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Mercury in the Calcasieu River/Lake Complex, Louisiana

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The Calcasieu River/Lake Complex is of great economic importance to southwestern Louisiana. Calcasieu Lake is an important fishing ground for shrimp and oysters. The Calcasieu Ship Channel allows large vessels to navigate to Lake Charles from the Gulf of Mexico, a distance of about 40 km. Since World War II, the area to the west of Lake Charles has undergone extensive industrial development, particularly along Bayou d'Inde.

The Calcasieu River/Lake Complex has been the focus of an interdisciplinary study to assess the types and areas of pollution along this important waterway. Particular attention has been given to Hg because of the toxicity of this metal (Nita, 1972), and the local importance of the chloralkali industry--an industry that is known to discharge Hg into the environment (Femreite, 1970; Compaan, 1971; Bothner and Carpenter, 1973; Loring and Bewers, 1976; Skei, 1978).

MATERIALS AND METHODS

The area of southwestern Louisiana sampled is shown in Figure 1. Water, sediment and biota were collected at stations in Calcasieu Lake, Calcasieu River, and along three bayou tributaries that were studied intensively. Intensive sampling included all stations along the particular bayou studied that month. The intensive surveys alternated among the three bayous, with the sampling sequence repeated every three months over a period of one year. Sampling stations on the bayous are numbered on the map as follows: Contraband Bayou (C1-C6), Bayou d'Inde (D1-D8), and Choupique Bayou (P1-P10). The samples were collected during the period from November 1983 to December 1985.

Water samples were collected with a 2-L van Dorn water

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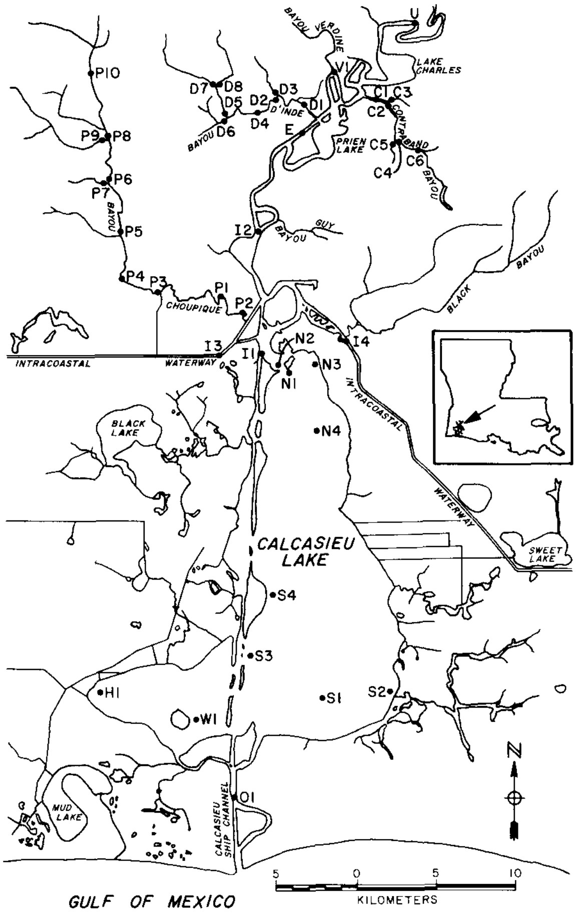

Figure 1. Area of southwestern Louisiana studied. Sampling stations are indicated by letters.

sampler. Samples were transferred to prewashed polyethylene bottles, acidified with nitric acid (HNO_3), and stored in a freezer at $4^{\circ}C$. Surface sediments (top 2 cm) were collected with a 0.05-m^2 Ekman grab sampler. Core samples were collected with a Wildco gravity core sampler. All samples were kept frozen until preparation for analysis. All biota samples were collected as part of the biological tasks within this interdisciplinary study. Oysters and mussels were collected either by tonging or by hand. All biota samples were dried to constant weight at $60^{\circ}C$ prior to chemical analysis (Bernhard, 1976).

Water samples were prepared by transferring 100 mL of sample to a 300-mL BOD bottle and adding 5 mL of 0.5N sulfuric acid and 2.5 mL of concentrated HNO_3. After mixing, ·15 mL of 5% (w/v) potassium permanganate solution were added. Additional portions of permanganate were added until the purple color persisted for at least 15 min. Then 8 mL of 5% (w/v) potassium persulfate solution were added and the bottles heated at 80°C for 2 h to oxidize any organic Hg present to the inorganic form. After cooling, 6 mL of sodium chloride/hydroxylamine chloride solution (12% w/v each) were added to reduce excess permanganate (EPA 1979, Method 245.1).

Sediment and biota samples were prepared by adding 10 mL of aqua regia to 2 g portions of dry sample which had been weighed into BOD bottles. Ten mL of aqua regia were added and the samples heated for 2 min at 80°C. Fifteen mL of 5% (w/v) potassium permanganate solution were then added and the mixture heated for 30 min at 80°C. After cooling, 6 mL of sodium chloride/hydroxylamine solution were added to reduce excess permanganate (EPA 1979, Method 245.3). A list of biota analyzed is given in Table 1.

The samples prepared as described above and standards containing known amounts of Hg in the same total volume were analyzed by the cold vapor atomic absorption method (EPA 1979, Method 245.1). A Perkin-Elmer Mercury Analysis System, in conjunction with a Perkin-Elmer Model 370A atomic absorption spectrophotometer, was used to analyze the samples. Five mL of 10% (w/v) stannous chloride solution were added to each bottle to reduce the Hg to the elemental form. The bottles were connected to an aerator and air bubbled through the bottle to carry reduced Hg into an absorption cell mounted in the spectrophotometer.

In order to determine sedimentation rates and the approximate time periods in which Hg was deposited in sediment, two radiochemical dating techniques involving ^{137}Cs and ^{210}Pb were used (Appleby and Oldfield, 1978; Robbine et al., 1978; Oldfield and Appleby, 1984). Both techniques are useful for dating sediments of less than 100 years of age, the time period of interest in this study.

Since ^{137}Cs is not a naturally occurring radionuclide but a result of nuclear fission, any ^{137}Cs appearing in the environment must be the result of nuclear fallout. Sedimentation rates may be estimated by assuming that the surface layer of sediment is of the present age and that the depth at which no ^{137}Cs is detected is the year 1954--the year in which ^{137}Cs was first injected into the environment in large quantities (Feely, 1965; Krey, 1968). The depth at which ^{137}Cs reaches a maximum should be about 1964 (Cooper et al., 1970; Beck et al., 1971).

^{137}Cs emits a gamma ray with an energy of 661 KeV. Approximately 100 g of dried sediment were counted using a 4096-channel Norland/Inotech Model 5400 multichannel analyzer with a Princeton-Gamma Tech Ge(Li) 12% crystal detector.

Another radioisotope useful for dating sediments is ^{210}Pb, which is continually produced in the environment from ^{226}Ra. A segmented core sample from Station D1 was digested in HNO_3 and the supernate coprecipitated with sulfide ion (Backman et al., 1984). The sample was then analyzed for ^{210}Pb by measuring the weak beta emission using a Beckman LS-1800 liquid scintillation counter. ^{226}Ra standards were used to plot a calibration curve.

From the amounts of ^{137}Cs and ^{210}Pb in the sediment core from Station D1, and by assuming a constant sedimentation rate, a calculation of the sedimentation rate was made. Both methods gave an approximate value of 0.74 cm per year. This sedimentation rate was then used to correlate Hg concentration with core depth and date of deposition.

RESULTS AND DISCUSSION

Mercury concentrations in water were nearly always below the detection limit (<0.1 ug/L). Mercury levels in Choupique Bayou were never above the detection limit during the course of the investigation. In fact, Hg was never detected in sediments in Choupique Bayou.

Mercury, however, was detected in water samples in the study area during the months of April and June, 1984. Mercury was detected over a small portion of the study area at levels of 2 to 3 ug/L. The presence of Hg in water samples probably originated near Bayou d'Inde or Bayou Verdine during April 1984. Subsequent transport down the Calcasieu River, to Station E located just downstream from Bayou d'Inde, and at stations N and W during May and June, 1984, may have occurred.

Table 1 gives the mean concentration of Hg measured in biota collected in the Calcasieu River/Lake Complex. Fish may absorb Hg from the water through the gills and skin (Norstrom et al., 1976) or through the digestive tract (Jernelov and Lann, 1971; Olson et al., 1973; Peterson et al., 1973; Bernhard and Zattera, 1975; Phillips, 1977). All species of fish

Table 1. Mean concentrations and standard deviations of Hg in various types of biota from the Calcasieu Estuary.

Species		Hg (mg/Kg dry weight)
Atlantic croaker	*Micropogonias undulatus*	0.25±0.09
Gulf menhaden	*Brevoortia patronus*	0.26±0.13
Spot	*Leiostomus xanthurus*	0.29±0.14
Blue catfish	*Ictalurus furcatus*	0.51±0.22
White shrimp	*Penaeus setiferus*	<0.2
Brown shrimp	*Penaeus aztecus*	<0.2
Oyster	*Crassotrea virginicus*	0.34±0.15
Blue crab	*Callinectes sapidus*	0.51±0.21
Mussel	*Ischadium recurvum*	0.15±0.07
Zooplankton	Mixed species	<0.2

measured in this study contain about the same Hg load-0.25 mg/kg (dry weight). The concentration of Hg in blue catfish (0.50 mg/kg) was the highest value found in any species of finfish.

The measured Hg content of the blue crab (*Callinectes sapidus*) was equal to the value for blue catfish (*Ictalurus furcatus*)-- 0.50 mg/kg. This may be related to the bottom feeding habits of these species and their interaction with the sediment/water interface. Methyl Hg is known to be produced in sediments by bacteria (Wood *et al.*, 1968) before it enters the food chain. Bottom feeders such as blue crabs might thus be expected to show higher levels of Hg (Renzoni *et al.*, 1973).

Mercury was measured in surface sediments collected at 36 locations throughout the Calcasieu River/Lake Complex. Mean surface Hg concentrations at station groupings are summarized in Table 2 and plotted demographically in Figure 2. This allows a comparison of the distribution of Hg across the study area. The absence of bars at some stations means that

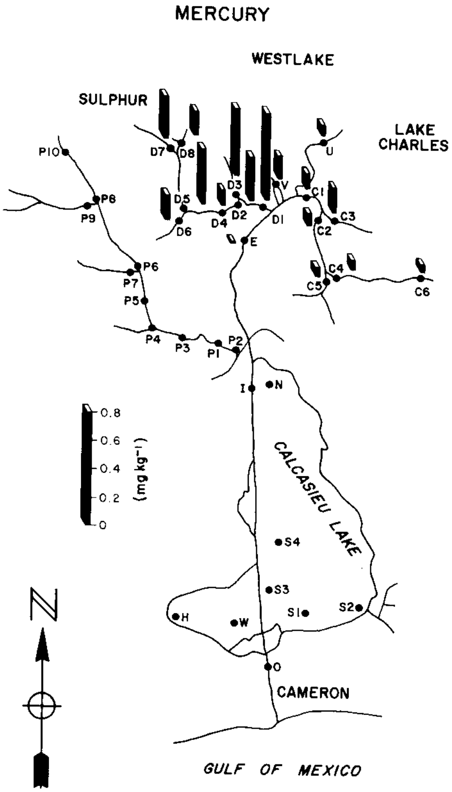

Figure 2. Demographic plot of mean Hg concentrations in surface sediments.

Table 2. Mean Hg concentrations in surface sediments at some locations from the Calcasieu River/Lake Complex

Location	Hg (mg/kg)
Bayou d'Inde	0.98 ± 0.45
Contraband Bayou	0.12 ± 0.06
Bayou Verdine	0.11 ± 0.08
Calcasieu Lake	<0.05
Calcasieu River	<0.05
Choupique Bayou	<0.05

the Hg concentration was below the detection limit of 0.05 mg/kg. Mercury was measured at all stations shown in Figure 2.

Mercury concentrations with depth and approximate date of deposition for four stations in Bayou d'Inde are plotted in Figure 3. Mercury first appeared in Bayou d'Inde in the late 1940's, increased during the 1960's, and reached peak concentrations during the early 1970's. At a depth of 20-28 cm, Hg was found in a very low concentration; below 38 cm (corresponding to the year 1933) Hg was not detected anywhere in the system.

Remarkably different patterns of Hg distribution are seen among the sampling stations along Bayou d'Inde. Stations DO (near the mouth of the bayou), D1A (on an industrial drainage ditch), and D1B (upstream from the industrial ditch and between D1 and D2) were added to the general sampling scheme to allow a better understanding of the distribution of Hg in sediments along Bayou d'Inde. The highest Hg levels were seen at Station D1A. Mercury levels began rising rapidly after 1964 at this station, but since 1978 there has been a decrease.

Station D1B was located upstream of D1. Mercury reached a maximum during the period between 1960 and 1976, after which there was a steady decrease. The difference between D1A and D1B may be attributed to one or more of the following: the point source may be located between these two stations; more than one source may exist; distribution patterns may have changed over time; or the sediments may have been disturbed over time.

Two stations, DO and D1, were located downstream of Station D1A. Both stations showed an increase in Hg over the years, with levels at DO still increasing and having a greater burden of Hg than D1. The change in Hg concentrations during the era sampled by the cores for stations D1B, D1, D1A, and DO are plotted (Figure 3) in order to compare the differences in distribution.

The remaining stations, D2 and D4, were located upstream from D1B. They both exhibited low levels of Hg; the distribution pattern at D2 was similar to that at DO, with a peak in the late 1970's. D4 showed fairly constant levels of Hg, reaching a maximum in the early 1980's.

Mercury levels in sediments from the rest of the sampled estuarine area were very low, and often below

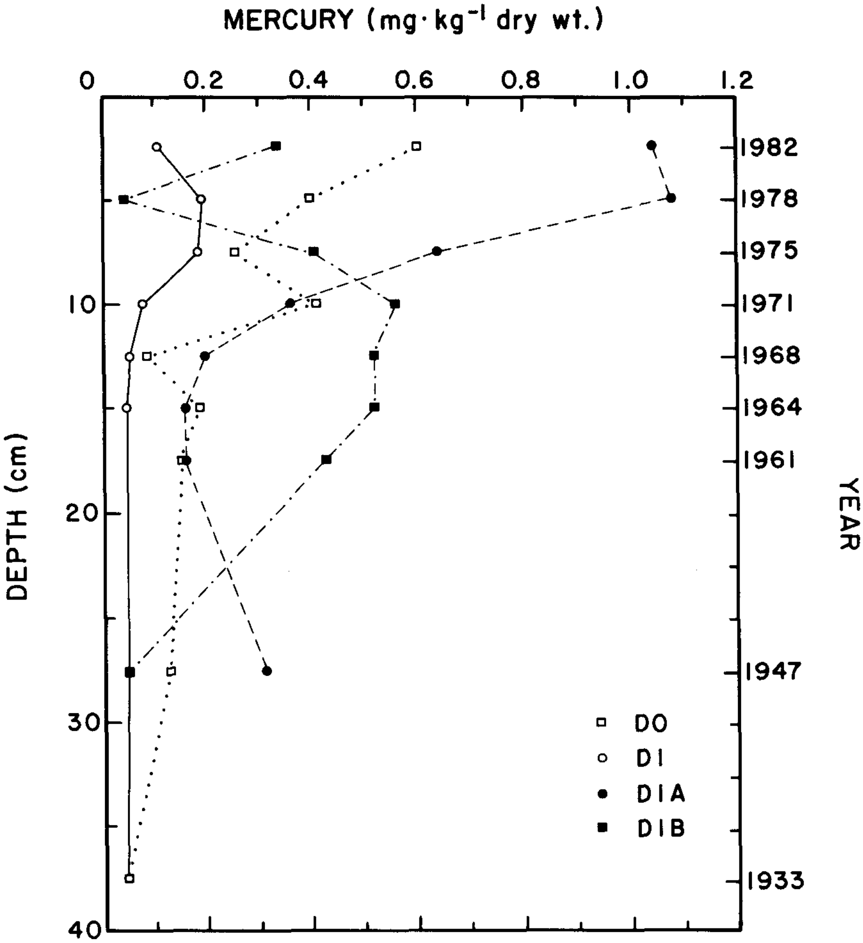

Figure 3. Mercury concentrations with depth and approximate date of deposition for sediment cores from four stations on Bayou d'Inde.

the detection limit (0.05 mg/kg dry weight). Slightly elevated levels of about 0.1 mg/kg were found in surface sediments from Contraband Bayou. The undetectable levels in Calcasieu Lake and Lake Charles demonstrate that Hg has not been transported in appreciable amounts to the remainder of the system. It is possible that future dredging or other activities within Bayou d'Inde could mobilize the Hg locked in the sediment.

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