FINAL REPORT

HAZARDOUS WASTE MANAGEMENT APPROACHES TO PROTECT WATER QUALITY

Interagency Cooperative Contract Between The University of Texas at Austin (Civil Engineering) and The Texas Water Development Board

Submitted to the

TEXAS WATER DEVELOPMENT BOARD
Austin, Texas
January 1989

Submitted by

The Civil Engineering Department
The University of Texas at Austin
Austin, Texas

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ABSTRACT

The objective of this project was to develop technical and scientific approaches to help protect the surface and ground water of the state of Texas from the improper disposal of hazardous wastes. Five separate research efforts were part of this project. Each effort was the responsibility of a specific faculty member at The University of Texas at Austin. The efforts and their overall results were as follows:

Genetic Engineering -- The objective of this effort was to apply new developments in recombinant DNA technology to the treatment of chemicals that have an adverse effect on water quality and the environment and are found in hazardous wastes. The results included:

(a) A mutant strain of bacteria was found to oxidize anthracene.

(b) Microorganisms were cultured that indicated the potential to degrade recalcitrant halogenated aromatic compounds.

Anaerobic Treatment -- The objective of this effort was to determine the effectiveness of an anaerobic process containing activated carbon to degrade phenols and chlorophenols. A simple, reliable methodology was developed for the evaluation of kinetic and preliminary design parameters for the anaerobic biodegradation of aromatic organic compounds.

In-Place Detoxification of Contaminated Soils -- This effort investigated the feasibility of biological decontamination methods that can be used directly with contaminated soils. The results indicated that, when operating conditions such as moisture content, amendments, aerobic conditions, and nontoxic conditions were properly controlled, polyaromatic hydrocarbons in the soil were degraded by microorganisms.

Early Detection Monitoring -- The feasibility of using inexpensive buried probes to indicate leakage from waste disposal sites was investigated. Fiberglass probes, gypsum blocks, an electric resistivity probe, and heat dissipation sensors were able to detect potential leakage in laboratory settings.

Multi-Phase Transport of Contaminants In Groundwater -- Source models that can be used to improve the understanding of multiphase transport of contaminants in groundwater were developed. The models allowed simulation of the fate and transport of spills and releases of organic fluids at or near ground surface. The resulting computer program has been installed in the Texas Water Commission computer system.

HAZARDOUS WASTE MANAGEMENT APPROACHES TO PROTECT WATER QUALITY

INTRODUCTION

Background -- In October 1985, a proposal with the above title was submitted to the Texas Water Development Board (TWDB) for evaluation and consideration. The research described in the proposal represented an integrated effort to develop technical and scientific approaches to help protect the surface and groundwater quality of the state of Texas from the improper disposal of hazardous wastes. The approaches that can be used for this purpose include:

a) treatment methods to reduce the hazard of wastes that ultimately must be disposed of,

b) disposal methods that minimize the movement of constituents in hazardous and other wastes so that surface and groundwaters are not contaminated,

c) better methods to detect and monitor contaminants that may be in soils, especially at ultimate disposal sites, and

d) a better understanding of the fate and transport of hazardous waste constituents that can occur in soil, groundwater and surface waters.

Considerable justification for such research existed at that time and still exists for relevant research:

a) Texas is attempting to retain and increase industries allied to petroleum refining and chemical production and to increase the number of micro-electronic related industries and similar "high tech" industries. The by-products of these industries (hazardous and other wastes) can have an adverse effect on water quality, particularly groundwater quality.

b) At the present time, over 85% of the hazardous waste in the United States may be disposed of by environmentally improper methods. These include a variety of land disposal methods (landfills and surface impoundments) as well as storage methods from which leakage can occur and ultimately reach groundwater or surface water. This is particularly important to Texas since about 60% of the state water needs are met from groundwater sources.

c) Using current federal estimates, Texas ranks first among the states in terms of the amount of hazardous wastes generated with about 13% of the national total.

d) The quantities of hazardous waste generated in the United States are large, roughly one metric ton (2200 pounds) of liquid, solid or slurry per person per year. Toxic chemicals from these wastes are having an adverse effect on public health and the environment, are one of the highest public concerns, and are likely to be a high continuing public concern for the next decades.

e) The costs of satisfactory hazardous waste treatment and disposal are not trivial. By 1990, the hazardous waste compliance costs to industry could rise to between $8.4 billion and $11.2 billion. These costs translate into a significant percentage of industry profits. As an example, for the chemical and allied products industry, hazardous waste management costs could range from 21 to 45% of profits.

Nine activities were included in the proposal. They included eight research projects and one information acquisition effort. These were topics in which the identified faculty have considerable expertise. The proposed research projects are natural extensions of relevant research being conducted by knowledgeable individuals at the forefront of their professions.

TWDB Support -- In two separate actions, the TWDB funded five of the identified research projects. At its November 1985 meeting, the TWDB authorized a contract for research on three research tasks:

> In-Place Detoxification of Contaminated Soils
> Early Detection Monitoring
> Multiphase Transport of Contaminants in Groundwater

These were tasks 4, 6, and 7 of the original proposal.

In January 1986, TWDB authorized support for two additional tasks:

> Genetic Engineering
> Anaerobic Treatment

These were tasks 1 and 2 of the original proposal. Dr. Tommy Knowles was identified as the TWDB Contract Manager.

Project Descriptions -- Each research task was the responsibility of specific faculty at The University of Texas at Austin. The following summarizes the objectives of each task and the faculty member who was the task principal investigator.

Genetic Engineering
Dr. David Gibson, Director
Center for Applied Microbiology

Recent rapid developments in recombinant DNA technology have opened new horizons in the use of microorganisms to treat industrial wastes. It is now possible to construct new strains of bacteria that will carry out reactions not found in any single organism. Enzyme levels can be increased dramatically by genetic engineering technology and enzymes can be subjected to site-specific mutagenesis to create new enzymatic activities.

The objective of this research was to apply these new approaches to chemicals that have an adverse effect on water quality and human health and the environment and are found in hazardous wastes. The specific objectives were:

-- isolation of the pathways used by microorganisms for the degradation of anthracene and phenanthrene

-- genetic engineering of microorganisms to construct strains that will efficiently remove anthracene and phenanthrene from polluted environments

-- conduct preliminary studies to screen fungi for ligninase activity. The ligninases will be studied in terms of their ability to degrade chlorinated environmental pollutants.

Anaerobic Treatment
Dr. Joseph F. Malina, Jr.
Department of Civil Engineering

Anaerobic biological treatment processes are particularly useful for synthetic organics that can be degraded anaerobically but not aerobically, such as chlorinated hydrocarbons found in hazardous wastes. This research was an engineering evaluation of the effectiveness of anaerobic microbiological technologies applied alone and in combination with activated carbon to enhance the degradation of aromatic organic compounds. The specific objectives were to determine:

-- the relative anaerobic degradation rate of phenol, p-cresol, p-nitrophenol and 2,3-dichlorophenol

-- acclimation time required for biodegradation of these compounds

-- toxic or inhibitory effects of these compounds on acidifiers and methanogenic bacteria

-- the effect of activated carbon on the degradation rate, acclimation time and toxic or inhibitory concentration of these compounds

-- the feasibility of the scanning electron microscope to examine the physical and structural characteristics of microbial growth on granular activated carbon

In-Place Detoxification of Contaminated Soils
Dr. Raymond C. Loehr
Department of Civil Engineering

Many soils in Texas are contaminated by organics as a result of spills and surface impoundments and ponds. The organics must be removed and stabilized as part of cleanup and closure operations. Laboratory research investigations were conducted with these soils to identify biological decontamination methods that can be used directly at sites having contaminated soils. This will: (a) avoid more expensive excavation and subsequent disposal methods, and (b) minimize contamination of groundwater at such sites. This research:

-- used contaminated soil from a petrochemical facility in Texas

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-- determined the loss rates of polyaromatic hydrocarbons (PAH) in the contaminated soil

-- identified operational factors that affect the loss rates

-- indicated how the results can be used to bioremediate contaminated soils

Early Detection Monitoring
Dr. David E. Daniel
Department of Civil Engineering

Texas has thousands of municipal waste landfills and a number of operating hazardous waste disposal facilities. Monitoring these facilities occurs by sampling groundwater periodically to determine whether leachate from the facility is degrading the groundwater quality. By the time contaminants reach groundwater monitoring wells, pollution has occurred.

Another approach is unsaturated zone monitoring in which detection probes are installed beneath a facility but well above groundwater resources. Such monitoring serves as an early warning system for leakage of contaminants. If leakage is detected early (detection monitoring), remedial measures can be undertaken to solve the problem before the solution becomes greatly expensive. By early action, groundwater resources are better protected from contamination.

The purpose of this research was to evaluate the feasibility of utilizing inexpensive buried probes in the unsaturated (vadose) zone of the soil to indicate leakage of contaminants from landfills and spills. The probes that were evaluated included tensiometers, thermocouple psychrometers, gypsum and fiberglass resistance blocks, resistivity probes and heat dissipation sensors.

Multi-Phase Transport of Contaminants in Groundwater
Dr. Randall J. Charbeneau
Department of Civil Engineering

When solvents, organics and water move through soils as a result of leaks and spills, multiphase flow occurs. Such flow results from the different solubilities of solvents and organics in the water percolating through the soil. This is a complex situation which results in contaminants moving faster than expected to and through the groundwater. Understanding the movement of multiphase pollutants is made difficult by the biotic and abiotic processes which control the transport and fate of the chemicals. These processes include advection, mixing, sorption, dissolution, volatilization and degradation.

This research focused on the basic physical and chemical mechanisms affecting multiphase contaminant transport. The objectives were to:

-- develop mathematical models, based on these basis mechanisms that will improve the understanding of multi-phase transport of contaminants

-- attempt to apply these models to situations relevant in Texas

Report Objective -- In addition to the identified faculty, staff and graduate students at The University of Texas at Austin participated in this research. Many of the graduate students used parts or all of this research for their theses and dissertations. As a result, the education and training of many students and staff occurred. In addition, information from this research has been included in many courses taught by the noted faculty and has been part of numerous technical presentations and papers. Thus, this research supported by the TWDB has had a broad impact, not only in acquisition of specific research findings but also in education, training and information transfer.

Throughout the project, quarterly project reports were supplied to the TWDB. At the end of the project, detailed technical reports for each project were provided to the TWDB.

Because of the extensive work that was undertaken and accomplished, a compilation of all the research details, pertinent literature and results would be voluminous. In discussion with the TWDB Contract Manager, it was agreed that a briefer, more readable extended executive summary that included the results from all five projects would constitute the final project report. This is that report.

USE OF RESULTS

This project consisted of five separate research efforts that had different objectives and different principal investigators. The overall objective was to develop technical and scientific approaches to help protect the surface and groundwater of the state of Texas.

The efforts included scientific (*Genetic Engineering*), engineering (*Anaerobic Treatment* and *In-Place Detoxification of Contaminated Soils*), monitoring (*Early Detection Monitoring*), and transport and fate estimation (*Multi-Phase Transport of Contaminants in Groundwater*) approaches. Each of the efforts was successful in that the overall objective was met and new knowledge was developed. In several cases, the results have helped advance current practice.

Because of the diverse nature of the efforts, the results will be most useful to different parts of the profession and the public. The following summarizes the information that was obtained and the groups likely to use that information.

Genetic Engineering -- Pertinent results include: (a) research protocols to identify microorganisms capable of degrading halogenated aromatic hydrocarbons, and (b) degradation pathways that occur when anthracene is degraded. The results will help other microbiologists and biochemical engineers develop improved bioremediation methods for residuals containing these compounds.

Anaerobic Treatment -- The anaerobic degradation of phenols and chlorophenols was demonstrated. In addition, a reliable methodology for the evaluation of design parameters for the anaerobic degradation of aromatic organic compounds was developed. The results will allow consulting engineers and those in industry to consider improved anaerobic treatment for certain industrial wastewaters.

In-Place Detoxification of Contaminated Soils -- The effort showed that soils contaminated with polyaromatic hydrocarbons from the petrochemical industry can be microbially degraded under proper operating conditions. The results indicated that the contaminated soils around the pits, ponds, and lagoons at industrial sites in Texas can be treated by this process, thus reducing the costs to these industries. This not only protects the groundwater, but also helps such industries to be more competitive. Industries increasingly are using bioremediation methods to treat and clean up contaminated soils, including the plant that furnished the soils for these experiments.

Early Detection Monitoring -- It is important to detect contamination before it leaches to the groundwater. This allows more rapid corrective action and avoids expensive and difficult treatment of contaminated groundwater. This effort investigated relatively inexpensive probes that could be used for such monitoring. Several did show potential under laboratory conditions. The results are pertinent to regulatory agencies which must approve soil-water monitoring systems and for industries which must install and utilize them.

Multi-Phase Transport of Contaminants in Groundwater -- Chemicals that enter the soil and percolate to the groundwater generally are a mixture of compounds. The ability to estimate what happens to such chemicals requires the use of mathematical models. These models must include reactions between all phases of the mixture. The mathematical model developed through this effort allows an understanding of what happens to any chemical, water, or organic solvent in a mixture. The results are useful to industry, consulting engineers, and regulatory agency personnel who must use such models to estimate the transport and fate of the chemicals in groundwater. This model has been installed on the computer system at the Texas Water Commission.

GENETIC ENGINEERING
Dr. David T. Gibson, Director
Center for Applied Microbiology
The University of Texas at Austin

OBJECTIVES

Rapid developments in recombinant DNA technology have considerable potential for the use of microorganisms to treat industrial wastes. New strains of bacteria can be constructed to carry out reactions not found in any single organism. In addition, enzyme levels can be increased dramatically and enzymes can be subjected to site-specific mutagenesis is to enhance enzymatic activities.

This project attempted to utilize genetic engineering technology to detoxify and degrade specific organics. The objectives of this research were:

1. Isolation of microorganisms capable of degrading anthracene and phenanthrene

2. Determination of the pathways used by microorganisms for the degradation of anthracene and phenanthrene

3. Genetic engineering of microorganisms to construct strains that will efficiently remove anthracene and phenanthrene from polluted environments

4. Preliminary studies to screen fungi for ligninase activity. The ligninases were studied in terms of their ability to degrade chlorinated environmental pollutants.

Each of these objectives is discussed separately.

ISOLATION OF MICROORGANISMS CAPABLE OF DEGRADING ANTHRACENE AND PHENANTHRENE

Results -- Conventional enrichment culture technology was ineffective in isolating pure cultures of bacteria that could grow with phenanthrene and anthracene as a sole source of carbon and energy. This may have been due to the low solubility of these aromatic hydrocarbons. Towards the end of the project an alternative technique was utilized which led to the isolation of organisms that can oxidize or solubilize phenanthrene and anthracene. This procedure involved growing cultures on a rich growth medium and then spraying the plates with an ether solution of phenanthrene or anthracene. After 48 hours incubation at 30°C, a clear zone around individual colonies was taken as an indication of hydrocarbon oxidation. This procedure led to the isolation of two organisms, each of which was able to oxidize both hydrocarbons. Since these organisms were isolated near the end of the project period, no metabolism studies were initiated.

Materials and Methods -- Conventional enrichment cultures were set up for the isolation of bacteria that would utilize phenanthrene and anthracene as sole sources of carbon and energy. Soil and sediment samples from Waller Creek, Town Lake, and a waste oil deposit were used as potential sources of organisms. Each sample was added to 50 ml of mineral salts medium in a 250 ml conical flask. Anthracene (0.1%)

or phenanthrene (0.1%) was added to each flask and all flasks were placed on a rotary shaker at 30°C. Each flask was observed for microbial growth over a period of 8 weeks.

An alternative procedure that would detect organisms capable of partial degradation of anthracene and phenanthrene was developed toward the end of the project period. Soil samples (1.0 g) were suspended in 5.0 ml of 0.05 M KH_2PO_4 buffer, pH 7.0 and 0.1 ml aliquots were applied directly to nutrient agar plates and incubated at 30° C for 48 hours. Plates that revealed the presence of isolated colonies were sprayed with a 0.5% solution of hydrocarbon in ether. Evaporation of the ether resulted in an even distribution of the solid hydrocarbon on the surface of the agar plate where it appeared as a fine white layer. The plates were then incubated for 48 hours at 30° C. Colonies that degraded or solubilized the individual hydrocarbons were easily detected by a clear zone around the colonies.

Discussion -- Polycyclic hydrocarbons that contain more than two aromatic rings are not very soluble in water. The specific approach was used because one can then be sure that such strains will oxidize phenanthrene and anthracene to carbon dioxide and water. In any biodegradation study, it is not sufficient to know that the hydrocarbon disappears. This is because partial oxidation products may be more toxic than the parent substrate. The direct isolation procedure did yield two organisms that would apparently oxidize both hydrocarbons. Another interpretation is that the organisms excreted an emulsifying agent that caused a clearing of the solid hydrocarbon on the surface on an agar plate. Further studies are required to determine the metabolic capability of these isolates.

PATHWAYS USED BY MICROORGANISMS FOR THE DEGRADATION OF ANTHRACENE AND PHENANTHRENE

Results -- Since new isolates capable of growth with phenanthrene and anthracene were not isolated, studies were conducted with a *Beijerinckia* species capable of growth with biphenyl as the sole source of carbon and energy. This effort focused on anthracene degradation. A mutant strain of *Beijerinckia* (B8/36) was shown to oxidize anthracene to *cis*-1,2-dihydroxy-1,2-dihydroranthracene as the major product. A second dihyrodiol was detected and tentatively identified as 2,3-dihydroxy-2,3-dihydroanthracene. In contrast, the parent strain of *Beijerinckia* oxidized anthracene and the degradation products were identified as 2-hydroxy-3-napthoic acid and 2,3-dihydroxynaphthalene. A metabolic pathway for the degradation of anthracene was proposed.

Materials and Methods -- The organism used throughout this study was a strain of *Beijerinckia* which was originally isolated from Waller Creek at The University of Texas at Austin. This organism can grow with biphenyl as the sole source of carbon and energy for growth. The organism was grown in a mineral salts medium containing 0.01% (wt/vol) yeast extract and 0.1% (wt/vol) sodium succinate. Growth was followed turbidimetrically.

· Culture flasks functioning under controlled environmental conditions with appropriate substrates were used for the growth of these organisms. The anthracene metabolites were isolated by extraction with ethyl acetate, partially drying the extract over anhydrous sodium sulfate and further reduction to dryness *in vacuo* at 30°C.

Partial purification of the residue was achieved on a deactivated (20%) silica column. The residues were analyzed by high performance liquid chromatography (HPLC), thin layer chromatography (TLC), or gas chromatography (GC) depending on the type of compound being determined. Mass spectra (MS) were obtained as part of these analyses.

Discussion -- As a result of the experiments, several metabolic intermediates were detected and confirmed. A preliminary pathway for the degradation of anthracene by the *Beijerinckia* organism was proposed from these results (Figure 1).

The mechanism by which 2,3-dihydroxynaphthalene is formed from 2-hydroxy-3-naphthoic acid is thought to be an oxidative decarboxylation. It is not known precisely how 2,3-dihydroxynaphthalene is metabolized to salicylate. In order to characterize the ring-fission mechanism of 2,3-dihydroxynaphthalene and to further identify the metabolic pathway of anthracene, selection techniques for mutants blocked in different stages of the metabolic pathway must be developed and applied in future studies.

GENETIC ENGINEERING OF MICROORGANISMS TO CONSTRUCT STRAINS THAT WILL EFFICIENTLY REMOVE ANTHRACENE AND PHENATHRENE

Results -- Preliminary studies were conducted but personnel and time constraints precluded further research. The preliminary studies with *Beijerinckia* have shown that the ability of this organisms to degrade biphenyl is correlated with the presence of a 20 megadalton plasmid. Cured strains of *Beijerinckia* that have lost the plasmid also lose the ability to grow with biphenyl and the capacity to oxidize anthracene. The observations suggest that the enzymes responsible for biphenyl degradation are also able to degrade anthracene.

STUDIES TO SCREEN FUNGI FOR LIGNINASE ACTIVITY

Results -- Attempts were made to develop procedures for determining ligninase activity in *Phanerochaete chrysosporium* and *Favolus alveolaris* cultures. A spectrophotmetric assay and Blue Dextran, an indicator dye used as a visual assay, were used to detect ligninase production. In general, the spectrophometric assay failed to detect ligninase activity, but the visual assay did indicate that ligninase was produced by cultures of both *P. chrysosporium* and *F. alveolaris*. The failure to develop a reliable assay for ligninase activity precluded screening of the fungal collection for organisms that could be used to degrade chlorinated environmental pollutants.

Background -- Lignin is decomposed primarily by basidiomycetous fungi that cause the form of wood decay known as white-rot. An H_2O_2-requiring enzyme with properties of both oxygenase and peroxidase has been isolated that is apparently catalytic in the degradation of lignin and lignin substructure compounds. This ligninase was found to oxidize many aromatic compounds with structures resembling the subunits of lignin. The catalytic activity of the enzyme occurs via a peroxidase mechanism.

The ligninolytic basidiomycete, *P. chrysosporium*, can degrade several halogenated phenolic compounds. This observation suggests the possibility that this
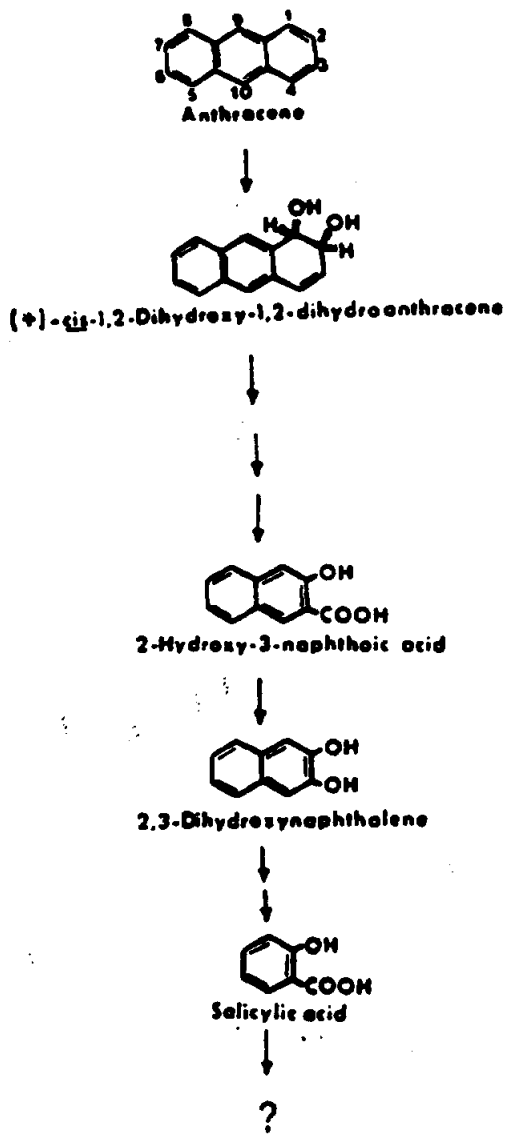
Figure 1. Preliminary evidence of the anthracene degradative pathway by *Beijerinckia sp. BI.*

organism, or others possessing ligninolytic properties, could be used in industrial waste treatment systems to degrade normally recalcitrant halogenated molecules which currently pose environmental and health hazards. Another fungus, *Favolus alveolaris*, has also exhibited ligninase potential.

One of the reactions catalyzed by the enzyme is the oxidation of 3,4-dimethoxybenzyl alcohol (veratryl alcohol) to 3,4-dimethoxybenzaldehyde (veratraldehyde). This reaction has served as the basis for determining ligninase activity of proteins isolated from supernatants of cultures of *P. chrysosporium* and of the unconcentrated supernatant itself.

Once the methodology involved in detecting ligninase activity in fluids obtained from cultures of *P. chrysosporium* and *F. alveolaris* has been perfected, the techniques can be used to develop a simple test for detecting and comparing ligninase activities produced by other fungi. Additionally, experiments can be designed to investigate the possibility of using the ligninase enzyme system to degrade halogenated aromatic compounds. Before either of these two objectives could be met, the ability to use procedures involved in isolating, purifying and manipulating the enzyme(s) had to be attained.

Materials and Methods -- Experiments were designed to detect ligninase production. Culture parameters were varied by incubating some cultures under air and some under oxygen at specific times in the incubation period. In addition, since it has been reported that ligninase production can be increased by the addition of veratryl alcohol and metals, these were added to some cultures. The effects of varying the buffer component, and its concentration, and the concentration of the other reaction mixture components was investigated.

Two strains of *P. chrysporium* were used in these experiments. Strain BKM-1767 was obtained from the Gray Freshwater Biological Institute.   Another strain was obtained from the U.S. Department of Agriculture, Forest Service, Madison, Wisconsin. *F. alveolaris*, wild type, was collected by David T. Gibson and maintained in his laboratory. All *P. chrysosporium* cultures were grown in a nitrogen-limited medium. *F. alveolaris* was grown on Potato Dextrose Agar (Difco) slants at 30°C.

All ligninase assays were performed using the same procedure, except that reactant concentrations were varied in an attempt to optimize the system. The procedure was that described by Tien and Kirk [1].

Discussion -- The decolorization of the dye, Blue Dextran, indicated that ligninase was probably being produced by some cultures. However, ligninase activity was not detected by the spectrophotometric determination of veratraldehyde production except in one instance in which low level activity was observed in *P. chrysosporium* cultures. Unfortunately, these results were not reproducible. The decolorization of the dye may be due to some extracellular enzyme other than ligninase produced by the organisms.

The fact that the Blue Dextran was decolorized by cultures of *P. chrysosporium* and *F. alveolaris* indicates that these organisms are probably producing ligninase. These cultures present a potential opportunity to develop a biological system by which

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recalcitrant halogenated aromatic compounds may be degraded. Before this can be done, however, a quantitative method of determining ligninase activity must be developed.

REFERENCES

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ANAEROBIC TREATMENT
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OBJECTIVES

The potential of anaerobic biotechnology for the treatment of aromatic organic compounds is evident. However, quantification of design parameters and fundamental research on the processes are required; specifically, the assessment of relative rates of anaerobic biodegradation of aromatic compounds, acclimation time, toxicity or inhibitory effects and the effect of activated carbon on these parameters.

This study was an engineering evaluation of the effectiveness of anaerobic microbiological technologies applied alone and in combination with activated carbon to enhance and accelerate the degradation of specific aromatic organic compounds. The study attempted to determine:

1. the relative rate of anaerobic biodegradation of phenol, p-cresol, p-nitrophenol and 2,3-dichlorophenol,

2. acclimation time required for biodegradation of these compounds,

3. toxic or inhibitory effects of these compounds on methanogenic bacteria and acidifiers,

4. the effect of activated carbon on the biodegradation rate, acclimation time and toxic or inhibitory concentration of these compounds, and

5. the feasibility of the scanning electron microscope to examine the physical and structural characteristics of microbial growth on granular activated carbon.

RESULTS

Phase I -- The first phase of experiments proved the feasibility of the research approach. The principal conclusions were:

a) For all phenol concentrations, excluding 2000 mg/L, the peak in gas production occurred at day 22.

b) Gas production increased toward the end of the 58-day incubation time.

c) Acetic acid degradation was not significantly affected up to a phenol concentration of 100 mg/L. At 600 mg/L there were signs of toxicity or inhibition. At 2000 mg/L, no significant degradation occurred, indicating strong toxicity or inhibition.

d) The degradation of propionic acid was similar to the patterns observed for the blank and for the 10 mg/L phenol concentration. At a phenol concentration of 100 mg/L there was a stimulation in the propionic acid degradation. At phenol

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MATERIALS AND SYSTEMS

A serum-bottle technique was developed to accomplish the research objectives. The research was divided into two phases. Phase I evaluated the technique and the quality of the seed sludge. In addition, isotherm data for the granular activated carbon were developed. Phenol was used in this phase at initial concentrations of 0, 10, 100, 600 and 2000 mg/L. In Phase I, all serum-bottles at each concentration were run in duplicate. The variability in the results was low. Therefore only one bottle was used for Phase II.

Phenol, p-cresol, p-nitrophenol, and 2,3-dichlorophenol were used in Phase II. The initial concentrations were 0, 100, 600 and 2000 mg/L. Granular activated carbon was added to some of the serum-bottles. The amount of activated carbon added was such that the initial ratio of activated carbon (GAC) to chemical compound (AOC) was maintained at 0.25 mg GAC/mg AOC/L. A single serum-bottle was tested for every chemical at each concentration per week.

The controls for both phases consisted of a mineral medium enriched with a mixture of acetic and propionic acids and a vitamin solution. Each serum-bottle was inoculated with anaerobic biomass. The parameters monitored were: gas volume and composition, concentration of acetic and propionic acid remaining, concentration of specific AOC remaining, total organic carbon in solution, and total and volatile suspended solids. Some carbon samples were examined by scanning electron microscopy to determine growth on the activated carbon surface and, if positive, to observe the physical relationship between the carbon and its attached growth.

A Phillips scanning electron microscope model SEM515 was used for the observation of the granular activated carbon particles. The non-biological specimens did not require any preparation prior to use. The particles that were exposed to active biomass were prepared by fixation of the specimen with a 2% glutaraldehyde solution in a 0.2 M cacodylic acid solution, followed by several dehydration steps with increasing concentrations of ethyl alcohol diluted in water and finally washed with increasing concentrations of amyl acetate diluted in ethyl alcohol. Specimens were stored in 100% amyl acetate prior to critical point drying.

DISCUSSION

The serum-bottle method to determine anaerobic treatability of these aromatic organic compounds was satisfactory to meet the project objectives. The compounds could be degraded anaerobically. However, the use of GAC and process operating conditions affected the rate and degree of degradation.

GAC enhanced biodegradation at most concentrations of the chemicals tested. This improvement may be explained in various ways. All of these compounds had an inhibitory or toxic effect on the microorganisms. When the bulk concentration of the specific chemical decreased because of adsorption on GAC, the toxic effect decreased.

Phenol and p-cresol were not as toxic as p-nitrophenol and 2,3-dichlorophenol. 2,3-dichlorophenol at a concentration of 100 mg/L with GAC degraded well. A

significant difference of the degradation with and without GAC was observed for this compound at this concentration.

Acetic acid degraded faster and more completely than propionic acid, independent of GAC addition and compound tested. In general, addition of GAC to the serum-bottles improved biodegradation of acetic and propionic acids. This improvement occurred mainly at the 100 and 600 mg/L levels of phenol, p-cresol, p-nitrophenol and 2,3-dichlorophenol. At a concentration of 2000 mg/L, only phenol and p-nitrophenol responded positively to the addition of GAC. The most dramatic effect due to GAC addition was observed at a 2,3-dichlorophenol concentration of 10 mg/L. Almost complete removal of acetic acid was noted with GAC compared to only 20 percent for the serum-bottles without GAC.

Scanning electron microscopy can be used to observe relationships between microorganisms and GAC. The topography of the GAC particle surface is highly favorable for microbial attachment and growth since there are recesses that protect the microorganisms against fluid shear forces. For the GAC exposed to biological activity, there is evidence of microbial attachment and growth (reproduction). No protozoa were found attached to the specimens examined. There was indication of more than one species on the GAC surface as evidenced by different bacteria size and morphology (rod-shaped and spherical). Colonization by microorganisms did not happen in a biofilm fashion but rather in a dispersed manner. Attachment seems to be due to slime formation in some cases. Precise quantification of the relationship between attached biological growth and the diffusional transport processes associated with adsorption may not be straightforward.

IN-PLACE DETOXIFICATION OF CONTAMINATED SOIL

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OBJECTIVES

Industrial organic residues require environmentally sound management. Many industrial sludges have been stored and disposed of in ponds, lagoons and other surface impoundments that can contaminate the surrounding soil. Even when the sludge in these units is removed, the contaminated soils remain as a source of potential groundwater contamination. Technical approaches are needed to treat and decontaminate such soils. Bioremediation can be such an approach since the soil contains active biological, chemical and physical mechanisms that can degrade organics and immobilize inorganics.

This research examined the potential of utilizing bioremediation for contaminated soils. The objectives were to: (a) examine the feasibility of this technology to decontaminate soils containing petrochemical wastes, and (b) develop data to determine if bioremediation is a viable closure alternative for the contaminated soils.

RESULTS

Bioremediation of contaminated soils containing polyaromatic (PAH) hydrocarbons was evaluated. Operational factors such as waste loading rates, soil moisture content and acclimated organisms were examined. The results indicated that PAH loss can occur when environmental factors are controlled.

When acclimated organisms were present, controlling the moisture to 80% of field capacity resulted in greater loss than when the moisture was 40% of field capacity. PAH loss did not occur when the contaminated soil was tested without the addition of uncontaminated soil or organic amendments. The microorganisms in the amendments acclimated rapidly to the PAH's and the conditions of the tests. No special acclimated organisms were needed to accomplish the degradation (loss).

MATERIALS AND METHODS

The contaminated soil came from the bottom of a pond used to store primary clarifier sludge at a petrochemical plant in Texas. The contaminated soil was mixed with varying quantities of uncontaminated soil to evaluate different loading rates. The uncontaminated soil was obtained from a rural area approximately four miles southwest of Austin, Texas. The soil was air dried, sieved and stored at 4°C in the dark until used.

Toxicity screening analyses estimated the potential impact of the material on soil biota. The analyses estimated the toxicity of the contaminated soil, the initial application rates used in the degradation studies and the detoxification that occurred.

The Microtox System (registered trademarks, Microbics Corporation) was the toxicity screening method.

Many preliminary and six detailed degradation tests were performed, each evaluating a different combination of environmental parameters that may affect the degradation rates of the organic compounds. The loss rate of specific compounds was determined using small soil microcosms and a consistent protocol. Each test consisted of sets of triplicate microcosms for each sampling interval. Controls containing only uncontaminated soil were included in the sets.

The microcosms were arranged in sample sets for sacrifice at intervals to provide at least seven data points to establish the degradation (loss) rate of the compounds. The reactors were incubated at 20°C in the dark. In four of the six tests, uncontaminated soil was mixed with the contaminated soil. The uncontaminated soil was acclimated to the environmental conditions of the test prior to use.

On each sampling date, a sample set was extracted with methylene chloride and concentrated. The extract was dried by passing through a sodium sulfate column, and the "dried" extract kept refrigerated until analyzed. First order degradation rates were calculated.

The contaminated soil contained a complex mixture of organic compounds. A sample of the concentrated extract from one of the experiments was characterized by a GC/MS analysis. The contaminated soil contained two, three and four-ring PAH's. Several were selected for evaluation in the degradation studies.

Gas Chromatography -- All concentrated extracts from the soil microcosms were analyzed by gas chromatography (GC) using a chromatograph equipped with a flame ionization detector (FID), a split injection system, and an integrator. All the tracked PAH's were confirmed by spiking a sample with known standards of each PAH or by cross-referencing with the GC/MS chromatogram.

DISCUSSION

The study evaluated the feasibility of using bioremediation to decontaminate soils containing petrochemical residues. The primary emphasis was on determining degradation (loss) rates of representative polyaromatic hydrocarbons (PAH).

Moisture Content -- The aerobic degradation of organics in soil is a function of the available soil moisture. Commonly, this is expressed in terms of percent of field capacity, i.e., the amount of water retained by the soil micropores. At moisture levels below 30-40 percent, activity is restricted due to low water concentrations, while at high moisture levels, aerobic microbial metabolism is reduced because the soil pores are near saturation and transfer of oxygen is inhibited.

Several experiments evaluated the hypothesis that the moisture content needed to be controlled. The conclusions were:

- The moisture level is a critical parameter for the degradation of 2, 3 and 4-ring PAH's. If moisture content is maintained at 80 percent of field capacity, degradation rates will be considerably greater than at 40 percent of field capacity.

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- For contaminated soil alone, maintaining the moisture content at 80 percent of field capacity did not result in PAH degradation. Other parameters such as acclimated microorganisms and nutrients also play an important role in achieving degradation of PAH compounds.

Amendments -- The total carbon content of the contaminated soil was 4.3 percent and the organic carbon content was 2.0 percent, both expressed on a dry basis. An organic amendment, dry waste-activated sludge, was added to determine the need for more organic matter, nutrients and/or bacteria. The results indicated that amendments that add nutrients, organic matter and active organisms can be of benefit in removing many PAH's in the contaminated soils.

Loading Rates -- Initial toxicity screening demonstrated that the contaminated soil was not toxic to indicator bacteria. Two contaminated soil:uncontaminated soil loading rates were evaluated to determine whether the dilution and the indigenous microorganisms in the uncontaminated soil affected the degradation rates. Results indicated that an increase in the waste-loading rates, within the limits of tests, increased the overall degradation rates of the PAH's in the contaminated soils.

Acclimated Microorganisms -- Acclimated microorganisms are important to successful bioremediation. Several tests evaluated whether the addition of organisms made a difference in the loss of the PAH compounds. The results demonstrated that, within limits of the research and under a range of environmental conditions, the uncontaminated soil contained an indigenous microorganism population capable of quickly initiating PAH degradation. This result is significant in that the uncontaminated soil was gathered from a rural location and had not been exposed previously to the PAH compounds in the contaminated soil. Specially developed microorganisms were not required to degrade the hydrocarbon contaminants. Combining the contaminated soil with uncontaminated soil resulted in significant hydrocarbon degradation.

on the probes and their readings; and (f) determine in column tests whether the probes can detect the passage of a moisture front.

The soil used was kaolin Hydrite R supplied by Georgia Kaolin Co. Seventy-five percent of the soil is finer than 2mm. The soil is essentially pure kaolinite, is readily available, has been used by numerous researchers, and is typical of many non-expandable clay minerals found in the U.S. .

Soil suction was measured with tensiometers and thermocouple psychrometers. Tensiometers were constructed from 1-bar porous ceramic cups that measured about 12 mm in diameter and were read with an electrical pressure transducer, voltmeter, and strip-chart recorder. The thermocouple psychrometers were Model PCT-55 units supplied by Wescor, Inc., and were read with a Keithley Model 155 microvoltmeter.

The cylindrical gypsum blocks were supplied by Soilmoisture Equipment Corp. and measured approximately 25 mm in length and 15 mm in diameter. The fiberglass cells were supplied by Soiltest, Inc. The resistance units were read with a Model 5910A meter supplied by Soilmoisture Equipment Corp. and with a Yellow Springs Instrument Model 31 conductivity bridge.

The resistivity probes used in this study were built by the investigators and measured 50 mm in length and 12.5 mm in diameter. Tin coated, 16 gauge copper wire was used for the electrodes and the probes were filled with a mixture of microcrystalline wax and paraffin to act as a sealer. A model 2350 Bison Instruments earth resistivity meter measured resistivity.

The heat dissipation sensors were A1001C AGWA-II soil matric potential sensors supplied by Agwatronics, Inc., and measured approximately 25 mm in length and 20 mm in diameter. An A1011 AGWAmeter was used to read the sensors.

Kaolin was compacted in molds measuring 150 mm in both diameter and height using standard Proctor (ASTM D698) compaction techniques. The moisture content of the soil was approximately 21% (g/g) at the time of compaction. The kaolin was sealed with end plates, and the various probes were installed through holes in the wall of the mold containing the compacted kaolin. The soil was moistened to a desired water content and readings were taken.

Column tests were also performed. In the columns, the soil was wetted at one end and the response of the probes was monitored.

DISCUSSION

Tensiometers and Psychrometers -- Thermocouple psychrometers yielded slightly higher suctions at high water contents than tensiometers because of the influence of osmotic suction on the readings of thermocouple psychrometers. Thermocouple psychrometers showed tolerable sensitivity to changes in moisture content for a volumetric water content (θ) between 0.24 and 0.45. Tensiometers were tolerably sensitive for $0.42 < \theta < 0.54$. These ranges correlate well to expectations based on data published in the literature for working ranges in suction. Tensiometers were insensitive to salinity effects, but psychrometers were significantly affected by soil

salinity. When the soil was wetted with slightly salty water, the salts masked the effects of soil wetting in the psychrometer readings. This can cause problems for monitoring of waste sites because leachate should contain many dissolved electrolytes.

Gypsum Blocks -- The relationship between electrical resistance and soil moisture content was determined for four gypsum blocks installed in soils moistened with distilled water. The results suggested tolerable sensitivity over a broad range in volumetric water content (0.24 to 0.50) for this soil. As the soil approached saturation, the gypsum blocks lost their sensitivity. There was a range in volumetric water content, θ, for this soil of 0.46 to 0.50 in which gypsum blocks were most sensitive to changes in moisture content.

The gypsum blocks functioned reasonably well over the full range of suctions studied (0.1 to 13 atm). This agrees fairly well with previously published data.

The effect of salinity was studied by moistening kaolinite with aqueous solutions of 0.01 M and 0.1 M NaCl. The 0.01 M NaCl solution had little influence upon the meter readings. For a given fluid content, the meter readings were much higher when 0.1 M NaCl was added. The addition of solutes lowered the electrical resistance and raised the meter reading. Fortunately, the effects of electrolytes suggest that gypsum blocks can be used to indicate leakage from waste storage or disposal facilities. If a leak occurred, the soil would be moistened and the electrolyte concentration would increase.

Five gypsum blocks, each embedded in soils with different moisture contents, were subject to a range of temperatures. The results varied with soil moisture content and temperature. For field applications, calibrated thermistors or thermocouples should be installed with gypsum blocks, and soil temperature should be measured to correct the readings from gypsum blocks.

Fiberglass Probes -- Two fiberglass probes were placed in specimens of compacted kaolinite which were moistened with distilled water to cover a range of water contents. These probes were relatively insensitive to changes in water content for $\theta < 0.45$ and were inferior to gypsum blocks in this respect. On the other hand, fiberglass probes were more sensitive than gypsum blocks at high water contents ($\theta > 0.50$).

Tests were conducted with the soil mixed with distilled water, 0.01 M, 0.1M and 2.8 M sodium chloride to identify the effect of salts. For soil with low salt content, below 0.1 NaCl, a higher salt concentration in the soil caused a higher meter reading (or lower electrical resistance) at the same volumetric fluid content. For volumetric fluid contents below 43%, the salinity influence became masked because of lack of sensitivity. For soil with 2.8 M NaCl, the salinity effects became very influential and expanded the sensitivity of the probes.

The readings from the fiberglass cells increased with an increase in moisture content and an increase in salinity. This is encouraging in terms of detecting leaks from waste disposal facilities.

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Four fiberglass cells were embedded in soil with different water contents and subjected to different temperatures. Readings increased as temperature increased and a different sensitivity to temperature change was found throughout the range of meter readings.

Electrical Resistivity Probe -- The relationship between soil moisture content and electrical resistivity was determined for six resistivity probes installed in soil moistened with tap water. The probes exhibited decreasing sensitivity with increasing moisture content. The influence of salinity on the response of the probes was studied by moistening the compacted kaolinite with a 0.2 M NaCl solution. The resistivity of the soil decreased more quickly with increasing moisture content for the soil moistened with the salt water solution compared to the soil moistened with tap water. There is no obvious problem in detecting leakages of saline water or, presumably, leachate from waste sites.

Heat Dissipation Sensors -- Three heat dissipation sensors were installed in compacted kaolinite and moistened with tap water. The sensitivity of the heat dissipation sensor was greatest for soils with a moisture content of about 0.4. All three heat dissipation sensors provided similar relationships and showed good response over a wide range in moisture contents.

Column Tests -- The column tests involved many detailed measurements. For brevity, the results are not presented here. However, the column tests led to the following observations: (a) tensiometers worked very well in detecting a moistening of the soil; (b) psychrometers also detected wetting of the soil, but salinity effects masked the results and led to data ambiguities; (c) gypsum blocks worked well; (d) fiberglass units worked well, except for some anomalous readings at high water contents; (f) resistivity probes generally worked well, but there were problems with shorting out of some probes; and (g) heat dissipation sensors worked well.

MULTI-PHASE TRANSPORT OF CONTAMINANTS IN GROUNDWATER

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OBJECTIVES

Releases of fluids containing contaminants to subsurface soils have a number of common characteristics. Sources tend to be localized, such as from spills or releases from leaky tanks. The fluids migrate downward through the unsaturated zone, and form a three-phase fluid system: water, organic fluid, and air. Upon reaching the water table, organic fluids which are less dense than water form a lense which grows in thickness and spreads laterally. Ultimately, the organic fluid will dissolve in the groundwater to the extent limited by its solubility, and be transported as a miscible groundwater contaminant. The situation is made complex through a number of physical, biotic and abiotic processes.

The objectives of this research were to: (a) develop source and risk models that will improve the understanding of multiphase transport of contaminants in groundwater, and (b) apply these models to several situations in Texas. The goal was to develop models which are computationally efficient, require a minimum of input data, and allow the user to assess the environmental consequences of a release of organic fluids at or near the ground surface and evaluate the sensitivity to various parameters while describing the fate and transport processes.

RESULTS

The models developed during this research allow one to simulate the fate and transport of spills and releases of organic fluids at or near the ground surface. Although a number of assumptions are made, the approach does include the appropriate physics which describes the problem quantitatively. There continues to be a need for field verification. The basic philosophy has been to balance data availability with model generality within the context of typical field sites.

One of the goals was to apply the model to specific sites. Unfortunately, neither time nor resources allowed much progress in this direction. However, the basis for such an effort is available through the model to examine the trade-off between use of time for further site characterization versus continued migration and spreading of a contaminant at a release site. Such questions are the focus of ongoing research, the results of which will be shared with the TWDB.

APPROACH AND METHODS

The mathematical model developed through this research encompasses three sub-models. The first simulates conditions resulting from a surface release of an organic fluid, which is referred to as an "oil". The first sub-model simulates the fate and transport of the oil, and any solutes which might be dissolved in the oil, as they migrate downward from the ground surface. The model considers gravity-induced flow of water and oil. Migration of the oil ceases onces its saturation decreases to its residual

saturation. The solute is allowed to partition between the oil, water, air, and soil phases. Degradation of the solute can occur in all phases while the oil phase itself can undergo degradation. Volatilization of the solute can occur from the air phase and is a function of the partitioning behavior of the solute, the air phase saturation, and the depth to which the solute has penetrated. The first sub-model can be used to determine whether a release will penetrate to the water table, how long it takes to do so, and the volume and mass flux past any horizon.

The second sub-model considers the development of an oil lense at the water table for an oil with a density less than that of water. The volume and mass flux into the lense is provided from the output from the first sub-model. As more and more oil is added to the lense, it grows in thickness and spreads laterally. Once the oil source is cut off, the thickness dissipates until the oil spreads to the extent controlled by its residual saturation. Partitioning of the solute between the water, oil and soil phases is again considered, as is degradation of the solute and oil. The solute can volatilize from the lense, and the amount of dissolution of the solute into the groundwater is calculated as a function of the groundwater velocity, lateral extent of the lense, and the water solubility of the solute.

The third sub-model considers migration of the solute as a miscible constituent within the aquifer. This sub-model was developed from the USGS Solute Transport Model, with a number of substantial changes. The new version of this model considers flow and transport in an unconfined aquifer. The original version only could deal with transport in a confined or semi-confined aquifer. Other changes have been made which greatly reduce the mass balance error. The source information for the third sub-model is obtained from the output of the second sub-model. The solute experiences, dispersion and decay, and is allowed to partition with the soil. The model simulates the concentration plume as it develops and dissipates over time.

DISCUSSION

General -- Each of the sub-models is described in more detail below. This discussion focuses on the capabilities, assumptions and limitations of the models. The discussion is qualitative in that equations are not presented nor are detailed presentations of the numerical methods used.

A mathematical statement of the physical laws which govern the multiphase flow and transport in the subsurface is developed through an extended form of Darcy's Law and the principle of conservation of mass (or volume, since the water and oil are assumed incompressible). The equations that govern these flows in porous media are coupled, nonlinear, partial differential equations. There is a mass conservation equation for each fluid and for each dissolved constituent in the system. There are also auxiliary relationships which incorporate various physical phenomena into the differential equations. An extended form of Darcy's Law is used to model the flux of the fluids. Two functions, the relative permeability and the capillary pressure, incorporate the physics of multiphase flows into Darcy's Law and couple the otherwise independent mass conservation equations.

Under unsaturated and multiphase conditions, the entire pore space is not filled with water or another fluid, but, rather, two or more immiscible fluids share the pore space. The relative permeability curve shows that the ability of the media to transmit

the other multiphase infiltration models. The presence of air is accounted for via the usage of the proper relative permeability function.

Second, imposed heads on the liquids and gravity are considered most important in driving infiltration. The differential mass conservation equation becomes a first order hyperbolic type and can be solved by the method of characteristics. In this equation, all quantities are expressed in terms of kinematic variables, hence the name kinematic model. In making this assumption, the leading edge of the invading water front is idealized as a sharp discontinuity. The sharp front is located so that the true and idealized profiles contain the same mass. To model the speed of the front, an integral form of the conservation equation is used. The speed is the same as the speed of some point on the true front. Thus the kinematic model can approximate the time at which a liquid arrives at a given depth. Due to the capillary pressure gradients, some amount of liquid, however, will arrive sooner than this model predicts. Taken together, the differential and integral equations comprise the approximate governing equation for the water.

The third assumption for the infiltration model is that in strongly wetted systems, the relative permeability of the wetting phase is independent of the other fluids present. This is because the wetting phase is so strongly attracted to the medium that it occupies the smallest pores no matter what other fluids are present. The extensive available literature shows that experimental results agree with this assumption.

The consequences of a strong wetting on kinematic infiltration allows the model to be extended to model oil and water flow. The mass conservation equations are coupled insofar as the flux equations are coupled. For the wetting liquid (water) in a strongly wetted system, the flux is independent of other fluids. Thus, the mass conservation equation for the water is independent of the other equations and can be solved first. For simulation of oil and solute migration from the ground surface down to the water table, one may use an average water infiltration rate (equal to the net precipitation minus runoff and evaporation). Recent work on simulation of the soil moisture profile has shown that below a depth of one or two meters, the moisture content (and water flux) remains relatively constant. Only near the ground surface are water contents highly variable over time. Since, for the most part, one will be interested in water tables which are considerably deeper than this, the assumption of an average water infiltration rate is used in this model.

After obtaining the solution of the water equation, the equation for the oil phase may be solved, under the Richards-Kinematic assumption, by the method of characteristics. Due to the relative complexity of the oil relative permeability function, no analytic solution exists for unsteady flow of oil.

In some important cases, the infiltrating oil may be supplied under imposed heads. This may occur during leaks for storage tanks, for example. Under the condition that the available pore space is filled by the oil, the well-known Green-Ampt model may be used to determine the speed of the infiltrating oil.

The oil may contain dissolved constituents that are soluble in water, volatile, and/or sorb onto the soil. Assuming no dispersive effects, the mass conservation equation for the constituents may be solved by the method of characteristics. If a dissolved constituent is volatile, it will be lost from the soil at the surface. A zone is

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assumed to develop that lacks any of the volatile constituents. The loss rate is determined by diffusion through the soil and through the atmospheric conditions as well as by the fluid saturations within the profile. If this speed is greater than the speed of the leading edge as determined above, at some point in time the constituent is entirely volatilized from the profile. Similarly, a component may disappear from the profile before reaching the water table because of biodegradation.

The input data includes: (a) parameters characterizing the porous matrix, many of which can be reasonably estimated from information based on soil texture, (b) parameters characterizing the fluids and the solute, (c) parameters describing the oil release characteristics, and (d) parameters controlling the numerical simulation. The output provides fluid and solute profiles at specified times and fluid flux and solute histories at specified depths. The latter are of direct interest in the second sub-model.

Lense Sub-Model -- The objective of this model is to determine the rate of spread of infiltrating oil on top of the water table if the oil is less dense than the water, and to determine the rate at which a solute carried down with the oil is dissolved into the underlying groundwater and carried away as a miscible contaminant. In light of the considerable uncertainty which characterizes the problem in the field, the model formulation has sought a simple representation which captures much of the relevant physical character without requiring an extensive data set or significant computational time expenditure.

As oil moves into the central core with oil and solutes entering from above, its thickness grows. Because of buoyancy, part of this thickness is carried above the water table and part below, in a proportion determined by the oil and water densities. As the thickness of the central core increases, a lateral head gradient develops causing the oil lense to spread. For the geometry of the lense, the model has adopted the Dupit-Forchheimer parabola in cylindrical coordinates. With the basic shape fixed, the entire volume of oil within the lense and central core is a function only of the oil-filled porosity (total porosity minus residual moisture content), the areal size of the central core, the thickness of the central core, and the lateral extent of the lense. Only the latter two parameters are a function of time.

Two basic equations describe the development of the lense. The first results from setting the time rate of change of oil volume within the lense and central core equal to the volume inflow from above (which comes from the first sub-model) less the rate at which oil is degraded, where the relationship between oil volume and core thickness and lateral extent is used. The second equation comes from Darcy's Law with the Dupuit-Forchheimer assumptions applied to the outer ring of the lense. This equation determines the flux of oil outward from the central core as a function of the core thickness and lateral extent of the lense. The result is two coupled nonlinear ordinary differential equations for the lense thickness and lateral extent, which are solved using the Runge-Kutta method.

With the lense size determined, the partitioning and fate of any solutes can be evaluated. Of particular interest is the rate at which the solute is released into the groundwater beneath the lense. The approach taken is to model this release as a vertical diffusion (or dispersion) process controlled by the extent of the lense, solubility of the solute, and speed of the underlying groundwater. The water immediately beneath the lense is considered to be saturated with solute. Concentration gradients

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then cause downward diffusion of the solute further into the aquifer during the time period within which the particular water column resides beneath the lense. The water columns are continually moving with the ambient groundwater flow, so that clean columns appear at the upstream edge of the lense. The solution is analytically tractable, and provides the mass flux from the lense as a function of time. In addition to dissolution, the solute also may experience biodegradation and volatilization, though these appear to be of somewhat less importance from the point of view of groundwater pollution.

The data requirements for the lense model are slight. One must estimate the central core area, which may be assumed to be the same as the source area which it is beneath. One also must know the oil viscosity and degradation rate, partition characteristics of any solutes, degradation rate constants, solute solubility in water, groundwater flow velocity, and effective vertical diffusion/dispersion coefficient within the aquifer.

Results indicate that a solute which would be expected to have very little mobility because of its high sorption potential can migrate significant distances if it is carried along by the solvent such as the oil modeled in the lense. Recognition of these mechanisms suggests methods of enhanced groundwater reclamation as well as mechanisms of facilitated support.

Aquifer Solute Transport Sub-Model -- The third sub-model considers the fate and transport of miscible solutes within an unconfined aquifer at the site of a spill or release of an organic fluid at the ground surface. The framework for the aquifer model comes from the U.S.G.S. Solute Transport Model, originally programmed by Konikow and Bredehoeft. The original model, while widely used throughout the country, is often criticized for its rather large mass balance errors. In addition, the model does not allow one to look at unconfined aquifers, which are actually of most concern with regard to groundwater contamination from surface activities.

This third sub-model allows simulation of the fate and transport of miscible organic contaminants as they migrate through an unconfined aquifer, allowing for anisotropic and nonhomogeneous conditions as well as hydraulic transient phenomena. Methods for improving on the mass balance error were considered.

The USGS model is already in use by the Texas Water Development Board, so its capabilities will not be presented. The following changes are of note. The numerical model has been modified for an unconfined aquifer where the saturated thickness depends on the hydraulics of the flow system. This has required a number of changes within the code, although no additional parameters are used (if one interprets the storage coefficient as the specific yield and the transmissivity as the hydraulic conductivity). In addition, a transient source from a lense, such as that modeled by the second sub-model, has been added, as has linear partitioning with the soil and first order degradation.

From a computational point of view, other significant changes have been made. The original model simulated advection processes through following the movement of fluid particles along flow paths within the aquifer and using arithmetic averaging of particle concentrations to find concentrations at finite difference node points. The advection and arithmetic averaging procedures are the major causes for the relatively

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large mass balance errors in the USGS model. The approach taken in the new version of the model is to look backwards along a streamline and move a particle to the same final location during each time step, and then use volume-averaging to estimate node point concentrations. For most cases, the mass balance errors are decreased significantly. In addition, certain of the stability requirements have been relaxed.