

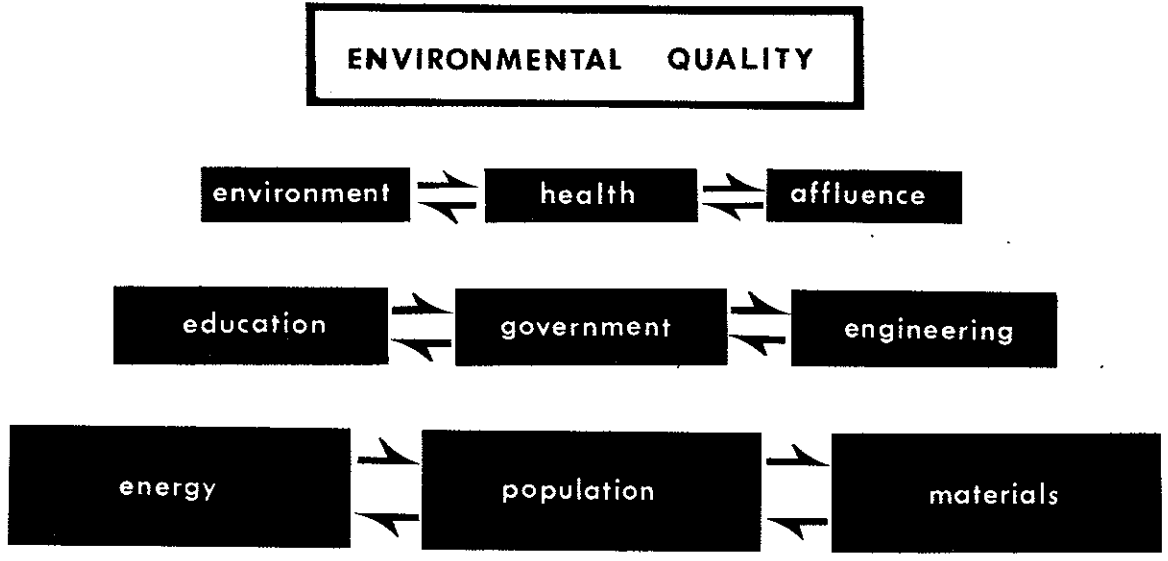
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## LEAD AND ARSENIC CONCENTRATIONS IN SOME SOUTH TEXAS COASTAL-ZONE SEDIMENTS

B. J. PRESLEY  
and  
J. H. CULP

EQN 09



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B. J. Presley

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Texas A&M University

Environmental Quality Note 09

August 1972

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Introduction

In recent years both scientists and the lay public have become increasingly concerned with the harmful effects of introducing man-produced toxic substances into the marine environment. These substances are likely to be especially harmful in the coastal zone, because this is where they are first introduced, and because this is the area of most intense biological activity. Monitoring of the pollutant levels in near-shore environments, especially those near industrial centers, has become commonplace and has resulted in the closing of important commercial fishing grounds in many parts of the world.

Monitoring of industrial and municipal wastes for pollutants should, and will, continue. In addition more attention needs to be paid to agricultural sources of toxic materials. The present study is part of a program initiated by Dr. Wayne Ahr, assistant professor, Department of Geology, Texas A&M University, which is intended to survey effects of agricultural practices on the concentration of

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\* Assistant Professor, Department of Oceanography, Texas A&M University.

\*\* Research Associate, Department of Oceanography, Texas A&M University.

toxic substances in the coastal environment. Dr. Ahr analyzed sediments for DDT and DDE, and we determined lead (Pb) and arsenic (As) on these same samples. We hope that data from this small pilot project will be useful in planning a more extensive study of the fate of agriculturally derived pollutants in the marine environment.

#### Background and description of the study area

The study area has been described in some detail by Ahr (1972) and is located in the Laguna Atascosa National Wildlife Refuge (Fig. 1). It is on the flanks of the Rio Grande delta, an area surrounded by croplands. In this pilot study, emphasis was placed on pollutant concentrations in sediment, most of which has been transported to the marine coastal zone by streams and deposited in areas of quiet water. Some of this sediment was once soil in the croplands surrounding the area and as such should reflect any unusual concentrations of substances in the cropland soil.

At the same time substances, especially heavy metals leached from soils, will be concentrated in the solid phase of sediments deposited by the leaching water. The reason for this is the enormous adsorbing power of fine-grained material suspended in stream water. A number of studies have shown that dissolved heavy metals are readily removed from stream water by adsorption on sediment particles (Duursma and Gross, 1971). Thus, in analyzing sediments, information on both dissolved and suspended loads of the contributing streams is gained.

Sediment analysis is unique in one respect: it gives an historical

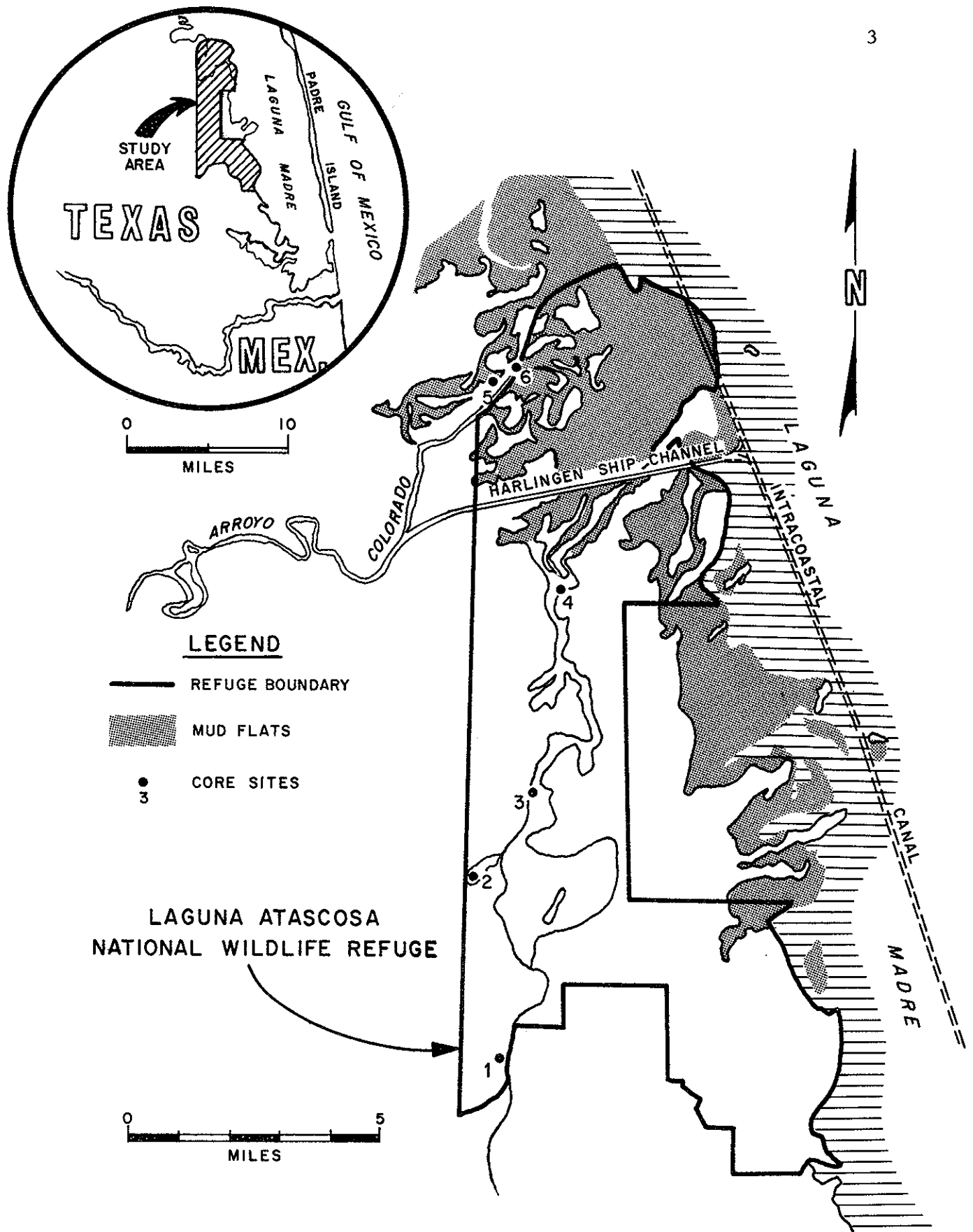


Fig. 1. Location of the study area showing core sites.

perspective. The layers of sediment were deposited at successively greater times in the past with depth in the sediment column, which allows one to compare old conditions with recent ones. This is, in fact, one of the primary reasons for the present study. It is well known that large quantities of lead arsenate and other metal-based insecticides were used in the Rio Grande Valley in the 1930s, but more recently these have been replaced by chlorinated hydrocarbons and other organic substances. We wanted to know if this change in agricultural practice was reflected in the sediments.

Concentrations of toxic substances in or on the surfaces of sediment particles also can be of direct importance to biological activity in the coastal zone. Many kinds of organisms ingest sediment in their search for food and in this way may transfer the toxic substance from the sediment to the marine food chain. This also can occur when organisms attach themselves to the sediment or to individual sediment particles either in larval stages of their development or in adult life.

Organisms also can pick up toxic substances indirectly from the sediment. That is, the substance first can dissolve or de-sorb from the sediment and then be ingested by an organism. This mechanism has been studied little, except in the case of nutrients (Lee, 1970), but may be of widespread importance because of the large reservoir of mineral matter which exists in the sediment. If this material is made available to organisms, serious consequences could result.

The physio-chemical conditions below the water-sediment interface



are very different from those in the overlying water. This is especially true where appreciable amounts of organic matter are trapped in the sediment, owing either to a rapid sedimentation rate or to high productivity in the overlying water. These changed physio-chemical conditions lead to several consequences that can directly affect environmental quality, especially if the sediment is mechanically disturbed.

At all but the upper few inches of the sediment, the pore water of the deposits will contain no oxygen, and organic matter will be utilized by sulfate-reducing bacteria. This produces highly toxic hydrogen sulfide gas as well as large amounts of carbon dioxide, methane, and other gases.

The sulfate reduction lowers the Eh and pH in the pore water, bringing into solution heavy metals that were insoluble in the overlying water. Enrichment factors of up to 4000 have been measured in some sediments in our laboratory.

At the same time large amounts of phosphate, ammonia, and other nutrients are released into the pore water; pesticides and herbicides are likely to behave in the same manner.

In most sediments the diffusion of material from the pore water to the overlying water is slow, especially because new sediment is continually added at the top. However, if the sediment is mechanically disturbed, potentially significant amounts of substances can be added to the water column, especially in shallow water areas. These substances may be highly toxic (heavy metals, H<sub>2</sub>S, pesticides) or may

stimulate productivity in the overlying water (phosphate, ammonia) to such an extent as to deplete all oxygen and kill desirable forms of life.

Thus a study of sediment concentrations of potentially toxic substances has more than academic interest, but only a few such studies have been initiated. This pilot study is intended to stimulate more such work.

#### Analytical methods

Considerable effort was devoted to development of analytical techniques in the early stages of this project. We were not interested in the total Pb and As in the sediment but only that part which may have come from the activities of man. In other words, the Pb and As tightly bound in the silicate structure of the sediment and thus originating in the weathered igneous rock was not important. We therefore devised an acid-leaching procedure which gave the desired results with a minimum of time and effort.

#### Method for lead

Sediment samples (2.00 g) were digested for acid-leachable lead by placing the sample in a Teflon bomb with 5.0 ml of concentrated HNO<sub>3</sub>. The bombs were placed in an oven at 105°C for three hours, removed, and allowed to cool to ambient temperature. The caps were removed under a hood because of NO<sub>2</sub> fumes, and the sides of the bombs were rinsed down with deionized water. The bombs were then placed in a centrifuge for two minutes to remove sediment from the aqueous layer, and the liquid was decanted into a 20.0 ml volumetric flask. The

sediment was washed two times with deionized water which was transferred to the volumetric flask and diluted to volume. The 20.0 ml sample was transferred to a separatory funnel to which 40.0 ml of a mixture of 6N HCl and 2.5N LiCl already had been added. Twenty milliliters of methyl iso-butyl ketone (MIBK) was added and the mixture was shaken for two minutes. The MIBK and aqueous layer were separated by allowing the aqueous layer, which still contained the lead, to drain out the bottom into a plastic beaker. The MIBK layer, which contained the iron chloride complex, was discarded. A pH electrode was placed in the plastic beaker, and the pH was adjusted to 3 with  $\text{NH}_3$  saturated with MIBK. The sample was transferred back to the separatory funnel and 10.0 ml of MIBK plus 6.0 ml of 1.0 percent ammonium pyrrolidine-dithiocarbamate (APDC) was added. The mixture was shaken again for two minutes, and the MIBK layer containing the lead was separated from the aqueous layer. The MIBK layer was analyzed by atomic absorption for lead at an analytical wavelength of  $2170 \text{ \AA}$ . Reagent blanks and standards were carried through the same procedure. For calibrations, commercial Pb standards were extracted into MIBK.

The estimated precision of the method is  $\pm 5$  percent relative standard deviation for the concentrations encountered.

#### Method for arsenic

The sediment samples were prepared for analysis by weighing a 2.00 g sample into a 125.0 ml Erlenmeyer flask with standard taper top. Seventy-five milliliters of 1N HCl was added to the flasks, and

they were brought to boiling on a hot plate which leached out the arsenic (Woolson et al., 1971). After the sample was cooled to ambient temperature, the arsenic was reduced for 30 minutes with KI and  $\text{SnCl}_2$ . During this reduction time period, the absorber of a Fisher Scientific Company No. 1-405 arsine generator was filled with 5.0 ml of  $\text{I}_2$ -KI solution. Three grams of zinc metal were added to the flask, and the absorber unit immediately was attached to the flask. The arsine gas, produced along with hydrogen, bubbled through the absorber, and the arsenic was retained by the  $\text{I}_2$  solution. The reaction was allowed to continue for one hour to insure complete recovery of the As.

The absorber solution was placed in a plastic vial, reduced with 0.2 ml of sodium metabisulfite, and 3.0 ml of molybdenum mixed reagent was added. The arsenic-molybdenum blue color was allowed to develop for one hour. The solution then was transferred to a 4.0 cm pathlength cuvette, and the absorbance at  $8400 \text{ \AA}^0$  was measured with a spectrophotometer. Reagent blanks and standards were carried throughout the procedure. For calibrations, Baker analytical reagent grade arsenious oxide dissolved in dilute acid solution was used. Precision for a single determination was about  $\pm 10$  percent for the concentration levels encountered.

#### Results and discussion

Listed in Table 1 are the results of the analyses of the 48 sediment samples we received. These samples had been collected at

nine different sites along a 15-mile north-south line running from the Arroyo Colorado to the southern boundary of the wildlife refuge (Fig. 1). Only one core was shorter than one meter in length, and most were almost one and one-half meters in length.

The sediment has been described in some detail by Ahr (1972) who also gave some geomorphological data on the sampling sites. It seems unnecessary to repeat his descriptions here, especially because there was so little variation in the Pb and As concentration of the sediment.

We found no evidence that the sediment has been contaminated by man-introduced Pb and As. The relatively small concentration variations we found appear not to correlate with depth in the sediment column or any of the variables measured by Ahr in his study. This is in spite of the fact that according to Ahr's data, the sediment ranges from Recent to Pleistocene in age and shows considerable differences in physical characteristics.

Relatively little data on Pb and As concentrations in Recent sediments are available, but Shimp et al. (1970, 1971) gave data for these and other trace elements on a large number of cores collected in Lake Michigan. They found strong evidence for man's influence, in that cores collected near metropolitan areas commonly had about 150 parts per million (ppm) lead in the upper few centimeters, but only 20 ppm or so at depth. Arsenic concentrations were up to 30 ppm at the surface but only 5 ppm or so at depth. In our south Texas cores, lead concentrations clustered around 5 ppm with no decided trend with

depth, while arsenic values were around 3 ppm with no obvious trends.

We analyzed a few sediment samples from the Mississippi River delta (table 1) and found them to be generally about two times richer in leachable lead than the south Texas cores but similar in arsenic. A surface soil sample from outside Bizzell Hall on the Texas A&M University campus gave 300 ppm Pb, but at 20.0 cm the value had dropped to 100 ppm. Our analytical procedure thus seems to be sound, and we can only conclude that there is no evidence for man-introduced lead and arsenic in the south Texas sediments we analyzed.

The fact that the sediments we analyzed were not enriched in Pb and As, despite large additions of these elements to the surrounding croplands in historical times, could mean that the sediments were not of the right age, that is, they may all have been too young or too old to show the expected pattern. This could happen in a coastal environment where stream channels are continually shifting as erosion and deposition occurs. It seems more likely, though, that the lead and arsenic added to croplands was retained on the land. Build-up of arsenic concentrations to the point of contamination of field soils is well known. In a study of this phenomenon Woolson et al. (1971) estimated that in some cases 95 percent of all arsenic added over a number of years has been retained by the soil.

This only reinforces statements made in this report concerning the ability of particulate material to adsorb potentially toxic heavy metals. If the metals are added in solution, as from industrial wastes, they will be adsorbed on the suspended matter in streams and

added to accumulating sediment in the coastal zone. If, however, the metals are added to cropland, they may be relatively immobile and simply accumulate in the soil.

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## TABLES

Table 1

## ACID LEACHABLE LEAD AND ARSENIC IN SOUTH TEXAS COASTAL-ZONE SEDIMENTS

Site Number	Depth (cm)	Pb mg/Kg	As mg/Kg	Site Number	Depth (cm)	Pb mg/Kg	As mg/Kg
1	10-15	10.1	7.4	6	10-15	4.0	1.0
1	40-45	8.9	6.0	6	43-46	5.4	3.0
1	68-73	7.3	3.1	6	90-94	6.2	4.0
1	101-106	8.0	2.4	6	109-121	8.8	2.3
1	127-132	9.9	3.0				
1	140-142	3.1	2.1	7	13-18	4.9	2.0
				7a	13-30	6.5	1.9
2	13-18	8.4	4.2	7	35-40	4.5	1.3
2	30-32	7.1	2.8	7a	74-81	3.6	3.6
2	65-67	6.2	0.8	7	84-89	5.4	3.1
				7a	101-106	4.5	4.7
3	0-8	3.4	3.0	7	127-132	5.7	3.0
3	63-68	4.9	3.0	7a	127-132	---	3.6
3	127-142	4.8	4.5	7a	132-135	6.0	2.0
4	6-12	9.6	3.0	8	10-15	7.3	2.5
4a	13-18	5.8	1.9	8	35-40	8.9	4.1
4	46-51	4.8	1.2	8	81-86	8.7	8.0
4a	58-63	5.0	2.3	8	111-116	5.4	1.1
4a	96-101	4.9	2.2				
4a	111-117	3.9	0.8	9	10-15	6.6	3.4
4	118-120	5.4	4.9	9	45-50	---	2.0
				9	81-86	6.2	3.3
5	7-12	1.9	1.3	9	99-106	7.7	1.6
5a	10-15	2.6	1.4				
5	40-46	0.9	1.7	33*	0-10	18.7	2.8
5a	46-51	3.4	2.3	35*	0-10	17.5	4.0
5	89-96	2.5	1.6	37*	0-10	16.0	2.9
5a	89-95	5.0	2.5	37*	50-60	10.9	3.0
5a	114-122	9.7	3.8				
5a	128-130	3.7	1.2				
				Average Marine Shale <sup>†</sup>		20.0	6.6

\*Mississippi River Delta

†Krauskopf (1967)