

Literature Survey

Subsurface and Groundwater Protection Related to Petroleum Refinery Operations

API PUBLICATION 800
SEPTEMBER 1988

American Petroleum Institute
1220 L Street, Northwest
Washington, D.C. 20005



Documents

Document Sharing Hub

Literature Survey

Subsurface and Groundwater Protection Related to Petroleum Refinery Operations

Refining Department

API PUBLICATION 800

American
Petroleum
Institute



SPECIAL NOTES

1. API PUBLICATIONS NECESSARILY ADDRESS PROBLEMS OF A GENERAL NATURE. WITH RESPECT TO PARTICULAR CIRCUMSTANCES, LOCAL, STATE, AND FEDERAL LAWS AND REGULATIONS SHOULD BE REVIEWED.
2. API IS NOT UNDERTAKING TO MEET THE DUTIES OF EMPLOYERS, MANUFACTURERS, OR SUPPLIERS TO WARN AND PROPERLY TRAIN AND EQUIP THEIR EMPLOYEES, AND OTHERS EXPOSED, CONCERNING HEALTH AND SAFETY RISKS AND PRECAUTIONS, OR UNDERTAKING THEIR OBLIGATIONS UNDER LOCAL, STATE, OR FEDERAL LAWS.
3. INFORMATION CONCERNING SAFETY AND HEALTH RISKS AND PROPER PRECAUTIONS WITH RESPECT TO PARTICULAR MATERIALS AND CONDITIONS SHOULD BE OBTAINED FROM THE EMPLOYER, THE MANUFACTURER, OR SUPPLIER OF THAT MATERIAL, OR THE MATERIAL SAFETY DATA SHEET.
4. NOTHING CONTAINED IN ANY API PUBLICATION IS TO BE CONSTRUED AS GRANTING ANY RIGHT, BY IMPLICATION OR OTHERWISE, FOR THE MANUFACTURE, SALE, OR USE OF ANY METHOD, APPARATUS, OR PRODUCT COVERED BY LETTERS PATENT. NEITHER SHOULD ANYTHING CONTAINED IN THE PUBLICATION BE CONSTRUED AS INSURING ANYONE AGAINST LIABILITY FOR INFRINGEMENT OF LETTERS PATENT.

Copyright 1988 American Petroleum Institute

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.

**Documents**

Document Sharing Hub

TABLE OF CONTENTS

	<u>Page</u>
1.0 INTRODUCTION	1
2.0 THE LITERATURE SEARCH	2
2.1 Computer Search	3
2.2 Manual Search	3
3.0 ANNOTATION PROCESS	3
4.0 PREVENTION ANNOTATIONS	5
5.0 DETECTION AND ASSESSMENT ANNOTATIONS	26
6.0 CONTAINMENT AND CLEANUP ANNOTATIONS	47
7.0 REGULATORY BACKGROUND	80
7.1 EPA Groundwater Protection Strategy	80
7.2 Selected Examples of Some State and Local Requirements	82
7.2.1 Illinois	83
7.2.2 Louisiana	83
7.2.3 New Jersey	84
7.2.4 Texas	84
8.0 REGULATORY ANNOTATIONS	86
8.1 Clean Water Act	87
8.1.1 Discharge of Oil	87
8.1.2 National Pollutant Discharge Elimination System	87
8.1.3 National Primary Drinking Water Standards	88
8.1.4 Dredge and Fill Operations	88
8.2 Safe Drinking Water Act	89
8.2.1 Underground Injection Control Program	89
8.2.2 Wellhead Protection Program	89
8.2.3 Sole Source Aquifer Program	90

	<u>Page</u>
8.0 REGULATORY ANNOTATIONS, continued	
8.3 Solid Waste Disposal Act	91
8.3.1 Land Disposal of Solid Wastes	91
8.3.2 Generation, Transportation, and Disposal of Hazardous Waste	92
8.3.3 Solid Waste Management Units	93
8.3.4 Surface Impoundments	94
8.3.5 Waste Piles	95
8.3.6 Land Treatment	95
8.3.7 Landfills	95
8.3.8 Interim Status Requirements	96
8.3.9 Management of Hazardous Waste at New Land Disposal Restrictions	96
8.3.10 Land Disposal Restrictions	97
8.3.11 Hazardous Waste Program	97
8.4 Toxic Substances Control Act	98
8.5 Comprehensive Environmental Response, Compensation and Liability Act of 1980	99
8.6 Regulatory Annotations from the General Literature	100
REFERENCES	103

TABLE 1 REFINERY GROUNDWATER AND SUBSURFACE OUTLINE



Documents

Document Sharing Hub

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 I).
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 quality 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, pyrolysis. 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 CO₂ 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 CO₂ 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 CO₂ 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, phenanthrene, 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 distribution 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-time 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/m³; concentrations in urban areas ranged from 0.1 to 61.0 ug/m³. 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. Finally 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/meter² 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 fertilization 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 CO₂. 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, inoculation 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 CO₂ evolution following stirring, suggested that O₂ 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 (K_f) and linear partition coefficient (K_p) were highly correlated with the organic content of the samples. The sorption constants (K_p), 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/m² 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 brome grass 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 significantly 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 European 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, I-223, 1983.

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

- o The properties and characteristics of various hazardous liquids.
- o The compatability of various tank and piping system materials with certain hazardous liquids.
- o The types of leaks and problems which can occur in bulk storage facilities.
- o The cause of corrosion.
- o 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.

Predvall, 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 quantified 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 study, 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 apparent lack of degradation were extended periods of extremely 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", API 45th Midyear Refining Mtg., Preprint 22-80, 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 chromatograph. 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 Cont. 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.

Houzm, 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 proceeds 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 exhaustor. 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, III-129, 1984.