

Heavy Metal Concentrations in Organisms from an Actively Dredged Texas Bay

R. R. Sims, Jr.* and B. J. Presley

*Department of Oceanography
Texas A&M University
College Station, Tex. 77843*

INTRODUCTION

Heavy metal pollution has usually been associated with industrial and municipal discharges into rivers, estuaries, and the air; however, it also has been related to dredging and spoil disposal (BELLA and MCCAULEY, 1972; CARMODY et al., 1973). In most near-shore environments, appreciable amounts of organic matter are trapped in the sediments and its degradation causes reducing conditions in all but the upper few centimeters of the interstitial water. This process lowers the Eh and pH of the interstitial water and brings into solution heavy metals that are insoluble in oxygenated water. Normally the diffusion of these metals from the interstitial to the overlying water would be slow, especially because new sediment is continually being added at the sediment surface. However, if the sediment is disturbed, as in dredging, the possibility of significantly increasing both the dissolved and particulate metal concentration in the water column exists.

Any redistribution or increase of metal concentrations, such as those just described, may allow organisms to take up greater amounts of metals from the water or from ingested particles. These effects may then be amplified up the food chain, resulting in adverse effects on organisms at higher trophic levels.

STUDY AREA

This study was part of an assessment of the environmental impact of dredging on San Antonio Bay and the adjacent Aransas National Wildlife Refuge. The San Antonio and the Guadalupe River which join a few miles before entering the northeast end of the bay, provide the main fresh water input to the area. The total drainage area of these two rivers is 24,848 square kilometers of largely agricultural land. The area of the bay itself is about 340 square kilometers with an average depth of about 2 meters. San Antonio

*Present address: Dept. of Marine Science, University of South Florida, 830 First Street South, St. Petersburg, Fla. 33701

Bay has no direct connection to the Gulf of Mexico, but connects to bays on either side which do. The Gulf Intracoastal Waterway (GIWW) which is 4-5 meters deep and 40 meters wide also crosses all the bays in this area, and another navigation channel, Victoria Barge Canal, runs along the eastern side of San Antonio Bay.

The construction and maintenance of these navigation channels, and the ship and barge traffic in them, disturbs the sediment in the area. Much more concern has been expressed, however, over the effect of removing oyster shell from San Antonio Bay. According to KERR (1967), shell was taken from fossil reefs in the bay by shovel and wheelbarrow as early as 1880, and by mechanical dredge as early as 1905. Hydraulic dredging began in 1912, and in that year the State of Texas received tax on 409,037 cubic meters of shell. By the 1950's, 7 to 9 million cubic meters of shell per year were being removed, but this has declined somewhat in recent years. Thus, the area has had a long history of intense dredging activity. In order to show an effect on the metal content of organisms or sediments as a result of this dredging, it is necessary to determine the background metal levels of the material studied and/or to relate metal levels observed to other similar near-shore areas. Such a comparison has been made for surface and sub-surface Bay sediments TREFRY (1974). This present report describes the work done on organisms.

METHODS

A total of 80 individuals from three groups of animals (molluscs, crustaceans, and bony fish) were collected from 23 sampling sites in San Antonio Bay. These sampling sites covered the entire bay, including dredged and undredged areas. Oysters and clams were collected by dredging. Shrimp, bony fish, and some crabs were collected with an otter trawl. A number of crabs were also collected from traps, which were placed in dredged and non-dredged areas. The oysters and clams were packed in ice and kept alive until they were returned to the laboratory. All other organisms were frozen in polyethylene bags immediately after collection.

All organisms and tissues were washed with deionized water to remove sand and clay and blotted with a Kimwipe to remove excess water. An aliquot was then dried at 105°C to determine water content. For cadmium, copper, lead, and zinc determination, 10 g of wet samples, when possible, were digested

in 15 ml of a 2:1 mixture of nitric and perchloric acids in covered tall form pyrex beakers. The samples were heated slowly to dryness, and if charring occurred, additional nitric acid was added. A small amount of water was then added to dissolve the residue and the volume was brought to 50 ml with pre-extracted pH 4 buffer. The metals were solvent extracted using an APDC-MIBK system (BROOKS et al., 1967) to free them from interfering ions. The organic solution was analyzed by atomic absorption spectrophotometry using standards carried through the same procedure.

Arsenic was determined on 2 gram tissue samples which were digested with a 5:2:2 mixture of nitric, perchloric and sulphuric acids. The arsenic was removed by distilling it as arsine gas and quantified by a molybdenum blue colorimetric methods essentially as described by VOGEL (1971), except that color development followed the PO_4 method of STRICKLAND and PARSONS (1968).

Mercury concentration was measured on 1 g samples which were oxidized with concentrated nitric acid in screw top culture tubes for three days at 60°C. The mercury analysis followed that of HATCH and OTT (1968).

The estimated precisions (coefficient of variation) of the various analyses based on replicate determinations are: As, 7%; Cd, 15%; Cu, 10%; Hg, 6%; and Zn, 2%.

RESULTS AND DISCUSSION

The objective of this study was to determine what effect, if any, dredging has on the concentration of heavy metals in the biota of San Antonio Bay. The elements chosen for analysis are known to be either potential toxins or physiological metabolites, and have been determined in a number of previous studies. The organisms analyzed are the most common and abundant in the bay and are divided into three taxonomic groups for discussion purposes.

Molluscs

The bivalve molluscs (Crassostrea virginica and Rangia cuneata) have the highest metal concentrations of the organisms studied. This observation is consistent with data given by VINOGRADOV (1953), SEGAR et al., (1971), and IDOE (1972). These high levels may be explained by the feeding habits and the biochemistry of this groups. Oysters, for example, are filter feeders which ingest suspended material from water. This material is known to be a good scavenger of heavy metals. In addition, copper and zinc are used by these organisms as metabolites.

Table I compares the arsenic, cadmium, lead, mercury, and zinc concentrations of oysters from San Antonio Bay with those from reportedly unpolluted and undredged waters of other areas. The metal concentrations, except for copper, proved to be lower than those from other areas along the the Gulf Coast (KOPFLER, 1966) and showed no relationship to areas of dredging in San Antonio Bay. The oysters from the bay also contained lower mercury and arsenic concentrations than oysters from other similar locations (PRESLEY et al., 1972; WINDOM, 1972).

Metal concentrations for the clam Rangia from San Antonio Bay (Table I) compare well with the finding of PRINGLE et al., (1967).

Table I. Average heavy metal concentrations in soft portions of whole molluscs (concentrations in ppm dry weight).

Organism	Location	As	Cd	Cu	Pb	Hg	Zn
Oyster	A	1.3	3.2	161	<0.8	0.05	322
"	B	-	40	-	6.5	0.13	268
"	C	<1.6	2.4	46	7.7	0.45	654
"	D	-	35	41	3.0	-	1103
"	E	-	-	126	-	-	1533
Clam	F	-	0.5	25	1.1	-	51
"	G	-	<1.0	15.5	<1.0	-	85

- A. San Antonio Bay (this study) 9 organisms analyzed
- B.. Flower Gardens, Texas (PRESLEY et al., 1972) 2 organisms analyzed
- C. U. S. Southeast Coast (WINDOM, 1972) 14 organisms analyzed
- D. Tasman Sea, New Zealand (BROOKS and RUMSBY, 1965), 6 organisms analyzed
- E. U. S. Gulf Coast (KOPFLER, 1966) 136 organisms analyzed
- F. San Antonio Bay (this study) 5 organisms analyzed
- G. Pongo River, North Carolina (PRINGLE et al., 1967)

Crustaceans

Crustaceans are, as a group, mobile, and thus any one organism could theoretically travel around all of San Antonio Bay and adjacent areas in its life time. This is especially true of shrimp which, after the juvenile stage, migrate out of the bay into the GIWW and the Gulf of Mexico. Because of this mobility, it would be meaningless to directly compare metal concentrations in shrimp from dredged with undredged areas. Therefore, these metal values too must be compared with those of other similar areas which are not considered polluted. As Table II shows, crustaceans in San Antonio Bay do not differ appreciably in heavy metal content from crustaceans in other regions.

Table II. Average heavy metal concentrations in whole crustaceans (concentrations in ppm dry weight).

Organism	Location	As	Cd	Cu	Pb	Hg	Zn
Brown shrimp	A	0.6	<0.4	34	<0.2	<0.02	14
" "	B	-	0.1	24	0.2	-	29
" "	C	11.0	<0.1	11.5	0.2	0.14	23
White shrimp	D	3.8	<0.2	17	<0.2	0.24	23
Blue crab	E	0.6	0.1	54	<0.2	-	14
" "	F	1.8	0.4	34	<3.5	-	75

- A. San Antonio Bay (this study) 8 organisms analyzed
- B. Northeast Mexican coast (PRESLEY et al., 1972)
2 organisms analyzed
- C. Mississippi River area (PRESLEY et al., 1972)
2 organisms analyzed
- D. U. S. Southeast coast (WINDOM, 1972) 6 organisms analyzed
- E. San Antonio Bay (this study) 4 organisms analyzed
- F. U. S. Southeast coast (WINDOM, 1972) 17 organisms analyzed

Bony fish

The bony fish are a very diverse and mobile group of organisms. However in this study it was found that the range of values for trace metals consistently overlaps from one species to another (Table III). The possible reason for such relative uniformity is the similar metabolism and biochemistry of the group as a whole.

Table III. Average heavy metal concentrations in various bony fish (concentrations in ppm dry weight).

Organism	Location	# Analyzed	Cd	Cu	Pb	Zn
Atlantic croaker ^a	S.A.B. ^c	10	<0.1	2.6	<0.3	6.3
Silverside ^a	S.A.B.	6	0.1	4.3	2.3	117
Spot ^b	S.A.B.	2	0.2	2.3	<0.6	25
"	U.S.S.E.C. ^d	5	0.5	8.4	8.6	20
White sea trout ^b	S.A.B.	2	1.8	1.9	1.0	24
Spotted sea trout ^b	S.A.B.	2	0.1	1.3	<0.2	19
" " "	U.S.S.E.C.	5	0.5	9.5	1.0	21
Bay anchovy ^a	S.A.B.	6	0.5	2.8	1.4	97
" " "	U.S.S.E.C.	6	6.1	10.0	6.1	397
Menhaden ^a	S.A.B.	7	<0.1	2.8	1.0	26
Gizzard shad ^a	S.A.B.	4	<0.1	4.0	<0.4	7.5
Southern flounder ^b	S.A.B.	1	0.3	2.2	0.9	37
" " "	U.S.S.E.C.	3	1.3	3.0	3.7	39

a. Whole fish analyzed

b. Flesh only analyzed

c. San Antonio Bay (this study)

d. U. S. Southeast Coast (WINDOM et al., 1972)

The bony fish from San Antonio Bay appear to be lower in cadmium, copper, lead, and zinc than fish of the same species from non-dredged and relatively unpolluted areas of the U. S. Southeast coast (Table III). Arsenic and mercury were also low in the San Antonio Bay; the range of arsenic in the flesh was <0.1 - 0.7 ppm, while mercury had a range of 0.08 - 0.16 ppm with an average of 0.10 ppm. WINDOM (1972) found average values of 2.0 ppm arsenic and 0.09 ppm mercury in these same species of bony fish from the Southeastern U. S.

Separate tissue samples were analyzed from some San Antonio Bay fish, and these showed a distinct preferential uptake by the various tissues. The liver proved to concentrate cadmium, copper, and zinc to the greatest extent, while the heart appeared to concentrate lead. The stomach and flesh showed lower concentrations of metals than other tissues. Similar results have been observed previously (PRESLEY et al., 1972; WINDOM, 1972).

CONCLUSIONS

Organisms from San Antonio Bay have been shown to have low heavy metal concentrations. This is most likely the result of low natural metal levels in the area and minimal man-introduced contamination due to the bay's location far from any dense industrial or population centers. In addition, vigorous shell dredging activity in the bay for more than 50 years has not in any obvious way increased the concentrations of heavy metals in the organisms found there.

Analyses have shown that metal concentrations in sediments from depths up to 2 meters (representing several centuries) are both low and uniform (TREFRY, 1974). This indicates that the sediments do not represent any unusual metal reservoir for dredging to disturb, and shows that no recent increase in metal input to the bay has occurred.

In general, organisms from San Antonio Bay were lower in almost every metal than organisms from other areas where dredging and pollution are thought to be minimal. Molluscs were observed to concentrate metals more than the other organisms studied, but the levels observed are very much lower than those thought to be lethal or toxic (BOWEN, 1966). Except for a few large fish, metal concentrations did not correlate significantly with the size or growth stage of the individual. In the fish, certain organs, such as the liver, were found to concentrate metals, in agreement with previous reports.

ACKNOWLEDGMENTS

We wish to thank Jake Hoffman for his help in field collections and John H. Trefry and Paul Boothe for advice during the writing of this paper. This research was supported through the U. S. Army Corps of Engineers contract no. DACW64-72-C-0046.

REFERENCES

- BELLA, D. A., and J. E. MCCAULEY: Environmental considerations for estuarine dredging operations. Proc. World Dredging Conf. 457 (1972).
- BOWEN, H. J. M.: Trace elements in biochemistry. Academic Press, London, 241 pp. (1966).
- BROOKS, R. R. and M. G. RUMSBY: The biogeochemistry of trace element uptake by some New Zealand bivalves. Limnol. Oceanogr. 10, 521-527 (1965).
- BROOKS, R. R., et al.: The APDC-MIBK extraction system for the determination of trace elements in saline waters by atomic absorption spectro-photometry. Talanta 14, 809 (1967).

- CARMODY, D. J., et al.: Trace metals in sediments of New York Bight. Mar. Poll. Bull. 4, 132 (1973).
- HATCH, W. R., and W. L. OTT: Determination of sub-microgram quantities of mercury by atomic absorption spectrophotometry. Anal. Chem. 40, 2085 (1968).
- IDOE: Baseline studies of pollutants in the marine environment. Background papers for a meeting at Brookhaven National Laboratory, 24-26 May 1972.
- KOPFLER, F. W. (ed.): Copper and zinc content of oysters (*Crassostrea virginica*) from selected areas of the South Atlantic and Gulf of Mexico. USD HEW, Public Health Ser. Tech. Memo. GCSSRC (FY 67-1), 9 pp. Unpublished report (1966).
- PRESLEY, B. J., et al.: A study program to identify problems related to oceanic environment quality-Gulf of Mexico and Caribbean (heavy metals), In: Baseline Studies of Pollutants in the Marine Environment (I.D.O.E.). 732. Brookhaven Nat. Lab., New York (1972).
- PRINGLE, B. H., et al.: Trace metal accumulation by estuarine molluscs. Unpublished report (1967).
- SEGAR, D. A., et al.: The distribution of the major and some minor elements in marine animals. Part II. Molluscs. J. Mar. Biol. Ass. U. K. 51, 131 (1971).
- STRICKLAND, J. D. H., and T. R. PARSONS: A practical handbook of sea water analysis. Fish. Res. Bd. Canada, 311 pp. (1968).
- TREFRY, J. H.: The distribution of potentially toxic heavy metals in the sediments of San Antonio Bay and the Northwest Gulf of Mexico - M.S. Thesis, Texas A&M University, College Station, Tx. (1974).
- VINOGRADOV, A. P.: The elementary chemical composition of marine organisms, In: Sears Found. for Mar. Res., Mem. II. Yale Univ., New Haven, 647 pp. (1953).
- VOGEL, A. L.: A textbook of quantitative inorganic analysis. Longman Ltd., London, 1216 pp. (1971).
- WINDOM, H. L.: Arsenic, cadmium, copper, lead, mercury, and zinc in marine biota-North Atlantic Ocean, In: Baseline Studies of Pollutants in the Marine Environment (I.D.O.E.). 121 Brookhaven Nat. Lab., New York (1972).