

Oil Spill Impacts

The Effects of the Apex Barge Oil Spill on the Fish of Galveston Bay

*Susanne J. McDonald, James M. Brooks, Dan Wilkinson,
Terry L. Wade, and Thomas J. McDonald*

Geochemical and Environmental Research Group, Texas A&M University

On July 28, 1990 the Greek tanker, *Shinoussa*, collided with three barges in the Houston Ship Channel in Galveston Bay, Texas. Over 700,000 gallons of petroleum product were released into the bay from one of the Apex barges. The spilled petroleum was a processed product known as a vacuum reformat that contained unusually high concentrations of the toxic polynuclear aromatic hydrocarbon (PAH), benzo[a]pyrene (BaP). The purpose of this study was to assess the effects of the spilled petroleum on the fish of Galveston Bay and to compare results obtained from more typical monitoring methods (i.e., PAH tissue residue concentrations) and a recently developed technique for detecting PAH metabolites in fish bile. Measuring the concentrations of biliary PAH metabolites in fish is a sensitive method that can provide an improved estimation of PAH exposure, early indications of habitat deterioration, and a clear association between pollutant source and resultant exposure. Data of this nature is beneficial for informed management and regulatory decisions.

Field crews were on Galveston Bay collecting fish as part of the Galveston Bay National Estuary Program (GBNEP) monitoring study the week following the oil spill. One of the designated stations in this study, Todd's Dump (or Eagle Point), is located within two miles of the Apex barge oil spill and was sampled on August 3, 1990, one week after the spill. Fish were collected using gill nets at the north/northwest end of Redfish Island and over the oyster reef at Todd's Dump. A prominent oil slick was observed in waters surrounding Redfish Island; whereas, no obvious slick was evident in waters over the oyster reef. Additionally, follow up studies resampled the Todd's Dump area for fish approximately four and sixteen weeks after the spill. The fish captured were analyzed for PAH metabolites in bile and PAH residue in liver and muscle tissues. The PAH metabolites analyzed were naphthalenes, phenanthrenes, and BaPs.

Fish rapidly metabolize lipophilic PAH to more polar and excretable metabolites. A number of polar metabolites formed by the enzymatic transformation of PAH in fish livers are excreted into bile and urine. Biliary PAH metabolites were analyzed using a non-radiometric technique employing HPLC and fluorescence detection. The advantages of this technique include the ease with which samples are collected and stored, the minimal sample preparation required, its sensitivity, its low cost, and that it is an *in vivo* measurement. Field studies have documented elevated concentrations of PAH metabolites in the bile of fish collected near hydrocarbon contaminated sediments and downstream from an oil spill. An increased incidence of idiopathic hepatic lesions and reduced ovarian maturation has been correlated with high concentrations of biliary PAH metabolites in fish.

The analysis of fish collected near Redfish Island, one week after the spill, revealed the highest biliary concentrations of PAH metabolites ever reported for fish. The mean concentration of naphthalene, phenanthrene and benzo[a]pyrene

metabolites was 4,200,000, 1,900,000, and 11,000 ng/g wet weight, respectively. Fish captured over the oyster reef, in waters that were not obviously oiled, had metabolite concentrations of 1,100,000 (naphthalene), 540,000 (phenanthrene), and 3,900 (BaP) ng/g. The high concentration of BaP metabolites is of particular concern since many of these compounds are highly carcinogenic and reflect the high concentration of BaP in the spilled petroleum. The mean biliary concentrations of PAH metabolites in fish captured four weeks after the spill were lower than those observed one week after the spill, but were still elevated (naphthalene = 900,000, phenanthrene = 290,000, and BaP = 2400 ng/g); whereas, fish collected sixteen weeks after the spill had significantly lower concentrations of PAH metabolites in their bile (naphthalene = 240,000, phenanthrene = 70,000, and BaP = 630 ng/g).

In contrast to results of the biliary analysis, the concentration of PAH residues in the tissues of fish captured one week after the spill are low to nondetected. Significant concentrations of PAH are seldom detected in fish, even when the adjacent environment contains high concentrations of PAH, because fish rapidly metabolize PAH to derivatives not detected by routine analytical techniques for monitoring hydrocarbon exposure. Evaluating the effects of the Apex oil spill only on the concentration of PAH residue in fish tissues would suggest no significant evidence of exposure. However, metabolite data indicates that the fish near Todd's Dump were exposed to high concentrations of PAH.

A Simple Method to Monitor Mutagenic Responses at Oil Spill Sites

C.S. Giam, T. L. Holliday, Y. Zheng, R. Li, and A. M. Landry
Texas A&M University at Galveston

and

S. Kira and T. Itoh
Okayama University Medical School

and

H. Hayatsu
Faculty of Pharmaceutical Sciences, Okayama City, Japan

This ongoing project was initiated to explore the mutagenic responses of "treated cloth" from sites different distances away from an oil spill. Eight sites in Galveston Bay were selected for sampling. Sampling was conducted five to seven days following the release of approximately 500,000 gallons of crude oil into Galveston Bay as a result of the collision between an oil tanker and a barge on July 28, 1990. The sites varied in their distance from the spill and included a "control site", i.e., at a remote (not obviously affected) site from the spill.

Treated cloth containing copper phthalocyanine trisulfonate is expected to preferentially bind polynuclear aromatic hydrocarbons (PAHs). Certain PAHs are well established mutagens. Treated cloth was suspended in polluted bodies of water for extended periods of time to monitor mutagenic pollutants. For this study, treated cloth was suspended in the water at a depth of 1-2 feet from the surface. After 24 hours, the treated cloth was collected. In the laboratory, the treated cloth was extracted with a methanol/ammonia solution. The extract was then subjected to the "Ames assay" using *Salmonella typhimurium* TA98 as the tester strain in the presence of an S-9 mix. This method could provide data on the amount of mutagens present during the *entire* monitoring period (24 hours) as opposed to conventional sampling methods which provide data on that brief period (minutes) during which the sample was taken.

In addition to determining the mutagenic responses of the treated cloth, conventional sampling of water, sediment and oysters were taken for chemical characterization. The objective was to see if there is a correlation between the levels of PAHs in these samples and mutagenicity of the treated cloth extract from the same site. Samples were taken at the sites immediately prior to placing the treated cloth in the water. Water samples were carefully collected in precleaned glass containers. Sediment samples were collected using an Ekman grab, and carefully transferred to precleaned glass jars. Oysters were collected by hand using a metal "crow bar" if necessary. They were rinsed with water at the site and wrapped in two layers of aluminum foil. Samples were sealed, then placed in plastic bags and transported to the laboratory on ice. In the laboratory, water samples were refrigerated, sediment samples were frozen, and oyster tissue was removed from the shell and frozen until time of analysis. For chemical analysis, samples were weighed and then extracted with pollutant-free solvents. Extracts were analyzed by capillary GC-MS and GC-FID, especially for hydrocarbons.

Treated cloth from sites in close proximity to the spill had higher mutagenic

responses than those from more distant sites and the control site.

Preliminary chemical analysis of the water samples indicated the presence of petroleum alkanes, polynuclear aromatic hydrocarbons, phthalates, and other organic compounds. Following completion of this analysis, attempts will be made to correlate the mutagenic responses of the treated cloth extracts with the presence of known mutagens in the samples.

The treated cloth used for this study was blue rayon supplied by Dr. S. Kira and Dr. H. Hayatsu. This work was partially supported by: EPA Projects 89-06444, 89-06445, NIH Project 5 P42ESO4917-03, Welch Project BD1161 and a Grant-in-aid (02557092) from the Ministry of Education, Science and Culture, Japan.