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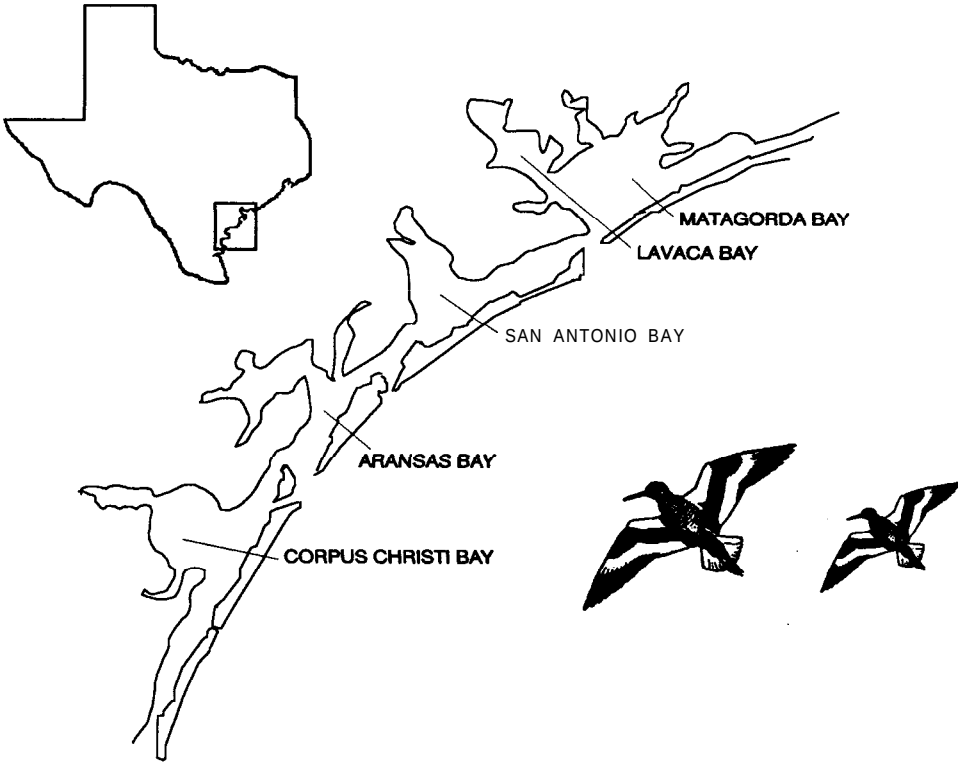
PHASE II REPORT



REGION 2
U.S. FISH AND WILDLIFE **SERVICE**
CORPUS **CHRISTI,** TEXAS, FIELD OFFICE

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ACCUMULATION OF MERCURY IN SEDIMENTS, PREY, AND SHOREBIRDS OF LAVACA BAY, TEXAS

PHASE II REPORT

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ABSTRACT

To continue the U.S. Fish and Wildlife Service's (Service) Lavaca Bay Natural Resource Damage Assessment (NRDA) Investigations, Phase II studies were initiated to include sediment, shorebird, and prey item components to demonstrate a pathway for mercury accumulation in shorebirds from Lavaca Bay. Two resident species, the American Oystercatcher *(Haemotopus palliatus)* and the Willet (*Catoptrophorus semipalmatus),* and one migratory species, the Long-billed Dowitcher (*Limnodromus scolopaceus*) were selected to represent the shorebird guild in Lavaca Bay. Sediments, prey items, oystercatcher adults and eggs, and adult Willets and dowitchers were collected from February to July 1993 from Lavaca Bay and a reference site. Analytical results indicate that mean mercury concentrations were significantly higher ($P < 0.05$) in sediments, shorebird livers, oystercatcher eggs, and in every prey species collected from Lavaca Bay when compared to the reference bay. Livers of Lavaca Bay dowitchers exhibited mercury levels 2.5 times higher than reference dowitchers (2.46 ppm vs. 0.91 ppm Hg dry wt.), while Lavaca Bay prey items of this species exhibited a four-fold increase (0.20 ppm dry wt. vs. < 0.05 detection limit). The mean mercury concentration in Lavaca Bay oystercatcher eggs exceeded reference eggs by three times; by comparison, the adult livers contained mercury concentrations four times higher than those from the reference group (5.13 ppm vs. 1.34 ppm). The most pronounced increase appeared in livers of Lavaca Bay Willets which exhibited a ten-fold increase in mercury concentration compared to the reference site (44.8 ppm vs. 4.53 ppm). Willets are known to feed heavily on fiddler crabs (*Uca* sp.), a prey species which also exhibited dramatically higher mercury concentrations (0.83 ppm dry wt. vs. < 0.05 detection limit) in Lavaca Bay compared to those collected from the reference site.

Information from the Service's Phase I Lavaca Bay Studies, and studies conducted by the U. S. Geological Survey, the National Marine Fisheries Service, and the Texas Department of Health support the results of current Phase II studies, indicating that elevated levels of mercury in Lavaca Bay sediments are bioaccumulating in the food chains of a variety of Lavaca Bay fish and wildlife, particularly shorebirds. A review of the literature and results of the above studies indicate that in the sediments, prey, eggs, hatchlings, and adult shorebirds of Lavaca Bay, mercury has potentially accumulated in sufficient quantity to seriously impact the Secretary of the Interior's trust natural resources and their supporting ecosystems, as defined in the National Contingency Plan. Quantification of the extent of the mercury-related impacts to the natural resources of Lavaca Bay is recommended through chronic toxicity studies of prey and histopathological and biomarker studies of serially dosed, pen-raised waterbirds that typically reside in Lavaca Bay.

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INTRODUCTION

Lavaca Bay, Texas was contaminated with mercury from the 1960's to the mid-1 970's as a result of operations of the Aluminum Company of America's (ALCOA) chlor-alkalai facility at Point Comfort, Texas (Figure 1). In the spring of 1991, the Corpus Christi Field Office of the U.S. Fish and Wildlife Service (Service) initiated Natural Resource Damage Assessment (NRDA) investigations to evaluate mercury-related injury to Lavaca Bay avian resources. Phase I studies examined accumulation and effects of mercury on: 1) nesting colonial waterbirds, 2) migratory waterfowl and cormorants that winter in Lavaca Bay, and 3) historical population trends in nesting colonial waterbirds. Phase II studies were expanded to include shorebird and shorebird prey investigations in order to demonstrate a pathway for mercury accumulation through the avian food chain. This study documents significant differences in mercury accumulation between Lavaca Bay and reference site sediments, prey, eggs, and adult shorebirds.

Two resident birds, the Willet (*Catoptrophorus semipalmatus*), and the American Oystercatcher (*Haematopus palliatus*) and one migratory shorebird, the Long-billed Dowitcher (*Limnodromus scolopaceus),* were selected to represent the shorebird guild utilizing the Lavaca Bay system. Willets and Oystercatchers are year-round residents that are territorial and site-specific; both species feed and nest within the Lavaca Bay system. Willet prey includes macrobenthos, insects, and small crustaceans, such as fiddler crabs *(Uca* sp.). Oystercatchers feed primarily on oysters, mussels, and benthic infauna. Long-billed Dowitchers breed in Alaska and Canada, and winter from California to Florida, south to Argentina, and throughout the Texas Gulf coast, feeding primarily in mudflats of bays, associated intertidal areas, and salt marshes. Prey items of dowitchers include marine worms, crustaceans, and mollusks obtained by probing in the mud or sand (Oberholser, 1974).

METHODS AND MATERIALS

Sediments

Ten surface (0.0-10.0 cm) sediment samples were collected with an Eckman dredge from shorebird feeding, loafing, and nesting areas in Lavaca Bay. Ten samples were also taken from similar shorebird habitat at the reference site in Aransas Bay (Figure 1). All stainless steel instruments used to collect and handle the sediments were chemically cleaned, and an aliquot of each sediment sample was placed in a labeled, certified chemically-cleaned sample jar and kept on ice until returned to the lab. The sediment samples were then kept frozen at -20°C until they were shipped to Geochemical & Environmental Research Group (GERG) at Texas A&M,

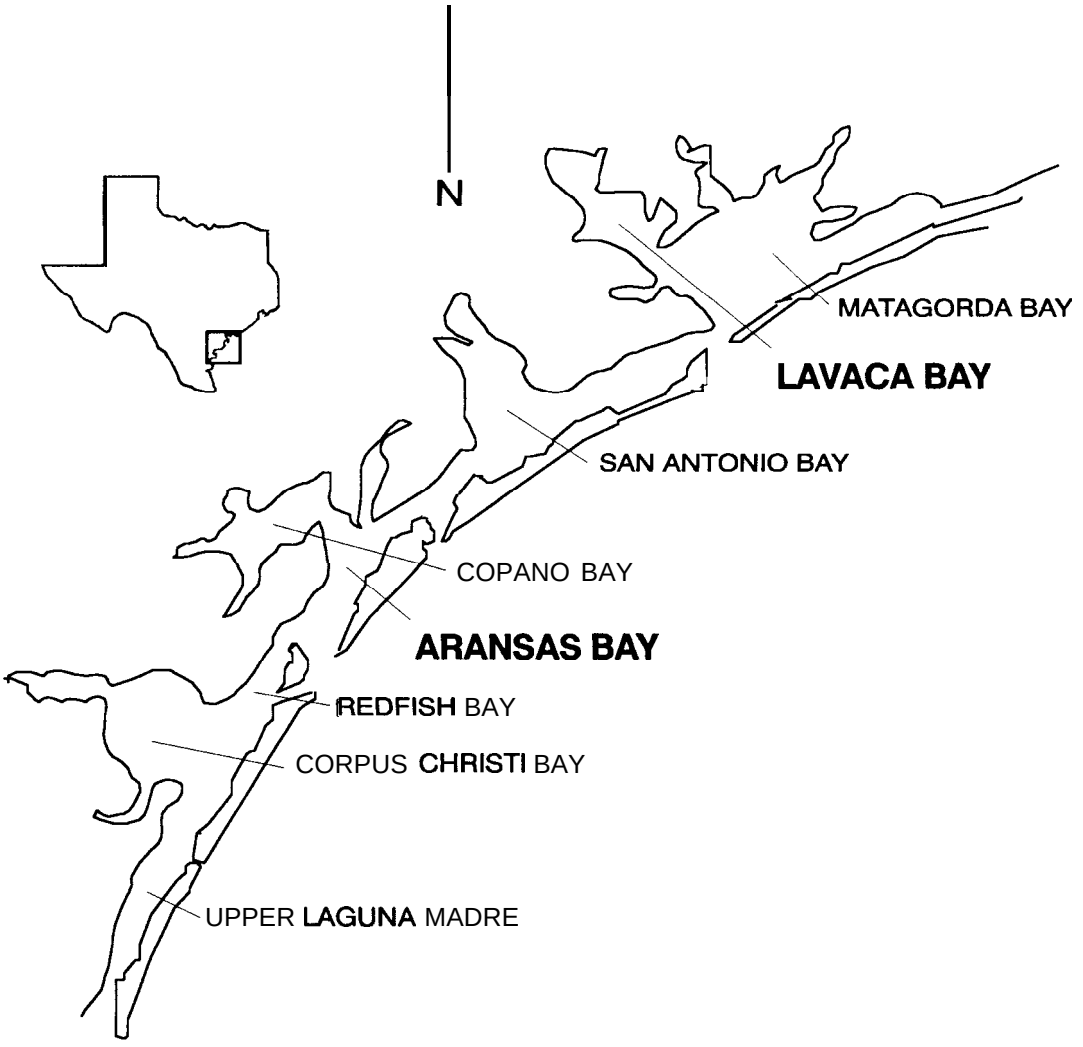

Figure 1. Location of Lavaca and Aransas Bays on the Texas coast.

College Station. Chain-of-custody protocol and documents accompanied all samples, and chemical methodology and reports met or exceeded Patuxent Analytical Control Facility (PACF) Quality Assurance Quality Control standards (Moore 1990). Concentrations of total mercury were measured for all samples using cold vapor atomic absorption spectrophotometery (Hatch and Ott 1968).

Prey Items

Shorebird prey item samples consisted of mussels (*Brachidontes exustus*), oysters (*Crassostea virginica*), polychaetes, small xanthid crabs, and fiddler crabs (*Uca* sp.) Mussels and oysters were removed from the shell prior to placing in the sample jars. Polychaetes were collected from sediments using chemically-cleaned, stainless steel sieves and forceps. All prey were placed in sample jars, labeled, and kept frozen at 20°C until they were sent to the PACF-approved analytical laboratory. Three composite samples of polychaetes were collected and analyzed for total mercury from both the study and reference sites; however, funding constraints limited analysis of other prey items to one composite sample of numerous individuals per group of organisms from both the study and reference sites.

Shorebird Eggs

One American Oystercatcher egg was collected from each of 10 nests at both the reference and study sites during late March and early April 1993. As each nest was approached, the egg nearest the collector was taken to insure random sampling. The eggs were placed in protective cartons and kept on ice until they were returned to the laboratory, where they were scored and the contents placed in sample jars. Egg contents were then frozen (-20°C) and later sent to a PACF-approved laboratory for total mercury analysis.

Shorebird Adults

Twenty Long-billed Dowitchers were collected from both Lavaca Bay and the reference site using a shotgun with steel shot in late February and early March 1993, prior to the nuptial molt and spring migration. Ten oystercatcher adults and twenty Willet adults were collected in mid-July from each site after the young had fledged. Birds were immediately tagged, placed in plastic bags, and kept on ice until dissection the following day. Livers were removed using Quality Assurance/Quality Control (QA/QC) procedures to prevent cross-contamination, placed in labeled sample jars, and frozen (-20°C) in a commercial freezer until they were sent to a PACF-approved laboratory.

T-tests were used to analyze for significant differences in mercury levels between sediments, prey items, oystercatcher eggs and adult shorebird livers from Lavaca Bay and the reference site.

RESULTS AND DISCUSSION

Sediments

Six of ten sediment samples collected from Lavaca Bay were above the detection limit for mercury (0.1 ppm dry weight (dw)); the maximum level was 1.18 ppm (Appendix). The mean dw mercury concentration in Lavaca Bay sediments was 0.26 ppm, whereas all reference site samples were below the detection limit (BDL) (Table 1). Sediment samples with the highest mercury concentrations were collected in the barge docking area adjacent to ALCOA (1.18 ppm dw), the mudflat near the Central Power and Light Company plant on Cox Bay (0.41 ppm dw), Lavaca 1 mudflats (0.33 ppm dw), and the mudflat at Point Comfort Turning Basin (0.25 ppm dw) (Figure 2). These results concur with those of Reigel (1990) who reported that mercury-contaminated sediments remain widespread throughout Lavaca Bay, concentrating around the ALCOA site. Decreasing mercury levels occurred with increasing distance from the plant, ranging from 0.101 to 1.86 ppm dw (Reigel 1990).

Table 1. Arithmetic means and ranges (in parentheses) of mercury in sediments and composite shorebird prey items (ppm dry weight) from Lavaca Bay, Texas and a reference site, 1993.

SAMPLE ITEM	LAVACA BAY	REFERENCE SITE
SEDIMENT (n=l 0)'	0.26 (0.05[1]-1.18) 6[2]	BDL[3]
MUSSEL (n=1)	0.27	BDL
OYSTER (n=l)	0.26	BDL
POLYCHAETE (n=3)	0.20 (0.15-0.26) 3	BDL
XANTHID CRAB (n=1)	0.18	BDL
FIDDLER CRAB (n=1)	0.83	BDL

[1] Assigned value of ½ detection limit (0.1 ppm dry weight).
[2] Number of samples above detection limit.
[3] All values below detection limit.
[4] n=number of samples taken from each bay

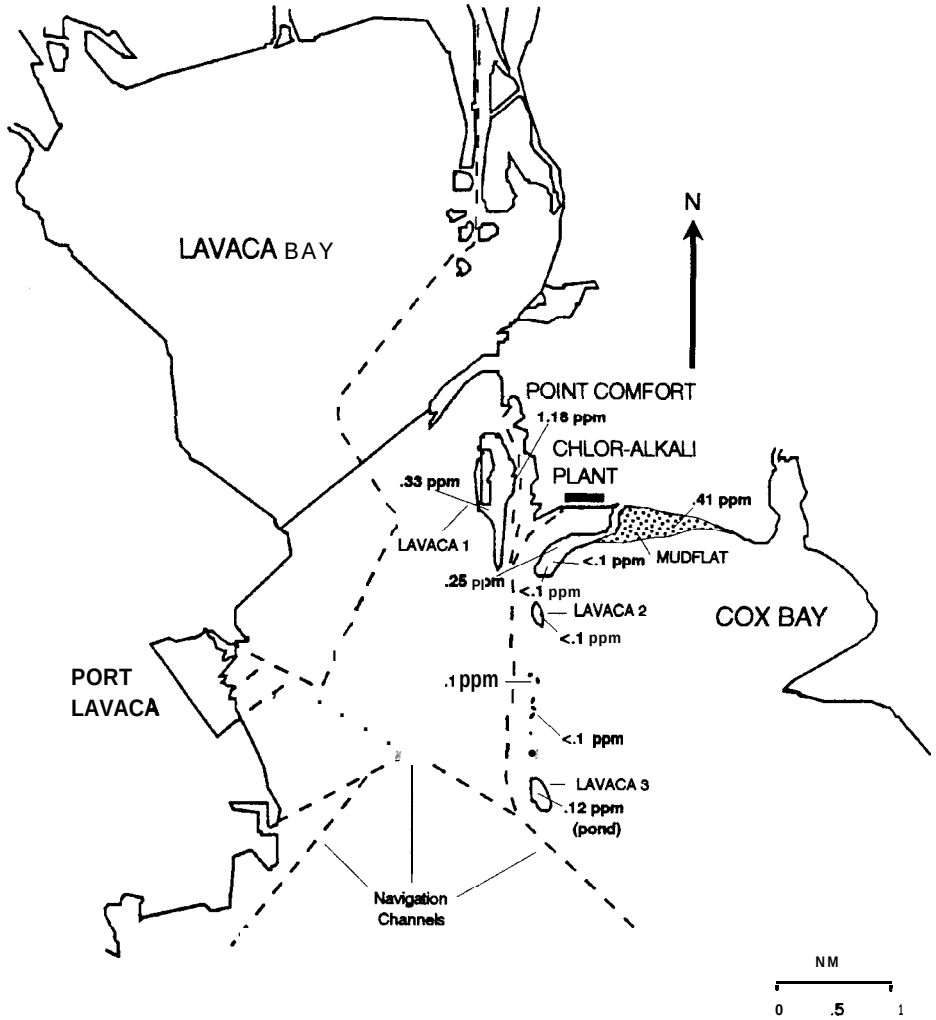

Figure 2. Map of Lavaca Bay showing concentration of mercury (ppm) in sediments.

Surface sediments maintain high mercury levels because mercury is strongly bound to fine-grained sediments that are easily resuspended. Current ongoing dredging activities in Lavaca Bay resuspend fine sediments, some of which are deposited on mudflats utilized by shorebirds for feeding. One species of particular concern which feeds on these mudflats is the Snowy Plover (*Charadrius alexandrinus*), a candidate for the endangered species list.

Prey Items

All shorebird prey items from Lavaca Bay were above the lower limit of detection for mercury whereas all reference site prey items were below the detection limit (Table 1). The mean total mercury whole body concentration was 0.27 ppm in mussels, 0.26 ppm in oysters, 0.20 ppm in polychaetes, and 0.18 ppm in xanthid crabs from Lavaca Bay. By comparison, Lavaca Bay oysters collected by Reigel (1990) in 1989 ranged from 0.2 to 3.2 ppm dw and mussels ranged from 0.8 to 2.1 ppm dw. Fiddler crabs from Lavaca Bay had the highest whole body mercury concentration of all the prey items collected for this study (0.83 ppm dw).

Marine invertebrates are known to uptake and accumulate concentrations of trace metals from the surrounding environment orders of magnitude higher than ambient environment levels. The literature reports that sedentary, suspension-feeding invertebrates with large permeable areas may uptake trace metals at rates that cannot be matched by excretion rates (Rainbow et al. 1990). In this study, fiddler crabs, which ingest sediments, had the highest level of mercury as opposed to filter feeding invertebrates, such as mussels and oysters. Reigel (1990) analyzed the carapace of blue crabs and suggested that the relatively low concentrations in the carapace may indicate that crabs do not depurate mercury through molting. This inability to depurate mercury could also explain why fiddler crab mercury residues were the highest of all the taxonomic groups of prey items. The combined mean of mercury in all prey items from Lavaca Bay was two times greater than that of the sediments, indicating that bioaccumulation of mercury is occurring at lower trophic levels (Figure 3).

Oystercatcher eggs

The mean concentration of mercury detected in Lavaca Bay American Oystercatcher eggs was 1.44 ppm dw, almost four times higher than the mean of 0.4 ppm dw detected in reference site eggs (Table 2 and Figure 4). Comparative data is unavailable on mercury residues in American Oystercatcher eggs collected from other locations. However, data have been collected for mercury in the eggs of several other species of shorebirds and wading birds from Texas. King et al. (1991) reported a mean mercury concentration of 0.40 ppm wet weight (ww) in Forster's Tern (*Sterna forsteri*) eggs and 0.46 ppm ww in Black Skimmer (*Rynchops niger*) eggs collected from Lavaca Bay in 1984. These means are slightly higher than that of the Lavaca

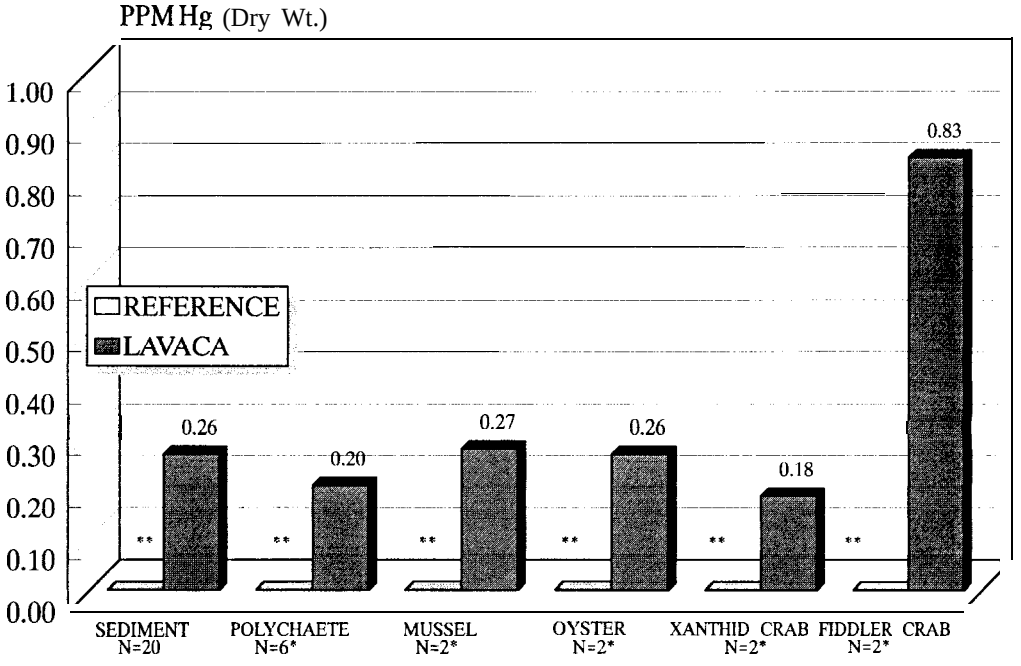

Figure 3. Mean mercury levels in Lavaca Bay shorebird prey items and sediments.

* EACH SAMPLE IS A COMPOSITE OF SEVERAL INDIVIDUALS
** SAMPLES WERE BELOW DETECTION LIMIT FOR MERCURY (0.1 PPM DRY WEIGHT)

Table 2. Mean mercury levels, range, standard deviation and total number of samples of American Oystercatcher eggs) and adult shorebird livers (American Oystercatcher, Willet, and Long-billed Dowitcher) from Lavaca Bay and the reference site. Mercury expressed as ppm mercury dry weight.

SAMPLE ITEM	LAVACA BAY	REFERENCE SITE	PROBABILITY (*P*)
OY STERCATCHER EGG	1.44 (1.00-2.57) 0.50 N=10	0.40 (0.21-0.70) 0.15 N=10	<0.0001
OYSTERCATCHER ADULT	5.13 (3.21-9.12) 1.77 N=10	1.34 (0.68-2.21) 0.41 N=10	<0.0001
WILLET ADULT	44.84 (5.29-161.12) 37.71 N=20	4.53 (2.12-7.74) 1.69 N=20	<0.0001
DOWITCHER ADULT	2.46 (0.62-4.93) 1.23 N=20	0.91 (0.49-1.45) 0.21 N=20	<0.0001

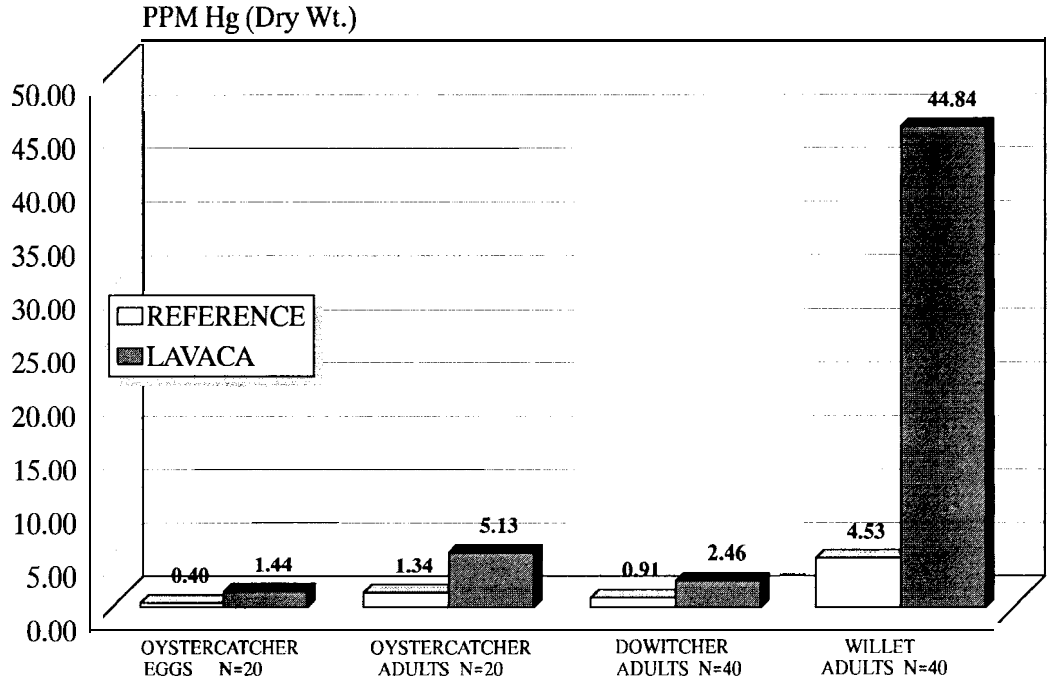

Figure 4. Mean mercury levels in Lavaca Bay shorebirds.

Bay American Oystercatcher eggs (0.34 ppm ww). Even so, the Lavaca Bay oystercatcher eggs had a higher mean mercury concentration than eggs from the two reference sites used by King et al. (1991), San Antonio Bay (0.22 ppm ww in Forster's Tern eggs) and Laguna Vista (0.19 ppm ww in Black Skimmer eggs).

In another study by King et al. (1983) Royal Tern (*Sterna maxima) eggs* were collected from Matagorda Bay and Corpus Christi Bay in 1978, and mean mercury levels of 1.27 ppm ww and 1.11 ppm ww, respectively, were reported. However, Matagorda Bay, which was used as the reference in that study, is included in mapped areas of mercury contamination originating from Lavaca Bay (Holmes 1977), and the Corpus Christi Bay site was also known to be contaminated.

Gamble et al. (1994) reported in Phase I of this project that the eggs of seven out of nine species of colonial nesting birds collected from Lavaca Bay in 1991 had higher mean mercury concentrations than eggs collected from reference sites. An examination of hatching success by Gamble et al. (1994) yielded inconclusive results, but it appears that colonial nesting birds, as well as other marine birds in the Lavaca Bay area, are laying eggs which contain more mercury than eggs of the same species from non-contaminated sites.

The implications of these data (i.e., mercury in the eggs of American Oystercatchers collected for this study) are not clear because little is known of the effects to the reproductive success of shorebirds caused by chronic exposure to environmental mercury contamination. Previous investigators have been unable to establish a clear cause-and-effect relationship between concentrations of mercury in the eggs of colonial nesting birds and reduced hatching success (Connors et al. 1975, King et al. 1983, King et al. 1991, and Gamble et al. 1994). Nonetheless, mercury has been shown to cause increased early mortality and behavioral problems in Mallard chicks (Heinz 1979) and the bioaccumulation of any mercury above background level may be considered potentially hazardous (Eisler 1987).

Shorebirds

Mean mercury concentrations in livers of all species of shorebird adults from Lavaca Bay were significantly higher than in reference site birds ($P < 0.0001$, Table 2). Results are summarized in Table 3. The average dry weights of mercury in the livers of Lavaca Bay shorebirds collected for this study were 5.13 ppm (1.44 ppm ww) for oystercatchers, 44.84 ppm (12.88 ppm ww) for Willets, and 2.46 ppm (0.801 ppm ww) for Long-billed Dowitchers; reference site oystercatchers, Willets, and dowitchers had residues of 1.34 ppm (0.36 ppm ww), 4.53 ppm (1.00 ppm ww), and 0.91 ppm (0.32 ppm ww), respectively. Lavaca Bay resident species, American Oystercatchers and Willets, had mean liver mercury concentrations four and ten times higher, respectively, than reference site birds. Lavaca Bay Long-billed Dowitchers, the migratory species, had a mean mercury concentration two and one-half times higher than reference birds (Figure 4).

No data is available from other studies regarding mercury in the tissues of American Oystercatchers; however, several area studies have determined concentrations of mercury in other shorebird livers, reporting results in both dry and wet weights. Mean mercury residues in the livers of wintering shorebirds collected in 1976-77 from contaminated areas near Corpus Christi, Texas ranged from 0.21 ppm ww in Lesser Yellowlegs to 0.83 ppm in Greater Yellowlegs (White et al. 1980) (Table 3). In a study by Custer and Mitchell (1991), Willets collected from three lower Laguna Madre locations and one upper Texas coastal location had mean mercury liver residues ranging from 2.0 to 3.8 ppm dw. By comparison, the mean dry weight in Lavaca Bay Willets collected for this study was 44.8 ppm dw. Mercury levels were also higher in Lavaca Bay Willets than in fish-eating birds from Galveston Bay (King and Cromartie 1986) and in Redhead ducks from Redfish and Baffin Bays (Gamble and Woodin 1993).

Lavaca Bay Willets had a mean concentration of mercury higher than that of any other bird studied on the Texas coast (Table 4), although concentrations in the livers of individual, migratory, Double-crested Cormorants from Lavaca Bay ranged up to 221

Table 3. Mercury levels in livers of adult shorebirds (American Oystercatcher, Willet, and Long-billed Dowitcher), and shorebird eggs (American Oystercatcher) from Lavaca Bay, Texas. Mercury expressed as ppm Hg dry weight.

Oystercatcher Adult REFERENCE N=10	Oystercatcher Adult LAVACA N=10	Willet Adult REFERENCE N=20	Willet Adult LAVACA N=20	Oystercatcher Egg REFERENCE N=10	Oystercatcher Egg LAVACA N=10	Dowitcher Adult REFERENCE N=20	Dowitcher Adult LAVACA N=20
0.99	3.79	6.87	27.04	0.46	1.18	0.49	1.13
1.14	4.44	6.37	9.28	0.40	1.00	0.99	1.26
2.21	3.74	3.11	27.3 1	0.58	1.87	1.16	3.26
1.50	9.12	7.53	50.55	0.37	1.38	0.78	4.43
1.20	4.19	4.12	38.36	0.23	2.57	0.92	1.75
0.68	7.44	4.53	127.07	0.43	1.01	1.21	1.49
1.07	3.21	3.87	26.27	0.23	1.08	0.91	1.21
1.38	5.18	2.78	57.35	0.21	1.91	0.98	1.66
1.47	5.94	3.64	43.23	0.37	1.41	0.66	4.04
1.75	4.24	3.44	18.80	0.70	1.00	0.95	0.62
		7.74	161.12			0.70	2.54
		2.79	23.37			1.06	1.65
		5.66	78.12			1.04	2.91
		3.64	20.54			0.86	4.00
		2.12	43.07			1.45	1.33
		3.35	54.14			0.69	1.80
		7.19	5.29			0.90	2.25
		3.34	26.73			0.92	3.71
		3.90	43.79			0.90	4.93
		4.56	15.43			0.71	3.18
MEAN 1.34	MEAN 5.13	MEAN 4.53	MEAN 44.84	MEAN 0.40	MEAN 1.44	MEAN 0.91	MEAN 2.46
MIN 0.68	MIN 3.21	MIN 2.12	MIN 5.29	MIN 0.21	MIN 1.00	MIN 0.49	MIN 0.62
MAX 2.21	MAX 9.12	MAX 7.74	MAX 161.12	MAX 0.70	MAX 2.57	MAX 1.45	MAX 4.93
STD 0.41	STD 1.77	STD 1.69	STD 37.71	STD 0.15	STD 0.50	STD 0.21	STD 1.23
t-test	*P*<0.0001	*t*-test	*P*<0.0001	*t*-test	*P*<0.0001	*t*-test	*P*<0.0001

Table 4. Mean mercury residues in the livers of avian species collected from the Texas coast from 1976 to 1992.

Species	Collection Date	N	Location	Mean Mercury Concentration (ppm)	Source
Avocet	1976-77	4	Oso Bay	0.22 ww	White *et al.*, 1980
Dunlin	1976-77	10	Nueces Bay	0.47 ww	White *et al.*, 1980
Greater Yellowlegs	1976-77	2	Nueces Bay	0.83 ww	White *et al.*, 1980
Least Sandpiper	1976-77	16	Nueces Bay	0.50 ww	White *et al.*, 1980
Lesser Yellowlegs	1976-77	13	Nueces Bay	0.21 ww	White *et al.*, 1980
Sanderling	1976-77	15	Oso Bay	0.67 ww	White *et al.*, 1980
Western Sandpiper	1976-77	15	Nueces Bay	0.43 ww	White *et al.*, 1980
Willet	1986	18	Laguna Atascosa	2.0 dw	Custer and Mitchell, 1991
Willet	1986	20	Port Mansfield	3.4 dw	Custer and Mitchell, 1991
Willet	1986	7	South Padre Island	2.8 dw	Custer and Mitchell, 1991
Willet	1986	10	Bastrop Bayou	2.4 dw	Custer and Mitchell, 1991
Redhead Duck	1988-89	10	Baffin Bay	0.24 dw	Gamble and Woodin, 1993
Redhead Duck	1988-89	9	Redfish Bay	0.07 dw	Gamble and Woodin, 1993
Olivaceous Cormorant	1981	10	Galveston Bay	1.60 ww	King and Cromatie, 1986
Laughing Gull	1981	10	Galveston Bay	0.75 ww	King and Cromartie, 1986
Black Skimmer	1981	10	Galveston Bay	1.42 ww	King and Cromartie, 1986
Double-crested Cormorants	1991-92	19	Lavaca Bay (early)	10.39 ww	Gamble *et al.*, 1994
Double-crested Cormorants	1991-92	19	Lavaca Bay (late)	7.87 ww	Gamble *et al.*, 1994

ppm ww in Phase I (Gamble et al. 1994) of this project. Questions still remain concerning the wintering site fidelity of cormorants on the Texas coast but Gamble et al. (1994) believed the source of mercury contamination was not accumulated from the nesting areas. Since cormorants are a relatively long-lived bird, accumulation of mercury in cormorant livers may occur over time, with age causing the variability found in individual mercury residues. Due to a suspected variablity in the ages of the birds sampled and their respective mercury residues, no significant differences were found in liver concentrations between cormorants collected early and at the end of the wintering season. Therefore, it was not possible to document an increase in mercury uptake during the overwintering period (Gamble et al. 1994). Willets, however, because of their territorial nature, remain in one location throughout the year; results of this study indicate that the resident population of Lavaca Bay Willets are constantly being exposed to mercury through consumption of their prey items and incidental ingestion of sediment. Likewise, oystercatchers, the other resident species in this study, had mercury liver concentrations higher than dowitchers which only wintered in the area.

Dose-controlled studies demonstrate acute mercury toxicosis occurring when liver concentrations approached 20 ppm in Red-tailed Hawks (Fimreite and Karstad 1971), but reproductive impairment has been documented in Mallard ducks with liver concentrations of 1 ppm ww (Heinz 1976). In Lavaca Bay, 100% of the Willets collected had liver concentrations of mercury greater than 1 ppm, and 15% exceeded 20 ppm. Low-level long-term exposure may allow birds to build up a tolerance to mercury without suffering acute or obvious effects, but chronic, sublethal reproductive and behavioral effects may be occurring instead. Since mercury is known to adversely affect reproduction, Willets may be experiencing problems with nesting success or hatchability, that, due to the secretive nature of their nesting habits and precociousness of their young, are undetectable by conventional methods of determining nesting success.

CONCLUSIONS AND RECOMMENDATIONS

Mercury can adversely affect reproduction, growth, behavior, metabolism, blood chemistry, histology, and other body functions in both birds and marine organisms (Eisler 1987). Residues of 0.5 to 1.5 ppm mercury in ring-necked pheasant (*Phasianus colchicus*) eggs caused reproductive failure (Fimreite 1971) and Heinz (1979) reported reproductive success lower in second and third generation Mallards (*Anas platyrhynchos*) with mean liver mercury concentrations of up to 1.49 ppm ww. Mercury has a high potential for bioaccumulation, which tends to be rapid in aquatic organisms, a strong tendency to biomagnify in food chains, and is slow to depurate (Eisler 1987). In this study, the mean mercury levels in sediments, prey, and

shorebirds were considerably higher in Lavaca Bay than at the reference site at each trophic level, indicating the pathway for bioaccumulation and biomagnification potentially detrimental to all Lavaca Bay avian species with similar food habits (Figure 5).

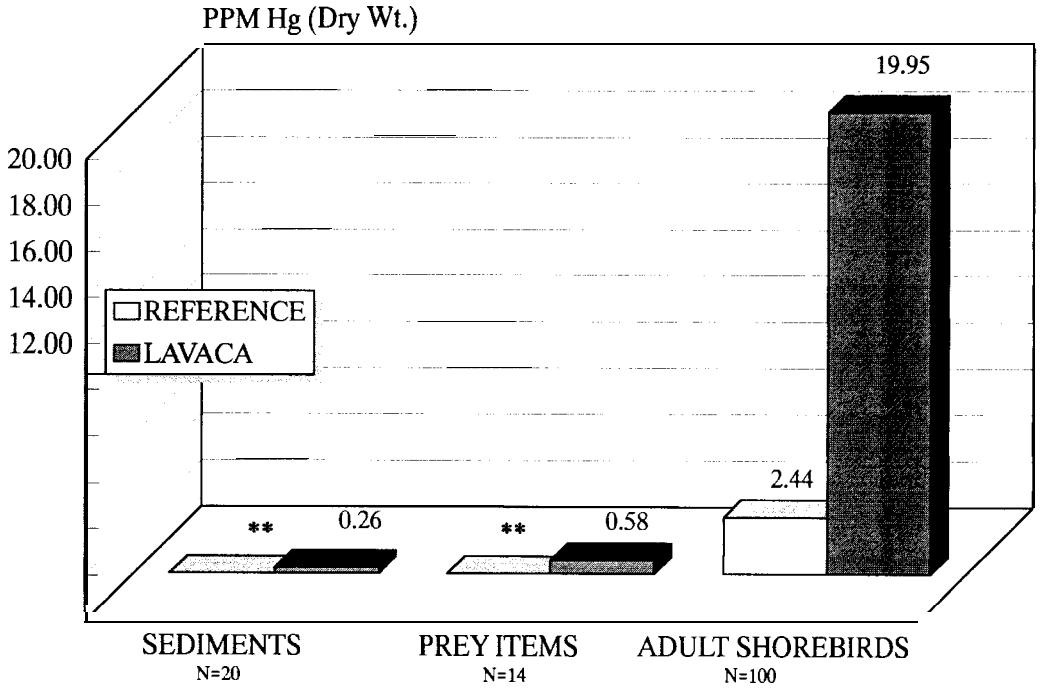

Figure 5. Mean mercury levels in sediments, prey items and shorebirds from Lavaca Bay, Texas and a reference site. Mercury expressed as PPM Hg - dry weight.

** All samples were Below Detection Limit, 0.1 ppm dry weight.

Based upon the results of previous studies (Evans and Engel 1994, Gamble et al. 1994) and a review of available literature, mercury has in the past and continues to be accumulated in sediments, prey, eggs, hatchlings, and adult shorebirds of Lavaca Bay. Results of this study indicate that mercury has accumulated in sufficient quantity to seriously impact the trust natural resources and the supporting ecosystems that are protected under the authority of the Secretary of the Interior, as described in the National Contingency Plan (Plan) (Federal Register 1994). By definition, as stated in the Plan, injury to sediments, water quality, and the prey organisms that constitute the supporting ecosystems for migratory birds, anadromous fishes, endangered species, certain marine mammals, and U. S. Fish and Wildlife Service lands requires the Secretary to assess the injury and to seek restoration and compensation for the trust resource injured, including their supporting ecosystems. In our view, there is sufficient evidence based on the results of this and other recent studies to indicate injury has occurred to the shorebirds, and their supporting ecosystems, in Lavaca Bay.

It is our recommendation that the biological effects of the mercury at concentrations detected in Lavaca Bay prey, eggs, and adults of shorebirds be evaluated through controlled dose-response wet lab and pen studies using histopathology, biomarker, and chemical analysis to quantify the potential injury to those and similar species of birds and their prey. Because Willets showed high accumulation rates of mercury, as did one of their chief prey, fiddler crabs, a closer examination of these species is critical.

LITERATURE CITED

Connors, P.G., V.C. Anderlini, R.W. Risebrough, M. Gilbertson, and H. Hays. 1975. Investigations of heavy metals in Common Tern populations. Can. Field Nat. 89: 157-162.

Custer, T.W. and C.A. Mitchell. 1991. Contaminant exposure of Willets feeding in agricultural drainages of the Lower Rio Grande Valley of south Texas. Environ. Monit. and Assess. 16: 189-200.

Eisler, R. 1987. Mercury hazards to fish, wildlife and invertebrates: a synoptic review. U.S. Fish Wildl. Ser. Biol. Rep. 85(1.10). 90 pp.

Evans, D.W. and D.W. Engel. 1994. Mercury bioaccumulation in finfish and shellfish from Lavaca Bay, Texas: descriptive models and annotated bibliography. NOAA Tech. Mem. NMFS-SEFSC-348. 89 pp.

Federal Register. 1994. The National Oil and Hazardous Substances Pollution Contingency Plan. 40 CFR Part 9-300, Vol. 59, No. 178:47384-47495.

Fimreite, N. 1971. Effects of dietary methylmercury on Ring-necked Pheasants. Occas. Pap. Can. Wildl. Serv. 9:1-37.

Fimreite, N and L. Karstad. 1971. Effects of dietary methyl mercury on Red-tailed Hawks. J. Wildl. Manage. 35:293-300.

Hatch, W.R. and W.L. Ott. 1968. Determination of submicrogram quantities of mercury by atomic absorption spectrophotometry. Annu. Chem. 40:2085-2087.

Heinz, G.H. 1976. Methylmercury: second-generation reproductive and behavioral effects on Mallard ducks. J. Wildl. Manage. 40:710-715.

Heinz, G.H. 1979. Methylmercury: reproductive and behavioral effects on three generations of Mallard ducks. J. Wildl. Manage. 43:394-401.

Holmes, C.W. 1977. Effects of dredged channels on trace-metal migration in an estuary. J. Research U.S.G.S. 5:243-251.

Gamble, L.R. and M.C. Woodin. 1993. Contaminants in Redhead Ducks wintering in Baffin Bay and Redfish Bay, Texas. U.S. Fish and Wildl. Serv., Ecological Services, Corpus Christi, TX. Unpublished document.

Gamble, L.R., C.R. Chandler, D.W. Potter, M.C. Lee, and L.L. Price-May. 1994. Preliminary investigation of mercury contamination in fish-eating waterbirds of Lavaca Bay, Texas: Phase I report. U.S. Fish and Wildl. Serv., Ecological Services, Corpus Christi, TX. Unpublished document.

King, K.A. and E. Cromartie. 1986. Mercury, cadmium, lead, and selenium in three waterbird species nesting in Galveston Bay, Texas, USA. Colonial Waterbirds. 9:90-94.

King, K.A., T.W. Custer, and J.S. Quinn. 1991. Effects of mercury, selenium, and organochlorine contaminants on reproduction of Forster's Terns and Black Skimmers nesting in a contaminated Texas Bay. Arch. Environ. Contam. Toxicol. 20:32-40.

King, K.A., C.A. Lefever, and B.M. Mulhern. 1983. Organochlorine and metal residues in Royal Terns nesting on the central Texas coast. J. Field Ornithol. 54:295-303.

Moore, J. 1990. Patuxent Analytical Control Facility Reference Manual: June 1990. U.S. Fish and Wildlife Service. Laurel, MD (Unpub. Rept.).

Oberholser, H.C. 1974. The bird life of Texas, Vol. I. Univ. Texas Press, Austin 530 pp.

Rainbow, P.S., D.J. Phillips, and M.H. Depledge. 1990. The significance of trace metal concentrations in marine invertebrates. Mar. Poll. Bull. 21:321-324.

Reigel, D.V. 1990. The distribution and behavior of mercury in sediments and marine organisms of Lavaca Bay, Texas. M.S. Thesis. Texas A&M Univ. College Station, TX. 113 pp.

White, D.H., K.A. King, R.M. Prouty. 1980. Significance of organochlorine and heavy metal residues in wintering shorebirds at Corpus Christi, Texas, 1976-1977. Pest. Mon. J. 14:58-63.

APPENDIX

LABORATORY REPORTS OF MERCURY ANALYSIS OF SEDIMENTS, SHOREBIRD PREY ITEMS, EGGS, AND ADULT SHOREBIRD LIVERS FROM LAVACA BAY AND REFERENCE SITE, 1993

Key to sample identication numbers:

93AA01BB

93 = Year of collection

AA = Sample type
- FC = Fiddler Crab
- MU = Mussel
- OY = Oyster
- PC = Polychaete
- XC = Xanthid Crab
- SD = Sediment
- DW = Dowitchers
- OE = Oystercatcher Egg
- OA = Oystercatcher Adult
- WA = Willet Adult

01 = Sample number

BB = Sample Location
- LB = Lavaca Bay
- AB = Aransas Bay

WEIGHT, % MOISTURE, % LIPID, TOTAL SUSPENDED SOLIDS

Sample Number	Sample Matrix	Sample Weight (g)	Percent Moisture	Percent Lipid	Total Suspended solids (%)
93FC01AB	Invertebrate		60.33		
93FC01LB	Invertebrete		66.25		
93MU01AB	Invertebrate		80.85		
93MU01LB	Invertebrate		78.45		
93OY01AB	Invertebrate		78.77		
930Y01LB	Invertebrate		82.56		
93PC01AB	Invertebrate		83.57		
93PC01LB	Invertebrate		86.57		
93PC02AB	Invertebrate		77.35		
93PC02LB	Invertebrate		74.76		
93PC03AB	Invertebrate		80.44		
93PC03LB	Invertebrate		77.78		
93XC01AB	Invertebrate		64.13		
93XCD1LB	Invertebrate		59.09		
93SD01AB	Sediments		33.61		
93SD01LB	Sediments		27.41		
93SD02AB	Sediments		21.62		
93SD02LB	Sediments		20.62		
93SD03AB	Sediments		28.63		
93SD03LB	Sediments		35.98		
93SD04AB	Sediments		30.14		
93SD04LB	Sediments		41.48		
93SD05AB	Sediments		28.21		
93SD05LB	Sediments		46.5		
93SD06AB	Sediments		30.23		
93SD06LB	Sediments		32.69		
93SD07AB	sediments		37.01		
93SD07LB	Sediments		29.7		
93SD08AB	Sediments		23.81		
93SD08LB	Sediments		46.18		
93SD09AB	Sediments		20.88		
93SD09LB	Sediments		27.49		
93SD10AB	Sediments		35.21		
93SD10LB	Sediments		48.18		

PROCEDURAL BLANKS

Analyte	Lab Sample Number	Result Total UC
Hg	BLANK A	< .1
	BLANK B	< .1
	BLANK C	< .1
	BLANK F	< .1
	BLANK H	< .1

REFERENCE MATERIALS

Analyte	Lab Sample Number	S.R.H. ID	S.R.M. Name	* Certified Reference Value (ppm / %)	95% Confidence Interval	Result (ppm / %)	Percent Recovery
Hg	ORCHLV-D	NIST 1571	Orchard Leaves	.155 Dry	.015	.15 Dry	96.77
	DOLT-2-G	NRCC DOLT-2	Dogfish Liver	1.99 Drv	.1	1.89 Drv	94.97
	DORM-C	NRCC DORM-I	Dogfish Muscle	.798 Dry	.074	.71 Dry	88.97
	MESS-2-D	NRCC MESS-2	Sediment	.092 Dry	.009	< .1 Dry	108.7
	MESS-2-E	NRCC MESS-2	Sediment	.092 Dry	.009	< .1 Dry	108.7
	MESS-2-G	NRCC MESS-2	Sediment	.092 Dry	.009	< .1 Dry	108.7

* Only certified analytes list a confidence interval - all others are considered reference values.

ANALYTICAL METHODS

Method Code	Method Description
002	LABORATORY: Geochemical & Environmental Research Group, Texas A&M

Tissue, Sediment and Uater Mercury

II. Mercury was determined by EPA method 245.5 with minor revisions. Sediment samples can be analyzed either freeze dried or on a uet basis. Sediment samples are homogenized by mixing before subsampling. The tissue samples uere homogenized in the original sample containers uith a Tekar Tissuniter and subsampled. Uater samples are acidified (0.5% v/v with high purity nitric acid, HNO3) in the original sample bottle. For sediments a 0.5 to 1.0 gram sample (dry ueight) was used. For tissues a 1.5 to 2.0 gram sample (wet ueight) was used. For uater the sample size is 20 ml.

For tissue and sediment, the sample is ueighed into a 50 ml polypropylene centrifuge tube. 2.5 ml of concentrated sulfuric acid (H2SO4) and 1.5 ml of concentrated nitric acid (HNO3) were added and the samples heated in a uater bath at 90 C for 15 min. After cooling 10 ml of distilled water and 15 ml of mixture of 3.3% (w/w) potassium permsnganate (KMnO4), and 1.7% (u/u) potassium persulfate (K2S208) uere added to each tube and the samples heated in a water bath at 90 C for 30 min. After cooling 5 ml of 10% (w/w) hydroxylamine hydrochloride (NH2OH HC1) was added to reduce excess permanganate and the volune brought to 35 ml uith distilled uater.

For uater samples, the sample is ueighed into a 50 ml polypropylene centrifuge tube, 1 ml of concentrated H2SO4 is added and the solution mixed vigorously with a vortex stirrer. Then 4.5 ml of the KMnOr/K2S208 is added and the resulting mixture heated in a 90 C uater bath for 2 hours. After cooling, 1.5 ml of a 10% (w/w) hydroxylamine hydrochloride (NH2OH HC1) solution is added, sample volume adjusted to a constant volume uith distilled uater and the resulting solution mixed vigorously.

CONTAMINANT CONCENTRATIONS

Analyte	Sample Number	Sample Matrix	Result (ppm Dry Wt.)	Detection Limit (ppm Dry Wt.)	Result (ppm Uet Wt.)	Detection Limit (ppm Uet Wt.)
Hg	93DUOlAB	Liver	.494	.06	.154918	.018816
	93DW01LB	Liver	1.132	.06	.375258	.01989
	93DW02AB	Liver	.994	.06	.309134	.01866
	93DW02LB	Liver	1.264	.06	.386658	.018354
	93DW03AB	Liver	1.163	.06	.382743	.019746
	93DW03LB	Liver	3.255	.06	1.02858	.01896
	93DW04AB	Liver	.781	.06	.274209	.021066
	93DW04LB	Liver	4.432	.06	1.325611	.017946
	93DW05AB	Liver	.918	.06	.301747	.019722
	93DW05LB	Liver	1.754	.06	.581977	.019908

PROCEDURAL BLANKS

Analyte	Lab Sample Number	Result Total UG
% Moisture	BLANK-A	
	BLANK-B	
	BLANK-C	
	BLANK-D	
	BLANK-E	
	BLANK-F	
	BLANK-G	
	BLANK-H	
Hg	BLANK-A	< .06
	BLANK-B	< .06
	BLANK-C	< .06
	BLANK-D	< .06
	BLANK-E	< .06
	BLANK-F	< .06
	BLANK-G	< .06
	BLANK-H	< .06

REFERENCE MATERIALS

Analyte	Lab Sample Number	S.R.M. ID	S.R.M. Name	• Certified Reference Value (ppm / %)	95% Confidence Interval	Result (ppm / %)	Percent Recovery
Hg	NBSOYS-A	NIST 1566a	Oyster Tissue	.0642 Dry	.0067	< .06 Dry	93.46
	NBSOYS-0	NIST 1566a	Oyster Tissue	.0642 Dry	.0067	.069 Drv	107.48
	NBSOYS-P	NIST 1566a	Oyster Tissue	.0642 Dry	.0067	.061 Dry	95.02
	NBSOYS-Q	NIST 1566a	Oyster Tissue	.0642 Dry	.0067	.061 Dry	95.02
	NBSOYS-R	NIST 1566a	Oyster Tissue	.0642 Dry	.0067	.068 Dry	105.92
	NBSOYS-X	NIST 1566a	Oyster Tissue	.0642 Dry	.0067	.064 Dry	99.69
	NBSOYS-Y	NIST 1566a	Oyster Tissue	.0642 Dry	.0067	.068 Dry	105.92
	DOLT2-C	NRCC DOLT-2	Dogfish Liver	1.99 Drv	.1	2.015 Dry	101.26
	DOLT2-F	NRCC DOLT-2	Dogfish Liver	1.99 Dry	.1	2.098 Dry	105.43
	DOLT2-I	NRCC DOLT-2	Dogfish Liver	1.99 Dry	.1	2 Dry	100.5
	DORM-B	NRCC DORM-l	Dogfish Muscle	.798 Dry	.074	.798 Dry	100
	DORM-D	NRCC DORM-l	Dogfish Muscle	.798 Dry	.074	.746 Dry	93.48
	DORM-E	NRCC DORM-I	Dogfish Muscle	.798 Dry	.074	.703 Dry	88.1
	DORM-G	NRCC DORM-l	Dogfish Muscle	.798 Dry	.074	.723 Dry	90.6
	DORM-H	NRCC DORM-l	Dogfish Muscle	.798 Dry	.074	.574 Dry	71.93

• Only certified analytes list a confidence interval - all others are considered reference values.

ANALYTICAL METHODS

Method Code	Method Description
002	LABORATORY: Geochemical & Environmental Research Group, Texas A&M

Tissue, Sediment and Water Mercury

II. Mercury was determined by EPA method 245.5 with minor revisions. Sediment samples can be analyzed either freeze dried or on a wet basis. Sediment samples are homogenized by mixing before subsampling. The tissue samples were homogenized in the original sample containers with a Tekar Tissumizer and subsampled. Uater samples are acidified (0.5% v/v with high purity nitric acid, HNO3) in the original sample bottle. For sediments a 0.5 to 1.0 gram sample (dry weight) was used. For tissues a 1.5 to 2.0 gram sample (wet weight) was used. For water the sample size is 20 ml.

For tissue and sediment, the sample is neighed into a 50 ml polypropylene centrifuge tube. 2.5 ml of concentrated sulfuric acid (H2S04) and 1.5 ml of concentrated nitric acid (HN03) were added and the samples heated in a water bath at 90 C for 15 min. After cooling 10 ml of distilled water and 15 ml of mixture of 3.3% (w/w) potassiun permanganate (KMn04), and 1.7% (w/w) potassiun persulfate (K2S208) were added to each tube and the samples heated in a water bath at 90 C for 30 min. After cooling 5 ml of 10% (w/w) hydroxylamine hydrochloride (NH2OH HC1) was added to reduce excess permanganate and the voluna brought to 35 ml with distilled water.

For water samples, the sample is weighed into a 50 ml polypropylene centrifuge tube, 1 ml of concentrated H2S04 is added and the solution mixed vigorously with a vortex stirrer. Then 4.5 ml of the KMnOr/K2S208 is added and the resulting mixture heated in a 90 C water bath for 2 hours. After cooling, 1.5 ml of a 10% (w/w) hydroxylamine hydrochloride (NH2OH HC1) solution is added, sample volume adjusted to a constant volume with distilled water and the resulting solution mixed vigorously.

ANALYTICAL METHODS (Cont.)

Method Code	Method Description
003	(wt. wet sample and beaker) - (wt. beaker)

Catalog: 2050039 Lab Name: GERG **23-Feb-94** Purchase Order: 85830-3-3433 Page: 1

WEIGHT, % MOISTURE, % LIPID, TOTAL SUSPENDED SOLIDS

Sample Number	Sample Matrix	Sample Ueight (g)	Percent Moisture	Percent Lipid	Total Suspended solids (%)
930E01AB	Avian Egg		76.49		
930E01 LB	Avian Egg		75.52		
930E02AB	Avian Egg		77.18		
930E02LB	Avian Egg		76.38		
930E03AB	Avian Egg		76.72		
930E03LB	Avian Egg		76.43		
930E04AB	Avian Egg		79.38		
930E04LB	Avian Egg		75.74		
930E05AB	Avian Egg		76.15		
930E05LB	Avian Egg		76.12		
930E06AB	Avian Egg		75.39		
930E06LB	Avian Egg		76.21		
930E07AB	Avian Egg		75.55		
930E07LB	Avian Egg		74.61		
930E08AB	Avian Egg		76.57		
930E08LB	Avian Egg		76.67		
930E09AB	Avian Egg		77.23		
930E09LB	Avian Egg		77.03		
930E10AB	Avian Egg		76.67		
930E10LB	Avian Egg		75.53		
930A01AB	Liver		71.3		
930A01 LB	Liver		73.33		
930A02AB	Liver		73.41		
930A02LB	Liver		72.24		
930A03AB	Liver		75.57		
930A03LB	Liver		71.49		
930A04AB	Liver		70.57		
930A04LB	Liver		71.06		
930A05AB	Liver		73.88		
930A05LB	L i v e r		72.55		
930A06AB	Liver		73.97		
930A06LB	Liver		72.84		
930A07AB	Liver		70.18		
930A07LB	Liver		71.9		

WEIGHT, % MOISTURE, % LIPID, TOTAL SUSPENDED SOLIDS (Cont.)

Sample Number	Sample Matrix	Sample Weight (g)	Percent Moisture	Percent Lipid	Total Suspended Solids (%)
93WA15LB	Liver		73.03		
93WA16AB	Liver		73.37		
93WA16LB	Liver		70.29		
93WA17AB	Liver		70.42		
93WA17LB	Liver		**73.99**		
93WA18AB	Liver		72.58		
93WA18LB	Liver		70.96		
93WA19AB	Liver		70.69		
93WA19LB	Liver		71.49		
93WA20AB	Liver		69.7		
93WA20LB	Liver		72.84		

CONTAMINANT CONCENTRATIONS **(Cont.)**

Analyte	Sample Nunber	Sample Matrix	Result (ppm Dry Wt.)	Detection Limit (ppm Dry Wt.)	Result (ppm Wet Wt.)	Detection Limit (ppm Uet Wt.)
Hg	930A08AB	Liver	1.38	.1	.388332	.02814
	930A08LB	Liver		.1	1.54105	.02975
	930A09AB	Liver	1.48	.1	.391902	.02666
	930A09LB	Liver	5.94	.1	1.609146	.02709
	930A10AB	Liver	1.75	.1	.4949	.02828
	930A10LB	Liver	4.24	.1	1.266064	.02986
	93WA01AB	Liver	6.87	.1	2.037642	.02966
	93UAOlLB	Liver	27.04	.1	8.08496	.0299
	93WA02AB	Liver	6.37	.1	1.706523	.02679
	93WA02LB	Liver	9.28	.1	2.606752	.02809
	93WA03AB	Liver	3.11	.1	863958	.02778
	93WA03LB	Liver	27.31	.1	7.832508	.02868
	93WA04AB	Liver	7.53	.1	2.298909	.03053
	93WA04LB	Liver	50.55	.1	15.766545	.03119
	93WA05AB	Liver	4.12	.1	1.42964	.0347
	93WA05LB	Liver	38.36	.1	12.48618	.03255
	93WA06AB	Liver	4.53	.1	1.356282	.02994
	93WA06LB	Liver	127.07	.1	35.185683	.02769
	93WA07AB	Liver	3.87	.1	1.22679	.0317
	93WA07LB	Liver	26.27	.1	7.024598	.02674
	93WA08AB	Liver	2.78	.1	.887932	.03194
	93WA08LB	Liver	57.35	.1	16.49386	.02876
	93WA09AB	Liver	3.64	.1	1.054872	.02898
	93WA09LB	Liver	43.23	.1	12.649098	.02926
	93UA10AB	Liver	3.44	.1	.817	.02375
	93UA10LB	Liver	18.8	.1	4.48004	.02383
	93UAllAB	Liver	7.74	.1	2.181132	.02818
	93UAllLB	Liver	161.12	.1	48.513232	.03011
	93WA12AB	Liver	2.79	.1	.71424	.0256
	93WA12LB	Liver	23.37	.1	6.87078	.0294
	93WA13AB	Liver	5.66	.1	1.705924	.03014
	93WA13LB	Liver	78.12	.1	20.764296	.02658
	93WA14AB	Liver	3.64	.1	1.042496	.02864
	93WA14LB	Liver	20.54	.1	5.336292	.02598
	93WA15AB	Liver	2.12	.1	.70172	.0331

PROCEDURAL BLANKS

Analyte	Lab Sample Number	Result Total UG
Hg	BLANK A	
	BLANK B	8
	BLANK C	0
	BLANK D	0
	BLANK E	
	BLANK F	8
	BLANK G	0
	BLANK H	0
	BLANK I	0

REFERENCE MATERIALS

Analyte	Lab Sample Number	S.R.H. ID	S.R.M. Name	• Certified Reference Value (ppm / %)	95% Confidence Interval	Result (ppm / %)	Percent Recovery
Hg	NBSOYS-D	NIST 1566a	Oyster Tissue	.0642 Dry	.0067	< .1 Dry	155.76
	NBSOYS-E	NIST 1566a	Oyster Tissue	.0642 Dry	.0067	< .1 Dry	155.76
	NBSOYS-G	NIST 1566a	Oyster Tissue	.0642 Dry	.0067	< .1 Dry	155.76
	DOLT2 C	NRCC DOLT-2	Dogfish Liver	1.99 Dry	.1	2.16 Dry	108.54
	DOLT2 D	NRCC DOLT-2	Dogfish Liver	1.99 Dry	.1	2.08 Dry	104.52
	DOLT2 F	NRCC DOLT-2	Dogfish Liver	1.99 Dry	.1	2.11 Dry	106.03
	DORM B	NRCC DORM-1	Dogfish Muscle	.798 Dry	.074	.69 Dry	86.47
	DORM C	NRCC DORM-1	Dogfish Muscle	.798 Dry	.074	.67 Dry	83.96
	DORM E	NRCC DORM-1	Dogfish Muscle	.798 Dry	.074	.73 Dry	91.48

* Only certified analytes list a confidence interval • all others are considered reference values.

ANALYTICAL METHODS

Method Code	Method Description
002	LABORATORY: Geochernical & Environmental Research Group, Texas A&M

Tissue, Sediment and Uater Mercury

II. Mercury was determined by EPA method 245.5 with minor revisions. Sediment samples can be analyzed either freeze dried or on a wet basis. Sediment samples are homogenized by mixing before subsampling. The tissue samples were homogenized in the original sample containers with a Tekar Tissunizer and subsampled. Water samples are acidified (0.5% v/v with high purity nitric acid, HNO3) in the original sample bottle. For sediments a 0.5 to 1.0 gram sample (dry weight) was used. For tissues a 1.5 to 2.0 gram sample(wet weight) uas used. For water the sample size is 20 ml.

For tissue and sediment, the sample is weighed into a 50 ml polypropylene centrifuge tube. 2.5 ml of concentrated sulfuric acid (H2SO4) and 1.5 ml of concentrated nitric acid (HNO3) were added and the samples heated in a water bath at 90 C for 15 min. After cooling 10 ml of distilled water and 15 ml of mixture of 3.3% (w/w) potassiun permanganate (KMnO4), and 1.7% (w/w) potassiun persulfate (K2S208) were added to each tube and the samples heated in a water bath at 90 C for 30 min. After cooling 5 ml of 10% (w/w) hydroxylamine hydrochloride (NH2OH HC1) was added to reduce excess permanganate and the volume brought to 35 ml with distilled water.

For uater samples, the sample is weighed into a 50 ml polypropylene centrifuge tube, 1 ml of concentrated H2SO4 is added and the solution mixed vigorously with a vortex stirrer. Then 4.5 ml of the KMnOr/K2S208 is added and the resulting mixture heated in a 90 C water bath for 2 hours. After cooling, 1.5 ml of a 10% (w/w) hydroxylamine hydrochloride (NH2OH HC1) solution is added, sample volune adjusted to a constant volw with distilled water and the resulting solution mixed vigorously.