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Literature Survey

Subsurface and Groundwater Protection Related to Petroleum Refinery Operations

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American Petroleum Institute
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Refining Department

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Petroleum
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FOREWORD

This literature survey was conducted under the direction of the API Committee on Refinery Environmental Control. The purpose of the study was to determine by means of a literature search what information has been published relating to the impact of petroleum refinery operations on subsurface soils and on groundwater with special reference to potential contamination problems.

The survey was performed by Woodward-Clyde Consultants under contract to the American Petroleum Institute.

Questions concerning the contents of this report should be addressed to the director of the Refining Department, American Petroleum Institute, 1220 L Street, NW, Washington, DC 20005.

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TABLE 1 REFINERY GROUNDWATER AND SUBSURFACE OUTLINE

LITERATURE SURVEY: SUBSURFACE AND GROUNDWATER PROTECTION RELATED TO PETROLEUM REFINERY OPERATIONS

1.0 INTRODUCTION

This report is the principal product of a study under contract to the American Petroleum Institute (API) to prepare the background basis for development of a series of monographs on subsurface and groundwater protection at petroleum refineries.

The study was designed to determine by a literature search what information has been published relating to the impact of petroleum refinery operations on subsurface soils and on groundwater with special reference to potential contamination problems. The study addresses this overall objective in the following phases:

1. Conducting a detailed literature search for existing publications, reports, papers, etc. that address specific topics enumerated in the initial outline prepared by the API (Table 1).
2. Preparation of an annotated bibliography for each pertinent literature citation based upon a review of the publications.
3. Supplying copies of the literature cited in the annotated bibliography.
4. Identifying topics for which no literature could be found and additional topics identified during the study for which literature is available and which are pertinent to refinery groundwater and subsurface soil considerations.

In accordance with the objectives of the study, this report contains: (1) an explanation of how the literature search was conducted, (2) annotations for pertinent articles, (3) a list of references including articles annotated and articles reviewed but not annotated, (4) a discussion of applicable Federal Statutes and Regulations, and annotations for pertinent regulatory programs under the five principal statutes that apply to petroleum refinery operations, and (5) a discussion of elements of the Refinery Groundwater and Subsurface Outline for which few or no references were found.

With respect to Item 4, the principal area in which the literature is notably deficient is low toxicity inorganic wastes produced at refineries. Other than textbook and manual coverages, the literature search yielded few references to common refinery contaminants of low toxicity, such as sulphides, chloride, phenols and nitrogen compounds, and spent acids and alkalis. Although these compounds make up the bulk of potential pollutants from refineries, they are handled routinely in wastewater treatment systems and are not generally perceived by the public or regulators as posing severe problems requiring remediation. This tolerant perception is likely to change, however, especially with respect to phenol compounds. Phenol, for example, is classed a hazardous chemical and was included in the list of priority pollutants under Section 110 of SARA (Superfund Amendments and Reauthorization Act), which may require regulation under the Safe Drinking Water Act. The federal water qualify criteria for carcinogenic risk at the 10^{-5} level is 3.5 ug/l for phenol. Furthermore, at least 23 states include phenol in Water Quality Standards or Criteria for protection of aquatic life.

Liquid effluents generally are treated by physical separation of oily components, chemical flocculation, and biological treatment (including biooxidation, trickling filters, or activated sludge treatment). The cleaned water, containing dissolved inorganic matter generally is discharged to surface waters, leaving a residue of organic and inorganic sludge consisting of mineral particles, recalcitrant organic compounds, and metals (mainly chromium, lead, and zinc). The sludge is commonly disposed of by land farming, which allows further biodegradation of recalcitrant organics including polynuclear aromatic hydrocarbons (PAHs).

Solid refinery wastes comprise a wide range of materials in addition to sludges, including spent metal catalysts, treatment clays, filter cake, ash, silt, etc. Some of these materials, such as spent metal catalysts, have value and, therefore, are recycled. However, most other solids have little salvage value, and if nonhazardous are disposed of mainly as landfill.

Information on the treatment and disposal of inorganic liquid and solid waste is scattered throughout the sanitary engineering literature and commonly is not identified as refinery or petroleum industry waste. Searching the literature for references only indirectly applicable to impacts of petroleum refining on groundwater would not be cost-effective in view of the ready availability of information on industrial waste treatment in textbooks and manuals.

2.0 THE LITERATURE SEARCH

The information needed for this project was obtained from computer and manual searches of the principal data bases relating to petroleum refining and groundwater. These were the API Central Abstracting and Indexing Service (CAIS) Data Base, the CAS ONLINE System of the American Chemical Society, the National Technical Information Service (NTIS), and Ground-Water On-Line, the National Ground Water Information Center Data of the National Water Well Association.

Manual searching of conference proceedings and published literature searches was employed to supplement the computer search, and as a quality check on the computerized data systems.

2.1 Computer Search

Carrying out a computer search required that a descriptor list be compiled that would lead to printouts of appropriate references without overwhelming the searcher with great masses of irrelevant material. It was found necessary to adapt this basic list to fit specific data systems, which have a thesaurus of terms that must be used to access their system.

The several data bases provided access to several hundred thousand references. CAS ONLINE, for example, draws upon 12,000 scientific and technical journals published in 140 nations. The computer searches yielded a total of 559 citations. Review of these citations indicated that 117 merited follow-up, after exclusion of foreign language sources, news magazine citations, redundancy and citations not appropriate to the project.

2.2 Manual Search

As many citations were to proceedings of conferences addressed to petroleum releases to groundwater, and to published literature searches on various aspects of these topics, these sources were scanned directly for additional citations. In this fashion, a target list of 1,375 citations to articles in English and pertinent to petroleum and groundwater contamination was compiled, which includes the 117 citations from the computer searches. The list includes such diverse topics as: gasoline spills from pipelines and service stations, land farming of refinery wastes, prevention and detection of tank leaks, biodegradation of hydrocarbons in the unsaturated zone, and management of hydrocarbon vapors in the subsurface, to name but a few. Although the majority of references annotated are not specific to refinery properties, essentially all are deemed to have at least some transfer value to refinery operations as related to ground water.

3.0 ANNOTATION PROCESS

Annotations were prepared following review of the subject document. They contain a brief description as appropriate to the author's approach, followed by a summary of the principal conclusions. In a small percentage (less than 10 percent) of the articles, the author's abstract was suitable for use without material modification. However, in general, authors' abstracts failed to describe the approach, and/or were not explicit about results.

The annotations are arranged alphabetically within four sections corresponding to the principal topic headings of the Groundwater and Subsurface Outline (Table 1); namely, prevention, detection and assessment, containment and cleanup, and regulatory background. Articles that spanned more than a single topic were classified according to the principal focus. Of the 111 articles annotated, 41 percent were classified as containment and cleanup, 29 percent as prevention (including equipment and operating practices), 26 percent as detection and assessment, and 4 percent as regulatory background. The regulatory component has been augmented by annotations to Federal statutes and regulations. In considering the breakdown shown above, it is well to keep in mind that some bias is built into the classification of containment and cleanup as compared to detection, because all descriptions of cleanups necessarily involve an element of detection of a problem before cleanup is undertaken and monitoring of the results. The same sort of overlap, however, does not apply to the other categories.

4.0 PREVENTION ANNOTATIONS

Annotations grouped under the heading Prevention lend themselves to a three-way subdivision into: (1) operational manuals, (2) articles describing ways of preventing groundwater contamination, and (3) land farming as a means of disposal of oil wastes, generally limited to refineries because of scale. In each subdivision some annotations are specific to refinery operations, some apply industry-wide, while some are specific to service station or petroleum transport and storage facilities. The latter group have been annotated because of their possible transfer value to refinery operations.

Manuals annotated include that of API on Disposal of Refinery Wastes, and the New York State "Recommended Practices for Underground Petroleum Storage", "Recommended Practices for Aboveground Storage of Petroleum Products" and "Technology for the Storage of Hazardous Liquids: A State of the Art Review" which apply to all aspects of the industry including refineries. API's "Recommended Practices for Bulk Liquid Stock Control at Retail Outlets" was annotated because stock control may apply to refinery operations as a means of avoiding groundwater contamination.

Of annotations on preventing groundwater contamination, five, by Blokker (1971), Geraghty and Miller (1980) and (1980), Knowlton (1985), and Thompson and Kuhlthau (1980) were specific to refineries. Five annotations applied to the petroleum industry generally and focused mainly on prevention and detection of underground tank leaks as a means of avoiding groundwater contamination, but included also articles on training of personnel, underground tank-spill risk analysis, and application of hydraulic protection methods to alleviating contamination hazards.

Land treatment is widely applied at refineries for disposal of organic waste in a way that poses minimal threat to groundwater supplies. Accordingly, several annotations deal with various aspects of land treatment of wastes. All the annotations can be considered as directly applicable to refinery operations because wastes generated elsewhere in petroleum operations generally do not justify the scale required for land treatment of oily wastes. API Pub. No. 4379 (1984) and Pal and Overcash (1980) present general overviews of land-treatment methods and their effectiveness. Several articles, including Bossert et al (1984), Sims and Overcash (1983), Weldon (1979), Streebin et al (1984), Bulman et al (1985), and Loehr et al (1985) focus on the fate of organic and inorganic constituents of oily wastes and land-treatment biodegradation rates. Other annotations deal with specific aspects of land treatment or specific locations, including sorption of polyaromatic hydrocarbons, Means et al (1980); separator-sludge degradation, Bagwandoss et al (1984); tank sludge, Mucsy et al (1984); crude-oil degradation by land treatment in Alaska, Mitchell et al (1979); sludge degradation in Eastern Canada, Norris (1981), low temperature land treatment, Loynachan (1978); and codisposal of oily wastes with municipal waste; Barber et al (1984).

To summarize the section on Prevention, the annotations indicate that: (1) with continued emphasis on refinery operations and training, the amounts of liquid wastes requiring treatment may be minimized, thereby reducing cost and lowering risk to groundwater, (2) the health effects of refinery operations as related to groundwater have generally been minor, and (3) land treatment of refinery wastes have had minimal impact on groundwater supplies due to the effectiveness of biodegradation, and the low solubility and high sorption of less degradable compounds.

American Petroleum Institute, "Manual on Refinery Wastes - Volume on Solid Wastes", Amer. Petrol. Inst., Washington, D.C., 27, 1980.

Discusses the impact of the Resources Conservation and Recovery Act (RCRA) on refinery operations as related to solid waste disposal. Suggest that refiners review their operations regarding: (1) relations with off-site waste disposers, (2) consideration of onsite treatment, storage, and disposal of wastes, (3) determination of alternatives to waste disposal, and (4) consideration of economics of waste segregation to reduce hazardous components.

The manual examines methods of source reduction as an alternative to disposal, resource recovery of process chemicals. and pre-treatment including concentration, incineration, pyrolosis. It concludes with a discussion of landfill and land farming as ultimate disposal of wastes with helpful information on ways to improve efficiency in both areas.

American Petroleum Institute, "The Land Treatability of Appendix VIII Constituents Present in Petroleum Industry Wastes", API Pub. No. 4379, 108p, appends, 1984.

Reports on a literature review of land treatment of petroleum-refinery wastes, with special reference to Appendix VIII (40 CFR 261) constituents, the so-called priority pollutants which include some 350 chemicals.

Land treatment has been used for more than 25 years to dispose of refinery wastes. The general approach is to mix the waste into the uppermost 1-foot of soil at a designed rate based on soil and climatic characteristics and other site-specific factors governing degradation rates. Approximately 50% of refinery wastes currently are disposed of in this fashion including most oily process wastes and bio-sludges from waste-water treatment systems. Total land treatment in the U.S., is about 72,000 tons per year.

The major degradation processes are aerobic biodegradation, chemical reactions with soils, and photo-chemical degradation. The principal classes of wastes disposed of by land treatment are monoaromatic hydrocarbons, polynuclear aromatic hydrocarbons (PAHs), phenolics, and phthalate esters. Toluene and naphthalene are the major components of oily wastes. The average removal rate of oily compounds is 78% per year. Approximately 10 to 30% of oily wastes accumulate in the soil during the active life of a land treatment facility. After termination these organics degrade slowly without special treatment.

Those priority pollutants in refinery wastes that are not subject to degradation, such as heavy metals and high molecular weight PAHs generally are poorly soluble in water and are immobilized by adsorption on clay minerals in the soil zone.

Properly designed and operated land treatment facilities can degrade or immobilize all the Appendix VIII constituents in refinery wastes. Locally increase in salinity may be of greater concern because the dissolved load of common inorganic constituents is not effectively reduced in land treatment.

American Petroleum Institute, "Recommended Practice for Bulk Liquid Stock Control at Retail Outlets", API Pub. No. 1621, pp. 1-7, appends., 1980.

Presents a manual for stock control at service stations, and recommends maintaining a daily inventory record in which a balance is maintained of deliveries, sales, onsite use, and inventory on hand. The average variance ranges from +0.27 to -0.40 percent. Although small variability should be expected, losses should not exceed 0.50 percent on a regular basis. Losses above this level, especially over extended periods, are suggestive of underground leakage. Other indicators are sudden unexplained variance from an established pattern, or small but growing daily losses.

Detailed procedures are given for inventory accounting, and for distinguishing between leakage, and other losses such as surface spillage, thefts and meter inaccuracy.

Bagwandoss, K. M., L. E. Streebin, J. M. Robertson, and P. T. Bowen, "Degradation of Petroleum Fractions from Oil Refinery Wastes - A Land Treatment Study", Proc., NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals - Prevention, Detection and Restoration, Nat'l. Water Well Association, Dublin, OH, 82-98, 1984.

Summarizes results of tests on fifty 9 x 30-foot plots treated at different loading rates and frequencies with API separator sludge from a refinery processing sweet crude. The focus was on degradation of oily fractions(asphaltenes, saturates, polar compounds, and aromatics) which were analyzed by fractionating oil extracted from the soil-oil matrix. The fractions are defined as follows: asphaltenes, pentane insolubles that can be separated from a solution of oil-in-n-pentane; saturates, material that on percolation in a n-pentane eluent is not adsorbed on clay or silica gel; polar compounds, materials adsorbed on clay after percolation in a n-pentane eluent; aromatics, materials that on percolation pass through adsorbent clay in n-pentane but are adsorbed on silica gel.

The concentrations of oil fractions applied were (in percent) asphaltenes, 1.5 to 4.3; saturates, 30 to 60; polar compounds, 43 to 58; and aromatics, 17 to 30. The overall losses on typical plots were 72 to 82 percent. Individual fraction losses were: asphaltenes 36-75%, saturates, 77-89%; polar compounds, 45-58%; and aromatics, 81-83%. Some variance was due to transformation of compounds from one fraction to another through biodegradation.

The most active degradation occurred in summer and fall; there was little degradation during cold winter months.

Barber, C., P. J. Maris, S. C. Bull and R. G. Johnson, "Codisposal of Oil Wastes with Domestic Solid Wastes in Landfills: Leaching and Persistence of Oil", Proc., Hazardous and Industrial Waste Management and Testing: Third Symposium, Am. Soc. Testing and Materials, Philadelphia, Spec. Tech. Publ. 851, 152-170, 1984.

Controlled landfill offers a possible alternative for the disposal of oily wastes, and research has been carried out in Great Britain to assess the impact of these practices using laboratory simulations and a site study.

These studies showed that oil emulsions (cutting oil and mousse) were rapidly broken down to free oil and an associated aqueous phase in the landfill. The oil was readily sorbed by domestic waste solids, whereas the aqueous phase was flushed out with leachate. Concentrations of oil in leachate were, in most cases, similar to those found in leachate from domestic wastes only (within the range of 5 to 10 mg/L). It was probable that under anaerobic conditions in the fill, oil was not significantly degraded by microorganisms, small losses of oil being mainly due to leaching.

It is concluded that water pollution (surface or groundwater) from the disposal of small volumes of oil wastes with domestic wastes will not be significantly greater than pollution by leachates from domestic wastes only. It is possible that, at small landfills, disposal of excessive quantities of aqueous oil emulsion wastes could exceed the sorptive capacity of the domestic wastes and give rise to leaching of oil.

The persistence of oil in a landfill for long periods of time is an additional problem, which has consequences for the long-term development of land "reclaimed" with wastes containing oils.

Blokker, P. C., "Prevention of Water Pollution from Refineries", in Water Pollution by Oil, P. Hepple (ed) Inst. of Petroleum, London, 21-36, 1971.

To maintain a low cost to benefit ratio in the remediation of water pollution, minimum requirements for refinery-effluent disposal in rivers should be set along with minimum standards for the quality of receiving water.

A summary of refinery operations is given. Based on these operations the main sources of pollution are: desalter effluent water, sour condensates, and phenolic condensates from cracking operations.

Suggested methods to decrease water pollution by refineries are: improve drainage systems, reduce cooling water and process water, stripping sulphides from process waters, remove oil by use of separators, remove oil and suspended solids by chemical flocculation, remove suspended solids by air flotation, remove dissolved oxygen consuming contaminants by biological purification, de-water sludge and incinerator ash as landfill.

Because of the high cost of effluent treatment other than by gravity oil separation, secondary treatment should only be used when essential.

Bossert, I., W. M. Kachel, and R. Bartha, "Fate of Hydrocarbons during Oily Sludge Disposal in Soil", Applied and Environmental Microbiology, V. 47, No. 4, 763-767, 1984.

A 1,280-day laboratory simulation of the "landfarming" process explored the fate in soil of polynuclear aromatics (PNAs) and total extractable hydrocarbon residues originating from the disposal of an oil sludge. In addition to the measurement of CO_2 evolution, periodic analyses of PNAs and hydrocarbons monitored biodegradation activity. The estimation of carbon balance and of soil organic matter assessed the fate of residual hydrocarbons. Seven sludge applications during a 920-day active disposal period were followed by a 360-day inactive "closure" period with no further sludge applications. A burst of CO_2 evolution followed each sludge addition, but substantial amounts of undegraded hydrocarbons remained at the end of the study. Hydrocarbon accumulation did not inhibit biodegradation performance. Conversion of hydrocarbons to CO_2 predominated during active disposal; incorporation into soil organic matter predominated during the closure period. In this sludge, the predominant PNAs were degraded more completely (85%) than total hydrocarbons. Both biodegradation and abiotic losses of three- and four-ring PNAs contributed to this result. Some PNAs with five and six rings were more persistent, but these constituted only a small portion of the PNAs in the sludge. The study confirmed that the microbially mediated processes of mineralization and humification remove sludge hydrocarbons from soils of landfarms with reasonable efficiency.

Brostoff, F. E., "Industry Training and Education in Spill Prevention (...Detection and Response)", Proc., NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water - Prevention, Detection, and Restoration, Nat'l. Water Well Association, Dublin, OH, 1-10, 1984.

Author stresses the need for an aggressive company training campaign reaching out to operating personnel to achieve maximum results in reducing operating spills. He outlines a campaign utilizing posters, bulletins, slide tapes, audioscans, and videotapes in the areas of spill prevention, inventory control, and leak/spill response. The key to success is to get operating personnel to think "environment" in the course of day-to-day activities.

Bulman, T. L., S. Lesage, P. J. A. Fowlie, and M. D. Webber, "The Persistence of Polynuclear Aromatic Hydrocarbons in Soil", PACE Rept. No. 85-2, Petroleum Assn. for Conservation of Canadian Environment, Ottawa, 51 p., appends.,1985.

Reviews information on sources and properties of polynuclear aromatic hydrocarbons (PAHs) and processes affecting their disposition when disposed of to soil; and presents results of field experiments to define the fate of PAHs in agricultural soils.

In general as molecular weight of PAH compounds increases, solubility decreases, and bioaccumulation potential, log octanol/water coefficient, and sorption coefficient all increase. The fate of PAHs in soils are of importance in refinery operations because waste-water treatment systems yield large volumes of PAH rich sludge which commonly is treated by land farming.

Measured amounts of naphthalene, phenanthene, anthracene, fluoranthene, pyrene, benzo(a) anthracene, chrysene, and benzo(a) pyrene (in order of increasing molecular weight) were added to agricultural soils and their disappearance over time was monitored. The low molecular weight components - naphthalene, phenanthrene, anthracene, fluoranthene, and pyrene - were reduced by 94-100 percent in 200 days; while the higher molecular weight compounds - benzo(a) anthracene, chrysene, and benzo(a) pyrene - were reduced by only 22-88 percent in 400 days. The half lives of benzo(a) pyrene were found to be 347 and 218 days for 5 and 50 mg/kg treatments, respectively.

In another field test carbon-14 labeled benzopyrene and fluoranthene were added to soil, and the distributioin of C-14 as volatile, adsorbed, or degraded product was determined. The anthracene decrease was ascribed mainly to volatilization and adsorption, while that for benzopyrene was due largely to adsorption. Microbial transformation of benzopyrene was negligible.

It was concluded that annual loadings exceeding 50 kg/ha for phenanthrene; 10 kg/ha for anthracene, fluoranthene, and pyrene; and 0.2-0.4 kg/ha for benzo(a) anthracene, chrysene, and benzo(a) pyrene likely would result in accumulation of those PAHs over time. However, the less degradable compounds are also the least mobile in solution.

Curran, S. D., "Prevention and Detection of Leaks from Underground Gasoline Storage Systems", Proc., Sixth Nat'l Ground-Water Quality Symposium, Nat'l Water Well Association, Dublin, OH, 93-100, 1982.

This paper presents general state-of-the-art technology and other development work underway in the field of underground petroleum storage leak prevention and detection methods as a means to reduce the potential of groundwater contamination. Underground product leaks occur as a result of mechanical or corrosion failures in storage tank systems. Mechanical failures are normally due to faulty installations but may result from subtle soil movements, such as those along natural fault lines, freeze/thaw cycles and natural subsidence. In addition, violent natural phenomena such as earthquakes, can result in loosened fittings and/or ruptured lines and tanks.

The primary cause of leaks in steel underground storage systems is corrosion, a continuing process that makes the precise time at which failure occurs difficult to determine. The factors that contribute to corrosion failure include tank installation, tank age, soil type, water-table level and the presence of electrical currents. To minimize corrosion failure of existing underground storage systems, preventive methods such as cathodic protection and interior and exterior coatings have proven effective. For newly installed storage-tank systems the use of non-corrosive materials (fiberglass reinforced plastic) has greatly enhanced the integrity and longevity of underground storage systems. Additionally, a detailed evaluation of varying sub-surface environments prior to new installations can aid in the prevention of corrosion.

Leak detection methods include tank and line tightness testing and continuous leak monitoring. Tightness testing of underground tankage on a one-tme basis can be effective in identifying existing leakers, but this periodic form of testing will likely not detect a leak at the time it occurs. Other methods have been proposed to continuously monitor underground systems for leaks, including line leak detectors, observation wells and strict inventory control.

Edwards, N. T., "Polycyclic Aromatic Hydrocarbons (PAHs) in the Terrestrial Environment - A Review", Journal of Environmental Quality, V. 12, No.4., 427-441, 1983.

This review, while touching on sources of polycyclic aromatic hydrocarbons (PAHs) and their degradation, emphasizes research that addresses their fate in the terrestrial environment. Typical ambient concentrations of PAHs in soil and vegetation range from 1 to 10 ug/kg and from 10 to 20 ug/kg, respectively, which are due to plant synthesis, forest and prairie fires, volcanoes, etc. Anthropogenic sources are primarily from fossil-fuel burning. Estimated annual release of benzo(a)pyrene (BaP) from fossil-fuel combustion is 4.6×10^6 kg. Concentrations of PAHs in air, soil, and vegetation vary with distances from known sources. Reported BaP concentrations in air of nonurban areas of the United States ranged from 0.01 to 1.9 ug/m^3; concentrations in urban areas ranged from 0.1 to 61.0 ug/m^3. Concentrations of BaP in soil may typically reach 1,000 ug/kg, and values exceeding 100,000 ug/kg have been reported near known sources. Typically, concentrations for total PAHs (usually the sum of 5 to 20 PAHs) exceed BaP concentrations by at least one order of magnitude.

The maximum PAH concentration in vegetation growing near a known source was 25,000 ug/kg, but values more typically range from 20 to 1,000 ug/kg. Reported BaP concentrations in vegetation ranged from 0.1 to 150 ug/kg. Concentrations in vegetation were generally less than those in soil where the plants were growing. Concentration ratios (concentration in vegetation/concentration in soil) ranged from 0.0001 to 0.33 for BaP and from 0.001 to 0.18 for the sum of 17 PAHs tested. However, laboratory experiments demonstrated that plants can concentrate PAHs above those found in their environment. Controlled experiments with a few PAHs demonstrated uptake by both leaves and roots and subsequent translocation to other plant parts. Washing leaves of vegetation contaminated with PAHs removes no more than 25% of the contamination. There is some evidence that plants can catabolize PAHs, but metabolic pathways have not been well defined.

Geraghty and Miller, Inc., "Assessment Guide for Refinery Wastewater Impoundment Impacts on Ground Water", Consultants Report to Amer. Petroleum Inst., Washington, D.C., 1-83, 1980.

Presents guidelines for use by refinery operators for evaluating the impact of their waste impoundments on groundwater resources and to assist in design of groundwater data programs needed for compliance with environmental regulations. The guidelines describe the principles of groundwater occurrence and movement, the movement of contaminants in ground water, and philosophy of groundwater monitoring.

The parameters needed to evaluate the hydrologic regime are given together with methods of estimating these parameters. Finallly an example of a typical assessment is presented. The criteria for the assessment include flooding potential, earthquake potential, flow rate in the unsaturated zone, flow rate in the saturated zone, point of discharge, groundwater quality, and regional water-supply sources.

Geraghty and Miller, Inc., "Assessment of Potential Hazard to Ground Water Posed by Refinery Wastewater Impoundments", Consultants Report to Amer. Petroleum Inst., Washington, D.C., 1-89, appends, 1980.

An unpublished but more comprehensive treatment of work annotated under Thompson, W.E., and R.H. Kuhlthau, 1980. Includes work sheets for compliance assessment of ten selected refineries' impoundments.

Jenkins, T. F., D. C. Leggett, and C. J. Martel, "Removal of Volatile Trace Organics from Wastewater by Overland Flow Land Treatment", Jour. Environ. Sci. Health, V. A15, No. 3, 211-224, 1980.

A prototype overland-flow land treatment system was studied to determine its effectiveness in removing volatile trace organics in municipal wastewater. Chlorinated primary wastewater, surface water collected from different points downslope, and runoff were applied at the top of a vegetated, gentle slope of low permeability soils and collected downslope in ditches. These samples were analyzed by a gas chromatograph/mass spectrometer unit with purge and trap sampler.

Results showed the efficient removal of many volatile organic substances including chloroform and toluene from the wastewater. Treatment is achieved by a combination of sedimentation, biochemical degradation, and plant uptake and possibly volatilization.

Knowlton, H.E., "A Discussion of Groundwater Contamination and Petroleum Refineries", Proc., Seminar on Groundwater and Petroleum Hydrocarbons, Petrol. Assoc. for Conservation of the Canadian Environment, Ottawa, XII-1 - XII-15, 1983.

The article outlines the principal sources of oil-refinery wastes as oily sludges, acid sludges, alkylation sludges, tank-water draws, tank leaks, line breaks, and spillage, and recommends corrective measures for on-site cleanup. The author recommends on-site cleanup as generally more effective than removal to off-site landfills, and stresses the importance of consideration of the resource value of oil wastes.

Oily sludge can be stabilized with cement-kiln dust to upgrade the land for other uses. Oily waste pits can be cleaned up by treating waste in a recovery system and using output for fuel in process units. Acid wastes and spills may require excavation and neutralization with lime or soda ash.

Loehr, R. C., J. H. Martin, E. F. Nauhauser, R. A. Noton, and M. R. Malecki, "Land Treatment of an Oily Waste - Degradation, Immobilization and Bioaccumulation", EPA Report 600/S2-85/009, 1-5, 1985.

Land treatment of an industrial oily waste was investigated to determine the loss and immobilization of waste constituents and the impact of the waste and the application process on soil biota.

The waste was applied to field plots of a moderately to slowly permeable heavy silt loam in New York. The field plots consisted of four replicates each of natural controls, rototilled controls, and low, medium, and high application rate plots. Wastes were applied in June 1982, October 1982, and June 1983. In June 1983, the plots that had received the low applications received a high application and became the high application plots. During the study, the waste was applied to the test plots at seven waste application rates that ranged from 0.17 to 9.5 kg total oil and grease/meter^2 or from 0.09% to 5.25% oil and grease in the zone of incorporation.

The application of the wastes increased the pH and volatile matter of the soils. Over the period of the study, the half life of the total oil and grease in the field plots ranged from about 260 to about 400 days. Not all of the applied oil was lost from the plots. The refractory fraction ranged from 20% to an apparent 50% of the applied oil and grease. The refractory fraction did not appear to adversely affect the soil biota.

Napthalenes, alkanes, and specific aromatics were rapidly lost from the soil, especially in the warmer months. The half life of these compounds generally was less than 30 days.

The waste applications increased the concentration of several metals in the upper 15 cm of the soil. Except for sodium, all of the metals were immobilized in the upper 15 cm of the plots.

Earthworms bioaccumulated cadmium, potassium, sodium, and zinc. The accumulation could not be related to waste application rates and occurred in worms from the control plots as well as in worms from the plots that received the wastes. The land treatment of these wastes did not cause any unexpected bioaccumulation of metals in the earthworms. The earthworms did not accumulate napthalenes, alkanes, or specific aromatics that were in the applied waste.

Rototilling and waste application reduced the numbers and biomass of earthworms and the numbers and kinds of microarthropods in the field plots. Both types of soil biota were able to recover from the rototilling and waste application.

Loynachan, T. E., "Low-Temperature Mineralization of Crude Oil in Soil", Journal of Environmental Quality, V. 7, No. 4, 494-500, 1978.

Reviews methods of enhancing crude oil mineralization at 10°C. Crude oil was added at 0, 3, and 6% wt. of oil to wt. of soil. Both mechanical stirring of the soil and fertilizatiion were effective in enhancing mineralization. Under the most favorable conditions of the study only small amounts (less than 20%) of the added C was evolved as CO_2. Nitrogen appeared to be the most stimulatory fertilizer; however, phosphorus in addition to nitrogen further enhanced carbon mineralization. Sawdust was added to decrease the hydrophobic nature of oiled soils and to improve the soil physical properties. Although added sawdust lessened aggregation of the stirred soil, degradation of the oil was not enhanced. Aerobic bacteria and actinomycetes were both initially active shortly after oil addition. This was followed somewhat later by population increases of bacteria growing anaerobically. Oil additions had no stimulatory effect on fungal populations. Time required for doubling of the indigenous aerobic bacterial population at 10°C was less than 2 days. This suggests that under conditions approximating those of this study, innoculation with appropriate organisms may be unnecessary in contaminated soils. Fertilization further reduced the doubling time by approximately one third.

As oiling rates were increased, the ratio of aerobic to anaerobic bacterial growth tended to decrease. This, along with increased CO_2 evolution following stirring, suggested that O_2 may limit further degradation.

Means, J. C., S. G. Wood, J. J. Hassett, and W. L. Banwart, "Sorption of Polynuclear Aromatic Hydrocarbons by Sediments and Soils", Envir. Sci. and Technol., 14:12, 1524-1538, 1980.

Reports on sorption of pyrene, 7, 12-dimethylbenzo(a) anthracene, 3-methylcholanthrene, and dibenzanthracene on 14 sediments and soil samples representative of a wide range of environments in the Mississippi River basin.

It was found that the equilibrium Freundlich constant (Kj) and linear partition coefficient (Kp) were highly correlated with the organic content of the samples. The sorption constants (Kp), when normalized to organic carbon content, were predictive of octanol/water partition coefficient. A significant negative correlation was found between organic content (log K_{OC}) and the log of water solubility for the compounds studied.

Mitchell, W. W., T. E. Loynachan, and J. D. McKendrick, "Effects of Tillage and Fertilization on Persistence of Crude Oil Contamination in an Alaskan Soil", Jour. of Environ. Quality, V.8, No. 4, 525-532, 1979.

The persistence of Prudhoe Bay crude oil was evaluated with cereal plantings over a 4-year period on field plots at Palmer, Alaska, oiled at 10 and 20 liters/m^2 with tillage and fertilization as treatments. Following the field study, soil was removed for greenhouse evaluations and analyses.

Tilling aided water infiltration on the oiled plots in the field. Oiled plots without tillage or fertilization produced negligible growth during the first three growing seasons and very poor growth (less than 10% coverage) in the fourth year. In the first year, only the 10-liter tilled plots provided tangible growth, about one-tenth that of the unoiled plots. The 20-liter plots required both treatments to produce growth in the second and third years, while either treatment sufficed for the 10-liter plots, with growth still much reduced from the controls. Oil decomposition was sufficiently advanced in the fourth year to permit over 75% coverage on the tilled 10-liter plots, about 50% coverage on the tilled and fertilized 20-liter plots, and about 25 to 40% coverage on the tilled, unfertilized 20-liter and on the fertilized, untilled 10-liter plots. Annual weeds were mostly unsuccessful in invading the oiled plots until the fourth year.

Greenhouse studies with oiled, fertilized soil removed from the field in the fourth year showed that tillage benefited growth of barley and bromegrass in the surface layer but was detrimental to growth in the 10- to 15-cm layer. Laboratory analyses corroborated the greater contamination of the deeper layers from the tilled plots. Field moisture levels were highly negatively correlated with residual oil contents, thus emphasizing the droughty effects of oil contamination. Residual oil contents of 13.5% completely inhibited germination of barley and brome, while levels under 7.5% allowed germination but reduced shoot heights. Decreasing levels of residual oil with increasing depth of tilled soil did not result in signifcantly greater plant growth. Beneficial degradation of oil may be retarded at depths in the soil, thus prolonging its phytotoxic effects. Tillage is best delayed to allow volatilization and some weathering to occur.

Moreau, M., "Some European Perspectives on Prevention of Leaks from Underground Storage Systems", Ground Water Monitoring Review, Nat'l. Water Well Association, Dublin, OH, V. 7, No. 1, 45-48, 1987.

Author reports on a brief survey of Western Europeran practices and standards for gasoline tanks, piping, and pump installations designed to prevent gasoline leakage to ground water.

In general, the requirements are much more stringent than in the United States. In most countries tanks are of double-wall steel construction having domed ends and full-thickness welds to withstand test pressures of 29-45 psi vs 5 psi in the U.S. Tanks are generally coated with asphalt and are tested electrostatically at the factory.

Piping generally is steel coated with plastic or PVC, and joints are welded or threaded but covered with asphalt applied in the field. All piping connections to tanks are made through a manhole cover to accommodate inspection.

Pumps are generally suction-type and plumbed so that if piping problems occur, product will drain back into the tank, not into the environment.

Mucsy, G., E. Kranicz-Pap, and G. Urbanyi, "Disposal of Oil-Containing Sludges on Farmlands", Proc., Hazardous and Industrial Waste Management and Testing: Third Symposium, Am. Soc. Testing and Materials, Philadelphia, Spec. Tech. Publ. 851, 135-151, 1984.

The response of soils and plants to oil-containing sludges was studied in Hungary by pot, small plot, and field experiments. The objective was to develop a simple method of farmland disposal without detrimental effects on the environment.

Dewatered sludge from a petroleum storage plant, in combination with nitrogen fertilizer, was found most suited to farmland disposal. The sludge was applied to sandy soil at rates from 3 to 8 grams oil per kilogram of soil, and during a single growing season (six months) 60 to 90 percent of the oil was decomposed. No oil was detected below a 60-cm depth. Some physical properties of the soil, particularly the texture and water-retaining capacity, were improved. The plants were analyzed for protein, phosphate, and potassium oxide and found to have suffered no detriment and no loss in crop yield. Disposal by conventional agrotechnical operations proved environmentally safe and economically superior to other alternatives.

New York State Department of Environmental Conservation, "Recommended Practices for Underground Storage of Petroleum", N.Y. Dept. Environ. Conservation, 1984.

This manual contains the New York State Department of Environmental Conservation's recommended practices for underground petroleum storage. Guidance includes: (1) the design of tanks and piping systems; (2) the installation of underground storage systems; (3) secondary containment; (4) leak detection; (5) overfill protection and transfer spill prevention; (6) storage-system tightness testing; (7) storage-tank rehabilitation; and (8) the closure of underground storage facilities.

The manual contains best management practices for underground tank systems, but they were not requirements at the date of publication.

New York State Department of Environmental Conservation, "Recommended Practices for Aboveground Storage of Petroleum Products", Environ. Conservation, 1987.

This manual is a companion to the 1984 guidance on underground storage, but is directed to aboveground facilities. Organization and recommended practices are comparable to the earlier reference.

New York State Department of Environmental Conservation, "Technology for the Storage of Hazardous Liquids: A State of the Art Review", N.Y. Dept. Environ. Conservation, 1-223, 1983.

This review addresses the following topics with respect to underground and above ground storage systems:

- The properties and characteristics of various hazardous liquids.
- The compatability of various tank and piping system materials with certain hazardous liquids.
- The types of leaks and problems which can occur in bulk storage facilities.
- The cause of corrosion.
- Other technical factors that must be considered prior to the storing of hazardous liquids.

As gasoline and petroleum products comprise the largest quantities of hazardous liquids handled in New York State, much attention is directed toward surface and underground petroleum leaks.

Norris, D. J., "Landspreading of Oily and Biological Sludges in Canada", Chem. Abs., American Chemical Society, V. 95, No. 2, p. 289, 1981.

Landspreading at a fullscale operational site and a test site in eastern Canada showed the feasibility of this method for the disposal of both oily sludge (from refineries) and waste activated sludge. The oily sludge and waste activated sludge contained oil 1-30 and less than 0.01, solids 1-20 and 1-10, and water 50-98 and 90-99 wt percent, respectively. The trace metals content was 1-10,000 mg/kg for both sludges. Oil and phenol did not leach into groundwater from the landspreading site; the level of NO_3 in shallow wells increased but still remained well below the drinking water standard of 10 ppm. The level of NO_3 in deep wells remained the same. Thus, shallow wells can provide an early warning of potential groundwater contamination. Disposal rates of greater than 200 m^3 of oil per hectare per year were achieved even though the operation was restricted to six months of the year with sludge being stored for the remaining six months. Further oily sludge additions were stopped whenever the oil content exceeded 10 percent; if the soil pH dropped to 6.5, lime was added to prevent solubilization of trace metals.

Pal, D., and M. R. Overcash, "Assessment of Land Treatment Technology for Petroleum Refinery Solid Wastes", Water Resources Research Inst. Univ. of N.C., Rept. No. 141, 1-29, 1980.

The report examines land treatment for aggregate refinery solid wastes. This land treatment differs from conventional land farming by using a site nondegradation approach which is more closely related to the RCRA approach to hazardous waste management.

A basic design procedure for the use of land treatment involves: (1) characterization of compounds in waste, and (2) site characterization to establish the plant-soil assimilating capacity for each constituent of the waste. This permits determination of the land limiting constituent (LLC) which is used to calculate land-area requirements.

All petroleum refineries in the U.S. were classified according to their operations and processes. The estimates of waste generation and characteristics were based on refineries with the largest range of activities. For soil assimilative capacity, sandy loam and clay loam soils were chosen. Calculations show the sandy loam decomposing oil at a rate of three percent soil weight per year (67,000 kg/ha/yr) and the clay loam decomposing six percent soil weight/yr (130,000 kg/ha/yr). For oil with a high nitrogen to carbon ration these rates can increase up to 50 percent. Values for assimilation rates of various constituents (organic compounds, salts, metals) are given in tables.

It was concluded that knowledge of the organic compounds in refinery wastes is incomplete and modifications must be made as more data becomes available. Fluoride was found to be the LLC in both sandy loam and clay loam soils. In the absence of fluoride land area required was reduced by three to five-fold and selenium, chromium and clay became LLCs.

PACE, "Underground Tank Systems: Review of State of the Art and Guidelines", PACE Report No. 82-3, Petroleum Association for Conservation of the Canadian Environment, Ottawa, 1-69, 1983.

This review and guidance manual addresses prevention of underground leaks from petroleum tanks through proper installation of tanks and piping, inventory control, and tank testing. Causes and control of corrosion are explained, methods for evaluating the underground environment and predicting tank condition are presented and proper methods for tank removal and disposal, or abandonment are recommended.

Fully successful installation of tanks and piping requires careful adherence to specifications, codes, and local regulations; soil investigation; proper selection of materials appropriate to the site; capable supervision and inspection during installation; and careful testing during and following installation.

Proper inventory control is identified as the first line of defense against damage from leaks in identifying leakage before damage is substantial. When careful review of inventory records confirms leakage, pipe and tank testing should be used to identify the source. Several testing systems are described and recommended.

Electrolytic corrosion is identified as the main cause of leakage from metal tanks, and the principal methods of control are described: coatings, cathodic protection, and internal linings. Methods for evaluating the environment with respect to corrosion include: electrical earth resistivity, soil pH, soil-moisture content, and presence of sulfides. Procedures for testing for these parameters are given, and a scoring system for the evaluation of underground environments is recommended. Using the Soil Aggressiveness Value (SAV) thus obtained together with age of installation, a system is presented for predicting tank condition.

Finally, guidelines are presented for the proper removal and disposal, or abandonment of underground petroleum tanks.

Predpall, D.F., W. Rogers, and A. Lamont, "An Underground Tank Spill Prevention Program", Proc. NWWA/API Conf. on Hydrocarbons and Organic Chemicals in Ground Water - Prevention, Detection, and Restoration, Natl. Water Well Assoc., Dublin, OH, pp. 17-32, 1984.

Authors apply decision analysis techniques in assigning action priorities in systems with large numbers of tanks to prevent or reduce spills. The general approach recommended is to: (1) develop an automated data processing data base on all tanks, (2) perform assessment- priority analysis, (3) develop spill prevention strategy, (4) investigate high risk tanks, and (5) implement remedial work.

Key to the approach is the assessment-priority analysis, i.e., where to invest the greatest effort. This step consists of four tasks; inventory reconciliation analysis, soil-corrosivity analysis, site-hazard analysis, and priority ranking. In the first two tasks, these factors are quantified in terms of probability of leaks for each tank. Site hazard analysis is addressed as two elements, environmental hazard and public-health hazard; and each element is quantitied in terms of probability. Once the leak probability and site risks have been calculated these figures are multiplied to give an overall risk figure. The overall risk is then used in assigning priority to leak-detection investigations.

Sims, R. C., and M. R. Overcash, "Fate of Polynuclear Aromatic Compounds (PNAs) in Soil-Plant Systems", Residue Reviews, V. 88, 1-68, 1983.

Polynuclear aromatic (PNA) compounds are a class of organics including hydrocarbon and heterocyclic species. Individual PNA compounds and isomers vary widely in their susceptibility to biodegradation; however, a consistent trend of decreasing biodegradation with increasing ring number is apparent. PNAs do decompose in soil systems, probably more rapidly than in any other waste management alternative or receiver systems involving biological activity. Conclusive rates of decomposition and soil levels above which application of PNA constituents adversely affects the food chain have yet to be established. Utilization of a soil assimilative capacity concept would allow treatment of PNA compounds in an environmentally acceptable and cost effective manner. Enhancement factors that increase degradation rates of PNAs increase the soil assimilative capacity and could provide land application as an alternative technology that may be the most economical for safe and acceptable disposal of PNA wastes.

Based on current information, it appears that with bacterial seeding or insitu acclimation of a land application site, a substantial degradation rate could be achieved for the PNA class of compounds. Of all degradation pathways considered, including volatilization and microbial degradation, the latter mechanism appears to be the most important in the environment.

Streebin, L.E., J.M. Robertson, A.B. Callender, L. Doty, and K. Bagwandoss, "Closure Evaluation for Petroleum Residue Land Treatment", EPA Report 600/S2-84-162, 1-6, 1984.

Three oily residue land treatment sites to which no waste applications had been made for six months, nine months, and six years, respectively, were sampled to define existing conditions. Runoff, zone of incorporation (0-25 cm), and unsaturated zone (26-152 cm) samples were collected at each site during the 15-month study period.

A considerable variation in residual oil content existed at the three sites. Site 2, a well-managed operating site which had received no waste for six years, had a residual oil concentration of 2-3 wt.% in the zone of incorporation. Sites 1 and 3, which had received waste applications within the 12 months previous to this tudy, contained 5-6 and 8-9 wt.% residual oil, respectively. Oil concentrations greater than background were detected as deep as 45-50 cm at all sites with the highest concentrations being found at site 3. Average concentrations of oil in soil remained relatively constant at each site during the study period; however, large variations in oil content of individual core samples were found within each site. Possible contributing factors to this apparant lack of degradation were extended periods of extrememly wet or dry soil, low available soil nitrogen levels giving extremely high carbon-to-nitrogen ratios, and the presence of persistent hydrocarbons. Thirteen or more organic priority pollutants were identified in samples collected at each site; however, only trace quantities were found below the zone of incorporation. Several of these priority pollutants also were identified in adjacent soil background samples.

Metals were immobilized in the top 25 cm of soil at all sites. Soil and soil pore water at each site contained high chloride levels. Barium, zinc, iron and manganese were present in high concentrations in the soil pore water.

Site 2 supported a lush growth of vegetation while sites 1 and 3 supported little or no vegetative growth.

Vegetation studies revealed that grasses were more tolerant than tree seedlings when planted in areas having an oil content of 5-6 wt.%. Root development was inhibited at levels of 4-5 wt.%. In areas having an oil content of 9-13 wt.%, survival rates for both were very low.

Thompson, W. E., and R. H. Kuhlthau, "Potential Hazard of Refinery Wastewater Impoundments to Ground-Water Systems", <u>API 45th Midyear Refining Mtg., Preprint 22-80,</u> Amer. Petrol. Inst., Washington, D.C., 108-117, 1980.

Wastewater impoundments at ten selected refineries in seven different groundwater regimes were evaluated with respect to their threat to groundwater resources and their ability to meet EPA regulatory requirements for solid and hazardous wastes. Despite minimal impact on groundwater all sites investigated failed EPA criteria on one or more counts. The most common shortcomings were (1) lack of low permeability soil barriers to impede downward leaching of chemicals and (2) less than five-foot separation between impoundment bottom and water table.

Among priority pollutants, chlorinated hydrocarbons and fused-ring aromatics are the compounds most likely to leach from refinery impoundments; among priority pollutants metals, arsenic, selenium, mercury, and cadmium are the most likely. However, the impact of common inorganic compounds, such as chloride, sodium, and calcium upon groundwater quality are likely to be greater than that of priority pollutants because of higher concentrations in wastewaters.

Many refineries are located along tidewater in industrial districts where the uppermost groundwater is not used for water supply. In these areas the impact of refinery impoundments on ground water is minimal. Refineries in inland areas such as the western alluvial basins, the High Plains, and the Northern Great Plains are more likely to have a serious impact on groundwater quality.

Weldon, R. A., "Biodisposal Farming of Refinery Oily Wastes", Proc., 1977 Oil Spill Conf. (Prevention, Behavior, Control and Cleanup), API Pub. No. 4308, Washington, D.C., 609-614, 1979.

Oily wastes, whether derived from refinery operations or oil-spill cleanups present similar disposal problems. The paper reports on a study of biodisposal farming.

Soils, initially oil-free, were checked for composition, depth to groundwater, pH, cation-exchange capacity, microflora populations and nutrient levels. The soils were amended with supplemental nutrients as required to maximize biooxidation activity and pH was adjusted with lime to avoid acidic conditions.

The operating procedure called for waste application, followed by incorporation into the tilled soil depth or mixing zone as soon as soil conditions would permit. The tilling was repeated approximately two weeks later, resulting in two soil aerations between applications. Waste was applied again four or five weeks following the previous spreading and the cycle was repeated. This procedure continued, weather permitting, until the onset of winter weather when activities were suspended. All sites were selected and operated so as to avoid anaerobic conditions for any significant period, which was of the utmost importance.

During the two-year period studied, oil disappearance rates were high. Centrifuge sludge applied at a rate of 1,260 barrels per acre (49,000 gallons) per year showed an oil loss of 950 barrels per acre per year for a 75 percent biodegradation rate (assuming negligible evaporative losses). The API separator sludge applied at a rate of 1,100 barrels of oil per acre per year showed an oil disappearance of 880 barrels per acre per year for an 80 percent biodegradation rate.

5.0 DETECTION AND ASSESSMENT ANNOTATIONS

For the most part, annotations under this heading relate to petroleum product releases at service stations, terminals and pipelines rather than at refineries. However, the chemicals and principles described may have transfer value to refinery operations. The annotations may be divided into four main categories: (1) physical and chemical characterization of petroleum wastes in water, (2) methods for remote detection of petroleum in the subsurface, (3) the behavior of petroleum chemicals in the subsurface environment, and (4) mechanisms of transport of petroleum in ground water.

Annotations on characterization of petroleum wastes include API Pub. 4296 (1978) and API Publ. 4346 (1981), which deal with chemical characterization of refinery wastes. Other annotations in this category include API Pub. 4395 (1985) and Leinonen and Mackay (1973) which report on experimental determination of the solubility of petroleum compounds in water, and Senn and Johnson (1987) describing the applicability of gas-chromotography to analysis of petroleum hydrocarbons.

Methods of remote detection of petroleum in the subsurface are treated by Dolezal (1978) and Saunders et al (1983) on geophysical surveys, by Ecklund (1985) and Pelikan et al (1978) on soil-gas surveys, and by Robbins and Nichols (1984) and Scheinfeld et al (1986) on tank-leak detection systems.

Annotations relating to behavior of petroleum in the subsurface include Birk (1978), Houzim (1978), Patrick et al (1986) and Yaniga (1984), and by Duffy et al (1977) in the section on Detection and Assessment. Descriptions of specific spill events are presented in case histories by Collins (1985), Reichmuth (1984), and Yaniga and Demko (1983). A description of the environmental fate of aromatics and PAHs spilled at a coal-tar plant, by Quinn et al (1985) was included because of the chemical similarity of the tarry coal wastes to some oil-refinery wastes. A magazine article (National Petroleum News, 1980) was annotated because it described a multimillion gallon product spill from one or more refineries.

Mechanisms of contaminant transport in ground water are discussed from the theoretical aspect by Corapcioglu and Baehr (1987), Fried and Zilliox (1978), Hinchee and Reisinger (1985), Mackay et al (1986), and Pfannkuch (1984), while Sellberg (1978) and van der Waarden et al (1971) present results of field and laboratory experiments of transport processes. Wood and McLaughlin (1984) reported on improvements in general in groundwater monitoring network design.

Petroleum product spills commonly are discovered through leakage of liquids or gases to sewers or other utility conduits, or to nearby buildings. Geophysical methods, chiefly the electrical resistivity technique, and soil-gas analysis have proven valuable as remote, non-invasive methods for delineating the subsurface extent of petroleum spills. Considerable information is available in the literature on degradation, sorption, and other changes in spilled product in soils and groundwaters. However, relatively little information has been published on pollutants stemming from refinery operations. Numerous theoretical discussions have been published on petroleum contaminant transport in ground water, but relatively little information is available based on field experience. In summary, the impacts of refinery operations on groundwater resources clearly are not perceived as being as serious as product spills from distribution systems.

American Petroleum Institute, "Analysis of Refinery Waste Waters for the EPA Priority Pollutants: Interim Report", API Pub. No. 4296, 1978.

Intake waters, wastewater feed to biotreatment units, and final effluent streams from 17 petroleum refineries were sampled by EPA to screen for the presence or absence of 129 chemicals on the EPA Priority Pollutant List. Split samples were taken for separate analysis at nine of the refineries. Among the organics, 38 were found in final effluent, and 13 trace metals were detected.

American Petroleum Institute, "Refinery Wastewater Priority Pollutant Study - Sample Analysis and Evaluation of Data", API Pub. No. 4346, 1-100, appends, 1981.

Presents and compares analytical data on priority pollutant organics and metals and traditional surrogate waste-water parameters (TOC, BOD, TSS, COD, oil and grease, and 4 AAP phenolics) during split-sampling study of influent and effluent wastewater at two refineries. Organic priority pollutants were analyzed by two EPA Standard Methods approaches, 624 and 625 (internal standards technique), and 1624 and 1625, (isotope dilution technique). Other parameters were analyzed by a single EPA Standard Method.

The methods were evaluated in terms of bias (systematic differences between measured concentrations and true or designated reference concentration), and within laboratory precision (variability resulting from random measurement errors).

The conclusions were:

The use of the isotope dilution procedure offered no advantage over the internal standard procedure in terms of eliminating between-laboratory bias or improving within-laboratory precision. The magnitude of the between-laboratory bias and the within-laboratory precision of either procedure remains a limitation of the methods' utility for regulatory purposes. The ICAP and AA methods of elemental analysis are essentially equivalent for measuring chromium and zinc in refinery wastewaters.

The concentrations of priority pollutants in the refinery effluents studied are too low to allow a valid assessment of the utility of using traditional parameters as surrogates for priority pollutants. Although a qualitative relationship between total chromium and total suspended solids was found, this is insufficient to show that a valid surrogate relationship exists.

Refinery treatment systems can reduce priority pollutants present in raw wastewater to very low levels. Much of the variability of final effluent concentrations is due to variability associated with the analytical methods currently available to measure effluent concentrations at the part-per-billion level. The two refineries were remarkably similar with respect to the pollutants present in the influent and effluent samples and the concentrations of these pollutants.

Continued evidence of the possibility of sample contamination with such priority pollutants as methylene chloride, benzene, toluene, chloroform, and phthalates indicates that analytical data for low levels (10 ug/l) of these pollutants is subject to question.

American Petroleum Institute, "Groundwater Monitoring and Samples Bias", API Pub. No. 4367, 1-206, 1983.

The report examines the various sources of bias encountered in monitoring of groundwater quality, describes how bias is introduced, and suggests means to minimize bias.

The main sources of bias include foreign materials introduced during drilling including drilling muds and chemical conditioners and biota. Other sources include contaminants introduced in filter packs, seals, and grout. Degassing and aeration of native groundwater during well construction can also affect the chemical character of the groundwater.

Purging and taking of samples from wells and their packaging and handling en route to the laboratory also can bias analytical results. The authors stress the need to minimize disturbance and exposure during sampling, and note the difficulty of obtaining representative samples for volatile organic analysis.

A discussion is presented of chemical parameters and the degree to which each is affected by sampling. While conservative constituents such as specific conductance and chloride are generally little affected, constituents sensitive to changes in pH and eH, such as iron and carbonate species can be greatly affected by degassing and oxygen invasion during sampling, as is true also of volatile organic constituents.

American Petroleum Institute, "Detection of Hydrocarbons in Groundwater by Analysis of Shallow Soil Gas/Vapor", API Pub. No. 4394, 1-73, 1985.

Measurement of hydrocarbon concentrations in soil gas is increasingly being used as a measure of the level of hydrocarbon contamination of ground water in the saturated zone. Several measurement methods were reviewed and evaluated with regard to practicability for field application.

The methods evaluated included grab samples of soil cores, surface flux chambers, down-hole flux chambers, accumulator devices, and ground-probe testing. In grab sampling, a core is taken in an airtight container and transported to the laboratory for head-space analysis. In surface and downhole flux testing an enclosure device samples gaseous emissions by sweeping contaminated air out of the chamber with clean air, and the contaminated air is measured at the exit point by a portable gas analyzer or gas chromotograph. In the accumulator technique, an adsorbing material is buried in an inverted can for a set period of time; the adsorber is recovered and transported to the laboratory for desorption and analysis. In the ground probe technique, steel probes with ports at the bottom are driven into the ground to a uniform depth. A vacuum is applied to the probe and vapor samples are extracted for analysis with a syringe from the vacuum line.

The following criteria were employed: (1) measuring a soil-gas concentration is preferable to measuring an emission rate, (2) rapid sampling and analytical turnaround is advantageous, (3) sampling site disturbance should be minimized, and (4) it is preferable to isolate the gas sample from the soil matrix rather than collecting soil samples for later analysis.

The methods tested were ranked as follows according to their applicability for ground water and soil contamination investigations: (1) ground probes, (2) accumulators, (3) surface-flux chambers, (4) grab sampling of cores, and (5) subsurface flux-chambers.

American Petroleum Institute, "Laboratory Study on Solubilities of Petroleum Hydrocarbons in Groundwater", API Pub. No. 4395, 1-21, appends, 1985.

Describes study to determine solubilities of API reference regular unleaded gasoline in distilled water under laboratory conditions at 13°C.

Concentrations dissolved ranged from a maximum of 65 mg/l for benzene to about 1 mg/l for 2-pentene, m-pentene, and a trimethyl benzene. Other organics quantified included : toluene, 33 mg/l; m-xylene, 11 mg/l; o-xylene, 6.9 mg/l; p-xylene, 4.4 mg/l; ethylbenzene, 4.3 mg/l; butane, 2.7 mg/l; 2-methyl butane, 3.7 mg/l, and 2-butene, 2.4 mg/l.

Partition coefficients for the aromatic compounds, calculated from published data on solubilities of the pure compounds in water, showed good agreement with the experimental data.

Birk, F. and C. Vovreyer, "The Behaviour of Oil in Fissured Rocks - Demonstrated by Typical Oil Incidents", Proc., Int'l Symposium on Ground Water Pollution by Oil Hydrocarbons, Prague, Czech., Int'l Association of Hydrogeologists, 107-125, 1978.

This paper presents problems encountered during investigations in which there is contamination of fissured aquifers. Fissured rocks are anisotropic media relative to void distribution and permeability. The oil migration proceeds discontinuously and depends on volume and orientation of joints, bedding planes and other cavities. The deviation from the behaviour of oil in porous media makes estimation of oil damage in fissured rocks very difficult.

The oil migration does not take a uniform areal course as in porous media, but moves along preferred joint cracks, transporting in some cases considerable quantities of oil. The mapping of a contaminated oil zone on the groundwater table by soundings is therefore very difficult. The irregular distribution of oil renders more difficult oil recovery by pumping from wells.

Joint planes transverse to the direction of groundwater flow often have the effect of trash boards. They retain the oil or at least deflect the oil in other directions. As a result, the oil spread commonly disagrees with the direction of groundwater flow. Pressure fluctuations associated with fissured rocks can open new avenues of flow, further spreading oil pollutants. The final phase of oil spreading in fissured rocks, and oil movement in general, is often reached long after the source has been defined and eliminated. Quantitative data about oil-retention capacity or oil thickness in earth materials is difficult to derive. The complexities of these effects require extensive investigations to design corrective actions for abatement.

Collins, M.A., "Ground-Surface Interaction in Promotion of Contamination by Underground Storage Tank Leakage: A Case Study", Proc., NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water -Prevention, Detection, and Restoration, Nat'l. Water Well Association, Dublin, OH, 90-110, 1985.

Reports a case history in which a telephone conduit in Houston, Texas was acting as a sump for gasoline leaking from three different service stations. The author concludes that the gasoline was carried with infiltrating rain to the shallow water table and that telephone conduits served as conduits for contaminant flow.

Corapcioglu, M. Y., and A. L. Baehr, "A Compositional Multiphase Model for Groundwater Contamination by Petroleum Products: I. Theoretical Considerations", Water Resources Research, V.23, No. 1, 191-200, 1987.

A mathematical model is developed to describe the fate of hydrocarbon constituents of petroleum products introduced to soils as an immiscible liquid from sources such as leaking underground storage tanks and ruptured pipelines. The problem is one of multiphase transport (oil (immiscible), air, and water phases) of a reactive contaminant with constituents such as benzene, toluene, and xylene found in refined petroleum products like gasoline. In the unsaturated zone, transport of each constituent can occur as a solute in the water phase, vapor in the air phase, and as an unaltered constituent in the oil phase. Additionally, the model allows for adsorption. Molecular transformations, microbially mediated or abiotic, are incorporated as sink terms in the conservation of mass equations. An equilibrium approximation, applicable to any immiscible organic contaminant is applied to partition constituent mass between the air, oil, water, and adsorbed phases for points in the region where the oil phase exists. Outside the oil plume the equilibrium approximation takes on a simpler form to partition constituent mass between the air, water, and adsorbed phases only. Microbial degradation of petroleum products is first discussed in a general model, then the conservation of mass equation for oxygen is incorporated into the analysis, which takes advantage of the key role played by oxygen in the metabolism of hydrocarbon utilizing microbes in soil environments. Approximations to two subproblems, oil-plume establishment in the unsaturated zone, and solute and vapor transport subsequent to immiscible plume establishment are then developed from the general model.

Dolezal, J., "The Aid of Geophysical Methods in Oil Spill Cleanups", Proc., Int'l Symposium on Ground Water Pollution by Oil Hydrocarbons, Prague, Czech., Int'l Association of Hydrogeologists, 319-330, 1978.

The use of geophysical methods can be used as a tool for obtaining information about geological structure of a contaminated area, groundwater regime and dynamics, and estimating the areal extent of an oil spill. Geophysical methods can be used both in prevention (monitoring), during emergency cleanup operations, and in proper design for abatement.

To obtain data on the detailed geological structure, mainly geoelectrical methods (resistivity profiling and vertical electrical sounding), seismic refraction or microgravitational methods have been used. The data serve to characterize structural features, to determine the composition of the cover, and to assess the depth of weathering. Based upon these data, the position of the groundwater table, and that of the aquifer can be determined, sandy and clayey layers can be distinguished, etc. Provided at least one borehole is available in the area of interest, electric logging methods can be applied to give details on the lithology of the borehole profile and to delineate porous or fissured aquifers. When several boreholes are available, they may be correlated over a relatively wide distance.

The use of various geophysical methods, in combination and cooperation with other disciplines, can supply information aiding in prevention or remediation of an oil spill environment.

Fried, J. J., and L. Zilliox, "The Dispersion Scheme in the General Mechanisms of Groundwater Pollution by Hydrocarbons", Proc., Int'l Symposium on Ground Water Pollution by Oil Hydrocarbons, Prague, Czech., Int'l Association of Hydrogeologists, 139-147, 1978.

Hydrodynamic dispersion is an important mechanism of pollution propagation in groundwater. An oil product entering unconsolidated earth materials will meet two other fluid phases, air and water. It flows as a polyphase flow of immiscible fluids in porous media. When an oil product massively enters the ground, it first infiltrates under gravity. If the amount of product exceeds the retention capacity of the materials oil reaches the capillary fringe above the water table. Under a sufficient pressure at the infiltration point, it can enter groundwater but then spreads horizontally in the capillary fringe. The surface of spreading is limited by capillary forces, and the free oil mass can be raised or lowered with the water-table fluctuations, thus oil at residual saturation can be found beneath the water table.

Exchanges between the oil product and groundwater creates an environment for hydrocarbon transfer. Exchanges can occur when the oil contacts the groundwater; soluble components are directly dissolved by the flow and carried to the water table. In cases in which the oil does not reach the saturated zone, water infiltrating vertically through the unsaturated zone can dissolve some of the oil product and carry it to the water table, where entrainment with flow will start.

The solute pollution source is the point of contact between oil and water. The major mechanism of this pollution is dispersion-convection, which governs its movement; carrying, spreading and diffusing the hydrocarbons.

Hinchee, R. E., and H. J. Reisinger, "Multi-Phase Transport of Petroleum Hydrocarbons in the Subsurface Environment: Theory and Practical Applications", Proc., NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water - Prevention, Detection and Restoration, Nat'l Water Well Association, Dublin, OH, 58-76, 1985.

The authors review the physical-chemical principles that govern transport of gasoline components in bulk liquid, dissolved, and vapor phases in the subsurface environment. Two specific site investigations are used to illustrate how ratios of gasoline components can be utilized to differentiate among transport mechanisms and ages of spills.

Subsurface movement of bulk liquid is largely a function of the physical properties of the liquid, such as density, viscosity, and hydrophobicity and bulk properties of the matrix, chiefly permeability and water content. Beneath a recent spill, gasoline components are found in ratios relating to the hydrocarbon/water partition coefficients of the several compounds. Volatilization into soil air is largely a function of vapor pressure and relative solubility of a compound in the bulk liquid phase. Ratios of gasoline components in the dissolved and vapor phases are distinctly different from those of the bulk liquid.

Hydrocarbons floating on the water table will partition into dissolved or vapor phases depending on local environmental conditions. Movement of floating product in the direction of groundwater flow will result in the retardation of the more sorbable components. Movement as a vapor plume in the vadose zone in similar fashion causes partitioning, and solution into the groundwater from the vapor phase can result in contamination of groundwater up the hydraulic gradient from a spill site.

Two specific site investigations are used to illustrate the effects of different transport mechanisms. At Site 1 gasoline contamination was confined mainly to unconsolidated overburden above Piedmont crystalline rocks. Two to three years had elapsed between the spill and its discovery and investigation. Samples from monitoring wells at differing distances from the spill show distinct differences in ratios of benzene, toluene, xylenes, and diisopropyl ether (DIPE) with DIPE relatively enriched as compared to benzene in more distant wells. The less soluble, more readily adsorbed toluene and xylenes commonly were below detection level in the distant wells.

At Site 2 a spill of the same type of product as at Site 1, was discovered and cleaned up promptly; thus, the hydrocarbons analyzed were less weathered than at Site 1. The authors show on the basis of hydrocarbon ratios that transport of hydrocarbons to a distant well was via vapor phase and solution into the groundwater rather than by transport as free product or in solution in groundwater.

Houzim, V., "Alterations of the Petroleum Substance in Rock-Water-Air and Rock-Water Systems", Proc., Int'l Symposium on Ground Water Pollution by Oil Hydrocarbons, Prague, Czech., Int'l Association of Hydrogeologists, 279-288, 1978.

This paper investigates the processes and changes to which petroleum products infiltrating into soil and rock media are subject. In rock-soil formations, petroleum products occur as gases, liquids, water solutions or water emulsions. In addition to the simple spread of petroleum products, various physical, physico-chemical, chemical, and microbial processes take place in the vadose and the water saturated zones of the rock-soil environments. A series of time-dependent processes can take place upon infiltration of the petroleum product into the naturally occurring systems of the rock-soil medium. These include sorption on rock-soil media, evaporation of the volatile fraction, dissolution of the native organic matter in the petroleum product, selective desorption and dissolution of the petroleum product in water, emulsification and deemulsification of the petroleum product in water, and chemical oxidation and reduction.

The author describes each of these processes with respect to the various chemical compositions of petroleum products.

Leinonen, P. J. and D. Mackay, "The Multicomponent Solubility of Hydrocarbons in Water", Canadian Jour. of Chemical Engineers, V. 51, No. 2, 230-233, 1973.

The most toxic and soluble components of petroleum hydrocarbons tend to be the most volatile. For toxicological assessment a method of calculating toxicity characteristics of water which has been contacted with a complex hydrocarbon mixture becomes essential. For experimental purposes the aqueous solubility of six binary hydrocarbon systems consisting of benzene and cyclohexane with each of 2-methyl-pentane, n-hexane, and 1-hexane were measured at 25°C. The high volatility of these hydrocarbon components was significant for analysis during the experiment. The solubility of each hydrocarbon component was found greater by from 6 to 35 percent than the value expected by prediction on the basis of the solubility of the hydrocarbon component being proportional to its mole fraction in the hydrocarbon phase. This positive deviation is partly attributable to the activity coefficient of the hydrocarbon in the hydrocarbon phase being slightly greater than unity. There is, however, additional solubility enhancement of from 1 to 25 percent with an average of 10.7% apparently due to the reduction of the hydrocarbon activity coefficients in the aqueous phase by the presence of other hydrocarbons. These results suggest that it will be possible to calculate the solubilities of individual hydrocarbon components present in complex oil mixtures provided information is available on the mole fraction and activity coefficient of the hydrocarbon in the hydrocarbon phase, and the pure component aqueous solubility.

Mackay, D. M., P. V. Roberts, and J. A. Cherry, "Transport of Organic Contaminants in Groundwater", Environ. Sci. Technology, V. 19, No. 5, 384-392, 1985.

Reviews the state of understanding of the physical, chemical, and biological processes that affect the movement of organic contaminants in ground water. These are mainly advection, dispersion, adsorption and desorption, and chemical and biological transformations.

The authors conclude that the extreme time lags that characterize contaminant transport suggest that groundwater contamination by hazardous chemicals is a long-term problem that can reach large proportions before being recognized. It is a problem that is likely to persist long after serious mitigation efforts have begun. It is important to recognize that the time constants for water quality changes in groundwater are large, approaching those that characterize oceans and large lakes and much greater than those for streams.

National Petroleum News, "Brooklyn Spill: 17-Million Gals. under the Sidewalks of New York", Ntl. Petrol. News, p.4, 1980.

A large body of petroleum product floating on the water table beneath Brooklyn, N.Y. came to public attention when oil was found seeping into Newtown Creek, which forms the boundary between Brooklyn and Queens Boroughs, New York City. A subsequent groundwater investigation initiated by the U.S. Coast Guard indicated that 17 million gallons of product 4 to 7 feet thick underlay about 52 acres in Brooklyn.

The vicinity of the spill is mainly industrial and several refineries have operated in the area dating back to 1860. The product appears to represent a mixture of gasoline, fuel oil, middle distillates, and kerosene. Calculations based on groundwater travel time suggest that the spill(s) occurred about or prior to 1950.

Despite the large volume of product floating underground, the spill does not represent an imminent hazard to public safety or health. The depth to fluid ranges from 7 feet near Newtown Creek to 40 feet further inland beneath residential neighborhoods. Also groundwater is no longer pumped for water supply in that area. At the time of writing, major cleanup efforts were in suspension pending resolution of which public agency had jurisdiction for cleanup and who the responsible parties may have been.

Patrick, G., J. F. Barker, R. W. Gillham, C. I. Mayfield, and D. Major, "The Behavior of Soluble Petroleum Product Derived Hydrocarbons in Ground Water: Phase II, PACE Rept. No. 86-1, Petrol. Assoc. for Conservation of the Canadian Environment, Ottawa, 1-59, 1986.

This report presents results as of Spring 1986 from a multiyear field experiment and laboratory research project investigation on transport of gasoline components (BTX) in groundwater.

Field experiments at Borden, Ont. indicated that 98 percent of BTX injected had disappeared within 410 days. The mass losses were initially linear with time followed by a period of tailing. Relative velocities of transport with respect to chloride and the groundwater itself were 90% for benzene and 65% for n-xylene. In the presence of oxygen, BTX in the groundwater generally is reduced to detection levels within a few weeks or months, but biodegradation prceeds much slower under anaerobic conditions.

Laboratory experiments suggest that biodegradation of BTX under anaerobic conditions is accelerated by the addition of nitrate.

The principal conclusions of the research are that in low organic-carbon sand aquifers the major attenuation of BTX is by biodegradation. Oxygen is required, and a major control of biodegradation rate is the rate of transport or mixing of oxygenated groundwater with the contaminants.

Pelikan, V., M. Kucera, and M. Polenka, "The Application of Soil Air Analysis in Order to Determinate the Extent of Groundwater Contamination Due to Petroleum Products", Proc., Int'l Symposium on Ground Water Pollution by Oil Hydrocarbons, Prague, Czech., Int'l Association of Hydrogeologists, 73-81, 1978.

When soils are contaminated by oil, the oil products are present in the soil medium both in the liquid and in the gaseous phases. The volatile components penetrate into the porous medium generating in the soil air a zone of increased hydrocarbon content that surrounds the rocks containing the liquid products. By measuring the soil air along a series of sampling points, an accurate map of the extent of contamination may be generated. Soil air is measured by driving a sampler with soil-air intake ports into the soil and evacuating surrounding air with a suction pump through a sampling tube. Soil air measurements may be obtained by mounting an indication tube for oil hydrocarbons upstream of the exhauster. For qualitative differentiation of the soil air, chromatographic analyses may be performed on the soil air sample.

In the field, sampling is started at the points of the presumed highest contamination and extended in the presumed direction of flow from the origin of the spill. If increased hydrocarbon content is found in the soil air, we proceed along a line leading from the contaminated point to an area where no increased hydrocarbon content can be found at three consecutive sampling points. This series of soil-air sampling is repeated for all areas of suspected contamination until the radial extent of the contamination plume can be defined.

It is a major advantage of soil-air analyses that they do not require drilling of sampling boreholes and that little space is needed to drive in the sampling tubes. Soil air can also be sampled from below buildings by drilling small holes into the floor of the basement rooms.

Of course, the method also has limitations due to which it cannot be used in all instances. The type of seeping oil product plays an important role, above all. The best results have been attained for various types of gasoline, crude oil, and kerosene containing the highest amount of volatile components. Diesel oil and fuel oils affect the quality of soil air to lesser degree. The petrography of the aeration zone also affects the diffusion of gaseous hydrocarbons which spread readily in sandy and stony soils. In clayey soils or where the aeration zone contains continuous clay layers, the potential generation of a zone of gaseous hydrocarbons is restrained. A depressed groundwater table may decrease gaseous hydrocarbons in the soil air, while a rising water table displaces the soil air toward the surface thus increasing the concentrations of gaseous hydrocarbons.

Pfannkuch, H-O., "Determination of the Contaminant Source Strength from Mass Exchange Processes at the Petroleum-Ground-Water Interface in Shallow Aquifer Systems", Proc., NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water - Prevention, Detection and Restoration, Nat'l. Water Well Association, Dublin, OH, 111-129, 1984.

The paper reviews the scientific literature on chemical mass transfer of petroleum to groundwater and summarizes as follows:

For most groundwater flow regimes mass transfer is predominantly diffusion controlled and therefore independent of flow rates. This is due to the generally low flow velocities in natural groundwater flow fields. The absolute amount of dissolved hydrocarbons found in the groundwater depends on the solubility of the particular hydrocarbon fractions.

Solubility dependence on velocity control is only rarely seen in natural settings with high flow regimes, as for example in highly transmissive aquifer units such as gravel materials, in high velocity regimes through fractured media, and near pumped wells. For experimental determination of mass transfer, laboratory conditions have to be dimensionally scaled to match the field conditions under investigation in order to transfer laboratory results to the field.

Appropriate source characterization in terms of the mass-transfer regime and bulk coefficients and the effective exchange interface area is an integral part of formulating predictive flow and mass-transport models. It is also important in the assessment and design of source-control schemes for pollution abatement procedures.

Quinn, E. J., T.N. Wasielewski, and H.L. Conway, "Assessment of Coal Tar Constituent Migration: Impact on Soils, Ground Water and Surface Water", Proc., NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water - Prevention, Detection, and Restoration, Nat'l Water Well Association, Dublin, OH, 111-127, 1985.

The authors present preliminary results of an investigation of a pre-1952 coal-gas plant near a river in Connecticut. The information has transfer value to refinery waste problems because the tarry coal wastes are chemically similar to some oil-refinery wastes.

The tar yield from coal ranges up to 12 percent by weight. The tarry wastes at the site consisted mainly of polynuclear aromatic hydrocarbons (PAHs), principally naphthalene, methylnapthalene, acenaphthalene, phenanthrene, and pyrene, with lesser amounts of phenolics and monoaromatics, mainly benzene, toluene, and xylenes. Some 300 million gallons of tar were produced at the site; however, the amount disposed of on site was not known. Tarry wastes remaining on site were mainly at the location of a former tar pond and in deposits in a former lake bed (now drained), to which the tar pond discharged.

Soils tested contained up to 370 ppm each of benzene, and toluene, and 540 ppm of xylenes. PAHs found were mainly those listed above, all of which were found at maximum levels exceeding 10,000 ppm.

Ground-water samples contained up to a total of 300 ppb of benzene, toluene, and xylene and PAHs at levels generally not exceeding 1,000 ppb. The principal dissolved PAH compounds were naphthalene, methylnaphthalene, and acenaphthalene. The concentration of organics decreased rapidly in the direction of groundwater discharges.

Samples from the river, which is degraded by upstream industrial discharges, showed little evidence of organic contamination from the site. However, sediments from the river bed both upstream and downstream of the site contained PAHs that may have originated at the site.

Reichmuth, D. R., "Subsurface Gasoline Migration Perpendicular to Ground Water Gradients - A Case Study", Proc., NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water - Prevention, Detection and Restoration, Nat'l. Water Well Association, Dublin, OH, 43-52, 1984.

Author uses a case history of a service-station spill to illustrate how gasoline vapors moved up the hydraulic gradient against the groundwater flow direction. Beginning in late 1978, occasional gasoline odors were detected in a restaurant and house which was near two gasoline stations. In January 1981 the local fire marshall detected high hydrocarbon concentrations and on the following day ordered the restaurant closed. Shortly thereafter a large leak was found in a distribution line of the more distant gasoline station. Tests indicated that the groundwater contours were perpendicular to a line passing through the restaurant and stations. This made it impossible for groundwater to carry the gasoline between the leak and the restaurant. The soil profile at the site was determined to consist of approximately 15 feet of silty clay covering a clean gravel. Additional inquiry established that odors increased during periods of high wind and during the winter and early spring. Also, the water table dropped at least 4.7 feet between September and February.

Further analysis demonstrated that the gasoline was transported to the restaurant area by gasoline vapors that migrated through the void space in the clean gravel. The silty clay beneath the leak had absorbed most of the gasoline so only small amounts of liquid reached the groundwater. The dip of the contact between the silty clay and gravel allowed the fumes to migrate laterally and slightly upward to the vicinity of the restaurant where the basements had penetrated most of the silty clay. There, the vapors moved upward into the basements. During summer periods when the water table was high this gravelly zone was saturated and the path was shut off. This caused the observed seasonal fluctuations in fumes.

Robbins, R. J., and D. G. Nichols, "Electrical Leak Detection Systems for Underground Stored Chemicals and Fuels", Proc., Seventh Nat'l Ground Water Quality Symposium, Nat'l Water Well Association, Dublin, OH, 40-44, 1984.

Many states now require leak-detection systems for existing tanks and for new tank installations for storage of hazardous liquids including petroleum products. The authors review various electrical systems which accomplish leak detection. They range in complexity from simple electrical sounders through pre-installed warning devices to devices that automatically sample a monitoring tube and analyze the sample automatically for Total Organic Carbon.

Several monitoring principles are available, including electrical capacitance, electrical conductivity, conductivity/pressure/temperature, ionic concentration, conductivity/refractivity, thermal conductivity, and semi-permeable membrane. Most of these do not lend themselves to retrofitting; however, systems which monitor or sample using a tube or well can be retrofitted.

The authors stress the need to consider local operations and environmental conditions in selecting a detection system.

Saunders, W.R., R.W. Castle, and C.R. Foget, C.R., "Delineation of Subsurface Petroleum Spills Using Terrain Conductivity Measurements", Proc., 1983 Oil Spill Conference, 415-417, 1983.

An explanation of the use of terrain conductivity for locating subsurface hydrocarbons. The advantages of this method are that soil contact is not required and the number of observation wells can be reduced. Factors affecting conductivity are: amount of pore space, interconnection of pore space, pore-filling liquid, and number of free ions in the pore-filling liquid. As the hydrocarbons are non-conducting, terrain conductivity can be used to determine location, extent and thickness of the contamination plume. Limitations to the method are primarily underground and include surface utilities, such as sewer lines, water mains and power lines. The meter can be oriented in such a way as to use the interfering object as a constant.

Two case studies are used to illustrate the method. The first involves a California gas-station spill in silty sand with the groundwater surface seven feet below grade. Ten transects were run with the terrain conductivity meter, revealing a pool of hydrocarbons beneath an alley and part of the street. Background noise (pipes, power lines, parked car) prevented determination of the oil thickness by conductivity, but observation wells show the thickness to exceed 17 inches locally.

The second study involved a large underground spill on the West Coast. The site was a hydraulic sand fill covered with impervious materials (asphalt, concrete) and underlain by water lines, underground power lines, and drain pipes. The groundwater was 10 feet below grade. With the terrain conductivity meter, readings were taken at 10-foot spacings at a depth of six meters. A line of readings was made where the observation wells showed the absence of hydrocarbons. This yielded background readings of 80 to 90 mmhos/m. In the areas of hydrocarbon pools readings were 28 to 70 mmhos/m depending on the thickness of hydrocarbon. A correlation was established between hydrocarbon thicknesses in wells and the conductivity values.

The terrain conductivity method has been shown to be cost effective and can reduce the number of observation wells by at least 50 percent.

Scheinfeld, R. A., J. B. Robertson, and T. G. Schwendeman, "Underground Storage Tank Monitoring: Observation Well Based Systems", Ground Water Monitoring Review, Vol. 6, No. 4, Water Well Journal Publ. Co., 49-55, 1986.

The 1984 RCRA Amendments (Subtitle I) direct the U.S. EPA to develop regulations and states to regulate underground storage tanks. As a result, state and local governments and petroleum-related companies require the use of release detection systems for underground petroleum storage tanks. These systems, which are installed in groundwater observation wells, vapor wells or u-tubes, include hydrocarbon-detecting paste, bailers, interface probes, electrical resistivity sensors, thermal-conductivity sensors, hydrocarbon-soluble devices, hydrocarbon-permeable materials and vapor detectors. This paper describes the available state-of-the-art technology for leak detection and the application for which each system is best suited.

Schwille, F., "Groundwater Pollution by Mineral Oil Products", Proc., Groundwater Pollution Symposium, Moscow, Int'l. Assoc. of Hydrological Sciences, Pub. No. 103, 226-240, 1975.

Reviews European experience in groundwater pollution from petroleum spills, which are due mainly to corrosion of underground tanks, overfilling of tanks, and road tanker accidents. The most serious spills have involved light fuel oil, diesel fuel, and gasoline.

The author describes oil migration in the unsaturated and saturated zones as non-aqueous phase liquid and as dissolved phase in solution in groundwater and presents model and field examples of the spread of petroleum. A discussion is presented of vapor-phase transport of volatile petroleum components in the unsaturated zone, and of microbial degradation of petroleum in the subsurface environment.

Remedial measures are discussed, including excavation of contaminated soil, recovery of floating product through skimmer wells and trenches, use of emulsifying agents, and pumping to prevent the transport of dissolved contaminants. The conclusion is reached that oil spills are so site specific and governed by local hydrogeologic heterogeneity that generic solutions offer little promise.

Sellberg, B., "The Rate of Spread of Petroleum Products", Proc., Int'l Symposium on Ground Water Pollution by Oil Hydrocarbons, Prague, Czech., Int'l Association of Hydrogeologists, 183-207, 1978.

This paper describes experiments in the field with No. 1 fuel oil and gasoline to determine the way in which these hydrocarbons spread in some saturated unconsolidated deposits, particularly bottom varves of glacial clay and sand on clay. In the investigations the rate of movement of No. 1 fuel oil varied from 0.1-0.2 m/day up to 1.0-1.6 m/day. Gasoline showed lower velocity ranging from 0.03-0.04 m/day to 0.09 m/day. Experiments covering a longer period showed that the maximum concentration greatly diminished in transport up to a distance of about 20 m.

The velocity calculations are based on the shortest route from the injection point to the sampling point. The oil and gasoline might have followed a longer route, but the figures do answer the question of how long it would take for the oil to spread from one point to another in the situations described.

Senn, R. B., and M. S. Johnson, "Interpretation of Gas Chromatographic Data in Subsurface Hydrocarbon Investigations", Ground Water Monitoring Review, Water Well Journal Publ. Co., Vol. 7, No. 1, 58-63, 1987.

Capillary-column gas chromatography (GC) is extremely useful in investigations of subsurface contamination by petroleum hydrocarbons. Fluid samples collected from observation wells are evaluated by GC methods to detect and analyze petroleum hydrocarbons in dissolved and liquid phases. The presence, types, and concentrations of many petroleum derived hydrocarbons dissolved in groundwater can be determined. GC analysis can also be used to determine the composition of liquid hydrocarbon products, including gasoline, distillates and heavier oils. The degree of degradation of sampled liquid hydrocarbon product can be estimated from GC information, and this information can be helpful in estimating the length of time the product has been in the subsurface. Determination of the hydrocarbon source and migration path can be made from GC analysis of fluid samples collected at two or more locations, by comparing ratios of highly volatile constituents of petroleum product to less volatile constituents. The interpretative techniques demonstrated in this paper can be used by hydrogeologists to facilitate detection, identification and mitigation of subsurface hydrocarbons.

Somers, J. A., "The Fate of Spilled Oil in the Soil", Hydrological Sciences Bulletin, Int'l. Assoc. of Hydrological Sciences, V. 19, No. 4, 501-521, 1974.

The behavior of spilled oil within the soil and subsoil is described in terms of known models for its movement and biochemical transformation. Application of Darcy's Law is used to formulate mathematical models of potential flow. In the case of multiple phase flow, the volume of the polluted soil can be calculated if the amount of lost oil is known and if there is insight into the pore volume and the irreducible minimum oil saturation, which functions as a limiting factor for migration. By defining the shape of the polluted area, the most questionable elements of the multiple phase flow, namely the determination of the specific permeability and of the interfacial potentials, are eliminated. For practical purposes the model has been reduced to a single phase flow because Kr-oil approximates 0 and Kr-water approximates 1 (relative permeability). When a single phase flow (hydrocarbons dissolved in groundwater) is concerned, Darcy's Law can be used to arrive at quantitative conclusions. These results can be used to decide on the line of action for remediation.

With respect to biological transformations, the model of hydrogen transfer is useful. However, a peroxidation for which molecular oxygen is necessary takes place during the first stage of oxidation; and an aerobic environment is essential. In the underground, free oxygen will therefore act as a limiting factor. The transformation velocities are highly dependent on the structure of the compound; account should be taken of the solubility of the transformation products which exceeds the solubility of the original hydrocarbons.

van der Waarden, M., A. L. A. M. Bridie, and W. M. Groenewald, "Transport of Mineral Oil Components to Groundwater-I, Model Experiments on the Transfer of Hydrocarbons from a Residual Oil Zone to Trickling Water", Water Research, 5:213-226, 1971.

Reports on model experiments in which water was trickled through columns packed with glass beads and saturated with gasoline, kerosene, and gas oil. It was found that the rate of leaching of water soluble components was determined by the partition coefficients of the components and the water/oil ratio. The experiments did not take account of adsorption of petroleum components on mineral particles, which would greatly retard hydrocarbon transport under natural conditions.

Wood, E. F., and D. McLaughlin, "Groundwater Monitoring Well Network Redesign", Proc., NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water - Prevention, Detection, and Restoration, Nat'l. Water Well Association, Dublin, OH, 198-209, 1984.

Demonstrates by use of a case example how the number of data points in a groundwater well network can be reduced without significant loss of information content. Redundant data points are eliminated by use of a geostatistical (kriging) model. Elimination of 26 percent of the wells reduced network efficiency to 0.74 to 0.83 of original level depending upon which data points were eliminated.

Yaniga, P. M., "Hydrocarbon Retrieval and Apparent Hydrocarbon Thickness: Interrelationships to Recharging/Discharging Aquifer Conditions", Proc., NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water - Prevention, Detection and Restoration, Nat'l. Water Well Association, Dublin, OH, 299-329, 1984.

The author discusses the relation of thickness of hydrocarbons floating on the water table as observed in wells to rise and decline of the water table. Maximum hydrocarbon thickness will be observed when the water table is stable. Sharp rises of the water table lead to reduction in thickness of floating hydrocarbons because some is trapped in pores beneath the water table. Similarly, sharp declines also lead to decreased thickness because some hydrocarbon is retained in the unsaturated zone.

Stress is placed on obtaining adequate water-level records over time as a basis for proper interpretation of records of hydrocarbon thickness.

Yaniga, P. M. and D.J. Demko, "Hydrocarbon Contamination of Carbonate Aquifers: Assessment and Abatement", Proc., Third Nat'l. Symposium on Aquifer Restoration and Ground Water Monitoring, Nat'l. Water Well Association, Dublin, OH, 60-65, 1983.

Using a 200,000 gallon fuel oil spill at a bulk storage and distribution center, the authors present a step-by-step outline for conducting a site assessment, and discuss their approach to cleanup.

The spill, caused by leakage from an underground pipe to a little-used loading rack, received little attention following initial plumbing repairs. Two years later fuel oil hydrocarbons were discovered downgradient from the site during construction of a water well. Further investigation revealed a free product plume floating on the water table in fractured dolomite bedrock, 300 x 900 feet in lateral extent and as much as 25 feet thick. The water table was about 50 feet below land surface. Observation wells were drilled at 100-150 feet spacing to delineate the spill, and hydrologic characteristics of the aquifer were estimated from slug tests and pumping tests.

Floating free product was recovered utilizing a two pump recovery system (one pump depresses the hydraulic surface; the other recovers floating product). The system was recovering 500 to 700 gallons per day of reusable fuel oil at the time of writing.

6.0 CONTAINMENT AND CLEANUP ANNOTATIONS

As is the case for the Detection and Assessment section, most annotations under this heading deal with cleanups of petroleum product releases at service stations, terminals, storage facilities, and from pipelines rather than at refineries. In like fashion, general discussions of methods of removing petroleum from the subsurface focus on gasoline and fuel oil as contaminants, rather than the broader spectrum of petroleum materials handled in refineries. Also the emphasis in the literature is almost entirely focused on cleanup rather than containment as such.

The annotations lend themselves to a fourfold subdivision: (1) general discussions of principles and processes for removing petroleum from the subsurface, (2) laboratory investigations, generally focused on a single principle, (3) field tests, also generally focused on a single factor, and (4) case histories of field cleanups commonly employing more than one principle.

API publications represent the majority of the annotations in the general discussion category. These include the API Underground Spill Manual (1980); literature surveys on various aspects of cleanup technology by in API Pubs. 4414 (1986) and 4415 (1985), API Pub. 4432 (1982); and reports of special studies in API Pubs. 4438 (1986) and 4429 (1986), IT Enviroscience (1983), and in API Pubs. 4438 (1986) and 4429 (1986). The remaining annotations in this category by Dennis (1977), Kobayashi and Rittman (1982), McGill (1977), Pelikan (1978), Wilson and Conrad (1984) and Yaniga (1982), are of discussions of the general principles of petroleum recovery or are general discussions of a single principle such as biodegradation.

Laboratory studies generally focused on a single aspect of cleanup such as biodegradation, sorption processes, or recovery of petroleum using surfactants. Papers by Jensen et al (1985), Kappeler and Wuhrmann (1978), API Pub. 4430 (1977) and White et al (1985) report the results of laboratory tests of bacterial degradation of petroleum hydrocarbons. Bouwer (1984) and Wilson and Rees (1985) report on increased rates of biodegradation through the addition of nutrients, and API Pubs. 4389 (1985) and 4428 (1986) report on enhanced biodegradation through the addition of hydrogen peroxide to the ambient water. Stetzenbach et al (1985) addressed specifically rates of biodegradation of polyaromatic hydrocarbons including those commonly found in refinery wastes. Manos et al (1985) and Rogers et al (1980) report on tests of sorption of petroleum compounds on various materials, and API Pubs. 4317 (1979) and 4390 (1985) discuss the use of surfactants to remove petroleum from sandpacks.

Field studies of enhanced biodegradation using hydrogen peroxide were reported by Brown and Norris (1984), and tests of the effectiveness of forced venting of the unsaturated zone for removal of volatiles were presented in API Pubs. 4410 (1985) and 4431 (1984).

Numerous case history presentations describe actual cleanups of releases (generally product) in a variety of natural environments. Cleanup by pumping and treating is discussed by Broscious et al (1984), Burke and Buzea (1984), Chafee and Weimar (1983), McIntyre (1983), Villaume (1979), and Willman (1983). A case history is discussed by Yamiga and Denko (1983) in the section on Detection and Assessment in which cleanup is described as a follow up to assessment of a large fuel-oil release. The complications of removal of floating product in tidal regimes, where the water table may fluctuate over several feet per day, is described by Haven and Jones (1985) and Littlefield (1984). Experience with forced venting of the unsaturated zone is discussed by API Pub. 4431 (1986), and the use of forced venting in combination with enhanced biodegradation is described by Minaugh et al (1983). O'Connor et al (1981) and O'Connor et al (1984) describe remediation of subsurface releases at an Alberta refinery, and Duffy et al (1977) discuss the persistence of crude oil in soils and ground waters based on tests of cores from release sites.

Cleanups, as reflected in case-history presentations, have to date focused on pumping and separating liquid-phase product floating on the water table. However, considerable laboratory and field research indicates that forced venting of the unsaturated zone, with or without enhanced biodegradation is highly effective for removing volatile petroleum constituents from soils and ground water. Rates of cleanup may be improved considerably by addition in feed water of nutrients and hydrogen peroxide to enhance bacterial growth. In the case of hydrocarbons dissolved in ground water, forced venting causes evaporation of volatile petroleum constituents from the water table, and biodegradation can be effective as well in reducing dissolved hydrocarbon concentrations.

The heavier non-aromatic petroleum hydrocarbons handled in refineries are not amenable to forced venting, and releases of heavy components must be remediated mainly by recovery from wells and trenches with surface separation of petroleum and water. As the heavier fractions are poorly soluble and highly sorptive they generally migrate slowly in the subsurface. Residual petroleum and dissolved hydrocarbons left after physical cleanup can be treated by enhanced biodegradation techniques. Recovered petroleum resulting from cleanups at refineries may be recycled onsite or may be shipped offsite for disposal.

American Petroleum Institute, "Beneficial Stimulation of Bacterial Activity in Groundwaters Containing Petroleum Products", API Pub. No. 4427, 1-141, appends., 1975.

Describes a highly successful cleanup of a major gasoline spill at Ambler, Pennsylvania, where a pipeline break resulted in loss of 135,000 gallons of high-octane gasoline to a fractured dolomite aquifer system, which was the water supply for the town.

Physical removal by groundwater depression pumping and skimming accounted for about two-thirds of the original gasoline spilled, but in less than 1 year recovery rates of gasoline had declined to a point where physical removal was no longer effective.

Injection of air, ammonium sulphate, and sodium phosphates stimulated naturally occurring bacteria to oxidize the remaining dissolved gasoline components. Nitrate and phosphate utilization data indicate that more than 40,000 gallons of gasoline were converted to microbial mass. Different bacterial strains utulized various components of gasoline. Bacteria of the genus Nocardia appeared responsible for degradation of paraffinic hydrocarbons, while Pseudomonas degraded the aromatic compounds.

American Petroleum Institute, "Bacterial Growth in and Penetration of Consolidated and Unconsolidated Sands Containing Gasoline", API Pub. No. 4426, 1-20, 1977.

Reports on laboratory studies in which washed sand samples and typical sandstone cores were first saturated with gasoline, and then flooded with groundwater containing gasoline - utilizing bacteria. The sand samples consisted of 97 percent material retained on an 80-mesh screen, with permeability of 3.5-200 darcys. The sandstone cores consisted of Berea Sandstone, with porosity 18-20 percent, and permeability 100-600 millidarcys.

The tests indicated that bacteria readily penetrated the sand samples and degraded the gasoline present. Penetration of sandstone cores of permeability as low as 19 to 75 millidarcys by bacteria was also observed. Bacteria were detected in significant numbers in the produced water from all samples tested.

American Petroleum Institute, "Field Application of Subsurface Biodegradation to Gasoline in a Sand Formation", API Pub. No. 4430, 1-137, 1978.

Reports on laboratory and field study of gasoline - spill cleanup at Millville, N.J., where several thousand gallons of gasoline was lost into an upper permeable sand overlying clayey strata. Floating product formed an elongated pancake-like body beneath an area of less than one-half acre. Gasoline thicknesses of as much as 20 inches were observed in test wells. Over a period of four months about 7,000 gals. were removed with a combination of pumping and skimming, but recovery rates declined to levels where physical removal was ineffective. At that time 8,000 to 10,000 gals. of product remained in the ground.

Naturally occurring aerobic bacteria were stimulated to degrade dissolved gasoline constituents by injecting air (for oxygen) and a solution consisting mainly of ammonium sulphate and sodium phosphate, but including also agar, magnesium sulfate, sodium carbonate, calcium chloride, manganese sulphate, and iron sulphate.

Gasoline component concentrations initially ranged from about 2,500 - 3,500 ppm. During the three and one-half month injection period, about eight pore volumes of water were injected in the area of contamination, resulting in the elimination of free gasoline at which point the study was terminated.
Major conclusions included: (1) optimum spacing of injection and recovery wells for site situation was about 60 feet, (2) importance of trace inorganics to bacterial growth was confirmed, (3) dissolved oxygen content of water was the limiting factor on bacterial growth throughout the tests, and (4) the major bacterial strains were Nocardia, Pseudomonas, and Flavobacterium.

American Petroleum Institute, "Underground Movement of Gasoline on Groundwater and Enhanced Recovery by Surfactants", API Pub. No. 4317 1-38, 1979.

Laboratory studies of surfactant effectiveness were carried out as part of a larger program of evaluating chemical surfactants to be used in conjunction with conventional techniques to enhance and accelerate recovery of gasoline from underground spills.

A combination of commercial nonionic and ionic surfactants was found to be effective in displacing gasoline from model sandpacks. It was found in modeling studies that both simple displacement in the saturated zone and draining of the zone of capillary water were effective mechanisms in gasoline recovery. In the latter case, it appears that previously immobile gasoline is drained to a narrower zone above a new capillary water zone, where the gasoline saturation is sufficiently high that it can flow toward a recovery point.

American Petroleum Institute, "Underground Spill Cleanup Manual", API Pub. No. 1628, First Edition, 1-34, 1980.

This manual cites basic information as to the nature and impact of hydrocarbon contamination on the environment. Evaluation techniques which may identify the source of contamination are presented as well as cleanup techniques designed to control the spread of migration and aid in product recovery are described.

The behavior and fate of petroleum products lost to the ground depends on the hydrogeology. The migration of released product is influenced by the structure and composition of the media through which it flows. At some point contact between the immiscible petroleum product and groundwaters will be made. It is this point of contact which normally results in the most environmentally damaging contamination by petroleum hydrocarbons. Under the influence of groundwater flow, free phase and water-soluble hydrocarbons begin to migrate laterally, increasing the areal extent of pollution.

An evaluation of a spill area must be conducted to ensure positive identification of the source of product loss. After terminating the polluting source, a geohydrologic investigation is carried out, which provides the necessary information for design of a recovery system most suited to the affected area.

American Petroleum Institute, "Literature Inventory: Treatment Techniques Applicable to Gasoline Contaminated Groundwaters", API Pub. No. 4432, 1-53, appends., 1982.

Reports on a literature survey in which focus was on mildly contaminated groundwaters (about 15 ppm gasoline constituents) and on surface treatment processes. The processes considered included: activated carbon adsorption, air stripping, ozone treatment, ultra-violet radiation, reverse osmosis, polyurethane foam adsorption, activated sludge treatment, solvent extraction, ultrafiltration, coagulation, and land treatment.

It was concluded that activated carbon adsorption and air stripping (at ambient and elevated temperatures) and combinations of these processes were the most practicable for groundwater cleanups in the concentration range considered. However, land treatment and biological treatment in existing treatment plants were considered practicable where land and facilities are available. Other methods are ruled out on basis of cost and unavailability of process equipment at scale needed for groundwater cleanups.

American Petroleum Institute, "Treatment Technology for Removal of Dissolved Gasoline Components from Ground Water", API Pub. No. 4369, 1983.

Laboratory evaluation, describes assessment of activated carbon adsorption and air stripping for treating groundwater containing gasoline components. Activated carbon adsorption was tested using 1-inch diameter miniplant columns and ¼-inch diameter microcolumns. Factors evaluated included influent concentrations, feed preparation method, height of column, hydraulic loading, and quantity of steam used for activated carbon regeneration.

Air stripping was tested using 1½-inch diameter columns packed with ¼-inch berl saddles. Factors evaluated included influent concentration, temperature, air-water ratio, and feed composition.

Both activated carbon adsorption and air stripping proved effective in removing gasoline components from water, although neither method removes t-butyl alcohol. Air stripping removes methyl t-butyl ether effectively, which is not removed by activated carbon absorption.

Cost comparisons evaluate economic efficiency of activated carbon adsorption vs. air stripping.

Costs of activated carbon adsorption treatment of contaminated water at 200 gpm flow rate ranged from $0.30/m gals at 1 ppm influent concentration to $2.10/m gals at 100 ppm. Cost of airstripping was not sensitive to influent concentration and was $0.75/m gals consistently. These cost curves intersected at a concentration of about 15 ppm. Thus, at higher input concentrations air stripping was more cost effective and offered the additional advantage of removal of methyl t-butyl ether.

American Petroleum Institute, "Forced Venting to Remove Gasoline Vapor from a Large-Scale Model Aquifer", API Pub. No. 4431, 1-60, 1984.

Describes laboratory experiments in which 3 x 3 x 1.2 meter sand filled tanks were used. A constant moving water table was maintained at constant temperature of 13°C. A gasoline spill was simulated by adding gasoline above the capillary zone. During the 134-day experiment 50 to 84 percent of the gasoline was recovered. Four tanks were used to simulate long and short flow paths and the effects of different extraction rates.

It was concluded that: (1) forced venting is a practical way to reduce gasoline-vapor concentrations in the unsaturated zone and can remove some gasoline from the saturated zone, (2) short screened sections in the zone of high vapor concentration are more effective than continuously screened wells, (3) sealing the surface will optimize recovery by restricting vertical air circulation, and (4) a high initial extraction rate is desirable, which can be followed by lower extraction rates after vapor concentrations in the extraction wells has stabilized.

American Petroleum Institute, "Feasibility Studies on the Use of Hydrogen Peroxide to Enhance Microbial Degradation of Gasoline", API Pub. No. 4389, 1-36, 1985.

Bench-scale and-sand column experiments were used to assess the effectiveness of hydrogen peroxide (H_2O_2) injection into sand aquifers as a source of oxygen to accelerate the growth of gasoline degrading microrganisms. As H_2O_2 is toxic to microorganisms it was important to assess the upper concentration at which H_2O_2 could be used effectively.

The results indicated:

(1) H_2O_2 is reasonably stable in media representative of likely field conditions. Iron salts tend to catalyze the decomposition of H_2O_2, but this can be countered by addition of phosphates.

(2) The maximum concentration of H_2O_2 tolerated initially by mixed cultures of gasoline degraders was 0.05%. By increasing the concentrations of H_2O_2 incrementally, the tolerance level could be raised to 0.2%.

(3) Microbial densities in sand columns increased significantly following application of H_2O_2. This was attributed to increased oxygen provided by the H_2O_2 treatment.

American Petroleum Institute, "Test Results of Surfactant Enhanced Gasoline Recovery in a Large-Scale Model Aquifer", API Pub. No. 4390, 1-59, 1985.

Laboratory studies of the efficiency of surfactant removal of gasoline from a simulated aquifer were carried out in a 10-ft x 10 ft x 4 ft tank with the water table 1 ft below the surface. The surfactant used was a 2% solution of Richonate YLA with 2% Hyonic PE-90 added to lower the viscosity. Gasoline was introduced just above the water table. Three types of surfactant applications were tested: (1) a single application by percolation through the sand, (2) multiple daily applications by percolation through the sand, and (3) multiple daily applications by injection into the water table. Gasoline removed totaled 6, 76, and 83 percent, respectively.

American Petroleum Institute, "Subsurface Venting of Hydrocarbon Vapors from an Underground Aquifer", API Pub. No. 4410, 102 p, appends., 1985.

Describes field experiments, in which vapor recovery from wells at a gasoline spill site was tested with several configurations of air-inlet-well production rates, and monitoring depths. Two recovery wells were screened from 14 to 20 feet below land surface, and air inlet wells spaced 20 and 40 feet from recovery wells were screened over the same depth interval. Vapor monitoring probes were installed at heights of one, two, and five feet above the capillary zones. Vapor samples were taken at three different production rates, 18.5 scfm, 22.6 scfm, and 39.8 scfm.

It was found that the radius of influence extended about 50 feet from the recovery wells at the lowest production rate, and about 110 feet at the highest rate. Decreases in vapor concentrations from pre-test levels ranged from 12 to 99 percent depending upon flow rates and distance of monitoring probe from recovery well over periods of 10 to 15 days. A total of 166 gallons of product was recovered during three tests. The concentration of vapors in the recovery-well discharge was relatively constant throughout the tests, thus cumulative recovery was linear with time of production.

It was concluded that subsurface vapor venting is effective not only for removing hazardous vapors from the unsaturated zone, but was effective also in removing volatile hydrocarbons from the groundwater by evaporation from the water table.

American Petroleum Institute, "Literature Survey: Hydrocarbon Solubilities and Attenuation Mechanisms", API Pub. No. 4414, 1-101, 1985.

This survey gives results of a literature search on solubilities of gasoline components and attenuation mechanisms which tend to remove these components from subsurface waters. The search focused on the 276 components through C_{12}. Most of the solubility data were for individual compounds in distilled water at $25^{o}C$. Factors affecting solubility significantly were temperature, salinity, and presence of dissolved organics in solution. Pressure and pH had little effect.

Benzene was the most soluble consitituent (about 1,800 ppm), followed by three conjugated dienes, and then low molecular weight olefins and cycloolefins. The substituted benzenes (xylenes, solubility 150-200 ppm; ethylbenzene, about 175 ppm; and toluene, about 600 ppm) dissolve readily in water. Alkanes generally are insoluble in water at $25^{o}C$. The solubility of olefins and paraffins varied inversely with molecular weight.

Effects of temperature are believed important due to reported increase in solubility below 17.5°C, however, most laboratory studies are carried out at 25°C and little information is available at other temperatures or under field conditions.

Biodegradation, sorption, and volatilization are the major mechanisms acting to attenuate gasoline constituents in the soil system. The capacity of hydrocarbons to be adsorbed decreases in the order of: olefins, aromatics, cycloalkanes, alkanes. Within groups the higher molecular weight compounds are adsorbed to a greater degree than low molecular weight compounds. Thus, sorption is generally inversely related to solubility.

Generally volatility varies inversely with solubility, that is, the higher the vapor pressure the lower the solubility; however, benzene is both highly volatile and highly soluble under laboratory conditions.

American Petroleum Institute, "Literature Survey; Unassisted Natural Mechanisms to Reduce Concentrations of Soluble Gasoline Components", API Pub. No. 4415, 1-73, 1985.

Reviews natural processes tending to reduce concentrations of gasoline components in surface and groundwaters. With respect to groundwaters, the main processes are adsorption, microbial degradation, and volatilization from soil grains in the unsaturated zone.

The review focuses on four aromatic constituents of gasoline, benzene, toluene, ethylbenzene, and xylenes, plus two additives, methyl-t-butyl ether, and t-butyl alcohol. These aromatic compounds are relatively insoluble in water, but are more soluble than the other major gasoline components, the alkanes.

The major factors identified as affecting hydrocarbon removal were temperature, character of sediments, and nutrient availability. The literature on sorption was so incomplete and contradictory that definite conclusions were impossible, beyond that sorption varies inversely with solubility.

Natural treatment processes offering promise for reduction of hydrocarbons in water are the use of holding ponds and lagoons to increase volatilization and photolysis, and land application/farming to increase volatilization and biodegradation.

American Petroleum Institute, "Cost Model for Selected Technologies for Removal of Gasoline Components", API Pub. No. 4422, 63, 1986.

A cost model was developed to provide conceptual level cost estimates of capital, operating, and maintenance costs related to aquifer restoration following a gasoline spill. Aromatic components of the spill were assumed as benzene, 25 mg/l; toluene, 14 mg/l; xylenes, 9 mg/l; ethyl benzene, 2 mg/l; additives (methyl-t-butyl ether (MTBE) or t-butyl alcohol (TBA), 10 mg/l. Other inputs to the cost model were obtained from the published literature.

The following conclusions were reached:

1. Aquifer restoration is a lengthy and complicated process, and will not likely result in the removal of gasoline components to non-detectable concentrations within a reasonable time period. In fact, under many aquifer conditions, it will be difficult to reduce aquifer hydrocarbon concentrations to less than 100 ppb, even when effluent recycle is practiced;

2. It is likely that the restoration period predicted by the cost model is underestimated, due to the fact that the contribution of phase-separated hydrocarbons to the groundwater was not considered;

3. Aquifer remediation is expensive, particularly when total costs over long restoration periods are considered;

4. Cleanup costs will significantly increase if required aquifer hydrocarbon cleanup target concentrations are decreased;

5. Treated effluent reinjection will decrease the aquifer-restoration period to some extent, most notably in the most permeable formations. Removal of hydrocarbons from poorly permeable formations appears to be less influenced by effluent recycle;

6. Only limited information on treatment technologies for MTBE and TBA removal from groundwater is available, particularly at low concentrations.

7. At present, carbon adsorption, air stripping, or a combination of the two technologies are the most applicable proven technologies for the restoration of an aquifer contaminated by a gasoline spill. Although other technologies such as biological treatment may be feasible, they are largely unproven at full scale remediation, particularly for compounds such as MTBE and TBA.

American Petroleum Institute, "Enhancing the Microbial Degradation of Underground Gasoline by Increasing Available Oxygen", API Pub. No. 4428, 1-25, appends., 1986.

The report describes a literature search on providing favorable conditions for aerobic microbial degradation of gasoline in the subsurface. It was concluded that the most cost-effective means of increasing oxygen supplies for bacteria was through the injection of a hydrogen peroxide solution.

Laboratory studies were carried out to determine the limit of hydrogen peroxide concentration beyond which the peroxide would be toxic to soil bacteria. It was found that newly established cultures were sensitive to peroxide at about 100 ppm, but that mature cultures could tolerate up to 1,000 ppm without significant damage.

American Petroleum Institute, "Examination of Venting for Removal of Gasoline Vapors from Contaminated Soil", API Pub. No. 4429, 1-25, 1986.

Simulation modeling was employed to analyze a process for removing hydrocarbon vapors from soil overlying a water table contaminated with gasoline. It was concluded that:

1. The very light fractions of gasoline contribute most to total vapor pressure of gasoline due to their high vapor pressure.
2. When vapor in equilibrium with gasoline is carried away from the liquid phase, the vapor is greatly enriched in the light fractions and the remaining liquid becomes richer in the heavier, less volatile fractions.
3. On the basis of air moved, reduced pressures are more efficient than increased pressures.

American Petroleum Institute, "Field Study of Enhanced Subsurface Biodegradation of Hydrocarbons Using Hydrogen Peroxide as an Oxygen Source", API Pub. No. 4448, 1-75, 1987

Reports on a field study of in-situ enhanced biodegradation of gasoline floating on groundwater in an unconfined sandy glacial aquifer. The objective of the study was to assess the effectiveness of using H_2O_2 as an oxygen source to stimulate biodegradation under the conditions described.

A test cell was formed by an infiltration barrier consisting of trenches. This was further subdivided by trenches into two zones containing 4,100 and 13,400 lbs. of hydrocarbon, respectively. Measured amounts of nutrients and H_2O_2 were injected over a 6.5 month period.

The principal conclusions were: (1) H_2O_2 was effective in stimulating microbial biodegradation, (2) hydrocarbon concentrations declined 60-70 percent, (3) microbial population densities corresponded to areas of greatest H_2O_2/nutrient injections, (4) aquifer permeability decreased significantly, presumably due to mineral precipitation, (5) cost was $65 to $100 per gallon of degraded hydrocarbon, and (6) site hydrogeology should be carefully evaluated prior to in-situ biodegradation.

Bouwer, E. J., "Biotransformation of Organic Micropollutants in the Subsurface", Proc., NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water - Prevention, Detection, and Restoration, Natl. Water Well Association, Dublin, OH, 66-80, 1984.

The paper presents theory and describes laboratory experiments with focus upon secondary utilization of contaminants by microorganisms. In primary utilization non-photosynthetic microorganisms, chiefly bacteria, obtain energy for growth by oxidation of hydrocarbons in the presence of an electron acceptor, such as oxygen under aerobic conditions, or nitrate, sulphate, or carbon dioxide under anaerobic conditions.

When the concentrations of organic nutrients in the subsurface environment is very low, microorganisms may not obtain sufficient energy from oxidation of ambient hydrocarbons to meet their maintenance requirements, and dissolved contaminants in water may not be degraded. However, simultaneous utilization of nutrients is possible; thus microorganisms can metabolize trace amounts of contaminants in the presence of other organics which provide energy needed for microrganism culture. This process, termed secondary utilization, permits microorganisms to degrade contaminants that could not otherwise be utilized, through providing an outside source of nutrients.

Laboratory continuous column experiments using acetate as the primary nutrient source and non-chlorinated aromatic priority pollutants, ethylbenzene, styrene, and naphthalene as secondary sources, showed that these compounds were degraded to near detection limits after five days acclimation time. In these experiments acetate in the feedwater was maintained at 1 mg/L concentration, and the priority pollutant at 10 to 30 ug/L. The detention time in the columns was about 20 minutes.

At the field scale secondary utilization can be stimulated for in-situ groundwater treatment by supplying suitable nutrients as a primary source of energy and oxygen as an electron acceptor. In situations where the contaminant plume is poorly defined, the same objective can be met by a bioreactor on the surface supplied with well water from the contaminated zone.

Broscious, J. A., V. Batu, and M. C. Plautz, "Recovery of Petroleum Product from a Highly Permeable Aquifer Under the Effects of Municipal Water Supply Wells", Proc., Sixth Nat'l Symposium and Exposition on Aquifer Restoration and Ground Water Monitoring, Nat'l Water Well Association, Dublin, OH 493-509, 1986.

This paper presents experience in a case study where the aquifer beneath a petroleum spill is highly permeable and located in an urban area, within the zone of influence of municipal water wells. In such circumstances the free product lens has the potential to migrate rapidly under influence of the individual production wells.

The spill area is underlain by two distinct geologic units. Similar response to pumping stresses demonstrates that the two units comprise a homogeneous hydrogeologic unit of high permeability (Transmissivity (T) = 3.7×10^3 ft^2/day, Hydraulic conductivity (K) = 371.0 ft/day). The impact of the municipal water supply wells situated approximately 400 feet from the spill site, was proven quite significant (water levels fluctuated approximately ±1.0 foot in a daily period).

Water-table fluctuation caused by pumping demands at production wells can reduce the accuracy of the calculated amount of product to be recovered, thus reducing the optimum rate of recovery. This is due to the fact that under a fluctuating water table, the thickness of product measured in the field can exhibit a large range of values. As the water table drops, some of the product migrates with the water table and the remainder will be absorbed by the soil it passes through. When the water table rises, the previously absorbed product will be picked up and once again be influenced by local groundwater gradients.

To reduce costs and maximize efficiency of recovery operations, the effect of local production wells needs to be analyzed and methods for monitoring and controlling these effects need to be implemented.

Brown, R. A., and R. D. Norris, "Oxygen Transport in Contaminated Aquifers with Hydrogen Peroxide", Proc., NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water - Prevention, Detection and Restoration, Nat'l. Water Well Association, Dublin, OH, 441-450, 1984.

Low solubility of oxygen in water and rapid depletion of oxygen by aquifer bacteria limit the effectiveness of bioreclamation in aerobic systems. The authors discuss how this limitation can be circumvented through injecting hydrogen peroxide into the aquifer through wells.

Typically the solubility of oxygen in water is 8-10 ppm. Column tests were conducted using air, pure oxygen, and hydrogen peroxide in environments in which gasoline utilizing bacteria had been established. The available oxygen averaged 8 ppm with air, 40 ppm with pure oxygen, and 200 ppm with hydrogen peroxide. It was found that bacterial growth was maximized by using peroxide. Peroxide must be used with care, however, because evolution of free oxygen can lead to blocking of porosity by bubbles, and hydrogen peroxide is toxic to bacteria at high levels.

Burke, M. R., and D. C. Buzea, "Unique Technology Applied to the Cleanup of Hydrocarbon Product from a Low Permeability Formation in a Residential Neighborhood in St. Paul, Minnesota", Proc., NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water - Prevention, Detection, and Restoration, Nat'l. Water Well Association, Dublin, OH, 377-399, 1984.

The paper describes a system used to clean up a large product spill floating on the shallow water table in poorly permeable glacial drift deposits in a residential neighborhood. Leakage of 60,000-90,000 gallons of product from a liquid petroleum pipeline resulted in a floating lens of product beneath an area of 120,000 square feet. Because of shallow depth to water strong odors were observed and several houses were evacuated.

Because of the shallow water table, low permeability of the glacial deposits, and residential character of the contaminated area, a recovery system consisting of 100 closely spaced four-inch diameter wells was constructed. The wells are connected by subsurface lines to a single centrifugal pump, which discharges to an oil-water separator and recovery system.

After six months of operation 45,000 gallons of product had been recovered, and a water-table depression had been maintained, thus alleviating problems of odors and product discharge.

Chaffee, W. T, and R. A. Weimar, "Remedial Programs for Ground-Water Supplies Contaminated by Gasoline", Proc., Third Nat'l Symposium on Aquifer Restoration and Ground Water Monitoring, Water Well Journal Publishing Co., Worthington, OH., 39-46, 1983.

Programs for the investigation and cleanup of groundwater supplies contaminated by gasoline are based on two case studies. In one a gasoline storage tank at a service station leaked 2,000 to 3,000 gallons of high octane unleaded gasoline which contaminated a nearby well field supplying 60 percent of a town's water supply. Initial investigation revealed contamination about 300 feet from the production wells. In the other a service station gasoline storage tank leak contaminated fractured rock formations being pumped by about 50 private wells belonging to nearby residents. The leak was first detected by a gasoline taste and odor in the water.

The primary techiques used for assessing the extent and movement of the gasoline are: (1) monitoring wells, (2) gasoline-lens detection, and (3) contaminant-plume detection.

(1) Monitoring wells are used to determine water levels, detect contaminants, monitor movement and evaluate cleanup measures.

(2) The thickness of the gasoline lens is measured using a steel tape with water and gasoline sensitive paste.

(3) In detecting the plume of contamination the methods used were: dissolved oxygen (lower in spill area), temperature (higher in spill area), microbial levels (gasoline-utilizing bacteria concentrations higher in spill area), Organic Vapor Analyzer (results are relative), laboratory analysis (most accurate and costly).

Final cleanup involved one of two alternatives: abandon the water supply temporarily or permanently, or rehabilitate the supply.

Three methods were considered in rehabilitation: (1) treat the aquifer with a bioreclamation process while temporarily using an alternate water supply. This would involve adding oxygen and nutrients to the contaminated water, (2) use the existing contaminated water supply but install an aeration and/or activated charcoal-treatment system, (3) create a closed system recirculation cell at the spill site by pumping contaminated groundwater through an aerator and activated charcoal system and back into the contaminated area.

In case study 1 investigations showed the development of a new permanent groundwater supply would be too expensive and it was decided to rehabilitate the aquifer according to method 3 above. This would involve a shallow upper recirculation cell pumping 75 gpm and a treatment process consisting of an oil/water separator, an air stripping tower, and two GAC vessels.

In case study 2 it was decided that the most cost effective alternative was to extend the existing municipal system to serve the threatened area.

Dennis, David, M., "Effectively Recovering Oil Spills to Groundwater", Proc., 1977 Oil Spill Conference, API Publ. 4284, 255-258, 1977.

Oil spills which do not reach surface waters are given little consideration but are probably the most difficult to clean up. These types of spills represent a long-term threat to health and the environment. Three methods of cleaning up this type of spill are proposed. These methods are 1) recovery trench, 2) recovery wells, and 3) crock recovery.

The recovery trench method employs a backhoe constructed trench downgradient of the spill. This trench intercepts contaminants moving downgradient and allows them to be pumped out and disposed of. The recovery wells system uses observation wells to depress the water table and cause contamination to flow to the wells for disposal. The recovery system, which employs large diameter casings, is used on low permeability material with little groundwater movement.

Duffy, J. J., M. F. Mohtadi, and E. Peake, "Subsurface Persistence of Crude Oil Spilled on Land and Its Transport in Groundwater", Proc., 1977 Oil Spill Conf. (Prevention, Behavior, Control and Cleanup), API Pub. No. 4284, 475-478, 1977.

The persistence of water-soluble hydrocarbons from crude oil releases on land was investigated as source of groundwater contamination by means of theoretical models, percolation experiments, and the analysis of core samples from release sites. Examination of a one-dimensional flow model of convection, dispersion, biodegradation, and adsorption of an oil-water solution beneath a water table revealed that under certain conditions adsorption has no effect on the maximum oil concentration reached at any given distance from a release. Chemical analysis of water percolated through an oil-release zone in a sand trough and also through soil cores taken at release sites revealed that it may take the equivalent of much more than 100 times the average annual rainfall of Calgary to diminish the water soluble components in the leachate to a level acceptable in drinking water. Measurements of the amount of alkanes and isoprenoids as functions of depth in field cores at release sites of various ages and locations indicated that biodegradation rates are much lower in the anaerobic zone than above. Theoretical predictions indicate that contaminated groundwater may extend in the direction of flow from less than one meter to several thousand meters from a release depending primarily on biodegradation rates and pore velocities. It is conclued that oil in the subsoil resulting from releases on land has the potential to pose very long-term threats to groundwater quality and, by the mechanism of resurfacing, to vegetation.

Haven, E. L., and D. E. Jones, "Petroleum Recovery in a Tidal Environment", Proc., Fifth Nat'l Symposium and Exposition on Aquifer Restoration and Groundwater Monitoring, Nat'l Water Well Association, Dublin, OH, 668-690, 1985.

A petroleum recovery system was designed and installed at a petroleum bulk storage terminal in Bangor, Maine in response to seepage into the adjacent Penobscot River. The recovery system had to be specially designed to take into account an average tidal fluctuation of 16 feet in the river with a corresponding 8-foot change in the groundwater beneath the site.

A hydrogeological investigation included the installation of groundwater monitoring wells to determine the hydraulic properties of the alluvial aquifer and the extent of free-floating petroleum. Periodic gauging of the wells showed a significant change in groundwater elevations and petroleum thicknesses with tidal fluctuations. A 36-hour survey of petroleum and groundwater levels in the wells was conducted to quantify these changes.

The petroleum thicknesses in all but one well were at a minimum at the high groundwater level, increasing to a maximum thickness as the water level dropped. The rapid increase in the petroleum thickness as the water level drops is due to preferential migration of the petroleum into the well. As the groundwater level declines, the soil pores remain partially full of water and the petroleum migrates into the well rather than vertically through the partially saturated soil. The minimum petroleum thickness at the high water level occurs as the groundwater level rises rapidly, forcing the petroleum out into the formation.

Based on the results of the hydrogeological study and tidal survey, a petroleum-recovery system was designed and installed. The system consists of a 12-inch diameter recovery well equipped with explosion-proof pumps and controls. The two-pump system includes: (1) a pump to depress the water table creating a gradient for petroleum to migrate to the well; and (2) a pump to evacuate petroleum as it accumulates in the well. The water level in the well is maintained below the low tide level through the entire tidal cycle.

The initial petroleum recovery rate of about 250 gallons per day (gpd) decreased to approximately 150 gpd following several weeks of operation. After two months of aeration the recovery rate decreased to about 50 gpd. Following a further mid-winter decline, the rate of recovery has again stabilized at approximately 50 gpd.

The continuing recovery operation has eliminated the seepage of petroleum into the river and significantly reduced the amount of petroleum on the groundwater.

Jensen, B., E. Arvin, and A. J. Gundersen, "The Degradation of Aromatic Hydrocarbons with Bacteria from Oil Contaminated Aquifers", Proc., NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water - Prevention, Detection, and Restoration, Nat'l. Water Well Association, Dublin, OH, 421-435, 1985.

Fixed film reactors and chemostrates were used to test the biodegradability at laboratory scale of toluene, xylene, trimethylbenzene, naphthalene, phenanthrene, and ethyl and methylnaphthalenes. The fixed film reactor consisted of two concentric plexiglass cylinders, the inner one of which was kept rotating. The rotation ensures mixing of the liquid and keeps the biofilm thickness even due to hydraulic sheer. The chemostate system is a reactor in which a bacterial culture is kept in suspension by magnetic stirring. Experiments were performed under aerobic conditions at 2 mg/l oxygen concentration and the bacteria were fed inorganic nutrients.

Tests with the biofilm reactor showed that water contaminated with gasoline, light fuel oil, and heavy fuel oil at the 1 ppm level could be scrubbed of dissolved hydrocarbons generally within 100 hours. Biphenyl generally was the most degradable compound, generally disappearing (1 ppb) within 30 to 70 hours. Phenanthrene was the most refractory compound. In one sample from a heavey fuel-oil release 60 ppb of phenanthrene remained after 148 hours, although that represented an order of magnitude reduction.

The main conclusion was that microorganisms are able to degrade one-and two ringed aromatic hydrocarbons down to 1 ug/l or lower with a fairly high reaction rate, given sufficient oxygen and nutrients. With naphthalene as the only carbon and energy source the microorganisms in a fixed biofilm can easily degrade the hydrocarbon down to 1 ug/l. Most surprising is the observation, that the Monod constant, K_s, appears to be about 1 ug/l or even lower, which indicates a zero order reaction for naphthalene in the concentration range of practical interest. Normal expectations are that the reaction rate for organic compounds is first order in the microgram per liter concentration range.

If groundwater is taken from an anaerobic gasoline or fuel oil contaminated area with no significant degradation activity, and oxygen and nutrients are then added, rapid degradation of the hydrocarbons down to one microgram per liter or less starts with little lag time. This however, requires an initial hydrocarbon concentration below about 10 mg/l. At higher concentrations a considerable adaptation time may be expected.

Kappeler, T. and K. Wuhrmann, "Microbial Degradation of the Water-Soluble Fraction of Gas Oil - I", Water Research Bull., V. 12, 327-333, 1978.

The report describes laboratory tests of the aerobic microbial degradation of components of gas oil in aqueous solution when the contaminated water is percolated through an unsaturated sand column.

Microbial degradation of the water soluble components of gas oil was measured both qualitatively and quantitatively. The mixed ambient flora in clean groundwater served as the inoculum in continuous percolation experiments. Concentration gradients of individual components and dissolved organic carbon were measured as a function of percolation time. A lag period of about five days at 10°C and 1 day at 25°C, respectively, preceded measureable attack of dissolved hydrocarbons. After steady state conditions were established, complete elimination of hydrocarbons occurred within a few decimeters of percolation depth.

Kobayashi, H., and B. E. Rittman, "Microbial Removal of Hazardous Organic Compounds", Envir. Sci. and Technol., 16/3: 170A-181A, 1982.

Reviews the broad spectrum of removal of hazardous organic compounds by biodegradation. Among hazardous organic compounds associated with oil refinery environments, such as benzene, toluene, and polynuclear aromatic hydrocarbons. Heterotrophic bacteria, such as Pseudomonas, and fungi of the genus Cunninghamella, are identified as having good potential for degrading hazardous petroleum components. Phototrophic organisms, while capable of biodegrading many hydrocarbons, would have little applicability to the groundwater regime.

Littlefield, K. V., N. E. Wehler, and R. W. Heard, "Identification and Removal of Hydrocarbons from Unconsolidated Sediments Affected by Tidal Fluctuations", Proc., Fourth Nat'l Symposium on Aquifer Restoration and Ground Water Monitoring, Nat'l Water Well Association, Dublin, OH, 316-322, 1984.

Multiple product losses occurred in a petroleum tank farm through its 80-year history. Accumulation of the product on the water table and subsequent migration resulted in seepage from the site into an adjacent creek. A thorough hydrogeological investigation was designed to identify variations in the subsurface that controlled migration of the hydrocarbons. Geologic logging of the soils, geophysical surveys and aquifer tests revealed the presence of abandoned stream channels, which acted as preferred conduits for the movement of hydrocarbons. Interlayered fine- and coarse-grained sediments resulted in the formation of natural traps where oil preferentially accumulated. Three major "pools" were located and an 8-inch recovery well was installed in each pool. Water-table depression pumps placed in these wells created cones of depression that induced oil flow from the aquifer. Complications in the recovery method due to tidal fluctuations and changes in pumping level caused by mineral precipitation in the well and depression pumps were overcome by the use of an automatic skimmer device to recover the floating hydrocarbons. This equipment automatically compensated for the changes in water level and product thickness and was used to successfully recover more than 24,000 gallons of product in the first 240 days of the operation. The recovery effort was completely automatic and required only weekly visits to monitor wells, gauge and empty recovery oil tanks, maintain groundwater depression pumps and adjust pumping rates. The recovery effort continues with noticeable decrease in oil seepage to the creek, oil thickness in the aquifer and oil recovery rate. Oil recovery rates decrease as oil must be induced from greater distances and becomes entrained in the soils.

Manos, C. G., Jr., K. R. Williams, W. D. Balfour, and S. J. Williamson, "Effects of Clay Mineral-Organic Matter Complexes on Gaseous Hydrocarbon Emissions from Soils", Proc., NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water - Prevention, Detection, and Restoration, Nat'l. Water Well Association, Dublin, OH, 189-206, 1985.

Effects on adsorption and desorption of n-pentane were tested in the laboratory by varying additions of natural silt-clay soils containing organic complexes. N-pentane emissions were reduced by one percent for each one percent addition of the silt-clay soil to a clean sand. After firing the organic soil at 400°C to remove organic matter, it was found that sorption had increased greatly. In those tests N-pentane emissions were reduced by four percent for each one percent addition of silt-clay soil. It was concluded that both soil organic matter and clay content significantly affect gaseous emissions of volatile compounds from soils.

McGill, W. B., "Soil Restoration Following Oil Spills - A Review", Jour. Canadian Petroleum Tech., V. 16, No.2, 60-67, 1977.

Presents techniques available for removal of residual oil in soil media after initial cleanup is completed. The effectiveness of various techniques depends on the type and amount of oil, and soil environment. Up to 40 percent of residual oil can be removed through non-biological mechanisms, primarily volatilization. Volatilization of oil components is most significant from exposed surfaces. Enhancement of volatilizaton may be achieved by mixing or tillage and through forced aeration of sub-soils. Other non-biological mechanisms of oil removal include burning and photo-oxidation.

Oil that is not removed from soil through physical and chemical means must be dealt with biochemically. Biological restoration generally requires nutrient additions, aeration, maintenance of a neutral pH, tillage or mixing to break surface crusts and some form of drainage in very wet spots. Stimulation of oil-degrading organisms by these methods has proven to increase the rate of restoration by several fold and sometimes an order of magnitude. It is noted, however, that some oil components are resistant to microbial attack and may persist for several years in soil.

McIntyre, D., "Underground Oil Spill Investigation and Cleanup", Proc., 1983 Oil Spill Conference, Amer. Petrol Inst., Washington, D.C., 393-396, 1983.

In April 1978 an investigation of an oily sheen on a Connecticut River revealed the presence of three underground storage tanks in an industrial park as the potential source of contamination. One 10,000 gallon tank belonged to Company A which also owns the park. The other tanks holding 10,000 and 11,000 gallons belonged to Company B, a tenant of the park. Company B's 10,000 gallon tank had leaked 500 gallons of No. 2 oil 14 months earlier. Its 11,000 gallon tank was less than five years old but both 10,000 gallon tanks were over 20 years old. Both companies declined responsibility but Company A participated in the investigation conducted by the EPA and the Connecticut DEP.

Investigation showed easiest access to the groundwater through a low lying area where the depth to groundwater is 8-10 feet as opposed to 30 feet near the tanks. A 100 foot long interceptor trench was dug here and partially filled with crushed rock. A 10-foot deep standpipe (diam. of 55 gal drum) was installed in the trench from which oil and water were pumped. Oil flow stopped by May 1978. Analysis showed No. 2 type oil. Company B's 10,000 gallon tank held No. 2 oil before its leak, at which time it was replaced by No. 4 oil. Responsibility was not determined by this investigation.

The flow of oil resumed on June 30, 1978 and was contained by curtain booms and sorbents. In August an abandoned water intake pipe carried oil from the initial release site to an area 130 feet downstream creating a new release which was contained. On September 2 additional recovery wells were drilled, one upstream and one downstream from the original release with the downstream well intercepting the new release. This system recovered an average of 400 gallons per month from November 1978 to March 1979 with the leakage stopped during this period. Leakage resumed in April 1979 at a reduced rate.

In August, ten 1.5-inch diameter observation wells were installed. They provided information on location and extent of contamination but not on its source. Final estimates of the maximum volume of oil in the ground ranged from 37,700 to 151,000 gallons.

The EPA assumed control of the project in April 1980 and replaced the recovery system with a 12-inch diameter metal well casing, 37 feet deep, installed near the old standpipe and an automatic pumping system feeding two 550 gallon tanks.

In August 1980, the tanks were excavated revealing that Company B had a badly scaled 10,000 gallon tank with oil saturated soil. In 1981 there was renewed leaching from the downstream site. A second 12-inch diameter recovery well was installed to handle the situation.

In conclusion, more than 95% of the oil was recovered before it reached surface water. This amounted to 100,000 gallons as of October 1982. Most recovery was achieved by the second recovery system. Environmental damage was negligible. It was necessary to excavate the tanks to determine responsibility for the contamination as all other methods failed in this respect.

Minugh, E. M., J. J. Patry, D. A. Keech, and W. R. Leek, "A Case History: Cleanup of a Subsurface Leak of Refined Product", Proc., 1983 Oil Spill Conference, Amer. Petrol. Inst., Washington, D.C., 397-403, 1983.

In October 1980, two restaurants 500 feet downgradient from a bulk plant handling refined products reported gasoline odor. Five out of 27 wells (2-inch diameter, 20 feet deep) drilled contained free hydrocarbons. Eleven of the fourteen test pits (13 feet deep) revealed free hydrocarbons floating on the groundwater surface with a two to three foot zone of contaminated soil above. The bulk plant was determined to be the the source of contamination. The plant has six surface tanks storing 100,000 gallons and two buried tanks storing 7,000 gallons. Testing showed the buried tanks were tight and that a buried tank not in service was leaking. Once excavated, evidence was found of former gasoline leaks.

A filter-scavenger oil-recovery device in the area of greatest contamination recovered 250 gallons of gasoline and diesel oil mixture in the first month of operation. During a subsequent field investigation nineteen 13-foot deep exploratory pits were dug and 27 exploratory wells were drilled. Groundwater flow rates and directions were determined, dynamic pumping tests were performed, soil and groundwater were analyzed for gasoline content and biostimulation of groundwater samples was conducted.

The area of greatest contamination was found to be a highly porous channel deposit bounded by low permeability alluvial-fan deposits. Groundwaters outside the channel were not contaminated. The bulk plant and restaurants are above this channel. The water-table gradient was nearly parallel to the gradient of the alluvial fan. Flow rates varied drastically as did dynamic pumping rates (0.9 to over 50 gallons per minute). Biostimulation studies showed biodegradation to be feasible.

Two recovery and cleanup systems were developed; one for the bulk plant and the other for the restaurants. The bulk plant's system consisted of three recovery wells in a line perpendicular to the hydraulic gradient located in the area of maximum contamination. Water produced by the depression of the water table was piped upgradient to injection trenches at which point nutrients would be added. An air compressor connected to an air line running the length of the injection trench with porous stone diffusers along the line was used to aerate the water. A similar system was used for the restaurants with modifications due to the proximity of traffic and a business area. Injection trenches were replaced by injection wells and a vapor elimination system was incorporated. This system consisted of five 2-inch air injection wells at 10-foot intervals on one side of the building and a similar array of vacuum wells on the other side. Air would flow between the two removing gasoline vapors. From October 11, 1981 to September 30, 1982 a total of 3,266 gallons of free hydrocarbons was recovered with 85 percent having been recovered in the first two months.

The biodegradation system began operation October 2, 1981 and from this time to September 1982, a total of 105 nutrient injections were made totaling 16.65 tons of chemicals. Nutrients first reached the bulk plant 12 days after and the restaurants three to five days after the initial injection. Dissolved oxygen first appeared five months later and at this time no free hydrocarbons were detected. The vapor elimination system had reduced hydrocarbon levels from an initial level exceeding the lower explosive limit for gasoline to negligible levels by July 1982. By August 1982 dissolved organic carbon in the water was under five ppm.

O'Connor, M. J., A. M. Wofford, and R. M. Richardson, "Contamination of Groundwater by Hydrocarbons from a Refinery - A Case History", Proc., 1981 Oil Spill Conference (Prevention, Behavior, Control, Cleanup), Amer. Petrol. Inst., Washington, D. C., 393-407, 1981.

The Gulf Canada Products Company Asphalt Plant and Terminal in Calgary, Alberta, operated for almost four decades without a serious environmental incident. In February 1978, however, hydrocarbons were discovered seeping from the bank of a lagoon in the Inglewood Bird Sanctuary, a wildlife preserve located adjacent to the refinery. An investigation was immediately undertaken to determine the origin and extent of the subsurface contamination. Measures were concurrently adopted to intercept the flow of petroleum products before their entry into the lagoon, so that any adverse effects on migrating waterfowl could be minimized. A subsurface horizontal box culvert and impermeable curtain assembly along the leading edge of the contaminant were designed and constructed. Hydrocarbons that accumulated in the box culvert were removed with a vacuum truck.

Subsequent studies, which comprised the drilling and monitoring of over 70 test holes, revealed that approximately 16 hectares under the Bow River floodplain had been contaminated by a layer of hydrocarbons up to 1 m in thickness and up to 8,000 m^3 (2 million gal) in volume. It was concluded that the petroleum products had been lost to the subsurface during the normal course of operations over 40 years and had accumulated on the water table in a stratigraphic trap under the plant site. The recent release of the contaminant was attributed to a unique set of hydrogeologic conditions.

Three abstraction wells were installed at critical locations within the contaminated area. Each well contained separate pumps for withdrawal of groundwater and petroleum products. Collection is facilitated by piezometric drawdown caused by pumping clean groundwater at a rate of approximately $6.8 \times 10^{-2} m^3/sec$ (1,080 gpm). This water is used to recharge the aquifer inside the plant site, thus diverting any future spillage to the abstraction facility. Hydrocarbons recovered from each well were pumped, via an underground pipeline directly back to the plant, where they were re-refined. Results of the cleanup were not available at the time of writing.

O'Connor, M. J., A. M. Wofford, and S. K. Ray, "Recovery of Subsurface Hydrocarbons at an Asphalt Plant - Results of a Five-Year Monitoring Program", Proc., NWWA/API Conf. on Petroleum Hydrocargons and Organic Chemicals in Ground Water - Prevention, Detection and Reclamation, Nat'l. Water Well Association, Dublin, OH., 359-376, 1984.

This presents an update of an article by J. M. O'Connor and others (1981) on the same spill. An interceptor trench installed near the leading edge of the hydrocarbon contaminant plume together with three recovery wells have prevented further product leakage to the wildlife-refuge lagoon over five years of operation.

Continuous operation of the recovery system from 1978-84 had resulted in recovery of 1,300,000 liters (340,000 gallons) of product. Maximum rate of recovery was observed in the second half of 1979 of 250,000 liters (66,000 gallons) after recovery wells were placed in service. By the second half of 1983 the recovery rate had declined to 30,000 l/half year (16,000 gal/year).

Calculations based on product recovery rate and normalized apparent spill volume suggest that all free product will be recovered by 1990.

Pelikan, V., "Hydraulic Protection of Ground Waters Against Oil Substances", Proc., Int'l Symposium on Ground Water Pollution by Oil Hydrocarbons, Prague, Czech., Int'l Association of Hydrogeologists, 61-71, 1978.

The term hydraulic protection comprises those measures taken to protect groundwaters which bring about an artificial change of the level of the hydrostatic water table. Lowering of the water table is necessary to prevent the spread of pollution and to be able to withdraw from the contaminated formation polluted waters and any free phase pollutants. The extent of pollution is limited by constructing systems of protection wells located in one or several rows perpendicular to the direction of flow of groundwater. The depression formed by pumping from the system of wells must be continuous and must extend throughout the plume of pollution. The distances between the wells must be calculated so that the depression cones which are thus formed overlap one another by one fourth to one third. If one fails the necessary depression can be maintained by the neighboring wells. By minimizing the contact of undergroundwaters with oil substances the extent to which these pollutants may migrate can be minimized and their recovery enhanced.

Raddell, C. F. and D. A. Palombo, "Monitoring and Recovery of Free Hydrocarbons from a Shallow Aquifer", Proc., Sixth Nat'l Symposium and Exposition on Aquifer Restoration and Ground Water Monitoring, Columbus, OH, Nat'l Water Well Association, 466-481, 1986.

A preliminary hydrogeologic assessment of an inactive petroleum bulk storage terminal resulted in the discovery of significant free product(s) atop a shallow water table. The site lies in a midwestern humid state where recharge occurs from direct precipitation. Most product was "trapped" beneath the aboveground storage tank area where underlying fine grained sediments appeared to be saturated with product from the capillary fringe to below the stable water table.

Investigations involving shallow test pits and test wells resulted in a series of recommendations for recovery of free product. The tank area and other areas of free product accumulation were controlled with different schemes of recovery. In the tank area, a series of trenches filled with gravel were effectively utilized with small air operated diaphragm pumps to quickly remove 30,000 gallons of product within a period of 10 weeks. This particular area was monitored on a frequent basis with wells in order to optimize the rate of recovery. The rate of product removal has been maintained between 200 and 300 gallons/per week by alternating pumping of collector wells.

In other portions of the terminal, product in smaller volume was flowing uncontrolled toward a major river. This area required the installation of wells to recover product. Air-diaphragm pumps were utilized in conjunction with a water-table depression pump. A 4-inch diameter well was used to depress the water table with a submersible pump while operating an air-diaphragm pump to skim off product accumulating in the well. This procedure removed free product at a rate of 20-30 gallons per day.

Several automatic recovery systems have been designed and used on this site. The basic approach was to pump both product and water from the wells to a separator tank. Once a thousand or so gallons of product were recovered in the separator tank, it would be pumped over to a second 10,000 skid mounted tank. When 8,000± gallons were stored in the 10,000 gallon tank, a local refiner would pick up a load, which would be reprocessed in the refinery at a final stage.

The recovery systems were continuing to remove product at the time of writing.

Rogers, R. D., J. C. McFarlane, and A. J. Cross, "Adsorption and Desorption of Benzene in Two Soils and Montmorillonite Clay", Envir. Sci. and Technol., V. 14, No. 4, 457-460, 1980.

Laboratory batch-equilibration sorption tests were conducted on two natural soils and on two purified montmorillonite clays saturated with aluminum and calcium ions, respectively. With benzene concentrations in water of 10, 100, and 1,000 ppb it was found that sorption was minimal for the soils and Ca-clay. Benzene sorption on the Al-saturated clay was seven times greater than for the soils and three times greater than for Ca-saturated clay. Benzene tended to resist desorption. The most likely route of benzene loss from soils is by volatilization.

It was concluded that sorption is not the major effect of soil on benzene, rather the soil provides a medium for benzene degradation chiefly by volatilization. The reason for Al-saturated clay retaining more benzene than natural soils or Ca-saturated clay remains unexplained.

Stetzenbach, L. D., L. M. Kelly, K. J. Stetzenbach, and N. A. Sinclair, "Decreases in Hydrocarbons by Soil Bacteria", Proc., Groundwater Contamination and Reclamation Symposium, Am. Water Resources Association, 55-60, 1985.

Degradation by "Naturally-occurring" microorganisms may significantly affect the persistance of pollutants in the environment. To assess the impact of microbial activity on the concentration of polyaromatic hydrocarbons (PAHs), randomly selected isolates from aseptically collected soil cores of petroleum contaminated and uncontaminaed background sites were incubated with naphthalene, fluorene, anthracene, and pyrene (PAHs present in the groundwater underlying the contaminant site). Significant decreases in the concentration of naphthalene was noted, using High Performance Liquid Chromatography with fluorescence detection, in cultures with isolates from both contaminant and background sites. Decreases in the concentration of fluorene was enhanced in cultures of bacteria from the contaminant sites above the decreases achieved by the isolates from the uncontaminated sites. Enumeration with acridine organge direct count and standard plate count demonstrated that bacterial numbers increased proportionally with decreased PAH concentration. Naphthalene concentrations were noted to decrease to background levels in four weeks. At the end of 13 weeks fluorene concentrations had decreased to background levels while pyrene and anthracene had decreased to remaining concentration levels of 45 and 30 percent respectively.

Villaume, J. F., B. H. Herre, and D. P. Voykin, "Cleanup of an Oil Spill into Ground Water at Williamsport, Pennsylvania - A Case History", Proc., 1979 Oil Spill Conference (Prevention, Behavior, Control, Cleanup), API Pub. No. 4308, Washington, D.C. 501-505, 1979.

Describes interim efforts to cleanup leakage of fuel oil at an electric generating station. During 1977, more than 75,000 gallons of No.2 fuel oil leaked into the ground from a 100,000-gallon storage tank at Pennsylvania Power and Light Company's Williamsport Combustion Turbine and Substation Site, located about 1,000 feet from the Susquehanna River in a highly industrialized area.

Pumping from drilled wells was the preferred interim method of recovery. To limit the extent of the spill and collect the oil, groundwater was artificially drawn down at several points. The clean water from the bottom of the drawdown-recovery wells was discharged to a storm sewer; the oil-water mixture from the top was passed through a gravity separator. The separator underflow was returned to the ground through an abandoned drill hole.

The initial oil-recovery rate was 1,000 gallons/day, dropping to 100 gallons/day after three months, for a total of almost 45,000 gallons recovered after nine months. Average recovery costs were about $2.50/gallon.

The overall success of the cleanup effort was considered good, although attempts to establish an unattended operation had to be abandoned. Major problems encountered include an influx of sludge and sediment into the wells, chronic pump failures, and numerous restrictions to drilling, which shows that standard practices can not be applied routinely in every case. Further recovery efforts remained to be decided at the time of writing.

White, K. D., J. T. Novak, C. D. Goldsmith, and S. Bevan, "Microbial Degradation Kinetics of Alcohols in Subsurface Systems", Proc., NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water - Prevention, Detection, and Restoration, Nat'l. Water Well Association, Dublin, OH, 140-159, 1985.

Reports on laboratory testing of biodegradation of methanol and tertiary butyl alcohol (TBA), both gasoline additives, under aerobic and anaerobic conditions. Soil samples from four gasoline release sites and from uncontaminated sites were tested. All samples to depths of 100 feet contained significant bacterial populations.

Under aerobic conditions both methanol and TBA biodegraded readily, methanol disappearing in 33 days and TBA in 62 days. Under anaerobic conditions samples not previously contaminated exhibited rapid methanol degradation, but TBA degraded slowly. Samples from gasoline spill sites showed similar degradation of methanol, but enhanced degradation of TBA.

Willman, J. C., "Case History: OPEC in Southern Idaho", 1983 Oil Spill Conference, Amer. Petr. Inst., Washington, D.C., 389-391, 1983.

Nampa, Idaho is located over a shallow aquifer with the water table 15-25 feet deep; irrigation causes annual fluctuations of 10 to 20 feet in the water table. Contamination first appeared in 1975 as oily vapors and residues in the basements of downtown businesses. The source could not be located and since the problem was intermittent it wasn't pursued at the time. In 1980 a significant amount of oil accumulated in a furniture store basement. Four thousand five hundred gallons of oil was recovered in a sump in the basement by pumping a shallow relief well outside in the alley. Although the problem worsened from Fall 1980 to Spring 1981, a well situated 10 feet from the sump remained uncontaminated indicating the presence of subsurface barriers restricting oil mobility.

In 1981 EPA drilled 65 wells in the vicinity of the furniture store. Soil cores were recorded and wells were tested with a photo-ionizer organic analyzer in an effort to locate negative readings, organic fumes or oil. Each well was then flushed and pumped and the groundwater elevation recorded. Results showed the contaminated area to be contained within a four-square block area. The source was found to be a tank located two blocks east and one block south of the furniture store, leaking three gallons per day of diesel. This tank was removed from service.

The City of Nampa was contracted by the EPA to construct a pumping station to recover the oil. In the area of greatest contamination a 70 x 4-foot "L" shaped trench filled with 450 yards of gravel was constructed to collect oil. A vertical, 20-foot deep, 30-inch perforated caisson located at the bend in the trench was used to collect oil and pump it to a buried 1,000-gallon tank. Two pumps were used in the caisson. One 100-gpm groundwater pump created a cone of depression and discharged groundwater to a storm sewer. The other was an oil scavenger capable of pumping recovered oil to the storage tank at a rate of 50 gpm at 20-foot head.

From the end of September 1981 to August 1982, 11,600 gallons of oil had been collected. The remaining volume is unknown. The total cost of the project was $74,300; with the groundwater wells costing $16,000, the tank test costing $4,500 and the recovery system costing $53,800. The collected oil sold for $7,500.

Wilson, B. H., and J. F. Rees, "Biotransformation of Gasoline Hydrocarbons in Methanogenic Aquifer Material", Proc., NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water - Prevention, Detection, and Restoration, Nat'l. Water Well Association, Dublin, OH, 128-139, 1985.

The authors report on laboratory tests of degradation of benzene, toluene, ethylbenzene and o-xylene in an anaerobic environment. Concentrations in water of 600 mg/l for benzene and toluene and 250 mg/l for ethylbenzene and o-xylene, were seeded with anaerobic bacteria obtained from floodplain deposits.

All the compounds tested degraded, with or without addition of nutrients. At the end of 20 weeks toluene content had been reduced by 80 percent, but little reduction was observed of the other compounds. However, after 40 weeks toluene was reduced by 98 percent, benzene by 72 percent, ethylbenzene by 74 percent, and o-oxylene by 78 percent. Tests with carbon-14 labeled toluene indicate that it was transformed mainly to carbon dioxide.

Wilson, J. L., and S. H. Conrad, "Is Physical Displacement of Residual Hydrocarbons a Realistic Possibility in Aquifer Restoration", Proc., NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water - Prevention, Detection, and Restoration, Nat'l. Water Well Association, Dublin, OH, 274-298, 1984.

The paper reviews the literature on multiphase flow of hydrocarbons and water and concludes that in planning for cleanups of hydrocarbon spills more attention needs to be given to the trapping of hydrocarbons in a porous matrix by capillary forces.

The migration of hydrocarbon essentially immiscible with water occurs as a continuous multi-phase flow under the influence of capillary, viscous and gravity forces. Once the source of hydrocarbon is disrupted, and the main body of hydrocarbon displaced, some of it is trapped in the porous media because of capillary forces. Hydrocarbon migration halts as this lower, residual saturation is reached. The trapped hydrocarbon remains as pendular rings and/or isolated, essentially immobile blobs. Residual hydrocarbons act as a continual source of contaminants, as for example, water coming into contact with the trapped immiscible phase leaches soluble hydrocarbon components. Because residual hydrocarbons exist as a discontinuous phase, continuum flow models may be inappropriate to simulate conditions under which residual hydrocarbons are mobilized.

Residual hydrocarbon can occupy from 15 percent to 40 percent or more of the pore space. Much more hydrocarbon is retained in the saturated zone as blobs, than in the vadose zone as pendular rings and blobs. Soil structure has much less influence on residual saturation in the saturated zone. Once trapped as isolated blobs in the saturated zone, residual hydrocarbon can be mobilized by increasing the hydraulic gradient or reducing the interfacial tension. In very permeable media, such as a gravel or coarse sand, it is theoretically possible to obtain sufficient hydraulic gradients to sweep all of the blobs out. In soils of medium permeability, such as a fine to medium sand, some of the residual can be hydraulically removed. In less permeable media hydraulic means are futile. Design curves are given for blob mobilization in the saturated zone.

Residual hydrocarbon can migrate; it is discontinuous, not "irreducible". Relative permeability and pore pressure - saturation curves must be modified to account for the dependence of residual saturation on the gradient. Blob size and shape distributions, of importance to mobilization calculations, are also of importance to investigators who are interested in hydrocarbon volatilization, solution and biodegradation. Finally, laboratory experiments on leaching, transport and degradation of residual hydrocarbon must not be run under high gradients, or they risk mobilizing the blobs.

For refinery spills enhanced oil recovery methods developed for petroleum production may have some applications. Thermal or steam flooding may prove feasible, and alcohol flooding may be practicable in the cases of large volumes of hydrocarbons in place.

Yaniga, P., "Alternatives in Decontamination for Hydrocarbon-Contaminated Aquifers", Ground Water Monitoring Review, Water Well Journal Publ. Co., 47-57, Fall 1982.

Selection of available alternatives for abatement of underground hydrocarbon contamination depends primarily on the amount and type of contaminant involved, the hydrogeology of the affected area, the proximity of sensitive resources that could be damaged by contamination, the potential for ignition, explosions or asphyxiating concentrations of hydrocarbon vapors, and background water quality.

The author lists and describes a variety of recovery systems whose selection and effectiveness is governed by local conditions of the affected area.

Application of a two pump system nested in one production well to free-product situations is reported superior to systems that rely on infiltration trenches, skimming pumps, and oil/water separation at the surface. For dissolved product abatement, aeration (air stripping) or filtration (activated charcoal) is cited as the most effective means of product removal. To facilitate aquifer restoration following the removal of dissolved contaminants, recirculation through contaminated areas has proven an effective means of physical desorption of hydrocarbons bound to the soil particles. Biodegradation via biostimulation is achieved by air sparging to increase dissolved oxygen levels and by nutrient addition to stimulate growth of hydrocarbon consuming bacteria.

The application of techniques described appear most suited to achieve optimum results when applied to aquifers of moderate-to-good primary or secondary permeability.

7.0 REGULATORY BACKGROUND

7.1 EPA Groundwater Protection Strategy

The policy of the U.S. Environmental Protection Agency with regard to groundwater protection is that the states are to have the predominant role in groundwater protection, with the EPA providing support for both development of the states' institutional capabilities and for provision of technical assistance for a number of program activities. A number of EPA documents have been issued to provide such assistance. There are approximately 270 EPA program activities that relate to 25 of 33 groundwater contamination sources identified by the Office of Technology Assessment (1984: Protecting the Nation's Groundwater from Contamination). Differences in activity objectives and organizational location within EPA has led to a series of publications of somewhat different focus dealing with related groundwater activities. Refinery personnel dealing with groundwater monitoring or groundwater contamination may find differences in methods in different guideline documents or procedures under different programs. One such example of different programs and methods is that of RCRA and Superfund (CERCLA).

EPA's Ground-Water Protection Strategy document was issued in August of 1984 by the Office of Ground Water Protection. The major components of that strategy are:

1) EPA support for state development of comprehensive groundwater protection programs;

2) Assessment of groundwater contamination from then unaddressed sources, including leaking underground storage tanks, surface impoundments, and landfills;

3) Development of internal guidelines for consistency in EPA groundwater protection and clean-up programs; and

4) Strengthening of EPA's organization for groundwater management and of EPA's cooperation with federal and state agencies. As part of that strategy, EPA adopted a groundwater classification to focus priorities in groundwater protection as follows:

Class I: Special groundwaters that are highly vulnerable to contamination because of hydrological characteristics of areas in which they occur and either of (a) "irreplacability, with no reasonable alternative source of drinking water available to substantial populations"; or (b) "ecologically vital, in that the aquifer provides base flow for a particularly sensitive ecological system, that, if polluted, would destroy a unique habitat";

Class II: Current and potential sources of drinking water and waters having other beneficial uses; and

Class III: Groundwaters not considered potential sources of drinking water and of limited beneficial use, that is, groundwaters having more than 10,000 mg/l total dissolved solids or are "otherwise contaminated beyond levels that allow cleanup using methods reasonably employed in public water system treatment." (Ground Water Protection Strategy, p.5-6).

Groundwaters classified as Class III waters may receive less protection than Class I or II waters, but in general, technology standards for hazardous waste facilities would be the same as for the two higher classes unless waived on a case-by-case basis. Waivers are not available when contamination from a facility downgraded the water quality so as to preclude future use.

There are a variety of EPA documents that amplify aspects of EPA and state requirements. These documents do not deal explicitly with petroleum in groundwater but rather cover general aspects of regulatory procedures. They are listed here for the convenience of the reader, should they appear to be relevant to specific problems being encountered with regulatory procedures.

1) Guidelines for Ground-Water Classification under the EPA Ground-Water Protection Strategy, 1986, Office of Ground Water Protection.

2) Selected State and Territory Ground-Water Classification Systems, 1985, Office of Ground Water Protection.

3) EPA Activities Related to Sources of Ground-Water Contamination, 1987, Office of Ground Water Protection.

4) Ground-Water Monitoring Strategy, 1985, Office of Ground Water Protection.

5) RCRA Ground-Water Monitoring Technical Enforcement Guidance Document, 1986, OSWER-9950.1.

6) Hazardous Waste Land Treatment, 1983, SW-874.

7) Management of Hazardous Waste Leachate, 1982, SW-871.

8) Guide to the Disposal of Chemically Stabilized and Solidified Waste, 1982, SW-872.

9) Hydrologic Simulation on Solid Waste Disposal Sites, 1982, SW-868.

10) Closure of Hazardous Waste Surface Impoundments, 1982, SW-873.

7.2 Selected Examples of Some State and Local Requirements

Some 900 state, territorial, and local agencies deal with some aspect of groundwater, including data collection, regulation, and so on. Owners and operators of facilities must contact relevant regulatory agencies (which represent only a relatively small part of the 900) for local requirements. Frequently these requirements are based upon the Federal programs described above, although their requirements may be more extensive or more stringent than Federal program requirements, which represent a minimum level of protection.

There are several summaries of state groundwater regulatory programs and requirements available for reference, such as the American Petroleum Institute's Publication Number 4416, "Guide to State Groundwater Programs and Standards" Overview of State Ground-Water Program Summaries", Vol 1, (March, 1985); "State Ground-Water Program Summaries", Vol 2, (March, 1985); and "Survey of State Ground-Water Quality Protection Legislation, 1985" (April, 1987). When accurate and current regulatory information is required for a given state or local area, it is advisable to contact the appropriate agency because regulatory revisions are frequent and summary volumes are often out-of-date by the time of publication. There can be one or more state regulatory agencies for the above-described Federal regulations, or state agencies may administer state regulations for which there is no Federal regulatory counterpart. Should a state not be delegated responsibility for a Federal program, that program is administered within the state by the USEPA. There are exceptions such as the Safe Drinking Water Act's Wellhead Protection Program, which does not provide for Federal administration in the absence of a Federally-approved state program. Several state summaries are included here to give an indication of the variety of state regulatory programs now in operation.

7.2.1 Illinois

In addition to the State's general water-quality statute, the Illinois Environmental Protection Act, the State has been delegated authority for non-hazardous and hazardous waste sites under RCRA, and for the Underground Injection Control (UIC) program, both of which are administered by the Illinois Environmental Protection Agency. That agency also administers Clean Water Act programs. Responsibility for the public drinking water program is delegated jointly to the Illinois Environmental Protection Agency and the State Health Department. Several State agencies are engaged in groundwater monitoring activities, for example, the State Water Survey.

7.2.2 Louisiana

In addition to the State Water Control Law and the Louisiana Solid Waste Management and Recovery Act, Louisiana has been delegated authority for nonhazardous and hazardous waste programs under RCRA, which are administered by the Department of Environmental Quality, Divisions of Solid Waste and Hazardous Waste, respectively. The UIC program is administered by the Office of Conservation, Injection and Mining Division, for all five classes of wells. Public water-supply authority is delegated to the State as well, being administered by the Department of Health and Human Resources, Office of Health Services and Environmental Quality. The state's emergency response program for leaking underground gasoline tanks and for hazardous materials that could contaminate groundwater is jointly operated by the Department of Environmental Quality and the Louisiana State Police, Hazardous Materials Division. Enforcement authority for most of the groundwater programs resides with the Department of Environmental Quality. Other agencies, such as the U.S. Geological Survey, cooperate in groundwater quality monitoring for background data.

7.2.3 New Jersey

New Jersey has several environmental and water laws in addition to delegated Federal programs. The State's Department of Environmental Protection Division of Water Resources, is the lead agency for groundwater protection. The program operates as part of the New Jersey Water Pollution Control Act's Pollutant Discharge Elimination System Permit Program, which is used to regulate both surface and groundwater. Discharges to groundwater are regulated by permit from the Bureau of Ground Water. Contamination evaluation or pollution incidents can involve the Bureau of Ground Water, Bureau of Water Supply, Division of Waste Management, and Enforcement Regions. The Division of Water Resources regulates both nonhazardous and hazardous industrial waste disposal. The Division of Waste Management monitors CERCLA and the State's Spill Fund. The Division of Water Resources and the Division of Waste Management monitor water quality under the RCRA program. Drinking water quality is under the authority of the Division of Water Resources. In addition to the State programs located in the Department of Environmental Protection, eight county agencies have or are instituting groundwater monitoring programs. The State has received delegation of UIC, RCRA, and public water-supply supervision authority.

7.2.4 Texas

The Texas Water Code, the Solid Waste Disposal Act, and the Natural Resources Code provide much of the basis for Texas's groundwater protection program. In addition, the Department of Water Resources and the Department of Health jointly administer RCRA programs under a delegation of Phase 1 and 2 interim programs, with monitoring of hazardous waste sites, permitting and enforcement being exercised by the Department of Water Resources. Transport of industrial solid waste is administered by the Department of Water Resources and the Department of Public Safety. Disposal of hazardous wastes by well injection under the UIC program is delegated to the Department of Water Resources, which has authority for administering the program for Class I, III, IV, Va wells; the Class II and Vb well program is administered by the Texas Railroad Commission. Protection of public water supplies is handled by the

Department of Health, Division of Water Hygiene. The primary responsibility on a state-wide basis for groundwater protection and planning lies with the Department of Water Resources, however, nine other state agecies and nine undergroundwater conservation districts also have some responsibility for management, control, and protection of groundwater. Special rules apply for activities in certain areas, such as in the recharge area of the Edwards Aquifer.

Groundwater protection standards are adopted for waste-management units to establish the parameters for which compliance monitoring is required and to provide action levels for corrective action programs. Where possible, the standards are based on National Primary Drinking Water Regulations establishing maximum contaminant limits (MCLs); for constituents for which such standards have not been established, any statistically significant increase in the background level of a contaminant in groundwater beneath the waste-management unit triggers corrective action.

8.0 REGULATORY ANNOTATIONS

Regulatory annotations have been grouped into: (1) annotations to Federal Statutes and Regulations, and (2) pertinent annotations from the general literature relating to regulatory background. Under the first group, the material has been organized by the five major statues under which the USEPA regulates groundwater; (1) the Clean Water Act, (2) the Safe Drinking Water Act, (3) the Solid Waste Disposal Act, (4) the Toxic Substances Control Act, and (5) the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). The latter statute was amended in 1986 by the Superfund Amendments and Reauthorization Act (SARA); however, most of the implementing regulations have not been published in the Federal Register at the time of this compilation. For each major category relating to groundwater, the appropriate sections in the Code of Federal Regulations are cited together with the authorizing statute and references to the United States Code or other places at which the statute can be found.

8.1 Clean Water Act

8.1.1 Discharge of Oil

40 CFR 110-114 (authority: Federal Water Pollution Control Act Amendments of 1972; 33 USC 1251 et seq.)

The provisions of 40 CFR 110 prohibit the discharge of oil to navigable surface waters in quantities that have been determined to be harmful to the public health or welfare, including such discharges as would violate applicable water quality standards or "cause a film or sheen upon or discoloration of the surface or emulsion to be deposited beneath the surface of the water or upon adjoining shorelines (40 CFR 110.3)." Onshore and offshore fixed facilities, including processing and refining facilities that could discharge oil in harmful quantities, are required to maintain Oil Spill Prevention Control and Countermeasure Plans (40 CFR 112). The requirements of section 112 for a given facility are extensive and detailed, specifically designed to prevent discharges and spills that would reach surface waters. Penalty provisions for failure to comply with section 112 are included in 40 CFR 114. A recent report on contamination of groundwater alledged to have occurred as a result of surface seepage and spills from surface facilities such as dumps, pipelines, and storage tanks has recently been issued by the Alaska Division of Geology and Geophysics (Report of Investigations 87-16).

8.1.2 National Pollutant Discharge Elimination System

40 CFR 122 et seq. (authority: The Clean Water Act, 33 USC 1251 et seq.)

The NPDES system is designed to regulate the discharge of treated wastewater to navigable surface waters. However, there are some provisions that relate to the disposal of pollutants into wells. Sec. 122.50 requires that applicable effluent standards and limitations for discharges allowed by a NPDES permit be adjusted to reflect the reduction in raw waste load resulting from injection of part of the waste stream into an injection well. Sec. 123.28 requires that state permit programs administering the NPDES system include authority to regulate the disposal of pollutants into wells. Most state programs utilize the Underground Injection Control program under the authority of the Safe Drinking Water Act (40 CFR 144 et seq.) to administer the requirements of sec. 123.28.

8.1.3 National Primary Drinking Water Standards

40 CFR 141 et seq. (authority: 42 USC 300g-1, g-3, j-4, j-9).

For requirements under the Resource Conservation and Recovery Act (RCRA) that make reference to either Primary or Secondary Drinking Water Standards, see 40 CFR 141.11 through 141.16 and 143.3. Sec. 141.50 has recommended maximum contaminant levels for organic contaminants and 141.51 has RMCLs for inorganic contaminants.

8.1.4 Dredge and Fill Operations

Guidelines for Specification of Disposal Sites for Dredged or Fill Material . CFR 230 et seq. (authority: Clean Water Act of 1977, secs. 404(b) and 401(a)(33 USC 1344 (b), 1361(a)).

This section makes reference primarily to effects on surface-water hydrology and quality and to ecological effects of dredge and fill operations and soil disposal. However, among the water uses for which impacts are to be evaluated are those on "Municipal and private water supplies" that consist of surface water or groundwater directed to the intake of a municipal or private water-supply system (40 CFR 230.50(a)). Evaluation of the effects of dredging, filling, and spoil disposal on water-supply uses are to be for both the quantity of water available and for water quality (230.50(b)). The evaluations of a variety of enviromental factors, including municipal water supply, are to be by both the Corps of Engineers and the U.S. Environmental Protection Agency (231.1 et seq).

8.2 Safe Drinking Water Act

8.2.1 Underground Injection Control Program

40 CFR 144 et seq. (authority: 42 USC 300f et seq.; 42 USC 6901 et seq.).

The authority for the Underground Injection Control (UIC) program for injection of fluids into subsurface strata derives from both the Safe Drinking Water Act and, to the extent that it deals with hazardous waste, from the Resource Conservation and Recovery Act. The purpose of the requirements is "to assure that underground injection of fluids will not endanger drinking water sources" (40 CFR 144.1). In the absence of state regulation of underground injection, or specific kinds of sources of injection, EPA administers UIC requirements. Sec. 144.6 contains the classification of well types; that most commonly anticipated to be present at a refinery would be Class I, a well used for the purpose of injecting hazardous waste "beneath the lowermost formation containing, within one quarter mile of the well bore, an underground source of drinking water" or a disposal well used to inject fluids "beneath the lowermost formation containing, within one quarter mile of the well bore, an underground source of drinking water." The regulations define underground sources of drinking water and exempted aquifers, prohibitions, requirements for wells and permits, therefore, authorization of injection by rule (as opposed to a well-specific permit), well construction, operation, and reporting requirements, as well as other matters (40 CFR 144 through 146). Approved State UIC programs are covered in sec. 147 et seq.

8.2.2 Wellhead Protection Program

(authority: Safe Drinking Water Act Amendments of 1986, sec. 205.)

Amendments to the Safe Drinking Water Act, enacted June 19, 1986, created a requirement that States establish Wellhead Protection Areas around wells and well fields that serve as sources of public water supply. EPA requirements and guidelines for the State programs have been published (52 FR 23888, 25 June 1987), giving States two years in which to delineate wellhead protection areas. Unlike most western European wellhead protection programs, which focus largely on risks of microbial contamination, the U.S. programs are to focus on protection of drinking water from the risk of contamination of chemicals. The result will be to significantly increase the area under control because many potential chemical contaminants are less subject to attenuation during transport to and in groundwater than are microbes. It appears likely that limitations on land use activity and emphasis on best practices for the handling, storage, and use of chemicals within a specified distance from public water supply wells and well fields will be the principal approaches to protection of the specified areas from contamination. Two significant aspects of the program interact to produce the final State regulatory requirements: first, the delineation of wellhead protection areas (methods for which are described in Guidelines for Delineation of Wellhead Protection Areas, Office of Ground Water Protection, U.S.E.P.A.), and second, specific limitations or restrictions that apply within such wellhead protection areas in order to control the risk of groundwater contamination.

8.2.3 Sole Source Aquifer Program

Section 1424(e), Safe Drinking Water Act (authority: 42 USC 330f, 300h); 40 CFR sec. 149.

Provisions relating to the program leading to a designation of a groundwater aquifer as a sole or principal source of drinking water result in a required separate review of all projects having Federally-assisted funding for their impact upon the aquifer and drinking water to be derived therefrom. An amendment to the Safe Drinking Water Act in 1986 created a Sole Source Aquifer Demonstration Program (sec. 1427, SDWA), providing funding for demonstration programs for Critical Aquifer Protection Areas associated with designated sole source aquifers. Although relatively few areas have been designated to date as sole source aquifers, as of 1987 the potential availability of Federal funds for aquifer-protection programs has created an additional incentive for new areas to seek designation in accordance with regulations revised on June 26, 1987 (52 FR 23986). Experience to date has been that these areas more frequently affect pipeline than refinery projects.

8.3 Solid Waste Disposal Act, As Amended by the Resource Conservation and Recovery Act

8.3.1 Land Disposal of Solid Wastes

Guidelines for the Land Disposal of Solid Wastes; 40 CFR sec. 241 et seq. (authority: Solid Waste Disposal Act of 1965 (P.L. 89-272), as amended by the Resource Recovery Act of 1970 (P.L. 91-512), sec. 209(a)).

The provisions of these regulations apply to the land disposal of municipal (and analogous industrial) wastes, commonly in facilities in which a large variety of wastes are co-disposed. The purpose of the regulations is to "protect public health and welfare", including air and water (including groundwater) quality. By specific approval, a disposal site can accept a variety of otherwise not-acceptable wastes, such as hazardous wastes, bulk liquids and semi-liquids, sludges containing free moisture, highly flammable or volatile substances, and certain industrial process wastes (241.201-2). It is required that the hydrogeology of a site be evaluated to design a facility to "protect or minimize the impact on groundwater resources" (241.202-2). Criteria used in the determination of acceptability of otherwise excluded wastes include "the hydrogeology of the site, the chemical and biological characteristics of the waste, alternative methods available, environmental and health effects, and the safety of personnel (241.201-1). Some sections of the 240. series specifically exclude coverage of industrial solid wastes, hazardous wastes, sludges, and construction and demolition wastes (e.g., sec. 243, storage and collection of residential, commercial, and institutional solid waste; sec. 246, source separation for materials recovery guidelines). However, sec. 256, guidelines for development and implementation of state solid-waste management plans, requires explicit state consideration of hazardous wastes, industrial wastes, processing, treatment, and disposal of such wastes (256.02). States are required to protect groundwater resources such that "A facility or practice shall not contaminate an underground drinking water source beyond the solid-waste boundary or beyond an alternative boundary specified in accordance with paragraph(b) of this section" (257.3-4). An underground drinking water source is defined to include "An aquifer supplying drinking water for human consumption" or "An aquifer in which the groundwater contains less than 10,000 mg/l total dissolved solids" (257.3-4(c)(4)).

A recommended state regulatory power to be included in state regulations is that "Every facility which produces leachate in quantities and concentrations that could contaminate groundwater in an aquifer should be required to monitor to detect and predict contamination" (256.22(b)(2)).

8.3.2 Generation, Transportation, and Disposal of Hazardous Waste

40 CFR 260 et seq. (authority: Solid Waste Disposal Act, as amended by the Resource Conservation and Recovery Act of 1976) (42 USC 6905 et seq.).

Provisions of 40 CFR 260 et seq. deal with a wide variety of responsibilities of generators, transporters, and disposers of hazardous wastes. They are voluminous and extensive in application. Persons responsible for operations involving hazardous wastes will need to make reference to numerous sections in addition to those pertaining specifically to groundwater. It will be necessary for the reader to determine whether Federal or state standards under an approved state program apply to the facility of concern. In some situations, Federal standards can apply when a state program has not received approval of requirements for the treatment, storage, or disposal of hazardous wastes. Interim status standards (40 CFR 265) rather than final standards (40 CFR 264) will apply to parties owning or operating a hazardous waste management facility on the date that the facility became subject to the requirement for a RCRA permit and the facility has qualified for interim status by virtue of compliance with 40 CFR 270.70. Requirements for state programs are that they have essentially the equivalent of 40 CFR 265 requirements, including requirements for groundwater monitoring, for Phase I interim approval and the equivalent of 40 CFR 264 requirements for Phase II approval (secs. 271.128 and 271.129). Approved state programs for hazardous waste management are listed in 40 CFR 272.

8.3.3 Solid Waste Management Units

In general, it can be considered that the provisions of subpart F, Releases from Solid Waste Management Units, secs. 264.91 through 264.101 are applicable to conditions of compliance with groundwater protection standards, compliance monitoring, detection monitoring, and corrective action programs, should any be required. Specifically, sec. 264.90 addresses the applicability of the subpart to "owners or operators of facilities that treat, store, or dispose of hazardous waste". "A surface impoundment, waste pile, and land treatment unit that receives hazardous waste after July 26, 1982 (a "regulated unit") must comply with the requirements of secs. 264.91 through 264.100 in lieu of sec. 264.101 for purposes of detecting, characterizing, and responding to releases to the uppermost aquifer (the shallowest water table aquifer)" (264.90(a)(2)). That section also contains criteria for exemptions from the section during the operating, closure, and/or post-closure periods. Sec. 264.91 requires that owners and operators must conduct 1) a monitoring and response program if hazardous constituents from a regulated unit are detected at the designated compliance point, or 2) institute a corrective-action program whenever the groundwater protection standard is exceeded or whenever leachate from a regulated unit exceeds specified concentration units (per sec. 264.94) in groundwater between the compliance point and the downgradient facility property boundary. In other cases, the owner or operator is required to conduct a detection monitoring program. Requirements of these various programs are to be specified in a facility permit issued by the USEPA Regional Administrator. Sec. 264.92 requires compliance with concentration limits, established under sec. 264.94, for hazardous constituents, determined and specified by sec. 264.93, "in the uppermost aquifer underlying the waste management area" at the point of compliance (sec. 264.95). Concentration limits established under sec. 264.94 are either those listed in 264.94(a) or are separately established by the Regional Administrator as an alternate concentration limit, using the provisions of 264.94(b).

Requirements for groundwater monitoring are found primarily in secs. 264.97, 264.98, and 264.99. The requirements include provisions for determination of background concentrations of constituents; sampling, analytical, statistical, sampling frequency and other procedures; and the period of time for which the monitoring program must be conducted. Detection monitoring is covered in sec. 264.98 and compliance monitoring is covered by sec. 264.99. The latter section also contains the procedures through which exceedances of the groundwater protection standard are determined and reported to the Regional Administrator and a corrective-action program is initiated.

Requirements of sec. 264.100 for corrective action programs are for the purpose of preventing hazardous constituents from exceeding their specified concentration limits by (1) removing the hazardous waste constituents, or (2) treating them in place. A corrective-action program is to be accompanied by a groundwater monitoring program that demonstrates the effectiveness of the corrective action. Sec. 264.101 requires that owners or operators seeking a permit for the treatment, storage, or disposal of hazardous waste must institute corrective action for all releases of hazardous waste or constituents from any solid-waste management unit at the facility, regardless of the time that the waste was placed in the facility. Such corrective action will be made part of the permit requirements for the facility.

Secs. 264.111 through 264.115 concern facility closure requirements and secs. 264.116 through 264.120 concern post-closure requirements, including those pertaining specifically to groundwater.

The August 24, 1987, revisions of the sec. 264 monitoring program specifications (40 CFR 264.91 et seq.) provide increased flexibility in dealing with the highly variable hydrogeologic conditions that have actually been encountered in program operations. The revisions apply to monitoring requirements and statistical analysis of data therefrom, with increased responsibility for the owner or operator to design and defend the design of compliance monitoring, detection monitoring, and corrective action programs.

8.3.4 Surface Impoundments

Requirements for the design and operation of surface impoundments including lagoons, ponds, and basins so as "to prevent any migration of wastes out of the impoundment to the adjacent subsurface soil or groundwater or surface water at any time during the active life (including closure period) of the impoundment are covered by 40 CFR 264.221. That section also contains provisions for exemption, including a list of factors related to hydrogeologic studies and data relevant to migration of leachate to groundwater that must be considered in an application for exemption. Sec. 264.228 includes closure requirements necessary to protect groundwater and a requirement for groundwater monitoring during the post-closure period if "waste residues or contaminated materials are left in place at final closure." In addition, sec. 264 and 265 requirements for storage and disposal facilities have requirements for unsaturated zone monitoring during the facility's active life and post-closure (40 CFR 264.278 and 265.278).

8.3.5 Waste Piles

Storage or treatment of hazardous wastes in piles exposed to precipitation such that runoff or leachate can be produced are regulated under sec. 264.250 through 264.259. Designs alternative to that specified by regulation can be considered for exemption if the design, operating practices, and location characteristics combined "will prevent the migration of any hazardous constituents...into the groundwater or surface water at any future time" (sec. 264.251(b)). Closed waste piles with hazardous wastes enclosed are regulated under subpart N, Landfills, secs. 264.301 through 264.317.

8.3.6 Land Treatment

Hazardous wastes disposed of through land treatment so that they are degraded, transformed, or immobilized, are regulated by 40 CFR secs. 264.270 through 264.283. Requirements for unsaturated zone monitoring of soil and soil-pore liquids are included in 264.278 and closure and post-closure requirements are covered by 264.280.

8.3.7 Landfills

Hazardous wastes disposed of in landfills are regulated by the requirements of 40 CFR 264.300 through 264.317. After final closure, the owner or operator must comply with the groundwater monitoring requirements of subpart F, secs. 264.90 through 264.101, as applicable (264.310(b)(3)).

8.3.8 Interim Status Requirements

Interim status regulations for groundwater monitoring require that a hazardous waste management facility "implement a groundwater monitoring program capable of determining the facility's impact on the quality of groundwater in the uppermost aquifer underlying the facility" unless the facility is exempt or it can be demonstrated that there is "a low potential for migration of hazardous waste constituents from the facility via the uppermost aquifer to water supply wells (domestic, industrial, or agricultural) or to surface water" (40 CFR 265.90). Additional provisions specify requirements for a groundwater monitoring system, for sampling and analysis procedures, preparation of a groundwater monitoring program plan, evaluation of initial sampling results, record keeping and reporting, and other details (265.91 through 265.94). There are groundwater monitoring requirements for the various activities analogous to those described under sec. 264 above provided for in the sec. 265 interim requirements.

8.3.9 Management of Hazardous Waste at New Land Disposal Facilities

Regulations contained in 40 CFR 267 apply to "new hazardous waste landfills, surface impoundments, land treatment facilities, and Class I underground injection wells (as defined in sec. 122.32(g) of (40 CFR)) that require individual RCRA permits under 40 USC 122." These provisions do not apply to those disposing of hazardous waste by underground injection by rule under sec. 122.26(b), among others; see sec. 267.1 for exemptions. In addition to compliance with sec. 267 provisions, new facilities must also comply with the requirements of sec. 264.18, concerning requirements for the location of new facilities, and with subparts B, C, D, E, G, and H of part 264 (40 CFR 267.2). Part 267 regulations had application until Part 264 regulations for new facilities became final or until February 13, 1983, whichever was earlier. Specific provisions dealing with groundwater are in secs. 267.10, 267.23 (closure and post-closure of land treatment); 267.59 through 267.53 (groundwater monitoring); and 267.60 through 267.64 (underground injection).

8.3.10 Land Disposal Restrictions

Subpart B of Part 268 contains a listing of wastes requiring evaluation for prohibition of disposal by land treatment by specific dates.

8.3.11 Hazardous Waste Permit Program

Part 270 contains the requirements for Part A and Part B permit applications, including requirements dealing with aspects of groundwater and site subsurface hydrogeology.

8.3.12 Underground Storage Tanks

40 CFR 280 (authority: Solid Waste Disposal Act, as amended; 42 USC 6912, 6991 (a, b, c, d, e, f, g, and h)

EPA proposed new regulations dealing with a variety of aspects of underground storage tanks, including technical, financial, and state program requirements (52 FR 12662, 17 April 1987), with supplements to the proposed rules for the same categories (52 FR 48638, 23 Dec. 1987). EPA's present schedule is for promulgation of the final regulations in May, 1988. Although refinery managers and operators will be concerned with aspects of both the financial and State program provisions of the proposed regulations, it is the technical requirements of the proposed regulations that will be of greatest interest. Subpart B, section 280.20 deals with the specific design, construction, and corrosion protection requirements for new tanks, with existing tanks to be upgraded to the standards for new tanks within ten years, to include cathodic protection, or to be closed in accordance with requirements of section 280.80. Separate requirements were proposed for tanks storing specifically-listed petroleum products (Subpart F, section 260 et seq.; see especially discussion and questions in the December notice) including provisions for soil and groundwater cleanup and reporting of above and subsurface releases. Many refineries associated with petrochemical operations or feedstocks may also have tanks that would be covered by requirements for hazardous substances. Groundwater protection aspects of the proposed regulations would require both soil vapor monitoring and groundwater monitoring wells (section 280.41). There are specific provisions for reporting releases and investigation, abatement and cleanup of material (sections 280.50 and 280.70), with special provisions for corrective actions in case of leakage of petroleum (280.60). Provisions of section 280.80 would deal with the requirements for both temporary and permanent closure, including surrounding the tank. Based on the number and variety of additional questions posed by the EPA in the December, 1987, publication on proposed rules, details of some portions of the initially-proposed rules may change significantly prior to promulgation of the final regulations in 1988.

8.4 Toxic Substances Control Act

40 CFR 700 et seq. (authority: Toxic Substances Control Act, 15 USC 2601 et seq.).

The purposes of the Toxic Substances Control Act are the control of importation, manufacture, and distribution of toxic chemicals. Explicit groundwater-related provisions of the Act are rather limited, although the broad interpretation of "Health and safety study" as used by Act includes "assessments of human and environmental exposure," which include "impacts of a particular chemical substance or mixture on the environment, including surveys, tests, and studies of: biological, photochemical and chemical degradation; structure/activity relationships; air, water, and soil transport; biomagnification and bioconcentration; and chemical and physical properties..." in addition to monitoring data (40 CFR 716.3). Reporting requirements for physical and chemical properties resulting from studies performed for the purpose of determining the environmental or biological fate of a substance include a number of parameters of concern to the fate of a chemical substance in groundwater. Sec. 717.12(c) requires the recording of significant adverse reactions to the environment, including "(6) Long lasting or irreversible contamination of components of the physical environment, especially in the case of groundwater, and surface water and soil resources that have limited sefl-cleaning capability."

Among the prohibitions in the regulations is the manufacture of any new chemical that causes, or whose impurities or byproducts cause, "significant environmental effects under anticipated conditions of manufacture, processing, distribution in commerce, use, or disposal...." (723.50). Such significant environmental effects clearly include adverse effects on groundwater. Provisions dealing with the disposal of polychlorinated biphenyls (PCBs) in chemical-waste landfills contain requirements for groundwater hydrologic information and for groundwater monitoring systems, with specifications given for the design of groundwater monitoring wells, analyses of water samples, leachate collection, and the use of suction lysimeters (761.75).

8.5 Comprehensive Environmental Response, Compensation, and Liability Act of 1980

40 CFR 300 et seq. (authority: sec. 105, P.L. 96-510, 42 USC 9605, and sec. 311(c)(2), P.L. 92-500, 33 USC 1321(c)(2); E.O. 12316 (Aug. 20, 1981); E.O. 11735 (Aug., 1973)).

Programs in this section, designated as Superfund Programs, include the National Oil and Hazardous Substances Pollution Contingency Plan, and all organizational and planning requirements associated with oil and hazardous substance spill and discharge cleanup operations. Specific provisions are included for remedial measures for releases so as to protect groundwater, and to treat contaminated water, soil, and sediment (sec. 300.70). Operational requirements involving groundwater contamination assessment and renovation will take place under secs. 300.52 and 300.53 for oil and 300.64, 300.65, 300.66, and 300.68 for hazardous substances. The Superfund Amendments and Reauthorization Act will create some changes in groundwater compliance standards and site-characterization requirements, possible as Interim Guidance for Applicable or Relevant Appropriate Requirements (ARARs).

8.6 Regulatory Annotations from the General Literature

American Petroleum Institute, "Guide to State Groundwater Programs and Standards", API Pub. No. 4416, 1986.

This guide recognizes that Federal and State laws, regulations and guidelines concerning the use and protection of groundwater present a rapidly moving target, accordingly the guide was issued in loose-leaf format. The first part, Chapters 1-4, provides an overview of technical and regulatory concepts and terminology and a summary of the Federal programs that form the basis for State regulation. A key chapter is that on Federal Groundwater Protection Programs, which discusses EPA's Groundwater Protection Strategy and gives brief explanations of how the six Federal laws under which EPA regulates water quality relate to groundwater protection.

Most of the volume consists of individual sections on State laws, regulations, and guidelines that relate to groundwater. A standard format is used giving classification, quality standards, drinking water standards, appropriation of groundwater, controlled use areas, sole source aquifers, well-construction rules, underground injection control, waste management and details of drinking water standards and monitoring requirements. Citations are provided for key regulatory officials.

Blevins, M.L., and D.E. Williams, "Management of Gasoline Leaks - A Positive Outlook", Proc. Seventh Nat'l Ground Water Quality Symposium, Nat'l Water Well Association, Dublin, OH, 45-83, 1984.

The author describes recent California legislation for regulation of underground storage of hazardous materials, and describes in detail three major underground spills that have affected ground water in Southern California.

Under legislation that was pending at the time of reporting, tank and sump owners would be subject to the following:

1. Permitting by local government of all existing and new tanks and sumps for storage of hazardous substances;
2. Monitoring of all new existing tanks and sumps;
3. Design standards including monitoring devices for all new tanks;
4. Annual reports covering any changes in tank operation;
5. Reports to permitting agency of any leaks or unauthorized releases within 24 hours;

6. Proper abandonment procedures for tanks and sumps; and
7. Penalties of $500 to $5,000 per day for non-compliance.

Horsley, S. W, and D. S. Blackmar, "Development and Implementation of Regulations to Control Underground Fuel Storage Tanks on Cape Cod", Proc., Seventh Nat'l., Ground Water Quality Symposium, Nat'l. Water Well Assoc., Dublin, OH, 29-39, 1984.

The paper reports on development of local regulatory structure to assure against hydrocarbon spills from underground tanks and assesses implementation of regulations over a five year period. Cape Cod is especially sensitive to ground-water contamination because the sole source of municipal and domestic water supply is a relatively shallow glacial sand and gravel aquifer. Some 130 municipal wells and 15,000 residential wells furnish nine billion gallons per year to the 15 jurisdictions (towns) on Cape Cod.

Stimulated by a 1978 subsurface gasoline spill at Truro, the Cape Cod Planning and Development Commission drafted model regulations/by-laws for control of underground storage tanks. Since 1979 all 15 towns that comprise Barnstaple County (Cape Cod) have adopted control regulations. These are generally enforced by the town Board of Health in conjunction with the Fire Department.

Major provisions of most of the town regulations are registration of underground tanks, inventory control requirements, leak testing, and specifications for new installations. In some towns registration is limited to commercial size tanks, but in some residential fuel tanks are covered also. Inventory control is generally enforced through spot checks rather than submittal of records. Most towns require annual pressure testing of tanks 15 years old or older; at 20 years non-conforming tanks must be removed for inspection for leaks. If a leak is discovered the subsequent investigation is at the owner's expense. New tank installations require approved design with protection against internal and external corrosion. Most towns prohibit or require special design for tanks within specified distances of water supply wells.

The experience through 1984 indicates:

1. Fourteen of fifteen towns require registration; 1,016 tanks have been registered. Problems have arisen in locating tanks, especially residential heating oil and non-service station commercial tanks.
2. Inventory control has proven poor and unreliable except for large losses, due to poor quality control of measurements.
3. Tank testing has resulted in early detection of 39 leaks prior to major damage. County-wide compliance has been 86 percent. Most owners have replaced old tanks rather than going into an annual testing schedule.

Zoch, R. M., Jr., "When an HPI Plant Shuts Down...", Hydrocarbon Processing, V.64, No. 10, 51-52, 1985.

Reviews the regulatory framework that applies to hydrocarbon processing plants, advises on development of closure plans, and gives a step-by-step procedure for what must be done to achieve closure at plants regulated under the Resource Conservation and Recovery Act (RCRA) and the Toxic Substances Control Act (TSCA).

The article was condensed from a longer presentation, but gives a succinct checklist of the many steps required by Federal and State law for final plant closure.

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TABLE 1
REFINERY GROUNDWATER AND SUBSURFACE OUTLINE

A. Technical and Operational Issues

1. Prevention

a. Equipment
- Aboveground and underground storage tanks
- Pipes, sewers, and sumps
- Process equipment
- Wastewater storage and treatment basins and tanks

b. Operating Practices
- Prevention, maintenance, and repair
- Loading and unloading
- Tank overfill and dewatering of tank farms
- Spill response procedures
- Sampling points
- Source control
- Solid waste handling practices
- Water wells
- Cathodic protection

2. Detection and Assessment

a. Hydrogeology Primer
- Soil structure
- Groundwater movement
- Fate of released hydrocarbons (on- and off-site)
- Contaminant characteristics (solubility and viscosity)

b. Source Monitoring
- Tank inventory monitoring
- Tank leak testing
- Waste site investigations
- Line leak testing
- Sump/sewer inspection and testing

c. Groundwater Monitoring
- Well construction, installation, and location (siting)
- Sampling and analysis
- Statistical methods and analysis
- Data interpretation
- Plume delineation
- Modelling and migration
- Source determination
- Plume volume estimates
- Vapor migration

3. Containment and Clean-up

   a. Plume containment
      - o Hydraulic containment
      - o Physical containment

   b. Plume Mitigation
      - o Product recovery wells and equipment
      - o Vapor venting and equipment
      - o Disposal of water and contaminated soil
      - o Dewatering wells for soluble plumes
      - o Site capping after cleanup

   c. Water Treatment - Aboveground
      - o Air stripping and recovery or incineration
      - o Biological treatment
      - o Activated carbon treatment
      - o Other

   d. In-situ Attenuation or Treatment
      - o Natural attenuation
      - o Induced biodegradation
      - o Sorption
      - o Volatilization

   e. Health and Safety Implications
      - o Vapors
      - o Explosion-proof equipment and procedures
      - o Investigation of implications

B. Regulatory Background

- o EPA Ground-Water Protection Strategy
- o State Requirements
- o Federal Laws
- o Federal and State Regulations and Guidelines

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