2004 Annual Report

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Chicot/Evangeline Aquifer of the Texas Gulf Coast, Groundwater Age and Pathways for Saltwater Contamination

Regina M. Capuano and Steven V. Lindsay

The Chicot/Evangeline aquifer is the primary, and in some cases only, source of fresh water for many of the small towns and rural areas of the Texas Gulf Coast, however, many parts of it are becoming increasingly salty and unusable. Saltwater contamination of this aquifer in neighboring Matagorda County has been attributed to seawater intrusion[1] and upwelling of oil-field brines from underlying sedimentary units.[2] The purpose of this study is to evaluate if upwelling brine contaminates the aquifer over a broader area than that identified by Bourgeois.[2] Also, we hope to determine if this process is more effective in areas where the Beaumont Formation (which overlies and confines the Chicot aquifer) has been deeply incised and replaced with more permeable fluvial sediments. The study area includes Fort Bend and Brazoria Counties, which lie north and northeast of Matagorda County (Fig. 1) and provide a transect of the aquifer from its proposed recharge area in the northwest to its discharge at the Gulf of Mexico.[1] The results of this research can be used in managing groundwater use in this region and can be extended to understanding saltwater contamination of other coastal aquifers in similar geologic settings.

Twenty-nine water samples were collected from the Chicot/Evangeline aquifer for this study (Fig. 1). Chemical (Na, K, Ca, Mg, Sr, Fe, B, Si, Al, P, NO_3, pH, Cl, SO_4, HCO_3, CO_3, acetate, I, and Br) and isotope (δD, δO^{18}, δC^{13}, and C^{14}) analyses of the samples are being completed. This study is markedly different from all previous studies of this aquifer (e.g., Dutton and Richter[3] and Bourgeois[2]) in that carbon isotope analyses (δC^{13}) were used to determine the source of carbon, which provided a new perspective on fluid flow in this aquifer. In this region, the Beaumont formation, which is a clay-rich layer that overlies the Chicot, is thought to be relatively impermeable preventing recharge or contamination of the aquifer in the study area. In addition, the replacement of the Beaumont in some areas by the more permeable incised valley fill and its effect on recharge has not been considered. The δC^{13} and C^{14} analyses completed to date indicate that younger and isotopically lighter carbon with a consistent δC^{13} value is being added to the aquifer water along its flow path, strongly suggesting there is recharge of younger water through these overlying units to the Chicot aquifer. Initially, a limited number of these carbon analyses were completed to evaluate their usefulness and now based on these results more samples will be analyzed to confirm these findings.

Prior predictions of the source of salt contamination in the Chicot aquifer water based on a hydrologic analysis suggests seawater intrusion,[3] where as a later study based on elemental tracers suggests contamination is likely the result of upwelling of oil-field brine from underlying aquifers rather than seawater intrusion.[2] Ion analyses indicate that the salt contamination in well 3 (Fig. 1) downstream from the Clemens dome is only from dissolution of halite in the dome. Other wells in the area show a contribution of salt from this same process. The Clemens dome and several others in this area penetrate into the Chicot, but the tops occur 100 m or more below the sampling depths. Ion analyses indicate that other samples from the vicinity of the salt domes and those from the coast are clearly altered by mixing with water from outside of that typically present in the aquifer. δC^{13} and C^{14} from a coastal well and a δC^{13} from near a salt dome support this. We await the additional carbon isotope analyses to determine whether it is seawater or upwelling brine.

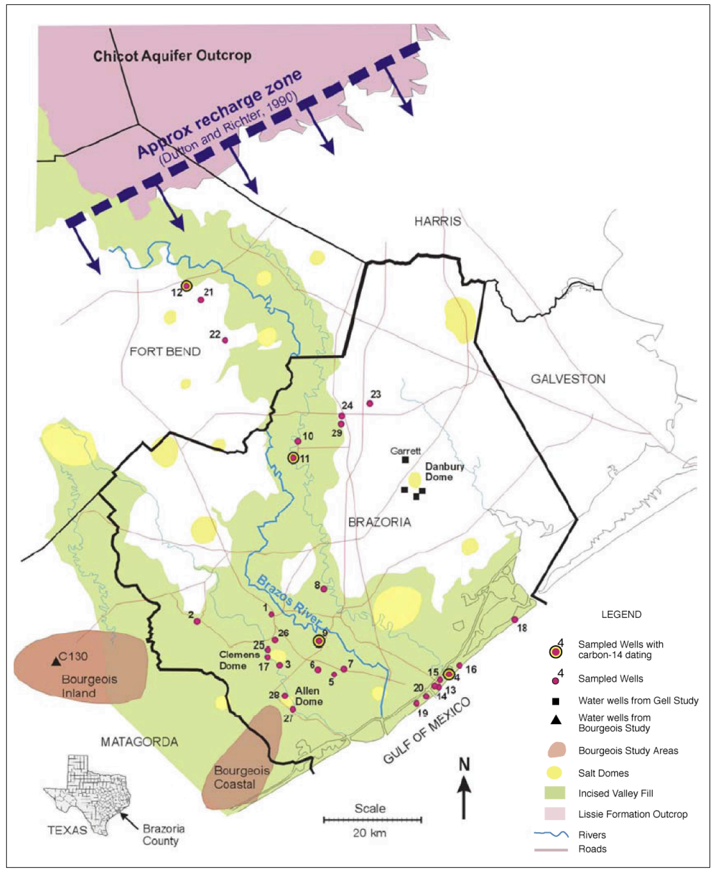

Figure 1. Location of wells sampled in this study. Area of incised valley fill,[4,5] salt dome locations,[6] Bourgeois' study area,[2] and Gell study area.[8] Base map from U.S.G.S. Houston Quadrangle, 1975.2.

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Scouting Studies of Simultaneous Soot Oxidation and NO_x Reduction in Diesel Engine Exhaust

Michael P. Harold and Pranav Khanna

During this eight-month project, we have carried out transient kinetics studies of NO_x adsorption and reduction on a model *Pt*/*BaO*/alumina catalyst. This is the first step toward the development of a combined NO_x and soot abatement converter for use in the exhaust after-treatment system of a diesel vehicle.

The main experimental tool we have used is the Temporal Analysis of Products reactor (TAP reactor). The TAP reactor enables the study of transient catalytic kinetics under well-characterized conditions (see Fig. 1). The system comprises a high-speed pulse valve system, reaction chamber, array of vacuum pumps, and a quadrupole mass spectrometer. The normal operating mode for the TAP reactor is a high vacuum (about 10^{-7} Torr) with the main transport mechanism being Knudsen diffusion. Pulsing experiments therefore yield data that can be analyzed in terms of intrinsic surface processes such as adsorption, reaction, and desorption. When coupled with a mathematical model that accounts for the Knudsen transport and surface chemical processes, one can elucidate key mechanistic issues and estimate kinetic parameters. This enables the development of a predictive microkinetic model that is incorporated into a reactor model for design purposes.

We have carried out a series of TAP experiments for the following reaction systems on the same model *Pt*/*BaO*/alumina powder catalyst:

(1) *NO* decomposition:

$$NO \rightarrow N_2 + O_2$$

(2) NO_2 storage and decomposition:

$$3NO_2 + BaO \rightarrow Ba(NO_3)_2 + NO$$

(3) $NO + O_2$ reaction:

$$NO + 0.5O_2 \rightarrow NO_2$$

(4) *NO* (or NO_2)/H_2 alternating pulses:

$$2NO + BaO + 0.5O_2 \rightarrow Ba(NO_2)_2$$
$$3H_2 + Ba(NO_2)_2 \rightarrow BaO + N_2 + 3H_2O$$

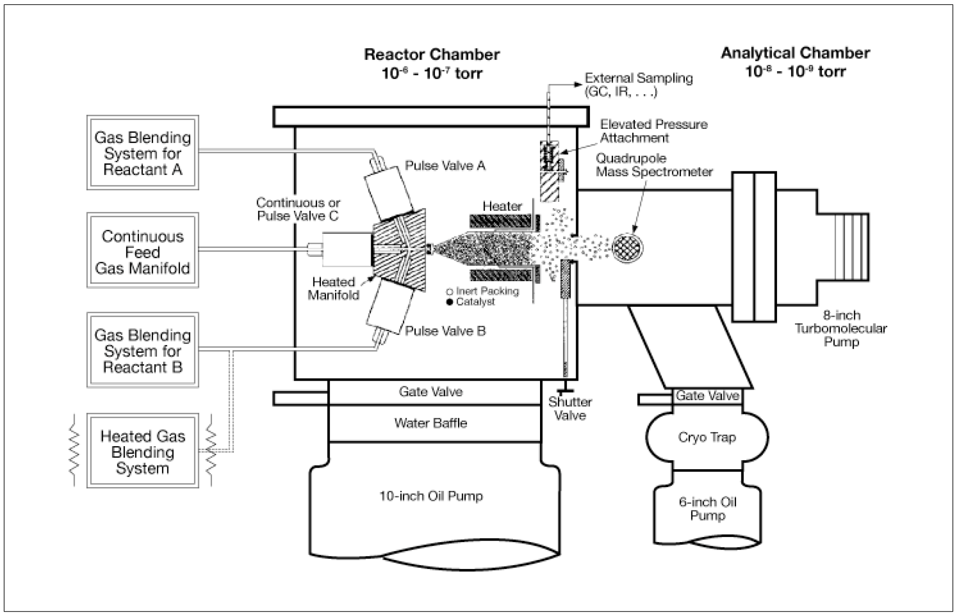

Figure 1. The TAP® Reactor System

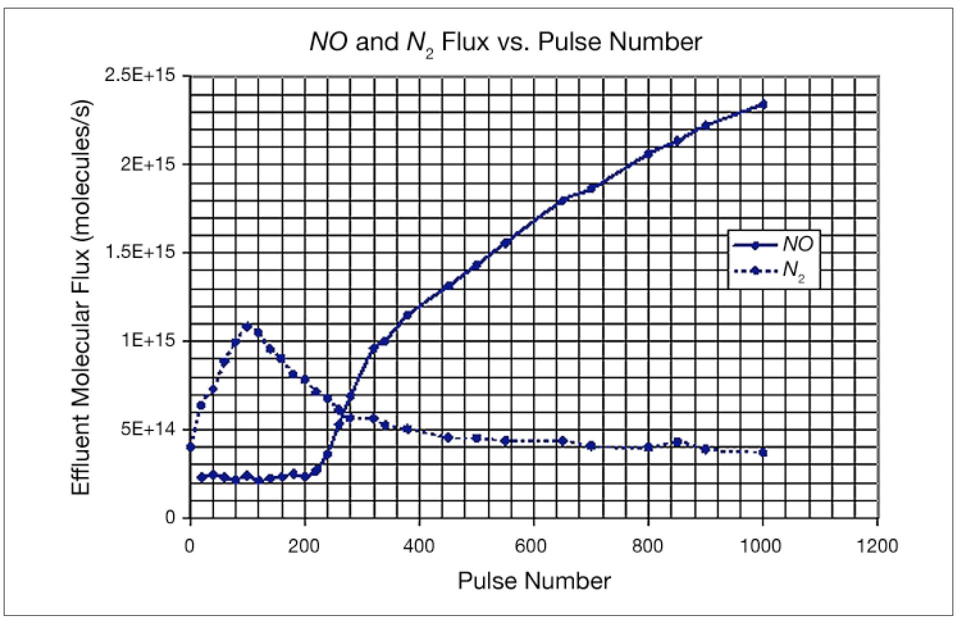

Figure 2. Dependence of Effluent Flux of N_2 and *NO* During the Sequential Pulsing of *NO* Over an Initially Oxidized *Pt*/*BaO*/Alumina Catalyst

Typical TAP data for the *NO* decomposition system are shown in Fig. 2. On an initially clean, oxidized *Pt*/*BaO* catalyst, a series of pulses of *NO* over a range of temperatures results in the temporary production of molecular nitrogen. The production of nitrogen achieves a maximum at an intermediate *NO* exposure (number of pulses) then gradually decreases. This trend is attributed to the accumulation of oxygen adatoms on the *Pt* surface which inhibit the adsorption and subsequent dissociation of *NO*. The effluent reactant *NO* and product N_2 signals reveal that the *NO* is more quickly detected than the N_2, an order opposite to that obtained with *Pt*/alumina catalyst. This indicates that the product *NO* exchanges with the barium storage component. The storage capability of the catalyst is even more evident in experiments in which NO_2 or NO/O_2 mixtures are pulsed to the catalyst. In the former, there is a long lag before NO_2 is detected, indicating an initial uptake on the storage compound. In a similar temperature range there is neligible production of NO_2 in the NO/O_2 experiments, indicating that the NO_2 that is produced is rapidly stored.

These studies are advancing our understanding of the main mechanism for NO_x storage and reduction on model NO_x trap catalysts. This understanding will help us design better catalysts and develop better predictive models which will be needed in the development of the more complex NO_x /soot abatement catalyst.

We have submitted a proposal to the EPA-sponsored Gulf Coast Hazardous Substance Research Center (GCHSRC) based on this work and related research sponsored by the State of Texas and Engelhard Corporation.

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Funding and proposals

Harold, M.P. (PI) and V. Balakotaiah (Co-I). “Development of an Integrated Particulate and NO_x Trap System for Diesel Engines,” Gulf Coast Hazardous Substance Research Center (GCHSRC), $183,401 over three years (*pending*).

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Characterization of Benthic Macroinvertebrate Communities in Restored/Created Salt Marshes and Natural Bayous Along the Houston Ship Channel and Upper Galveston Bay

Cindy Howard and Jim Dobberstine

RECENT REPORTS HAVE INDICATED THAT in certain areas of the Houston Ship Channel-Galveston Bay (HSC-GB) system, water and sediment quality, species diversity, and biological productivity are in decline as a result of the introduction of anthropogenic contaminants.[1-4] Contaminants enter Galveston Bay from numerous point and non-point sources along the bay itself and its supply waters, which include the HSC. The development of total daily maximum load (TMDL) programs in the HSC-GB system often requires evaluation of the resident benthic macroinvertebrate communities. Benthic organisms make good indicator species because they are found only in areas that are suitable for their survival and differ in their tolerance to pollution and other environmental stressors.[5] Unfortunately, accurate assessments of benthic macroinvertebrate communities at impacted sites in the HSC-GB system have been historically hampered by the lack of comparable reference sites. The purpose of this study was to identify at least one potentially acceptable reference community for current and future TMDL studies in the HSC and Galveston Bay.

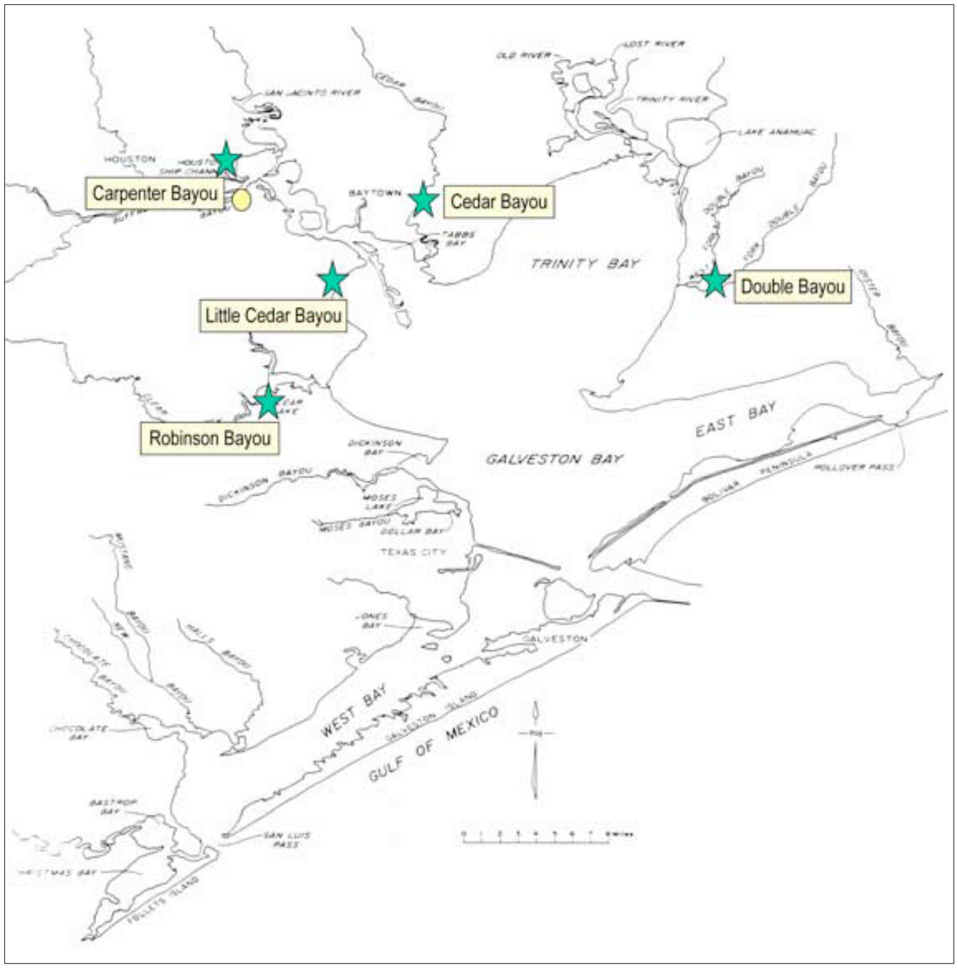

Figure 1. Location of Sites Selected for Potential Reference Bayous for the Houston Ship Channel-Galveston Bay System

Five bayous were selected for the study based on available physical, chemical, and biological data (Fig. 1). Sediment samples were collected from three stations along each bayou in May 2004 and July 2004. At each station, standard water quality parameters (salinity, conductivity, pH, dissolved oxygen, and total dissolved solids) were measured. Five replicate 4.2-inch core samples were collected for benthic macroinvertebrate community analysis and additional samples were collected for two standard EPA sediment toxicity tests, characterization of sediment type, and heavy metals analyses.

Following are preliminary results of the study. Results of the first round of toxicity tests on the amphipod *Leptocheirus plumulosus* and mysid shrimp *Mysidopsis bahia* indicate that sediments from all five bayous are not toxic (no significant difference in mortality and growth compared to control, $p \leq 0.05$). Benthic macroinvertebrate species richness and diversity is notably higher in Cedar Bayou than in the other bayous, and the lowest number of species is found in Carpenter Bayou. There also appears to be a notable difference in benthic species composition among the bayous, even though the water quality and sediment type variables are comparable. Other analyses are still in progress and will be completed by November 2004.

A third sampling event is planned for December 2004. Before then, the bayou system that appears to be the best candidate for a HSC-GB reference site will be selected for additional, more intensive study. Following collection of the last set of data, all five sites will be analyzed along with data from impacted sites in the region using standard diversity indices and the benthic index[6] to determine the potential of at least one of the study sites to serve as a reference community for TMDL studies in the HSC-GB.

SEDIMENT SAMPLING—Jim Dobberstine collected five replicate 4.2-inch sediment samples for benthic macro-invertebrate community analysis.

Acknowledgments
We gratefully acknowledge John Huffman, U.S. Fish and Wildlife Service, for providing boat transportation and assistance with collecting sediment samples, and Jim Horne, PBS&J, for facilities, supplies, test organisms, and assistance in conducting the toxicity bioassays.

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Remotely Sensed Digital Change Detection for Studying Urban Development and its Relationship to Flooding in Houston, Texas

Shuhab D. Khan

For this study, four Landsat TM images were selected for path 25 and row 39 to examine changes caused by urbanization in the Houston area from 1984 to 2003. The data for selected scenes were acquired in November 5, 1984, December 19, 1994, January 10, 2000, and January, 18, 2003. For classification and change detection of these images, a combination of post-classification and manual on-screen digitization methods was used. The main disadvantage faced in this process was that only changes with large spectral differences were identifiable; small changes in land-cover types were difficult and timeconsuming to detect. It was found, however, that the neural network model proved to be more useful to classify the images for different years. Therefore, the neural network technique was used to classify the images into five land use classes. The five classes included vegetation, asphalt, concrete, bare ground, and water and were selected based on their relevance to flooding and urbanization. Figure 1 shows the results of classification for 1984, 1994, 2000, and 2003.

For change detection the post-classification comparison technique, which is the most commonly used quantitative method of change detection, was used. It requires rectification and classification of each remotely sensed image. The resulting two maps are then compared on a pixel-by-pixel basis using a change detection matrix.

Two maps of different dates were selected as initial and final states maps and from these a change image map consisting of brightness value for each class was created. Table 1 shows the initial state classes in the columns and the final state classes in the rows. For each initial state class (i.e., each column), the table indicates how these pixels were classified in the final state image. The change-in-pixels row indicates the total number of initial state pixels that changed classes.

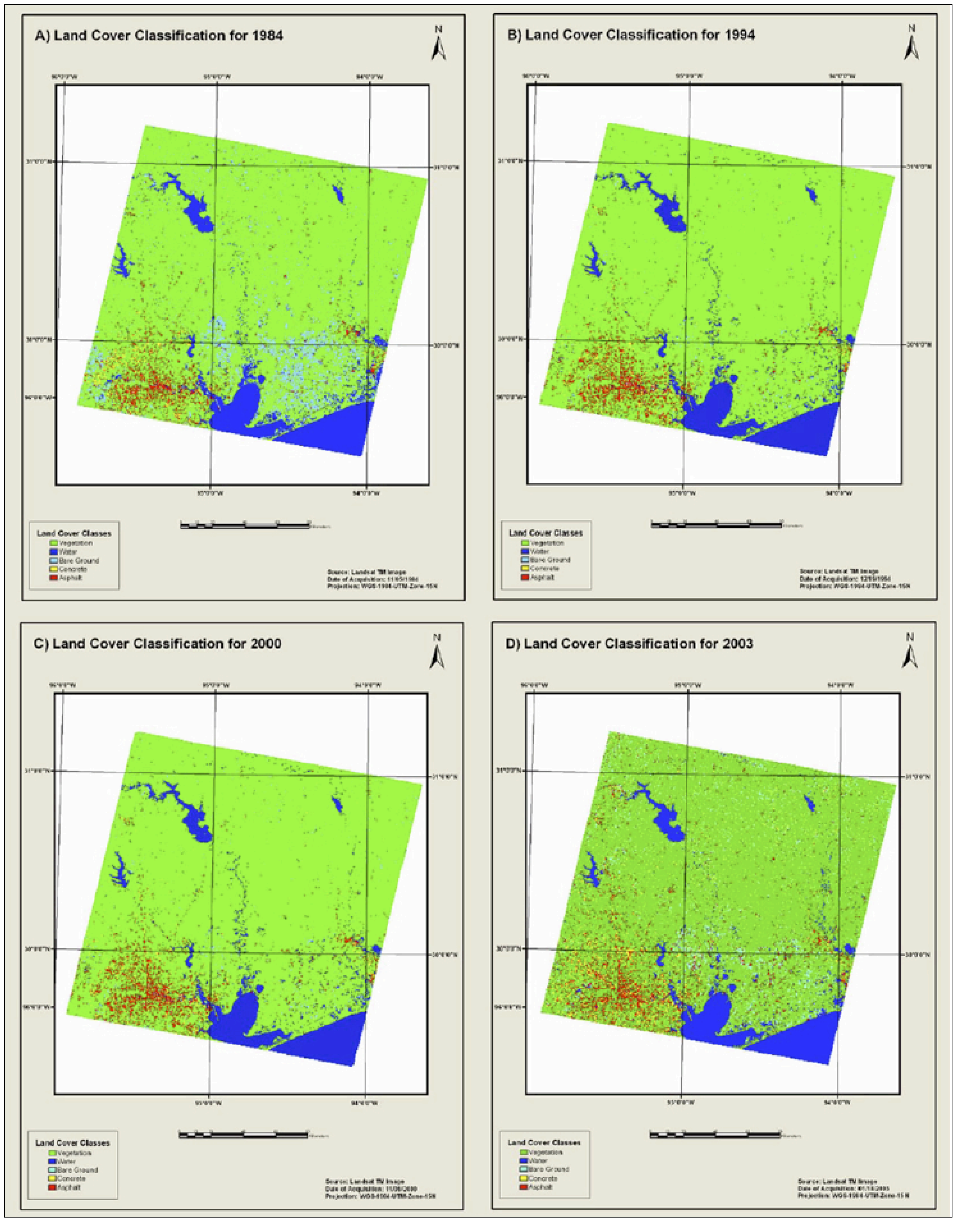

Figure 1. Land Classification Using Neural Network Technique for Houston Area

The results of the land cover classification of the Houston area from 1984, 1994, 2000, and 2003 show that concrete and asphalt increased by about 21 percent from 1984 to 1994, by 39 percent from 1994 to 2000, and by 114 percent from 2000 to 2003. In contrast, vegetation increased by 13 percent from 1984 to 1994 but decreased by 1 percent from 1994 to 2000 and by 8 percent from 2000 to 2003. The increase in concrete and asphalt, and overall decreases in vegetation clearly show increase in urbanization.

In order to estimate flooding and its relation to urbanization, the relationship between rainfall and runoff was examined by means of the runoff ratio (R/P), which is a measure of overall basin hydrologic response. The runoff ratio data show an overall

Table 1. Land Cover Change in the Greater Houston Area Using Landsat TM (Unit: %), 1984–2003

	Asphalt	Vegetation	Water	Concrete	Bare Ground	Total
1984	2.72%	75.55%	10.40%	1.29%	10.04%	100%
1994	3.01%	84.07%	9.32%	1.38%	2.22%	100.00%
1984 (pixels)	990,264	27,532,126	3,788,861	471,785	3,658,539	36,441,575
1994 (pixels)	1,114,049	31,105,962	3,447,473	510,239	821,084	36,998,807
Change(1984–1994)	13%	13%	-9%	8%	-78%	
1994	3.01%	84.07%	9.32%	1.38%	2.22%	100.00%
2000	3.88%	83.28%	8.22%	1.54%	3.07%	100.00%
1994 (pixels)	1,114,049	31,105,962	3,447,473	510,239	821,084	36,998,807
2000 (pixels)	1,428,806	30,644,216	3,025,128	568,317	1,129,671	36,796,138
Change (1994–2000)	28%	-1%	-12%	11%	38%	
2000	3.88%	83.28%	8.22%	1.54%	3.07%	100.00%
2003	4.50%	75.96%	9.09%	3.04%	7.40%	100.00%
2000 (pixels)	1,428,806	30,644,216	3,025,128	568,317	1,129,671	36,796,138
2003 (pixels)	1,660,479	28,045,989	3,357,351	1,123,331	2,732,585	36,919,735
Change (2000–2003)	16%	-8%	11%	98%	142%	

increase in surface runoff with the exception of a few sites, such as the Neche River in Rockland, where the decrease in runoff can be attributed to the construction of a new reservoir in the area.

A web-based application is being developed that will provide results of our work to the public via ArcIMS (ARC Internet Map Server) through the following site: <http://geoinfo.goesc.uh.edu/Houston>

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Synthesis of New Flame Retardants For Pollution Prevention

Jack Y. Lu

THE MOST POPULAR COMMERCIAL FLAME RETARDANTS USED IN plastic products—from computers to automobiles—are halogenated compounds such as polybrominated diphenyl ethers (PBDE). Recently, flame retardants have come under fire from environmental groups because of their increasing presence in the environment.[1] The pollution from these flame retardants is caused by a vapor-phase mechanism in the retardant and its solubility in water. These problems may be solved by designing and synthesizing new flame retardants that are insoluble in water and prefer condensed-phase mechanism. With the environmental concerns of flame-retardants, metal-organic coordination polymers could provide a new alternative.

Among the new materials synthesized in our laboratory, UnHuClFr 1 and UnHuClFr 2 are insoluble in water and common organic solvents. They were blended into a commercial polymer, HIPS, a flammable polymer. The material was tested for ignition resistance using the industry-standard UL-94 flame test. A 30 and 28 wt% loading of UnHuClFr in HIPS gave an industry-standard UL-94 V-0 result. To obtain a V-0 rating, the plastic must self-extinguished within 10 seconds after each of two sequential ignitions (an ignition consisting of the bar being immersed in the flame for 10 seconds).

The research activities in our laboratory also produced large pore containing porous materials for potential environmental applications. Copper-dipyridal complex has a single-net open-framework structure. It displays very attractive anion exchange, as well as molecular exchange capabilities. Further research on its applications is in progress.

A new 2-D covalent network coordination polymer uniquely sandwiched by alternating 1-D intra-hydrogen bonding networks (Fig. 1) has also been synthesized and characterized by single crystal x-ray structure and thermal analysis.

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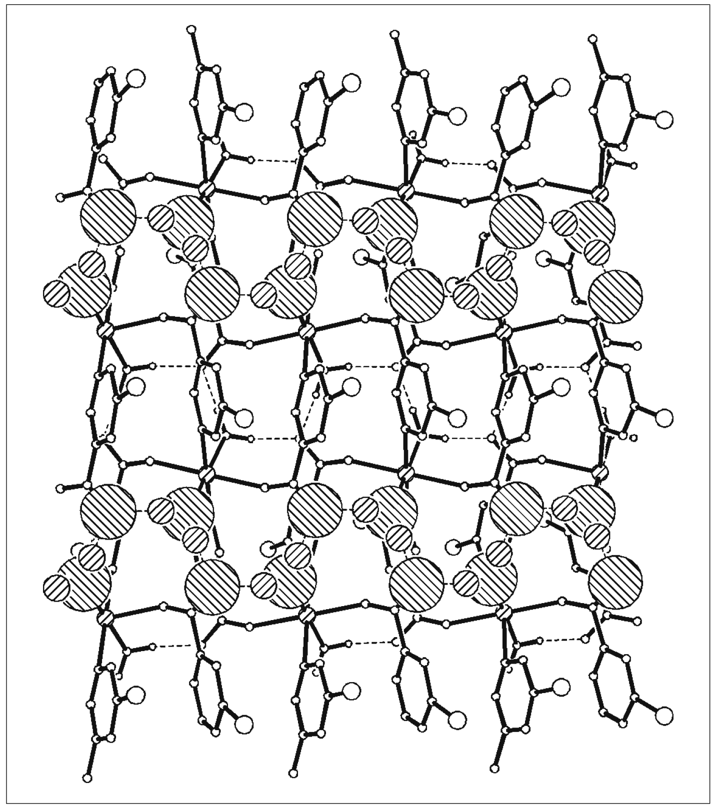

Figure 1. A Covalent Layer Sandwiched by Alternating 1-D Intra-hydrogen Bonding Networks Extending along the *c* Axis

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Environmental Variation and the Diversity of Texas Salt Marsh Plant Communities

Steven C. Pennings

Understanding the factors mediating local species richness is complicated by the fact that species richness is affected both by large-scale evolutionary and biogeographic factors that create the regional species pool and local ecological processes that determine which limited number of species from the species pool will exist at a particular site. One approach to solving this problem is to compare habitats that share a similar species pool but have different local patterns of diversity, such as the salt marsh ecosystems of the Atlantic (Georgia) and Gulf (Texas) coasts. These two different marsh systems have relatively similar species pools in richness and species composition, but differ in local diversity. By comparing these two systems we can explore the ecological factors mediating diversity while minimizing effects from regional differences in the richness of the species pool or differences in the traits of the species that make up the flora.

Although marshes in Georgia and Texas share a similar species pool, marshes of Georgia appear to have discrete zones of vegetation that form across an edaphic elevational gradient.[1,2] These zones result from competitive dominants excluding subordinate species to more stressful habitats and from subordinates dominating zones in which dominants cannot survive.[3-5] In contrast, Texas marsh zones appear to be patchy and overlap broadly, creating areas of high local diversity. One possible explanation for this would be that the irregular tidal schedule of the Gulf Coast does not allow competitive dominants to form strict monospecific zones. Although Georgia and Texas marshes visually appear to have different patterns of zonation and local diversity, data that would allow rigorous comparisons of the two systems are lacking.

We studied two relationships commonly used to quantify biodiversity: (1) the species-area relationship and (2) the diversity-biomass relationship. We hypothesized that the power law of the species-area curve would have a shallower slope in Texas than in Georgia because of greater species richness in small areas and a similar total species pool. In accordance with the unimodal diversity-biomass relationship described by Grime[6], we hypothesize that the diversity-biomass curve would differ between Georgia and Texas in two ways. First, for any given level of biomass, the diversity of Texas marshes would be greater. Second, this difference between the two curves would be greatest at levels of high biomass where competition is more likely to limit richness in Georgia marshes.

We selected four marshes for intensive study in each geographic region. Marshes that were chosen were exposed to full strength seawater and were similar in overall species composition. In future work, we will expand to include more sites in each region.

Species-area Relationship

Species-area curves were determined for eight zones of vegetation in Georgia: (1) Shrubs, (2) *Juncus roemerianus*, (3) High Meadow, (4) Salt Pan, (5) Mid Meadow, (6) Low Meadow, (7) Short *Spartina*, and (8) Tall *Spartina*. In Texas, the same zones were used but the two *Spartina* zones could not be reliably distinguished and were combined into one, giving a total of seven zones. A series of nested quadrats starting at 0.2 × 0.2 m and increasing in area up to 1 × 10 m were examined; all plant species present were recorded. Six replicate sets of nested quadrats were sampled in each zone at each site.

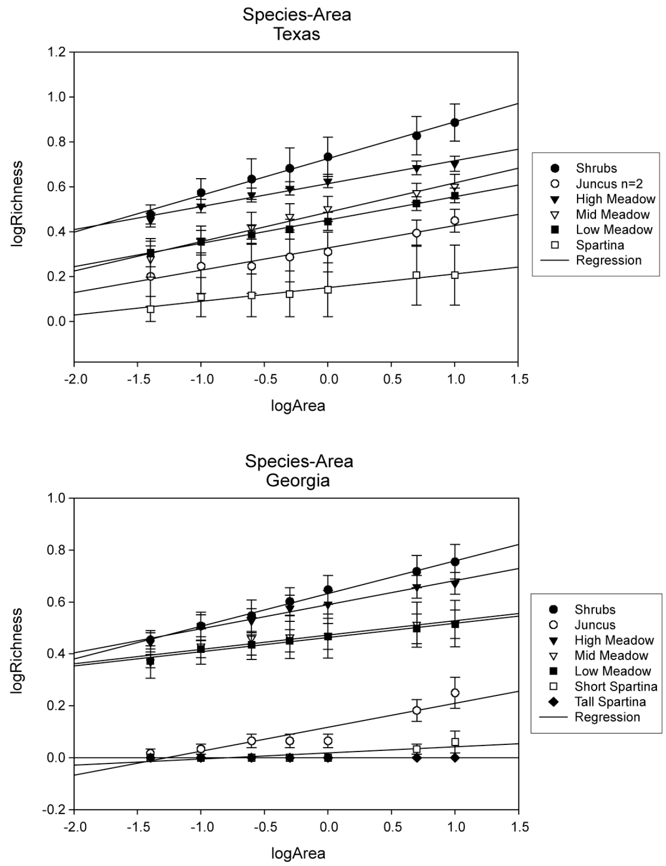

Figure 1. Relationship Between Sampling Area and Species Diversity in Comparable Zones of Texas (*top*) and Georgia (*bottom*) Salt Marshes

In contrast to predictions, all Texas species-area slopes were steeper (range 0.06 to 0.16) than results from comparable Georgia zones (range 0.01 to 0.13) (see Fig. 1). When individual zones were compared between regions with *t*-tests, these differences were not significant, except for the case of the Mid-Meadow zone ($p = 0.04$). When average slopes of all zones were compared between regions using a paired *t*-test, slopes from Texas were significantly greater than slopes from Georgia ($p = 0.002$) (see Table 1). The existence of steeper species-area slopes in Texas is contrary to our initial

Table 1. Species richness in comparable vegetation zones in Georgia and Texas salt marshes. Shown are coefficients for species-area curves, estimates of species richness at 10 m^2 from the species-area curves, and actual numbers of species observed in each zone during all sampling.

	Y-intercept			Slope			Species Richness at 10m^2			Actual Richness		
Zone	**GA**	**TX**	***P*-value**	**GA**	**TX**	***P*-value**	**GA**	**TX**	***P*-value**	**GA**	**TX**	***P*-value**
Shrubs	0.63	0.73	0.39	0.13	0.13	0.1	6.19	8.62	0.29	9.75	13.25	0.14
Juncus	0.12	0.33	**0.04**	0.09	0.1	0.87	1.53	2.91	0.16	3.25	4.5	**0.06**
High Meadow	0.59	0.61	0.64	0.09	0.1	0.62	5.06	5.46	0.56	6.33	6.73	0.68
Mid Meadow	0.47	0.49	0.89	0.06	0.13	**0.04**	3.63	3.55	0.95	4.25	5.25	0.41
Low Meadow	0.46	0.45	0.84	0.05	0.1	0.16	3.54	3.85	0.57	3.86	5.25	**0.07**
Spartina-all	9.40E-03	0.15	0.29	0.01	0.06	0.26	1.08	1.98	0.29	1.38	2.25	0.2
Combined			**0.009**			**0.001**			**0.01**			**0.007**

hypothesis. We predicted that Texas marshes would be more diverse than Georgia marshes in the smallest plots, but that final diversity in the largest plots would be similar in both regions. Instead, diversity was greater in Texas at all spatial scales. This result could occur if species were more widely distributed across the marsh in Texas than in Georgia (i.e., each species occurred in more zones), if the total species pool was greater in Texas than in Georgia, or both. We are currently analyzing data on zonal distributions of each species, but our observations suggest that, in Texas, individual species do occur in more zones than in Georgia.

The total species pool was estimated by using species richness data from the above surveys. This was done by taking a total richness count per zone across replicate transects and also predicting a best estimate of richness at the 10 m^2 scale. Species richness in comparable zones was greater in Texas in both actual count and in estimations; although, differences were significant when all zones were compared using paired *t*-tests, but usually not when individual zones were compared using two-sample *t*-tests (Table 1). Similarly, the total of all species seen in each marsh (the species pool) was greater for Texas sites (17) than for Georgia sites (12.8, two-sample *t*-test, $p = 0.04$). In sum, our results suggest that regional differences in richness within individual marsh zones were caused by (1) individual species being more widely distributed across the marsh and (2) a greater species pool in Texas than in Georgia.

One concern with this approach is that we examined only presence/absence data, and ignored the relative abundance of each species. Thus, rare species had an impact on the results that was disproportionate to their abundance. In the diversity-biomass relationships described next, we looked at relative abundance data to get a better measure of diversity.

Diversity-biomass Relationship

The same sites and zones used for the species-area data were also sampled to quantify the diversity-biomass relationship. In each zone, we measured vegetation height to estimate biomass and species richness of each species in 20 1 × 1 m quadrats in each zone. Relative abundance was taken in eight 0.5 × 0.5 m quadrats in the same transect of each zone. Height data will be converted to biomass using relationships derived from four to six additional harvested plots in each zone. Biomass was obtained by harvesting all above-ground material from a 0.25 × 0.25 m plot centered in the quadrat, drying at 60 degrees to a constant weight, and weighing the dried material. All samples have been collected. Sample processing and data analysis is ongoing.

Together, these two approaches have provided an extensive set of data that will allow rigorous comparisons to be made between geographic regions and between zones in each region. We began the work with the subjective impression, based on non-quantitative observations, that diversity patterns differed between Gulf Coast and Southeastern Atlantic Bight salt marshes. These data will clarify exactly what aspect of diversity differs between the geographic regions. We plan next to expand the scope of our work by taking selected measurements at a larger number of sites in each geographic region. This will ensure that the differences we have observed are typical (not biased by the four sites we selected in each region) and will allow us to document spatial patterns in diversity among sites within each geographic region.

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Investigating the Metabolic Pathway of Anaerobic Biodegradation of Unsaturated Hydrocarbons in Marine Sediment

Deborah J. Roberts and Ken Butler

SYNTHETIC-BASED DRILLING FLUIDS (SBFs), which can contain unsaturated hydrocarbons (olefins), are used to lubricate drill bits during deep-sea oil drilling operations in the Gulf of Mexico. Concern about the environmental impact of the discharge of drill cuttings by the Environmental Protection Agency (EPA) has resulted in the enactment of rules requiring that all SBFs be certified as biodegradable by microorganisms indigenous to the marine sediment. Metabolic intermediates of the anaerobic biodegradation of the SBF may provide a rapid and sensitive means to reveal intrinsic biodegradability potential. In addition, this research aims to advance the state of knowledge concerning the fate of hydrocarbon pollutants in the natural environment.

Preliminary efforts in this research have been directed at obtaining active olefin-degrading, sulfate-reducing cultures and developing the gas chromatography/mass spectroscopy (GC/MS) techniques needed to analyze for the metabolites.

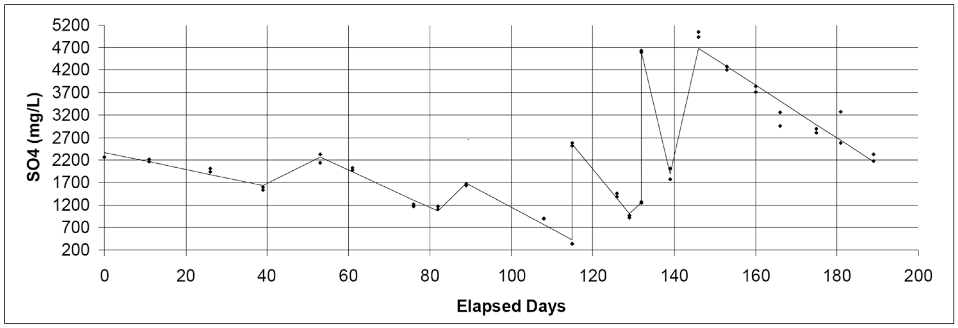

Figure 1. Sulfate Loss in Mother Culture. On days where spikes occur, the culture was amended with K_2SO_4.

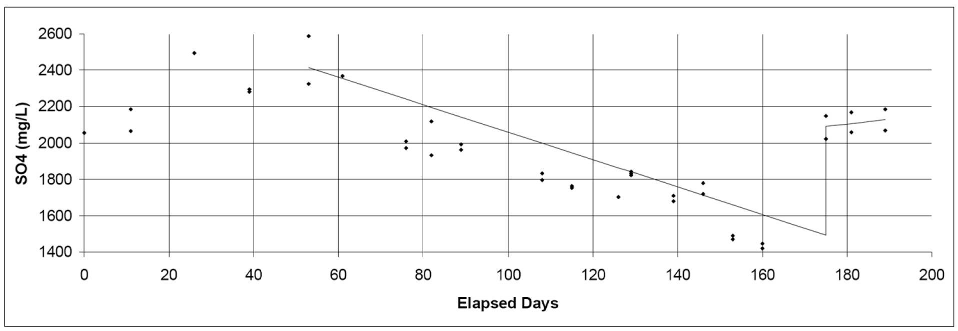

Figure 2. Sulfate Loss in First Daughter Culture. On days where spikes occur the culture was amended with K_2SO_4.

Culture Development

The mother culture was started in May 2003 by adding to a 500 ml flask about ten milliliters of ocean sediment collected from Galveston Bay to 260 ml of a sulfate-containing brackish medium prepared as described by Widell and Bak.[1] From May 2003 to December 2003, the culture was enriched by four transfers to fresh media, and amended with 250 to 1000 ul 1-tetradecene during two of the four transfers.

In early February 2004, a daughter culture was prepared by transferring 50 ml of enriched media from the flask to a serum bottle containing 50 ml of fresh media, and adding 500 ul of 1-tetradecene. In early May 2004, a second daughter culture was prepared in the same manner. All three enrichment cultures were periodically amended with sulfate and 1-tetradecene.

Since the overall oxidation-reduction reaction between sulfate and 1-tetradecene is:

$$10.5SO_4^{2-} + C_{14}H_{28} + 15.75H^+ \rightarrow 14CO_2 + 5.25H_2S + 5.25HS^- + 14H_2O$$

a decrease in the sulfate ion concentration indicates that 1-tetradecene is being biodegraded; therefore, the biodegradation of 1-tetradecene is monitored by periodically determining the sulfate ion concentration $[SO_4^{2-}]$ using ion chromatography. Results for two of the cultures are shown in Figs. 1 and 2.

The figures indicate that the mother culture and the first daughter culture are actively degrading 1-tetradecene. The rate of sulfate removal, and thus the projected rate of tetradecene removal, is improving with time in the mother culture. This suggests that the enrichment process is occurring. The first daughter culture is still removing sulfate very slowly suggesting more time for enrichment is needed. For the second daughter culture, the sulfate concentration remained relatively constant (not shown).

GC/MS Method Development

From the literature review[2,3] it is anticipated that the following compounds may be produced during the biodegradation of 1-tetradecene:[3]

- 1-tetradecanol,
- 2-tetradecanol,
- 1,2-epoxytetradecane,
- 1-tetradecanoic acid, and
- 2-tetradecylsuccinic acid.

Table 1. Retention Times of Compounds

Compound	Retention Time (min)
1-tetradecene	15.7
1-tetradecano	30.7
2-tetradecanol	26.7
1,2-epoxytetradecane	27.6
1-tetradecanoic acid-TMS Ester	23.9

To develop a method for the analysis of these compounds, standards of the compounds (500 mg/L dichloromethane) were prepared. It was not possible to purchase 2-tetradecylsuccinic acid, so *n*-tetradecylsuccinic anhydride was purchased and used to prepare 2-tetradecylsuccinic acid. Additionally, the acids were converted to trimethylsilyl (TMS) ester after reaction with *N*,*O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) since this is required before they can be analyzed using GC/MS.

All of the anticipated compounds were detected using GC/MS with the exception of 2-tetradecylsuccinic acid-TMS ester. Identification of the standards was made by comparing the obtained spectra to the NIST mass spectra database. In the case of 1-tetradecanoic acid-TMS ester the identity of this compound was further confirmed by comparing the retention time of the compound to a published retention time of the compound under identical instrument conditions.[4]

The retention times of the identified compounds are shown in Table 1.

Gas chromatography conditions are being adjusted in an attempt to detect 2-tetradecylsuccinic acid-TMS ester. If continued efforts to detect 2-tetradecylsuccinic acid-TMS ester are unsuccessful, the base hydrolysis reaction procedure on tetradecylsuccinic anhydride will be repeated.

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Pharmaceuticals, Hormones and Other Endocrine Disrupting Chemicals in Susceptible Waters in the Houston Area

Chunlong Zhang, Leticia Vega, Joseph L. Hedrick, and Zlata Grenoble

Water quality research and monitoring have been generally focused on the U.S. EPA priority pollutants (114 organic and 15 inorganic compounds) such as aliphatic/aromatic hydrocarbons, halogenated hydrocarbons, and pesticides. However, the occurrence, fate and transport, and toxic effects of pharmaceuticals, hormones, and other endocrine disrupting chemicals (PHEDCs) remain largely unknown. Many of these compounds are hormonally active and have the potential to alter functions of the endocrine system in humans and wildlife. PHEDCs also pose potential effects including abnormal physiological processes, reproductive impairment, increased incidences of cancer, and the development of antibiotic-resistant bacteria.[1]

The technological advances in analytical instrumentation particularly during the last ten years have extended our concern to these emerging compounds of low concentrations. A recent USGS survey detected a wide variety of PHEDC compounds in the U.S. streams.[2] The most frequently detected compounds are in the categories of steroids and hormones, wastewater-related compounds, and nonprescription drugs. This USGS survey also indicates that common estrogens are detected at a frequency of 2.8 -21.4% by GC/MS methods. They include natural female hormone 17β-estradiol (E2), its oxidation product estrone (E1), and the synthetic contraceptive additive 17α-ethynylestradiol (EE2).[2,3]

Table 1. Target Estrogen Compounds and Major Ions Detected Using LC/MS-APPI

	Formula	MW	Major ions detected using APPI negative scan
Estrone (E1)	$C_{18}H_{22}O_2$	270.4	269
17β-Estradiol (E2)	$C_{18}H_{24}O_2$	272.4	271
Estriol (E3)	$C_{18}H_{24}O_3$	288.4	289
17α-Ethynylestradiol (EE2)	$C_{20}H_{24}O_2$	296.4	295

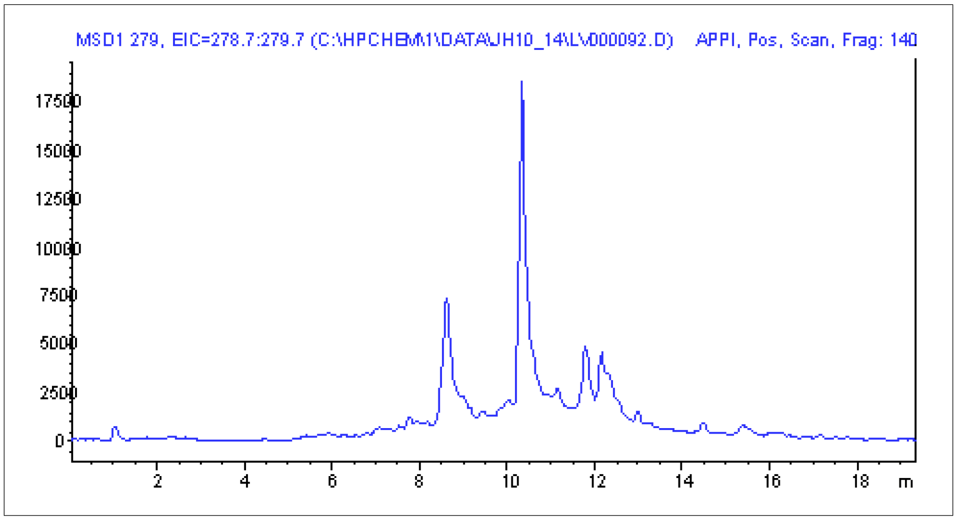

Figure 1. Extraction of m/z 279 Ion in the Effluent of a Simulated Bioprocess Water Recovery System

Our research focus at the early stage of this study was to develop pre-concentration and analytical methods (GC/MS and LC/MS) for the identifications and quantification of PHEDCs. Four estrogens were selected for this purpose (Table 1). Initial work focused on LC/MS by employing Agilent 1100 Model LC/MS system equipped with two ion sources—electrospray and atmospheric pressure photoionization (APPI). Estrone (E1), estradiol (E2), estriol (E3), and the synthetic ethynylestradiol (EE2) (each at 100 mg/L in methanol) were analyzed using flow injection analysis (FIA) mode to directly deliver each analyte to the ion source and to determine the most appropriate ionization source and scan mode. APPI negative mode was identified as the suitable operating mode for optimum peak intensity of the estrogens. Major ions detected for E1, E2, E3, EE2 were 269, 271, 289, and 295, respectively.

Subsequent studies were initiated to determine the occurrence and concentration ranges of target compounds in local representative water and wastewater samples that may be susceptible to PHEDC discharge. Wastewater samples from a contained wastewater recovery system were chosen because of the high contaminant concentration associated with its low volume waste stream relative to municipal wastewaters. While mestranol, 17β-estradiol, and estrone were not detected, ethynylestradiol was detected in both feed and effluent samples at a level of approximately 2 μg/L (Fig. 1). There was a significant amount of residual organics in the effluent that interfere with analyte determination. Optimal conditions were determined as follows:

(a) Extractions: Conditioned cartridges with 5 mL methanol and water; Added 10 mL wastewater sample and applied vacuum; Rinsed cartridge with 3 mL 70:30 water-methanol solution; Eluted sample with 5 mLs methanol; Concentrated sample to 200 μL under a nitrogen stream.

(b) Chromatographic conditions: Zorbax SB-C18 column (5 μ, 2.1 × 150 mm at 50ºC); gradient flow at 0.4 mL/min (A = water, B = methanol, gradient start at 20% B; 10 min, 100%

B; 20 min, 100% B);

(c) Diode-array detector: signal A – 215, 8 nm, reference – 360, 100 nm; signal B – 254, 8 nm, reference – 360, 100 nm; MS Source: APPI, positive mode, Vcap: 1100 V positive mode; Nebulizer: 20 psig, Drying gas: 4.0 L/min at 325ºC; Vaporizer: 320ºC; Scan range: 200-350amu, Peak width: 0.1 min, Time filter: ON, Fragmentor: 140 volts.

Experiments are underway to develop a robust method applicable to routine determination of low concentration PHEDC compounds in complicated matrices. On-going studies are to fine-tune the current LC-MS method (perhaps with the combined use of GC/MS) using a wide variety of sample matrices (water, wastewater, and sludge) in the Houston area. Experiments have also been initiated to investigate the dissipation mechanisms (sorption and biodegradation) of PHEDCs in a simulated activated sludge reactor system using sludges collected from Airport Wastewater Treatment Plant in Galveston.

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Recharging the Science Lab: One Link in the UHCL–McWhirter Partnership

Bonnie Mackey

The UHCL–McWhirter Professional Development Lab School represents an innovative partnership between the University of Houston-Clear Lake (UHCL) and McWhirter Elementary School. Couched within the goals of this lab school are two over-riding themes: (1) the intertwining of the expertise and pedagogical experiences of faculty and staff from both sites, and (2) the desire to enhance the scientific and environmental knowledge base of McWhirter elementary teachers and students. We addressed both goals by aquiring additional equipment for environmental and science activities within the lab. We also by developed exemplary lesson plans that use the new supplies and equipment in teaching pre-kindergarten through fifth grade students. In addition, 85 percent of the McWhirter faculty participated in a six-hour Project Learning Tree workshop that dealt with infusing environmental education into the curriculum for McWhirter students.

The target audience consisted of pre-kindergarten through fifth grade students at the McWhirter Professional Development Lab School (PDLS). With the guidance of Dr. Brenda Weiser, Project Learning Tree in the City coordinator, Marlene Morgan and Sarah Maxcey, UHCL graduate students, taught within the science lab lessons that instilled environmental education within the elementary science curriculum. A second target audience consisted of the faculty at McWhirter PDLS. The faculty participated in a six-hour Project Learning Tree workshop that was conducted at the McWhirter campus in spring 2004. By providing faculty with the environmental education workshop, the faculty acquire the skills, the hands-on experiences, and the activity book to implement environmental education themes within their everyday teaching. Awareness of their campus environment enables teachers and students to become more responsible and knowledgable citizens who strive to respect and cherish Earth's ecological and geographical components.

Objectives

The objectives of this project were (1) to organize the science lab by labeling supplies in both English and Spanish; (2) to utilize the science lab facility throughout the school day; and (3) to infuse environmental education issues within teacher professional development. Through the hard-working and dedicated commitment of Ms. Morgan and Ms. Maxcey, all of the stated objectives in this EIH grant were accomplished.

Products and Services Produced

Several final products resulted from this grant. They include:

(1) an organized and dual-language labeled science lab;
(2) teacher handbooks in both English and Spanish that describe the organization of the science lab and present exemplary lessons concerning environmental education themes for each grade level, pre-kindergarten through fifth grade;
(3) teacher training workshops (Project Learning Tree) that model the development and implementation of environmental education lesson plans which align with the Texas Essential Knowledge and Skills curriculum; and
(4) a colorful, informative tree guide of the McWhirter campus.

The dissemination of materials was handled in the spring and summer of 2004. Ms. Morgan and Ms. Maxcey developed a bilingual teacher handbook for all McWhirter faculty in grades pre-kindergarten through fifth. This teacher handbook included: (1) an explanation and visual layout of the reorganized science lab, (2) exemplary lessons concerning environmental education concepts for each grade level (pre-k-fifth grade), and (3) alignment of those exemplary environmental education lessons with the state curriculum, Texas Essential Knowledge and Skills (TEKS). Under the direction of Ms. Morgan and Ms. Maxcey, third, fourth, and fifth grade classes were selected to help produce a tree guide of the McWhirter campus. After learning about the various trees on their campus, elementary students gave their input as Ms. Morgan and Ms. Maxcey developed the tree guide. The colorful and interactive guide includes photos of the trees, a campus map that delineates the location of each tree, and ideal growing environments for each tree.

Benchmarks

Progress was measured throughout the grant period by the completion of each task identified on the timeline. The following tasks were completed on their designated schedule:

November–December, 2003
- Organized and labeled items in lab

January–May, 2004
- Developed teacher handbooks with description and layout of newly organized science lab
- Developed and implemented lessons concerning environmental education issues
- Developed tree guides of McWhirter campus

May–July, 2004
- Conducted educator workshops

Publications

Mackey, B., M. Morgan, and S. Maxcey. *Organizing the Elementary School Science Lab*: *Preparations, Procedures, and Performances*. Worthington, OH: Linworth Publishing Company, 2005 (*potential book contract*).

Bonnie Mackey is a an assistant professor of early childhood education in the School of Education, University of Houston-Clear Lake. She can be reached at mackey@cl.uh.edu. Marlene Morgan and Sarah Maxcey are graduate students in the School of Education.

Science Lab Teacher Guide

Produced by Marlene Morgan and Sarah Maxcey
Graduate students – University of Houston Clear Lake
Principle Investigator: Dr. Bonnie Mackey
Sponsored by the Environmental Institute of Houston
2004

El Método Científico

* ***Observa el mundo a tu alrededor***: haz preguntas de lo que ves.
* ***Haz una hipótesis***: una suposición razonable de lo que pudiera ocurrir. Tu predicción puede estar basada en investigación, conocimiento previo y/o experiencia.
* ***Crea un experimento***: el cual será usado para probar tu hipótesis.
* ***Recolecta información***: documentando e interpretando los resultados de tu experimento
* ***Saca conclusiones:*** necesaria para ver si tu hipótesis es correcta. Si es necesario, revisa y prueba nuevas hipótesis.
* ***Publica:*** o presenta tus resultados.

Science Lesson Plan

Title of Lesson: Who Needs You Baby?	Date: May, 2004
Author(s): Morgan, Maxcey and Lesh	School District: CCISD Campus: McWhirter Elementary
Subject Area: Science and Literacy	Grade Levels: 3rd and 4th

State Standards (Texas: TEKS)	3.1(a) 4.1(a) 3.2(b) 4.2(b) 3.2(c) 4.2(c) 3.2(d) 4.2(d) 3.4(a) 4.4(a) 3.8(a) 4.5(a) 3.8(b) 4.8(a) 3.8(d) 4.8(b) 3.9(a) 3.9(b) **LA:** *3.1,3.4, 3.8, 3.9, 3.10, 3.14, 3.15, 3.17, 3.18* **LA:** *4.1, 4.3, 4.11, 4.15, 4.16, 4.18, 4.19, 4.25*
Stated Objective(s)	Student's will find signs of animals and other living things in the schoolyard and describe ways the school environment provides those living things with what they need to survive. Students will hypothesize how organisms are dependent on each other to survive.
Anticipatory Set (Focus)	Teacher or librarian will read "The Great Kapok Tree" before the lesson. Ask open-ended questions that relate to the story to get students thinking about what organisms need to live.
Explanation	Remind students of the *Great Kapok Tree* book by asking questions about how animals and insects depend on trees and other living things in the environment to live. Students will work in groups and go outside to various trees and record living items they find. This information will be recorded in journals and measure tree width, bugs in and around trees, weight of branches on the ground. Students will work in groups to convert their outside field trip findings by drawing and labeling items on a classroom environmental bulletin board sheet. Students will hypothesize how organisms are dependent on each other to survive.
Guided Practice	Teachers will use the paper trees in the lab to demonstrate how to observe and record their findings. Bugs, moss and other items will be placed in and around the tree before the teacher discusses the lesson. Check that they understand the process they will follow before going outside by asking open-ended questions.
Independent Practice	Students go outside with pencils or pens, paper to record their findings, and hand lenses to investigate the school environment. Students examine their chosen tree(s) in groups of three or four

	people for open discussion.
Assessment or Evaluation	Students will identify and draw or label at least three living organisms found around their chosen tree.
Enrichment/Extension	Students will design an environment based on their findings from outside observations and draw them on a classroom bulletin board or chalkboard space that is covered with paper. Students could be given a journal to write and illustrate what they have observed on a daily basis over the course of the predetermined amount of time set by the teacher.
Closure	Students will be gathered back together while outside and asked open-ended questions. Questions could be: What living organisms did you find on and around the tree? What do you think this organism needs to live from the tree.
Materials	Hand lenses, paper, pens, pencils, clipboards, paper trees in lab. Various critters planted on and around the paper trees for the guided practice, white paper sheets to cover the bulletin board or chalk board in each classroom, markers for enrichment to environmental poster, scales.

Excerpts from the *Science Lab Teacher Guide* Produced by Marlene Morgan and Sarah Maxcey for McWhirter Elementary School

Texas State Envirothon

Brenda Weiser

The Canon Envirothon is North America's largest high school environmental education competition. The Envirothon is an academic, extra-curricular environmental and natural resource education program and competition designed for high school students.

Teams consist of five high school-aged students from participating U.S. states and Canadian provinces. The competition focuses on five areas of study: aquatics, forestry, soils, wildlife, and a current environmental issue, which changes every year. In addition to field experience, students also participate in an oral component focusing on a local environmental problem. This unique combination of learning experiences and breadth of study is part of what has made the Envirothon a success with students and educators. Winning state/provincial teams compete for recognition and scholarships by demonstrating their knowledge of environmental science and natural resource management.

Nine teams participated in the 2004 Texas State Envirothon on April 18 and 19 at Bear Creek Park, Houston. Six schools were represented in the fourth annual competition: Chapel Hill High School (two teams), Clear Lake High School, John Cooper High School (two teams), Paschal High School, Magnolia High School, and North Lamar High School. The competition began on Sunday afternoon at Bear Creek Park with the field test. Teams rotated through several field stations answering questions relating to each study area. To answer questions in the time allowed, teams had to think deductively, combine knowledge from all five subject areas, use the appropriate field equipment, and employ a total team effort.

Sunday evening, the teams participated in the oral component of the competition. Students were presented with information focusing on urban resource management and were asked to develop a proposal addressing the rapid growth of the northwest portion of Harris County. Areas of consideration included wildlife habitat, management of natural resources, and environmentally responsible behavior. The teams also considered the impact on economic, environmental, and societal issues such as water quality, air quality, quality of life, and transportation issues in their presentations. Dr. George Guillen, executive director of the Environmental Institute of Houston at the University of Houston-Clear Lake, presented background information on the current issue to the students. The students were then sequestered, with supervision, for four hours to work on their presentations. The presentations were delivered to a panel of judges on Monday morning.

Awards were presented to the top scoring teams on the field

***Top*—Prior to the competition, teams receive training on the use of the instruments they will encounter in the field.**
***Middle*—A team examines one of five water sources as part of the field competition's written exam.**
***Bottom*—Soil identification is part of each field station.**

1st Place: Conroe Academy of Science and Technology High School, Conroe

2nd Place: John Cooper High School–Team A, The Woodlands

(written) exam by subject, and for the top team in the oral presentation. The winners were:

- Aquatics: Chapel Hill HS–Team B
- Forestry: John Cooper HS–Team A
- Soils: Conroe Academy
- Wildlife: Conroe Academy and John Cooper HS
- Current Issue: Conroe Academy
- Oral Presentation: John Cooper HS–Team B

The overall results were based on composite scores. The winners were:

- 1st Place: Conroe Academy of Science and Technology
- 2nd Place: John Cooper HS–Team A
- 3rd Place: John Cooper HS–Team B

Conroe Academy of Science and Technology High School represented Texas at the International Canon Envirothon in West Virginia, July 26 through August 1, 2004.

Envirothon is a year round project, requiring continuous revamping. Steps are being executed to create a 2004–2005 Texas State Envirothon Steering Committee. Through this committee, decisions will be made regarding the location, creation of a study packet and test materials, finances, teacher training, and sponsorship for the 2005 Texas State Envirothon.

3rd Place: John Cooper High School–Team B, The Woodlands

Brenda Weiser is the Environmental Education Program Manager for EIH. Weiser also lectures on teacher education through the University of Houston-Clear Lake's School of Education. She can be reached at weiser@cl.uh.edu.

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