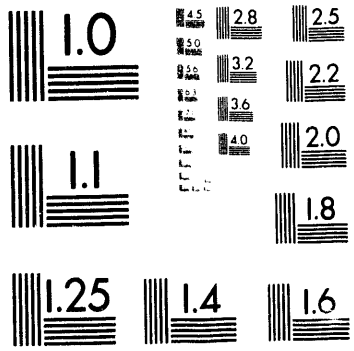
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1 of 1

DOE/EW/53023--T3

Tulane/Xavier University
Hazardous Materials in Aquatic Environments of the Mississippi River Basin
Quarterly Project Status Report
(July 1, 1993 - September 30, 1993)

Administrative Activities

During this quarter, approval was given by DOE for purchase of equipment. Equipment purchases were initiated and much of the equipment has been received and installed.

The committees in charge of coordination of sampling and analyses associated with the collaborative research groups continued to meet and address these issues. Sampling has been done in the lower part of Devil's Swamp and in the Devil's Swamp Lake area. In addition, extensive sampling has been done in Bayou Trepagnier and in Bayou St. John.

During this period, Tulane and Xavier Universities continued working closely with Oak Ridge National Laboratories (ORNL). The ORNL 1993 summer student internship program was completed. Plans were made for expanding the program to support 8 students next summer. Leonard Price, a Xavier University Chemistry professor and John Walz, a Tulane University Engineering professor each spent 5 weeks at ORNL. During this time these faculty worked with ORNL researchers exploring mutual interests and discussing possible future collaborations. In September, Drs. Carl Gehrs, Lee Shugart and Marshall Adams of ORNL, visited the Tulane and Xavier campuses. They presented two seminars and met with several of the investigators being supported by the ERWM contract.

Tulane/Xavier project administrators participated in the Office of Technology Development's "New Technologies and Program Exhibition" in the Rayburn House Office Building on September 23 and in the Hart Senate Office Building on September 27.

Below is a brief progress report from each of the research and education projects that are currently funded through the ERWM contract.

Collaborative Cluster Projects

Project Title: Biological Fate and Transport of Toxic and Hazardous Materials

Principal Investigator: A.A. Abdelghani, Ph.D.

All subclusters reported having begun their research on the effects of contamination on aquatic organisms in Devil's Swamp. Staff from the respective subclusters have made trips to the swamp and collected fish, frogs, crawfish, plants, water and sediment for study. Staffing is generally complete (or is expected to be complete soon). Equipment has been ordered some of which has already been delivered.

I. Ecology Subcluster: Members of the subcluster spent much of the quarter becoming familiar with the Devil's Swamp System. The group had difficulty accessing the northern section, and

thus, focused their sampling on Devil's Swamp Lake, which is drained by the northern section of the swamp, and the middle and lower parts of the swamp proper. Water, sediment, crawfish, plants, frogs and fish were collected in three sampling trips in August and September. These will be used to establish contaminant levels in the lake and lower swamp, and for health assessment and cancer screening studies (fish). The stomachs were removed from fish and sent to Xavier for content analysis, which will help determine links in the foodchain. Foodchain organisms will be the focus of future sampling expeditions.

The electrofishing boat should be ready later in October.

Cypress trees are being cored in Bayou Trepagnier and Cat Island on the Mississippi River; 55 cores have been taken from areas ranging from heavily contaminated to uncontaminated. Cores are awaiting heavy metal analysis. Collection coordinates have been computerized. Cores will be taken from trees on the next trip to Devil's Swamp.

A colony of wading birds has been observed near Bush, LA. The colony is within feeding distance of the swamp system. Feathers and droppings have been collected, and observation of the birds' feeding habits in the swamp will begin.

Examination of the fish digestive tracts from the Ecology group is being conducted by Xavier senior staff.

II. Biomarkers: The normal neurological and immunological parameters of frogs not exposed to Devil Swamp contaminants are being studied and experiments to treat frogs with measured doses of pollutants have begun. In initial studies, methylmercury doses as small as 5 ppb dramatically altered tad pole development. A sampling trip into Devil's Swamp produced seven adult Rana catesbiana. Nervous tissues and immune cells were removed from these frogs to study indicators of exposure to heavy metal contamination. Additional sampling for frogs from Devil's Swamp is planned during the third quarter.

Studies on the first fish and water samples collected from Devil Swamp have begun. Samples (about 25) of adult fish from polluted areas are being examined for disease and environmentally associated cancer. The fish are currently being processed for histopathological examination. Chemical analysis of the fish tissue for hexachlorobenzene (HCB) and hexachlorobutadiene (HCBD) are in progress.

Studies have started on exposing embryos of the Japanese medaka fish (Oryzias latipes) to several water and sediment samples from Devil Swamp. These water samples should contain mixtures of chemicals including HCB and HCBD. The results of the developmental studies will be confirmed by more controlled laboratory studies using Devil Swamp chemicals in the future. The field water samples being used in these developmental studies are being analyzed for pollutants at Devil Swamp.

A senior investigator was trained to use "state of the art" microinjection procedures at Woods Hole, MA. He has modified procedures to accommodate the large medaka fish oocyte, eggs and embryos and to permit the delivery of reproducible quantitative amounts of chemicals to the developing animals. Test solutions and extracts from Devil Swamp water samples can be microinjected. Transgenic microinjections are also being considered in a similar manner. Establishment of a transgenic facility will enable us to produce a transgenic medaka to serve as a sentinel of pollution.

The power supply for electrophoresis is on back order, and the film developer machine has been ordered but not yet delivered. Sample catfish livers have been taken and isolated for microsome work, and procedure will begin once the research assistant has been hired. The candidate needs

a change of visa status before accepting the position.

III. Exposure

A. Plant Uptake and Metabolism: Acute toxicities of several heavy metals affecting the vegetative reproduction of *Lemna gibba* have been determined. Growth data for cadmium, lead, and uranyl are complete and corresponding data for arsenate and thorium are well in hand. The information, when complete, will form the basis for uptake and accumulation studies. Other methods of determining measurements of cadmium, lead, and uranyl are being explored. Field studies are just starting at Bayou Trepagnier. Lab-grown plants are being exposed in the field and will be returned for analysis to determine uptake, accumulation, and metabolism.

A site in New Brunswick, Canada was identified as another possible field-site study for heavy metal pollution. It is a wetland within 150 yards of a zinc smelter. Although shellfish are known to be contaminated with heavy metals, especially lead and zinc, the extent of contamination of the fresh water ecosystem adjacent to the plant has not been determined. No members of the *Lemna* family were found in the area, but samples of water and bulrush leaves were obtained. If these are found to be significantly contaminated a field study with duckweed from central New Brunswick will be considered next summer.

Concentrations of HCB and HCBD attained in the growth media for *Lemna* show little effect on the growth rate; examination of the ability of duckweed to accumulate HCB and HCBD are underway.

Certain biochemical effects of cadmium exposure on invertebrates was observed, and may have potential as biomarkers.

The uptake of cadmium and lead ions into zeolite X is being investigated. Cadmium is efficiently taken up by the zeolite. Sealing the zeolite by application of organosilanes is also being studied. The derivitization of minerals to enhance their ability to adsorb and immobilize heavy metals is also being examined.

One post doctoral fellow has been hired and will work with processing brain samples for neurotransmitter and their metabolizing enzymes. Brain tissue from catfish caught in Devils' Swamp August 5 were received by the Xavier group and histopathological evaluation is underway.

B. Toxicity and Aquatic Organism Uptake: One expedition to Devil's Swamp was taken to collect environmental samples. Samples included soil, sediment, water, vegetation, and aquatic organisms. Samples are currently being prepared for chemical analysis. Another field trip to the swamp is scheduled during the last week in October, with subsequent sampling trips scheduled in January, April, and August 1994, and every quarter during the following two years.

Most of the supplies for toxicity testing and uptake have been received. Preparation for testing are in progress and should start within two weeks.

Abiotic testing (adsorption and desorption) studies are being planned; isolation and identification of soil and sediment microorganisms are in progress.

A post doctoral fellow has been identified and the remaining staff and graduate students have been hired. Equipment has been ordered and delivered or awaiting delivery. Software packages have also been ordered. QA/QC laboratory procedures have been finalized. Laboratory equipment and analytical methods have been tested and necessary modifications are being made. Liver tissue from catfish caught at Devil's Swamp were received and histopathological evaluation is underway.

Project Title: Assessment of Mechanisms of Metal-Induced Reproductive Toxicity in Aquatic Species As A Biomarker of Exposure

Principal Investigator: Mary Bitner Anderson, Ph.D.

Field Studies: Due to unusual hot weather we were unable to acquire catfish fingerlings from catfish farms for stocking the pens in Bayou Trepagnier. Next quarter we will obtain catfish (2 to 3 pounds each) from a seafood wholesaler to stock the pens for field exposure studies.

Laboratory Studies:

Metal-exposures of crayfish: Based upon the results of metal analyses of Bayou Trepagnier, we selected two metals (lead and chromium) for laboratory study. Male and female crayfish were exposed to 150 ppb lead, 150 ppb chromium or no metal for a period of 4 weeks. During this time period, water and metal solutions were changed daily and samples taken twice weekly for determination of metal concentrations at the initiation and conclusion of a 24 hour exposure period. At the end of four weeks the crayfish were weighed, hemolymph collected, and the crayfish were sacrificed. Hepatopancreas, gills and gonads were weighed, and then collected for metal analyses and histological study. Results demonstrated no significant difference in body weights or hepatopancreatic weights among the experimental groups. However, a significant increase in ovarian weight was noted in the lead-exposed group when compared to the control group when expressed as ovarian weight (77.4 ± 10.6 mg. vs. 44.82 ± 5.1 mg) or as percent of body weight ($4.0 \pm .3\%$ vs. $2.8 \pm .3\%$). Testicular weight in the lead-exposed group was elevated but was not significantly different when compared to control values (12.5 ± 2.5 mg vs. 8.8 ± 1.3 mg). Histological studies of the tissues and metal analyses of the tissues are currently being conducted.

The continuation of this experiment involves 8 week-exposures which will be concluded in two weeks. These will be evaluated in the same way as described above. From these studies we can determine the amounts and time course of metal accumulation in the hemolymph, gills, hepatopancreas and gonads in relationship to the water concentrations. Histological studies will let us determine if any histopathology exists in the tissues of interest as a result of such exposures.

Reproductive evaluation in male crayfish: Electrical stimulation was used to attempt the collection of spermatophores from the gonopores located at the base of the fifth pair of walking legs. We found that the customized probe which we currently have is not suitable for use on crayfish being too large for this species. In addition, a suitable low voltage/amperage stimulator with readable monitors is required for such studies. We consulted with the Department of Orthopaedics at LSU Medical Center Rehabilitation Laboratory for suitable probes and low level electrical stimulator for this purpose which should soon be available for our use.

We employed an alternate method for collecting spermatophores by removing the vas deferens and homogenizing it in phosphate buffered saline. This method was used to collect spermatophores from crayfish for morphological and biochemical studies of sperm. Using this approach we were able to retrieve sperm for quantitative expression of results in our subsequent studies. The following parameters are being standardized at present:

(1) Measurement of sperm concentrations in the homogenate using Makler chamber
(2) Determination of sperm viability using eosin Y dye exclusion method
(3) Analysis of superoxide dismutase (SOD) activity by nitrite method

Samples collected from the vas deferens of the metal-exposed and control crayfish (see above)

are being evaluated.

In order to investigate whether exposure of crayfish to heavy metals induces generation of free radicals, SOD activity in the hemolymph was evaluated. A significant SOD-like activity was observed in samples obtained from control and metal-treated crayfish. However, further studies are required to establish the role/presence of this specific enzyme in hemolymph.

Cluster Meetings: Monthly meetings are held the first Thursday of each month. In addition, members of our cluster met with Dr. Gary McPherson's for discussion of collaborative studies.

Professional Visits: We met with Drs. Shugart and Adams of ORNL. Our discussion focused on the development of specific markers of reproductive risk assessment in aquatic species. The meeting was very productive and we are in the process of obtaining relevant published materials from them.

Project Title: Bioremediation of Selected Contaminants in Aquatic Environments of the Mississippi River Basin

Principal Investigator: Sanjoy Bhattacharya, Ph.D.

The Devil's Swamp area was visited again; some samples have been collected from Bayou St. John and analyzed for metals. Additional equipment has been ordered and mutant proteins have been purified. Microorganism isolation from contaminated soils and fungi enrichment has continued. Toxicity tests have begun, and personnel staffing has been completed.

Site Visit: An attempt to reach Devil's Swamp Lake to view the area for a better understanding of the regional geography was made by several investigators and students on September 28, 1993. All roads to the lake went through private property.

Sampling: During the site visit above, samples of water and sediment were collected from a swampy area on the east side of Baton Rouge Harbor just north of Southern University in Baton Rouge (coordinates 30°32.15' N, 91°12.40' W measured using a Geographical Positioning System), located near Devil's Swamp. Water and sediment samples were also collected from Bayou St. John, a natural water body connected to Lake Pontchartrain. Samples from Bayou St. John were collected to conduct sediment analysis as a function of depth. The samples have been distributed between Xavier and Tulane laboratories for analysis and characterization relative to bioremediation. We should be able to acquire our next Bayou St. John samples from our rubber dinghy.

Experimental: Work has continued on protein engineering methods to reshape the substrate binding site of the cytochrome $P\text{-}450_{BM\text{-}3}$ (BM-3) from *Bacillus megaterium* with a goal of producing novel isozymes capable of oxidizing selected organic compounds contaminating Devil's Swamp. The wild type BM-3 and two mutant proteins have been purified, and a BM-3 with an altered substrate specificity for fatty acids has been produced with a mutation that changed the methionine at position 5 to glycine. Armed with an August, 1993 determination of the crystalline structure of BM-3, a more systematic approach toward altering the shape of the substrate binding site by directed mutagenesis is being taken.

Isolation of microorganisms from contaminated soils continue. Standard dilution plating with selected media containing anti-bacterial agents are being used to enrich for fungi. Standard curves for HPLC assays for benzo(a)pyrene have been developed to supplement thin layer chromatography. A study of basidiomycete germplasm for novel, putative ligninase activity

has begun. Formulation studies on the white rot fungus *Phanerochaete chrysosporium* have continued.

A bioreactor system to study the kinetics of CCl_4 degradation has been set up. Initial studies are using acetate as a substrate to perfect experimental technique. Data will be analyzed by constrained nonlinear regression analysis.

Sediment samples from Devil's Swamp and Bayou St. John are being cultivated for anaerobic bacteria to be used in CCl_4 toxicity experiments.

Sediment samples from Bayou St. John have been analyzed for trace metals. Results on four of the fourteen metals assayed show concentrations as high as: lead, 800 ppm; zinc, 650 ppm; cadmium, 3 ppm; and manganese, 300 ppm.

Equipment: The gas chromatograph has been received and awaits installation and setup. Several items of laboratory equipment and field equipment to facilitate sampling in the Devil's Swamp area have been ordered, including a global-positioning system, an inflatable dinghy and an outboard motor. October receipt is expected.

Interaction with Oak Ridge: Graduate students spent two weeks in Oak Ridge (August 16 through 27) working with Dr. Tommy Phelps' group. During the first week, they went through standard orientation and training procedures. They took with them samples of a bacteria culture from the Tulane Environmental Engineering Lab, which were used to prepare more than 80 serum bottle experiments. The test serum bottles were spiked with carbon tetrachloride, chloroform, or tetrachloroethylene. Samples were analyzed by gas chromatography and ICP. The primary aim of these experiments was to become familiar with the analytical instruments and procedures.

Personnel: Undergraduate and graduate student staffing is complete.

Project Title: Pore-Level Flow, Transport, Agglomeration and Reaction Kinetics of Microorganisms

Principal Investigator: Lisa J. Fauci, Ph.D.

Goals: Understanding the detailed pore-level behavior of microorganisms through porous media is essential for the development of effective *in situ* bio-remediation strategies. We are developing integrated experimental and computational models of the pore-level behavior of microorganisms. Our models will include the detailed analysis of convection and diffusion within the pores and the convection and chemotactic responses of swimming microorganisms to the local concentration gradients. Additionally, these models will include microbial adhesion to each other and the surrounding pore structure, and the reaction kinetics of these organisms to the toxic contaminant.

Accomplishments:
(1) *Experiments*
We are continuing our experimental investigations of chemotaxis through small pores constructed of glass capillary tubes. Thus far, the apparatus has been constructed, and image analysis techniques are being used to track individual *E. Coli* bacteria as they progress through a field of constant nutrient gradient.

(2) *Coordinated analytical approach*
Meetings were held on a weekly basis to formulate the mathematical model that couples fluid dynamics, contaminant transport and microorganism motility and adhesion. These coupled non-linear partial differential equations are complex. Initially, we will solve simplified versions of this model, in order to validate our computational methods and improve our intuition of the system. A post doctoral fellow who is an expert in computational methods relevant to our investigations joined our group in September. Thus far, he has successfully formulated and computed concentration field estimates of contaminants within single pores using a finite-difference approximation of the convection-diffusion equation. Presently, he is coupling the contaminant transport equation to the fluid flow equations. The computational solution of the fluid equations have been developed and validated. Coupling these two physical mechanisms will permit us to incorporate complex particle/structure interactions and thus allow us to model the flow and agglomeration of bacteria in individual pores. Initial simulations using this coupled algorithm will involve a single particle in a pore moving under fluid convection and chemotaxis. These initial simulations will be completed in the next quarter. We will then study multi-particle systems using physico-chemical properties derived from the experimental investigations.

(3) *Student involvement and training*
Two undergraduates, one from Tulane University and one from Xavier University, were employed full-time during the summer as research assistants. They worked at Tulane, and coded the numerical solution of a contaminant reaction-diffusion in both two and three spatial dimensions. A Silicon Graphics Personal Iris graphics workstation was used to visualize the results.

In addition, two Tulane graduate students have been working on aspects of this project. A Chemical Engineering graduate student has conducted our experimental studies and a Mathematics graduate student has started preliminary numerical investigations of contaminant transport.

(4) *Equipment purchase*
During the last quarter, we received the computational facilities that are necessary for our simulations. This system, an IBM RS/6000 Model 580, is housed within the Tulane Department of Mathematics, and is being supported by that department.

(5) *Consulting arrangements*
Dr. Aaron L. Fogelson, a professor of mathematics at the University of Utah, has agreed to serve as a consultant on this project. Dr. Fogelson has ongoing collaboration with the PI, and is an expert in the computational modeling of cell transport and adhesion in biological flows. His first visit to Tulane will be in October. In addition, Dr. Charles S. Peskin, a professor of mathematics at the Courant Institute of Mathematical Sciences, will visit in December. Dr. Peskin is a world-renowned expert in the computational biological fluid mechanics and he pioneered the computational approaches used in our studies.

Project Title: Natural and Active Remediation of Toxic and Radioactive Metals in Aquatic Environments

Principal Investigator: Gary McPherson, Ph.D.

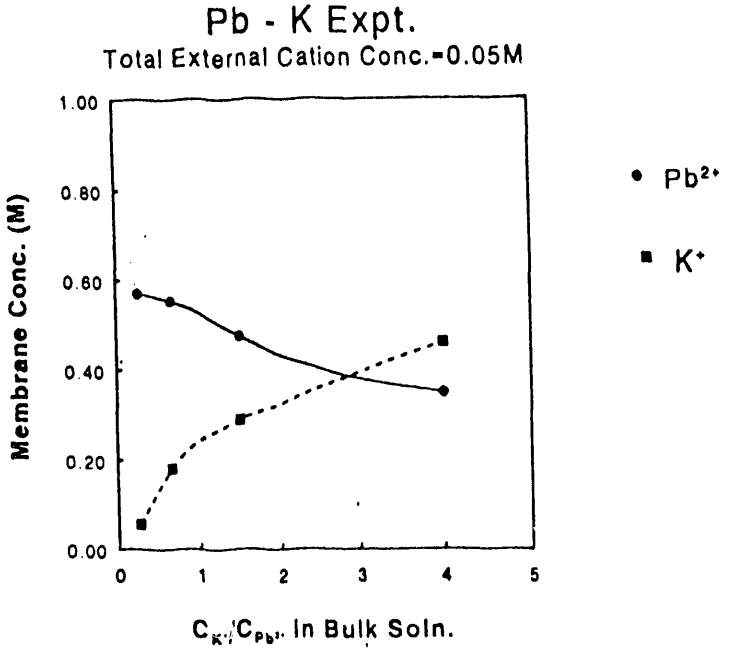
Equipment: The instrumentation for trace metal analysis (ICP spectrometer and graphite furnace AA) have arrived and are being installed in the satellite CIF facility in Dinwiddie Hall. This equipment should be operational in the first week of November.

I. Metal Ion Up-take on Selective Ion Exchange Membranes

In order to evaluate the performance of new membranes materials such as sulfonated polyphosphazene membranes for treating heavy metal contaminated waste water, Cd^{2+} and Pb^{2+} equilibrium uptake experiments were performed in the laboratory with a commercially available Nafion 117 cation exchange membrane (a perfluorosulfonic acid membrane manufactured by E. I. DuPont de Nemours & Co., Inc.).

Nafion absorption selectivity for univalent and divalent cations was investigated experimentally by soaking membranes for 24 hours in prepared aqueous mixtures of $Pb(NO_3)_2$ and KNO_3. The total salt concentration in the soak solution was held constant at 0.05 M and the potassium ion/lead ion ratio was varied from 0.2 to 4.2. The membranes were than removed from the soak solution, excess electrolyte was wiped from the film surfaces, and the membranes were placed in distilled water (for 24 hours) and 2.0 M H_2SO_4 (24 hours) to remove all absorbed cations and anions. The concentration of cations in the leach solutions was determined by atomic absorption spectrophotometry. The swelling properties of the membranes (membrane porosity and wet membrane density) were also measured, for a given lead nitrate/potassium nitrate soak solution. Similar equilibrium uptake experiments were performed with cadmium nitrate and potassium nitrate salts.

The results of the Pb^{2+}/K^+ absorption experiments follow. Preferential absorption of lead by Nafion was observed when the potassium/lead concentration ratio in the external bulk solution was < 3. The Pb^{2+}/K^+ and Cd^{2+}/K^+ uptake results with Nafion is to be used as base line data for assessing quantitatively the performance of new cation exchange membranes which will be synthesized by this research cluster.



II. Exchange of Metal Ions on Sediments and Well Defined Clay's

With the arrival of the new intercoupled plasma instrumentation (ICP) we have decided to shift our attention to developing the technology required to determine metal contents of metals

adsorbed on montmorillonite clays. To do this we are in the process of duplicating previous results obtained using europium as the adsorbate at a pH of 5.5. In these studies the amount of europium adsorbed as a function of temperature was as follows:

T °C	Irreversible adsorption (meq/100g clay)
20	33.2
100	75.2
160	102.5
200	137.8
280	155.2

Because the CEC capacity of the clay is only 89.3 meq/100mg clay, it is clear that this cationic exchange capacity is exceeded at temperatures larger than about 100 °C. A major problem with that was an indirect analytical method was used to arrive at these results, i.e., the amount of europium released from the clay following washing with triply deionized water was analyzed polarographically for Eu and was then subtracted from the total amount adsorbed (a quantity subject to considerable error). A problem with this procedure was that the clay was not digested. Therefore these adsorption results are regarded with suspicion. With the new instrumentation it will be possible for us to completely digest the clay. This should enable us to obtain more meaningful results.

The reason for retracing our steps is to gain confidence in the use of the more sophisticated instrumentation. After we clear up the adsorption results on the lanthanides, studies on the adsorption of Pb will be initiated. At this point we feel that such a study will be easier than focusing on the adsorption of Fe which would require subtracting framework Fe.

A full time graduate student is now involved in this study. Mr. Aiguo Liu from the salt Water Institute in China has joined our group. In addition a postdoctoral student under the PI's supervision will be participating in a supervisory role on the project.

To complete the adsorption studies of the Lanthanides on montmorillonite, to develop confidence in the use of ICP and to initiate studies on the adsorption of Pb.

Project Title: Expert Geographical Information System for Assessing Hazardous Materials in Aquatic Environments"

Principal Investigator: James L. Regens, Ph.D.

Summary of Project Activities: The project team successfully completed a series of activities during the second quarter. Primary accomplishments are summarized below:

(1) The series of DOE facility visits for Phase I to identify an appropriate site(s) was conducted from July through September. All major DOE facilities with ArcInfo-based GIS capabilities that applied to Solid Waste Management Unit (SWMU) characterization and remediation were contacted by the DOE/ERWM technical liaison, Mr. Bryan Albers, to explore their potential interest in cooperating with the project team. The following sites indicated willingness to host a site visit: Los Alamos National Laboratory, Sandia National Laboratories, Remote Sensing Laboratory/Nevada Test Site, Savannah River Site, Oak Ridge National Laboratory, Rocky Flats Site, and Hanford Site. Accompanied by the DOE/ERWM technical liaison, the PI visited each of the sites to assess their suitability. Based on the preliminary visits, an agreement

delineating the relationship between the project team and the appropriate site(s) will be finalized during the next quarter.

(2) The project team held a series of meetings devoted to refining the management plan for coordinating interaction among the faculty researchers at Tulane University Medical Center, Tulane's School of Engineering, and Xavier University.

(3) The research group developed, through individual effort and several joint meetings, a set of guidelines regarding the required capabilities and features of the Spatial Analysis Research Laboratory to be located in the J. Bennett Johnston Health and Environmental Research Building at the Tulane University Medical Center. Guidelines regarding satellite facilities to be established in the Tulane School of Engineering and Xavier campus were also developed.

(4) Overall project research plans and goals for year 1 were revised and adjusted to reflect the budget changes imposed on the project. Since the equipment budget was cut by over 50 percent and operating expenses also were substantially reduced, the senior personnel decided to concentrate this year's budget on establishing a state-of-the-art main facility in the Spatial Analysis Research Laboratory. In addition, preliminary development of the two satellite facilities with remote access to the main facility will be initiated.

(5) An equipment list was prepared and submitted to DOE for approval. Subsequent to DOE approval in July, a purchase order was issued to procure equipment from vendors.

(6) One sociology graduate student assigned to the project conducted a preliminary literature review of GIS applications. He prepared a brief paper summarizing the technical possibilities for social and demographic data analysis with geographical information systems.

(6) A review of the literature addressing the association between pesticide/herbicide use and non-Hodgkins lymphoma (NHL) was initiated. Preliminary identification of incidence and mortality data sources for NHL and birth defects was started.

(7) Three engineering graduate students with degrees in hydrology, geology, and computer science were hired to the expert system (ES) component of the project in July. A literature review was conducted during the summer on published and on-going research on GIS and ES applications in hydrology, water resources, and environmental and geotechnical engineering. Contacts were established with local organizations developing GIS systems such as the Corps of Engineers (COE). Discussions have started regarding sharing the geotechnical information currently available in the COE database.

(8) The programs MODFLOW, a ground water flow model, and MT3D, a dissolved contaminant transport model, were obtained and compiled. Other models, for both surface and ground water quantity and quality aspects of the research project, will be evaluated in the near future and added to our library. Development of the expert interface software has started and will continue during the Fall semester.

(9) Dr. Bakeer and his associates initiated preliminary PC-based work using two expert systems shells--NASA's CLIPS and Information Builders' LEVEL5, Microsoft FoxPro for database management, and Microsoft FORTRAN and C compilers currently available on the Department of Civil and Environmental Engineering's personal computers.

(10) Four graduate students with backgrounds in environmental health sciences and engineering, policy analysis, quantitative methods, and law joined the project staff in August.

Education Project

Project Title: Enhancement of Environmental Education at Tulane and Xavier Universities

Project Investigator: Sr. Monica Loughlin

The planning and implementation of the environmental science and engineering (ESE) educational programs continued. Both universities met with their faculty to evaluate their current programs and to begin to make plans for a strategic implementation of new courses and curricula.

Curriculum Development: To help in their planning efforts, Xavier and Tulane Universities conducted two workshops focusing on ESE curriculum development. The first one, held on July 30, 1993, was led by Dr. Robert Ford, Director of the Center for Energy and Environmental Studies at Southern University in Baton Rouge. At the workshop, issues which were relevant to designing a successful program were discussed, as were the problems which led to the demise of an early program at Southern University. At the second workshop, led by Dr. Dilip Shah, Professor of Industrial Hygiene and Safety at North Carolina A & T, discussions on the importance of including courses on the safety of workers and the workplace took place. Dr. Shah elaborated on the various tracks available to the students in the School of Technology at North Carolina A & T. Additionally, Dr. Shah gave a seminar (attended by the public) on environmentally-conscious manufacturing and its importance in today's economy and the economic health of industries. Although both workshops were hosted by Xavier, faculty, staff and students from both universities attended.

The development of several new courses were initiated during the quarter. At Xavier, these include the following: Survey of Environmental Chemistry (Sr. Henry), Environmental Ecology (Martinat), Communications of Environmental Risk (Duplantier) and Environmental Toxicology (Mielke). An Environmental Studies course is being developed at Tulane by Dr. Bhattacharya, and an Environmental Chemistry course by Dr. Apblett.

A survey of the curriculum content of environmental sciences and environmental studies programs at other major universities and colleges was completed. The survey indicated that well developed environmental programs share three common components: strong science foundation, internship opportunities or public service, and a major thesis or project paper.

The Tulane Liberal Arts and Sciences (LAS) Environmental Committee met three times during the quarter. The following faculty members serve on the committee: Allen Apblett, Chemistry; Stuart Bamforth, Ecology, Evolution, and Organismal Biology; Joan Bennett, Cell and Molecular Biology; John McDowell, Geology; and Michael Zimmerman, Philosophy. The Committee has tentatively designed a course of study for various coordinate majors (upon approval of other departments) that clarifies and adds focus to the present environmental curriculum. At the same time, the Committee has identified some course gaps in the present program. This has led the Committee to begin the process of developing a "dream curriculum." Also, the Committee is studying ways to develop more internship programs, and the feasibility of a five year Master's Degree Program in Environmental Studies.

In August, the Tulane LAS Environmental Committee developed an Environmental Studies brochure which was handed out at the entering freshmen reception in early September. Extra copies were then sent to the Admissions Office for further distribution. Also, the Committee

surveyed past students of the program. Overall, their comments were positive. Finally, the Committee has invited Dr. Robert Watts from the National Institute for Global Environmental Change to give a lecture in November.

Environmental Programs Office and Staff: One of the goals of the project is to establish an institutional infrastructure that will foster the implementation of a comprehensive environmental education initiative at both campuses. In order to attain this goal and to better serve the needs of the Xavier students, an Office of Environmental Programs was created to carry out the activities of this DOE grant. Dr. Sally O'Connor was named as Director and a building on campus was identified as the center for the activities of the grant. The new structure replaced the old Center for Environmental Programs. The Office has now been staffed with a full-time assistant and a secretary/administrative personnel. Since the creation of the Office, its Director has been named a Regional Director of the Alliance for Environmental Education, an international organization comprised of over 500 institution members dedicated to the environmental education and literacy of US citizens and other nationals. Both Xavier and Tulane Universities are members of the Alliance, and its affiliation with the organization should enable the universities to enhance their environmental programs through linkages with other educational institutions.

ER/WM Scholars Program at Xavier: During the quarter, the Xavier Environmental Education Committee, comprised of O'Connor (Chemistry), Henry (Chemistry), Crockett (Environmental Programs), Dixon (Environmental Programs), Vincent (Physics), Fulginiti (Biology), Hamilton (Biology), Eatman (Philosophy) and Duplantier (Communications), met four times to discuss issues regarding the DOE-sponsored scholars program. Discussions focused on the preparation of a brochure to describe the program, the guidelines for the environmental scholarships, and the process of selection of the scholars. The committee decided to call the program *LIFE Scholars Program*, LIFE being an acronym for Living Intelligently to Foster Earthcare. A brochure describing the availability of scholarships to those students interested in a career in environmental restoration and waste management was distributed to the students during their Fall semester registration. The guidelines for the scholarship were published including the eligibility requirements, the benefits, the requirements of the program, and the selection process. A total of 35 applications were received by the Office by the designated deadline date. The committee met again on October 7th to review and evaluate all applications. The four students selected to be LIFE scholars will be officially named during the next quarter. The LIFE scholars will be placed under the mentorship of Xavier and/or Tulane faculty who have on-going research projects in the environmental areas. The scholars will be encouraged to spend the summer at a DOE lab to further enhance their education.

Other Activities:
(1) At Xavier, the survey of institutional capability in the environmental areas is nearing completion. With the exception of a few departments, all information has been gathered. It is expected that the survey will be reported to the agency by the end of the Spring semester. This survey is intended to assess the progress of the grant in implementing various educational efforts at Xavier. A similar survey is being conducted at Tulane University.

(2) An RFP for faculty mini-grants was sent out to all Xavier faculty. The RFP is the first step in the plan for retooling/retraining existing faculty to enable them to participate in the following activities: a) to infuse current courses with environmental issues, b) to develop new courses with significant environmental content, and c) to improve and enhance environmental literacy on campus.

(3) A university-wide curriculum development workshop is being planned for the Spring semester to further encourage faculty to participate in the planning and implementation of the environmental educational programs.

(4) During the quarter, the Office of Environmental Programs initiated a campus-wide effort to educate Xavier students in environmental literacy by meeting with all freshmen to discuss the availability of an environmental studies program, the opportunities available to them through the Office of Environmental Programs and to encourage students who are interested in an environmental career. An Environmental Club was founded during the quarter with initial membership numbering more than 40 students, and plans are underway for the Office to be involved in the university-sponsored Wellness Week.

(5) On September 13-15, 1993, Dr. O'Connor participated in the Training/ Education Session of the Hanford Summit, "A National Forum on Environment, Technology and the Economy," held in Richland, WA. Concerns regarding the training and education of the nation's existing and future workforce were discussed. Initial action plans were laid out, with follow-up to occur in about 6 months.

Initiation Projects

Project Title: Heavy Metal Immobilization In Mineral Phases

Principal Investigator: Allen Apblett, Ph.D.

We are developing methodology whereby toxic metals may be encapsulated and immobilized in a very durable ceramic material. This waste form will be designed such that the pollutants are locked in the same crystalline mineralogical phases in which they occur naturally (i.e. materials that have a demonstrated ability to sequester the metals for billions of years).

One wastestream that we are investigating is from wet lime-gypsum flue gas desulfurization plants[1]. This contains mainly harmless metals (calcium, magnesium, sodium, iron, and aluminum) but does contain significant amounts of heavy metals (manganese, cadmium, chromium, copper, mercury, nickel, lead, zinc and tin). The challenge is to separate the toxic metals from the others in such a manner that they may be easily incorporated into the ceramic wasteform. We have reacted each of the above metals with potassium ethylxanthate and found that ethylxanthate is very efficient at precipitating the heavy metals while leaving calcium, magnesium, and sodium in solution. All the precipitates were characterized by X-ray diffraction and their solubilities in common organic solvents determined. Thermal gravimetric analysis indicated that the ethylxanthate complexes decompose at extremely low temperatures (ca.120^{o}C) to sulfide materials.

Our target wasteform is the mineral sphlaerite (ZnS) which has the ability to form solid solutions with heavy metal sulfides[2]. Our xanthate complexes may be used in two ways to accomplish entrapment of heavy metals in sphlaerite;
(1) zinc ions may be added to contaminated water and it and the heavy metals may be co-precipitated by addition of potassium ethylxanthate to the solution
(2) separated xanthate precipitates and zinc bis (ethylxanthate) may be dissolved in a high-boiling organic solvent (e.g. xylene) and the subsequent solution refluxed to deposit a homogeneous sulfide ceramic.

We have used a single toxic metal in our initial investigation in order to simplify the chemistry. Cadmium is often found at up to two and a half percent in naturally-occuring zinc sulfide and we therefore chose this amount for the amount of waste-loading. A solution of cadmium chloride and zinc chloride in appropriate amounts was treated with potassium ethylxanthate

and the precipitate thus obtained was filtered off and dried. X-Ray diffraction indicated that the cadmium and zinc precipitate homogeneously i.e. as a solid-solution of zinc and cadmium ethylxanthates. We are currently investigating the pyrolysis of this precursor to a ceramic material.

As well, we have demonstrated that a refluxing solution of cadmium bis-ethylxanthate in xylene rapidly forms cadmium sulfide as a very fine powder that is excellent for processing into a sintered body. We are currently pursuing the simultaneous deposition of a mixed cadmium and zinc material using this technique.

A recent development in the preparation of metal sulfides has prompted us to attempt another approach to sulfide ceramic wasteforms. Barron and Landry[3] demonstrated that sulfide semiconductors can be prepared by microwaving a mixture of metal powders and sulfur. While most metals do not pose a biological hazard in the metallic form, mercury metal is certainly an exception. We therefore have successfully tried the microwave approach for the preparation of mercury sulfide from mercury metal. We are now applying this technology to remediation of the waste from mercury porosimetry measurements performed on the coke by-product of the petrochemical industry. The initial results are encouraging since all visible traces of mercury disappear. However, the amount of reduction of mercury vapor and the leachabilty of the final wasteform remains to be determined as soon as the necessary analytical equipment is available.

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[1]Lefers, J.B., W.F. Broeke, H.W. Venderbosch, J. DeNiet, and A. Ketterlarij, (1987), "Heavy Metal Removal from Waste Water from Wet Lime (Stone) - Gypsum Flue Gas Desulfurization Plants," Water Resources, 21: 1345.

[2]Duda, R. and L. Rejy "Minerals of the World" (Arch Cape Press, New York, 1986).

[3]Barron A. and C. Landry, (1993), "Synthesis of Polycrystalline Chalcophyte Semiconductors by Microwave Irradation," Science, 260: 1653.

Project Title: A Pilot Study of the Applicability of Polarography to Exposure and Bioremediation Problems in Aquatic Systems

Principal Investigator: K. J. Bundy, Ph.D.

A main concern of this quarter has been the preparation of a revised version of the manuscript "Polarographic Trace Level Analysis Can Be Applied to the Detection of Environmental Contaminants," which has been submitted for consideration for publication in the Proceedings of the Annual Meeting of the Society for Environmental Geochemistry and Health.

Progress has been made in getting samples from Devil's Swamp for polarographic analysis. Five gallons of water and one gallon of mud have been obtained for sampling. We have not yet been able to analyze this material because of a recent equipment failure. The apparatus is expected to be operational within a couple of weeks and analyses will begin then.

To build up our capability to perform chemical analyses of heavy metal concentrations in tissue, we have performed several preliminary studies, as enumerated below. A suitable supporting electrolyte for analysis of lead has been identified, 0.1 M citric acid with NH_4OH added to pH 3. Measurements with lead standard solutions have shown that, so far, our lower threshold detection limit is 10 ppb. We should be able to diminish this value as we "fine tune" our analytical technique. Since the best information that we have indicates that the lead concentration in the swamp is about 150 ppb, there should not be a problem in terms of our detection sensitivity, unless other swamp components present interferences.

Additionally, specimens of bovine liver were obtained so that we could begin development of our analytical methods for frog tissue. The liver is one of the organs that we will be analyzing in this project. The samples were first soaked in a lead bearing solution. Two processes were examined for extracting the heavy metal from the tissue to obtain a form amenable for polarographic measurement: dry ashing and acid digestion. 74.9 ppb was the polarographically measured concentration of the dry ash residue. 65.5 ppb was the value determined with acid digestion. The similarity of the values lends confidence for the use of either technique.

Based on the results above and the previous experience in our laboratory with respect to the analysis of chromium in a variety of tissues, we do not at this time anticipate that there are any technical barriers which will impede our ability to detect lead or chromium in frog tissue.

Steps have been taken with respect to separation of the various fractions in water and mud samples. Aqueous and mud specimens from a site in St. Charles Parish were obtained. Using our filtration systems we able to separate out the aqueous component using a 0.1 μm filter. The course particulates were separated from the clays using a 105 μm filter. We will in the future employ an intermediate filter to fractionate the fine particulate moiety.

At present we are investigating the appropriate means for extraction of lead and chromium from the particulate material. We want to only analyze for the amounts which are relatively easily leached from the particles themselves into the aqueous phase or which could be leached out by the action of frog digestive fluids, as opposed to those amounts which are tightly bound in the structure of the minerals. We have identified solutions of varying aggressiveness which can be used for this purpose, but at this point we are still investigating which is most relevant for extraction of pollutants.

Project Title: Bioenvironmental Analytical Support Services

Principal Investigator: William J. George, Ph. D.

During this quarter of the DOE funding period, the Analytical Support Laboratory has moved to the Johnston CBR Building. We have continued both analytical and field work, interacting to varying degrees with three DOE cluster groups.

Approximately 300 tissue and water samples have been received for analysis from the Metals-Induced Reproductivity Cluster (M.B. Anderson). Site assessment of Bayou Trepagnier has continued for this project.

A meeting was held with Drs. McPherson, Flowers, and Koplitz from the Chemical and Natural Remediation Cluster. The analytical interests common to both groups were discussed, and a foundation was laid for collaborative efforts in the future.

Drs. Rani and Thien from the Bioremediation Cluster have also discussed with us ways in which we may provide both field and analytical support for the projects which they oversee.

Bayou Trepagnier Site Evaluation: Values for the concentrations of metals in surface sediments from 5 sites along Bayou Trepagnier are presented below. Sediment digests prepared by EPA Method 3050 were analyzed by inductively coupled plasma emission spectroscopy (ICP).

The sampling locations cover the roughly 3 mile length of the Bayou. A station designated as "headwaters" is nearest the Shell Refinery, and the station where Bayou Trepagnier ends, joining

Bayou LaBranche, is nearest Lake Pontchartrain. Of the three intermediate sampling stations, two are located at the point of entry of side streams into Bayou Trepagnier--designated as the "upstream inflow" and "downstream inflow" sites--and the third is a grassy marsh area not far above the Bayou Trepagnier/Bayou LaBranche junction.

Concentration of Metals
in Bayou Trepagnier Sediments
(mg metal per kg sediment)

Metal	Headwaters	Upstream Inflow	Downstream Inflow	Grassy Marsh	At Bayou LaBranche
Iron	>6000	3312	5586	>6000	5920
Aluminum	7044	1265	2778	7473	3284
Lead	605	256	499	41	34
Chromium	48	34	315	37	29
Manganese	229	41	85	263	175
Zinc	160	88	163	111	97
Vanadium	17	5	10	15	9
Cobalt	15	4	7	13	8
Nickel	13	3	6	11	7
Copper	12	5	11	13	6
Selenium	Present at low levels. Exact quantitation pending				
Arsenic	Present at low levels. Exact quantitation pending				
Cadmium	All values less than practical quantitation for ICP				
Beryllium	All values less than practical quantitation for ICP				

Control values for each metal were within 13% of nominal value. Recovery of pre-digestion aqueous spike (Cr, Pb, and Zn) was greater than 97%.

Iron and aluminum were present in the sediments in the highest concentrations. Lead (maximum observed level of 605 mg/Kg) and chromium (maximum observed level of 315 mg/Kg) were highest of metals of particular toxicological interest, and these were selected to be the focus in future work for field bioaccumulation studies and laboratory reproduction studies for the Cluster working on Metals-Induced Reproductive Toxicity.

Zinc was also an abundant metal in the sediments. Dr. Lynn Koplitz (Chemical and Natural Bioremediation Cluster) used x-ray diffraction methodology to analyze the sediments from neighboring Engineer's Canal at a locations where waters from Bayou Trepagnier enter. Our reported values for zinc in the soils (maximum 163 mg/Kg) are similar in magnitude to her findings.

Comparing the values from the different locations, the higher concentrations of metals were generally found in the headwater sediments nearest the refinery. High values for lead, chromium and zinc were also found in sediments at the downstream inflow station.

In the water specimens taken from the same sampling stations and screened by ICP for the above metals, only iron and manganese were found to be high enough to be within detectable range. Maximum observed concentrations for iron and manganese were 2110 ppb and 622 ppb respectively, with the highest values for both being found in water taken from the upstream

inflow site. Although in later studies graphite furnace atomic absorption spectrophotometry may be used to investigate the composition of metals in the water column with greater sensitivity, screening results indicate that Bayou Trepagnier water are not grossly contaminated by metals.

Quantitation of metals in field samples of organisms is still being evaluated.

Methylene chloride extracts of the soils from the 5 sampling stations were analyzed by gas chromatography/mass spectroscopy (GC/MS). In general, the compounds detected consisted of a broad range of saturated and unsaturated hydrocarbons and a significant quantity of elemental sulfur. Both constituents are characteristic of petroleum contamination. Absent were the light weight substituted benzenes characteristic of gasoline. Oil and grease, non-volatile petroleum constituents, also appear to be present in the soils in large quantities.

While a some hydrocarbons and a large quantity of sulfur was present in all sediments collected, hydrocarbons were most prominent in the sediments taken from the downstream inflow and the headwaters sampling stations. The quantity of hydrocarbons from other stations was dramatically lower.

Killifish taken throughout the bayou were found also to contain hydrocarbon compounds. A typical chromatogram of fish extract contained 8 different chemical compounds felt to be derived from petroleum sources, with high percentage chemical library matches to substituted forms of octane, hexadecane, cycloundecane, hexene, undecene, hexacosane, heptadecane, and pentatriacontane. As an added item of interest, in the general observations made at the time the fish were collected, notation was made that some fish exhibited grossly enlarged abdomens.

Some physical parameters of bayou waters sampled in situ on the June 29 collection trip are presented below:

	Headwaters	Upstream Inflow	Downstream Inflow	Grassy Marsh	At Bayou LaBranche
Temperature (deg C)	30.0	33.1	32.6	31.4	30.2
Dissolved solids (g/L)	1.22	1.43	1.41	1.37	1.17
Conductivity (ms/cm)	2.45	2.82	2.82	2.74	2.33

Additional Metals analyses: During this quarter, the analytical support laboratory has also completed the analyses of 225 tissues (kidneys, liver, and bone specimens) for lead content. Quantitation of methyl mercury in 1028 other animal tissues (spleen, adrenal gland, gonads, liver, brain, kidney, whole blood and plasma) are presently underway.

Project Title: Evaluation of the Carcinogenic, Reproductive, and Developmental Effects of Mixtures of Contaminants on the Medaka Fish (Oryzias latipes).

Principal Investigator: William R. Hartley, Ph.D.

Three experiments are currently in progress. These experiments are to determine the developmental and reproductive effects of cadmium on the Japanese medaka using an embryo

exposure protocol. A review of the literature indicates that cadmium toxicity is dependent on water hardness for most aquatic organisms. Therefore an experiment was designed to determine the possibility of using distilled water (low hardness) for growing embryos. The artificial embryo rearing solution usually used has high water hardness due to nutrient/salts. Growth of the embryo was attempted in distilled water, distilled water and methylene blue mold inhibitor, and regular embryo rearing solution with methylene blue. The result of this experiment was high mortality and severely reduced hatch in distilled water and distilled water plus methylene blue. Development was normal with almost 100 percent hatch in the embryo rearing solution. Approximately 120 embryos were involved in this experiment and the surviving fry are currently undergoing evaluation.

A second experiment is in progress in which embryos are being exposed to 0.0, 0.1, 0.3, and 0.5 mg Cd/L with low water hardness. The third experiment in progress involves the exposure of the medaka fish embryos to 5, 10, and 15 mg Cd/L with 100 ppm hardness. We have modified the proposed embryo exposure protocol by exposing each embryo in an individual vial. This allows us to follow the complete development course of each embryo. Abnormalities are being documented by photography.

Upon completion of these and other planned experiments in the third quarter we hope to establish the hardness dependent EC50 for developmental effects in the medaka exposed to cadmium and begin range finding with trichloroethylene.

Project Title: The Removal of Phenolics and Aromatic Amines from Aqueous Streams through Enzymatic Polymerization

Project Investigator: Vijay T. John, Ph.D.

Preliminary data has been collected. An undergraduate student has worked on the project along with a doctoral student who is continuing to do his research. Preliminary results are promising and very exciting, although we need to validate and duplicate some of our results.

Our objective was to use surfactants to facilitate removal of phenolics and aromatic amines from aqueous streams. The methodology was to enzymatically polymerize these compounds to insoluble oligomers and polymers that drop out of solution. While the basic enzymatic reaction for the removal of phenols has been described in the literature, our objective was to take the science further by coming up with a technology to increase the efficiency of the process.

In carrying out the research, we have found an interesting observation that may be of much consequence in the removal of aromatics from aqueous streams. The concept is based on the coupling of enzymatic polymerization to a classical reaction known as the Fenton reaction. When H_2O_2 is added to an aqueous solution containing Fe^{2+} and an aromatic, a very reactive hydroxyl radical is formed through the reaction

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet$

The aromatic is subsequently hydroxylated. For example, if the aromatic is benzene (M) the following reactions can occur

$M + OH^\bullet \rightarrow MOH^\bullet$

$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^-$

$2\ MOH^\bullet \rightarrow M\text{-}M + 2\ H_2O$

$MOH^\bullet + Fe^{3+} \rightarrow Fe^{2+} + MOH$

The two major products are phenol (MOH) and biphenyl (M-M), which is insoluble and drops out as a precipitate. Then, we conduct the enzymatic polymerization to convert phenol to polyphenol which is insoluble and also precipitates from solution.

We have been able to completely remove benzene from water in a controlled experiment using the concept of coupling the Fenton reaction to enzymatic polymerization. Our continuing studies address the extension of this concept to mixtures of contaminants, and methods to measure kinetics of decontamination. We believe that this is feasible, relatively inexpensive, and novel technology that is of practical use.

Papers: One paper (to Environmental Science and Technology, or to the Journal of Water Research) is in preparation.

Project Title: Genetically Engineered Microorganisms: Aromatic Hydrocarbon Biodegradation Genes From Rhodococcus.

Principal Investigator: Kevin J. Kendall, Ph.D.

This quarter has been spent isolating fragments of DNA from *Rhodococcus* sp. ATCC 19070 that bear strong resemblance to DNA from *Pseudomonas putida*.

We have found that, despite the fact that *Rhodococci* are very different bacteria from *Pseudomonas*, both of our strains contain some DNA that is very similar to DNA in *Pseudomonas*. In particular, there is very strong similarity to DNA that encodes enzymes required to metabolize benzoic acid, an intermediate in the biodegradation of toluene. This similarity was found using the technique of Southern blot analysis. This suggests that we may be able to use *Pseudomonas* DNA to clone toluene biodegradation genes from *Rhodococcus*.

We have constructed a gene bank of *Rhodococcus* DNA cloned in *E. coli* and have identified a clone that contains sequences homologous to the *Pseudomonas putida* TOL plasmid. It is possible that this clone contains genes that encode enzymes similar to the ones utilized by *Pseudomonas* to degrade aromatic hydrocarbons. This clone is currently being characterized and prepared for sequencing.

We are currently identifying additional clones that contain DNA that is similar to *Pseudomonas*. These clones will also be sequenced to identify the enzymes that are encoded by the DNA. Clones encoding biodegradation enzymes will then be analyzed in more detail as a first step towards creating genetically manipulated strains of *Rhodococcus* with enhanced biodegradation potential.

Papers and presentations:

A presentation was delivered to the Fifth Annual Symposium on Emerging Technologies in Hazardous Waste Management for the American Chemical Society: Sandra Haddad, Kristie Beaton, John Lofgren and Kevin Kendall. "Alternative Bacteria For Bioremediation." I&EC Special Symposium, American Chemical Society, Atlanta, GA, Sept. 27-29, 1993.

John Lofgren, Sandra Haddad, and Kevin Kendall. "Metabolism of alkanes by *Rhodococcus erythropolis*." Submitted to the Journal of Environmental Science and Health.

Project Title: Laser Ablation/Ionization Studies Related to the Removal of Nuclear Materials from Metal Surfaces

Principal Investigator: Brent Koplitz, Ph.D.

Overview: As a research initiation project, we use our existing laser and mass spectrometer technology to study laser ablation/ionization processes that are relevant to the removal of nuclear material from metal surfaces. Methods to understand and improve laser ablation studies as well as containment issues related to the ejected material are being studied. The benefit for DOE is an improved understanding of laser ablation processes. If successful, these studies will assist laser clean-up efforts where laser ablation is concerned. In fact, one of our approaches to particle containment, laser ionization of the ablated material, complements existing suction-type removal methods.

Progress: A new experimental apparatus for conducting ablation/ionization experiments is now working in our laboratory. The system is being tested by multiphotoionizing N_2O with 193 nm light and calibrating the resulting mass spectrum. Experiments involving the ablation of Ni are now being tackled.

Project Title: Asymmetric PVDF Pervaporation Membranes for the Removal of Organic Contaminants from Waste Water

Principal Investigator: Peter N. Pintauro, Ph.D.

Objective: To fabricate and test a new class of asymmetric polyvinylidene fluoride (PVDF) pervaporation membranes for the selective removal of non-polar organic contaminants from waste water.

Approach: Investigate the piezoelectric properties of asymmetric PVDF films and examine the separation performance of such membranes.

Asymmetric PVDF membranes were fabricated using a solution of 14% dry PVDF polymer, 13% dimethyl acetamide (DMAc), and 73% acetone. Membranes were cast on a flat glass plate with a 12 minute air dry time (at 65% relative humidity and 25°C) followed by 30 minute immersions in three 15°C precipitation baths (the first bath was composed of 50% water, 40% acetone, and 10% DMAc; the second bath contained 60% water and 40% acetone; the third bath was pure water).

The performance of the PVDF membranes for the pervaporation separation of benzene from water was evaluated. Using a standard flat sheet membrane pervaporation apparatus, benzene was selectively extracted (at 25°C and 0.05 atm. downstream pressure) from a 150 ppm benzene in water feed solution. The benzene concentration in the permeate was found to be 251,868 ppm (which corresponds to a benzene separation factor of 1616). The benzene flux through the membrane was 6.1 g/m^2-hr. After performing the benzene separation experiment, the PVDF membrane was polled by pressing together two PVDF films and applying a voltage of 4.0 kV across the films for 50 minutes. The membrane films showed high piezoelectric activity, as noted by the production of a 40 V signal when the film was struck mechanically (as compared to a 35 V signal which was found when a commercially available polled PVDF film was tested). The benzene separation performance of the polled PVDF film was examined next using the pervaporation apparatus with a 145 ppm benzene in water feed solution at 25°C. The benzene concentration of the permeate was found to be 255,579 ppm (a separation factor

of 1775) and the benzene flux was 5.7 g/m^2-hr. These flux and separation factor numbers were essentially identical to that found with the PVDF membrane which was not polled.

The next experiments to be performed will examined pervaporation of a benzene/water feed solution with a PVDF membrane which is polled with a voltage higher than 4 kV to see if higher applied voltages will produce more piezoelectric activity in the film and better benzene/water separation. Methods which can accurately quantify the piezoelectric activity of the PVDF films will be examined and a more precise comparison of the piezoelectric activity of the asymmetric PVDF membranes and commercially available films will be made.

Project Title: Grant to Establish a Collaborative Research Relationship between the Tulane/Xavier CBR and the Institute of Radioecological Problems of the Academy of Sciences of Belarus in Minsk, Belarus

Project Investigator: Samuel C. Ramer, Ph.D.

Background: The goal of this grant was to lay the groundwork for a program of collaborative research between the Tulane/Xavier CBR and the Institute of Radioecological Problems of the Academy of Sciences of Belarus (IREP), which is located in Minsk, Belarus.

During the past quarter we have made progress in setting up the technical infrastructure for collaborative work. An e-mail connection with the Institute of Radioecological Problems in Minsk required the purchase and setup of computers with adequate software and fax/modems both here in New Orleans and in Minsk. During July and August equipment was set up at Tulane. During August and September the requisite computer hardware, software, and fax/modem for our partners in Minsk was purchased. We have not yet established a connection on Internet, but we are exploring this with the help of the Tulane Computer Center. We now know that the IREP can gain access to the Internet in Minsk. A connection should be established during the coming months.

While in Minsk, we met with one of the graduate students at the IREP and urged him to apply to Tulane's graduate program in physics. His preliminary application materials have been received. However, it is not yet clear whether it would be better to place him in physics or in a division of engineering that is more closely involved with computer modeling and environmental remediation.

Project Title: Risk, Stress, and Restructuring: A Case Study from Louisiana

Principal Investigator: J. Timmons Roberts, Ph.D.

The survey instrument, a 16-page questionnaire on work content and job stress has been completed. The instrument is to be self-administered by oil refinery and chemical plant workers. It includes adjusted indices of job content, hazardous exposures, job pressures, job control, supervision, self-esteem, depression, anxiety, stress, and a number of items specific to the petroleum industry. These latter indices seek to elicit unbiased assessments of the role of subcontractors in the overall safety of the plant. Literature review and documentation of the survey has been finished.

Negotiations are finalized to administer the survey at two facilities. One is a large oil refinery and the other a is medium-sized chemical factory. The survey is scheduled to begin at the chemical plant in November and at the refinery in January.

Based on analysis of data from the General Social Survey* the following paper has been submitted to *Social Forces*:: "Hazardous Workplaces, Class and Stress: An Eleven Nation Comparison." A second paper is in progress. Initial results will be presented at the Eastern Sociological Society meetings in Baltimore, MD on March 17-20.

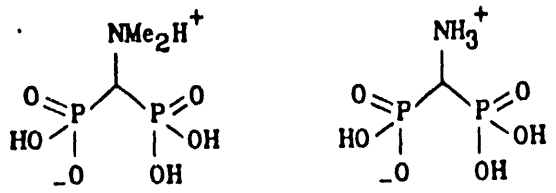
Drs. Robert Karasek and Carol Aneshensel have been invited to speak at the University.

*The General Social Survey examined the relationship between the workplace, hazardous exposures, class and stress. This research, administered through the International Social Survey Project, was conducted on representative samples totaling 8,000 workers in eleven nations.

Project Title: Synthesis of New Resins for the Absorption of Actinide Ions

Principal Investigator: D. M. Roundhill, Ph.D.

During the past quarter we have completed the refinement of the stability constant data for the complexation of UO^+ with MAMDP and AMDP (Figure 1). The stability

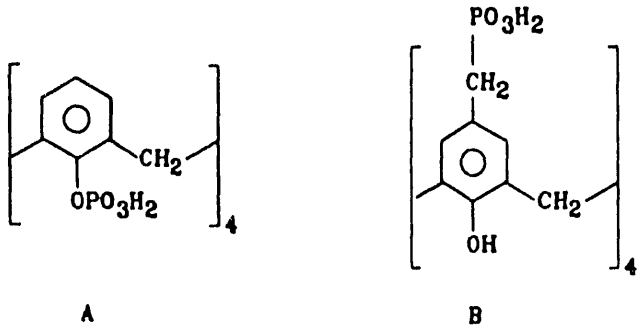


MAMDP (H_4L) AMDP (H_4L)

Figure 1

and protonation constants have all been evaluate, and it has been found that the amino group exerts a significant increase in the stability constant over those observed with phosphonates that do not contain such a group.

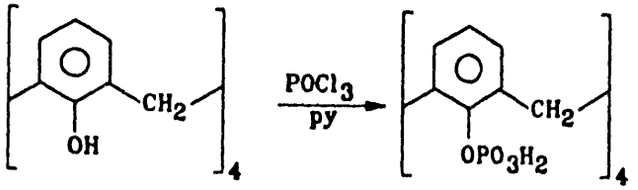
We have begun to synthesize new calixarenes with phosphonate groups attached to the lower rim, and phosphonate groups to the upper rim. These compounds are shown as A and B in Figure 2. Preliminary titration data has been obtained with the



A B

phosphonate B. We have already determined the solution conditions that need to be used to obtain this experimental data, and we have determined the concentration conditions that need to be used to avoid precipitation of the uranyl complex.

The phosphonate compound A has been prepared by reacting calix[4]arene with $POCl_3$ and pyridine (equation 1). At present we have not succeeded in obtaining a



single compound in pure form, but efforts are underway to achieve this goal.

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