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Heavy Metals in Oysters and Clams of St. Louis Bay, Mississippi

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St. Louis Bay is a shallow embayment lying at the western end of the Mississippi Sound. Two rivers, the Jourdan and Wolf enter this basin at opposite ends and drain an area of approximately 720 square miles. Of the bays along the Mississippi coast, St. Louis Bay suffers the least from anthropogenic input of pollutants. Only scattered residential areas and a few very small industrial parks spoil a virtually pristine area. The placement of a large TiO_2 refinery in 1979 on the north bay shore was responsible for great concern over discharge of metal pollutants from ore by-products.

The present study was designed to establish "typical" values of 17 metals in the water, sediment and biota of St. Louis Bay before operation of the ore refinery began. Though previous studies in this bay have included heavy metal analyses in the sediments and water (BRENT et al. 1972, LYTLE 1973 and U.S. GEOLOGICAL SURVEY unpublished data), no prior study has included biota.

In deciding upon the organisms to include in the study, consideration was given to the criteria: (1) is the organism a resident throughout the year, (2) is the organism ecologically important or can the organism be of some economic significance.

Because of their ability to concentrate pollutants of various kinds from their environment, certain marine animals have been found useful as indicator organisms. LATOUCHE & MIX (1981), GORDON et al. (1980), KUMARAGURU & RAMAMOORTHL (1979), and ROMERIL (1979) have documented the decided advantage of selecting members of the bivalve community for pollution monitoring efforts. During 1978 it was found that the clam, Rangia cuneata and oyster, Crassostrea virginica were the only organisms that reasonably met the sampling criteria in St. Louis Bay. Specimens of both were analyzed to compare metal uptake and to see whether their microphageous behavior is reflected in the relationship of body weight burden of trace metal to levels in the sediments and water column.

The metals chosen for analysis were arsenic (As), antimony (Sb), beryllium (Be), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), mercury (Hg), molybdenum (Mo), nickel (Ni), selenium (se), strontium (Sr), titanium (Ti), vanadium (V) and zinc (Zn).

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MATERIALS AND METHODS

In December, 1978 specimens of C. virginica were collected by hand from a reef near the southwest shore of St. Louis Bay, and the R. cuneata were collected by hand from the northwest shore region of the bay. Oysters varied in size from 4.5 g to 11.7 g (wet weight shucked). Individual specimens of oysters were analyzed separately. Three batches of 14 adult clams were homogenized and the composite analyzed.

Clams were opened using a knife constructed of polycarbonate. This device was not suitable for the oysters which required a one minute steam treatment before being pried open. All tissue and liquid were removed, weighed and included for analysis. Digestion and analysis of sample materials generally followed the protocol of the U.S. ENVIRONMENTAL PROTECTION AGENCY (no date). The digestion for all metals but Hg consisted of treatment of 5 g wet tissue with conc. HNO_3 (5 mls) and conc. H_2SO_4 (6 mls) which was simmered five minutes. Five mls more HNO_3 were added with an additional five minute heating. Sufficient 30% H_2O_2 was added during a one hour digestion to maintain a light-colored sample.

The digest was made up to volume and aspirated directly into the flame of an atomic absorption spectrophotometer for all metals but As, Sb, Se and Hg. As, Sb and Se were analyzed by introducing aliquots of the digested tissue to a hydride generation flask where upon delivery of $NaBH_4$ the metal hydride was swept by Ar gas into a heated quartz tube in the path of an atomic absorption light beam (U.S. ENVIRONMENTAL PROTECTION AGENCY no date and U.S. ENVIRONMENTAL PROTECTION AGENCY 1976).

Hg was measured by digestion of a separate set of samples. Since there was not sufficient clam tissue, only oyster tissue was used for analysis; 5 g of homogenized tissue from 11 specimens were digested with 8 mls conc. H_2SO_4 and 2 mls conc. HNO_3. After reduction with $SnCl_2$ the Hg vapor was flushed through a cell in the atomic absorption spectrophotometer after the method of U.S. ENVIRONMENTAL PROTECTION AGENCY (1976).

Water was collected at eight sites including the areas of clam and oyster collections. The collections on alternate months during 1978 were separated into soluble and particulate phases by 0.45 μ membrane filtration. Surface sediments were collected twice during the year at the oyster-clam sites and 12 other collection sites. Details of analysis and results may be found elsewhere (LYTLE 1978).

All analyses were conducted in a laboratory especially designed to prevent contamination during each stage of analysis. The laboratory was equipped with positive pressure high efficiency filtered air; water was prepared with glass distillation followed by ion exchange and quartz distillation; only J. T. Baker Ultrex grade chemicals were used throughout.

Along with samples, blanks and standards, three reference materials were analyzed to assess recovery for metals in organisms, a bovine liver from the National Bureau of Standards and soluble fish tissue and dried copepods from the International Atomic Energy Agency.

RESULTS AND DISCUSSION

Results of analysis of the oysters and clams are contained in Table 1. For comparison the mean values for water and sediment samples taken near the organism collection sites are included. Ten of the elements occur in these organisms at such low levels that they are not detected by currently standardized procedures. Only As, Cd, Cu, Se, Zn, Fe and Hg occurred at detectable levels in the oysters and clams.

The variabilities of metal concentrations as shown by % relative standard deviations displayed in Table 1 do not seem to be a function of whether composite samples are used in analysis (as for *R. cuneata*) or individual specimens (*C. virginica*). Little improvement in analytical variability was achieved by using the 14-sample composites for *R. cuneata*.

Both As and Se are concentrated by these bivalves though not to the same degree. As accumulates in *C. virginica* to levels approximately twice those accumulated in *R. cuneata*, but Se is twice as effectively concentrated by *R. cuneata*. Concentrations of As and Se in the water and sediments will not explain this divergence for these metals. VAHL (1973) and GRIEG & WENZLOFF (1978) have demonstrated that bivalves, especially *C. virginica* are very efficient retainers of particulate matter and may obtain their metal levels from particulate matter and sediment. Successful accumulation of As in oyster and clams in St. Louis Bay is not surprising considering the high levels in both particulates and sediments of the bay. Based solely on levels of As and Se in the particulates and sediments, Se is apparently more efficiently accumulated from the surroundings by both organisms than is As.

As and Se occur at levels less than those found at similar locations for the same organisms in the southeastern U.S., typified by values listed in Table 2. Considering the high particulate water value of As found in St. Louis Bay some question arises over the values in this report. A look at results of our analysis *vs* certified values for standard reference materials (SRMs) in Table 3 reveals the greatest discrepancy for As and Se. The U.S. ENVIRONMENTAL PROTECTION AGENCY (no date) method used in this survey is designed for wet tissue; all SRMs are dried materials. The discrepancy may arise because the analysis method is not suitable for dried materials. More likely, however, the method results in considerable loss of As and Se or suffers from inefficient degradation of As and Se bonding sites in the wet oyster-clam tissue. In this case, As and Se would have been much higher in both organisms than reported, and the efficacy of the method would be in doubt.

TABLE 1. Results of trace metal analysis in organisms, water, and sediments of St. Louis Bay, Mississippi.

Sample		As	Sb	Be	Cd	Co	Cr	Cu	Pb	Mo
C. virginica	mean (μg/g wet wt.)	0.12216	<0.05	<0.08	1.61	<0.4	<0.1	31.5	<0.5	<2
(Sta. I)	% rel. std. dev.	96.59%			16.59%			51.56%		
Water	soluble (μg/l)	<2	<2	<0.2	<3	<20	<100	<10	<20	<80
(Sta. I)	particulate (μg/l)	0.151	<0.02	<0.2	<0.19	<1.4	<2.1	<1	<2.1	<16
	particulate (μg/g solids)	13.88	<0.025	<0.075	<0.087	<0.35	<2.	<0.32	<3.4	<4.7
Sediment (Sta. I)	(μg/g dry wt.)	6.72	<0.025	0.689	<0.087	7.54	9.73	10.34	13.8	<4.7
R. cuneata	mean (μg/g wet wt.)	0.0560	<0.05	<0.08	<0.05	<0.4		2.46	<0.5	<2
(Sta. II)	% rel. std. dev.	40%						28%		
Water	soluble (μg/l)	<2	<2	<0.2	<3	<20	<100	<10	70	<80
(Sta. II)	particulate (μg/l)	0.118	<0.02	<0.2	<0.19	<1.4	<2.1	<1	<2.1	<16
	particulate (μg/g solids)	20.17	<0.025	<0.075	<0.087	<0.35	<2	<0.32	<3.4	<4.7
Sediment (Sta. II)	(μg/g dry wt.)	7.38	<0.025	0.888	<0.087	8.35	11.6	9.74	16.9	<4.7

Sample		Ni	Se	Sr	Ti	V	Zn	Fe	Hg
C. virginica	mean (μg/g wet wt.)	<0.2	0.284	<10	<2	<2	821	57.4	0.0746
(Sta. I)	% rel. std. dev.		46.09%				25.6%	20.48%	20.93%
Water	soluble (μg/l)	<30	<2	1712.8	<300	<200	73.4	58.78	<0.2
(Sta. I)	particulate (μg/l)	<3.9	<0.01	<2.5	<73	<15	47.53	414.62	
	particulate (μg/g solids)	<0.95	<0.13	<1.2	<20	<6.4	6495.8	23,600	
Sediment (Sta. I)	(μg/g dry wt.)	8.26	<0.13	<1.2	277.5	<6.4	73	21,000	0.107
R. cuneata	mean (μg/g wet wt.)	<0.2	0.493	<10	<2	<2	16.5	720	n.r.[1]
(Sta. II)	% rel. std. dev.		48%				10.6%	17.2%	
Water	soluble (μg/l)	<30	<2	1997.7	<300	<200	78.37	49.05	
(Sta. II)	particulate (μg/l)	<3.9	<0.01	<2.5	<73	<15	27.72	305.483	
	particulate (μg/g solids)	<0.95	<0.13	<1.2	<20	<6.4	4071.6	40,006	
Sediment (Sta. II)	(μg/g dry wt.)	10.43	<0.13	<1.2	358.5	<6.4	65.7	21,800	

[1] not reported

TABLE 2. Results of previous analysis of trace metals in oysters and clams of the Southeastern U.S.

Location	As	Cd	Cr	Cu	Pb	Hg	Se	Zn	Fe	Reference
C. virginica										
San Antonio Bay, TX[1]	1.3	3.2		161	<0.8	0.05		322		SIMS & PRESLEY 1976
Flower Garden, TX[1]		40			6.5	0.13		268		SIMS & PRESLEY 1976
U.S. Southeast Coast[1]	<1.6	2.4		46	7.7	0.45		654		SIMS & PRESLEY 1976
U.S. Gulf Coast[1]				126				1533		SIMS & PRESLEY 1976
Bayou Casotte, MS[2]		0.16			0.35	0.25				HARVEY & KNIGHT 1978
Biloxi, MS[2]		0.17			0.07	0.13				HARVEY & KNIGHT 1978
Deer Island, MS[2]		0.13			0.12	0.13				HARVEY & KNIGHT 1978
Biloxi Yacht Club, MS[2]		0.04			0.05	0.30				HARVEY & KNIGHT 1978
Graveline Bayou, MS[2]		0.575	2.99	21.6	1.09			618		HARVEY et al. 1982
Texas Gulf Coast[2]	0.57	0.48	0.43	41		0.07	0.14	103	31	GUTHRIE et al. 1979
R. cuneata										
Texas Gulf Coast[2]	2.39	1.19	0.99	23		0.11		13	71	GUTHRIE et al. 1979
San Antonio Bay, TX[1]		0.5		25	1.1		0.54	51		SIMS & PRESLEY 1976
Pongo River, NC[1]		<1.0		15.5	<1.0			85		SIMS & PRESLEY 1976
Graveline Bayou, MS[2]		0.224	0.92	2.95	1.53			7.57		HARVEY et al. 1982

[1] μg/g dry wt.

[2] μg/g wet wt.

TABLE 3. Results of Standard Reference Material Analysis.

Reference Material	As	Sb	Be	Cd	Co	Cr	Cu	Pb	Mo
Bovine Liver									
GCRL[2]	n.d.[3]	n.d.	n.d.	n.d.	n.d.	n.d.	237	n.d.	n.d.
NBS[4]	(0.055)[5]	n.r.[6]	n.r.	0.27	(0.18)	n.r.	193	0.34	(3.2)
Dried Copepod									
GCRL	0.363	n.d.	n.d.	0.324	n.d.	n.d.	5.01	0.839	n.d.
IAEA[7]	6.7	0.07	n.r.	0.85	0.9	1.7	7.8	3.8	n.r.
Soluble Fish Tissue									
GCRL	0.175	n.d.	n.d.	0.0802	n.d.	n.d.	2.95	n.d.	n.d.
IAEA	14.5	n.r.	n.r.	n.r.	0.220	0.714	5.25	n.r.	n.r.
	Ni	Se	Sr	Ti	V	Zn	Fe	Hg	
Bovine Liver									
GCRL[2]	n.d.	n.d.	n.d.	n.d.	n.d.	255	339		
NBS[4]	n.r.	1.1	(0.14)	n.r.	n.r.	130	270	0.016	
Dried Copepod									
GCRL	0.585	0.499	n.d.	n.d.	n.d.	172	42.3		
IAEA[7]	2.0	3.4	n.r.	n.r.	n.r.	157	61	0.35	
Soluble Fish Tissue									
GCRL	0.218	0.860	n.d.	n.d.	n.d.	21.3	643		
IAEA	n.r.	3.07	n.r.	n.r.	n.r.	18.9	565	73.9	

[1] Values expressed in ppm (µg/g).

[2] Value obtained in trace metal lab at Gulf Coast Research Laboratory.

[3] n.d. = not detected (see Table 1 for detection limits).

[4] National Bureau of Standards certified value.

[5] Parentheses indicate results not certified.

[6] n.r. = not reported

[7] International Atomic Energy Agency certified values.

The fact that Cu and Zn are very effectively accumulated by *C. virginica* even more than *R. cuneata* in St. Louis Bay is amply documented in other studies of these two species in the southeastern U.S. (see Table 2 and WRIGHT 1978 and ZAMUDA & SUNDA 1982). Only for Cu in *R. cuneata* do bivalves in St. Louis Bay have significantly lower Cu or Zn than these bivalves in other locations of the Southeast U.S.

Table 1 indicates a greater enrichment of Fe in *R. cuneata* *vs* *C. virginica* which is also supported by previous studies (Table 2) and other reports of Fe in oysters and clams (WRIGHT 1978). The high values of Fe in the water column (Table 1) could easily account for high accumulations in the bivalves.

Only oysters were of sufficient size to conduct the multi-element analysis on individual specimens. Correlation coefficients calculated for metal *vs* weight, contained in Table 4 demonstrate no significant positive correlation for any metal. Significant negative correlations were found for selenium and iron *vs* weight suggesting a decline in metal level with age of oyster, a phenomenon encountered in other studies of metal *vs* weight studies (WRIGHT 1978).

TABLE 4. Correlation coefficients of weight and trace metals in oysters from St. Louis Bay.

	Weight	As	Cd	Cu	Se	Zn
Hg[1]	-0.589					
As[2]	-0.168					
Cd	-0.006	0.317				
Cu	0.364	-0.735*	0.133			
Se	-0.776*	0.096	0.324	-0.357		
Zn	0.155	-0.962**	-0.311	0.695	-0.123	
Fe	-0.713*	0.266	0.596	-0.217	0.805*	-0.184

[1] df for Hg = 9

[2] df for other metals = 6

*Significant at 95% confidence level

**Significant at 99% confidence level

Correlation between metals was strongest with negative correlation of As with both Cu and Zn and positive correlation of Se and Fe. WRIGHT (1978) discusses significant positive correlation with Zn and Cu occurring in other studies of *C. virginica*. The correlation of Cu with Zn was not as strong in the present study but nevertheless gives further evidence that the metal behavior of *C. virginica* and *R. cuneata* in St. Louis Bay prior to the introduction of heavy industry is consistent with that observed in other bays throughout the Southeastern United States.

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