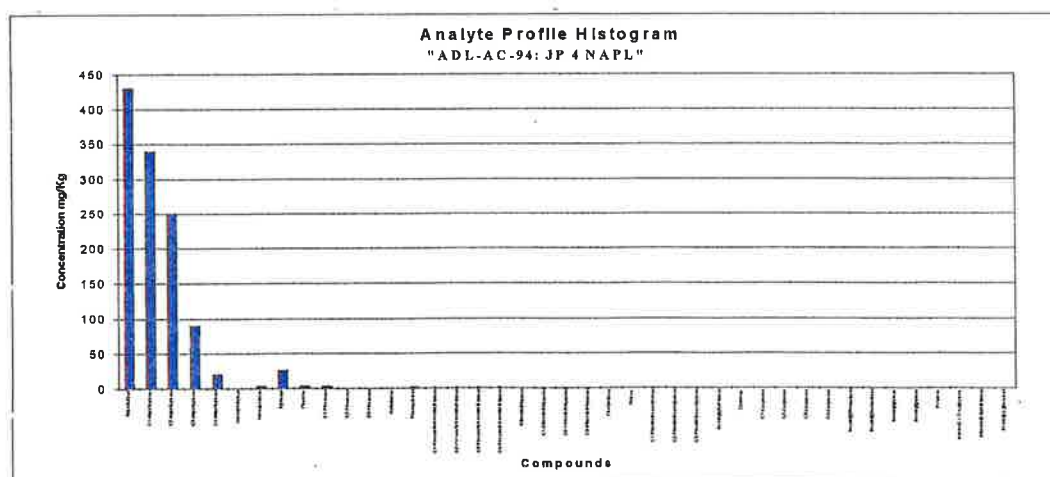
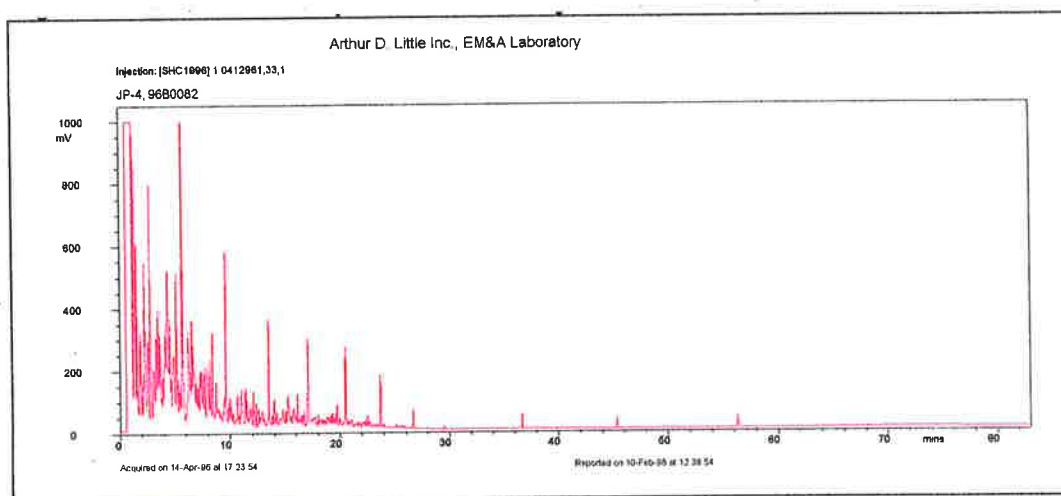
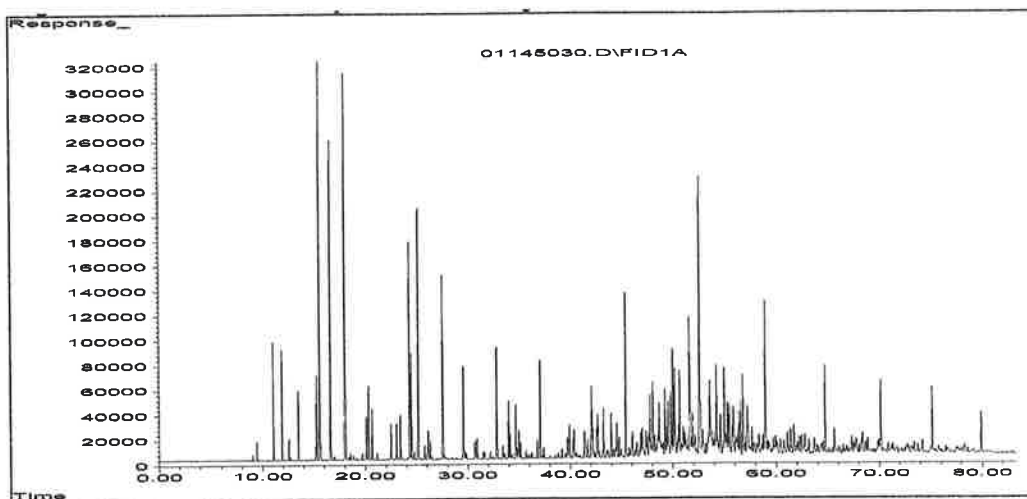




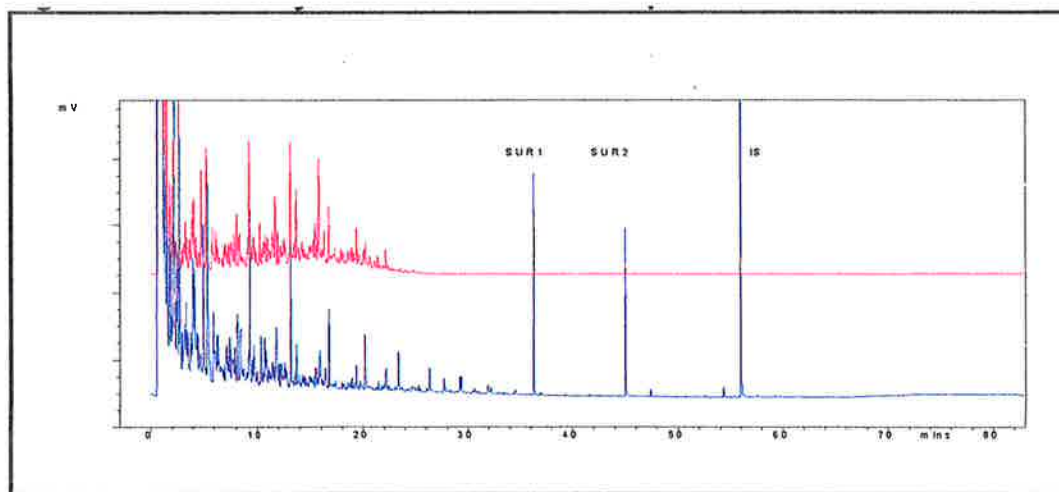
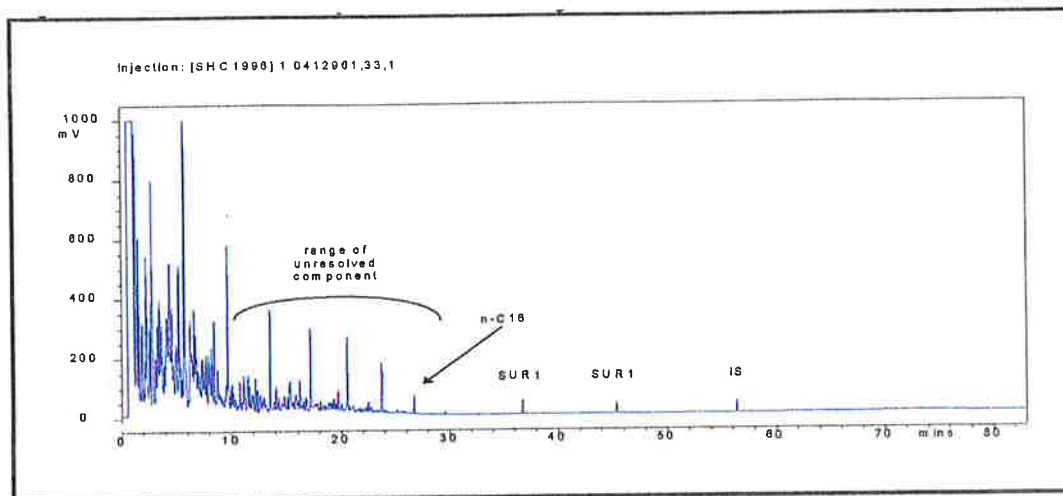
Source: Samples MW-1A, MW-11, MW-2, MW-3, MW-4 from F&B analysis in Malcolm Pirnie
(1997) report (converted from wt %); all others Arthur D. Little

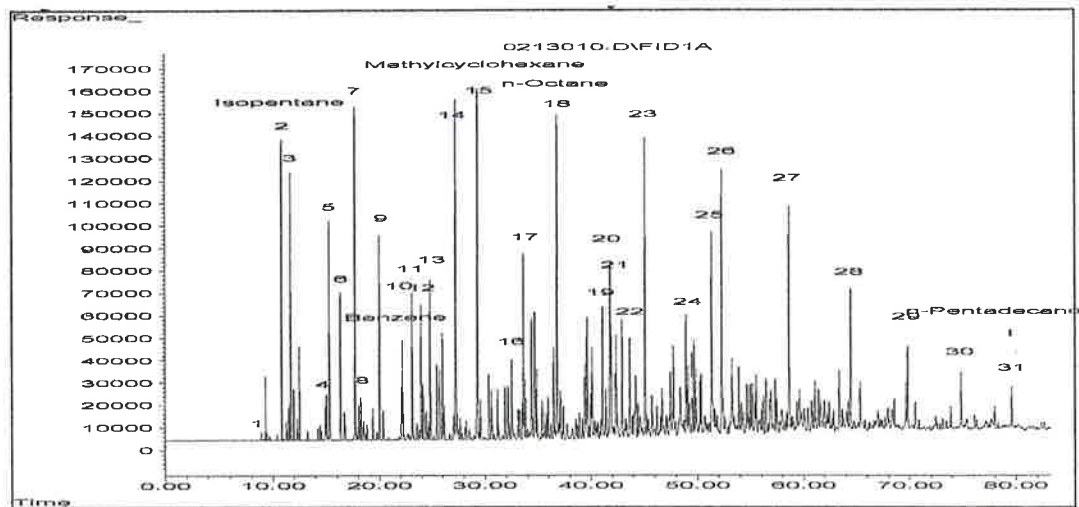
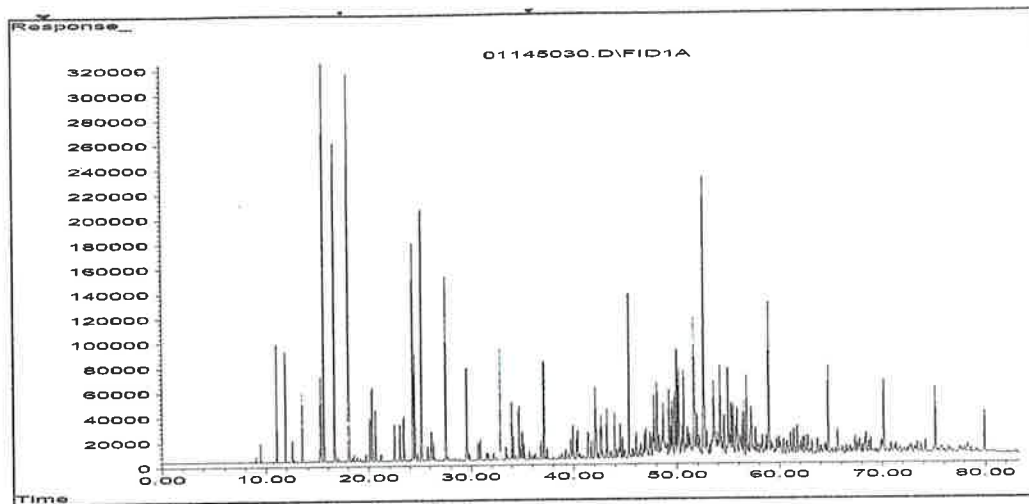
INTEGRATED SCIENCE & TECHNOLOGY, INC.	DRAWN BY: CWS	REVIEWED: PKH	APPROVED: HJR
	DATE: 20 FEB 1998	PROJECT NO. SU001H	DWG. NO.
	Diagnostic Evaluation of Selected Olefin Compounds		FIGURE 7-14

STUDY AREA
PHILADELPHIA, PENNSYLVANIA



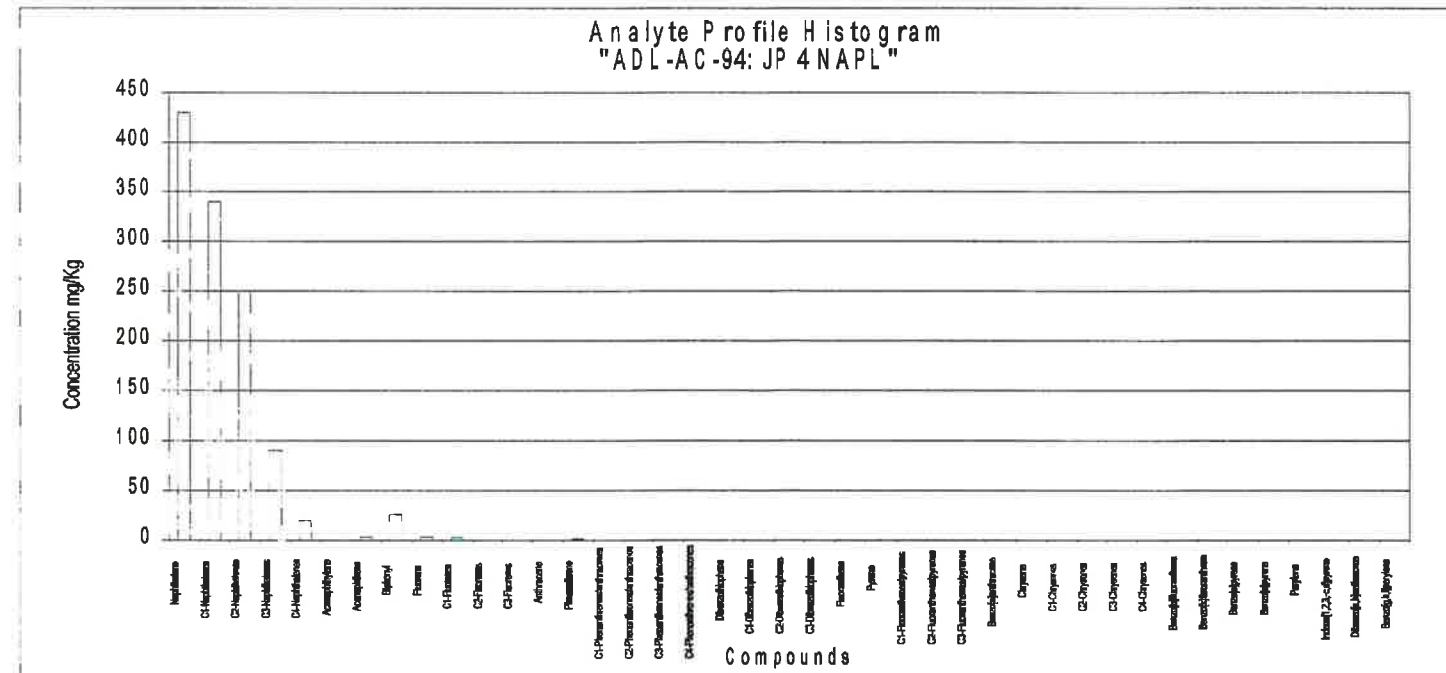
GRO, SHC: 96B0082





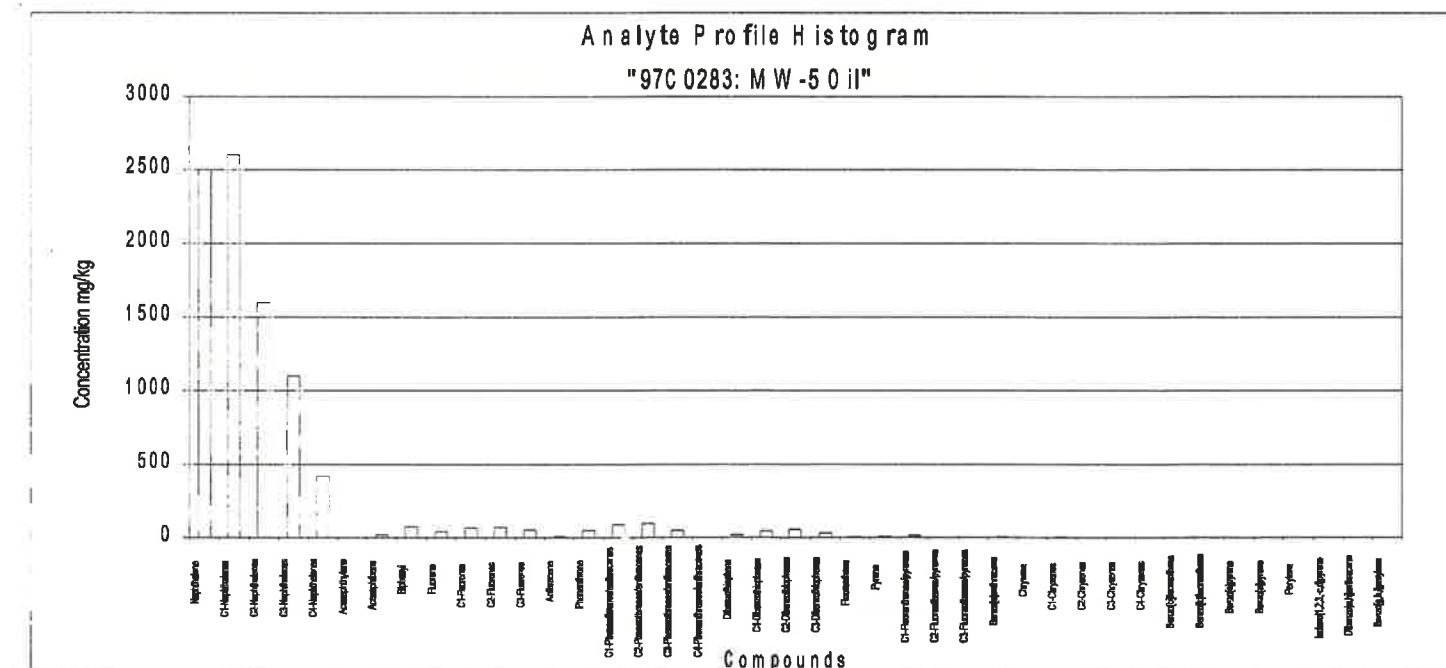
7.18a

JP-4 STANDARD PAH Distribution

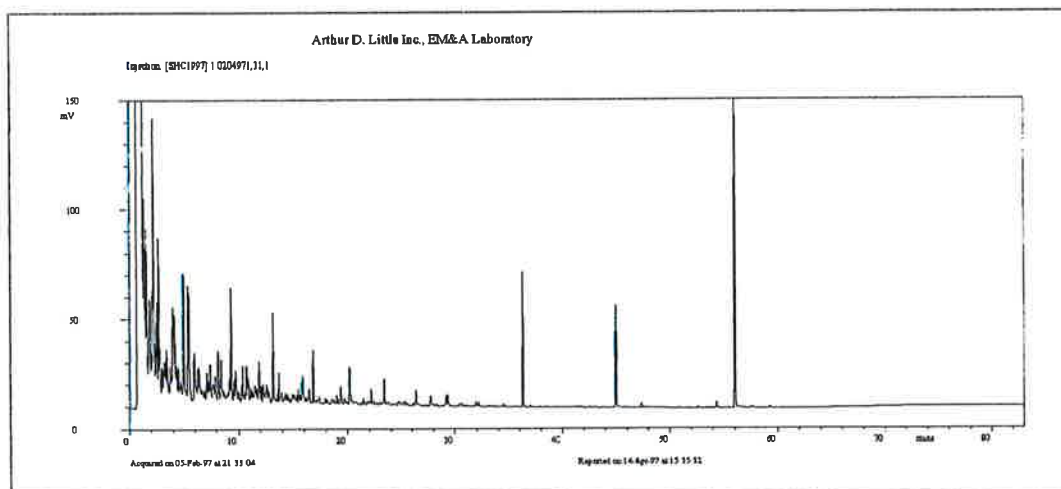
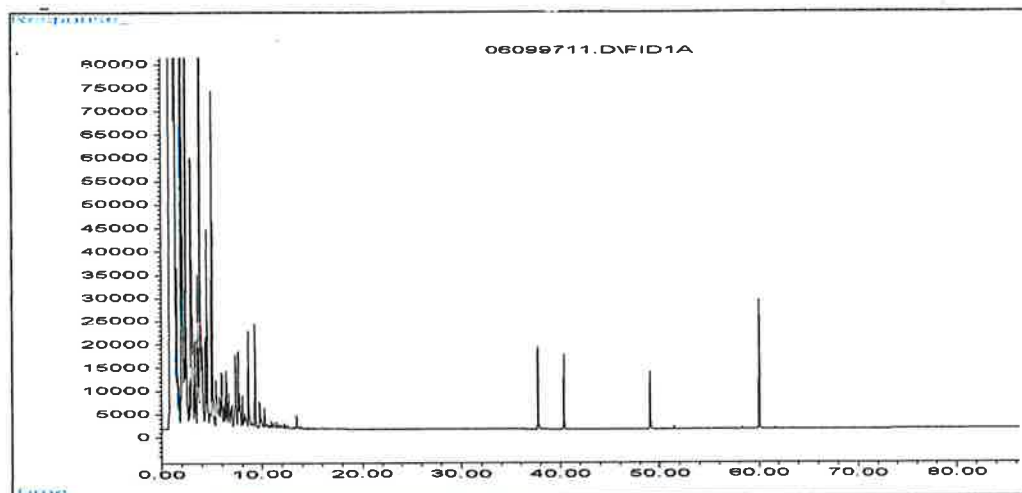


7.18b

Sample MW-5 PAH Distribution



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COMPARISON OF JP-4 STANDARD PAH DISTRIBUTIONS WITH DSCP MW-5 NAPL PAH DISTRIBUTIONS STUDY AREA PHILADELPHIA, PENNSYLVANIA		FIGURE 7-18

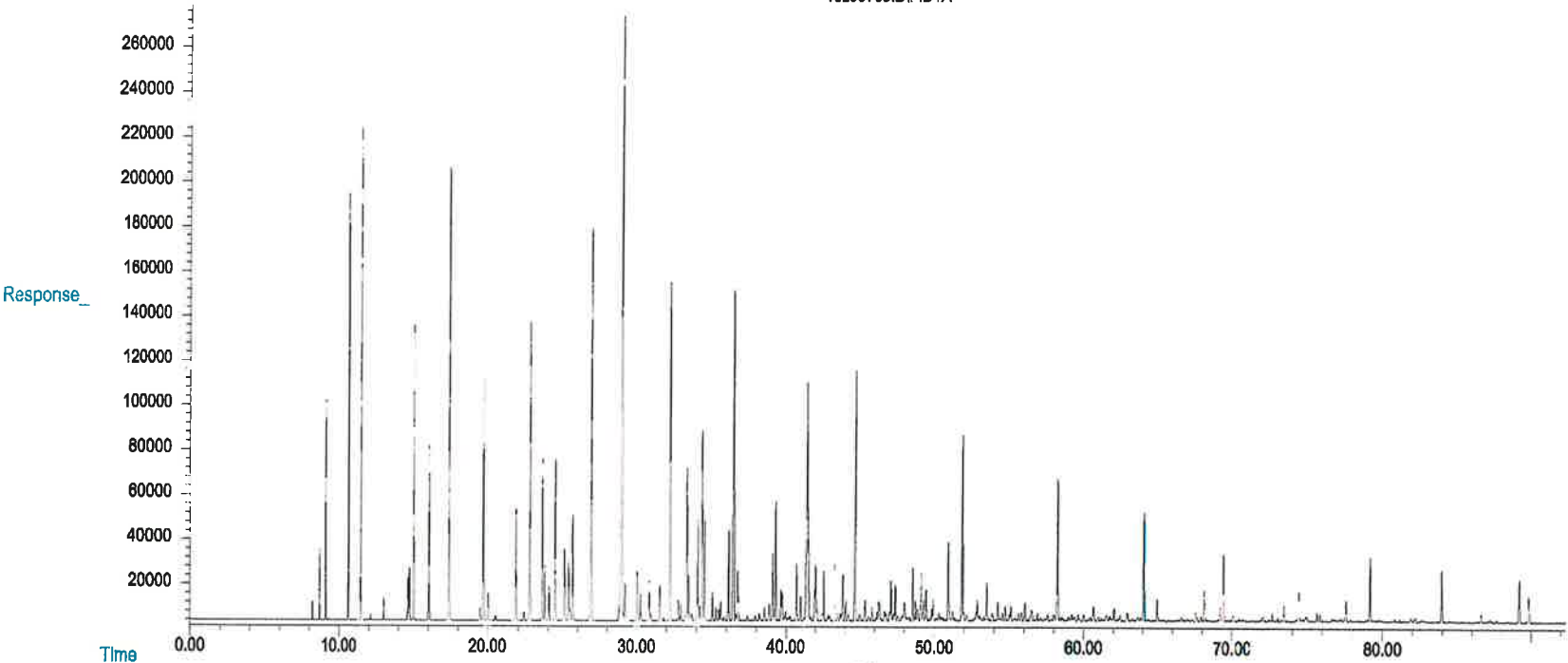


DRAWN BY: EG	REVIEWED: PKH	APPROVED: HJR
DATE: MARCH 1998	PROJECT NO. SU001H	DWG. NO. *****
GC/FID Comparison of Sun Refinery Heavy Naptha and DSCP MW-6 NAPL Study Area, Philadelphia, PA		
FIGURE 7-19		

7.20a

Condensate Sample GRO Chromatogram

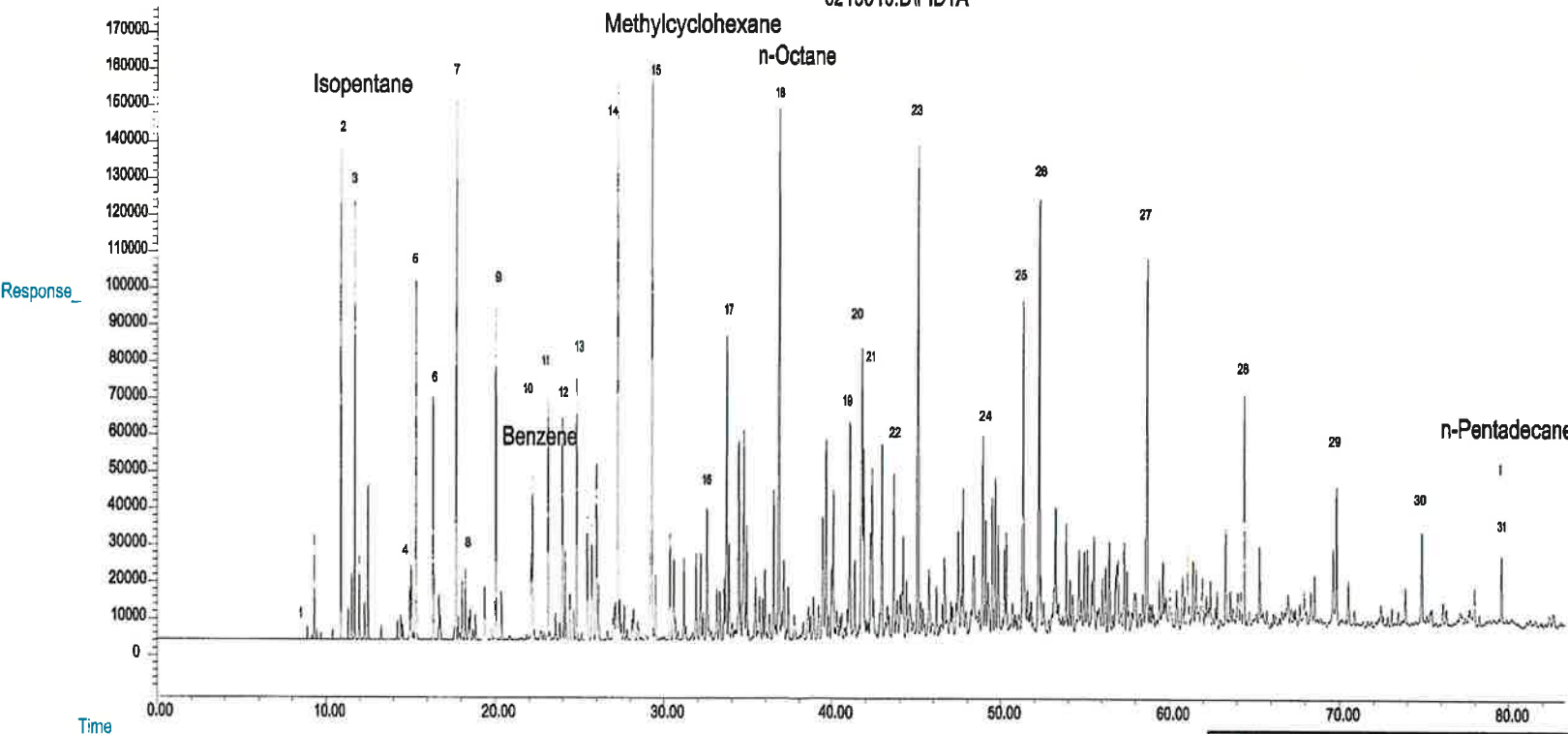
10289709.D\FID1A



7.20b

Sample MW-5 GRO Chromatogram

0213010.D\FID1A

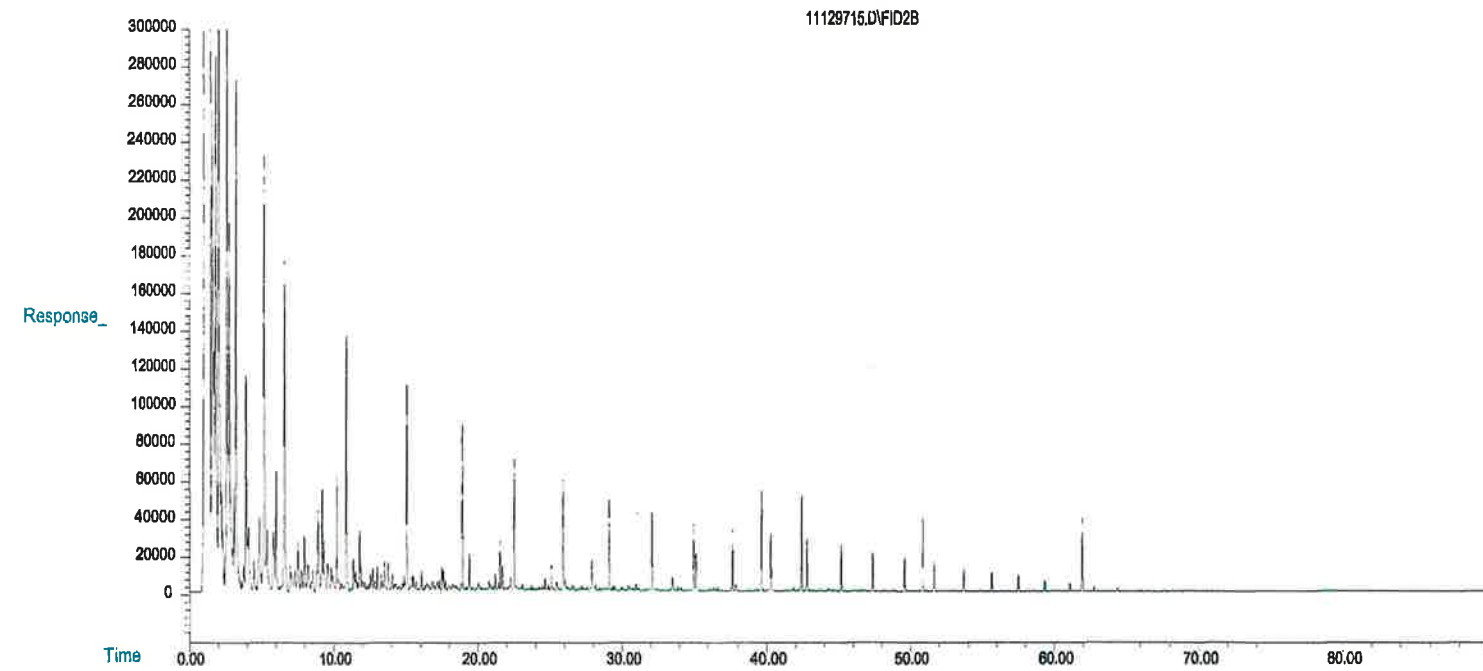


	DRAWN BY: CWS	REVIEWED: PKH	APPROVED: HJR
	DATE: 5 MAR 1998	PROJECT NO. SU001H	DWG. NO.
	COMPARISON OF NATURAL GAS CONDENSATE GRO DISTRIBUTIONS WITH DSCP MW-5 NAPL GRO STUDY AREA PHILADELPHIA, PENNSYLVANIA		

FIGURE
7-20

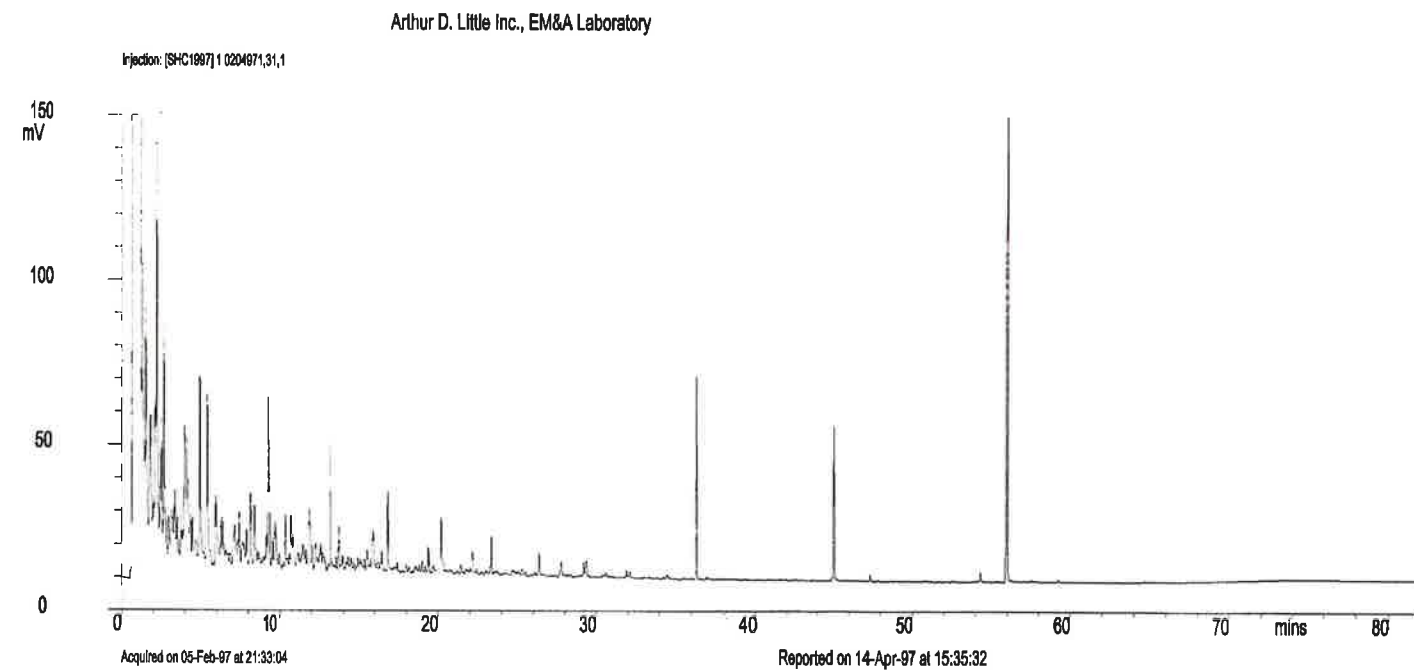
7.21a

Condensate Sample GC/FID Chromatogram



7.21b

Sample MW-5 GC/FID Chromatogram

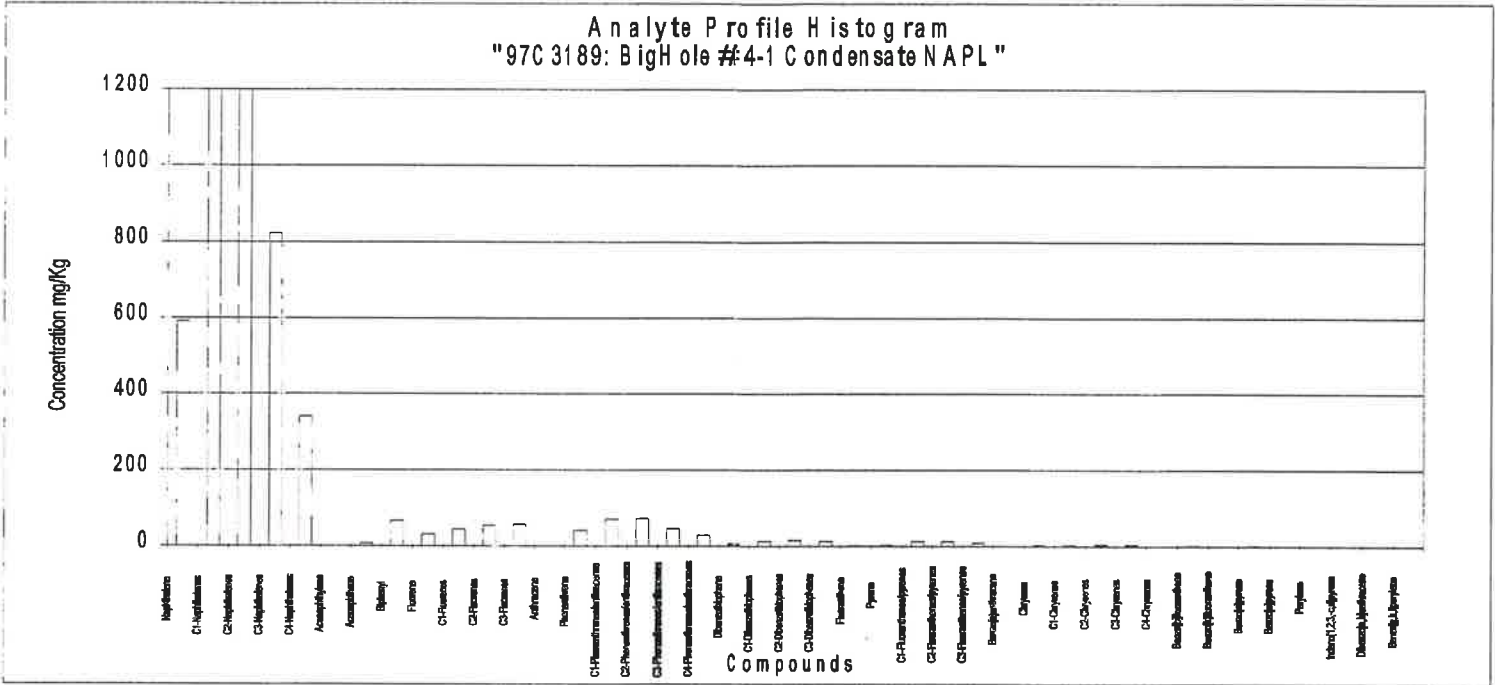


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COMPARISON OF NATURAL GAS CONDENSATE GC/FID DISTRIBUTIONS WITH DSCP MW-5 NAPL GRO STUDY AREA PHILADELPHIA, PENNSYLVANIA		FIGURE 7-21

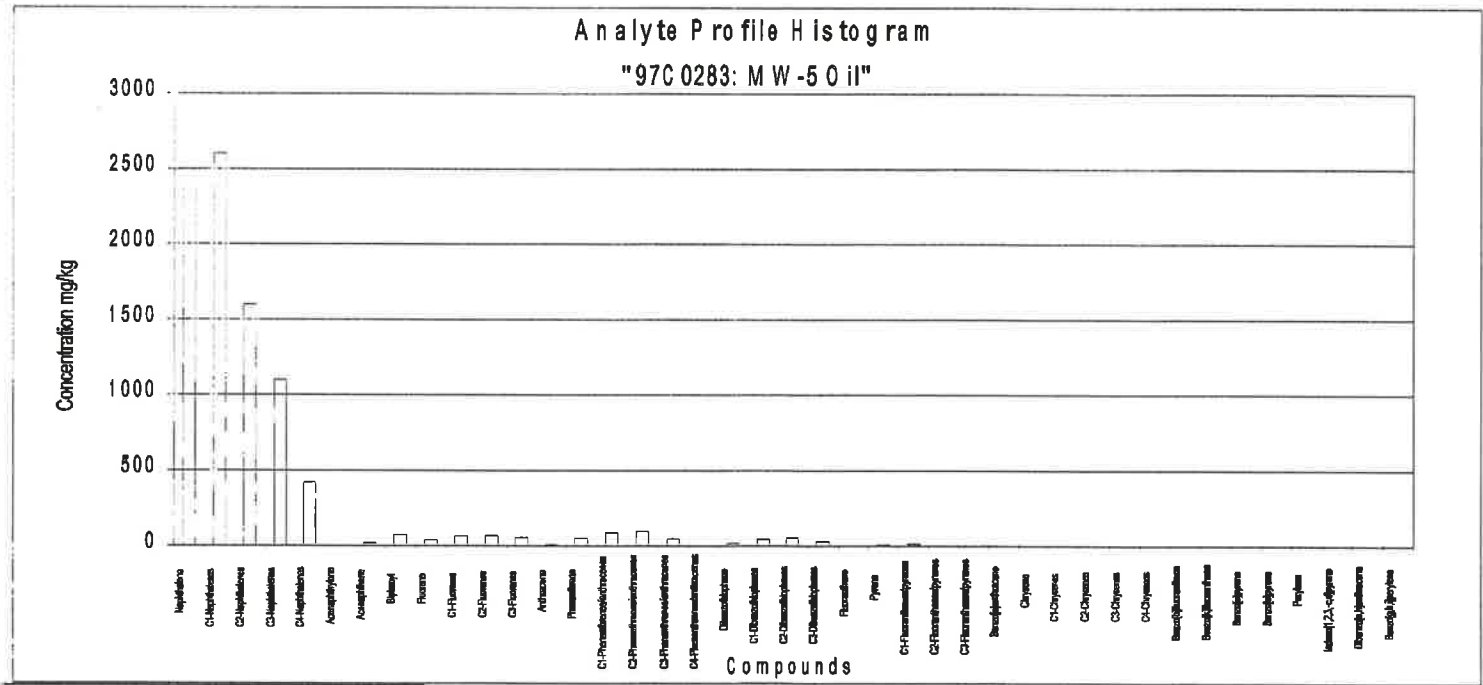
7.22a

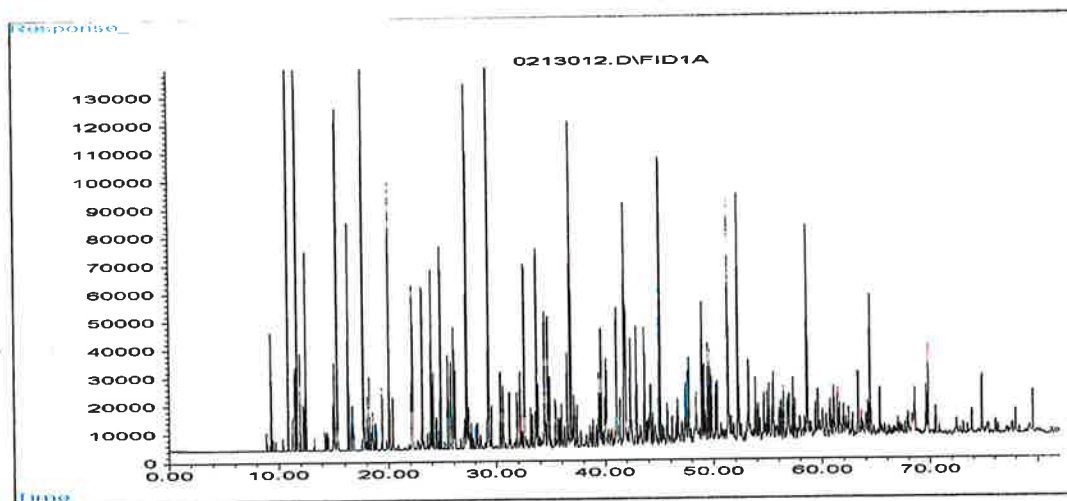
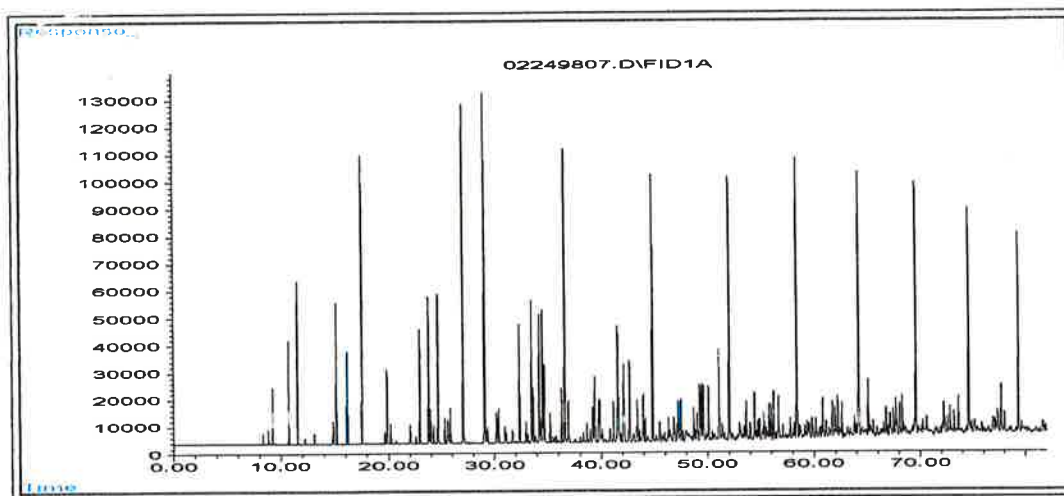
Condensate Sample PAH Distribution



7.22b

Sample MW-5 PAH Distribution





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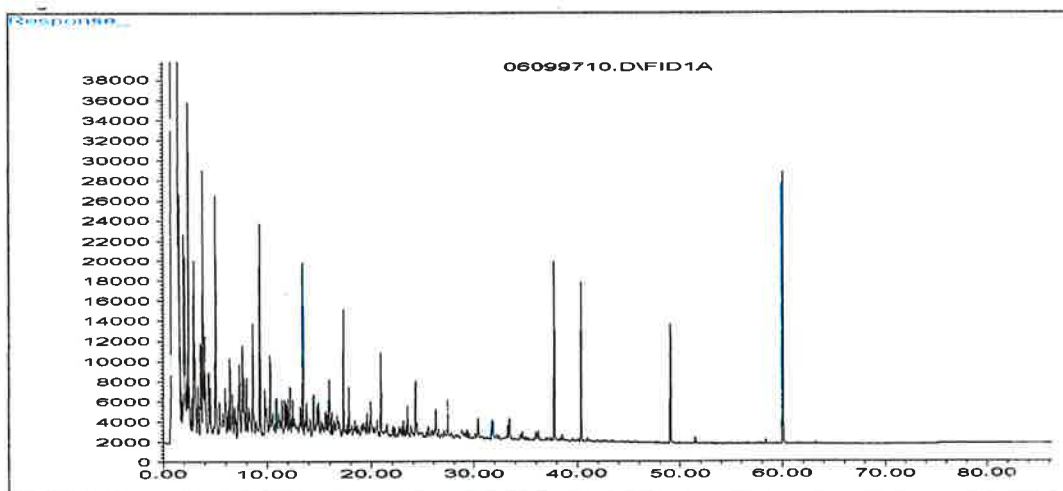
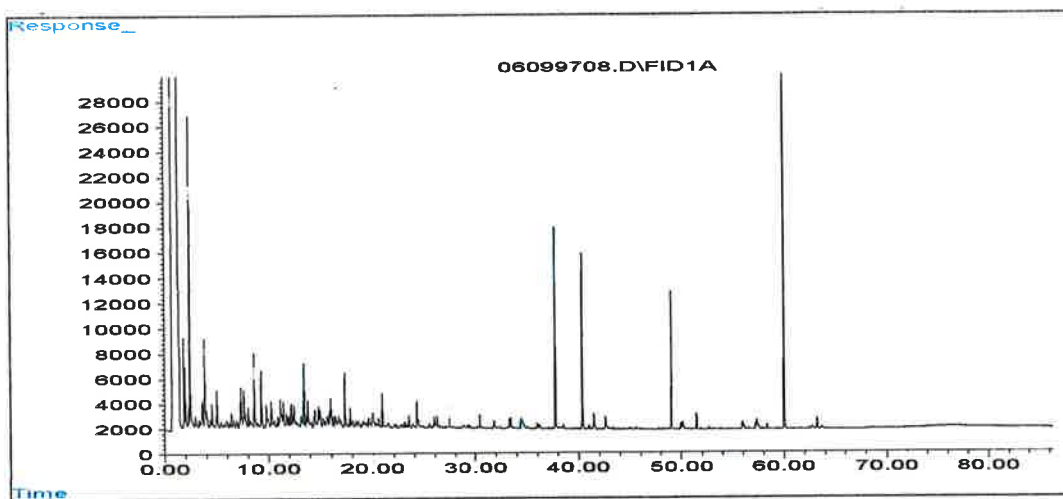
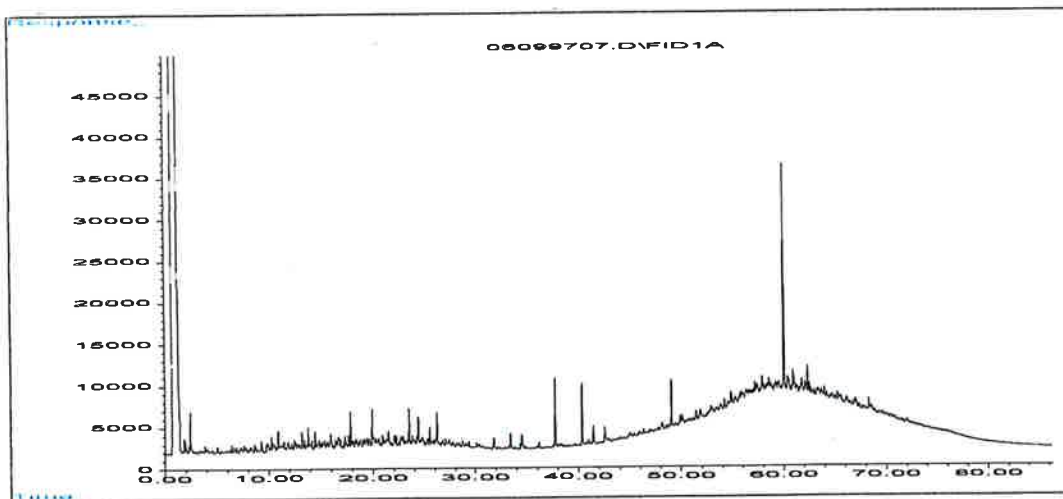
DWG. NO.

GC/FID Comparison of Gas Condensate and DSCP
MW-6 NAPL

Study Area, Philadelphia, PA

FIGURE

7-23



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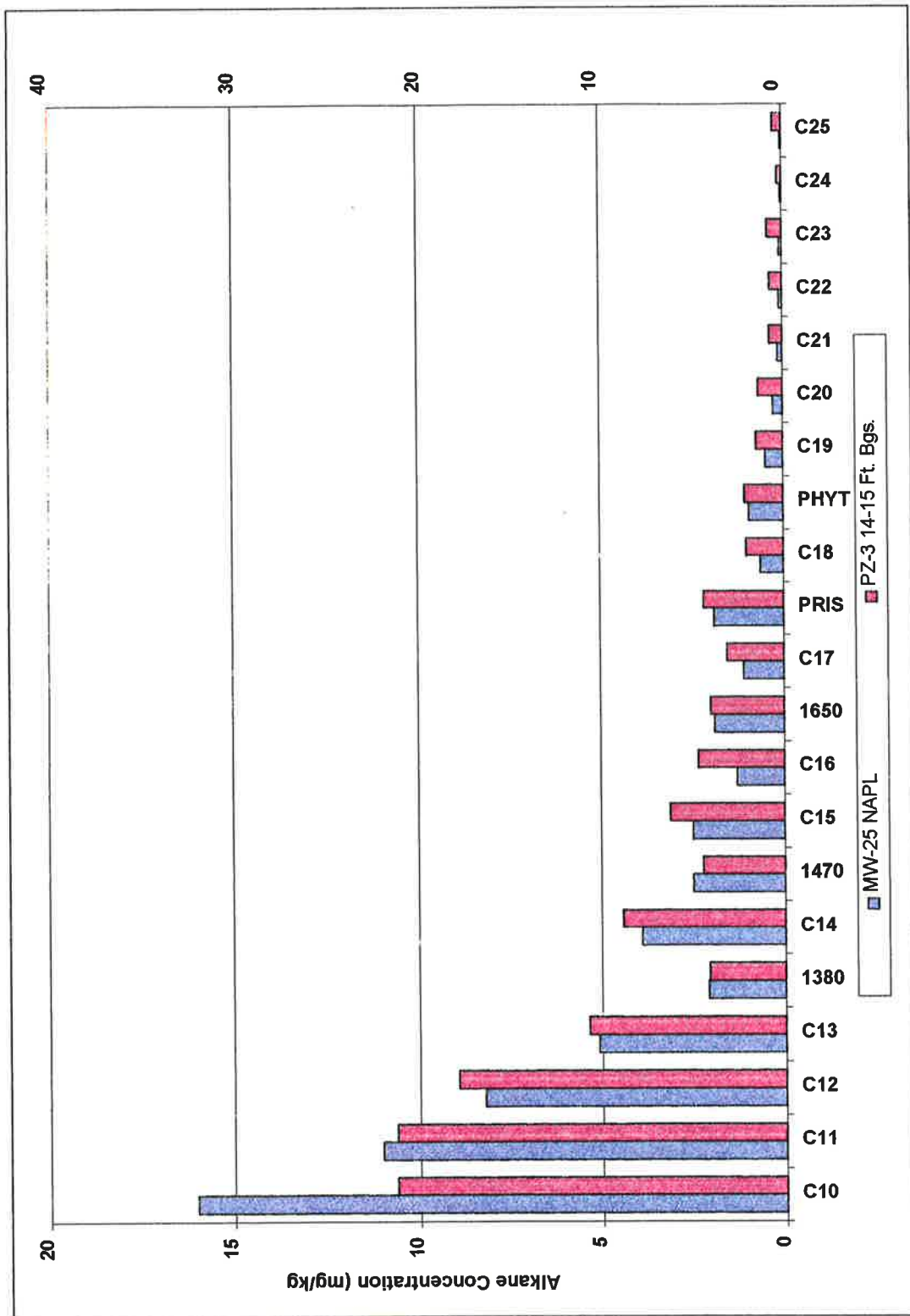
DWG. NO.

GC/FID Comparison of DSCP Soil Samples PZ-2 (10-12-ft), PZ-3 (14-15-ft) and NAPL from MW-25

Study Area, Philadelphia, PA

FIGURE

7-24

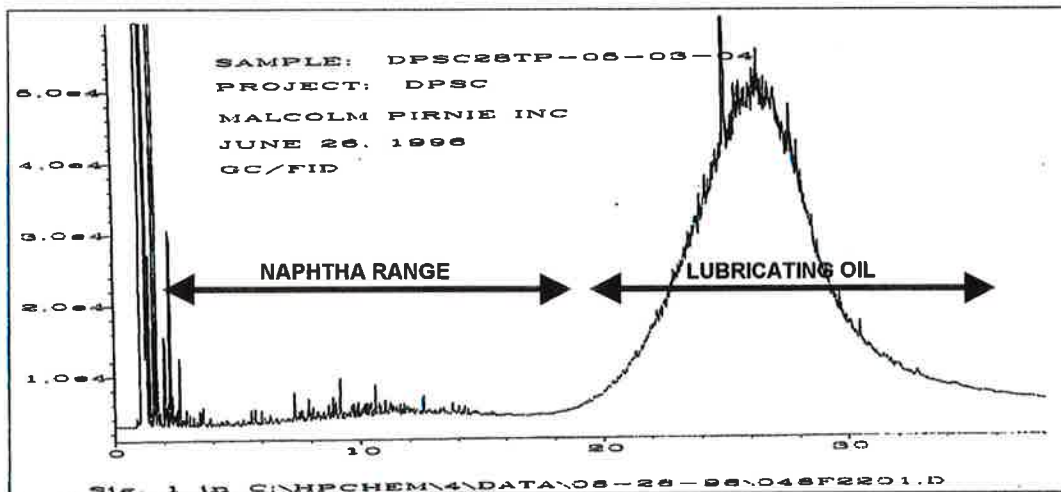


ALKANE DISTRIBUTIONS

STUDY AREA, Philadelphia, PA

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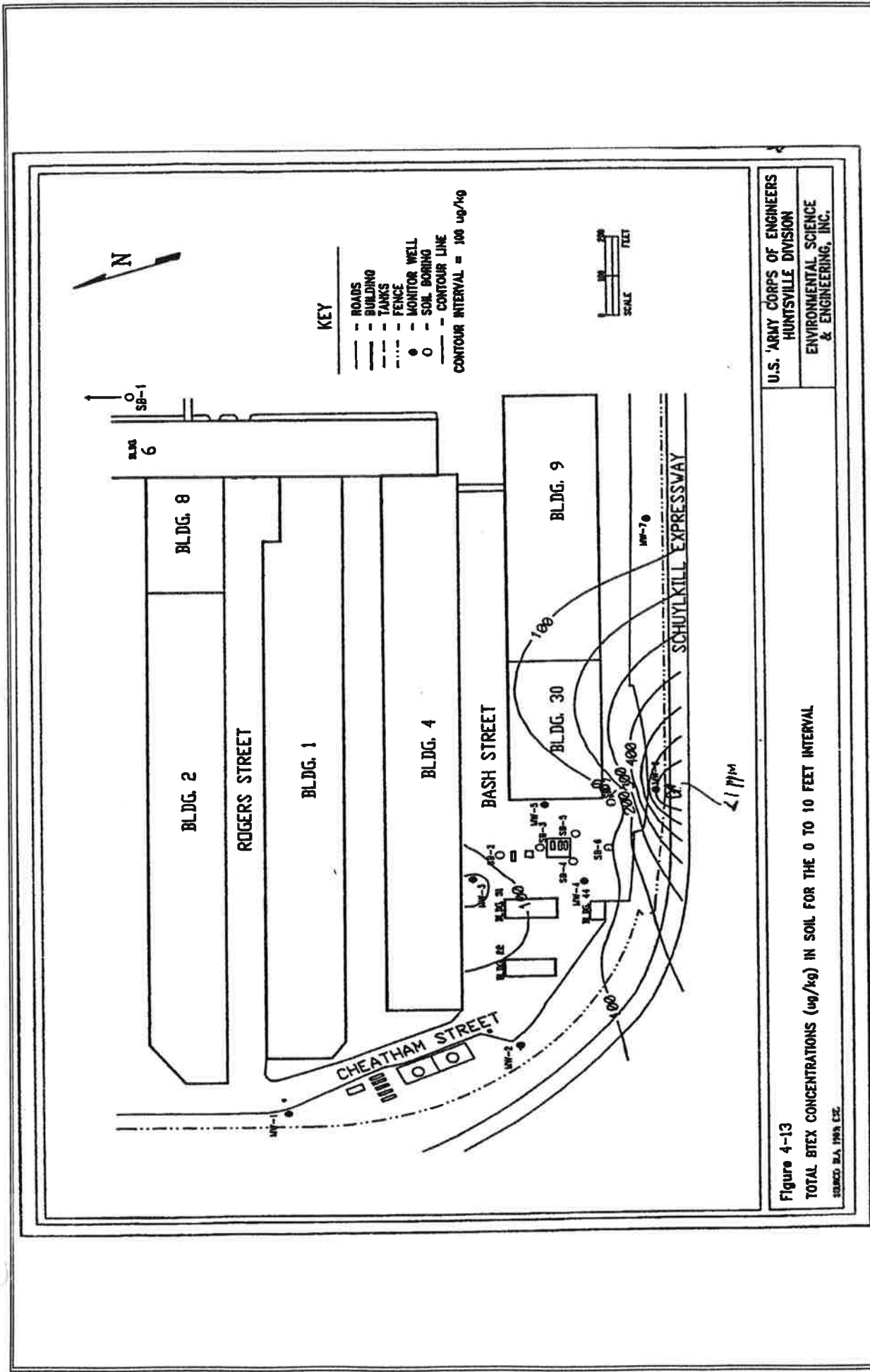
DWG. NO.

DSCP Analysis of Sample
 Near Building 28 Gasoline Station

Study Area, Philadelphia, PA

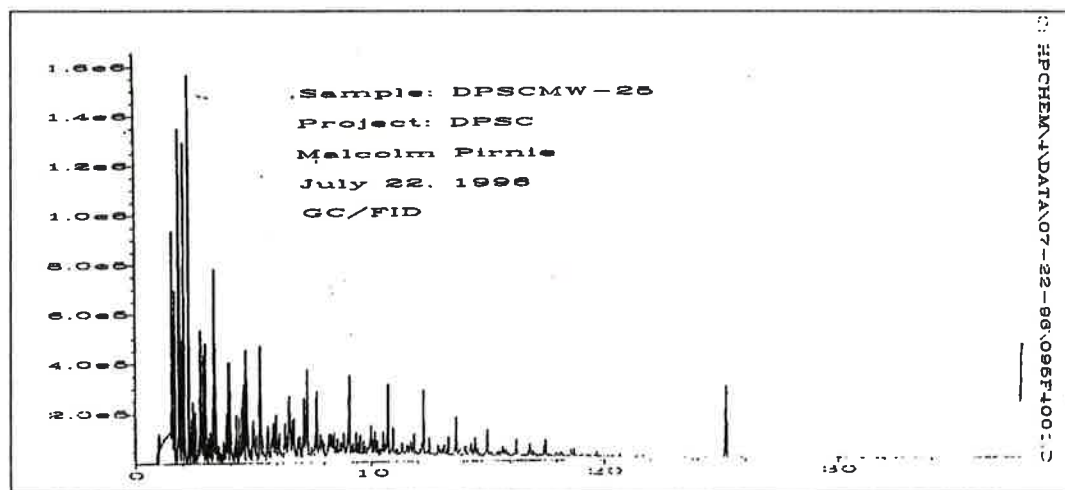
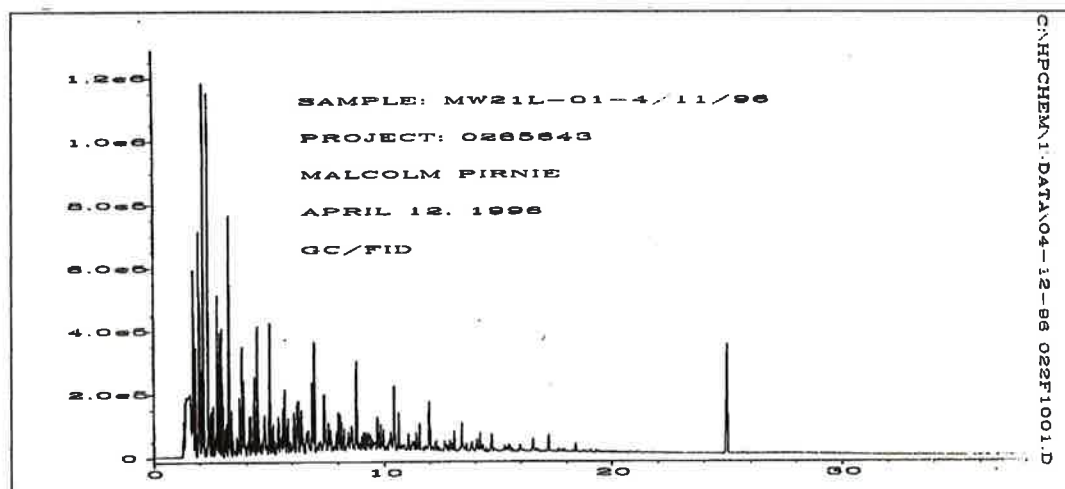
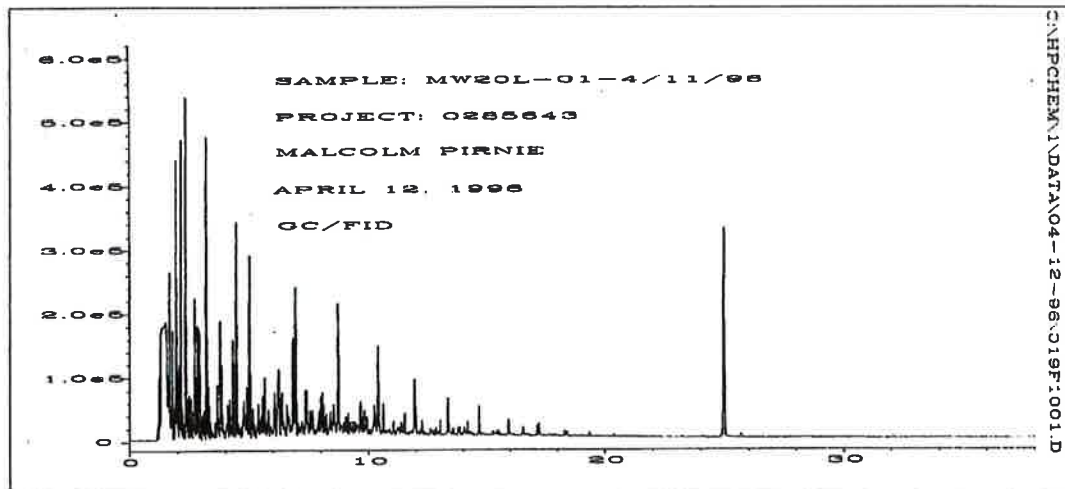
FIGURE

7-26

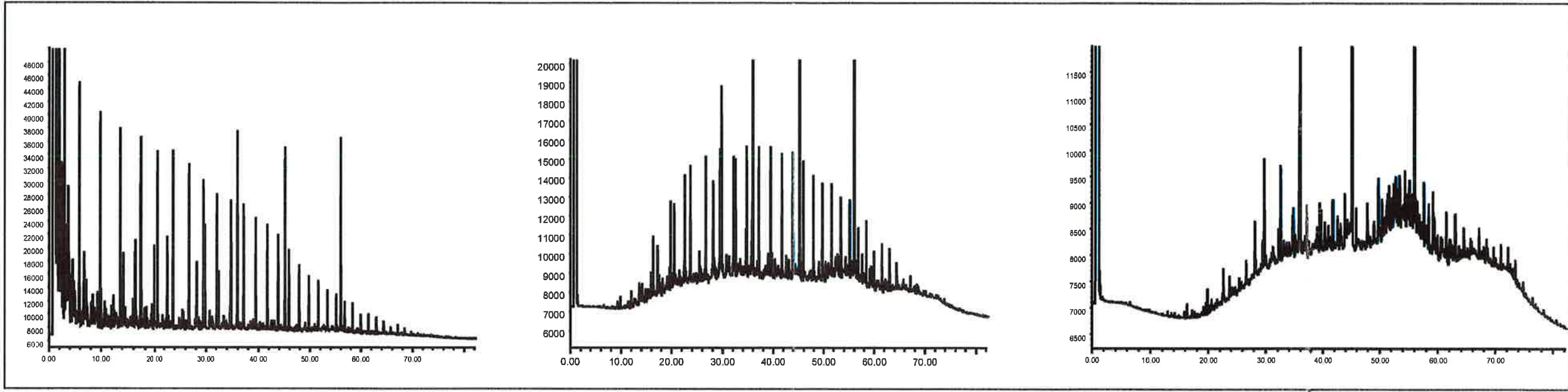


SOURCE: ES&E Report

INTEGRATED SCIENCE & TECHNOLOGY, INC.	DRAWN BY:	DATE:	BTEX Concentrations Near Building 28 Gasoline Station STUDY AREA, Philadelphia, PA	FIGURE 7-27
	EG	MARCH 1998		
	REVIEWED: PKH	PROJECT NO. SU001H		
	APPROVED: HJR	DWG. NO. *****		

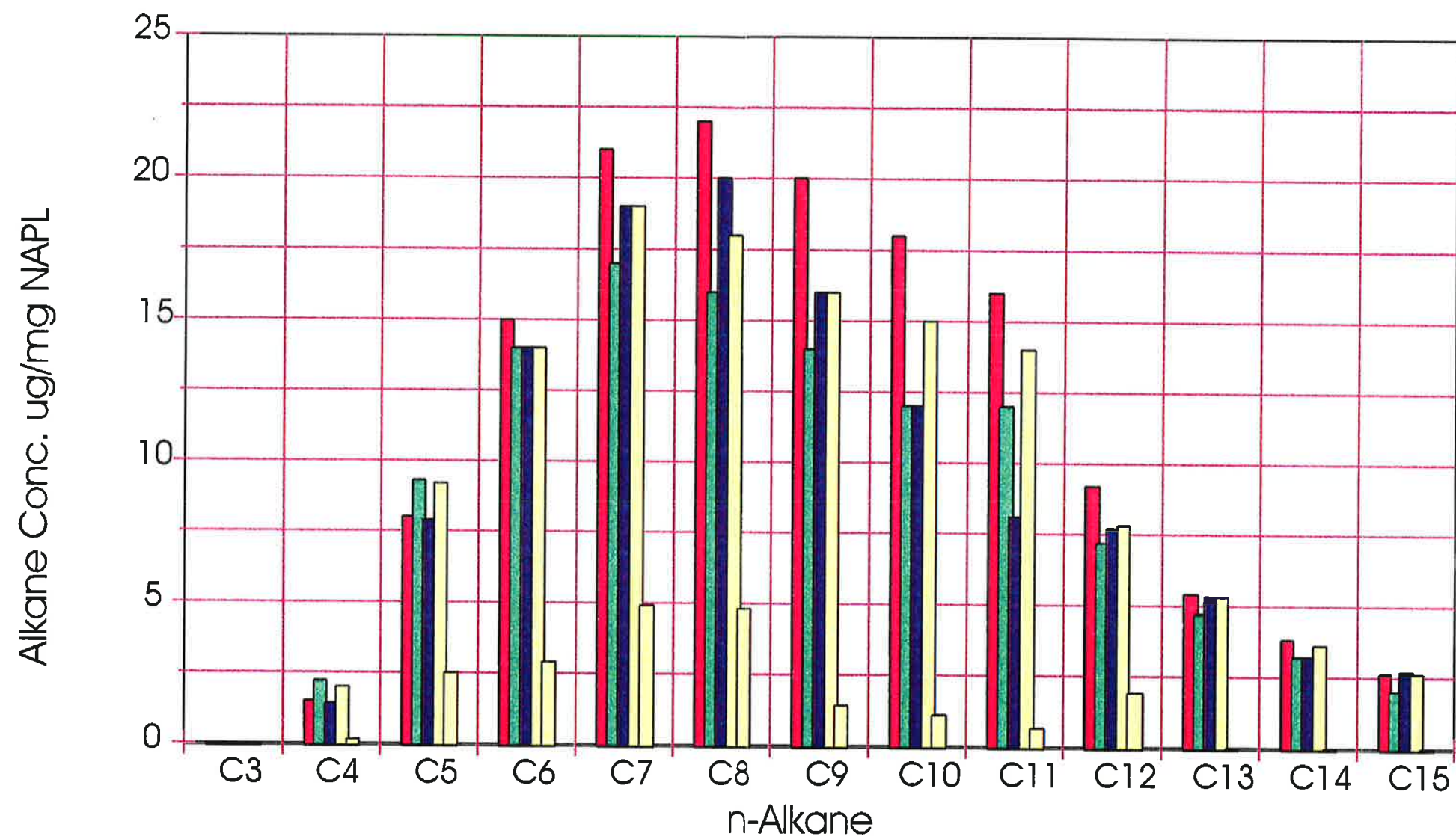


INCREASING WEATHERING

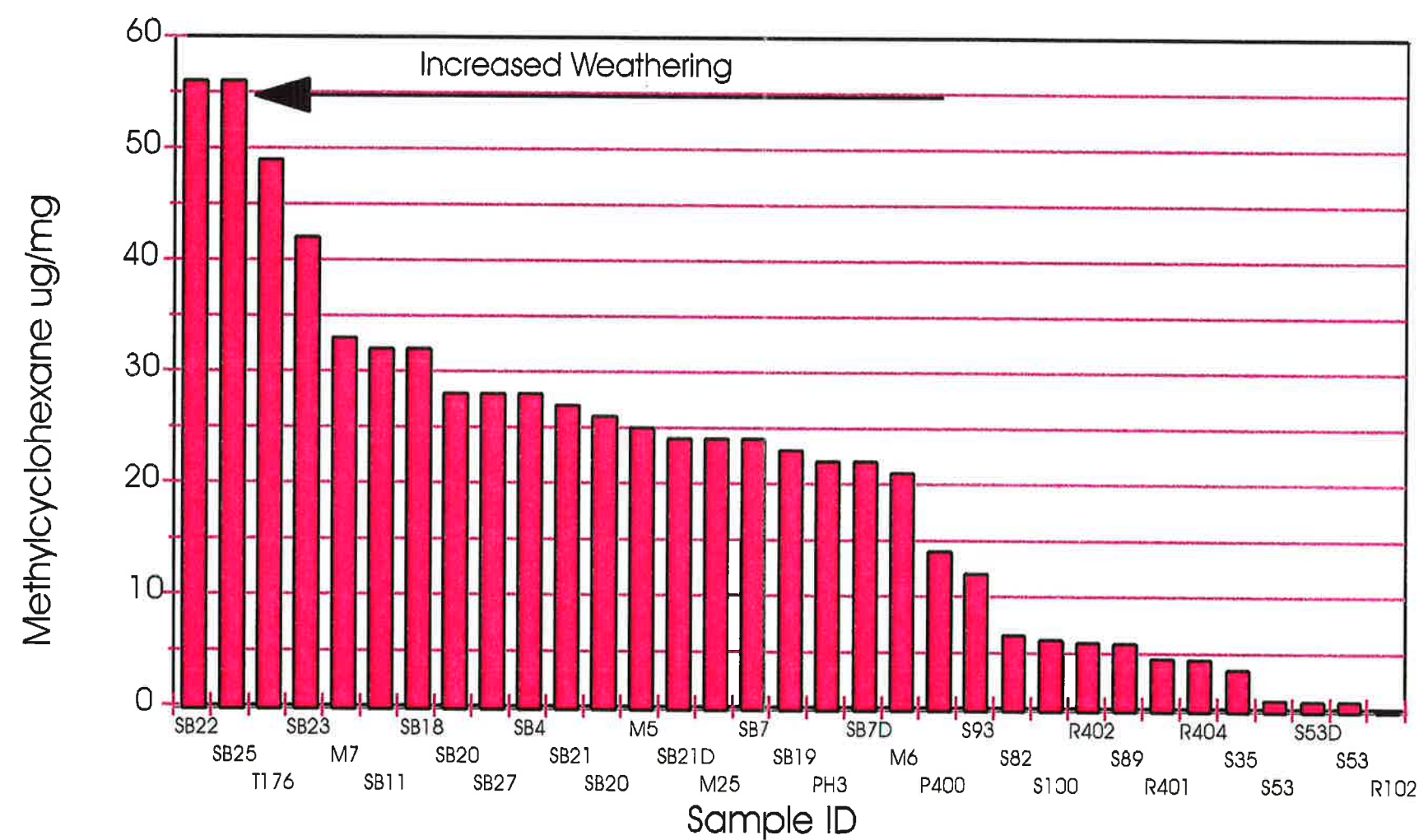


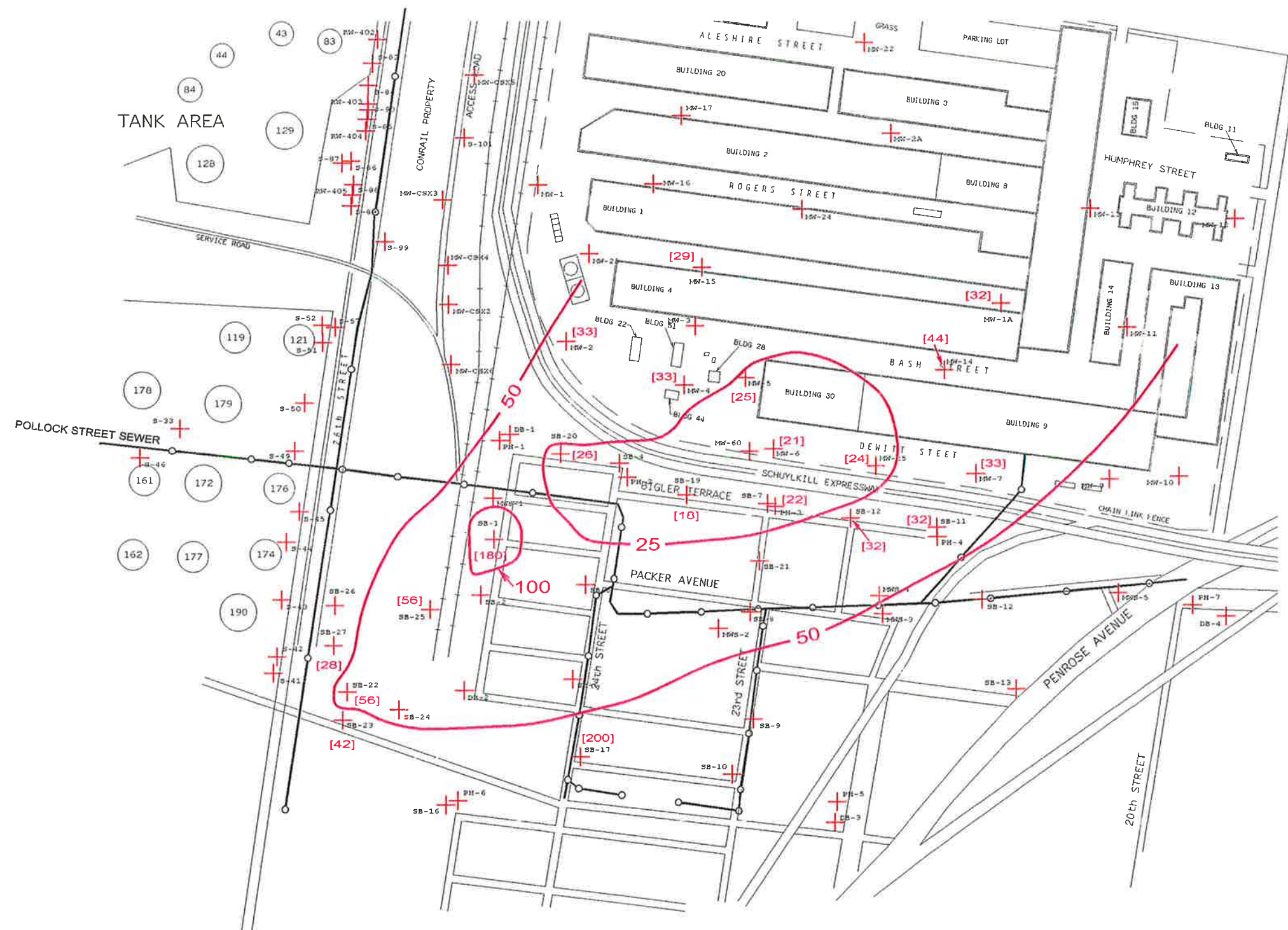
DESIGNED BY: CWS	REVIEWED PKH	APPROVED HJR
DATE 5 MAR 1998	PROJECT NO. SU001H	DWG. NO.
GC/MS CHROMATOGRAMS DEMONSTRATING WEATHERING PATHWAY OF CRUDE OIL STUDY AREA PHILADELPHIA, PENNSYLVANIA		

FIGURE
7-29

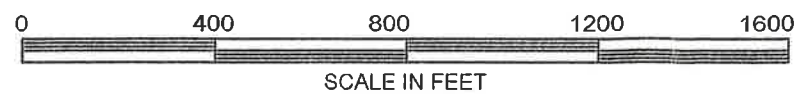


Methylcyclohexane NAPL Weathering Plot



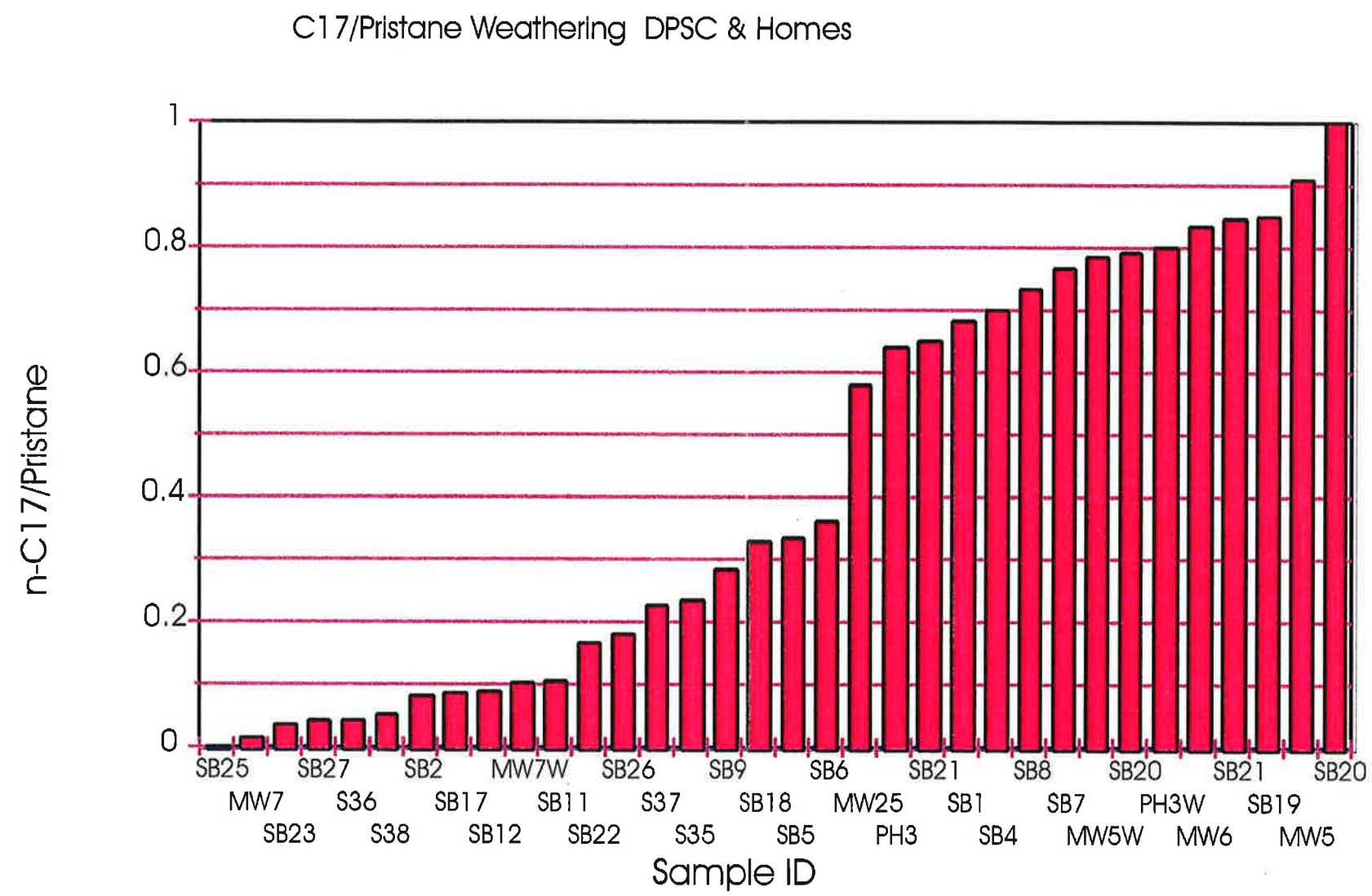


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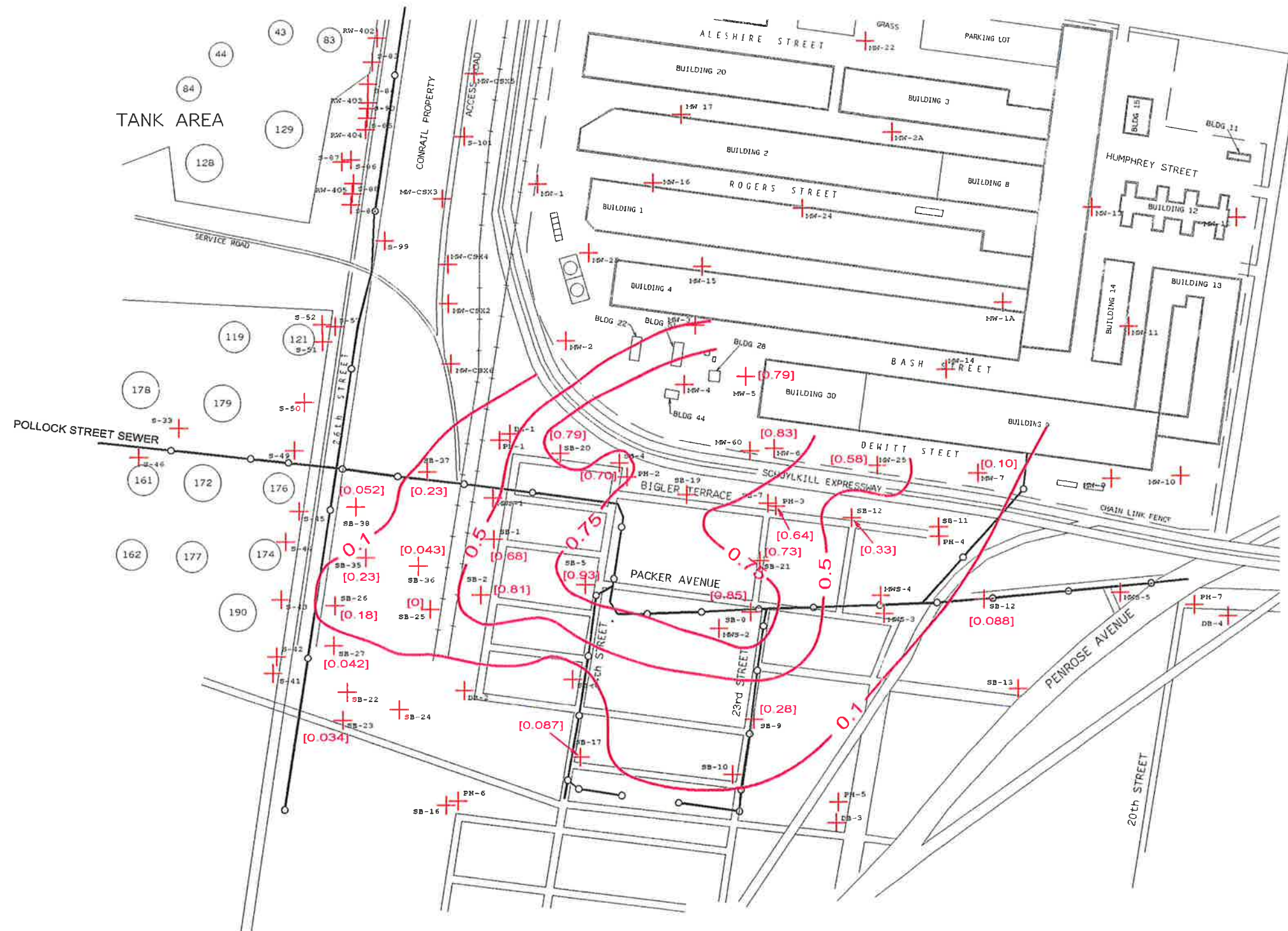
CONCENTRATION OF METHYLCYCLOHEXANE IN NAPL	FIGURE
STUDY AREA, Philadelphia, PA	7-33



 I N T E G R A T E D S C I E N C E & T E C H N O L O G Y , I N C .	DRAWN BY: CWS	REVIEWED: PKH	APPROVED: HJR
	DATE: 5/31/2011	PROJECT NO. SU001H	DWS. NO.
	C17/PRISTANE WEATHERING DSCP & PHILADELPHIA HOUSING AUTHORITY STUDY AREA PHILADELPHIA, PENNSYLVANIA		

LEGEND

- + SB-21 – SAMPLING LOCATIONS
- ~ 50 – CONTOUR LINE
- [25] – MEASURED VALUE
- 222 – TANKS



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	APPROVED: HJR	DWG. NO. 11400138
n-C17/PRISTANE IN NAPL		FIGURE
STUDY AREA, Philadelphia, PA		7-35

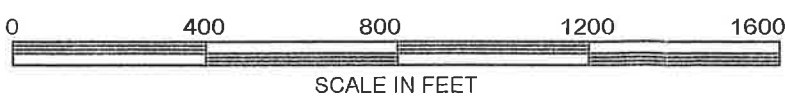
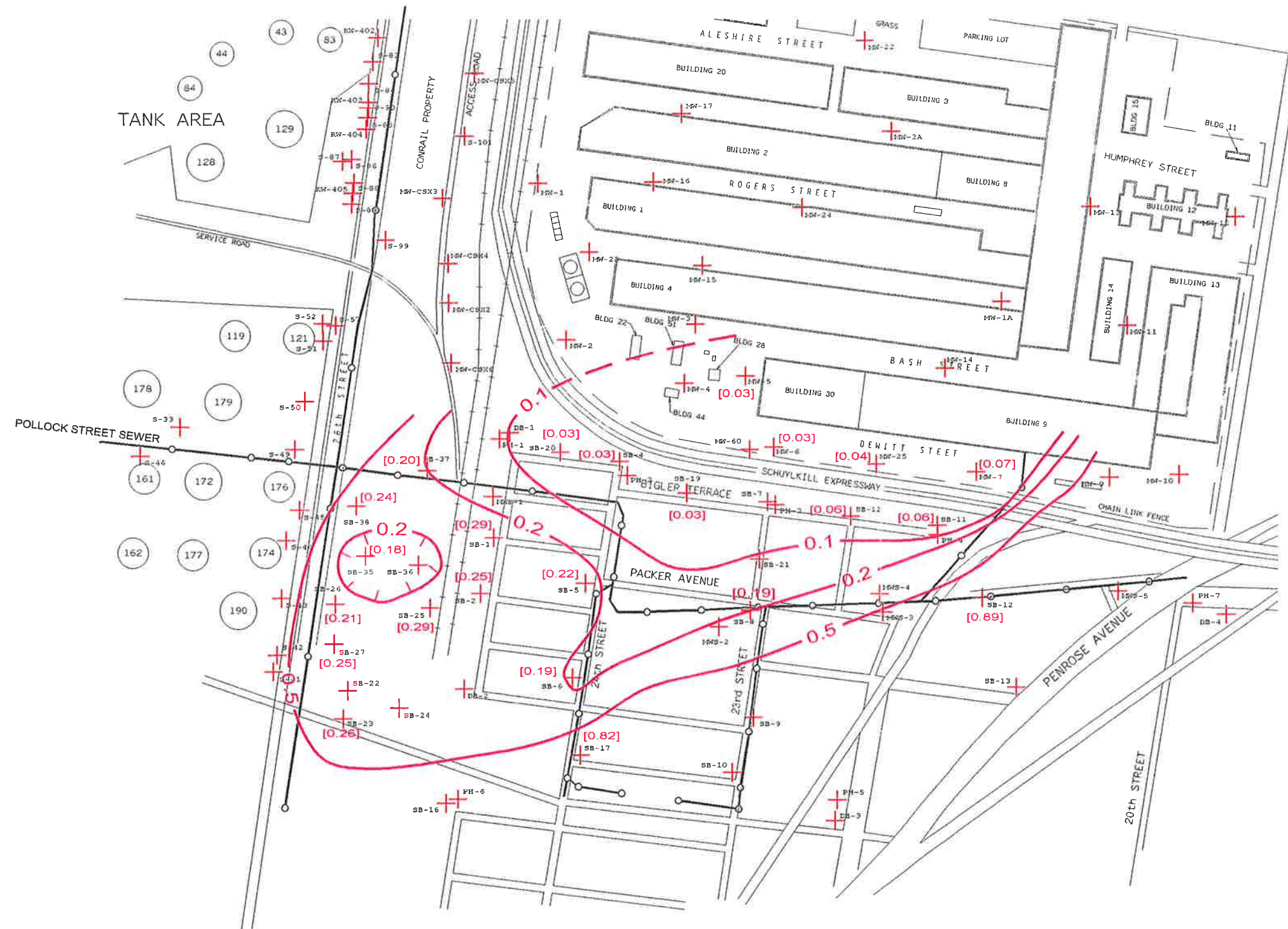
LEGEND

 — SAMPLING LOCATIONS

 50 — CONTOUR LINE

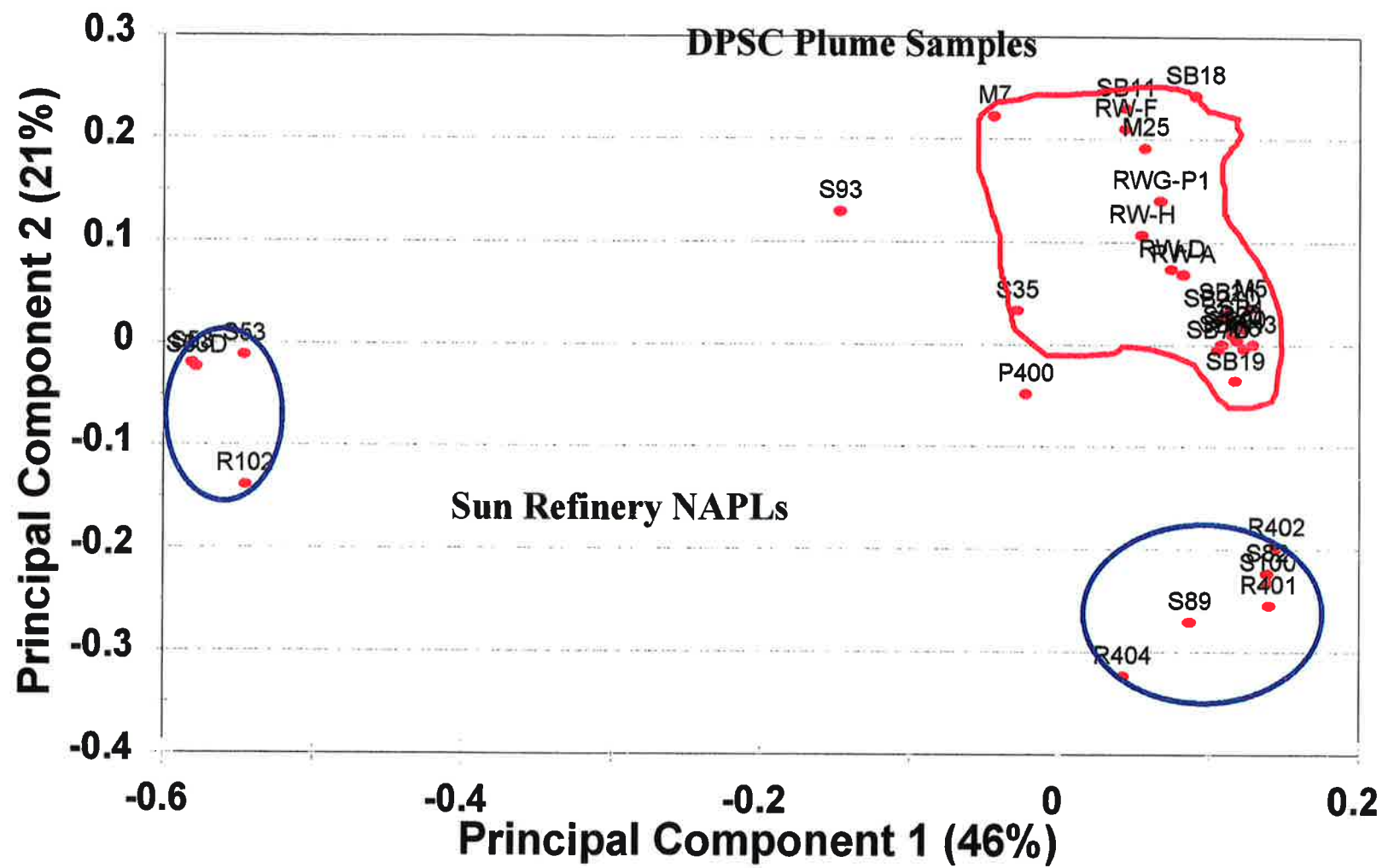
[25] — MEASURED VALUE

 222 — TANKS



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	APPROVED: HJR	DWG. NO. 11400138
PERCENT PHENANTHRENE IN NAPL		FIGURE
STUDY AREA, Philadelphia, PA		7-36

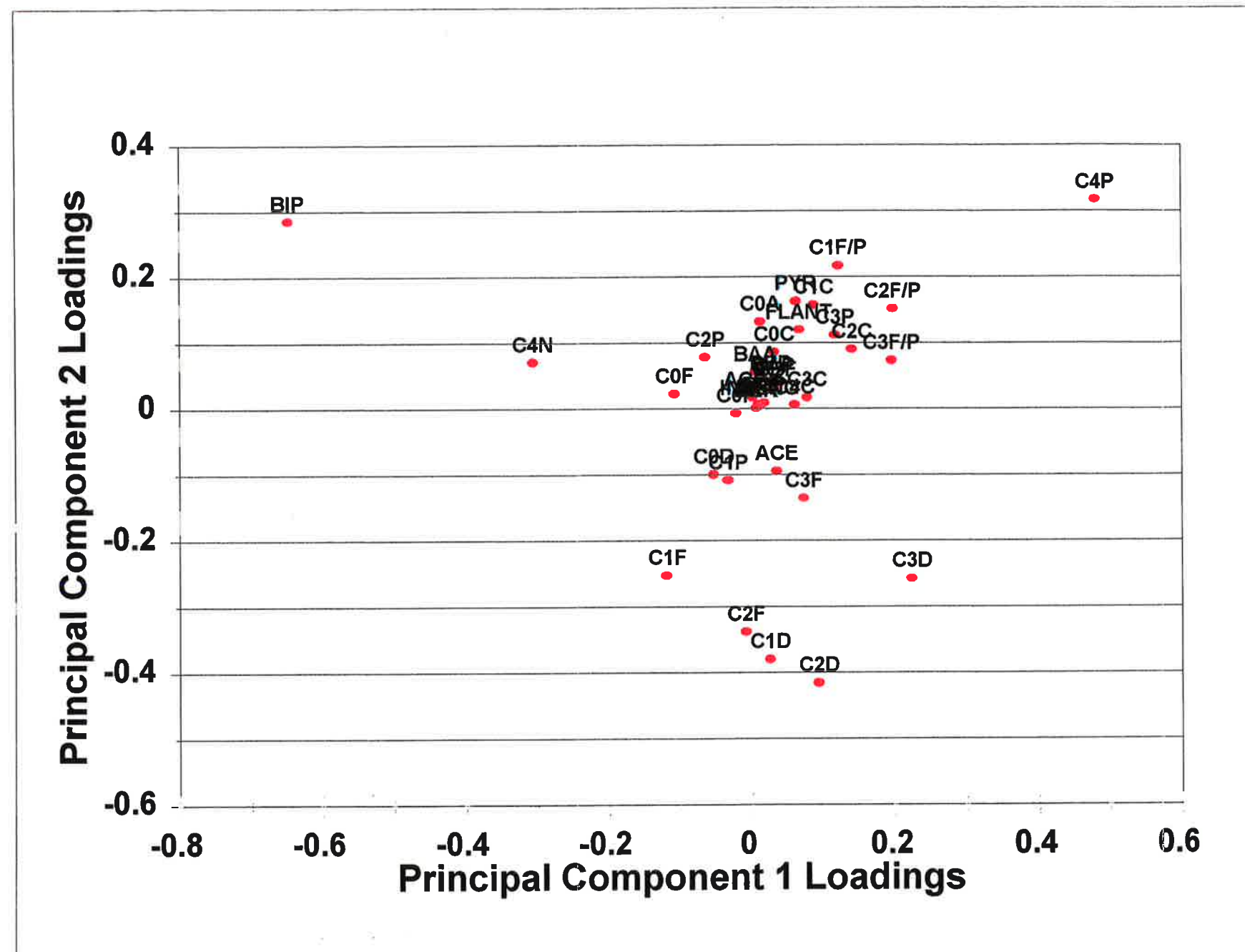


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PCA SCORES OF NAPL GRO DATA COLLECTED FROM THE DPSC PLUME AND THE SUN REFINERY STUDY AREA PHILADELPHIA, PENNSYLVANIA		
FIGURE 7-37		



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PCA LOADINGS OF NAPL GRO DATA COLLECTED FROM THE DSPC PLUME AND THE SUN REFINERY STUDY AREA PHILADELPHIA, PENNSYLVANIA		FIGURE 7-38

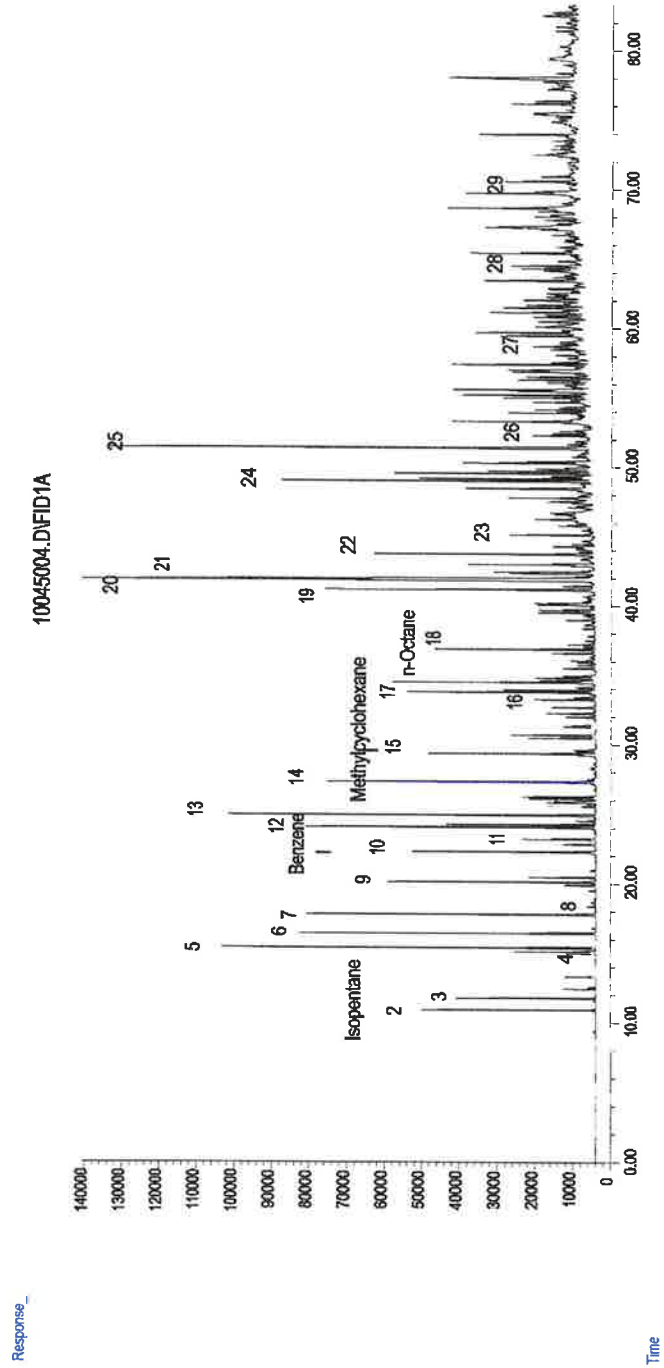


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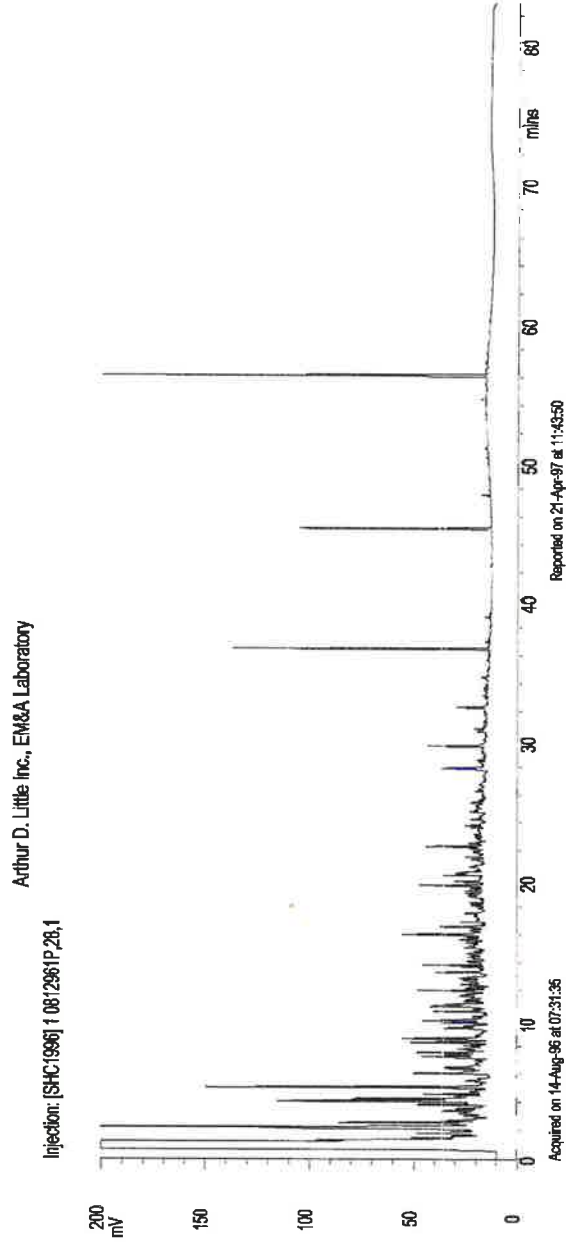
DRAWN BY: CWS	REVIEWED: PKH	APPROVED: HJR
DATE: 20 FEB 1998	PROJECT NO. SU001H	DWG. NO.
PCA-PAH LOADINGS OF NAPL/SHEEN SAMPLES COLLECTED FROM THE DSCP AREA AND SUN #1 TANKFARM STUDY AREA PHILADELPHIA, PENNSYLVANIA		

FIGURE
7-40

GRO Analysis of Sun Refinery NAPL Sample S-89



GC/FID Analysis of Sun Refinery NAPL Sample S-89



PAH Analysis of Sun Refinery NAPL Sample S-89



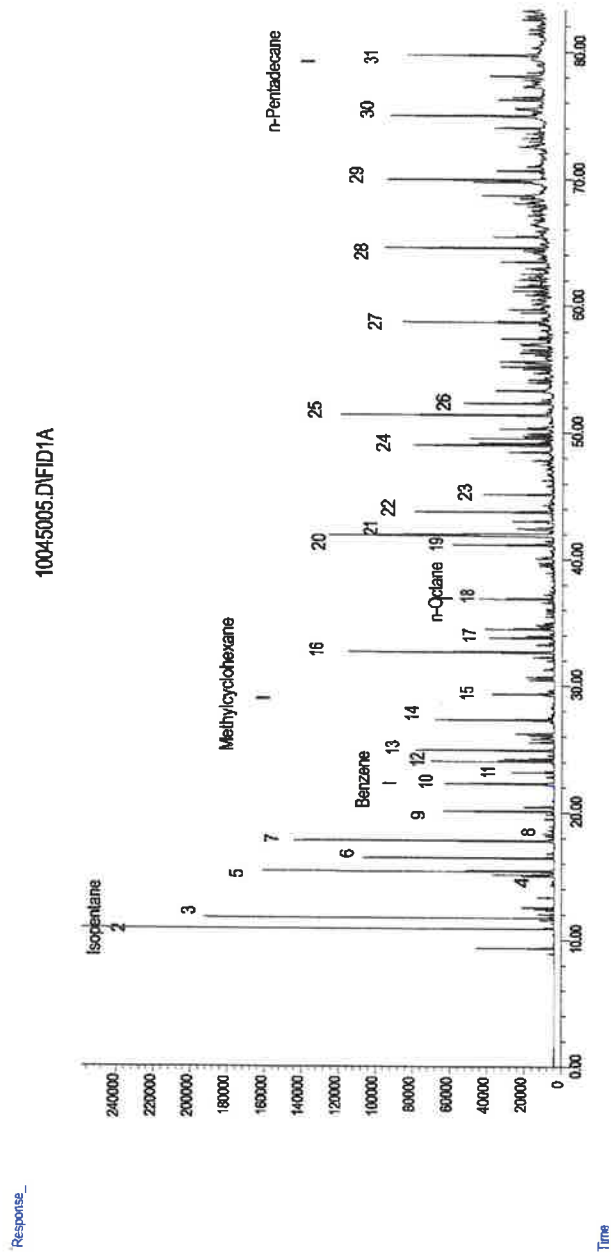
DRAWN BY:	DATE:
REVIEWED:	5 MAR 1998
APPROVED:	PROJECT NO. SU00TH
	DWG. NO.

CHEMICAL ANALYSES OF NAPL SAMPLES
FROM SUN WELL S-89

STUDY AREA
PHILADELPHIA, PENNSYLVANIA

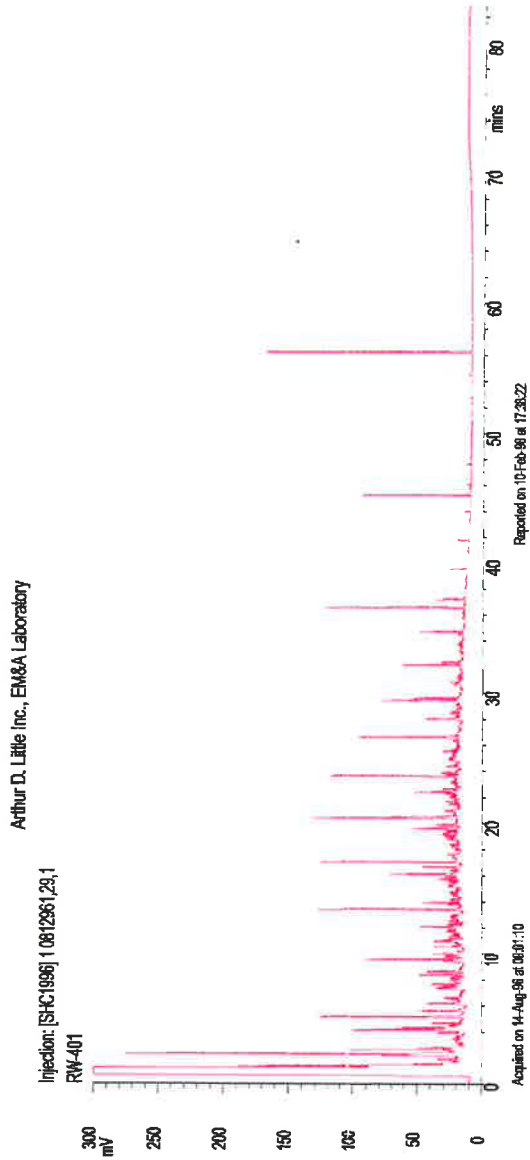
GRO Analysis of Sun Refinery NAPL Sample RW-401

a



GC/FID Analysis of Sun Refinery NAPL Sample RW-401

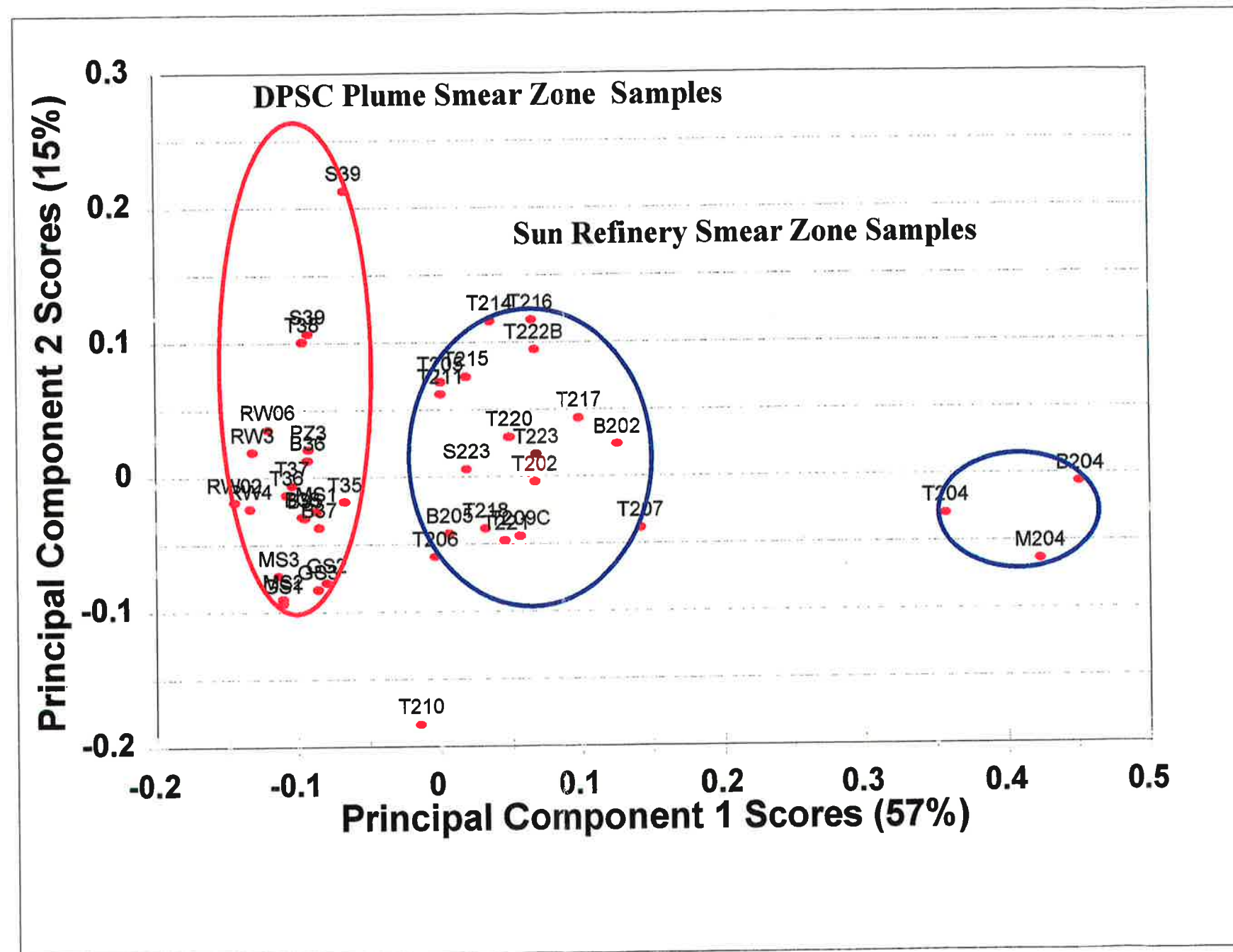
b



PAH Analysis of Sun Refinery NAPL Sample RW-401

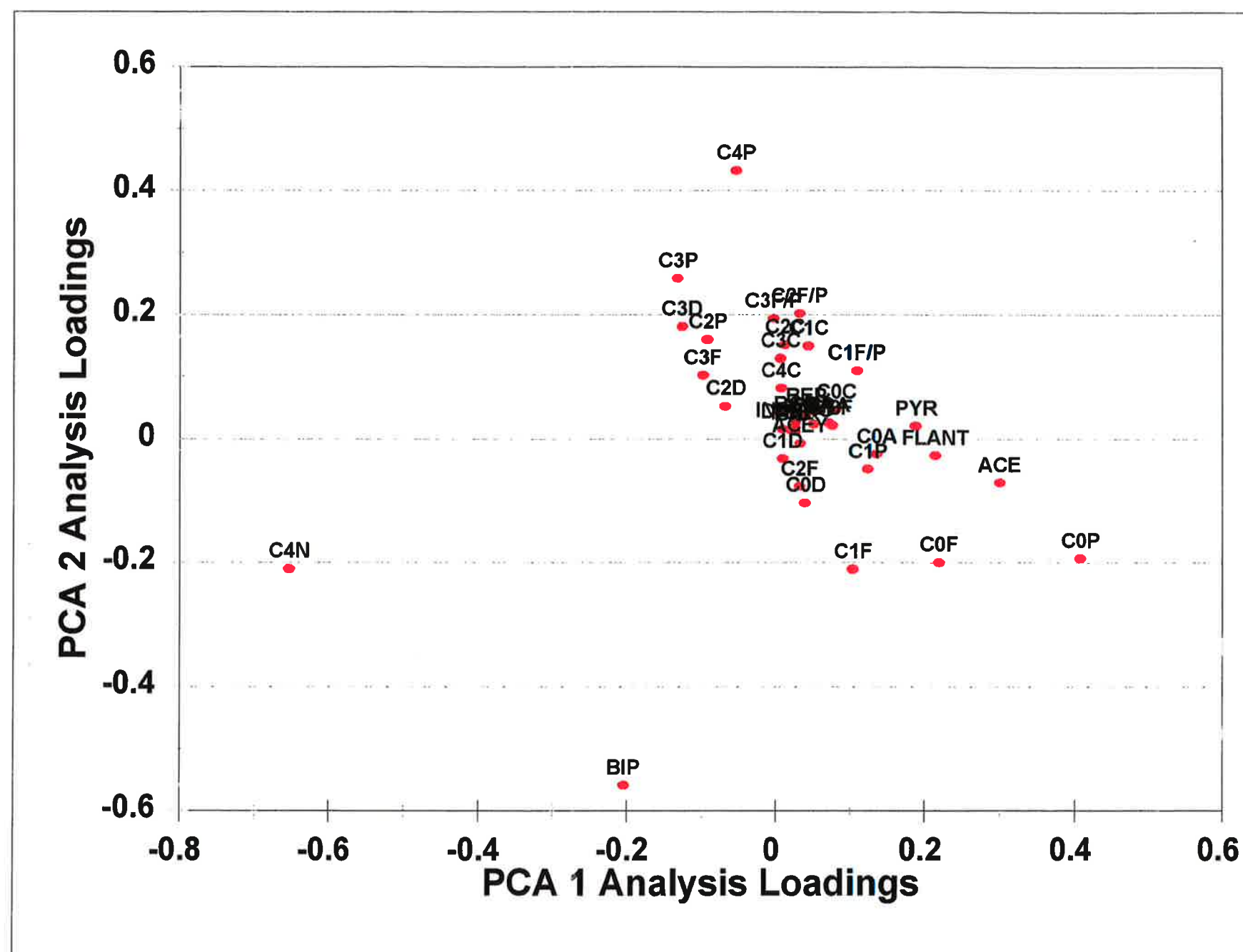
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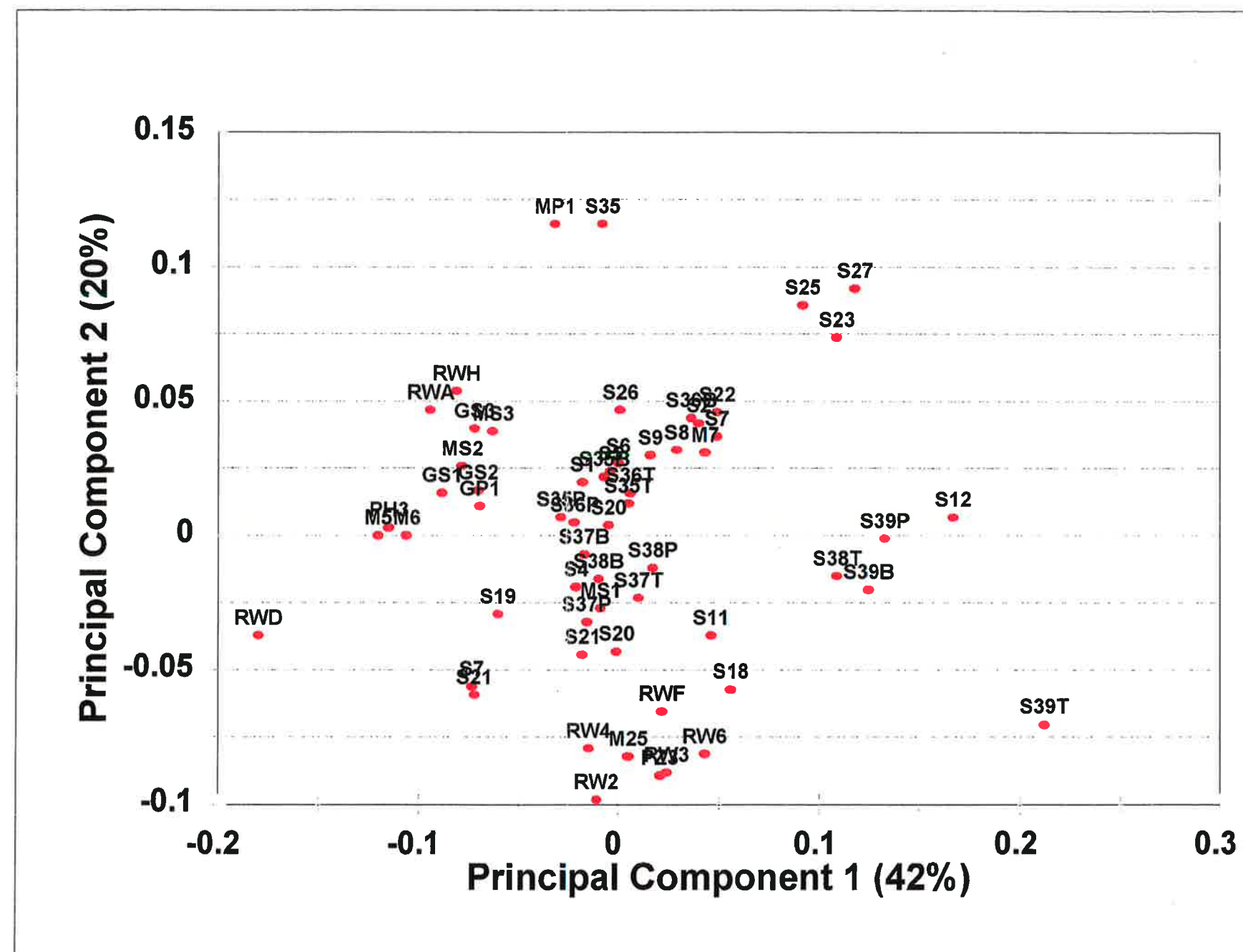
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PCA SCORES OF SMEAR ZONE PAH DATA COLLECTED FROM THE DSPC PLUME AND THE SUN REFINERY		FIGURE
STUDY AREA PHILADELPHIA, PENNSYLVANIA		7-43



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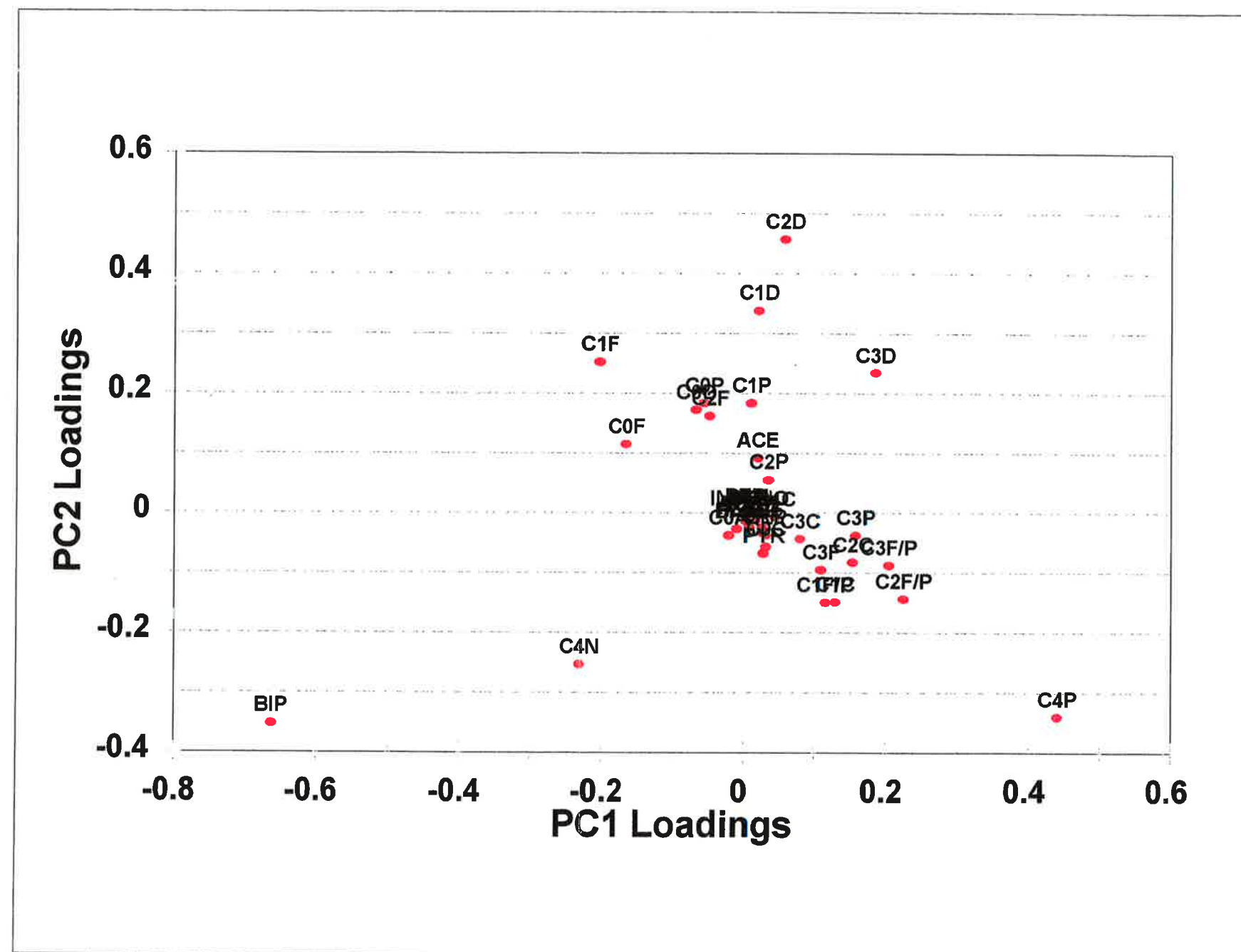
DRAWN BY: CWS	REVIEWED: PKH	APPROVED: HJR
DATE: 20 FEB 1998	PROJECT NO. SU001H	DWG. NO.
PCA LOADINGS OF SMEAR ZONE PAH DATA COLLECTED FROM THE DSPC PLUME AND THE SUN REFINERY STUDY AREA PHILADELPHIA, PENNSYLVANIA		FIGURE 7-4



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PCA SCORES ANALYSIS OF NAPL/SHEEN AND SMEAR ZONE SAMPLES COLLECTED FROM THE DSCP PLUME AREA STUDY AREA PHILADELPHIA, PENNSYLVANIA		

FIGURE
7-45



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PCA LOADINGS OF NAPL/SHEEN AND SMEAR ZONE SAMPLES COLLECTED FROM THE DSCP PLUME AREA STUDY AREA PHILADELPHIA, PENNSYLVANIA		

FIGURE
7-46

TABLE 7-2: Listing of Samples Analyzed

Lab ID	Field ID	Batch ID	Matrix	Date Coll'd	Date Rec'd	Water Prep	Rinse Prep	Oil Prep	Soil Prep	GC/FID	PAH	GRO	OTHER
97C0281	S-35	Batch SUB 2	Product	01/21/97	01/23/97								SIMDIS,PB
97C0282	PH-3	Batch SUB 2	Product	01/21/97	01/23/97								SIMDIS,PB
97C0283	MW-5	Batch SUB 2	Product	01/22/97	01/23/97								SIMDIS,PB
97C0284	MW-7	Batch SUB 2	Product	01/22/97	01/23/97								SIMDIS,PB
97C0285	MW-6	Batch SUB 2	Product	01/22/97	01/23/97								SIMDIS,PB
96B2182	S-100	Batch GRO 1	Product	06/25/96	06/28/96							X	
96B2183	S-89	Batch GRO 1	Product	06/25/96	06/28/96							X	
96B2184	RW-401	Batch GRO 1	Product	06/26/96	06/28/96							X	
96B2185	RW-402	Batch GRO 1	Product	06/26/96	06/28/96							X	
96B2186	RW-404	Batch GRO 1	Product	06/26/96	06/28/96							X	
96B2187	PZ-400	Batch GRO 1	Product	06/25/96	06/28/96							X	
96B2518	S-53	Batch GRO 1	Product/Water	07/30/96	07/31/96							X	
96B2518 DUP	S-53 DUP	Batch GRO 1	Product/Water	07/30/96	07/31/96							X	
96B2520	S-93	Batch GRO 1	Product/Water	07/30/96	07/31/96							X	
96B2523	RW-102	Batch GRO 1	Product/Water	07/30/96	07/31/96							X	
96B2867	SB-4	Batch GRO 1	Product	09/10/96	09/13/96							X	
96B2869	SB-7	Batch GRO 1	Product	09/10/96	09/13/96							X	
96B2869 DUP	SB-7 DUP	Batch GRO 1	Product	09/10/96	09/13/96							X	
96B2870	SB-11	Batch GRO 1	Product/Water	09/10/96	09/13/96							X	
96B2952	SB-18	Batch GRO 1	Product	09/20/96	09/25/96							X	
96B2953	SB-19	Batch GRO 1	Product	09/20/96	09/25/96							X	
96B2954	SB-20	Batch GRO 1	Product	09/24/96	09/25/96							X	
96B2962	SB-20	Batch GRO 1	Product/Water	09/24/96	09/27/96							X	
96B2963	SB-21	Batch GRO 1	Product/Water	09/26/96	09/27/96							X	
96B2963DUP	SB-21	Batch GRO 1	Product/Water	09/26/96	09/27/96							X	
97C0279	S-82	Batch GRO 2	Product	01/21/97	01/23/97							X	
97C0280	S-53	Batch GRO 2	Product	01/21/97	01/23/97							X	
97C0281	S-35	Batch GRO 2	Product	01/21/97	01/23/97							X	
97C0282	PH-3	Batch GRO 2	Product	01/21/97	01/23/97							X	
97C0283	MW-5	Batch GRO 2	Product	01/22/97	01/23/97							X	
97C0284	MW-7	Batch GRO 2	Product	01/22/97	01/23/97							X	
97C0285	MW-6	Batch GRO 2	Product	01/22/97	01/23/97							X	
96B3824	SB-22	Batch GRO 3	Product/Water	10/15/96	11/14/96							X	
96B3825	SB-23	Batch GRO 3	Product/Water	10/28/96	11/14/96							X	
96B3826	SB-25	Batch GRO 3	Product/Water	10/30/96	11/14/96							X	
96B3828	SB-27	Batch GRO 3	Product/Water	10/30/96	11/14/96							X	
96B2866	SB-1	Batch GRO 3	Product/Water	09/10/96	09/13/96							X	
96B2961	SB-2	Batch GRO 3	Product/Water	09/25/96	09/27/96							X	
96B2959	SB-17	Batch GRO 3	Product	09/19/96	09/25/96							X	

TABLE 7-2: Listing of Samples Analyzed

Lab ID	Field ID	Batch ID	Matrix	Date Coll'd	Date Rec'd	Water Prep	Rinse Prep	Oil Prep	Soil Prep	GC/FID	PAH	GRO	OTHER
97C0737	DPSC-MW25	Batch GRO 4	Product	04/28/97	05/19/97							X	
97C0738	Tank 176	Batch GRO 4	Product	05/14/97	05/19/97							X	
96B2514	SS-1	Batch SVOC 1	Product/Water	07/10/96	07/31/96								FS GC/MS
96B2524	RW-105	Batch SVOC 1	Product/Water	07/30/96	07/31/96								FS GC/MS
96B2525	RW-106	Batch SVOC 1	Product/Water	07/30/96	07/31/96								FS GC/MS
96B2526	CAUFER DAM	Batch SVOC 1	Product/Water	07/30/96	07/31/96								FS GC/MS
96B2679	DB-217W	Batch 3A	Product/Water	08/21/96	08/27/96		X			X	X		
96B2680	DB-210W	Batch 3A	Product/Water	08/22/96	08/27/96		X			X	X		
96B2681	DB-114W	Batch 3A	Product/Water	08/20/96	08/27/96		X			X	X		
96B2666	SB-1	Batch 3A	Product/Water	09/10/96	09/13/96		X			X	X		
96B2667	SB-4	Batch 3A	Product	09/09/96	09/13/96			X		X	X		
96B2667 DUP	SB-4 DUP	Batch 3A	Product	09/09/96	09/13/96			X		X	X		
96B2668	SB-5	Batch 3A	Product/Water	09/11/96	09/13/96		X			X	X		
96B2669	SB-7	Batch 3A	Product	09/09/96	09/13/96			X		X	X		
96B2670	SB-11	Batch 3A	Product/Water	09/10/96	09/13/96			X		X	X		
96B2952	SB-18	Batch 3A	Product	09/20/96	09/25/96			X		X	X		
96B2953	SB-19	Batch 3A	Product	09/20/96	09/25/96			X		X	X		
96B2954	SB-20	Batch 3A	Product	09/24/96	09/25/96			X		X	X		
96B2955	SB-8	Batch 3A	Product	09/13/96	09/25/96		X			X	X		
96B2956	SB-12	Batch 3A	Product	09/17/96	09/25/96		X			X	X		
96B2957	SB-9	Batch 3A	Product	09/18/96	09/25/96		X			X	X		
96B2958	SB-6	Batch 3A	Product	09/16/96	09/25/96		X			X	X		
96B2959	SB-17	Batch 3A	Product	09/19/96	09/25/96		X			X	X		
96B2961	SB-2	Batch 3A	Product/Water	09/25/96	09/27/96		X			X	X		
96B2962	SB-20	Batch 3A	Product/Water	09/24/96	09/27/96			X		X	X		
96B2963	SB-21	Batch 3A	Product/Water	09/26/96	09/27/96			X		X	X		
96B3822	SB-14	Batch 3B	Product/Water	11/01/96	11/14/96		X			X	X		
96B3823	SB-21	Batch 3B	Product/Water	09/26/96	11/14/96		X			X	X		
96B3824	SB-22	Batch 3B	Product/Water	10/15/96	11/14/96		X			X	X		
96B3825	SB-23	Batch 3B	Product/Water	10/28/96	11/14/96		X			X	X		
96B3826	SB-25	Batch 3B	Product/Water	10/30/96	11/14/96		X			X	X		
96B3827	SB-26	Batch 3B	Product/Water	10/31/96	11/14/96		X			X	X		
96B3828	SB-27	Batch 3B	Product/Water	10/30/96	11/14/96		X			X	X		
96B2867RE	SB-4	Batch DDT 1	Product	09/10/96	09/13/96			X					PEST/PCB
96B2869RE	SB-7	Batch DDT 1	Product	09/10/96	09/13/96			X					PEST/PCB
96B2870RE	SB-11	Batch DDT 1	Product/Water	09/10/96	09/13/96			X					PEST/PCB
96B2952RE	SB-18	Batch DDT 1	Product	09/20/96	09/25/96			X					PEST/PCB
96B2953RE	SB-19	Batch DDT 1	Product	09/20/96	09/25/96			X					PEST/PCB

TABLE 7-2: Listing of Samples Analyzed

Lab ID	Field ID	Batch ID	Matrix	Date Coll'd	Date Rec'd	Water Prep	Rinse Prep	Oil Prep	Soil Prep	GC/FID	PAH	GRO	OTHER
96B2954RE	SB-20	Batch DDT 1	Product	09/24/96	09/25/96			X					PEST/PCB
96B3822	SB-14	Batch DDT 1	Product/Water	11/01/96	11/14/96		X						PEST/PCB
96B3823	SB-21	Batch DDT 1	Product/Water	09/26/96	11/14/96		X						PEST/PCB
96B3824	SB-22	Batch DDT 1	Product/Water	10/15/96	11/14/96		X						PEST/PCB
96B3825	SB-23	Batch DDT 1	Product/Water	10/28/96	11/14/96		X						PEST/PCB
96B3826	SB-25	Batch DDT 1	Product/Water	10/30/96	11/14/96		X						PEST/PCB
96B3827	SB-26	Batch DDT 1	Product/Water	10/31/96	11/14/96		X						PEST/PCB
96B3828	SB-27	Batch DDT 1	Product/Water	10/30/96	11/14/96		X						PEST/PCB
97C0272	S-82 WATER	Batch 4	Water	01/21/97	01/23/97	X				X	X		PEST/PCB,VOC
97C0273	S-53 WATER	Batch 4	Water	01/21/97	01/23/97	X				X	X		PEST/PCB,VOC
97C0274	S-35 WATER	Batch 4	Water	01/21/97	01/23/97	X				X	X		PEST/PCB,VOC
97C0275	PH-3 WATER	Batch 4	Water	01/21/97	01/23/97	X				X	X		PEST/PCB,VOC
97C0276	TRIP BLANK 1	Batch 4	Water	01/21/97	01/23/97								VOC
97C0277	MW-5 WATER	Batch 4	Water	01/22/97	01/23/97	X				X	X		PEST/PCB,VOC
97C0278	MW-7 WATER	Batch 4	Water	01/22/97	01/23/97	X				X	X		PEST/PCB,VOC
97C0279	S-82	Batch 4	Product	01/21/97	01/23/97			X		X	X		PEST/PCB,VOC
97C0280	S-53	Batch 4	Product	01/21/97	01/23/97			X		X	X		PEST/PCB,VOC
97C0281	S-35	Batch 4	Product	01/21/97	01/23/97			X		X	X		PEST/PCB,VOC
97C0282	PH-3	Batch 4	Product	01/21/97	01/23/97			X		X	X		PEST/PCB,VOC
97C0283	MW-5	Batch 4	Product	01/22/97	01/23/97			X		X	X		PEST/PCB,VOC
97C0284	MW-7	Batch 4	Product	01/22/97	01/23/97			X		X	X		PEST/PCB,VOC
97C0285	MW-6	Batch 4	Product	01/22/97	01/23/97			X		X	X		PEST/PCB,VOC
97C0286	TRIP BLANK 2	Batch 4	Water	01/22/97	01/23/97								VOC
97C0857	PZ-2 (10-12)	Batch 5	Soil	05/23/97	05/29/97			X		X	X		
97C0858	PZ-3 (14-15)	Batch 5	Soil	05/23/97	05/29/97			X		X	X		
97C0859	PZ-3 (19)	Batch 5	Soil	05/23/97	05/29/97			X		X	X		
97C0737	DPSC-MW25	Batch 5	Product	04/28/97	05/19/97			X		X	X		
97C0738	Tank 176	Batch 5	Product	05/14/97	05/19/97			X		X	X		
97C1146	S-35 22.5	Batch 6	Soil	07/02/97	07/11/97			X		X	X		
97C1147	S-35 32	Batch 6	Soil	07/02/97	07/11/97			X		X	X		
97C1147DUP	S-35 32 DUP	Batch 6	Soil	07/02/97	07/11/97			X		X	X		
97C1148	S-36 24.5-25	Batch 6	Soil	07/02/97	07/11/97			X		X	X		
97C1149	S-36 35	Batch 6	Soil	07/02/97	07/11/97			X		X	X		
97C1150	S-37 21	Batch 6	Soil	07/07/97	07/11/97			X		X	X		
97C1151	S-37 31	Batch 6	Soil	07/07/97	07/11/97			X		X	X		
97C1152	S-39 21	Batch 6	Soil	07/07/97	07/11/97			X		X	X		
97C1153	S-39 31-33	Batch 6	Soil	07/07/97	07/11/97			X		X	X		
97C1154	S-38 20-21	Batch 6	Soil	07/07/97	07/11/97			X		X	X		
97C1155	S-38 31	Batch 6	Soil	07/08/97	07/11/97			X		X	X		
97C1158	S-35	Batch 6	Product/Water	07/08/97	07/12/97	X				X	X		

TABLE 7-2: Listing of Samples Analyzed

Lab ID	Field ID	Batch ID	Matrix	Date Coll'd	Date Rec'd	Water Prep	Rinse Prep	Oil Prep	Soil Prep	GC/FID	PAH	GRO	OTHER
97C1159	S-36	Batch 6	Product/Water	07/08/97	07/12/97	X				X	X		
97C1160	S-37	Batch 6	Product/Water	07/11/97	07/12/97	X				X	X		
97C1161	S-38	Batch 6	Product/Water	07/11/97	07/12/97	X				X	X		
97C1162	S-39	Batch 6	Product/Water	07/11/97	07/12/97	X				X	X		
96B2183	S-89	Batch DDT 2	Product	06/25/96	06/28/96			X					PEST/PCB
96B2183MS	S-89 MS	Batch DDT 2	Product	06/25/96	06/28/96			X					PEST/PCB
97C0279	S-82	Batch DDT 2	Product	01/21/97	01/23/97			X					PEST/PCB
97C0282	PH-3	Batch DDT 2	Product	01/21/97	01/23/97			X					PEST/PCB
97C0283	MW-5	Batch DDT 2	Product	01/22/97	01/23/97			X					PEST/PCB
97C0284	MW-7	Batch DDT 2	Product	01/22/97	01/23/97			X					PEST/PCB
97C0285	MW-6	Batch DDT 2	Product	01/22/97	01/23/97			X					PEST/PCB
96B2952	SB-18	Batch DDT 2	Product	09/20/96	09/25/96			X					PEST/PCB
96B2953	SB-19	Batch DDT 2	Product	09/20/96	09/25/96			X					PEST/PCB
97C0737	DPSC-MW25	Batch DDT 2	Product	04/28/97	05/19/97			X					PEST/PCB
96B3828	SB-27	Batch DDT 2	Product/Water	10/30/96	11/14/96			X					PEST/PCB
96B2182	S-100	Batch PB 1	Product	06/25/96	06/28/96								PB
96B2183	S-89	Batch PB 1	Product	06/25/96	06/28/96								PB
96B2184	RW-401	Batch PB 1	Product	06/26/96	06/28/96								PB
96B2185	RW-402	Batch PB 1	Product	06/26/96	06/28/96								PB
96B2186	RW-404	Batch PB 1	Product	06/26/96	06/28/96								PB
96B2187	PZ-400	Batch PB 1	Product	06/25/96	06/28/96								PB
96B2518	MW-53	Batch PB 1	Product/Water	07/30/96	07/31/96								PB
96B2520	MW-93	Batch PB 1	Product/Water	07/30/96	07/31/96								PB
96B2523	RW-102	Batch PB 1	Product/Water	07/30/96	07/31/96								PB
96B2524	RW-105	Batch PB 1	Product/Water	07/30/96	07/31/96								PB
96B2867	SB-4	Batch PB 1	Product	09/10/96	09/13/96								PB
96B2869	SB-7	Batch PB 1	Product	09/10/96	09/13/96								PB
96B2870	SB-11	Batch PB 1	Product/Water	09/10/96	09/13/96								PB
96B2952	SB-18	Batch PB 1	Product	09/20/96	09/25/96								PB
96B2953	SB-19	Batch PB 1	Product	09/20/96	09/25/96								PB
96B2962	SB-20	Batch PB 1	Product/Water	09/24/96	09/27/96								PB
96B2963	SB-21	Batch PB 1	Product/Water	09/26/96	09/27/96								PB
97C0280	S-53	Batch PB 1	Product	01/21/97	01/23/97								PB
97C0281	PH-3	Batch PB 1	Product	01/21/97	01/23/97								PB
97C0282	MW-5	Batch PB 1	Product	01/21/97	01/23/97								PB
97C0283	MW-7	Batch PB 1	Product	01/22/97	01/23/97								PB
97C0284	MW-6	Batch PB 1	Product	01/22/97	01/23/97								PB
97C0285	DPSC-MW25	Batch PB 1	Product	04/28/97	05/19/97								PB
97C0737	Tank 176	Batch PB 1	Product	05/14/97	05/19/97								PB

TABLE 7-2: Listing of Samples Analyzed

Lab ID	Field ID	Batch ID	Matrix	Date Coll'd	Date Rec'd	Water Prep	Rinse Prep	Oil Prep	Soil Prep	GC/FID	PAH	GRO	OTHER
97C1968	SB-206 20-25	Batch 7	Soil	08/05/97	08/09/97				X	X	X		
97C1969	SB-204 40-45	Batch 7	Soil	08/05/97	08/09/97				X	X	X		
97C1970	SB-207 30-35	Batch 7	Soil	08/07/97	08/09/97				X	X	X		
97C1971	SB-204 25-30	Batch 7	Soil	08/05/97	08/09/97				X	X	X		
97C1972	SB-202 30-35	Batch 7	Soil	08/04/97	08/09/97				X	X	X		
97C1972MS	SB-202 30-35	Batch 7	Soil	08/04/97	08/09/97				X	X	X		
97C1972MSD	SB-202 30-35	Batch 7	Soil	08/04/97	08/09/97				X	X	X		
97C1973	SB-204 30-35	Batch 7	Soil	08/05/97	08/09/97				X	X	X		
97C1974	SB-202 25-30	Batch 7	Soil	08/05/97	08/09/97				X	X	X		
97C1983	SB-211 25-30	Batch 7	Soil	08/13/97	08/16/97				X	X	X		
97C1984	SB-205 25-30	Batch 7	Soil	08/12/97	08/16/97				X	X	X		
97C1985	SB209C 35	Batch 7	Soil	08/11/97	08/16/97				X	X	X		
97C1986	SB-205 30-35	Batch 7	Soil	08/12/97	08/16/97				X	X	X		
97C1987	SB-210 25-30	Batch 7	Soil	08/11/97	08/16/97				X	X	X		
97C2168	SB-214 20-25	Batch 7	Soil	08/18/97	08/25/97				X	X	X		
97C2169	SB-215 25-30	Batch 7	Soil	08/19/97	08/25/97				X	X	X		
97C2170	SB217B 15-20	Batch 7	Soil	08/19/97	08/25/97				X	X	X		
97C2171	SB-218 25-30	Batch 7	Soil	08/20/97	08/25/97				X	X	X		
97C2172	SB-216 15-20	Batch 7	Soil	08/20/97	08/25/97				X	X	X		
97C2173	SB-220 20-25	Batch 7	Soil	08/21/97	08/25/97				X	X	X		
97C2174	SB-222B 25-30	Batch 7	Soil	08/22/97	08/25/97				X	X	X		
97C2174MS	SB-222B 25-30	Batch 7	Soil	08/22/97	08/25/97				X	X	X		
97C2174MSD	SB-222B 25-30	Batch 7	Soil	08/22/97	08/25/97				X	X	X		
97C2279	NR5-S 6.5	Batch 7	Soil	08/26/97	08/29/97				X	X	X		
97C2280	NR3-S 5.5	Batch 7	Soil	08/26/97	08/29/97				X	X	X		
97C2315	SB-221 30-35	Batch 7	Soil	08/27/97	08/30/97				X	X	X		
97C2316	SB-219 25-30	Batch 7	Soil	08/26/97	08/30/97				X	X	X		
97C2317	SB-223 25-30	Batch 7	Soil	08/25/97	08/30/97				X	X	X		
97C2318	SB-224 35-40	Batch 7	Soil	08/27/97	08/30/97								
97C2319	SB-225 25-30	Batch 7	Soil	08/25/97	08/30/97								
97C3724	15	Batch 8	Product	11/20/97	11/26/97			X		X	X	X	
97C3725	13	Batch 8	Product	11/24/97	11/26/97			X		X	X	X	
97C3824	RW-301	Batch 8	Product	10/29/97	12/04/97			X		X	X	X	
97C3989	RWM-S1	Batch 8	Soil	12/15/97	12/17/97				X	X	X		
97C3990	RWM-S2	Batch 8	Soil	12/15/97	12/17/97				X	X	X		
97C3991	RWM-S3	Batch 8	Soil	12/15/97	12/17/97				X	X	X		
97C3992	RWM-P1	Batch 8	Water	12/15/97	12/17/97	X				X	X		
97C3993	RWG-S1	Batch 8	Soil	12/16/97	12/17/97				X	X	X		
97C3994	RWG-S2	Batch 8	Soil	12/16/97	12/17/97				X	X	X		
97C3995	RWG-S3	Batch 8	Soil	12/16/97	12/17/97				X	X	X		

TABLE 7-2: Listing of Samples Analyzed

[illegible]

8. DSCP SOURCE ANALYSIS

8.1 INTRODUCTION

The DLA contends that the DSCP never used petroleum hydrocarbon products similar to that in the NAPL plume beneath the DSCP property. Based on the history of activities that were carried out at DSCP over the years and its environmental history, it is clear that significant amounts of petroleum products including gasoline, naphtha, and naphtha-like products, such as those in the plume were handled and used. In fact, based on the capacity of known tankage on DSCP's property for light petroleum products, these tanks could have released from 330,000 gallons to 700,000 gallons over the years and still have been considered tight or leak-free under current Pennsylvania tank standards.

DSCP argues there is no data from its facility indicating that it was the source. The absence of data is the DSCP's responsibility. DSCP is charged under BRAC and has responsibility under Federal and State environmental laws to ensure that its facility was fully characterized, that there were no risks to human health and the environment, and that it take responsibility for the contamination it caused. A primary focus of DSCP's physical investigation of its facility has been whether soil impacted by known releases from tanks requires remediation under UST regulations. In fact, all DSCP's many investigations were approached as corner gas station assessments. Table 8-1 summarizes these previous UST investigations. DSCP tries to bootstrap these analyses into the forensic question of whether these areas investigated are potential sources of the contamination that exists. Reference to current UST regulations and remediation standards is not warranted for defining the scope of an investigation into sources.

PADEP has pointed out that the DSCP's physical investigations have been inadequate for assessing possible sources on DSCP's facility. One example is a 3 July 1997 letter in which PADEP was addressing the relationship of BRAC and plume issues. W. Stanley Sneath, PADEP's attorney for the plume, said that PADEP, "has not see enough information to make any ... determination," that three sites for which DSPC was seeking BRAC closure were not possible sources of the plume.

The DSCP's historical investigation besides focusing primarily on tanks in place since Pennsylvania's UST law became effective (i.e., 1989) compounded its bias against finding evidence of sources by focusing on shallow soil contamination. This type of focus is particularly problematic in more coarse-grained soils because NAPL from a source would tend not to spread as it migrated vertically. Thus, unless the investigation was planned to consider this eventuality, it would very likely miss many sources. A particular concern with DSCP's investigations is that their assumptions and objectives essentially overwhelm the data's quality and render the analyses virtually useless for assessing whether there was a source of the NAPL plume on its site. In many instances, the investigatory assumptions prior to and during the studies resulted in conclusions unsupportable by the body of data. These perfunctory conclusions, in turn, were used as a basis for not collecting the necessary data to fully characterize the potential sources on the DSCP site. Figure 8-1 lists 36 potential sources of the plume, most of which have not been adequately studied.

DSCP's fact-finding investigation into historical operations was woefully inadequate to ascertain the type and quantity of petroleum products DSCP handled over the years. DSCP interviewed less than 20 individuals and did little to develop historical facts about petroleum product use. Sun has identified names of over 200 former or current employees who could provide valuable information into past operations.

Sun has long suspected that DSCP's primary goal for the NAPL Plume Study and for studies as early as Kemron/Versar was to build a case that the refinery was responsible and that DSCP was not. DSCP rejected Sun's proposals to work together on a fifty-fifty basis to objectively investigate all potential sites on the refinery, on DSCP and other locations and to design and implement a common, objective, scientific investigation. Sun has recently developed evidence that this indeed was DSCP's primary motive.

In the minutes of two 1995 meetings involving representatives of DSCP, USACE, Versar, and PADEP, it is clear that DSCP was not interested in looking for sources on its site, but rather on making a case that the refinery was responsible for the NAPL plume.

The minutes of a 5 January 1995 meeting state the following:

“The free product petroleum hydrocarbon plume appears to contain approximately 10,000,000 gallons of product. Based solely on the above volume, this finding suggests that [DSCP] and most of the surrounding properties could not have caused a plume of this size and that a major off-site source is responsible for the plume.”

This is pure speculation. DSCP had not yet investigated its own potential on-site sources and the very same minutes reflect DSCP's and its consultants' feelings about Sun as a source. In response to the direct question, “[Do we have] enough evidence to go after Sun as a PRP right now?” a representative of Versar said, “We do not have enough evidence, particularly because there is not a good geometric connection of the free product plume to the Sun Property.” Versar then said, “we have to develop a chemical connection of the plume to the Sun property to have sufficient evidence.”

Suggestions were made at that meeting that, “jet lubricating oil” fingerprints were identified in the plume and that the Nike missile assembly area, formerly Building 26, may be a potential source. Yet this area has not been evaluated. The minutes also refer to planned installation of two monitor wells on Conrail property, being studied to assess whether a “pathway” existed. Once these wells were drilled, the results (as discussed in Section 5) provided no evidence that a pathway existed. Thus, the lack of a geometric connection that Versar acknowledged in January 1995 was buttressed after these wells were drilled and analyzed. Yet, Malcolm Pirnie, with no new evidence, concluded that such a pathway exists.

Minutes of a March 1995 meeting, reflected in a 5 May 1995 letter from Versar to USACE, Philadelphia District, continue to reflect that “there was not a strong geometric connection to the Sun property.” For some reason, these minutes contain a statement that, “there was significant evidence that the petroleum hydrocarbon plume did not originate from the [DSCP]....” As shown above, the minutes of the 5 January 1995 meeting, however, stated that the only reason DSCP was not considered a source was the estimated size of the plume (then estimated to be over 10,000,000 gallons). Since no further studies were done on DSCP sources between these two meetings, no evidence supports the proposition that DSCP was not a source.

The remainder of this section identifies some of the many potential source areas on DSCP's property and on two off-site locations.

8.2 OVERVIEW OF DSCP OPERATIONS

The study area has been industrialized for well over 80 years. Over that period, while there have been operational changes, DSCP maintained the same basic manufacturing objectives: it manufactured clothing, printed documents, maintained and painted vehicles, warehoused food, and otherwise supported the DoD mission. The Government's tenants of DSCP performed extensive vehicular maintenance as well as maintenance on Nike missiles (PRC 1994). The DSCP was developed in 1917, significantly upgraded in the early 1940s, and has been used since to support the various branches of the United States military. Activities carried out at the site included cloth storage, clothing manufacture, clothing preservation (including mothiciding, clothing cleaning and pressing), storage and maintenance of vehicles of all sorts (i.e., trucks, forklifts, locomotives, etc.), food storage, and research related to the manufacture of clothing. Because the Philadelphia facility was one of the largest and most active of its type, there were also a large number and variety of support activities carried out at the facility. These operations included boiler operation (gas fired with oil backup) to provide heat and steam, a small-scale rail system to move supplies and goods, a locomotive maintenance facility, a printing facility, a vehicle painting operation, a pesticide storage and application facility, and gasoline and diesel filling stations on at least three locations on the site. At its peak, the facility employed 8,728 personnel. As is the case at most military installations, the DSCP site was essentially a self-contained facility capable of carrying out its mission with very little assistance from off the site, save importing raw materials. As such, it is valid to assume that the facility carried out all of the activities that would be expected to be carried out in any small town or village. This is borne out by historical documents.

Given the importance of the various war efforts which DSCP supported, specifications for materials used were important to enforce uniformity of quality. Recycling, reclamation, and re-use were not as widely practiced as they are today. Materials were either consumed or disposed. This appears to be the case with petroleum solvents, such as naphtha, that were used in the mothproofing operations in Building 9, which were extensively disposed of down the sectional clay-pipe floor drains. The drains backed up repeatedly, causing an evacuation and a series of inspections. The inspections clearly determined that the cause of the problems was hydrocarbon solvent disposal, sewer leakage, and contamination of soil beneath Buildings 9 and 13 (PRC 1994). Given the construction and age of these sewers, solvent would have most certainly leaked into the soil and

ultimately impacted the groundwater. Also, undocumented other waste naphtha streams from the painting or vehicle and locomotive maintenance process were very likely similarly disposed.

8.3 SPECIFIC SOURCE AREAS

To provide order to the ensuing discussions, source areas will be discussed at individual areas on the DSCP site. A logical starting point for the discussion is to build on known site characteristics, such as the plume morphology (as discussed in Section 5). Figure 8-2 presents the product thickness distribution at the DSCP site. Based on the isopach contours and the understanding that NAPL plumes have the greatest apparent thickness near the source, there are several immediate conclusions as discussed in Section 3.2:

- Several apparent source areas exist on the site (i.e., several areas indicate NAPL thicknesses that suggest proximity to a source)
- The apparent source areas do not correspond exclusively to the historically identified tank locations
- The general contours of NAPL thickness, which include large areas, may result from the lack of data coverage over much of the site and the lack of wells between NAPL occurrences. This could result in an overestimation of the overall plume volume.

The relative contribution of each potential source identified in Figure 8-1 to the NAPL plume at DSCP is not clear because many have never been investigated, and those that were, were addressed with a bias toward USTs. Furthermore, the UST-based studies, since they focus on shallow soil remediation rather than on analyses to assess potential on-site sources, cannot be used to rule out potential sources.

8.3.1 On-Site Sewer System

Utility construction practices in 1942, when the facility received its most recent complete renovation, typically included the use of terracotta clay pipe. Leakage and release from such piping is not only possible, but is a near certainty given its age. With the diversity of processes carried out at the site that included dry cleaning, insecticide fogging, and laboratory testing, the use and disposal of petroleum products, including solvents, had to be widespread at the site. Laboratory photographs from the 1950s show large extraction processes that likely included solvents. These were placed

directly over long horizontal drains. Spent solvents probably were discharged in the sewers. Drains next to sponging and mothciding operations have been observed and are likely to be a direct connection to the drains and sewers. The sewer system, as documented in 1992 (CH2M Hill) is shown serving every bay of the warehousing and manufacturing facilities. Waste water from the DSCP flows directly to the city's sewer mains. Consideration of specific source areas are described below. Since the sewers are generally above the water table, material would leak out and make its way to the water table. The site sewer system has been inadequately investigated with regard to source evaluation.

8.3.2 Gas Condensate

Gas supply enters the DSCP facility at two separate locations, one along Oregon Avenue and the other along 20th Street. The gas supply from the Philadelphia Gas Works that enters the DSCP site from 20th Street is through a 20-in main at 35 psi, which is reduced to 25 psi in Building 11. It is known that gas condensate accumulates in gas-distribution systems. As shown in Section 7, gas condensate looks remarkably like the material in the plume. Since condensate can be characterized as a naphtha material, the subsurface near the gas line or adjacent to any drip pots on the site should be further characterized. Previously referenced incidents in 1952 and 1953 suggest the potential for heavy end gas condensate as a potential source at Building 13. Figure 8-1 shows the gas distribution system on the DSCP site.

During 1993, DSCP used 231,323-McF of natural gas. Using comparable gas-supply statistics, in a similar distribution system, several thousand gallons of condensate per year can be produced by such a large volume. During more active years (i.e., 1940s and 1950s), the production of condensate could have been substantially greater.

8.3.3 Building 12/Main Gate

Building 12 contained photo-chemicals and painting chemical storage in the basement. Photocopying and printing was also performed in the basement of this building. Further investigation, including the area near sewers for printing solvent and paint solvents, may identify potential sources.

8.3.4 Building 6

MW-1A, in which NAPL has been observed, is located on the northeastern edge of Building 4 and immediately west of Building 6. Building 6 contained many different offices in past years and small laboratories have occupied the building since 1942. It has also housed small fabrication shops, water deionizing operations for the laboratory, testing for ultraviolet light exposure and the photography lab. Since subsurface structures such as USTs have not been known to exist in the area, the source of the NAPL in MW-1A may be related to other subsurface structures such as sewers or gas condensate that may have conveyed NAPL.

A letter from the DLA to the EPA, but addressed to PADEP, on 26 June 1992 indicated that the excavation contractor for the new elevator shaft near Building 6 indicated that "product" was encountered 14-ft BLS. This encounter is approximately 4-ft above historical ground-water level, indicating an on-site source.

8.3.5 Building 13/Building 14

At the eastern portion of the site, an apparent NAPL thickness of 1.5-ft was observed in MW-11 near Building 14 in November 1997. This suggests that a source exists in the vicinity of Buildings 13 and 14. Reportedly high vapor concentrations have been detected in the sewer and in the steam-piping conduit of Building 13. Kemron/Versar (1995) reported elevated TPH soil concentrations (10,000 mg/kg) and NAPL in this area. The relation of the observed NAPL in MW-11 with that observed near Building 6 (MW-1A) is not clear. However, the lack of monitoring wells to differentiate the plumes may lead to the conclusion that a source of NAPL may exist in the area.

8.3.6 Bash Street Gasoline Station

The status of the USTs at the Bash Street Gasoline Station has never been satisfactorily resolved. The USTs reportedly contained gasoline for the site vehicles. No record of the tank removals has been found. Borings around the apparent concrete subsurface vault indicated that the highest TPH-GRO concentrations were in the 12- to 14-ft interval (probably the depth of the bottom of the tanks and vaults) at 20,000 µg/kg (sample GSUST 04), and the highest lead concentration (146 mg/kg) was detected in its 10- to 12-ft interval (sample GSUST 04). Obviously, releases have occurred from this area.

8.3.7 Building 9, Former Building 5, and The DDT Tanks

Building 9 was the area where sponging and mothiciding was performed. Building 5 was the old factory. The basement of Building 9 contained pesticide (DDT) mixing equipment, and the sponging equipment was on the first floor. Historical photographs of the sponging operation show large vats of material above areas where the sponging fluid was applied. Drains apparently were in the mixing rooms and under the sponging equipment to remove the excess and drippings. With the historic information that one of the preferred solvents for the sponging and mothiciding was deodorized kerosene, a naphtha, drains from any areas where this was performed likely would have been sources if discharges occurred to leaking sewers. Spent sponging and mothiciding fluids likely were also disposed through the clay sewer system. This inadequately characterized area is over the NAPL plume and must, therefore, be considered a source worthy of further investigation. Appendix M contains specifications of solvent used in DDT spraying operations.

MW-7 and MW-9 are located near the former DDT USTs. During the removal of the DDT tanks, 1,400,000-lb of soil and other waste was disposed. During the removal process, the mixing room in Bay B of Building 9 was observed to have drains leading to the storm-sewer system. The drains and connection to the sewer were removed the same time the tanks were removed. Soil concentrations at the tanks were 900 mg/kg DDT at the tanks and 52,000 mg/kg under the concrete building floor. TPH concentrations were 242 mg/kg. The maximum observed DDT concentrations and TPH concentrations under the mixing room floor (8-in deep) were 220 mg/kg and 35 mg/kg, respectively.

Although DDT was not detected in the NAPL plume, it is possible that naphtha was stored in what were later called DDT tanks before it was mixed with DDT or that straight naphtha was stored at other undocumented locations. Thus, the release of naphtha without DDT is possible. This is a logical theory since records indicate that water-soluble DDT was not used until 1951 or later and that the DDT was mixed into the solvent at Building 9.

8.3.8 Building 30 Tank

A tank with unknown contents was in Building 30. This tank was believed to be a 600-gallon tank. However in 1990 and 1991, when the tank was being pumped out in preparation for closure, 2,000 gallons of liquid were removed with no depletion of the liquid in the tank. The status and contents of this tank are still unknown. Therefore, this area must be considered a potential source.

8.3.9 Building 30, Oil-Water Separator

The west bay of this building was used for locomotive maintenance. Steam cleaning and a paint booth for painting equipment were also housed in this building. Solvents and chemicals were stored within the building before the designation of the hazardous waste storage facility near Building 46. The contents of the separator are still unknown, but this area must be considered a source.

8.3.10 Building 28 USTs

According to information on file with the PADEP, the pre-1971 fuel USTs at Building 28 gas station had remote fill lines running south from the tanks to the rail tank car unloading headers. An exploratory trench was installed near Building 28, and high levels of soil contamination near the leak and along the entire 50-ft length of trench at a depth of 3-ft were observed. This indicates that product from piping leaks flowed along the pipe trenches, probably back to the tankpit. Tank-car distribution is a notoriously sloppy operation. Soil sample GS004 in the piping trench contained very high levels of diesel and gasoline constituents and lead. Malcolm Pirnie completed soil borings in the area and observed TPH-GRO concentrations as high as 110,000 $\mu\text{g/kg}$ at a 14-ft depth (boring 28UST-05), but the highest photoionization detector (PID) reading in the boring was at a depth of 11-ft. Malcolm Pirnie did not collect a sample from this interval. In general, the highest PID field observations at this location did not correspond with the samples selected for analyses; thus, the characterization is suspect. Also, little or no correlation exists between the PID readings and the TPH-GRO concentrations detected during laboratory analyses. PID readings of 5 to 7 ppmv have corresponding soil concentrations of 45,000 $\mu\text{g/kg}$, but PID readings one order of magnitude higher have TPH-GRO concentrations that are that much lower. This lack of correlation is troublesome, and the conclusion that there was no significant petroleum loss at this location based on PID screening lacks support. In addition to the lack of correlation between field screening and

laboratory analytical results in this area, analyses to determine lead concentrations in the soil were not performed. Since leaded gasoline was likely stored in the USTs in this area (given the time when this was used), soil samples should have been analyzed for this parameter.

In conclusion, numerous operational source areas have not been resolved with the existing data. Further investigations to evaluate the contribution of these potential sources to the DSCP NAPL plume is necessary before any of these potential sources of the NAPL plume beneath the DSCP can be ruled out.

8.4 SOURCE QUANTITY AT DSCP

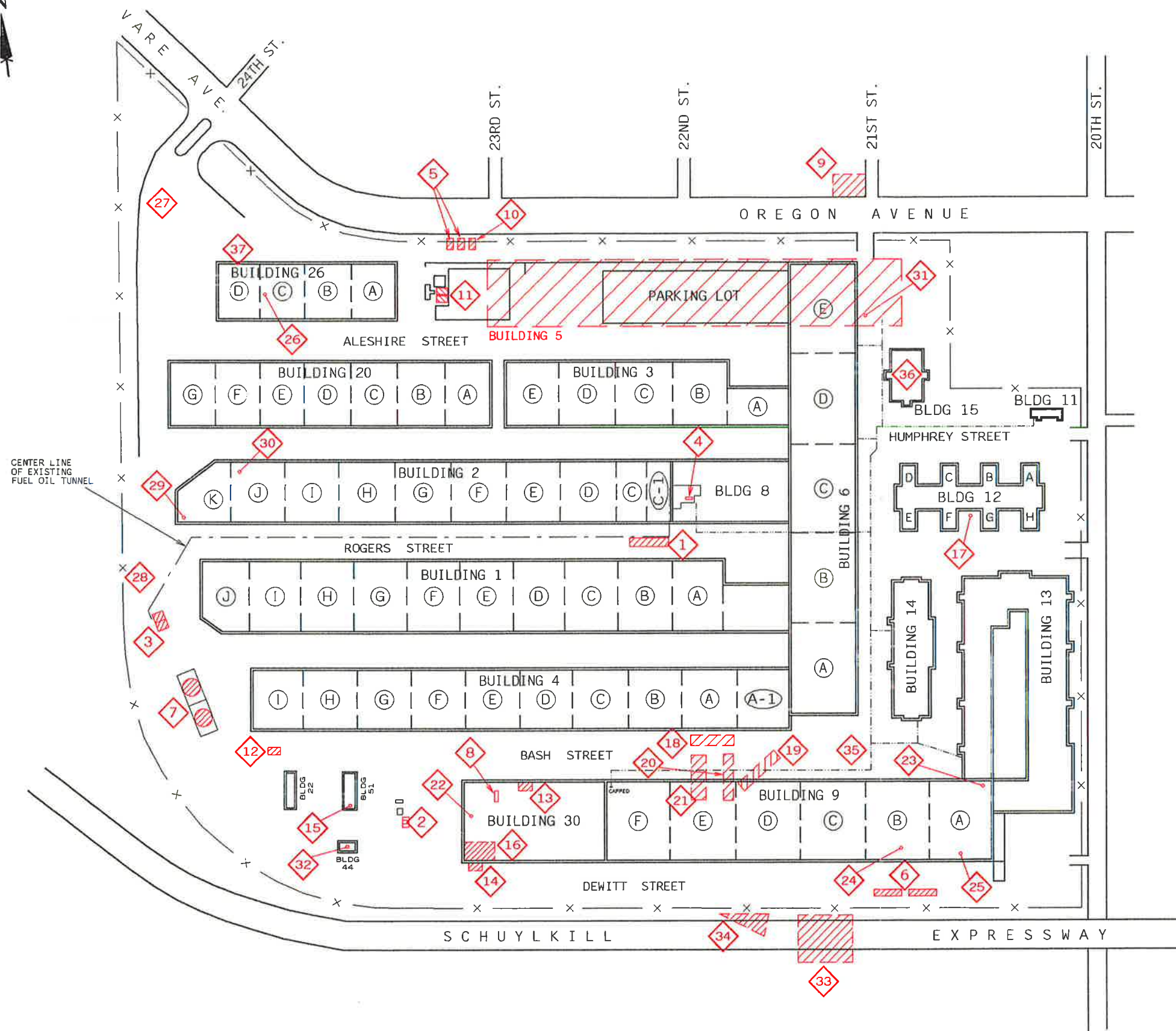
To further evaluate the potential for onsite sources at DSCP, the known storage capacities and operational periods for known USTs on the site were compared with the regulatory standard for documenting a "tight system" to quantify potential releases. Such documentation has been recorded with PADEP in the tank closure reports. The total capacity of the known tankage was 118,719 gallons. (To be conservative, the large ASTs that held No. 6 fuel oil have not been included in this analysis.) The period of service for the tanks is unknown in many instances. DSCP also reports conflicting periods of service for the same tank in its documentation. The total years in operation for all the known tanks at DSCP is estimated to be between 384 and 788 years. Assuming a potential leak of 0.01 gal/hr, the standard for tank-tightness testing (PADEP Chapter 245, EPA 40CFR43(c)), a potential release between 330,000 and 700,000 gallons is possible with no leak detection. This quantity is clearly a conservative estimate since there are documented reports of leaking product lines and tanks with holes identified during their removal. This cursory analysis shows that DSCP did handle sufficient petroleum products (in the known tanks) to have been the source of the NAPL beneath their site.

8.5 MONTGOMERY BROTHERS/SHERWOOD BROTHERS

Both of these former industrial facilities were located above one of the apparent thickest portions of the NAPL plume. Based on historical photographs, Montgomery Brothers remained in operation until the construction of the Schuylkill Expressway in 1953. Little is known about either of the facilities except that Montgomery Brothers manufactured liquid rubber cement and Sherwood Brothers produced betholine. Both are expected to have used naphtha in their production

processes. Further, an AST labeled “naphtha” was discovered on the Sherwood Brothers site on the 1922 Sanborn map. Therefore, they deserve consideration as potential sources to the NAPL plume of DSCP.

In summary, DSCP has conducted numerous subsurface investigations on its site. However, all of them focused on USTs and on meeting UST regulations. Thus, they were biased toward post-1989 activities and they focused more on the near surface environment. DSCP’s process apparently included an element of pre-screening, in that they did not investigate areas that they deemed incapable of being major plume contributors. This led to broad and significant oversights. Sun’s analysis has identified numerous uninvestigated or inadequately investigated potential source areas that combined with previously identified source areas (by DSCP), could easily have produced the plume on their site.



POTENTIAL HYDROCARBON SOURCES

- 1 30,000 GAL. DIESEL UST
- 2 (3) 10,000 GAL. GASOLINE/DIESEL UST
- 3 (5) 25,000 GAL. #6 OIL UST
- 4 550 GAL. WASTE OIL UST
- 5 (2) 10,000 GAL. HEATING OIL UST (SAND FILLED)
- 6 (2) 10,000 GAL. DOT UST (SAND FILLED)
- 7 (2) 200,000 GAL. #6 OIL AST
- 8 1,440 GAL. WASTE OIL AND SOLVENT SEPARATOR
- 9 GAS STATION
- 10 10,000 GAL. HEATING OIL UST
- 11 (2) SIZE AND CONTENTS UNKNOWN - NOT CONFIRMED
- 12 550 GAL. GASOLINE UST
- 13 SIZE AND CONTENTS UNKNOWN - UST
- 14 500 OR 600 GAL. WASTE OIL/USED MOTOR OIL UST
- 15 PESTICIDE MIXING ROOM (AREA)
- 16 LOCOMOTIVE REPAIR BAY
- 17 PAINTING
- 18 PLUMBING AND CARPENTER SHOP
- 19 PAINT SHOP
- 20 PRINTING SHOP
- 21 LABORATORY
- 22 PAINT BOOTH
- 23 GAS STATION
- 24 SPONGING AND DRYING
- 25 PESTICIDE MIXING (BASEMENT)
- 26 REFUSE BURNER
- 27 PAINT AND OIL STORAGE
- 28 OIL STORAGE
- 29 DIESEL STORAGE
- 30 PESTICIDE STORAGE
- 31 SPONGING AND PESTICIDE APPLICATION
- 32 FLAMMABLE STORAGE BUILDING
- 33 SHERWOOD BROTHERS BETHOLINE MANUFACTURING (OFF-SITE)
- 34 MONTGOMERY BROTHERS LIQUID RUBBER CEMENT FACTORY (OFF-SITE)
- 35 GAS DISTRIBUTION SYSTEM
- 36 C&T LAB (BLDG 15)
- 37 NIKE MISSILE OPERATIONS

LEGEND

—X— FENCE LINE

SOURCE OF BASE MAP:
SITE DRAWING BY
VERSAR, INC., LANGHORNE, PA.
DATED 9/1/93

THIS MAP WAS COMPILED FROM BASE DRAWINGS
AND/OR SKETCHES SUPPLIED BY OTHERS.
IT IS TO BE USED ONLY AS AN APPROXIMATE SOURCE OF REFERENCE.
WE ASSUME NO RESPONSIBILITY FOR THE ACCURACY OR
BASE MAP RELATED INFORMATION CONTAINED HEREIN.

0 50 100 150 300 600
APPROXIMATE SCALE IN FEET

INTEGRATED
SCIENCE &
TECHNOLOGY, INC.

DRAWN BY: EG	REVIEWED: PKH	APPROVED: HJR
DATE: 04 MAR 1998	PROJECT NO. SU001A	DWG. NO. 11422116
POTENTIAL HYDROCARBON SOURCE AREAS		
STUDY AREA Philadelphia, PA		
FIGURE 8-1		

TABLE 8-1
Summary of DSPC Storage Tanks
(Taken from the NAPL Plume Confirmation Study)

TANK NO. ^A	BRAC TANK NO. ^B	CAPACITY (gal)	CONTENTS	LOCATION	USE	DATE INSTALLED	TANK CONDITION ^C	CONTAMINATION	COMMENTS
USTs (001 through 005)	7 through 11	25,000 each tank ^{2,3,12}	No. 6 fuel oil ^{3,11}	Bldg. 18 tank farm (between Bldg. 18 and ASTs)	Active ^{2,3,12}	Jan 1942 ^{2,3}	Cleaned and precision-tested in fall 1994 - tested tight ³	Several releases of fuel oil near Bldg. 18 have been documented ⁽¹²⁾	In operation from 1942 to present ⁽¹²⁾ . Tanks encased in concrete ^(3,10) connected in two AST's and pump house (Bldg. 18). Supplies fuel to Bldg. 8 boiler as backup power supply ⁽³⁾ .
006	4	10,000 ^{1,2,3,5,12,18}	Unleaded gas ¹				All in good condition		
007	5	10,000 ^{1,2,3,5,12,18}		South of Bldg. 28 (gas station) Top of each tank is 3-ft bgs ⁽¹⁸⁾	Removed 5/94 ^{1,2}	1942 ¹⁰ Jan 1971 ^{1,2,3}	All tanks and piping tightness tested in 1988 - no leaks ^{3,9}	Removed 20 cy of contaminated soil - additional contaminated soil left in place ¹ . Removed 50 cy ³	In operation from 1971 to 1994. ¹² Used for on-site automotive consumption; replaced with one 2,000 gallons and one 4,000-gallon tank (ASTs Nos. 004A and 005A, respectively).
008	6	10,000 ^{1,2,3,5,12}	Diesel ^{1,2,12}				Leak in Tank 008 fuel line discovered and repaired 10/87 ⁸		
9	17	30,000 ^{1,2,3,4,12,18}	Diesel ¹² and No. 2 fuel oil ^{3,4}	Rogers Street Between Bldgs. 1 and 8. Top of tank is 3-ft bgs	Removed 2/95 ¹²	Jan 1971 ³ , Jan 1973 ^{1,2,4,12} early 1970s ¹⁰	Intact, no evidence of leakage from tank or piping ¹	No VOC or TPH contamination observed beneath tank ^{1,3}	In operation from 1973 to 1993. ¹² Supplied fuel to Bldg. 8 standby emergency diesel generators. ^{1,3} out of service for 10 years. ³
010	18	550 ^{1,2,3,5,12,18}	Waste oil ^{3,12} (used motor oil) ^{1,4}	Courtyard of Bldg. 8 (center of site)	Removed 5/94 ^{2,12}	Jan 1973 ^{1,2,3,4,12}	Intact, no holes or evidence of leakage in tanks or piping during removal ¹	Minor release beneath tank (TPH = 1,200 ppm). No contaminated soil found during tank removal. ¹	Exact contents of the tank are unknown. ¹² In operation from 1973 to 1992. ¹² Waste-oil tank for two standby emergency diesel generators in Bldg. 8. ¹
011 012	14 15	6,000 ^{1,2,3,5}	Diesel or No. 2 fuel, ³ No. 4 fuel oil ⁴ , heating oil ¹² .	Along Oregon Ave., North of Bldg. 46	Removed 7/94 ^{2,12}	January 1922 ^{1,3,4,12}	Intact, no holes or evidence of leakage ¹	Contamination beneath one tank; (TPH = 9,800 ppm at 14-ft bgs) ⁷⁷ . Soil around and under tanks observed as contaminated. ³ No release from the USTs has been identified ¹²	In operation from 1922 to 1941. Exact contents are unknown. ¹² Out of service since 1940s. ³ Fuel-oil storage for former boiler plant in Bldg. 10 (demolished and piping removed), filled with sand previously. ⁷⁷ Tanks were cut up during removal, extract capacity not confirmed. ¹⁶

TABLE 8-1
Summary of DSPC Storage Tanks
(Taken from the NAPL Plume Confirmation Study)

TANK NO. ^a	BRAC TANK NO. ^b	CAPACITY (gal)	CONTENTS	LOCATION	USE	DATE INSTALLED	TANK CONDITION ^c	CONTAMINATION	COMMENTS
013	1	10,000 ^{1,2,3}	DDT and other contaminants ^{2,5}	South of Bldg. 9 (Dewitt St.)	Removed 7/95 ¹	Jan 1942 ^{1,2}	Intact with no sign of leakage ^{1,3}	High DDT contamination; TPH = 242 ppm, VOC = 10 ppb xylene. ³	Filled with sand in 1983. ³ Supplied chemicals to a room in Bldg. 9. ^{1,3} In operation from 1942 to 1973. ¹²
014	2	5,12 ^{1,8}	DDT ^{1,3} pesticide ¹²	Top of tank is 3-ft bgs					More than 1.4 million pounds of contaminated soil, liquids, solids, and debris were removed from the site. ⁸
015	16	10,000 ^{1,2,3,5}	Heating oil, ¹² diesel or No. 2 fuel, ³ No. 4 fuel oil ^{1,4}	Along Oregon Ave., north of Bldg. 46.	Closed in place 2/95	Unknown ^{1,2,4} 1922 ¹²	1/2-in hole in bottom of tank ¹	Visible soil contamination encountered ^{1,18}	Exact contents are unknown. ¹² Discovered during removal of two adjacent tanks; fuel storage for Bldg. 10 boilers. Demolished in mid-1900s (piping also demolished). ¹ Filled with foam ¹ in operation from 1922 - 1941. ¹²
NR1	12	Unknown ¹²	Unknown ¹²	East end of Bldg. 46	Inactive ¹²	Unknown ¹² Prior to May 1935 ¹⁷	Unknown	No release from Bldg. 46 has been documented ¹²	The existence of these tanks has not been confirmed ¹²
NR2	13	Unknown ¹²	Unknown ¹²	Within Bldg. 30 on north side	Inactive ¹²	Unknown ¹²	Unknown	Unknown	Oil-water separator, exact contents are unknown. ¹² Bldg. 30 was used as a vehicle maintenance facility from 1960s to 1980s; ¹³ from early 1970s to early 1980s.
NR-4a through NR-4d	22	5,049, 8,130, 550 and 1,090	Gasoline ¹²	Dash Street between Bldgs. 6, 9 and 14	Inactive ¹²	Unknown ¹² Prior to May 1935	Unknown	Unknown	Tanks supplied fuel to former gasoline station. ¹² The 550-gal tank is indicated as "leaky tank - disconnected" ²⁰
NR-5	-	Unknown but believed to be 600 ^{1,13}	Unknown ¹²	Within Bldg. 30	Unknown ¹³	Unknown ¹³	Unknown	Unknown	2,000 gal of liquid pumped from tank, but contents could not be depleted. ¹³ pH was low upon initial pumping of liquid, became neutral over time. ¹⁸
AST's 001A	3	600 ¹⁵ or 500 ^{2,5,12}	Waste oil, ¹² used motor oil ⁶	Southwestern exterior wall of Bldg. 30. ¹²	Removed 1991, ² 1992 ¹²	Jan 1950 ²	Unknown	Unknown	In operation from 1950 to 1992. ¹⁵ No tank closure report available
002A	20	200,000 ^{2,12}	No. 6 fuel ^{1,17,12}	Southwest corner of site,	Active ^{2,12}	Jan 1942 ^{2,12}	Unknown	Unknown	Supplies fuel to boiler in Bldg. 8 as backup power system. In operation from 1942 to present ¹²
003A	21	each		south of Bldg. 18					

TABLE 8-1
Summary of DPSC Storage Tanks
(Taken from the NAPL Plume Confirmation Study)

TANK NO. ^a	BRAC TANK NO. ^b	CAPACITY (gal)	CONTENTS	LOCATION	1996 USE	DATE INSTALLED	TANK CONDITION ^c	CONTAMINATION	COMMENTS
004A		2,000 ^{2,3}	Diesel ¹	South of Bldg. 28	Active ²	July 1994 ²	Unknown	Unknown	These two ASTs replaced three USTs that were removed in May 1994
005A		4,000 ^{2,3}	Unleaded gas ²						
NR6A		200,000 each ¹⁵	Water	East of Bldg. 1 beneath present location of Bldg. 6	Removed ¹⁰	Unknown	Unknown	Unknown	Water storage tanks used in former boiler house to supply steam lines. Tank NR8A was a water tower. ¹⁰
NR7A									
NR8A		75,000							

Reference C112M-1111. 1996.

NOTES:

^a Tank numbers are designated in sources (1), (2), and (4). Tanks designated as "NR" are additional tanks discovered, which are not included on the PADER tank registration forms.

^b Tank numbers are designated on source (12).

^c Observations on tank condition generally were obtained from tank closure reports. The reports do not specify if testing or analysis (e.g., pressure testing) was performed to confirm the observations.

Sources of Information

- ¹ UST Closure Report Form
- ² Registration of storage tanks
- ³ Final Phase I RI/FS report, prepared by Kenron/Versar
- ⁴ UST closure notification form
- ⁵ DLA letter to PADER regarding Registration of Storage Tanks, 7/12/94
- ⁶ UST sampling at Oregon Avenue, Figure 2, prepared by Versar, Inc., 5/19/94
- ⁷ Plan View of 10,000 Gallon Storage Tank Located along Oregon Avenue." Drawing No. L9407101, prepared by Versar, Inc.
- ⁸ DPSC Tank Closure Report, prepared by Rollins Environmental Site Services, June 30, 1995.
- ⁹ Draft Feasibility Report for Replacement of USTs at DPSC, prepared by Baker Environmental, Inc., December 1992.
- ¹⁰ Installation Assessment of DPSC, prepared by Chemical Systems Laboratory, September 1982.
- ¹¹ Final Engineering Report for DPSC, prepared by Environmental Science & Engineering, Inc., November 1991
- ¹² BRAC Cleanup Plan for DPSC, Final Report Update 0.1, prepared by Defense Logistics Agency, June 15, 1995.
- ¹³ Preliminary Screening Assessment, Buildings 30 and 44, DPSC, prepared by ENSR Consulting and Engineering, September 1991.
- ¹⁴ "Location of Main Stream Supply and Return Lines," Drawing No. 6214-172, dated July 16, 1918.
- ¹⁵ DPSC Personnel
- ¹⁶ "General Plan Showing City Water Main, Domestic Water Lines and Fire Protection Mains." Drawing No. P.D.M. 145, dated May 28, 1935.
- ¹⁷ "Underground Storage Tank Removals and Gas Station Tank Replacement." Drawing No. 1088001, sheets 1 through 7 of 7, dated 6/15/93.
- ¹⁸ "PQMD-Building No. 9 Sponging Plant, Liquid Handling Equipment with Equipment Room and Piping." Drawing No. PQMD 34-51-?, dated 3/5/51.
- ¹⁹ "Underground Gasoline Storage Tanks," Drawing No. P.D.M. 7, dated 1/3/39.

Reference: "Draft Environmental Assessment, Disposal and Re-use of Defense Personnel Support Center, Philadelphia, PA. 1996.

9. SUMMARY AND CONCLUSIONS

Sun has carried out a detailed, comprehensive, and integrated evaluation of all available data with bearing on the origin of the NAPL plume beneath the DSCP facility. Sun's evaluation was carried out to determine the merit of a series of allegations made by DLA as part of a dispute over the source of the plume. These allegations included the following:

- DSCP contends that the source of the NAPL plume beneath its site is the Sun refinery which is located to the west
- DSCP contends that this NAPL migration was possible because groundwater flowed from west to east during the time when the release occurred
- DSCP contends that the NAPL released migrated through a pathway beneath 26th Street and the CSX right of way and onto their site
- DSCP contends that the NAPL from Sun accumulated on their site to form a plume with the morphology and in the configuration that exists today
- DSCP contends that the NAPL beneath their site is a light refinery naphtha characteristic of JP-4 and that this aviation fuel was never used on their site
- DSCP contends that NAPL migration occurred during a 12- to 14-year time frame defined by release of the military specification for JP-4 and completion of construction of the 26th Street sewer.
- DSCP contends that they did not use materials such as those found in the NAPL plume in sufficient quantities to have caused the plume.

The database constructed to carry out this evaluation included information from the various environmental, cultural, and historical investigations that have been carried out as part of the BRAC process; data generated by governmental agencies related to regional geology and hydrogeology; data generated in the course of the many public works projects carried in the area surrounding the study area; and new and historical data generated and gathered by Sun. Sun used this comprehensive database to address the following major issues germane to assessing the following questions:

- Was the groundwater table ever configured such that NAPL from the refinery could have been transported to the DSCP site?

- Does a pathway exist through which NAPL from the refinery could have migrated to the DSCP site?
- Is the morphology of the NAPL plume beneath the DSCP site consistent with one formed as a result of migration from the refinery?
- Is the chemical character of the NAPL in the plume beneath DSCP consistent with a source on the refinery?
- Are there areas or have there been activities carried out on the DSCP site that could have led to creation of the NAPL plume?

Each of these issues was thoroughly, carefully, and objectively evaluated using all available valid data regardless of source and state-of-the-art tools. Initially, each issue was examined independently, then it was examined further using an integrated approach that encompassed all applicable disciplines. This type of approach allowed multiple arguments and lines of evidence to be developed. Taken together, the multiple evaluations render conclusions more valid and defensible. Based on the examination and analyses performed, the following conclusions have been drawn on an issue-specific basis:

- Groundwater in the site area flows predominately from north to south with a westerly component. It always has. Pumping on the refinery since the 1930s has enhanced or augmented the westerly flow component in the vicinity of the refinery. Conventional analyses, supplemented by vector analyses, support this conclusion. Pumping from wells on the Navy Yard 1.2 miles south of the refinery and DSCP had little or no direct effect on the direction of groundwater flow in the study area. In contrast, the installation of the 26th Street sewer and the dewatering associated with those activities did. Leaks in the sewer continue to enhance flow from the DSCP to the west. For NAPL migration to have occurred as DSCP alleges, groundwater would have needed to flow nearly due east. This has never been the case, nor has DSCP postulated that this has ever been the case.
- No geological or chemical evidence of a pathway through which NAPL migrated from the refinery to the DSCP site exists, either at the elevation of the current water table or at the elevation of the water table in the time window alleged by DSCP. Also, no geological evidence suggests the presence of a highly conductive zone, which would have been required. Further, no evidence of hydrocarbon in concentrations suggestive of residual saturation (10,000 to 20,000 mg/kg) is present, as would need to be the case if a pathway were present. Dissolved-phase hydrocarbon concentrations in the alleged pathway are at or less

than the limits of detection. Had hydrocarbon migrated through the area, the dissolved-hydrocarbon concentrations would be in the range of 20,000 to 50,000 µg/L.

- The morphology of the NAPL plume beneath the DSCP site is entirely consistent with sources on the DSCP site. The plume is elliptical with a long axis oriented northeast to southwest; the same direction as the flow of groundwater. Further, the thickest aspect of the plume is in the vicinity of four probable sources on the site, and it thins in all directions. This is consistent with the physics of immiscible multi-phase transport. The plume is also least weathered near the thickness centroids and is most weathered nearest its margins. This is also consistent with transport theory because more recently released NAPL pushes NAPL that has been in the subsurface longer.
- The material in the DSCP NAPL plume is not JP-4 or light refinery naphtha; instead, it is primarily a mixture of gasoline and naphtha or naphtha-like products. It differs distinctly from the NAPL and soil-residual hydrocarbon observed beneath the refinery, where the character of the NAPL is diverse. This is the case both near the current water-table elevation as well as the elevation of the water during the time window in which DSCP alleges NAPL migration occurred.
- Numerous locations on the DSCP site are known or potential NAPL sources. The investigations carried out to date on the DSCP property have been woefully inadequate. They did not focus on areas where leaks and spills were documented. They were not designed to find a plume source. Rather they were designed to achieve closure under the Pennsylvania UST program.

In summary, the refinery is not the source of the NAPL plume beneath the DSCP site. Based on an analysis of all relevant factors, the source is DSCP itself.

REFERENCES

- American Petroleum Institute (API). 1985. Laboratory Study of Solubilities of Petroleum Hydrocarbons in Groundwater. API Publication No. 4395, 21 pp.
- Alexander, Martin. 1961. Introduction to Soil Microbiology. John Wiley & Sons, Inc., New York. Chapter 17, pp. 293-308.
- Atlas, R.M. 1981. Microbial degradation of petroleum hydrocarbons: an environmental perspective. *Microbiological review* 45(1), 180-209.
- Bear, J. 1972. Dynamics of Fluids in Porous Media. American Elsevier, New York.
- Beckett, G. D. and D. Huntley. 1998. Soil Properties and Design Factors Influencing Free-Phase Hydrocarbon Cleanup. *Environmental Science and Technology*. Vol. 32, No. 2, 287-293.
- Beery, et al. 1975. Assessment of JP-8 as a Replacement of the Air Force Standard Jet Fuel JP-4 Part I. USAF RPT AFAPL-TR-74-71.
- Berg, T. M. 1980. Geologic Map of Pennsylvania. Pennsylvania Geologic Survey, 1 sheet, scale 1:250,000.
- Blake, S. B. and R. A. Hall, 1984. Monitoring Petroleum Spills with Wells; Some Problems and Solutions: Proceedings of the Fourth National Symposium on Aquifer Restoration and Groundwater Monitoring, NWWA.
- Boehm, P.D., G.S. Douglas, W.A. Burns, P.J. Mankiewicz, D.S. Page, and A.E. Bence. 1997. Advances in petroleum hydrocarbon chemical fingerprinting and allocation techniques after the Exxon Valdez oil spill. *Marine Pollution Bulletin*. (In Press)
- Boehm, P.D., G.S. Douglas, and J.S. Brown. 1995. Advanced chemical fingerprinting for oil spill identifications and natural resource damage assessments. Proceedings, 1995 Oil Spill Conference, Long Beach, CA.
- Borden, Robert C. 1994. *Natural Bioremediation of Hydrocarbon-Contaminated Ground Water* in Handbook of Bioremediation. Lewis Publishers. Boca Raton, Florida.
- Bouwer, H. and P. C. Rice. 1976. "A Slug Test for Determining Hydraulic Conductivity of Unconfined Aquifers with Completely or Partially Penetrating Wells." *Water Resources Research* 12(3):423-428.
- Bouwer, H. 1989. "The Bouwer and Rice Slug Test--An Update." *Ground Water* 27(3):304-309.
- Brooks, R. H. and A. T. Corey. 1966. Hydraulic Properties of Porous Media. American Society of Civil Engineering 92 (61-88).

REFERENCES (CONTINUED)

- Bruce, Lyle, Toney Miller, and Bob Hockman. 1991. Solubility Versus Equilibrium Saturation of Gasoline Compounds: A Method to Estimate Fuel/Water Partition Coefficient Using Solubility or K_{oc}. Proceedings of the 1991 Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration. Ground Water Management 8. Houston, Texas.
- Bruce, L.G., and G.W. Schmidt. 1994. Hydrocarbon fingerprinting: case studies. AAPG Bulletin, V. 78, No. 11, pp 1692-1710.
- Burris, D. R. and W. G. MacIntyre. 1985. "Environmental Toxicology and Chemistry" 4:371-377.
- C Tech Development Corporation. Environmental Visualization System, Version 2.60 for Windows NT 1994. Port Angeles, Washington.
- CH2M Hill. 1996. Draft Environmental Assessment: Disposal and Reuse of Defense Personnel Support Center, Philadelphia, Pennsylvania, July 1996.
- Chapelle, Francis H. 1993. Ground-Water Microbiology and Geochemistry. John Wiley and Sons, Inc. New York, New York.
- Chemical Systems Laboratory, Environmental Technology Division. 1982. Installation Assessment of Defense Personnel Support Center, Philadelphia, PA. September.
- Chiou, C. T., D. E. Kile, and R. L. Malcolm. 1988. "Environmental Science and Technology" 22 (3):288-303.
- Dames & Moore. 1997. Offsite Free-Phase Hydrocarbon Delineation Interim Report. Sun Company, Inc. Defense Personnel Support Center Project, Philadelphia, Pennsylvania
- Davis, John C. 1986. Statistics and Data Analysis in Geology, Second Edition. John Wiley & Sons, Inc., New York. Chapter 2, pp. 383-405.
- Department of Defense. 1990. Military Standard – Hydrocarbon compounds and solvent distillates, technical grade. MIL-STD-1448, 22 August, 1990.
- Douglas, G.S., A.E. Bence, R.C. Prince, S.J. McMillen, and E.L. Butler. 1996. Environmental stability of selected petroleum hydrocarbon source and weathering ratios. *Environ. Sci. Technol.* Vol. 30, No. 7, pp 2332-2339.
- Douglas, G.S., R.C. Prince, E.L. Butler, and W.G. Steinhauer. 1994. The use of internal chemical indicators in petroleum and refined products to evaluate the extent of biodegradation. In R.E. Hinchee, B.C. Alleman, R.E. Hoeppel, R.N. Miller (Eds.), *Hydrocarbon Bioremediation*. Ann Arbor, Mich.: Lewis Publishers.

REFERENCES (CONTINUED)

- Douglas, G.S., and A.D. Uhler. 1993. Optimizing EPA methods for petroleum contaminated site assessments. *Env. Test. Anal.* 2:46-53.
- Douglas, G.S., K.J. McCarthy, D.T. Dahlen, J.A. Seavey, W.G. Steinhauer, R.C. Prince, and D.L. Elmendorf. 1992. The use of hydrocarbon analysis for environmental assessment and remediation. In: P.T. Kostecki and E.J. Calabrese (Eds.), *Contaminated Soils: Diesel Fuel Contamination*. Ann Arbor, Mich.: Lewis Publishers.
- Douglas, G.S. 1991. Fingerprinting of petroleum hydrocarbons in water. In 14th Annual EPA Conference on Analysis of Pollutants in the Environment. Norfolk, Va. Invited paper.
- Dragun, J. 1988. *The Soil Chemistry of Hazardous Materials*. Silver Springs, MD, Hazardous Materials Control Research Institute, pp. 75-152.
- Drake, E.N., G.S. Douglas, and R.C. Prince. 1997. Nutrient stimulated biodegradation of aged landfarm hydrocarbons in soil. In *proceedings: 1997 Bioremediation Conference*, New Orleans, April 28-30.
- Drake, E.N., K.E. Stokely, P. Calcavecchio, R.E. Bare, S.J. Rothenburger, G.S. Douglas, and R.C. Prince. 1995. Nutrient-stimulated biodegradation of aged refinery hydrocarbons in soil. In R.E. Hinchee, G.S. Douglas, Say Kee Ong (Eds.), *Monitoring and Verification of Bioremediation*. Columbus Ohio: Battelle Press.
- Eastcott, Linda, Wan Ying Shiu, and Donald Mackay. 1988. "Environmentally Relevant Physical-Chemical Properties of Hydrocarbons: A Review of Data and Development of Simple Correlations". *Oil and Chemical Pollution* 4 (1988) 191-216.
- Eckberg, David K., and Daniel K. Sunada. 1984. Nonsteady Three-Phase Immiscible Fluid Distribution in Porous Media. *Water Resources Research* 20, no. 12:1891-97.
- Eiceman, G.A., F.R. Sprester, J.L. Gardea and N.Y. Nan. 1985. Distribution of hydrocarbons in soil through contamination from a leaking natural gas pipeline. *Amer. J. Environ. Anal. Chem.* Vol 23, pp 21-35.
- Elmendorf, D.L., C.E. Haith, G.S. Douglas, and R.C. Prince. 1994. Relative rates of biodegradation of substituted polycyclic aromatic hydrocarbons. In R.E. Hinchee, A.E. Leeson, L. Semprini, and S.K. Ong (eds.), *Bioremediation of Chlorinated and Polycyclic Aromatic Hydrocarbon Compounds*. Ann Arbor, Mich.: Lewis Publishers.
- Environmental Systems and Technologies, Inc (ES&T). 1994a. SpillCAD®, Data Management And Decision Support for Hydrocarbon Spills, User and Technical Guide, Version 3.2.

REFERENCES (CONTINUED)

- Environmental Systems and Technologies, Inc (ES&T). 1994b. Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Practical for Site Assessment and Remediation. May 23 - 26, 1994. San Diego, California. Environmental Systems & Technologies, Inc., Blacksburg, Virginia.
- Essaid, H. I. And W. N. Herkelrath, 1993. Simulation of Fluid Distribution observed at a Crude Oil Spill Site Incorporating Hysteresis, Oil Entrapment, and Spatial Variability of Hydraulic Properties. Water Resources Research. 29(b). pp. 1753 - 1770.
- Feenstra, S. 1996. Spatial Variability of Source Zones and Plums. The Princeton Remediation Course, A Short Course by Princeton Groundwater in, Orlando, Florida, June 3 to 7, 1996, 76 pp.
- Fenneman, N. M. 1937. Physiography of the Eastern United States. McGraw Hill. New York.
- Fetter, C. W. 1988. Applied Hydrogeology - 2nd Edition. Merrill Publishing Company, Ohio, 92 p.
- Fetter, C. W. 1993. Contaminant Hydrogeology. Macmillan Publishing Company, New York.
- Fluor Daniel GTI. 1997. Conceptual Design Report: Free Product Hydrocarbon Recovery Operations, Defense Personnel Support Center (DPSC) and the Passyunk Homes Area, Philadelphia, PA. August 22, 1997. Fluor Daniel GTI, West Chester, Pennsylvania.
- Fogel, M. M., A. R., Taddeo, and S. Fogel. 1986. Applied and Environmental Microbiology. 51(4):720-724.
- Freeze, R. A. and J. A. Cherry. 1979. Ground Water. Prentice Hall, Inc., Englewood Cliffs, New Jersey.
- GES. 1993. Groundwater Assessment: Jackson Street Sewer, Pollack Street Sewer, and 26th Street Sewer; Sun Company, Inc. Philadelphia Refinery, Philadelphia, Pennsylvania, 23 September 1993.
- Gibbs, L.M. (1993) How gasoline has changed. In. SAE Technical Paper Series. Fuels and Lubricants Meeting and Exposition. October 18-21, 1993. Philadelphia, Pennsylvania.
- Golden Software. 1997. Surfer[®]. Version 6.0.
- Graham, J. B. 1946. Ground-Water Resources in the Philadelphia Area, Pennsylvania. Report of the Board of Consulting Engineers, Appendix B, South Philadelphia Well Supply, 12 pp.
- Greenman, D. W., D. R. Rima, W. N. Lockwood, and H. Meisler. 1961. Ground-Water Resources of the Coastal Plain Area of Southeastern Pennsylvania. Pennsylvania Geological Survey Water Resource Report 13, 375 pp.

REFERENCES (CONTINUED)

- Guthrie, V. B. 1960. Petroleum Products Handbook. McGraw-Hill Book Company, New York, New York.
- Guymon, G. L. 1994. Unsaturated Zone Hydrology. PTR Prentice Hall, Englewood Cliffs, New Jersey, 210 pp.
- Haggard, John V. 1956. Manufacture of Clothing: 1945-53. QMC Historical Studies, Series II, No. 1. Historical Branch, Office of the Quartermaster General, Washington, D.C. 287 pp.
- Harroun, Inc. 1970. Engineering Soil and Foundation Analysis: Tanks Nos. 128 and 129, South Yard Philadelphia Refinery. Atlantic Richfield Company.
- Hinchee, R. E. and H. J. Reisinger. 1987. Groundwater Monitoring Review, Winter: 84-92.
- Howard, Philip H. 1990. Handbook of Environmental Fate and Exposure Data for Organic Chemicals. Lewis Publishers, Inc., Chelsea, Michigan.
- Hunter Research. 1994. Cultural Resources Survey, Defense Personnel Support Center, City of Philadelphia, Philadelphia County, Pennsylvania. U.S. Army Corps of Engineers, Philadelphia District, Philadelphia, Pennsylvania, dated November 1994.
- Jacob, C. E. 1963. Determining the Permeability of Water-Table Aquifers. U.S. Geological Survey Water-Supply Paper 1536-1, p. 1245-1271.
- Jury, W. A., W. F. Spencer, and W. J. Farmer. 1983. Journal of Environmental Quality, 12:558-564.
- Kaplan, I. R., Y. Galperin, S. Lu, and R. Lee. 1997. Forensic Environmental Geochemistry: Differentiation of Fuel Types, Their Sources, and Release Time. Organic Geochemistry--Linking the Biosphere and the Geosphere. From the Organic Geochemical Division (Geochemical Society) Symposium, 27 October 1996, Denver, Colorado. European Association of Organic Geochemists. Elsevier Science Ltd, London.
- Kaplan, I.R. and Y. Galperin. 1996. How To Recognize Hydrocarbon Fuel In The Environment And Estimate Its Age Of Release. Groundwater and Soil Contamination: Technical Preparation and Litigation Management" by Thomas J. Bois and Bernard J. Luther, John Wiley & Sons, July 1996.
- Kaplan, I.R., Galperin, Y., Alimi, H., Lee, R.P. and Lu, S.T. 1996. Patterns of chemical changes during environmental alteration of hydrocarbon fuels. Groundwater Monitoring and Remediation 16 (4), 113-124.
- Karickhoff, S. 1985. "Pollutant Sorption in Environmental Systems," in Environmental Exposure From Chemicals. Vol. 1. W. Brock Neely and Gary E. Blau, eds. Boca Raton, FL: CRC Press, Inc. pp. 49-64.

REFERENCES (CONTINUED)

- Kemron/Versar. 1995. Remedial Investigation/Feasibility Study, Defense Personnel Support Center, Philadelphia, Pennsylvania. U.S. Army Corps of Engineers, Baltimore District, Baltimore, Maryland.
- Land, C. S. 1968. Calculation of Imbibition Relative Permeability for Two- and Three-Phase Flow from Rock Properties. Trans. Am. Inst. Min. Metall. Pet. Eng. 243 (149-1565).
- Lane, J.C. (1980) Gasoline and other motor fuels. In Kirk-Othmer Encyclopedia of Chemical Technology, ed. M. Grayson, Vol 11, pp 652-695, John Wiley and Sons, New York.
- Lenhard, R. J. and J. C. Parker. 1990. Estimation of Free Hydrocarbon Volume from Fluid Levels in Observation Wells. Ground Water. V 28, p 57-67.
- Levorsen, A. I. 1967. Geology of Petroleum. Second Edition. W. H. Freeman and Company, San Francisco, 689 pp.
- Lide, David R. 1993. CRC Handbook of Chemistry and Physics, 74th Edition. CRC Press. Ann Arbor, Michigan.
- Lyman, W. J., W. F. Reehl, and D. H. Rosenblatt. 1982. Handbook of Chemical Property Estimation Methods. McGraw-Hill Book Company, pp. 4-1 through 4-33.
- Malcolm Pirnie, Inc. 1996. Draft Final Phase II Expanded Site Investigation Report and Quality Control Summary Report for Defense Personnel Support Center, Philadelphia, Pennsylvania, March 1997. US Army Corps of Engineers, Baltimore District, Baltimore, Maryland.
- Malcolm Pirnie, Inc. 1997a. Draft Final NAPL Plume Study for Defense Personnel Support Center, Philadelphia, Pennsylvania, March 1997. US Army Corps of Engineers, Baltimore District, Baltimore, Maryland.
- Malcolm Pirnie, Inc. 1997b. Response to Sun Company, Inc. - June 1997, August 1997.
- Manly, B.F.J. 1986. Multivariate statistical methods. A primer. Chapman and Hall, London, (1986).
- McAuliffe, C. 1966. Solubility in water of paraffin, cycloparaffin, olefin, acetylene, cycloolefin and aromatic hydrocarbons. Journal of Physical Chemistry 70(4). Pp 1267-1275.
- McMillen, S.J., N.R. Gray, J.M. Kerr, A.G. Requejo, T.J. McDonald, and G.S. Douglas. 1995. Assessing Bioremediation of Crude Oil in Soils and Sludges. In R.E. Hinchee, G.S. Douglas, Say Kee Ong (Eds.), Monitoring and Verification of Bioremediation. Columbus Ohio: Battelle Press.
- Metcalf and Eddy, Inc.. 1991. Wastewater Engineering: Treatment, Disposal, and Reuse. Third Edition. McGraw Hill, Inc., New York, New York, 1240 pp.

REFERENCES (CONTINUED)

- Miget, R. J., H. Oppenheimer, H. I. Kator, D. A. Larock. 1969. Proceedings of the Joint Conference on prevention and Control of Oil Spills. American Petroleum Institute. Washington, D.C. pp. 237-331.
- Owens, J. P. and J. P. Minard. 1979. Upper Cenozoic Sediments of the Lower Delaware Valley and the Northern Delmarva Peninsula. New Jersey, Pennsylvania, Delaware, and Maryland.: U.S. Geological Survey Professional Paper 1067-D, 47p.
- Page, D.S., P.D. Boehm, G.S. Douglas, and A.E. Bence. 1995. Identification of hydrocarbon sources in benthic sediments of Prince William Sound and the Gulf of Alaska following the *Exxon Valdez* oil spill. In: Exxon Oil Spill: Fate and Effects in Alaskan Waters, ASTM Special Technical Publication #1219, Peter G. Wells, James N. Butler, and Jane S. Hughes, eds., American Society for Testing and Materials, Philadelphia, 1995.
- Page, D.S., P.D. Boehm, G.S. Douglas, A.E. Bence, W.A. Burns, and P.J. Mankiewicz. 1997. Pyrogenic polycyclic aromatic hydrocarbons in sediments record past human activity: A case study in Prince William Sound Alaska. Submitted to Marine Pollution Bulletin. (Submitted 3/6/97)
- Page, D.S., P.D. Boehm, G.S. Douglas, A.E. Bence, W.A. Burns, and P.J. Mankiewicz. 1997. An estimate of the annual input of natural petroleum hydrocarbons to seafloor sediments in Prince William Sound, Alaska. Marine Pollution Bulletin. (in press).
- Page, D.S., P.D. Boehm, G.S. Douglas, A.E. Bence, W.A. Burns, and P.J. Mankiewicz. 1996. The natural petroleum hydrocarbon background in subtidal sediments of Prince William Sound, Alaska, USA. *Environmental Toxicology and Chemistry*. Vol 15, No. 8, pp 1266-1281.
- Parker, J. C., R. J. Lenhard, and T. Kuppusamy. 1987. A Parametric Model for Constitutive Properties Governing Multiphase Flow in Porous Media. Water Resource Res., v 23, p 618-624.
- Parker, J. C., J. J. Kaluarachchi, V. J. Kremesec, and E. L. Hockman. 1990. Modeling Free Product Recovery at Hydrocarbon Spill Sites. Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water. NWWA, p 641-655.
- Parker, J. C. 1994. Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Practical Models for Site Assessment and Remediation. A Short Course by ES&T and IGWMC in San Diego, California, May 23 to 26, 1994.
- Paulachok, G. N. and C. R. Wood. 1984. Water-Table Map of Philadelphia, Pennsylvania. 1976-1980. U.S. Geological survey Hydrologic Investigations Atlas HA-676, 1 sheet, scale 1:50,000.
- Paulachok, G. N., C. R. Wood, and L. J. Norton. 1984. Hydrologic Data for Aquifers in Philadelphia, Pennsylvania. U.S. Geological Survey Open-File Report 83-149, 104 pp.
- Paulachok, G. N. 1991. Geohydrology and Ground-Water Resources of Philadelphia, Pennsylvania. U.S. Geological Survey Water-Supply Paper 2346, 79 pp.

REFERENCES (CONTINUED)

- Perry, Robert H. and Don W. Green, Editors. 1997. Perry's Chemical Engineers' Handbook, 7th Edition. McGraw Hill. New York, New York.
- Philadelphia Quartermaster. 1944. Illustrative Appendix. A History of Storage and Distribution at the Philadelphia Quartermaster Depot, 1917 - 1943, December 1944.
- PRC Environmental. 1994. Environmental Baseline Survey for Defense Personnel Support Center, Philadelphia. Defense Logistics Agency, Alexandria, Virginia, dated December 16, 1994.
- Prince, R.C., E.N. Drake, P.C. Madden, and G.S. Douglas. 1997. Biodegradation of polycyclic aromatic hydrocarbons in historically contaminated soil. In *proceedings: 1997 Bioremediation Conference*, New Orleans, April 28-30.
- Prince, R.C., E.N. Drake, S.J. Rothenburger, Karen E. Stokely, and G.S. Douglas. 1996. Biodegradation of polynuclear aromatic hydrocarbons in the environment. In *Proceedings: American Chemical Society Meeting: Division of Environmental Chemistry*. New Orleans, LA, March 24-29.
- Prince, R.C., J.R. Clark, J.E. Lindstrom, E.L. Butler, E.J. Brown, G. Winter, M.J. Grossman, P.R. Parrish, R.E. Bare, J.F. Braddock, W.G. Steinhauer, G.S. Douglas, J.M. Kennedy, P.J. Barter, J.R. Bragg, E.J. Harner, and R.M. Atlas. 1994. Bioremediation of the Exxon Valdez oil spill: Monitoring safety and efficacy. In R.E. Hinchee, B.C. Alleman, R.E. Hoeppel, R.N. Miller (Eds.), *Hydrocarbon Bioremediation*. Ann Arbor, Mich.: Lewis Publishers.
- Prince, R.C., D.L. Elmendorf, J.R. Lute, C.S. Hsu, C.E. Haith, J.D. Senius, G.J. Dechert, G.S. Douglas, and E.L. Butler. 1994. 17a (H) 21 β (H)-hopane as a conserved internal marker for estimating the biodegradation of crude oil. *Environ. Sci. Technol.* Vol. 28, No. 1. pp 142-145.
- Prince, R.C., S.M. Hinton, J.R. Bragg, D.L. Elmendorf, J.R. Lute, M.J. Grossman, W.K. Robbins, C.S. Hsu, G.S. Douglas, R.E. Bare, C.E. Haith, J.D. Senius, V. Minak-Sernero, S.J. McMillen, J.C. Roffall, and R.R. Chianelli. 1993. Laboratory studies of oil spill bioremediation; toward understanding field behavior. ACS.
- Reinout L., W. Pool, M. van Vulpen, R. D. Norris. 1995. In Situ Electrobioreclamation in Low-Permeability Soils. *Applied Bioremediation of Petroleum Hydrocarbons*, R. E. Hinchee, J. A. Kittel, and H. J. Reisinger, ed. Battelle Press, Columbus, Ohio, pp. 287-292.
- Reisinger, H. J. 1995. Hydrocarbon Bioremediation - An Overview. *Applied Bioremediation of Petroleum Hydrocarbons*, R. E. Hinchee, J. A. Kittel, and H. J. Reisinger, ed. Battelle Press, Columbus, Ohio, pp. 1-9.
- Roberts, A. J. and T. C. Thomas. 1986. Characterization and Evaluation of JP-4, Jet-A, and Mixtures of These Fuels in Environmental Water Samples. *Environmental Toxicology and Chemistry*. Volume 5, pp. 3-11.

REFERENCES (CONTINUED)

- Van Genuchten, M. Th. 1980. A Closed-form Equation for Predicting the Hydraulic Conductivity of Unsaturated Soils. *Soil Science Society of America Journal*, v. 44:p 892-898.
- Vogel, T. M. and P. L. McCarty. 1985. *Applied and Environmental Microbiology*. 49 (5):1080-1083.
- Weber, Walter J., Jr., and GiGiano, Francis A. 1996. Process Dynamics In Environmental Systems. John Wiley & Sons, Inc. New York, New York.
- West, T. F. and G. A. Campbell. 1952. *DDT and Newer Insecticides*. Chemical Publishing Co., Inc., New York, New York.
- Wold, S., K. Esbensen and P. Geladi. 1987. Principal Component Analysis. *Chemometrics and Intelligent Laboratory Systems* 2, pp 37-52.
- Zimmerman, O. T. and Irvin Lavine. 1946. *DDT: Killer of Killers*. Industrial Research Service, Dover, New Hampshire.