INTERPRETATION OF ANTHROPOGENIC ENRICHMENT OF METAL CONCENTRATIONS IN SEDIMENTS FROM A SAVANNAH HARBOR BOAT SLIP

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REFERENCE: *Proceedings of the 2005 Georgia Water Resources Conference,* held April 25-27, 2005, at the University of Georgia. Kathryn J. Hatcher, editor, Institute of Ecology, The University of Georgia, Athens, Georgia.

Abstract. Metal contamination of estuarine sediments, especially in industrialized and highly developed areas such as the Savannah Harbor, have been a persistent and increasing problem in Georgia and elsewhere. Previous studies (Chen, 1993 and Alexander et al., 1997) of radiotracer-dated sediment cores from a relic Savannah Harbor boat slip (Slip 1) showed increasing metal concentrations in the 1940s and 1950s, followed by a decrease in the late 1960s. These trends have been attributed to the increased development of Savannah's port facilities in the 1950s and 1960s, with the beneficial effect of pollution controls explaining the decreasing trend. As part of recent studies of Slip 1 sediments conducted by ATM, metal concentrations in sediment cores from 1998 and 2004 have been normalized to a reference element (e.g., aluminum) and compared to benchmarks of anthropogenic enrichment. This comparison showed that sediments deposited in Slip 1 since the 1940s had the greatest anthropogenic enrichment. Recent samples reflecting sediments deposited since 1998 showed overall lower levels of anthropogenic enrichment and may indicate that the pollution controls of recent decades are working. However, these samples also showed that lead is ubiquitous in Slip 1 sediments and that there must be continuing sources of arsenic, chromium, manganese, and zinc in the Savannah Harbor.

INTRODUCTION

Slip 1 Sediments

Information on the history of Slip 1 is imperfect, but the original excavation was apparently created in the 1880s by a ship repair company for use as a dry dock. Shortly thereafter, an unknown corporation purchased the property and excavated Slips 1 to its areal extent before work began on the present project. By 1925, wharves and warehouse buildings lined both sides of the slip; these facilities were reportedly used for the storage and transportation of cotton and naval stores such as turpentine, lumber, salt, etc. Shortly after World War II, the slip was abandoned and over the years completely filled in with sediments settling out from the water column. Slip 1 remained relatively undisturbed until 1998 when it was dredged to a depth of (-)15.5 ft MLW in support of the development of Hutchinson Island. ATM's investigation of Slip 1 in 1998 was aimed at (1) analyzing the sediments deposited in Slip 1 since regular maintenance dredging of the slip stopped after World War II, and (2) evaluating the potential effects of dredging and disposing of these sediments.

BACKGROUND AND PREVIOUS STUDIES

Slip 1 is one of several boat slips on Hutchinson Island associated with relic shipping terminals that had been abandoned for over fifty years. Much information about the sediment quality, rate of deposition, and source of material in Slip 1 was determined through previous investigations by Alexander et al. (1997) and Chen (1993).

After abandonment, the slip began to fill in with material eroded from the Savannah River watershed. As evidenced by the geologic cores and results of grain size analysis, the slip filled in with clay size particles falling out of suspension from the water column. It was assumed that the original depth of the boat slip was (-)21 ft MLW, the same depth of the Savannah River Channel in 1911. The rate of deposition in Slip 1 was calculated to range from 3.3 to 19.3 cm per year (Chen 1993). The rate of deposition ranged significantly due to the influences of a changing depositional environment.

Pollution History of the Savannah Estuary

The Savannah River Estuary study detailed in the report *Pollution History of the Savannah Estuary* (Alexander et al., 1997) is a product of research to gather information on long term trends in contamination of US coastal and estuarine sediments. The study included the collection of dated cores from different sites in the Savannah Estuary and analysis for sixteen metals. Ages were assigned to different depth intervals within each core by use of two radiotracers, ^{210}Pb and ^{137}Cs. Changes in the concentrations of contaminants in the cores were used to reconstruct the history of contaminant input to the Savannah Estuary. In summary, the study presents evidence of relatively large inputs of anthropogenic metals (e.g., mercury, chromium and lead) during the 1950s and 1960s into the Savannah Estuary. This was followed by a gradual decrease of these metals over the past 20 to 30 years.

Mercury, lead and chromium all showed significant temporal changes down dated cores in the Savannah Estuary. The changes were most pronounced in Core H, which was collected from Slip 1 on Hutchinson Island. Core H was collected to a depth of 5.25 m (-17.2 ft MLW) and represented sediments aged between 1920 and 1993. Chromium concentrations in Core H rose during the 1940s and early 1950s followed by a decrease in the late 1950s, 1960s and 1970s. In 1968 there was a sharp peak in mercury concentrations in Core H. Lead concentrations increased in the 1940s and 1950s followed by a decrease in the late 1960s. The increase in metal concentrations is likely due to the increased development of the port of Savannah in the 1950s and 1960s. The subsequent decrease in the concentration is presumably due to the effect of pollution controls applied to those industries, since industrial growth has continued up to the present.

Trace Element Distributions in Salt Marsh Sediments: The Relative Importance of Non-Steady State and Diagenetic Processes

This thesis (Chen, 1993) is a study of non-steady state and diagenetic processes in the Savannah and Ogeechee estuaries. The study includes the testing of sediment samples for 13 metals. Similar to Alexander et al. (1997), ages were assigned to different depth intervals within each core by use of two radiotracers, ^{210}Pb and ^{137}Cs.

Chen used the same sediment cores as those used in Alexander et al. (1997). The core labeled Core A-2 in Chen (1993) corresponds to Core H from Alexander et al. (1997), which was collected from Slip 1. Although Chen (1993) uses the identical core sample, the tests were conducted on different depth intervals of the core — i.e., Chen (1993) tested core depth intervals 0-2 cm, 5-7 cm, 10-12 cm, etc., and Alexander et. al (1997) tested core depth intervals 0-1 cm, 19-20 cm, 39-40 cm, etc.

Since the tests performed on Core A-2 (Chen, 1993) and Core H (Alexander et al., 1997) used different sediments from the same core, the results for both Core A-2 and Core H can be mathematically composited. This yields an average concentration of each contaminant for the entire core sample, representing sediments from 1920 to 1993, which is presented in Table 1.

METHODS

ATM developed Sampling and Analysis Plans for Slip 1 in 1998 and in 2004 in support of environmental effects evaluations of dredged sediments from the slip. Four sediment cores were collected from the slip using vibracore technology in 1998 and again from approximately the same locations in 2004. The existing depth of sediments at the sample locations ranged from (-)0.5 ft MLW to (+)4.0 ft MLW in 1998. The existing depth of sediments at the sample locations in 2004 ranged from (-)4.0 ft MLW to (+)4.0 ft MLW. The depth of penetration for the four cores ranged from (–)17 ft MLW to (-)19 ft MLW. All sediments samples were submitted in laboratory-supplied sample containers to an analytical laboratory for chemical analysis. A sample from each core vertically composited over the entire core was also analyzed for grain size distribution.

Vibracore Sampling

Athena Technologies, Inc. (ATI) performed the vibracore collection work for the Slip 1 Hutchinson Island work in 1998 and 2004. ATI employed a 46-foot research vessel (Lady Athena) as the primary sampling platform. Final site coordinates were taken by a portable differential GPS unit. Water depths were taken using a Hummingbird^{tm} depth sounder or lead line at the sites accessible to Lady Athena. Upon reaching a vibracore station, Lady Athena was triple-point anchored to ensure that the desired position was held during the vibracoring procedure. Vibracore samples were collected aboard Lady Athena using a 23-foot long, 3-inch diameter, decontaminated aluminum sample barrel. Vibracoring was performed until penetration met desired depth. The vibracore sample was extracted from the sample barrel aboard Lady Athena by vibrating the sample out of the core tube into a stainless steel pan. An ATI geologist logged the core as it was extracted from the sample barrel. The sample was then sub-sampled, placed in sample jars provided by the analytical laboratory and iced down inside coolers to keep the samples at 4°C.

Four vibracores were taken from the extraction site (SHHIS1VC*x* where *x* is 1 through 4), with two cores collected from each side of the slip. The four cores were homogenized in the laboratory and tested for an extensive list of metallic elements.

Sediment Chemical Analysis

The individual vibracores were analyzed for a list of sixteen metals including two reference elements: Aluminum (Al) and Iron (Fe), which are usually expressed as percentages, and

Table 1. Mathematically Averaged Sediment Data for Core A-2/H

ANALYTE	UNITS	VALUE
Aluminum	(%)	12.2
Cadmium	ppm	0.297
Chromium	ppm	84.7
Copper	ppm	35.7
Iron	(%)	6.05
Lead	ppm	47.1
Manganese	ppm	760
Nickel	ppm	31.9
Zinc	ppm	118

Source: Alexander et al. (1997) and Chen (1993); calculations by ATM fourteen target metals: Antimony (Sb), Arsenic (As), Beryllium (Be), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Manganese (Mn), Mercury (Hg), Nickel (Ni), Selenium (Se), Silver (Ag), Thallium (Tl), and Zinc (Zn).

To properly utilize applicable Sediment Quality Guidelines and the metals interpretive tool, "total" digestion of the sediment using hydrofluoric acid was performed on the metals samples. Results from the previous studies described in the Background section (Core A-2/H; Chen, 1993; Alexander et al., 1997) also used total digestion.

FINDINGS AND CONCLUSIONS

According to geologic logs and in comparison with grain size analysis, the dominant feature shown from physical analysis of the 1998 Slip 1 vibracores was the homogeneous nature of the clay-sized material (71.3 to 78.8%) present in Slip 1 in 1998. In 2004, the percent of clay-sized material in the sediment samples decreased slightly with a corresponding slight increase in sand and silt content over the 1998 samples. Table 2 summarizes pertinent physical and descriptive information gathered on the 1998 and 2004 sediment samples.

Based on depth of penetration, the 1998 Slip 1 cores (depth of penetration (-)17 to (-)19 ft MLW) represent a similar distribution of sediment as the A-2/H cores collected and analyzed by Alexander et al. (1997) and Chen (1993), which had a depth of penetration of (-)17.2 ft MLW. In contrast, reflecting the dredging of Slip 1 that occurred after the 1998 sampling event, the 2004 cores represented approximately 80% maintenance material and 20% "new work" material (i.e., material between (-)15.5 to (-)17.0 ft MLW). Based on comparison to depth and radiotracer dating for Core A-2/H, the "new work" material in the 2004 core samples should be similar to the oldest section of Core A-2/H (e.g., from the 1920s).

Metals Interpretive Tool—Aluminum Normalization

Since metals naturally occur in sediments at varying concentrations, a metal enrichment test is particularly important. The most promising tool for testing for anthropogenic enrichment is a metals interpretive tool that normalizes metal concentrations to a reference element (usually Al). Schropp et al. (1990) developed such a tool for eight metals with uncontaminated estuarine sediments from Florida and Georgia. For other metals not included in this set, the regression coefficients were obtained from work conducted on data by Hanson and Evans (1990) and Hanson et al. (1993). Only two elements, Sb and Be did not have regression values. The Schropp et al. (1990) values were log transformed and were based on a large regional data set. The Hanson and Evans values were linear regression and did not appear to fit the data as well.

Table 3 summarizes the results of the metal concentrations for all samples normalized to 8.01% Al (the concentration in world average shale; Hanson and Evans, 1990). World average shale, Schropp et al. (1990) means, and Hanson and Evans (1990) mean metal concentrations are provided with the normalized Slip 1 data for comparison. Where the table reveals that the cored Slip 1 sediments are dissimilar from the reported means at the top of the table, anthropogenic enrichment is suggested. The results indicate potential anthropogenic enrichment in all samples analyzed.

DISCUSSION

The results presented in Table 3 suggest that the February 1998 sample cores reflect the most anthropogenic enrichment

Table 2. Summary of Slip 1 Sediment Core Sample Characteristics

Sample	%Al	%Fe	%Solids	%TOC	%Fines (<63 um)	%Gravel	%Sand	%Silt	%Clay
2004 Cores									
SHHIS1VC1	9.6	5.6	40	2.2	97.7	0.0	2.3	35.2	62.5
SHHIS1VC2	6.4	4.9	37	2.2	88.5	0.0	11.5	35.0	53.5
SHHIS1VC3	10.3	5.9	44	2.3	96.7	0.0	3.3	33.2	63.5
SHHIS1VC4	8.7	5.0	42	2.2	99.2	0.0	0.8	49.2	50.0
1998 Cores									
SHHIS1VC1	5.0	5.7	35	3.2	96.2	0.0	1.3	24.3	74.4
SHHIS1VC2	2.1	6.0	40	2.4	97.6	0.0	0.4	24.7	74.9
SHHIS1VC3	8.1	5.5	39	3.3	96.2	0.0	1.2	27.5	71.3
SHHIS1VC4	4.6	6.1	41	2.5	97.5	0.0	0.2	24.0	75.8

Note: The silt and clay fractions (mud) do not sum to the "% Fines" because the laboratory used the #200 sieve (74µm) for the fine sand and silt division. The 63µm (#230 sieve) cut-off is reported as "% Fines" for consistency with NOAA's NS&T Program.

Table 3. Comparison of Normalized (8.01% Al) Metals in Slip 1 and Comparable Sediments

			Concentration (ppm)									
Sample	**Al (%)**	**Fe (%)**	**As**	**Cd**	**Cr**	**Cu**	**Pb**	**Mn**	**Hg**	**Ni**	**Ag**	**Zn**
World Average Shale	8.01%	4.7%	13	0.3	90	45	20	850	0.4	68	0.07	95
Schropp et al. Means	8.01%	NA	17.8	0.166	39	13.5	25.2	NA	0.21	11.4	NA	53
Hanson & Evans Means	8.01%	3.9%	13.3	0.173	72	15.3	26.8	662	0.091	23.1	0.078	90
Slip 1 (May 2004)												
SHHIS1VC1	8.01%	4.7%	14.7	<0.2	67	31	32	838	0.14	31	<0.2	102
SHHIS1VC2	8.01%	6.2%	21.9	<0.3	112	40	43	1,005	0.16	40	<0.2	151
SHHIS1VC3	8.01%	4.6%	14	<0.2	51	29	34	925	0.13	29	<0.2	99
SHHIS1VC4	8.01%	4.6%	16	<0.2	66	32	36	819	0.14	30	<0.2	107
Slip 1 (February 1998)												
SHHIS1VC1	8.01%	9.1%	29	3.0	160	64	78	1,538	0.2	59	2.9	208
SHHIS1VC2	8.01%	22.9%	65	8.0	339	183	160	4,196	0.6	156	6.9	496
SHHIS1VC3	8.01%	5.4%	19	2.0	96	40	40	949	0.2	35	2.1	129
SHHIS1VC4	8.01%	10.6%	31	3.7	157	84	73	2,264	0.3	70	3.5	226
Slip 1 (1993)												
Core A-2/H	8.01%	4.0%	7	0.2	56	23	31	499	0.1	21	0.2	77

Notes: All sediments normalized to 8.01% Al; the concentration in World Average Shale. Concentrations of Al and Fe are given as percents of the dry weight sample; minor element concentrations are in parts per million (ppm).

when compared to world average shale and the Schropp et al. (1990) and Hanson & Evans (1990) means. While the 1998 core samples and Core A-2/H represent the same distribution of sediments based on depth of penetration, the 1998 samples clearly exhibit greater anthropogenic enrichment than the Core A-2/H sediments. Both of these cores reflect sediments deposited in Slip 1 from the 1920s through the 1990s, and therefore represent the greatest period of industrial activity on the Savannah River. However, the disparity of these results is likely due to different methods of sample preparation. The 1998 cores were collected and individually composited over their entire depth before chemical analysis. In contrast, specific depth intervals were collected from Core A-2/H, analyzed individually and mathematically composited. Given that over 56% (9.7 ft) of the 17.2-ft A-2/H core represents sediments from the 1920s and 1930s, the mathematical composite is overly weighted toward the less-enriched older section of the core.

Table 3 also shows that the 2004 cores are much less enriched than the corresponding 1998 core samples. The 2004 samples were collected after Slip 1 was dredged to a depth of (-)15.5 ft MLW in 1998, and therefore primarily represent sediments deposited since 1998. The 2004 cores do reflect that the pollution controls of recent decades may be working, however the cores also reflect that Pb is ubiquitous in Slip 1 sediments and that there must be continuing sources of As, Cr, Mn and Zn in the Savannah Harbor.

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