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QUALITY CONTROL FOR MAFLA IV AND SOUTH TEXAS II INVESTIGATIONS

Final Report
to the
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DEPARTMENT OF ANALYTICAL CHEMISTRY

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FINAL REPORT

TRACE METAL ANALYSIS: QUALITY CONTROL FOR MAFLA IV AND SOUTH TEXAS II INVESTIGATIONS

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Chapter I

Executive Summary

A comprehensive quality control program, Contract No. 08850-CT5-49, was conducted by Gulf South Research Institute (GSRI) in support of the MAFLA OCS Monitoring and South Texas OCS Baseline Program for the Bureau of Land Management, Department of the Interior.

A total of 241 marine environmental samples including 10 suspended particulates, 31 zooplankton, 19 paint chip samples, 75 sediment, and 106 epifauna samples were subjected to quality control trace metal analysis. All samples were chosen at random from the samples analyzed by the prime contractor. Those samples delivered to GSRI consisted of three sample groups composed of a total of five different sample types: South Texas Baseline - suspended particulates, zooplankton, sediments, and epifauna; MAFLA Monitoring - zooplankton, paint chips, sediments and epifauna; MAFLA Rig Monitoring - sediments and epifauna. All samples were analyzed for cadmium, chromium, copper, lead, nickel, and vanadium. Additional metals were determined with each of the three groups. South Texas Baseline samples were analyzed for zinc; South Texas sediment and epifauna samples were also analyzed for barium. MAFLA Monitoring and MAFLA Rig Monitoring samples received iron analysis. The MAFLA Monitoring paint chip samples and sediments and Rig Monitoring sediment samples were also analyzed for barium.

GSRI analyzed 10 suspended particulate samples. The high, low, and average concentration for metals of interest are listed in Table 1 in

units of micrograms per liter of water filtered.

An accuracy study was funded by BLM in anticipation of errors and interferences in analysis of biota similar to those encountered by GSRI during previous analyses of BLM sediment samples. The hot nitric acid digestion procedure cited in Contract No. 08850-CT5-49 was studied and was found to be too costly in addition to yielding poor results. A liquid fire digestion was tested which gave relatively imprecise data and is hazardous to the user. A third procedure, referred to as the Ten-Day procedure, utilized the principle of the Parr bomb. The three procedures were tested by digesting aliquots of four biota pools provided by BLM (shrimp, oyster, sand dollars, and flounder). Data showing trace metal analyses of the pools by each of these methods are presented. The analysis of the pools made them useful as in-house standards for the analyses of epifauna samples. The Ten-Day procedure was approved by BLM for digestion of the epifauna and zooplankton samples on the basis of the results of the accuracy study.

The 31 zooplankton samples received by GSRI included 15 from the MAFLA Monitoring phase of the study and 16 from the South Texas Baseline survey. A summary of high, low, and average metal contents on the South Texas zooplankton samples are shown in Table 2. The high, low, and average value of the trace metals measured for the MAFLA Monitoring samples are presented in Table 3.

Seventeen paint chip samples from the MAFLA Baseline were analyzed for all eight trace metals. The average, low, and high concentrations are shown in Table 4. Two paint chip samples from the South Texas study had similar concentrations of lead, nickel, and vanadium while barium and copper content was very dissimilar.

Concentration (µg/l of water filtered)

Metal	Average	Low	High
Cd	0.0053	0.0001 (243M)[a]	0.001 (243B)
Cr	0.011	0.001 (155M)	0.42 (156B)
Cu	0.009	0.0004 (243M)	0.028 (243T)
Ni	0.015	0.0008 (155T)	0.055 (156B)
Pb	0.0095	0.0012 (155M)	0.045 (243T)
V	0.022	0.004 (243M)	0.081 (156B)
Zn	0.13	0.019 (155M)	0.37 (243T)

[a]Numbers and/or letters in parenthesis indicate BLM sample designation.

Table 1. Summary of Data for Suspended Particulate Matter Samples.

Concentration (ppm, dry weight basis)

Metal	Average	Low	High
Cd	3.6	0.27 (AIZ-ZPL-QC-tm)[a]	8.8 (CGN-ZPL-QC-tm)
Cr	5.1	0.55 (EDJ-ZPL-QC-tm)	47.0 (ARJ-ZPL-QC-tm)
Cu	15	4.1 (AIZ-ZPL-QC-tm)	45.8 (CGN-ZPL-QC-tm)
Ni	14	1.7 (CTG-ZPL-QC-tm)	26.0 (ETG-ZPL-QC-tm)
Pb	63	3.6 (CTG-ZPL-QC-tm)	527 (APJ-ZPL-QC-tm)
V	42	3.3 (AHZ-ZPL-QC-tm)	378 (AOG-ZPL-QC-tm)
Zn	97	21.5 (AIZ-ZPL-QC-tm)	162 (ARJ-ZPL-QC-tm)

[a]Numbers and/or letters in parenthesis indicate BLM sample designation.

Table 2. Summary of Data for Zooplankton Samples - South Texas Baseline.

	Concentration (ppm, dry weight basis)		
Metal	Average	Low	High
Cd	17	5.0 (1101)[a]	79 (1310)
Cr	1.1	0.46 (1414)	2.6 (1308)
Cu	27	9.6 (1207)	65.7 (1204)
Fe	242	75 (1308)	751 (1310)
Ni	16	8.5 (1206)	36.2 (1308)
Pb	20	10.3 (1207)	34.5 (1205)
V	19	4.3 (1207)	122 (1413)

[a]Numbers in parenthesis indicate BLM sample designation.

Table 3. Summary of Data for Zooplankton Sample - MAFLA Monitoring.

Metal	Unit of Concentration	Average	Low	High
Ba	ppm	273	21.4 (PCM-4)[a]	1310 (PCM-1)
Cd	ppm	3.7	<0.2 (6 samples)	33.9 (PCM-2)
Cr	%	0.18	0.006 (PCM-12)	0.56(PCM-11)
Cu	ppm	424	31.5 (PCM-4)	3763 (PCM-8)
Fe	%	4.7	0.31(PCM-5)	34.4 (PCM-4)
Ni	ppm	44	6.3 (PCM-1)	158 (PCM-2)
Pb	%	3	0.05(PCM-15)	13.0 (PCM-8)
V	ppm	28	4.9 (PCM-1)	163 (PCM-4)

[a]Numbers and/or letters in parenthesis indicate BLM sample designation.

Table 4. Summary of Paint Chip Data - MAFLA Monitoring.

The metals present in large quantities in the sediments which dissolve along with trace metals during digestion of the samples include aluminum, calcium, iron, magnesium, potassium, and sodium. Barium, chromium, copper, nickel, and vanadium in sediments, were measured against aqueous standards and matrix-matched standards since a matrix effect was observed for these five trace constituents. The average, low, and high values for each metal are listed in Table 5 (MAFLA Rig Monitoring) and Table 6 (MAFLA Monitoring). The dissolved barium content for the latter was measured by flameless AAS. The trace metal analyses of twenty-nine sediment samples from the South Texas Baseline Study (U.S. Geological Survey) showed very different levels of barium, chromium, and vanadium for the total versus partial digestion methods. The average, low, and high concentration of metals of interest are summarized in Table 7.

The in-house standard reference sediments, Sample A and Sample B, employed for quality control purposes for the MAFLA Baseline Survey, were also used for this investigation. In addition, a third bulk sediment, Sample C, was incorporated into the present study. Quality Control Charts are presented for these three sediments for the trace metal determinations. Percent recovery data for the three in-house standard reference sediments are also presented.

The 106 epifauna samples received by GSRI for trace metal analysis included 30 from the South Texas Baseline (University of Texas), 39 from the MAFLA Monitoring, and 37 from MAFLA Rig Monitoring. The majority of the South Texas Baseline samples were analyzed by flameless AAS for all trace metals of interest except copper and zinc. The average, low, and high

Concentration (dry weight basis)

Metal		Partial Digestion	Total Digestion
Ba	average	82 ppm (131 ppm)[a]	446 ppm (510 ppm)[a]
	low	33.0 ppm (551301 TSQC 4)[b]	215 ppm (551301 TSQC 4)
	high	189 ppm (591901 TSQC 2)	1390 ppm (551001 TSQC 2)
Cd	average	c	c
	low	<0.04 ppm (2 samples)	<0.04 ppm (11 samples)
	high	0.19 ppm (551401 TSQC 4)	0.15 ppm (551401 TSQC 3)
Cr	average	35 ppm (38 ppm)[a]	52 ppm (55 ppm)[a]
	low	16.9 ppm (510501 TSQC 3)	30.7 ppm (510501 TSQC 3)
	high	52.1 ppm (592501 TSQC 2)	60.6 ppm (592101 TSQC 2)
Cu	average	14 ppm (15 ppm)[a]	13 ppm (15 ppm)[a]
	low	7.3 ppm (510501 TSQC 3)	3.2 ppm (551401 TSQC 3)
	high	18.8 ppm (510801 TSQC 2)	17.9 ppm (592501 TSQC 2)
Fe	average	0.4%	1.9%
	low	0.05% (55100 TSQC 2)	0.8% (510901 TSQC 4)
	high	1.1% (592101 TSQC3)	2.7% (510601 TSQC 2)
Ni	average	27 ppm (26 ppm)[a]	38 ppm (40 ppm)[a]
	low	14.6 ppm (510501 TSQC 3)	14.2 ppm (510901 TSQC 4)
	high	58.6 ppm (551301 TSQC 3)	61.1 ppm (591901 TSQC 2)
Pb	average	26 ppm	26 ppm
	low	15.8 ppm (510501 TSQC 3)	18.8 ppm (591901 TSQC 2)
	high	33.2 ppm (510801 TSQC 2)	31.1 ppm (592301 TSQC 4)
V	average	82 ppm (62 ppm)[a]	128 ppm (102 ppm)[a]
	low	33.2 ppm (551401 TSQC 4)	76.4 ppm (510501 TSQC 3)
	high	121 ppm (591901 TSQC 2)	192 ppm (510901 TSQC 3)

[a] Matrix -matched Standards.

[b] Numbers and/or letters in parentheses indicate BLM sample designation.

[c] Average not applicable - one or more analyses below detection limit.

Table 5. Summary of Data for Sediment Samples - MAFLA Rig Monitoring.

Concentration (dry weight basis)

Metal		Partial Digestion	Total Digestion
Ba	average	18 ppm	89 ppm
	low	2.4 ppm (2642)[a]	16.5 ppm (1642)
	high	71.8 ppm (2530R)	156 ppm (2209J)
Cd	average	0.08 ppm	0.06 ppm
	low	<0.04 ppm (2 samples)	<0.04 ppm (13 samples)
	high	0.13 ppm (2208J, 2212J)	0.24 ppm (2645)
Cr	average	13 ppm (23 ppm)[b]	15 ppm (14 ppm)[b]
	low	<0.1 ppm (2642)	0.7 ppm (2419K)
	high	25.5 ppm (2313J)	24.2 ppm (2535R)
Cu	average	8 ppm (8 ppm)[b]	5 ppm (5 ppm)[b]
	low	0.8 ppm (2642)	0.5 ppm (2419K)
	high	15.3 ppm (2212J)	9.0 ppm (2213J)
Fe	average	0.20%	0.27%
	low	0.02% (2642)	0.03% (2419K)
	high	0.98 (2213J)	0.96% (2213J)
Ni	average	18 ppm (19 ppm)[b]	16 ppm (22 ppm)[b]
	low	1.7 ppm (2622)	0.6 ppm (2642)
	high	30.9 ppm (2535R)	37.4 ppm (2212J)
Pb	average	33 ppm	21 ppm
	low	2.1 ppm (2642)	4.1 ppm (2642)
	high	47 ppm (2645)	35.6 ppm (2535R)
V	average	21 ppm	17 ppm
	low	1.5 ppm (2642)	2.0 ppm (2642)
	high	39.9 ppm (2645)	44.8 ppm (2535R)

[a]Numbers and/or letters in parenthesis indicate BLM sample designation.

[b]Matrix-matched Standards.

Table 6. Summary of Data for Sediment Samples - MAFLA Monitoring.

Metal		Concentration (dry weight basis) Partial Digestion	Total Digestion
Ba	average	66.3 ppm (64 ppm)[a]	380 ppm (393 ppm)[a]
	low	28.9 ppm (235)[b]	309 ppm (241)
	high	99.7 ppm (164)	481 ppm (273)
Cd	average	c	c
	low	<0.04 ppm (5 samples)	<0.04 ppm (142)
	high	0.28 ppm (176)	0.38 ppm (235)
Cr	average	30 ppm (33 ppm)[a]	52 ppm (54 ppm)[a]
	low	18.1 ppm (230)	25.2 ppm (230)
	high	39.3 ppm (226)	79.7 ppm (165)
Cu	average	11 ppm (12 ppm)[a]	14 ppm (14 ppm)[a]
	low	6.4 ppm (8)	3.6 ppm (32)
	high	16.0 ppm (226)	58.9 ppm (245)
Ni	average	17 ppm (8 ppm)[a]	19 ppm (18 ppm)[a]
	low	6.8 ppm (236)	8.5 ppm (230)
	high	24.7 ppm (88)	31.8 ppm (32)
Pb	average	16 ppm (16 ppm)[a]	22 ppm
	low	9.0 ppm (165)	11.0 ppm (137)
	high	25.1 ppm (176)	34.7 ppm (245)
V	average	66 ppm (64 ppm)[a]	129 ppm (106 ppm)[a]
	low	43.6 ppm (238)	60.2 ppm (30)
	high	93.6 ppm (176)	189 ppm (88)
Zn	average	79 ppm	75 ppm
	low	32.4 ppm (230)	36.9 ppm (230)
	high	273 ppm (235)	123 ppm (226)

[a]Matrix-matched Standards.

[b]Numbers and/or letters in the parenthesis indicate BLM sample designation.

[c]Average not applicable. One or more analyses below detection limit.

Table 7. Summary of Data for Sediment Samples - South Texas Baseline.

concentration of trace metals analyzed are shown in Table 8. Flame AAS was applicable to the analyses of the majority of the MAFLA Monitoring samples. A summary of average, low, and high measurements is presented in Table 9. The data summary for the MAFLA Rig Monitoring sample is given in Table 10. All metals except copper and iron were determined by flameless AAS. Fourteen replicates of NBS SRM 1577 were analyzed with the 106 epifauna samples for quality control purposes. The selection of duplicates, concentration for spiked samples, in-house standards, and NBS SRM's is described in detail. The trace metal determinations for SRM 1577 and SRM 1571 are given in Table 11 along with the values certified by the National Bureau of Standards.

Concentration (ppm, dry weight basis)

Metal	Average	Low		High	
Ba	1.5	0.4	(END-EPI-QC-tm)	3.7	(ETM-EPI-QC-tm)
Cd	0.3	0.02	(CTM-EPI-QC-tm)	4.1	(DGL-EPI-QC-tm)
Cr	a	<0.1	(28 samples)	11.9	(BGQ-EPI-QC-tm)
Cu	15.5	0.7	(CQE-EPI-QC-tm)	99.8	(DGL-EPI-QC-tm)
Ni	a	0.1	(15 samples)	26.7	(END-EPI-QC-tm)
Pb	a	<0.02	(2 samples)	3.4	(CND-EPI-QC-tm)
V	0.3	<0.3	(all 30 samples)	<0.3	
Zn	30.9	9.7	(EGT-EPI-QC-tm)	102	(DGL-EPI-QC-tm)

[a]Average not applicable - one or more analyses below detection limit.

Table 8. Summary of Data for Epifauna Samples - South Texas Baseline.

Concentration (ppm, dry weight basis)

Metal	Average	Low		High	
Cd	1.7	0.03	(2 samples)	8.3	(IV-B C-6)
Cr	a	<0.1	(8 samples)	6.5	(V-A A-4)
Cu	10.8	2.2	(III-B C-6)	80.9	(IV-B C-6)
Fe	316	7.8	(I-B C-8)	4230	(VI-B A-8)
Ni	a	<0.1	(3 samples)	86.7	(V-A A-4)
Pb	20.4	<0.02	(2 samples)	59.3	(247-A-15)
V	a	<0.3	(3 samples)	48.5	(VI-A C-2)

[a]Average concentration not applicable - one or more analyses below detection limit.

Table 9. Summary of Data for Epifauna Samples - MAFLA Monitoring.

	Concentration (ppm, dry weight basis)		
Metal	Average	Low	High
Cd	0.3	0.01 (4517 TEQC 2)	2.6 (4919 TEQC 3)
Cr	a	<0.1 (21 samples)	1.3 (4923 TEQC 4)
Cu	33.6	8.6 (4510 TEQC 2)	92.9 (4106 TEQC 5)
Fe	78.2	4.5 (4918 TEQC 2)	517 (4510 TEQC 2)
Ni	2.7	0.3 (5 samples)	10.8 (4102 TEQC 5)
Pb	a	<0.02 (7 samples)	4.7 (4510 TEQC 1)
V	a	<0.3 (29 samples)	52.9 (4923 TEQC 4)

[a]Average concentration not applicable - one or more analyses below detection limit.

Table 10. Summary of Data for Epifauna Samples - MAFLA Rig Monitoring.

	Concentration (ppm, dry weight basis)			
	NBS SRM 1577		NBS SRM 1571	
Metal	Expt.	Certified	Expt.	Certified
Cd	0.30±0.12	0.27±0.04	0.10±0.03	0.11±0.02
Cu	186±19	193±10	10.6±0.6	12±1
Fe	257±33	270±20	151±6	300±20
Ni	a	a	1.2±0.5	1.3±0.2
Pb	1.56±0.93	0.34±0.08	41.9±3.9	45±3
Zn	115±14	130±10	23.0±0.5	25±3

[a]Not certified for trace metal of interest

Table 11. Summary of Data for NBS SRM 1577 and SRM 1571.

CHAPTER II

INTRODUCTION

The data for the trace metal analyses of suspended particulate matter, biota, and sediment is presented in the chapters to follow. A detailed Sample Log Summary is included as Appendix A. The BLM cruise number and sample number is listed with the date each sample was received by Gulf South Research Institute.

The biota accuracy study data and discussion is contained in a chapter (IV) separate from the actual trace metal analysis information (Chapter VI). The sediment analyses and all quality control information for the sediment sets is discussed in Chapter VII.

The analysis of empty sample containers is discussed with the appropriate group of samples. The epifauna sample bags are discussed in Chapter VI and the sediment tube analysis is presented in Chapter VII. Another check for potential contamination was performed involving the analysis of paint chip samples scraped from the sampling vessels. The paint chip data is included at the end of the report as Appendix B.

All data charts are contained in the individual chapters for ease of referral during discussions of anomalies and results. The epifauna data tables in Chapter VI include a facing page which lists the scientific name of each species and the percent solids for each. The captions for the tables and figures are listed both as part of the Table of Contents and under each presentation.

CHAPTER III

SUSPENDED PARTICULATE MATTER

Ten samples of suspended particulate matter were received for analysis for the South Texas Baseline Survey. Blank filters were not received and the weights on the particulate matters were not recorded following collection. The volume of water passed through each filter was approximately ten liters.[1]

The membrane filter containing the insoluble material was transferred from the sealed, plastic container to a two hundred fifty (250) ml Griffin beaker. Three (3) ml of concentrated ULTREX HNO_3 was added, the beaker was covered with a ribbed beaker cover, and the beaker was gently heated to dissolve the membranes. The temperature of the hot plate was increased to digest the material. The acid was evaporated and the beaker and cover cooled. Three (3) ml of concentrated ULTREX HNO_3 was added and heating was continued until digestion was complete, indicated by a light-colored residue. Two (2) ml of 1:1 ULTREX HCl was added to the dry residue and the beaker gently warmed to dissolve the material. The beaker and cover were washed with deionized distilled water and the sample was filtered to remove silicates and other insoluble material. The final volume was adjusted to 10.0 ml.

The analysis of the prepared solutions for trace metal content was performed without using extraction methods since these techniques are difficult to apply due to instability of the metal chelate complexes.

[1] Telecon from C. Holmes, USGS, Corpus Christi, via E. D. Wood, COAR.

The analysis for zinc, chromium, nickel, vanadium, cadmium, lead, and copper was performed directly by flameless atomic absorption spectrophotometry.

The results of analyses for trace metals in particulate samples were to be reported on a dry weight basis to the nearest one-tenth part-per-billion (weight/volume). Since the weight of the solid material was not recorded the data will be reported in units of microgram metal per liter of water filtered based on a ten liter water filtration volume. The trace metal data given in these units is presented in Table 12. The sample described 156T(M) was received as 156T (identical to another sample). The choice of which sample labeled 156T to rename 156T(M) was made by observing that the trace metal data for other members of top, bottom, and middle groups showed the top sample to be highest in most metal levels. This may not be a correct assumption since this rule does not hold for every case. No samples were supplied in duplicate for these samples.

The interpretation of this data will remain very difficult since the weight of solid material is unknown. The best method of comparing data from the Quality Control Laboratory with the other laboratories will be to convert all data to the same units.

BLM Cruise No.	BLM Sample No.	V ($\times 10^{-3}$)	Cd ($\times 10^{-3}$)	Pb ($\times 10^{-3}$)	Ni ($\times 10^{-3}$)	Cu ($\times 10^{-3}$)	Cr ($\times 10^{-3}$)	Zn ($\times 10^{-3}$)
B	155T	15.5	0.47	5.9	0.8	4.8	7.1	35.0
B	155M	10.2	0.13	1.2	3.2	0.7	1.2	18.5
B	155B	26.0	0.70	9.1	11.0	8.8	16.2	84.0
B	156T	20.5	0.23	4.0	21.1	7.2	4.7	65.5
B	156T(M)	10.5	0.71	2.6	30.1	7.3	7.5	195
B	156B	81.0	0.76	15.8	55.4	17.4	42.2	280
B	157T	7.4	0.66	3.7	10.6	7.6	2.9	114
B	243T	23.0	0.52	44.5	10.9	28.4	18.7	365
B	243M	4.0	0.11	1.6	1.2	0.4	4.6	36.5
B	243B	22.0	1.00	6.9	8.0	7.8	2.5	94.5

Table 12. Trace Metal Quality Control Data for Suspended Particulate Matter Samples for BLM Cruise B - South Texas Baseline.

Concentration Units: µg metal per liter of water filtered.

CHAPTER IV

BIOTA ACCURACY STUDY

A. General

Due to the errors noted by GSRI for sediment analysis, BLM funded an accuracy study for the biota procedure to be employed in this study. The parameters investigated in the program were as follows:

1. Type and amount of digestion media.
2. Size of sample required for attainment of acceptable minimum detection limits.
3. Loss of any trace metal during heating process (using spiked samples).
4. Time required for the digested sample to reach the clear, colorless state.
5. Dilution volume required for attainment of acceptable minimum detection limits.
6. Identification of potential interferences affecting trace metal analysis by AAS.
7. Precision and accuracy.

The study was performed using four large biota pools of shrimp, oysters, sand dollars, and flounder. The pooled samples were prepared by cleaning, drying, and grinding each of the four biota types. Grinding was accomplished with an electric grinder using aliquots of the pools. Multiple grinding and mixing was performed until the samples were as homogeneous as possible.

The digestion procedure to be studied (contained in Contract No. 08850-CT5-49) did not correspond reasonably well to any of the four methods recommended by the participants in the BLM Standardization Workshop held in Washington, D.C. on September 10-12, 1975. GSRI believed these four methods should be evaluated by the accuracy study but was requested instead to use the contracted method.

In addition to the analysis of the four biota pools, the analysis of 40 BLM biota samples, ten for each of the four pool species, was performed as part of the accuracy study. A pool of freeze-dried oysters obtained from the Food and Drug Administration (FDA) and a pool of freeze-dried tuna supplied by the National Bureau of Standards (NBS) were used for quality control purposes throughout the study. NBS Standard Reference Materials 1571 (orchard leaves) and 1577 (bovine liver) were also studied. These SRM's are of different matrices than the biota samples under investigation so interpretation of data for these samples should be made with caution.

B. Pool Preparation

1. Shrimp

Each container of shrimp was thawed and the shrimp were cleaned using plastic cleaners. All inedible portions were removed including shell and digestive apparatus. The total wet weight of shrimp remaining following cleaning was 1955 grams. The shrimp were dried to constant weight at 105^{o}C in clean, acid-washed, tared beakers. Seven days and nights (168 hours) of drying time was required on the average for this

step to be completed. The dry weight of shrimp was 415 grams. The average percent moisture lost during drying was 78.8%.

2. Flounder

The flounder species were thawed and cleaned; all inedible portions were removed and only the fleshy portions were retained for analysis. It was necessary to use a stainless steel knife to separate the skin of these fish from the flesh. A new knife was purchased and cleaned prior to use. Since this step involves potential contamination, the flesh at the beginning of the skinning process where the knife was necessarily in direct contact was removed using a Teflon coated spatula. This flesh portion (very small percentage of the total) was retained to determine if contamination did result. The total wet weight of flounder prepared was 3,383 grams. The flounder were dried to constant weight in a 105°C oven for an average of 5 days and nights (120 hours). The dry weight of prepared flounder obtained was 758 grams corresponding to a 77.6 percent moisture loss.

3. Oyster

The frozen oysters received by GSRI for the biota accuracy study were shucked by the sampling team prior to shipment. The shucked oysters were thawed and placed in acid-cleaned, dry, tared beakers. The total wet weight of the oyster pool was 2,294 grams. The beakers with oysters were placed in a 105°C oven for 5 days and nights (an average of 120 hours) to be dried to constant weight. The weight of dried oysters resulting was 331 grams corresponding to an 85.6 percent moisture loss.

4. Sand Dollars

The sand dollar samples were thawed at room temperature overnight. The entire organism was prepared for analysis for this species. The total wet weight of the sand dollar pool was 1430 grams. The samples were placed in acid-cleaned, dry, tared beakers and dried in a 105°C oven for 88 hours. The weight of the dried sand dollars was 1093 grams corresponding to 23.6 percent moisture loss.

C. Experimental

The experiments performed using the four biota pools will be described below in chronological order. The sand dollar pool was not included in early experiments since information requested from BLM regarding the preparation of the pool did not arrive until part of the study had been completed.

1. Experiment I

The digestion procedure used for the preparation of the first set of samples for trace metal analyses is that cited in Contract No. 08850-CT5-49. The procedure is as follows:

a. Weigh a one (1) gram sample of biota into a clean beaker.

b. Add three (3) ml of concentrated ULTREX HNO_3.

c. Cover the beaker with a watch glass and heat the contents until the solution is clear and colorless, adding HNO_3 as needed.

d. Evaporate the solution almost to dryness.

e. Add a small quantity of distilled water and 0.5 ml HNO_3 to resolubilized the salts.

f. Transfer the contents quantitatively to a 10.0 ml volumetric flask and dilute to volume with distilled water.

g. Analyze for trace metal content by flame or flameless AAS.

The first set of samples to be analyzed for trace metal content included the following:

a. 15 one-gram replicates of the dried shrimp pool;

b. 1 replicate of the shrimp pool spiked with 10 ppm vanadium;

c. 1 replicate of the shrimp pool spiked with 10 ppm copper;

d. 5 replicates of the freeze-dried oysters obtained from FDA;

e. 5 replicates of the freeze-dried tuna fish obtained from the National Bureau of Standards;

f. One sample determination of NBS Standard Reference Material (SRM) 1571 (orchard leaves);

g. Two sample determinations of NBS SRM 1577 (bovine liver); one 0.5 gram sample size and one 1.0 gram sample size. Two final concentrations of bovine liver SRM were used in order to better approximate the expected metal levels in the shrimp supplied by BLM.

h. Six reagent/glassware blanks.

A significant problem was encountered with this digestion procedure. Step (c.) in the procedure above required 32 hours to accomplish for some samples while the clear and colorless condition was not even achieved for all sample digestions. The quantity of ULTREX HNO_3 used was considerable ranging from 20 to 90 ml per sample. Concentrating such large volumes of acid to 10 ml induced large blanks even for the very pure (low trace metal levels) ULTREX acid. Since several days were spent digesting the samples, blanks were prepared for commercially available HNO_3 certified suitable for mercury determinations. (The low Hg nitric acid costs $9.00 for the usual 7 lb size while ULTREX HNO_3 costs $60 for 500 ml quantities.) Sixty ml of HNO_3, both ULTREX and low-Hg, were concentrated for blank measurements. Comparison of the blanks for the two HNO_3 acids is shown in Table 13. Surprisingly, the ULTREX blanks yielded higher trace metal levels than low-Hg HNO_3 for iron, chromium, zinc, and nickel. Vanadium, copper, and lead blanks were comparable for both varieties of HNO_3 while cadmium content was higher in the low-Hg HNO_3 blank. However, both sets of blanks contained significant quanties of the trace elements of interest.

In addition to economic considerations and problems with relatively high reagent blanks, the lengthy digestion procedure

Trace Metal	ULTREX HNO_3	Low-Hg HNO_3
V	0.5	0.5
Fe	1.4	0.7
Cu	0.2	0.3
Cr	2.3	0.7
Zn	1.3	0.7
Ni	0.04	0.01
Pb	0.12	0.15
Cd	0.008	0.018

Table 13. Concentration of Trace Metals (ppm) Determined for ULTREX and Low-Hg HNO_3 in Experiment I.

presents logistic difficulties. If one is required to add HNO_3 repetitively to a sample container in 3 ml aliquots as many as 20 to 30 times, the following problems may be anticipated:

a. Chances for metal contamination are increased;

b. Chances for metal losses are enhanced;

c. Spilling of samples may occur since hot beaker covers must be lifted with tongs held in one hand while acid is added with the other hand; the covers must then be replaced without disturbing the beaker.

d. Keeping constant watch over a set of samples being digested is difficult since small 3 ml volumes can evaporate simultaneously for several samples and require further addition of acid to more than one sample.

The total number of samples prepared in this first set was 30 (excluding blanks). Five samples of the 30 were spilled during this sample preparation step. One beaker cover was dropped and broken and three others were dropped and washed before replacing. Other difficulties encountered during the digestion were recorded and will be discussed below with the data presentation where appropriate.

The one-gram sample size and 10.0 ml final dilution volume permitted metal determinations to be made by flame AAS for iron, copper, lead, chromium and zinc. Flameless AAS was employed to measure nickel, lead, and cadmium content. Analysis for vanadium

in the shrimp samples was unsuccessful by both flame and flameless AAS. The flame procedure failed due to lack of sensitivity and the flameless analysis was unsuccessful due to high noise levels. The vanadium analysis problem was solved during the course of later experiments by using different procedures.

The data obtained for the remaining trace metals of interest will be presented for the set of 15 replicate shrimp samples and the two samples spiked alternately with vanadium or copper. The labeling system employed included the use of initials SP corresponding to shrimp pool followed by consecutive arabic numerals. Samples SP-3, SP-9, SP-11, and SP-12 were spilled and are omitted in data tabulations. The samples spiked with vanadium and copper were labeled SP-V-1 and SP-Cu-1 (the numeral one corresponding to the first spike determination) respectively. These spiked samples represent two additional replicate analyses except for vanadium or copper determinations.

The trace metal data is presented in Table 14 for nickel, lead, cadmium, iron, copper, chromium, and zinc analyses. The data in Table 14 was statistically analyzed for mean, standard deviation, and percent recovery of spikes. This information is presented in Table 15. Values omitted from mean and standard deviation calculations are noted where appropriate. The criteria arbitrarily selected for omission of data is the following: if the standard deviation of one or two values was more than four times the standard deviation

Sample	Ni[1] (ppm)	Pb[1,3] (ppm)	Cd[1] (ppm)	Fe[2] (ppm)	Cu[2] (ppm)	Cr[2] (ppm)	Zn[2,3] (ppm)
SP-1	0.27	<D.L.	0.29	81.6	16.1	4.4	57.1
SP-2	0.18	<D.L.	0.30	72.8	15.6	2.4	52.2
SP-4	0.22	<D.L.	0.23	94.2	16.0	7.0	57.8
SP-5	0.23	<0.04	0.65	67.9	68.4	1.6	76.8
SP-6	0.18	<D.L.	0.20	75.8	16.1	2.3	57.7
SP-7	0.17	<D.L.	1.04	80.8	16.4	4.9	56.8
SP-8	0.17	<D.L.	0.16	87.2	14.9	2.7	52.4
SP-10	0.17	<D.L.	0.13	75.8	11.2	2.8	46.7
SP-13	0.21	<D.L.	0.30	72.4	16.1	4.8	55.2
SP-14	0.17	<D.L.	0.10	60.9	14.8	4.9	50.0
SP-15	0.19	<D.L.	0.47	74.5	15.3	2.7	52.8
SP-V-1	0.24	<D.L.	0.27	59.6	15.0	D.L.	52.4
SP-Cu-1	0.29	<D.L.	0.17	73.4	23.5	5.4	55.0

1: Flameless AAS.
2: Flame AAS.
3: <D.L. refers to less than minimum detection limit. No numerical D.L. will be specified since high reagent blanks substrated from the sample measurements set the D.L. rather than instrumental or methodology consideration.

Table 14. Trace Metal Analysis of Replicate Shrimp Pool Samples Expressed in Units of Parts-per-Million- Experiment I.

Trace Metal	Mean Value (ppm)	Standard Deviation (ppm)	Excluded Samples	% Recovery
Ni	0.20	0.03	None	
Pb	a	a	--	
Cd	0.24	0.11	SP-5,SP-7	
Fe	76.9	9.1	None	
Cu	15.3	1.5	SP-5	82
Cr	3.3	1.2	SP-4	
Zn	53.8	3.7	SP-5	

[a] Indeterminate

Table 15. Statistical Analysis of Trace Metal Data for Shrimp Pool from Table 5 - Experiment I.

calculated without the values, these data were omitted in the final statistical calculations.

The five replicate samples of freeze-dried oysters were analyzed for the same trace metals as the BLM shrimp pool. All metals of interest except vanadium were determined. The data and statistical analyses is presented in Table16 for nickel, lead, cadmium, iron, copper, chromium, and zinc analyses.

The five replicate tuna samples were taken from one of 14 containers given to GSRI by the National Bureau of Standards. In order to properly identify the particular container used the samples were labeled with TF (Tuna Fish) followed by the arabic numeral corresponding to container number and then finally sequential lower case letters distinguish each replicate. The first sample, TF-1-a, was spilled during digestion. Data for the remaining four replicates is presented in Table 17 for trace metal determinations and statistical parameters including mean and standard deviations.

The trace metal data for NBS SRM 1571 (orchard leaves) and two concentrations of NBS SRM 1577 (bovine liver) is presented in Table 18. The tabulated data includes the value obtained by GSRI and the certified NBS value. NBS SRM 1577-1 represents the ∿0.5 gram sample size while NBS SRM 1577-2 represents ∿ 1.0 gram sample preparation.

Sample	ppm Ni[1]	ppm Pb[1]	ppm Cd[1]	ppm Fe[2]	ppm Cu[2]	ppm Cr[2]	ppm Zn[2]
OP-1	1.31	0.08	6.22	287	187	5.1	4200
OP-2	1.32	0.06	6.64	313	180	3.1	3970
OP-3	1.36	0.04	6.95	305	194	5.7	4300
OP-4	1.38	0.03	6.95	312	189	6.3	4250
OP-5	1.39	<D.L.[3]	7.29	309	202	8.9	4680
Mean	1.35	0.05	6.81	305	190	5.8	4280
Standard Deviation	0.04	0.02	0.40	11	8	2.1	260

1: Flameless AAS
2: Flame AAS
3: Value excluded for mean and standard deviation.

Table 16. Trace Metal Data and Statistical Analysis for FDA Oyster Samples - Experiment I.

Sample	ppm Ni[1]	ppm Pb[1]	ppm Cd[1]	ppm Fe[2]	ppm Cu[2]	ppm Cr[2]	ppm Zn[2]
TF-1-b	0.44[3]	0.06	0.04	78.7	3.7	10.2	14.7
TF-1-c	0.06	0.06	0.02	61.2	3.2	5.2	12.5
TF-1-d	0.08	0.08	0.06	90.7	3.9	16.2	15.2
TF-1-e	0.16	0.01	0.07	74.3	3.7	6.7	16.5
Mean	0.10	0.05	0.05	76.2	3.6	9.6	14.7
Standard Deviation	0.05	0.03	0.02	10.5	0.3	4.9	1.7

1: Flameless AAS
2: Flame AAS
3: Value excluded for mean and standard deviation.

Table 17. Trace Metal Data and Statistical Analysis for NBS Tuna Fish - Experiment I.

Sample	ppm Ni		ppm Pb		ppm Cd		ppm Fe	
	GSRI	NBS Certified Range	GSRI	NBS Certified Range	GSRI	NBS Certified Range	GSRI	NBS Certified Range
NBS-SRM 1571	1.12	1.3 ± 0.2	36.5	45 ± 3	0.15	0.11 ± 0.2	302	300 ± 20
NBS-SRM 1577-1 (0.5 gram)	1.56	[a]	0.35	0.34 ± 0.08	0.26	0.27 ± 0.04	219	270 ± 20
NBS-SRM 1577-2 (1.0 gram)	1.40	[a]	0.36	0.34 ± 0.08	0.26	0.27 ± 0.04	265	270 ± 20

	ppm Cu		ppm Cr		ppm Zn	
	GSRI	NBS Certified Range	GSRI	NBS Certified Range	GSRI	NBS Certified Range
NBS-SRM 1571	12.0	12 ± 1	9.0	[a]	28.7	25 ± 3
NBS-SRM 1577-1	156	193 ± 10	2.5	[a]	118	130 ± 10
NBS-SRM 1577-2 (1.0 gram)	185	193 ± 10	--		125	130 ± 10

[a] Not certified for Ni or Cr.

Table 18. Trace Metal Data for NBS SRM 1571 and NBS SRM 1577 - Experiment I.

The excellent agreement for trace metal data obtained for NBS Standard Reference Materials in Table 18 was surprising in light of the comparatively poor precision obtained for the BLM shrimp pools. The precision for the FDA oyster samples and NBS tuna was also better than the BLM shrimp pool. This difference might be due to less homogeneity for the BLM shrimp pool. The average amount of acid required for digestion of the sample groups described above is as follows:

BLM shrimp pool:	56 ml
FDA oysters:	42 ml
NBS tuna:	42 ml
NBS SRM's:	58 ml

No significant difference in digestion amounts exist that would explain the abnormal differences in precision.

2. Experiment II

In order to determine if the 32 hour acid digestion is required for accurate analyses, a kinetics study was performed. The shrimp biota pool and NBS-SRM 1577 (bovine liver) were analyzed for trace metal content using variable digestion times. The following samples comprised a set:

3 Shrimp Pool Replicates

1 NBS SRM 1577

1 Reagent/Glassware Blank

1 Shrimp Sample Spiked with 10 ppm Copper

Six sets of the above 6 samples were digested for 2, 4, 8, 16, 24 and 32 hours to ascertain the optimum digestion time required for accurate metal determinations. The low-Hg HNO_3 was used in this study since blanks comparable to ULTREX acid were obtained in Experiment I. The average quantity of HNO_3 used for the kinetic studies is as follows:

2 hours - 12.5 ml

4 hours - 25.0 ml

8 hours - 55.0 ml

16 hours - 121.0 ml

24 hours - 184.2 ml

32 hours - 209.8 ml

The color of the samples was not the same following digestion for those samples that had been heating for the same length of time. The observance of dense red fumes just prior to attaining dryness was noted. The use of hotplates for heating may possibly be inadequate since irregularities in temperature depending on location of the beakers on the hotplate were observed.

The analyses for chromium, lead, cadmium, and nickel did not demonstrate sufficient sensitivity or reproducibility to provide comparable time-dependent data. The data obtained for iron, zinc, and copper permit analysis digestion times to be evaluated. The determinations for these trace metals are presented in Table 19. The sample identifications were numerically continued as in Experiment I. The NBS SRM and spiked samples were identified by a number corresponding

Sample	Digestion Time (hours)	ppm Zn	ppm Fe	ppm Cu
SP-16	2	54.7	45.0	13.3
SP-17	2	53.5	50.3	13.2
SP-18	2	79.0	44.0	13.4
SP-Cu-2K	2	56.6	47.7	24.3
SP-1577-2K	2	104	209	15.3
SP-19	4	54.4	52.1	14.6
SP-20	4	52.5	51.8	14.4
SP-21	4	55.6	56.9	15.1
SP-Cu-4K	4	51.6	56.0	22.6
SRM 1577-4K	4	106	207	15.2
SP-22	8	54.8	192	14.9
SP-23	8	54.5	54.6	14.5
SP-24	8	60.1	51.8	12.7
SP-Cu-8K	8	59.1	102	22.7
SRM 1577-8K	8	132	246	176
SP-25	16	53.7	47.4	14.2
SP-26	16	51.9	46.2	13.5
SP-27	16	58.0	74.7	14.1
SP-Cu-16K	16	46.4	41.0	11.5
SRM 1577-16K	16	99	181	139
SP-28	24	62.7	81.3	15.3
SP-29	24	34.8	38.0	8.5
SP-30	24	47.4	42.9	12.9
SP-Cu-24K	24	43.5	48.6	18.8
SP 1577-24K	24	128	233	179
SP-31	32	41.1	37.4	11.6
SP-32	32	41.3	56.9	11.3
SP-33	32	38.8	60.7	11.2
SP-Cu-32K	32	42.9	50.9	21.2
SRM 1577-32K	32	100	189	151

Table19. Trace Metal Determinations for Zinc, Iron, and Copper for Kinetic Study - Experiment II.

to digestion time followed by a "K" (Kinetics). The average value for each metal and standard deviation are presented in Table 20. The percent recovery of copper spikes is also shown in Table 20. The values obtained at each time for the NBS SRM may be compared to the certified values in Table 21.

Comparison of the data in Tables 20 and 21 shows some inconsistencies and suggests some general trends. The standard deviations increase, with some exceptions, as the digestion time increases (Figure 1). The average metal concentrations for the three replicate shrimp sample analyses decreases as digestion time increases suggesting that some metal content may be lost (Figures 2 and 3). The accuracy of the NBS SRM 1577 (bovine liver) is poor for the 2 and 4 hour digestion times and is best for the 8 hour digestion. The percent difference between the value obtained and the NBS certified value increases for the 16, 24, and 32 hour digestions. The percent recovery of copper spikes is 86.8 for the 8 hour determination. The comparison of the data in Tables 19, 20 and 21 suggests that the optimum digestion time for this procedure is 8 hours. The peak heights for the 8 hour blanks were 1.4% of average sample peak height for zinc, 1.1% for copper, and 2.0% for iron. The peak heights for the 32 hour blanks for zinc, copper, and iron were 21.0%, 4.81% and 20.5% of the average sample peak heights, respectively. The large blanks obtained with lengthy digestion times due to large quantities of acid being concentrated is more significant for those metals present in very small amounts such

Digestion Time (hr)	Mean and Standard Deviation (ppm) Zn	Fe	Cu	Recovery of Cu Spikes
2	60.9 ± 12.1	46.8 ± 2.8	13.3 ± 0.1	110
4	53.5 ± 1.8	54.2 ± 2.6	14.7 ± 0.4	78.8
8	57.1 ± 2.9	53.2 ± 2.0[a]	14.0 ± 1.2	86.8
16	52.5 ± 4.8	52.3 ±15.2	14.0 ± 0.4	[b]
24	47.1 ± 11.6	52.7 ±19.5	12.2 ± 3.4	66.0
32	41.0 ± 1.7	51.5 ±10.2	11.3 ± 0.2	98.2

[a] One value omitted
[b] Spike omitted

Table 20. Statistical Analysis of Kinetic Data - Experiment II.

Digestion Time	ppm Zn			ppm Fe			ppm Cu		
	GSRI	NBS Certified Value	% Difference	GSRI	NBS Certified Value	% Difference	GSRI	NBS Certified Value	% Difference
2	104	130±10	19.8	209	270±20	22.4	15.3	193±10	92.1
4	106	130±10	18.2	207	270±20	23.4	15.2	193±10	92.1
8	131	130±10	1.1	246	270±20	8.9	178	193±10	8.8
16	99.3	130±10	23.6	181	270±20	33.1	139	193±10	28.0
24	128	130±10	1.4	233	270±20	13.7	179	193±10	7.2
32	99.8	130±10	23.2	189	270±20	29.8	151	193±10	21.7

Table 21. Comparison of Zinc, Iron, and Copper Content Determined in NBS SRM 1577 - Experiment II.

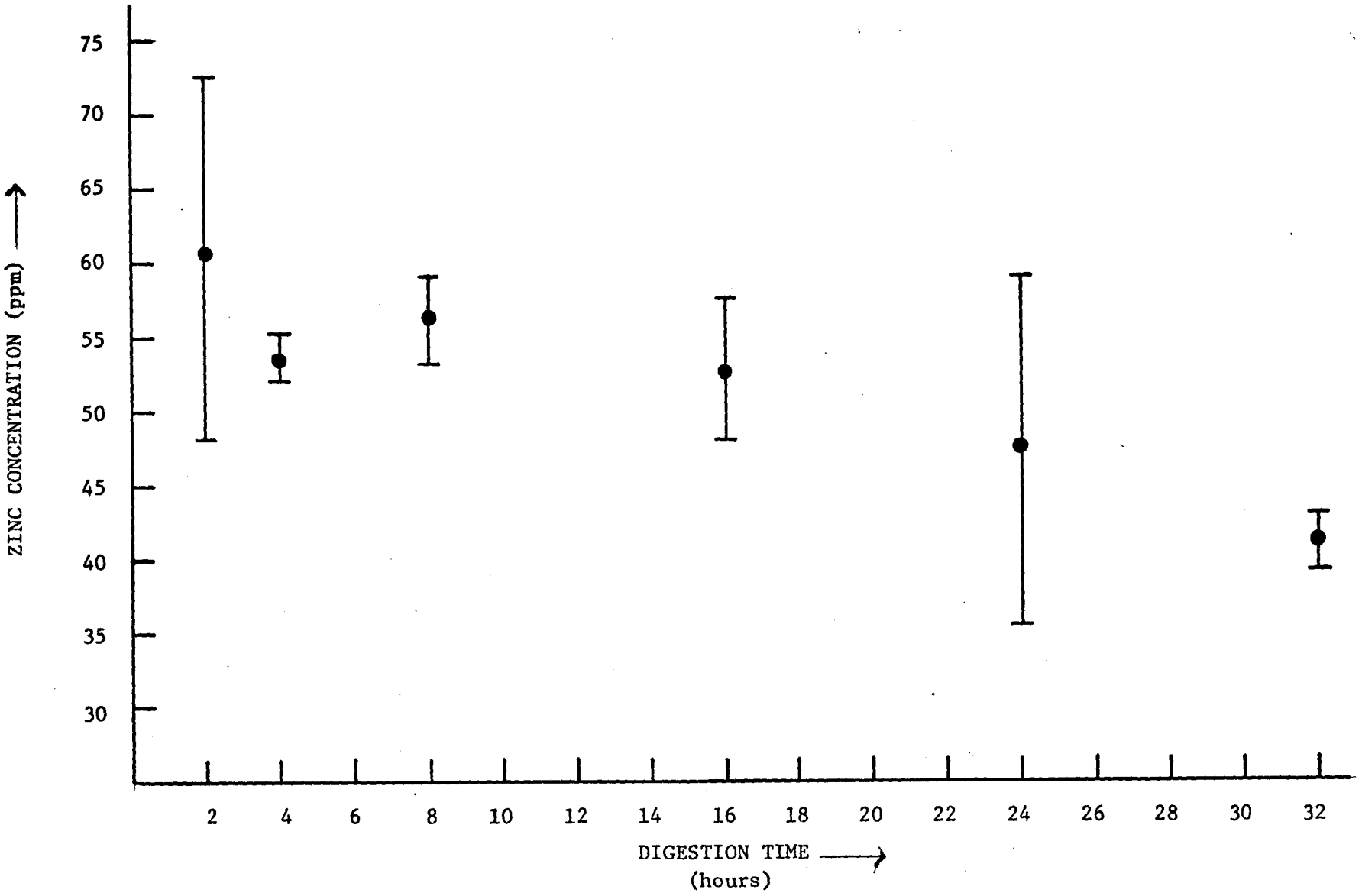

Figure 1. KINETIC STUDY: Zinc: Mean and Standard Deviation of 4 Replicate Determinations.

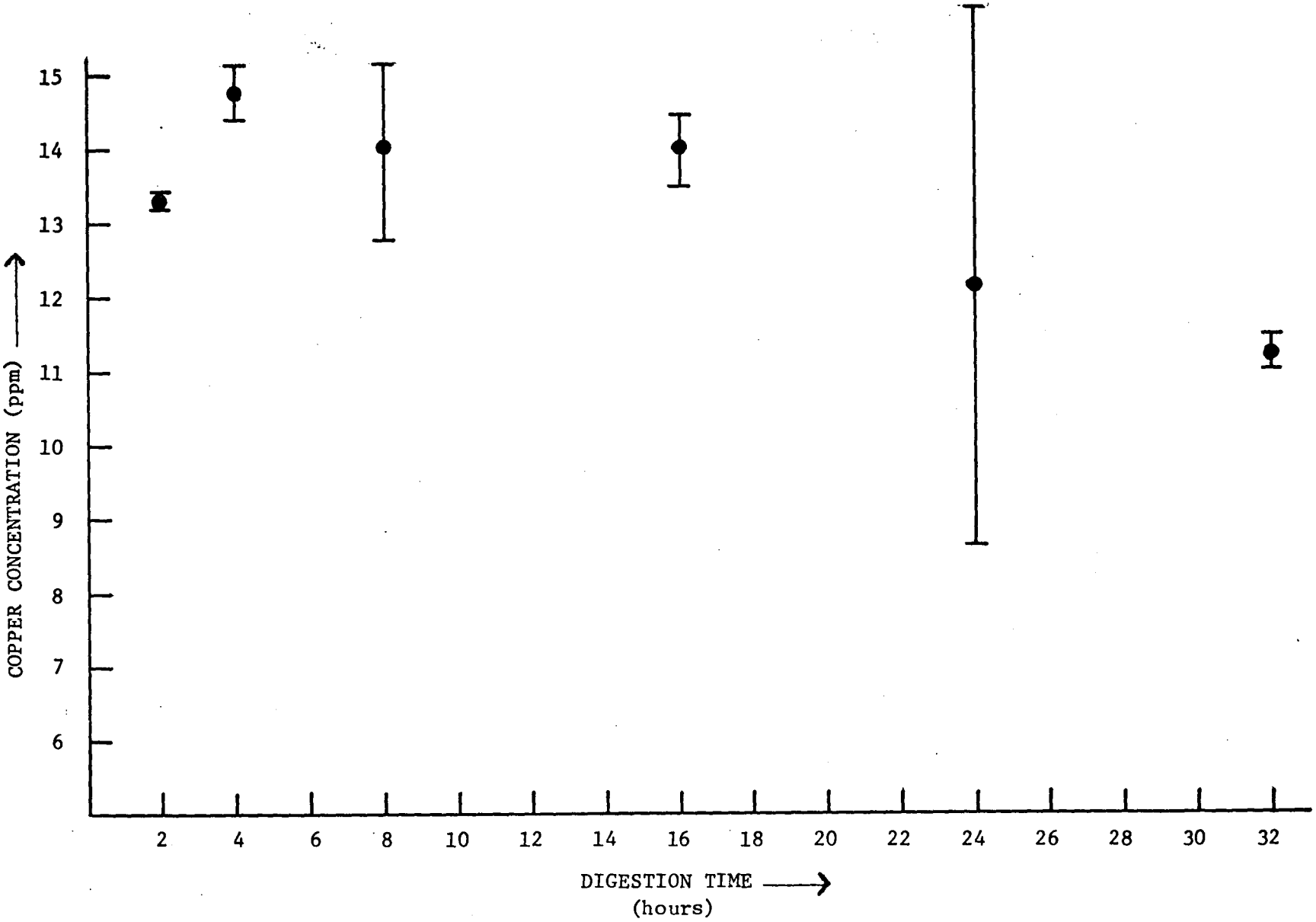

Figure 2. KINETIC STUDY: Copper: Mean and Standard Deviation of 3 Replicate Determinations.

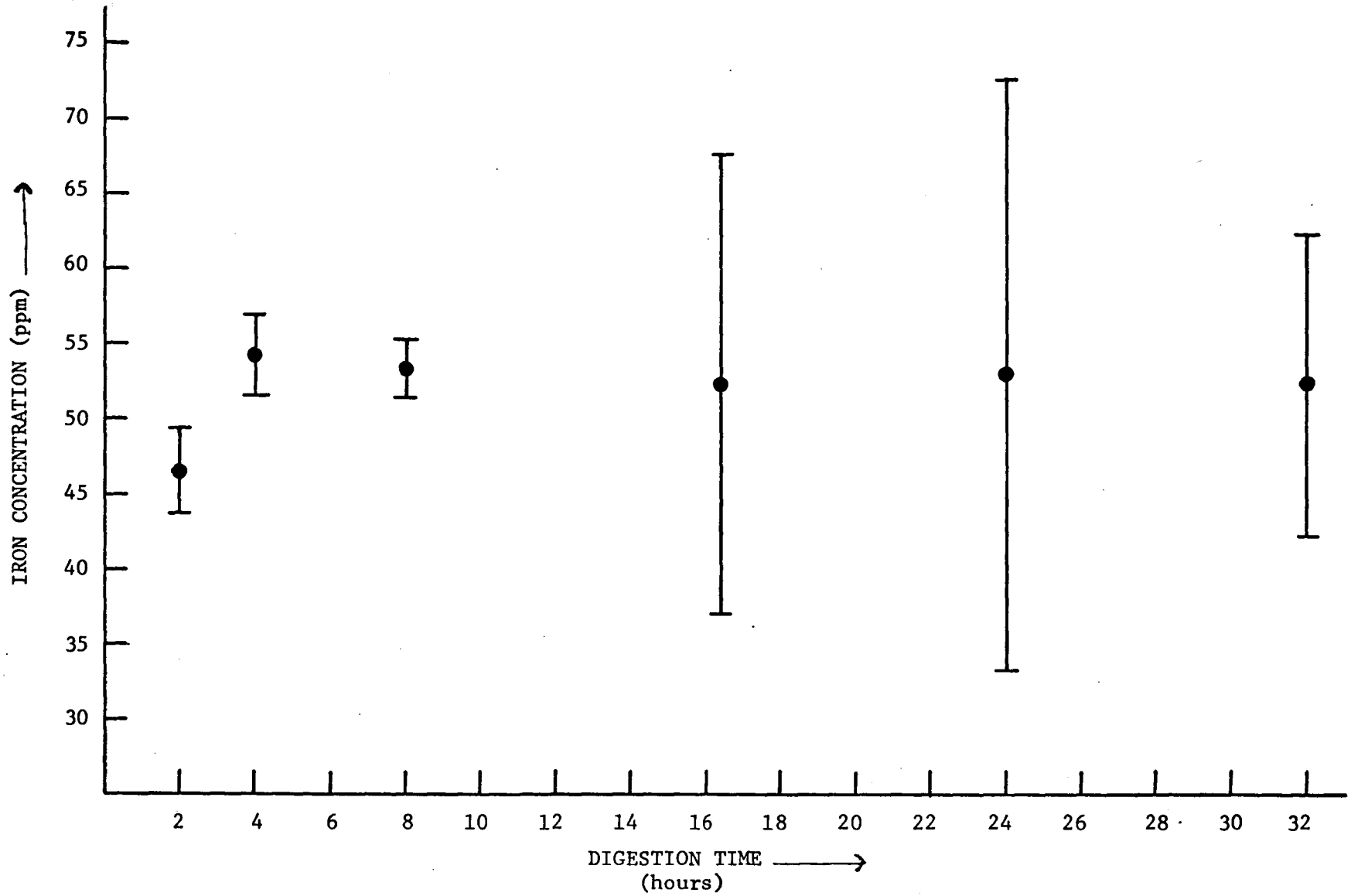

Figure 3. KINETIC STUDY: Iron: Mean and Standard Deviation of 4 Replicate Determinations.

as cadmium, nickel, and lead. In many cases for these metals, the blank peaks are slightly greater than or equal to the sample peaks rendering the analysis useless.

3. Experiment III

A second digestion procedure was studied since the nitric acid digestion was found to be a poor method. The National Bureau of Standards routinely performs biota analyses using a perchloric-nitric acid digestion. The procedure is as follows:

a. Weigh one (1) gram of predried material.

b. Add 5-10 ml concentrated ULTREX HNO_3.

c. Preash at reflux temperature for ½-1 hour to oxidize organic material.

d. Add 10-15 ml concentrated $HClO_4$.

e. Heat in beaker with cover until solution is clear, adding HNO_3 immediately if white $HClO_4$ fumes are observed.

f. Dilute to desired volume.

g. Analyze for trace metal content by flame and flameless AAS.

Four digestion runs were made using this procedure. Two sets of shrimp, one oyster set, and a set of flounder samples were studied. The recommended one gram sample size was reduced to 0.5 grams in order to obtain a final dilution volume to ten milliliters.

The time required to digest a set of 25-30 samples varied from 9 to 12 hours. The appearance of dense, white, $HClO_4$ fumes was noted frequently during the analysis.

The data for the $HClO_4$-HNO_3 digestion of the two sets of shrimp pool samples is given in Table 22 for copper, zinc, and iron. Since the time remaining for the accuracy study was growing short at this time the flameless parameters were excluded. The instrumental analysis time required to determine the three metals that could be done by flame AAS was approximately 20 percent of the total for all metals. The data for the shrimp pool includes the average value for each metal, the standard deviation, and the percent recovery of spikes added prior to initiation of digestion. The observed precision was acceptable for all three metals but recovery of copper and iron spikes was poor. The data for the oyster pool is given in Table 23. Both precision and percent recovery were unacceptable for this set of samples. Very poor precision and accuracy is indicated in Table 24 for the flounder pool analysis. The standard deviation is greater than the average for both copper and iron. The values obtained for the analysis of NBS SRM 1577 (bovine liver) are given in Table 25. The percent error shown is both poor and inconsistent. Due to the poor data obtained for the four digestion runs, the perchloric-nitric digestion was abandoned. In addition, this method is extremely hazardous for use with biota samples.

Metal	Average ± Standard Deviation (ppm)	Percent Recovery
Cu	11.5 ± 2.2	65.0
Zn	102 ± 4	Not Spiked
Fe	42.2 ± 2.9	59.5

Table 22. Trace Metal Data for Two Sets of Shrimp Pool Samples - Experiment III.

Metal	Average ± Standard Deviation (ppm)	Percent Recovery
Cu	150 ± 5	70.0
Zn	2920 ± 230	Not Spiked
Fe	550 ± 70	33.3

Table 23. Trace Metal Data for Oyster Pool Samples - Experiment III.

Metal	Average ± Standard Deviation (ppm)	Percent Recovery
Cu	2.0 ± 3	48.6
Zn	30.0 ± 7.2	Not Spiked
Fe	11.3 ± 17	0

Table 24. Trace Metal Data for Flounder Pool Samples - Experiment III.

Metal	Average Concentration (ppm)	Percent Error
Cu	162	-16.1
Zn	230	+77.4
Fe	206	-23.9

Table 25. Trace Metal Data for NBS SRM 1577 (Bovine Liver) - Experiment III.

4. Experiment IV

A third digestion procedure based on the principle of the Parr bomb techniques was tested for feasibility. The Parr bomb technique has been used successfully by several investigators but was not studied due to the investment required to purchase the expensive bombs. The procedure studied, referred to as the Ten-Day Procedure, uses the pressure development by the action of nitric acid on the biota. The procedure examined is as follows:

a. Weigh 0.5 gram of predried material in a 15-30 ml polyethylene vial with screw cap.

b. Add 2-3 ml of ULTREX HNO_3

c. Cap each vial and allow to stand at room temperature.

d. Relieve the pressure frequently the first day and at least once each day for ten days.

e. Add 5 ml of distilled water.

f. Filter and dilute filtrate to 10.0 ml.

g. Analyze for trace metal content by flame and flameless AAS.

This procedure gave the best precision of all methods studied. The percent recovery of spikes was good in most cases with the exception of zinc. The average and standard deviation of 4 replicate shrimp pool analyses is given in Table 26. The oyster pool data shown in Table 27 is not as good as that for shrimp especially the percent recovery of spikes. The oyster samples exhibited the most difficulty for all sample preparation procedures. Immediately following addition

Metal	Average ± Standard Deviation (ppm)	Percent Recovery
Cu	12.5 ± 0.2	94.6
Zn	40.8 ± 1.6	83.9
Fe	27.2 ± 1.8	70.8

Table 26. Results of Shrimp Pool Analysis Using Ten-Day Procedure - Experiment IV.

Metal	Average ± Standard Deviation (ppm)	Percent Recovery
Cu	125 ± 6	61.2
Zn	1060 ± 240	a
Fe	260 ± 12	68.5

[a]Quantity of zinc too large for spiked determinations.

Table 27. Results of Oyster Pool Analysis Using Ten-Day Procedure - Experiment IV.

of acid, extensive foaming and coagulation was observed. While most samples appeared to have been dissolved following the ten day digestion, these samples required the most filtration. The metal levels are greater than shrimp by a factor of ten to twenty which also complicated the spiking procedure; zinc was so high that spikes were not included. The flounder and sand dollar pool analyses shown in Tables 28 and 29 respectively demonstrated low recovery of zinc spikes. The precision is good for all metals and percent recovery of copper and iron spikes is much improved over previously examined methods. The FDA oyster pool, NBS tuna pool, and NBS SRM 1577 were also analyzed with the ten day nitric acid procedure. The data for these samples given in Table 30 illustrates excellent precision but low values for SRM 1577.

The data obtained for this experiment suggested that the ten-day nitric acid digestion was the best of the methods studied especially for precision. The percent recovery of spikes was not excellent, however, the recovery of spikes was better than for the other methods studied. The data for SRM 1577 was low but still inconclusive since this was the first data collected for these samples. It was decided to perform further experiments with this method.

5. Experiment V

The objective of this experiment was to determine if the ten-day nitric acid procedure could provide accurate data for NBS SRM 1577.

Metal	Average ± Standard Deviation (ppm)	Percent Recovery
Cu	0.72 ± 0.31	81.3
Zn	13.9 ± 0.7	61.3
Fe	4.0 ± 0.7	89.3

Table 28. Results of Flounder Pool Analysis Using Ten-Day Procedure - Experiment IV.

Metal	Average ± Standard Deviation (ppm)	Percent Recovery
Cu	4.4 ± 0.2	79.0
Zn	4.7 ± 0.6	41.7
Fe	32.8 ± 7.3	73.3

Table 29. Results of Sand Dollar Pool Analysis Using Ten-Day Procedure - Experiment IV.

Sample	Cu Ave ± Std. Dev.	Zn Ave ± Std. Dev.	Fe Ave ± Std. Dev.
Oysters - FDA	147 ± 1.2	1940 ± 285	188 ± 27
Tuna Fish - NBS	2.6 ± 0.1	15.3 ± 0.4	45.6 ± 2.0
NBS SRM 1577	118 ± 5	109 ± 8	163 ± 3
Certified Value (1577)	193 ± 10	130 ± 10	270 ± 20

Table 30. Ten-Day Procedure Results for Reference Materials - Experiment IV.

The data for this sample and the pooled samples were expedited and analyzed prior to the sample analysis in progress for which these materials served as quality control checks. In this set of samples was included:

3 shrimp pool samples

3 oyster pool samples

3 flounder pool samples

3 sand dollar pool samples

3 NBS tuna samples

2 NBS SRM 1577

The trace metal data for this set of samples is given in Table 31. For the most part, the precision observed was good. The NBS Tuna Pool did not yield precise data for copper, zinc, lead, and nickel and might not be homogeneous. The values for NBS SRM 1577 were somewhat low but later use of this procedure gave both high values and values exactly in the certified range. The percent recovery of spiked samples analyzed with this set of samples is given in Table 32.

6. Experiment VI

Forty actual environmental samples were to be analyzed for trace metal content as part of the accuracy study. Ten of each of the types for which pools had been sampled and analyzed were to be selected according to the contract. The selection of these samples was coordinated with the BLM New Orleans OCS office since no immediate grouping could be made. For example, no oyster samples were received

Sample	ppm Cu	ppm Fe	ppm Zn	ppm Pb	ppm Cd	ppm Ni	ppm Cr	ppm V
Shrimp-1	14.1	26.7	33.3	0.02	0.20	0.84	0.05	0.3
Shrimp-2	14.4	24.2	36.4	0.02	0.26	0.70	0.05	0.3
Shrimp-3	15.5	25.0	32.0	0.02	0.29	0.33	0.05	0.3
Oyster-1	140	308	3200	0.02	7.3	2.4	0.05	0.3
Oyster-2	192	385	4500	0.02	6.2	3.4	0.05	0.3
Oyster-3	161	363	3400	0.02	7.5	3.5	0.05	0.3
Flounder-1	1.2	<Blank	11.3	0.02	0.22	0.1	0.05	0.3
Flounder-2	1.3	<Blank	11.2	0.02	0.21	0.1	0.05	0.3
Flounder-3	1.2	15.8	12.8	0.02	0.22	0.1	0.05	0.3
Sand dollar-1	5.9	31.2	3.7	4.2	0.04	0.1	0.05	4.5
Sand dollar-2	5.5	21.8	2.9	5.9	0.05	0.1	0.05	3.9
Sand dollar-3	5.4	19.9	2.0	4.6	0.04	0.1	0.13	4.8
NBS Tuna-1	2.9	43.7	11.3	0.18	0.01	0.1	0.05	0.3
NBS Tuna-2	6.2	36.2	12.6	0.35	0.01	1.1	0.05	0.3
NBS Tuna-3	3.0	41.2	3.2	0.04	0.01	4.0	0.05	0.3
NBS SRM 1577-1	165	197	86	0.22	0.48	0.1	0.5	0.3
NBS SRM 1577-2	187	211	90	0.19	0.16	0.1	0.05	0.3
NBS certified value for SRM 1577	193 ± 10	270 ± 20	130 ± 10	0.34 ± 0.08	.27 ± 0.04	[a]	[a]	[a]

[a] Not certified

Table 31. Trace Metal Data for Ten-Day Procedure - Experiment V.

Sample	10 ppm Cu	25 ppm Fe	50 ppm Zn	10 ppm Pb	10 ppm Cd	10 ppm Ni	10 ppm Cr	10 ppm V
Shrimp	101	92	93	71	100	87	80	84
Crab	84	85	a	64	108	89	79	101
Fish	85	75	34	89	88	75	56	84
Flounder	98	a	64	109	105	108	77	100
Sand dollar	71	60	61	99	89	111	79	60

[a] Spike omitted

Table 32. Percent Recovery for Spiked Samples - Experiment V.

to be included with the oyster pool. In this case, crab samples were substituted since these fall in the same general category. Starfish and sand dollars were both analyzed with the sand dollar pool. Since only four actual flounder were received, seven other fish were substituted for use with the flounder pool. A sufficient quantity of shrimp was received. In some cases two organisms representing one sample were analyzed separately in order to provide enough samples to match each biota pool. These replicate analyses will not be considered part of the total contracted number of samples; instead the analyses were performed as part of the accuracy study.

The forty samples were analyzed using the ten-day nitric acid digestion in three sets. The first set was made up of shrimp, stomatopod, and crab. The shrimp samples included 4102-TEQC4, 4106-TEQC2,4510-TEQC4, 4513-TEQC2, 4514-TEQC1, 4919-TEQC4, and 4293-TEQC3. The five stomatopods analyzed were 4102-TEQC3, 4106-TEQC1, 4513-TEQC3, 4514-TEQC2, and 4919-TEQC3. Seven crabs were analyzed including API-EPI-QC-tm (#4 of 4), II-A-C-6 (#2 of 5), IIA-C-6 (#3 of 5), IB-C-8, IIB-C-2, ETM-EPI-QC-tm (#1 of 2), and 4918-TEQC2. The quality control check for the analysis of these sample included two reagent/glassware blanks, three shrimp pool samples, and three oyster pool samples. The data for eight trace metals (copper, iron, zinc, lead, cadmium, nickel, chromium, and vanadium) is given in Table 33. The samples analyzed in duplicate are designated by small letters a and b while SP is used to refer to spiked samples. The second

BLM SAMPLE NO.	ppm Cu	ppm Fe	ppm Zn	ppm Pb	ppm Cd	ppm Ni	ppm Cr	ppm V
4102-TEQC 4-a	37.2	19.0	53.9	0.23	0.22	3.6	<0.05	<0.3
4102-TEQC 4-b	31.0	9.3	38.8	0.12	0.22	3.4	0.06	<0.3
4106-TEQC 2	29.1	18.2	29.9	0.27	0.22	2.5	<0.05	<0.3
4106-TEQC 2-SP	39.2	64.0	76.6	3.6	5.1	11.2	8.0	8.4
4510-TEQC 4	29.4	43.1	45.7	<0.02	0.20	0.6	0.4	<0.3
4513-TEQC 2	29.3	47.1	37.2	0.02	0.23	0.6	<0.05	<0.3
4514-TEQC 1	21.5	36.0	25.3	<0.02	0.19	0.3	<0.05	<0.3
4919-TEQC 4	26.2	41.6	32.1	0.05	0.22	1.1	<0.05	<0.3
4921-TEQC 4	24.9	70.6	29.3	0.04	0.18	0.7	<0.05	<0.3
4923-TEQC 3	20.3	33.2	30.2	<0.02	0.20	0.3	<0.05	<0.3
4102-TEQC 3	69.7	29.0	77.4	<0.02	0.09	8.5	<0.05	<0.3
4106-TEQC 1	80.3	27.1	76.2	0.08	0.06	2.2	<0.05	<0.3
4513-TEQC 3	61.8	26.8	56.8	0.09	0.09	2.2	0.07	<0.3
4514-TEQC 2	29.6	11.6	20.8	<0.02	0.02	4.7	<0.05	<0.3
4919-TEQC 3	31.8	11.6	57.8	<0.02	2.6	2.2	<0.05	<0.3
API-EPI-QC-tm	209	73.0	129	<0.02	2.0	3.1	<0.05	<0.3
IIA-C-6-2	133	45.7	93.0	0.26	2.4	3.7	0.4	<0.3
IIA-C-6-3	39.8	19.2	57.5	<0.02	2.1	1.8	0.07	<0.3
IB-C-8	55.0	7.8	57.7	<0.02	2.9	1.1	<0.05	<0.3
IIB-C-2-a	56.2	20.8	56.1	<0.02	1.3	1.5	0.08	<0.3
IIB-C-2-b	60.0	5.6	72.0	0.12	1.8	1.6	0.08	<0.3
ETM-EPI-QC-tm	86.2	56.6	91.1	<0.02	0.18	3.0	<0.05	<0.3
ETM-EPI-QC-tm-SP	128	98.6	93.7	3.5	3.9	11.9	7.9	10.1
4918-TEQC 2	41.9	4.5	47.2	<0.02	0.25	5.9	<0.05	<0.3

Table 33. Trace Metal Quality Control Data for Biota Set 1.

set of samples included only flounder and fish. The flounder analyzed were API-EPI-QC-tm, AVP-EPI-QC-tm, CJZ-EPI-QC-tm, FGT-EPI-QC-tm and fish samples were DJO-EPI-QC-tm (# 1 of 2 and # 2 of 2), FJY-EPI-QC-tm, FAM-EPI-QC-tm, EJZ-EPI-QC-tm, EGT-EPI-QC-tm, and END-EPI-QC-tm. Three flounder pool replicates and three NBS tuna samples were analyzed concurrent with the flounder / fish set. The data for this set of samples is given in Table 34 . The third set of samples included four sand dollars designated as IV-A-A-2, IV-A-A/B-3, VI-A-C-6, and IV-A-C-2 and five starfish labeled 4510-TEQC2, 4510-TEQC3, 4511-TEQC2, 4923-TEQC4, and 4929-TEQC3. Three sand dollar pool replicates and NBS SRM 1577 in duplicate were analyzed with this set of samples for quality control purposes. The data for the sand dollars and starfish is presented in Table 35 . The average and standard deviation of duplicates and percent recovery of spikes is shown in Table 36 for all three sets of biota included in the accuracy study.

D. Conclusions

The accuracy study performed for BLM led to a modification of Contract 08550-CT5-49. The procedure recommended for biota analysis is as follows:

1. A one (1) gram sample of pre-dried and fragmented material will be placed in a thirty (30) milliliter pre-cleaned, screw cap polyethylene vial.
2. Three (3) milliliters of ULTREX HNO_3 will be added cautiously.

SAMPLE NO.	ppm Cu	ppm Fe	ppm Zn	ppm Pb	ppm Cd	ppm Ni	ppm Cr	ppm V
DJO-EPI-QC-tm-1	1.2	77.6	10.8	0.30	0.03	1.2	<0.05	<0.3
DJO-EPI-QC-tm-2	0.8	73.2	11.0	0.14	< 0.01	0.7	<0.05	<0.3
FJY-EPI-QC-tm	0.8	1.8	17.8	3.32	0.04	2.5	<0.05	<0.3
FAM-EPI-QC-tm	1.0	2.5	13.2	0.11	0.07	0.5	<0.05	<0.3
EJZ-EPI-QC-tm	2.9	4.3	18.5	0.28	0.16	5.4	0.05	<0.3
EGT-EPI-QC-tm-a	0.8	14.1	9.7	0.29	0.03	0.8	<0.05	<0.3
EGT-EPI-QC-tm-b	1.1	23.7	9.7	0.15	0.09	0.1	<0.05	<0.3
END-EPI-QC-tm	0.8	6.3	10.5	0.12	0.07	26.7	<0.05	<0.3
END-EPI-QC-tm-SP	43.3	43.7	178	4.3	4.6	34.2	5.6	8.4
API-EPI-QC-tm-a	1.9	5.5	11.4	0.14	0.21	0.7	<0.05	<0.3
API-EPI-QC-tm-b	1.4	6.8	11.1	0.18	0.21	0.7	<0.05	<0.3
AVP-EPI-QC-tm	1.7	7.2	14.0	0.48	0.17	0.9	0.05	<0.3
AVP-EPI-QC-tm-SP	11.5	9.1	45.9	4.6	4.6	12.2	7.7	10.0
CJZ-EPI-QC-tm	3.0	4.2	13.8	0.12	0.17	2.6	<0.05	<0.3
FGT-EPI-QC-tm	1.2	29.8	12.6	<0.02	0.16	0.5	<0.05	<0.3

Table 34. Trace Metal Quality Control Data for Biota Set 2.

BLM SAMPLE NO.	ppm Cu	ppm Fe	ppm Zn	ppm Pb	ppm Cd	ppm Ni	ppm Cr	ppm V
VI-A-A-2-a	5.9	167	9.3	0.44	0.10	0.3	0.1	43
VI-A-A-2-b	5.2	166	9.7	0.44	0.09	0.3	0.1	43
IV-A-A/B-3	5.6	27.5	4.7	0.21	0.03	<0.1	0.08	39
IV-A-A/B-3-SP	12.7	57.5	35.2	5.9	3.8	11.1	7.9	45
VI-A-C-6	4.7	202	6.0	0.68	0.09	<0.1	0.07	41
VI-A-C-2	5.6	199	5.8	0.46	0.03	<0.1	0.1	48
4510-TEQC2	8.6	517	144	0.52	0.17	0.3	0.2	37
4511-TEQC2	11.6	378	158	0.42	0.25	10.4	0.2	48
4510-TEQC3	9.6	357	164	0.77	0.19	0.3	0.3	42
4923-TEQC4	17.8	495	158	0.70	0.23	5.6	1.3	53
4929-TEQC3	9.1	324	161	0.39	0.23	6.2	0.3	45

Table 35. Trace Metal Quality Control Data for Biota Set 3.

Duplicates

	AVERAGE ± STANDARD DEVIATION (ppm)							
SAMPLE NO.	Cu	Fe	Zn	Pb	Cd	Ni	Cr	V
4102-TEQC4	34.1±4.4	14.2± 6.9	46.4±10.7	0.2± .08	0.22±0.00	3.50±0.1	0.05± .01	< 0.3
IIB-C-2	58.1±2.7	13.2±10.8	64.0±11.2	[a]	1.55± .35	1.5 ±0.1	0.08±0.00	< 0.3
EGT-EPI-QC-tm	1.0±0.2	18.9± 6.8	9.7± 0.0	0.2±0.10	0.06±0.04	[a]	< 0.05	< 0.3
API-EPI-QC-tm	1.6±0.4	6.2±0.9	11.2± .2	0.2±0.03	0.21± .00	0.7± 0.00	< 0.05	< 0.3
VI-A-A-2	5.6±0.5	166±1	9.5± 0.3	0.4±0.00	0.10±0.01	0.3± 0.0	0.1±0.0	43±0

[a] One value less than detection limit

Spikes

	Percent Recovery							
SAMPLE NO.	Cu	Fe	Zn	Pb	Cd	Ni	Cr	V
4106-TEQC2	101	92	93	71	100	87	80	84
EMT-EPI-QC-tm	84	85	Omitted	64	108	89	79	101
END-EPI-QC-tm	85	75	34	89	88	75	56	84
AVP-EPI-QC-tm	98	Omitted	64	109	105	108	77	100
IVA-A/B-3	71	60	61	99	89	111	79	60

Table 36. Average and Standard Deviation of Duplicates and Percent Recovery of Spikes for Experiment VI.

3. Each vial will be capped and allowed to stand at room temperature.

4. The pressure will be relieved frequently the first day and as needed each day (at least once a day) for ten (10) days. Two (2) to three (3) milliliters of additional HNO_3 may be added during digestion as needed.

5. Following ten (10) days of digestion, five (5) milliliters of distilled water will be added to each vial.

6. The resulting digestate will be filtered, transferred to a twenty-five (25) milliliter volumetric flask, and diluted to volume with distilled water.

7. The solution will then be analyzed by flame atomic absorption techniques for the metals listed in Item 1.A.3. If increased sensitivity is required, flameless AA techniques will be used (graphite furnace).

The amount of sample employed or reagents used, as described in the preceeding stepwise procedures, can be modified to achieve lower detection limits, more sensitive analyses, or more complete sample dissolutions.

This procedure gave the best precision and accuracy of all the procedures investigated. The original nitric acid procedure lead to high reagent blanks and cost ineffectiveness due to the copious quantities of ULTREX nitric acid required. The perchloric

acid digestion, in addition to being extremely dangerous to perform, did not yield precise trace metal data. The ten-day nitric acid digestion method was by far the most cost effective techniques since only 2-3 milliliters of ULTREX acid is required per sample. The polyethylene vials are much less expensive than bombs and provide a suitable pressure vessel if the pressure is relieved frequently as described in the modification. These containers are easily cleaned and may be recycled if required. GSRI recommends that new containers be used for each analysis, however, since the cost is quite reasonable. The quality control data for the analysis of the remaining biota samples given in later chapters further illustrates the utility of the ten-day nitric acid digestion method.

CHAPTER V

ZOOPLANKTON

Five zooplankton samples were received from each of the BLM Cruises 12, 20, and 28 for the MAFLA Monitoring. Sixteen samples were received from the South Texas Baseline study for a total of 31 zooplankton samples. The trace metals of interest for both the MAFLA and South Texas studies include vanadium, cadmium, lead, nickel, copper, and chromium. The seventh metal determinations was iron for the MAFLA group and zinc for the South Texas samples.

The samples were prepared for analysis by filtering the excess liquid and drying to constant weight. Some samples contained over 99% water which precluded obtaining a wet weight for the material. These samples were probably not filtered after collection by the sampling team since this is an unusually large quantity of water. The dried zooplankton samples were ground and dried once again to constant weight. All of the dried zooplankton was used in all but a few cases leading to sample sizes of 0.1 to 0.5 grams.

The zooplankton was digested in ULTREX nitric acid using the Ten-Day digestion procedure recommended following the biota accuracy study. Two reagent/glassware blanks were analyzed and NBS SRM 1571 (orchard leaves) was used for the quality control purposes. In addition four samples were analyzed in duplicate and four samples were spiked with 40 ppm of each trace metal of interest.

The trace metal data for the MAFLA monitoring samples is presented in Table 37 in units of ppm. The South Texas data is shown in Table 38. The high metal levels observed for the zooplankton

BLM Cruise No.	BLM Sample No	V	Cd	Pb	Ni	Cu	Cr	Fe
12	1101	14.8	9.6	13.2	10.5	25.9	2.4	165
12	1204	12.8	22.1	24.6	19.1	65.7	1.4	351
12	1205	18.9	24.7	27.9	14.1	44.5	0.75	229
12	1207	10.0	14.7	22.5	16.0	9.6	1.3	87
12	1308	10.7	6.4	17.3	13.5	9.8	0.37	75
20	1101	7.8	5.0	11.6	11.0	20.8	1.1	89
20	1205	7.0	12.4	34.5	11.8	38.3	1.6	178
20	1207	4.9	8.2	10.3	10.8	20.4	0.28	107
20	1308	21.9	16.3	31.6	36.2	30.6	2.6	196
20	1413	122	10.7	14.5	15.2	21.8	0.23	167
28	1206	8.0	12.3	15.5	8.5	10.1	0.56	245
28	1207	4.3	12.9	16.8	13.4	10.4	0.68	116
28	1309	7.3	7.5	15.7	14.9	60.0	1.3	311
28	1310	25.4	79.1	23.2	35.1	15.8	1.9	751
28	1414	8.8	6.5	13.5	12.4	13.4	0.46	568

Table 37. Trace Metal Quality Control Data for Zooplankton Samples for BLM Cruises 12, 20, and 28 - MAFLA Monitoring.

Concentration Units: ppm (dry weight basis).

BLM Cruise No.	BLM Sample No.	V	Cd	Pb	Ni	Cu	Cr	Zn
02	AHZ-ZPL-QC-tm	3.3	1.9	6.6	7.2	10.3	0.72	66.3
02	AIZ-ZPL-QC-tm	3.5	0.27	9.7	5.1	4.1	1.2	21.5
02	AOG-ZPL-QC-tm	378	5.3	20.6	13.9	10.8	1.3	109
02	APM-ZPL-QC-tm	29.7	7.0	527	17.2	11.6	10.5	103
02	ARJ-ZPL-QC-tm	15.5	2.1	133	14.1	20.0	47.0	162
05	BBA-ZPL-QC-tm	132	1.7	54.3	8.2	15.8	6.6	126
07	CDJ-ZPL-QC-tm	9.7	4.3	12.0	12.8	13.6	1.2	97.4
07	CGN-ZPL-QC-tm	10.0	8.8	26.1	14.0	45.8	1.6	109
08	CMX-ZPL-QC-tm	12.1	2.0	18.6	13.4	11.1	1.5	137
11	CTG-ZPL-QC-tm	6.7	2.4	3.6	1.7	9.2	1.0	89.0
09	DJI-ZPL-QC-tm	17.2	6.7	24.8	13.0	21.1	1.9	105
12	EDJ-ZPL-QC-tm	14.1	3.7	14.1	22.5	13.5	0.55	69.3
12	EGN-ZPL-QC-tm	10.1	4.4	16.9	18.2	16.1	1.2	81.9
13	EMX-ZPL-QC-tm	12.5	4.1	19.2	20.4	11.6	1.7	88.7
13	ETG-ZPL-QC-tm	9.9	1.1	26.4	26.0	7.5	0.93	95.8
14	FJS-ZPL-QC-tm	7.9	3.0	95.0	17.2	10.0	2.0	95.6

Table 38. Trace Metal Quality Control Data for Zooplankton Samples for BLM Cruises 02, 05, 07, 08, 09, 11, 12, and 14 - South Texas Baseline.

Concentration Units: ppm (dry weight basis).

enabled most analyses to be performed by flame atomic absorption spectrophotometry. The flameless technique was required for chromium, a few cadmium analyses, and for the majority of the vanadium determinations.

The data for NBS SRM 1571 is presented in Table 39 for four replicate determinations. The average and standard deviations given for each metal and the NBS certified value is included for comparison. The accuracy is excellent with the exception of iron. Iron should be solubilized in nitric acid and is not low for all NBS standard reference materials. The average and standard deviation and percent recovery of the eight zooplankton samples used for quality control purposes is given in Table 40. The selection of samples to be spiked in duplicate was based on the quantity of material available. Sufficient zooplankton was provided only in the case of the South Texas samples. The samples were not analyzed separately according to region so the quality control sample selection was valid. The precision is very good for all trace metals of interest; the percent recovery of spikes is good in most cases since no trends, either high or low, are noted. The analyses of the zooplankton from MAFLA and South Texas for trace metal content was in-control.

NBS SRM 1571

	Concentration (ppm)							
Standard No.	V	Cd	Pb	Ni	Cu	Cr	Fe	Zn
#1	1.5	0.11	44.7	4.3	10.8	0.31	129	22.7
#2	1.5	0.07	43.8	4.3	12.0	0.31	136	24.0
#3	1.0	0.05	43.2	0.86	9.5	0.38	151	21.0
#4	1.2	0.05	44.0	0.40	10.6	0.75	145	22.3
Average ± Standard Deviation	1.3±0.2	0.07±0.03	43.9±0.6		10.7±1.0	0.44±0.21	144±10	22.5±1.2
Certified Value	a	0.11±0.02	45±3	1.3±0.2	12±1	a	300±20	25±3

[a] Not certified for trace metal of interst.

Table 39. Trace Metal Quality Control Data for NBS-SRM 1571 for Zooplankton Samples.

Duplicates

	Average ± Standard Deviation (ppm)							
Sample No.	V	Cd	Pb	Ni	Cu	Cr	Fe	Zn
AHZ-ZPL-QC-tm	3.3±0.1	1.9±0.1	6.6± 1.4	7.2±0.4	10.3±0.2	0.72±0.8	421± 11	66.3± 6.1
ARJ-ZPL-QC-tm	15.3±0.5	2.1±0.2	246 ± 0.5	14.1±0.5	20.0±3.4	47.0 ±0.7	3200± 40	162 ± 5
CMX-ZPL-QC-tm	12.1±0.2	2.0±0.1	18.6± 1.0	13.4±0.0	11.1±1.0	1.5 ±0.3	1980±180	137 ±67
ETG-ZPL-QC-tm	9.9±0.2	1.1±0.1	26.4±12.6	26.0±1.5	7.5±0.4	0.93±0.27	307±0	95.8± 6.1

Spikes

	Percent Recovery							
Sample No.	V	Cd	Pb	Ni	Cu	Cr	Fe	Zn
AIZ-ZPL-QL-tm	88	91	102	89	91	100	a	78
DJI-ZPL-QL-tm	147	100	81	86	96	109	a	b
BBA-ZPL-QL-tm	65	85	81	102	79	121	73	133
CTG-ZPL-QL-tm	93							

[a] Content of trace metal too high to do spiked sample.

[b] Spike omitted.

Table 40. Average and Standard Deviation of Duplicates and Percent Recovery of Spikes for Zooplankton Samples.

CHAPTER VI

EPIFAUNA

A. General

Of the one hundred six epifauna samples analyzed for trace metal content, thirty were from the South Texas Baseline, thirty-nine belonged to the MAFLA Monitoring group, and thirty-seven were MAFLA Rig Monitoring samples. The majority of the samples belonged to one of the following categories: shrimp, fish, crab, starfish, sand dollar, coral, squid, flounder, or sponge.

The percent solid of each sample was determined before it was ground and homogenized. The Ten Day nitric acid digestion method was employed to extract the metals from the samples. Flame and flameless AA was used to determine the concentration of the metals of interest in the acid extracts.

B. Procedure

For those biota samples possessing edible portions (fish, shrimp, crab, etc.), that portion was removed and placed in a pre-weighed, (hot HCl) washed beaker and weighed again. The remaining samples (sand dollar, coral, sponges, etc.) were rinsed in deionized water, air dried and placed in clean pre-weighed beakers and weighed. All samples were dried in a 105°C oven until a constant weight was obtained. This step required only two or three days for most samples since such small quantities were being dried. After drying and cooling, the weight was taken again to determine the percent solid of the samples.

Mortars and pestles or an electric mortar-grinder were used to grind and homogenize each sample. All glassware, mortars and pestles, and plastic-ware were thoroughly washed in detergent, nitric acid and hot hydrochloric acid. After grinding and re-drying, portions of each sample were weighed for digestion. The remainder of each dried sample was frozen in a sterile plastic bag for future use if needed.

All epifauna were digested using the Ten-Day Nitric Acid Digestion Procedure. A one-half gram sample size and ten mililiter dilution volume was used for the 40 BLM samples analyzed in the accuracy study. This small dilution volume was insufficient for analysis of all metals so the remainder of the digestions utilized a one gram sample weight and a final volume of 25 ml. However, because of the small sample quantities delivered to GSRI some of the digested samples weighed between 0.3 and 1 gram.

C. Analysis Scheme

The biota samples were divided into eight sets, each consisting of an average of 14 BLM epifauna samples, 2 reagent-glassware blanks, 3 duplicates, 3 spiked samples, 3 in-house standards and from two to five NBS SRM's. Related species were analyzed together whenever possible. This scheme was employed to maintain better quality control since each type of sample was expected to digest differently; the proper in-house standards were digested with each set.

The samples were divided as follows: set 1 - crabs and shrimp, set 2 - fish and flounders, set 3 - sand dollars and starfish, set 4 -

primarily fish and squid, set 5 - mostly sponges, set 6 - shrimp, set 7 - coral and sponges, set 8 - shrimp. Sample types other than the ones listed were included in some sets when appropriate.

NBS SRM 1577 (Bovine Liver) was included in all sets except #5 (sponges). NBS SRM 1571 (Orchard Leaves) was used in this case because orchard leaves are more similar in matrix to sponges than bovine liver. However, because of the fine consistency of the particles in the 1571 Standard Reference Material a considerable amount of time was required for filtration and rinsing was difficult. Therefore, orchard leaves were used only for this set.

Samples to be duplicated and spiked were chosen based upon sample size since many samples consisted of less than 2 grams. The concentrations of the spikes added to the first forty samples analyzed were experimental since the approximate trace metal concentrations of each species was unknown. The concentrations of the initial spikes (in units of ppm in the sample) were: set 1 (shrimp) and set 3 (sand dollars) - 50 ppm of Fe and Zn plus 10 ppm of Cu, Ni, Cd, Pb, Cr, and V, set 2 (flounder) - 50 ppm of Zn and 10 ppm of Cu, Fe, Ni, Cd, Pb, Cr, and V, set 1 (crab) and set 2 (fish) - 50 ppm of Cu, Fe, Zn and 10 ppm of Ni, Cd, Pb, Cr, and V.

Trace metal concentrations added to spiked samples were more consistent for the remaining sets. Sets 4,6, and 8 received the same spikes as sets 1 (crab) and 2 (fish). 40 ppm of Cu, Fe, Zn, Ni, Cd, Pb, Cr, and V was added to spiked samples in set 5 and set 7.

The primary type of epifauna being analyzed determined the in-house standard which was digested with each set. The biota pools prepared for

the accuracy study were used as in-house standards in most cases. The Oyster Pool and the Shrimp Pool were used for set 1. Set 2 included NBS Tuna Fish and the Flounder Pool. Samples of the Sand Dollar Pool were analyzed with set 3, and the Flounder Pool was included in set 4. No in-house standards were used for set 5 since no standards similar in matrix to sponges were available. The Shrimp Pool was utilized for sets 6 and 8, and finally, the Sand Dollar Pool was analyzed with set 7.

Included in the sample deliveries were six empty sample bags; the inside surfaces of these were analyzed for trace metal content. Table 41 shows the very low results obtained for each of the nine trace metals analyzed indicating absence of contamination.

D. South Texas Baseline

Thirty samples from South Texas were analyzed for barium, vanadium, lead, nickel, copper, chromium and zinc. Approximately half of these samples were fish; the remainder consisted of squid, shrimp, flounder, and crab. These samples were analyzed along with other samples in four different sets (sets 1, 2, 4 and 6).

The trace metal data is reported in units of ppm (on a dry weight basis) in Tables 42, 43, and 44. The scientific names and percent solid data is presented in tabular form on the pages facing each of these three tables and for the biota tables to follow. For the most part only Cu and Zn were present in concentrations high enough to be detected by flame AA. No vanadium was found in any of the samples, while only two samples contained enough chromium to be detected.

	Concentration (µg/bag)								
Blank No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Fe	Zn
#1	<0.5	<0.2	<0.05	<0.1	0.8	0.3	0.6	<6.0	6.0
#2	<0.5	<0.2	<0.05	0.2	0.2	<0.3	0.6	<6.0	<6.0
#3	<0.5	<0.2	<0.05	0.1	0.6	<0.3	1.4	<6.0	<6.0
#4	<0.5	<0.2	<0.05	0.2	3.5	0.8	0.2	<6.0	6.0
#5	<0.5	<0.2	<0.05	<0.1	0.5	<0.3	0.6	<6.0	<6.0
#6	<0.5	<0.2	<0.05	0.1	0.5	0.3	2.9	<6.0	<6.0
Average ± Standard Deviation	<0.5	<0.2	<0.05	[a]	1.0 ± 1.2	[a]	1.0 ± 1.0	<6.0	[a]

[a] Average and standard deviation not applicable - one or more results less than detection limit.

Table 41. Trace Metal Quality Control Analysis of Blank Epifauna Sample Bags.

BLM Cruise No.	BLM Sample No.	Sample Identity	Percent Solid
02	AIN-EPI-QC-tm	Chaetodipterus faber	21.7
02	AJG-EPI-QC-tm	Centropristes philadelphicus	24.1
02	ALJ-EPI-QC-tm	Serranus atrobranchus	19.1
02	AOM-EPI-QC-tm	Stenotomus coprinus	19.6
02	API-EPI-QC-tm	Loligo pealei	21.3
02	ASK-EPI-QC-tm	Trachurus lathami	22.2
05	AVP-EPI-QC-tm	Syacium gunteri	20.8
05	BDO-EPI-QC-tm	Loligo pealei	22.1
05	BDQ-EPI-QC-tm	Upeneus parvus	22.0
05	BGQ-EPI-QC-tm	Cynoscion arenarius	22.5

Sample Identities and Percent Solids Data for Epifauna Samples from BLM Cruises 02 and 05 - South Texas Baseline.

BLM Cruise No.	BLM Sample No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Zn
W. 74-75-II & III	BO2 AIN-EPI-QC-tm	1.2	<0.3	0.11	1.0	<0.1	2.6	<0.1	19.3
W. 74-75-II & III	BO2 AJG-EPI-QC-tm	1.1	<0.3	1.0	1.3	0.9	85.5	0.2	56.1
W. 74-75-II & III	BO2 ALJ-EPI-QC-tm	1.1	<0.3	0.06	0.81	<0.1	0.9	<0.1	16.2
W. 74-75-II & III	BO2 AOM-EPI-QC-tm	1.3	<0.3	0.05	1.1	0.1	1.8	<0.1	17.8
W. 74-75-II & III	BO2 API-EPI-QC-tm	0.78	<0.3	0.06	0.77	<0.1	1.6	<0.1	13.2
W. 74-75-II & III	BO2 ASK-EPI-QC-tm	1.1	<0.3	0.46	0.82	<0.1	2.8	<0.1	29.0
W. 74-75-IV	BO5 AVP-EPI-QC-tm	1.2	<0.3	0.17	0.48	0.9	1.7	<0.1	14.0
W. 74-75-IV	BO5 BDO-EPI-QC-tm	1.1	<0.3	0.05	1.7	0.1	20.8	<0.1	45.9
W. 74-75-IV	BO5 BDQ-EPI-QC-tm	1.0	<0.3	0.06	1.1	<0.1	1.7	<0.1	15.5
W. 74-75-IV	BO5 BGQ-EPI-QC-tm	0.57	<0.3	0.11	1.1	<0.1	7.5	11.9	14.1

Table 42. Trace Metal Quality Control Data for Epifauna Samples for BLM Cruises BO2 and BO5 - South Texas Baseline.

Concentration Units: ppm (dry weight basis).

BLM Cruise No.	BLM Sample No.	Sample Identity	Percent Solid
07	CBF-EPI-QC-tm	Urophycis floridanus	22.6
07	CEF-EPI-QC-tm	Stenotomus caprinus	24.5
11	CGT-EPI-QC-tm	Pristipomoides aquilonaris	20.8
08	CJZ-EPI-QC-tm	Syacium gunteri	20.8
08	CND-EPI-QC-tm	Penaeus aztecus	25.6
11	CQE-EPI-QC-tm	Pristipomoides aquilonaris	22.8
11	CTM-EPI-QC-tm	Cynoscion nothus	23.8
11	DAM-EPI-QC-tm	Penaeus aztecus	25.1
11	DGL-EPI-QC-tm	Squilla chydaea	50.4
09	DJO-EPI-QC-tm	Pristipomoides aquilonaris	20.3

Sample Identities and Percent Solids Data for Epifauna Samples from BLM Cruises 07, 08, 09 and 11 - South Texas Baseline.

BLM Cruise No.		BLM Sample No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Zn
Sp 75-I	07	CBF-EPI-QC-tm	2.0	<0.3	0.05	1.4	<0.1	1.3	<0.1	19.2
Sp 75-I	07	CEF-EPI-QC-tm	2.0	<0.3	0.06	1.5	<0.1	14.4	<0.1	69.6
Sp 75-II & III	11	CGT-EPI-QC-tm	1.9	<0.3	0.09	1.6	<0.1	0.8	<0.1	11.8
Sp 75-II & III	08	CJZ-EPI-QC-tm	0.56	<0.3	0.17	0.12	2.6	3.0	<0.1	13.8
Sp 75-II & III	08	CND-EPI-QC-tm	1.5	<0.3	0.34	3.4	1.4	33.7	<0.1	56.6
Sp 75-II & III	11	CQE-EPI-QC-tm	1.8	<0.3	0.04	1.5	<0.1	0.7	<0.1	14.5
Sp 75-II & III	11	CTM-EPI-QC-tm	1.5	<0.3	0.02	1.5	<0.1	1.5	<0.1	19.2
Sp 75-II & III	11	DAM-EPI-QC-tm	1.3	<0.3	0.16	3.1	<0.1	38.6	<0.1	65.2
Sp 75-II & III	11	DGL-EPI-QC-tm	3.5	<0.3	4.1	2.7	2.0	99.8	<0.1	102
Sp 75-IV	09	DJO-EPI-QC-tm	2.4	<0.3	0.03	0.3	1.2	1.2	<0.1	10.8

Table 43. Trace Metal Quality Control Data for Epifauna Samples for BLM Cruises 07, 08, 09 and 11 - South Texas Baseline.

Concentration Units: ppm (dry weight basis).

BLM Cruise No.	BLM Sample No.	Sample Identity	Percent Solid
12	EBF-EPI-QC-tm	Loligo pealei	14.4
12	EEF-EPI-QC-tm	Centropristis philadelphicus	20.3
12	EGT-EPI-QC-tm	Pristipomoides aquilonaris	21.0
13	EJZ-EPI-QC-tm	Micropogon undulatus	19.4
13	END-EPI-QC-tm	Pristipomoides aquilonaris	19.3
13	EQE-EPI-QC-tm	Penaeus aztecus	21.2
13	ETM-EPI-QC-tm	Callinectes similis	19.9
13	FAM-EPI-QC-tm	Stenotomus caprinus	22.7
14	FGT-EPI-QC-tm	Syacium gunteri	20.7
14	FJY-EPI-QC-tm	Pristipomoides aquilonaris	21.6

Sample Identities and Percent Solids for Epifauna Samples from BLM Cruises 12 13 and 14 - South Texas Baseline.

BLM Cruise No.		BLM Sample No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Zn
Su 75-I	12	EBF-EPI-QC-tm	2.0	<0.3	0.47	1.2	<0.1	13.0	<0.1	49.9
Su 75-I	12	EEF-EPI-QC-tm	2.0	<0.3	0.07	.88	<0.1	1.1	<0.1	17.8
Su 75-I	12	EGT-EPI-QC-tm	0.74	<0.3	0.60	0.22	0.4	1.0	<0.1	9.7
Su 75-II & III	13	EJZ-EPI-QC-tm	2.1	<0.3	0.16	0.28	5.4	2.9	<0.1	18.5
Su 75-II & III	13	END-EPI-QC-tm	0.43	<0.3	0.07	0.12	26.7	0.8	<0.1	10.5
Su 75-II & III	13	EQE-EPI-QC-tm	1.2	<0.3	0.22	1.6	<0.1	34.0	<0.1	61.5
Su 75-II & III	13	ETM-EPI-QC-tm	3.7	<0.3	0.18	<0.02	3.0	86.2	<0.1	91.1
Su 75-II & III	13	FAM-EPI-QC-tm	1.5	<0.3	0.07	0.11	0.5	1.0	<0.1	13.2
Su 75-IV	14	FGT-EPI-QC-tm	1.3	<0.3	0.16	<0.02	0.5	1.2	<0.1	12.6
Su 75-IV	14	FJY-EPI-QC-tm	1.0	<0.3	0.04	3.3	2.5	0.8	<0.1	17.8

Table 44. Trace Metal Quality Control Data for Epifauna Samples for BLM Cruises 12, 13 and 14 - South Texas Baseline.

Concentration Units: ppm (dry weight basis).

Four samples analyzed in duplicate are: AOM-EPI-QC-tm (set 4), BDQ-EPI-QC-tm (set 4), CQE-EPI-QC-tm, and EGT-EPI-WC-tm (set 2). Averages and standard deviations are reported in Table 45.

The following six samples received trace metal spikes: API-EPI-QC-tm (set 4), AVP-EPI-QC-tm (set 2 - flounder), BGQ-EPI-QC-tm (set 4), CTM-EPI-QC-tm (set 4), END-EPI-QC-tm (set 2 - fish), and ETM-EPI-QC-tm (set 1 - crab). Percent recoveries are presented in Table 45.

E. MAFLA Monitoring

Half the thrity-nine samples for this group were sponges, while the remainder were usually crabs, coral, or sand dollars. The majority of trace metal analyses of the sponges and coral samples (sets 5 and 7) could be determined by flame AAS. Analyses for cadmium, lead, nickel, vanadium, and chromium were required by flameless AAS for about half the samples. The vanadium determinations were done by the flameless graphite furance technique. The elements of interest include vanadium, cadmium, lead, nickel, copper, chromium and iron. Tables 46, 47, and 48 show the trace metal data for these samples.

Samples duplicated for MAFLA Monitoring include: 247-A-8 (set 5), VI-A-A-2 (set 3), II-B-C-2 (set 1), 151-A-6 (set 5), IV-B-A-8 (set 5), VI-C-C-4 (set 7), 062-A-10 (set 7), 151 (set 8), and 251-A-4 (set 7). The average and standard deviation for each pair of duplicates is indicated in Table 49.

The spiked samples for this set consist of: 64-A-2 (set 5), IV-A-A/B-3 (set 3 - sand dollars), 64-A-13 (set 5), 247-A-13 (set 5), 064-A-4 (set 7), 247-A-17 (set 7), 047-A-2 (set 7). The spiked

Duplicates

		Average ± Standard Deviation							
Sample No.	Set #	Ba	V	Cd	Pb	Ni	Cu	Cr	Zn
AOM-EPI-QC-tm	4	1.3 ±0.2	<0.3	0.05±0.01	1.1 ±0.0	0.1±0.0	1.8±0.1	<0.1	17.8±1.0
BDQ-EPI-QC-tm	4	1.0 ±0.1	<0.3	0.06±0.01	1.1 ±0.0	<0.1	1.7±0.2	<0.1	15.5±0.1
CQE-EPI-QC-tm	4	1.7 ±0.1	<0.3	0.04±0.01	1.6 ±0.1	<0.1	0.7±0.2	<0.1	14.5±0.1
EGT-EPI-QC-tm	2	0.74±0.25	<0.3	0.06±0.03	0.22±0.07	0.8/<0.1	1.0±0.2	<0.1	9.7±0.0

Spikes

		Percent Recovery							
Sample No.	Set #	Ba	V	Cd	Pb	Ni	Cu	Cr	Zn
API-EPI-QC-tm	4	c	88	97	74	97	93	129	82
AVP-EPI-QC-tm	2	c	100	105	109	113	98	76	64
BGQ-EPI-QC-tm	4	c	95	103	62	101	84	b	76
CTM-EPI-QC-tm	4	c	91	102	82	97	98	131	91
END-EPI-QC-tm	2	c	84	88	89	75	85	56	335[a]
ETM-EPI-QC-tm	1	c	101	108	64	89	84	79	b
Average % Recovery			93±7	101±7	80±18	95±13	90±7	104±30	78±11

[a]Results excluded from average and standard deviation calculations.

[b]Spike omitted

[c]Samples not spiked with Ba

Table 45. Average and Standard Deviation of Duplicates and Percent Recovery of Spikes for South Texas Baseline Epifauna Samples.

BLM Cruise No.	BLM Sample No.	Sample Identity	Percent Solid
11	047-A-16	Tethya	21.8
11	64-A-2	Tethya	26.5
11	146-B-19	Tethya	29.3
11	151-A-14	Tethya	25.3
11	247-A-8	Tethya	24.1
11	251-A-5	Tethya	25.8
13	V-A A-6	Stylocidaris affinis	61.5
13	VI-A A-2	Clypeaster sp.	54.0
15	I-B B-2	Tropiometra sp.	54.5
15	I-B C-8	Portunus spinicarpus	22.2
15	II-A C-6	Portunus gibbesi	22.2
15	II-B C-2	Portunus spinicarpus	21.8
15	IV-A A/B-3	Encope sp.	56.3

Sample Identities and Percent Solids for Epifauna Samples from BLM Cruises 11, 13 and 15 - MAFLA Monitoring for First Period.

BLM Cruise No.	BLM Sample No.	V	Cd	Pb	Ni	Cu	Cr	Fe
11	047-A-16	3.7	1.2	10.1	4.1	4.3	<0.1	68.4
11	64-A-2	2.5	5.2	8.6	11.6	4.6	<0.1	98.0
11	146-B-19	6.8	1.2	17.3	42.0	5.2	2.4	209
11	151-A-14	3.5	1.9	8.6	27.1	4.8	0.2	81.4
11	247-A-8	10.2	1.6	16.1	26.4	5.3	1.8	184
11	251-A-5	2.6	1.5	2.4	20.3	4.0	<0.1	94.7
13	V-A A-6	22.9	0.17	56.6	56.1	5.9	0.7	149
13	VI-A A-2	43.4	0.10	0.44	0.3	5.6	0.1	167
15	I-B B-2	14.5	0.15	55.3	51.6	5.9	0.4	47.0
15	I-B C-8	< 0.3	2.9	< 0.02	1.1	55.0	<0.1	7.8
15	II-A C-6	< 0.3	2.1	< 0.02	1.8	39.8	<0.1	11.2
15	II-B C-2	< 0.3	1.6	[a]	1.6	58.1	<0.1	13.2
15	IV-A A/B-3	39.3	0.03	0.21	< 0.1	5.6	<0.1	27.5

[a] Sample analyzed in duplicate - Average not applicable since one result less than detection limit

Table 46. Trace Metal Quality Control Data for Epifauna Samples for BLM Cruises 11, 13 and 15 - MAFLA Monitoring for First Period.

Concentration Units: ppm (dry weight basis).

BLM Cruise No.	BLM Sample No.	Sample Identity	Percent Solid
19	047-A-16	Tethya	25.7
19	64-A-13	Tethya	35.2
19	146-B-3	Tethya	22.7
19	147-A-5	Tethya	22.1
19	151-A-6	Tethya	21.9
19	247-A-13	Tethya	21.7
19	247-A-15	Madracis decactis	75.4
19	251-A-12	Tethya	20.9
22	II-A A-5	Tethya	29.1
22	III-B C-6	Sponge "C"	25.6
22	V-A A-4	Sponge "B"	45.1
22	VI-A C-6	Clypeaster sp.	50.5
22	VI-B A-8	Sponge "A"	22.0

Sample Identities and Percent Solids Data for Epifauna Samples from BLM Cruises 19 and 22-MAFLA Monitoring for Second Period.

BLM Cruise No.	BLM Sample No.	V	Cd	Pb	Ni	Cu	Cr	Fe
19	047-A-16	2.4	1.7	10.8	19.2	4.7	0.1	76.2
19	64-A-13	4.2	2.0	11.6	10.4	2.8	< 0.1	90.8
19	146-B-3	1.5	2.6	14.1	23.1	4.0	0.7	96.6
19	147-A-5	1.3	1.9	5.7	19.3	3.9	0.1	55.1
19	151-A-6	3.1	1.7	13.2	22.2	4.2	[a]	97.2
19	247-A-13	1.4	1.5	9.2	18.7	3.1	0.3	76.6
19	247-A-15	15.2	0.15	59.3	45.7	5.9	0.3	17.8
19	251-A-12	4.6	1.6	10.4	19.5	4.4	0.4	101
22	II-A A-5	2.7	5.2	1.1	0.62	3.2	0.2	135
22	III-B C-6	0.7	0.27	0.73	9.0	2.2	0.2	38.0
22	V-A A-4	24.3	3.7	49.4	86.7	5.7	6.5	3570
22	VI-A C-6	41.0	0.09	0.68	<0.1	4.7	<0.1	202
22	VI-B A-8	10.2	6.8	30.7	29.8	7.3	1.8	4230

[a]Sample analyzed in duplicate - Average not applicable since one result less than detection limit

Table 47. Trace Metal Quality Control Data for Epifauna Samples for BLM Cruises 19 and 22 - MAFLA Monitoring for Second Period.

Concentration Units: ppm (dry weight basis).

BLM Cruise No.	BLM Sample No.	Sample Identity	Percent Solid
30	VI-A C-2	Clypeaster sp.	44.9
30	VI-C C-4	Urchin "A"	39.1
32	062-A-10	Lytechinus variegatus	40.5
32	064-A-4	Tethya	77.5
32	151-A-20	Trachygellius cinachyra	22.2
32	247-A-6	Verongia	26.0
32	247-A-17	Madracis decactis	76.6
33	I-B C-7	Comactina echinoptera	51.3
33	II-A A-15	Lytechinus variegatus	44.9
33	IV-B C-5	Cypeaster raveneli	39.0
33	IV-B C-6	Portanis spinicarpus	24.9
34	047-A-2	Poutes divarecata	70.3
34	251-A-4	Poutes divarecata	70.5

Sample Identities and Percent Solids Data for Epifauna Samples from BLM Cruises 30, 32, 33 and 34 - MAFLA Monitoring for Third Period.

BLM Cruise No.	BLM Sample No.	V	Cd	Pb	Ni	Cu	Cr	Fe
30	VI-A C-2	48.5	0.03	0.46	<0.1	5.6	0.1	199
30	VI-C C-4	3.9	0.30	45.4	14.1	7.4	2.3	842
32	062-A-10	2.8	0.29	49.3	10.8	7.4	1.7	167
32	064-A-4	6.2	5.7	8.2	0.5	4.8	1.7	205
32	151-A-20	3.1	1.1	0.79	9.6	4.9	0.9	57.3
32	247-A-6	3.1	0.52	10.5	27.0	11.0	0.3	112
32	247-A-17	4.9	0.14	47.5	12.0	6.7	0.7	26.4
33	I-B C-7	3.1	0.37	50.6	11.7	6.7	1.0	34.3
33	II-A A-15	3.4	0.40	47.5	12.4	6.7	1.8	248
33	IV-B C-5	3.3	0.17	45.5	11.1	6.1	1.4	194
33	IV-B C-6	2.5	8.3	0.34	9.4	80.9	0.4	252
34	047-A-2	4.9	0.12	49.6	9.3	7.2	1.0	22.2
34	251-A-4	3.2	0.60	47.5	11.2	6.9	0.6	22.2

Table 48. Trace Metal Quality Control Data for Epifuana Samples for BLM Cruises 30, 32, 33, and 34 - MAFLA Monitoring for Third Period.

Concentration Units: ppm (dry weight basis).

Duplicates

Sample No.	Set #	Average ± Standard Deviation (ppm) V	Cd	Pb	Ni	Cu	Cr	Fe
247-A-8	5	10.2±0.6	1.6 ±0.2	16.1 ±1.5	26.4±1.8	5.2±0.3	1.8±1.1	184 ± 28
VI-A-A-2	3	43.4±0.6	0.10±0.01	0.44±0.00	0.3±0.0	5.6±0.3	0.1±0.0	167 ± 1
II-B-C-2	1	<0.3	1.6 ±0.2	<0.02/0.12	1.6±0.1	58.1±1.9	<0.1	13.2± 7.6
151-A-6	5	3.1±0.3	1.7 ±0.1	13.2 ±1.7	22.2±1.4	4.2±0.6	<0.1/0.2	97.2± 11
VI-B-A-8	5	10.2±0.9	6.8 ±1.2	30.7 ±0.1	29.8±3.2	7.3±0.6	1.8±0.1	4234 ±249
VI-C-C-4	7	3.9±0.2	0.30±0.08	45.4 ±0.4	14.1±2.3	7.4±0.2	2.3±0.1	842 ±135
062-A-10	7	2.8±0.1	0.29±0.02	49.3 ±2.7	10.8±0.1	7.4±0.6	1.7±0.2	167 ± 30
151-A-20	8	3.1±0.1	1.1 ±0.1	0.79±0.05	9.6±0.4	4.9±0.1	0.9±0.0	57.3± 1.3
251-A-4	7	3.2±0.1	0.60±0.61	47.5 ±0.1	11.2±0.3	6.9±0.0	0.6±0.0	22.2± 0.0

Spikes

Sample No.	Set #	Percent Recovery V	Cd	Pb	Ni	Cu	Cr	Fe
64-A-2	5	130	95	91	94	91	114	89
IV-A-A/B-3	3	60	89	99	111	71	79	60
64-A-13	5	145	99	94	91	95	120	107
247-A-13	5	120	92	80	73	89	111	89
064-A-4	7	50	79	94	96	97	89	186[a]
247-A-17	7	88	70	71	82	83	81	71
047-A-2	7	83	69	53	84	81	79	102
		97±36	85±12	83±16	90±12	87±9	96±18	86±18

[a] Result excluded from average and standard deviation calculations.

Table 49. Average and Standard Deviation of Duplicates and Percent Recovery of Spikes for MAFLA Monitoring Epifauna Samples.

concentrations added for each set are as listed in section C. The percent recoveries for these samples are presented in Table 49.

F. MAFLA Rig Monitoring

The MAFLA Rig Monitoring samples were analyzed for cadmium, chromium, copper, iron, lead, and nickel. All trace elements were determined with the graphite furnace except for Cu and Fe. The majority of these samples were shrimp, but several of the epifauna were crabs or starfish. These samples were analyzed with the epifauna in sets 1, 3, 6 and 8. The trace metal data is presented in Tables 50 and 51.

Sample numbers 4102 TEQC4 (set 1), 4102 TEQC1 (set 6), 4515 TEQC1 (set 6), and 4922 TEQC (set 6) were processed in duplicate. Table 52 displays the averages and standard deviations for these epifauna. Vanadium and chromium could not be detected in the majority of the samples.

Trace metal spikes as described in section C were added to each of these four biota: 4102 TEQC6 (set 8) 4511 TEQC1 (set 6), 4921 TEQC1 (set 6), and 4924 TEQC1 (set 6). Listed in Table 52 are percent recoveries for these samples.

G. NBS Standard Reference Materials

Fourteen replicates of NBS SRM 1577 (bovine liver) were analyzed for quality control purposes with the epifauna samples. The trace metal values and the averages and standard deviations for each metal are shown in Table 53. Most analyzed values show very good correlation with the NBS certified values presented in Table 53.

Set 5 included NBS SRM 1571 (orchard leaves). Five replicates were analyzed with this set: The trace metal data, averages, and

BLM Cruise No.	BLM Sample No.	Sample Identity	Percent Solid
24	4102 TEQC1	Penaeus setiferus	24.5
24	4102 TEQC2	Trachypenaeus sp.	22.2
24	4510 TEQC1	Penaeus setiferus	25.2
24	4510 TEQC2	Astropecten sp.	49.5
24	4511 TEQC1	Penaeus setiferus	24.5
24	4511 TEQC2	Astropecten sp.	49.5
24	4513 TEQC1	Trachypenaeus sp.	72.8
24	4515 TEQC1	Penaeus setiferus	24.3
24	4515 TEQC2	Trachypenaeus sp.	21.8
24	4516 TEQC1	Penaeus setiferus	24.1
24	4516 TEQC2	Trachypenaeus sp.	21.7
24	4517 TEQC1	Penaeus setiferus	23.6
24	4517 TEQC2	Trachypenaeus sp.	21.5
24	4918 TEQC2	Callinectes sapidus	23.5
24	4921 TEQC1	Penaeus setiferus	23.9
24	4922 REQC1	Penaeus setiferus	24.1
24	4924 TEQC1	Penaeus setiferus	24.1

Sample Identities and Percent Solids Data for Epifauna Samples from BLM Cruise 24 - MAFLA Rig Monitoring

BLM Cruise No.	BLM Sample No.	V	Cd	Pb	Ni	Cu	Cr	Fe
24	4102 TEQC1	<0.3	0.25	4.3	1.1	25.0	a	10.5
24	4102 TEQC2	<0.3	0.05	1.9	3.6	26.1	< 0.1	15.2
24	4510 TEQC1	<0.3	0.03	4.7	0.3	22.3	< 0.1	9.9
24	4510 TEQC2	37.4	0.17	0.52	0.3	8.6	0.2	517
24	4511 TEQC1	<0.3	0.03	3.6	0.6	25.4	0.1	10.3
24	4511 TEQC2	48.7	0.25	0.42	10.4	11.6	0.2	378
24	4513 TEQC1	<0.3	0.03	1.5	1.4	27.4	0.2	22.2
24	4515 TEQC1	<0.3	0.04	3.7	1.2	24.8	a	5.3
24	4515 TEQC2	<0.3	0.02	1.1	1.4	27.1	< 0.1	15.0
24	4516 TEQC1	<0.3	0.02	3.7	1.4	27.2	< 0.1	5.3
24	4516 TEQC2	<0.3	0.04	1.1	0.9	27.0	< 0.1	33.3
24	4517 TEQC1	<0.3	0.03	2.7	2.6	31.5	< 0.1	13.8
24	4517 TEQC2	<0.3	0.01	0.96	1.0	22.8	0.1	23.2
24	4918 TEQC2	<0.3	0.25	<0.02	5.9	41.9	< 0.1	4.5
24	4921 TEQC1	<0.3	0.06	2.2	1.6	30.8	0.3	21.0
24	4922 TEQC1	<0.3	0.03	2.6	2.3	22.3	a	18.2
24	4924 TEQC1	<0.3	0.02	4.6	0.9	25.6	< 0.1	5.3

[a] Sample analyzed in duplicate - Average not applicable since one result less than detection limit.

Table 50. Trace Metal Quality Control Data for Epifauna Samples for BLM Cruise 24 - MAFLA Rig Monitoring.

Concentration Units: ppm (dry weight basis).

BLM Cruise No.	BLM Sample No.	Sample Identity	Percent Solid
27	4102 TEQC3	Stomatopod "A"	20.5
27	4102 TEQC4	Peneaus setiferus	21.8
27	4106 TEQC1	Stomatopod "A"	18.5
27	4106 TEQC2	Peneaus setiferus	23.4
27	4510 TEQC3	Astropectens duplicatus	45.8
27	4510 TEQC4	Trachypeneaus sp.	24.0
27	4513 TEQC2	Trachypeneaus sp.	23.4
27	4513 TEQC3	Stomatopod "A"	21.8
27	4514 TEQC1	Trachypenaeus sp.	23.1
27	4514 TEQC2	Stomatopod "A"	21.6
27	4919 TEQC3	Stomatopod "A"	17.9
27	4919 TEQC4	Peneaus setiferus	24.2
27	4921 TEQC4	Trachypeneaus sp.	23.7
27	4923 TEQC3	Trachypeneaus sp.	23.1
27	2923 TEQC4	Astropectens duplicatus	48.5
27	4929 TEQC3	Astropectens duplicatus	49.7
36	4102 TEQC5	Squilla empusa	18.3
36	4102 TEQC6	Penaeus duorarum	23.6
36	4106 TEQC5	Squilla empusa	19.5
36	4106 TEQC6	Squilla chydaea	23.6

Sample Identities and Percent Solids Data for Epifauna Samples from BLM Cruises 27 and 36 - MAFLA Rig Monitoring

BLM Cruise No.	BLM Sample No.	V	Cd	Pb	Ni	Cu	Cr	Fe
27	4102 TEQC3	<0.3	0.09	<0.02	8.5	69.7	<0.1	29.0
27	4102 TEQC4	<0.3	0.2	0.2	3.5	34.1	<0.1	14.2
27	4106 TEQC1	<0.3	0.06	0.08	2.2	80.3	<0.1	27.1
27	4106 TEQC2	<0.3	0.2	0.3	2.5	29.1	<0.1	18.2
27	4510 TEQC3	42.1	0.2	0.8	0.3	9.6	0.3	357
27	4510 TEQC4	<0.3	0.2	<0.02	0.6	29.4	0.4	43.1
27	4513 TEQC2	<0.3	0.2	0.02	0.6	29.3	<0.1	47.1
27	4513 TEQC3	<0.3	0.09	0.09	2.2	61.8	<0.1	26.8
27	4514 TEQC1	<0.3	0.2	<0.02	0.3	21.5	<0.1	36.0
27	4514 TEQC2	<0.3	0.02	<0.02	4.7	29.6	<0.1	11.6
27	4919 TEQC3	<0.3	2.6	<0.02	2.2	31.8	<0.1	11.6
27	4919 TEQC4	<0.3	0.2	0.05	1.1	26.2	<0.1	41.6
27	4921 TEQC4	<0.3	0.2	0.04	0.7	24.9	<0.1	70.6
27	4923 TEQC3	<0.3	0.2	<0.02	0.3	20.3	<0.1	33.2
27	4923 TEQC4	52.9	0.2	0.7	5.6	17.8	1.3	495
27	4929 TEQC3	45.1	0.2	0.4	6.2	9.1	0.3	324
36	4102 TEQC5	0.3	1.0	0.17	10.8	79.2	0.5	45.2
36	4102 TEQC6	<0.3	0.07	0.36	0.6	30.2	0.2	15.7
36	4106 TEQC5	0.4	1.8	0.15	5.5	92.9	0.2	34.0
36	4106 TEQC6	0.3	1.2	0.04	5.3	88.5	<0.1	104

Table 51. Trace Metal Quality Control Data for Epifauna Samples for BLM Cruises 27 and 36 - MAFLA Rig Monitoring.

Concentration Units: ppm (dry weight basis).

Duplicates

		Average ± Standard Deviation (ppm)						
Sample No.	Set #	V	Cd	Pb	Ni	Cu	Cr	Fe
4102 TEQC4	1	0.3	0.22±0.00	0.18±0.08	3.5±0.1	34.1±3.0	0.1	14.2±5.0
4102 TEQC1	6	0.3	0.25±0.19	4.3 ±0.0	1.1±0.0	25.0±0.5	a	10.5±1.8
4515 TEQC1	6	0.3	0.41±0.01	3.7 ±0.2	1.2±0.1	24.8±0.9	a	5.3±3.7
4922 TEQC1	6	0.3	0.03±0.01	2.6 ±0.3	2.3±0.6	22.3±0.5	a	18.2±6.5

Spikes

		Percent Recovery						
Sample No.	Set #	V	Cd	Pb	Ni	Cu	Cr	Fe
4106 TEQC2	1	84	100	71	87	101	80	92
4102 TEQC6	8	91	96	125	98	84	96	66
4511 TEQC1	6	102	86	83	83	99	94	97
4921 TEQC1	6	98	81	81	81	87	88	92
4924 TEQC1	6	98	80	117	80	87	110	93
Average ± Standard Deviations	all	95±7	87±9	95±30	86±7	92±8	94±11	88±12

[a] Average and standard deviation not applicable - one result less than detection limit

Table 52. Average and Standard Deviation of Duplicates and Percent Recovery of Spikes for MAFLA Rig Monitoring Samples.

NBS SRM 1577

Standard No.	Set No.	Concentration (ppm) Ba	V	Cd	Pb	Ni	Cu	Cr	Fe	Zn
#1	1,2,3	[a]	<0.3	0.48	0.22	<0.1	165	<0.1	197	86.5
#2	1,2,3	[a]	<0.3	0.16	0.09	<0.1	187	<0.1	211	90.4
Avg ± Std Deviation	1,2,3	[a]	<0.3	0.32±0.23	0.16±0.09	<0.1	176±15	<0.1	204±10	88.5±2.8
#1	4	<0.5	<0.3	0.42	1.8	<0.1	180	0.3	273	101
#2	4	<0.5	<0.3	0.47	1.6	<0.1	180	0.1	275	111
#3	4	[a]	[a]	0.27	[a]	<0.1	221	0.6	291	120
#4	4	[a]	[a]	0.25	[a]	<0.1	175	0.7	233	118
Avg ± Std Deviation	4	<0.5	<0.3	0.35±0.11	1.7±0.1	<0.1	189±21	0.4±0.3	268±25	113±8
#1	6	<0.5	<0.3	0.16	3.2	0.3	206	<0.1	287	114
#2	6	<0.5	<0.3	0.20	2.7	<0.1	209	<0.1	275	123
#3	6	<0.5	<0.3	0.19	2.7	<0.1	211	<0.1	274	125
Avg ± Std Deviation	6	<0.5	<0.3	0.18±0.02	2.9±0.3	[b]	209±3	<0.1	279±7	121±6
#1	7	[a]	<0.3	0.30	1.4	2.4	186	<0.1	289	130
#2	7	[a]	<0.3	0.32	1.2	<0.1	181	<0.1	273	129
#3	7	[a]	<0.3	0.22	1.4	<0.1	182	0.2	275	126
Avg ± Std Deviation	7	[a]	<0.3	0.28±0.05	1.3±0.1	[b]	183±3	[c]	279±9	128±2
#1	8	[a]	<0.3	0.29	1.3	<0.1	164	<0.1	236	122
#2	8	[a]	<0.3	0.28	1.2	<0.1	157	0.2	210	117
Avg ± Std Deviation	8	[a]	<0.3	0.29±0.01	1.3±0.1	<0.1	161±5	[c]	223±18	120±4
Avg ± Std Deviation	all	<0.5	<0.3	0.29±0.11	1.6±0.9	[c]	186±19	[c]	257±33	115±14
NBS Certified Value		[b]	[b]	0.27±0.04	0.34±0.08	[b]	193±10	[b]	270±20	130±10

[a] Analysis not required.
[b] Not certified for trace metal of interest.
[c] Average and standard deviation not applicable - one or more results less than detection limit.

Table 53. Trace Metal Quality Control Data for NBS-SRM 1577 for Epifauna Samples.

standard deviations are contained in Table 54. Comparison with NBS certified values reveals excellent results except for iron. Similar comparisons were observed for SRM 1571 during analysis of the zooplankton samples. However, very good comparison was observed for iron analysis of SRM 1577. This observation shows that the Ten-Day Nitric Acid Digestion is capable of efficient extraction of iron from biota. The reason for the poor comparison observed may lie in the dissimilarity of matrix composition of the reference material.

H. In-House Reference Standards

During the accuracy study the BLM Shrimp, Oyster, Flounder, and Sand Dollar Pools and several replicates of the NBS Freeze-Dried Tuna Fish were analyzed for copper, iron, and zinc using the Ten-Day Procedure. These results are compared with those obtained from the same standards analyzed with the Epifauna samples in Table 55. The epifauna results are generally higher than those from the accuracy study. However, the very low blanks obtained with the epifauna digestions indicate that the higher results are not due to contamination. The accuracy study represents the first trial for the Ten-Day Procedure and subsequent runs would be expected to yield higher results as the technique is perfected.

NBS SRM 1571

Standard No.	Set	Concentration (ppm) V	Cd	Pb	Ni	Cu	Cr	Fe	Zn
#1	5	1.2	0.12	45.2	0.7	10.4	0.1	151	22.4
#2	5	1.1	0.12	44.8	0.9	10.8	0.4	166	22.9
#3	5	1.1	0.07	42.3	0.9	11.4	2.7	159	22.7
#4	5	a	0.07	35.4	1.6	9.8	1.0	123	23.4
#5	5	a	0.12	41.7	1.8	10.7	1.0	154	23.6
Average ± Standard Deviation		1.1±0.1	0.10±0.03	41.9±3.9	1.2±0.5	10.6±0.6	1.0±1.0	151±6	23.0±0.5
Certified Value		b	0.11±0.02	45±3	1.3±0.2	12±1	b	300±20	25±3

[a] Analysis not required
[b] Trace metal values not certified for metal of interest

Table 54. Quality Control Data for NBS SRM 1571 for Epifauna Samples.

Standard	Set No.	Concentration (ppm) Ba	V	Cd	Pb	Ni	Cu	Cr	Fe	Zn
BLM Shrimp Pool	1	b	<0.3	0.29±0.03	0.02	0.6 ±0.3	14.7±0.7	<0.1	25.3±1.3	33.9±2.3
BLM Shrimp Pool	6	b	<0.3	0.22±0.10	3.9 ±0.2[a]	0.9 ±0.6	14.9±0.3	c	32.7±0.4	56.5±7.5
BLM Shrimp Pool	8	b	<0.3	0.29±0.09	0.21±0.09	0.7±0.1	13.9±0.6	<0.1	30.8±1.1	49.7±4.1
BLM Shrimp Pool	Biota Accuracy Study	b	b	b	b	b	12.5±0.2	b	27.2±1.8	40.8±1.6
BLM Sand Dollar Pool	3	b	43.8±4.6	0.04±0.01	4.9±0.9	<0.1	5.6±0.3	c	24.3±6.1	2.9±0.9
BLM Sand Dollar Pool	7	b	4.0±0.2	0.12±0.01	58.9±2.0	10.4±0.3	6.3±0.4	0.8±0.1	48.2±3.8	7.3±0.8
BLM Sand Dollar Pool	Biota Accuracy Study	b	b	b	b	b	4.4±0.2	b	32.3±7.3	4.7±0.7
BLM Flounder Pool	4	1.6±0.1	<0.3	0.08±0.03	1.2±0.2	<0.1	c	c	5.8±1.3	15.7±0.3
BLM Flounder Pool	2	1.2±0.5	<0.3	0.22±0.01	<0.02	<0.1	1.2±0.1	<0.1	c	11.8±0.9
BLM Flounder Pool	Biota Accuracy Study	b	b	b	b	b	0.7±0.3	b	4.0±0.7	13.4±0.7
BLM Oyster Pool	1	b	<0.3	7.0±0.7	<0.02	3.1±0.6	164±26	<0.1	352±40	3700±706
BLM Oyster Pool	Biota Accuracy Study	b	b	b	b	b	125±6.	b	257±12	1060±238
NBS Tuna Fish	2	b	<0.3	<0.01	0.19±0.15	c	4.0±1.9	<0.1	38.7±2.5[a]	12.0±0.7[a]
NBS Tuna Fish	Biota Accuracy Study	b	b	b	b	b	2.7±0.1	b	45.7±2.0	15.3±0.5

[a] One replicate deleted from calculations
[b] Analysis not required
[c] Average not applicable - one or two samples less than detection limit

Table 55. In-House Quality Control Samples for Epifauna.

CHAPTER VII

SEDIMENT ANALYSIS

A. General

The sediments analyzed for trace metal content for quality control purposes were analyzed using two digestion techniques. The two sample preparations are commonly referred to as a partial digestion and a total digestion. Both methods have been used for OCS Environmental studies and may be jointly evaluated from the data collected in this study.

The selection of a digestion procedure suitable for trace metal analysis of sediments has not been established uniformly for environmental purposes. The partial versus total digestion has led to lively scientific debate at recent conferences addressing methodology. GSRI has advocated the use of the partial digestion for environmental studies of sediments.[1] The quantity of toxic metals bioavailable is of prime importance for evaluation of environmental impact due to offshore drilling operations. The partial digestion technique

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[1] Montalvo, J.G., Jr., and McKown, M.M., Environmental Implications of Sediment Bulk Analysis Techniques for Trace Metals in Off-Shore Well-Drilling Operations, presented to the EPA Conference on Environmental Aspects for Chemical Use in Well-Drilling Operations. Houston, Texas, May 21-23, 1975, published by the EPA Office of Toxic Substances, September, 1975.

utilizes nitric and hydrochloric acid for leaching of metal content. The total digestion employs hydrofluoric and perchloric acids thereby having the potential to remove metals from the crystal lattice. The metals in these sites should not be bioavailable and therefore not of interest for environmental impact evaluation.

The total digestion method is expected to yield higher metal level determinations than the partial digestion when used for the analysis of identical samples. This trend is followed for some metals; the opposite situation or equivalent concentrations have also been observed during this study. For the cases where significantly higher concentrations are detected with the total digestion sample treatment it would be more difficult to observe an environmental impact. On the other hand, it would be easier to observe a change (increase or decrease) for metals measured in smaller concentrations. The most valid argument in favor of the total digestion is that reproducibility will be better if all of the metal is extracted. Since absolute extraction of all metals from the sediment matrix has not been proven for the total digestion this advantage may not be realized.

B. Procedures

The sediment samples are mixed while wet either in the sample container or a beaker. An aliquot is removed from the bulk sample, placed in a beaker, and dried to constant weight at 103°-105°C. The dried sample is ground in a mortar and pestle to increase homo-

geneity of the sediment and to break the caked sediment into weighable form. The dried sediment is digested according to the procedures detailed below for partial or total sample preparation.

1. Partial Digestion[1]

   a. Weigh 3-4 g of dry (103°C) sediment into a 250 ml erlenmeyer flask.

   b. Add 100 ml of water, 1.0 ml conc. HNO_3 and 10.0 ml conc. HCl.

   c. Heat at 95°C until volume is reduced to 15-20 ml (approximately 3 hours).

   d. Cool.

   e. Clarify the sample by filtering.

   f. Dilute to 50 ml.

   g. Proceed with atomic absorption analyses for trace mental content.

2. Total Digestion

   a. Dry entire sample at 105°C and then grind to a fine powder with a procelain-lined mixer mill.

   b. Ash 1 gram of the sediment by heating in a muffle furnace at 400-450°C for 8 hours.

   c. Transfer samples to Teflon beakers.

   d. Add 3 ml of concentrated nitric acid, 5 ml of concentrated ULTREX hydrochloric acid, and 2 mls of concentrated ULTREX $HClO_4$.

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[1]Tentative Digestion of Sediments for Metal Analysis, Environmental Protection Agency, Region IV, Chemical Services Branch, June 28, 1973.

e. Heat to near dryness.

f. Add a second mixture of 3 ml of hydrofluoric and 2 ml of perchloric.

g. Heat again to dryness.

h. Redissolve residue in 5 ml of 5N ULTREX hydrochloric acid.

i. Dilute with deionized water to 25 ml.

C. Analysis Scheme

The sediments were analyzed in sets of 15-20 including the following quality control samples:

1. Three samples analyzed in duplicate;
2. Three samples spiked with known quantities of trace metals;
3. Six in-house standard reference sediments including:
   a. Sample A
   b. Sample A spiked
   c. Sample B or Sample C analyzed in duplicate
   d. Sample B or Sample C spiked in duplicate
4. Two reagent/glassware blanks;
5. NBS Plastic Clay Standard Reference Material.

The major constituents of the sediments were determined prior to trace metal analysis including calcium, iron, aluminum, sodium, magnesium, and potassium. The matrix was quantitated in order to prepare matrix-matched standards to provide corrections for matrix interferences. Two matrices were observed for the sediments analyzed in this program. The sediments from the area offshore

Mississippi, Alabama, and Florida (MAFLA) contained very high calcium levels while the samples from the South Texas area were low in calcium. Average matrices were determined for each set of sediments. It was necessary to take the Rig Monitoring samples originally planned for the MAFLA area from South Texas. The matrix for MAFLA Rig Monitoring therefore corresponds to the South Texas samples rather than the MAFLA Monitoring sediments. The sediment analyses will be described below according to the phase of the program under investigation. The data is presented in tables in the order used by BLM for sample inventory lists (by request).

D. South Texas Baseline

Twenty-nine sediments were analyzed for trace metal content for quality control of the South Texas Baseline study. The trace metals of interest included barium, vanadium, cadmium, lead, nickel, copper, chromium, and zinc. The sediments were analyzed as two sets in groups of fifteen and fourteen samples each. The cadmium content was low enough to require flameless atomic absorption analysis. The flame AAS technique was adequate for the analysis of the remaining metals with a few exceptions for isolated samples. Trace metal data is presented for the South Texas Baseline samples in Tables 56, 57, 58 , and 59 in units of parts-per-million (dry weight basis). The data is given for the partial digestion with aqueous calibration standards in Table 56 and for matrix-matched calibration standards in

BLM Cruise No.	BLM Sample No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Zn
A	8	70.0	47.6	<0.04	9.7	12.4	6.4	21.1	51.1
A	24	69.0	62.2	<0.04	10.4	17.2	9.9	29.6	62.1
A	32	67.7	67.0	<0.04	13.0	16.7	8.8	28.6	66.8
A	42	82.7	72.3	<0.04	13.7	19.4	12.7	32.0	70.7
A	88	61.3	85.0	0.25	12.2	24.7	13.7	37.3	79.3
A	110	51.6	72.1	0.08	15.9	19.9	11.1	34.6	90.4
B	137	64.5	84.3	<0.04	11.6	24.2	13.8	37.0	82.4
B	146	85.5	61.0	0.04	11.6	17.1	10.6	28.7	66.4
B	149	94.6	71.1	0.05	14.2	20.0	12.0	33.0	93.8
B	155	56.3	80.0	0.07	14.7	23.4	12.7	36.0	76.0
B	156	73.1	81.8	0.08	16.4	22.8	14.7	38.3	85.3
B	157	66.4	79.1	0.07	15.6	21.9	13.1	37.8	88.0
B	160	67.7	77.2	0.06	12.3	20.1	11.4	36.7	75.6
B	164	99.7	74.8	0.04	15.1	20.9	14.5	35.4	97.3
B	165	93.3	67.7	0.06	9.0	18.3	11.5	32.5	64.0
B	176	62.4	93.6	0.28	25.1	19.4	15.5	36.6	130
B	185	89.2	71.8	0.18	22.4	20.4	14.4	34.0	105
B	226	92.5	81.1	0.20	24.9	20.4	16.0	39.3	164
B	230	31.0	49.6	0.04	11.0	7.4	6.4	18.1	32.4
C	235	28.9	44.9	0.11	13.0	8.0	7.5	18.4	273
C	236	32.0	45.6	0.06	13.8	6.8	6.5	18.6	32.5
C	238	38.4	43.6	0.04	13.8	8.5	6.9	20.3	32.6
B	241	73.0	68.6	0.10	22.9	19.4	13.1	36.1	64.6
C	243	87.9	85.0	0.19	24.5	20.4	15.5	39.0	66.6
B	245	63.3	49.5	0.05	15.8	11.1	9.0	22.1	42.8
C	259	35.7	47.1	0.09	14.4	10.1	7.8	20.0	48.0
C	265	80.4	51.6	0.15	17.1	11.9	9.2	24.4	46.3
C	269	71.6	65.6	0.14	20.6	15.4	11.0	29.4	56.2
C	273	35.1	43.7	0.11	13.9	8.8	6.5	20.0	46.5

Table 56. Trace Metal Quality Control Data for Sediment Samples for BLM Cruises A,B, and C - South Texas Baseline.

Concentration Units: ppm (dry weight basis)
Digestion: Partial
Calibration Standards: Aqueous.

BLM Cruise No.	BLM Sample No.	Ba	V	Cd[a]	Pb	Ni	Cu	Cr	Zn[a]
A	8	66.7	34.8		10.2	13.4	6.8	23.8	
A	24	65.8	49.8		10.9	18.6	10.6	33.4	
A	32	64.5	49.6		13.7	18.1	9.4	32.2	
A	42	79.2	53.5		14.4	20.9	13.6	36.0	
A	88	58.2	62.9		12.8	26.7	14.7	42.5	
A	110	48.8	53.4		17.0	21.4	11.9	38.9	
B	137	61.4	62.4		12.2	26.2	14.8	41.7	
B	146	81.9	45.2		12.2	18.4	11.3	32.3	
B	149	90.9	52.6		14.9	21.6	12.8	37.2	
B	155	53.3	59.2		15.4	25.2	13.6	40.4	
B	156	69.8	60.5		17.3	24.6	15.8	43.1	
B	157	63.2	58.5		16.5	23.7	14.0	42.6	
B	160	65.0	57.1		12.9	21.7	12.2	41.3	
B	164	95.9	55.4		15.9	22.6	15.5	39.8	
B	165	89.6	50.1		9.5	19.8	12.4	36.5	
B	176	60.5	71.4		26.2	20.9	17.1	38.0	
B	185	86.6	54.8		23.4	22.0	15.9	35.4	
B	226	89.8	61.9		26.0	22.0	17.6	40.8	
B	230	30.1	37.9		11.5	7.9	7.0	18.8	
C	235	28.0	34.3		13.6	8.6	8.3	19.2	
C	236	31.0	34.8		14.4	7.4	7.1	19.3	
C	238	37.2	33.3		14.4	9.2	7.6	21.0	
B	241	70.9	52.4		23.9	20.9	14.5	37.5	
C	243	85.3	64.9		25.6	22.0	17.1	40.5	
B	245	61.4	37.8		16.4	12.0	9.9	23.0	
C	259	34.7	35.9		15.0	10.9	8.6	20.7	
C	265	78.0	39.4		17.9	12.8	10.2	25.3	
C	269	69.4	50.1		21.6	16.6	12.1	30.6	
C	273	34.0	33.4		14.5	9.5	7.2	20.8	

[a]Matrix-Matched Standards not required

Table 57. Trace Metal Quality Control Data for Sediment Samples for BLM Cruises A,B, and C - South Texas Baseline.

Concentration Units: ppm (dry weight basis)
Digestion: Partial
Calibration Standards: Matrix-Matched.

BLM Cruise No.	BLM Sample No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Zn
A	8	448	78.5	0.04	11.6	11.3	9.8	33.3	53.0
A	24	316	110	0.09	13.4	16.5	11.7	48.0	57.3
A	32	409	142	< 0.04	27.8	28.9	3.6	41.0	66.3
A	42	458	151	0.07	16.1	18.3	17.3	57.0	82.9
A	88	460	189	0.26	14.1	27.0	18.5	73.2	84.1
A	110	445	145	0.14	18.0	19.9	13.1	61.2	78.6
B	137	404	181	0.21	11.0	24.6	17.8	76.8	112
B	146	382	131	0.16	14.2	18.2	14.9	58.7	76.1
B	149	412	143	0.14	17.5	20.3	14.8	58.1	83.7
B	155	341	167	0.26	19.6	23.8	16.4	75.1	92.5
B	156	319	160	0.17	20.2	23.7	18.1	72.2	93.2
B	157	367	154	0.14	19.2	20.9	14.6	70.0	81.3
B	160	421	131	0.14	20.6	18.9	12.6	71.8	76.7
B	164	365	126	0.13	22.2	17.5	14.5	59.1	79.8
B	165	353	183	0.19	22.0	23.0	16.6	79.7	109
B	176	344	170	0.14	31.0	23.0	17.5	78.9	105
B	185	363	126	0.14	11.8	20.0	15.0	58.1	73.7
B	226	387	173	0.27	21.6	29.8	19.5	73.2	123
B	230	356	60.2	0.22	14.4	8.5	6.7	25.2	36.9
C	235	394	72.3	0.38	18.0	9.0	7.8	28.0	44.3
C	236	383	80.2	0.32	13.2	9.5	7.4	28.9	42.2
C	238	369	152	0.14	16.9	8.0	7.3	29.1	39.1
B	241	309	147	0.18	21.0	19.8	15.0	66.4	104
C	243	304	125	0.11	18.0	16.5	12.8	57.9	82.6
B	245	377	85.1	0.13	34.7	13.0	58.9	39.0	47.3
C	259	339	80.0	0.15	31.9	11.7	9.0	34.0	54.5
C	265	376	74.0	0.18	12.5	12.8	9.6	31.4	65.5
C	269	380	122	0.18	20.1	17.0	13.9	58.0	85.1
C	273	481	82.7	0.23	12.5	10.5	8.3	32.9	39.9

Table 58. Trace Metal Quality Control Data for Sediment Samples for BLM Cruises A,B, and C - South Texas Baseline.

Concentration Units: ppm (dry weight basis)
Digestion: Total
Calibration Standards: Aqueous.

BLM Cruise No.	BLM Sample No.	Ba	V	Cd[a]	Pb[a]	Ni	Cu	Cr	Zn[a]
A	8	461	63.4			11.3	9.8	33.4	
A	24	325	88.8			16.5	11.8	48.1	
A	32	467	49.6			31.8	3.6	41.1	
A	42	472	122			18.3	17.4	57.1	
A	88	474	153			26.9	18.6	73.3	
A	110	429	124			19.9	13.2	61.3	
B	137	416	146			24.6	17.9	77.0	
B	146	393	106			18.2	15.0	58.8	
B	149	424	116			20.2	14.9	58.2	
B	155	352	135			23.8	16.5	75.2	
B	156	329	129			23.6	18.2	72.3	
B	157	378	124			20.8	14.7	70.1	
B	160	434	106			18.9	12.7	71.9	
B	164	374	102			17.5	14.6	59.2	
B	165	364	148			23.0	16.7	79.8	
B	176	354	137			23.0	17.6	79.0	
B	185	374	102			20.0	15.1	58.2	
B	226	399	140			29.7	19.6	73.3	
B	230	367	48.6			8.5	6.7	25.2	
C	235	406	58.4			9.0	7.8	28.0	
C	236	395	64.8			9.5	7.4	29.0	
C	238	380	123			8.0	7.3	29.2	
B	241	319	119			19.8	15.1	66.5	
C	243	313	101			16.5	12.9	58.0	
B	245	388	68.7			13.0	60.1	39.1	
C	259	349	64.6			11.7	9.0	34.1	
C	265	387	59.8			12.8	9.6	31.5	
C	269	392	98.5			17.0	14.0	58.1	
C	273	495	66.8			10.5	8.3	33.0	

[a]Matrix-Matched Standards not required

Table 59. Trace Metal Quality Control Data for Sediment Samples for BLM Cruises A,B, and C - South Texas Baseline.

Concentration Units: ppm (dry weight basis)
Digestion: Total
Calibration Standards: Matrix-Matched.

Table 57. The total digestion analysis is presented in Table 58 for aqueous standards and Table 59 for matrix-matched calibration standards. The average matrix for the South Texas sediments by the partial digestion contained 2.7% Al, 1.2% Ca, 2.0% Fe, 1.0% Mg, 2.1% Na and 0.59% K. The total digestion matrix contained 4.6% Al,1.2% Ca, 2.6% Fe, 1.2% Mg, 1.7% Na, and 1.1% K.

Six of the South Texas sediments were analyzed in duplicate including 8, 110, 155, 185, 236, and 265. The six samples spiked with known quantities of trace metal (50 ppm for Ba, V, Pb, Ni, Cu, and Cr; 25 ppm for Cd) were numbers 24, 88, 157, 230, 241, 273. These samples were used for duplicates and spiked samples for both the partial digestion and total digestion sample preparations. The average and standard deviation of duplicate analyses and percent recovery of spikes is presented in Tables 60, 61, 62, and 63. The division of data according to digestion method and aqueous or matrix-matched standards corresponds to that used for the trace metal data presentation. The precision determined for the duplicate analyses is excellent for all metals; copper is the most precise analysis while zinc is the least precise. The percent recovery data is good with the exception of a few cases. The percent recovery for the total digestion is somewhat poorer than for the partial technique. Chromium spikes were omitted for samples 24, 88, and 157. The percent recovery for vanadium continued to illustrate the elevation of vanadium absorbance due to the sediment matrix. Percent recovery values for matrix-matched standards were more quantitative as predicted from previous studies.

Duplicates

	Average ± Standard Deviation (ppm)							
Sample No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Zn
8	70.0±0.5	47.6±0.2	<0.04	9.7±0.6	12.4±0.1	6.6±0.0	21.2±0.1	51.1± 2.5
110	51.6±0.06	72.1±1.3	0.08±0.02	20.9±8.8	19.9±0.2	11.1±0.2	34.7±3.0	90.4±20.4
155	56.3±8.3	80.1±3.1	0.07±0.03	14.7±1.4	23.4±0.2	12.7±0.0	36.1±0.7	78.7± 3.8
185	89.2±0.5	71.8±0.8	0.18±0.02	22.4±0.2	20.4±1.9	14.4±0.0	34.0±0.9	105±5
236	31.9±0.1	45.6±0.4	0.06±0.02	13.8±0.1	6.8±1.1	6.5±0.0	18.6±0.4	32.5± 0.2
265	80.4±5.3	51.6±2.6	0.15±0.01	15.8±3.0	11.9±0.0	9.2±0.3	24.4±0.5	46.3± 2.1

Spikes

	Percent Recovery							
Sample No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Zn[b]
24	90.0	122	90.7	86.9	87.5	89.6	a	
88	106	120	79.0	87.5	80.4	84.1	a	
157	107	147	76.5	91.6	90.6	91.3	a	
230	91.4	140	99.8	97.2	94.0	91.9	96.0	
241	105	145	103	93.3	86.1	86.2	101	
273	96.4	106	104	93.3	89.0	90.8	102	

[a]Spike omitted
[b]Spikes not required

Table 60. Average and Standard Deviation of Duplicates and Percent Recovery of Spikes for Sediment Samples for South Texas Baseline.

Digestion: Partial
Calibration Standard: Aqueous

Duplicates

Sample No.	Average ± Standard Deviation (ppm)							
	Ba	V	Cd[a]	Pb	Ni	Cu	Cr	Zn[a]
8	66.7±0.5	34.8±0.8		10.2±0.6	13.4±0.1	6.8±0.0	23.8±0.2	
110	53.3±8.1	53.4±0.9		22.0±9.2	21.4±0.2	11.9±0.2	38.9±3.3	
155	48.7±0.1	59.3±2.3		15.4±1.5	25.2±0.3	13.6±0.0	40.5±0.8	
185	86.6±0.5	54.8±0.6		23.4±0.2	22.0±2.1	15.9±0.0	35.3±0.9	
236	31.0±0.0	34.8±0.3		14.4±0.1	7.4±1.2	7.1±0.0	19.3±0.4	
265	78.0±5.1	39.4±2.0		17.9±1.1	12.8±0.0	10.2±0.3	25.3±0.6	

Spikes

Sample No.	Percent Recovery							
	Ba	V	Cd[a]	Pb	Ni	Cu	Cr	Zn[a]
24	87.2	90.3		91.5	94.4	96.0	b	
88	104	88.6		92.1	86.9	90.1	b	
157	105	109		96.5	97.9	97.8	b	
230	88.7	106		102	101	101	92.0	
241	96.4	94.2		97.4	92.6	95.1	99.3	
273	93.5	81.3		98.0	95.8	100	106	

[a] Matrix-matched standards not required
[b] Spike omitted

Table 61. Average and Standard Deviation of Duplicates and Percent Recovery of Spikes for Sediment Samples for South Texas Baseline.

Digestion: Partial
Calibration Standard: Matrix-Matched.

Duplicates

	Average ± Standard Deviation (ppm)							
Sample No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Zn
8	448±18	78.5±2.9	0.04±0.01	11.6±1.0	11.3±0.1	9.8±0.3	33.3±4.1	53.6±1.3
110	445±18	144± 5	0.14±0.03	17.9±0.1	19.9±0.3	13.1±0.0	61.3±1.8	79.7±2.1
155	341±30	167±13	0.26±0.02	19.5±0.2	23.8±1.0	16.3±2.0	75.1±1.0	92.7±0.3
185	363±80	127± 9	0.13±0.03	11.6±0.5	20.0±0.4	15.0±0.5	58.1±5.4	87.8±6.7
236	383± 4	80.3±2.0	0.33±0.02	13.2±2.9	9.5±1.7	7.4±0.0	28.9±1.6	44.8±3.7
265	375±11	74.0±5.9	0.18±0.05	12.5±0.2	12.7±0.7	9.6±0.8	31.5±0.9	52.6±4.5

Spikes

	Percent Recovery							
Sample No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Zn[a]
24	100	89	89	78	78	88	90	
88	117	123	92	78	79	89	100	
157	91.8	124	93	83	75	93	92	
230	96.2	124	104	118	94	116	103	
241	87.5	125	93	93	86	92	87	
273	[b]	107	94	67	61	89	79	

[a] Spikes not required
[b] Spike omitted

Table 62. Average and Standard Deviation of Duplicates and Percent Recovery of Spikes for Sediment Samples for South Texas Baseline.

Digestion: Total
Calibration Standard: Aqueous

Duplicates

	Average ± Standard Deviation (ppm)							
Sample No.	Ba	V	Cd[a]	Pb[a]	Ni	Cu	Cr	Zn[a]
8	448±18	78.5±2.9			11.3±0.1	9.8±0.3	33.3±4.1	
110	445±18	144± 5			19.9±0.3	13.1±0.0	61.3±1.8	
155	341±30	167±13			23.8±1.0	16.3±2.0	75.1±1.0	
185	363±80	127± 9			20.0±0.4	15.0±0.5	58.1±5.4	
236	383± 5	80.3±2.0			9.5±1.7	7.4±0.0	28.9±1.6	
265	375±11	74.0±5.9			12.8±0.7	9.6±0.8	31.5± 9	

Spikes

	Percent Recovery							
Sample No.	Ba	V	Cd[a]	Pb[a]	Ni	Cu	Cr	Zn[a]
24	112	72			78	88	91	
88	131	99			79	90	100	
157	103	100			75	93	92	
230	108	100			94	117	103	
241	979	101			86	91	109	
273	b	86			71	90	79	

[a]Matrix-matched standards not required
[b]Spike omitted

Table 63. Average and Standard Deviation of Duplicates and Percent Recovery of Spikes for South Texas Baseline.

Digestion: Total
Calibration Standard: Matrix-Matched.

Comparison of partial digestion and total digestion values show similar levels for zinc, copper, nickel, and lead. The level of cadmium increased for some samples by a factor of two. Chromium content was also higher for the total digestion samples corresponding to a fifty percent increase. The vanadium levels increased two-fold on the average. The most remarkable difference observed for the partial versus total analysis was for barium. The average barium content measured for the twenty nine samples was 66.3 ppm by the partial digestion and 380 ppm by the total digestion which illustrates a 5.7 fold increase for the total method. Precision and accuracy appear similar for the two techniques based on the average and standard deviation for duplicates and percent recovery of spikes. Comparison of data for in-house standard reference sediments and plastic clay will be presented below.

E. MAFLA Monitoring

Twenty-one sediments were subjected to trace metal quality control analysis for the MAFLA Monitoring program. Barium, vanadium, cadmium, lead, nickel, copper, chromium, and iron content were determined for these sediments. Some of the samples from the MAFLA Monitoring were delivered to GSRI at the same time as MAFLA Rig Monitoring samples from South Texas. The twenty one MAFLA Monitoring sediments were analyzed in three sets concurrent with the Rig Monitoring sediments. Since two matrices were prevalent per set due to the mixture of MAFLA and Texas samples the two groups would have been analyzed separately if the geographical sources had been known in advance. The average concentration of major constituents for these samples is as follows: 0.2% Al, 16% Ca,

0.2% Fe, 0.7% Mg, 0.6% Na, and 0.06% K for the partial leaching process and 0.6% Al, 12% Ca, 0.3% Fe, 0.7% Mg, 0.3% Na, and 0.1% K for the total digestion.

The analysis for barium and cadmium was performed by the flameless graphite furnace atomic absorption technique. Selected sample analyses for the other trace metals required flameless determinations but the large majority were detectable by routine flame AAS. Barium determinations were made by the flameless AAS method due to the extremely large quantities of calcium present in the matrix causing a serious flame emission noise interference.

The trace metal data (ppm-dry weight basis) for the twenty-one MAFLA Monitoring program sediments is present in Table 64 (partial digestion, aqueous standards), Table 65 (partial digestion, matrix-matched standards), Table 66 (total digestion, aqueous standards), and Table 67 (total digestion, matrix-matched standards). All samples listed in Tables 65 and 67 for matrix-matched standards are those analyzed by flame AAS. Matrix-matched standards may not be employed for the flameless method due to impurities in the chemicals. These samples are footnoted as not requiring matrix-matched standards. In addition lead does not require these standards since lead determinations are not subject to significant matrix interferences. Iron is, of course, a matrix constituent and is not affected by the other elements of the matrix. The samples analyzed in duplicate include 2101, 2209J, 2103, 2535R and 2642. Four samples were analyzed with trace metal spikes including 2645,

BLM Cruise No.	BLM Sample No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Fe (x 10^3)
10	2101	6.6	16.4	0.05	26.2	12.2	7.2	8.3	0.9
10	2426	9.6	18.8	0.06	31.4	18.8	8.2	15.3	3.4
10	2645	13.1	39.9	0.11	47.0	28.4	9.1	16.7	2.8
14	2207J	7.2	19.6	0.10	25.6	12.4	7.4	10.3	0.6
14	2208J	17.4	27.9	0.13	44.0	23.5	7.0	16.1	1.1
14	2209J	14.9	23.2	0.12	43.2	18.9	8.8	13.4	1.1
14	2211J	21.2	23.7	0.10	43.9	21.9	10.0	17.0	1.8
14	2212J	19.2	31.2	0.13	44.7	29.7	15.3	23.2	8.5
14	2213J	19.0	24.4	0.09	45.0	30.8	15.2	25.5	9.8
14	2316J	21.3	20.3	0.10	43.4	22.7	7.8	11.4	1.0
14	2317J	2.5	30.6	0.09	46.6	21.9	7.1	12.1	2.5
29	2102	2.5	5.4	<0.04	14.9	7.3	3.5	10.0	0.5
29	2103	8.8	12.1	0.06	23.2	14.2	4.0	10.8	1.4
29	2105	13.2	15.8	0.07	35.0	18.6	5.2	9.8	0.7
29	2208K	5.3	18.5	0.07	34.6	20.3	8.5	12.3	1.0
29	2209K	13.6	13.8	0.10	32.2	17.8	7.4	12.7	1.2
29	2419K	9.0	9.2	<0.04	8.0	2.5	1.2	2.5	0.3
29	2530R	71.8	8.8	0.08	26.7	11.1	4.0	8.6	1.9
29	2535R	57.2	41.7	0.07	31.9	30.9	9.2	18.8	6.8
29	2641	4.9	7.8	0.01	4.0	3.5	2.5	5.3	1.8
29	2642	2.4	1.5	0.02	2.1	1.7	0.8	<0.1	0.2

Table 64. Trace Metal Quality Control Data for Sediment Samples for BLM Cruises 10, 14, and 29 - MAFLA Monitoring.

Concentration Units: ppm (dry weight basis)
Digestion: Partial
Calibration Standards: Aqueous

BLM Cruise No.	BLM Sample No.	Ba[a]	V	Cd[a]	Pb	Ni	Cu	Cr	Fe[a] (X10^3)
10	2101		12.9			13.3	8.0	8.2	
10	2426		14.8			20.3	9.1	15.1	
10	2645		31.3			30.8	10.1	16.5	
14	2207J		15.4			13.4	8.2	10.2	
14	2208J		21.9			25.5	7.8	15.9	
14	2209J		18.2			20.5	9.8	13.2	
14	2211J		18.6			23.7	11.0	16.8	
14	2212J		24.5			32.1	17.0	22.9	
14	2213J		19.1			33.4	16.9	25.2	
14	2316J		15.9			24.5	8.6	11.3	
14	2317J		24.0			23.7	7.8	11.9	
29	2102		a			7.9	3.9	9.8	
29	2103		9.5			15.5	4.4	10.6	
29	2105		12.4			20.3	5.8	9.6	
29	2208K		14.5			22.1	9.4	12.1	
29	2209K		10.8			19.4	8.2	12.4	
29	2419K		5.9			2.6	1.2	4.7	
29	2530R		5.7			11.6	4.0	15.8	
29	2535R		26.7			32.2	9.2	34.7	
29	2641		6.1			3.8	2.7	5.2	
29	2642		a			1.9	0.9	<0.1	

[a]Matrix-Matched Standards not required

Table 65. Trace Metal Quality Control Data for Sediment Samples for BLM Cruises 10, 14, and 29 - MAFLA Monitoring.

Concentration Units: ppm (dry weight basis)
Digestion: Partial
Calibration Standards: Matrix-Matched.

BLM Cruise No.	BLM Sample No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Fe ($x10^3$)
10	2101	48.2	13.8	<0.04	14.4	18.8	3.3	10.7	1.5
10	2426	58.8	17.6	<0.04	17.1	19.5	4.0	13.9	2.9
10	2645	110	38.3	0.24	28.9	31.5	6.4	17.9	9.5
14	2207J	99.9	9.6	<0.04	13.2	17.7	3.8	9.2	1.4
14	2208J	68.7	27.1	<0.04	19.9	26.9	5.8	15.8	1.4
14	2209J	156	13.5	0.12	20.0	28.6	4.6	13.0	1.2
14	2211J	150	13.3	0.08	25.5	28.3	4.8	14.6	2.1
14	2212J	147	20.5	0.14	28.0	37.4	8.3	20.2	7.5
14	2213J	87.7	28.0	0.08	28.6	34.6	9.0	21.3	9.6
14	2316J	123	20.1	<0.04	19.4	26.4	4.0	12.3	2.8
14	2317J	143	23.2	0.27	24.2	33.4	4.5	12.8	2.5
29	2102	46.1	2.0	<0.04	9.8	9.7	1.6	8.1	0.5
29	2103	45.7	2.2	<0.04	17.0	12.6	4.0	13.4	1.3
29	2105	114	2.5	<0.04	25.4	17.7	5.7	13.3	0.6
29	2208K	99.9	3.9	<0.04	23.8	15.4	5.2	15.8	1.1
29	2209K	100	8.2	<0.04	23.9	28.2	4.8	12.8	1.2
29	2419K	26.9	8.8	<0.04	7.5	5.9	0.5	0.7	0.3
29	2530R	65.1	26.5	0.13	26.7	13.2	2.2	10.6	2.2
29	2535R	113	44.8	0.19	35.6	22.9	8.2	24.2	5.4
29	2641	47.4	7.6	<0.04	8.4	8.7	2.9	10.5	1.9
29	2642	16.5	2.0	<0.04	4.1	0.6	1.6	4.8	0.5

Table 66. Trace Metal Quality Control Data for Sediment Samples for BLM Cruises 10, 14, and 29 - MAFLA Monitoring.

Concentration Units: ppm (dry weight basis)
Digestion: Total
Calibration Standards: Aqueous.

BLM Cruise No.	BLM Sample No.	Ba[a]	V	Cd[a]	Pb[a]	Ni	Cu	Cr	Fe[a] (x10^3)
10	2101		10.4			19.0	3.3	11.4	
10	2426		13.3			19.7	4.1	14.8	
10	2645		28.9			31.8	6.4	19.0	
14	2207J		7.3			17.9	3.8	9.8	
14	2208J		20.5			27.2	5.9	16.8	
14	2209J		10.2			28.9	4.6	13.8	
14	2211J		10.0			28.6	4.9	15.6	
14	2212J		15.5			37.7	8.4	21.5	
14	2213J		21.2			34.9	9.1	22.7	
14	2316J		15.2			26.7	4.0	13.1	
14	2317J		17.6			33.7	4.0	13.7	
29	2102		a			9.8	1.6	8.6	
29	2103		a			13.1	4.0	14.2	
29	2105		a			19.5	5.7	14.1	
29	2208K		a			16.9	5.2	16.7	
29	2209K		a			28.4	4.9	13.6	
29	2419K		6.7			6.3	0.5	0.8	
29	2530R		20.1			14.1	2.4	12.2	
29	2535R		34.1			24.4	8.9	27.9	
29	2641		a			8.8	3.0	11.2	
29	2642		a				1.6	5.1	

[a]Matrix-Matched standards not required

Table 67. Trace Metal Quality Control Data for Sediment Samples for BLM Cruises 10, 14, and 29 - MAFLA Monitoring.

Concentration Units: ppm (dry weight basis)
Digestion: Total
Calibration Standards: Matrix-Matched.

2213J, 2208K, and 2530R. The average and standard deviation of duplicate analyses and percent recovery of spikes is presented in Tables 68, 69, 70, and 71.

F. MAFLA Rig Monitoring

A total of 25 samples were analyzed for trace metals by the quality control laboratory for MAFLA Rig Monitoring. The metals determined included barium, vanadium, cadmium, lead, nickel, copper, chromium, and iron. The samples were taken from the South Texas geographical area and consequently are low in calcium corresponding to the matrix of the sediments for the South Texas Baseline. The concentration of major constituents in these samples was 2.9% Al, 1.5% Ca, 1.9% Fe, 0.9% Mg, 1.1% Na and 0.5% K. The cadmium analysis was performed by flameless atomic absorption in addition to selected determinations for some sediments. The remaining determinations were accomplished with flame AAS.

The trace metal data for sediment samples for MAFLA Rig Monitoring are presented in Table 72 (partial digestion, aqueous standards), Table 73 (partial digestion, matrix-matched standards), Table 74 (total digestion, aqueous standards), and Table 75 (total digestion, matrix-matched standards). Three samples were analyzed in duplicate including 592301 TSQC2, 510901 TSQC3, and 510701 TSQC4. Four samples were spiked with known quantities of trace metals including 551301 TSQC 2, 510701 TSQC3, 551301 TSQC3, and 551401 TSQC4. The average and standard deviation of duplicates and percent

Duplicates

	Average ± Standard Deviation (ppm)							
Sample No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Fe(x10^3)
2101	6.6±0.1	16.4±4.4	0.05±0.00	26.2±0.6	12.2±0.6	7.2±0.3	8.3±0.8	1.14±0.02
2209J	14.7±2.2	23.2±3.1	0.12±0.04	43.2±0.4	18.9±3.2	8.8±2.6	13.4±1.9	0.87±0.04
2103	8.8±0.3	12.1±0.2	0.06±0.01	23.2±0.3	14.2±3.3	4.0±0.5	10.8±0.3	1.37±0.09
2535R	57.2±5.4	41.7±5.0	0.07±0.00	31.9±1.8	30.9±12.3	9.2±0.3	18.8±0.5	6.10±0.70
2642	2.4±0.0	1.5±0.1	0.04	2.1±1.5	1.7±0.4	0.80±0.10	0.6±0.1	0.20±0.18

Spikes

	Percent Recovery							
Sample No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Fe[a]
2645	102	113	85.2	103	88.3	89.0	83.7	
2213J	70	126	89.2	79.2	90.5	93.5	106	
2208K	125	105	110	106	101	93.5	98.6	
2530R	92.8	102	100	97.5	101	85.1	96.5	

[a]Spikes not required

Table 68. Average and Standard Deviation of Duplicates and Percent Recovery of Spikes for Sediment Samples for MAFLA Monitoring.

Digestion: Partial
Calibration Standards: Aqueous

Duplicates

	Average ± Standard Deviation (ppm)							
Sample No.	Ba[a]	V	Cd[a]	Pb[a]	Ni	Cu	Cr	Fe[a]
2101		12.9±3.5			13.3± 0.7	8.0±0.3	8.2±0.8	
2209J		18.2±2.4			20.5± 3.5	9.8±2.9	13.2±1.9	
2103		9.5±0.2			15.5± 3.6	4.4±0.6	10.6±0.3	
2535R		26.7±3.2			32.2±12.8	9.2±0.3	34.7±0.9	
2642		a			1.8±0.4	0.86±0.08	a	

Spikes

	Percent Recovery							
Sample No.	Ba[a]	V	Cd[a]	Pb[a]	Ni	Cu	Cr	Fe[a]
2645		88.9			96.3	98.9	82.4	
2213J		99.1			98.7	104	104	
2208K		82.6			110	104	97.1	
2530R		80.2			110	94.6	95.1	

[a]Matrix-matched standards not required.

Table 69. Average and Standard Deviation of Duplicates and Percent Recovery of Spikes for Sediment Samples for MAFLA Monitoring.

Digestion: Partial
Calibration Standards: Matrix-Matched

Duplicates

	Average ± Standard Deviation (ppm)							
Sample No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Fe(X10^3)
2101	48.2±1.8	13.8±5.2	<0.04	14.4±1.3	18.8±0.4	3.3±0.0	10.7±1.3	1.47±0.63
2209J	156±0	13.5±0.8	0.12±0.07	20.9±1.3	28.6±0.3	4.6±0.8	13.0±0.3	1.18±0.02
2103	45.7±1.7	2.2±0.0	<0.04	17.0±1.1	12.6±0.4	4.0±0.1	13.4±2.4	1.29±0.19
2535R	113±5	44.8±0.6	0.19±0.01	35.6±2.7	22.9±0.6	8.2±0.5	24.2±0.3	5.37±1.37
2642	16.5±3.5	2.0±0.1	<0.04	4.1±1.7	0.6±0.0	1.6±0.0	4.8±0.5	0.54±0.10

Spikes

	Percent Recovery							
Sample No.	Ba[a]	V	Cd	Pb	Ni	Cu	Cr	Fe[a]
2645		107	92.3	88.2	86.0	94.0	113	
2213J		107	93.6	80.9	79.9	90.0	83.6	
2208K		120	103	95.4	120	91.0	102	
2530R		116	95.4	93.2	83.3	80.0	74.3	

[a]Spikes not required

Table 70. Average and Standard Deviation of Duplicates and Percent Recovery of Spikes for Sediment Sample for MAFLA Monitoring.

Digestion: Total
Calibration Standards: Aqueous

Duplicates

	Average ± Standard Deviation (ppm)							
Sample No.	Ba	V	Cd[a]	Pb[a]	Ni	Cu	Cr	Fe[a]
2101	a	10.4±4.0			19.0±0.4	3.3±0.0	11.4±1.3	
2209J	a	10.2±0.6			28.9±0.3	4.6±0.8	13.8±0.3	
2103	a	a			13.1±4.9	4.0±0.1	14.2±2.5	
2535R	a	34.1±0.5			24.4±0.6	8.9±0.5	27.9±0.3	
2642	18.8±4.0	a			a	1.6±0.1	5.1±0.5	

Spikes

	Percent Recovery							
Sample No.	Ba[a]	V	Cd[a]	Pb[a]	Ni	Cu	Cr	Fe[a]
2645		80.6			86.9	94.7	121	
2213J		80.6			79.7	90.7	87.9	
2208K		90.4			118	92.0	109	
2530R		87.4			94.2	87.4	85.6	

[a]Matrix-matched standard not required

Table 71. Average and Standard Deviation of Duplicates and Percent Recovery of Spikes for Sediment Samples for MAFLA Monitoring.

Digestion: Total
Calibration Standards: Matrix-Matched

BLM Cruise No.	BLM Sample No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Fe ($x10^3$)
24	510601 TSQC2	162	99.8	0.08	30.5	34.1	17.5	50.9	1.8
24	510701 TSQC2	145	82.1	0.07	25.7	19.7	14.4	33.7	1.9
24	510801 TSQC2	161	97.7	0.08	33.2	34.5	18.8	46.9	2.4
24	551301 TSQC2	182	90.7	0.10	30.0	31.8	16.7	43.4	2.3
24	551401 TSQC2	124	94.4	0.15	28.6	31.5	16.7	47.4	1.7
24	551701 TSQC2	151	77.9	0.04	27.6	26.9	15.1	40.0	1.9
24	591901 TSQC2	189	121	0.14	29.8	26.1	16.7	51.7	1.5
24	592301 TSQC2	131	91.2	0.06	27.6	29.8	15.9	43.4	2.2
24	592501 TSQC2	153	110	0.08	30.2	30.6	17.7	52.1	2.6
27	510501 TSQC2	128	71.6	0.05	23.2	26.0	13.0	30.7	1.7
27	510701 TSQC3	139	67.2	0.06	22.6	24.5	12.6	32.5	1.6
27	510901 TSQC3	148	101	0.08	25.2	26.6	13.7	35.7	2.1
27	551001 TSQC2	142	77.5	0.06	24.9	26.4	13.4	35.3	0.5
27	551301 TSQC3	85.7	73.9	0.06	21.5	58.6	12.9	33.9	2.5
27	551401 TSQC3	178	85.7	0.08	26.6	23.2	14.0	41.4	1.7
27	592101 TSQC2	148	81.0	0.06	26.5	26.0	14.6	35.4	2.2
27	592301 TSQC3	142	80.2	0.10	23.3	28.5	13.0	37.0	2.5
36	510501 TSQC3	47.2	57.3	<0.04	15.8	14.6	7.3	16.9	7.5
36	510701 TSQC4	53.3	78.9	0.15	20.6	20.9	12.0	24.7	4.9
36	510901 TSQC4	49.4	78.7	0.07	23.1	21.0	11.8	24.7	5.7
36	551001 TSQC3	38.5	63.4	0.13	28.0	20.0	11.3	22.1	5.1
36	551301 TSQC4	33.0	80.9	0.05	22.0	20.5	11.9	25.0	6.7
36	551401 TSQC4	38.1	33.2	0.19	24.9	22.7	13.9	25.1	11.0
36	592101 TSQC3	35.5	82.0	<0.04	23.2	22.1	12.8	25.3	11.4
36	592301 TSQC4	129	67.2	0.14	25.1	20.9	11.1	21.5	9.1

Table 72. Trace Metal Quality Control Data for Sediment Samples for BLM Cruises 24, 27, and 36 - MAFLA Rig Monitoring.

Concentration Units: ppm (dry weight basis)
Digestion: Partial
Calibration Standard: Aqueous.

BLM Cruise No.	BLM Sample No.	Ba	V	Cd[a]	Pb[a]	Ni	Cu	Cr	Fe[a] (x10^3)
24	510601 TSQC2	185	81.5			39.0	19.0	51.6	
24	510701 TSQC2	166	67.0			22.5	15.6	34.2	
24	510801 TSQC2	184	79.8			39.4	20.4	47.5	
24	551301 TSQC2	208	74.0			36.4	18.1	44.0	
24	551401 TSQC2	142	77.0			36.0	18.2	48.0	
24	551701 TSQC2	172	63.6			30.8	16.4	40.5	
24	591901 TSQC2	216	99.0			29.8	18.1	52.4	
24	592301 TSQC2	148	74.4			34.1	17.3	44.0	
24	592501 TSQC2	175	89.5			35.0	19.2	52.8	
27	510501 TSQC2	131	58.4			18.4	14.1	37.5	
27	510701 TSQC3	142	54.8			18.2	13.6	33.4	
27	510901 TSQC3	152	82.3			20.1	14.8	36.8	
27	551001 TSQC2	145	63.3			17.9	14.6	36.3	
27	551301 TSQC3	87.6	60.3			20.5	14.0	34.9	
27	551401 TSQC3	182	70.0			20.2	15.2	42.6	
27	592101 TSQC2	151	66.1			18.2	15.8	36.4	
27	592301 TSQC3	145	65.5			20.1	15.1	37.0	
36	510501 TSQC3	54.2	39.7			16.2	7.6	22.7	
36	510701 TSQC4	64.9	54.5			23.2	12.4	33.2	
36	510901 TSQC4	63.1	54.4			23.4	12.2	33.2	
36	551001 TSQC3	49.2	43.8			22.2	11.7	29.7	
36	551301 TSQC4	42.2	56.0			22.8	12.3	33.6	
36	551401 TSQC4	48.7	23.0			25.2	14.4	33.8	
36	592101 TSQC3	45.3	56.7			24.6	13.3	34.0	
36	592301 TSQC4	165	46.5			23.2	11.5	28.9	

[a]Matrix-Matched Standards not required

Table 73. Trace Metal Quality Control Data for Sediment Samples for BLM Cruises 24, 27, and 36 - MAFLA Rig Monitoring.

Concentration Units: ppm (dry weight basis)
Digestion: Partial
Calibration Standards: Matrix-Matched.

BLM Cruise No.	BLM Sample No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Fe ($x10^3$)
24	510601 TSQC2	410	117	<0.04	25.9	49.3	17.6	60.4	27.0
24	510701 TSQC2	355	101	<0.04	20.3	49.0	13.6	45.6	18.9
24	510801 TSQC2	305	121	<0.04	26.8	46.1	16.3	57.6	25.0
24	551301 TSQC2	431	124	<0.04	23.0	47.4	15.5	56.0	22.4
24	551401 TSQC2	286	129	<0.04	24.5	48.9	15.8	57.2	24.9
24	551701 TSQC2	266	117	<0.04	22.1	43.9	16.1	51.8	23.7
24	591901 TSQC2	301	121	<0.04	18.8	61.1	15.9	60.3	22.6
24	592301 TSQC2	300	116	<0.04	20.2	43.2	15.0	52.8	22.5
24	592501 TSQC2	388	130	0.05	22.2	42.4	17.9	57.8	24.0
27	510501 TSQC2	281	142	0.11	26.9	33.6	15.2	51.8	26.1
27	510701 TSQC3	885	140	0.06	30.2	31.0	5.9	44.1	18.6
27	510901 TSQC3	512	192	<0.04	30.2	35.3	6.2	50.6	26.2
27	551001 TSQC2	1390	139	0.04	28.7	32.5	4.5	46.2	23.0
27	551301 TSQC3	415	116	0.08	25.6	46.6	15.0	52.4	22.9
27	551401 TSQC3	384	157	0.15	26.0	27.0	3.2	41.6	21.2
27	592101 TSQC2	321	139	0.07	29.4	49.9	17.2	60.6	16.4
27	592301 TSQC3	387	156	<0.04	27.9	30.4	7.1	46.2	23.3
36	510501 TSQC3	308	76.4	0.06	22.5	23.6	7.4	30.7	11.0
36	510701 TSQC4	449	118	0.04	29.7	30.0	12.0	42.3	9.4
36	510901 TSQC4	791	115	0.05	27.0	14.2	12.2	45.3	8.0
36	551001 TSQC3	432	121	<0.04	26.3	30.9	12.1	44.3	9.3
36	551301 TSQC4	215	121	0.08	27.0	29.5	13.3	44.1	10.6
36	551401 TSQC4	462	123	0.10	29.1	43.7	14.6	50.8	11.8
36	592101 TSQC3	477	135	0.05	30.0	32.5	12.8	47.8	13.0
36	592301 TSQC4	400	135	0.04	31.1	33.0	12.2	46.8	13.0

Table 74. Trace Metal Quality Control Data for Sediment Samples for BLM Cruises 24, 27, and 36 - MAFLA Rig Monitoring.

Concentration Units: ppm (dry weight basis)
Digestion: Total
Calibration Standard: Aqueous.

BLM Cruise No.	BLM Sample No.	Ba	V	Cd[a]	Pb[a]	Ni	Cu	Cr	Fe[a] (x10^3)
24	510601 TSQC2	469	94.5			49.3	17.7	60.4	
24	510701 TSQC2	405	81.5			49.0	13.6	45.7	
24	510801 TSQC2	348	98.1			46.1	16.4	57.8	
24	551301 TSQC2	492	100			47.3	15.6	56.0	
24	551401 TSQC2	327	104			48.9	15.9	57.3	
24	551701 TSQC2	304	94.9			43.8	16.2	51.9	
24	591901 TSQC2	344	97.8			61.0	16.0	60.4	
24	592301 TSQC2	343	93.7			43.1	15.1	53.0	
24	592501 TSQC2	443	105			42.3	18.0	57.8	
27	510501 TSQC2	320	115			37.2	15.2	51.8	
27	510701 TSQC3	1011	115			34.4	5.9	44.1	
27	510901 TSQC3	566	103			39.3	6.2	50.7	
27	551001 TSQC2	1588	147			36.1	4.5	46.2	
27	551301 TSQC3	474	93.5			46.6	15.1	52.4	
27	551401 TSQC3	439	116			30.0	3.2	41.6	
27	592101 TSQC2	367	113			49.9	17.3	60.6	
27	592301 TSQC3	442	115			33.8	7.1	46.2	
36	510501 TSQC3	352	61.9			26.2	8.5	42.4	
36	510701 TSQC4	513	95.2			33.4	13.7	59.3	
36	510901 TSQC4	904	93.2			15.8	14.0	62.6	
36	551001 TSQC3	493	98.0			34.4	13.8	61.1	
36	551301 TSQC4	246	98.0			32.8	15.2	60.9	
36	551401 TSQC4	528	99.6			48.6	16.6	70.1	
36	592101 TSQC3	545	109			36.2	14.6	66.0	
36	592301 TSQC4	457	109			36.7	13.9	64.6	

[a]Matrix-Matched standards not required

Table 75. Trace Metal Quality Control Data for Sediment Samples for BLM Cruises 24, 27, and 36 - MAFLA Rig Monitoring.

Concentration Units: ppm (dry weight basis)
Digestion: Total
Calibration Standards: Matrix-Matched.

recovery of spikes is shown in Tables 76, 77, 78 and 79. The MAFLA Rig Monitoring sediments were analyzed in the three sets with the MAFLA Monitoring samples as described above.

G. Standard Reference Sediments

The total number of sediments analyzed by the Trace Metal Quality Control Laboratory included twenty-nine for the South Texas Baseline, twenty-one for MAFLA Monitoring, and twenty-five for MAFLA Rig Monitoring for a total of seventy-five samples. Five analysis sets were constructed containing an average of 15 sediments. The number of in-house standard reference sediments analyzed concurrent with these samples was 30. Sample A and Sample A spiked with trace metals was analyzed with all five sets both for partial and total digestion. Samples B in duplicate and Sample B spiked in duplicate was analyzed with three of the sets. Sample C in duplicate and Sample C spiked in duplicate was analyzed with two sets. This in-house reference sediment was not analyzed under the previous contract. Sample C has been analyzed as 20 replicates in order to obtain an average and standard deviation for the quality control charts. This sample will eventually replace Sample B since the quantity of this bulk sample available has decreased significantly.

The South Texas Baseline sediments were analyzed in sets 1 and 2; MAFLA Monitoring and MAFLA Rig Monitoring sediments were analyzed together in sets 3, 4, and 5. Iron and zinc were both determined for the Sample A replicates although zinc was required only for the South Texas samples while iron was included only in the MAFLA program.

Duplicates

	Average ± Standard Deviation (ppm)							
Sample No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Fe(X10^3)
592310 TSQC2	131±21	91.2± 2.2	0.06±0.01	27.6±0.4	29.8±0.4	15.9±0.2	43.4±0.9	2.2±0.4
510901 TSQC3	148±45	101±3	0.08±0.04	25.2±0.1	26.6±0.6	13.7±0.9	35.7±2.7	2.1±0.2
510701 TSQC4	530±6.0	78.9±11.0	0.15±0.06	20.6±0.3	20.9±1.0	12.0±0.2	24.7±2.1	4.9±0.0

Spikes

	Percent Recovery							
Sample No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Fe(X10^3)
551301 TSQC2	97.5	100	70.0	100	96.5	95.8	97.2	
510701 TSQC3	b	131	80.2	94.0	83.0	95.2	102	
551301 TSQC3	86	107	69.1	97.0	85.0	95.8	97.2	
551401 TSQC4	b	102	89.3	89.1	72.4	90.1	91.3	

[a] Spikes not required
[b] Spike omitted

Table 76. Average and Standard Deviation of Duplicate and Percent Recovery of Spikes for Sediment Samples for MAFLA Rig Monitoring.

Digestion: Partial
Calibration Standards: Aqueous

Duplicates

	Average ± Standard Deviation (ppm)							
Sample No.	Ba	V	Cd[a]	Pb[a]	Ni	Cu	Cr	Fe(x10^3)[a]
592301 TSQC2	148±25	74.4±2.5			34.1±0.4	17.3±0.3	44.0±1.3	
510901 TSQC3	152±46	82.3±2.6			20.1±0.5	14.9±1.0	36.8±4.0	
510701 TSQC4	65±12	54.5±7.6			23.2±1.1	12.4±0.3	33.2±2.8	

Spikes

	Percent Recovery							
Sample No.	Ba	V	Cd[a]	Pb[a]	Ni	Cu	Cr	Fe(x10^3)[b]
551301 TSQC2	110	81.6			105	99.0	98.5	
510701 TSQC3	c	107			95.0	98.4	103	
551301 TSQC3	97.2	87.3			97.3	99.0	98.5	
551401 TSQC4	c	83.2			82.8	93.1	92.6	

[a] Matrix-matched standards not required
[b] Spike not required
[c] Spike omitted

Table 77. Average and Standard Deviation of Duplicates and Percent Recovery of Spikes for Sediment Samples for MAFLA Rig Monitoring.

Digestion: Partial
Calibration Standards: Matrix-Matched

Duplicates

	Average ± Standard Deviation (ppm)							
Sample No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Fe(x10^3)
592301 TSQC2	467±26	116±3	0.04	20.2±0.0	43.2±0.3	15.0±0.0	52.8±1.1	22.5±0.3
510901 TSQC3	512±22	192±7	0.04	30.2±1.2	35.3±1.3	6.2±0.5	50.6±1.2	26.2±2.1
510701 TSQC4	449±29	118±1	0.04±0.01	29.7±0.4	30.0±2.6	12.0±0.1	42.3±0.6	9.41±2.42

Spikes

	Percent Recovery							
Sample No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Fe(x10^3)[a]
551301 TSQC2		131	97.3	94.8	92.8	95.0	98.1	
510701 TSQC3		120	103	86.4	94.6	93.2	89.4	
551301 TSQC3		119	104	96.0	89.5	97.0	88.7	
551401 TSQC4		126	94.2	85.7	66.3	84.0	75.8	

[a]Spikes not required - major constituent

Table 78. Average and Standard Deviation of Duplicates and Percent Recovery of Spikes for Sediment Samples for MAFLA Rig Monitoring.

Digestion: Total
Calibration Standards: Aqueous

Duplicates

	Average ± Standard Deviation (ppm)							
Sample No.	Ba	V	Cd[a]	Pb[a]	Ni	Cu	Cr	Fe(x10^3)[a]
592301 TSQC2	300± 7	93.7±2.8			48.1±0.3	15.1±0.0	53.0±1.1	
510901 TSQC3	584±26	141±6			39.3±1.5	6.2±0.3	50.7±0.8	
510701 TSQC4	513±33	95.2±0.4			33.4±2.9	13.7±0.1	59.3±0.4	

Spikes

	Percent Recovery							
Sample No.	Ba	V	Cd[a]	Pb[a]	Ni	Cu	Cr	Fe(x10^3)[a]
551301 TSQC2	113	106			103	95.6	98.5	
510701 TSQC3	83.5	96.9			105	93.8	89.7	
551301 TSQC3	113	96.1			99.6	97.6	89.0	
551401 TSQC4	89.2	102			73.8	84.6	76.1	

[a]Matrix-matched standards not required

Table 79. Average and Standard Deviation of Duplicates and Percent Recovery of Spikes for Sediment Samples for MAFLA Rig Monitoring.

Digestion: Total
Calibration Standards: Matrix-Matched

The trace metal analysis of in-house standard reference sediment Sample A by the partial digestion is shown in Table 80. This data is presented as quality control charts compared to the average and standard deviation of 55 replicate analyses of Sample A performed previously.

These charts are presented for barium (Figure 4), vanadium (Figure 5), lead (Figure 6), nickel (Figure 7), copper (Figure 8), chromium (Figure 9), and zinc (Figure 10) where $\bar{x}$ corresponds to the average of the 55 replicates and σ represents the standard deviation. The quality control charts for Sample A illustrate that the analyses were in-control for all five sets. The trace metal data for Sample A analyzed by the total digestion is shown in Table 81. The in-house standard reference sediments have not been analyzed by the total digestion procedure a sufficient number of times to construct quality control charts with the average of several replicates shown. As time permits these replicate determinations will be made for future use.

The percent recovery of spikes for Sample A is presented in Table 82 (partial) and Table 83 (total) for both aqueous and matrix-matched standards when appropriate. Only aqueous standards are employed for the quality control chart data presented above since matrix-matched standards may not be used in flameless analysis. The pattern of vanadium elevation and barium depression is observed with this percent recovery data as noted above for the actual samples. The spikes were omitted for set 1 and 2 for the total digestion; sufficient other information was available to determine that the analysis was in-control so these runs were not repeated.

Set No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Zn	Fe(x10^3)
1	97.5	39.4	<0.04	24.9	6.3	6.1	18.5	45.2	8.46
2	106	52.6	<0.04	33.6	7.6	8.4	25.8	32.8	9.71
3	82.4	42.4	<0.04	36.2	12.4	9.7	26.0	39.6	7.72
4	87.6	42.2	<0.04	31.8	11.4	8.3	20.9	33.2	7.42
5	72.1	42.6	<0.04	30.1	7.9	6.2	13.6	37.4	7.42
Average	89.1	43.8	<0.04	31.3	9.1	7.7	21.0	37.6	8.15
Standard Deviation	13.2	5.1	0	4.2	2.6	1.6	5.2	5.1	0.97

Table 80. Trace Metal Quality Control Data for Sample A.

Concentration Units: ppm (dry weight basis)
Digestion: Partial
Calibration Standards: Aqueous

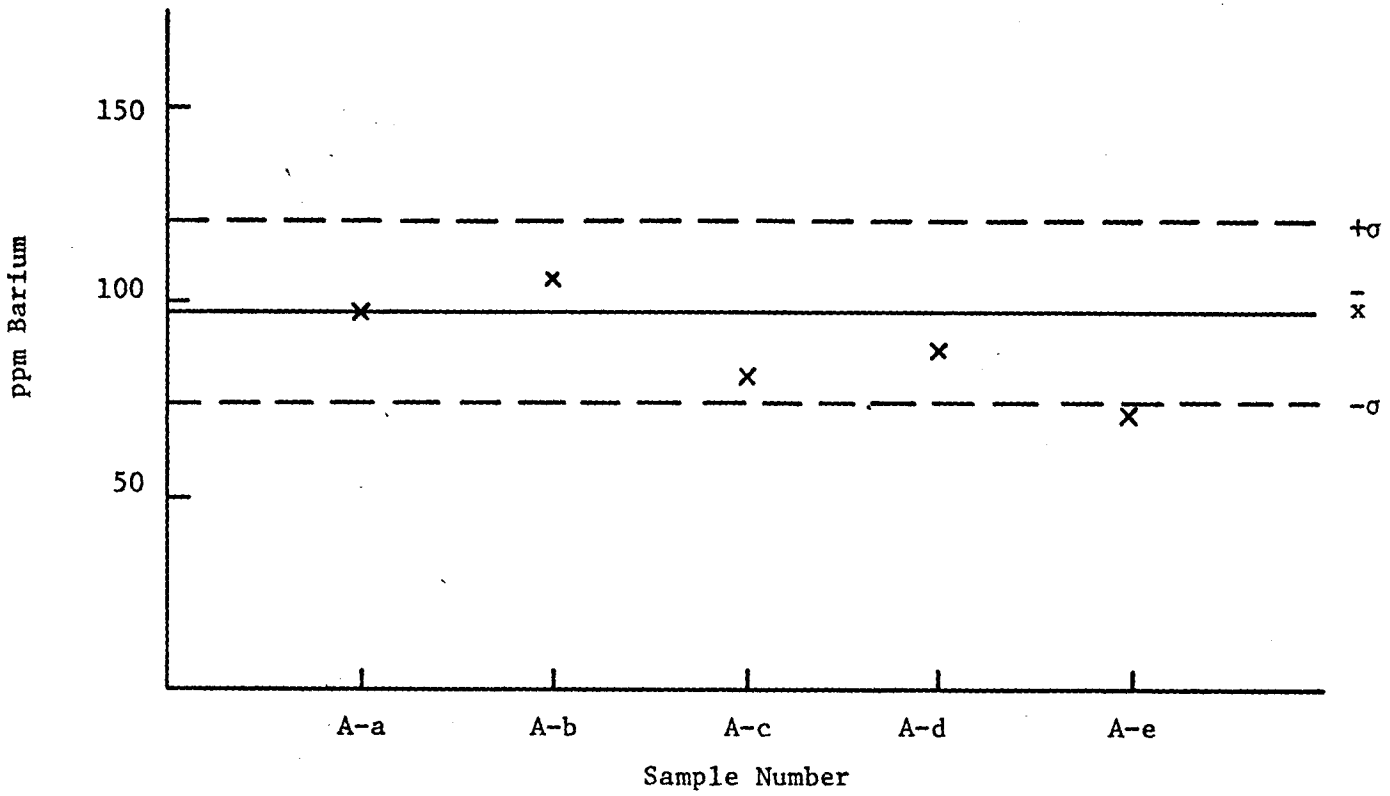

Figure 4. Barium Quality Control Chart - South Texas and MAFLA Sediments.

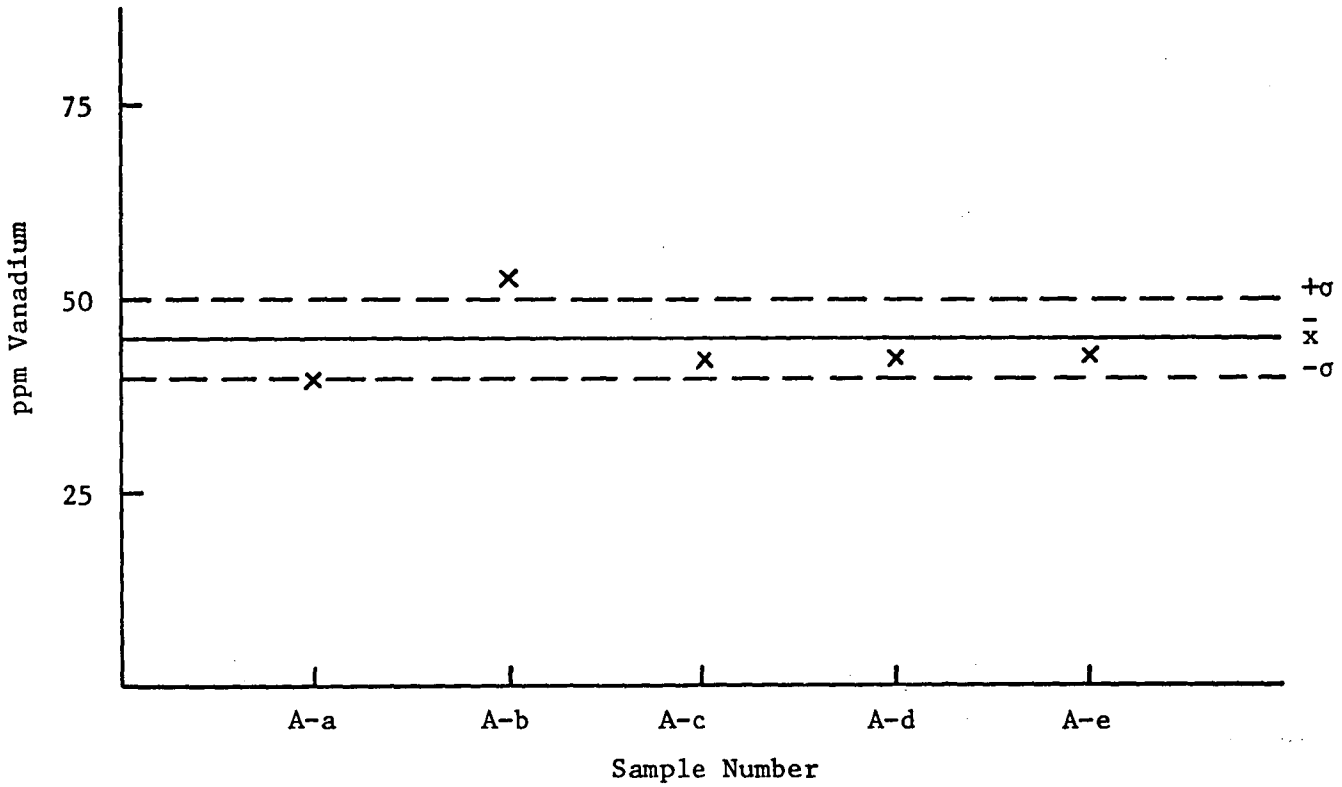

Figure 5. Vanadium Quality Control Chart - South Texas and MAFLA Sediments.

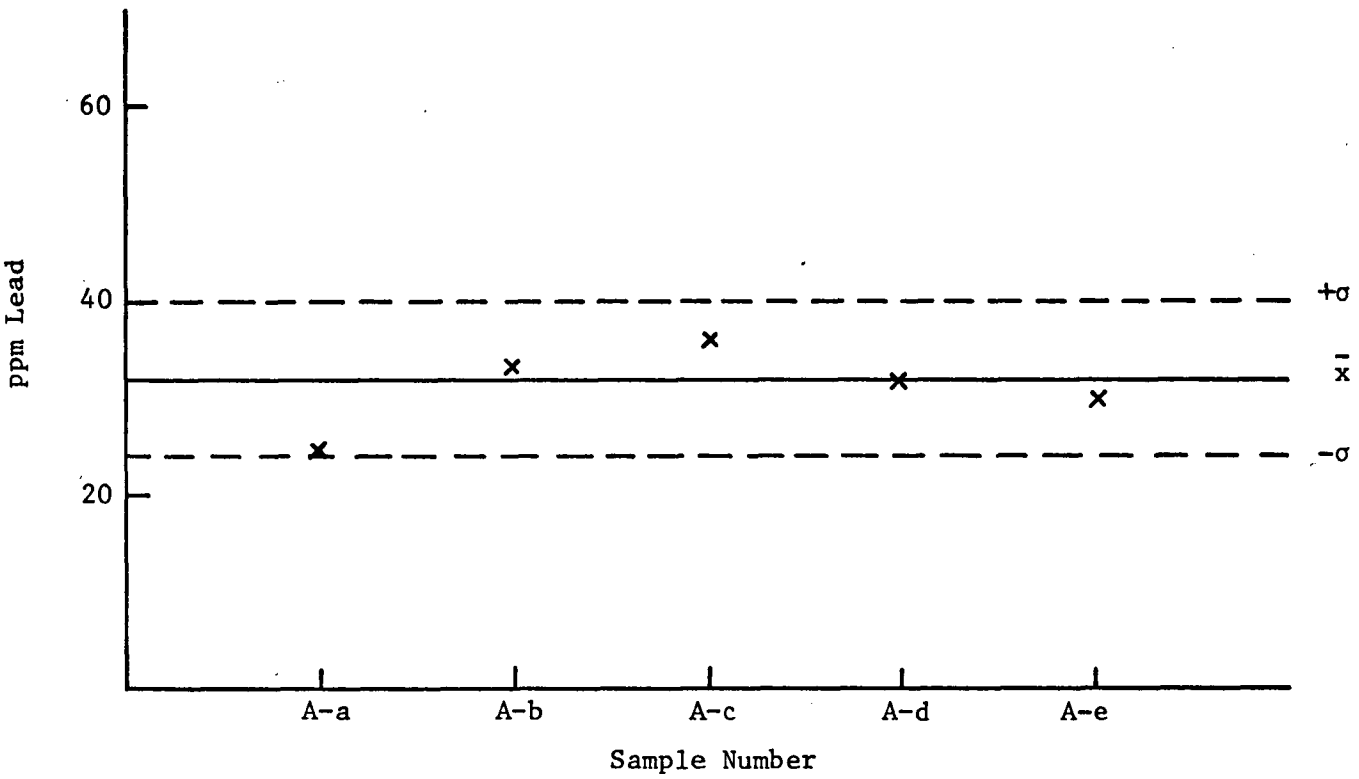

Figure 6. Lead Quality Control Chart - South Texas and MAFLA Sediments.

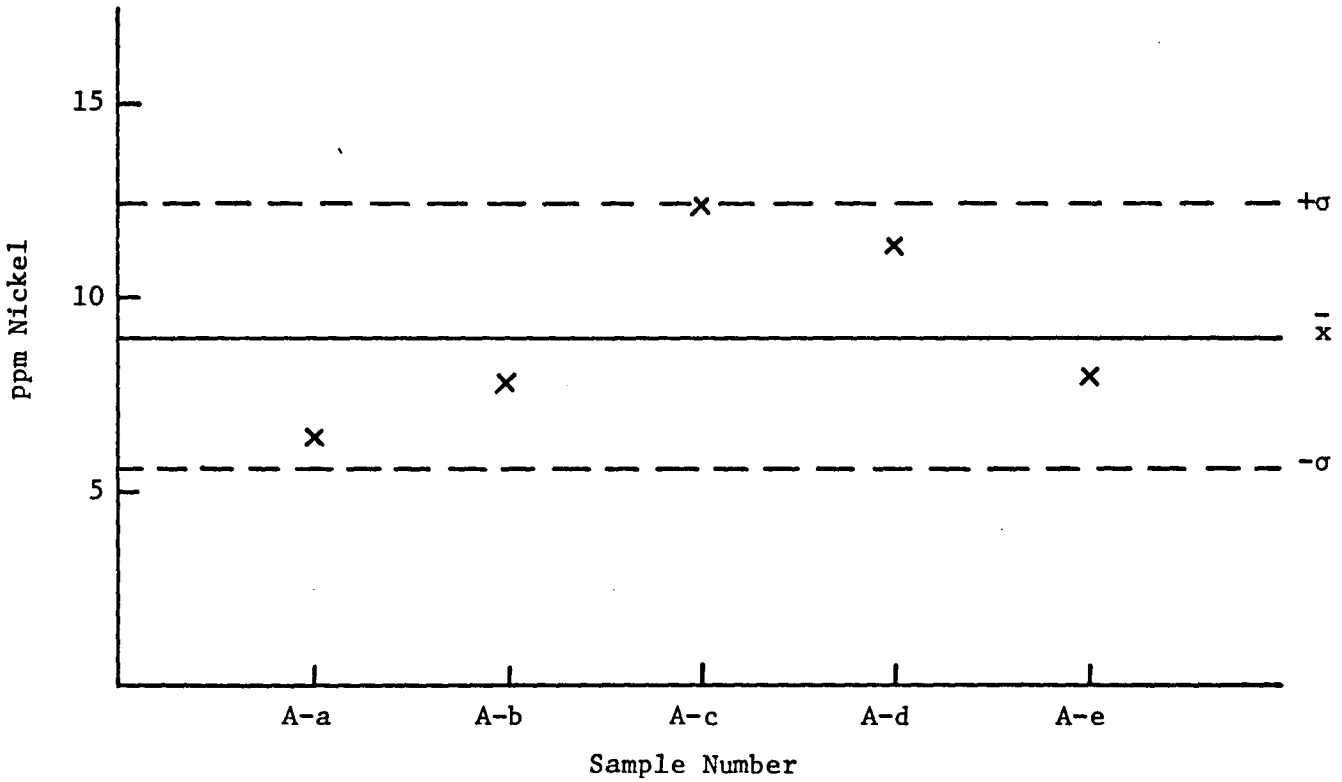

Figure 7. Nickel Quality Control Chart - South Texas and MAFLA Sediments.

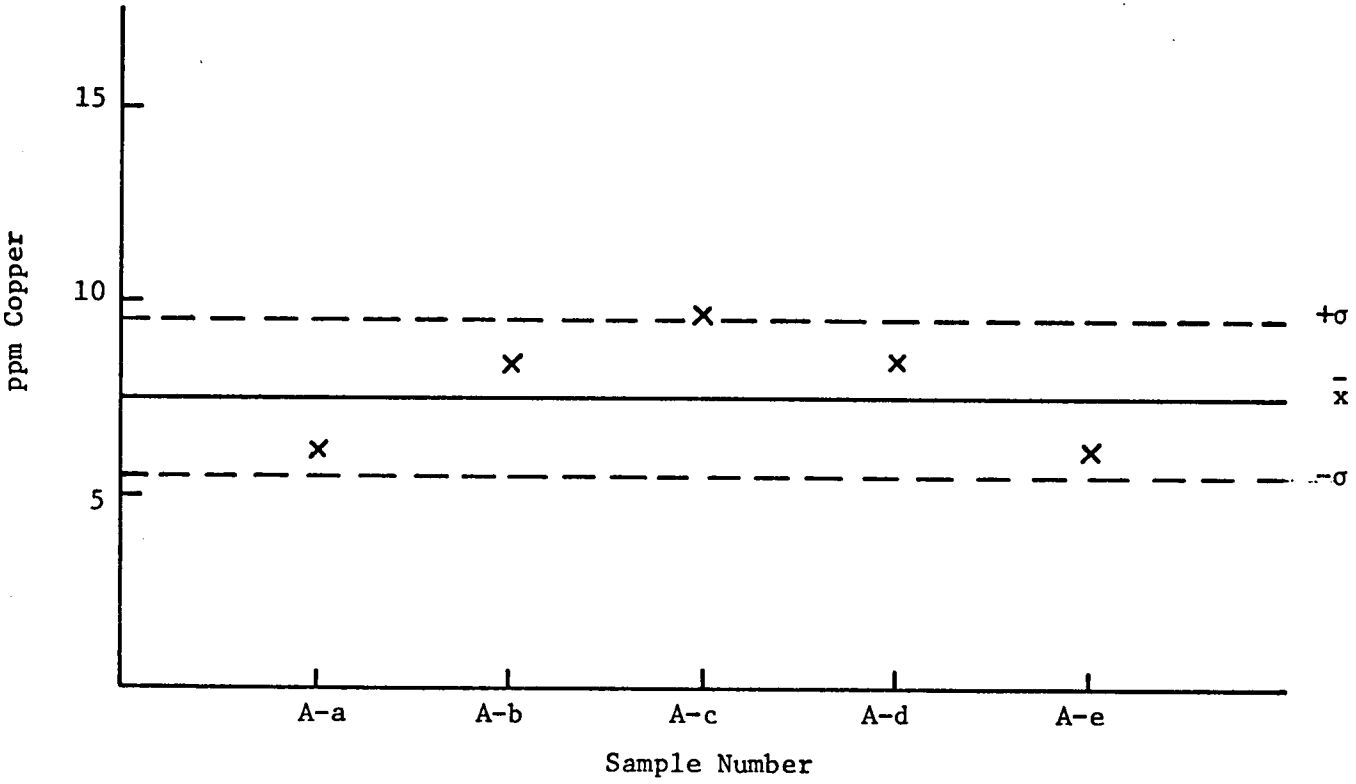

Figure 8. Copper Quality Control Chart - South Texas and MAFLA Sediments.

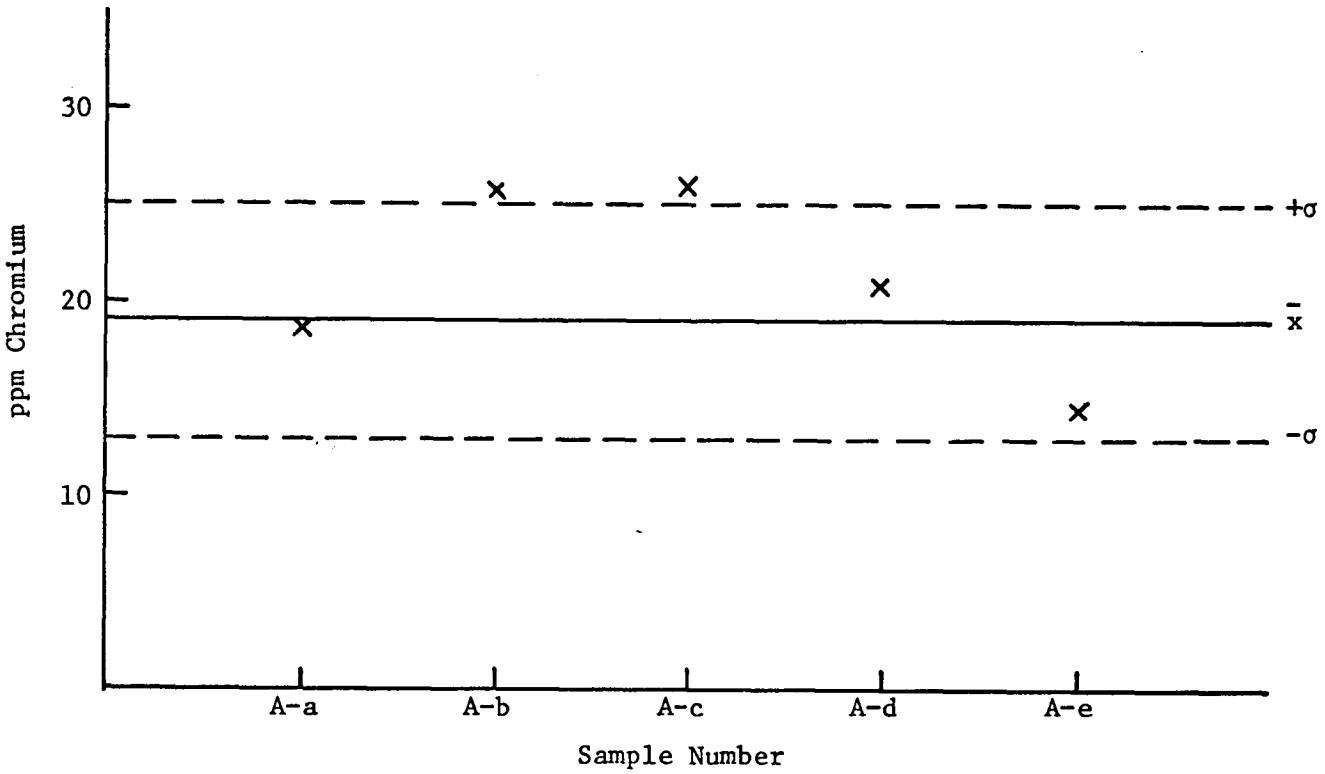

Figure 9. Chromium Quality Control Chart - South Texas and MAFLA Sediments.

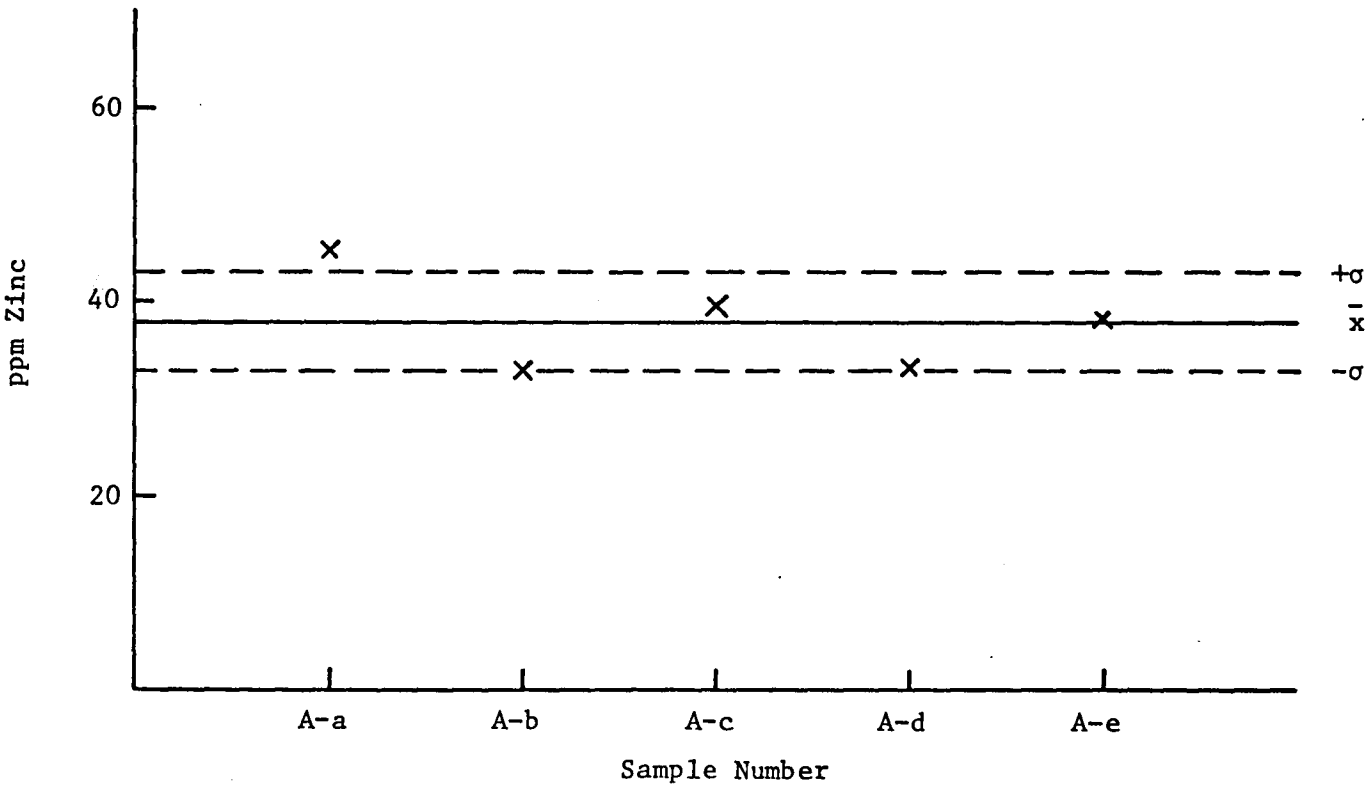

Figure 10. Zinc Quality Control Chart - South Texas and MAFLA Sediments.

Set No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Zn	Fe(x10^3)
1	180	81.9	0.05	33.6	18.6	10.1	42.5	40.5	15.4
2	192	74.7	0.04	36.0	19.8	10.6	47.3	38.5	15.5
3	229	69.4	<0.04	33.2	20.4	11.1	28.9	a	14.5
4	196	108	0.05	31.8	20.1	10.2	31.4	a	12.7
5	201	82.4	<0.04	35.6	17.8	8.8	36.1	a	12.8
Average	200	83.2	<0.04	34.0	19.3	10.2	37.2	39.5	14.2
Standard Deviation	18.2	14.8	----	1.8	1.1	0.9	7.6	1.4	1.4

[a]Analysis not required for set

Table 81. Trace Metal Quality Control Data for Sample A.

Concentration Units: ppm (dry weight basis)
Digestion: Total
Calibration Standards: Aqueous

Set No.	Ba		V		Cd	Pb	Ni		Cu		Cr	
	Aq	MM	Aq	MM			Aq	MM	Aq	MM	Aq	MM
1	87.2	89.9	134	103	95.1	94.0	97.1	105	94.6	101	a	a
2	a	a	99.7	76.1	97.1	90.9	90.8	98.1	92.0	98.6	91.7	99.9
3	104	107	138	105	96.0	108	99.5	107	93.8	100	95.8	104
4	84.8	87.4	112	85.6	104	88.2	87.7	94.8	85.1	91.2	111	121
5	a	a	112	85.6	83.9	106	87.1	94.1	101	108	99.6	108
Average	92.0	94.8	138	91.1	95.2	97.4	92.4	99.8	93.3	99.8	99.5	108

[a]Spike omitted

Table 82. Percent Recovery of Spikes for Sample A by the Partial Digestion Technique for Aqueous (Aq) and Matrix-Matched (MM) Standards.

Set No.	Bu		V		Cd	Pb	Ni		Cu		Cr	
	Aq	MM	Aq	MM			Aq	MM	Aq	MM	Aq	MM
1[a]												
2[a]												
3	a		139	112	96.4	90.3	66.8	74.2	96.0	106	73.2	101
4	105	117	118	95.4	98.4	103	102	113	98.8	108	74.7	103
5	106	118	103	83.2	99.2	a	89.1	99.0	87.1	95.7	79.8	110
Average	105	117	120	96.9	98.0	96.6	86.0	95.4	94.0	103	75.9	105

[a]Spike omitted

Table 83. Percent Recovery of Spikes for Sample A by the Total Digestion Technique for Aqueous (Aq) and Matrix-Matched Standard.

The trace metal data for in-house standard reference sediment Sample B is shown in Table 84 for the partial digestion and in Table 85 for the total digestion. The average and standard deviation reported for these samples is well within experimental error. The percent recovery of trace metal spikes is shown in Table 86 (partial digestion) and Table 87 (total digestion. Data for aqueous and matrix-matched standards is presented for comparison. In some cases the matrix-matched recovery is not an improvement over the aqueous case. This event may be due to the make-up of the matrix which corresponded to the BLM sediments in the set rather than the in-house standard reference sediments. Quantitative recovery of spikes is noted in the majority of the analyses. The data from Table 84 was employed to construct Quality Control Charts for Sample B for each metal with sets 3, 4, and 5. These charts are shown in Figure 11 (barium), Figure 12 (vanadium), Figure 13 (cadmium), Figure 14 (lead), Figure 15 (nickel), Figure 16 (copper), and Figure 17 (chromium). The mean ($\bar{x}$) and standard deviation (σ) shown on these charts represent the statistical analysis of 55 replicates analyzed previously for the trace metals in the BLM OCS program.

The trace metal concentrations determined for in-house standard reference sediment Sample C are exhibited in Table 88 (partial digestion) and Table 89 (total digestion). The average and standard deviation shown indicate good analytical precision. The percent recovery data for these

Samples	Set No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Fe(x10^3)
B-1	3	20.5	16.6	1.2	10.9	3.6	12.6	73.1	4.24
B-2	3	15.9	16.2	1.4	13.7	3.5	15.1	80.5	4.39
B-1	4	18.3	11.4	1.0	12.0	3.8	9.6	70.1	3.42
B-2	4	19.2	13.4	1.0	12.1	3.6	10.6	57.6	3.09
B-1	5	18.0	10.2	1.3	10.9	3.6	10.3	76.0	3.81
B-2	5	15.1	16.8	0.9	11.5	3.2	10.4	68.1	3.64
Average		17.8	14.1	1.1	11.8	3.6	11.4	70.9	3.77
Standard Deviation		2.0	2.9	0.2	1.0	0.2	2.1	7.8	0.49

Table 84. Trace Metal Quality Control Data for Sample B.

Concentration Units: ppm (dry weight basis)
Digestion: Partial
Calibration Standards: Aqueous

Sample	Set No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Fe(x10^3)
B-1	3	72.7	19.4	1.5	9.6	5.6	12.7	46.9	4.69
B-2	3	94.7	23.3	1.5	13.6	4.5	12.6	53.2	6.18
B-1	4	77.6	25.0	1.7	8.1	3.9	10.2	42.8	3.80
B-2	4	73.8	19.7	1.7	8.1	4.2	11.8	47.6	4.35
B-1	5	71.3	20.4	1.7	15.0	3.7	11.4	47.2	3.08
B-2	5	66.3	20.4	1.7	12.4	4.5	8.9	42.5	2.64
Average		76.1	21.4	1.6	11.1	4.4	11.3	46.7	4.12
Standard Deviation		9.8	2.3	0.1	3.0	0.7	1.5	3.9	1.26

Table 85. Trace Metal Quality Control Data for Sample B.

Concentration Units: ppm (dry weight basis)
Digestion: Total
Calibration Standards: Aqueous

Sample	Set No.	Ba		V		Cd	Pb	Ni		Cu		Cr	
		Aq	MM	Aq	MM			Aq	MM	Aq	MM	Aq	MM
B-1	3	93.8	115	126	94.1	97.2	94.0	95.2	103	101	108	97.5	109
B-2	3	83.7	102	124	92.6	88.2	113	87.2	94.1	94.5	101	93.5	105
B-1	4	75.2	92.1	137	102	108	99.0	95.0	102	100	107	99.2	112
B-2	4	87.3	107	132	98.6	111	102	98.2	106	103	110	101	114
B-1	5	75.0	91.9	119	88.9	86.0	98.2	87.3	94.2	103	110	90.8	102
B-2	5	88.0	108	122	91.1	90.3	102	95.6	103	92.5	99.1	106	119
Average		83.8	103	127	94.6	96.8	101	93.1	100	99.0	106	98.0	110

Table 86. Percent Recovery of Spikes for Sample B by the Partial Digestion Technique for Aqueous (Aq) and Matrix-Matched (MM) Standards.

Sample	Set No.	Ba		V		Cd	Pb	Ni		Cu		Cr	
		Aq	MM	Aq	MM			Aq	MM	Aq	MM	Aq	MM
B-1	3	96.5	108	123	99.4	98.4	92.5	85.9	95.2	96.8	110	90.2	124
B-2	3	a	a	120	97.0	105	78.9	86.5	95.6	102	116	86.7	119
B-1	4	99.4	110	114	92.1	108	88.0	105	116	104	118	99.2	137
B-2	4	112	124	113	91.3	96.0	97.0	95.0	105	103	117	93.2	128
B-1	5	98.6	110	94.6	76.4	99.0	99.8	93.1	103	87.4	99.5	93.6	129
B-2	5	102.5	114	95.4	77.1	101	103	87.8	97.3	92.2	105	101	139
Average		102	113	110	88.9	101	93.2	92.2	102	97.6	111	94.0	129

[a]Spike omitted

Table 87. Percent Recovery of Spikes for Sample B by the Total Digestion Technique for Aqueous (Aq) and Matrix-Matched (MM) Standards.

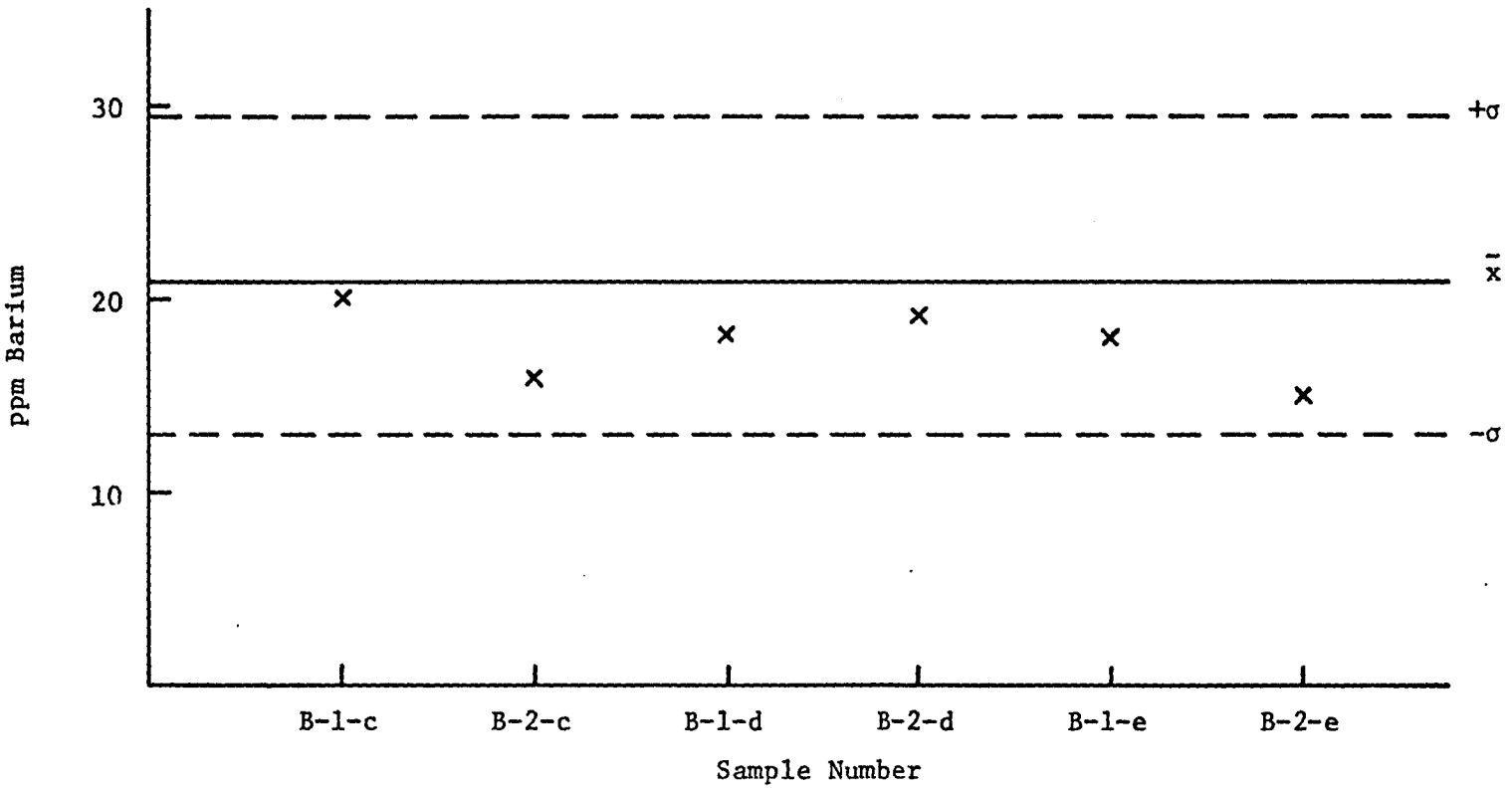

Figure 11. Barium Quality Control Chart - MAFLA Monitoring and MAFLA Rig Monitoring Sediments.

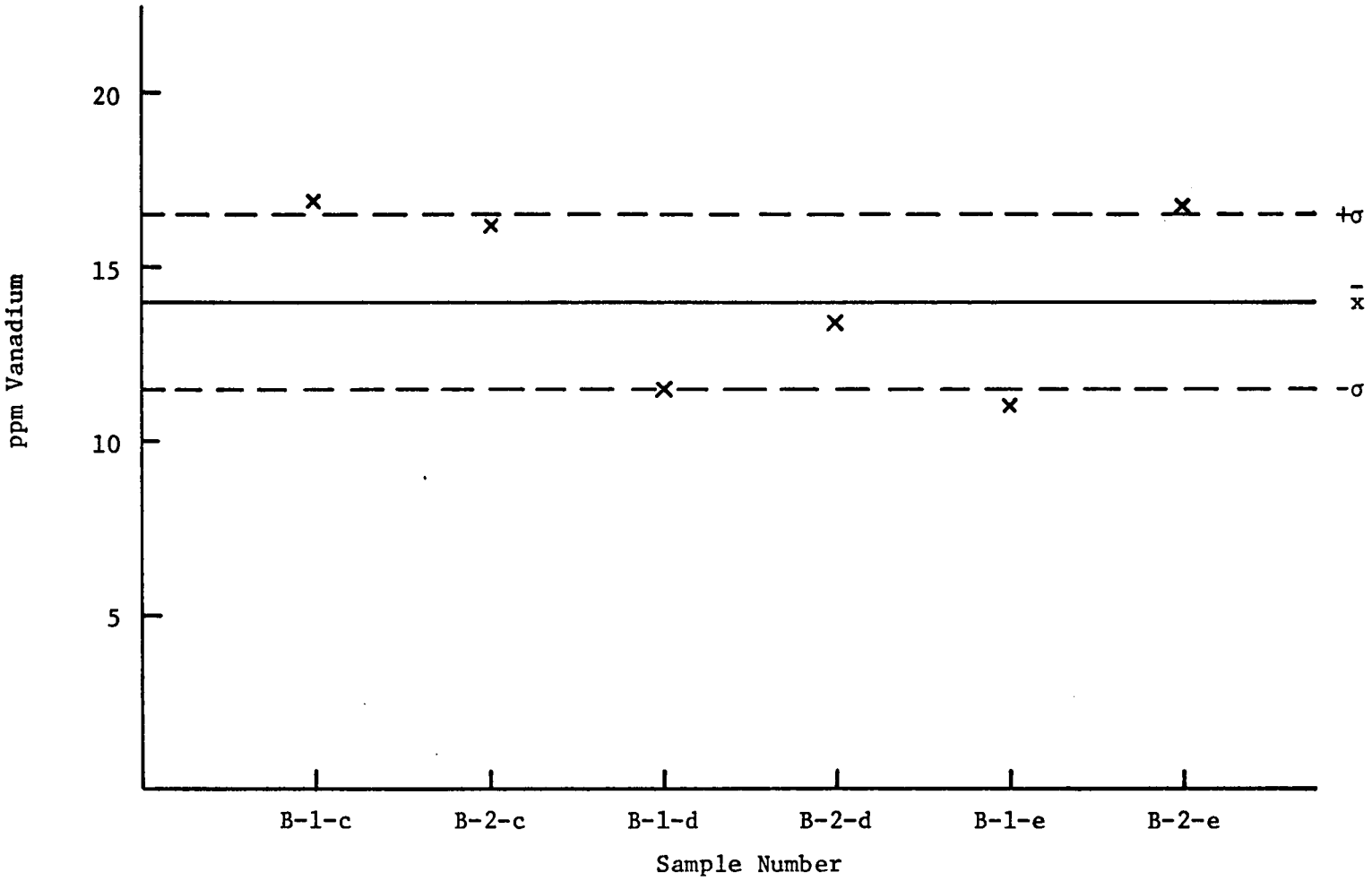

Figure 12. Vanadium Quality Control Chart - MAFLA Monitoring and MAFLA Rig Monitoring Sediments.

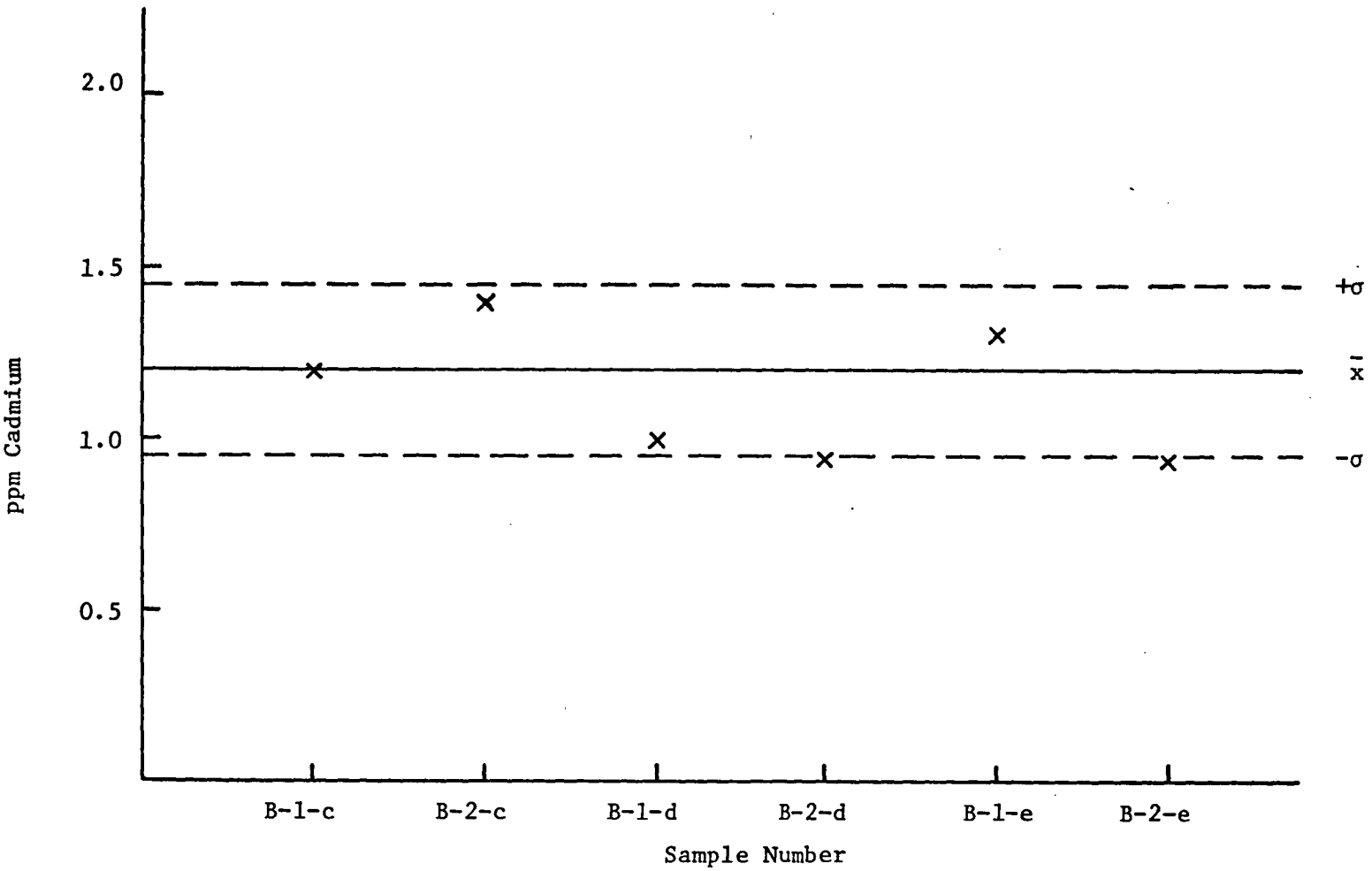

Figure 13. Cadmium Quality Control Chart - MAFLA Monitoring and MAFLA Rig Monitoring Sediments.

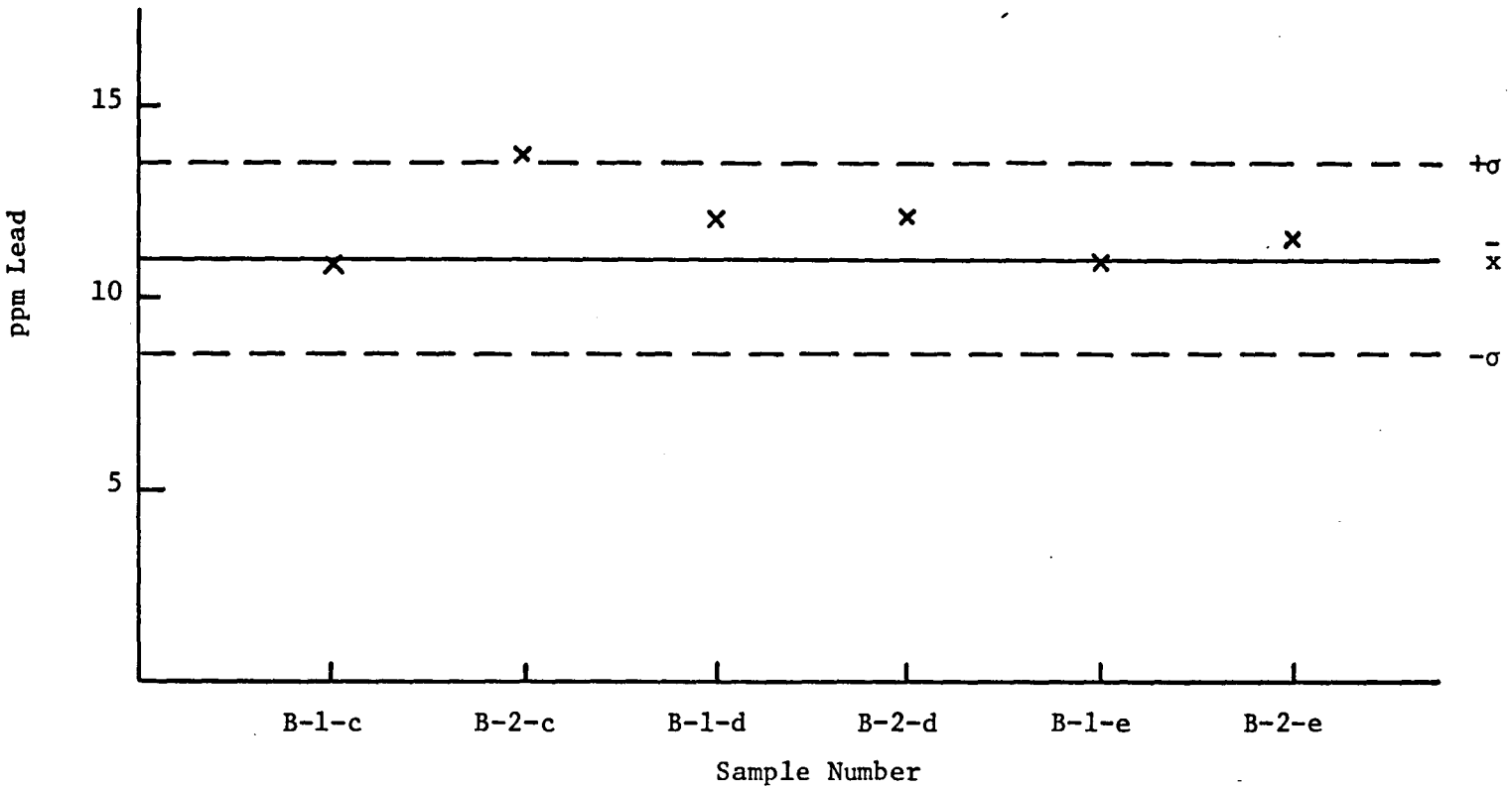

Figure 14. Lead Quality Control Chart - MAFLA Monitoring and MAFLA Rig Monitoring Sediments.

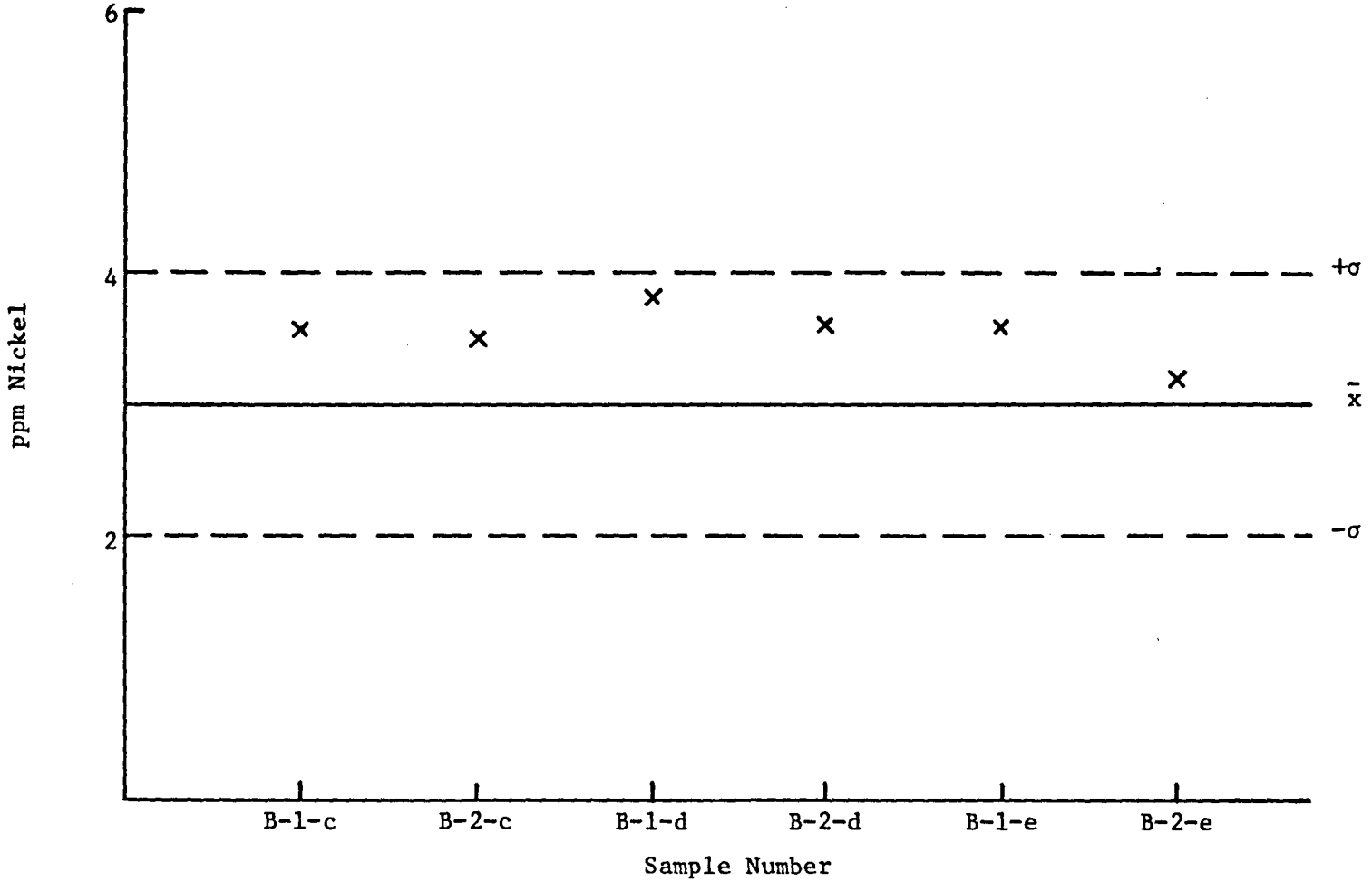

Figure 15. Nickel Quality Control Chart - MAFLA Monitoring and MAFLA Rig Monitoring Sediments.

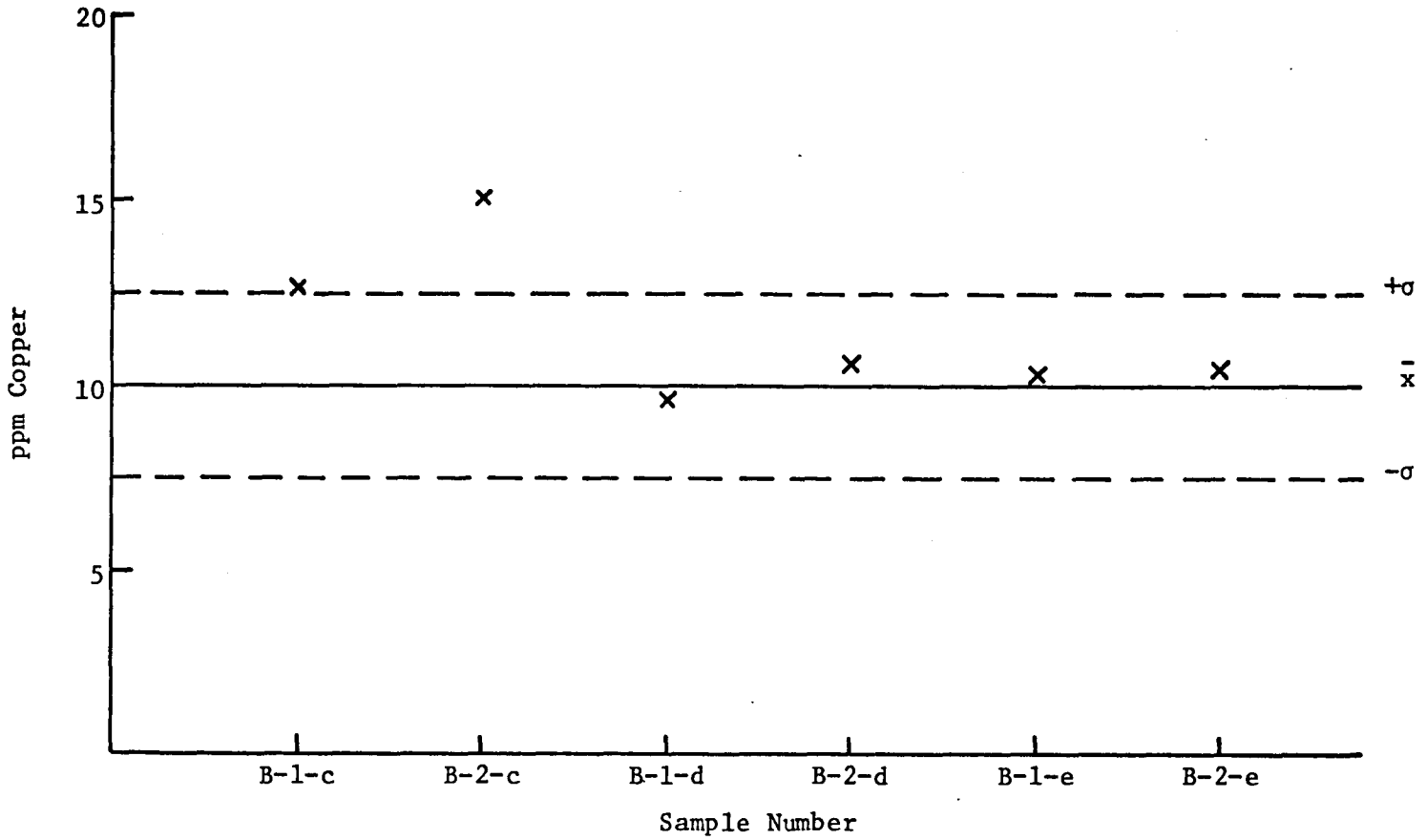

Figure 16. Copper Quality Control Chart - MAFLA Monitoring and MAFLA Rig Monitoring Sediments.

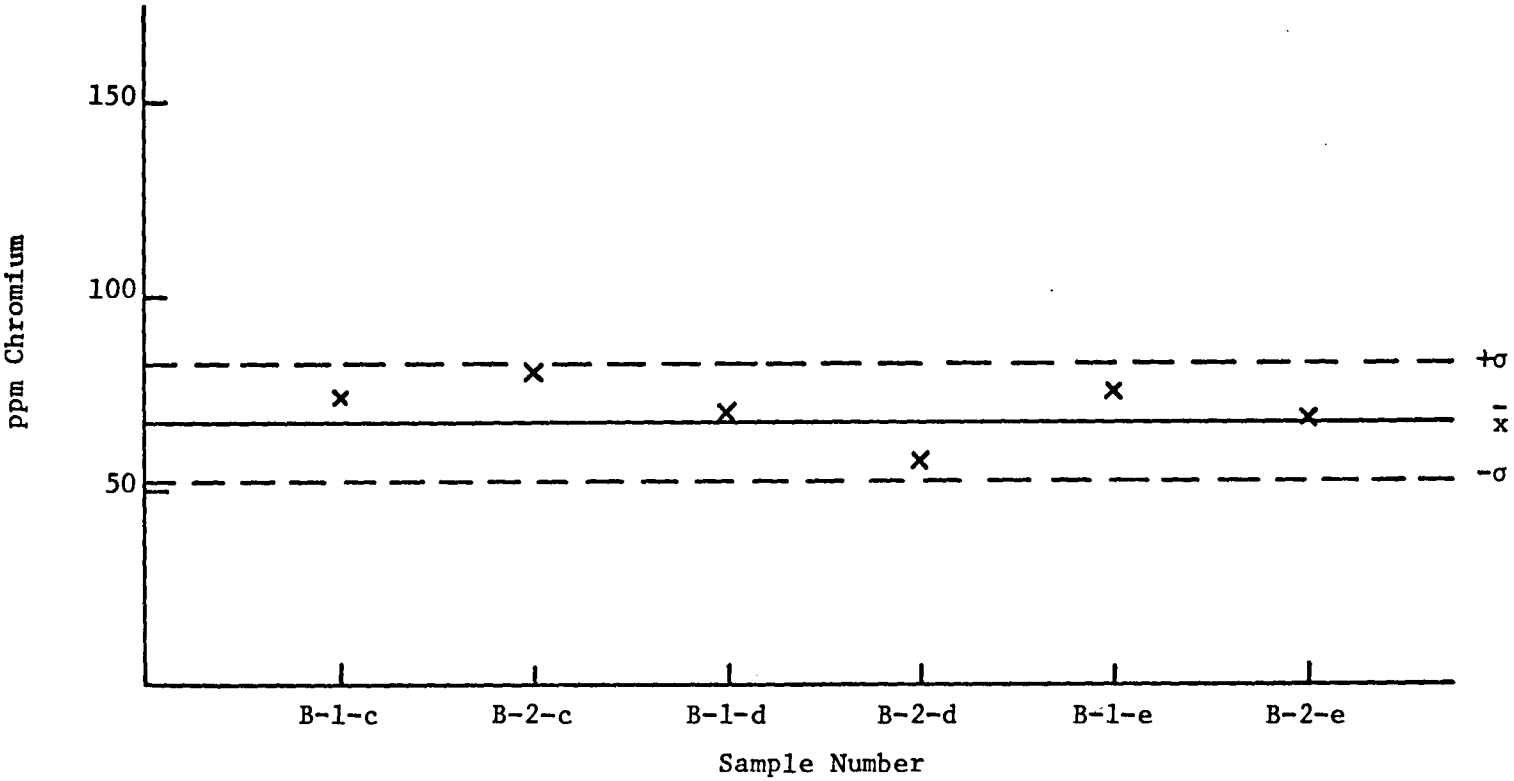

Figure 17. Chromium Quality Control Chart - MAFLA Monitoring and MAFLA Rig Monitoring Sediments.

Sample	Set No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Zn	Fe(x10^3)
C-1	1	21.7	14.8	5.3	18.2	22.0	28.9	272	47.8	3.52
C-2	1	20.9	13.8	5.1	17.2	18.1	27.9	273	43.0	3.48
C-1	2	26.8	13.5	5.0	19.8	23.1	27.1	276	39.3	4.68
C-2	2	23.1	13.1	5.1	19.6	18.0	26.1	294	41.9	4.16
Average		23.1	13.8	5.1	18.7	20.3	27.5	278	43.0	3.96
Standard Deviation		2.6	0.7	0.1	1.2	2.6	1.2	10.3	3.6	0.57

Table 88. Trace Metal Quality Control Data for Sample C.

Concentration Units: ppm (dry weight basis)
Digestion: Partial
Calibration Standards: Aqueous

Sample	Set No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Zn	Fe(x10^3)
C-1	1	77.4	29.6	4.8	17.2	3.8	34.7	278	50.5	7.36
C-2	2	97.5	32.8	3.4	20.1	3.3	35.2	252	54.7	6.19
C-1	1	93.8	27.3	5.2	22.1	3.0	34.9	250	50.7	6.76
C-2	2	85.5	27.1	4.7	23.3	2.2	37.0	230	52.8	6.80
Average		88.6	29.2	4.5	20.7	3.1	35.4	252	52.2	6.78
Standard Deviation		9.0	2.6	0.8	2.7	0.7	1.0	19.7	2.0	0.48

Table 89. Trace Metal Quality Control Data for Sample C.

Concentration Units: ppm (dry weight basis)
Digestion: Total
Calibration Standards: Aqueous

samples determined with the partial digestion is shown in Table 90. The Quality Control Charts for Sample C employed with sets 1 and 2 are presented as Figure 18 (barium), Figure 19 (vanadium), Figure 20 (cadmium), Figure 21 (lead), Figure 22 (nickel), Figure 23 (copper), Figure 24 (chromium), and Figure 25 (zinc). These charts indicate that both sets of analyses were in-control.

The plastic clay Standard Reference Material (98a) issued by the National Bureau of Standards was analyzed with each set of BLM sediments. Only three trace metals of interest in the OCS environmental studies is certified by NBS for this SRM: barium, chromium, and iron. For this reason SRM 98a is not an ideal quality control check. The data obtained for NBS SRM 98a is shown in Table 91 (partial digestion) and Table 92 (total digestion). The average and standard deviation for five replicates by each technique is presented in addition to the NBS certified value. The precision is good for both digestion techniques indicating that either digestion procedure yields consistent metal concentrations. The certified value for iron is not achieved for either digestion. The barium and chromium content is low for the partial technique and in the proper range for the total digestion. The metal levels in this SRM that are certified are in the proper range for the BLM studies. Copper and perhaps nickel are higher than environmentally observed in sediments for the most part.

Sample	Set No.	Ba		V		Cd	Pb	Ni		Cu		Cr	
		Aq	MM	Aq	MM			Aq	MM	Aq	MM	Aq	MM
C-1	1	75.8	92.8	129	96.3	99.6	92.0	97.9	106	89.3	95.7	a	a
C-2	1	76.0	93.1	124	92.6	93.7	92.5	104	112	85.3	91.4	a	a
C-1	2	89.7	108	127	94.8	96.8	95.0	109	118	86.6	92.8	116	130
C-2	2	100	122	131	97.8	100	95.6	92.2	99.5	103	110	96	108
Average		85.4	104	128	95.4	96.7	93.8	100	109	91.0	97.5	106	119

[a]Spike omitted

Table 90. Percent Recovery of Spikes for Sample C by the Partial Digestion Technique for Aqueous (Aq) and Matrix-Matched (MM) Standards.

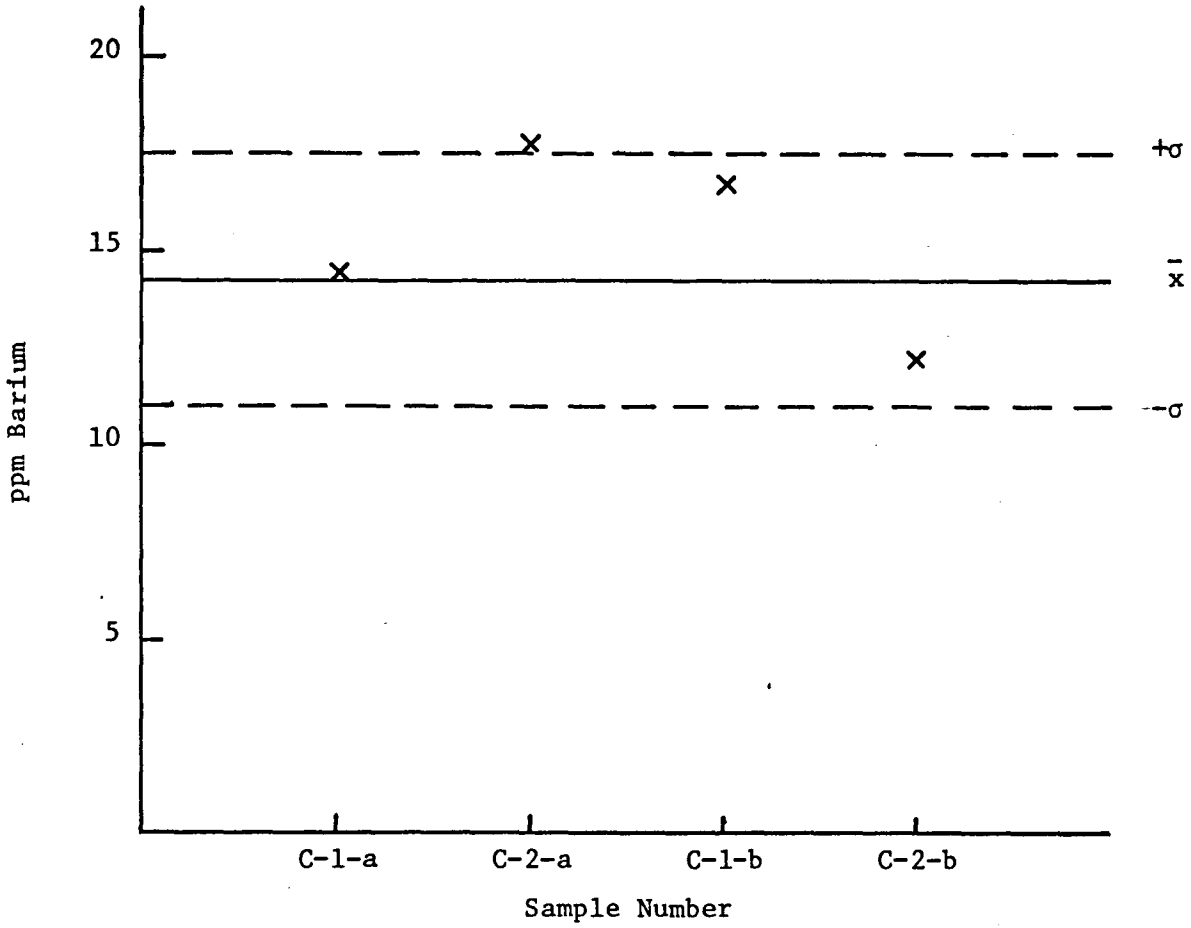

Figure 18. Barium Quality Control Chart - South Texas Baseline Sediments.

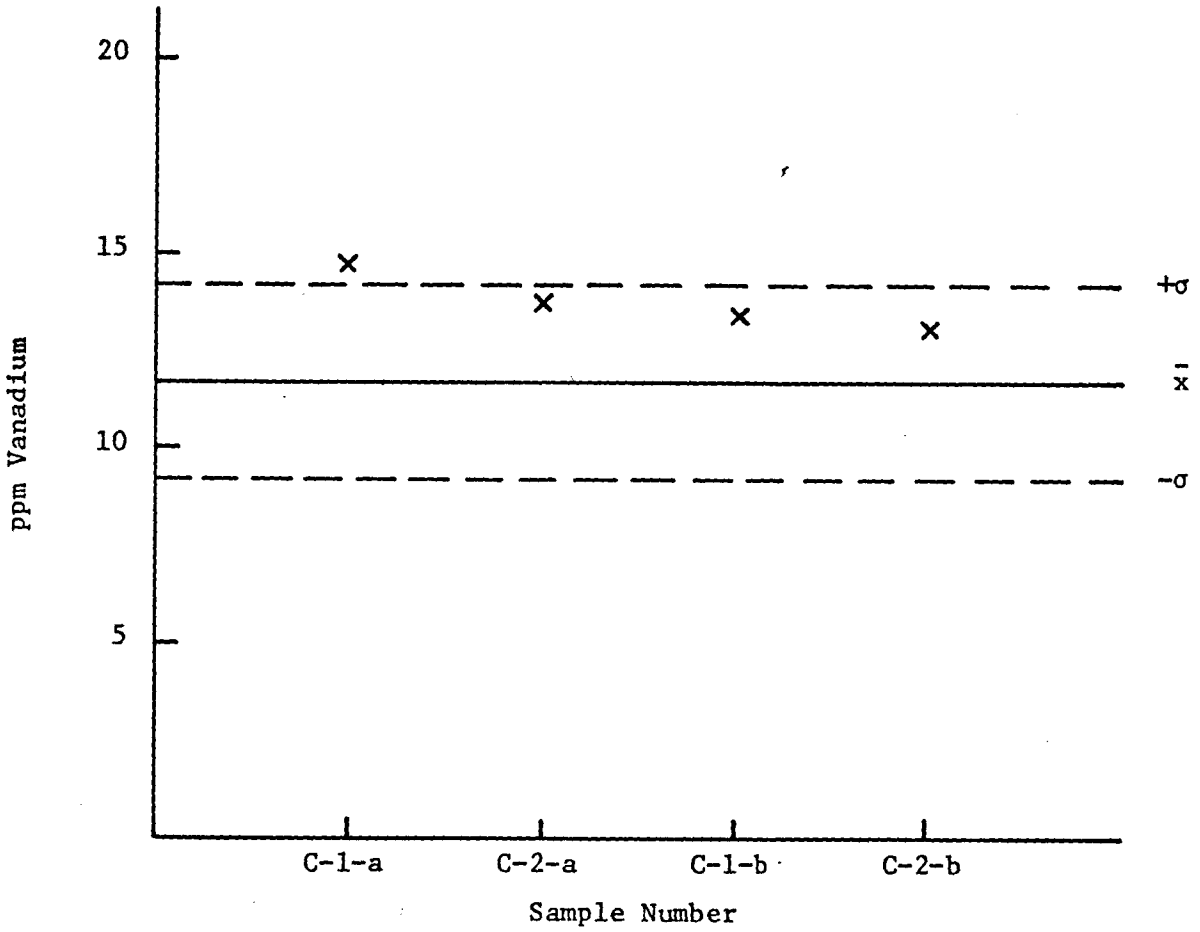

Figure 19. Vanadium Quality Control Chart - South Texas Baseline Sediments.

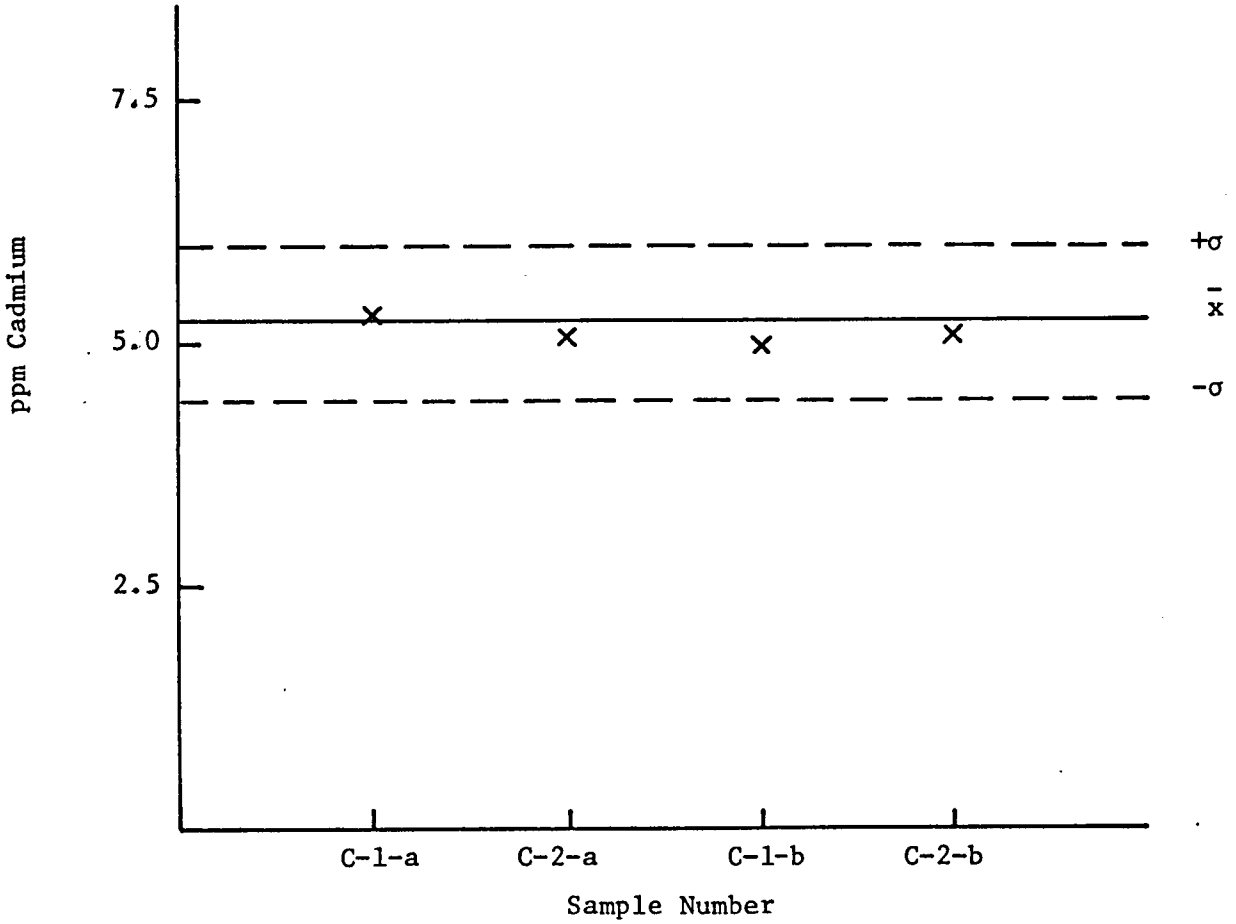

Figure 20. Cadmium Quality Control Chart - South Texas Baseline Sediments.

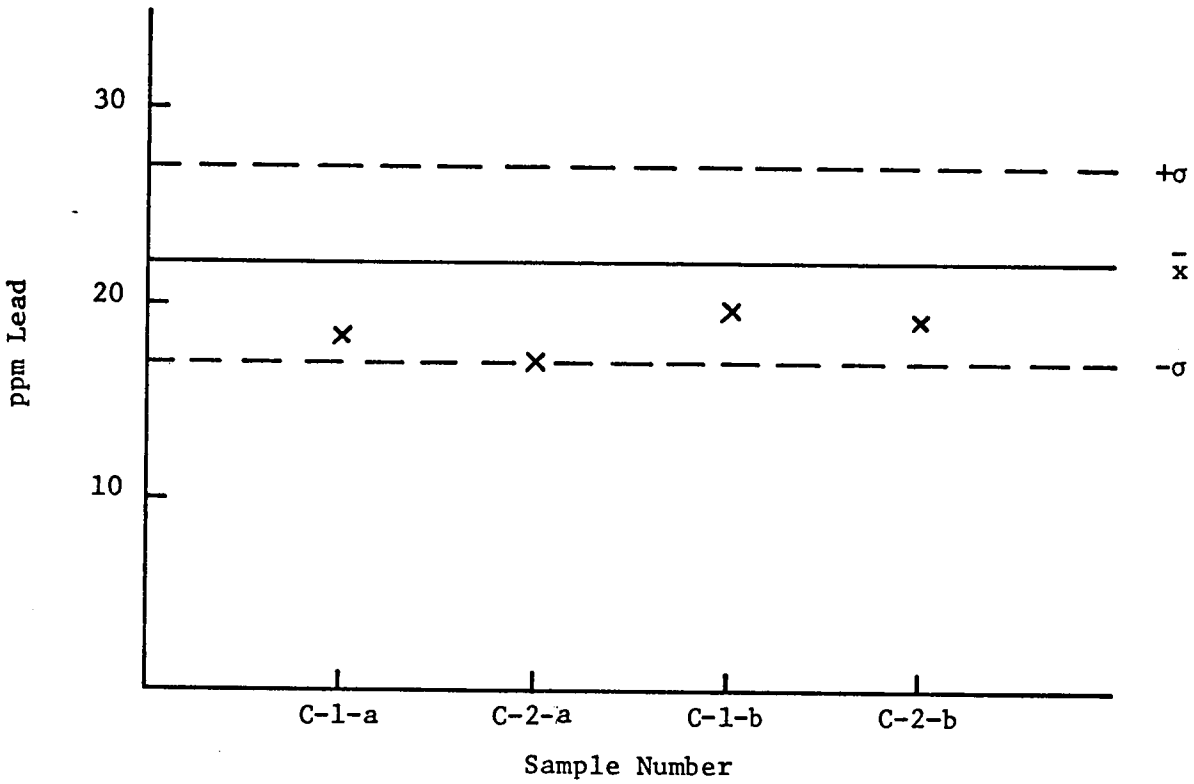

Figure 21. Lead Quality Control Chart - South Texas Baseline Sediments.

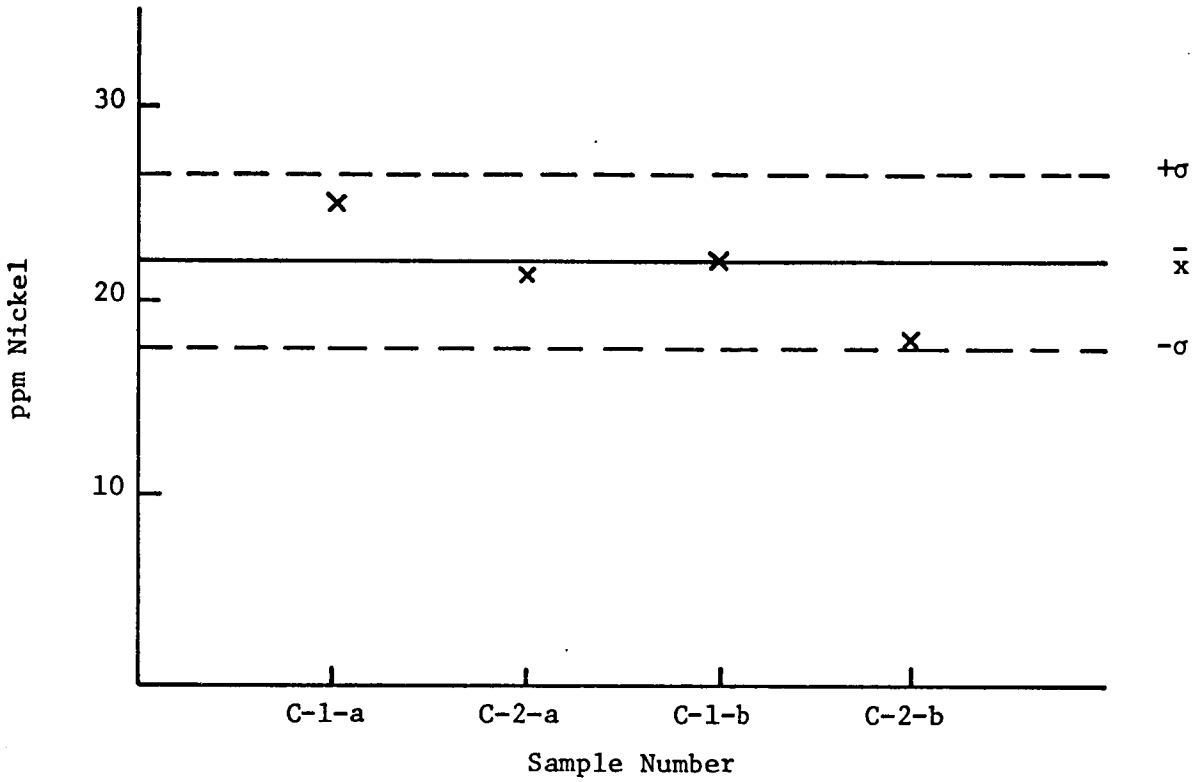

Figure 22. Nickel Quality Control Chart - South Texas Baseline Sediments.

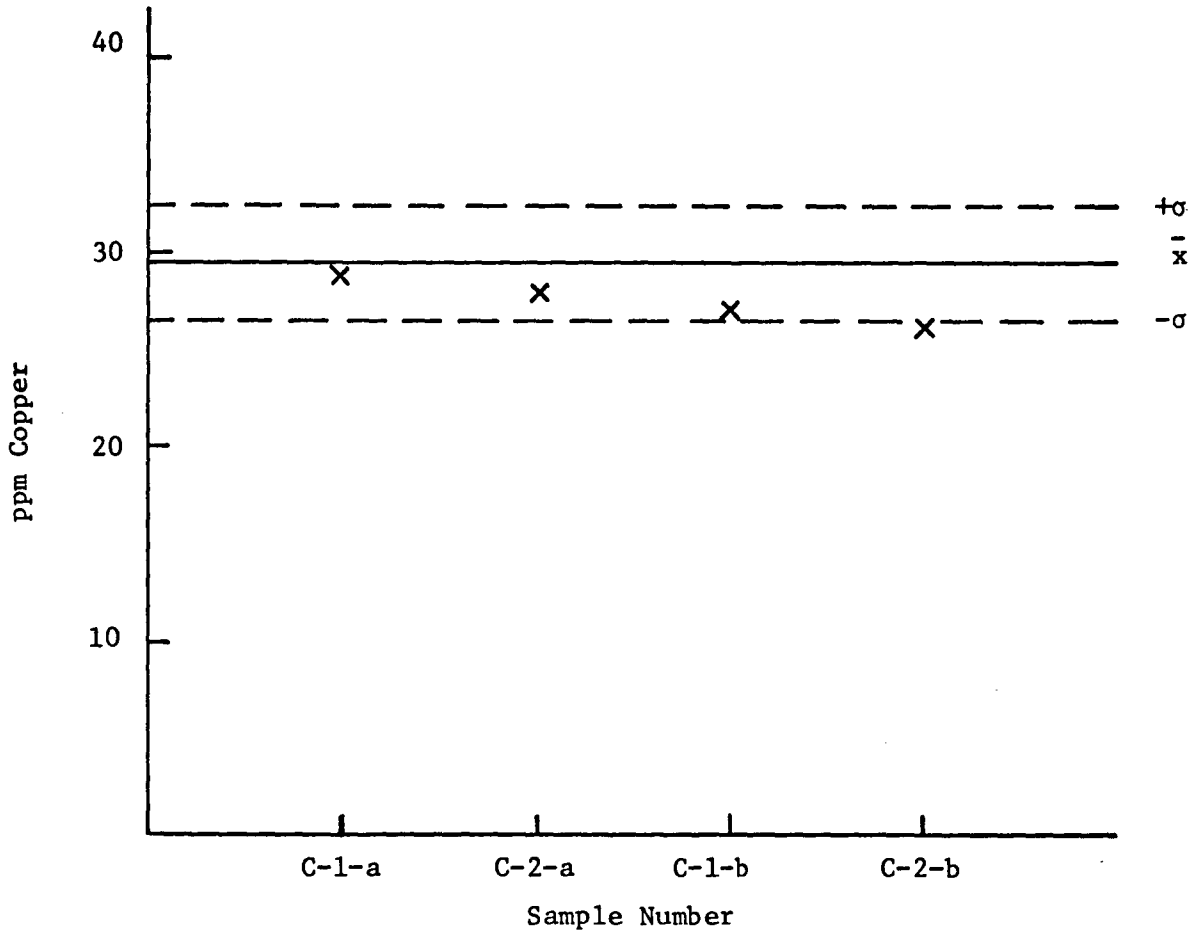

Figure 23. Copper Quality Control Chart - South Texas Baseline Sediments.

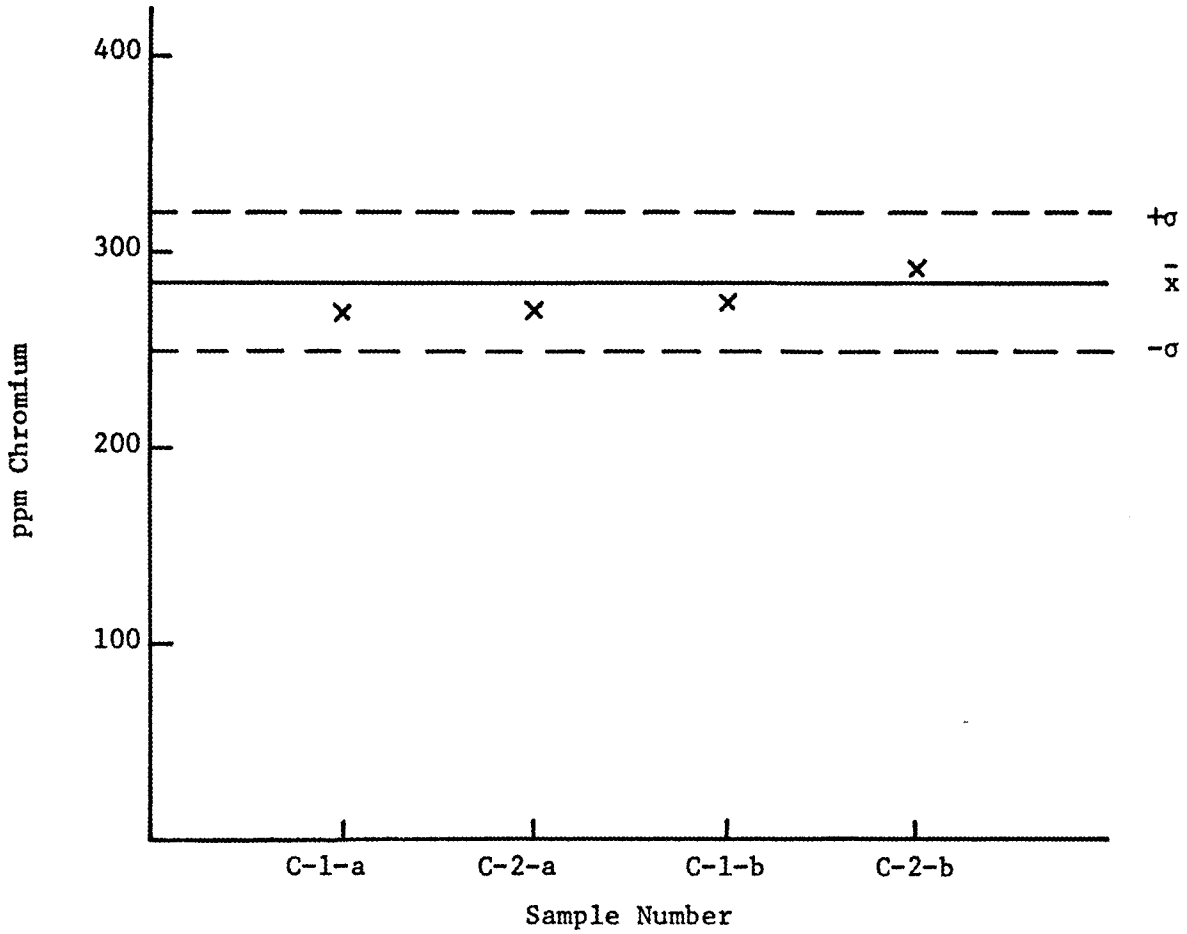

Figure 24. Chromium Quality Control Chart - South Texas Baseline Sediments.

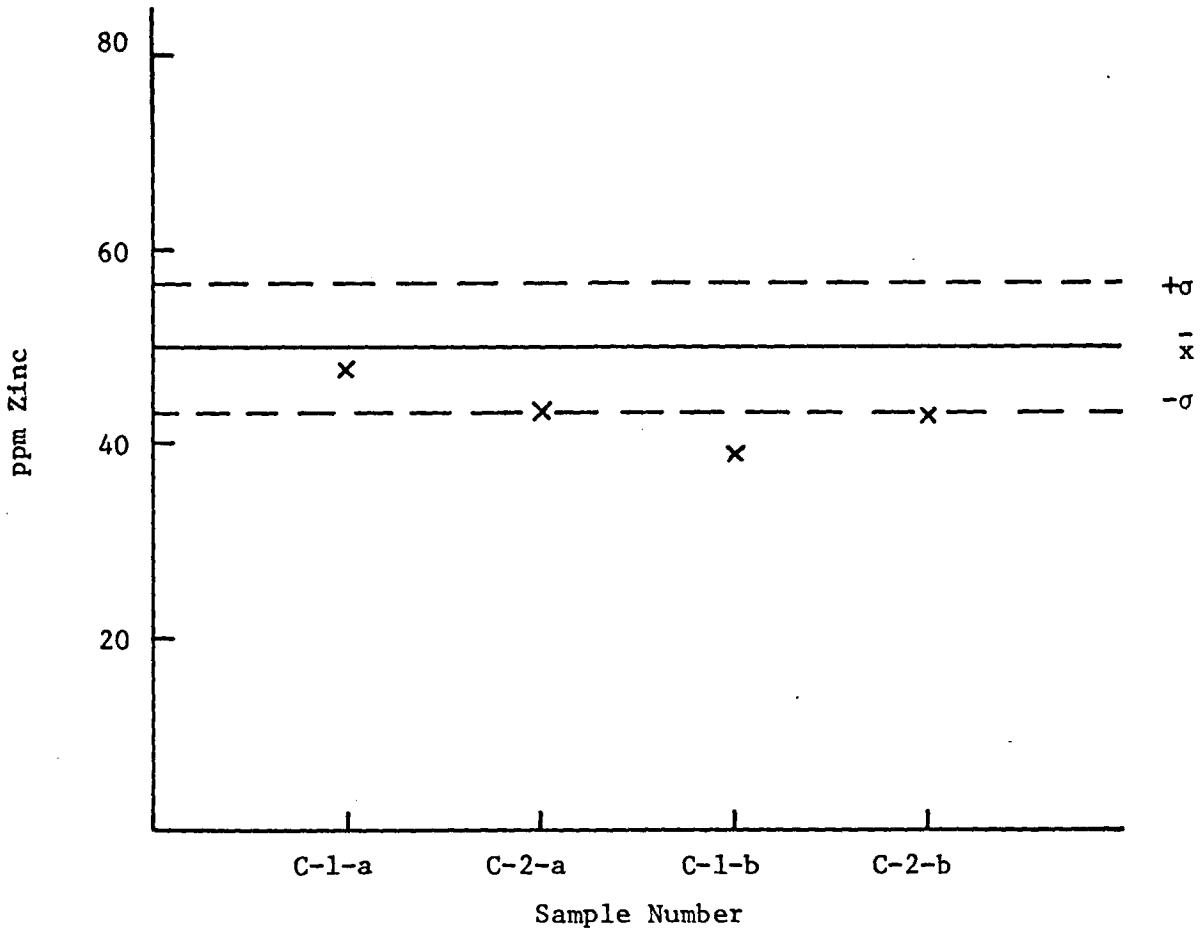

Figure 25. Zinc Quality Control Chart - South Texas Baseline Sediments.

Sample No.	Set No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Zn	Fe
98a-1	1	178	128	<0.04	52.7	63.3	142	40.4	10.6	a
98a-2	2	161	119	<0.04	47.8	62.0	174	37.7	11.8	3760
98a-3	3	152	102	<0.04	51.9	56.9	173	32.5	9.9	2500
98a-4	4	176	134	<0.04	48.7	60.9	146	40.0	8.8	3100
98a-5	5	a	a	<0.04	40.8	64.2	135	35.6	11.5	2030
Average		167	121	<0.04	50.5	60.8	159	37.2	10.5	3120
Standard Deviation		12	14	0	2.1	2.8	17	3.3	1.2	630
Certified Value		269	b	b	b	b	b	200	b	9400

[a]Insufficient sample remained for analysis

[b]Not certified

Table 91. Trace Metal Data for NBS SRM 98a (Plastic Clay) for the Partial Digestion Technique.

Sample No.	Set No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Zn	Fe
98a-1	1	255	403	<0.04	63.9	121	196	219	a	3940
98a-2	2	222	401	<0.04	64.9	125	197	216	27.4	4090
98a-3	3	246	385	<0.04	60.4	113	197	214	25.2	5210
98a-4	4	233	393	<0.04	62.6	121	189	213	26.5	4600
98a-5	5	222	396	<0.04	60.5	119	194	214	19.5	5160
Average		236	396	<0.04	62.5	120	195	215	24.7	4600
Standard Deviation		15	7	0	2.0	4.4	3.4	2	3.6	588
Certified Value		269	b	b	b	b	b	200	b	9400

[a]Insufficient sample remained for analysis

[b]Not certified

Table 92. Trace Metal Data for NBS SRM 98a (Plastic Clay) for the Total Digestion Technique.

H. Sediment Sample Tube Blanks

Six sediment sample tube blanks were analyzed for trace metal content to determine if contamination could be present. There are no widely accepted techniques for performing such an analysis. The method used was a hot aqua regia rince (25 ml) of the tube with stoppers. The volume was reduced to approximately 5 ml and diluted to 25.0 ml with distilled water. The analyses for trace metals was performed by flameless AAS for all trace metals of interest. The iron and zinc analyses were performed for all six sediment tubes. The data obtained is presented in Table 93 in units of micrograms of metal per tube. The average and standard deviation is presented except for the cases where selected samples are below the minimum detection limit cited in the table. The levels of iron and zinc determined were in excess of the other trace metals. These metals are also in environmental samples in large quantities.

	Concentration (µg/tube)								
Table No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Fe	Zn
1	<0.5	<0.2	<0.05	<0.1	<0.2	<0.3	0.1	6	29
2	<0.5	<0.2	<0.05	<0.1	0.5	0.9	0.1	13	11
3	<0.5	<0.2	<0.05	<0.1	0.8	0.9	<0.1	4	20
4	<0.5	<0.2	<0.05	0.3	<0.2	<0.3	<0.1	3	10
5	<0.5	<0.2	<0.05	1.3	2.4	<0.3	<0.1	4	18
6	<0.5	<0.2	<0.05	0.6	3.5	2.0	0.1	3	27
Average	<0.5	<0.2	<0.05	a	a	a	a	5	19
Standard Deviation	0	0	0	a	a	a	a	4	8

[a]Not applicable - one or more samples below detection limit

Table 93. Trace Metal Quality Control Data for Sediment Tube Analyses.

APPENDIX A

SAMPLE LOG SUMMARY

SAMPLE LOG SUMMARY

A. General

A total of two hundred ninety-five (295) environmental samples were delivered to Gulf South Research Institute for trace metal quality control analysis under BLM Contract No. 08850-CT5-49. GSRI's contract required the analysis of two hundred thirty-seven (237) of these samples. The specific samples to be analyzed from the 295 received were determined by the COAR for BLM, Dr. Ed Wood of the New Orleans OCS office. Each sample will be listed below in groups corresponding to those from the BLM sample inventory. The number of the cruise during which the sample was taken and the date of delivery to GSRI will be listed. The separation of groups below will be made according to sampling area rather than chronologically. Each sample delivery was reported in chronological order in Progress Reports I, II, III, IV, Special, and V submitted to BLM by GSRI.

B. MAFLA Monitoring

1. Zooplankton

Cruise No.	Delivery Date	Sample No.
12	10/8/75	1101
12	10/8/75	1204
12	10/8/75	1205
12	10/8/75	1207
12	10/8/75	1308
20	10/30/75	1101
20	10/30/75	1205

20	10/30/75	1207
20	10/30/75	1308
20	10/30/75	1413
28	3/15/76	1206
28	3/15/76	1207
28	3/15/76	1309
28	3/15/76	1310
28	3/15/76	1414

2. Sediment

Cruise No.	Delivery Date	Sample No.
14	8/8/75	2207J
14	8/8/75	2208J
14	8/8/75	2209J
14	8/8/75	2211J
14	8/8/75	2212J
14	8/8/75	2213J
14	8/8/75	2316J
14	8/8/75	2317J
10	10/8/75	2101
10	10/8/75	2426
10	10/8/75	2645
29	2/19/76	2102
29	2/19/76	2103
29	2/19/76	2105
29	2/19/76	2208K
29	2/19/76	2209K
29	3/15/76	2419R
29	3/15/76	2530R
29	3/15/76	2535R
29	2/19/76	2641
29	2/19/76	2642

3. Epifauna

Sample numbers placed in parentheses in the following logs for epifauna refer to samples deleted by BLM due to the excess of samples delivered to GSRI.

a. First Period

Cruise No.	Delivery Date	Sample No.
11	10/8/75	047-A-16
11	10/8/75	(047-A-18)
11	10/8/75	(62-A-7)
11	10/8/75	64-A-2
11	10/8/75	(146-B-12)
11	10/8/75	146-B-19
11	10/8/75	(147-A-2)
11	10/8/75	(147-A-5)
11	10/8/75	151-A-14
11	10/8/75	247-A-8
11	10/8/75	251-A-5
13	8/8/75	V-A A-6
13	8/8/75	VI-A A-2
13	8/8/75	(I-A A/B-3)
15	8/8/75	I-B B-2
15	8/8/75	(I-B C-6)
15	8/8/75	I-B C-8
15	8/8/75	II-A C-6
15	8/8/75	II-B C-2
15	8/8/75	(III-A C-4)
15	8/8/75	IV-A A/B-3

b. Second Period

Cruise No.	Delivery Date	Sample No.
19	10/8/75	047-A-16
19	10/8/75	(047-A-17)
19	10/8/75	64-A-13
19	10/8/75	146-B-3
19	10/8/75	(146-B-5)
19	10/8/75	147-A-5
19	10/8/75	(147-A-7)
19	10/8/75	151-A-6
19	10/8/75	(151-A-8)
19	10/8/75	247-A-13
19	10/8/75	247-A-15
19	10/8/75	251-A-12
19	10/8/75	(251-A-14)
22	10/30/75	(I-B A-8)
22	10/30/75	II-A A-5

22	10/30/75	III-B C-6
22	10/30/75	V-A A-4
22	10/30/75	VI-A C-6
22	10/30/75	VI-B A-8

c. Third Period

Cruise No.	Delivery Date	Sample No.
30	2/19/76	(V-A A-8)
30	2/19/76	VI-A C-2
30	2/19/76	(VI-B C-10)
30	2/19/76	VI-C C-4
32	3/15/76	062-A-10
32	3/15/76	064-A-4
32	3/15/76	(147-A-12)
32	3/15/76	(147-A-13)
32	3/15/76	151-A-20
32	3/15/76	(151-A-21)
32	3/15/76	247-A-6
32	3/15/76	(247-A-15)
32	3/15/76	247-A-17
33	3/15/76	(I-A C-10)
33	3/15/76	I-B C-7
33	3/15/76	II-A A-15
33	3/15/76	(II-A A-16)
33	3/15/76	(III-B A-2)
33	3/15/76	IV-B C-5
33	3/15/76	IV-B C-6
34	3/15/76	047-A-2
34	3/15/76	(047-A-15)
34	3/15/76	(146-A-4)
34	3/15/76	(146-A-6)
34	3/15/76	251-A-4
34	3/15/76	(251-A-19)
34	3/15/76	(251-A-24)

4. Paint Chips

Cruise No.	Delivery Date	Sample No.
10	8/8/75	PCM-1
11	8/8/75	PCM-2
12	8/8/75	PCM-3
14	8/8/75	PCM-4
15	8/8/75	PCM-5
19	10/8/75	PCM-6
20	10/30/75	PCM-7
22	10/30/75	PCM-8
28	3/15/76	PCM-11
29	3/15/76	PCM-12
30	3/15/76	PCM-13
32	3/15/76	PCM-14
33	3/15/76	PCM-15
34	3/15/76	PCM-16

C. MAFLA Rig Monitoring

1. Sediment

Cruise No.	Delivery Date	Sample No.
24	12/8/75	510601 TSQC2
24	12/8/75	510701 TSQC2
24	12/8/75	510801 TSQC2
24	12/8/75	551301 TSQC2
24	12/8/75	551401 TSQC2
24	12/8/75	551701 TSQC2
24	12/8/75	591901 TSQC2
24	12/8/75	592301 TSQC2
24	12/8/75	592501 TSQC2
27	2/19/76	510501 TSQC2
27	2/19/76	510701 TSQC3
27	2/19/76	510901 TSQC3
27	2/19/76	551001 TSQC2
27	2/19/76	551301 TSQC3
27	2/19/76	551401 TSQC3
27	2/19/76	592101 TSQC2
27	2/19/76	592301 TSQC3
36	4/8/76	510501 TSQC3
36	4/8/76	510701 TSQC4
36	4/8/76	510901 TSQC4

36	4/8/76	551001 TSQC3
36	4/8/76	551301 TSQC4
36	4/8/76	551401 TSQC4
36	4/8/76	592101 TSQC3
36	4/8/76	592301 TSQC4

2. Epifauna

a. Cruise 24

Delivery Date	Sample No.
12/8/75	4102 TEQC1
12/8/75	4102 TEQC2
12/8/75	4510 TEQC1
12/8/75	4510 TEQC2
12/8/75	4511 TEQC1
12/8/75	4511 TEQC2
12/8/75	4513 TEQC1
12/8/75	4515 TEQC1
12/8/75	4515 TEQC2
12/8/75	4516 TEQC1
12/8/75	4516 TEQC2
12/8/75	4517 TEQC1
12/8/75	4517 TEQC2
12/8/75	(4918 TEQC1)
12/8/75	4918 TEQC2
12/8/75	(4919 TEQC1)
12/8/75	(4919 TEQC2)
12/8/75	(4920 TEQC1)
12/8/75	(4920 TEQC2)
12/8/72	4921 TEQC1
12/8/75	4921 TEQC2
12/8/75	4922 TEQC1
12/8/75	4922 TEQC2
12/8/75	4923 TEQC1
12/8/75	4923 TEQC2
12/8/75	4924 TEQC1
12/8/75	4924 TEQC2
12/8/75	4925 TEQC1
12/8/75	4925 TEQC2

b. Cruise 27

Delivery Date	Sample No.
2/19/76	4102 TEQC3
2/19/76	4102 TEQC4
2/19/76	4106 TEQC1
2/19/76	4106 TEQC2
2/19/76	4510 TEQC3
2/19/76	4510 TEQC4
2/19/76	4513 TEQC2
2/19/76	4513 TEQC3
2/19/76	4514 TEQC1
2/19/76	4514 TEQC2
2/19/76	4919 TEQC3
2/19/76	4919 TEQC4
2/19/76	4921 TEQC4
2/19/76	4923 TEQC3
2/19/76	4923 TEQC4
2/19/76	4929 TEQC3

c. Cruise 36

Delivery Date	Sample No.
4/8/76	4102 TEQC5
4/8/76	4102 TEQC6
4/8/76	4106 TEQC5
4/8/76	4106 TEQC6
4/8/76	4510 TEQC5
4/8/76	4510 TEQC6
4/8/76	4513 TEQC5
4/8/76	4513 TEQC6
4/8/76	4514 TEQC3
4/8/76	4514 TEQC4
4/8/76	4919 TEQC5
4/8/76	4919 TEQC6
4/8/76	4921 TEQC5
4/8/76	4921 TEQC6
4/8/76	4923 TEQC5
4/8/76	4923 TEQC6

3. Paint Chips

Cruise No.	Delivery Date	Sample No.
24	12/8/76	PCM-9
27	3/15/76	PCM-10
36	4/8/76	PCM-17

D. South Texas Baseline

1. Zooplankton

Cruise No.		Delivery Date	Sample No.
W 74-75-II & III	02	3/25/75	AHZ-ZPL-QC-tm
W 74-75-II & III	02	3/25/75	AIZ-ZPL-QC-tm
W 74-75-II & III	02	3/25/75	AOG-ZPL-QC-tm
W 74-75-II & III	02	3/25/75	APM-ZPL-QC-tm
W 74-75-II & III	02	3/25/75	ARJ-ZPL-QC-tm
W 74-75-IV	05	3/25/75	BBA-ZPL-QC-tm
Sp 75-I	07	6/20/75	CDJ-ZPL-QC-tm
Sp 75-I	07	6/20/75	CGN-ZPL-QC-tm
Sp 75-II & III	08	6/20/75	CMX-ZPL-QC-tm
Sp 75-II & III	11	6/20/75	CTG-ZPL-QC-tm
Sp 75-IV	09	6/20/75	DJI-ZPL-QC-tm
Sp 75-I	12	9/23/75	EDJ-ZPL-QC-tm
Sp 75-I	12	9/23/75	EGN-ZPL-QC-tm
Su 75-II & III	13	9/23/75	EMX-ZPL-QC-tm
Su 75-II & III	13	9/23/75	ETG-ZPL-QC-tm
Su 75-IV	14	9/23/75	FJS-ZPL-QC-tm

2. Epifauna

Cruise No.		Delivery Date	Sample No.
W 74-75-II & III	02	3/25/75	AIN-EPI-QC-tm
W 74-75-II & III	02	3/25/75	AJG-EPI-QC-tm
W 74-75-II & III	02	3/25/75	ALJ-EPI-QC-tm
W 74-75-II & III	02	3/25/75	AOM-EPI-QC-tm
W 74-75-II & III	02	3/25/75	API-EPI-QC-tm
W 74-75-II & III	02	3/25/75	ASK-EPI-QC-tm
W 74-75-II & III	02	3/25/75	AVP-EPI-QC-tm
W 74-75-IV	05	3/25/75	BDO-EPI-QC-tm
W 74-75-IV	05	3/25/75	BDQ-EPI-QC-tm
W 74-75-IV	05	3/25/75	BGO-EPI-QC-tm

Sp 75-I	07	6/20/75	CBF-EPI-QC-tm
Sp 75-I	07	6/20/75	CEF-EPI-QC-tm
Sp 75 II & III	11	6/20/75	CGT-EPI-QC-tm
Sp 75-II & III	08	6/20/75	CJZ-EPI-QC-tm
Sp 75-II & III	08	6/20/75	CND-EPI-QC-tm
Sp 75-II & III	11	6/20/75	CQE-EPI-QC-tm
Sp 75-II & III	11	6/20/75	CTM-EPI-QC-tm
Sp 75-II & III	11	6/20/75	DAM-EPI-QC-tm
Sp 75-II & III	11	6/20/75	DGL-EPI-QC-tm
Sp 75-IV	09	6/20/75	DJO-EPI-QC-tm
Su 75-I	12	9/23/75	EBF-EPI-QC-tm
Su 75-I	12	9/23/75	EEF-EPI-QC-tm
Su 75-I	12	9/23/75	EGT-EPI-QC-tm
Su 75-II & III	13	9/23/75	EJZ-EPI-QC-tm
Su 75-II & III	13	9/23/75	END-EPI-QC-tm
Su 75-II & III	13	9/23/75	EQE-EPI-QC-tm
Su 75-II & III	13	9/23/75	ETM-EPI-QC-tm
Su 75-II & III	13	9/23/75	FAM-EPI-QC-tm
Su 75-IV	14	9/23/75	FGT-EPI-QC-tm
Su 75-IV	14	9/23/75	FJY-EPI-QC-tm

3. Paint Chips

Cruise No.		Delivery Date	Sample No.
W 74-75-I	01	3/25/75	QC-3/I
Sp 75-II & III	11	6/20/75	CK-I.

4. Suspended Particulate Matter

Cruise No.	Delivery Date	Sample No.
B	2/26/75	155T
B	2/26/75	155M
B	2/26/75	155B
B	2/26/75	156T
B	2/26/75	156T(M)
B	2/26/75	156B
B	2/26/75	157T
B	2/26/75	243T
B	2/26/75	243M
B	2/26/75	243B

5. Sediments

Cruise No.	Delivery Date	Sample No.
A	2/26/75	8
A	2/26/75	24
A	2/26/75	32
A	2/26/75	42
A	2/26/75	88
A	2/26/75	110
B	2/26/75	137
B	2/26/75	146
B	2/26/75	149
B	2/26/75	155
B	2/26/75	156
B	2/26/75	157
B	2/26/75	160
B	2/26/75	164
B	2/26/75	165
B	2/26/75	176
B	2/26/75	185
B	2/26/75	226
B	2/26/75	230
C	2/26/75	235
C	2/26/75	236
C	2/26/75	238
B	2/26/75	241
C	2/26/75	243
B	2/26/75	245
C	2/26/75	259
C	2/26/75	265
C	2/26/75	269
C	2/26/75	273

APPENDIX B

PAINT CHIP SAMPLES

PAINT CHIP SAMPLES

A total of nineteen paint chip samples were received which were taken from the sampling vessels for purposes of monitoring contamination. Fourteen of the samples were from MAFLA monitoring operations for BLM cruises 10, 11, 12, 14, 15, 19, 20, 22, 28, 29, 30, 32, 33, and 34. Three samples were from the MAFLA Rig Monitoring for BLM Cruises 24, 27, and 36. Two samples were obtained from the South Texas study identified as QC-3/I and CK-I.

The procedure employed for the determination of trace metals in the paint chips samples is as follows[1]:

1. A one hundred milligram sample is ashed at 500°C in a muffle furnace.
2. To this residue is added ten milliliters of concentrated ULTREX nitric acid.
3. The solution is heated gently until it has evaporated to half of its original volume.
4. The solution is cooled and clarified by centrifugation and transferred to a 25 ml volumetric flask and diluted to volume with distilled deionized water.
5. The solution is ready for analysis for trace metal content by flame and flameless atomic absorption spectrophotometry.

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[1]Determination of Metals in Paints and Vinyl Additives, Appl. Spec., (1971), 25(3): p. 313.

The analysis for lead, iron, chromium and copper was easily accomplished by usual flame AAS. The content of lead, iron, and chromium was so high that the data is presented in units of percent for these trace metals. The majority of the samples required the flameless graphite furnace AAS technique although some samples could be read in the flame mode of operation. Barium, nickel, cadmium, and vanadium were analyzed by flameless AAS and the data reported in units of parts-per-million. The data for the MAFLA samples is present in Table B-1 and the data for South Texas samples is shown in Table B-2.

The paint chip samples were very heterogeneous. Duplicates were not analyzed since no meaningful information could be obtained from such a determination. A sufficient quantity of each sample was received to follow the procedure given; however, some samples were exhausted with the one analysis.

BLM Cruise No.	BLM Sample No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Fe
10	PCM-1	1310	4.9	<0.2	0.21	6.3	99.9	0.03	0.57
11	PCM-2	274	7.2	33.9	0.25	158	57.3	0.12	1.26
12	PCM-3	48.8	10.6	<0.2	0.63	19.3	91.6	0.18	2.55
14	PCM-4	21.4	163	1.4	1.31	79.3	112	0.015	34.4
15	PCM-5	447	12.1	15.3	0.21	16.2	31.5	0.018	0.31
19	PCM-6	32.6	3.6	<0.2	5.55	21.9	34.7	0.008	0.88
20	PCM-7	67.4	11.0	<0.2	0.68	16.4	117	0.29	3.14
22	PCM-8	141	7.2	0.89	13.0	44.2	3763	0.017	3.54
24	PCM-9	1120	6.9	0.39	2.49	41.9	74.5	0.11	0.64
27	PCM-10	365	17.2	281	0.64	21.4	275	0.22	3.58
28	PCM-11	50.1	8.4	1.7	0.45	42.3	1820	0.56	0.94
29	PCM-12	84.0	5.9	0.52	10.6	29.9	196	0.006	2.32
30	PCM-13	109	11.0	0.34	6.12	42.2	159	0.023	3.93
32	PCM-14	59.2	18.1	304	0.63	23.6	65.2	0.14	2.96
33	PCM-15	294	43.1	<0.2	0.045	104	76.0	0.16	16.2
34	PCM-16	82.2	124	2.4	7.37	20.7	134	0.10	0.39
36	PCM-17	129	17.8	<0.2	0.62	59.7	110	1.00	5.86

Table B-1. Trace Metal Quality Control Data for Paint Chip Samples - MAFLA Monitoring and MAFLA Rig Monitoring.

Concentration Units: ppm (dry weight basis)--Ba, V, Cd, Ni, Cu
% (dry weight basis)--Pb, Cr, Fe.

Cruise No.	BLM Sample No.	Ba	V	Cd	Pb	Ni	Cu	Cr	Fe
W 74-75 I 01	QC-3/I	376	12.4	0.59	9.62	37.6	52.2	1.31	0.32
Sp 75-II & III 11	CK-I	1240	13.2	<0.2	8.21	24.4	2460	3.30	0.080

Table B-2. Trace Metal Quality Control Data for Paint Chip Samples--South Texas Baseline.

Concentration Units: ppm (dry weight basis)--Ba, V, Cd, Ni, Cu
% (dry weight basis)--Pb, Cr, Fe.

The Department of the Interior Mission

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering sound use of our land and water resources; protecting our fish, wildlife, and biological diversity; preserving the environmental and cultural values of our national parks and historical places; and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to ensure that their development is in the best interests of all our people by encouraging stewardship and citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.

The Minerals Management Service Mission

As a bureau of the Department of the Interior, the Minerals Management Service's (MMS) primary responsibilities are to manage the mineral resources located on the Nation's Outer Continental Shelf (OCS), collect revenue from the Federal OCS and onshore Federal and Indian lands, and distribute those revenues.

Moreover, in working to meet its responsibilities, the **Offshore Minerals Management Program** administers the OCS competitive leasing program and oversees the safe and environmentally sound exploration and production of our Nation's offshore natural gas, oil and other mineral resources. The MMS **Minerals Revenue Management** meets its responsibilities by ensuring the efficient, timely and accurate collection and disbursement of revenue from mineral leasing and production due to Indian tribes and allottees, States and the U.S. Treasury.

The MMS strives to fulfill its responsibilities through the general guiding principles of: (1) being responsive to the public's concerns and interests by maintaining a dialogue with all potentially affected parties and (2) carrying out its programs with an emphasis on working to enhance the quality of life for all Americans by lending MMS assistance and expertise to economic development and environmental protection.