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Trace Metal Contamination in Sediments of Barataria Bay, Louisiana

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Louisiana's coastal zone is extremely valuable to the sustained economic growth of the region. Not only does the economy depend heavily on the oil and natural gas industry but also on a highly productive fishery. Sixty-six percent of the total commercial seafood catch in the Gulf of Mexico since 1950 has been attributed to south Louisiana (Chesney et al., 2000). It is feared that pollutants produced by the oil industry and its associated activities will be incorporated into the fish of the system as has occurred in other places (Vazquez et al., 2001).

Located within this region of extreme economic importance (between the Mississippi and Atchafalaya River channels) is the Barataria estuarine system. In order to develop a baseline data set, the Barataria-Terrebonne Estuarine Program (BTNEP) funded a project to collate all the environmental data that has been collected over the past 20 years (Rabalais et al., 1995). Because of the potential for bioaccumulation, trace metals were of particular concern. Unfortunately, little water column and no sediment trace metal data existed to be included in this report and the data reported was of suspicious quality due to lack of clean sample collection and analysis techniques. This may have lead to the possibly faulty conclusion that trace metal concentrations in the system were decreasing over time.

In estuarine systems, trace metals sources are both natural and anthropogenic. It is often difficult to distinguish between these two sources due to highly variable concentrations in the water column. Many studies have shown the usefulness of sediments in understanding the anthropogenic contribution to trace metal burdens in estuarine systems (Alexander et al., 1993; Helz, 1976; Windom et al., 1989, Wong and Moy, 1984). Therefore this study collected sediments from the Barataria estuarine system and analyzed them for trace metal content. This data is compared to crustal abundance data (Wedepohl, 1995) to evaluate the importance of anthropogenic input and the data is also plotted versus depth in order to better understand the history of metal input.

MATERIALS AND METHODS

The Barataria estuary is located west of the main Mississippi River channel

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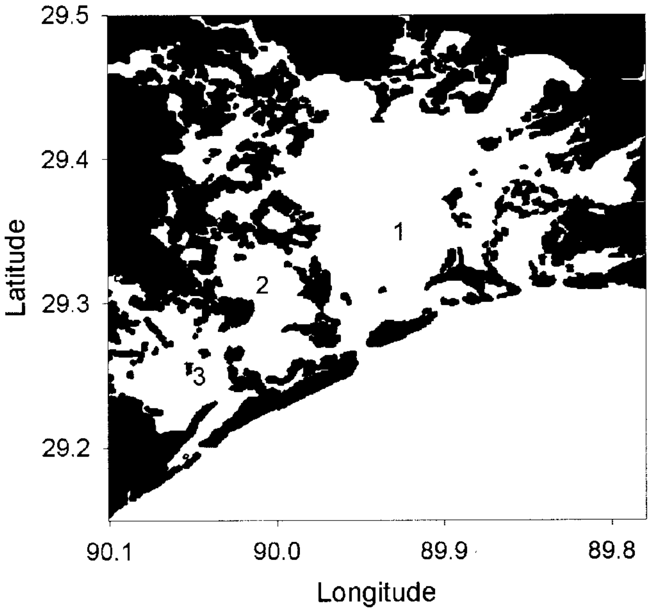

Figure 1. Station locations in the Barataria estuarine system. Station 1 is located in Barataria Bay. Stations 2 (Bay Des Illetes) and 3 (Caminada Bay) represent areas with different sedimentation rates, sediment types and waterway usage.

(Figure 1). Historically, the system acted as a natural distributary for the Mississippi River and the sediment in the system was replenished by river flooding. Today, the estuary is fed only by a diffuse flow from the north, which passes through several lakes. The main flow passes through the Barataria Bay region and there is some exchange to the open Gulf of Mexico in the western part of the estuary through Caminada Pass. While the deposition may have remained constant in this region (McKee, personal communication), the sources of this sediment are not constant as reflected in the highly variable aluminum content (an indicator of non-anthropogenic terrestrial material) in Barataria Bay and BDI (Figure 2). The flow from offshore and low freshwater flow in Caminada Bay is reflected in the relatively constant supply of aluminum. The estuary is bounded on the south by a series of barrier islands including Grand Isle, which is used extensively for recreation and commercial applications. Sedimentation rates range from approximately 0.1 cm/yr in the central estuary (Barataria Bay and Bay Des Illetes) to 0.25 cm/yr in Caminada Bay.

Sediment cores were collected at the three sites using acid-cleaned (0.5 M HCl) acrylic core tubes attached to a PVC pipe corer with a one-way check valve. The cores were sealed and transported to the laboratory at LUMCON where they were extruded and sectioned into clean centrifuge tubes using acid cleaned spatulas.

The cores from Barataria Bay and BDI were sampled down to 18 cm while the Caminada Bay core was sampled down to 30 cm in order to give a history of input for approximately the last 100 years. The sections were dried at 60°C for 4 days. The sections were then ground with an agate mortar and pestle until a fine powdery consistency was reached. The sediment was then stored in acid cleaned snap-cap vials until digestion.

The digestion procedure consisted of weighing approximately 25 mg of sediment into a small Teflon screw cap vial. Then 2 mL of 6M sub-boiling quartz distilled HCl (Q-HCl) and 1 mL of concentrated Q-HNO_3 were added. The vials were sealed and refluxed (70°C) overnight in a laminar flow hood. The samples were then cooled and 0.5 mL of concentrated Optima HF was added. The sample was refluxed an additional 24 hours before the cap was removed and the samples dried. The residue was reconstituted in 4 mL of 0.5M Q-HNO_3. Samples were analyzed using graphite furnace atomic adsorption on a Perkin Elmer Aanalyst 800 with Zeeman background correction. Procedure blanks and recovery checks were processed and analyzed with each batch of samples (1 blank and 1 standard for each 10 samples). Blanks were never more than 2% of the lowest sample and recoveries for a standard reference material (Buffalo River Sediment, NIST #8704) ranged from 93 to 104% for all metals.

RESULTS AND DISCUSSION

Station choice was initially focused on sampling a range of sedimentation rates (0.08, 0.10 and 0.25 cm/yr for Barataria Bay, Bay Des Illetes and Caminada Bay respectively). Areas with a higher sedimentation rate may dilute any signal due to pollution while areas with low sedimentation rates may have very high metal concentrations preserved in the sediments. After analysis of the sediments for metals, more differences are apparent between the sites. Organic carbon contents range from 0.5% at Caminada Bay to 3% at Bay Des Illetes. Figure 2 demonstrates how the different sites plot distinct from one another when considering Fe and Al (two crustal elements). If all the sediment was deposited and not re-worked, one might expect to find an Fe/Al ratio close to the crustal ratio (Wedepohl, 1995), or at least for all samples to plot close together since they have the same sediment source. However, it appears that the 3 sites have very different Fe/Al ratios. This may be an indication of redox processes releasing much of the Fe in both Bay Des Illetes and Caminada Bay. Iron oxyhydroxides have a high affinity for many other metals (Davis and Leckie, 1978), therefore, if all inputs are the same for the 3 sites, it would be expected that the Barataria Bay site would have a higher trace metal content and better preserve any historic anthropogenic impact.

The ratio of Pb, Cu, Zn and Cr to Al at all sites was greatly elevated over the ratios from average crustal material (Wedepohl, 1995). If plotted on Figures 3 and 4, the average crustal ratio would appear to be the y-axis. Thus even though some sites are elevated over others (discussion below) all sites show significant signs of anthropogenic impact. Association with organic matter is not the

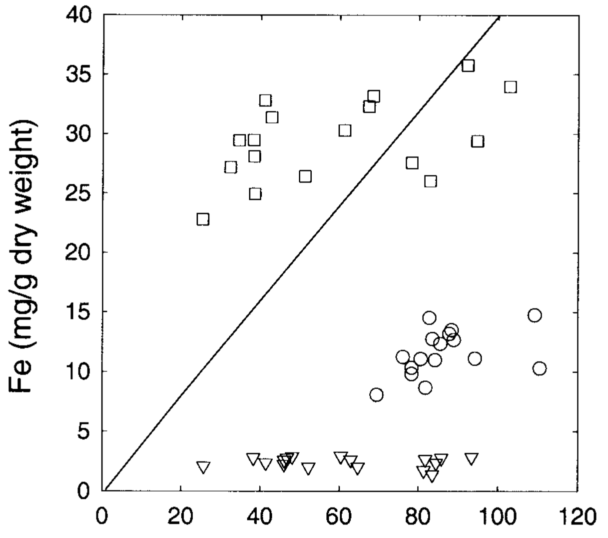

Figure 2. Concentration of Fe (mg/g) is plotted versus the concentration of Al (mg/g) at the 3 stations (Barataria Bay □, Bay Des Illetes ∇, and Caminada Bay ○). For reference, the global crustal ratio is plotted as a solid line.

controlling factor as Bay Des Illetes has the lowest metal concentration but the highest organic carbon content. These impacts may either be from the ships and boats using the bay or the oil industry in the area. Several petroleum production sites within the bay generated produced waters, which were elevated in many metals (Boesch and Rabalais, 1989). The production of these waste waters was to stop by January 1999 however several sites may still be active in the estuary as a result of an emergency order by the Louisiana Department of Environmental Quality (Rabalais et al., 1998). The discharge of this effluent may have lead to elevation of metal concentrations in the entire bay with higher concentrations near the produced water outflow. To date, no cores taken show a decrease at the surface which would indicate lower input in recent years (Figures 3 and 4). Since most discharge has been discontinued, if produced waters were the main contaminant source, it might be expected that cores taken 10 or 20 years in the future would show decreased metal concentrations.

The Barataria Bay site does have high concentrations of all four metals measured (Figures 3 and 4). However, Caminada Bay is elevated for Zn and Bay Des Illetes is elevated in Cr (Figure 4). This would imply that sorption onto Fe oxyhydroxide surfaces is not the only factor which determines sediment metal concentrations in this system. One possible explanation is that the elevated levels of Zn and Cr are driven by the location in correlation to the source of the metal. Caminada Bay is heavily utilized by both recreational and commercial boats and the Zn may be a result of anode use. While, Bay Des Illetes, because of its shallowness (less than 1 meter), is not as heavily used by boats and therefore

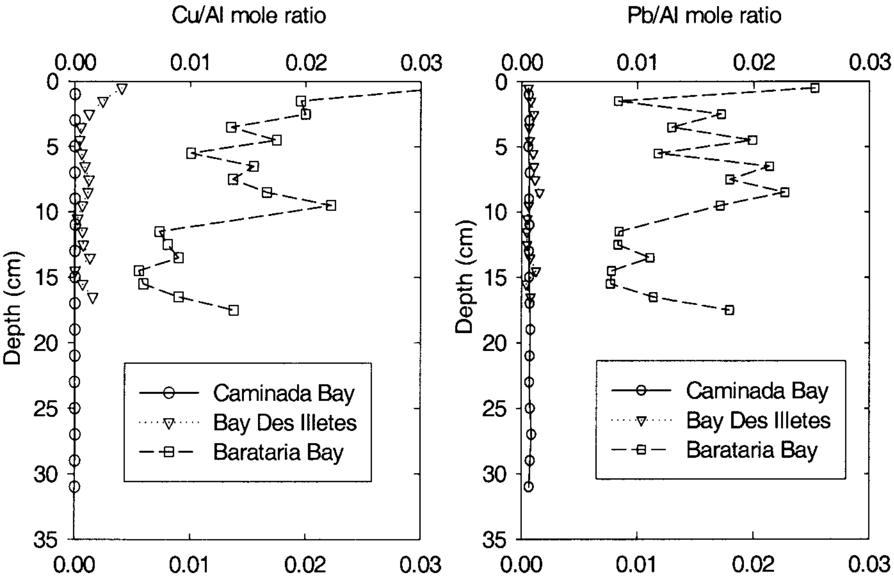

Figure 3. Cu/Al and Pb/Al mole ratios plotted versus depth for the 3 sampling sites (symbols are the same as in figure 2). Note that there is no apparent decrease at the surface with possibly even and increase.

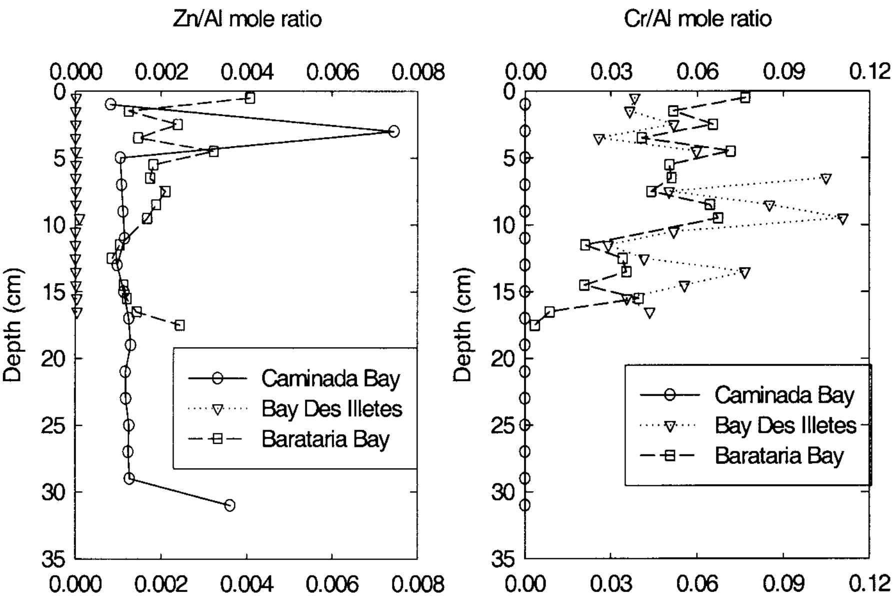

Figure 4. Zn/Al and Cr/Al ratios plotted versus depth (symbols the same as in figures 2 and 3). Note that Barataria Bay is elevated for both metals while Caminada Bay is elevated for Zn and Bay Des Illetes is elevated for Cr.

inputs would be low in this area. The elevated level of Cr in Bay Des Illetes remains relatively unexplained. Mayer and Fink (1980) suggested that surface area was the dominant factor controlling Cr concentrations in several Maine estuaries. This seems unlikely in the Barataria system since all sediment is from the same source. Also, it is unlikely that the surface area for Bay Des Illetes could be so different from Caminada Bay when their Fe/Al ratios are similar. It would seem that there must be a local source of Cr in the bay however this has not been identified.

In summary, trace metal concentrations in the sediments of the Barataria estuarine system are elevated above what is predicted from average crustal material. There is a large difference in the crustal material at the 3 sites sampled (as evidenced by the highly variable Fe/Al ratio). There is little trend with depth in the cores, however some metals at some sites show what may be increases in surficial sediment possibly indicating a recent increase in the metal source. Differences between sites are large and comparable to differences between other estuarine systems (Alexander et al, 1993). The range in sediment concentrations are hypothesized to be due to differences in sources (boats and produced waters) however this cannot be proven at this time.

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REFERENCES

Alexander CR, Smith RG, Calder FD, Schropp SJ, Windom HL, (1993) The historical record of metal enrichment in two Florida Estuaries. Estuaries 16: 627-637.

Chesney EJ, Baltz DM, Thomas RG, (2000) Louisiana estuarine and coastal fisheries and habitats: perspectives from a fish's eye view. Ecol Appl 10: 350-366.

Davis JA, Leckie JO, (1978) Effect of adsorbed complexing ligands on trace metal uptake by hydrous oxides. Environ Sci Technol 12: 1309-1315.

Helz GR, (1976) Trace element inventory for the northern Chesapeake Bay with emphasis on the influence of man. Geochim Cosmochim Acta 40: 573-580.

Mayer LM, Fink Jr LK (1980) Granulometric dependence of chromium accumulation in estuarine sediments in Maine. Est Coast Sci 11: 491-503.

Rabalais NN, Smith LE, Henry Jr CB, Roberts PO, Overton EB (1998) Long-term effects of contaminants from OCS produced-water discharge at Pelican Island facility, Louisiana. OCS Study MMS 998-0039. U.S. Department of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, LA. 88 pp.

Rabalais NN and others (1995) Status and Trends of Eutrophication, Pathogen Contamination, and Toxic Substances in the Barataria-Terrebonne Estuarine System, Publication # 22, Barataria-Terrebonne National Estuary Program.

Vazquez FG, Sharma VK, Mendoza QA, Hernandez R (2001) Metals in fish and shrimp of the Campeche Sound, Gulf of Mexico. Bull Environ Contam Toxicol 67: 756-762.

Wedepohl KH, (1995) The composition of the continental crust. Geochim Cosmochim Acta 59: 1217-1232.

Windom HL, Schropp SJ, Calder FD, Ryan JD, Smith RG, Burney LC, Lewis FG, Rawlinson CH (1989) Natural trace metal concentrations in estuarine and coastal marine sediments of the Southeastern United States. Environ Sci Technol 23: 314-320.

Wong GTF, Moy CS (1984) Cesium-137, metals and organic carbon in the sediments of the James River Estuary, Virginia. Est Coast Shelf Sci 18: 37-49.