# FISCAL YEAR 1984 PROGRAM REPORT

Louisiana Water Resources Research Institute

Louisiana State University Baton Rouge, Louisiana Fiscal Year 1984 Program Report
Grant NUmber 14-08-0001-G-909

for

U.S. Department of Interior Geological Survey

bу

Louisiana Water Resources Research Institute
Louisiana State University
Baton Rouge, LA 70803

Vijay P. Singh, Acting Director November 1985

"The research on which the report is based was financed in part by the United States Department of the Interior, Geological Survey, through the Louisiana Water Resources Research Institute."

"Contents of this publication do not necessarily reflect the views and policies of the United States Department of the Interior, nor does mention of trade names or commercial products constitute their endorsement by the United States Government."

# TABLE OF CONTENTS

Abstract				Page
Austract	•	•	• •	i
Water Problems and Issues of Louisiana	•	•		1
Program Goals and Priorities				6
Research Project Synopses		•		11
Assessment of Uncertainty is Hydrologic Models for Flood Frequency Analysis - V. P. Singh	•			12
A Technique for the Development of Management-Oriented Groundwater Models for Multilayered Apuifers - T. H. Illangasekare	•	•	•	14
Biological Removal of Chlorinated Hydrocarbons from Water - P. H. Templet	•	•		16
Oxidation of Trace Contaminants in Drinking Water - F. H. Groves, Jr		•	•	.21
Biodegradation of Hazardous Chemical Wastes - W. Pelon and M. L. Murray		•	•	23
Information Transfer Activities		•		26
Training Accomplishments	•	• •		27
University Contacts	•	•	•	28
Advisory Roards				20

#### ABSTRACT

The focus of the Fiscal Year 1984 Louisiana Water Resources

Research Institute Program was to support both applied and theoretical

projects. The applied projects were of immediate value to Louisiana,

while theoretical projects concurrently assisted in the solution of long
range problems.

Water resources problems were addressed relating to flood technology, ground water, water treatment and hazardous waste contamination. Project 02 on oxidation of trace contaminants in drinking water investigated the use of potassium ferrate for decomposition of organics in drinking water. Project 03 developed a special management oriented groundwater model for simulation and management of multilayered aquifers. Project 04 initiated biodegradation studies of hazardous chemical wastes using groundwater samples which were found to be both mutagenic and toxic. Project 05 used the principle of maximum entropy to develop criteria for assessment of uncertainty of using duckweeds for removing phenols and chlorophenols from water and offered the possibility of biological treatment of polluted waters.

# WATER PROBLEMS AND ISSUES OF LOUISIANA

Water-related problems are receiving increasing attention in Louisiana. There is growing realization that their timely resolution is crucial for continuing prosperity and economic well-being of the State, and for maintaining high quality of life. The water resources problems in Louisiana stem from the need for accelerated energy development, past and present practices of waste disposal, increased food production, industrial expansion, environmental protection, interaction with hydrologic environment, forest clearing and cutting, and safe and orderly urban and rural development. [They are intensified by shifting of population from a rural society to an urban one and population growth; and they are compounded by climatic and hydrologic fluctuations (droughts and floods), and the complexity and interdependence of the political, economic, social, technological and natural systems involved in the development, management and use of water and environmental resources.] Municipal and industrial waste generation, water pollution associated with urban runoff, effects of urban and other major land use changes on climatological and hydrological processes, flood damage protection, surface and groundwater contamination and management, and provisions of adequate municipal and industrial water supplies are of major concern.

Water resources research plays an important role in providing the technology to ensure an adequate supply of high quality water for many competing uses and with safe drinking water. To this end the Institute has, due to financial constraints, tried to promote high priority research areas. A short discussion of those problem areas which the Institute perceives to be of high priority is given below. The Institute conducted a survey to seek input from water resources

community including local and State government departments, educational institutions, private sector, planners, administrators, managers and practitioners on water resources problems and research priority needs. The outcome of this survey formed the basis for articulating water resources problems and deciding on funding of research projects to address them.

Analysis of Floods: Flooding in the U.S. accounts for considerable loss of life, personal tragedy and property damage each year. This is perhaps even more true in Louisiana. The devastation of property alone results in billions of dollars in losses. The losses have tended to prevail over the years despite the continuous expenditure of considerable sums of money. Research is needed to forecast the timing, magnitude and extent of flooding as a result of a specified rainfall event. To accomplish this, stochastic models of floods are needed. Also needed is a better procedure for assessment of flood damage. The flood insurance program administered by the Federal Emergency Management Administration (FEMA) cannot survive for long without revised guidelines for determining insurance premiums. Thus, the entire hydrology of flooding is a crucial area for investigation.

Hydrology of Ungaged Basins: Most basins in the United States are not gaged, despite extensive climatologic and streamflow network systems. This is certainly true in Louisiana. Mathematical models are therefore needed to investigate and predict hydrologic response of such basins. More reliable criteria are needed for classifying basins based on hydrologic similarity. Improved hydrologic procedures are needed if these basins are undergoing land use changes.

Integrate Analysis of Physical, Chemical and Biological Facets of Hydrologic Environment: When chemical wastes are introduced within and between ground and surface water environments, they undergo chemical and biological changes and, in turn, alter physical characteristics of the hydrologic conduits (aquifers, lakes, rivers, etc.) transporting them. Chemical wastes, hydrologic system and geochemical processes interact dynamically with each other. Integrated approaches considering physical, chemical and biological factors must be developed for determining migration and eventual fate of contaminants if we are to develop desired technology for their treatment and safe disposal. Likewise, integrated approaches must be developed for modeling movement of water and contaminant as a continuum, since water moves over and below the ground in a dynamically coupled manner.

Groundwater Research: Substantial achievements in the analysis of aquifer properties important to prediction of the future response of aquifers to alternate pumping and recharge decisions have been made. Major research challenges, however, remain. Some of these are: groundwater quality modeling, regional predictive capacity, prediction of water use, analysis of institutional adoption for groundwater management, use of aquifers for storage of waste heat through injection of heated water, use of aquifers to store compressed air, and new uses for resources previously thought unusable for quality or cost reasons, i.e., storage of fresh water in saline aquifers.

Aquifer Management: The framework for establishing property rights in groundwater has not yet been established in Louisiana. Recharge districts to salvage the seasonal surplus of water cannot be formed yet.

The lack of proper management framework is causing increasing pumping lifts in some areas and increased use of power for water supplies.

Urban Water Research: A shifting of the population from rural to urban society has resulted in approximately 75 percent of the Nation's population living on approximately two percent of the land. The principal problems associated with this shift include: (1) municipal and industrial waste generation, (2) water pollution associated with urban runoff, (3) effects of urbanization on local climate and hydrological processes, (4) flood damage protection, and (5) provision of adequate municipal and industrial water supplies. Examples of continuing research to solve these problems include: (1) research and development of procedures for detecting, measuring and predicting nonpoint sources of pollution and (2) research to provide solutions for the ultimate discharge of treatment plant effluents and the disposal of the tremendous volumes of sludge that are generated by the treatment process. A further goal of research is to develop integrated management for water supply, wastewater collection and disposal, and storm water management.

Environmental Protection Research: The quality of our environment must be maintained and enhanced in concert with other national goals. Research is required to establish the scientific base for environmental standards, regulations and practices. Research should continue on:

(1) environmental loading and contamination associated with human activities and natural sources (including radionuclides); (2) environmental processes that result in pollutant transformation, transport and removal; (3) pollutant identification, characterization and measurement; (4) determination of health and ecological effects; and (5) development

of alternate control technologies for environmental enhancement and restoration.

### PROGRAM GOALS AND PRIORITIES

The LWRRI funded five research projects of outstanding quality.

These projects addressed critical problems identified in the Institute's Five-Year Plan as well as in the Southern Plains Region Five-Year Plan for water resources research. The research projects addressed some of the critical water quality concerns and the techniques to quantify and alleviate these problems. A summary of these projects is presented and their relevance briefly reviewed.

Louisiana experiences flooding virtually every year. Of the many facets of flooding, frequency analysis constitutes the core. There has been a proliferation of mathematical models for performing frequency analysis. A research project was directed to develop hydrologic models for flood frequency analysis and assess their uncertainty. By employing the principle of maximum entropy (POME), a unified framework was developed for derivation of frequency distributions and estimation of their parameters. This framework utilized limited data in terms of constraints and hence has a lot of potential for application in data-scarce regions.

The major findings of this project are: (1) POME can be used to derive any frequency distribution provided appropriate constraints are specified. (2) POME provides a unique method of parameter estimation which is either superior to or at least as good as the existing methods of parameter estimation. (3) A method of assessing uncertainty associated with a given frequency distribution is derived by using POME. (4) POME provides a method to evaluate the worth of data. In other words, how long is long enough for hydrologic records.

The increasing demand placed on groundwater as a source of supply for both industrial and public use is expected to cause a decline in the potentiometric head in the water producing layers of the Baton Rouge aquifers. It is therefore necessary that the aquifer system be managed effectively to protect against drastic and continuous decline in head and consequent decline in quality. A project was funded to address the management of groundwater in multilayered aquifers.

This project developed a special management oriented groundwater model for the simulation and management of multilayered aquifers. A modeling technique referred to as the discrete kernel approach which is based on Green's function solution to linear partial differential equations was used in the design of the model. The three dimensional flow in the multilayered aquifer was simulated using a quasi-three dimensional flow in the horizontal direction. The flow in the confining aquitard layers were assumed vertical. A discrete kernel formulation was developed to simulate these assumed flow conditions.

The discrete kernel generator programs for the aquifer layers and aquitard and the numerical simulation model were developed. The multi-aquifer simulation model uses the kernel coefficients to compute the transient head distribution in the aquifer and aquitard layers and the leakage flux. Detailed user's manuals with instructions on data input to the three models were prepared.

Contamination of drinking water by traces of organic chemicals is of special concern because of health effects of these materials.

Louisiana waters are especially susceptible to this contamination because of industrial discharges stemming from large petrochemical industries. A project was funded to investigate the possibility of

decomposing organic contaminants by treatment with a powerful oxidizing agent.

Chlorinated organics in drinking water can arise from industrial effluents or from chlorination of naturally occurring organics during disinfection. The goal of this project was to study the use of a powerful oxidizing agent, potassium ferrate, for the decomposition of organics in drinking water. Benzene, dichloroethane, trichloroethylene, chloroform, chlorobenzene, and tetrachloroethylene at 100 ppb in water were treated at room temperature with ferrate. Fifty to one hundred parts of ferrate by weight were used per part of organic. The pH was in the 6.5 - 7.5 range. Only trichloroethylene was much affected by ferrate. It was 41 to 87 percent decomposed. The other organics were less than 25 percent decomposed. Our conclusion is that potassium ferrate is unlikely to be generally useful in oxidizing chlorinated organics in water.

With the hope of finding an inexpensive and simple solution to the problem of cleanup of contaminated water, a project was supported to investigate the role of freshwater plants in wastewater treatment. The use of duckweeds (Lemnaceae) to remove phenol and 2-chlorophenol from water offers an inexpensive and simple solution to the cleanup of contaminated water. The rate at which the organic compounds were removed from water by a known amount of duckweed was determined for three different concentrations of phenol and with three different amounts of duckweed for 2-chlorophenol. The duckweed removed phenol from water at a rate which is dependent on the phenol concentration and average 107 ug phenol removed/hr/g duckweed for the first 48 hours at 10 ppm initial concentration of phenol in water. The removal rate for 2-chlorophenol

was investigated at a lower initial concentration (2.3 ppm) and the removal rate was slower and a function of the quantity of duckweed present even when normalized to a constant duckweed level. The rate increased for the first 4-6 days and average 33 ug chlorophenol removed/day/g duckweed at the sixth day. The results support the hypothesis that duckweeds can be used to feasibly remove phenols and chlorophenols from water and offers the possibility of biological treatment of polluted waters.

Another project, funded by the Institute, related to hazardous chemical wastes which has been a problem of national concern. It is of particular concern to Louisiana because of its large petrochemical industrial base. Under natural conditions, the biodegradation of hazardous organic chemical wastes is often a slow process. Although appropriate microbial populations are present where such wastes exist, their biodegrading activities are often hampered as the result of low population densities, population pressures, and also by the presence of alternate carbon sources that are preferentially metabolized.

Our current interest involves the enhanced biodegradation of hazardous organic chemical wastes through the use of "synthesized" mixed microbial population that has attained a steady state of growth while using hazardous organics present in water samples as their sole source of carbon, biodegrading them to where recognized assay systems can no longer detect toxicity and/or mutagenicity. Individual members within such a population will be isolated, propagated under optimal conditions, then mixed to form a dense synthetic population that would permit more rapid biodegradation by the presence of sheer numbers.

Pond water from the Cleve Reber waste dump site was initially selected but was found to be neither toxic nor mutagenic, an observation that was subsequently confirmed by the US EPA. Recently a second sample of groundwater obtained from the Petro Processor Waste Dump site in north Baton Rouge was assayed and found to be both mutagenic and toxic. Biodegradation studies are being initiated using the water as the substrate and soil samples from the site as the inoculum.

|--|--|--|--|--|--|--|--|



# RESEARCH PROJECT SYNOPSES

Synopses of the research projects funded by the Institute are provided in the following order:

Assessment of Uncertainty in Hydrologic Models for Flood Frequency Analysis, by V. P. Singh

A Technique for the Development of Management-Oriented Groundwater Models for Multilayered Aquifers, by T. H. Illangasekare

Biological Removal of Chlorinated Hydrocarbons from Water, by P. H. Templet

Oxidation of Trace Contaminants in Drinking Water, by F. H. Groves, Jr.

Biodegradation  ${}^{\smallfrown} f$  Hazardous Chemical Wastes, by W. Pelon and M. L. Murray

# Synopsis

<u>Project Number</u>: 05 <u>Start</u>: 10-1-84 End: 9-30-85

<u>Title</u>: Assessment of Uncertainty in Hydrologic Models for Flood Frequency Analysis

<u>Principal Investigator</u>: Vijay P. Singh, Louisiana State University, Baton Rouge

## Project's Purpose and Objectives:

The objectives of this project were (1) to employ the principle of maximum entropy (POME) to develop a rational criterion for choosing amongst mathematical models for flood frequency analysis, (2) to assess uncertainty associated with these models, and (3) to verify the results by using streamflow data from river basins in Louisiana and elsewhere.

## Methods and Procedures:

The principle of maximum entropy (POME) was employed to develop a unified mathematical approach for derivation of a frequency distribution provided appropriate constraints were specified. These constraints were specified from data and were, therefore, a measure of information needed for derivation of the distribution. This procedure of derivation yielded a unique method of estimating the distribution parameters. Further, POME provided a quantitative measure of uncertainty associated with the distribution. In this way, it was possible to assess the various methods of parameter estimation for a given distribution and evaluate and compare the various distributions for the goodness of fit to empirical annual flood maxima. Observed streamflow data were used to test the procedures.

## Principal Findings and their Significance:

This project obtained the following important results: (1) The method of parameter estimation based on POME is either superior to or at least as good as other well-known existing methods. (2) A quantitative measure of uncertainty associated with a given frequency distribution is given by POME. (3) POME does not require complete data series; all that it needs is constraints. Consequently, it can be applied in data-scarce regions. (4) POME provides a quantitative measure of information contained in a given set of data.

#### Conclusions:

The following conclusions can be drawn from this study: (1) The existing flood frequency distributions can be derived from the general mathematical framework based on POME. (2) Parameters of these frequency distributions can be more easily and efficiently estimated by using POME. (3) POME requires less data than existing methods of deriving distributions. (4) POME can be extended to multivariate stochastic analysis which is currently being investigated.

# List of Publications and Manuscripts Produced:

Several manuscripts are under preparation. However, the following list includes those submitted for publication:

- 1. "Derivation of Some Frequency Distributions Using the Principle of Maximum Entropy," submitted to Advances in Water Resources.
- 2. "Three Parameter Lognormal Distribution Derived from the Principle of Maximum Entropy (POME)," submitted to <u>Transactions</u>, Institution of Engineers, Australia.
- 3. "Derivation of the Pearson Type (PT) III Distribution by Using the Principle of Maximum Entropy (POME)," Journal of Hydrology, Vol. 80, pp. 197-214.
- 4. "Estimating Parameters of EV1 Distribution for Flood Frequency Analysis," submitted to <u>Water Resources Bulletin</u>.
- 5. "Derivation of Log-Pearson Type III Distribution," submitted to ASCE Journal of Hydraulic Engineering.
- 6. "A Comparison of Transformation Methods for Flood Frequency Analysis," submitted to Water Resources Bulletin.
- 7. "A Stochastic Model for Sediment Yield," presented at the Fourth International Hydrology Symposium held July 15-17, 1985, in Fort Collins, Colorado.
- 8. "Comparing Methods of Transformation for Flood Frequency Analysis," presented at the Fourth International Hydrology Symposium held July 15-17, 1985, in Fort Collins, Colorado.
- 9. "Energy Dissipation in Tidal Waterways," Proceedings of the ASCE Specialty Conference on Hydraulics and Hydrology in the Small Computer Age, pp. 260-265, Lake Buena Vista, Florida.
- 10. "Sediment Transport in Vertically Two-Dimensional Man-Made Canals," <u>Proceedings of the 21 IAHR Congress</u>, Vol. 3, pp. 577-582, Melbourne, Australia.

# Synopsis

<u>Project Number:</u> 03 <u>Start:</u> 10-1-84 End: 9-30-85

<u>Title</u>: A Technique for the Development of Management-Oriented Groundwater Models for Multilayered Aquifers

<u>Principle Investigator</u>: Tissa H. Illangasekare, Louisiana State University, Baton Rouge

# Project's Purpose and Objectives:

Problems related to the management of groundwater in multilayered aquifers is addressed. Multilayered aquifers consist of water bearing aquifer layers separated by sufficiently permeable confining aquitard layers which permit significant leakage flow. Management decisions have to be taken on the locations of wells or recharge sites, timing of pumping and quantities to be pumped from different layers of the aquifer. The decisions are subjected to physical, environmental, institutional, economic, legal and political constraints. Any model designed to be used as a management tool should have the capability to simulate both the physical and operational behavior of the system.

# Methods and Procedures:

The discrete kernel method of groundwater modeling, a proven effective tool for management modeling of large aquifers, was used. This approach is based on the classical solution of partial differential equations by the use of Green's function method. The approach makes use of the fact that once the solution (kernels) of Green's function to a linear partial differential equation is known, the response to any type of excitation can be obtained by convoluting the excitations with Green's function. The three dimensional flow in the multilayered aquifer was simulated using a quasi-three dimensional flow model. The flow in each aquifer layer is modelled as two dimensional flow in the horizontal direction. The flow in the confining aquitard layers are assumed vertical. The discrete kernel formulation was developed to simulate these assumed flow conditions.

The kernels for the aquifer layers are generated by solving the two dimensional saturated groundwater flow equations using an implicit finite difference scheme. The kernels for the aquitard are generated by solving the one dimensional saturated ground water flow equation using Galerkin finite element method. The multilayered simulation model uses these kernel coefficients to compute the transient head distribution in the aquifer and aquitard layers and the leakage flux. Procedures were developed to couple a finer grid system to the coarser grid system of the model to obtain higher resolution solutions in the aquifer and in the sub-region of the aquifer.

# Principal Findings and Significance:

In this research a methodology was developed to explicitly express the state variables (e.g., piezometric head in aquifer, leakage flux, etc.) as functions of the decision variables (e.g., aquifer pumping) and the initial conditions. The models, developed based on this methodology, will be both cost effective for frequent use as decision making tool and capable of easy linkage with a management model. Also these explicit relationships between the state and decision variables can be used to formulate the management problem as a mathematical optimization problem to arrive at optimum management schemes. The developed model will be useful to ascertain the best strategies of operation for water conservation, to investigate different alternatives for water management and in developing the initial framework for establishing property rights in groundwater in the State.

# Conclusions:

Models and modeling techniques which are specifically useful for the management modeling of large multiaquifer systems were developed. The techniques are valid only if the governing partial differential equations are linear. The actual flow which takes place in the aquifer system is three dimensional. By decomposing the aquifer to separate aquifer and aquitard layers, the flow equations could be linearized to apply the discrete kernel method. The conventional modeling techniques still have their use in simulating systems in which the linearization assumptions could not be justified. In situations where the accuracy of solution could be compromised to some degree to achieve high computational efficiency needed in the use of the model as a decision making management tool, the models developed in this research could be effective.

# List of Publications and Manuscripts Produced:

- 1. "Aquifer Management Using Discrete Kernels in Microcomputers," Proceedings of the ASCE Hydraulics Division Specialty Conference, Orlando, Florida, 1985, pp. 999-1004.
- 2. "A Discrete Kernel Simulator for Simulation of Multilayered Aquifers," Completion Report, Louisiana Water Resources Research Institute, 49 pp. and three appendices.
- 3. "Management Modeling of Multilayered Leaky Aquifers," under preparation to be submitted to Water Resources Research.
- 4. "A Management Simulator for Baton Rouge Multiaquifer," under preparation to be submitted to Water Resources Bulletin.

# Synopsis

<u>Project Number</u>: 06 <u>Start</u>: 10-1-84 End: 9-30-85

Title: Biological Removal of Chlorinated Hydrocarbons from Water

<u>Principal Investigators</u>: Paul H. Templet and Barbara Carr, Louisiana State University, Baton Rouge

# Project's Purpose and Objectives:

The purpose of this research was to evaluate the possibility of using aquatic plants (duckweeds-Lemnaceae) to remove various phenols from water. The objective was to measure the uptake rate of phenol and chlorophenol from water solutions and compare the rates of removal to controls.

# Methods and Procedures:

Phenol and 2-chlorophenol were investigated in this study and their uptake rates by duckweed were measured. The compounds were dissolved in water at various concentrations and known amounts of duckweed added (wet weight). At selected intervals aliquots of water were removed and analyzed by GC/FID for the phenol of interest. A control was also analyzed, the control contained the phenol but no duckweed.

In testing phenol ( ${\rm C_6H_5OH}$ ), three concentrations were prepared, 20, 10 and 5 ppm and analyzed immediately by direct injection into a GC/FID. Duckweed was then added to the duplicate flasks: 0.32 g in the 5 ppm flasks, 0.30 g in the 10 ppm flasks and 0.40 g in 20 ppm flasks. With the passage of time, the flasks were periodically analyzed. The GC used a 10 m x 0.53 mm SE-30 column which was operated isothermally at 200°C. Duplicates of each concentration were run throughout the experiment. The duplicate controls contained 1, 5 and 10 ppm phenol but no duckweed. The duckweed was kept at ambient temperature (20°C) and exposed to artificial light 12 hours per day.

For the 2 Cl-phenol experiment, 4 sterilized flasks containing 200 ml of water, 1 ml of solution A and 1 ml of solution B of Hunter's Medium as nutrient and the following amount of duckweed were kept at 25°C and exposed to artificial light during 16 hours a day:

Duckweed (a)

	Duckweed	(6)
#1	3.20 g	
#2	1.38 g	
#3	0.67 g	
#4	0.00 g	(blank)
	#2 #3	#2 1.38 g #3 0.67 g

An amount of 0.462~mg of 2-chlorophenol was added to each sample resulting in a concentration of 2.31~ppm.

At different periods of time, 10 ml of each sample were passed through a C-18 Sep-pak (Millipore, Waters Associates) to extract the phenols from the water, and eluted with 3 ml of methylene chloride. One ul of this extract was injected in the Gas Chromatograph (Hewlett Packard 5890)/FID using a capillary column (5% Ph Me Silicone 50 m x 0.25 mm ID).

To find the response factor of these compounds, a standard phenols mixture was used (604-M Environmental Analyses Standard producted by SUPELCO Chromatograph Supplies) and original phenol concentration and diluted samples were run.

		<u>Original</u>	Sample #1	Sample #2
1. 2. 3. 4. 5. 6. 7. 8. 9. 10.	Phenol 2-Chlorophenol 2-Nitrophenol 2,4-Dimethylphenol 2,4-Dichlorophenol 4-Chloro-3-methylphenol 2,4,6-Trichlorophenol 2,4-Dinitrophenol 4-Nitrophenol 2-Methyl-4,6-dinitrophenol Pentachlorophenol	0.5 mg/ml 0.5 mg/ml 0.5 mg/ml 0.5 mg/ml 0.5 mg/ml 2.5 mg/ml 1.5 mg/ml 2.5 mg/ml 2.5 mg/ml 2.5 mg/ml 2.5 mg/ml	5 ppm 5 ppm 5 ppm 5 ppm 5 ppm 25 ppm 15 ppm 15 ppm 25 ppm 25 ppm 25 ppm 25 ppm	10 ppm 10 ppm 10 ppm 10 ppm 10 ppm 50 ppm 30 ppm 30 ppm 50 ppm 50 ppm 50 ppm

GC conditions included: Init temp:  $70^{\circ}$ C; Init time: 5 min; Rate: 15 deg/min; Final temp:  $270^{\circ}$ C; Final time: 5 min; Inj temp:  $250^{\circ}$ C; Det temp:  $310^{\circ}$ C.

Dividing the area by the concentration, the following response factors were found:

1.	$2.53 \times 10^{-5}$ $3.37 \times 10^{-5}$ $4.67 \times 10^{-5}$	6. 7.	2.86 5.34 2.52	x x	$10^{-5}$ $10^{-5}$ $10^{-5}$
4.	2.32 x 10 <sup>-5</sup>	8.	2.52	x	10 5
	4.20 x 10 <sup>-5</sup>	9.	7.63	x	10 5

The response factors of the last two compounds were not possible to determine because they were not consistent.

A sample of 32.78 ppm of 2-Chlorophenol was run in order to verify the response factor of GC, the following results were found: 35.41; 31.74; 28.83.

The experiment began on July 23, 1985, with 2.31 ppm of 2-Chlorophenol (10 ml of sample, extracted with 3 ml of methylene chlorine).

The flask containing sample #2 broke and the sample had to be transferred to a sterilized flask. Subsequently the duckweed died giving anamolous results.

On August 7, 1985, the duckweed from sample #1 was taken out of the flask and weighed, remaining close to the original amount (3.01 g). It was washed with deionized water and ground with 200 ml of water. From this new sample, 10 ml was poured through the Sep-pak and extracted with 3 ml of methylene chloride. A sample of this extract was injected in the GC, without any chlorophenol detected.

Sample #3 (0.67 g) = 0.6 ppm

Sample #4 (0.00 g) = 2.2 ppm

On August 13, 1985, the extraction from sample #3 exhibited 0.4 ppm. The amount of duckweed from sample #3 was removed and weighed (1.02 g). It has been found to have grown 0.35 g from the original weight (0.67 g). Table 1 contains the results of the experiment.

# Principal Findings and their Significance:

A sample of the results of the two experiments is shown in Table 1. The conclusion is that duckweed does remove both phenol and 2 Cl-phenol from water and that the rate of removal is dependent on both the amount of duckweed present and the concentration of the compound being removed.

### For Phenol

- (1) At the higher concentrations of phenol the removal rate is linear for the first several days, then slowly approaches a constant rate as the concentration of phenol diminishes.
- (2) The extraction rate/g duckweed is greater at higher phenol concentrations.
- (3) The average extraction rate/hr/g duckweed increases with phenol concentration.

# For 2-Chlorophenol

- (1) The decrease of 2-chlorophenol with time is approximately linear for the first 6 days.
- (2) The lowest concentration of duckweed had the highest removal rate per g of duckweed.
- (3) The removal rate peaked at day 4-6 for all 3 samples.

#### Significance

This research is significant in that it illustrates that duckweeds can be used to remove phenols and chlorinated phenols (and probably other organic) from water within a reasonable amount of time. The approach is inexpensive and feasible.

Table 1. Phenols Remaining in Solution as a Function of Time.

Time	Hours Elapsed	Exp 1 Phenol	Exp 2 Pheno1	Exp 3 Phenol	Control 1 (ppm)	Control 2 (ppm)	Control 3 (ppm)
5/1/85				The state of the s			
1244 1800	0 5.3	5.0 4.6	10.1	20.3	1.0	4.8	8.9
1812 1823	5.5 5.6		8.9	18.5		. •	
5/2/85							
1235 1240 1255	23.8 23.9 24.2	3.9	6.1	12.3			
5/3/85							
1515 1520 1530	50.5 50.6 50.8	0.5	0.3	3.6			ù.
5/6/85							
1115	120	0.6	0.3	0.4			
4/30/85	24 45 72 90				1.0 1.0 0.6 0.4	4.4 3.6 3.2 3.8	10.3 7.0 6.7 6.7

2-Chlorophenol Remaining in Solution

Date	Days Elapsed	Sample 1 (ppm)	Sample 2 (ppm)	Sample 3 (ppm)	Control (ppm)
7/23/85	0	2.3	2.3	2.3	2 2
7/27/85	4	1.1	1.5	1.8	2.3
7/29/85	6	0.5	0.8	1.3	2.2 2.2
8/4/85	12	0.3	1.1	1.0	2.2
8/5/85	13	0.2	1.2	0.8	2.2
8/7/85	15		1.8	0.6	2.2

<sup>(</sup>The phenol concentrations presented are the average of duplicates)

# Conclusions:

The conclusion is that duckweed does remove both phenol and 2 Cl-phenol from water and that the rate of removal depends upon both the amount of duckweed present and the concentrations of the compound being removed.

# List of Publications and Manuscripts Produced:

"The Biological Removal of Chlorinated Hydrocarbons from Water," in preparation, 1985.

## Synopses

<u>Project Number</u>: 02 <u>Start</u>: 10-1-84 End: 9-30-85

Title: Oxidation of Trace Contaminants in Drinking Water

Principal Investigator: Frank R. Groves, Jr., Louisiana State

University, Baton Rouge

## Project Purpose and Objectives:

Contamination of drinking water by traces of organic chemicals is of special concern because of the health effects of these materials. New Orleans water is specially susceptible to this contamination because of industrial discharges into the Mississippi River and because of reaction of naturally occurring organic materials with chlorine during heavy chlorination for disinfection. The goal of this research was to investigate the possibility of decomposing organic contaminants by treatment with a powerful oxidizing agent, potassium ferrate. Benzene, ethylenedichloride, trichloroethylene, chloroform, chlorobenzene, and tetrachloroethylene were treated at the 100 ppb level in water.

## Methods and Procedure:

Potassium ferrate was prepared by the method of Schreyer, et al. (1953), oxidation of ferric nitrate by freshly prepared hypochlorite in strongly basic solution. The yield of ferrate was 0.86 g. The ferrate was analyzed by the method suggested by Schreyer, et al. (1953) and was found to be 42 percent pure.

Solutions of the organic materials were prepared in water at a concentration of approximately 100 ppb. A phosphate buffer (5 ml per liter of solution) was added to bring the pH to 6.5 to 7.5. Potassium ferrate was then added at a level to 50 to 100 times the concentration of organic. The solutions were set aside at room temperature for several hours to allow the ferrate to react completely. Samples were then analyzed using EPA method 624 (purge - trap with GC/MS). The chromatographic column was one percent SP-1000 on 60/80 mesh CARBOPACK B, 1/8 inch OD stainless steel, 10 feet long.

## Principal Findings and their Significance:

Of the materials studied, only trichloroethylene was significantly decomposed by ferrate at the treatment level and pH used. Percentage decomposition of trichlorethylene ranged from 41 to 87 percent. The other organics studied were less than 25 percent decomposed. The preparation of potassium ferrate was found to be a difficult procedure involving strongly basic solutions, ill suited to scaleup from laboratory to commercial scale.

# Conclusions:

It appears unlikely that potassium ferrate will be generally useful for decomposing chlorinated organics in water. If ferrate is used for disinfection, it should probably be used in the form of an impure basic solution. Isolation of pure solid potassium ferrate is unlikely to be economical on a commercial scale.

# Publications and Manuscripts Produced:

A manuscript is planned reporting the results of this work. Completion date is end of December 1985.

## Synopsis

<u>Project Number:</u> 04 <u>Start:</u> 10-1-84 End: 9-30-86

Title: Biodegradation of Hazardous Chemical Wastes

<u>Principal Investigators</u>: William Pelon and Michael L. Murray, LSU Medical Center, New Orleans

# Project Purpose and Objectives:

The numerous dump sites in Louisiana in which hazardous organic chemical wastes have been buried now pose a threat to public health. Surface water runoff, ground waters, and existing aquifers all risk contamination by deposited chemical wastes escaping from deteriorating containers at the waste dump sites. This project seeks a practical approach towards reducting this threat by exploiting naturally-occurring biological systems, and by amplifying their biodegrading activities. This is being achieved through the fulfillment of the following objectives:

- 1. The confirmation of the toxic and mutagenic nature of the water samples under investigation.
- 2. The isolation of an autochthonous mixed bacterial population that will effectively biodegrade toxic and/or mutagenic organic chemicals present in waste-contaminated water to the point where such properties are no longer evident.
- 3. The isolation and identification of individual members within such a population so that practical methods may be developed utilizing them to modify existing situations.

### Methods and Procedures:

Pond water samples, considered to be chemically contaminated by the Hazardous Waste Division of the Louisiana State Department of Environmental Quality, were collected from the Cleve Reber Hazardous Waste Dump Site (on the US EPA's Superfund list) near Sorrento, Louisiana. These were filter-sterilized and stored at 4°C. Groundwater samples were also obtained from the Petro Processor, Inc., Waste Dump Site, in north Baton Rouge, Louisiana. These were similarly stored. Soil samples were also gathered from each of the locations, since on the basis of other investigations, there was evidence that autochthonous organisms, capable of biodegrading organic compounds, but existing in only low population densities, would be present at those particular sites.

Toxicity Assays. The toxicity of the organic chemically-contaminated water samples were to be determined using two recognized short-term toxicity assays, the Lethal Concentration  $_{50}$  (LC  $_{50}$ ) assay, that used the water flea (Daphnia magna), and the Growth Rate  $_{50}$  assay that employed the raddish seed (Raphanus sativus). In this latter

assay, two parameters, germination and root elongation were evaluated. For reasons to be later explained, these two assays are being supplemented through the use of the diploid human embryonic lung cell, WI-38, and the use of primary cultures of embryonic Syrian hamster cells. These two systems provide not only information on toxicity, but also on the capacity of substances in the water samples to transform normal cells into a malignant state.

Mutagenicity Determinations. The Liquid Suspension Mutant Fraction Assay, developed for the US EPA, a modification of the Standard Ames Assay, using the five currently recommended test strains of Salmonella typhimurium, is being employed for mutagenicity determinations. The assay is carried out both directly, and in the presence of rat liver microsomal fractions. This system has the advantage that erroneous results obtained as the result of naturally-occurring histidine being present in the water sample are avoided.

Biodegradation Studies. Biodegradation studies are based upon three premises. First, the hazardous chemical wastes contain a mileu of unknown organics of varying complexities, some of which may be toxic or mutagenic (carcinogenic). Second, a given organism may be limited as to the extent that it may metabolize a particular organic compound(s). The partially biodegraded compound then requires a different organism(s) that may use it as an energy source through further metabolic activity. This process is repeated over and over again until the original compound(s) in mineralized. Third, appropriate mixed bacterial populations that can carry out such biodegradation processes exist where such organic compounds are present, although perhaps in low population densities, and become evident under the proper conditions.

Sterilized water samples or their dilutions will serve as the culture medium after being supplemented with appropriate inorganic salts. The existing organic content of the sample will serve as the carbon sources.

Studies will be conducted using continuous culture procedures where fresh medium will be added at a given flow rate and the metabolized medium being expended at a comparable rate. The inoculum will consist of soil samples collected at the site of water sample collection. The population growth will be monitored using turbidometric and dry weight techniques until the bacterial populations reach a steady state of growth. Samples of expended medium will be removed, sterilized by positive pressure filtration, and assayed for toxicity and for mutagenicity utilizing the methods described earlier. The original water samples will be simultaneously assayed.

Upon the loss of toxicity and/or mutagenicity as the result of biodegradation, individual members of the mixed microbial population will be isolated and identified. Individual isolates will be propagated under optimal conditions. These will be later mixed in an effort to synthesize the original population. The synthesized mixed bacterial population will be added to the original sample medium to determine whether the biodegradation process will be repeated at a greater rate, and also to establish whether greater concentrations of the organic mixtures will be both tolerated and effectively metabolized.

A recent article (Science, 288: 1434, 1985) described the oxidation of persistent environmental chemicals by an enzyme produced by a white rot fungus species (Phanerochaete chrysosporium). Culture of this fungus have been obtained, and studies are being conducted on a limited scale to determine whether it may have application towards the objective of this study.

# Principal Findings and their Significance:

As investigations are currently in progress, the principal findings obtained thus far are limited. The pond water samples collected from the Cleve Reber Hazardous Waste Dump site were found to be neither toxic nor mutagenic. In conversations with the staff of the Louisiana Department of Environmental Quality, it was recently learned that comparable findings were obtained by the US EPA. Drainage of the pond without further treatment of its waters is currently under consideration.

Ground water samples were recently obtained from the Petro Processors, Inc., Hazardous Waste Site at the suggestion of Mr. DeVille, Hazardous Waste Division, Louisiana State Department of Environmental Quality. The sample was reported to be saturated with a variety of highly chlorinated hydrocarbons, with hexachlorobutadiene being present in greatest abundance. The sample was found to be bacteriologically sterile. When assayed with the raddish seed assay, it was found to be toxic on the basis of seed germination as well as root growth. Earlier studies with the Cleve Reber pond water showed that the toxicity assay using Daphnia magna, although recommended for use with pure or known compounds, did not lend itself to the assay of unknown materials present in the pond water samples. In lieu of the Daphnia assay, the Petro Processor ground water sample is currently being evaluated for both toxicity and for its cell transforming capability using the normal human embyronic lung cell line WI-38.

The ground water sample has also been assayed using the Liquid Suspension Mutant Fraction Assay for mutagenicity. It was found to be mutagenic to two of the five mutant strains of Salmonella typhimurium employed. Mutagenicity could not be detected when rat liver microsomal fractions were employed in the assay. The reason for this is uncertain, but it is speculated that the liver enzymes may have become inactivated by one or more of the organic components present in the water sample.

Since the Petro Processor group water sample has been only recently obtained, biodegradation studies are currently being initiated.

#### Conclusions:

Because of the reasons stated above, it is not possible to draw any conclusions at this time.

# Publications and Manuscripts Produced:

None

# INFORMATION TRANSFER ACTIVITIES

The Louisiana Water Resources Research Institute (LWRRI) has been engaged and continues to engage in a variety of activities which help transmission of research results to the user. The Institute deems this activity as vital to accomplish its mission. Specifically, the Institute requires each principal investigator to prepare a detailed documentation at the conclusion of his research project which also serves as a completion report and is published by the Institute as a technical report. These reports are made available to the public free of charge. Individual users, private companies, government organizations and others may receive them upon request. Many of the reports have been in high demand. If a particular user wants to use the results or methodology of a research project, then the Institute helps bring the principal investigator and the user together and assists the two in every possible way in their efforts to bridge the gap between research and practical application.

The Institute is called upon, from time to time, to identify individuals with certain specialized skills to perform a given task. In addition, the Institute offers advice on water related problems to individual users, local and state government organizations, as well as private companies.

To help the user keep abreast of current research and technological developments, the Institute encourages and sponsors/co-sponsors seminars, lectures, workshops, conferences, or symposia on topics of current and future interest. These forums provide unique opportunities to the researcher, the educator, the user, and the manager to be together and engage in fruitful discussions.

# TRAINING ACCOMPLISHMENTS

TOTAL

The number of individuals participating in projects financed in part with grant funds are shown by fields of study and training levels.

# Training Category Training Level Undergraduate Graduate Master's Ph.D. Post Degree Degree Ph.D. Total Engineering Agricultural Chemical 1 1 2. Civil Environmental Industria1 Biology **Ecology** Fisheries, Wildlife and Forestry Agronomy Chemistry 2 1 3 **Hydrology** 2 1 1 Resource Planning Law Economics Geography Geology Other - Specify

3

4

1

1

# UNIVERSITY CONTACTS

There were no cooperative arrangements with other Louisiana schools during fiscal year 1984.

# MEMBERSHIP, UNIVERSITY ADVISORY BOARD

Dr. Adam T. Bourgoyne, Professor Department of Petroleum Engineering

Dr. Dudley D. Culley, Professor Forestry & Wildlife Management

Dr. Leo J. Guedry, Professor Agricultural Economics & Agribusiness

Dr. Robert A. Muller, Chairman Department of Geobraphy & Anthropology

Dr. Dan Jackson, Professor Department of Invironmental Studies

Dr. Vijay P. Singh, Acting Director (Ex Officio)
La. Water Resources Research Institute

### MEMBERSHIP, STATE ADVISORY BOARD

Colonel Thomas A. Sands, District Engineer United States Corps of Engineers

Dr. Charles Groat, Director and State Geologist Louisiana Geological Survey

Mr. R. M. Hansen, Field Development Manager Kaiser Aluminum & Chemical Corporation

Mr. Darwin Knockenmus, Director United States Geological Survey

Dr. Bobby E. Price, Director Water Resources Center Louisiana Tech University

Mr. Charles S. Staples, Executive Director Soil and Water Conservation Committee

Dr. Walter C. Vodrazka, Chairman Department of Civil Engineering University of Southwestern Louisiana

Dr. Darrell Williamson Louisiana Department of Public Works Department of Transportation and Development