CONCENTRATIONS OF Hg, Pb, Zn, Cd, AND As IN TIMBALIER BAY AND THE LOUISIANA OIL PATCH

by J. G. Montalvo, Jr., and D. V. Brady

ABSTRACT

The purpose of this two-year study was to determine if petroleum drilling and/or production activities in Timbalier Bay and in the Louisiana oil patch contributed certain toxic metals to the marine environment—specifically, the extent of the contribution, if any, to the water column.

Samples were analyzed for total mercury, lead, cadmium, zinc, and arsenic. Sampling locations included areas near oil platforms, at various distances and directions from the platforms, and at locations remote from the oil platforms.

Over the sampling period, in bay water column samples, mercury ranged from <0.3 to 6.9 μ g/l with an average of 0.6 μ g/l. Cadmium ranged from <0.1 to 22.5 μ g/l with a mean of 0.6 μ g/l; lead from <0.5 to 50 μ g/l with an average of 2.8 μ g/l. Zinc varied between <0.2 and 66 μ g/l with a mean of 8.5 μ g/l. All of the arsenic values were below 10 μ g/l, the limit of detection.

Over the study period in the offshore area, mercury ranged from <0.3 to 7.5 μ g/l with an average of 0.4 μ g/l. Cadmium varied between <0.1 and 20 μ g/l with a mean of 0.3 μ g/l. Lead ranged from <0.5 to 50 μ g/l with a mean of 1.5 μ g/l; zinc from <0.2 to 66 μ g/l with an average of 6.8 μ g/l. All of the arsenic values were below the 10 μ g/l limit of detection.

When this investigation was conducted, J. G. Montalvo, Jr., was manager of the Analytical Chemistry Department and D. V. Brady was Chief Chemist at the Gulf South Research Institute, New Orleans, LA.

On several occasions the levels of zinc were found to decrease with increasing distance from the immediate vicinity of the oil platforms.

INTRODUCTION

The purpose of this study was to determine if petroleum drilling and/or production activities in Timbalier Bay and in the Louisiana oil patch contributed certain toxic metals to the environment, and the extent of the contribution, if any, to the water column.

This toxic metal program was limited to the determination of the levels of mercury, arsenic, zinc, cadmium, and lead in the water column. Samples were collected near oil platforms, at various distances and directions from the platforms, and at locations remote from the oil platforms.

Another purpose of the program was to establish scientifically sound baselines, but since oil production has been going on in the general area off the Louisiana Coast for many years, it is questionable if the values obtained, even in areas remote from oil platforms, can be considered truly representative of conditions that existed before oil exploration began. The data can, of course, be usefully compared to data obtained in the future.

Toxic metals could conceivably be contributed to the environment from accidental spillage of petroleum products, drilling fluids and cuttings, lubricating oils and fuels, brines, and the corrosion of platform metals.

The fate and effects of trace metals in marine and estuarine waters have until recently been studied mainly in laboratory investigations. It is known that certain metals concentrate in sediments and bioconcentrate in marine life (Horne 1969; Bender et al. 1972).

El-Sayed et al. (1972) presented available data on various metals in the Gulf and noted that the data were exceedingly sparse. For example, they presented data on only 15 samples for iron, nickel, and lead, and 63 samples for zinc. Essentially all of these samples were from the Texas Coast.

METHODS

Laboratory

Arsenic was determined by the silver diethyldithiocarbamate method, in which inorganic arsenic is reduced to arsine, which in turn reacts with silver salt forming a soluble red complex that is suitable for photometric measurement (American Public Health Association 1971). Quantitation was performed photometrically and the detection limit for the method was $10 \mu g/l$.

Cadmium, lead, and zinc were determined by atomic adsorption spectrophotometry after complexation with ammonium pyrolidine-dithiocarbamate (APDC) at pH 4 and extraction with methyl isobutyl ketone (MIBK), as described in Standard Methods (American Public Health Association 1971).

Mercury was determined by cold vapor atomic adsorption spectrophotometry. Samples were oxidized with sulfuric acid, nitric acid, potassium permanganate, and potassium persulfate. Reduction to elemental mercury was achieved with sodium chloride-hydroxylamine sulfate and stannous sulfate.

With these methods, the limits of detection were 0.3 μ g/l for Hg, 0.1 μ g/l for Cd, 0.2 μ g/l for Zn, and 0.5 μ g/l for Pb.

Metal recoveries as determined from spiked water samples were as follows: Cd - 95%; Pb - 77%; Zn - 89%; and Hg - 116%. Relative standard deviations expressed as percentage of the mean were 22% for Cd, 16% for Pb, 14% for Zn, and 11% for Hg.

Field

The general locations of the stations sampled in Timbalier Bay and along a transect into the offshore region are shown in figure 1. More samples were taken in the immediate vicinity of the platforms, i.e., within 1,000 meters, than at the control sites.

RESULTS

Bay

Over the sampling period in the bay water column samples, mercury ranged from <0.3 to 6.9 μ g/l with an average of 0.6 μ g/l. Cadmium ranged from <0.1 to 22.5 μ g/l with a mean of 0.6 μ g/l; lead ranged from <0.5 to 50 μ g/l with an average of 2.8 μ g/l. Zinc varied between <0.2 and 66 μ g/l with a mean of 8.5 μ g/l. All of the arsenic values were below 10 μ g/l, the detection limit.

Shown in table 1 are comparisons for the bay ambient stations (AB-1 and 2) and the platform sites during two periods for which at least 5 samples were available from each location. An analysis of variance performed on these data indicated no significant differences between locations at the 0.05% level.

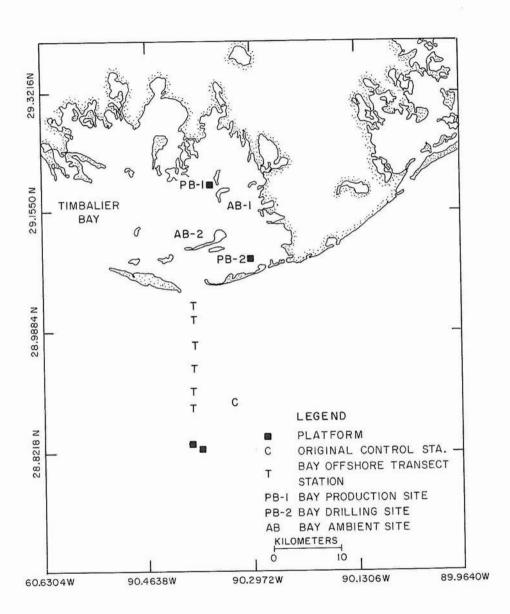


FIG. 1. THE OEI STUDY AREA SHOWING THE STATIONS SAMPLED.

	September 1972			October 1972		
	Production	Drilling	Ambient	Production	Drilling	Ambien
Zn	4.3	4.5	4.3	10.8	10.3	11.1
Cd	0.2	0.3	0.2	0.2	0.5	0.8
Pd	1.1	1.7	1.1	4.5	6.9	6.6
Hg	1.6	0.7	1.0	0.5	0.5	0.4

TABLE 1 TIMBALIER BAY—METAL LEVELS (\bar{x} in $\mu g/l$)

On occasion in the offshore region, zinc levels were shown to be elevated in the immediate vicinity of the platforms. As shown in figure 2, these elevations were of limited extent and probably represent metals from the sacrificial zinc anodes.

Variations in metal levels from the bay to the offshore platforms are shown in figures 3 and 4. These data represent the metal concentrations determined within the sectors shown in figure 5 over the study period. The platforms were located in sectors 2, 5, and 12.

Levels of cadmium and zinc (figure 3) were generally higher in the bay, decreasing along the transect into the Gulf. No clear platform effects are indicated from these data. As shown in figure 4, however, lead levels, although extremely variable, did appear elevated in the sector encompassing the workover platform in the bay. Mercury levels as shown in figure 4 were generally higher in the Gulf than in Timbalier Bay.

DISCUSSION

Data collected in close proximity to the platforms did indicate increased levels of Zn in the offshore area and Pb near the workover rig in the bay. Even these localized elevations were below those estimated as chronically toxic to marine life by the National Academy of Sciences (1972). For example, they estimated safe levels for zinc to be $20~\mu g/l$ and $10~\mu g/l$ for lead. As shown in figures 3 and 4, these levels were not exceeded, on the average, at the platform sites. In addition, it must be remembered that the Academy criteria are based on dissolved metals, and the values reported here are totals. Cadmium levels are estimated to be hazardous to marine life if they exceed $10~\mu g/l$. The highest mean value for cadmium reported in this study was $0.6~\mu g/l$ at the bay production platform.

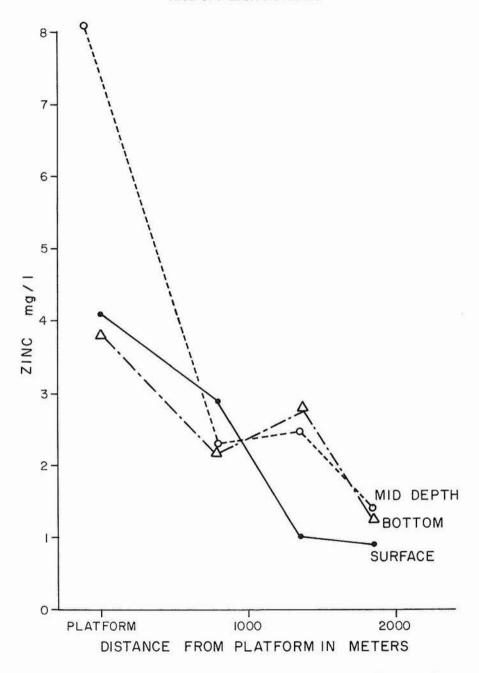


FIG. 2. WATER COLUMN ZINC LEVELS AT PLATFORM HOR-54A, SEPTEMBER 1972.

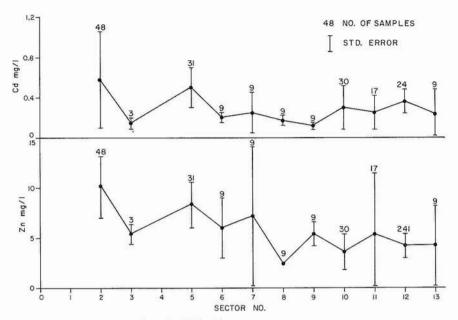


FIG. 3. OEI—BAY TO OFFSHORE.

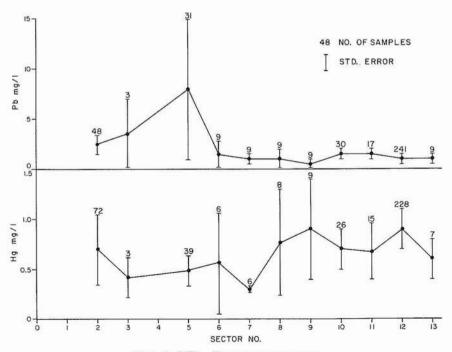


FIG. 4. OEI—BAY TO OFFSHORE.

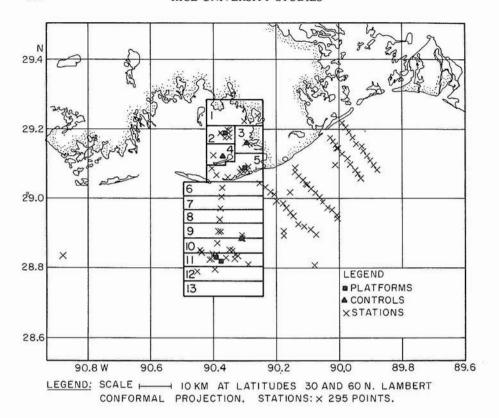


FIG. 5. METAL CONCENTRATIONS.

CONCLUSIONS

Utilizing the criteria set forth by the Academy and the data reported here, we do not predict a risk of chronic biological effects due to the metals zinc, lead, or cadmium originating from oil production platforms.

REFERENCES CITED

American Public Health Association, Standard Methods, 13th Edition. 1971. Washington, D.C.

Bender, M. E., R. J. Huggett, and H. D. Slone. 1972. Heavy metals—an inventory of existing conditions. The Fate of Chesapeake Bay. Journal of the Washington Academy of Science 62:144-153.

- El-Sayed, S. Z. and K. W. Fucik, 1972. Chemistry, primary productivity and benthic algae of the Gulf of Mexico. American Geographical Society, Folio 22.
- Horne, R. A. 1969. Marine Chemistry: The Structure of Water and the Chemistry of the Hydrosphere. New York: Wiley—Interscience.
- National Academy of Science and National Academy of Engineering. 1972. Water Quality Criteria. Washington, D.C.: U.S. Government Printing Office.