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# Concentrations of Selected Chlorinated Pesticides in Shrimp Collected from the Calcasieu River/Lake Complex, Louisiana

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Portions of the Calcasieu River Basin are extensively developed, particularly Greater Lake Charles, which includes the cities of Sulphur, Westlake, and the surrounding industrial complex. The section most affected by this development is the Calcasieu Estuary from the salt water barrier to the Intracoastal Waterway (Figure 1). This section of the ecosystem experiences wide fluctuations in water quality. The water quality is affected by numerous point discharges, by diffuse nonpoint sources, and by stream channelization.

The assimilative capacity and wasteload allocation for water quality management of the Calcasieu Estuary has been determined by Clarke et al. (1980). Pollutant loads from various land use areas are generally based on drainage area, estimated flow from a reference stream gauge, and studies done elsewhere in the United States. Approximately one-half of the pollutant load in this stream segment is estimated to be from diffuse nonpoint sources.

For several decades inland and coastal aquatic ecosystems have been affected by a multitude of synthetic chemical substances. This is a consequence of population growth and increased industrial and agricultural activity. Each year new chemical products are produced by industry. Many of these chemicals, the by-products of their production, and degradation products ultimately find their way into the aquatic environment as pollutants. The extent to which these pollutants affect the environment and its inhabitants depends largely upon the quantity and nature of the particular compounds involved.

Halogenated hydrocarbons, particularly polychlorinated biphenyls (PCBs), and the pesticide DDT and its degradation products have received much attention as

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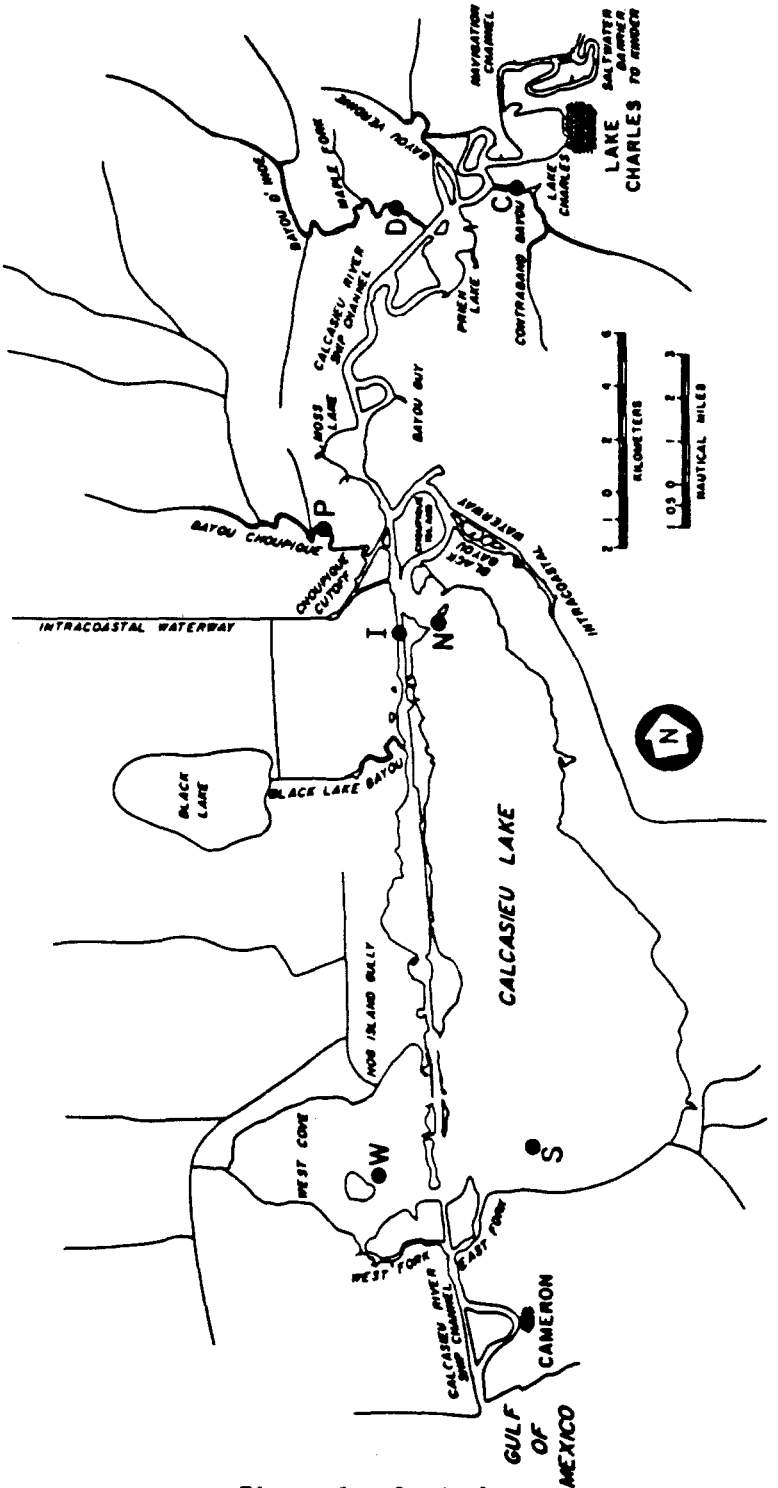


Figure 1. Study Area

environmental pollutants. The effects of these compounds on marine organisms have been studied, and both acute and chronic effects have been evaluated in laboratory studies (Nimmo et al. 1975; Vernberg et al. 1977). Many other halogenated organic compounds have also been reported in the marine environment (Butler and Schutzmann 1978; Pereira et al. 1988; Wade et al. 1988).

Because of the economic importance of the shrimping industry to southwest Louisiana, the objective of this study was to analyze shrimp collected from the Calcasieu River/Lake Complex for the presence of selected chlorinated pesticides. The presence of these compounds within shrimp tissues would serve as an indicator for the extent of pollution throughout this important estuarine system.

**MATERIALS AND METHODS**

For the purpose of investigating the extent of chemical pollution within the Calcasieu River/Lake Complex, this study focused on the portion of the Calcasieu River south of the salt water barrier (Figure 1) to the southern most part of Calcasieu Lake. Sampling stations were also established in three major tributaries of the Calcasieu River. These tributaries included Bayou d'Inde (D), Choupique Bayou (P), and Contraband Bayou (C). The three bayous investigated were chosen because their individual input of pollutants were from entirely different sources. Bayou d'Inde was chosen to represent industrial (mainly petrochemical) input and also sewage input from further upstream. Contraband Bayou was chosen to investigate impact upon the river due to urban runoff and sewage input. Choupique Bayou drains a relatively large, sparsely populated area and was thus felt to represent agricultural and marsh runoff.

Shrimp (*Penaeus setiferus* and *Penaeus aztecus*) were collected either with a 4.9 m commercial trawl (1.9 cm square mesh) with otter boards (60.5 x 31 cm), towed at 6 km $hr^{-1}$ for 10 minutes or with a 9.1 m bag-seine, 5 mm mesh. Samples were then placed in Whirl-Pak bags and frozen until analysis. A total of 652 shrimp samples at a combined weight of 1,373 grams were used for analyses. The average weight of each pooled sample analyzed was 44 grams. Tissue samples spiked with 100 $\mu$L of 1-Fluoronaphthalene at a concentration of 100 mg $L^{-1}$ and processed identically to other tissues, yielded a mean recovery of 84% and a standard deviation of $\pm$29%.

Solvents used in this study were of pesticide quality. Glassware and other materials used in the processing of samples were washed with Micro cleaning solution

(International Products Corporation), rinsed with distilled water and heated at 250°C overnight. Just prior to use, glassware was rinsed with pesticide-grade acetone and petroleum ether.

For extraction of synthetic organics, tissues were placed into a stainless steel Waring blender and homogenized twice using 20% acetone/acetonitrile for each extraction. Extracts were filtered and placed into a 1-L separatory funnel containing 5% NaCl solution. The combined extracts were then extracted 3 times with petroleum ether (PE). The samples were concentrated using an Evapotec™ Rotary Film Evaporator. Clean-up was accomplished by passing the sample through a Pasteur pipette containing fully activated alumina (80-200 mesh). The sample was then eluted with 5 mL PE and evaporated to 1 mL under a gentle stream of clean nitrogen. The procedure for sample extraction was a modification of existing methods currently used in this laboratory (Giam et al. 1980; EPA 1978).

Organic analyses were done using a Model 5890 Hewlett-Packard (HP) gas chromatograph coupled to a Model 5970 HP mass selective detector (MSD). A HP high performance (SE-52) cross-linked 5% phenyl methyl capillary column with a film thickness of 0.11 μm, an internal diameter of 0.20 mm, and a length of 25 m, was used for all organic analyses.

The tuning calibration compound used was perfluorotributylamine (PFTBA). PFTBA is a stable chemical that produces fragments throughout the entire mass range. Three of its mass peaks at m/z 69, 219, and 502 were used for tuning the Autotune and Quicktune programs. After the tuning was completed the normalization factors were calculated. These factors were used to adjust the relative intensities of the PFTBA mass peaks to match the values that would occur if the MS had been tuned with decafluorotriphenylphosphine (DFTPP), the EPA-approved reference standard.

Selected organic compounds were quantitatively analyzed in a selected ion mode (SIM) utilizing the molecular ions of the compounds of interest.

Environmental analysis standards for EPA Consent Decree Water Protocol were obtained from Supelco. Anthracene-$d_{10}$ was obtained from the EPA and used as an internal standard. The internal standard was added to each sample just prior to GC/MS analysis.

Commercial standards were periodically analyzed to determine recovery (accuracy). A midpoint laboratory standard was run with each batch of samples to check

performance of analytical methods. This standard was repeated for every tenth sample. Reagent blanks were run with each batch of samples. Externally-prepared reference and performance (unknown) samples were analyzed on a routine basis. These samples were obtained from the EPA or a commercial source (e.g., ERA). In addition, tissue samples were spiked with 100 $\mu$L of 1-Fluoronaphthalene at a concentration of 100 mg $L^{-1}$ and processed identically to the other tissues.

**RESULTS AND DISCUSSION**

Concentrations ($\mu g\ g^{-1}$) of chlorinated pesticides found in a mixture of Penaeus setiferus (white shrimp) and Penaeus aztecus (brown shrimp) are reported in Table 1. As can be seen from the table, shrimp containing various concentrations of these chlorinated compounds are distributed throughout the estuarine system. These sporadic and uneven distributions appear to be typical of what might be expected with analysis of nektonic species that tend to migrate from place to place. The chlorinated pesticides that were found in this study can be attributed to agricultural runoff into surrounding surface water. Yearly pesticide usage for agricultural purposes in Calcasieu Parish (which includes the area north of stations I and N) is between 600,000 and 1,000,000 lbs, while pesticide usage for Cameron Parish (which includes the area south of stations I and N) is between 100,000 and 300,000 lbs (LA DEQ 1985).

In general, the upper portion of the estuarine system (including the bayous) yielded the highest concentrations of pollutants found in this study. Since there are no established FDA Action Levels for these chlorinated pesticides in seafood edible portions, it is difficult to ascertain the significance of the concentrations reported in this study. Recent water quality criteria (EPA 1986) has been published which does provide guidelines for acceptable concentrations of various chlorinated pesticides to protect freshwater and saltwater aquatic life. These data are then used to establish some degree of risk to human health from the consumption of seafood from areas where pesticides have been detected. However, the correlation of water contamination with tissue contamination has not been firmly established with all chlorinated pesticides.

There is presently an urgent need to establish firm FDA Action Levels for pesticides and other synthetic organic compounds in seafood edible portions.

Table 1. Concentrations ($\mu g\ g^{-1}$)[1] of pesticides found in shrimp.

| Compound Name | Station and Cruise Date[2] C8509 (10)[3] | C8510 (7) | C8606 (7) | D8509 (18) | P8411 (41) | P8509 (12) | P8510 (28) | P8604 (3) |
|---|---|---|---|---|---|---|---|---|
| Delta-BHC | ND[4] | 0.63 | ND | 0.47 | ND | 0.38 | ND | 1.41 |
| Heptachlor | ND | ND | ND | 0.26 | ND | ND | ND | 0.75 |
| Aldrin | ND | ND | ND | ND | ND | ND | ND | 0.12 |
| Endrin | 0.25 | 9.47 | 0.80 | 0.57 | 0.15 | 5.36 | 0.40 | 5.12 |
| Endosulfan II | ND | ND | ND | 1.31 | ND | ND | ND | 2.57 |
| Endrin Aldehyde | 0.18 | 0.66 | ND | 0.09 | ND | 0.69 | ND | 0.50 |

| Compound Name | Station and Cruise Date P8605 (20) | I8509 (12) | I8510 (34) | I8603 (14) | I8604 (5) | I8605 (26) | I8606 (8) | I8607 (8) |
|---|---|---|---|---|---|---|---|---|
| Beta-BHC | ND | ND | ND | 0.07 | 0.04 | ND | ND | ND |
| Delta-BHC | ND | 0.29 | 0.05 | 0.15 | 0.18 | 0.11 | ND | ND |
| Heptachlor | 0.08 | ND | 0.02 | 0.02 | 0.12 | ND | ND | 0.02 |
| Aldrin | ND | ND | ND | ND | 0.02 | ND | ND | ND |
| Endrin | ND | 1.15 | 1.72 | 0.69 | 0.53 | ND | ND | 0.05 |
| Endosulfan II | ND | ND | ND | 0.82 | 0.36 | ND | ND | 0.15 |
| DDD | 0.25 | ND | ND | ND | 0.01 | ND | ND | ND |
| Endrin Aldehyde | ND | ND | 0.02 | 0.35 | 0.04 | ND | ND | 0.01 |

| Compound Name | Station and Cruise Date N8509 (33) | N8510 (32) | N8512 (25) | N8603 (16) | N8604 (8) | N8606 (5) | N8607 (15) | N8608 (22) |
|---|---|---|---|---|---|---|---|---|
| Beta-BHC | ND | ND | ND | ND | ND | ND | ND | 0.15 |
| Delta-BHC | ND | 0.06 | ND | ND | 0.19 | ND | ND | ND |
| Heptachlor | ND | ND | ND | 0.01 | 0.06 | ND | ND | 0.06 |
| Aldrin | 0.04 | ND | ND | 0.01 | 0.06 | ND | ND | 0.06 |
| Endrin | 0.50 | ND | 0.10 | 0.68 | 2.88 | ND | 0.05 | ND |
| Endrin Aldehyde | 0.22 | ND | 0.03 | 0.03 | 0.08 | ND | 0.01 | ND |

| Compound Name | Station and Cruise Date S8510 (34) | S8511 (113) | S8603 (18) | S8604 (30) | W8511 (20) | W8603 (8) | W8604 (20) |
|---|---|---|---|---|---|---|---|
| Beta-BHC | ND | 0.56 | ND | ND | ND | ND | ND |
| Delta-BHC | ND | 0.06 | ND | ND | ND | 0.13 | ND |
| Heptachlor | ND | 0.03 | ND | ND | ND | ND | ND |
| Aldrin | ND | 0.02 | ND | ND | ND | ND | ND |
| Endrin | 0.05 | 1.20 | ND | ND | 1.35 | ND | ND |
| Endosulfan II | ND | 0.14 | 0.66 | ND | ND | ND | ND |
| Endrin Aldehyde | 0.03 | 0.05 | ND | ND | 0.30 | ND | ND |

[1] All values are in ppm (wet weight); all analyses are of edible portions

[2] Letters indicate stations (Figure 1) and numbers indicate year and month of cruise (e.g., C8509 means Station C, February 1985)

[3] Number of shrimp analyzed are given in parentheses

[4] Not detectable; <0.01 $\mu g\ g^{1}$

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