

# **Toxicants in Aquatic Organisms**

## Toxic Contamination of Aquatic Organisms in Galveston Bay

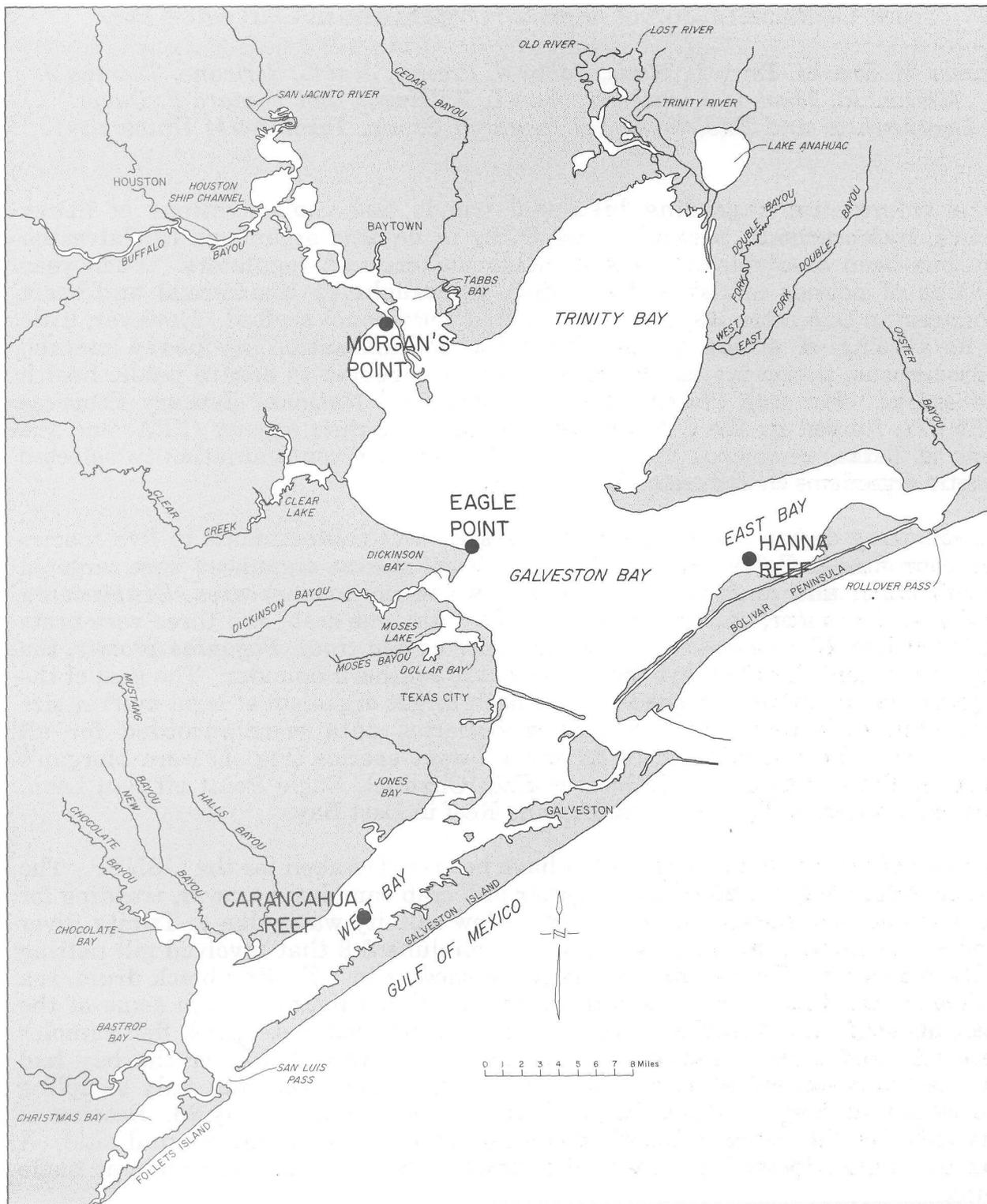
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Little information regarding historical trends and concentrations of heavy metals, hydrocarbons, pesticides and PCBs in aquatic organisms in Galveston Bay has been available to guide decision makers and regulators. Each year millions of pounds of fish and shellfish are caught by commercial and sport fishermen in Galveston Bay and consumed as nutritional seafood. However, little or no testing of edible tissues for toxic contamination by heavy metals, hydrocarbons, pesticides and PCBs has been conducted to assure public health and safety. For this reason, the Galveston Bay National Estuary Program (GBNEP), funded by the U.S. Environmental Protection Agency (EPA) and the State of Texas, undertook this study to characterize contamination in selected aquatic organisms in Galveston Bay.

The sampling design called for the analysis of trace contaminants in five species from four sites in Galveston Bay. Five species of marine organisms were targeted for collection and analyzed as follows: two macroinvertebrates, *Crassostrea virginica*, the oyster, and *Callinectes sapidus*, the blue crab; and three vertebrate marine fishes, *Cynoscion nebulosus*, the spotted sea trout, *Pogonias cromis*, the black drum, and *Paralichthys lethostigma*, the southern flounder. The goal of the program was to collect ten specimens of each target organism of legal market size from each collection site. Standard fisheries data were recorded for all collections. The collection sites for these target species (Fig. 1) were Morgan's Point, at the mouth of the Galveston Ship Channel, Eagle Point off San Leon, Carancahua Reef in West Bay, and Hanna Reef in East Bay.

Four samplings of aquatic organisms have been undertaken for the GBNEP. The first sampling May 23-25 collected oyster and crab samples; however, trawling for fish was not very successful as a result of low salinity water due to Trinity River flooding. A second sampling was undertaken June 6-8 that involved gill netting at the four sites. This sampling had some success in collecting black drum, sea catfish (*Arius felis*), spotted sea trout and southern flounder from some of the sites, although not in sufficient quantities for most analyses. Most fish samples were collected from a sampling from July 30 to August 3 after the bay had returned to a somewhat normal salinity regime. However, late July sampling was complicated by the Apex Barge oil spill that occurred on July 28. Because of this spill, few fish were collected near Eagle Point (close to the oil spill site). A final sampling trip on September 4-6 completed the remaining sampling at Eagle Point.

The analytical program called for the analyses of ten individual specimens of the five target organisms from each site (200 edible muscle tissue samples). Fifty liver samples were composited for analyses from the approximately 120 fishes. Trace contaminants measured included heavy metals, polynuclear aromatic hydrocarbons (PAHs), pesticides and PCBs and a GC-MS scan for other EPA



**Figure 1. Collection sites for tissue samples.**

organic priority pollutants. Trace elements of interest in this study were those on the EPA Priority Pollutant List (PPL) which included: arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), silver (Ag), and zinc (Zn). PAHs determined by GC/MS/SIMs included 39 two- to five-ring aromatics and selected alkylated homologs. Pesticides and PCBs were determined by gas chromatography with electron capture detection (ECD). Selected chlorinated pesticides (aldrin, chlordane, dieldrin, endrin, heptachlor, BHC, heptachlor epoxide, hexachlorobenzene, lindane, mirex, trans-nonachlor, toxaphene, DDTs, DDDs and DDEs) and individual PCB congeners were quantitated. Analytical methods for trace organic analyses followed those of the NOAA National Status and Trends Mussel Watch Program.

None of the average concentrations of trace metals or trace organic contaminants in fish tissue, oysters, or crabs collected in this study pose a risk to human health associated with consumption of seafood based on the U.S. EPA (1989) guidance manual for assessing human health risks for chemically contaminated fish and shellfish. In general, trace contaminants were higher in oyster and crab tissues than fish tissue. This was especially true for trace organics and certain trace metals such as zinc, lead, nickel, copper, cadmium and silver. Mercury showed the opposite trend with higher concentrations in fish tissue. Most PAHs in Galveston Bay seem to originate from combustion sources (atmospheric deposition or runoff) and not from petroleum inputs based on the distribution of PAHs and their alkylated homologs. The chlorinated hydrocarbons were represented by low levels of DDT and its metabolites (DDD and DDE). As expected, higher contaminant levels were generally found in the upper portion of Galveston Bay (Morgan's Point) near the Houston Ship Channel.

## **Trace Organic Contamination in Galveston Bay: Results from the NOAA National Status and Trends Mussel Watch Program**

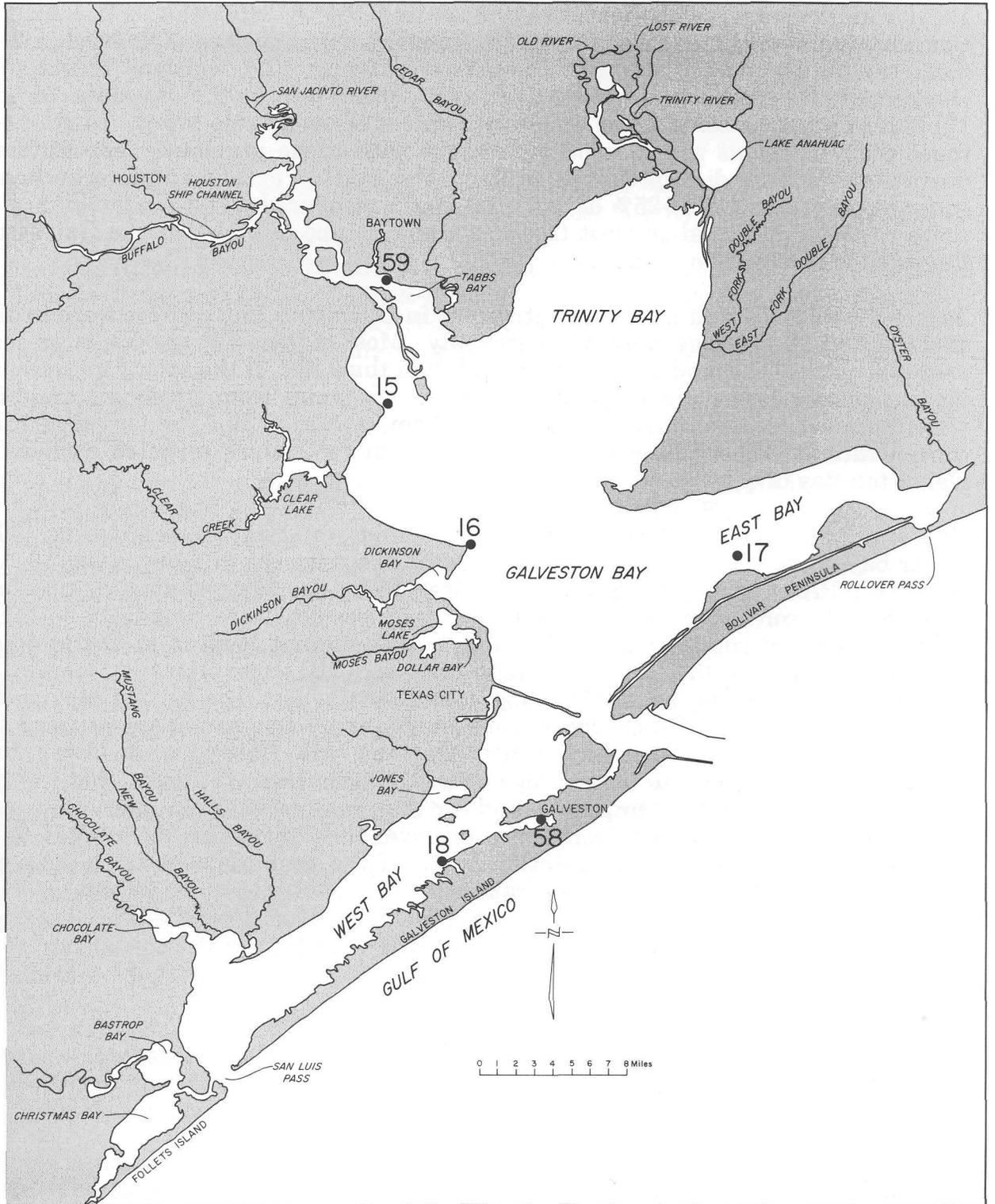
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In order to determine the current status and long-term trends for selected environmental contaminants in U.S. coastal areas, the National Oceanic and Atmospheric Administration (NOAA) established the National Status and Trends (NS&T) Mussel Watch Program. As part of the NS&T Program, sediment and oyster samples have been collected and analyzed from over 70 estuarine sites in the Gulf of Mexico representing all major Gulf Coast estuaries. Sampling sites were located in areas not influenced by known point sources of inputs.

Oysters have been employed as sentinel organisms because they are cosmopolitan, sedentary, known to bioaccumulate contaminants of interest, able to provide an assessment of bioavailability, not readily capable of metabolizing contaminants, able to survive pollution loading, readily found as locally stable populations, transplantable, and commercially valuable. Oysters are, therefore, excellent biomonitors for contamination in estuarine areas.

The Galveston Bay system is one of the largest and most economically important estuaries along the Texas Gulf Coast. This area has been the recipient of various contaminant inputs because of an aggressively growing urban and industrial region. Houston, Deer Park, Baytown, Texas City and Galveston, surrounding Galveston Bay to the north and west, are some of the most heavily industrialized areas in Texas. Hundreds of industrial plants bordering the Galveston Bay estuarine system, including petrochemical complexes and refineries, as well as runoff, are likely to introduce significant amounts of organic contaminants into the bay. In general, ecological studies have suggested that the waters of Galveston Bay contained contaminants in sublethal amounts which caused stress to organisms resulting in significant changes in the estuarine community structure.

Samples were collected at six locations in Galveston Bay (Fig. 1). Sampling was conducted each winter and began January of 1986 at four sites (15-18), and in December of 1987 at two other sites (58-59). Additional samples were collected at some of these sites to provide information on seasonal trends in contaminant concentrations. Sediments (top 1 cm) and oysters (20) were collected at three stations at each site and analyzed for polynuclear aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated pesticides (e.g DDT, chlordane) and tributyltin. All sample analyses were performed using Standard Operating Procedures to provide high quality, precise, accurate and reproducible data. Data quality was further assured by participation in NOAA/NIST intercalibration exercises. This allows for direct comparison of NS&T Gulf Coast data with NS&T data for the East and West Coasts.



**Figure 1. Galveston Bay sampling sites included the Ship Channel (59), Yacht Club (15), Todd's Dump (16), Hanna Reef (17), Offatt's Bayou (58) and Confederate Reef (18).**

Total PAH average concentrations ranged from 54 to 2400 ng/g. The higher concentrations were measured in oysters from the upper portion of Galveston Bay (i.e., stations 15 and 59) and near the City of Galveston (i.e., stations 18 and 58). Oyster samples from areas farther away from urban centers (i.e., stations 16 and 17) had average concentrations one to two orders of magnitude lower. In general, these concentrations are in good agreement with those previously encountered during temporal studies in Galveston Bay. Two PAHs, pyrene and fluoranthene, generally accounted for >25% of the total PAHs measured. The predominance of these compounds would suggest that the major source of PAHs in the Galveston Bay area is combustion products.

Average total PCB and DDT concentrations in Galveston Bay oysters were in the 48-1100 and 12-240 ng/g ranges, respectively. Most of the DDT residue is present as metabolites, DDE and DDD. In general, less than 10% of the total contaminant load in oysters is the parent compound, DDT. Samples from stations 15 and 59 were the most contaminated, while oysters from Station 17 had the lowest residue concentrations. These concentrations agree with the ranges reported earlier for Galveston Bay bivalves.

Contaminant concentration patterns were similar for most contaminants. The upper bay sites (15, 59) had higher concentrations than the mid-bay sites (16, 17) for DDT, PAH, PCB and butyltins. Sites from the lower bay (18, 58) had intermediate concentrations. This most likely results from proximity to large urban areas and runoff inputs. The lower contaminant loading in the mid-bay region probably results from dilution effects. The concentrations found in Galveston Bay are similar to the range found throughout the Gulf of Mexico for the NS&T Program. The concentrations in the upper bay are above average for the Gulf of Mexico, mid-bay concentrations are below, and lower bay concentrations are close to the average Gulf of Mexico concentrations. Most of the sites show no consistent temporal trend for the organic contaminants. However, there is a general decrease in concentrations over time at Station 15 for PAH, PCB and DDT. Sample collections at other times of the year indicate some seasonal variability of contamination concentrations.

## Trace Metals in Galveston Bay Oysters

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Oysters and other bivalves have been used as "sentinel" organisms for assessing the pollution status of marine water bodies for almost twenty years. For example, Goldberg, *et al.*, (1983) report data for a U.S. EPA funded "Mussel Watch" program conducted in 1976-78 and the current NOAA funded "National Status and Trends Program" (NS&T) is an outgrowth and extension of the "Mussel Watch" concept. Bivalves are widely recognized as being responsive to changes in pollutant levels in the environment, good accumulators of pollutants, widely distributed along coasts, and easy to collect and analyze. They integrate pollutant levels in the environment over weeks to months and therefore allow areas to be compared even when sampling is done only once or twice per year.

Oysters (*Crassostrea virginica*) were collected at six different sites in Galveston Bay during 1986-1989 as part of NS&T (see Fig. 1, page 69). Each site was on an identifiable oyster reef and at each, twenty oysters were taken from each of three stations, the stations being 100 to 500 m apart. Each site was sampled once each year, except two of the sites (stations 58, 59) were not sampled the first two years. The twenty oysters from each station were combined and analyzed as a single sample each year. In most cases stations were located hundreds of meters to many kilometers away from any obvious point sources of pollutant inputs in an attempt to characterize large areas of Galveston Bay, rather than to identify specific point sources of pollutant input.

Frozen oysters were returned to the lab where they were opened under clean room conditions. The oyster tissue was put into teflon jars which were loaded into an industrial paint shaker and shaken vigorously for 15-20 minutes to completely homogenize the samples. An aliquot of the combined and homogenized sample was freeze-dried, re-homogenized by ball milling in plastic, and weighed into a digestion vessel. Digestion of the approximately 200 mg dry weight samples of oyster tissue used three ml of a four to one mixture of ultra-pure nitric and perchloric acids.

Two blanks and two reference materials were digested with every set of 20-40 samples. Repeated analysis of these reference materials and participation in several intercalibration exercises give an estimate of ten percent or better for both the precision and accuracy of the data reported here.

All data reported here were obtained by atomic absorption spectrophotometry (AAS). The samples were analyzed for Ag, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Si, Sn, and Zn. Flame AAS was used for Cu, Fe, and Zn which exhibit high concentrations in oysters, cold vapor AAS for mercury, and graphite furnace AAS for the remaining elements.

Trace metal concentrations found in oysters collected along the entire Gulf of

Mexico coastline during the first four years of NS&T were generally similar to those reported in oysters taken from non-contaminated water in other parts of the world (Texas A&M Geochemical and Environmental Research Group, 1990). Only a few sites showed obvious trace metal pollution and these were restricted geographically such that nearby sites were usually unaffected. Abnormally high or low values at a site did, however, usually repeat year after year suggesting local control. Abnormal sites for most metals were just as likely to be visibly pristine as to be highly industrialized.

The oysters collected in Galveston Bay for NS&T were similar in trace metal content to those collected elsewhere along the Gulf coastline, i.e., there is no indication of generalized trace metal pollution in Galveston Bay (Table 1). The average Ag, Cd, Cr, Fe, Mn and Pb in Galveston Bay oysters differs by 10% or less from the Gulf-wide average. Copper is 13% higher in Galveston Bay, while Ni is 15% higher and Se is 16% higher. A "t-test" of the significance of those differences shows that only the Se averages are significantly different at the 95% confidence level. Arsenic in Galveston Bay oysters is less than one-half the Gulf-wide average, but the Gulf average is greatly influenced by several sites in southern Florida that produce oysters greatly enriched in As. Oysters from other Texas and Louisiana bays are similar in As content to those in Galveston Bay. Tin seems to be about 20% lower than Gulf averages in Galveston Bay, but all Sn values are near the detection limit of the method used and a 20% difference is not significant. Finally, Zn is 43% higher in Galveston Bay oysters than in Gulf-wide average oysters.

*Table 1. Average trace metal concentrations in 1200 oysters from Galveston Bay and 14,000 oysters from the entire U.S. Gulf coastline. All elements in ppm, µg/g dry wt.*

	<u>Ag</u>	<u>As</u>	<u>Cd</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Hg</u>	<u>Mn</u>	<u>Ni</u>	<u>Pb</u>	<u>Se</u>	<u>Sn</u>	<u>Zn</u>
GB avg.	2.35	4.74	4.29	0.53	166	279	.0815	16.2	2.01	0.66	3.46	0.26	3220
GOM avg.	2.13	9.94	4.06	0.57	148	309	0.135	15.1	1.75	0.68	2.96	0.33	2250
GB/GOM	1.10	0.48	1.06	0.93	1.12	0.90	0.60	1.07	1.15	0.97	1.17	0.79	1.43

Discussion of metals in Galveston Bay oysters averaged over all sites and all years obviously cannot show possible geographic and temporal trends within the bay. In the case of Zn, for example, three of the six Galveston Bay sites had oysters with near Gulf average Zn, with relatively little year to year variation. The other three sites had much higher Zn. Two of the high Zn sites, Ship Channel and Yacht Club, are in extreme northwestern Galveston Bay near industrial waste water inputs and boat basins where Zn contamination might be expected. The other high Zn site was in Offatt's Bayou on Galveston Island and is surrounded by residential development and private boat moorings. This apparent local control on Zn, and in some cases on other metals, is seen not only in Galveston Bay but also throughout the Gulf of Mexico. Large site to site and time to time changes in trace metal concentration might be due to man, but the exact activity responsible has not been identified.

Cadmium, Pb, Ag and Hg are often added to the environment by man in amounts rivaling those added by nature but there is no evidence of anthropogenic inputs of these metals in the Galveston Bay oyster data. Rather, except for Zn, trace metal concentrations in oysters from Galveston Bay are similar to those in oysters from pristine areas elsewhere and do not reflect the big differences in proximity to population and industrialization of the different sites in the bay.

#### Literature Cited

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- Goldberg, E. D., M. Koide, V. Hodge, A. R. Flegal and J. Martin. 1983. U.S. mussel watch: 1977-1978 results on trace metals and radionuclides. *Estuarine, Coastal and Shelf Science*, 16: 69-93.

## Transplanted Oysters as Sentinel Organisms in Monitoring Studies

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Coastal marine environment contamination by a number of organic compounds of synthetic or natural origin has received increasing attention over the last several years. Biomonitoring of these compounds in the aquatic environment is well established and bivalves are generally preferred for this purpose. The rationale for the "Mussel Watch" approach using different bivalves, e.g., mussel, oysters and/or clams, has been summarized by different authors and its concept has been applied to many monitoring programs during the last decade.

The National Oceanic and Atmospheric Administration (NOAA) National Status and Trends (NS&T) Program, for example, is designed to monitor the current status and long-term effects of selected organic and inorganic contaminants of environmental concern, i.e., polynuclear aromatic hydrocarbons (PAHs), chlorinated pesticides, polychlorinated biphenyls (PCBs), and trace metals. Concentrations of these contaminants in bivalves are measured along the coasts of the U.S.A. over several years. During the first five years of this program (1986-1990) the objective was to sample all the locations prescribed by NOAA; however, this goal was compromised by locations depleted of living oysters because of diseases, predators, excessive freshwater runoff, harvesting or dredge material burying entire reefs. Therefore, in some instances, it was not possible to obtain samples. At the end of the first five years of the NS&T program, nearly 20% of the original locations presented some of the above mentioned sampling problems that left the data base with missing values. Transplantation of bivalves to areas where indigenous individuals were not originally present or have been lost because of natural or man-induced actions could be a potentially useful tool in monitoring environmental pollution.

The present study was designed to examine the uptake and depuration of selected organic contaminants, PAHs and PCBs in oysters (*Crassostrea virginica*) through transplantation experiments in two locations in Galveston Bay, Texas.

Approximately 250 oysters of similar dimensions (e.g., 6-8 cm) were collected from a relatively uncontaminated area in Galveston Bay, Hanna Reef, and transplanted in 24x70 cm net bags, containing 25-30 individuals per bag, to a new location near the Houston Ship Channel (HSC) in the upper part of the bay. Composite samples of 20 transplanted and 15 indigenous oysters were collected at zero, three, seven, 17, 30, and 48 days during the first phase of the transplantation experiment. The remaining Hanna Reef oysters were then back-transplanted to their original location in Galveston Bay. At the same time, approximately 150 indigenous oysters from the HSC site were also transplanted to the Hanna Reef area. Composite samples of 20 oysters from each population were collected at three, six, 18, 30, and 50 days after transplantation.

The concentrations of most organic contaminants in oysters transplanted from Hanna Reef to the HSC increased dramatically during the seven-week exposure

period. Comparatively, concentrations of individual PAHs and PCBs in indigenous oysters during the first phase of this experiment were fairly constant. The analyte concentrations in native oysters represent the time-integrated contaminant concentrations available to the oysters in solution, adsorbed onto particles and incorporated into food.

Initial concentrations of total PAHs in transplanted oysters increased from 290 ng/g to a final value of 4360 ng/g. Two- and three-ring PAHs were detected in low concentrations in transplanted and indigenous oysters. Four- and five-ring compounds were accumulated to the highest concentrations in Hanna Reef oysters. By the end of the first 48 days, transplanted oysters accumulated these PAHs to levels that were not statistically differentiable from the concentrations measured in native individuals. The PAHs accumulated to the highest concentrations were: pyrene > fluoranthene > chrysene > benzo(e)pyrene > benzo(b)anthracene.

Hanna Reef and HSC oysters showed statistically significant depuration ( $p < 0.05$ ) of four- and five-ring PAHs after relocation to the Hanna Reef area. Depurations of these aromatic compounds by both groups of oysters were approximately exponential. The half-lives ranged from 10.4 and 12.4 days for pyrene to 25.6 and 38.5 days for fluoranthene in Hanna Reef and HSC oysters, respectively. Most of the values were, however, between ten and 16 days.

PCB concentrations in transplanted oysters increased from 30 ng/g to 850 ng/g after the 48-days exposure period. Pentachlorobiphenyls were the compounds accumulated to the highest concentrations in transplanted and native oysters. In comparison, practically no octa-, nona- or decachlorobiphenyls were detected in either oyster group. Unlike the PAHs, not all the PCB homologs measured in transplanted oysters reached the concentration encountered in indigenous individuals by the end of the first phase of this experiment. While there were no statistically significant differences in the tri- and tetrachlorobiphenyl concentrations measured in transplanted and native oysters, significant differences were observed in the total concentrations of penta- and hexachlorobiphenyls. It is evident that a longer exposure period is needed for the higher molecular weight PCB to reach a steady state concentration.

Hanna Reef and HSC oysters showed statistically significant depuration ( $p < 0.05$ ) of low molecular weight PCBs when relocated to the Hanna Reef area. Originally uncontaminated oysters depurated PCBs at a faster rate than chronically contaminated oysters. The clearance rates of high molecular weight PCBs were significantly slower in both oyster populations. Biological half-lives for these PCBs in Hanna Reef and HSC oysters ranged from 21 to 129 days and from 20 days to > year, respectively.

Transplanted oysters can be considered valuable bioindicators of environmental contamination by PAHs and PCBs in areas lacking indigenous oysters. However, in order to avoid misleading interpretations of environmental data collected using transplanted bivalves, it is imperative to understand that some trace organic compounds need extremely long time, i.e., several months, to reach equilibrium concentrations.