ACCUMULATION OF CONTAMINANTS FROM URBAN RAINFALL RUNOFF IN BLUE CRABS: A PILOT STUDY

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March 1997

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ACKNOWLEDGEMENTS

Several people contributed to this pilot study and their help is gratefully acknowledged.

o Charlie Sanchez, former regional contaminant coordinator, helped secure funds for the project.

o Steve Robertson, the current regional contaminant coordinator, provided necessary support for the completion of this report.

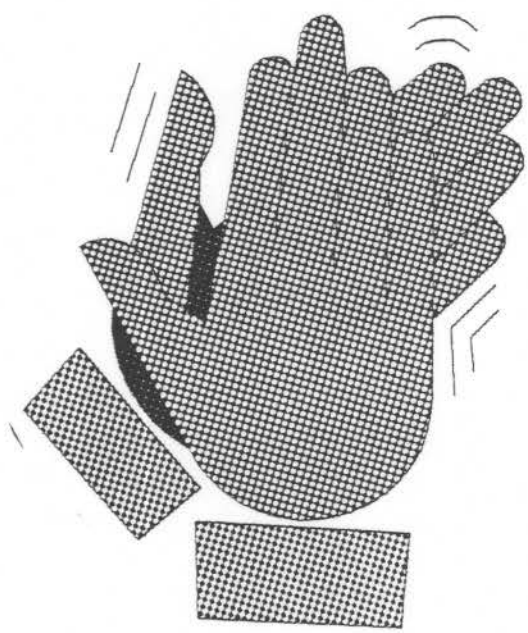
o Bryan Pridgeon was instrumental in collecting the samples.

o The Texas City Flood Control District provided access to their facilities for trap placement and security.

o Personnel from the Patuxent Analytical Control Facility in Laurel, Maryland were very helpful in securing chemical analysis of samples and performing quality control on the analytical results.

o Clare Lee and Kirke King, contaminant biologists with the Service, reviewed and improved this report.

o Special thanks go to Janice Deaton Santafede and Mary Lou Jones for their typing skills and the organization of the final report.



INTRODUCTION

Coastal estuaries near large urban or industrial facilities receive several classes of contaminants from point-source discharges, urban drainage systems, and non-point runoff (Cole et al. 1984, Hoffman et al. 1984, Bates et al. 1987, and Ellis et al. 1987). Hydrocarbons are also deposited from the atmosphere into coastal estuaries (Dickhut and Gustafson 1995). Nearly 50 percent of the hydrocarbons aerially deposited into the Chesapeake Bay were anthropogenic compounds (Webber 1983). Most contaminants of concern such as heavy metals, polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides, and other industrial chlorinated organic compounds are known to adsorb to suspended particulate matter in the water and settle into the sediment layer.

Sediments in estuaries receiving urban and industrial discharges are known to accumulate contaminants and may be a source of these chemicals to estuarine fish and shellfish species (Shuster and Pringle 1969, Winger et al. 1990, and Sanders 1995). Residues of hydrocarbons associated with stormwater suspended solids ranged between 1.7 to 6.2 percent of the total solid mass in the runoff (Ellis et al. 1985). McCain et al. (1990) reported aromatic hydrocarbons were detected 100-times higher in sediments receiving urban runoff than from estuaries receiving rural runoff. Published reports indicate that levels of PAHs are often several orders of magnitude higher in sediments than the overlying water column (Clements et al. 1994, Eisler 1987).

Several species of estuarine aquatics have been used for bioaccumulation or in-situ bioassay studies to determine uptake of contaminants or adverse biological effects to the organisms. Ekelund et al. (1987) determined that hydrophobic contaminants are more bioavailable if uptake by food determines the steady state concentration of the compound in the organism.

Galveston Bay is the largest estuary on the Texas coast in terms of fish and shellfish production. This shallow, 600 square-mile, embayment is adjacent to Houston and Texas City, Texas, which together is the world's second largest center for petrochemical production. Water quality problems in Galveston Bay have been recognized for over 30 years (Gloyna and Malina, 1964), and lately sediment quality problems have been discovered (Cain 1989, Carr 1993). The priority environmental problems identified by the Galveston Bay National Estuary Program (1994) included habitat loss, urban runoff, sewage bypasses and overflows, and toxic contamination of water and sediments. The objective of this pilot study was to determine the feasibility of using caged blue crabs *Callinectes sapidus* to monitor accumulation of contaminants in urban runoff during a rainfall event.

STUDY SITE DESCRIPTION

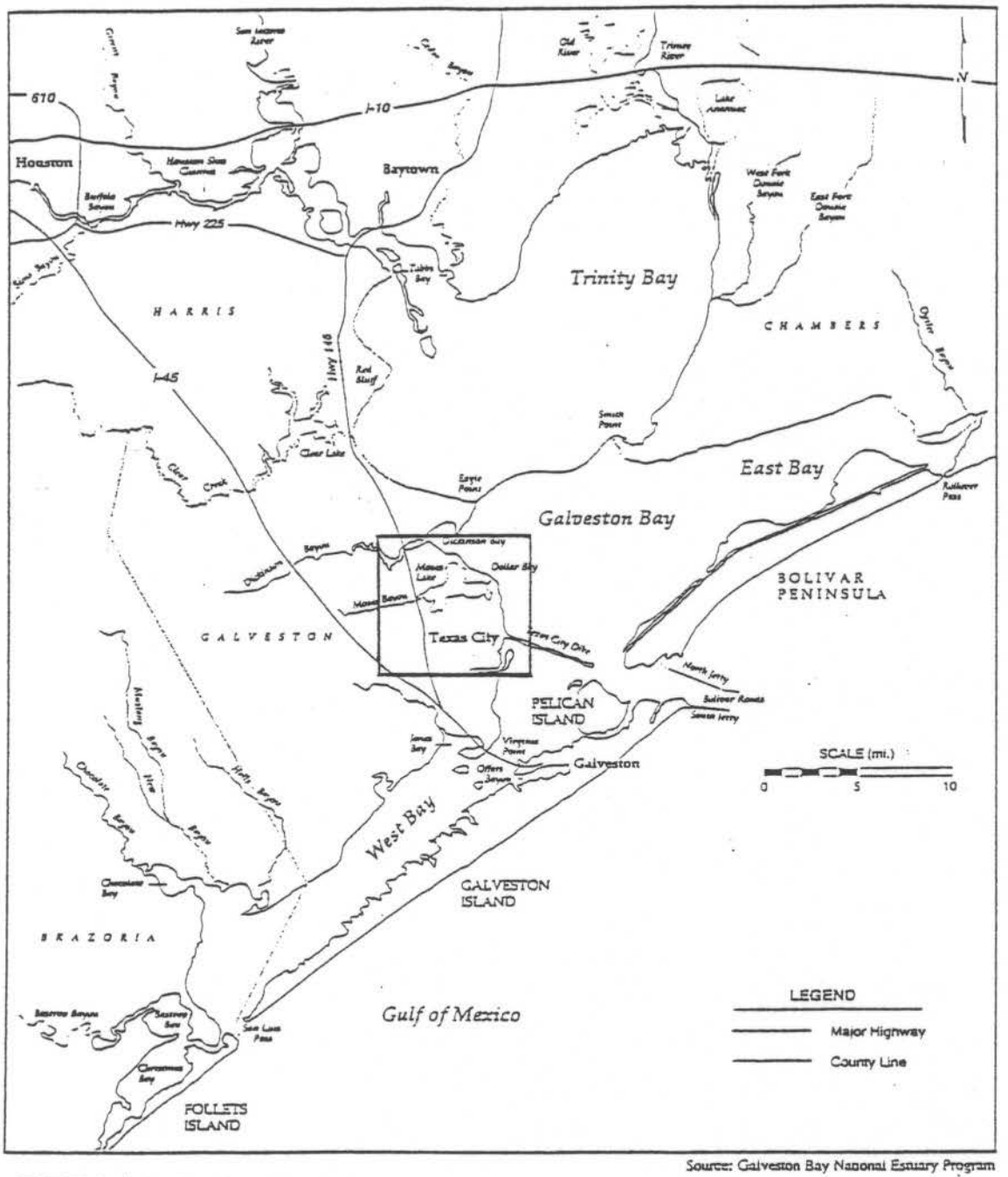
The study area is located within the city limits of Texas City, Texas on the southwest side of Galveston Bay (Fig. 1). The surrounding area is flat coastal land that drains slowly and is heavily developed with residential and industrial facilities. Texas City is a major shipping port for crude oil imports and petrochemical exports. Most of the chemical facilities are on the southeast side of Texas City. During the year prevailing winds are out of the southeast and deposition of any air releases would fall over the area.

Texas City is protected on the North, East, and South sides by a hurricane levee that was 70 percent constructed in 1963 and completed in 1979 (USACOE 1979). The levee (Fig. 2) was built to protect Texas City from the frequent tropical storms that may hit the area with storm surges as high as 15 feet (USACOE 1979). Rainfall from these storms may average 11-14 inches which creates a need for rapid drainage inside the levee back to Galveston Bay.

Three pump stations located in the urban drainage ditches lift the urban runoff water into either Dollar Bay (Station A). Moses Lake (Station B) or the industrial canal (Station C), see Figure 2.

The dimensions of the hurricane levee and its assorted discharge structures were evaluated and described in an environmental impact assessment document (USACOE 1979).

The pump station A on the east side of Texas City drains the old section of town which is predominately urban dwellings as well as old business structures. Pump station B receives runoff from the newer section of Texas City that drains residential and light industrial areas. The



Source: Galveston Bay National Estuary Program

FIGURE 1. Study Area Location.

pump at station C receives runoff from the heavy industrial side of Texas City that includes several petroleum or petrochemical facilities as well as one facility (Tex-Tin) that was recently put on the EPA's National Priority List (NPL). The ditch from pump station C also receives the treated effluent from the Gulf Coast Waste Disposal Authority facility. This drainage ditch was recognized as a heavily contaminated area by Cain (1993).

The reference site selected for this study was in Galveston Bay just North and East of

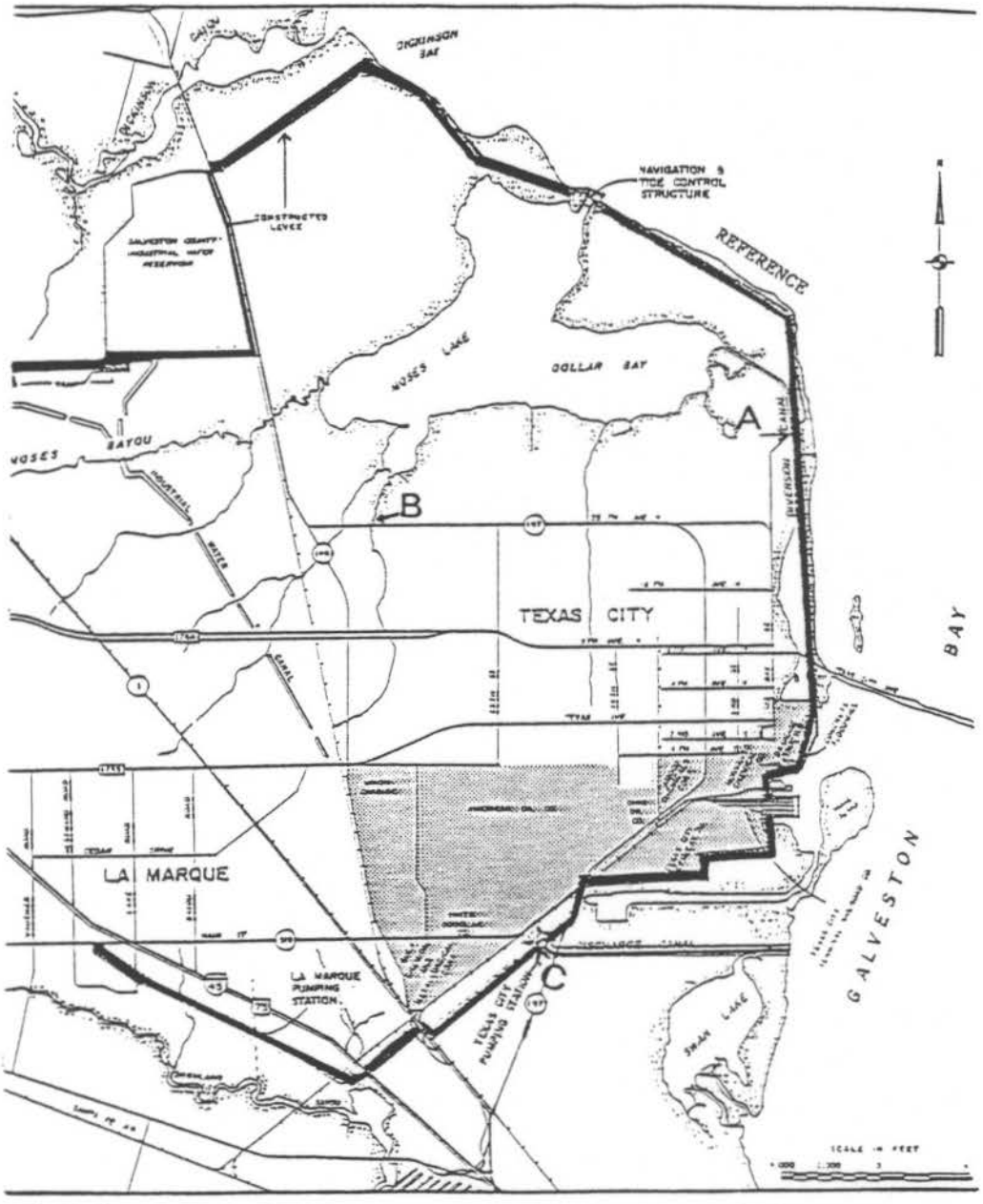


FIGURE 2. Location of sample collection sites for urban runoff from Texas City. (See A, B, C & REFERENCE above)

Dollar Bay (Fig. 2). This area is shallow water with a sandy bottom that gently slopes to about three meters (10 feet) deep. There is no known source of contamination entering the bay at this point.

METHODS

Blue crabs were collected on five occasions from an uncontaminated portion of Galveston Bay during the months of June through October 1992 whenever a rainfall event was predicted by the National Weather Service for the Texas City area. Crab traps were baited with chicken necks for 24 hours and any crab captured was placed in a holding cage and provided chicken necks during this bioaccumulation study. It was assumed that any contamination in the chicken necks would be similar for each set of crabs.

Five crabs per holding cage were placed in the urban drainage ditches for at least 3 days. The cages were placed in the discharge area of the pumps at Station A and Station C, but in the receiving water before the pump at Station B. At the end of the exposure period the crabs were removed from the holding cages, chilled and transported to the laboratory. There the crabs were dissected and the viscera, which included lung tissue, was removed and placed in a glass jar and frozen. A one-liter sediment sample was taken with a coring device from each location as well as a one-liter water sample. All samples were sent to an analytical laboratory under contract to the U. S. Fish and Wildlife Service and analyzed for heavy metals, polycyclic aromatic hydrocarbons (PAHs), and aliphatic hydrocarbons (Table 1). Analytical procedures are too extensive to reproduce in this report but are available from the Patuxent Analytical Control Facility in Laurel, Maryland upon request. A brief description of the analytical techniques is provided in Appendix I.

Table 1. Analytes from sediment, water, and blue crabs tissue.

Heavy Metals	Petroleum Hydrocarbons	
	Aromatics	Aliphatics
Aluminum	Anthracene	Dodecane
Antimony	Acenaphthene	Tridecane
Barium	Acenaphthylene	Tetradecane
Beryllium	Benzo(a)anthracene	Pentadecane
Boron	Benzo(a)pyrene	Hexadecane
Cadmium	Benzo(b)fluoranthrene	Pristane
Chromium	Benzo(ghi)perylene	Octadecane
Copper	Benzo(k)fluoranthrene	Phytane
Iron	Biphenyl	Nonadecane
Lead	Chrysene	Eicosane
Magnesium	Dibenzanthracene	
Manganese	2,6-Dimenthylnaphthlene	
Molybdenum	Fluoranthrene	
Nickel	Fluorene	
Strontium	Indenopyrene	
Thallium	1-Methylnaphthalene	
Tin	2-Methylnaphthalene	
Vanadium	1-Methylphenanthrene	
Zinc	Naphthalene	
	Perylene	
	Phenanthrene	
	Pyrene	
	2,3,4-Trimethylnaphthalene	

Acceptable performance (a recovery variation of <20%) of all chemical analyses in spikes, blanks, and duplicates was documented in quality control reports from the laboratory.

RESULTS AND DISCUSSION

Water Samples

One water sample was collected from each location 5 days after a major rainfall over Texas City. The only heavy metals detected in these water samples were aluminum, copper, iron, and manganese (Tables 2-5). Levels of these contaminants were at low concentrations and would not impair the water quality. There were no petroleum hydrocarbons detected in the water samples (Table 2-5).

Sediment Samples

Aluminum and iron were detected at the highest concentrations in sediments from the reference area (Table 2). This area does not receive urban road runoff, which has been reported as a major source of heavy metal contamination in estuaries, due to motor vehicles (Bourcier and Sharma 1980). Aluminum is the most abundant metal in the earth's crust (Haug 1984) averaging 81,000 ppm (Brooke and Stephan 1988). It is more soluble in acidic and basic solutions than in circumneutral (pH 7) solutions. Aluminum forms soluble complexes with ions such as chloride, fluoride, nitrate, phosphate, and sulfate (Brooke and Stephan 1988) which allows for easy mobility in the environment.

All the other heavy metals detected in the reference sediment fall within the normal levels reported for sediment from uncontaminated portions of the Galveston Bay system (Cain 1989, Cain 1993).

Mercury was detected only in the sediment sample collected from the pump station that received the new-urban runoff (Table 3). There is at present no explanation for this high level (10 ppm) at this one location. Mercury has not been a widespread contaminant in Galveston Bay sediment and is rarely detected in urban drainage ditch sediment (Cain 1993).

Concentrations of several heavy metals were highest in the sediment collected from the industrial-runoff site (Table 5). Cadmium, copper, chromium, manganese, nickel, lead, selenium and zinc were all found at elevated levels in the sediment from this site. At the present time it is not known if these contaminants are bioavailable and are accumulating in the sediment biota.

Petroleum hydrocarbons (aliphatic and polycyclic aromatic) were not detected in the sediment from the reference site (Table 2). All 20 of the PAHs were detected in the sediment samples from the new-urban runoff site (Table 3), but at very low levels. In sediment from the old-urban runoff site (Table 4) there were 18 PAHs detected at low levels. Higher concentrations of 19 PAHs were detected in the sediment from the industrial-runoff site (Table 5).

The total concentration of PAHs in the sediment from the industrial site is known to be correlated with elevated cancer frequencies in freshwater catfish (Black 1982).

The majority of polycyclic aromatic hydrocarbons entering aquatic environments remain close to the deposition site where they accumulate in sediments until benthic organisms either biotransform or biodegrade the compounds (Eisler 1987). Sediments considered heavily contaminated with polycyclic aromatic hydrocarbons generally contain more than 10 ppm total residues. Ellis et al. (1985) concluded that PAH levels in urban channel sediments can be very high and the sediments act as a reservoir of organic pollutants to the water column during storm surges.

Environmental effects of aliphatic hydrocarbons are less known from studies than the effects of PAHs (IARC 1983). Ten aliphatic hydrocarbons were detected in the sediment samples from the urban-runoff sites and the industrial-runoff site. The sum total of

Table 2. Contaminants in samples collected from the reference area, ppm wet weight.

	Blue Crab	*Sediment*	*Water*
Heavy Metals			
Aluminum	21.91	3610	0.39
Arsenic	1.05	2.52	BDL
Cadmium	0.09	BDL	BDL
Chromium	1.17	4.61	BDL
Copper	17.72	4.07	0.01
Iron	28.39	5709	0.42
Mercury	BDL	BDL	BDL
Manganese	5.31	106.91	0.01
Nickel	0.56	5.13	BDL
Lead	0.13	7.10	BDL
Selenium	0.44	BDL	BDL
Zinc	19.45	8.96	BDL
Petroleum Hydrocarbons-Aromatic			
dibenzanthracene	BDL	BDL	BDL
bonzanthracene	BDL	BDL	BDL
trimethyl-naphthalene	BDL	BDL	BDL
acenaphthalene	BDL	BDL	BDL
acenaphthene	BDL	BDL	BDL
anthracene	BDL	BDL	BDL
benzo(a)pyrene	BDL	BDL	BDL
benzo(b)fluoranthene	BDL	BDL	BDL
benzo(c)pyrene	BDL	BDL	BDL
benzo(g,h,i)perylene	BDL	BDL	BDL
benzo(k)fluoranthene	BDL	BDL	BDL
biphenyl	BDL	BDL	BDL
chrysene	BDL	BDL	BDL
fluoranthene	BDL	BDL	BDL
fluorene	BDL	BDL	BDL
indeno(1,2,3-cd)pyrene	BDL	BDL	BDL
naphthalene	BDL	BDL	BDL
perylene	BDL	BDL	BDL
phenonthrene	BDL	BDL	BDL
pyrene	BDL	BDL	BDL
Petroleum Hydrocarbons-Aliphatic			
n-dodecane	BDL	BDL	BDL
n-eicosane	BDL	BDL	BDL
pristane	0.23	BDL	BDL
n-hexadecane	0.04	BDL	BDL
n-nonadecane	BDL	BDL	BDL
n-octadecane	BDL	BDL	BDL
n-pentadecane	0.48	0.02	BDL
n-tetradecane	BDL	BDL	BDL
n-tridecane	BDL	BDL	BDL
phytane	0.08	BDL	BDL

Table 3. Contaminants in samples from new-urban runoff site (Station B), ppm wet weight.

	Blue Crab	*Sediment*	*Water*
Heavy Metals			
Aluminum	162.56	1150	0.82
Arsenic	0.98	1.82	BDL
Cadmium	0.10	BDL	BDL
Chromium	1.01	7.83	BDL
Copper	18.96	2.07	0.01
Iron	185.71	4397	0.77
Mercury	BDL	10.05	BDL
Manganese	23.04	92.04	0.03
Nickel	0.53	4.65	BDL
Lead	0.34	10.32	BDL
Selenium	0.37	BDL	BDL
Zinc	16.39	28.78	BDL
Petroleum Hydrocarbons-Aromatic			
dibenzanthracene	BDL	0.01	BDL
bonzanthracene	BDL	0.03	BDL
trimethyl-naphthalene	BDL	0.02	BDL
acenaphthalene	BDL	0.02	BDL
acenaphthene	BDL	0.01	BDL
anthracene	BDL	0.01	BDL
benzo(a)pyrene	BDL	0.03	BDL
benzo(b)fluoranthene	BDL	0.03	BDL
benzo(c)pyrene	BDL	0.03	BDL
benzo(g,h,i)perylene	BDL	0.04	BDL
benzo(k)fluoranthene	BDL	0.03	BDL
biphenyl	BDL	0.01	BDL
chrysene	BDL	0.03	BDL
fluoranthene	BDL	0.06	BDL
fluorene	BDL	0.01	BDL
indeno(1,2,3-cd)pyrene	BDL	0.02	BDL
naphthalene	BDL	0.01	BDL
perylene	BDL	0.04	BDL
phenonthrene	BDL	0.03	BDL
pyrene	BDL	0.10	BDL
Petroleum Hydrocarbons-Aliphatic			
n-dodecane	BDL	0.01	BDL
n-eicosane	0.02	0.07	BDL
pristane	1.19	1.21	BDL
n-hexadecane	0.14	0.08	BDL
n-nonadecane	0.27	0.06	BDL
n-octadecane	0.16	2.04	BDL
n-pentadecane	0.66	7.02	BDL
n-tetradecane	0.17	0.26	BDL
n-tridecane	0.05	1.24	BDL
phytane	0.12	1.04	BDL

Table 4. Contaminants in samples from old-urban runoff site (Station A), ppm wet weight.

	Blue Crab	*Sediment*	*Water*
Heavy Metals			
Aluminum	81.43	674	BDL
Arsenic	1.30	1.81	BDL
Cadmium	0.10	0.15	BDL
Chromium	1.56	1.24	BDL
Copper	19.20	2.24	0.01
Iron	68.30	1678	BDL
Mercury	BDL	BDL	BDL
Manganese	14.20	17.60	0.04
Nickel	0.67	BDL	BDL
Lead	0.12	4.76	BDL
Selenium	0.46	BDL	BDL
Zinc	23.06	10.30	BDL
Petroleum Hydrocarbons-Aromatic			
dibenzanthracene	BDL	0.01	BDL
bonzanthracene	BDL	0.03	BDL
trimethyl-naphthalene	BDL	0.03	BDL
acenaphthalene	BDL	0.01	BDL
acenaphthene	BDL	BDL	BDL
anthracene	BDL	0.01	BDL
benzo(a)pyrene	BDL	0.03	BDL
benzo(b)fluoranthene	BDL	0.02	BDL
benzo(c)pyrene	BDL	0.02	BDL
benzo(g,h,i)perylene	BDL	0.02	BDL
benzo(k)fluoranthene	BDL	0.02	BDL
biphenyl	BDL	0.01	BDL
chrysene	BDL	0.03	BDL
fluoranthene	BDL	0.05	BDL
fluorene	BDL	BDL	BDL
indeno(1,2,3-cd)pyrene	BDL	0.02	BDL
naphthalene	BDL	BDL	BDL
perylene	BDL	0.01	BDL
phenonthrene	BDL	0.03	BDL
pyrene	BDL	0.05	BDL
Petroleum Hydrocarbons-Aliphatic			
n-dodecane	BDL	0.01	BDL
n-eicosane	BDL	BDL	BDL
pristane	0.30	0.12	BDL
n-hexadecane	0.03	0.09	BDL
n-nonadecane	0.01	0.08	BDL
n-octadecane	0.01	0.01	BDL
n-pentadecane	0.47	0.16	BDL
n-tetradecane	0.03	0.04	BDL
n-tridecane	BDL	0.03	BDL
phytane	0.07	1.10	BDL

Table 5.
Contaminants in samples from industrial-urban runoff site, (Station C), ppm wet weight.

	Blue Crab	*Sediment*	*Water*
Heavy Metals			
Aluminum	571	1623	0.07
Arsenic	0.97	2.96	BDL
Cadmium	0.08	0.26	BDL
Chromium	8.82	68.79	BDL
Copper	17.93	23.32	0.01
Iron	433	3813	0.10
Mercury	BDL	0.06	BDL
Manganese	952	145	0.03
Nickel	7.52	7.91	BDL
Lead	0.65	18.35	BDL
Selenium	0.35	0.95	BDL
Zinc	25.11	110.37	BDL
Petroleum Hydrocarbons-Aromatic			
dibenzanthracene	1.174	0.024	BDL
bonzanthracene	BDL	0.054	BDL
trimethyl-naphthalene	BDL	0.173	BDL
acenaphthalene	BDL	0.030	BDL
acenaphthene	BDL	0.013	BDL
anthracene	BDL	0.054	BDL
benzo(a)pyrene	BDL	0.090	BDL
benzo(b)fluoranthene	BDL	0.027	BDL
benzo(c)pyrene	BDL	0.239	BDL
benzo(g,h,i)perylene	BDL	0.158	BDL
benzo(k)fluoranthene	BDL	0.029	BDL
biphenyl	BDL	BDL	BDL
chrysene	BDL	0.144	BDL
fluoranthene	BDL	0.038	BDL
fluorene	BDL	0.016	BDL
indeno(1,2,3-cd)pyrene	.312	0.040	BDL
naphthalene	BDL	0.380	BDL
perylene	BDL	0.052	BDL
phenonthrene	BDL	0.042	BDL
pyrene	BDL	0.226	BDL
Petroleum Hydrocarbons-Aliphatic			
n-dodecane	BDL	BDL	BDL
n-eicosane	BDL	0.283	BDL
pristane	0.193	0.345	BDL
n-hexadecane	BDL	0.064	BDL
n-nonadecane	BDL	0.106	BDL
n-octadecane	BDL	0.230	BDL
n-pentadecane	0.176	0.202	BDL
n-tetradecane	BDL	0.009	BDL
n-tridecane	BDL	0.010	BDL
phytane	BDL	1.890	BDL

aliphatics was eight times higher in sediments from the new-urban runoff site (Table 3) than from the industrial-runoff site (Table 5). This was surprising because the industrial site is an area that receives runoff from frequent oil spills.

There is no information on the possible environmental effects of aliphatic hydrocarbons in sediments at these levels. Most of the aliphatics are insoluble in water and reported toxicity to aquatic life is low at these levels. Aliphatics are probably bioremediated by bacteria as the sediment get disturbed by dredging or other turbulence and do not accumulate to high levels.

Crab Tissue Samples

Aluminum was found in all crab samples collected from each area. In crab tissue from the reference area aluminum averaged 21.9 ppm (Table 2), 162.5 ppm from the new-urban site (Table 3), 81.4 ppm from the old-urban site (Table 4), and 571.5 ppm from the industrial-runoff site (Table 5). The aluminum levels at the two urban-runoff sites and the reference area are similar to levels reported by Gamble et al. (1988) for oysters in the lower Rio Grande Valley of Texas. Sparling and Lowe (1996) were only able to find one reference concerning aluminum toxicity to an invertebrate estuarine species. Aluminum toxicity is increased with a decrease in the pH of water.

The ambient water quality criteria for aluminum set by the EPA recommends that a 4-day average concentration in freshwater not exceed 87 ppb more than once every 3 years when the ambient pH is between 6.5 and 9.0 (Brooke and Stephan 1988). There is no saltwater criteria or sediment criteria for aluminum, and it was not considered as a major soil contaminant by Beyer (1990).

Several human and animal studies in recent years link aluminum uptake with several disorders such as osteomalacis dialysis osteodystrophy, encephalopathy (King et al. 1981), runted fetuses, microcaudia, gonad agenesis, fused ribs and vertebrae, and absence of leg bones (McCormack et al. 1979, Gilani and Chatzinoff 1981). A primary mechanism for aluminum toxicity is the free-ion ($Al^{3}+$) substitution for magnesium at critical enzyme sites in some cellular functions (Macdonald and Martin 1988). There are no scientific papers on the effects of aluminum on reptiles, and in general, diets with less than 1000 ppm aluminum are not considered harmful to birds (Sparling and Lowe 1996). Aluminum at the levels detected in blue crabs for this pilot study are not likely to have serious ecological consequences.

Chromium was at least nine times higher in the sediment from the industrial-runoff site (Table 5) than the other sites, and six times higher in the crab tissue when compared to the crabs from the other three sites. Chromium is listed as one of 14 noxious heavy metals and is on the EPA priority pollutant list (Keith and Telliard 1979).

Chromium appears in several valence states (+1 to +6) but the +6 valence form is the most toxic to aquatic organisms. The potential for accumulation of chromium is high in mollusks and crustaceans (Jenkins 1981). Little is known however, about the relation between concentrations of total chromium in a particular environment and biological effects on the organisms living there (Eisler 1986). The most sensitive saltwater organism tested was a polychaete that had a maximum acceptable toxicant concentration (MATC) range of 0.017 to 0.038 ppm (Eisler 1986). Chromium can be scavenged by colloidal iron and readily moved from an estuary to the ocean.

Manganese in blue crabs collected from the industrial runoff site was 40 times higher (Table 5) than tissue residues from the other sites (Table 2-4). Manganese is a macronutrient in most animals and is not often reported as an environmental contaminant, however the levels reported in blue crab tissue in this study suggest further consideration of this metal is warranted.

Nickel was at the highest concentration in both the sediment and the crab tissue collected from the industrial-runoff site (Table 5). Nickel occurs naturally in rivers due to soil erosion and will usually be elevated in sediments that receive

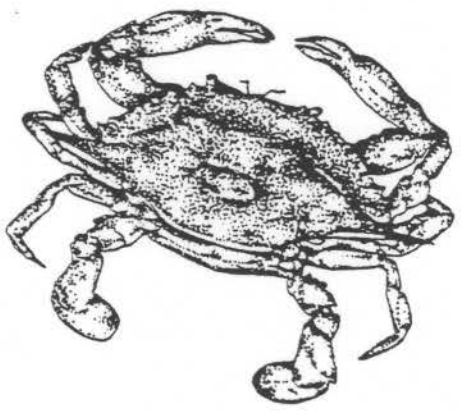
urban and industrial runoff. Bioaccumulation of nickel in birds and mammals is low but will readily accumulate in mollusks, crustacea, and algae (Jenkins 1981). The National Status and Trends Program of the National Oceanic and Atmospheric Administration, concluded that the potential for biological effects of nickel contamination is low in estuaries if sediments have less than 30 ppm nickel (Long and Morgan 1990). Ingersoll and Nelson (1989) classified sediments in the Great Lakes as "non polluted" if nickel residues were less than 20 ppm. This study indicates that nickel may be a contaminant in the sediment of the industrial-runoff site, and should be monitored through additional studies for possible bioaccumulation in aquatic organisms.

Petroleum hydrocarbons are usually discussed as two classes of compounds that affect fish and wildlife species (i.e., aliphatics and polycyclic aromatic hydrocarbons). Fish and crustaceans possess enzymes to activate aromatic compounds during metabolism (Eisler 1987), which generally results in low concentrations of these compounds in their tissue. There were no PAHs detected in the blue crab tissue samples from the reference area (Table 2), the new-urban runoff site (Table 3), or the old-urban runoff site (Table 4). Only two PAH compounds were detected in crab tissue from the industrial-urban runoff site (Table 5). Cain (1993) reported levels of 14 PAHs in crab tissue samples collected from this industrial canal averaged 140 ppb. This pilot in-situ bioassay study indicates that PAH contamination is present in the industrial-urban runoff area, and can be accumulated by blue crabs in a 3-day period.

Aliphatic hydrocarbons were detected in the crab tissue samples from the reference area (Table 2) as well as all three of the urban runoff areas (Table 3-5). These compounds were at very low levels and would not indicate any gross contamination of blue crabs from the urban runoff.

CONCLUSIONS

Blue crabs can be collected from an uncontaminated portion of an estuary and transported to other areas to do an accumulation study.Placement of crabs in urban runoff drainage ditches before a rainfall event are useful as an in-situ bioassay organism and will yield results in as little as 3 days. Heavy metals and petroleum hydrocarbons are apparently carried into receiving waters of urban runoff and may pose a problem to organisms closely associated with the sediment. This study suggests that a long-term monitoring study of urban runoff contamination may be useful, in order to successfully implement management options for reducing the contaminant loading to coastal estuaries.



LITERATURE CITED

Bates, T. S., P. P. Murphy, H. C. Curl, Jr. and R. A. Freely. 1987. Hydrocarbon distribution and transport in an urban estuary. Environ. Sci. & Technol., 21:193.

Black, J. 1982. Field and laboratory studies of environmental carcinogenesis in Niagara River fish. J. Great Lakes Res. 9:326-335.

Bourcier, D. R. and R. P. Sharma. 1980. Heavy metals and their relationship to solids in urban runoff. Inter. J. Environ. Anal. Chem., 7:273.

Brooke, L. T. and C. E. Stephan. 1988. Ambient water quality criteria for aluminum - 1988. EPA 440/5-86-008. NTIS, Springfield, VA. 56 pp.

Beyer, W. N. 1990. Evaluating soil contamination. U. S. Fish and Wildl. Service Rept., 90(2), 25 pp.

Cain, B. W. 1989. Contaminant assessment of maintenance dredge material from the Houston Ship Channel Galveston Bay, Texas. U. S. Fish & Wildl. Service Rept., Houston, TX., 36 pp.

Cain, B. W. 1993. Contaminant assessment of the upper Texas Coast. U. S. Fish & Wildl. Service Rept., Houston, TX., 46pp.

Carr, R. S. 1993. Sediment quality assessment survey of the Galveston Bay System. Galveston Bay National Estuary Program Publication GBNEP-30., 101 pp.

Clements, W. H., J. T. Oris and T. W. Wissing. 1994. Accumulation and food chain transfer of fluoranthene and benzo[a]pyrene in Chironomus riparius and Lepomis macrochirus. Arch. Environ. Contam. Toxicol., 26:261.

Cole, R. H., R. E. Frederick, R. P. Healy and R. G. Rolan. 1984. Preliminary findings of the priority pollutant monitoring project of the nationwide urban runoff program. J. Water Pollut. Control Fed., 56:898.

Dickhut, R. M. and K. E. Gustafson. 1995. Atmospheric inputs of selected polycyclic aromatic hydrocarbons and polychlorinated biphenys to southern Chesapeake Bay. Mar. Pollut. Bull., 30:385.

Eisler, R. 1986. Chromium hazards to fish, wildlife, and invertebrates: a synoptic review. U. S. Fish and Wildl. Serv. Biol. Rept. 85(1.6) 60 pp.

Eisler, R. 1987. Polycyclic aromatic Hydrocarbon hazards to fish, wildlife, and invertebrates: a synoptic review. U. S. Fish Wildl. Service Biol. Rept. 85(1.11), Wash., D.C., 81 pp.

Ekelund, R., A. Granmo, M. Berggren, L. Renberg and C. Wahlberg. 1987. Influence of suspended solids on bioavailability of hexachlorobenzene and lindane to the deposit-feeding marine bivalve, Aba nitida (Muller). Bull. Environ. Contam. Toxicol., 38:500.

Ellis, J. B., D. M. Revitt and D. Gavens. 1985. Polyaromatic hydrocarbon distributions in sediments of an urban catchment. Inter. J. Environ. Anal. Chem., 21:161.

Ellis, J. B., D. M. Revitt, D. O. Harrop and P. R. Beckwith. 1987. The contribution of highway surfaces to urban stormwater sediments and metal loadings. Sci. Total Environ., 59:339.

Galveston Bay National Estuary Program. 1994. The state of the bay. A characterization of the Galveston Bay ecosystem. Galveston Bay National Estuary Program Publication GBNEP-44, Webster, TX., 232 pp.

Gamble, L. A., G. Jackson, and T. C. Maurer. 1988. Organo-chlorine, trace element and petroleum hydrocarbons contaminants investigation of the Lower Rio Grande Valley, Texas, 1985-1986. U. S. Fish & Wildl. Service Rept., Corpus Christi, TX, 34 pp.

Gilani, S. H., and M. Chatzinoff. 1981. Aluminum poisoning and chick embryogenesis. Environ. Res. 24:1-5.

Gloyna, E. F. and J. F. Malina, Jr. 1964. Galveston Bay water quality study -- historical and recent data. Center for

Research in Water Resources, U. of Texas, Austin, TX., 130 pp.

Haug, A. 1984. Molecular aspects of aluminum toxicity. CRC Critical Reviews in Plant Sciences, 1:345-373, CRC Press.

Hoffman, E., G. L. Mills, J. S. Latimer and J. G. Quinn. 1984. Urban runoff as a source of polycyclic aromatic hydrocarbons to coastal waters. Environ. Sci. Technol., 18:580.

IARC (International Agency for Research on Cancer) 1983. IARC monograph on the evaluation of the carcinogenic risk of chemicals to humans: polynuclear aromatic compounds, Part I. IARC Press: Lyon. 477pp.

Ingersoll, C. G. and M. K. Nelson. 1989. Testing sediment toxicity with Hyallella asteca (Amphipoda) and Chironomus reparius (Diptera). ASTM STP 13th. Sym., Atlanta, GA. 43 pp.

Jenkins, D. W. 1981. Biological monitoring of toxic trace elements. EPA 600/53-80-90. NTIS, Springfield, VA. 9 pp.

Keith, L. H. and W. A. Telliard. 1979. Priority pollutants: 1.- a perspective view. Environ. Sci. and Toxicol. 13: 416-423.

King, S. W., J. Savory, and M. R. Wills. 1981. The clinical biochemistry of aluminum. CRC Critical Reviews in Clinical Laboratory Science, 14, CRC Press.

Long, E. R. and L. G. Morgan. 1990. The potential for biological effects of sediment-sorbed contaminants tested in the national status and trends program. NOAA Tech. Memo. NOS OMA 52, Seattle, WA. 175 pp.

Macdonald, T. L. and R. B. Martin. 1988. Aluminum ion in biological systems. Trends in Biochem. Sci. 13:15-19.

McCain, B. B., D. C. Malins, M. M. Krahn, D. W. Brown, W. D. Gronlund, L. K. Moore and S.-L. Chan. 1990. Uptake of aromatic and chlorinated hydrocarbons by juvenile chinook salmon (Oncorhynchus tshawytscha) in an urban estuary. Arch. Environ. Contam. Toxicol, 19:10.

McCormack, K. M., L.D. Otlosen, V.L. Sanger, S. Sprague, G.H. Mayor, and J.B. Hook. 1979. Effects of prenatal administration of aluminum and parathyroid hormone on fetal development in the rat. Proc. Soc. Exp. Biol. Med. 161:74-77.

Sanders, M. 1995. Distribution of polycyclic aromatic hydrocarbons in oyster (Crassostrea virginica) and surface sediment from two estuaries in South Carolina. Arch. Environ. Contam. Toxicol., 28:397.

Shuster, C. N. Jr. and B. H. Pringle. 1969. Trace metal accumulation by the American eastern oyster, Crassostrea virginica. Proc. Nat. Shellfish Assoc., 59:91.

Sparling, D. W. and T. P. Lowe. 1996. Environmental hazards of aluminum to plants, invertebrates, fish, and wildlife. Reviews Environ. Contam. and Toxicol., 145:1-127

USACOE, 1979. Final environmental statement Texas City and vicinity, Texas hurricane-flood protection project. U. S. Army Engineer District, Galveston, TX. 62pp.

Webber, D. B. 1983. Aerial flux of particulate hydrocarbons to the Chesapeake Bay estuary. Mar. Pollut. Bull., 14:416.

Winger, P. V., D.P. Schultz and W.W. Johnson. 1990. Environmental contaminant concentrations in biota from the lower Savannah River, Georgia and South Carolina. Arch. Environ. Contam. Toxicol., 19:101.

APPENDIX

METAL ANALYSIS

Samples were lyophilized prior to sample digestion. If necessary, the dried sample was then passed through a 2 mm plastic sieve and a split was then ground using a mortar and pestle. Percent moisture was determined using Standards Methods for the Examination of Water and Wastes, 14th ed. (Section 208A).

Digestions for ICP analysis were performed in accordance with "Procedures for Handling and Chemical Analysis of Sediment and Water Samples", US EPA/COE, Technical Report EPA/CE-81-1, May 1981. One gram aliquots of the dried samples were digested in a vigorous nitric acid-hydrogen peroxide procedure with a final aqueous matrix dilution of 100 mm after filtration. The sample results are reported in mg/kg dry weight. No extraordinary reactions or color changes were noted for the ICP digestion.

One sample was spiked and duplicated. Summaries of the ICP QC pages follow:

1. **Digestion Blanks** - Two blanks were digested with the samples. Normal contamination levels for several analytes were found in the blanks.

2. **Initial Calibration Checks** - The ICP spectrometer was calibrated properly as indicated by the percent recoveries of the elements analyzed (within 10% windows) in the initial check solutions.

3. **Initial Interference Check** - Background correction factors for selected analytes were properly determined as indicated by percent recoveries for the interference check solutions (within 20% windows).

4. **Duplicate Analysis** - The duplicate precision, as indicated by the Relative Percent Differences (RPD), was acceptable (inside the 20% windows) for all elements with the exception of Al and Pb. Al is only slightly high (21%). The high Pb RPD, at 30%, is probably due to the variability normally found when concentrations are near the IDL.

5. **Spike Analysis** - Spike recoveries in the sample were within 75 to 125% for most elements. Sb, B, Ag, and Sn were all low. Low recoveries are typically seen for these elements. As a result, the sample results are probably biased low.

6. **Reference Materials** - A solid EPA laboratory control sample (0287) was used as a reference material. Recoveries for certified analyte values which could be quantitated at a level above the reporting limit were all within +/- 25% with the exceptions of Ag. Ag recoveries are typically low with this type of digestion.

ORGANOCHLORINE AND AROCHLOR ANALYSIS

Twenty-four sediment samples were analyzed by Patuxent methods.

A subsample of each well-mixed sediment (5.0 g to 7.3 g), and sodium sulfate (heat treated at 550°C) were blended in a one-half-pint food blender. This mixture was added to a fiber extraction thimble (pre-extracted with petroleum ether). Internal standard solution from a syringe was placed on the sample in the thimble. The sample was extracted with petroleum ether (B&J distilled in glass) for at least 20 hours. The extract was concentrated to 10 mL with a Kuderna-Danish on a steam bath. During the concentration stages, the extract was never allowed to go to dryness.

The 9 mL of extract was exchanged into methylene chloride (Omnisolve distilled in glass) and brought to a 10 mL volume. A volume of extract equivalent to approximately 1 g of sample was loaded into a loop on the GPC unit

(ABC model No. 1002A) and injected. The GPC unit transfers the eluted fraction containing the chlorinated organics to an autoconcentrator that concentrates during elution and exchanges the solvent to hexane for a final volume of 10 mL.

The sample was concentrated to 1 mL by nitrogen blowdown and subjected to alumina micro column cleanup. The alumina (Biorad neutral alumina AG7, 100 to 200 mesh) was ignited and then deactivated with distilled water (7% by weight). The analytes were eluted with 10 mL of 4:1 hexane/methylene chloride. The eluent was concentrated to 1 mL for GC capillary analysis.

Percent moisture was determined by placing 2 g of the homogenate into a tared aluminum pan and placed in a drying oven (105°C) for at least 48 hours. The weight was recorded after cooling in a desiccator overnight.

For organochlorine analysis, six chlorinated biphenyl congeners were added before extraction of the sample and served the following purposes:

1. Monitoring sample extract losses due to extraction efficiency, GPC cleanup, or extract transfer.

2. Estimating detection limits.

3. Increasing accuracy of predicted retention times ($\pm$0.005 min) for the analytes.

4. Providing backup internal standards in the event of sample matrix interference with the normal quantification internal standard.

Before organochlorine GC analysis, two additional internal standards were added to the sample. These were used for monitoring the instrument's health; e.g., to indicate if there were any problems with the injection of each sample.

A Hewlett-Packard 5880A GC equipped with dual capillary column/dual ECD detectors was used for the organochlorine and arochlor analysis. The analysis was a single splitless (Grob) injection onto two 30-meter columns (DB-1 and DB-1701) of different polarities. The dual column analysis, besides providing confirmation of the pesticides, checks for coelution of unknowns with each individual pesticide. Because of the high resolving power of the capillary columns, coelution by an unknown on both columns is improbable.

Except as explained below, the amount and variance shown on the sample report pages was calculated from the values given by the two GC columns for each compound detected. If the variance was greater than 15% of the mean, it was assumed that coelution was occurring on the column showing the higher amount and only the lower amount was reported. In that case, a variance indicator NA (Not Applicable) was printed in the "Variance" list. Also, if near coelution occurs, where a positive identification on one of the GC columns was not possible, then only the amount given by the GC column that allows positive identification was reported. In this case, the variance indicator NA also was printed. The indicator NA also was used in the "Variance" list in cases where nothing was found above the detection limits on either column where the indicator ND was printed in the "Amount" list.

The temperature program was 50°C for two minutes to 280°C at 3°C/minute and a post-run temperature of 290°C for 5 minutes. Linear flow rate was at 30 cm helium/second.

Quantitation was done on the Hewlett-Packard 5880A GC. Due to the narrowness of the capillary peaks, all data were based on peak height, resulting in less biasing due to tailing, near coelution and baseline drift ("Assessment of the Results from Data Processing Systems using a Digital Chromatogram Simulator", R.J. Hunt, Journal of High Resolution Chromatography Communications, Vol. 8, July 1985, pp. 347-355). All data were collected directly from the GC into databases in an Amiga computer. The databases, besides providing report generation, allow the monitoring of the standard curves and internal standards over time. The data on the Amiga also was used for pattern recognition in arochlor analysis and to develop the organochlorine pesticide "unknowns" report.

The batch size for soxhlet extraction was 12 (11 samples and 1 blank). Two batches went onto the GPC at a time. No analytes were detected in the blank at concentrations greater than 0.5 ppb.

No GC/MS confirmation was done since no analytes were detected.

ALKANE AND AROMATIC ANALYSIS

Sample preparation for the alkanes and aromatics was as follows. Five micrograms deuterium labeled surrogate spikes were added to 5-15 g of the sample homogenate. There were labeled analogs for each of the polyaromatic hydrocarbons to be analyzed except benzo(e)pyrene and perylene. Aqueous potassium hydroxide (4 N) was added to each of the mixtures and the sample saponified in a steam bath for 2 hours. The centrifuge tubes were vortex mixed every 40 minutes. The hydrolysates were actified with hydrochloric acid, the mixture transferred to a separatory funnel and extracted three times with 25 mL methylene chloride each time. The aqueous layer was discarded. Soil and sediment samples were not hydrolyzed. The samples were mixed with sodium sulfate and soxhlet-extracted overnight with methylene chloride. The combined organic extract filtered through muffled NA_2SO_4 and rotary-evaporated to several millimeters. One hundred mL petroleum ether and 0.7 mL iso-octane was added prior to initial evaporation and the extract again reduced to several millimeters.

The alkanes and aromatics were fractionated on a column of 20 g 2.0% water-deactivated silica gel. Alkanes were eluted with 100 mL 40% methylene chloride in petroleum ether and an additional 60 mL methylene chloride. Each fraction was concentrated by rotary evaporation followed by nitrogen evaporation. The alkane fraction was evaporated to 1 mL, internal standards added and the extract transferred to a vial in preparation for GC analysis.

The aromatic fraction was concentrated to 10 mL and cleaned by gel permeation chromatography on Bio-Beads SX-3. The collected gel permeation fraction was first rotary-evaporated, then nitrogen-evaporated to 1 mL and finally shaken with aqueous sodium hydroxide. This step removed residual fatty acids. An injection internal standard was added to each extract and it was transferred to a vial in preparation for GC analysis.

Three compounds, n-undecane, n-docosane, and n-triacontane were added to each of the final alkane extracts before GC analysis to serve as quantitation internal standards.

Gas chromatography was done using a 30 M DB-5 capillary column with splitless injection on a Hewlett-Packard 5880A GC with flame ionization. The temperature program was 60°C for 3 minutes to 310°C at 6°/minute for alkanes and a post run temperature of 320°C for 2 minutes. Linear flow rate was 30 cm helium/second.

Internal standards for the polyaromatic hydrocarbons were the deuterium labeled compounds added at the saponification stage. The deuterium labeled fluorene has been found to deuterium/hydrogen exchange during base hydrolysis. Thus, D_{10} phenanthrene was used as the internal standard for fluorene.

Use of these internal standards automatically compensates for any losses during sample preparation. An injection internal standard was added to each extract before analysis on the GC/MS and was used to determine if recovery of labeled compounds were within the normal expected range.

Gas chromatography was done using a 30 M DB-5 capillary column with splitless injection on a Hewlett-Packard 5890 GC in conjunction with a Finnigan-MAT INCOS 50 mass spectrometer. The temperature program was 50°C for 2 minutes to 320°C at 8°/minute. The mass spectrometer scanned from 35 to 450 m/z in 0.56 seconds at 70 eV.

The target polyaromatic hydrocarbons were purchased from Supelco (Supelpreme) and mixtures of isotope labeled compounds were purchased from MSD Isotopes. Responses of the labeled compounds to 2,2'-difluorobiphenyl internal standard and of the target to the labeled

compounds was used to create a polyaromatic hydrocarbon library response list. The response curves for the target polyaromatic hydrocarbons were generated from 1 to 50 ng on column and were linear in this range.

The mass spectrometer was calibrated and an on-going calibration verification standard at either 1 or 2 ng on column injected daily. Compounds were searched for and quantified with "TCA", a program available from Finnigan-MAT for the analysis of target compounds. Mass spectra were examined manually to verify identification.