

# Variations in Trace Metal Concentrations in American Oysters (*Crassostrea virginica*) Collected From Galveston Bay, Texas

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**ABSTRACT:** Nearly one thousand oysters (*Crassostrea virginica*) were collected at 15 sites on four sampling trips to Galveston Bay during 1992-1993. Iron, silver, arsenic, cadmium, copper, lead, and zinc were determined in the whole soft part of the individual oysters. Trace metal concentrations were found to vary among individuals within a site on a given trip, and spatially and temporally around the Galveston Bay estuarine system. Differences in metal concentrations from site to site were a factor of 5 or more for some metals, and similar differences were found from time to time at a given site. Zinc was found in anomalously high concentrations at several sites, mainly along the west side of Galveston Bay. Isolated high values of other metals were found scattered throughout the bay; however, only one site (GBSL, near Swan Lake in lower Galveston Bay) was found to have significantly higher than average concentrations for several metals (Ag, Cu, Pb, and Zn). One obvious trend found in this study was that metal concentrations, except for As, were highest in the summer, followed by the fall, and lowest in the winter and spring. The temporal changes in metal concentrations in oysters cannot be explained by changes in body weight in different seasons, and are apparently caused by changes in environmental conditions (e.g., metal input, salinity) or biological activity (e.g., metabolism, depuration).

## Introduction

Bivalves have been used extensively in environmental monitoring studies in recent decades (Phillips 1977; Goldberg et al. 1978; Rainbow 1990; O'Connor and Ehler 1991). Accumulation of trace metals by bivalves has been shown to be relatively rapid and to reflect ambient exposure level (Zarogian et al. 1979; Beasley et al. 1982). On the other hand, the excretion of metals is thought to be relatively slow (National Academy of Sciences 1980) so they integrate ambient metal levels over some time period.

Great variation in metal concentrations in bivalves has been reported from many parts of the world. Even in relatively small areas (e.g., a specific estuary), concentrations of some metals can vary by a factor of 10 to 100 (Eisenberg and Topping 1984; Presley et al. 1990; Morse et al. 1993). Thus, extensive spatial and temporal sampling is needed to characterize an area using bivalve analyses.

The American oyster (*Crassostrea virginica*) is the dominant bivalve in the southern United States coastal and estuarine areas. Since 1986 the National Status and Trends (NS&T) Program, an outgrowth of an earlier "Mussel Watch" conducted in 1976-1978 (Goldberg et al. 1978), has been collecting and chemically analyzing bivalve mollusks at over 150 sites around the United States, includ-

ing sites in Galveston Bay (O'Connor and Ehler 1991).

Trace metal concentrations in oysters from the Galveston Bay sites of the NS&T Program for the period 1986-1990 have been published (Morse et al. 1993). These samples were collected in the winter (December-January) each year in order to minimize seasonal variation in metal concentrations. Because the NS&T is a long-term, large-scale monitoring program, it does not investigate a single estuary in great detail. Morse et al. (1993) reported, based on the first 5 yr of the NS&T Program, that most trace metal concentrations in oysters from Galveston Bay were similar to average concentrations in oysters from other Gulf of Mexico sites. Average concentrations of Cd, Cr, Cu, Mn, and Pb in Galveston Bay oysters differed by 10% or less from the Gulf-wide averages. Silver, Ni, Se, Sn, and Zn were, however, higher in Galveston Bay by 23%, 16%, 14%, 24%, and 35%, respectively.

The main purpose of the present study was to investigate trace metal distribution patterns and variability in metal content in oysters over a 1-yr period in order to detect potential pollution problems in Galveston Bay that might have been missed in the somewhat restricted sampling of the NS&T Program. An important question concerning trace metal concentrations in oysters, which is not well documented in previous work in Texas bays, is how fast and how much the concentrations change on

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a short-term basis. Another feature of the present work was the analysis of individual oysters, instead of pooled samples (20 individuals for NS&T), so as to provide information about size-dependency of metal concentrations and individual variability.

#### AREA DESCRIPTION

Throughout this paper, reference to Galveston Bay (Fig. 1), which is located in southern Texas, USA, includes its adjacent parts (East, West and Trinity bays.) The Trinity River provides most of the fresh water to Galveston Bay and carries domestic and industrial wastes from the Dallas-Ft. Worth area 1000 km upstream. The San Jacinto River, heavily industrialized along the inland part of the Houston Ship Channel, brings industrial wastewater into Galveston Bay from Houston and adjacent areas. The Bolivar Peninsula and Galveston Island, at the entrance to Galveston Bay, leave only a narrow outlet from the bay into the Gulf of Mexico. The Texas City Dike extends almost 8 km from the western shoreline of lower Galveston Bay toward the outlet of the bay. It limits water exchange between lower Galveston Bay and West Bay. All of Galveston Bay is shallow, with a depth less than 3 m almost everywhere, except for dredged ship channels. The western shore of Galveston Bay, from Houston to Galveston, is heavily industrialized, with petroleum, petrochemical, and chemical industries dominating.

Several factors contribute to potential pollution problems in Galveston Bay: wastewater from large cities (Dallas-Ft. Worth and Houston), heavy industrialization along the shore, shallow water and restricted exchange with the Gulf of Mexico, and extensive recreational activities (fishing and boating) by the large adjacent population. This study did not attempt, however, to characterize the sources of pollution to the bay. Instead, metal concentrations in oysters were determined under various conditions in order to evaluate use of oyster data as an indicator of pollution.

#### Methods

##### SAMPLING

Oyster collection for this project covered all four seasons (June 29–July 2, 1992; September 28–October 1, 1992; January 5–8, 1993; March 18–21, 1993). Sampling locations (Fig. 1) were re-occupied by using GPS and/or LORAN-C navigation and positioning systems in open-water areas, and by referencing permanent landmarks near the collecting sites nearshore. Nearshore oysters were hand-picked 5 m to 25 m from the shoreline. At least 20 individuals of randomly selected body sizes were collected from as small an area as possible at each site (usually within 10 m). An oyster dredge,

operated from a boat, was used to collect oysters from open-water locations. Towing distances were up to several hundred meters in order to collect enough individuals. The number of individuals collected differed from time to time because of varying dredging efficiency. However, 20 or more oyster individuals were collected from most sites. Samples were quick-frozen (using dry ice) upon collection and were stored in zippered plastic bags. They were kept frozen in the laboratory until processed further.

##### SAMPLE PROCESSING

Oysters were removed from the freezer, allowed to thaw, and mud was brushed from the exterior shells. They were then rinsed with deionized water and shucked using a stainless steel oyster knife. Oyster tissue (the whole soft part) was separated from the shells and rinsed sparingly with deionized water in order to remove sediment adsorbed to the tissue surface. Each oyster individual was then placed in a pre-weighed plastic vial, weighed, freeze dried, and reweighed. They were then powdered and homogenized in a Spex mixer (ball mill) by adding 2–3 acid-cleaned TPE Teflon balls (0.5 cm diameter) to the vial.

##### CHEMICAL ANALYSES

Oyster digestion was slightly modified from the standard NS&T procedures described by Presley et al. (1990). Aliquots of ~200 mg of oyster tissue, which had been dried, powdered, and homogenized, were placed in 60-ml capacity screw cap vessels of PFA Teflon (Savillex Corp., Minnetonka, Minnesota, USA, model 561). Three milliliters of ultra-pure nitric acid (J. T. Baker) were added to each vessel (3 ml of 1:1 HNO<sub>3</sub>-HCl for Ag measurement) and the vessels were allowed to sit overnight with the matching screw caps on but not tightened. The caps were tightened and the vessels were then heated at 130°C in a conventional drying oven for 1 h, 2 h, 4 h, and overnight (10–12 h) in separate heating steps. Before each heating step, the vessels were cooled and the caps were loosened to release CO<sub>2</sub> pressure, then tightened again. Blanks, spikes, replicates, and reference materials (1566 oyster tissue from the National Institute of Standards and Technology, NIST, formally NBS) were processed with each digestion batch. Dilution factors were calculated by dividing the final digest volume by the exact sample weight. The final volume was derived from the known empty digestion vessel weight, the final vessel weight, and solution density (average 1.067). Digestion solutions were stored in Nalgene 30-ml capacity polypropylene bottles until analyzed.

The trace metals determined were chosen be-

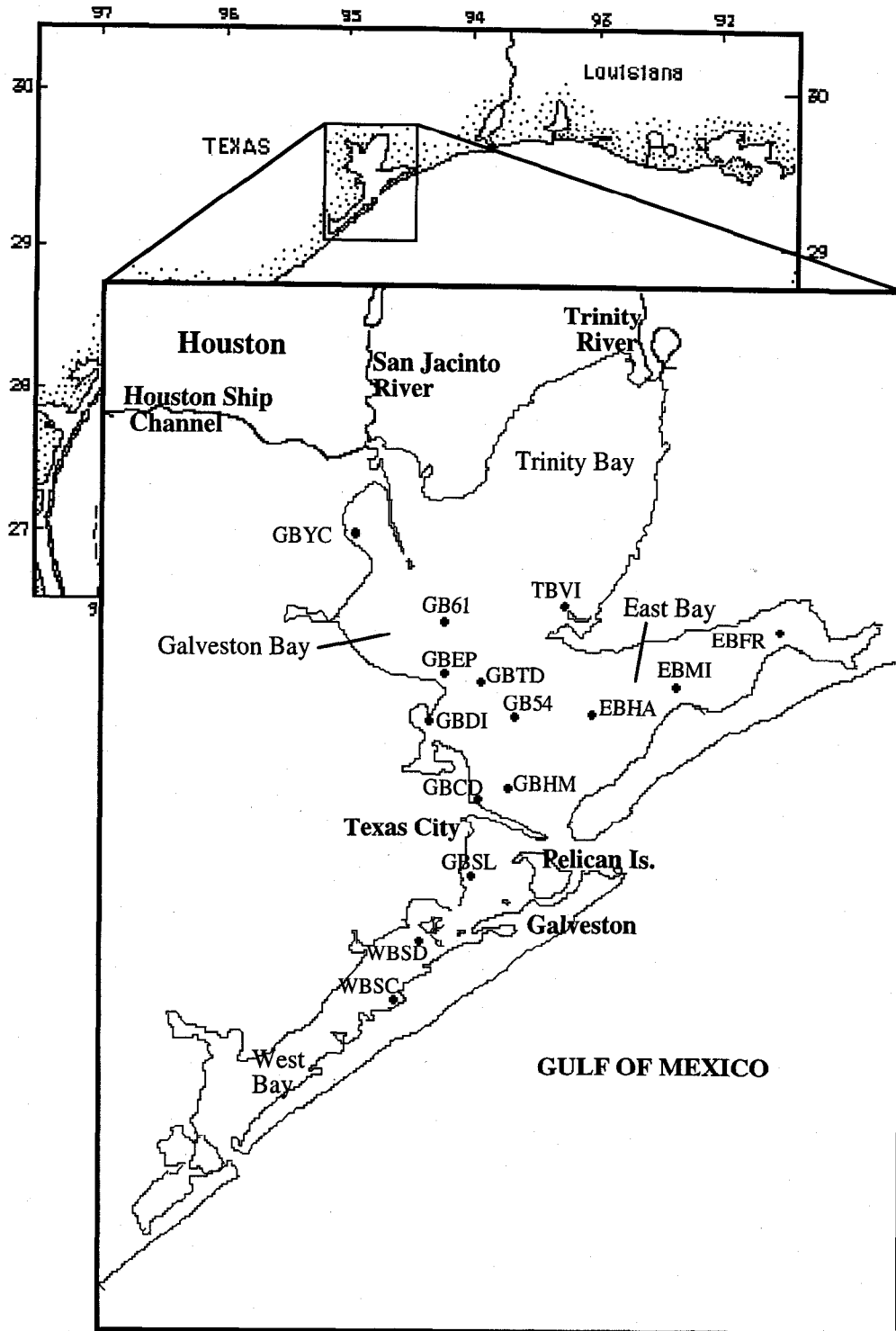


Fig. 1. Oyster sampling locations in Galveston Bay during 1992-1993.

cause of their possible environmental damage, physiological importance, and/or possible human health effects. Determinations of Fe, Cu, and Zn in oysters were performed by a Perkin-Elmer Mod-

el 306 Flame Atomic Adsorption Spectrometer, while the other analyses used a Perkin-Elmer model 3030Z Graphite Furnace Atomic Adsorption Spectrometer equipped with an HGA 600 furnace,

TABLE 1. Data for the reference material analyzed with the oyster samples during this study.

	Fe	Ag	As	Cd	Cu	Pb	Zn
Detection limit (ppm)	13	0.06	0.20	0.01	1	0.11	2
NIST 1566 (n = 21)							
Certified value (ppm)	539	1.68	14.00	4.15	66	0.37	830
Measured average (ppm)	528	1.68	13.41	3.82	63	0.36	807
Standard deviation (ppm)	9	0.11	0.94	0.17	3	0.06	26
Recovery (%)	98	100	96	92	94	97	97
Maxima (ppm)	542	1.98	15.34	4.17	68	0.50	865
Minima (ppm)	511	1.51	11.75	3.60	58	0.27	773

an AS-60 Autosampler, and Zeeman correction system. Standard solutions with appropriate concentrations for each element were made fresh from 1000 ppm AAS or ICP stock standards (VWR Scientific, Philadelphia, Pennsylvania, or Johnson Matthey Specture, Johnson Matthey Company, Ward Hill, Massachusetts). These were verified by quality assurance check samples which had been certified by the United States Environmental Protection Agency.

Analysis of the reference material, NIST 1566 oyster tissue, yielded 92%–100% recovery for seven metals (Table 1). Matrix spikes recoveries were 92%–106% on average for the same seven elements. Precision was good for most duplicate samples (two aliquots of a sample taken from the same individual), with relative percentage difference (RPD) mostly less than 10%.

#### DATA ANALYSIS

Average trace metal concentrations at each location on each trip were calculated by averaging all the individual oysters analyzed from that location. However, concentrations from individual oysters were used for all statistical tests from which spatial and temporal variations in trace metal concentrations were derived. Statistical methods applied include analysis of variance (general linear model and rank-based), linear regression model and t-test. Analysis of variance, including Duncan's multiple range test, and t-test were used to identify sites where concentrations were significantly higher than the others. Linear regression was performed between pairs of metals and between metal concentration and oyster dry weight. Most statistical work was performed using the SAS system (SAS Institute Inc., Cary, North Carolina).

#### Results and Discussion

##### TRACE METAL CONCENTRATIONS IN INDIVIDUAL OYSTERS

Large variations in trace metal concentrations among individual oysters collected at the same site and time were found for several metals. More specifically, As and Cd concentrations were relatively

constant among individuals at a given site on a given trip, whereas Fe, Ag, Cu, Pb and Zn showed significant intra-station variation. The coefficient of variation (CV) (1 standard deviation/mean) of As and Cd was usually less than 30% within a site on a given trip, while most datasets (any site-trip combination) for Fe, Cu, Pb, and Zn gave CVs higher than 30%. Metals with the greatest range in concentrations in individual oysters were Fe, Ag, Cu, and Zn, which differed by up to a factor of 5 or more. These variations were found in many different datasets.

A test was performed to determine the number of individuals required to provide a representative mean concentration. Several datasets with 25 individuals or more were chosen and for each dataset average concentrations were derived using various numbers of individuals that were randomly chosen. When 15 to 20 individuals were used, in most cases, to derive a mean concentration, the average is within 20% of the average value obtained using all individuals ( $n > 25$ ). This observation is consistent with that of Wright et al. (1985).

It is interesting to note that the maximal or minimal concentrations of Fe and Pb were often found in the same individuals, when samples collected at a given site on a given trip were compared. More specifically, maximal Fe and Pb concentrations were often observed when the oyster dry weights were the lowest while the minimal Fe and Pb concentrations were found in oysters with the largest dry weights. The negative relationship between logarithmic transformed Pb concentration and individual dry weight is not always very strong ( $R^2$  values range from 0.03 to 0.80); however, it is obvious that higher Pb concentrations occurred in smaller oyster individuals (Fig. 2).

The Fe and Pb correlation in individual oysters is illustrated in Fig. 3. The slopes of the correlations were generally about 20 (Fe in weight percent) except for a few sites where higher slopes or, in other words, higher Pb:Fe ratios were observed. Only winter data are shown in Fig. 3 to simplify the illustration of correlation. However, correlations

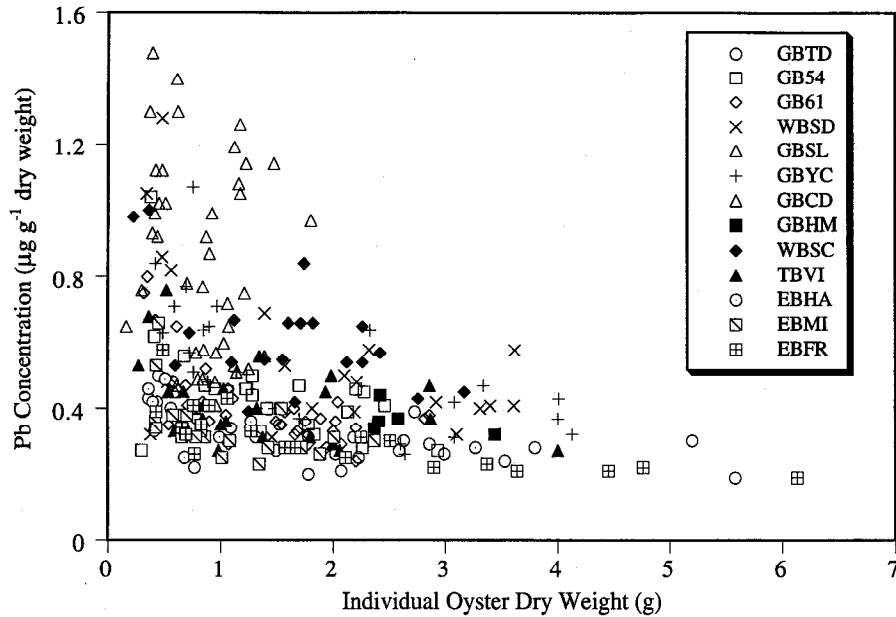


Fig. 2. Relationship between Pb concentration and dry weight of individual oysters. Higher concentrations were observed in individuals with smaller body dry weight.

between Pb and Fe in other seasons are similar to that in Fig. 3. In addition to the relationship between Pb and Fe, correlations were also found for Zn and Cu (Fig. 4) and Cu and Ag (Fig. 5). In 48 sample sets (site-trip combinations) with five or more individuals, 46 sets showed significant ( $p < 0.01$ ) linear regression between Fe and Pb in individual oysters and most  $R^2$  values are greater

than 0.8 (statistical data available upon request). For Zn and Cu,  $R^2$  values are generally greater than 0.7 and only six datasets have significance values ( $p$ ) larger than 0.01. Correlation between Cu and Ag is generally strong, with most  $R^2$  values greater than 0.8. Only three out of 48 sample sets have significance values ( $p$ ) larger than 0.01. Other pairwise correlations were tested, including metal con-

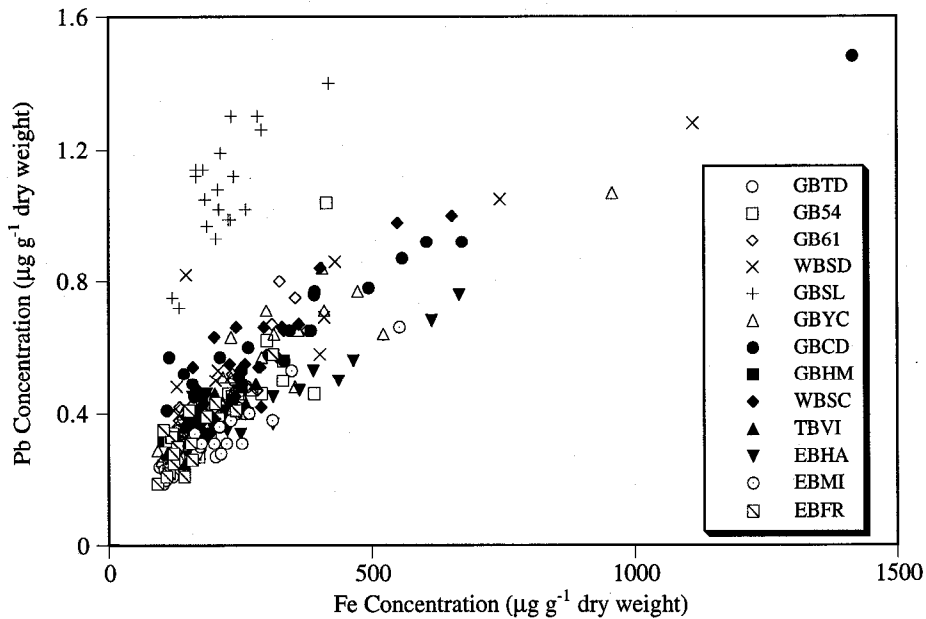


Fig. 3. Relationship between Pb and Fe concentrations in individual oysters (winter data shown). Linear correlation was found everywhere and different slopes were observed at different locations.

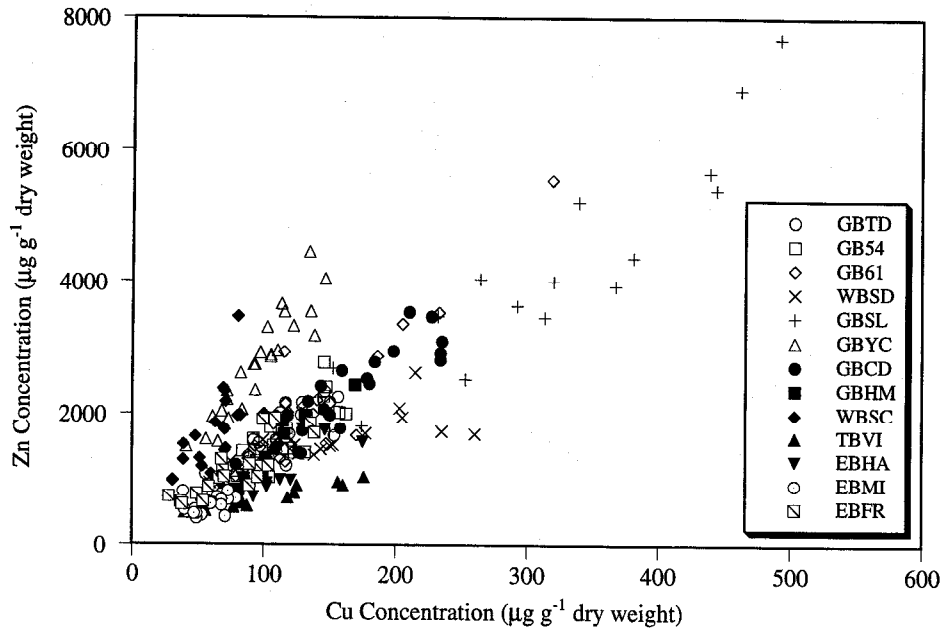


Fig. 4. Relationship between Zn and Cu concentrations in individual oysters (winter data shown). Linear correlation was found everywhere and different slopes were observed at different locations.

centration and individual oyster dry weight, but no significant correlations were found.

The good correlation between certain pairs of metals in individual oysters found in this study has been noted in few previous studies. Although the intercept of linear regression between these metal pairs is not always close to zero, the relatively constant ratios of Pb:Fe, Cu:Ag, and Zn:Cu (Table 2)

must be considered when speculating on reasons for spatial and temporal changes in metal concentrations.

GENERAL TEMPORAL AND SPATIAL VARIATIONS OF TRACE METALS IN GALVESTON BAY OYSTERS

Average trace metal concentrations at 15 sites on four sampling trips are shown in Fig. 6 (a-g). Sta-

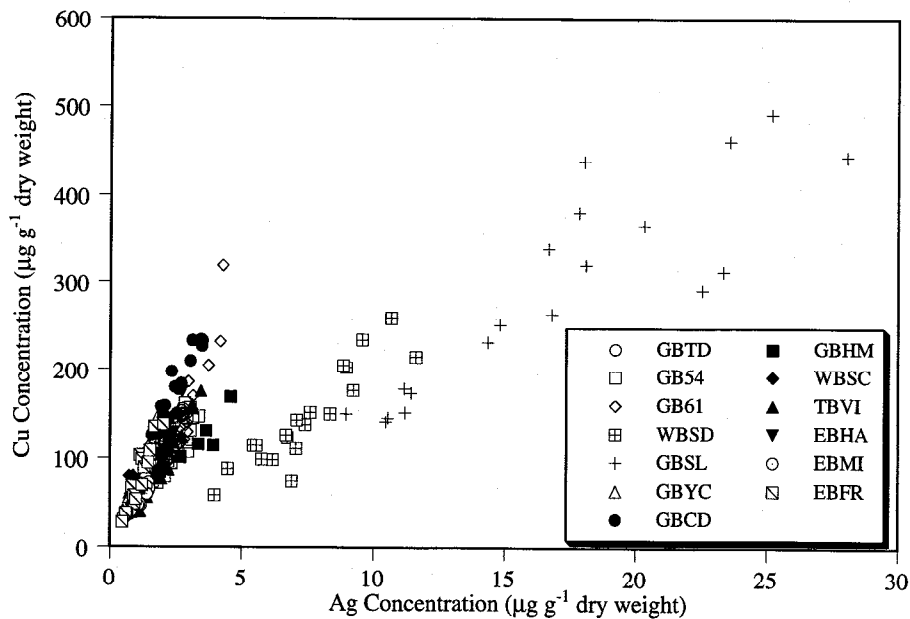


Fig. 5. Relationship between Cu and Ag concentrations in individual oysters (winter data shown). Linear correlation was found everywhere and different slopes were observed at different locations.

TABLE 2. Ratios of Pb and Fe, Cu and Ag, and Zn and Cu in oysters at each site on each trip.

	Pb:Fe				Cu:Ag				Zn:Cu			
	Summer	Fall	Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall	Winter	Spring
EBFR	14.6	11.6	21.2	11.3	73.3	65.6	68.4	67.0	11.2	12.4	14.4	11.6
EBHA	13.6	9.9	15.2	17.2	60.9	58.2	50.3	60.9	10.7	11.7	10.3	11.4
EBMI	14.9	8.7	15.5	12.7	79.8	65.7	51.2	76.6	11.2	12.8	9.7	13.6
GBCD	18.3	14.3	18.2	18.1	115.6	92.7	69.5	88.8	15.2	15.1	14.2	14.7
GBDI	14.1	10.5		20.3	89.7	75.1		76.7	12.2	13.1		13.1
GBEP	19.1	14.2			101.3	79.6			15.1	15.6		
GBHM	17.0		21.8		46.8		34.9		14.5		14.8	
GBSL			49.3	32.7			17.2	18.9			13.2	13.7
GBTD	27.2	12.6	20.3	21.9	83.2	67.0	55.1	71.2	17.6	12.8	14.4	14.3
GBYC			18.8	25.0			67.9	84.1			28.8	26.6
GB54	15.4	11.9	18.0	17.5	73.1	56.1	46.1	54.4	14.7	17.2	14.1	13.5
GB61	14.3		21.2	26.5	67.6		50.8	65.5	15.7		14.8	13.7
TBVI		8.8	21.5	18.3		44.4	46.5	51.8		6.6	6.8	7.6
WBSC	35.2	20.9	20.3	20.9	72.6	76.2	69.7	88.0	28.8	33.2	27.9	21.6
WBSD	16.6	15.5	19.4	21.0	31.6	18.5	19.5	25.1	7.7	10.2	11.1	11.7
Average	18.4	12.6	21.6	20.2	74.6	63.6	49.8	63.8	14.6	14.6	15.0	14.4

tistical results show that temporal variations in metal concentrations were significant at most sites (statistical data available upon request) when all individuals at a site were tested (Kruskal-Wallis test). Sites with less than three sample sets were not tested for temporal variability. Among the 11 sites that could be tested, WBSC and TBVI were the sites with the most constant metal concentrations (Ag, As, Cu, and Zn) in oysters. This is due possibly to environmental conditions; WBSC had relatively constant salinity (25–30 PSU) year round and is located away from potential contaminant inputs, whereas TBVI being closest to the freshwater input to Galveston Bay, has low salinity all year.

Comparing average metal concentrations at each site (each trip) to the averages of other sites by t-tests, localized effects were identified. By this procedure, several sites were found to have significantly higher than average metal concentrations (statistical data available upon request). Excess Zn was found at sites along the industrialized western shoreline at most times and in upper East Bay in the summer. High Ag concentrations were consistently observed at site GBSL near Swan Lake in lower Galveston Bay and site WBSD in eastern West Bay. Significantly high Cu was noted at western Galveston Bay sites and deep East Bay (summer only). Lead was found to be significantly higher at site GBSL and site WBSC in the middle of West Bay. In general, these sites are either close to the shoreline, boating and fishing activities, industrial areas, or areas of high population density, or they are affected by unusual natural conditions, such as low salinity. Details of the variations in metal concentrations will be discussed in the following sections.

#### TRENDS OF VARIATIONS IN INDIVIDUAL METALS

Metals determined in this study can be classified into three groups by comparing metal concentrations in oysters to those in area bottom sediments (Presley et al. 1992; Morse et al. 1993). Concentrations (dry weight basis) of Ag, Cd, Cu, and Zn in oysters are an order of magnitude higher than those in sediments. Arsenic concentrations are relatively similar. Iron and lead concentrations in oysters are normally only a few percent of those in sediments. As stated earlier, we found that Ag, Cu, and Zn correlated well with one another as did Fe and Pb. Apparently, oysters have greater ability to uptake Ag, Cu, and Zn (and Cd, although it does not correlate with these) than Fe and Pb.

#### COPPER, SILVER, AND ZINC

Spatial variations in metal concentrations in Galveston Bay oysters were large, for example a factor of 6 for Cu and Zn, and 10 for Ag, as shown in Figs. 6(a–c). Variations were larger in the summer than in winter and spring, except for a few sites with suspected localized effects. Site GBSL near Swan Lake in lower Galveston Bay was found to have abnormally high Cu, Zn, and Ag concentrations 1.5–7 times higher compared to other sites. This site is very close to an industrial area (Texas City). Consistently higher concentrations over time were also found at site GBEP (Cu and Zn, 1.5 times), GBYC (Zn, 2 times), and site WBSD (Ag, 2–3 times). Site GBEP is located close to shore and industrial areas. Site GBYC is located outside of the harbor of the Houston Yacht Club. Site WBSD is near the City of Galveston and is very close to a NS&T site in Galveston Bay where high Ag concentrations were reported for several years (Morse et al. 1993).

Overall, higher concentrations were usually observed at sites in western and upper Galveston Bay, which are physically close to areas having higher population and where industrial and recreational activities are most intense. Site WBSC, where the lowest Ag and Cu concentrations were found, is located mid-way down West Bay of Galveston Island, and is visually pristine. East Bay is also visually pristine and is remote from population and industry compared to sites in western Galveston Bay. Nevertheless, high Ag, Cu, and Zn concentrations (1.4–1.7 times higher) were found in upper East Bay (EBFR) probably due to low salinity (discussed in next paragraph). In West Bay, significant difference in Ag concentrations in oysters were found at two sites only a few miles apart, with 4–8 ppm at WBSD and ~0.9 ppm at WBSC. Environmental conditions such as salinity, temperature, turbidity, and current speed do not differ much between these two sites and it is hard to believe that the oysters are genetically different. It seems more likely that a yet unidentified source of Ag exists near site WBSD.

In East Bay, Cu, Ag, and Zn concentrations increased significantly from the mouth to the head in summer (Fig. 7). It is possible that salinity played a role in this geographic trend. In summer 1992, salinity was 28 PSU at EBHA, at the mouth of East Bay, 8 PSU at EBMI in mid-bay, and 5 PSU at EBFR, deep into East Bay. This strong salinity gradient was caused by heavy rains in the area. Average Cu concentrations at these three sites were 170 ppm, 226 ppm, and 360 ppm, respectively; thus there was an inverse correlation between Cu (and Ag and Zn) concentration in oysters and salinity. This relationship was found only in the summer because salinity did not vary in East Bay at other times. We have no Cu data for the low salinity water coming into East Bay.

Fresh water also comes into Trinity Bay but oysters were not analyzed for Cu at the site (TBVI) closest to the very low salinity found there in the summer of 1992. At other times, Cu was relatively high and salinity low there. We believe that salinity played an important role in regulating Cu concentrations in oysters based on the observations just presented and the fact that salinity has previously been reported to be one of the most important factors controlling Cu bioavailability to organisms (Bryan and Langston 1992). In both field studies and laboratory experiments, inverse relationship between Cu concentration in bivalves and salinity have been observed (Wright and Zamuda 1987; Sanders et al. 1991; Riedel et al. 1995). Greater availability of Cu in low salinity water could be due to enhanced supply, stronger complexation of Cu in high salinity waters, desorption of Cu from par-

ticulate matter during initial mixing of fresh water and salt water or other processes (Knezovich 1994).

Bioavailability of Ag is considered to be salinity dependent because of strong chloro complexing (Wright and Zamuda 1987; Sanders et al. 1991). The more stable salinity at our sites TBVI (higher Ag and Cu concentrations) and WBSC (lower, consistent Ag, Cu, and Zn concentration) support the suggestion that salinity strongly affects Ag, Cu, and Zn concentrations in Galveston Bay oysters. Although Cu:Ag and Zn:Cu ratios in oysters stayed relatively constant, it is unlikely that the bioavailable concentration of Ag, Cu, and Zn stayed proportional at each of the three sites in East Bay around the year. Riedel et al. (1995) suggested that salinity may cause a specific physiological effect on the accumulation of trace metals in oysters. Constant ratios in East Bay oysters over time in this study lead us to believe that salinity affected the physiology of oysters and regulated their Ag, Cu, and Zn concentrations in similar ways.

The ratios of Cu:Ag and Zn:Cu (Table 2) are surprisingly consistent over time at a given site, in most cases, even though the concentrations of Ag, Cu, and Zn changed significantly in different seasons. These consistent ratios among Ag, Cu, and Zn suggest oysters have the capability to regulate levels of these three elements during accumulation and depuration. Sanders et al. (1991) also reported a strong correlation between Cu and Ag concentrations in Chesapeake Bay oysters. Although the relationship between Cu and Zn was not discussed in detail, it appeared that these two metals had similar temporal variations in *Crassostrea gigas* (Boyden and Phillips 1981).

In general, Cu, Ag, and Zn concentrations were highest in the summer, followed by fall, and lowest in winter and spring. The largest decrease in Zn concentration from summer to spring at a given site was observed at EBFR, where average Zn concentration decreased from ~4000 ppm in the summer to < 1000 ppm in the spring. This is in contrast to the relatively constant Zn (and Cu) concentrations seen at site WBSC, in middle West Bay, over the four seasons. Large temporal variations in Cu, Ag, and Zn concentrations were common at sites located in upper Galveston Bay and deep East Bay (Figs. 6a, b) where the differences in seasonal average concentrations were usually a factor of 2 or more. It may be significant that the sites where Cu, Ag, and Zn varied the most were also the sites with the greatest salinity variations.

Some authors have attributed decreases of metal concentrations in oysters to growth (i.e., the effect of tissue dilution; cf. Rainbow 1990). However, in the present work, few relationships between Ag,



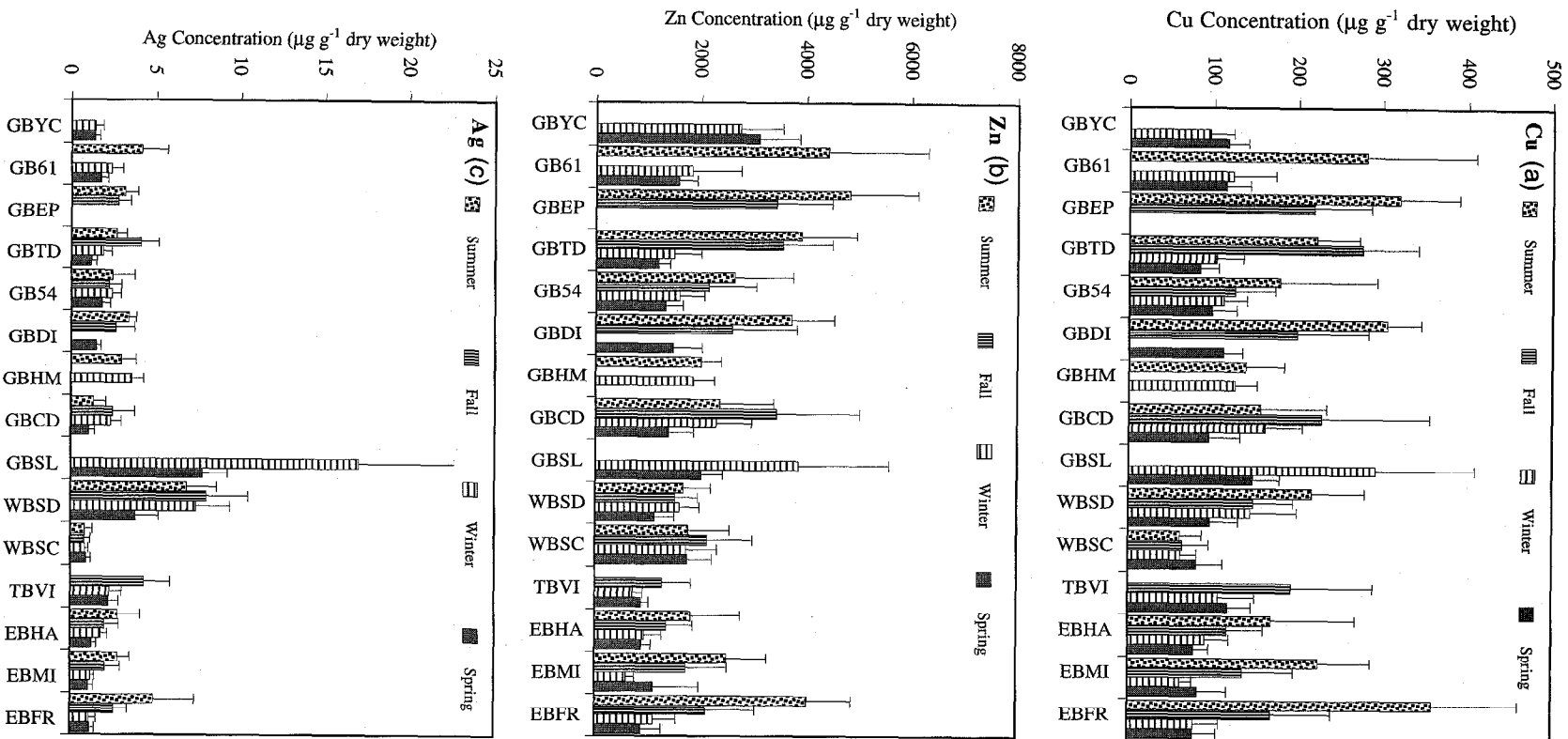


Fig. 6. Spatial and temporal variations in metal concentrations in oysters from Galveston Bay. Bars are average concentrations and error bars represent one standard deviation. (a) Cu, (b) Zn, (c) Ag, (d) Cd, (e) As, (f) Pb, (g) Fe.

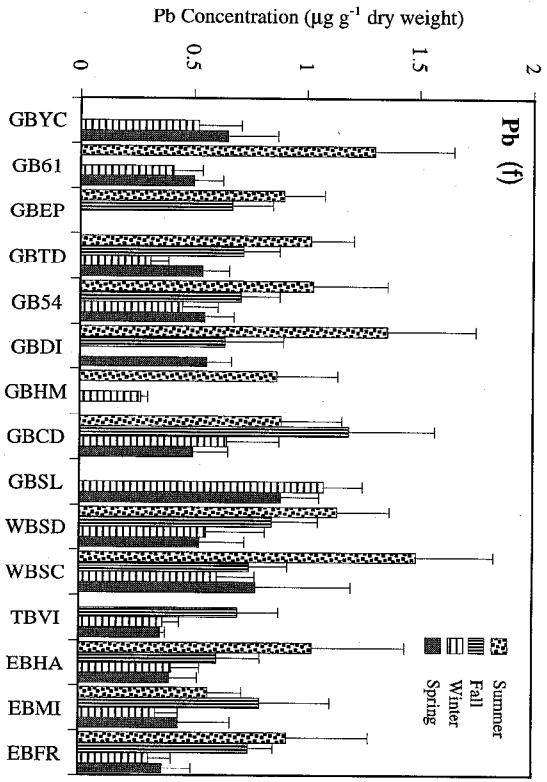
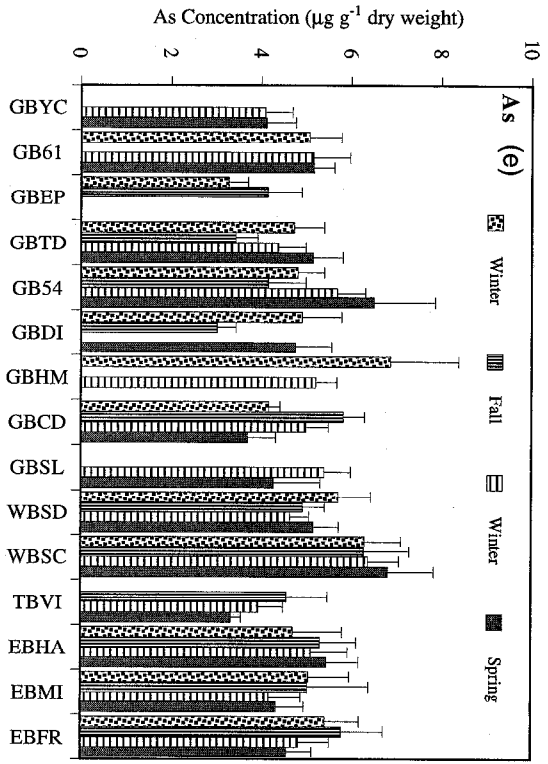
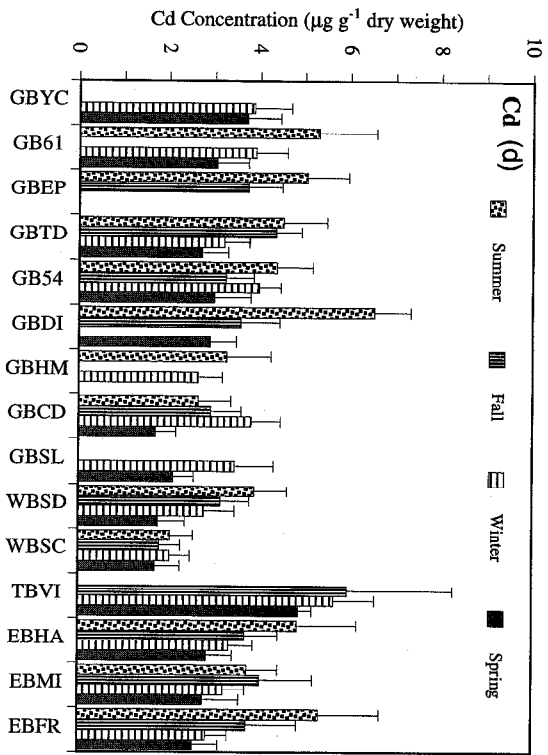


Fig. 6. Continued.

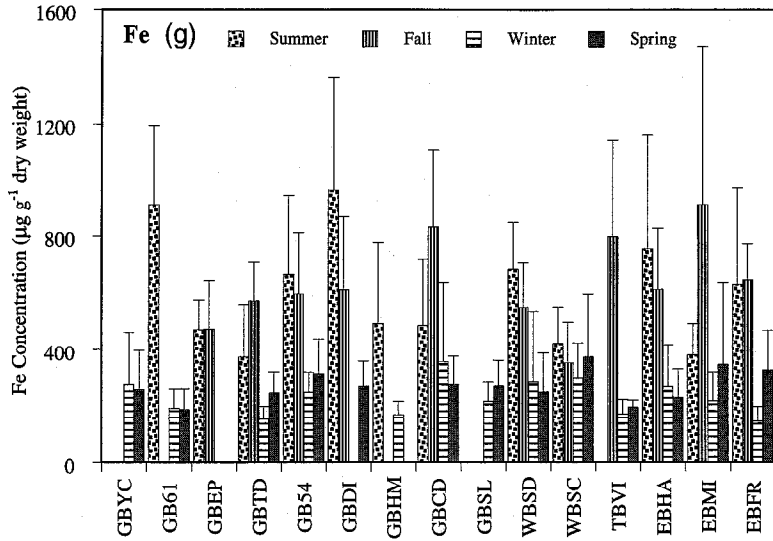


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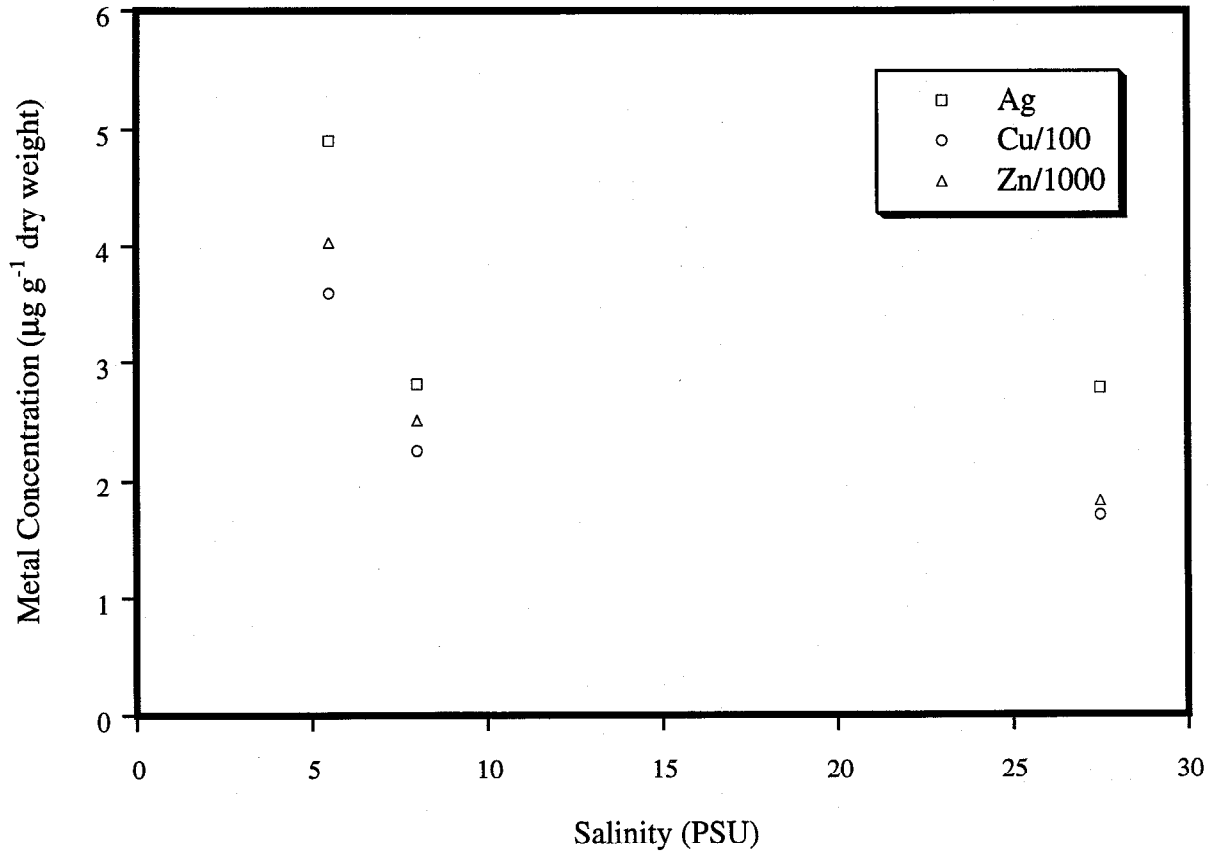


Fig. 7. An inverse correlation was observed between metal concentration (Ag, Cu, and Zn) in oysters and salinity in East Bay in the summer of 1992. This strong salinity gradient was not found in other seasons, nor were there large differences in metal concentrations among three sites.

Cu, or Zn concentration and oyster size (measured as dry weight) could be established. Changes in metal concentration and oyster dry weight sometimes had the same sign. Individual oyster dry weight did not have any consistent correlation with Ag, Cu, or Zn. At site WBSC, the change of average dry weight was a factor of 3 (0.69 g in the summer to 2.25 g in the spring) while Ag, Cu, and Zn stayed almost constant. In contrast, at site EBMI, average dry weight changed very little from summer to spring (1.02 g–1.56 g) and average Cu concentration decreased from 226 ppm in the summer to 62 ppm in the winter and 82 ppm in the spring. Although at some sites the oyster dry weights were higher, in general, when Ag, Cu, and Zn concentrations were lower in winter and spring, inconsistent and unproportional changes between dry weight and metal concentrations led us to conclude that the changes in oyster dry weight were not a dominant factor in controlling metal concentrations.

#### CADMIUM

Like Ag, Cu, and Zn, Cd concentration in oysters is normally an order of magnitude higher than that in sediment. However, Cd behaved differently in oysters. It showed less intra-sample variation and did not correlate well with the other three elements. Cadmium concentrations were generally higher in the summer (Fig. 6d) but large decreases from summer to winter were only found at site WBSD (eastern West Bay) and the three sites in East Bay (EBHA, EBMI, and EBFR). Temporal variations were significant at all sites ( $p < 0.01$ ) except TBVI ( $p = 0.178$ ).

Comparing average Cd concentrations from place to place, lower Cd concentrations were found at sites in lower Galveston Bay and West Bay, which are away from industrial and population areas. At some sites Cd seemed to correlate with Cu in temporal variation (decreasing from summer to winter), but the Cd changes were smaller and less consistent.

#### ARSENIC

Arsenic showed the least spatial and temporal variation in Galveston Bay oysters. The range 4 ppm to 6.5 ppm covers both temporal and spatial variations (Fig. 6e). Differences in As concentration were more pronounced, however, from site to site than within a site (significance test for spatial variation,  $p < 0.01$  on each trip). Most sites showed less than 10% temporal variation. At several sites these small temporal variations were statistically significant. Apparently, oysters get As from the water column, which is relatively constant in As concentration (Tripp 1988). It is also possible that As

has a longer half-life in oysters than other metals (Okazaki and Panietz 1981).

#### LEAD AND IRON

Iron showed almost exactly the same changes in concentrations in oysters as did Pb, both spatially and temporally. Great changes in Fe and Pb concentrations in oysters over time were found, as shown in Figs. 6f, g. Like most other metals, Pb concentrations were high in the summer at almost every site (1 ppm to 1.5 ppm) and low in the winter and spring (0.3 ppm to 0.5 ppm) except for a few sites where the highest concentrations were found in the fall. Temporal variation was significant at every site. Concentrations in the spring were slightly higher than those in the winter at some sites. Extraordinarily high average Pb concentrations were observed at GBSL (lower Galveston Bay) in the winter and spring compared to other sites sampled on the same trips, indicating GBSL may have a localized Pb input (1.7–2.4 times higher than the other sites,  $p < 0.01$ ). Lead concentrations in oysters at WBSC, in West Bay, were significantly above average on three of four trips (1.3–1.5 times higher than the others,  $p < 0.01$ ).

In general, concentrations of Fe and Pb in oysters are about 1–5% of the concentrations in sediments. We are concerned, therefore, that sediment in the oyster soft parts might affect Fe and Pb concentrations measured in the oyster. Because of the small samples (200 mg dry weight) digested in the procedures used here and the fact that the digestion removes 60–70% of the Pb and Fe from typical fine-grained sediment, even 2–10 mg of pure fine sediment could yield the amounts of Fe and Pb found in oysters.

We determined the Pb:Fe ratios in the sediments collected during our oyster sampling. If the Fe and Pb in oysters came primarily from included sediment, Pb:Fe ratios in oysters and in bottom and suspended sediments should be similar. Most of our Pb:Fe ratios fall into such a relative small range that linear regression does not show a strong correlation ( $R^2 \sim 0.4$ ), but, in fact, the ratios are similar. This is a possible explanation for the fact that Fe and Pb concentrations in oysters have an inverse relationship with oyster dry weight (Fig. 2). Similar negative correlations between Fe concentration and body weight have also been found in other bivalves, *Saccostrea cucullata* and *Isognomon isognomon* (Brown and Kumar 1990).

#### BAYWIDE AVERAGES

Average metal concentrations at each site on each trip were used to calculate an overall average value to represent concentrations in Galveston Bay oysters for each season (Table 3). Notice that av-

TABLE 3. Average metal concentrations and summary statistics (Kruskal-Wallis test) for temporal variations in trace metal concentrations in oysters collected from Galveston Bay during 1992–1993. All concentrations in ppm dry weight. Small significance values indicate at least one trip was different from the others.

Trip		Fe	Ag	As	Cd	Cu	Pb	Zn
Summer	Mean (12 sites)	604	3.20	5.09	4.30	220	1.04	2,973
	Standard deviation	199	1.58	0.94	1.26	86	0.25	1,133
Fall	Mean (11 sites)	633	3.10	4.78	3.66	170	0.76	2,299
	Standard deviation	162	1.89	1.02	1.02	60	0.16	844
Winter	Mean (13 sites)	232	3.53	4.92	3.45	120	0.49	1,720
	Standard deviation	65	4.38	0.69	0.88	59	0.21	877
Spring	Mean (13 sites)	274	2.07	4.88	2.75	100	0.54	1,440
	Standard deviation	55	1.88	1.01	0.88	21	0.15	600
All	Significance value	< 0.001	0.036	0.916	0.004	< 0.001	< 0.001	< 0.001

verage Ag concentrations in winter and spring for the entire Galveston Bay are strongly affected by site GBSL, which had a very high 17 ppm average in the winter and 7.77 ppm in the spring. This site was not sampled in either summer or fall. If GBSL is excluded, average baywide Ag concentrations become 2.40 ppm in the winter and 1.60 ppm in the spring. High concentrations at GBSL (Cu, Pb, Zn) and GBYC (Zn) also affected, by about 10–20%, Galveston Bay average concentrations of Cu, Pb, and Zn in winter and spring.

Except for Ag ( $p = 0.036$ ) and As ( $p = 0.916$ ), temporal variations were significant for all metals analyzed ( $p < 0.01$ ). Significance tests (Kruskal-Wallis) were performed by using average metal concentrations at each site on each trip. In general, average trace metal concentrations in Galveston Bay oysters, except for As, were higher during hot seasons (summer and fall) and decreased dur-

ing winter. Typical decreases in metal concentration from summer to winter was about 50%. For example, average Fe concentration decreased from ~600 ppm during summer to 230 ppm in the winter, and average Zn concentration decreased from ~3000 ppm to ~1400 ppm.

Table 4 compares the year-round averages in this study with data from other estuarine systems. The winter data from this study (Table 3) is similar to the Galveston Bay NS&T data (Morse et al. 1993) from 1986 to 1990 except for Zn, which was lower in this study. The NS&T Program only sampled six sites in Galveston Bay and the averages could be strongly affected by local inputs. Trace metal concentrations in Galveston Bay oysters are not much different from the averages of the entire Gulf of Mexico (NS&T data), except for As, which is much lower in Galveston Bay. Comparing Galveston Bay with another important seaport for shipping in

TABLE 4. Comparison of trace metal concentrations in oysters from different estuarine systems (all values in ppm dry weight).

	Ag	As	Cd	Cu	Fe	Pb	Zn
This study <sup>a</sup>	2.96 (0.84–17)	4.92 (3.03–6.83)	3.52 (1.71–6.55)	150 (61–360)	424 (146–966)	0.7 (0.27–1.49)	2,082 (602–4,819)
Galveston Bay <sup>b</sup>	2.77	4.5	4.33	165	275	0.71	3,263
US Gulf of Mexico <sup>c</sup>	2.24	9.69	4.2	156	320	0.69	2,417
Corpus Christi Bay <sup>d</sup>	1.66 (0.6–2.7)	10.31 (6.6–13)	6.87 (3.85–12.5)	163 (76–250)	247 (120–470)	0.84 (0.34–3.0)	4,150 (1,900–6,700)
Tampa Bay <sup>e</sup>	1.21 (0.2–2.7)	8.57 (3.5–26)	2.59 (1.0–5.4)	80 (7–195)	261 (155–530)	0.82 (0.08–2.05)	2,268 (430–8,600)
Hong Kong <sup>f</sup>		(15–20)	(6–8)	(400–950)		(4–8)	(1,500–2,400)
Chesapeake Bay <sup>g</sup>	(3–25)			(100–600)			
Chesapeake Bay <sup>h</sup>				(150–600)			(5,000–17,000)
Chesapeake Bay <sup>i</sup>			6.1 (0.3–39)	159 (15–718)		0.96 (0–79)	3,975 (60–12,800)
England <sup>j</sup>			(1–9)	(100–7,000)	(150–800)	(4–15)	(1,000–16,000)

<sup>a</sup> Year-round average of this study (49 samples of about 20 oysters each).

<sup>b</sup> NS&T 1986–1990, 78 pooled samples of 20 oysters each; Morse et al. (1993).

<sup>c</sup> NS&T 1986–1990, 874 pooled samples of 20 oysters each; Morse et al. (1993).

<sup>d</sup> NS&T Corpus Christi 1986–1988, 18 pooled samples of 20 oysters each; Presley et al. (1990).

<sup>e</sup> NS&T Tampa Bay 1986–1988, 37 pooled samples of 20 oysters each; Presley et al. (1990).

<sup>f</sup> *Crassostrea gigas*, pooled samples of 20 oysters; Ashton (1991).

<sup>g</sup> Pooled samples of 10 oysters; Riedel et al. (1995).

<sup>h</sup> Averages of 25 oysters; Wright et al. (1985).

<sup>i</sup> Averages of 985 oysters (assuming 80% water content by weight); Eisenberg and Topping (1984).

<sup>j</sup> Averages of 17 or 25 oysters; Boyden and Phillips (1981).

Texas, Corpus Christi Bay, most trace metal concentrations (except Ag) are lower in Galveston Bay. When Galveston Bay is compared with another estuary surrounded by a high population area, Tampa Bay, only Ag is higher in Galveston Bay, largely due to two sites (GBSL and WBSD) with strong localized Ag inputs. Notice NS&T data are used for Corpus Christi and Tampa bays (winter sampling) and they are compared to our winter data. Comparing Galveston Bay to other estuarine systems with large urbanization effect (Hong Kong, Chesapeake Bay, and Fal Estuary, England), we conclude that trace metal contamination problems are less serious in Galveston Bay.

#### TEMPORAL CHANGES IN METAL CONCENTRATIONS

Decreasing metal concentrations from summer to winter, by a factor of 3–4, were commonly found at most sites in this study. Similar results of high metal concentrations in oysters during summer months that decreased by a factor of 3–5 have been observed in Chesapeake Bay (Wright et al. 1985; Sanders et al. 1991; Riedel et al. 1995) and England (Boyden and Phillips 1981).

Okazaki and Panietz (1981) calculated the biological half-life for trace metals in northern California *Crassostrea virginica* by transplanting oysters containing higher metal concentrations to a relatively pristine site (Cu, 156 d; Ag, 149 d; Zn, 183 d; Fe, 73 d). In Galveston Bay, Ag, Cu, and Zn concentrations decreased to about half the starting values in time periods of 3 mo to 9 mo (e.g., EBFR from summer to fall; GBSL from winter to spring; most other sites from summer to winter or spring). This shows that the half-life of these metals in undisturbed oysters can be less than 100 d but is likely to vary considerably over a small geographic area.

#### Conclusion

Significant spatial and temporal variations were observed for all trace metal concentrations, except for As, determined in this study. Within a site at a given time, Ag, Cu, Fe, Pb, and Zn concentrations in individual oysters varied greatly (coefficients of variation from 13% to 86%), with skewed distribution. The high coefficient of variation of trace metal concentrations in oysters within a site suggests that in order to obtain representative metal concentrations, a large number of individuals (15–20) would be needed, including different sizes from the same population. Among the metals having large intra-sample variability, Fe and Pb concentrations were negatively correlated with body size (individual dry weight). Iron and lead concentrations in oysters seemed to be directly related to concentration in sediments at each location, possibly due to sediment in the oyster soft parts.

The most dramatic spatial variations of trace metal concentrations in oysters were seen along a salinity gradient at three East Bay sites. Concentrations of Ag, Cu, and Zn increased with decreasing salinity. At the westernmost site, EBHA (high salinity), Ag, Cu, and Zn concentrations were significantly lower than the overall bay averages but were significantly higher at the easternmost site (EBFR) in the summer. Salinity seemed to play a major role in determining bioaccumulation of Ag, Cu, and Zn in this visually pristine area.

The site GBSL near Swan Lake at lower Galveston Bay had Ag, Cu, Pb, and Zn concentrations in oysters much higher than the overall bay averages, suggesting that this site has above average anthropogenic trace metal inputs, probably from industry at nearby Texas City. Data from a few other sites also suggest localized metal inputs compared with baywide averages. Looking at the Galveston Bay estuarine system as a whole, however, trace metal pollution problems are not serious compared to many other estuarine systems (e.g., Chesapeake Bay, Hong Kong, and Fal Estuary).

Seasonal changes in metal concentrations were a factor of 3–5 at many sites in Galveston Bay oysters. Copper concentration decreased from 224 ppm in the summer to 122 ppm in the winter, thus yielding an average half-life near 200 d. Excluding two sites only sampled in winter and spring, the overall average Zn concentration changes from summer to winter by almost a factor of 3 in 9 mo, or a factor of 2 in 6 mo. These changes are consistent with observations of Okazaki and Panietz (1981). These large temporal variations in trace metal concentrations indicate that, even under natural environmental conditions, oysters are able to depurate trace metals (Ag, Cu, Zn, and Fe) rapidly. These oysters seemed to accumulate and depurate trace metals in response to changes in environmental conditions. Under conditions such as constant high salinity, they maintained trace metal concentrations (Ag, Cu, and Zn) at constant levels. Spawning could not be documented as a cause of variation in metal concentrations in oysters in this study. In any case, a weight change due to spawning can only account for part of the change in Cu concentration because it changed by up to a factor of 5 while the body weights only changed by a factor of 2–3.

The strong correlations between Fe and Pb, Zn and Cu, and Cu and Ag found almost everywhere during this study suggest that these metals change proportionally due to changes in environmental conditions (such as salinity, DOC, or turbidity). It seems unlikely, but not impossible, that anthropogenic inputs of two metals would change over time to the same extent. Additional data on many en-

environmental conditions are needed in order to determine the reasons for variations in trace metal concentrations in oysters because both water and sediment characteristics can have an influence.

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