

## **Project Number 1**

Fate and Transport of Particle-Reactive Normal, **Alkylated** and **Heterocyclic**  
Aromatic Hydrocarbons

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## ABSTRACT

The overall study framework is designed to investigate the fate, transport and chemical transformations of normal, **alkylated** and **heterocyclic** aromatic hydrocarbons associated with spilled oil, operational discharges and produced water discharges in coastal marine and **estuarine** environmental systems. In the present research, the nature of the particle reactivity or sorption/desorption equilibria which control the fate, transport and chemical transformations of hydrocarbons has been investigated through: 1) studies of the sorption/desorption equilibria and kinetics of selected normal, **alkylated** and **heterocyclic polynuclear aromatic hydrocarbons (PAH)** on various sediment types (a range of organic carbon and particle sizes) over a range of **salinities**; 2) studies of the relationship between the carbon **fraction** of sediments and the **equilibrium  $K_{oc}$**  (partition coefficient) for selected normal, **alkylated** and **heterocyclic PAH**; and 3) study of the role of colloidal organic material in the facilitated transport of hydrocarbons through aquatic systems and in mediating the particle reactive **nature** of selected normal, **alkylated** and **heterocyclic PAH**. This information may be used by environmental **managers** to determine or predict the extent and spatial distribution of hydrocarbon impacts of operational and accidental discharges of hydrocarbons as the result of increased oil production in marine and **estuarine** environments.

## PROJECT GOALS AND OBJECTIVES

**The investigations** carried out under **this** research grant have been designed to test the following **hypotheses**:

- 1) Both the **kinetics** and extent of sorption of normal, **alkylated** and **heterocyclic PAHs** will be a **function** of the aqueous volatility of the the compound.
- 2) The sorptive capacity of coastal sediments for normal, **alkylated** and **heterocyclic PAHs** will be related to the organic carbon fraction of the sediment and the particle size (surface area).
- 3) Increases in salinity will result in significant increases in sorption coefficients and will result in slower resorption kinetics for normal, **alkylated** and **heterocyclic PAHs**.
- 4) Colloidal organic matter will facilitate the transport of normal, **alkylated** and **heterocyclic PAHs** in marine and **estuarine** systems and will mediate (lower) **sediment-water partition** coefficients in interstitial water in bedded sediments.

## ACCOMPLISHMENTS TO DATE

### Field Collections of Sediments

The above hypotheses have been tested using both laboratory and field assessment techniques. In laboratory studies equilibrium partition coefficients on field collected sediments are being determined using standardized procedures (Means et. al., 1979, 1980). Resorption kinetics are being investigated **using**: batch (Means et. al., 1979); dynamic (Means and Barrington, unpublished data) and **sediment** microcosms (developed as part of the present study). Studies of sorption on **colloids** are being performed using the methods of Means and **Wijayaratne**, 1982. Delays in the **identification** of study sites encountered during the **first** year were overcome and **sufficient** contaminated and uncontaminated sediments were obtained for study. Some relatively contaminated sediments were collected at Grand Isle and Pass **Fourchon**, La. on Feb. 6-8, 1990 and from the Eugene Island Block

18 OCS platform in Nov. 1989 for use in studies. These sediments have been extensively characterized for **NAH-PAH** using new analytical techniques developed as part of this grant and reported below so that sorption/resorption experiments can be carried out. A second set of OCS cores for these studies were collected surrounding two active off-shore platforms between April 17 and 19, 1990. These sediments have been extensively characterized using the *new analytical* methods for **alkylated** and **heterocyclic** PAH isomers reported below.

**Although some** information on the equilibrium sorption of PAHs to sediments (Means et.al., 1980, 1982), and **colloids** (Wijayarathne and Means, 1984) has been developed, little is **known about the kinetics of the** sorption/resorption process in marine/estuarine sediments where salinity changes may influence these processes. Also, very little is known about the competitive interactions of **colloids** and sediments in marine systems for normal, **alkylated** and **heterocyclic** PAH although such interactions have been clearly demonstrated with **PCBs** in marine sediments. We are continuing to study these complex interactions **but**, results of these experiments are still preliminary at this time.

In **order to** determine effects of previous sediment contamination on fate and transport of new contaminant inputs, attempts at labeling of compounds associated with **petrogenic** contamination was performed. The **alkylated** and **heterocyclic polynuclear** aromatic hydrocarbons (**PAHs**) were chosen to encompass a range of **solubilities** of PAH compounds and ensure adequate analytical resolution at low detection limits. **Deuteration** was chosen over **tritiation** or **<sup>14</sup>C labelling** because of cost considerations as well as handling and disposal methods. Continued attempts to synthesize **deuterated** compounds with sufficiently high degrees of **deuterium** substitution to make the compounds detectable in the mass spectrometer were unsuccessful. In order not to compromise the broader goals of the proposed **research**, we embarked upon an extensive methods development effort which was **directed** at the trace determination of a number of specific positional isomers of **alkylated** naphthalenes, phenanthrenes and dibenzothiophenes. Table 2 lists the compounds for which **trace** detection methods have been developed. The mean detection limits achieved for water samples (100 ml) and sediment samples (c2 g) using selected ion monitoring gas chromatography/mass **spectrometry** are 0.05 ppb and 0.5 ppb, respectively. The methods used are presented in the Findings section of this report. These methods have been applied to analysis of surface sediments and cores from the **field**, core sections from microcosm resorption experiments, pore water samples and dynamic resorption experiment%

#### Isolation and Concentration of Colloidal Organic Carbon from Natural Waters

We tested several methods of concentrating **suspended**, dissolved and colloidal organic carbon (**OC**) from natural waters. Our objectives were: to select a filtration method which allows us to process large volumes of water without either adding components **from** the filters themselves or retaining filterable **OC** on the filters, to minimize pretreatment of the water samples or **OC** which may change the reactive nature of the OC, and to use a system which allows flexibility in choosing **molecular** size ranges. The **Amicon** system **purchased** on the grant has been **used** to collect colloidal **organic** matter from seawater using both the hollow fiber system and a tangential flow system. This material is being used in ongoing **sorption** studies.

#### Effects of Salinity on PAH Sorption - Desorption by Sediments

In order to determine the effects of salinity on sorption of PAHs by uncontaminated sediments, we performed a series of batch sorption and resorption equilibrium isotherms. During the first year, we performed a set of batch equilibrium sorption and resorption isotherms using two **<sup>14</sup>C-labelled** compounds (**DDT** and **PCB**), two sediments of

differing organic carbon contents and four salinity regimes (0, 9, 18, and 35% salinity). Results of these experiments were discussed in the first year report. No further experiments were performed this year **but**, we plan a series of experiments using **alkylated** compounds during year three.

### Microcosm Development and Testing of PAH Desorption Kinetics

The goal of this aspect of the research was to develop a microcosm system which could be used to study the resorption of **alkylated** PAH from contaminated sediments under a variety of conditions. As suggested by the **scientific advisory board**, we wanted to be able to use the microcosms for studies involving **benthic** organisms as well as **abiotic** conditions. Figure 1 shows the microcosm design which was developed and which has been used to study resorption of **alkylated** PAH from contaminated sediments over time courses up to 120 days.

## SIGNIFICANT FINDINGS

### A. Method Development

#### 1. Sample preparation

The sediment extraction method is a modification of that described by **MacLeod**, et al. (1985), where samples of sodium sulfate and DCM are rolled for 8-16 hours, followed by decanting. This procedure is repeated three times. Twelve samples and a reagent blank are typically prepared at one time. A suite of **deuterated** PAH (Ultra Scientific, US-108) is added to each sample jar as surrogate standards to monitor extraction efficiency. The decanted DCM is filtered through sodium **sulphate**, concentrated by **rotoevaporation**, and then further concentrated under a nitrogen stream with solvent exchange to **hexane**. Final volumes range **from** 200-500  $\mu$ l. Fine granular copper was added to reduce **sulphur** interferences. Extracts **from** the tumbling procedure were not subjected to further cleanup or fractionation. Analysis of the "whole" extract was performed to allow for simultaneous estimation of aromatic and **aliphatic** hydrocarbon concentrations in one analysis.

#### 2. GC/MS Analysis

A Hewlett-Packard 5890 Gas Chromatography directly interfaced to a Hewlett-Packard 5970B Mass Selective Detector was operated using the parameters presented in Table 1. A series of linear temperature ramps was necessary for the maximal separation of isomers of **alkylated PAH's** and for separation of parent PAH compounds **from alkylated PAH's** with interfering ions, while keeping analysis time (60 min.) and band-broadening to a minimum.

Table 2 lists the target **analytes** and **deuterated** reference standards, their abbreviations, and the mass fragments used for quantitative evaluation ("primary ion") and for confirmation of identity ("confirming ion"). **Alkylated** PAH standards were purchased from **Chiron Laboratones A.S.** (Norway). The standards represent the two isomers of methyl naphthalene, all 10 of the **dimethylnaphthalene** isomers, isopropylnaphthalene and **1,6,7-trimethylnaphthalene** for the class "C3" (three substituted carbon groups) **naphthalenes**, all four possible isomers of methyl dibenzothiophene, **1,2-dimethyl dibenzothiophene** for the class "C2" dibenzothiophenes, five of five possible methyl phenanthrenes, 16 of 25 isomers of **dimethyl phenanthrene**, and **1,2,8-trimethylphenanthrene** for the class of "C3" phenanthrenes. Retention order of the **alkylated** PAH isomers was determined by preparing 10 ppm dilutions in **hexane** containing one of each type of isomer, i.e., a methyl naphthalene, a **dimethylnaphthalene**, a methyl phenanthrene, a **dimethylphenanthrene**, etc. A final **standard**, containing **all** parent

Figure 1. Microcosm design for sediment resorption studies.

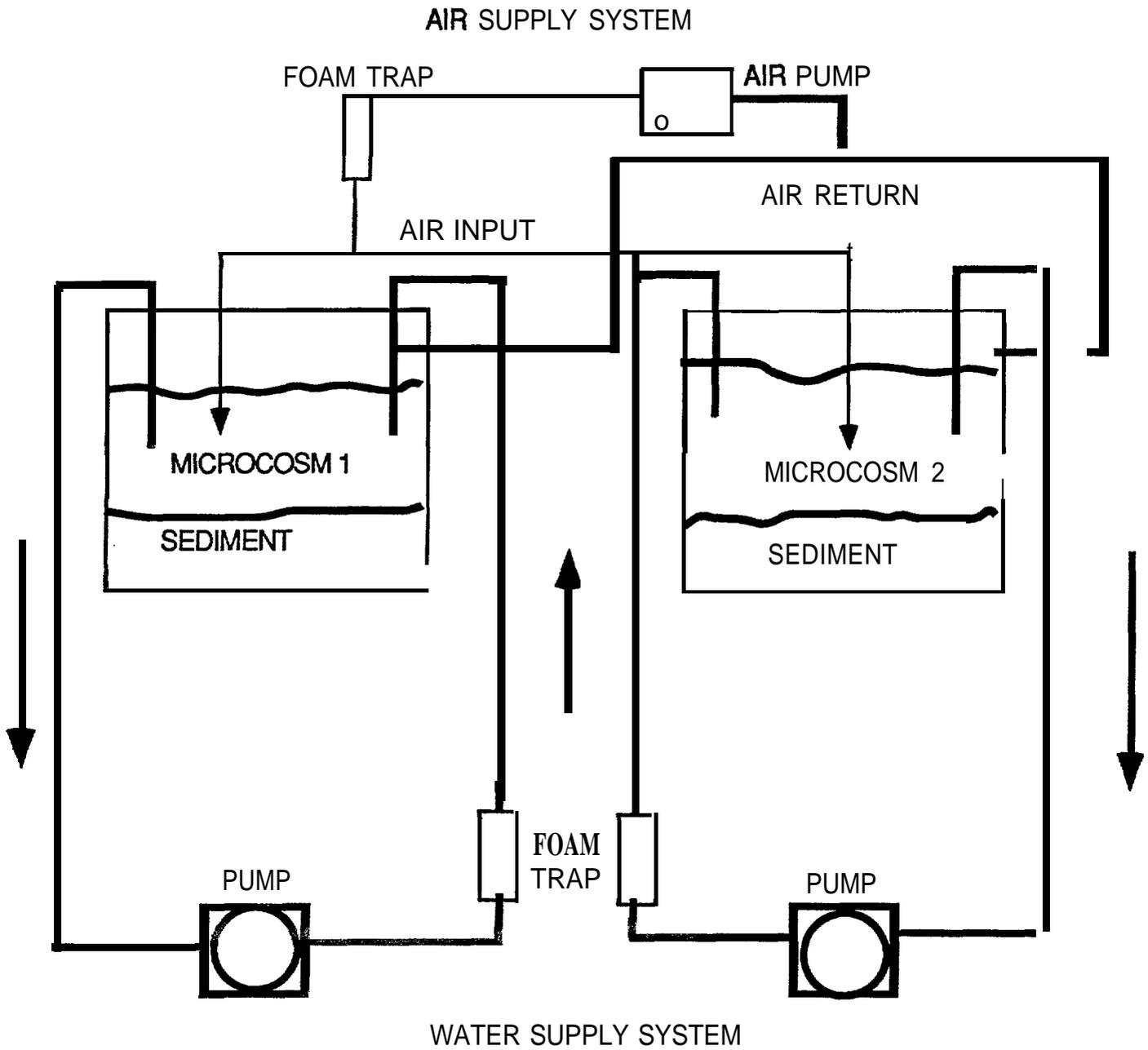


Table 1. Instrumental Parameters.

A. Heated Zones

Splitless Injection Port Temperature:	235°C.
Purge Time:	0.5 min.
GC/MS Transfer line temperature	280°C

B. Gas Chromatography Column

column:	DB-5, 30 meter, 0.25µ film thickness, 0.25 mm I.D. J&W Scientific, Inc.
Carrier Gas:	Helium
Linear velocity	40 cm/sec (butane injection at 100°C)

C. Gas Chromatography Temperature Program

Initial Column Temperature:	50°C
Time at Initial Temperature:	3 min.
Temperature Ramp #1:	6°C/min to 120°C
Temperature Ramp #2:	3°C/min to 190°C
Temperature Ramp #3	12°C/min to 280°C
Time at Final Temperature:	14.5 min.

D. Mass Spectrometer Data Acquisition

Scan Range:	45-450 amu.
Scan Rate:	1.06 scans/sec

**Table 2. Target Analytes**

Peak No.	Analyte	Abbreviation	Primary Ion	Confirming ion
1	<b>Naphthalene</b>	<b>Naphthalene</b>	128	129
2	2-Methylnaphthalene	2-MN	142	141
3	<b>1-Methylnaphthalene</b>	1-MN	142	141
4	2-Ethylnaphthalene	2-EN	156	141
5	<b>1-Ethylnaphthalene</b>	1-EN	156	141
6	<b>2,6/2,7-Dimethylnaphthalene</b>	<b>2,6/2,7-DMN</b>	156	141
7	<b>1,3/1,7-Dimethylnaphthalene</b>	<b>1,3/1,7-DMN</b>	156	141
8	<b>1,6-Dimethylnaphthalene</b>	<b>1,6-DMN</b>	156	141
9	<b>1,4/2,3-Dimethylnaphthalene</b>	<b>1,4/2,3-DMN</b>	156	141
10	<b>1,5-Dimethylnaphthalene</b>	<b>1,5-DMN</b>	156	141
11	<b>Acenaphthylene</b>	<b>Acenaphthylene</b>	152	153
12	<b>1,2-Dimethylnaphthalene</b>	<b>1,2-DMN</b>	156	141
13	<b>2-Isopropylnaphthalene</b>	<b>2-IPN</b>	170	155
14	<b>1,8-Dimethylnaphthalene</b>	<b>1,8-DMN</b>	156	141
15	<b>Acenaphthene</b>	<b>Acenaphthene</b>	153	154
16	<b>Fluorene</b>	<b>Fluorene</b>	166	165
17	<b>Dibenzothiophene</b>	<b>Dibenz.othiophene</b>	184	185
18	<b>Phenanthrene</b>	<b>Phenanthrene</b>	178	179
19	<b>Anthracene</b>	<b>Anthracene</b>	178	179
20	<b>4-Methyldibenzothiophene</b>	<b>4-MDBT</b>	198	197
21	<b>2/3-Methyldibenzothiophene</b>	<b>2/3-MDBT</b>	198	197
22	<b>1-Methyldibenzothiophene</b>	<b>1-MDBT</b>	198	197
23	<b>3-Methylphenanthrene</b>	3-MP	192	191
24	<b>2-Methylphenanthrene</b>	2-MP	192	191
25	<b>4/9-Methylphenanthrene</b>	<b>4/9-MP</b>	<b>192</b>	191
26	<b>1-Methylphenanthrene</b>	<b>1-MP</b>	192	191
27	<b>4,5-Dimethylphenanthrene</b>	<b>4,5-DMP</b>	206	191
28	<b>3,6-Dimethylphenanthrene</b>	3,6-DMP	206	191
29	<b>3,5-Dimethylphenanthrene</b>	3,5-DMP	<b>206</b>	191
29	<b>2,6-Dimethylphenanthrene</b>	<b>2,6-DMP</b>	206	191
30	<b>2,7-Dimethylphenanthrene</b>	<b>2,7-DMP</b>	206	191
31	<b>3,9-Dimethylphenanthrene</b>	<b>3,9-DMP</b>	206	191
32	<b>1,6/2,5/2,9-Dimethylphenanthrene</b>	<b>1,6/2,5/2,9-DMP</b>	206	191
33	<b>1,7-Dimethylphenanthrene</b>	<b>1,7-DMP</b>	<b>206</b>	191
34	<b>1,9/4,9-Dimethylphenanthrene</b>	<b>1,9/4,9-DMP</b>	<b>206</b>	191
35	<b>Fluoranthene</b>	<b>Fluoranthene</b>	<b>202</b>	101
36	<b>1,5-Dimethylphenanthrene</b>	<b>1,5-DMP</b>	<b>206</b>	191
37	<b>1,8-Dimethylphenanthrene</b>	<b>1,8-DMP</b>	<b>206</b>	191
38	<b>1,2-Dimethylphenanthrene</b>	1,2-DMP	<b>206</b>	191
39	<b>9,10-Dimethylphenanthrene</b>	9,10-DMP	<b>206</b>	191
40	<b>Pyrene</b>	<b>Pyrene</b>	<b>202</b>	101
41	<b>Benzo(a)anthracene</b>	<b>Benzanthracene</b>	<b>228</b>	226
42	<b>Chrysene</b>	<b>Chrysene</b>	<b>228</b>	226
43	<b>Benzo(b)fluoranthene</b>	<b>Benzo(b)fluor</b>	<b>252</b>	253
44	<b>Benzo(k)fluoranthene</b>	<b>Benzo(k)fluor</b>	<b>252</b>	253
45	<b>Benzo(a)pyrene</b>	<b>Benzo(a)pyrene</b>	<b>252</b>	253

Table 2. (cont'd.)

Peak No.	Analyte	Abbreviation	Primary Ion	Confirming ion
46	Indeno(1,2,3-cd)pyrene	Indenopyrene	276	278
47	Dibenz(a,h)anthracene	Dibenzanthracene	278	276
48	Benzo(g,h,i)perylene	Benzoperylene	276	278
<b>Deuterated Internal/Surrogate Standards</b>				
	d8-Naphthalene	d8-Naph	136	
	d10-Acenaphthene	d10-Ace	164	
	d10-Phenanthrene	d10-Phen	188	
	d12-Chrysene	d12-Chrys	240	
	d12-Perylene	d12-Peryl	264	

PAH compounds (Ultra Sci., US-106), alkylated PAH, and deuterated surrogate standards was prepared at 5 ppm by dilution with dichloromethane and was analyzed with hexamethylbenzene (HMB) as an internal standard. HMB was also coinjected into the GC/MS with each sample aliquot to monitor performance of the instrument and injection technique, but was not used in the calculations of analyte final concentrations. Quantifications are made using the internal standard (I.S.) method based on the corresponding deuterated surrogate standard for each analyte, as shown in Table 3.

Chromatographic data (Table 3) for parent and alkylated PAH were obtained from 20 daily calibration analyses of the standard mixture. In addition to the analytes listed, C4- and C5-naphthalenes, C3-dibenzothiophenes, and C3-phenanthrenes can be estimated using relative response factors generated from similar class analytes represented by the standard mixture. For example, the C3-dibenzothiophenes are estimated using the relative response factor for C2-dibenzothiophenes, 1,2-dimethyldibenzothiophene. In this way, we are able to quantitate additional compound classes without the considerable expense of these additional standards. C1-C3-fluorenes are estimated using the response factor from the parent compound.

### 3. Quality Assurance/Quality Control

Standard QA/QC procedures are followed, including analysis of duplicate and spiked samples, and daily tuning and calibration of the GC/MS system. Table 4 shows the reproducibility of the extraction and analysis method. Data was obtained using our in-house laboratory reference sediment. Table 5 presents results from the analysis of three samples collected near produced water discharges and spiked with the standard mixture just prior to extraction. Table 6 shows an example from the database that has been accumulated for sediments collected near produced water discharge sites in south Louisiana.

### **B. Field Applications**

An extensive body of information has been acquired for surface and depth sections of cores collected seasonally at various distances from produced water discharges located at Pass Fourchon, Bayou Rigaud and Eugene Island (OCS) in South Louisiana. Figures 2-5 show examples of data for alkylated PAH homologs in samples collected at Pass Fourchon during two seasons. Variations in the relative concentrations of alkylated and heterocyclic PAH can be seen at various distances from the discharge site, however, similarities in pattern are apparent between the two seasons shown. These figures illustrate the

complexity of processes impacting the sediments, such as discharge parameters and weather patterns. Figure 6 shows depth profile data for cores taken at a single site over four seasons, and illustrate again the dynamic nature of processes affecting these sediments. Note the similarity between cores from three seasons (one season had no detectable concentrations of any PAH except phenanthrene). The pattern of a subsurface decrease followed by an increase in concentrations lower in the core is often seen, and may indicate that chemical processes have more effect on PAH distributions than discharge parameters or sedimentation rates. We are applying ratioing of analytes in order to further examine this data to determine if there are selective mobilization/removal processes which may be active in the field for various members of the class of alkylated and heterocyclic PAH. These field data are also being compared to microcosm data to compare and further elucidate transport processes.

Table 3. Chromatographic Data for Target Analytes

ANALYTE	1.S.	MEAN R.R.T*	RSD R.R.T. %	MEAN RRF	RSD RRF %	Ave. Est. DL ng
Naphthalene	d8-Naph	1.005	0.012%	0.80	22%	0.1
2-MN	"	1.223	0.019%	1.02	2.9%	0.3
1-MN	"	1.259	0.018%	1.12	3.2%	0.3
2-EN	d10-Ace	0.878	0.025%	1.29	3.6%	0.7
1-EN	"	0.883	0.012%	1.45	4.1%	0.8
2,6/2,7-DMN	"	0.894	0.018%	0.80	3.4%	0.4
1,3/1,7-DMN	"	0.915	0.010%	0.67	2.3%	0.3
1,6-DMN	"	0.920	0.012%	0.74	3.9%	0.4
1,4/2,3-DMN	"	0.943	0.010%	0.87	2.9%	0.5
1,5-DMN	"	0.948	0.013%	0.87	3.9%	0.3
Acenaphthylene	"	0.956	0.009%	0.49	2.4%	0.1
1,2-DMN/2-IPN	"	0.966	0.039%	1.29	4.2%	0.2
2-IPN	"	0.969	0.012%	1.80	3.6%	1.0
1,8-DMN	"	0.996	0.012%	0.88	3.2%	0.4
Acenaphthene	"	1.008	0.013%	0.71	2.3%	0.2
Fluorene	"	1.155	0.023%	0.64	4.6%	0.2
Dibenzothiophene	d10-Phen	0.976	0.016%	0.80	1.6%	0.2
Phenanthrene	"	1.005	0.009%	0.92	2.1%	0.1
Anthracene	"	1.015	0.009%	0.93	2.2%	0.1
4-MDBT	"	1.081	0.014%	1.26	3.4%	0.3
2/3-MDBT	"	1.101	0.012%	1.23	3.3%	0.3
3-MP	"	1.124	0.010%	1.24	4.5%	0.3
1-MDBT	"	1.125	0.010%	1.49	3.8%	0.4
2-MP	"	1.129	0.013%	1.06	3.5%	0.3
4/9-MP	"	1.149	0.010%	1.31	4.5%	0.3
1-MP	"	1.153	0.012%	1.07	7.1%	0.2
4,5-DMP	"	1.178	0.032%	2.46	27.9%	0.2
3,6-DMP	"	1.220	0.040%	1.56	7.3%	0.4
3,5-IMP	"	1.223	0.040%	1.98	8.3%	0.3
2,6-DMP	"	1.225	0.039%	0.92	7.1%	0.3
2,7-DMP	"	1.228	0.042%	1.08	6.5%	0.2
3,9-DMP	"	1.236	0.042%	1.16	7.6%	0.3
1,6/2,5/2,9-DMP	"	1.240	0.041%	1.44	5.7%	0.3
1,7-DMP	"	1.243	0.044%	1.06	7.2%	0.2

Table 3. (cont'd.)

ANALYTE	I.S.	MEAN R.R.T*	RSD R.R.T. %	MEAN RRF	RSD RRF %	Ave. Est. DL ng
1,9/4,9-DMP	"	1.249	0.042%	<b>1.47</b>	<b>6.5%</b>	<b>0.3</b>
Fluoranthene	"	1.250	0.042%	<b>0.77</b>	<b>7.1%</b>	<b>0.1</b>
1,5-DMP	"	1.252	0.043%	<b>1.69</b>	<b>7.6%</b>	<b>0.3</b>
1,8-DMP	"	1.256	<b>0.046%</b>	<b>1.11</b>	<b>8.0%</b>	<b>0.3</b>
1,2-DMP	"	<b>1.264</b>	0.048%	1.49	8.1%	0.2
9,1 O-DMP	"	1.275	0.050%	1.56	9.0%	0.3
Pyrene	"	1.276	0.047%	0.79	10.7%	0.1
Benzantracene	<b>d12-Chrys</b>	0.999	0.005%	0.82	2.9%	0.1
Chrysene	"	1.001	0.032%	0.89	2.6%	0.1
Benzo(b)fluor	<b>d12-Peryl</b>	0.972	0.017%	0.62	9.7%	0.2
Benzo(k)fluor	"	0.974	0.020%	0.58	9.2%	0.2
Benzo(a)pyrene	"	0.995	0.009%	0.79	3.7%	0.3
Indenopyrene	"	1.107	0.05190	1.14	25.7%	1.3
Dibenzanthracene	"	1.112	0.043%	1.16	24.8%	3.5
Benzoperylene	"	1.138	0.073%	1.17	33.3%	1.0

IS= Internal Standard Reference Compound

R.R.T. = Relative retention time=  $R.T. x / R.T. IS$

R.R.F. = Relative response factor=  $(Cone. x / Area x) / (Cone. IS / Area IS)$

\* n=20, data from daily calibrations over a 2-month period.

Table 4. Replicate analyses of a laboratory reference sediment.

Analyte	A-01	A-02	A-03	MEAN	STD.	R.S.D.
	rig/g	ng/g	ng/g	ng/g	DEV.	%
DET. LIMIT*	<b>7.1</b>	<b>5.9</b>	<b>6.0</b>	6.3	<b>0.6</b>	<b>11%</b>
Naphthalene	8.6	10	<b>11</b>	9.9	<b>1.2</b>	12%
2-MN	19	<b>19</b>	<b>23</b>	20	<b>2.3</b>	<b>11%</b>
1-MN	21	<b>20</b>	<b>34</b>	25	<b>7.8</b>	31%
2-EN	<b>trc</b>	<b>trc</b>	<b>nd</b>	<b>trc</b>	NA	<b>NA</b>
1-EN	<b>trc</b>	<b>nd</b>	<b>nd</b>	<b>nd</b>	NA	<b>NA</b>
2,6/2,7-DMN	25	22	19	22	<b>3.0</b>	14%
1,7/1,3-DMN	18	20	20	19	<b>1.2</b>	<b>6%</b>
1,6-DMN	17	18	15	17	<b>1.5</b>	<b>9%</b>
2,3/1,4-DMN	<b>trc</b>	<b>6.9</b>	<b>10</b>	8.5	<b>2.2</b>	<b>26%</b>
1,5-DMN	8.1	9.1	9.3	8.8	<b>0.64</b>	7%
Acenaphthylene	<b>nd</b>	<b>trc</b>	<b>trc</b>	<b>trc</b>	NA	NA
1,2-DMN/2-IPN	<b>tr</b>	<b>tr</b>	<b>tr</b>	<b>tr</b>	NA	NA
2-IPN	<b>nd</b>	<b>nd</b>	<b>nd</b>	<b>nd</b>	NA	NA
1,8-DMN	<b>nd</b>	<b>nd</b>	<b>nd</b>	<b>nd</b>	NA	NA
Acenaphthene	16	14	15	15	1.0	7%
Fluorene	22	22	21	22	0.58	3%
Dibenzothiophene	18	16	14	16	2.0	13%
Phenanthrene	58	<b>58</b>	<b>59</b>	58	0.58	1%
Anthracene	26	<b>30</b>	<b>27</b>	28	2.1	8%
4-MDBT	40	<b>39</b>	<b>35</b>	38	2.6	7%
2/3-MDBT	26	<b>25</b>	<b>23</b>	25	1.5	6%
1-MDBT	15	18	17	17	1.5	9%
3-MP	22	21	18	20	2.1	10%
2 - w	19	17	<b>20</b>	19	1.5	8%
4/9-MP	25	<b>19</b>	<b>29</b>	24	5.0	21%
1-MP	14	<b>trc</b>	14	14	0.21	2%
3,6-DMP	32	<b>29</b>	<b>26</b>	29	3.0	10%
3,5-DMP	27	<b>30</b>	<b>26</b>	28	2.1	8%
2,6-DMP	<b>nd</b>	<b>nd</b>	<b>nd</b>	<b>nd</b>	NA	NA
2,7-DMP	13	12	11	12	<b>1</b>	<b>8%</b>
3,9-DMP	<b>53</b>	<b>57</b>	<b>48</b>	53	4.5	9%
1,6/2,9/2,5-DMP	40	37	37	38	1.7	5%
1,7-DMP.	<b>trc</b>	<b>trc</b>	<b>trc</b>	<b>trc</b>	NA	NA
1,9/4,9-DMP	<b>8.5</b>	<b>8.0</b>	<b>7.4</b>	8.0	0.55	<b>7%</b>
Fluoranthene	420	430	390	413	21	5%
1,5-DMP	<b>nd</b>	<b>nd</b>	<b>nd</b>	<b>nd</b>	NA	NA
1,8-DMP	<b>nd</b>	<b>nd</b>	<b>nd</b>	<b>nd</b>	NA	NA
1,2-DMP	<b>nd</b>	<b>6.3</b>	<b>7.2</b>	6.8	0.64	<b>9%</b>
9,1 O-DMP	<b>nd</b>	<b>nd</b>	<b>nd</b>	<b>nd</b>	NA	NA
Pyrene	440	<b>450</b>	<b>390</b>	427	32	8%
Benzo(a)anthracene	91	87	82	87	4.5	5%
Chrysene	131	133	126	130	3.6	<b>3%</b>
Benzo(b)fluoranthene	68	61	57	62	5.6	9%
Benzo(k)fluoranthene	150	160	140	150	10	7%

Table 4. (cont'd.)

Analyte	A-01	AU2	A-03	MEAN	STD. DEV.	R.S.D.
	ng/g	ng/g	ng/g	ng/g		%
Benzo(a)pyrene	41	24	31	32	8.5	27%
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	NA	NA
Dibenz(a,h)anthracene	43	65	23	44	21	48%
Benzo(g,h,i)perylene	nd	nd	nd	nd	NA	NA
<b>Average</b>						<b>11%</b>
<b>R.S.D.</b>						

Table 5. Recovery of target analytes spiked into sediment from near produced water discharges.

ANALYTE	Spike Amount ng/ul	EW9	EW3	PF400N F	MEAN
		% Recov	% Recov	% Recov	RECOV
d8-Naph	20	63%	64%	39%	5s%
d10-Ace	20	74%	82%	52%	69%
d10-Phen	20	94%	149%	35%	93%
d12-Chrys	20	67%	99%	20%	62%
d12-Peryl	20	76%	68%	22%	55%
Naphthalene	20	75%	77%	85%	79%
2-MN	20	73%	88%	95%	86%
1-MN	20	80%	91%	104%	92%
2-EN	20	90%	97%	112%	100%
1-EN	20	87%	86%	129%	101%
2,6/2,7-DMN	40	92%	101%	99%	98%
1,3/1,7-DMN	39	94%	104%	86%	95%
1,6-DMN	20	97%	102%	112%	104%
1,4/2,3-DMN	40	100%	108%	103%	104%
1,5-DMN	20	97%	102%	100%	100%
Acenaphthylene	20	90%	105%	84%	93%
1,2-DMN/2-IPN	38	93%	106%	132%	110%
2-IPN	18	89%	98%	139%	109%
1,8-DMN	19	105%	114%	144%	121%
Acenaphthene	20	104%	108%	124%	112%
Fluorene	20	116%	130%	116%	121%
Dibenzothiophene	10	87%	83%	104%	91%
Phenanthrene	20	81%	91%	106%	93%
Anthracene	20	78%	100%	98%	92%
4-MDBT	10	85%	100%	81%	88%
2/3-MDBT	16	88%	111%	65%	88%
3-MP	20	84%	116%	58%	86%
1-MDBT	14	81%	103%	33%	72%
2-MP	30	79%	97%	72%	83%
4/9-MP	30	77%	110%	50%	79%
1-MP	20	81%	111%	48%	80%
3,6-DMP	10	94%	144%	8%	82%
3,5-DMP	10	80%	NA	NA	80%
2,6-DMP	10	69%	91%	8%	56%

**Table 5.** (cent' d.)

<b>ANALYTE</b>	<b>Spike Amount ng/μl</b>	<b>EW9 % Recov</b>	<b>EW3 % Recov</b>	<b>PF400N F % Recov</b>	<b>MEAN RECOV</b>
2,7-DMP	5	75%	108%	31%	71%
3,9-DMP	10	54%	122%	-23%	51%
1,6/2,9/2,5-DMP	32	72%	124%	17%	71%
1,7-IMP	11	76%	121%	18%	71%
1,9/4,9-DMP	18	82%	123%	24%	76%
Fluoranthene	20	72%	124%	21%	72%
1,5-DMP	8	70%	131%	0%	67%
1,8-DMP	9	82%	123%	17%	74%
1,2-DMP	10	73%	133%	0%	69%
9,1 O-DMP	10	67%	133%	30%	76%
Pyrene	20	60%	117%	21%	66%
Benzoanthracene	20	73%	108%	120%	100%
Chrysene	20	75%	108%	127%	103%
Benzo(b)fluor	20	63%	77%	212%	118%
Benzo(k)fluor	20	58%	86%	112%	85%
Benzo(a)pyrene	20	62%	80%	0%	47%
Indenopyrene	20	60%	133%	0%	64%
Dibenzanthracene	20	60%	133%	0%	64%
Benzoperylene	20	70%	149%	0%	73%
AVE NAPHS=					101%
AVE DBTS =					83%
AVE PHENS=					73%

**Table 6.** Example of a dataset for samples collected in the vicinity of produced water discharges in South Louisiana.

Analyte	PF--400	NORTH				SOUTH
		600	800	900	1000	600
Naphthalene (ng/g)	31	nd	37	tr	5.1	tr
2-Methylnaph.	trc	nd	68	nd	8.4	trc
1-Methylnaph.	20	41	84	tr	6.6	trc
2-Ethyl-naph.	nd	nd	43	nd	nd	nd
1-Ethyl-naph.	nd	nd	nd	nd	nd	nd
2,6/2,7-Dimethylnaph.	140	300	300	tr	trc	trc
1,3/1,7-DMN	140	370	230	nd	6.2	trc
1,6-DMN	nd	tr	120	nd	trc	nd
1,4/2,3-DMN	93	200	110	nd	trc	tr
1,5-DMN	32	72	46	nd	nd	nd
1,2-DMN/2-IPN	nd	trc	trc	nd	nd	nd
2-IPN	nd	be	nd	nd	nd	nd
1,8-DMN.	nd	nd	nd	nd	nd	nd
C1-Naphthalenes, total	20	41	150	tr	15	tr
C2-Naphthalenes, total	410	940	850	tr	6	tr
C3-Naphthalenes	3,100	6,400	3,200	nd	33	trc
C4-Naphthalenes	5,300	5,000	920	nd	tr	nd
C5-Naphthalenes	1,800	tr	1,100	nd	tr	t-d
Acenaphthylene	nd	nd	nd	nd	nd	nd
Acenaphthene	nd	nd	nd	nd	trc	nd
Fluorene	47	77	77	tr	nd	nd
C1-Fluorenes	250	500	410	nd	tr	tr
C2-Fluorenes	500	1600	630	nd	tr	tr
C3-Fluorenes	890	1400	720	nd	36	160
Dibenzothiophene	tr	27	31	tr	nd	nd
4-MDBT	120	270	150	trc	trc	15
2/3-MDBT	32	120	65	trc	nd	nd
1-MDBT	30	72	25	nd	nd	nd
C1-Dibenzothiophenes, total	180	460	240	tr	tr	15
C2-Dibenzothiophenes, est.	1,000	1,400	670	be	7.0	150
C3-Dibenzothiophenes, est.	1,200	1,500	860	nd	11	330
Phenanthrene	nd	nd	180	10	18	14
3-MP	230	540	320	tr	7.8	tr
2-MP	35	120	270	tr	6.0	tr
4/9-MP	240	570	364	nd	8	tr
1-MP	150	310	260	nd	tr	tr
3,6-DMP	330	490	270	trc	11	49
3,5-DMP	nd	nd	nd	Id	nd	nd
2,6-DMP	150	310	180	tr	5	tr
2,7-DMP	170	250	110	tr	5	37
3,9-DMP	610	1,078	530	be	15	74
1,6/2,5/2,9-DMP	480	800	400	tr	12	65
1,7-DMP	160	320	160	tr	5	tr
1,9/4,9-DMP	190	270	150	nd	b	31
1,5-DMP	nd	nd	nd	nd	nd	nd
1,8-DMP	78	120	75	nd	tr	18
1,2-DMP	51	98	47	nd	tr	nd
9,1 O-DMP	nd	nd	36	nd	nd	tr
C1-Phenanthrenes, total	660	1,500	1,200	tr	22	tr

Table 6. (cont'd.)

Analyte	PF--40C	NORTH				SOUTH
		600	800	900	100C	600
C2-Phenanthrenes, total	2,20C	3,700	2,000		tr 53	270
C2-Phenanthrenes, est.	2,30C	3,900	2,000		trc 61	300
C3-Phenanthrenes, est.	2,40C	3,400	1,800		tr 44	610
Anthracene	nd	nd	27		3.5 3.7	12
Fluoranthene	180	190	110	23	54	110
Pyrene	150	190	110	20	56	110
Benzoanthracene	74	94	46	10	13	38
Chrysene	230	340	140	11	15	70
Benzo(b)fluoranthene	nd	nd	nd	8.0	15	nd
Benzo(k)fluoranthene	nd	nd	nd	6.0	8.2	nd
Benzo(a)pyrene	nd	nd	nd	7.4	tr	nd
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd	nd
Dibenzo(a,h)anthracene	nd	nd	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd	nd	nd
Total Pyrogenic PAH	710	920	760	99	190	350
Total Pyrogenic PAH	20,010	28,041	14,750	tr	234	1,565
Total PAH	21,000	29,000	16,000	99	430	1,900
FFPI	0.92	0.92	0.90	0.05	0.52	0.80
Saturated Hydrocarbons						
Resolved	32,000	57,000	68,000	480	2,100	3,600
unresolved	458,000	523,000	302,000	1,720	2,200	106,400
Total	490,000	580,000	370,000	2,200	4,300	110,000
MDL (ng/g)	19	24	21	2.5	3.6	9.9

MDL: Minimum Detection Lim

nd: Not detected

tr: Trace; one ion present, but below detection limits

trc: Trace confirmed; two ions present, but below detection limits

n/a: not analyzed

## C. Microcosm Studies

### 1. Design of the Seth<sup>™</sup> Merit Microcosm

The microcosm test apparatus was designed with the intent to limit possible complicating variability while retaining a necessary amount of flexibility. The test apparatus (Figure 1) consists of two 5 gallon aquaria in which are situated 28 clear, graduated glass sample jars of 110 ml volume, 24 of which have been filled with 100 ml of the test sediment. The jars have been arranged in four rows of seven with the four corner sample jars not filled with sediment but filled with cleaned glass spheres. Other sub-microcosms may also be used or a single bed of sediment can be used in the system. The pumping system can accommodate up to 6 additional microcosms.

The remaining volume of the tanks is filled, except for a 2 cm depth air space below the lids, with water having a salinity of 14 parts-per-thousand prepared from deionized water and Instant Ocean in this particular experiment. This water is circulated in such a manner to

effect five water exchanges (volume of aquarium) in a **24** hour period. This exchange rate is satisfactory for biological experiments as well. The water enters and exits from opposite ends of the tanks via four nozzles which are situated 1 cm above the sample jar tops and are aligned with the 4 columns of sample jars that run the length of the aquaria. The nozzles are **manifolded** to a common carrier line that feeds or accepts flow from the nozzles evenly.

Upon exiting the tanks the water passes through a foam plug trap which removes the hydrocarbons that may have **desorbed** into solution. The water is then introduced to the other tank that **from** which it was removed by the action of a peristaltic pump and the manifold/nozzle system previously **discussed**. The process of mixing the waters between tanks should prevent any variability in the waters flowing over the samples. The water volume of the system as well as the **arrangement** of the sample jars is preserved in the tanks after sampling events by replacing the samples taken with jars filled with clear glass spheres.

The potential for flow variation over the samples necessitated two design features. The first, already mentioned, is that the corner sample jars in the aquaria were not used due to poor water flow characteristics in these areas. Secondly, the flow and mixing within the tanks is enhanced by the use of an air-bubbling system. The 2200 ml of air per minute that are pumped into each tank via a submerged airstone create mixing and flows throughout the tank. The air from both tanks is recirculated constantly as the air that is pumped into the water is drawn **from** the airspace above the water and **passed** through a urethane foam plug trap to remove any volatilized hydrocarbons.

The entire microcosm test apparatus is operated in a compartmentalized enclosure to exclude light and to provide thermal stability. The enclosure is only opened for brief periods for sampling and maintenance procedures which are performed under low light conditions.

## 2. Modifications of Analytical Methods for Sediment Desorption Experiments

### Extraction of *microcosm* soil cores

Two methods of extraction were evaluated for preparation of sediment **core** samples. The **method** chosen for use is as follows: Three core jars were **removed from** each microcosm tank at sampling times of 0, 1,3,7, 14,28,60 and 120 days, for a total of 8 samples. The jars were capped and refrigerated until the day before extraction, when **the** overlying water was removed and the capped jar frozen overnight at -20°C. For extraction, the jar was broken and the frozen core placed in a coring device designed for these experiments. The device consisted of a **longform** beaker, with the same diameter as the core jars, to which a caliper was attached. The frozen **core** was placed into the device top side down and a glass plunger pushed through from the opposite end to force the core against a scraper while aligned with the caliper. The **core** was scraped against Stanley **Sureform** scrapers, a separate scraper for each 2-mm section, and which were **sonicated** in DCM and baked at **200°C** overnight prior to each use. The scrapers were supported over 500 ml tared jars and the soil allowed to fall into the jar for each section. Residual soil on the scrapers was removed by tapping the scrapers against the lip of the jars. A **subsample** of --0.5 gm was removed for dry-weight determination and the jar reweighed to obtain the wet weight of the sample. Wet weights were typically 2-3 g and moisture content averaged **60%**, and was generally 1-2% higher in the top sections. **Dichloromethane** was added to each jar, then an **aliquot** of the **deuterated surrogate** standards, and finally 30 gm of sodium sulfate was mixed in thoroughly using a stainless steel spatula. The jars were **sonicated** for 10 minutes in an ice-coded bath, and the solvent decanted through sodium sulfate. This procedure was repeated three times. **The** resulting extract was concentrated as described previously and sulfur removed by activated copper.

### **GC/MS analysis of microcosm extracts and determination of resorption rates for alkylated PAH**

Extracts were analyzed by **GC/MS** operated in the selected ion monitoring mode for enhanced sensitivity of the target analytes, utilizing the same temperature program as previously described for the GC. The standard mixture was diluted to 1 ppm for calibration of the instrument. Injections into the **GC** were made by **autosampler**, and **hexamethylbenzene** was added to **each extract** to monitor instrument performance. Figure 7 shows an example of data obtained for cores representing a "0-day" sample (**ie.**, cores were capped and stored immediately after the sediments were bedded), a day-28 core and a day-60 core taken **from the microcosm tanks**. **In** spite of the lack of treatment of the "**0-day**" samples, concentrations of **analytes were significantly** lower in the top segment of the core. This may be the result of **freezing** the core, or due to rapid resorption into overlying water that separated **from** the sediment during the bedding process. The data for the day 28 core shows that resorption of some PAHs is occurring **from** the top sections of the core while some other compounds such as **1-ethylnaphthalene** (1-EN) appear to be unchanged with depth. By day 60, several of the dimethylnaphthalenes are greatly depleted in the core while 1-EN is still found at very similar concentrations with depth, Figure 8 shows the ratios of several dimethylnaphthalenes to 1-EN as a **function** of depth and core age in the resorption microcosm. These data suggest that while the ratios of these **alkylated** species remain relatively constant with depth, they are increasing with time. From these data and other data obtained on these and other cores, we are developing estimates of the resorption rate constants of **alkylated** and **heterocyclic** PAHs **from** sediments under **different conditions** of salinity, **OC** and **colloid** enrichments. Further, because of the new analytical methodology which we have developed and **employed**, we are able to make several independent estimates of these rates for several positional isomers of the same compound (**ie.** 10 dimethylnaphthalenes) having similar sorption constants and aqueous volatility.

### **PROBLEMS OR DELAYS ENCOUNTERED AND PROPOSED SOLUTIONS**

The primary delays incurred in the projects thus far have been in the identification and sampling of active off-shore produced water discharge sites. Miscommunication with the principal investigator of another project prevented **us from collecting any further cores from** these sites during the year. However, with the initiation of the joint project with Dr. Winston which contains its own ship funds we plan to revisit some of these OCS sites in the summer of **1991**.

**The salinity** isotherms were repeated several times in order to **verify** that unexpected trends in the data are real.

### **REVISED SCHEDULE FOR REMAINDER OF THE PROJECT**

**Although** some **delays** have been incurred during the first two years of the **project**, the addition of a doctoral student funded by a **University** Fellowship and a second **masters** student **funded by** a teaching assistantship **to the team** has helped to put the project back on schedule. Further, Dr. Means has devoted an additional 15-20% of his time to this effort in conducting experiments and will continue to do so in the **third** year of the study. **All** objectives will be met.

### **PROJECT PARTICIPANTS**

Dr. Jay C. Means, Professor and Principal Investigator-study design, data interpretation  
Ms. Jing-wen Ma, Graduate **student**, ENVS-sorption/desorption experiments

Ms. Debra **McMillin**, Res. Assoc., **ENVS-analytical** methods development (**c.v.** attached)  
Mr. William **Glover**, Graduate student, **CHEM-microcosm** design, resorption experiment

#### RELATED PUBLICATIONS AND PRESENTATIONS

- Daniels, C.B.** and **J.C.** Means. Assessment of the **genotoxicity** of produced water discharges associated with oil and gas production using a fish egg and larval test. *Marine Environmental Research*. **28:303-307.1990.**
- Daniels, C.B.**, **C.B.** Henry and **J.C.** Means. Coastal oil drilling produced waters: Chemical characterization and assessment of the **genotoxicity** using **chromosomal** aberrations in *Cyprinodon variegates*. pp 356-371 in **Aquatic Toxicology and Risk Assessment**. Landis and Van Der **Schalle, eds.** ASTM, Philadelphia% PA, 1990.
- Sigleo, A.C.** and **J.C.** Means. Organic and inorganic components of **estuarine colloids**: implications for transport of pollutants. *Rev. Environ. Toxicol. Contam.* 112:123-147. 1990.
- St. Pe', K. M, **J.C.** Means, C. Milan, M. **Schenkler** and S. Courtney. "An Assessment of Produced Water Impacts to Low-Energy, Brackish Water Systems in Southeast Louisiana A Project Summary". pp 31-42, **Proc.** 1st International. Symposium. **Oil and Gas Waste Management**, New Orleans, **LA, 1990.**
- Rabalais, N.N.**, **J.C.** Means and **D.F.Boesch.** "Fate and Effects of Produced Water Discharges in Coastal Environments". pp 503-514, **Proc.** 1st. International. Symposium **Oil and Gas Waste Management**, New Orleans, LA, 1990.
- Means, J. C., C. Milan and **D.J. McMillin.** **Bioaccumulation** of produced water associated aromatic hydrocarbons by **estuarine** invertebrates. *Marine Environmental Research* (*in press*). 1991.

In addition, several abstracts covering some aspects of this work and other MMS **funded** research on produced water transport and fate studies have been presented or accepted for presentation at a variety of symposia and national meetings.

Figure 2. Selected **alkylated naphthalenes** concentrations in surface sediments collected at Pass Fourchon, Louisiana, at two time periods.

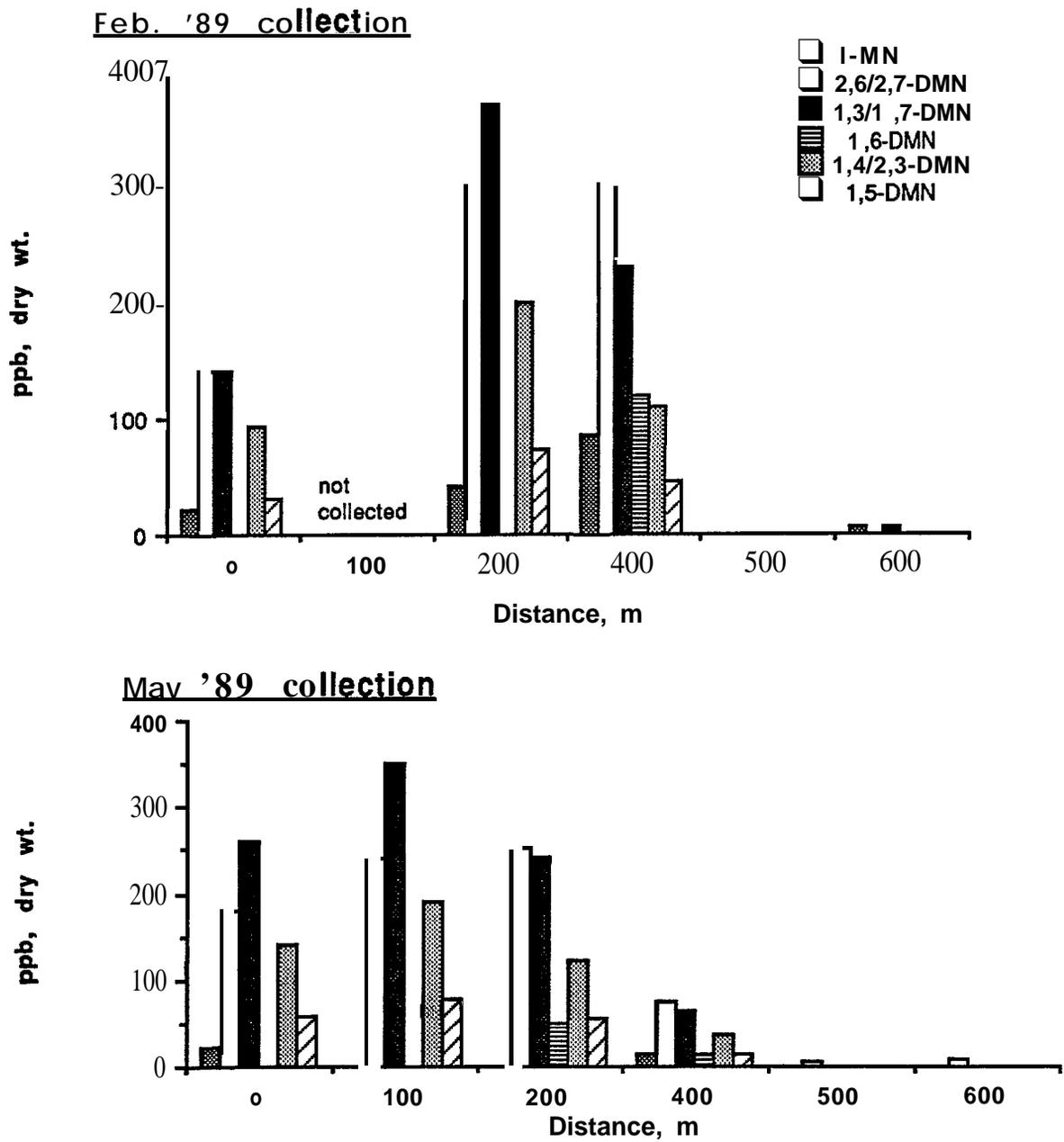


Figure 3. Methyl dibenzothiophenes concentrations in surface sediments collected at Pass Fourchon, Louisiana, at two time periods.

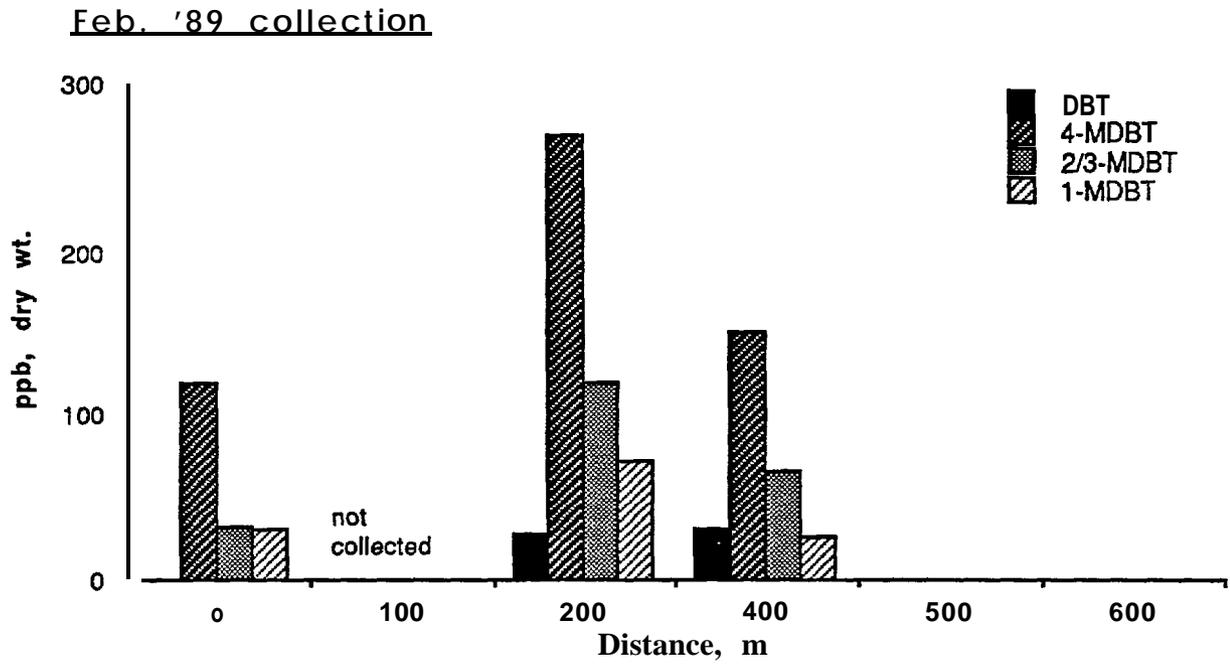


Figure 3. (cont'd)

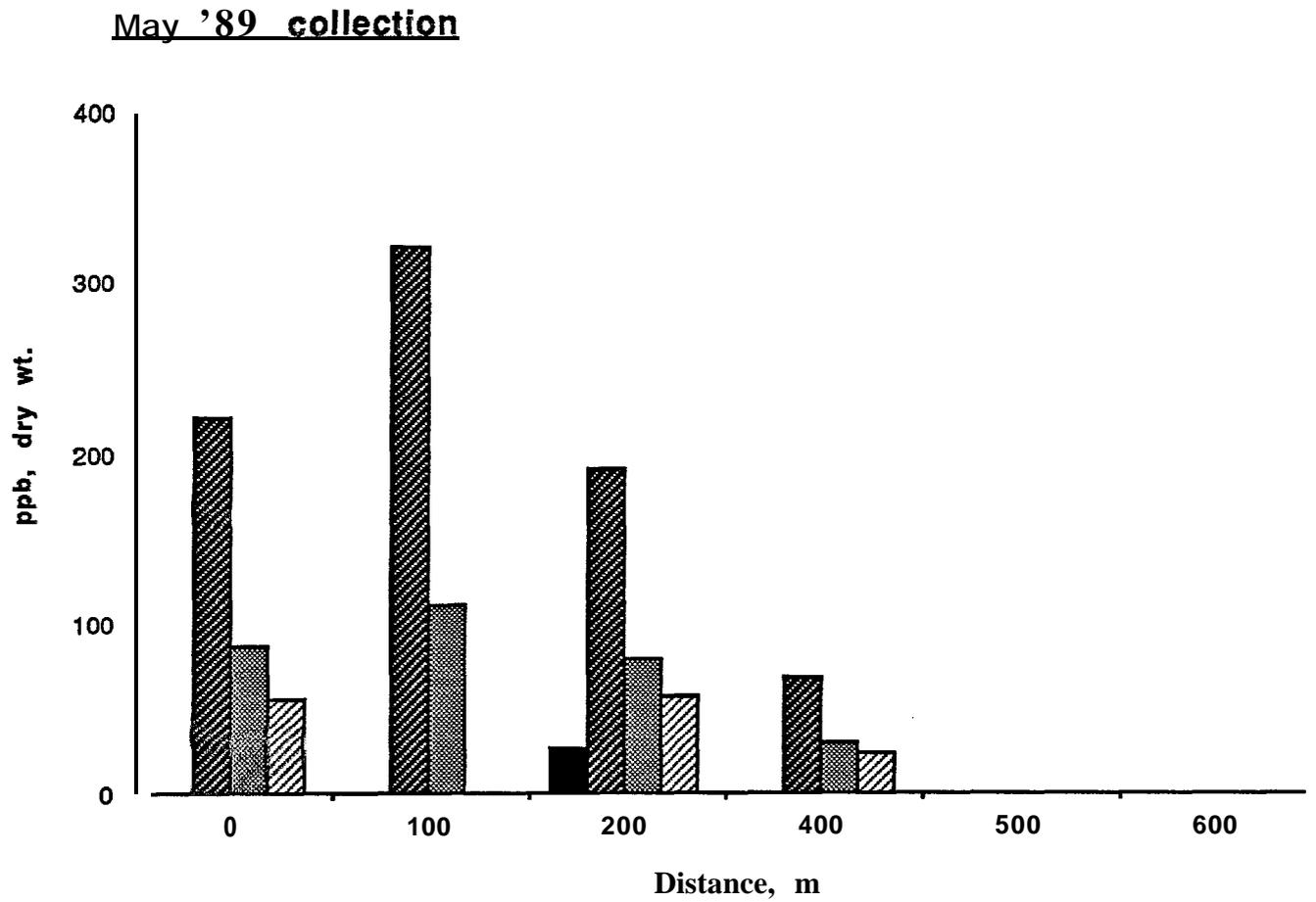


Figure 4. Methyl phenanthrenes concentrations in surface sediments collected at Pass Fourchon, Louisiana, at two time periods.

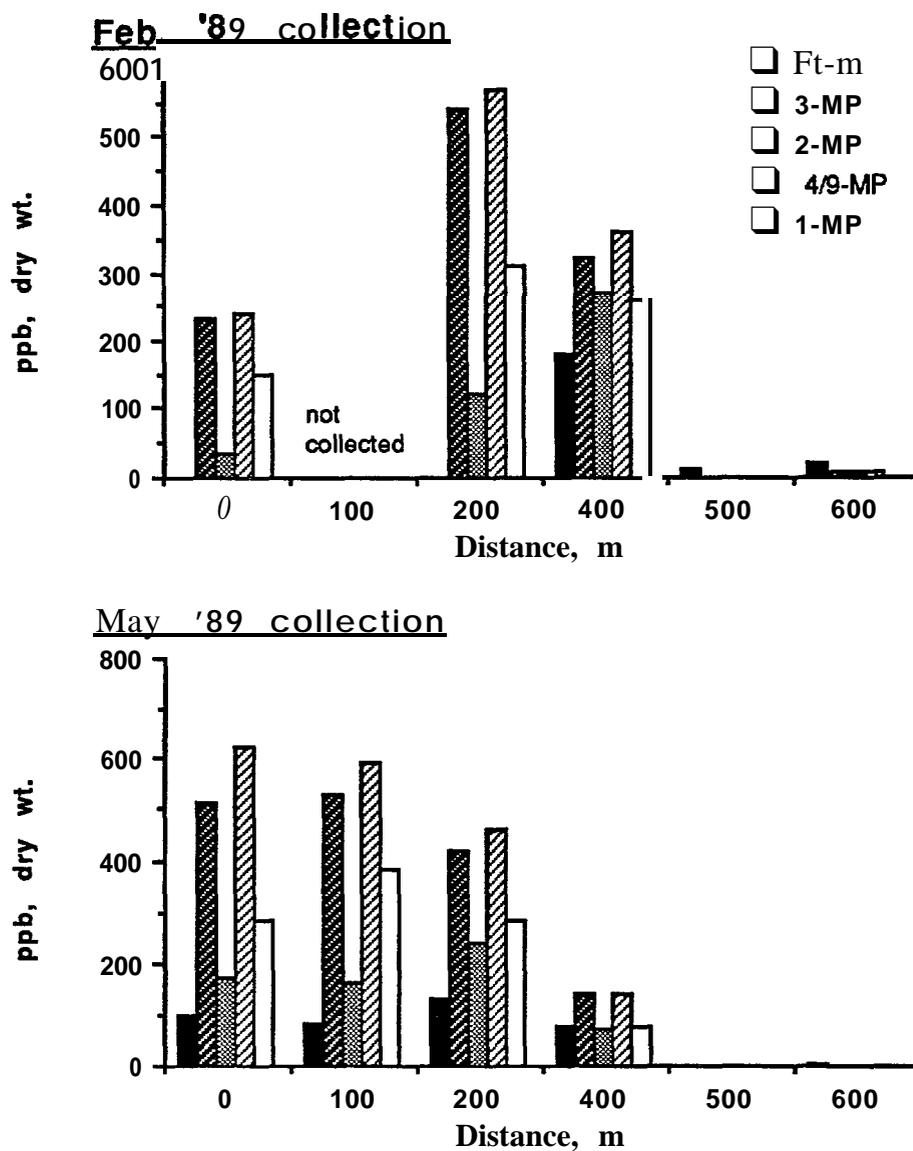


Figure 5. Dimethyl phenanthrenes concentrations in surface sediments collected at Pass Fourchon, Louisiana, at 2 time periods.

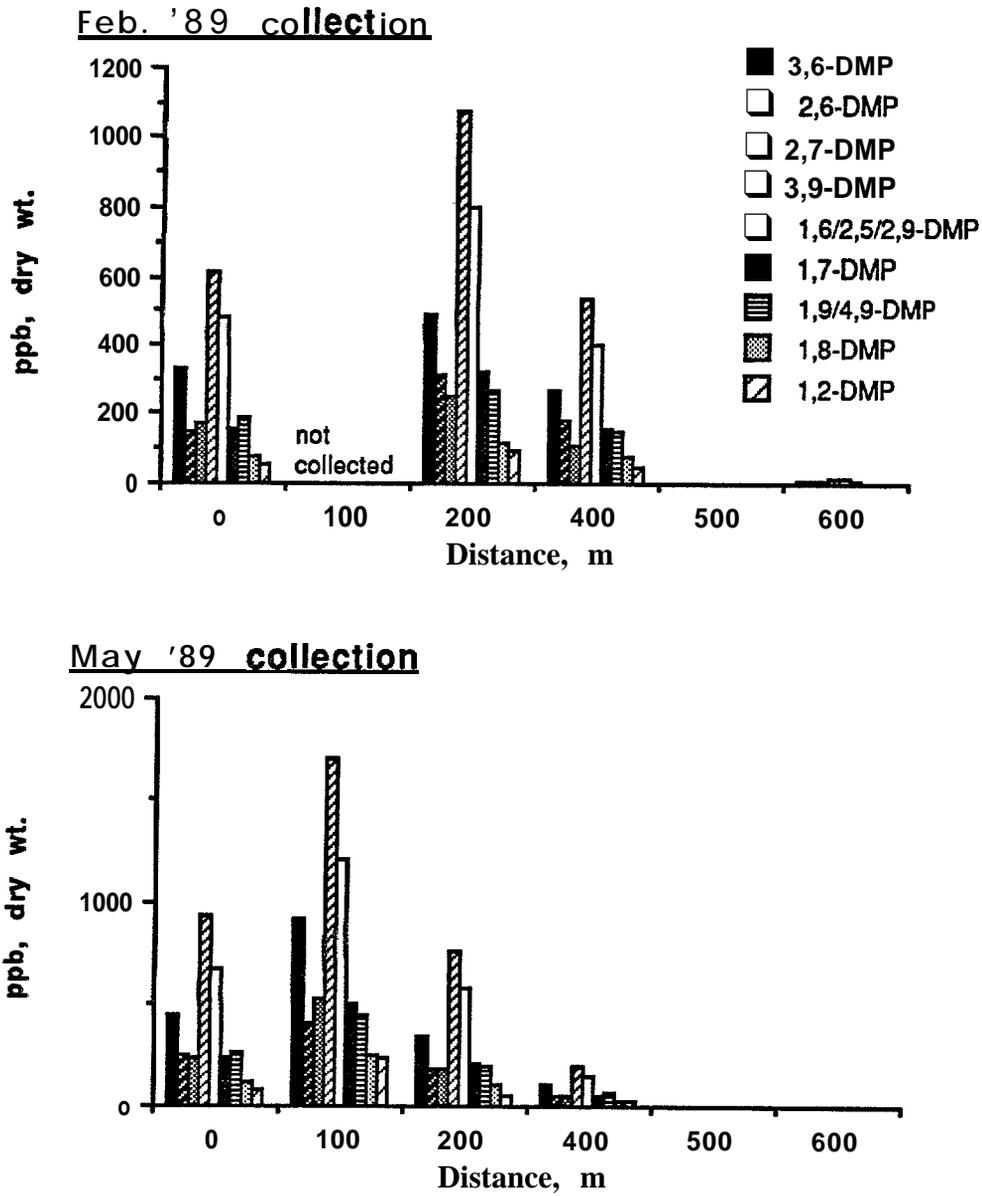


Figure 6. Depth profiles for selected **alkylated naphthalenes** concentrations in cores taken at a single Pass Fourchon site over three seasons.

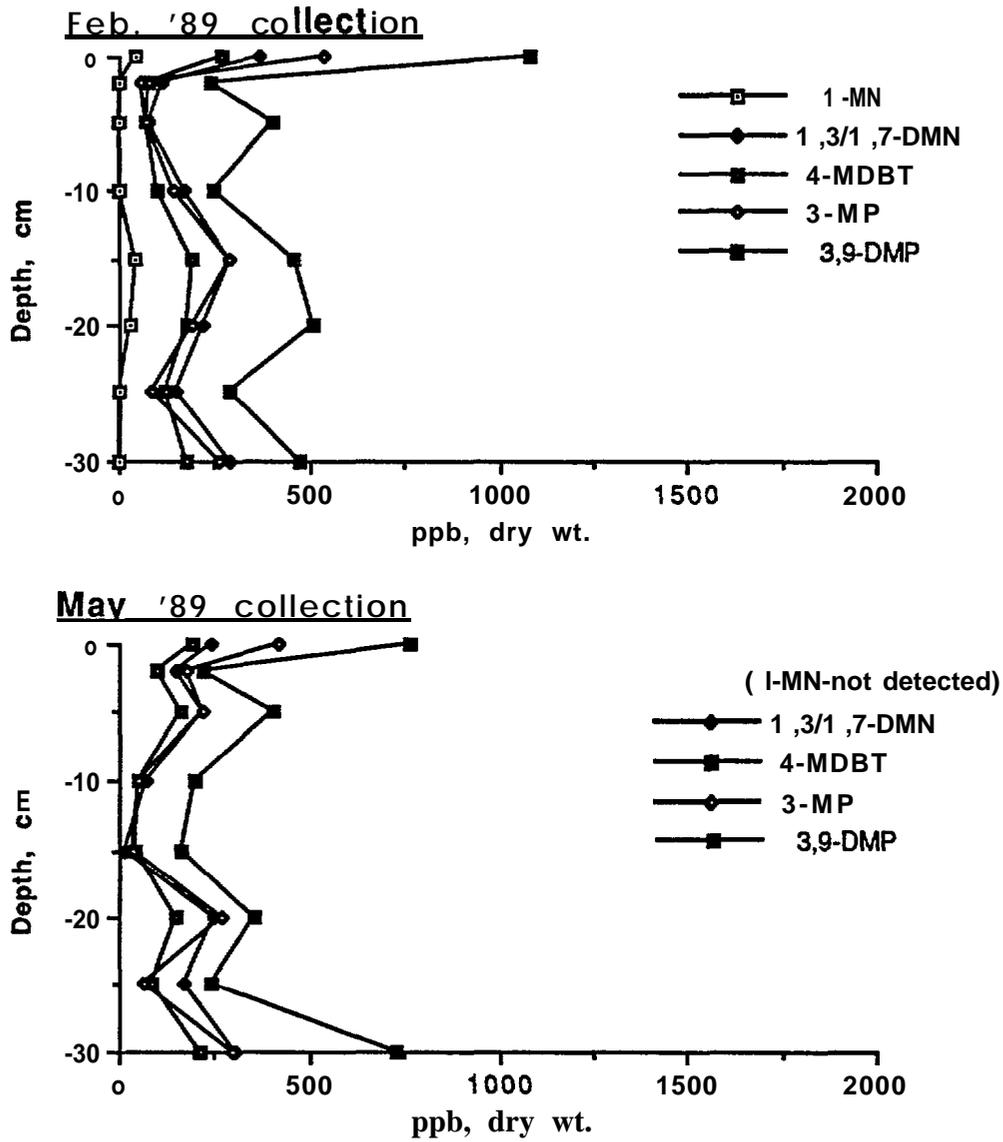


Figure 6. (cont'd.)

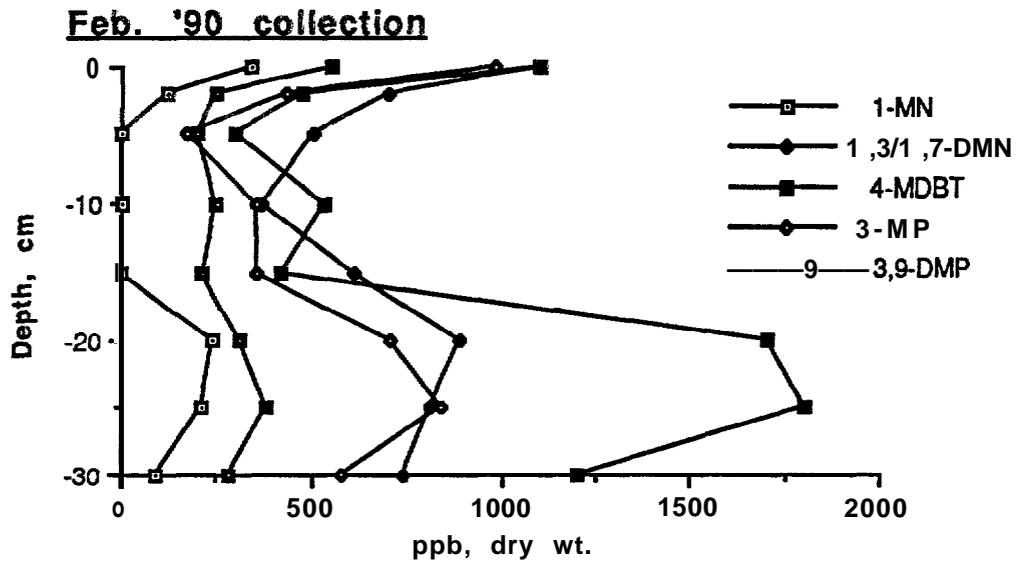


Figure 7. Depth profiles for selected **alkylated naphthalenes** concentrations in microcosm cores representing three sampling periods.

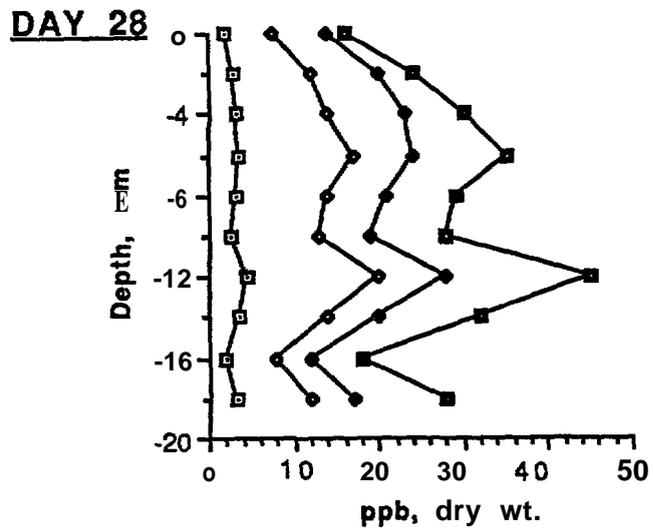
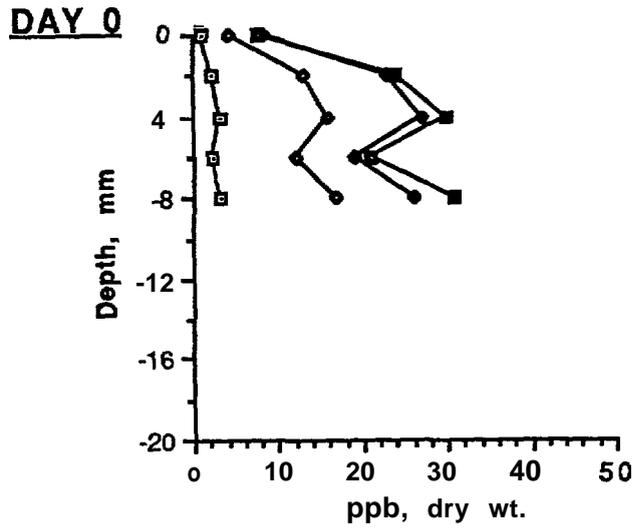


Figure 7. (cont'd.)

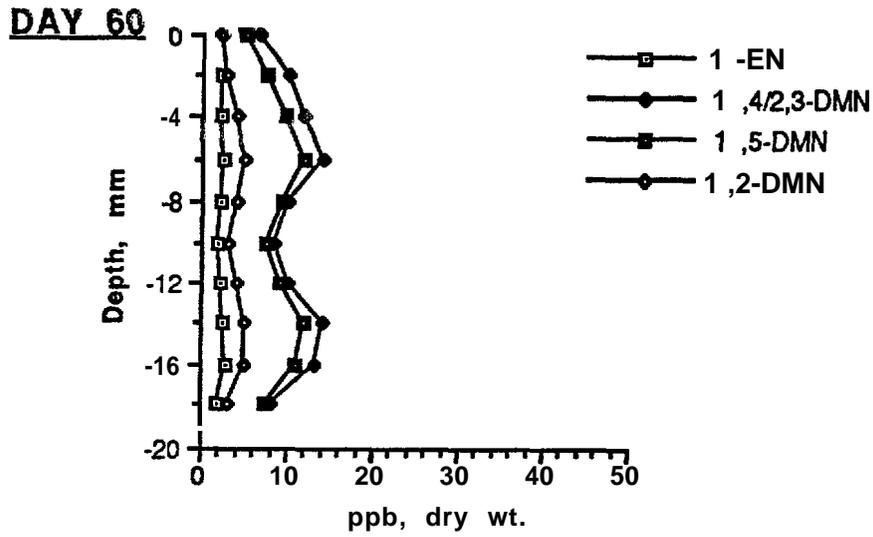


Figure 8. Ratios of selected alkylated naphthalenes concentrations (1-Ethyl naphthalene: 1,4/2,3 dimethylnaphthalene, 1,5-dimethylnaphthalene, and 1,2-dimethylnaphthalene) in microcosm cores representing three sampling periods.

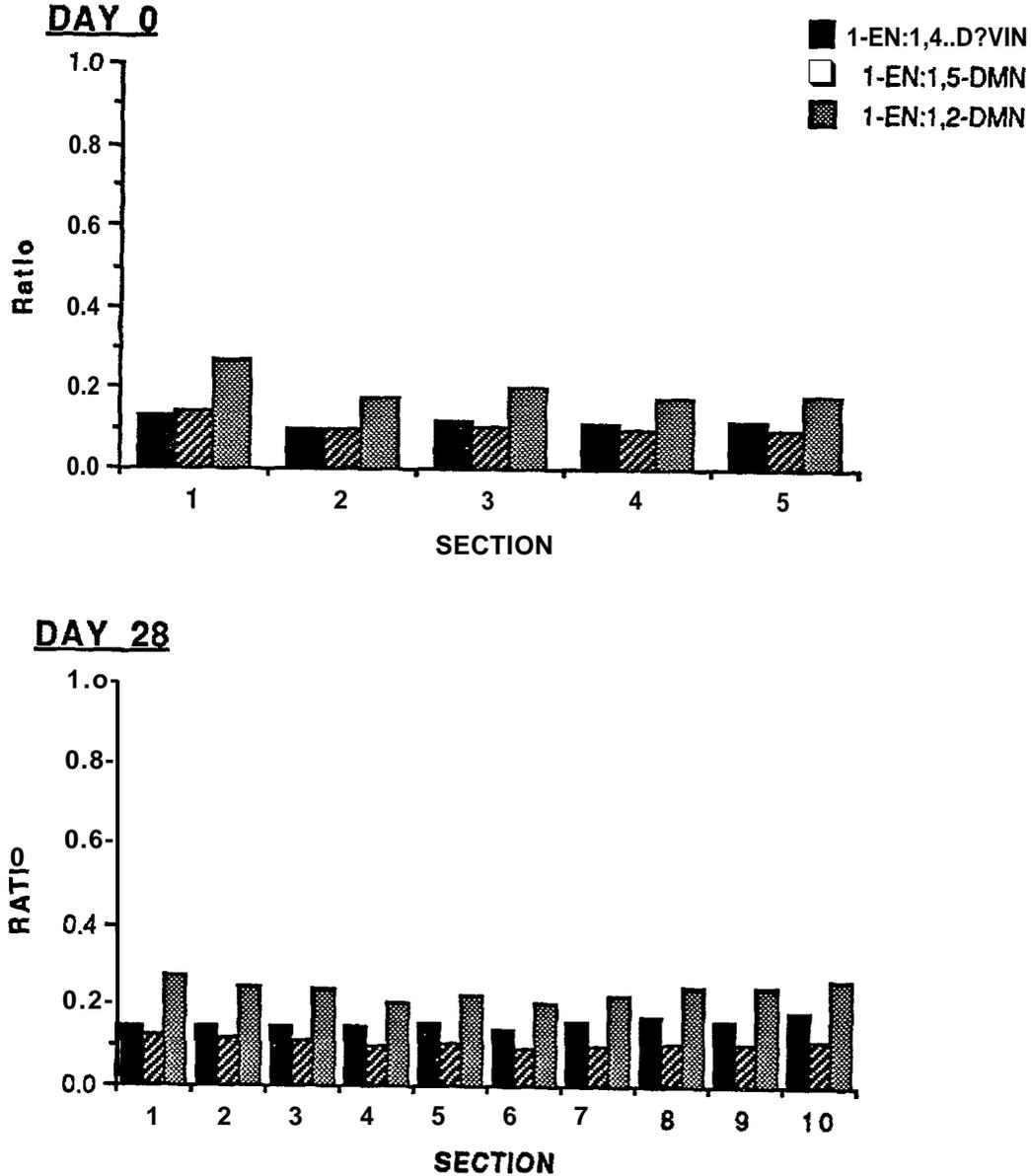
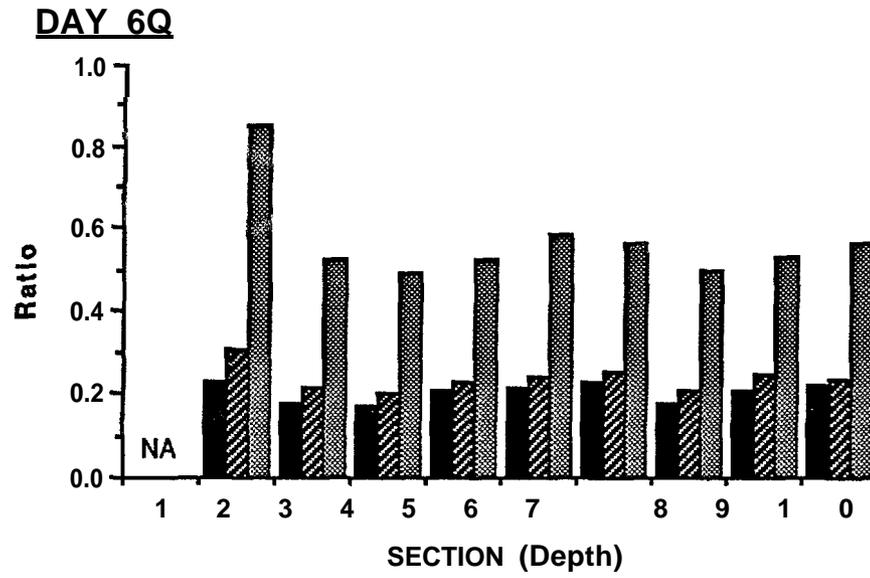


Figure 8. (cont'd.)



## Appendix 1

**Debra Jacobs McMillin**  
Research Associate IV

### **PROFESSIONAL EXPERIENCE**

**August, 1988 to present:**

RESEARCH ASSOCIATE IV, Institute for Environmental Studies, Louisiana State University, Baton Rouge, LA 70803. Co-investigator on several **projects** assessing impact of produced waters on coastal sediments. Performed **GC/MS** analyses of sediment and water samples. Developed methodology for analysis of analogs of **polynuclear** aromatic hydrocarbons. Supervised laboratory technician **in** preparation of soil samples. Trained co-workers and graduate students **in** use analytical instrumentation. Co-investigator on project to evaluate a prototype analytical **instrument**, the **PYRAN Thermal Chromatograph/Mass Spectrometer**, for applicability to sediment samples. Began developing methodology for assessment of DNA **adducts** using **HPLC** and **HPLC/MS**. Trained in use of **triple-quadropole** mass spectrometer with **thermabeam HPLC** interface. Assisted in preparation of research proposals, reports, and manuscripts.

**August, 1984 to August, 1988:**

RESEARCH ASSOCIATE III, Institute for Environmental Studies, Louisiana State University, Baton Rouge, LA 70803. Analysis of environmental samples using **HPLC**, **GC/FID**, and **GC/MS**. Methods development for assessment of **microsomal benzo(a)pyrene** metabolizes, ambient air **volatiles**, sediment hydrocarbons, coffee mutagens, and various pesticides. Experience with genetic engineering techniques, including **electrophoresis**. Duties include supervision of student workers, maintenance and repair of instruments, cost-estimation and invoicing for contracted analyses, and writing and editing reports.

**August, 1981 to June, 1984:**

RESEARCH ASSOCIATE, Food **Science Department**, Louisiana State University, Baton Rouge, LA 70803. **Research** on **quantitation** of nutrients **in** meat using **HPLC**, AutoAnalyzer, and **microbial** techniques. Independent work in methodology, **equipment**, and supply **determination**. Developed sampling procedures, supervised 6 graduate student workers in processing of samples. Instructed graduate students in use of **HPLC** and other lab and safety procedures. Wrote and reviewed **project** reports, research proposals, equipment requests, and bid specifications.

**June, 1978 to December, 1979:**

GRADUATE RESEARCH ASSISTANT, Department of Animal Science, **Iowa State University**, Ames, IA 50010. **Master's** thesis research using various types of **food** processing and **laboratory equipment**, including micro-Kjeldahl, KramerShear, fat extraction, moisture **determination**. Supervised lab **workers** and coordinated a **monthly** sensory panel of over 100 consumers.

**May, 1977 to June, 1978:**

LAB TECHNICIAN, Department of Animal Science, Iowa State University, Ames, IA 50010. Gathered data for research project on mechanism of nitrite reactions **in** cured meat products. Lab procedures included nitrite assay, **Kjeldahl** protein assay, use of **Sephadex** gel **column** chromatography, seaming **W spectrophotometer**, preparation of lab reagents.

### **EDUCATION**

	<b><u>Institution</u></b>	<b><u>Date</u></b>	<b><u>Grade</u></b>
M.S. Animal Sci. & Food Tech.	Iowa State Univ., Ames, IA	May, 1981	3.76 (4.0)
B.S. Food Technology	Iowa State Univ., Ames, IA	May, 1978	3.64 (4.0)

## **PROFESSIONAL IMPROVEMENT**

Waters Separations Development Course, Boston, MA, December, 1985  
Waters Ion Chromatography Course, Boston, MA, January, 1986  
Attended "Environmental Toxicology" class, LSU, Spring, 1986  
**Attended "HPLC '86," San Francisco, CA, May, 1986**  
**Waters WISP Maintenance School, New Orleans, LA, July, 1986**  
Attended "Chemical Separations" class, LSU, **Spring, 1987**  
Gas **Chromatography/Mass Spectrometry** ACS Short Course, Pittsburgh Conference, New Orleans, 1988  
**EXTREL Triple Quadropole** Mass Spectrometer Operator Training, LSU, January, 1989; Pittsburgh, OH, June, 1990.  
Attended ACS Environmental Chemistry Division Symposium on Organic Substances and Sediments in Water, Boston, MA, April, 1990.

## **PUBLICATIONS AND PRESENTATIONS**

- Jacobs, D.K., and **J.G. Sebranek**. 1980. Use of **prerigor** beef for **frozen** ground beef patties. *J. Food Sci.* **45:648-651**. **Presented** at 39th Annual Meeting of the Institute of Food Technologists, June 13, 1979.
- McMillin, D.J., J.G. Sebranek, and A.A. Kraft**. 1981. Microbial quality of hot-processed frozen ground beef patties processed after various holding times. *J. Food Sci.* 46:488-490. Presented at the 40th Annual Meeting of the Institute of Food Technologists, June 11, 1980.
- McMillin, D.J., K.W. McMillin, A.M. Mullins, and F.H. Hoskins**. 1985. Nutrient content of edible beef. *The Louisiana Cattleman*. 7:13.
- Henry, C.B., and **D.J. McMillin**. 1986. A Quick (But Not So Dirty) Method for the Analysis of Chlorinated Hydrocarbons in Whale Blubber. **Abstract**. Poster, Sixteenth Annual Symposium on Advances in Applied Analytical Chemistry. New Orleans Chromatography-Analytical Discussion Group, **Louisiana** Section American chemical Society. May 8, 1986.
- Jewell, C. S., G.W. Winston, and D.J. McMillin**. 1986. Characterization of the **Hepatopancreas** and Green Gland **Microsomal Mixed Function Oxidase** System of the Red Swamp Crawfish, *Procambarus Clarkii*. Abstract. Society of Environmental Toxicology and Chemistry Seventh Annual Meeting. November 2-5, 1986.
- Shane, B.S., A.M. **Troxclair, D.J. McMillin, and C.B. Henry**. 1987. Comparative Mutagenicity & Nine **Brands of Coffee** to Salmonella Typhimurium TA100, TA102, and TA104. *Environmental Mutagenicity*. Vol 11: In press.
- McMillin, D.J., and G.W. Winston**. 1987. Analysis and Verification of **Benzo(a)pyrene Metabolites** by HPLC using Combined Fluorescence and Multi-Channel, Programmable **UV** Detectors. Abstract. **Presented** at Seventeenth Annual Symposium on Advances in Applied Analytical Chemistry. New Orleans **Chromatography-Analytical** Discussion Group, **Louisiana** Section **American** Chemical Society, April 30, 1987.
- Winston, G.W., B.S. Shane, **C.A. Traynor, L.S. Ortego, C.B. Henry, and D.J. McMillin**. 1987. Induction of **Xenobiotic** Activation by Channel Catfish (*Ictalurus punctatus*)

- from a Contaminated River Basin Swamp **Ecosystem**. Extended **Abstract**, 194th ACS National Meeting, New Orleans, **LA**. Aug **30-Sept. 4**, 1987. Vol 27, p 89-92.
- Henry, C.B., **D.J. McMillin**, and **E.B. Overton**. 1988. Thermal Extraction **GC/MS** Analysis of **Semivolatile** Compounds in Hazardous Waste. Abstract. Eighteenth Annual Symposium on Advances in **Applied** Analytical Chemistry. New Orleans Chromatography-Analytical Discussion Group, Louisiana Section American Chemical Society, May 11, 1988.
- McMillin**, D.J., **C.B. Henry**, and **E.B. Overton**. 1989. Baseline Monitoring of Hydrocarbons by Thermal **Extraction-GC/MS** Compared to Conventional Methods. Abstract. Poster Presentation at Pittsburgh Conference and Exposition on Analytical Chemistry and Applied **spectroscopy**. **Atlanta**, GA. Mar 6-10, 1989.
- Overton, E. B., **L.H. Grande**, **R.H. Sherman**, **E.S. Collard**, **T.H. Backhouse**, and **D.J. McMillin**. Air Monitoring for Volatile Organic Compounds in an Industrial **Area**. Air Pollution Control Association Meeting. May, 1989.
- Milan, C. S., **D.J. McMillin**, **C.B. Henry**, **J.C. Means**, and **E.B. Overton**. 1989. Fate of Petroleum Hydrocarbons **from** Produced Water Discharges **in** Marsh Environments. Abstract. 197th ACS National Meeting, Dallas, TX. April, 1989.
- Rabalais**, N.N., **J.C. Means**, **D.J. McMillin**, **C.S. Milan**, and L. Smith. 1989. Characterization of produced Water (Chapter 5), Bayou Sale Study Site (Chapter 6), **Lafitte** Study Site (Chapter 7), and Golden Meadow Study Site (Chapter 8). In Environmental Impact of Produced Water Discharges in Coastal **Louisiana**, Boesch, D.F. and **Rabalais**, N.N., eds. Report prepared for the Louisiana Division of the Mid-Continent Oil and Gas Associates. (Under review).
- Overton, E.B., **L.H. Grande**, **R.W. Sherman**, **E.S. Collard**, **T.H. Backhouse**, and **D.J. McMillin**. 1989. Air Monitoring for Volatile Organic Compounds in an Industrial Area. Proceedings of the Air Pollution Control Association Annual Meeting, May 10, 1989. **In Press**.
- Daniels**, C.B., **D.J. McMillin**, and **J.C. Means**. 1989. Maternal Uptake and Transfer of a **Promutagen (Cyclophosphamide)** by an **Estuarine** Fish, *Cyprinodon Variegates*. Abstract. Fifth International Conference on Environmental Mutagens. July 10-15, 1989. Cleveland, OH.
- Means, J. C., **D.J. McMillin**, and A. **Atherton-Wilson**. 1990. An Analysis of Temporal and Historical Trends in Contaminant Concentrations in Sediments and **Biota** in Long Island Sound. Report to Ocean Assessments Branch, National Oceanic and Atmospheric Administration, **Rockville**, MD.
- McMillin**, D.J., **C.S. Milan**, and **J.C. Means**. 1990. Characterization and Impact Assessment of Produced Water Discharges. Abstract. Poster presentation. **La**. State Univ. Chemistry Department Open House, Nov., 1990.
- Means, J. C., **D.J. McMillin**, and **C.S. Milan**. Impacts of Gil-Field Brine-Associated Contaminants in Coastal **Estuarine** Environments. Abstract. State of the Estuary Conference, San Francisco, CA. May 30-31, June 1, 1991.
- McMillin**, D.J., **Milan**, C. S., and **J.C. Means**. 1991. Characterization of Petroleum **Hydrocarbons from** Produced Water Discharges and **Impacts on Estuarine** Systems. Abstract. SETAC 12th Annual Meeting, Nov. 3-7, 1991. Submitted.

## **MAJOR PROJECTS AND REPORTS**

- 1985-1986      **Old Inger: Biological Treatment. Provided HPLC screening of** biologically-treated oil sludge samples from an abandoned hazardous waste (Superfund) site.
- 1985-1988      **Louisiana Offshore Oil Pipeline (LOOP)/Louisiana Department of Wildlife and Fisheries Baseline Monitoring Project.** Analysis for hydrocarbon contamination by **HPLC, GC, and GC/MS.** Interstitial salinity measurements. Provided data and interpretation of results through quarterly **reports.**
- 1987-1988      St. Gabriel Air Quality Monitoring, Ascension Parish Air Quality Monitoring. **GC/MS** method development and analysis of charcoal trap air samples from local industrial site provided for comparison with newly developed field **sampling/analytical** devices.
- 1987-1988      **Impacts** of Produced Waters in Sensitive Coastal Habitats, sponsored by Minerals Management Service, U.S. Dept. of Interior, through Louisiana Universities Marine Consortium. Assisted in data acquisition and analysis.
- 1988-1989      **Environmental** Impacts of Produced Water Discharges in Coastal Louisiana, Mid-Continent Oil and Gas Association through Louisiana Universities Marine Consortium. **GC/MS** analyses and data synthesis of sediment and water samples. **Supervision** of laboratory technician in preparation of sediment samples.
- 1989-1990      Assessment of Produced Water Impacts to Low-Energy, Brackish Water Systems in Southeast Louisiana Kerry St. Pe', editor. Chapter VI. Hydrocarbons and trace metal concentrations in Produced Water Effluents and Proximate Sediments. **J.C. Means, C.S. Milan, and D. J. McMillin.**
- 1989-1991      Fate and Effects of Nearshore Discharges of OCS Produced Waters. Sponsored by Minerals Management Service, U.S. Dept. of Interior through Louisiana Universities **Marine** Consortium. **GC/MS** analyses and data synthesis of sediment and water samples. Contributor to final report.
- 1990-1991      Capitol Lakes Rehabilitation **Project:** Environmental Investigations and Planning Studies, sponsored by Capitol Lakes Task Force. "Report on contamination of Capitol Lake Sediments." J. Collins, C. Durham, **D.J. McMillin,** and **J.C. Means.** Feb. 4, 1991. Provided analyses for hydrocarbons, **PCB's** and pesticides in sediment samples and directed students in preparation of samples.
- 1990-1991      **Biomonitoring** to Assess the Impacts of Corridor Development upon contamination of Louisiana's **Estuarine** Living Resources. Sponsored by **Louisiana** Department of Environmental Quality. Preparation of samples **for trace metals** analyses, arranged for sub-contractor analyses.
- 1990-present      Fate and Transport of Particle-Reactive **Normal, Alkylated** and **Heterocyclic** Aromatic Hydrocarbons. Development of analytical methodology for determination of desorption kinetics of **petrogenic** hydrocarbons from contaminated sediments.