

HEAVY METAL ANALYSES OF BOTTOM SEDIMENT ON THE WEST FLORIDA SHELF

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INTRODUCTION

In continuation of the baseline evaluation of the Mississippi-Alabama-Florida continental shelf sponsored by the Bureau of Land Management, SUSIO has sampled stations along the six transects depicted in Figures 1 and 2. As seen in Figure 2, four of the transects pass through the five areas blocked off during the original baseline survey conducted in 1974-75. Within the scope of this baseline continuation study, we have received and analyzed surface sediment samples from 42 of the 45 stations. 21 of these stations were sampled on two different occasions resulting in a total of 63 samples (station data is contained in Appendix I).

This report presents the results of our analyses of these 63 samples for barium, cadmium, chromium, copper, iron, lead, nickel and vanadium.

METHODS

Samples were prepared for analysis by initially drying the entire aliquot (~50 g) of wet sediment at 105°C and then reducing it to a fine powder with a porcelain-lined Spex mixer-mill. Cadmium, chromium, copper, iron, lead and nickel were determined by atomic absorption spectrophotometry after dissolution of the sediment. Barium and vanadium were determined by instrumental neutron activation analysis of the solid sample.

For total dissolution, approximately two grams of finely powdered sediment were heated in a muffle furnace at 350°C for eight hours to ash the organic matter present. After heating, the samples were transferred

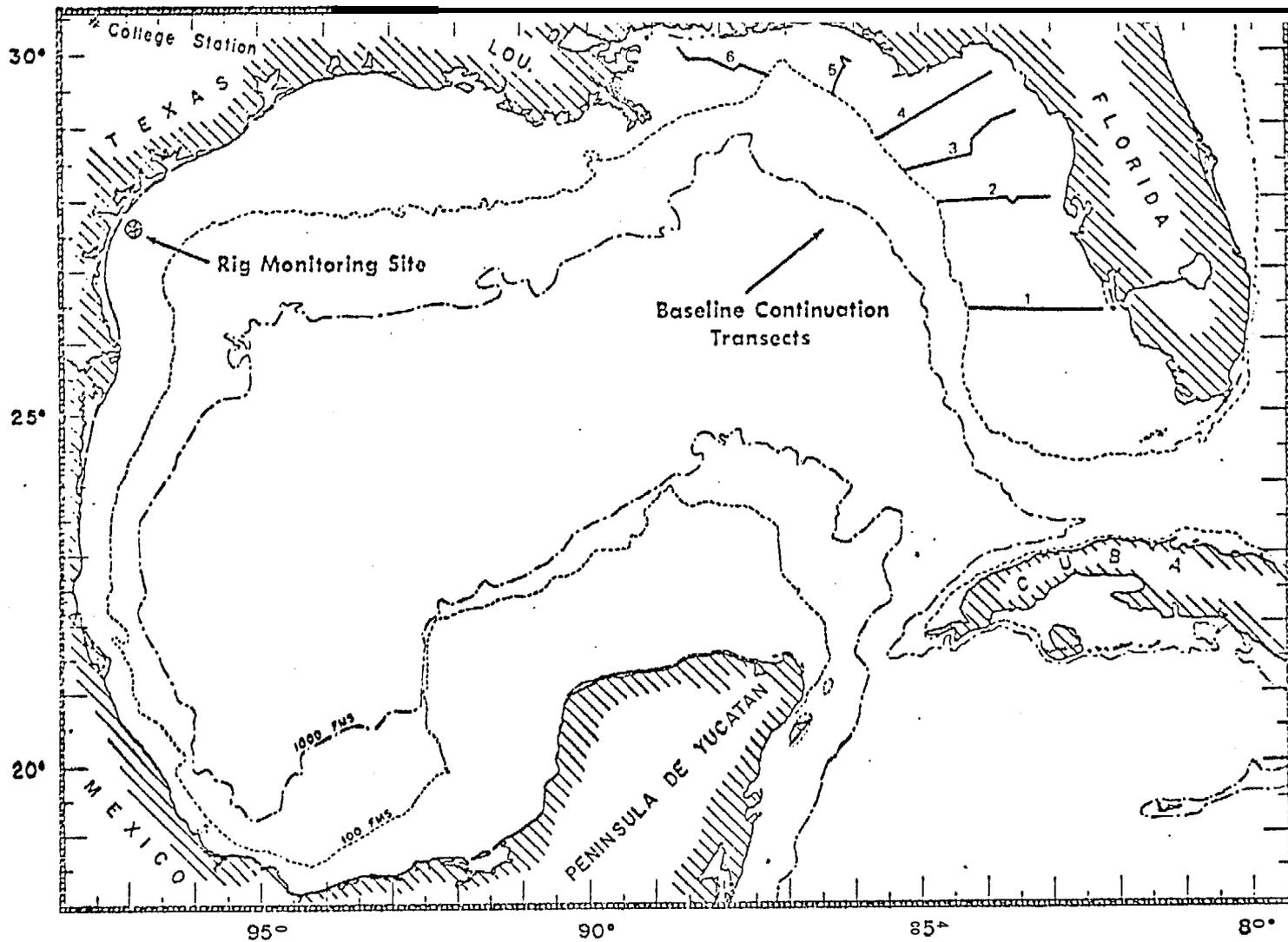
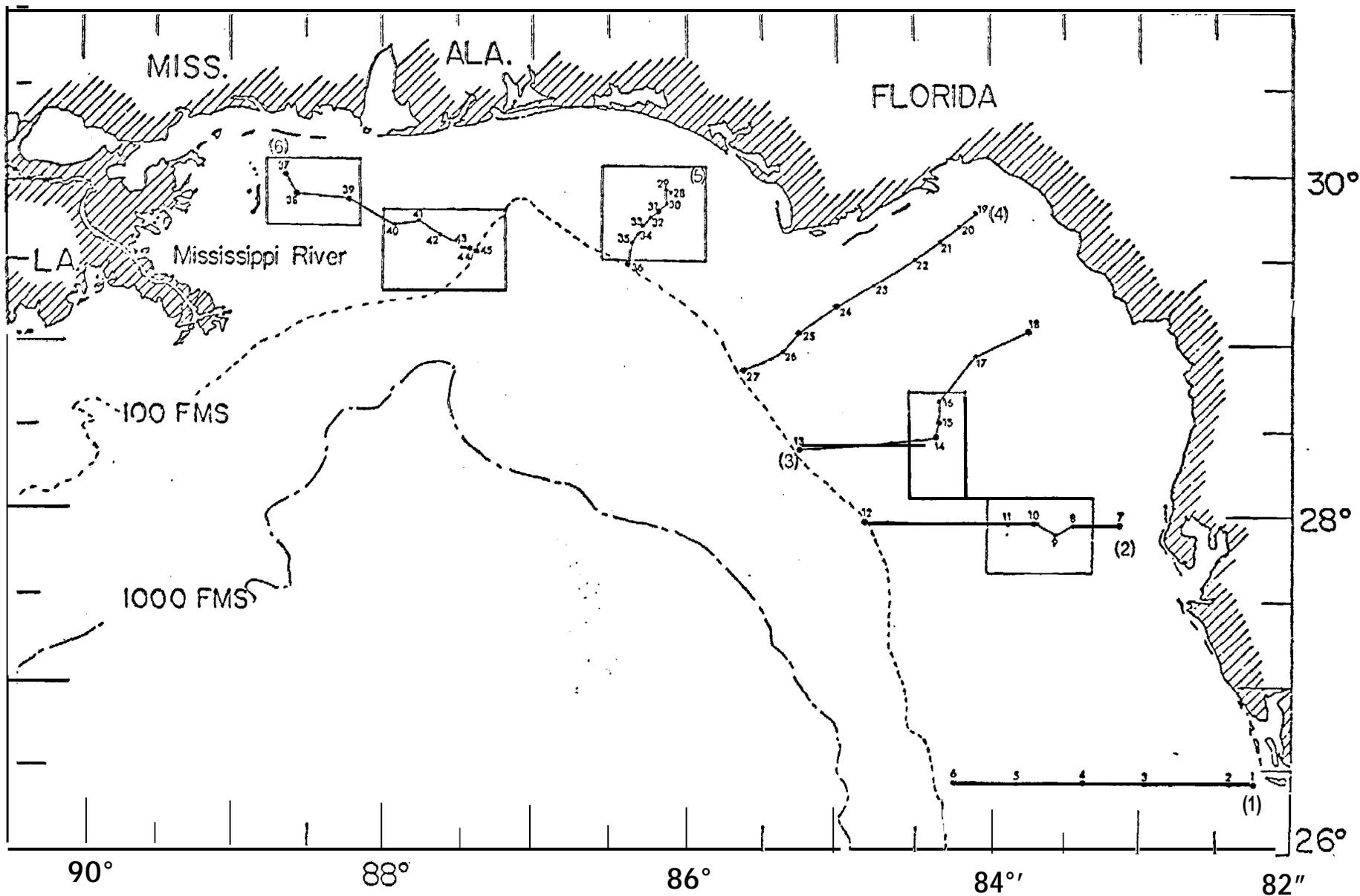


Fig. 1. Sampling areas for the MAFLA Rig Monitoring and Baseline Continuation Studies.



MAFLA Baseline Continuation sampling stations. Numbers in () indicate transect. Blocked sections indicate quadrants from MAFLA Baseline study. Large circles (●) indicate stations sampled for sediment trace metals during both periods (21); small circles (*) indicate those sampled only during first period (45).

to teflon beakers and the CaCO_3 was reacted by dropwise addition of 1 N HNO_3 , and the resulting solution removed. Next, five milliliters of HF (48%) and two milliliters of HClO_4 were added and the acid-sediment mixture was refluxed for approximately two hours before heating to near dryness. A second acid mixture (three milliliters HF, two milliliters HClO_4) was then added and again heated to near dryness. The residue was redissolved in two milliliters of 16 N HNO_3 , recombined with the CaCO_3 solution, and diluted to .25 ml with deionized water.

Cadmium, chromium, copper, lead and nickel were determined by direct aspiration into a Jarrell-Ash model 810, two channel atomic absorption spectrophotometer. Iron was determined after appropriate dilution by the same technique. Background absorbance, due to molecular absorption was monitored, where necessary, by simultaneously measuring the absorbance of a non-resonance line and the analytical line of the element of interest. Cadmium and chromium concentrations were also checked by flameless atomic absorption techniques using a Perkin-Elmer 306 atomic absorption spectrophotometer equipped with an HGA-2100 graphite atomizer and a deuterium background corrector.

Instrumental neutron activation analysis was used for vanadium determination. Initial preparation for neutron activation involved accurately weighing about 0.5 g of sediment, which had been dried at 105°C , into a small one gram capacity polyethylene vial. The vial was heat-sealed to prevent any loss of sample during the analysis. The marked, encapsulated samples were irradiated by the one MW Triga reactor at the Texas A&M University Nuclear Science Center. Each sample was irradiated separately for two minutes. This process was facilitated by a pneumatic

transport system which can rapidly transfer samples in and out of the reactor core. The sample vial was placed in a secondary polyethylene vial, together with an aluminum flux monitor, and transported to the core for the two minute time period.

After return of the sample and a one minute delay, the aluminum flux monitor was counted by a multichanneled pulse height analyzer. After an appropriate delay period (usually three to five minutes, so that the dead time was <30%) the irradiated sediment sample was placed on an Ortec Ge(Li) detector and counted using a separate GEOS Quanta 4096 channel multichannel pulse height analyzer. The analyzer was set for a gain of 1.0 keV per channel. The vanadium peak for the ^{52}V analyzed is at 1434 keV. After a five minute counting period, the spectrum was stored on magnetic tape.

Data reduction was done using the program HEVESY. The program calculates peak intensities and converts these to concentration by comparison with appropriate USGS standard rocks (DTS-1 and AGV-1). Corrections are made for varying delay times, dead times, and neutron fluxes.

Barium analysis was also done by activation analysis. In the barium procedure the sediments were irradiated for a 14 hr period in aluminum Swagelok tubes along with standards and blanks which were set in a rotisserie in the reactor core. After irradiation the samples were allowed to "cool" for two weeks. The irradiated samples were counted for two hours using an Ortec Ge(Li) detector and a Canberra model 8700, 1024 channel multichannel pulse height analyzer. The peak of interest was that produced by xenon X-rays at 29 keV; the gain was set so that the

peak was recorded in channel 1.60. After the two hour counting period, the spectrum was stored on magnetic tape and data reduction performed by HEVESY using the USGS standard rock W-1 as a basis for sample concentration calculation.

USGS standard rocks were analyzed to obtain some idea of the accuracy of our analyses. Our agreement for replicate analyses is, overall, quite good with our results being consistently within 10% of the published values. The precision of the metal analyses were considerably lower for sediments with high metal content than for sediment with low metal content. Quadruplicate dissolutions and analyses were made on separate sediment aliquots for five of the study samples. The selected sediments are representative of the predominance of low metal-bearing samples received. Precision were calculated by dividing standard deviation by the mean and are as follows: Cd, 35%; Cr, 20%; Cu, 12%; Fe, 9%; Pb, 15%; Ni, 11%; and V, 25%.

RESULTS AND DISCUSSION

Sediment metal concentrations for the 63 samples analyzed during the baseline continuation study are listed in Table 1. Wide variations in the % Fe (Figure 3), % CaCO₃ (Figure 4) and % fine-grained material (Figure 5) are observed not only for the overall MAFLA area but even within each transect. Trace metal concentrations show a similar variability, no doubt primarily in response to the changes in both chemistry and mineralogy implied by the grain size, CaCO₃ and Fe variations. Past experience has shown that high metal concentrations are found with fine-grained material, organic matter and Fe and Mn hydrous oxides, whereas lower concentrations

Table 1. Surface Sediment Trace Metal Concentrations, MAFLA Baseline
Continuation Study. (See Figure 2 and Appendix I for Station Location).

Station Number	Sample Period	Ba (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (%)	Pb (ppm)	Ni (ppm)	V (ppm)	CaCO ₃ (%)	Fines (%)	Water Depth (m)
2101	I	53±27	< .05	2	1	.13	6	5	9	47.8	8.6	11.0
	II		0	3.2	1.1	.13	3.7	1.5	24	42.4	13.9	11.3
2102	I	<30	< .05	2	1	.07	5	5	5	27.5	3.8	17.4
2103	I	<32	.06	9	1	.22	8	6	3	61.3	4.0	36.6
2104	I	<34	.10	4	2	.09	9	8	4	90.1	4.7	53.3
	II	<86	.13	5.1	1.7	.10	5.0	1.5	3	88.2	13.0	53*3
2105	I	<36	.10	6	3	.07	10	9	4	92.0	4.0	89.6
2106	I	<44	.10	8	4	.39	10	13	5	83.0	14.2	161.5
	II	<41	.20	7.8	2.9	.33	5.8	7.0	7	91.2	28.0	167.6
2207	I	<41	.10	3	1	.08	7	2	7	43.5	11*0	18.3
	II		.11	3.9	0.6	.08	2.0	1.1	-	37.6	10.5	19.2
2208	I	<73	< .05	6	1	.12	9	9	4	83.4	58.6	34.1
2209	I	<36	< .05	8	1	.13	10	5	6	83.6	42.4	29.3
2210	II	<79	.04	6.0	1.1	.11	5*9	1.3	5	90.1	37.8	37.2
2211	I	<34	.10	8	1	.20	10	8	5	93.2	11.9	42.1
2212	I	<53	.10	14	5	.81	11	14	13	88.0	43.4	186.5
	II	<97	.13	13*3	4.8	.678	5.3	7.9	11	86.8	47*7	189.6

Table 1. (continued)

Station Number	Sample Period	Ba (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (%)	Pb (ppm)	Ni (ppm)	v (ppm)	CaCO ₃ (%)	Fines (%)	Water Depth (m)
2313	I	< 58	.10	16	5	1.05	12	18	13	85.1	58.0	164.6
	II	< 102	0	13.8	3.6	.74	2.2	9.1	15	80.4	67.4	176.8
2314	II	< 89	.12	5.4	2.3	.17	8.1	5.2	6	63.6*	29.4*	29.0
2315	II	..	.13	0.7	1.0	.06	4.1	0.9	3	62.3	30.6	38.1
2316	I	< 34	.10	6	1	.13	9	8	6	70.6	8.4	37.2
2317	I	< 41	.10	6	1	.21	12	10	6	79.5	19.2	29.3
2318	I	< 65	<.05	1	1	.02	2	2	2	10.8	1.8	18.9
	II	< 47	0	2.4	0.5	.00	0.8	0.0	7	3.7	2.7	20.4
2419	I	< 30	<.05	1	1	.06	4	2	4	19.2	2.2	9.8
2420	I	< 32	.06	3	1	.26	7	8	5	46.9	2.5	14.6
2421	I	< 35	.07	3	1	.16	7	6	5	51.6	10.0	19.2
2422	I	< 35	.07	4	2	.25	6	9	9	43.8	9*3	24.1
2423	I	< 54	.95	5	2	1.67	11	9	27	72.5	14.5	29.6
2424	I	< 24	<.05	5	1	.08	2	2	3	9.0	4.0	28.3
	II	< 59	0	4.6	0.7	.10	2.0	1.4	7	7.8	7.2	32.6
2425	I	81±25	.05	3	1	.08	3	3		8.3	1.5	36.6
	II	< 49	.04	3.4	0.4	.05	2.2	1.2	10	14.5	4.0	35.7
2426	I	< 43	.09	5	2	.38	8	8	7	35.4	4.2	86.3

Table 1. (continued)

Station Number	Sample Period	Ba (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (%)	Pb (ppm)	Ni (ppm)	V (ppm)	CaCO ₃ (%)	Fines (%)	Water Depth (m)
2427	I	<67	.07	17	7	1.70	11	17	20	-	59.6	172.3
	II	<123	.08	14.9	6.4	1.29	9.5	12.4	24	70.3	64.8	175.0
2528	I	<35	.08	3	2	.31	7	7	12	58.7	5.2	37.2
	II	<35	.10	4	2	.61	8	8	9	71.9	2.0	37.5
2530	I	<35	.15	6	2	.44	8	8	9	74.7	1.4	40.2
2531	I	<39	.15	13	2	.60	9	11	8	84.7	2.6	44.5
	II	<80	.10	10.8	1.8	.52	6.1	9.2	8	88.3	2.2	44.8
2532	I	<42	-	10	2	.54	8	9	8	75.8	8.3	50.3
2533	I	<45	.15	10	2	.59	10	11	13	86.9	2.6	66.4
2534	I	<44	.10	11	1	.66	17	9	15	88.0	4.7	72.5
2535	I	<73	.98	26	5	.95	17	14	31	70.1	76.1	115.8
2536	I	<76	.70	23	8	1.34	15	20	45	-	79.7	180.4
	II	<138	.52	13.4	5.9	1.05	10.1	14.2	39	67.5	85.6	189.6
2637	I	321±76	.08	35	8	2.17	15	14	78	13.3	62.9	21.3
	II	-	.07	36.7	8.3	1.87	16.1	15.0	-	8.2	59.4	19.5
2638	I	288±72	.10	45	10	2.87	15	22	101	17.6	78.2	25.6
	II	288±77	.05	48.3	10.5	2.34	18.0	16.7	-	12.3	78.9	23.8
2639	I	<59	<.05	12	3	.94	12	8	23	20.8	14.3	32.0
	II	<89	0	14.1	2.3	.78	8.2	0	19	16.4	19.4	32.0

Table 1. (continued)

Station Number	Sample Period	Ba (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (%)	Pb (ppm)	Ni (ppm)	v (ppm)	CaCO ₃ (%)	Fines (%)	Water Depth (m)
2640	I	<31	.06	3	1	.33	5	1	6	19.7	1.7	35.7
2641	I	<34	<.05	6	3	.16	3	2	7	5.3	4.1	35.1
2642	I	136±45	<.05	5	1	.09	3	1	2	6.5	1.7	36.0
2643	I	<72	.10	10	2	1.63	18	12	28	84.0	5.9	68.0
	II	<86	.04	14.6	2.1	1.43	11.0	7.5	23	76.4	3.9	71.6
2644	I	<75	.10	10	2	1.12	20	9	31	88.6	3.0	70.7
	II	<76	.70	10.1	1.7	1.05	5.4	5.1	29	87.5	4.6	73.8
2645	I	<59	.10	13	3	1.04	20	9	18	84.3	11.4	107.3
	II	107±34	.07	11.3	2.4	.80	9.0	4.0	21	84.7	13.0	106.7

% Error From
Replication

35% 20% 12% 9% 15% 11%

509 Holmes, 1973 (N.W. Gem. Aug.)
 140 Holmes, 1973 (N.E. Gem. Shelf Aug.)
 66 Holmes, 1973 (S. Florida Shelf Aug.)
 35 Horn and Adms, 1966 (World Wide Carbonate Arz.)
 233 Horn and Adams, 1966 (Mobile belt Aug.)

xx< indicates limit of detection determined for each sample.

* Sediment Data from Sample Period III

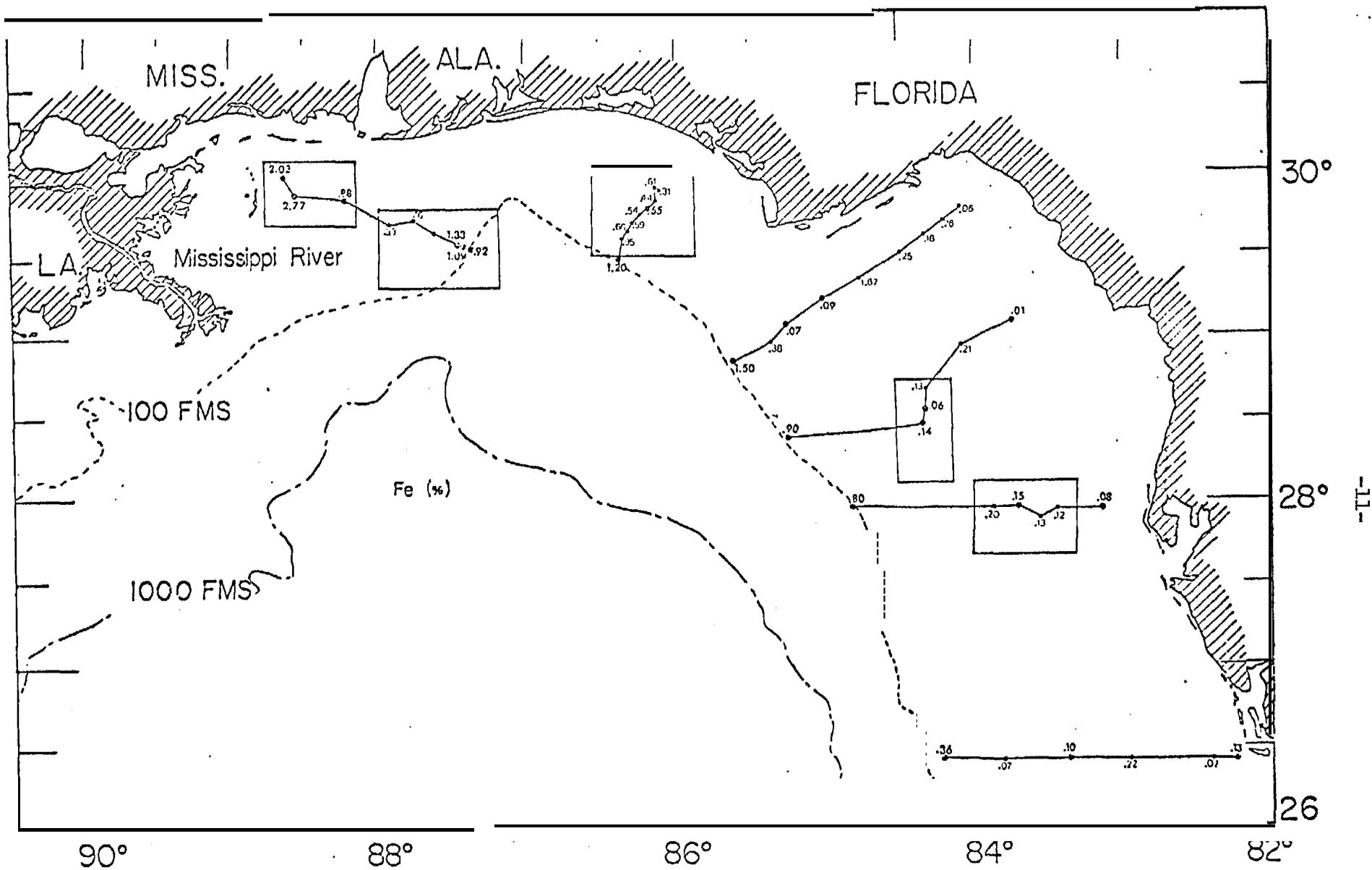
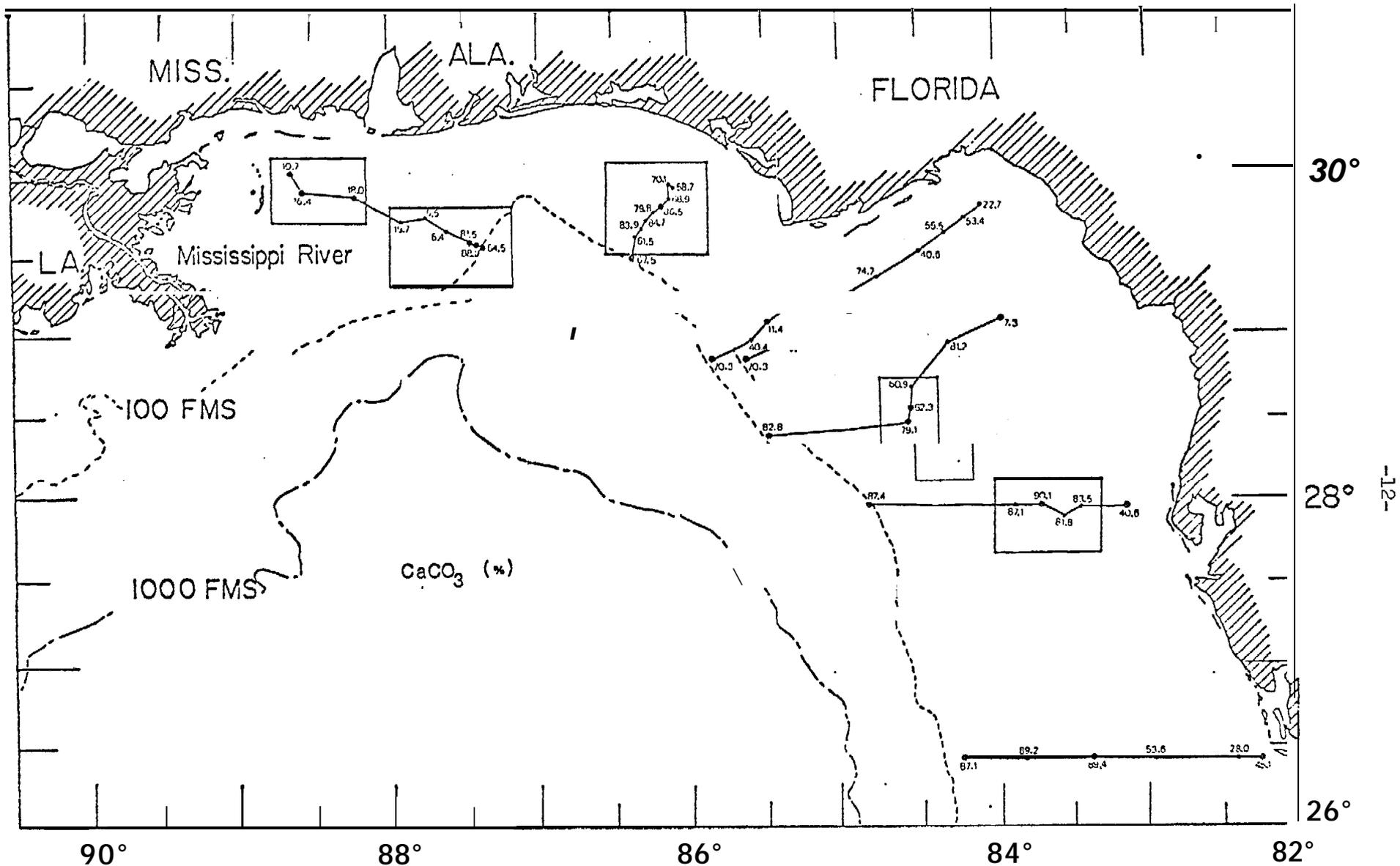


Fig. 3. Surface sediment iron content (%) averaged for two sampling periods of MAFLA Baseline Continuation Study.



rig. 4. Surface sediment calcium carbonate content (%) averaged for two sampling periods of MAFLA Baseline Continuation Study.

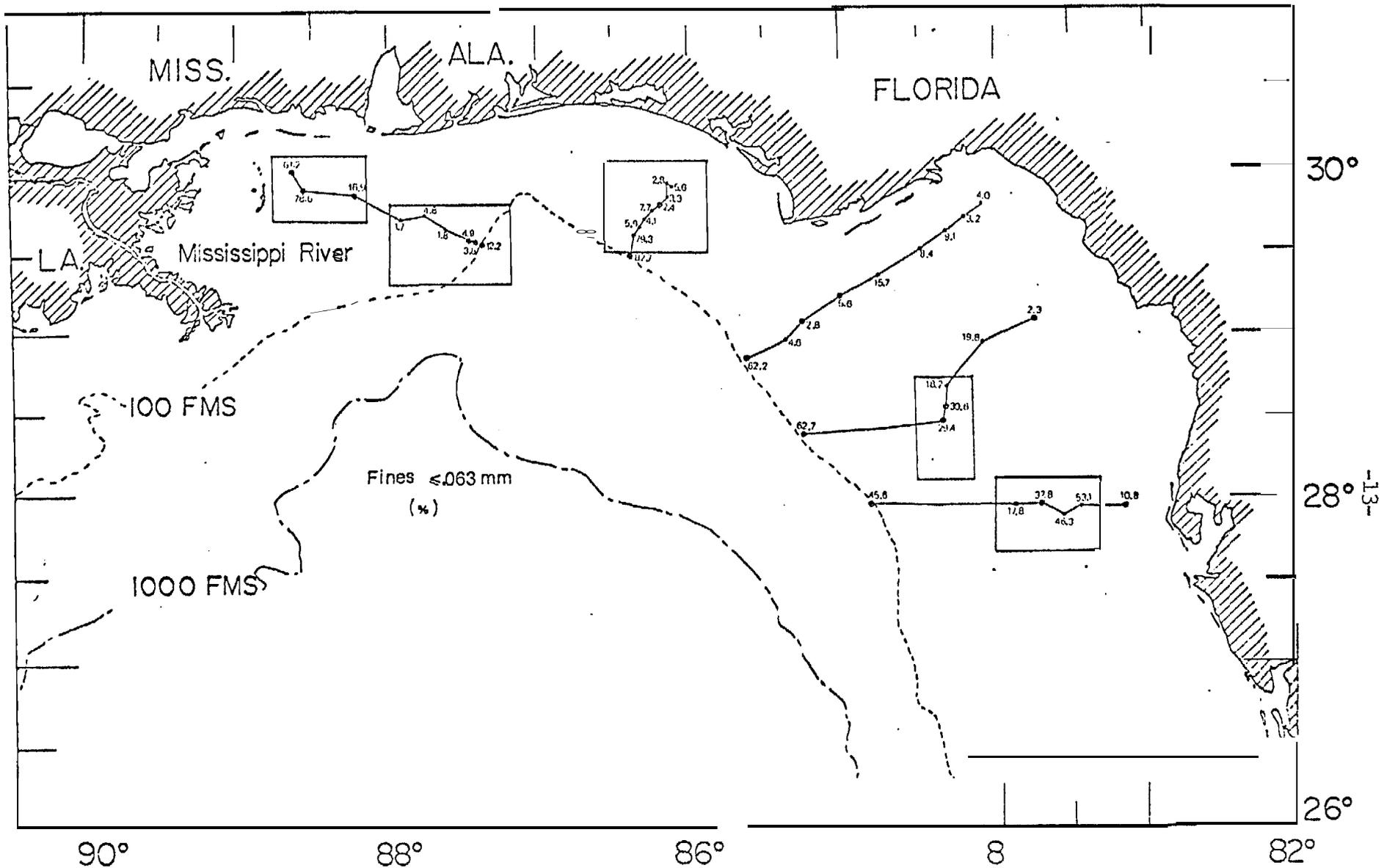


Fig. 5. Surface sediment fine grain ($\le .063\text{ mm}$) content (%) averaged for two sampling periods of MAFLA Baseline Continuation Study.

are observed when sediments contain appreciable amounts of quartz, carbonate and coarse-grained material.

To examine the interrelationships between possible controlling factors and metal concentrations, Trefry, et al.(1976) and Trefry and Presley (1976) have normalized metal concentrations to Fe. Sediment with metal concentrations which deviate from their expected ratio to Fe have been cited as having an anthropogenic contribution. This is reasonable because metals, including Fe, are well correlated with grain size, organic matter, CaCO_3 , etc., but Fe is unlikely to be added by man in amounts which would increase natural levels.

At the completion of the initial study of the MAFLA area, we showed that metal concentrations correlated well with the fundamental sediment characteristics and that there was no indication of metal pollution (Presley, et al., 1975). This observation also holds for the 63 second year samples. To examine all of the interrelationships between metal concentrations and their controlling factors would require an extensive analytical program and a rigorous statistical treatment of the data. It is more convenient to normalize observed metal concentrations to a single index which encompasses the more important concentration controlling factors. As mentioned, Fe provides such an index and in an effort to evaluate the distributions found in this study we have applied this approach to the data presented in Table 1.

Figures 6-10 give the metal to Fe scatter plots for the 1974-1976 MAFLA sediment data. In each case, there is a significant linear correlation of the metals with Fe. This occurs despite the three areas of provenance for MAFLA sediments. The plots provide a prediction interval for evaluating

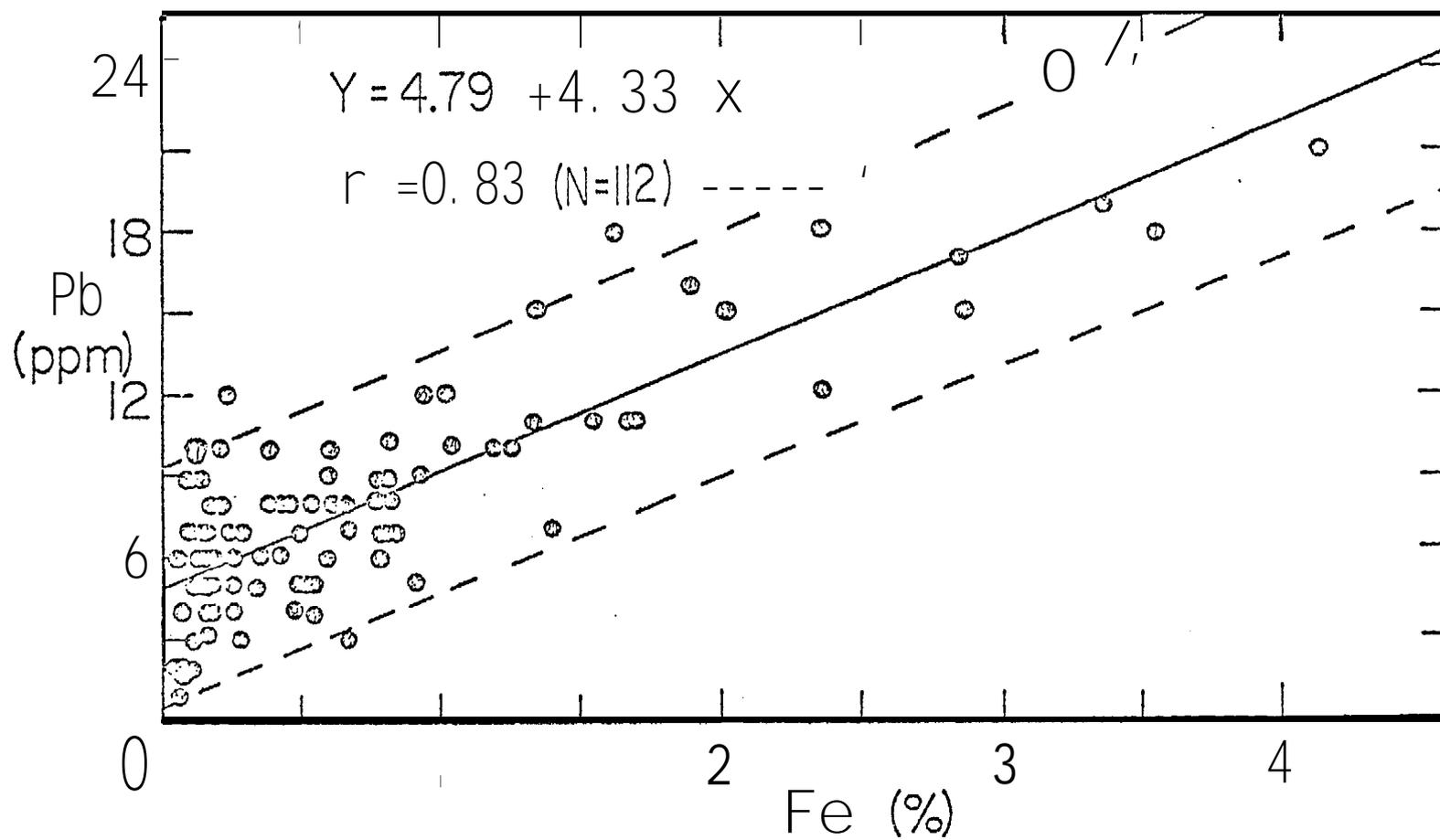


Fig. 6. Pb vs Fe scatter plot for MAFLA shelf sediments with 95% prediction interval.

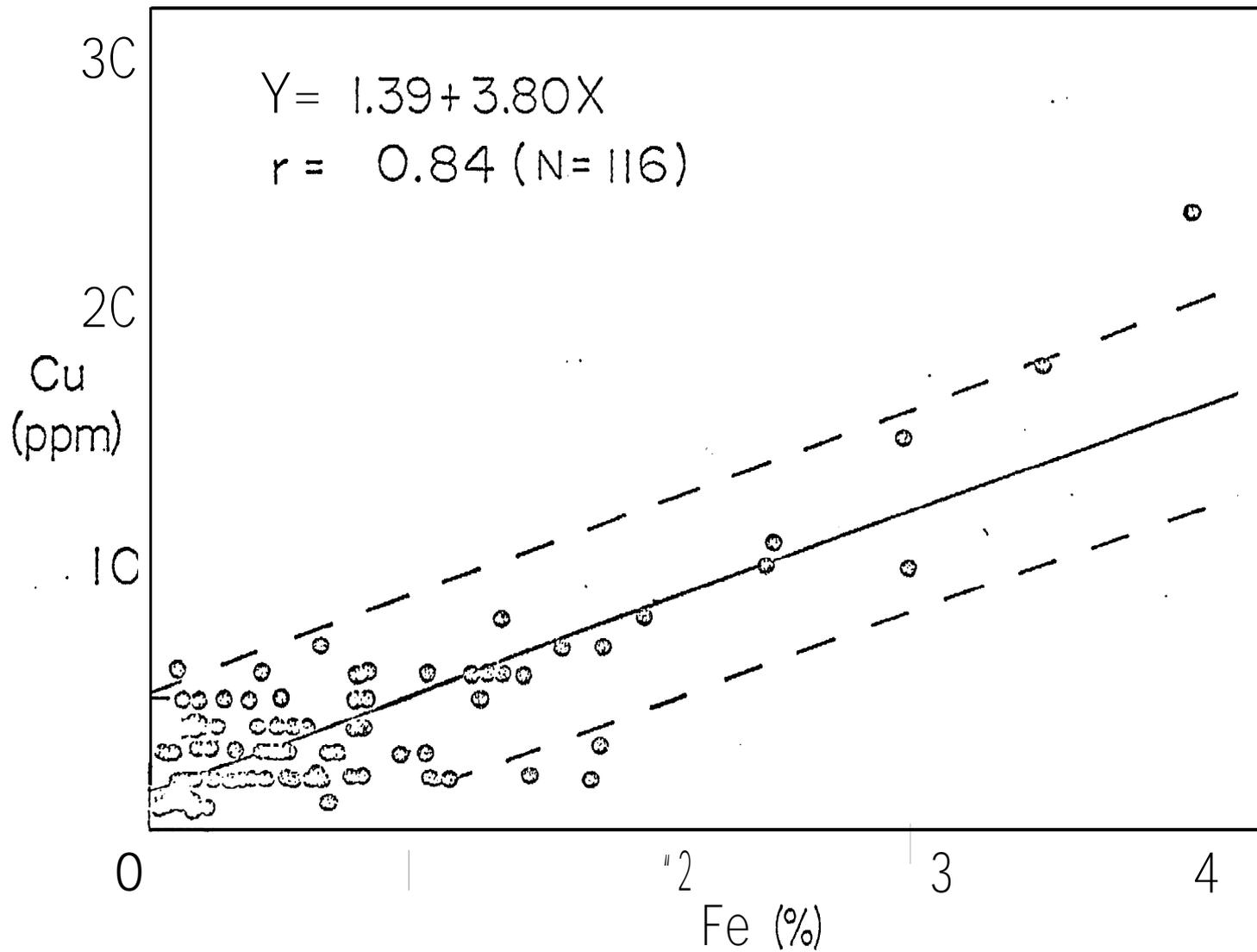


Fig. 7. Cu vs Fe scatter plot for MAFLA shelf sediments with 95% prediction interval.

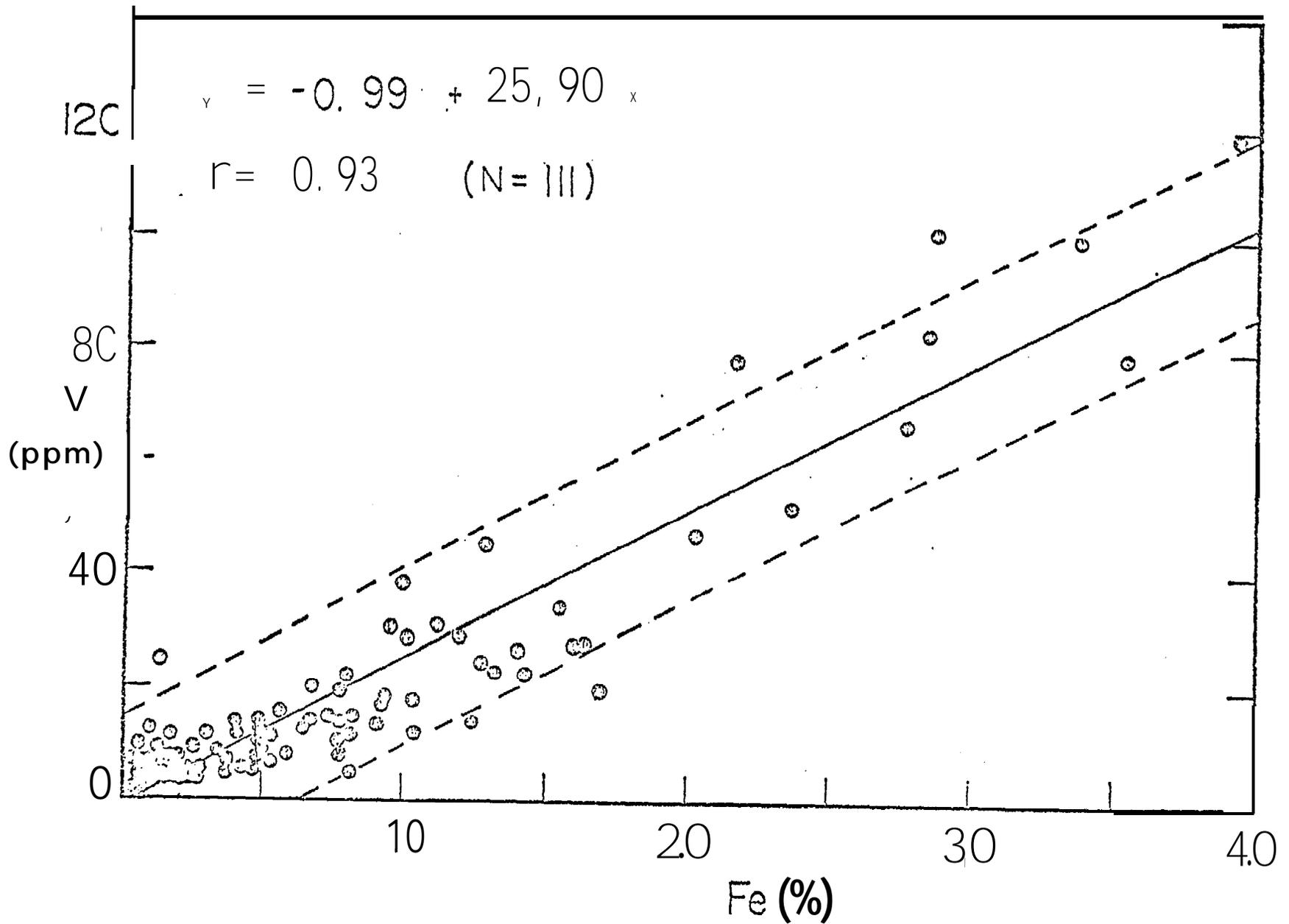
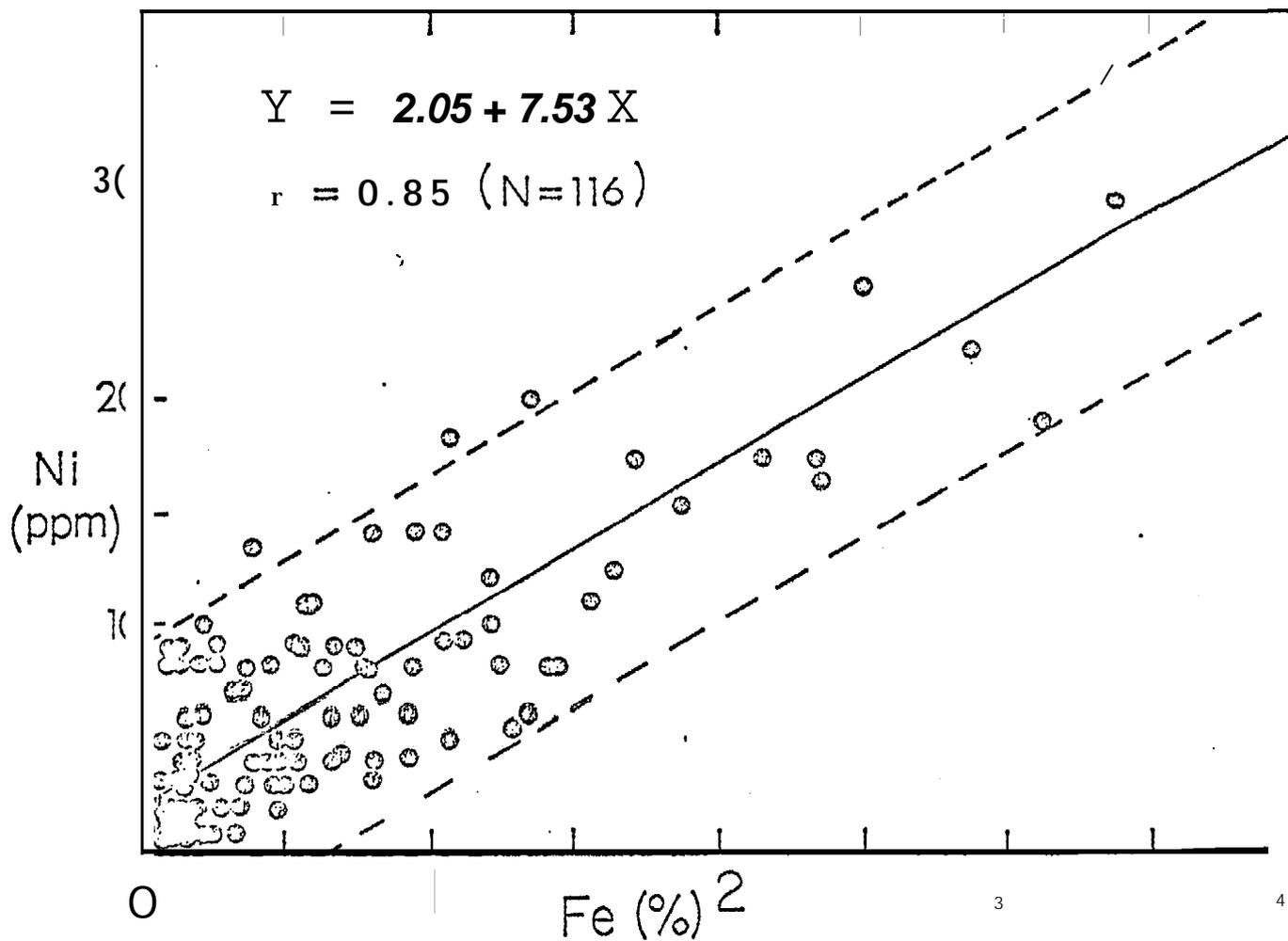


Fig. 10. V vs Fe scatter plot for MAFLA shelf sediments with 95% prediction interval.



Ni vs Fe scatter plot for MAFLA shelf sediments with 95% prediction interval.

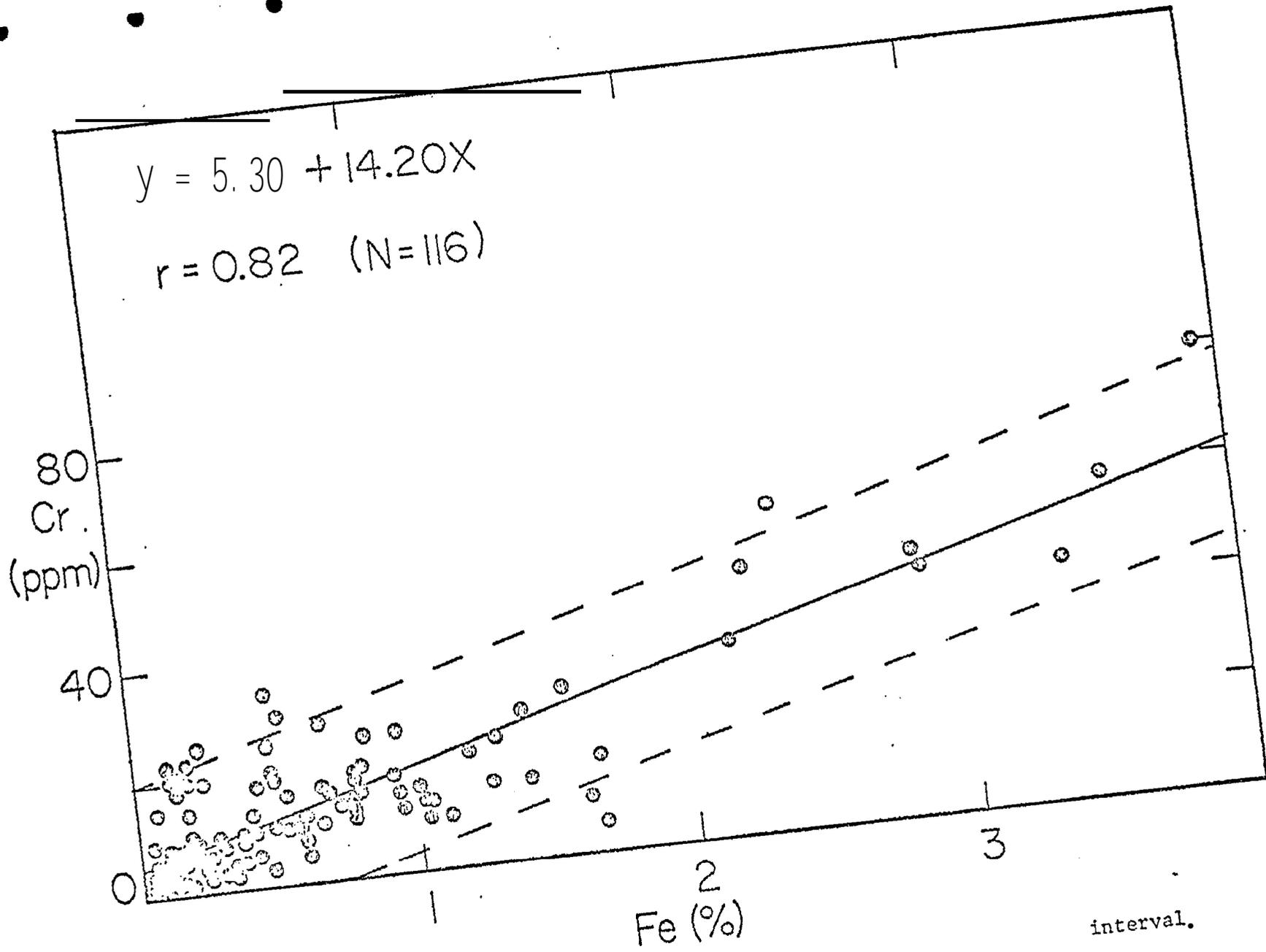


Fig. 9. Cr vs Fe scatterplot for MAFLA shelf sediments with 95% prediction

future sediment analyses and show no present-day evidence of pollution. Any input of trace metals from oil-related activities would result in , data points which deviate from linearity in the positive y-direction on the scatter plots, assuming that anthropogenic Fe input is not high enough to influence the normal sediment Fe content and that trace metal concentrations could be more easily and noticeably increased. Such an approach may be subject to difficulty in some of the extremely low iron Florida shelf areas; however, any appreciable metal increase to these areas will be observable due to the very low natural levels.

We have now characterized the basic metal distribution patterns for the MAFLA area and have shown that Fe may be used as an index for predicting trace metal concentrations, thus providing a means for assessing possible future anthropogenic input. The next step in this study should be to evaluate the form and "biological availability" of the naturally occurring toxic metals, so as to allow comparisons to man-introduced metals.

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APPENDIX I

Station locations for box cores
taken during sampling periods
1 and 2 of the MAFLA Baseline
Continuation Study

Sampling Period 1

<u>Cruise Number</u>	<u>Station Number*</u>	<u>Latitude</u>	<u>Longitude</u>	<u>Date</u>
10	2101	26°25'00"	82°15'01"	75 05 28
10	2102	26 25 00	82 25 01	75 05 28
10	2103	26 24 59	82 5802	75 05 28
10	2104	26 24 59	83 23 00	75 05 29
10	2105	26 24 59	83 49 59	75 05 29
10	2106	26 24 58	84 15 03	75 05 29
10	2637	30 02 02	88 37 02	75 06 01
10	2638	29 55 31	88 33 29	75 0602
10	2639	29 53 28	88 12 24	75 06 02
10	2640	29 43 31	87 54 32	75 0602
10	2641	29 45 35	87 46 41	75 06 02
10	2642	29 40 28	87 37 01	75 06 02
10	2643	29 36 24	87 27 07	75 0603
10	2644	29 36 10	87 23 32	75 06 03
10	2645	29 35 00	87 19 59	75 06 03
10	2528	29 54 59	86 05 00	75 06 04
10	2529	29 55 59	86 06 28	75 06 04
10	2530	29 50 59	86 06 30	75 06 04
10	2531	29 47 59	86 09 30	75 06 04
10	2532	29 45 58	86 12 28	75 06 04
10	2533	29 42 59	86 15 29	75 0605
10	2534	29 39 59	8616 59	75 06 05
10	2535	29 36 59	8619 59	75 06 05
10	2536	29 30 01	86 25 01	75 06 05
10	2419	29 46 58	84 05 01	75 0606
10	2420	29 51 48	84 11 01	75 06 06
10	2421	29 36 58	84 17 01	75 06 06
10	2422	29 30 00	84 27 01	75 06 07
10	2423	29 20 00	84 44 02	75 06 08
10	2424	29 13 00	84 59 59	75 06 08
10	2425	29 04 58	85 15 03	75 0608
10	2426	28 57 57	85 23 01	75 06 08
10	2427	28 49 59	85 37 06	75 06 08
10	2318	29 04 59	83 45 01	75 0609
10	2317	28 56 00	84 06 01	75 06 09
14	2207	27 56 59	83 09 00	75 07 22
14	2208	27 55 57	83 27 32	75 07 22
14	2209	27 52 30	83 34 00	75 07 22
14	2210	27 57 35	83 42 27	75 07 23
14	2211	27 56 29	83 53 02	75 07 23
14	2212	27 57 03	84 48 02	75 07 23
14	2313	28 24 04	84 14 53	75 07 24
14	2317	28 56 02	84 06 04	75 07 25
14	2316	28 42 01	84 20 01	75 07 25
17	2314	28 29 00	84 21 01	75 07 31
17	2315	28 34 00	84 20 13	75 07 31

* Second digit of station number indicates transect number as per Figure 1.

Sampling Period 2

<u>Cruise Number</u>	<u>Station Number*</u>	<u>Latitude</u>	<u>Longitude</u>	<u>Date</u>
21	2101	26°25.01	82°15.0'	75 09 15
21	2102	26 25.0	82 25.0	75 09 15
21	2103	26 25.0	82 58.0	75 09 15
21	2104	26 25.0	83 23.0	75 09 15
21	2105	26 25.0	83 50.0	75 09 16
21	2106	26 25.0	84 15.0	75 09 16
21	2207	27 57.0	83 09.0	75 09 16
21	2208	27 56.0	83 27.5	75 09 16
21	2209	27 52.5	83 34.0	75 09 17
21	2210	27 57.5	83 42.5	75 09 17
21	2211	27 56.5	83 53.0	75 09 17
21	2212	27 57.0	84 48.0	75 09 17
21	2313	28 24.0	85 15.1	75 09 18
21	2314	28 29.0	84 21.0	75 09 19
21	2315	28 34.0	84 20.1	75 09 19
21	2316	28 42.0	84 20.0	75 09 19
21	2317	28 56.0	84 06.0	75 09 19
21	2318	29 05.1	83 45.1	75 09 19
21	2419	29 47.0	84 05.0	75 09 19
21	2420	29 42.0	84 11.0	75 09 19
21	2421	29 37.0	84 17.0	75 09 20
21	2422	29 30.0	84 27.0	75 09 20
21	2423	29 20.0	84 44.0	75 09 20
21	2424	29 13.0	85 00.0	75 09 21
21	2425	29 05.0	85 15.0	75 09 21
21	2426	28 58.0	85 23.0	75 09 21
21	2427	28 50.0	85 37.1	75 09 22
21	2528	29 54.9	86 05.0	75 09 25
21	2529	29 56.0	86 06.5	75 09 25
21	2530	29 50.9	86 06.4	75 09 25
21	2531	29 48.0	86 09.5	75 09 25
21	2532	29 45.9	86 12.3	75 09 25
21	2533	29 42.9	86 15.5	75 09 26
21	2534	29 40.0	86 17.0	75 09 26
21	2535	29 37.0	86 20.0	75 09 26
21	2536	29 30.0	86 24.9	75 09 26
21	2645	29 35.0	87 20.1	75 09 26
21	2644	29 36.2	87 23.5	75 09 27
21	2643	29 36.5	87 27.0	75 09 27
21	2642	29 40.5	87 37.0	75 09 27
21	2641	29 45.5	87 46.5	75 09 27
21	2640	29 43.5	87 54.5	75 09 27
21	2639	29 53.5	88 12.5	75 09 27
21	2638	29 55.5	88 33.5	75 09 28
21	2637'	30 02.0	88 37.0	75 09 28

* Second digit of station number indicates transect number as per Figure 1.