COPPER AND OTHER CONTAMINANTS IN KING'S BAY AND CRYSTAL RIVER (FLORIDA) SEDIMENTS: IMPLICATIONS FOR IMPACT ON THE WEST INDIAN MANATEE

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ABSTRACT: Contaminant concentrations were measured in 25 sediment samples collected from King's Bay, the headwaters of the Crystal River, Florida. Total organic carbon content ranged from 0.17 to 9.95% dry weight. No organochlorine pesticides, pesticide metabolites or polychlorinated biphenyls (PCBs) were detected at concentrations above the detection limit of 0.01 ppm (0.10 ppm for total PCBs and toxaphene). Antimony, cadmium, silver and tin were not detected; however, arsenic, barium, chromium, iron, magnesium, manganese, selenium, strontium and vanadium were present at above-detection-limit concentrations at all locations sampled. Aluminum data were used to normalize all other metals concentration data. Arsenic, iron, and zinc concentrations at some sampling sites; and copper concentrations (range=<3.5-237 ppm dry weight) at all sample locations; appeared to be elevated due to anthropogenic influence. If transported through the food chain, copper concentrations at the most contaminated sites may be sufficient to adversely impact the West Indian manatee (Trichecus manatus).

KEY WORDS: copper, manatee, heavy metals, sediments

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INTRODUCTION

During the late 1970's, copper-based herbicides were used extensively for hydrilla (Hydrilla verticillata) control in the Crystal River, Citrus County, Florida. From 1 November 1978 through 30 October 1979, for example, over 6 metric tons of elemental copper was introduced into this river system. Most herbicide applications occurred during the time when endangered West Indian manatees (Trichechus manatus) were most abundant.

O'Shea et al. (1984) investigated copper and other contaminant concentrations in selected tissues of 39 dead manatees. They found that, with the exception of copper, manatee contaminant loads were relatively low. When organochlorine pesticides or PCB residues were detected in more than a small percentage of the total number of animals tested, concentrations of those contaminants were also low. Lead and cadmium concentrations were found in liver and kidney tissues, respectively, from all animals examined; however, they were not great enough to warrant concern.

Copper concentrations in liver tissue ranged from 4.4 to 1,200 ppm dry weight (n=54). The six highest copper concentrations (600 to 1,200 ppm) were in manatees from the northwest coast of Florida, and five of the six were determined to be from the Crystal River population.

Although recent aquatic plant control efforts in the Crystal River have relied on alternatives other than copper-based herbicides, especially when manatees were present, the U.S. Fish and Wildlife Service (Service) suspected that significant concentrations of copper might be present in the sediments. I here report the results of an investigation to determine present (1989) copper and other contaminant concentrations in the sediments of the Crystal River-King's Bay system (Fig.1)[1].

MATERIALS AND METHODS

The top 15 cm of sediment from 25 separate sites (Fig. 2) in King's Bay, Citrus County, Florida, was double-sampled using a 50.8 cm long stainless steel hand-coring tool fitted with a lexan nosepiece. A clean CAB plastic insert was used to collect each core. At five of the 25 sites (1, 5, 6, 7 and 8; Fig. 2), two additional samples were collected. For each of these, only the bottom 7.5 cm of the 15 cm-core was retained

[1]Samples were collected and submitted for analysis by Robert J. Pennington, the former Environmental Contaminant Specialist in the Vero Beach Field Office. Current address: U.S. Army Corps of Engineers, Jacksonville, Florida.

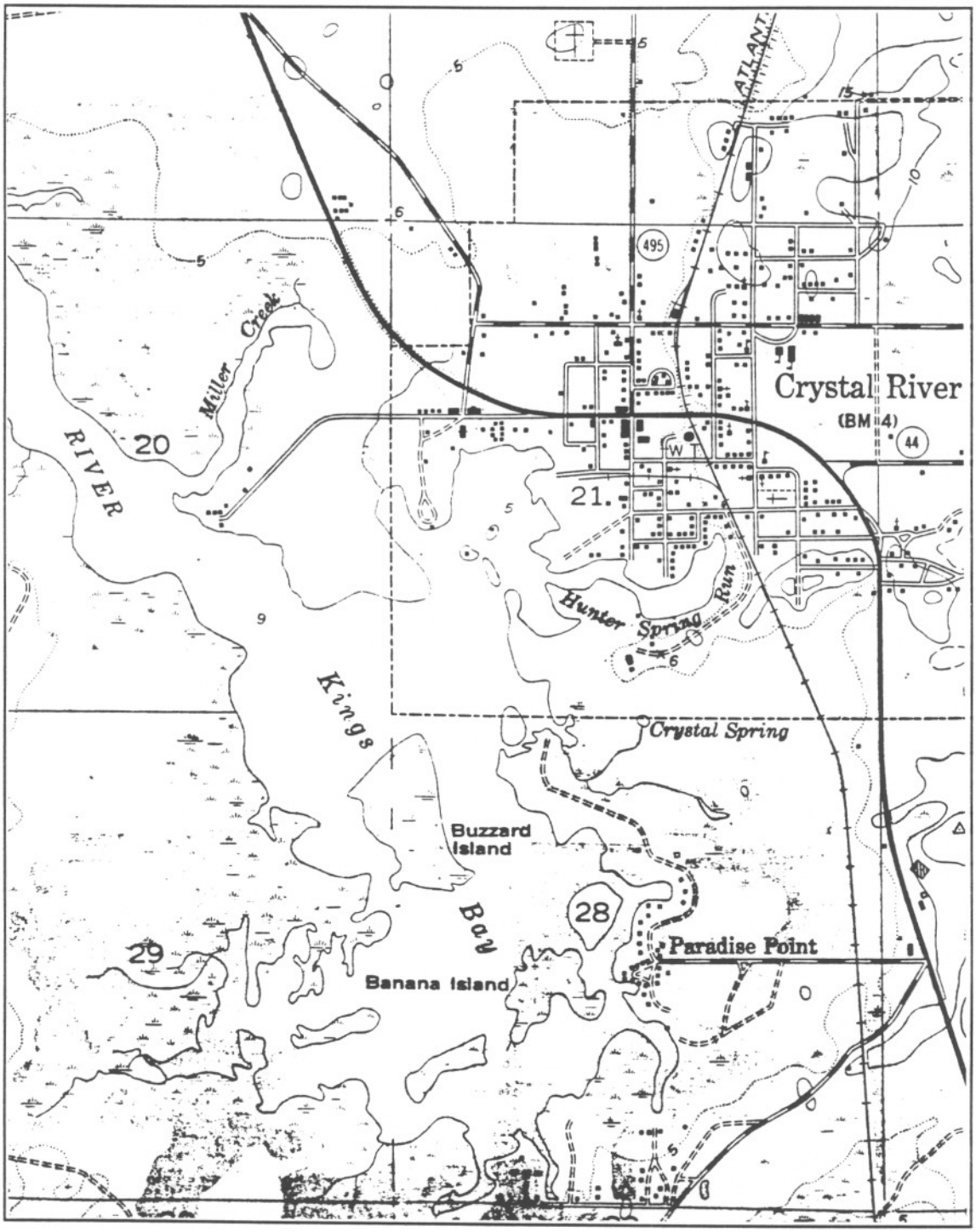

Figure 1. Map of King's Bay, upper Crystal River, and surrounding area.



Figure 2. Location of sampling sites.

to enable the detection of differences in contaminant concentrations with depth. Individual samples were placed in chemically-clean glass jars fitted with teflon-lined lids and stored on wet ice for 24 to 48 hours awaiting and during transport to the Vero Beach Field Office laboratory. On arrival at the laboratory, excess water was decanted from each jar and the samples were frozen (-15°C) awaiting shipment to the analytical facility. Samples were packed in dry ice for shipment.

One complete set of thirty samples was sent to the Geochemical and Environmental Research Group, Texas A&M University, College Station, TX, for total organic carbon (TOC), organochlorine pesticide and polychlorinated biphenyl (PCB) analyses. Quantitative analyses were performed using capillary gas chromatography (CGC) with an electron capture detector for pesticides and PCBs, CGC with a flame ionization detector for aliphatic hydrocarbons, and a mass spectrometer in the SIM mode for aromatic hydrocarbons.

Inorganic contaminant analysis was performed by the Research Triangle Institute, Research Triangle Park, NC. Quantitative analyses for aluminum (Al), antimony (Sb), barium (Ba), beryllium (Be), boron (B), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), silver (Ag), strontium (Sr), tin (Sn), vanadium (V), and zinc (Zn) were performed by inductively coupled plasma (ICP) emission measurement. Graphite furnace and cold vapor atomic absorption methods were used to measure arsenic (As) and selenium (Se), and mercury (Hg) concentrations, respectively. All concentrations are reported as ug/g (ppm) dry weight. Raw data are presented in the Appendix.

Statistical analysis was performed using log-transformed data. When the concentration at any given site was less than the detection limit (DL), a value equal to 0.75 x DL was used in the calculations. Between-group differences were determined using a single-factor analysis of variance. If significant (α=0.05) differences were found, differences between means were determined by using Duncan's multiple-range test. Student's t test was used to test for differences in contaminant concentrations due to sediment depth. All statistical analyses followed either Steel and Torrie (1960) or Zar (1974).

The method described by Windom et al. (1989) was used to determine whether inorganic contaminants were naturally occurring or likely of anthropogenic origin.

RESULTS

Organochlorine pesticides, PCBs and TOC:

Analyses were performed for α-, β-, γ-, and δ-BHC (1,2,3,4,5,6-hexachlorocyclohexane), HCB (hexachlorobenzene), heptachlor, heptachlor epoxide, α- and γ-chlordane, oxychlordane, *cis*-and *trans*-nonachlor, aldrin, dieldrin, endrin, mirex, *o*,*p*'- and *p*,*p*'-DDE, *o*,*p*'- and *p*,*p*'-DDD, *o*,*p*'- and *p*,*p*'-DDT, PCBs and toxaphene. No organic contaminants were found in any of the sediment samples at above detection limit concentrations (0.10 ppm for total PCBs and toxaphene; 0.01 ppm for all others tested). TOC content is presented in Table 1.

Inorganic contaminants:

Samples from the 25 locations (Fig. 2) were grouped according to location in the bay to facilitate statistical analysis. Seven distinct locations were recognized: Miller Creek (MC; site 1), East King's Bay (EKB; site 5), North King's Bay (NKB; sites 2-4), South King's Bay (SKB; sites 7-11), West King's Bay (WKB; sites 12-16), Central King's Bay (CKB; sites 6 and 17-20) and the Upper Crystal River (UCR; sites 21-25). Considering those elements which were detectable at all 25 locations, with the exceptions of lead and manganese, there were no significant differences between mean concentrations from the latter five locations. MC was considered singly due to geographic location. EKB was not included with any other group due to high contaminant concentrations. In many cases, contaminant concentrations in the sediment from this location were 1 to 2 orders of magnitude greater than concentrations found at any other location (see Figs. 3-27). Although mean contaminant concentrations in the entire core sample (0-15cm depth) were always greater than in the 7.5 to 15cm segment (Table 2), the difference was only significant in the case of copper ($t \approx 2.349$, $p < 0.05$).

Aluminum. Concentrations ranged from 520 to 17,900 ug/g at sites 9 (SKB) and 5 (EKB), respectively. The only location, other than EKB, where the aluminum concentration was greater than 10,000 ug/g was site 19 (CKB), near the southwest tip of Buzzard Island, where the level was 11,500 ug/g. Mean concentrations (range=1,519 to 4,470 ug/g) and distribution in the bay are shown in Figures 3 and 4. Aluminum is not commonly associated with anthropogenic inputs (Windom et al. 1989) and it was assumed that all aluminum in the sediments sampled was of natural origin. Thus, aluminum concentrations were used to normalize other data as suggested by Windom et al. (1989).

Table 1. Total organic carbon (TOC; % dw) content of King's Bay and upper Crystal River sediment samples. Values presented are geometric means. The standard error of the mean is in ()[a].

Location[b]	n	Minimum	Maximum	Mean
MC	1	-	-	4.26 (NA)
EKB	1	-	-	3.36 (NA)
NKB	2	0.32	1.23	0.63 (1.96)
SKB	5	0.17	2.95	0.76 (1.77)
WKB	5	1.36	8.38	2.57 (1.39)
CKB	4	0.52	9.61	3.10 (1.99)
UCR	5	0.23	9.95	2.68 (1.96)

[a] To determine the upper and lower intervals, multiply or divide the mean by the given value.

[b] Location: MC=Miller Creek, EKB=East King's Bay, NKB=North King's Bay, SKB=South King's Bay, WKB=West King's Bay, CKB=Central King's Bay, UCR=Upper Crystal River (see text for sample sites included in each general location.

Table 2. Mean (x/÷ S.E.) contaminant concentrations in sediments from 0 to 15 cm in depth vs. sediments from 7.5 to 15 cm (at sites 1,5,6,7 and 8). Values are ug/g dry weight.

	Depth					
	0-15 cm			7.5-15 cm		
Contaminant	Minimum	Maximum	Mean	Minimum	Maximum	Mean
Al	960	17900	3081 (1.75)	340	5160	1777 (1.63)
As	0.44	9.1	2.4 (1.87)	<0.3	6.6	1.6 (1.95)
Ba	7.0	35	13 (1.35)	3.8	18	9.7 (1.32)
Be	<0.25	0.54	0.26(1.25)	<0.25	0.31	0.23(1.12)
B	<8.0	39	14 (1.46)	<8.0	21	11 (1.26)
Cr	9.6	123	30 (1.64)	4.8	59	27 (1.58)
Cu	6.5	237	27* (2.04)	<3.5	19	3.9*(1.49)
Fe	660	16200	3409 (1.90)	160	11800	1682 (2.12)
Pb	<10	62	12 (1.53)	<10	<10	<10 (1.00)
Mg	250	2900	978 (1.66)	<100	2520	482 (1.78)
Mn	4.1	54	13 (1.57)	<3.0	44	8.6 (1.67)
Hg	<0.02	0.25	0.04(1.67)	<0.02	0.05	0.02(1.28)
Mo	<4.0	<4.0	<4.0 (1.00)	<4.0	4.1	3.2 (1.07)
Ni	<4.0	10.2	4.5 (1.30)	<4.0	5.5	3.4 (1.13)
Se	0.58	4.6	1.5 (1.49)	<0.3	2.5	0.93(1.49)
Sr	30	171	85 (1.47)	4.0	128	28 (1.81)
V	3.3	45	12 (1.60)	1.8	25	8.1 (1.55)
Zn	<3.5	72	9.1 (1.84)	<3.5	22	4.3 (1.52)

* Mean concentrations significantly different at α=0.05.

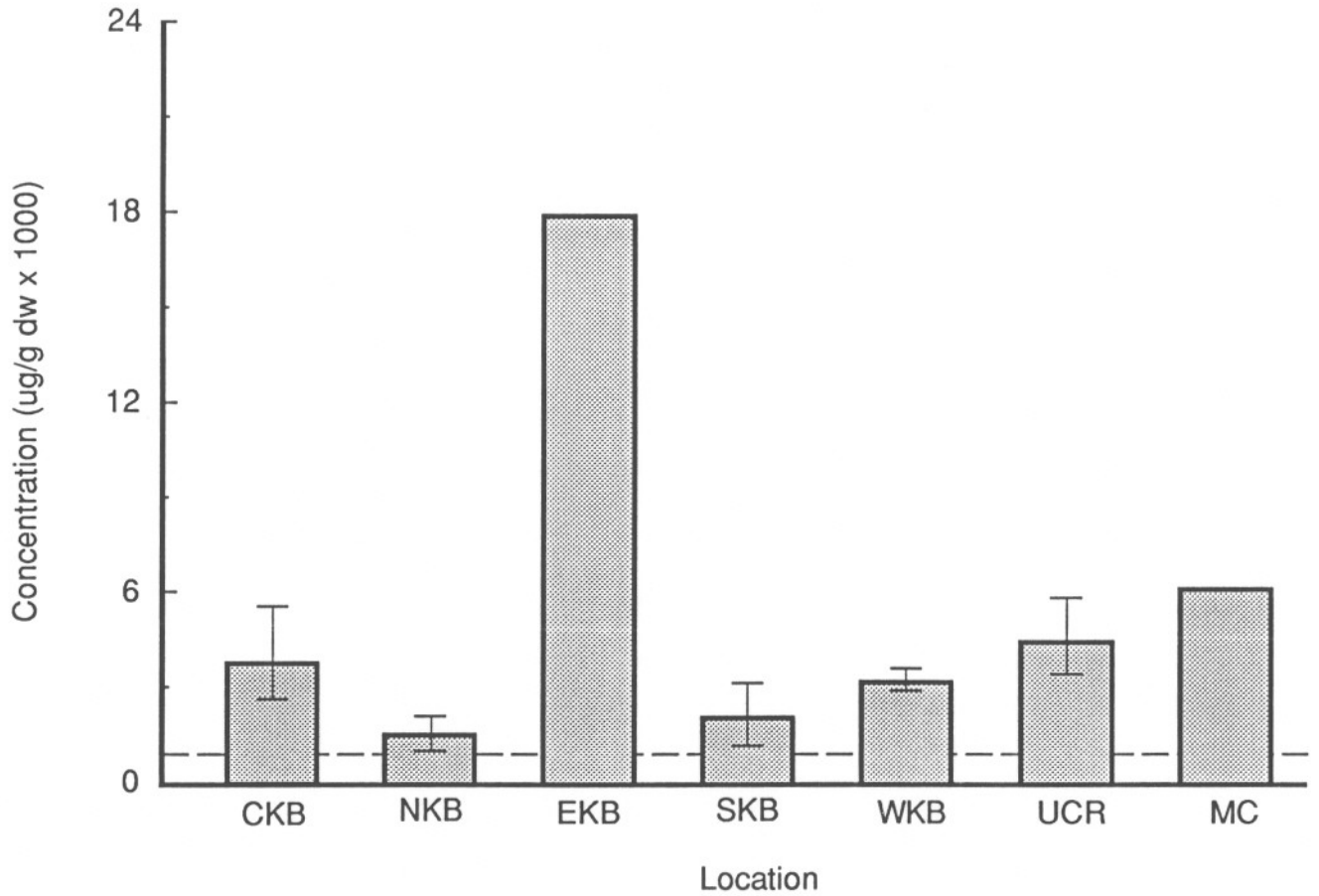

Figure 3. Mean (± S.E.) aluminum concentrations in King's Bay sediments (see text for location identification). Detection limit indicated by broken line.



Figure 4. Distribution of aluminum concentrations in King's Bay and upper Crystal River sediments.

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Antimony. Antimony was not detected at above-detection-limit (=25 ug/g) concentrations. However, the analytical laboratory stated that antimony recovery by ICP is usually low and that little confidence should be placed in the accuracy of the analysis.

Arsenic. Mean group concentrations, which ranged from 1.03 to 1.59 ug/g, are shown in Figure 5. Individual site sediment concentrations ranged from 0.336 to 9.08 ug/g and were weakly correlated with aluminum (r=0.55; Fig. 28) at all but two sites; 1 (MC) and 7 (SKB). Levels at these two sites (9.08 and 5.26 ug/g, respectively), in relation to aluminum, were much greater than expected.

Barium. Individual site concentrations ranged from 5.97 ug/g (site 9; SKB) to 35.5 ug/g (EKB). Mean concentrations (Fig. 6) varied from 10.4 to 11.3 ug/g. Barium concentrations were correlated with aluminum at all sites sampled (r=0.87; Fig. 28).

Beryllium. Beryllium concentrations ranged from below detection limits (17 of 25 sites) to 0.54 ug/g. Levels at EKB and MC (Fig. 7) were greater than those noted at other sites (range≈0.19 to 0.23 ug/g). Due to only eight values above the detection limit, a possible correlation between beryllium and aluminum was not determined.

Boron. Mean boron concentrations (Fig. 8) were more variable (range=8.0 to 19.5 ug/g) than most of the other elements included in the analysis. This may be attributable to the fact that boron recovery by ICP is often questionable. Site-specific concentrations ranged from below detection limits, in all general locations other than WKB, to 39.5 ug/g at EKB. Boron and aluminum concentrations were correlated (r=0.87; Fig. 28).

Cadmium. Cadmium was not detected in any of the samples at levels above the detection limit (=1.0 ug/g).

Chromium. The range of chromium concentrations in bay sediments varied from 7.22 ug/g at site 9 (SKB) to 123 ug/g at EKB. Mean group concentrations (range=16.0 to 34.9 ug/g) are shown in Figure 9. The estimated distribution (Fig. 10) was somewhat similar to that of aluminum (Fig. 4) as would be expected as there was a high degree of correlation between the two (r=0.96; Fig. 28).

Copper. Copper concentrations in bay sediments ranged from less than detection limits (2 sites; 2 in NKB and 8 in WKB) to 237 ug/g at EKB. Mean group concentrations (Fig. 11) ranged from 13.1 to 27.4 ug/g. General distribution of this element in the bay is shown in Figure 12. Copper and aluminum were

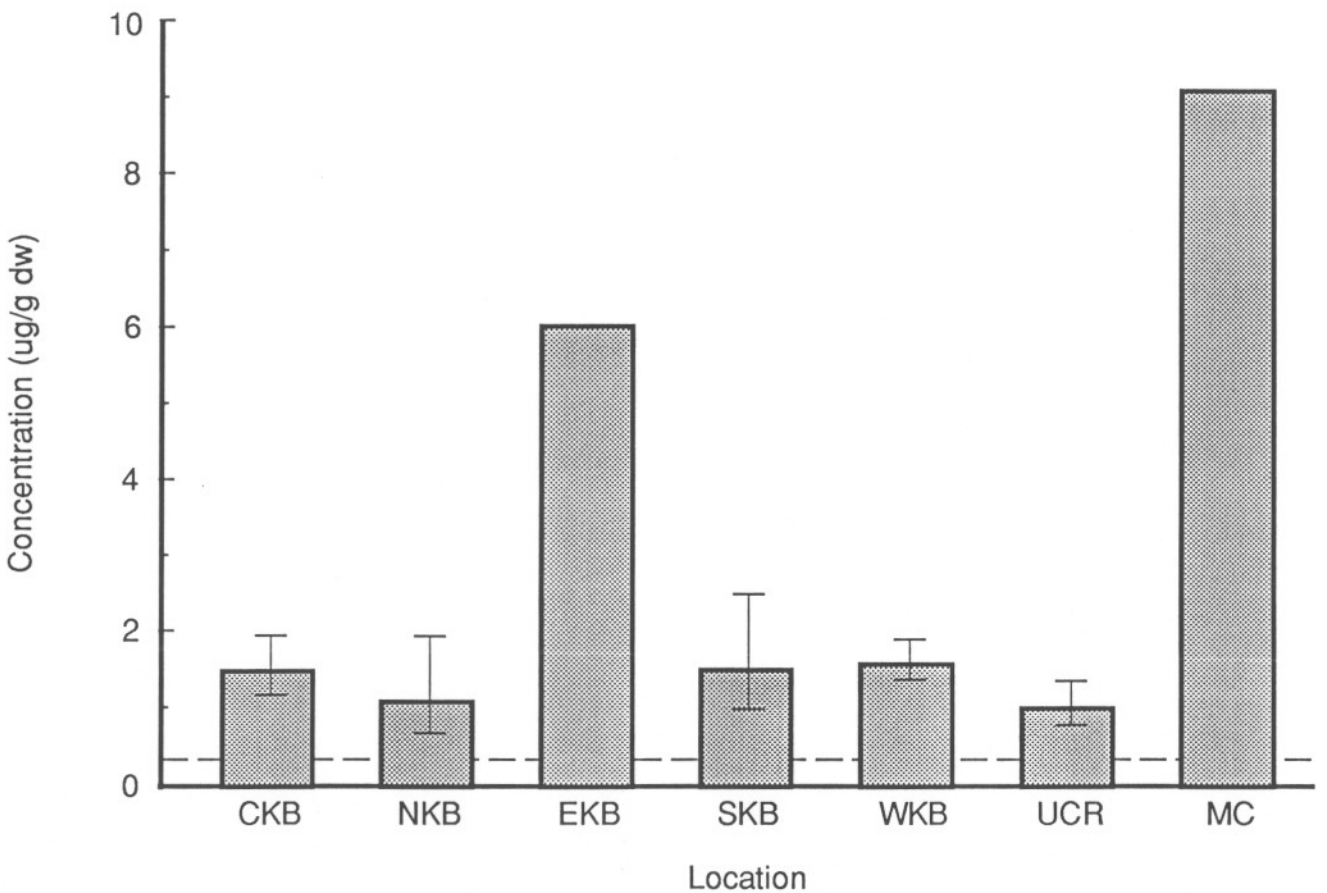

Figure 5. Mean (± S.E.) arsenic concentrations in King's Bay sediments (see text for location identification). Detection limit indicated by broken line.

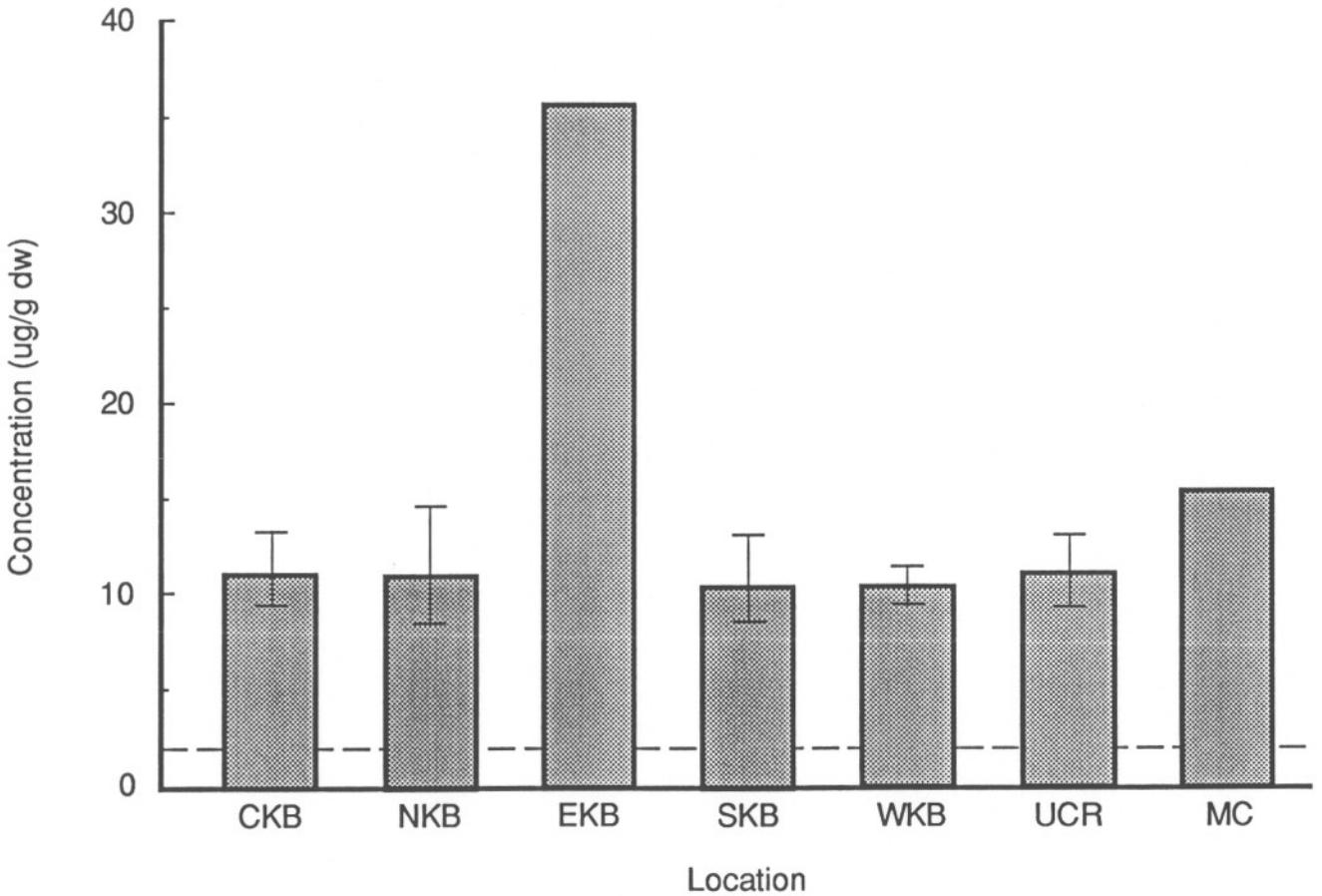

Figure 6. Mean (± S.E.) barium concentrations in King's Bay sediments (see text for location identification). Detection limit indicated by broken line.

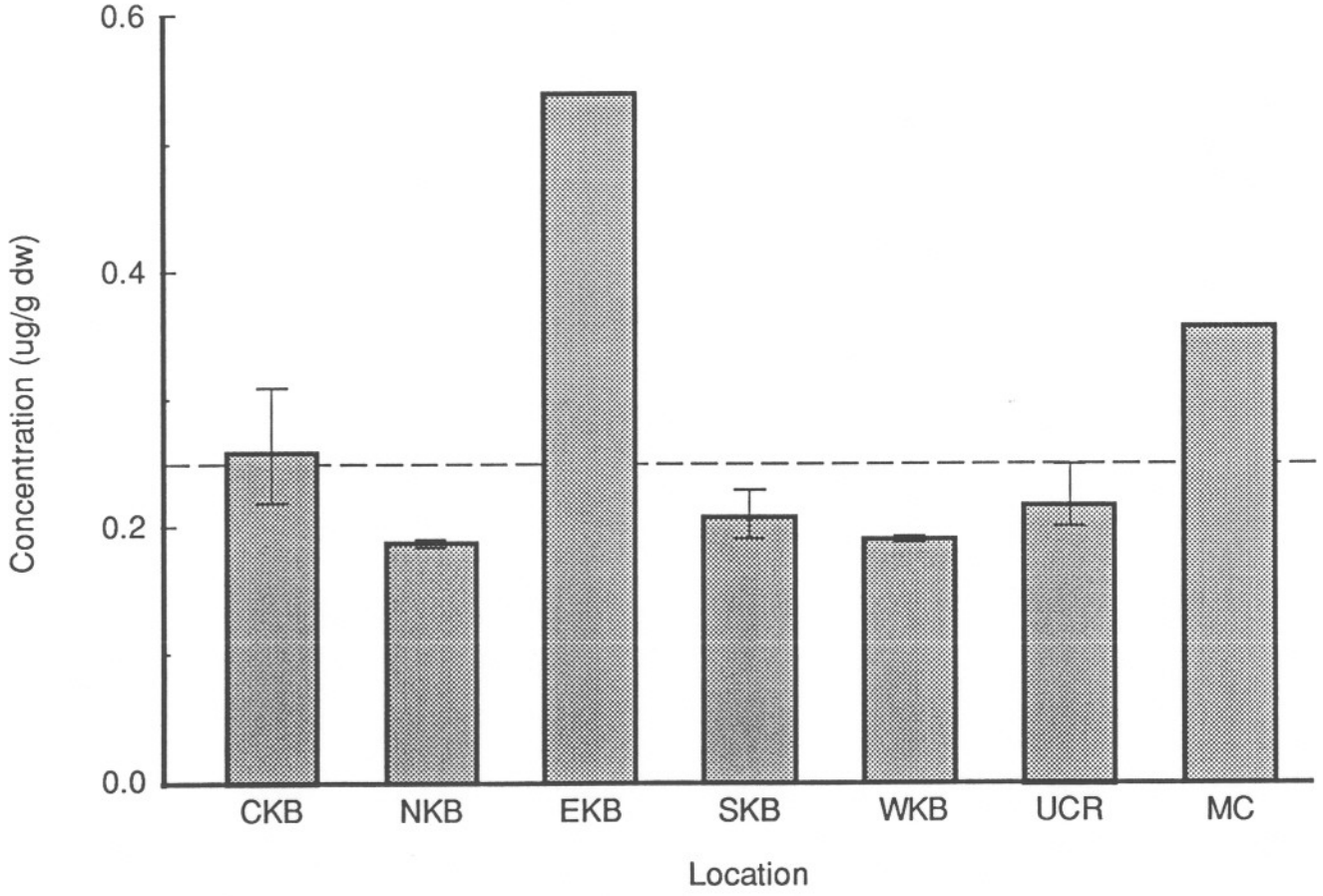

Figure 7. Mean (± S.E.) beryllium concentrations in King's Bay sediments (see text for location identification). Detection limit indicated by broken line.

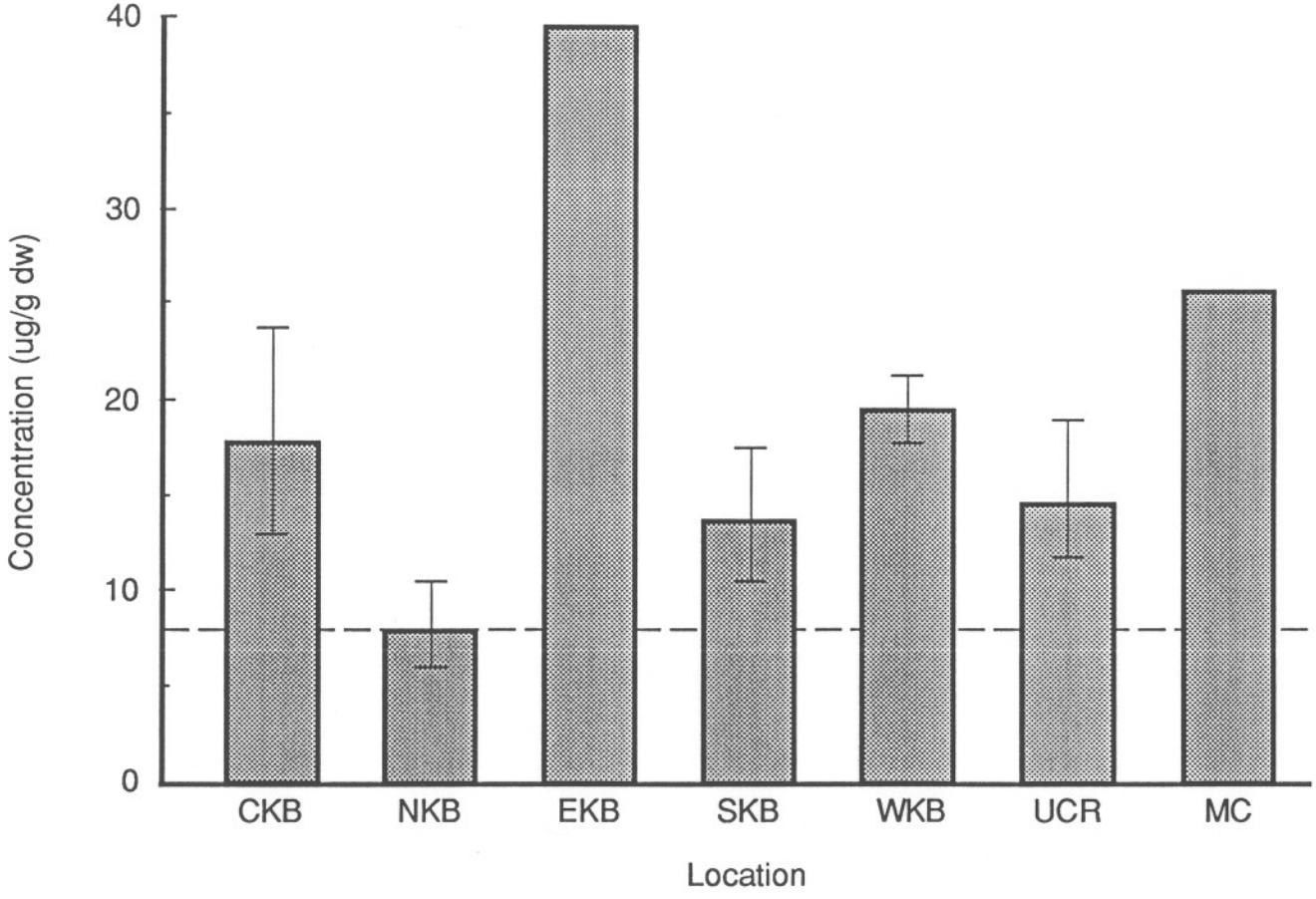

Figure 8. Mean (± S.E.) boron concentrations in King's Bay sediments (see text for location identification). Detection limit indicated by broken line.

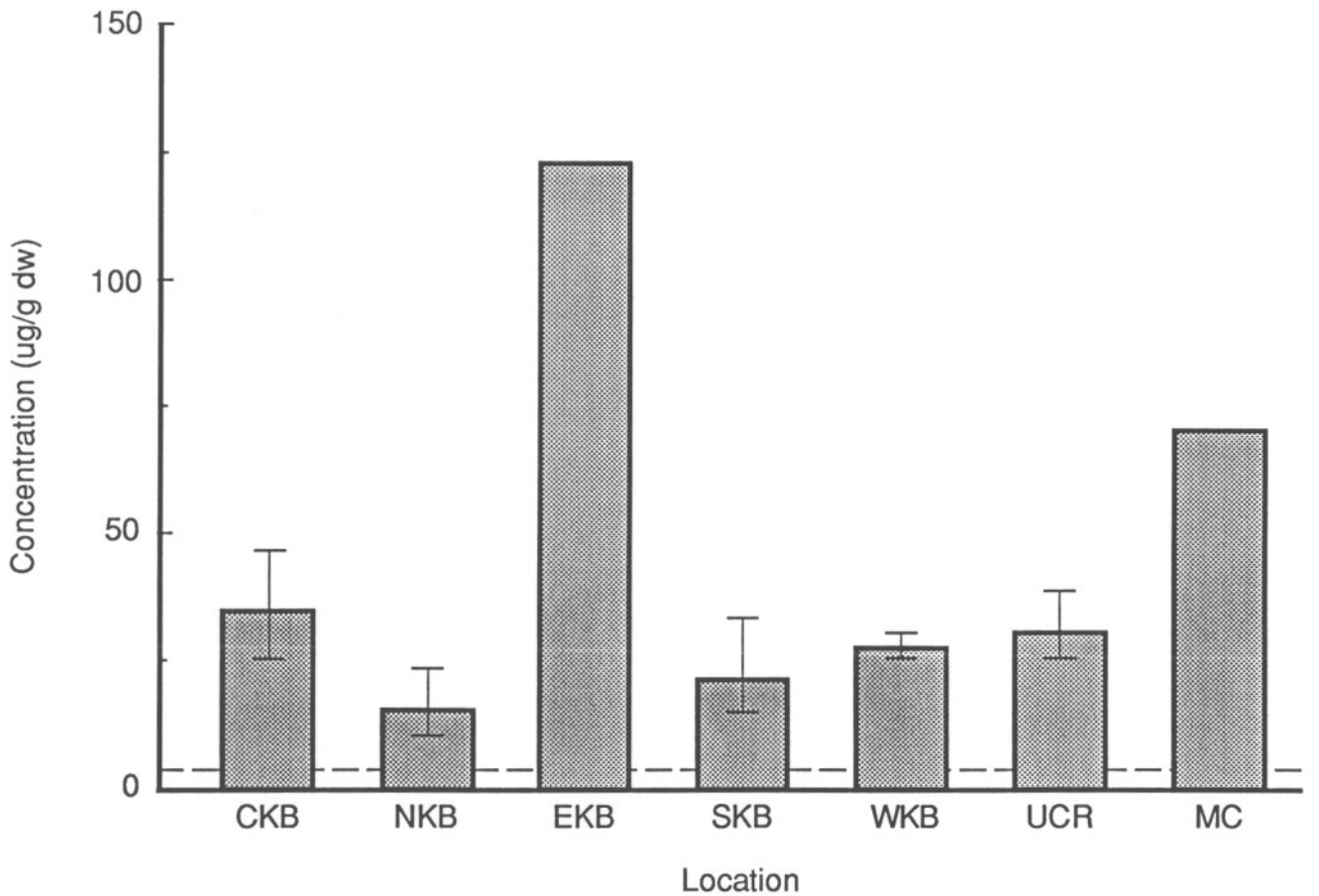

Figure 9. Mean (± S.E.) chromium concentrations in King's Bay sediments (see text for location identification). Detection limit indicated by broken line.



Figure 10. Distribution of chromium concentrations in King's Bay and upper Crystal River sediments.

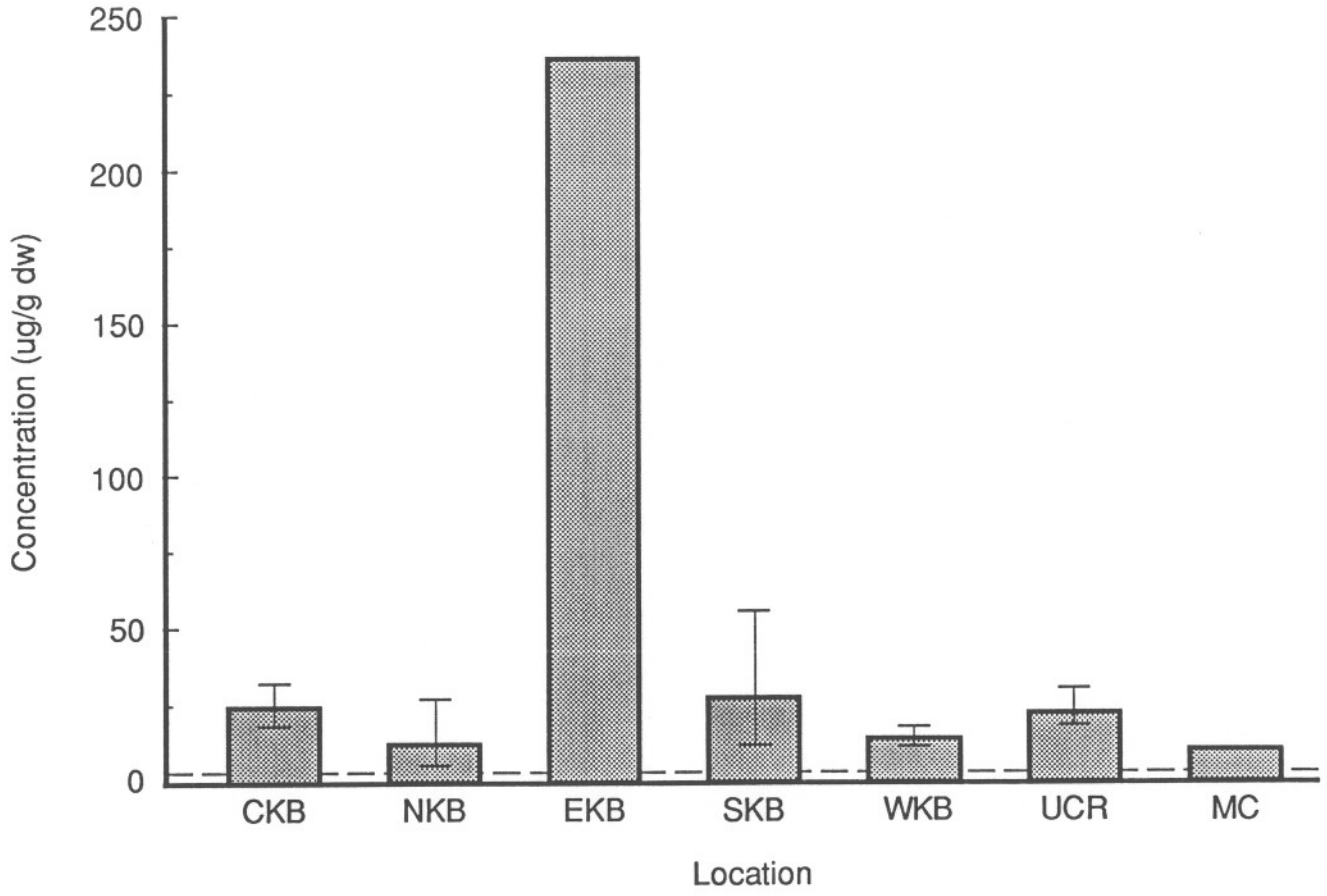

Figure 11. Mean (± S.E.) copper concentrations in King's Bay sediments (see text for location identification). Detection limit indicated by broken line.



Figure 12. Distribution of copper concentrations in King's Bay and upper Crystal River sediments.

correlated (r=0.75; Fig. 28), but the correlation was greatly influenced by the level noted at EKB. With this value removed, the correlation coefficient (r) was only 0.38.

Iron. Levels ranged from 550 ug/g (site 4, NKB) to 16,200 ug/g at MC. Mean group concentrations (range=902 to 3,887 ug/g) and iron distribution in bay sediments are reported in Figures 13 and 14, respectively. Correlation with aluminum was evident (r=0.79; Fig.28), however the concentration noted at MC was much greater than expected when compared to aluminum present at the same site.

Lead. Lead concentrations were below the limit of detection at 13 of the 25 sites. As was generally true for other elements, the maximum concentration (62.5 ug/g) was noted at EKB. Mean group concentrations (range≈7.5 to 17.4 ug/g) were as shown in Figure 15. The mean lead concentration at CKB was significantly greater than those from the other three general locations (p<0.01 when compared with NKB, WKB and SKB; p<0.05 for comparison with UCR), and the mean concentration in UCR sediments was significantly greater (p<0.05) than the mean from NKB. Correlation analysis was not performed.

Magnesium. Levels varied between a low of 250 ug/g at sites 4 (NKB) and 8 (SKB) and a high of 2,900 ug/g at EKB. Mean group levels (range=343 to 1,083 ug/g) are shown in Figure 16. Correlation with aluminum was noted (r=0.85; Fig. 29).

Manganese. Concentrations ranged from 3.01 ug/g to 25.1 ug/g at sites 4 (NKB) and 5 (EKB), respectively. Mean group concentrations ranged from 4.9 to 17.9 ug/g and are shown in Figure 17. Mean manganese concentrations in groups NKB and SKB were significantly less (p<0.05) than those at CKB, WKB and UCR, however SKB was not different from CKB and WKB. A weak correlation with aluminum concentrations was evident (r=0.53; Fig. 29).

Mercury. Mercury concentrations were low; ranging from below detection limits at 13 of 25 sampling sites to 0.56 ug/g at site 20 (CKB). Mean concentrations (range≈0.017 to 0.075 ug/g) are shown in Figure 18. There was little correlation (r=0.43) between mercury and aluminum levels in bay sediments (Fig. 30) verifying results reported by Windom et al. (1989).

Molybdenum. Molybdenum concentrations were generally below detection limits (20 of 25 sites). At the other five locations, concentrations ranged from 4.2 ug/g (site 24; UCR) to 7.6 ug/g (site 17; CKB). Mean gruop concentrations (range≈3.0 to 5.1 ug/g) are reported in Figure 19.

Nickel. Concentrations of nickel were above detection limits at only 40 percent of the sampling sites, and ranged from 4.0

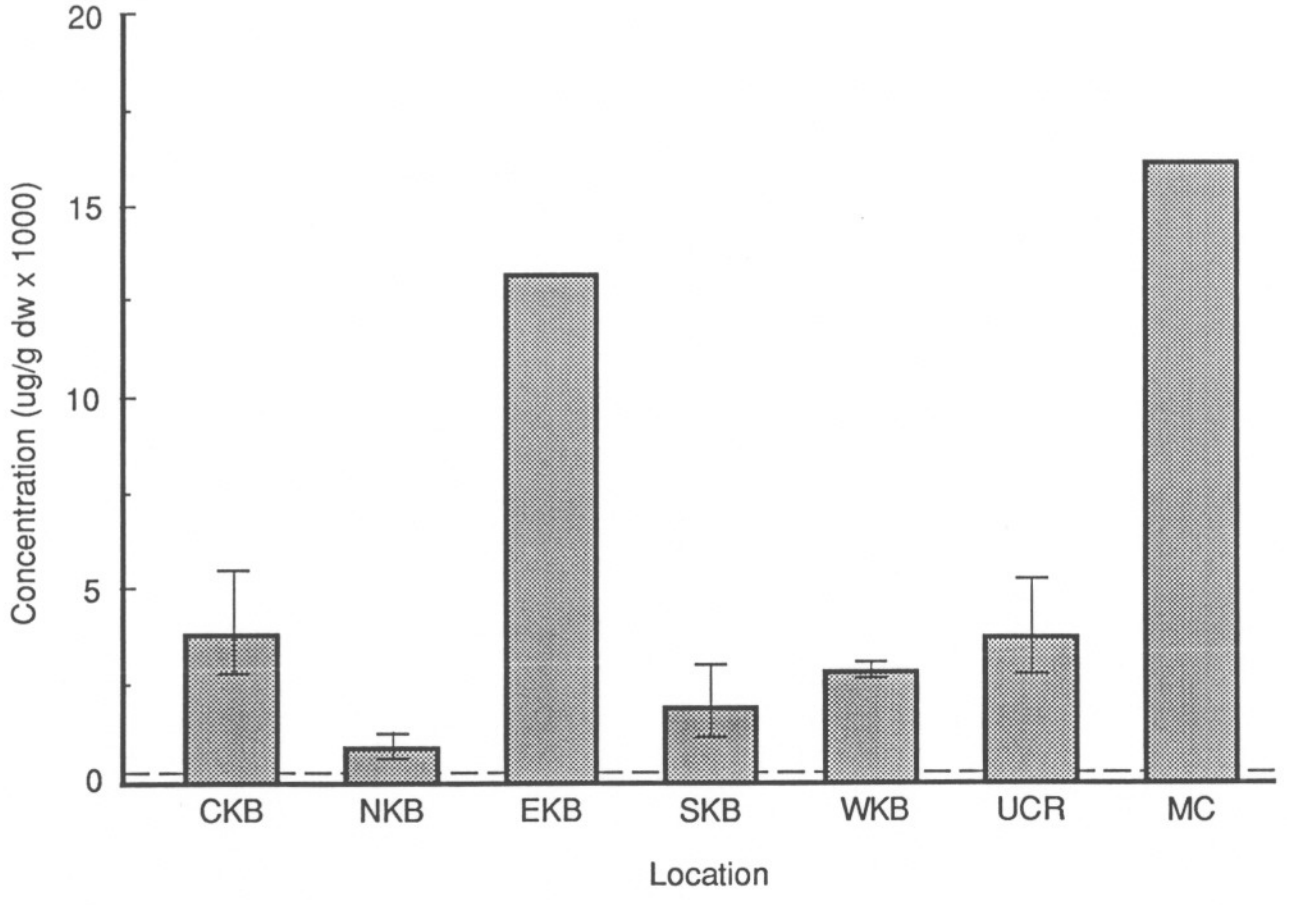

Figure 13. Mean (± S.E.) iron concentrations in King's Bay sediments (see text for location identification).



Figure 14. Distribution of iron concentrations in King's Bay and upper Crystal River sediments.

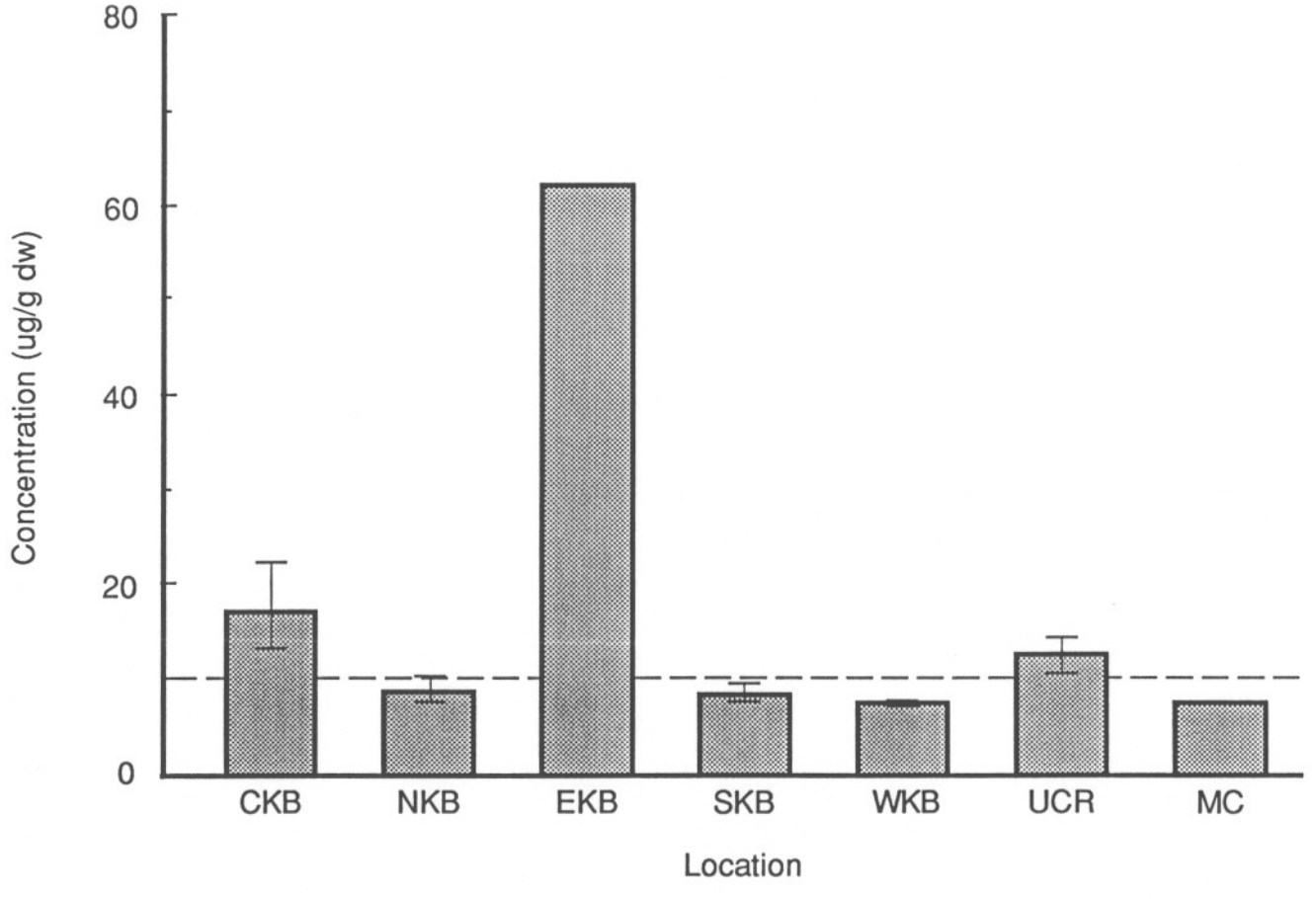

Figure 15. Mean (± S.E.) lead concentrations in King's Bay sediments (see text for location identification). Detection limit incdicated by broken line.

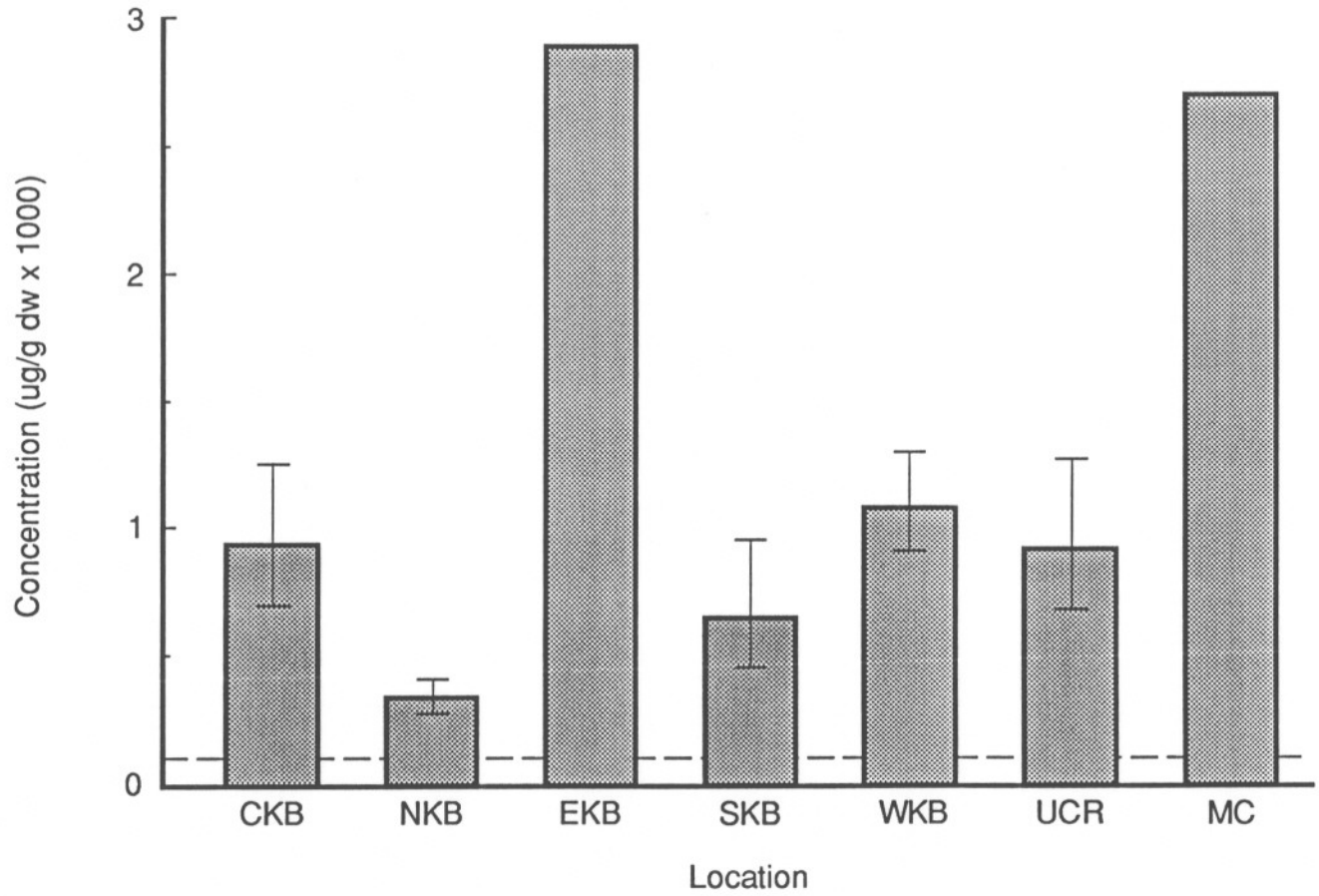

Figure 16. Mean (± S.E.) magnesium concentrations in King's Bay sediments (see text for location identification). Detection limit indicated by broken line.

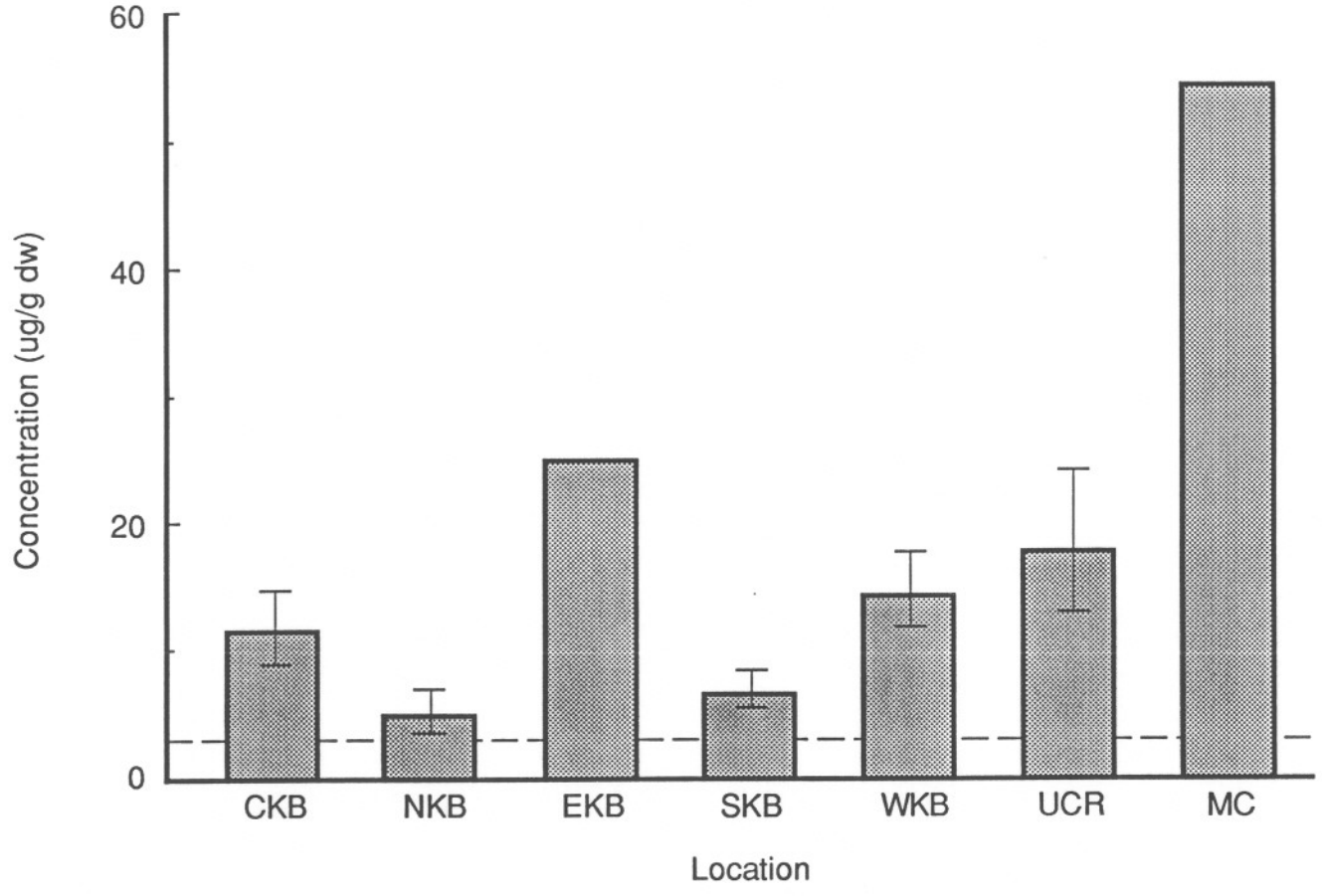

Figure 17. Mean (± S.E.) manganese concentrations in King's Bay sediments (see text for location identification). Detection limit indicated by broken line.

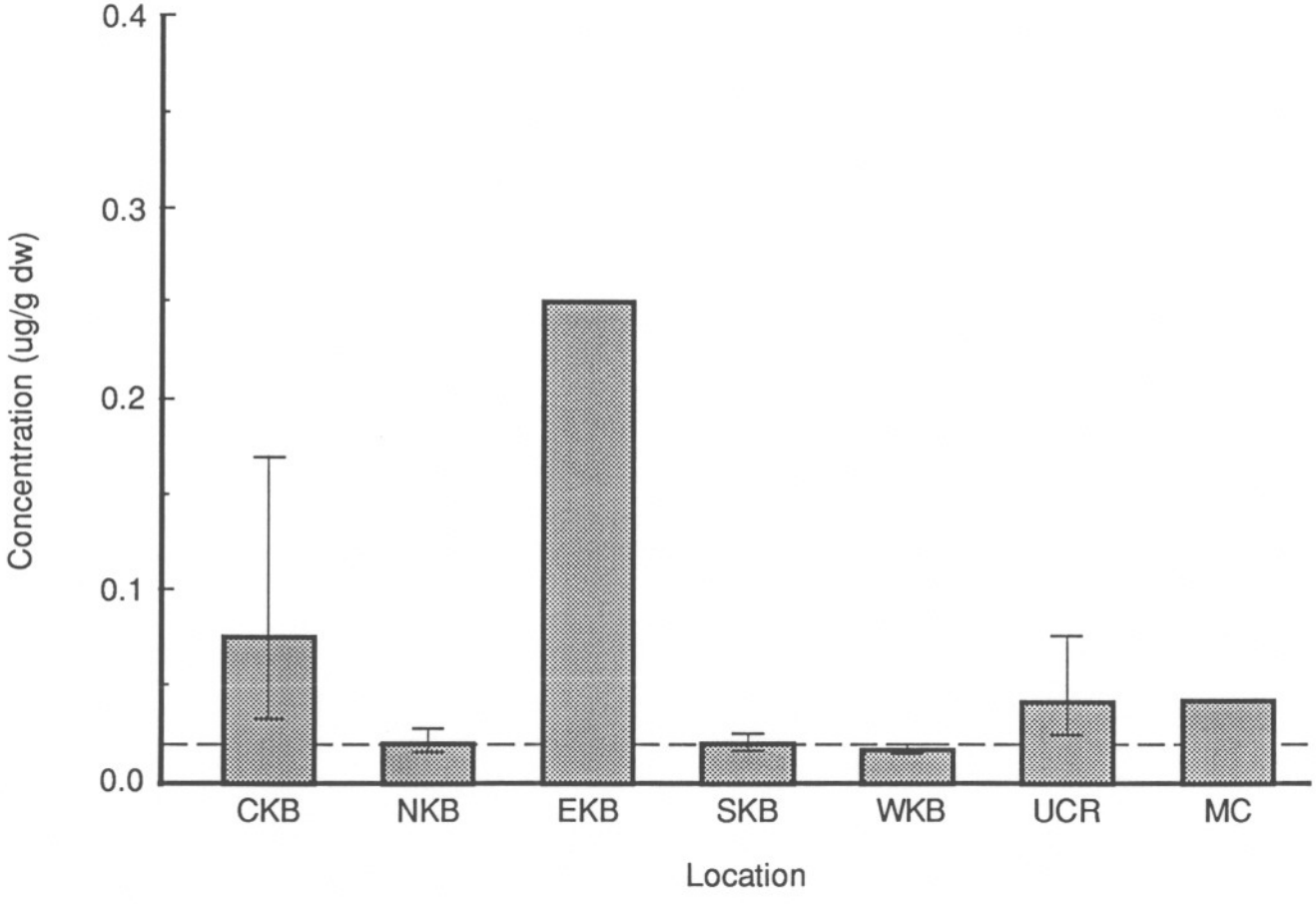

Figure 18. Mean (± S.E.) mercury concentrations in King's Bay sediments (see text for location identification). Detection limit indicated by broken line.

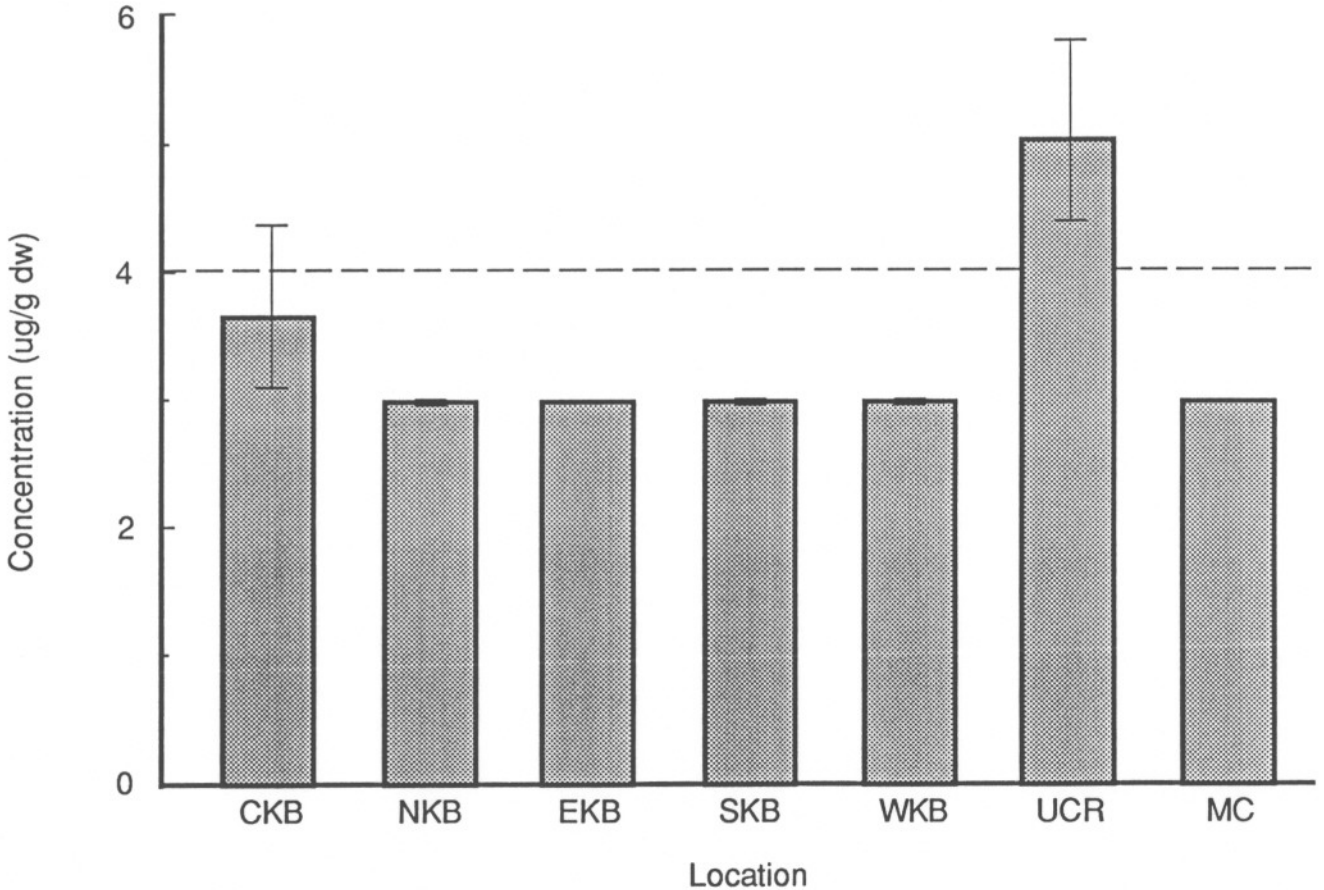

Figure 19. Mean (± S.E.) molybdenum concentrations in King's Bay sediments (see text for location identification). Detection limit indicated by broken line.

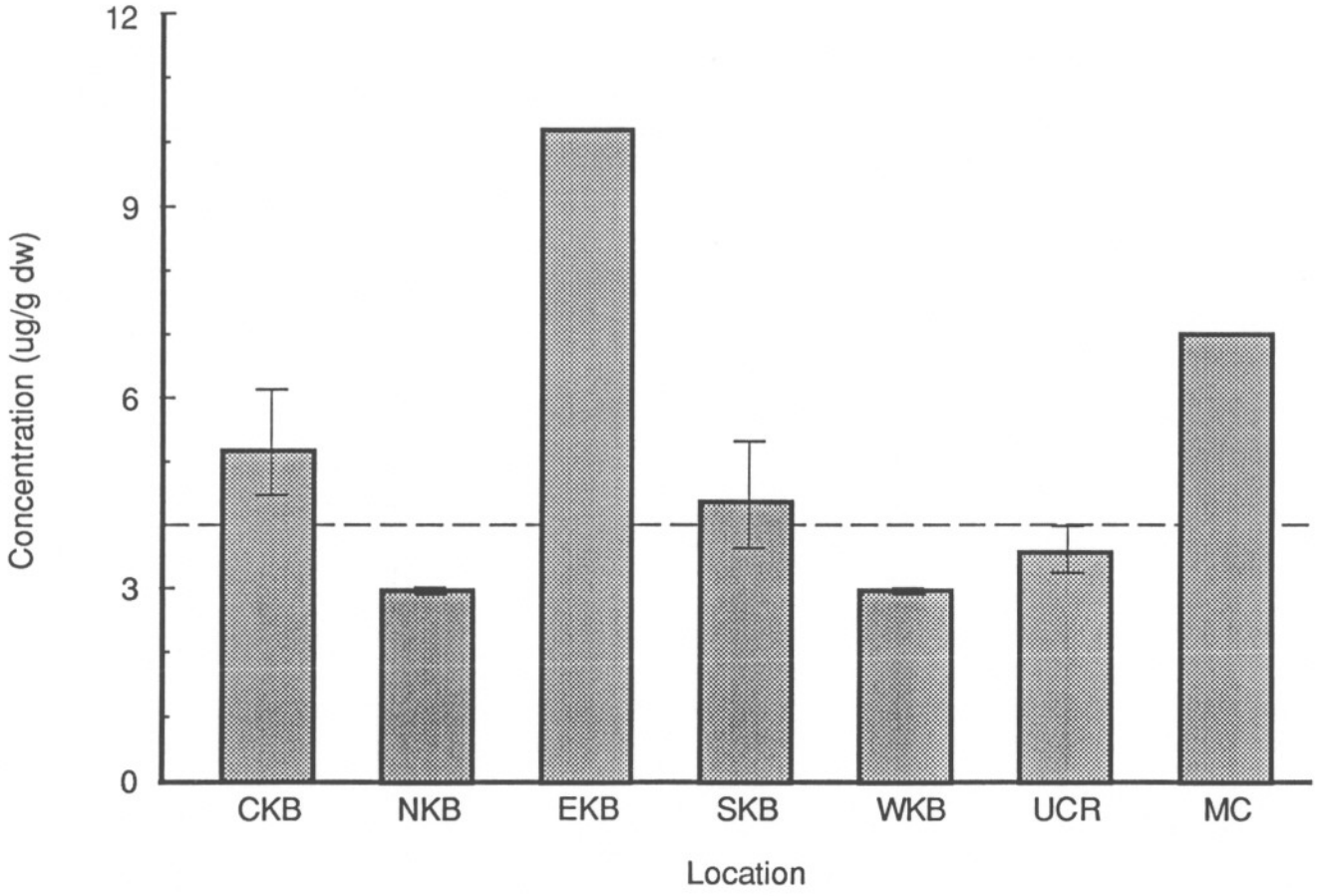

Figure 20. Mean (± S.E.) nickel concentrations in King's Bay sediments (see text for location identification). Detection limit indicated by broken line.

ug/g (the detection limit) at site 23 in UCR to 10.2 ug/g at EKB. Figure 20 shows the mean group concentrations (range≈3.0 to 5.2 ug/g) in the different areas of the bay.

Selenium. Selenium was present in measurable quantities at all sites. Concentrations ranged from 0.53 ug/g at site 9 (SKB) to 4.6 ug/g at EKB. Mean group levels (range=0.83 to 1.73 ug/g) and correlation with aluminum (r=0.84) are shown in Figures 21 and 29, respectively.

Silver. Silver was not detected in any of the samples (detection limit = 10 ug/g), but caution is advised as, like antimony, recovery of silver by ICP is usually low and of questionable accuracy.

Strontium. Strontium concentrations in bay sediments ranged from 10.4 ug/g at site 24 (UCR) to 171 ug/g at MC. Mean group levels (range=28.6 to 54.9 ug/g) and distribution in bay sediments are shown in Figures 22 and 23, respectively. Strontium and aluminum were somewhat correlated (r=0.48; Fig. 29).

Tin. Tin was not present at above-detection-limit (=30 ug/g) quantities in any of the sediments. The same word of caution previously expressed for antimony and silver also is applicable for tin.

Vanadium. Levels of vanadium in bay sediments varied from a low of 2.6 ug/g at site 9 (SKB) to 45.7 ug/g at EKB. Mean group concentrations (range=6.8 to 12.9 ug/g) and overall distribution are shown on Figures 24 and 25, respectively. Vanadium was highly correlated with aluminum (r=0.91; Fig. 29).

Zinc. Zinc was primarily concentrated in sediments from EKB and adjacent areas (Fig. 29). Mean group concentrations (Fig. 26) ranged from 5.1 to 10.7 ug/g. Correlation with aluminum was relatively strong; r = 0.76.

DISCUSSION

The major purpose of this study was to investigate the potential for adverse impact upon the West Indian manatee that might be imposed by the presence of copper residues in sediments from King's Bay and the upper reaches of the Crystal River. Therefore, most of this discussion will be addressed to that specific question. However, the answer to this general question can only be obtained by answering three basic questions: (1) are above-background concentrations of copper present in the sediments, (2) is there a pathway whereby the manatee may be exposed to copper in bay sediments, and (3)

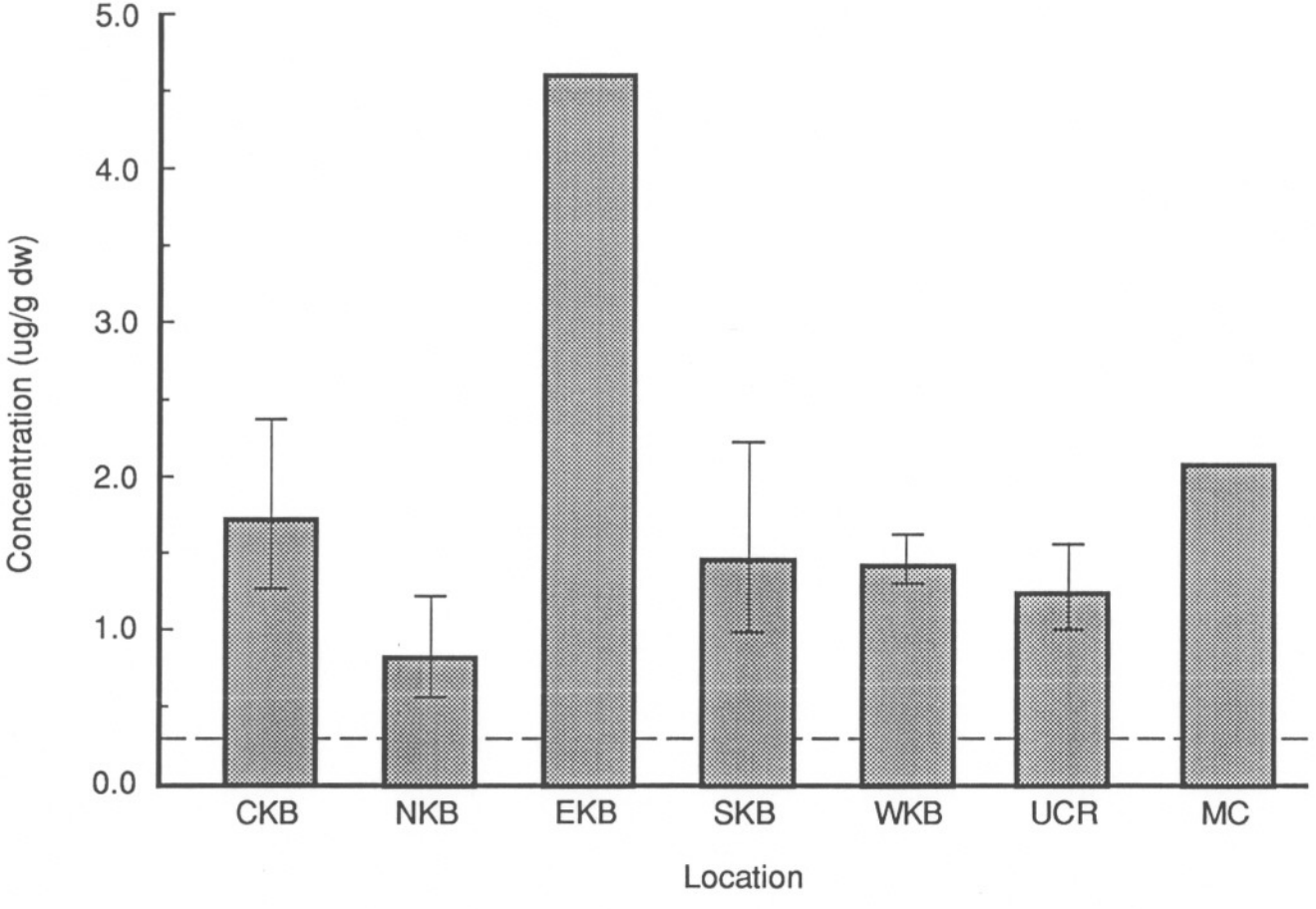

Figure 21. Mean (± S.E.) selenium concentrations in King's Bay sediments (see text for location identification). Detection limit indicated by broken line.

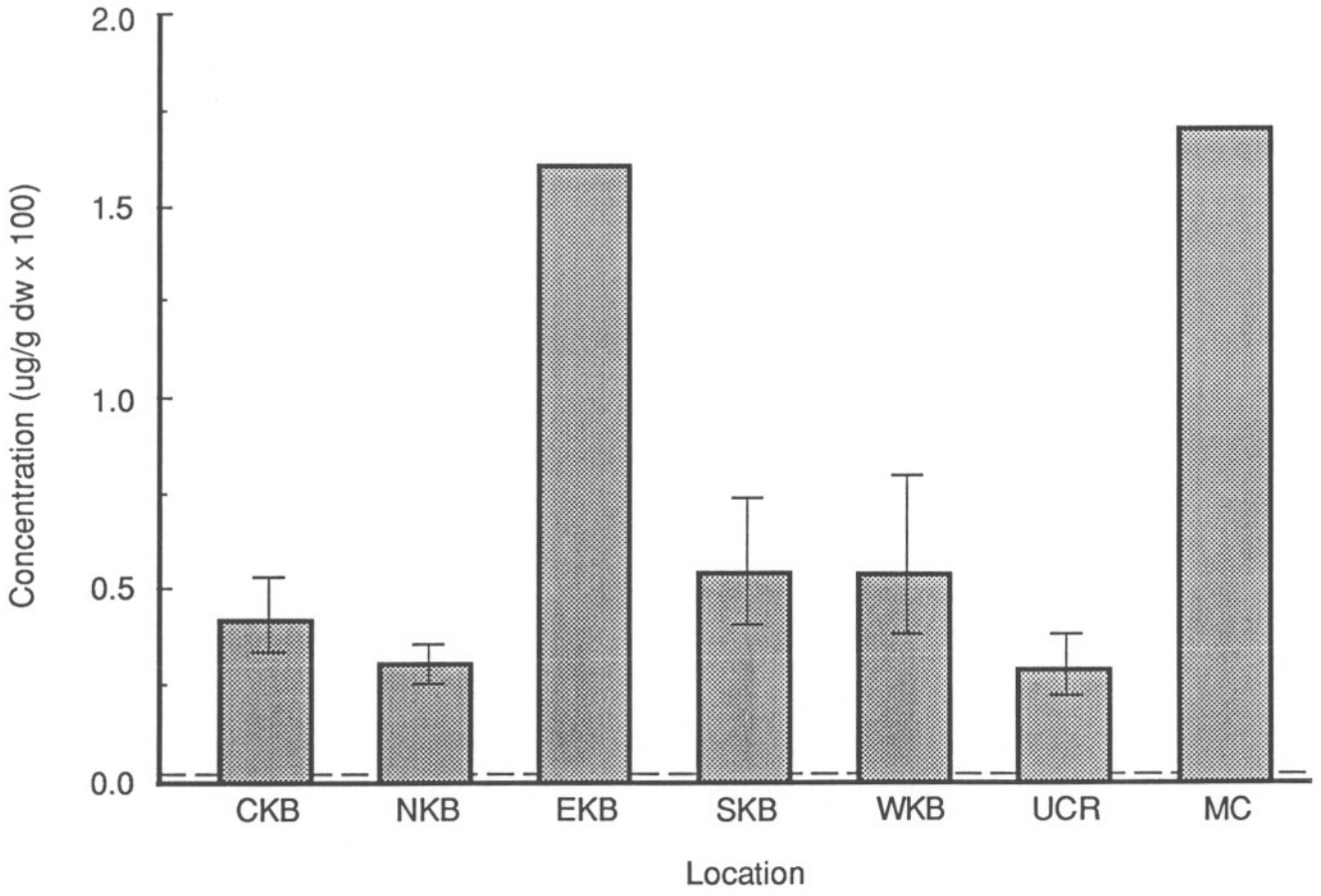

Figure 22. Mean (± S.E.) strontium concentrations in King's Bay sediments (see text for location identification). Detection limit indicated by broken line.

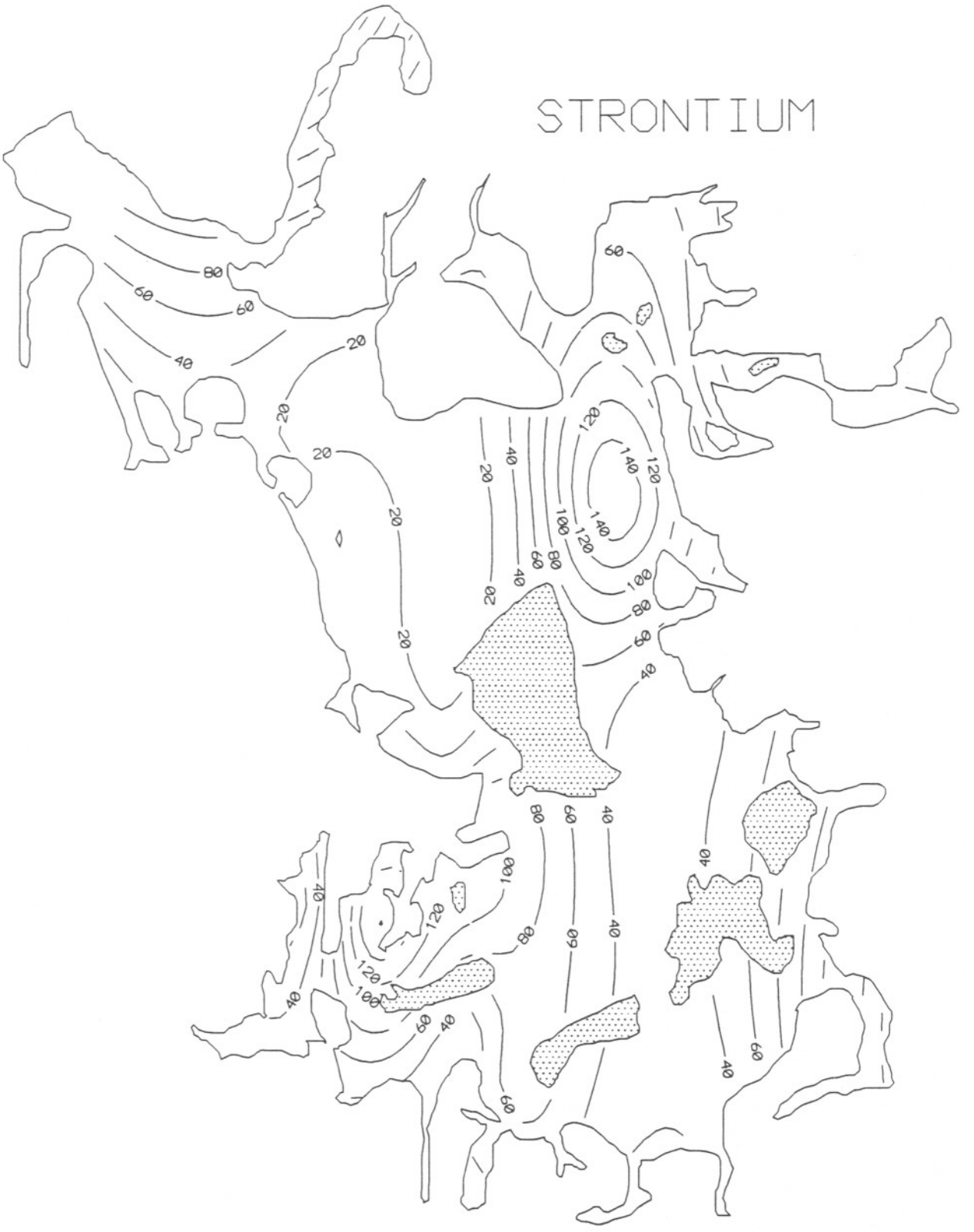

Figure 23. Distribution of strontium concentrations in King's Bay and upper Crystal River sediments.

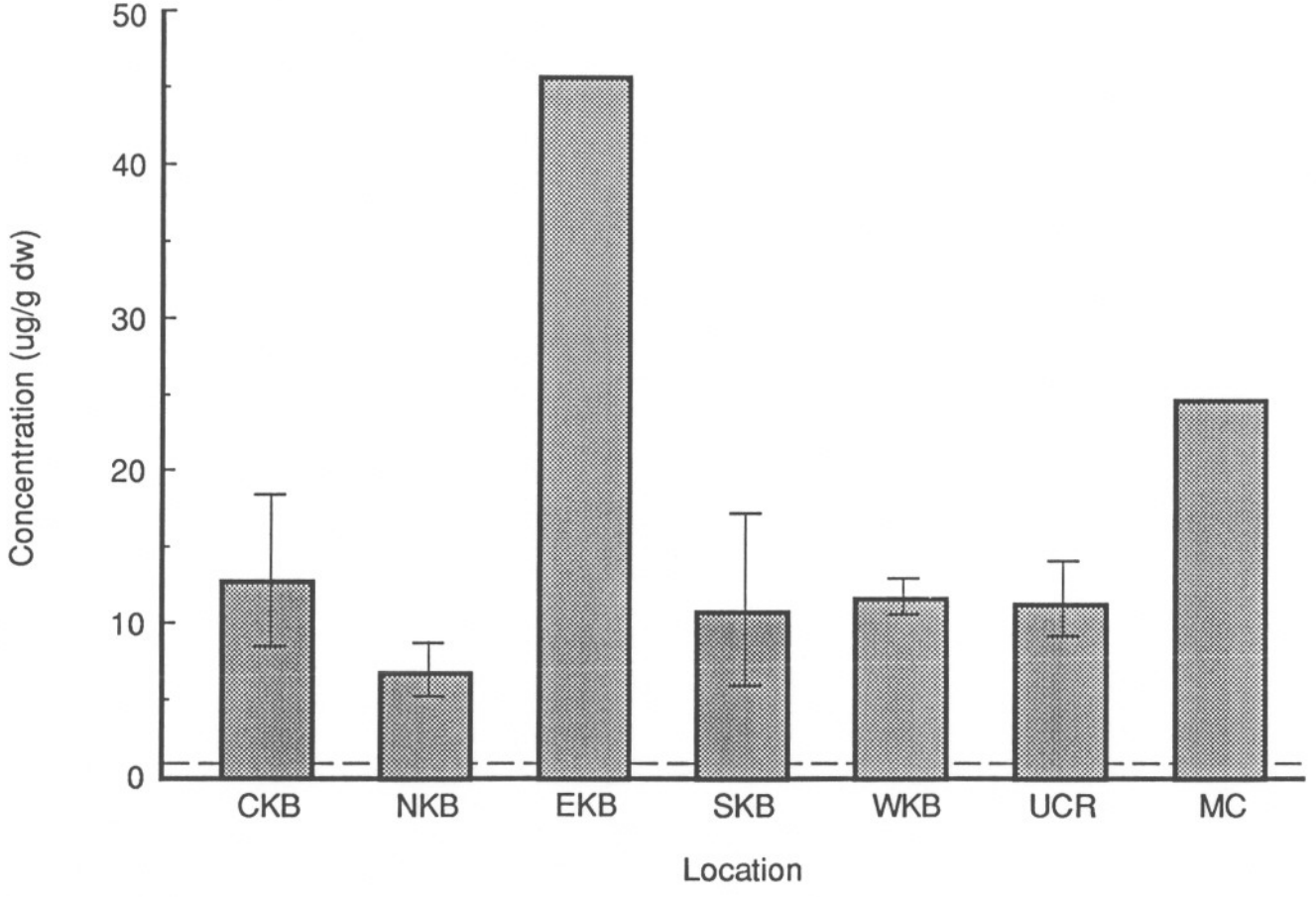

Figure 24. Mean (± S.E.) vanadium concentrations in King's Bay sediments (see text for location identification). Detection limit indicated by broken line.



Figure 25. Distribution of vanadium concentrations in King's Bay and upper Crystal River sediments.

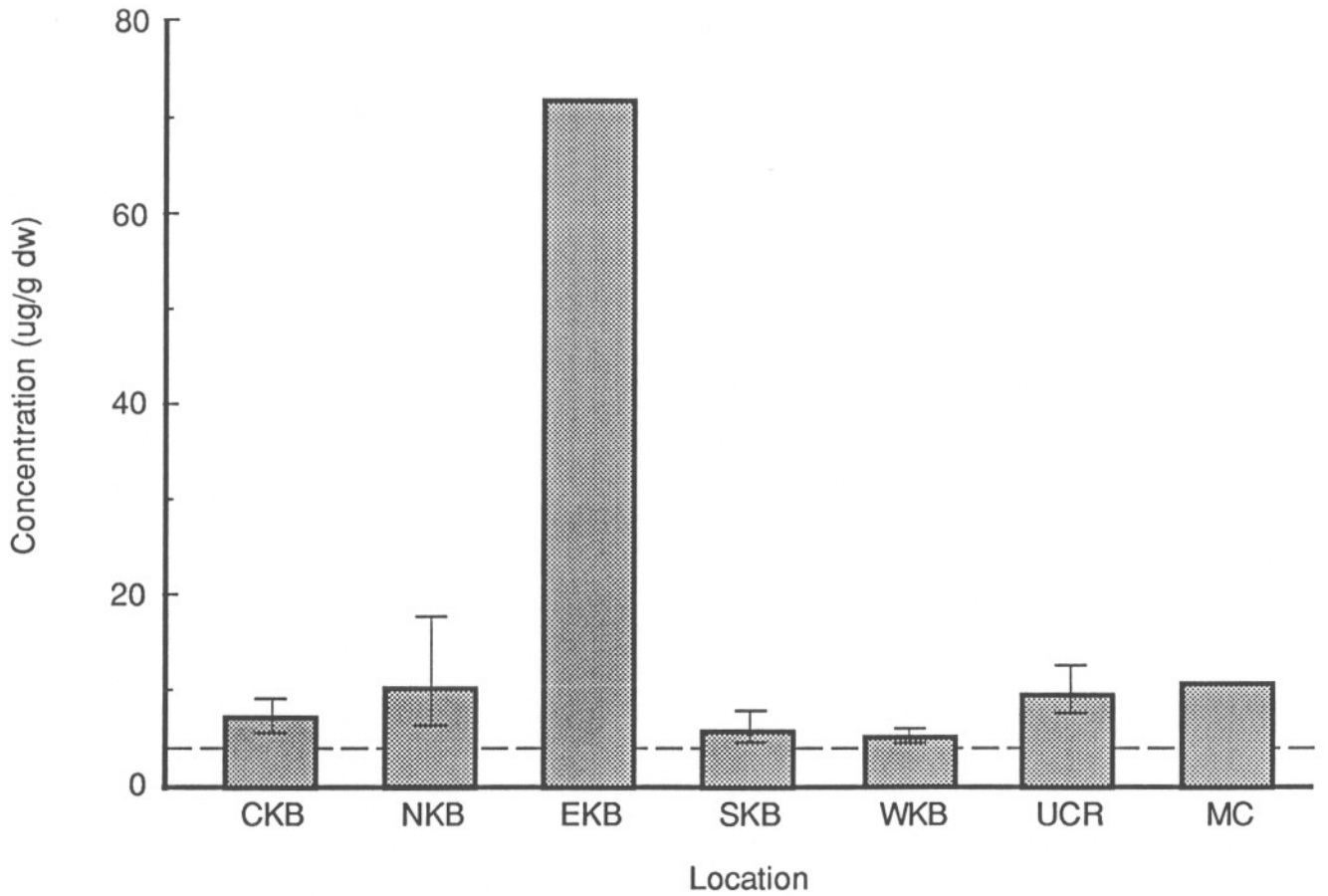

Figure 26. Mean (± S.E.) zinc concentrations in King's Bay sediments (see text for location identification).



Figure 27. Distribution of zinc concentrations in King's Bay and upper Crystal River sediments.

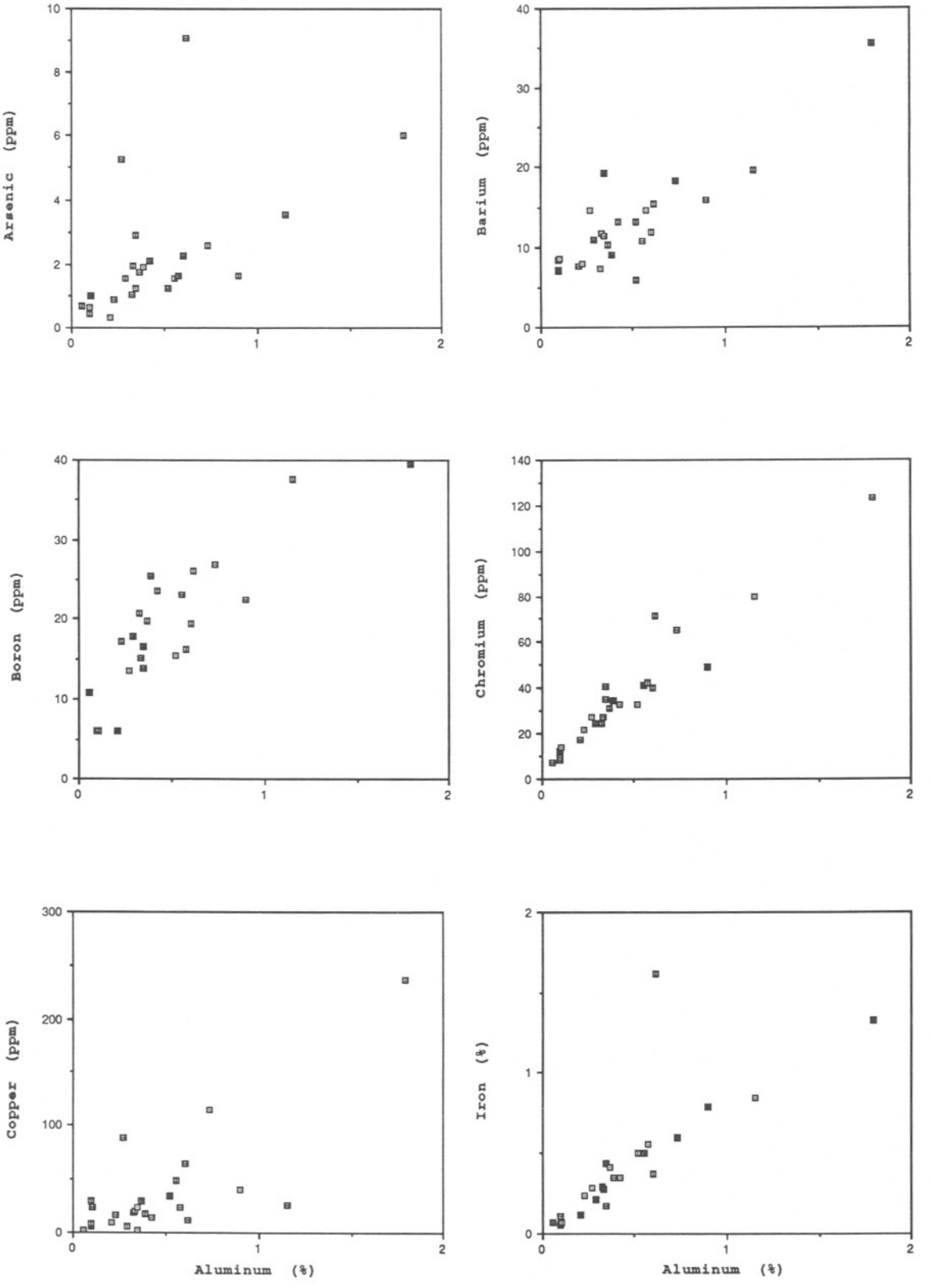

Figure 28. Arsenic, barium, boron, chromium, copper and iron concentrations in Crystal River and King's Bay sediments versus aluminum.

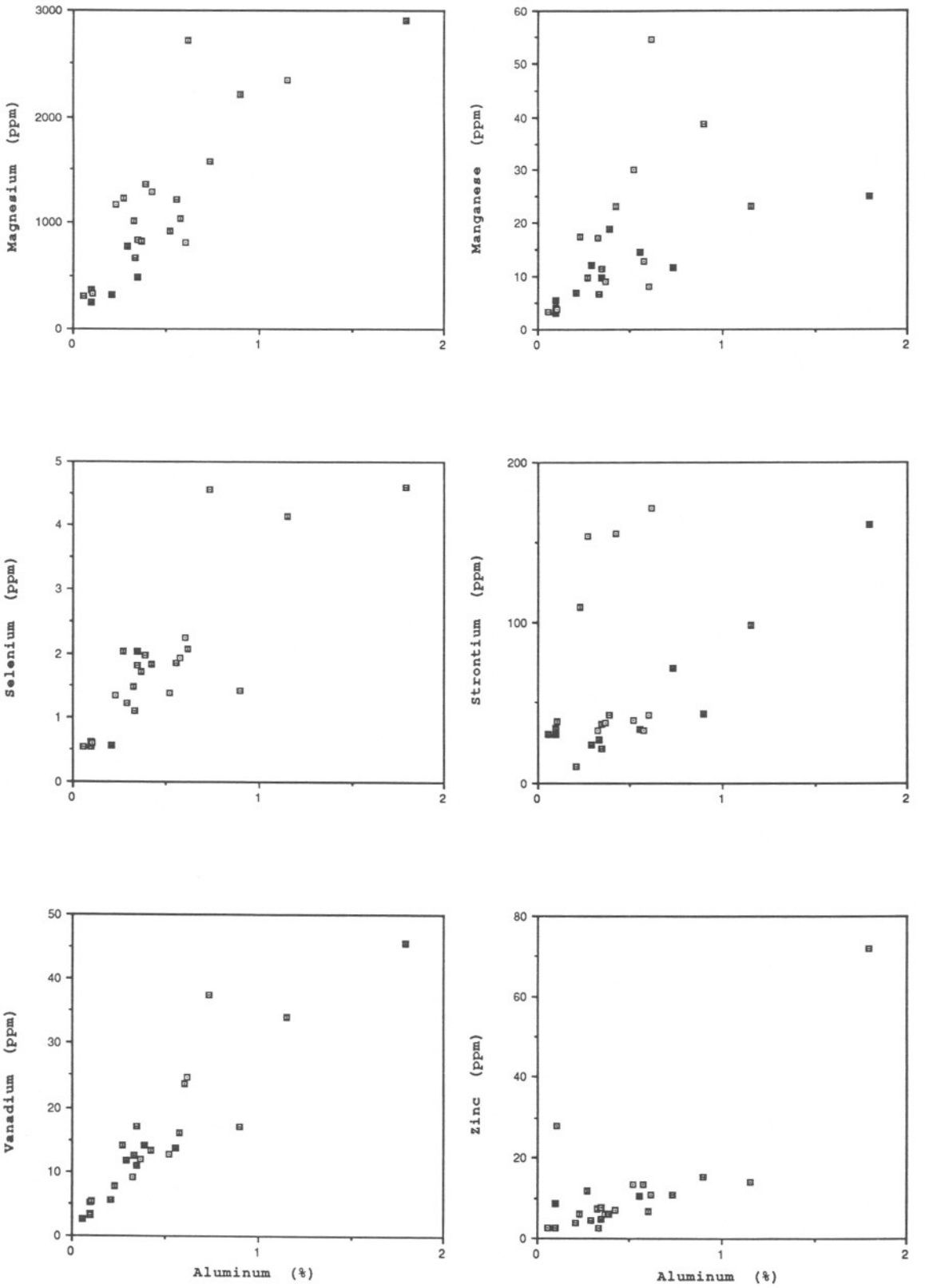

Figure 29. Magnesium, manganese, selenium, strontium, vanadium and zinc concentrations in Crystal River and King's Bay sediments versus aluminum.

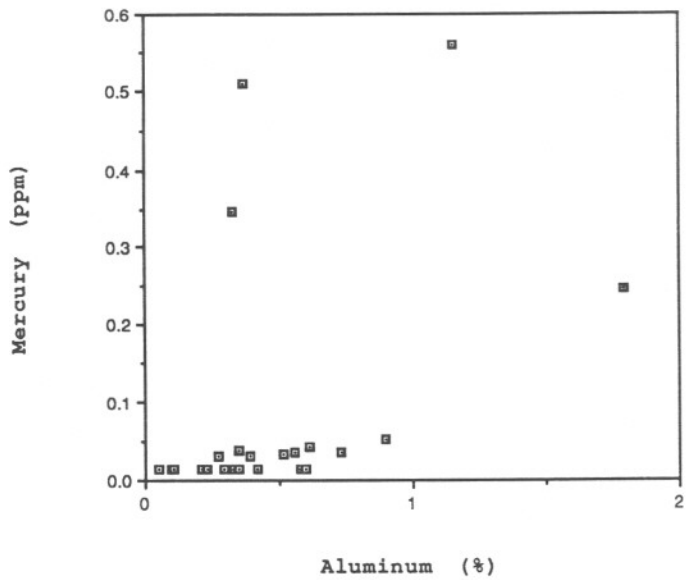

Figure 30. Mercury concentrations in Crystal River and King's Bay sediments versus aluminum.

what is the toxicological hazard to the manatee? Each of these will be addressed separately.

Copper in King's Bay and Crystal River sediments. Windom et al. (1989), in a study of naturally-occurring trace elements in sediments of estuaries and coastal areas of the United States, found that copper and many of the other elements detected in King's Bay and Crystal River sediments during this present study were found at levels which were directly proportional to aluminum concentrations. This finding suggested that natural aluminosilicate minerals are the dominant natural metal-bearing phases in these sediments, and further that the covariance of these metals with aluminum can provide a basis for identification and comparison of anthropogenic inputs to coastal and estuarine sediments. Using methodology described in Windom et al. (1989), I found that, although copper in King's Bay and Crystal River sediments did covary with aluminum as expected, the slope was much different [$M = 97.4(Al) - 7.3$ in this study vs. $M = 1.8(Al) - 1.4$ in Windom et al. (1989)].

Windom et al. (1989) also reported that, in natural, uncontaminated soils, the copper(ppm):aluminum(%) ratio was approximately 4.8. In this study, I found that copper was, on the average, 90.2 (S.E.=16.6; $n=25$) times greater than aluminum. Consequently, all of the copper concentrations found in King's Bay and Crystal River sediments were above the

"normal" range as reported by Windom et al. (1989). This suggests that copper concentrations in the bay have been greatly influenced by human activity.

The greatest concentration of copper found during this study, 237 ug/g at site 5 (EKB), was comparable with the mean level (204 ug/g; n=56) reported by the Florida Department of Environmental Regulation for surface sediments from Hillsborough Bay, which was also determined to be above the concentration one would expect given the amount of aluminum present (Long et al. 1991).

Exposure pathways. If copper from bay sediments is to have an impact on the manatee, the manatee must first be exposed. Manatees have been observed in King's Bay and the Crystal River during all seasons of the year, but data indicate the heaviest use during the period from October through March (Rathbun et al. 1990, Kochman et al. 1985, Powell and Rathbun 1984). The greatest number of animals were generally seen to the southeast of Banana Island. Kochman et al. (1985) indicated that this area was used most heavily from November through February, and that the Tarpon Spring area north of Banana Island received low but consistent use for the 6-month period from October through March. During the remainder of the year, relatively small numbers of animals were observed; most of them congregating in the northern half of the bay (west of Buzzard Island; Rathbun et al. 1990, Kochman et al. 1985). Powell and Rathbun (1984) and Hartman (1979) indicated that seasonal changes in distribution corresponded to changes in water temperature along the coast; the manatees seeking the comfort of King's Bay/Crystal River when the coastal waters become colder than the upwelling springs within the bay. At any rate, the bay is widely used by manatees of varying numbers throughout the year.

Manatees are herbivores. Using hydrilla as a food source, Etheridge et al. (1985) estimated that a manatee calf consumed up to 15.7 percent of its body weight, or approximately 8.5 kg of the plant, in a 5-hr period. Adults were reported to eat about five and one-half times this amount (45.5 kg; =7.1% of body weight) in the same time period.

Aquatic vegetation has been shown to be an efficient mechanism for moving copper from water and sediments to manatees. Sutton et al. (1970) reported that tissues of hydrilla contained 4,400 ug copper/g tissue after immersion for eight days in water containing 1.0 ppm copper. Parrotfeather (Myriophyllum brasiliense), a plant preferred by the manatee, is not particularly susceptible to copper, but does bioaccumulate the metal. Sutton and Blackburn (1971) noted that parrotfeather root tissues contained concentrations ranging from 70 to 170 ug/g two weeks after treatment with

0.25 to 1.0 ppm copper. All of these data were correlated with copper concentrations in water during, or immediately after, exposure rather than with uptake from known sediment concentrations.

Schroeder et al. (1988) reported the mean copper concentration in sediments from an evaporation pond in the Tulare basin (San Joaquin Valley, CA) as 39(±4) ug/g. Copper concentrations in widgeongrass (Ruppia maritima) from the same area ranged from 13 to 35 ug/g with a mean of 21 ug/g. In a similar study, Waddell and Coyner (1990) found that 14 ug/g copper in sediments resulted in concentrations of 17.5 and approximately 30 ug/g in hardstem bulrush (Scirpus acutus) and widgeongrass, respectively. Working in the Stillwater Wildlife Management Area (Nevada) and adjacent lands, Hoffman et al. (1990) reported copper concentrations in hardstem bulrush root material ranging from <4.0 to 281 ug/g associated with sediment copper levels ranging between 22 and 56 ug/g (NOTE: copper apparently was not measured in sediments from the area where 281 ug/g copper was found in bulrush). Sago pondweed (Potamogeton pectinatus) plants contained similar levels of copper (range=1.8 to 229 ug/g), but concentrations in cattail (Typha sp.) root and stem material were less; ranging from <0.88 to 8.8 ug/g and from 3.6 to 41.7 ug/g, respectively.

Based on these data, it would appear that aquatic plants do not bioconcentrate copper from sediments to any appreciable extent, and that copper concentrations in plant material in King's Bay should not exceed, except randomly, those concentrations noted in the sediments. Thus, maximum exposure would occur in an area, EKB, that is less utilized by the manatees than other, less contaminated, areas. However, to be on the safe side, I chose to use the maximum level observed in bay sediments, 237 ug/g, to determine exposure to the manatee.

Toxicological hazard to the manatee. Let us assume that: (1) the bioconcentration factor (BCF) for copper in aquatic plants native to King's Bay and the Crystal River area equals 1.0, (2) manatee calves and adults consume 8.5 and 45.5 kg of plant material/5-hr period (Etheridge et al. 1985), and (3) manatees spend, on the average, 18.5% (267±70 min/24-hr period) of their time feeding (Etheridge et al. 1985; Table 5). It then follows that calf and adult manatees could ingest approximately 1.8 and 9.6 g of copper per day, respectively.

Whereas no data exist relative to retention of copper by manatees, an adult human retains, on the average, 56 percent of that ingested (Demayo et al. 1982). These authors also suggest that the percentage of copper absorbed decreases with increased copper uptake and that the main copper repositories within the human body are the muscle, liver and brain; the

highest concentrations (9.2 to 46.8 mg/kg) being found in the liver. In humans, the ingestion of gram quantities of ionic copper has been shown to cause ulcerations of the gastrointestinal tract, hemolysis, jaundice, hepatic necrosis and renal damage (NAS 1977). Demayo et al. (1982) stated that symptoms of copper toxicity in sheep appeared at liver concentrations of approximately 150 mg/kg wet weight. This is much less than liver concentrations noted in some manatees. O'Shea et al. (1984) reported maximum copper concentrations of 1,200 mg/kg dry weight (≈300 mg/kg wet wt., assuming approx. 75% moisture in liver tissue) in livers of manatees from the Crystal River (Florida) population, and noted that copper concentrations reported for manatees in their study were well above those reported for at least 36 other species of mammals. O'Shea (personal communication) stated that he had no knowledge of evidence of copper toxicity in manatees; most animals found dead were decomposed to the extent that histopathological examination was impractical. Thus, it appears that there may be sufficient copper in at least some manatees, particularly those from the Crystal River and King's Bay population, to produce toxic effects.

Long and Morgan (1990) indicated that copper concentrations in sediments within the range of ≥70 to <310 ug/g as those "at or above which" toxic effects were detected in some species. Sediments from three of the sites sampled in King's Bay and the upper Crystal River contain levels of copper within this range and would seem to be sufficient to cause the level of contamination found in the animals.

Other metals. Of those other metals detected in King's Bay/Crystal River sediments, there were only a few that seemed to be present at levels indicative of human activity. Arsenic concentrations at sampling sites 1 and 7 (Fig. 2) were higher than would be expected from natural deposition, but were well within the limit of "normal" background concentrations (<15 ug/g; Eisler 1988). Iron concentrations were greater than expected, at four locations: 1, 5, 19 and 25. However, iron in soils is usually not toxic and, in some cases, biologically unavailable (USEPA 1976). Zinc concentrations at sites 5 and 25 were elevated; apparently from anthropogenic influences. No data regarding the toxicity of zinc to marine mammals was found.

Recommendations. As copper is highly persistent in a system once it is adsorbed by sediments, the further use of copper-based herbicides should be curtailed, regardless of the timing of application in relation to the presence of manatees. A monitoring program should be initiated [preferably as part of the Service's new Biomonitoring of Environmental Status and Trends (BEST) Program] to monitor copper concentrations, not only in the sediments of King's Bay and the Crystal River, but

also in the aquatic vegetation and in the manatee population utilizing the area. In addition, the population should be monitored for clinical signs of copper toxicosis, and deceased animals should be examined for histopathological symptoms of copper poisoning as well as copper concentrations in liver and other body tissues.

ACKNOWLEDGEMENTS

The author would like to thank Wade Bryant for providing the isopleths illustrating the distribution of various heavy metals in bay and river sediments, and Dr. Donald P. Schultz for his critical review and helpful suggestions.

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APPENDIX

QA\QC AND ANALYTICAL RESULTS

34

RESEARCH TRIANGLE INSTITUTE

CHEMICAL ANALYSIS OF ENVIRONMENTAL MATERIALS FOR RESIDUES OF INORGANIC CONTAMINANTS

Catalog 5928
Sediment Sample Analysis
ICP Data
AA Data
QC/QA Data

March 1990
FWS Contract No. 14-16-0009-87-009
RTI Contract 91U-3907

Prepared by

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Patuxent Wildlife Research Center
Laurel, MD 20708

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DEPARTMENT OF INTERIOR
FISH AND WILDLIFE SERVICE

Contract No. 14-16-0009-87-00 (RTI No. 91U-3907)

Catalog 5928

Sediment Sample Analysis Results
ICP Analyses

TABLE 1: AVERAGE RECOVERY OF SPIKED ANALYTE FROM SAMPLES ANALYZED BY THE RESEARCH TRIANGLE INSTITUTE USING ICP (DIRECT)

	AVERAGE	STANDARD DEVIATION	NUMBER
MATRIX: TISSUE			
Aluminum	98	9.0	42
Antimony	82	13.	30
Barium	98	7.0	56
Beryllium	100	16.	56
Boron	96	7.9	43
Cadmium	101	4.6	56
Cobalt	97	7.4	55
Chromium	99	4.2	56
Copper	101	8.1	55
Iron	101	12.	40
Lead	100	11.	56
Magnesium	100	13.	28
Manganese	100	5.3	52
Molybdenum	102	8.1	44
Nickel	99	5.1	44
Silver	57	36.	53
Strontium	100	14.	43
Tin	69	39.	29
Vanadium	99	5.6	43
Zinc	100	12.	50
MATRIX: SEDIMENT			
Antimony	91	12.	22
Barium	92	17.	6
Beryllium	92	10.	26
Boron	80	28.	25
Cadmium	95	5.9	30
Cobalt	96	8.4	18
Chromium	96	11.	28
Copper	97	11.	30
Lead	96	11.	28
Manganese	90	19.	12
Molybdenum	94	11.	28
Nickel	93	8.0	30
Silver	81	32.	28
Strontium	86	25.	26
Tin	90	25.	27
Vanadium	95	9.4	27
Zinc	98	13.	29

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SAMPLE INTEGRITY REPORT

CATALOG # 5928 PURCHASE ORDER # 85800-89-08094 LAB RTI

Original # of samples to be shipped 30

Actual # of samples received 30

Arrival date: initial sample shipment DATE: 9-21-89 FROM: Submitter

final sample shipment _____ _____

General sample condition Good, Frozen

Comments: _____

[X] All ASPECTS CORRECT (i.e. purchase order matches the catalog which matches the samples received) Samples will now enter laboratory queue.

OR

[ ] PROBLEMS EXIST, the following is required

Action Item	Comments
_____ Amend Purchase Order	_____
_____ Modify Catalog	_____
_____ Resolve Sample Problem	_____

Please return this form to Patuxent Analytical Control Facility as soon as all information can be provided.

TABLE 1: AVERAGE RECOVERY OF SPIKED ANALYTE FROM SAMPLES ANALYZED BY THE RESEARCH TRIANGLE INSTITUTE USING ATOMIC ABSORPTION

	AVERAGE	STANDARD DEVIATION	NUMBER
MATRIX:TISSUE			
Arsenic	98	7.3	63
Selenium	102	8.9	62
Mercury	96	9.7	72

	AVERAGE	STANDARD DEVIATION	NUMBER
MATRIX:SEDIMENT			
Arsenic	97	7.4	31
Selenium	96	7.9	30
Mercury	98	10.	30

TABLE 2: ESTIMATED 95 % CONFIDENCE INTERVAL FOR ANALYSES PERFORMED BY THE RESEARCH TRIANGLE INSTITUTE USING ATOMIC ABSORPTION

	± CONFIDENCE INTERVAL AS % OF SAMPLE CONCENTRATION	
SAMPLE CONCENTRATION*	2-10 LOD	>10 LOD
MATRIX:TISSUE	25	15
Arsenic	INS	INS
Selenium	INS	10
Mercury	20	15

	± CONFIDENCE INTERVAL AS % OF SAMPLE CONCENTRATION	
SAMPLE CONCENTRATION*	2-10 LOD	>10 LOD
MATRIX:SEDIMENT	20	15
Arsenic	INS	INS
Selenium	INS	INS
Mercury	INS	INS

* FOR ANY CONCENTRATION LESS THAN 2 LOD, THE 95 % CONFIDENCE INTERVAL IS ESTIMATED AT ± 2 LOD.

LOD= LIMIT OF DETECTION

INS=INSUFFICIENT DATA TO CALCULATE ON AN INDIVIDUAL ANALYTE BASIS

TABLE 2: ESTIMATED 95 % CONFIDENCE INTERVAL FOR ANALYSES PERFORMED BY THE RESEARCH TRIANGLE INSTITUTE USING ICP (DIRECT)

MATRIX: SEDIMENT

SAMPLE CONCENTRATION*	± CONFIDENCE INTERVAL AS % OF SAMPLE CONCENTRATION 2-10 LOD	>10 LOD
ALL ANALYSES	25	20
Aluminum	INS	30
Antimony	INS	INS
Barium	INS	20
Beryllium	INS	INS
Boron	INS	INS
Cadmium	INS	INS
Cobalt	INS	INS
Chromium	INS	15
Copper	INS	INS
Iron	INS	10
Lead	INS	INS
Magnesium	INS	35
Manganese	INS	15
Molybdenum	INS	INS
Nickel	INS	INS
Silver	INS	INS
Strontium	INS	INS
Tin	INS	INS
Vanadium	INS	15
Zinc	INS	INS

* FOR ANY CONCENTRATION LESS THAN 2 LOD, THE 95 % CONFIDENCE INTERVAL IS ESTIMATED AT $\pm$ 2 LOD.

LOD= LIMIT OF DETECTION

INS=INSUFFICIENT DATA TO CALCULATE ON AN INDIVIDUAL ANALYTE BASIS

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ANALYTICAL REPORT INTEGRITY FORM

Catalog #: 3178 Lab: KTI Region: 4

☑ Initial QA/QC Review -- Report Correct

DATE	INITIALS	PROBLEMS/ACTION
3-14-90	JM	OK
3-14-90	CPR	Ltr
		Sed. I.C.P BTX

Sample Analysis
Sediment - ICP
Results in µg/g (dry weight)

	Sample Number				
Element	CR001A	CR001C	CR002A	CR003A	CR004A
Al	6120	4520	3470	1040	970
Sb	<25.0	<25.0	<25.0	<25.0	<25.0
Ba	15.4	14.2	19.3	8.63	8.38
Be	0.363	0.306	<0.250	<0.250	<0.250
B	26.1	21.2	13.8	<8.00	<8.00
Cd	<1.00	<1.00	<1.00	<1.00	<1.00
Cr	71.5	59.1	35.1	13.7	8.33
Cu	11.7	<3.50	<3.50	24.3	29.5
Fe	16200	11800	1780	750	550
Pb	<10.0	<10.0	<10.0	12.8	<10.0
Mg	2710	2320	490	330	250
Mn	54.6	43.6	9.70	3.79	3.01
Mo	<4.00	<4.00	<4.00	<4.00	<4.00
Ni	7.03	5.54	<4.00	<4.00	<4.00
Ag	<10.0	<10.0	<10.0	<10.0	<10.0
Sr	171	128	21.4	38.4	33.2
Sn	<30.0	<30.0	<30.0	<30.0	<30.0
V	24.7	21.2	10.9	5.42	5.22
Zn	10.7	3.57	4.83	28.1	8.49

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Sample Analysis
Sediment - ICP
Results in µg/g (dry weight)

	Sample Number				
Element	CR005A	CR005C	CR006A	CR006C	CR007A
Al	17900	5160	970	1630	2720
Sb	<25.0	<25.0	<25.0	<25.0	<25.0
Ba	35.5	18.6	7.10	7.36	14.7
Be	0.540	0.296	<0.250	<0.250	<0.250
B	39.5	17.2	<8.00	9.18	13.5
Cd	<1.00	<1.00	<1.00	<1.00	<1.00
Cr	123	52.6	12.1	35.4	27.1
Cu	237	19.1	8.42	<3.50	88.6
Fe	13300	5240	1140	760	2840
Pb	62.5	<10.0	<10.0	<10.0	<10.0
Mg	2900	680	370	310	1230
Mn	25.1	12.2	5.44	3.71	9.87
Mo	<4.00	4.14	<4.00	<4.00	<4.00
Ni	10.2	<4.00	<4.00	<4.00	<4.00
Ag	<10.0	<10.0	<10.0	<10.0	<10.0
Sr	161	32.4	30.1	11.3	154
Sn	<30.0	<30.0	<30.0	<30.0	<30.0
V	45.7	25.1	3.28	3.35	14.2
Zn	72.0	22.2	<3.50	<3.50	11.8

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Sample Analysis
Sediment - ICP
Results in µg/g (dry weight)

	Sample Number				
Element	CR007C	CR008A	CR008C	CR009A	CR010A
Al	1370	960	340	520	3990
Sb	<25.0	<25.0	<25.0	<25.0	<25.0
Ba	11.3	6.95	3.84	5.97	11.9
Be	<0.250	<0.250	<0.250	<0.250	<0.250
B	8.96	<8.00	<8.00	10.9	19.4
Cd	<1.00	<1.00	<1.00	<1.00	<1.00
Cr	24.9	9.55	4.79	7.22	40.3
Cu	<3.50	6.50	<3.50	<3.50	64.9
Fe	1790	660	160	710	3720
Pb	<10.0	<10.0	<10.0	<10.0	<10.0
Mg	650	250	<100	310	810
Mn	10.6	4.08	<3.00	3.45	8.09
Mo	<4.00	<4.00	<4.00	<4.00	<4.00
Ni	<4.00	<4.00	<4.00	<4.00	5.82
Ag	<10.0	<10.0	<10.0	<10.0	<10.0
Sr	77.7	34.4	3.98	30.5	42.4
Sn	<30.0	<30.0	<30.0	<30.0	<30.0
V	7.76	3.46	1.75	2.58	23.7
Zn	<3.50	<3.50	<3.50	<3.50	6.63

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Sample Analysis
Sediment - ICP
Results in µg/g (dry weight)

	Sample Number				
Element	CR011A	CR012A	CR013A	CR014A	CR015A
Al	7280	3290	3860	2930	4200
Sb	<25.0	<25.0	<25.0	<25.0	<25.0
Ba	18.3	11.8	9.04	11.0	13.2
Be	0.300	<0.250	<0.250	<0.250	<0.250
B	27.0	15.1	25.5	17.9	23.6
Cd	<1.00	<1.00	<1.00	<1.00	<1.00
Cr	65.4	27.2	34.6	24.8	33.1
Cu	115	20.8	18.0	6.07	14.2
Fe	5940	2820	3470	2190	3540
Pb	13.7	<10.0	<10.0	<10.0	<10.0
Mg	1580	670	1360	780	1790
Mn	11.8	6.65	18.9	12.2	23.3
Mo	<4.00	<4.00	<4.00	<4.00	<4.00
Ni	9.25	<4.00	<4.00	<4.00	<4.00
Ag	<10.0	<10.0	<10.0	<10.0	<10.0
Sr	71.5	26.8	42.2	24.0	155
Sn	<30.0	<30.0	<30.0	<30.0	<30.0
V	37.4	12.6	14.2	11.7	13.4
Zn	10.9	<3.50	6.20	4.56	7.10

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Sample Analysis
Sediment - ICP
Results in µg/g (dry weight)

	Sample Number				
Element	CR016A	CR017A	CR018A	CR019A	CR020A
Al	2290	3650	3450	11500	5540
Sb	<25.0	<25.0	<25.0	<25.0	<25.0
Ba	7.91	10.3	11.4	19.6	10.8
Be	<0.250	0.270	<0.250	0.501	0.251
B	17.2	19.8	16.5	37.6	23.1
Cd	<1.00	<1.00	<1.00	<1.00	<1.00
Cr	21.5	31.3	40.6	79.5	41.3
Cu	17.2	30.4	23.8	25.9	49.2
Fe	2410	4170	4400	8480	5000
Pb	<10.0	19.4	13.4	26.7	29.9
Mg	1170	830	840	2340	1220
Mn	17.5	9.06	11.5	23.2	14.6
Mo	<4.00	7.63	<4.00	<4.00	<4.00
Ni	<4.00	4.51	5.41	8.72	5.64
Ag	<10.0	<10.0	<10.0	<10.0	<10.0
Sr	110	37.7	37.0	96.5	33.1
Sn	<30.0	<30.0	<30.0	<30.0	<30.0
V	7.77	11.9	17.1	34.0	13.8
Zn	5.99	6.06	7.77	14.1	10.4

Sample Analysis
Sediment - ICP
Results in µg/g (dry weight)

	Sample Number				
Element	CR021A	CR022A	CR023A	CR024A	CR025A
Al	3250	5730	5160	2070	8970
Sb	<25.0	<25.0	<25.0	<25.0	<25.0
Ba	7.31	14.6	13.2	7.61	16.0
Be	<0.250	0.252	<0.250	<0.250	0.317
B	20.7	16.3	15.5	<8.00	22.5
Cd	<1.00	<1.00	<1.00	<1.00	<1.00
Cr	24.4	42.3	32.7	17.3	49.3
Cu	19.6	24.1	34.6	9.60	40.5
Fe	2920	5550	5010	1160	7920
Pb	<10.0	16.3	11.1	13.1	17.1
Mg	1010	1040	920	320	2210
Mn	17.2	12.8	30.0	6.82	38.8
Mo	<4.00	6.66	6.19	4.20	6.10
Ni	<4.00	<4.00	4.00	<4.00	5.38
Ag	<10.0	<10.0	<10.0	<10.0	<10.0
Sr	32.7	32.7	39.3	10.4	42.7
Sn	<30.0	<30.0	<30.0	<30.0	<30.0
V	9.18	16.2	12.8	5.55	17.1
Zn	7.23	13.4	13.5	3.85	15.3

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Sediment Sample Analysis Results
AA Analyses

Sample Analyses
Sediment - AA

Results in µg/g (dry weight)

	Sample Number					
Element	CR001A	CR001C	CR002A	CR003A	CR004A	CR005A
As	9.08	6.61	2.89	1.00	0.446	6.02
Hg(CV)	0.0430	<0.02	0.0392	<0.02	<0.02	0.246
Se	2.08	1.47	1.81	0.589	0.543	4.61
% Mois.	50.7	52.4	64.6	63.5	52.4	84.4

	Sample Number					
Element	CR005C	CR006A	CR006C	CR007A	CR007C	CR008A
As	3.50	0.638	0.443	5.26	4.06	0.439
Hg(CV)	0.0514	<0.02	<0.02	0.0304	<0.02	<0.02
Se	2.47	0.580	0.894	2.03	0.937	0.617
% Mois.	71.7	58.4	31.0	86.8	39.6	40.9

	Sample Number					
Element	CR008C	CR009A	CR010A	CR011A	CR012A	CR013A
As	<0.3	0.684	2.28	2.57	1.94	1.90
Hg(CV)	<0.02	<0.02	<0.02	0.0356	<0.02	0.0305
Se	<0.3	0.534	2.26	4.56	1.09	1.98
% Mois.	22.6	55.5	65.7	80.5	72.2	85.0

Sample Analyses
Sediment - AA

Results in µg/g (dry weight)

Element	Sample Number					
	CR014A	CR015A	CR016A	CR017A	CR018A	CR019A
As	1.54	2.11	0.858	1.74	1.24	3.53
Hg(CV)	<0.02	<0.02	<0.02	0.0510	<0.02	0.0559
Se	1.21	1.84	1.33	1.71	2.04	4.15
% Mois.	71.3	78.3	73.1	68.6	61.4	87.0

Element	Sample Number					
	CR020A	CR021A	CR022A	CR023A	C4024A	CR025A
As	1.57	1.02	1.63	1.24	0.336	1.64
Hg(CV)	0.0358	0.0346	<0.02	0.0345	<0.02	0.0523
Se	1.86	1.47	1.94	1.37	0.548	1.42
% Mois.	75.9	72.2	60.1	65.6	31.0	59.8

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Sediment Sample Analysis/ICP

QC/QA
Detection Limits
Duplicate Sample Analyses
Spike Analyses
SRM Sample Analyses
Method Blank Analyses

ICP Method Detection Limits

Results in µg/g (dry weight)

Element	Sediment
Al	100
Sb	25
Ba	2.0
Be	0.25
B	8.0
Cd	1.0
Cr	3.0
Cu	3.5
Fe	100
Pb	10
Mg	100
Mn	3.0
Mo	4.0
Ni	4.0
Ag	10
Sr	2.0
Sn	30
V	1.0
Zn	3.5

AA Method Detection Limits

Results in µg/g (dry weight)

Element	Sediment
As	0.3
Hg(CVAA)	0.02
Se	0.3

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QC/QA--Duplicate Sample Analyses
Sediment - ICP

Results in µg/g (dry weight)

Element	CR001A Sample	CR001A Dup.	CR010A Sample	CR010A Dup.	CR019A Sample	CR019A Dup.	----- Sample	----- Dup.
Al	6120	6130	3990	3820	11500	13300		
Sb	<25	<25	<25	<25	<25	<25		
Ba	15.4	15.5	11.9	11.6	19.6	22.0		
Be	0.363	0.380	<0.25	<0.25	0.501	0.527		
B	26.1	28.6	19.4	19.1	37.6	39.9		
Cd	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0		
Cr	71.5	72.9	40.3	39.1	79.5	87.2		
Cu	11.7	13.7	64.9	63.4	25.9	27.3		
Fe	16200	16700	3720	3610	8480	9160		
Pb	<10	<10	<10	13.8	26.7	26.0		
Mg	2710	2720	810	760	2340	2610		
Mn	54.6	58.9	8.09	7.06	23.2	24.7		
Mo	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0		
Ni	7.03	6.87	5.82	4.67	8.72	9.69		
Ag	<10	<10	<10	<10	<10	<10		
Sr	171	170	42.4	32.7	96.5	111		
Sn	<30	<30	<30	<30	<30	<30		
V	24.7	26.0	23.7	23.8	34.0	38.1		
Zn	10.7	10.0	6.63	6.57	14.1	15.6		

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QC/QA--Spike Analyses

Sediment - ICP

Results in µg/mL

Element	Expec.	CR001C Found	% Rec.	Unspiked Sample	Expec.	CR021A Found	% Rec.	Unspiked Sample
Al	10.0	6	*	24	10.0	12.7	*	16.3
Sb	2.00	1.78	89.0	<0.05	2.00	1.61	80.5	<0.05
Ba	1.01	0.793	78.5	0.07	1.01	0.787	77.9	0.04
Be	1.00	0.863	86.3	<0.01	1.00	0.847	84.7	<0.01
B	1.01	0.910	90.1	0.10	1.01	0.896	88.7	0.10
Cd	1.00	0.921	92.1	<0.01	1.00	0.853	85.3	<0.01
Cr	1.00	0.870	87.0	0.27	1.00	0.868	86.8	0.12
Cu	1.00	0.865	86.5	<0.01	1.00	0.864	86.4	0.10
Fe	10.0	10	*	50	10.0	14.4	*	14.6
Pb	5.20	4.62	88.8	<0.05	5.20	4.46	85.8	<0.05
Mg	10.0	9	*	12.5	10.0	14.0	*	5.05
Mn	1.00	0.85	85.0	0.21	1.00	0.839	83.9	0.09
Mo	1.00	0.941	94.1	<0.01	1.00	0.871	87.1	<0.01
Ni	5.00	4.43	88.6	0.02	5.00	4.31	86.2	0.01
Ag	0.200	0.120	60.0	<0.01	0.200	0.053	26.5	<0.01
Sr	1.00	0.800	80.0	0.61	1.00	0.915	91.5	0.16
Sn	2.00	1.56	78.0	<0.05	2.00	1.55	77.5	<0.05
V	1.00	0.828	82.8	0.09	1.00	0.803	80.3	0.05
Zn	1.00	0.942	94.2	0.01	1.00	0.837	83.7	0.04

*Spike:Background Ratio <1

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QC/QA--SRM Sample Analyses
Sediment - ICP

Results in µg/g (dry weight)

	PACS-1		PACS-1		-----		-----	
Element	Expec.	Found	Expec.	Found	Expec.	Found	Expec.	Found
Al	-----	9000	-----	10100				
Sb	171	180	171	146				
Ba	-----	494	-----	552				
Be	-----	0.900	-----	0.900				
B	-----	93.0	-----	95.8				
Cd	2.38	2.00	2.38	2.60				
Cr	113	71.9	113	75.4				
Cu	452	372	452	378				
Fe	-----	39000	-----	39000				
Pb	404	373	404	394				
Mg	-----	11000	-----	12000				
Mn	470	386	470	388				
Mo	12.3	11.6	12.3	11.8				
Ni	44.1	36.5	44.1	33.9				
Ag	-----	<10	-----	<10				
Sr	277	210	277	223				
Sn	41.1	<30	41.1	<30				
V	127	102	127	103				
Zn	824	755	824	749				

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Method Blank Analyses
Sediment - ICP

Results in µg/g (dry weight)

Element	Sample Number					
	1	2	-----	----	-----	-----
Al	<100	<100				
Sb	<25	<25				
Ba	<2.0	<2.0				
Be	<0.25	<0.25				
B	<8.0	11.8				
Cd	<1.0	<1.0				
Cr	<3.0	<3.0				
Cu	<3.5	<3.5				
Fe	<100	<100				
Pb	<10	<10				
Mg	<100	<100				
Mn	<3.0	7.18				
Mo	<4.0	4.30				
Ni	<4.0	<4.0				
Ag	<10	<10				
Sr	<2.0	<2.0				
Sn	<30	<30				
V	<1.0	<1.0				
Zn	<3.5	<3.5				

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Sediment Sample Analysis/AA

QC/QA
Duplicate Sample Analyses
Spike Analyses
SRM Sample Analyses
Method Blank Analyses

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QC/QA--Duplicate Sample Analyses

Sediment - AA

Results in µg/g (dry weight)

Element	CR010A Sample	CR010A Dup.	CR019A Sample	CR019A Dup.	----- Sample	----- Dup.	----- Sample	----- Dup.
As	2.28	2.17	3.53	3.63				
Hg(CV)	<0.02	<0.02	0.0559	0.0698				
Se	2.26	2.37	4.15	3.72				

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QC/QA--Spike Analyses

Sediment - AA

Results in µg/mL

Element	Expec.	CR011A Found	% Rec.	Unspiked Sample	Expec.	CR021A Found	% Rec.	Unspiked Sample
As	0.200	0.189	94.5	0.0260	0.200	0.206	103	0.0104
Hg(CV)	0.0240	0.0265	110	0.000360	0.0240	0.0264	110	0.000354
Se	0.200	0.202	101	0.0461	0.200	0.213	106	0.0150

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QC/QA--SRM Sample Analyses

Sediment - AA

Results in µg/g (dry weight)

Element	NBS 1645 Expec.	NBS 1645 Found	NBS 1645 Expec.	NBS 1645 Found	NBS 2704 Expec.	NBS 2704 Found	PACS-1 Expec.	PACS-1 Found
As	66	62.9	66	72.5	-----	-----	-----	-----
Hg(CV)	-----	-----	-----	-----	1.44	1.56	4.57	4.61
Se	-----	-----	-----	-----	1.1	0.941	1.09	1.19

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Method Blank Analyses
Sediment - AA

Results in µg/g (dry weight)

	Sample Number					
Element	1	2	-----	-----	-----	-----
As	<0.3	<0.3				
Hg(CV)	<0.02	<0.02				
Se	<0.3	<0.3				