

Toxicants in Water

Dissolved and Particulate Trace Metals in the Galveston Bay Water Column

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Heavy metals are among the most toxic, ubiquitous, and persistent contaminants in estuarine habitats. Metals that are dissolved or suspended in the water column can degrade water quality and can become available to floating and swimming organisms and bottom-dwelling filter feeders. Also, although the majority of environmental metals reside in bottom sediments, the principal transport pathway is in the water column. Unfortunately, almost nothing is known about the physical and chemical pathways of these toxicants in the aquatic environment. Worse still, for Texas estuaries there has been *no* reliable data on even the concentration of trace metals. This abstract describes what we believe to be the first reliable, systematic measurements of trace metals in the water column of Galveston Bay.

Trace metals (zinc, lead, copper, and silver) were measured in water samples collected from throughout Galveston Bay in summer and fall, 1989. Metals were differentiated between operationally defined dissolved and particulate forms, depending on whether or not they passed through 0.4 μm filters. Parallel measurements were made of salinity, alkalinity, dissolved organic carbon (DOC), nutrients (P and N species), and suspended particulate matter (SPM). Ultraclean techniques were used during all stages of sample collection, transport, handling, processing, and analysis. Metals were pre-concentrated on columns of silica-immobilized 8-hydroxyquinoline, eluted with acid, and analyzed by graphite furnace atomic absorption spectrophotometry. Our method extensively uses blanks, controls, and certified reference seawaters. The extreme care and high sensitivity of our method make these the first reliable and accurate measurements of trace metals in Galveston Bay waters. Our measured metal concentrations are typically 100 to 1000 times lower than previous measurements.

Samples were collected over salinities ranging from 0.1 to 27.4 ‰, and particulate matter levels from 2.4 to 48.4 mg/l. Particulate matter did not show a consistent trend with salinity on the two sampling dates. In August, there was a mid-salinity SPM maximum, while in October, there was an SPM minimum at intermediate salinities. The differences at a given location probably reflect different levels of wind-driven mixing and turbulence, and consequent variable sediment entrainment in the water column of this shallow estuary.

DOC levels in the fresh water samples on the two dates were 5.5 ± 1.4 and 5.3 ± 0.2 mg/l, while in the Gulf of Mexico samples it was 0.1 ± 0.3 and 0.29 ± 0.14 mg/l. DOC showed very consistent behavior on the two dates, decreasing non-conservatively across salinity in both cases. There is clearly a sink for DOC within Galveston Bay, and this is consistent with previously observed removal of DOC via flocculation with increasing ionic strength. Alkalinity was nearly constant at about 2 meq/l across all salinities in this estuary.

In general, trace metals concentrations were only slightly higher than open ocean values, and are similar to measurements from other estuaries, conducted by careful analysts. Average metal concentrations and standard deviations are given in Table 1.

Table 1. Mean and standard deviations for trace metal concentrations.

	Dissolved ($<0.4 \mu\text{m}$)	Particulate ($>0.4 \mu\text{m}$)
Zinc (ppb)	1.68 ± 1.14	1.04 ± 0.66
Lead (ppb)	$0.071 \pm .029$	$0.209 \pm .150$
Copper (ppb)	0.86 ± 0.33	0.15 ± 0.10
Silver (ppt)	3.2 ± 2.7	2.8 ± 1.5

Dissolved metals did not show systematic variations with salinity, while particulate metals showed trends that were broadly similar to suspended particulate matter.

Galveston Bay is very shallow, so SPM levels, and their trace metal burdens, should be dominated by resuspension and settling of bottom sediments. Because of this close coupling, it seems likely that particulate metals in the water column will reflect levels in surficial bottom sediments. As expected, the concentrations of metals on suspended particles (calculated per mass of SPM) vary over a range that brackets the average values in surface sediments. We have also observed that particulate metal concentrations (per mass of SPM) decrease with increasing SPM levels. This is because low levels of SPM are composed mainly of fine sediments, which preferentially bind trace metals.

Dissolved trace metals do not show a simple pattern relative to salinity or SPM concentration. Based on our research using naturally occurring radionuclides, we believe that trace metals are scavenged and released very rapidly in Galveston Bay waters. This means that dissolved trace metal levels are the result of rapid adsorption to and desorption from SPM, which in turn is derived by resuspension of bottom sediments. Thus dissolved trace metal levels are controlled mainly by the coupling of two processes: 1) resuspension of bottom sediments to yield particulate metals; and 2) steady-state or equilibrium partitioning of metals between solid and liquid phases. As a result, dissolved trace metal levels should depend both on the quantity of suspended particles, and on its partitioning characteristics. Further research is needed to elucidate the details of this relationship.

Important Factors and Parameters in Monitoring Organic Pollution in Galveston Bay

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The Galveston Bay system is of extreme importance to many industries in Texas including fisheries, chemical industries, and tourism/recreational activities. For example, more than half of the nation's petrochemical industries contribute to the economy of the areas surrounding the Bay. Some of the users of the bay have conflicting requirements. While it is a vital nursery ground for the shell and fin fish industries, it may also be polluted by the chemical users. Thus, a well-managed bay by all users is a desirable aim. Pollution of Galveston Bay, whether accidentally or by negligent acts, can result in adverse or even fatal consequences to components of the ecosystem. Management of pollution in Galveston Bay (and knowledge of other nearshore waters) requires detailed and reliable information. This includes sources of pollution, distribution or circulation of pollutants, understanding of mechanisms of sinks and fates of the pollutants, concentrations of pollutants present in the water, and pollutant biological effects.

Anthropogenic organic pollutants, i.e., organic compounds introduced into the estuary by industry or other man-related activities (e.g., industrial discharges and chemical spills) are important sources of aquatic pollution. However, readily available published referenced reports on levels of organic pollutants and their toxic effects on aquatic life in Galveston Bay are extremely scarce. Thus, recently (1989) the Galveston Bay National Estuary Program funded creation of a Galveston Bay Bibliography and reference collection, to be accomplished by the Galveston Bay Information Center. When available, reports on pollutants are often not comparable and they may reflect different periods, sites, sampling methodologies and precautions, analytical protocols, and sampling matrices. For example, a literature survey on distribution of organics and physiological effects in Galveston Bay accessed only 24 publications for the period 1900-1989. Of these publications, 18 had data on man-made organics in Galveston Bay but they are not sufficient to predict present or future trends. A systematic history of pollution by organics in Galveston Bay is not available.

Where available, there are generally four types of organic analyses of environmental samples. The first includes biological oxygen demand (BOD), chemical oxygen demand (COD), and oil and grease determinations. These tests are commonly used by state and other regulatory agencies. Use of data from these studies for monitoring pollution in the bay are very limited at best due to the large number of factors that influence these determinations.

The second category is hydrocarbon analysis, including polycyclic aromatic hydrocarbons. This type of analysis may provide information on total or individual hydrocarbon concentrations. Data on individual hydrocarbons is useful, but limited to monitoring of oil pollution rather than other industrial organic discharges. Recent levels of compounds in category two detected in Galveston Bay sediment samples were at part per billion (ppb) levels and included

benzo(a)pyrene, anthracene, phenanthrene, chrysene, pyrene, and naphthalene (Giam, 1990; Landry, *et al.*, 1989; Murry, *et al.*, 1981). Benzo(a)pyrene (at ppb levels) has also been detected in flounder and blue crab (Murray *et al.*, 1981).

Thirdly, levels of "insecticides" may be determined. Sources of these compounds include agriculture and "home usage." Compounds in category three detected in Galveston Bay sediment (at ppb levels) and water (at part per trillion [ppt] levels) include lindane, DDT, and dieldrin (Ray *et al.*, 1983).

The fourth category is man-associated or anthropogenic organic compounds. Compounds in category four detected in Galveston Bay sediment (at ppb levels), water (at ppt levels) and biota (at ppb levels) include phthalates, polychlorinated biphenyls, hexachlorobenzene and pentachlorophenol (Giam, 1990; Landry, *et al.*, 1989; Murry, *et al.*, 1981). Many compounds in categories three and four are toxic to bay inhabitants and as such their concentrations should be monitored closely. (Because of the absence of intercalibrations among other analysts for pollutants, only our measurements are discussed in this paper. Our laboratory has successfully participated in national and international intercalibration exercises.)

Good measurements of organic pollutants in the marine environment are demanding; they require special samplers (Atlas and Giam, 1986; Giam and Chan, 1976), pre-cleaned and appropriate sample containers (Atlas and Giam, 1986; Giam and Chan, 1976), sensitive and specific analytical procedures (Giam, 1990; Landry, *et al.*, 1989; Murry, *et al.*, 1981; Atlas *et al.*, 1981; and Giam *et al.*, 1978), and critical evaluation of data (Giam, 1990; Landry, *et al.*, 1989; Murry, *et al.*, 1981; Atlas *et al.*, 1981; and Giam *et al.*, 1978). Thus, it is critical that the samplers and sampling containers be of materials that will not contaminate the samples, e.g., plastic bags, containers, tubing, shovels, etc. are not acceptable (Atlas and Giam, 1986; Giam and Chan, 1976). Highly sensitive analytical techniques are available for the measurement of very low levels (ppt) of complex pollutants in different sample matrices (Giam, 1990; Landry, *et al.*, 1989; Murry, *et al.*, 1981; Atlas *et al.*, 1981; and Giam *et al.*, 1978); they are required for estimating annual fluxes of pollutants in the marine environment. However, not many laboratories have such experience in the measurement of ubiquitous man-made organics.

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