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SCIENCE APPLICATIONS, INC.

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BENTHIC, YEAR TWO
VOLUME II, REPORT 9.0

VANADIUM, BARIUM, AND OTHER TRACE METALS IN SEDIMENT AND BIOLOGICAL SAMPLES USING NAA

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VOLUME II, REPORT 9.0

VANADIUM, BARIUM, AND OTHER TRACE METALS IN SEDIMENT AND BIOLOGICAL SAMPLES USING NAA

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ABSTRACT

Sediment trace metal results followed expected trends. Reliable concentration data for total and leachable (1 N HNO_3) sedimentary vanadium (V), barium (Ba), aluminum (Al), chromium (Cr), and iron (Fe) have been obtained by neutron activation analysis (NAA). In general, geographic differences can be seen, isolating sites with apparent anthroopogenic inputs from those with natural geochemical controls. Vanadium trends coherently with the other transition metals assayed for in this program (Cr and Fe). The most striking contrast is that between the high carbonate sediments of the outer regions (low in V) and the clay-rich sediments of the inner basins (high in V). Barium concentrations can be seen to relate most closely to sedimentary $CaCO_3$.

Extremely low metal concentrations were found in virtually all the fish liver samples. Compounded by small sample size, large replicate variances largely obscured geographical, seasonal and intraspecies comparisons even though the most sensitive NAA techniques available were utilized. Nevertheless, a definite seasonal contrast (higher V and Ba in winter) was seen. This is thought to be brought about by a general reduction in the liver weight in the winter, accompanied by a resultant decrease in elemental concentrations.

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9.1 INTRODUCTION

Petroleum exploration and recovery in the Outer Continental Shelf (OCS) are potential contributors of certain trace metals to the marine environment. Among these are barium (Ba), existing as barite (as high as 90% by weight) in drilling muds, and vanadium (V), notoriously enriched in crude oils from its association with organic porphyrin systems (Krauskopf, 1967). Because of the potential injections of these two elements into marine systems being exploited for petroleum, the Bureau of Land Management (BLM) has included them in their list of geochemical parameters to be surveyed and investigated under the OCS Environmental Studies program. While neither of these elements has been demonstrated to be particularly toxic to marine biotal systems (or individuals), little is known about their toxic thresholds (if there are any) or of any long-term chronic effects that abnormal amounts of either might have on biological communities.

This is especially true in the case of Ba where it has been shown that drilling activity can alter the normal geochemical levels of that element remarkably. Unpublished data from the OCS Environmental Study sponsored by BLM in the eastern Gulf of Mexico (MAFLA) during 1975/76 (Presley et al., 1976a) compares the distribution of whole sediment Ba levels sampled on a 2000-m diameter grid about a proposed drilling site, the same grid three months later during drilling operations, and six months later after drilling operations. There were found significant perturbations of the resident levels of Ba within the near vicinity of the rig site. What the environmental effect of such a Ba elevation might be is unknown, but at least we must be aware that it is possible to alter the geochemical system noticeably from a mass balance standpoint.

In the marine environment, trace elements may enter the biosphere through a number of pathways. One such pathway that has come about with the increased demand for energy, is the possible introduction of potentially toxic metals via offshore drilling and production. Metals, both dissolved and particulate, may enter the water column and biosphere through resuspension of reduced bottom sediments due to drilling and/or by crude oils which have been shown to contain as much as 300 ppm V (Yen, 1975).

Several conditions are desireable in order to usefully evaluate the distributions of metals in organisms for baseline (and subsequently, monitoring) purposes. The organism should concentrate the metals of interest. The elements of interest must be in sufficient concentration in the test organism to be above analytical background levels. Also the test organism should be readily available for continued sampling from control and polluted areas.

Although several test organisms were proposed, the two that were finally decided upon were two fish: Sebastes saxicola, stripetail rockfish which feeds on macroplankton and Lyopsetta exilis, slender sole which feeds on infauna (Phillips, 1964 and Best 1961).

The main purpose of this study was to provide background information on the levels of Ba and V in several individuals of each species of fish from several locations in the California Bight area during the winter and summer seasons. A secondary purpose was to test for trends both geographical and seasonal.

This report provides data which characterizes the Southern California OCS (Figure 11-9.0-1) with respect to surficial sediment and demersal fish Ba and V levels. The area surveyed by bottom sampling in this study is one of the most complex outer continental shelves found in the world's oceans (Shepard, 1973). It is an environment containing coasts and submarine terraces of wide geochemical variety, deep basins which are efficient sediment traps and which have steep slopes that are sedimentologically unstable, and a series of islands of varied origin and mineralogy. In addition to the complexity of the setting, the geochemical sources contributing to the submarine sediments are equally varied, including as example the organically rich, upwelled waters filling the more seaward areas, the Pollutant effluents draining from the highly urban coastal areas, the erosive volcanigenic substrates found on the mainland and inland shores, and the natural petroleum seeps near the mainland coast in the northern regions.

The complexity just described makes an impossible task of trying to assign geochemical distributions either a priori or from a few data points as can often be done in more homogeneous settings. Therefore, in this continued effort to establish a useable baseline of barium and vanadium distributions for the Bill, sampling was performed in a design to provide substantial information about certain areas (e.g., coastal zones, the pristine area south of the Channel Islands, the Tanner Bank region, the Los Angeles area shelf) and more cursory data to represent other selected environments (e.g., the offshore basins). Figure 11-9.0-2 shows the benthic sampling stations.

Due to the insensitivity of atomic absorption spectrophotometry in the analysis of Ba and V, neutron activation analysis (NAA) was used to obtain concentration data for these elements from the sediment and biota samples collected during this study (as well as for suspended particulate and particle interceptor trap (PIT) samples; see Volume 111, Appendix to Report 7.0

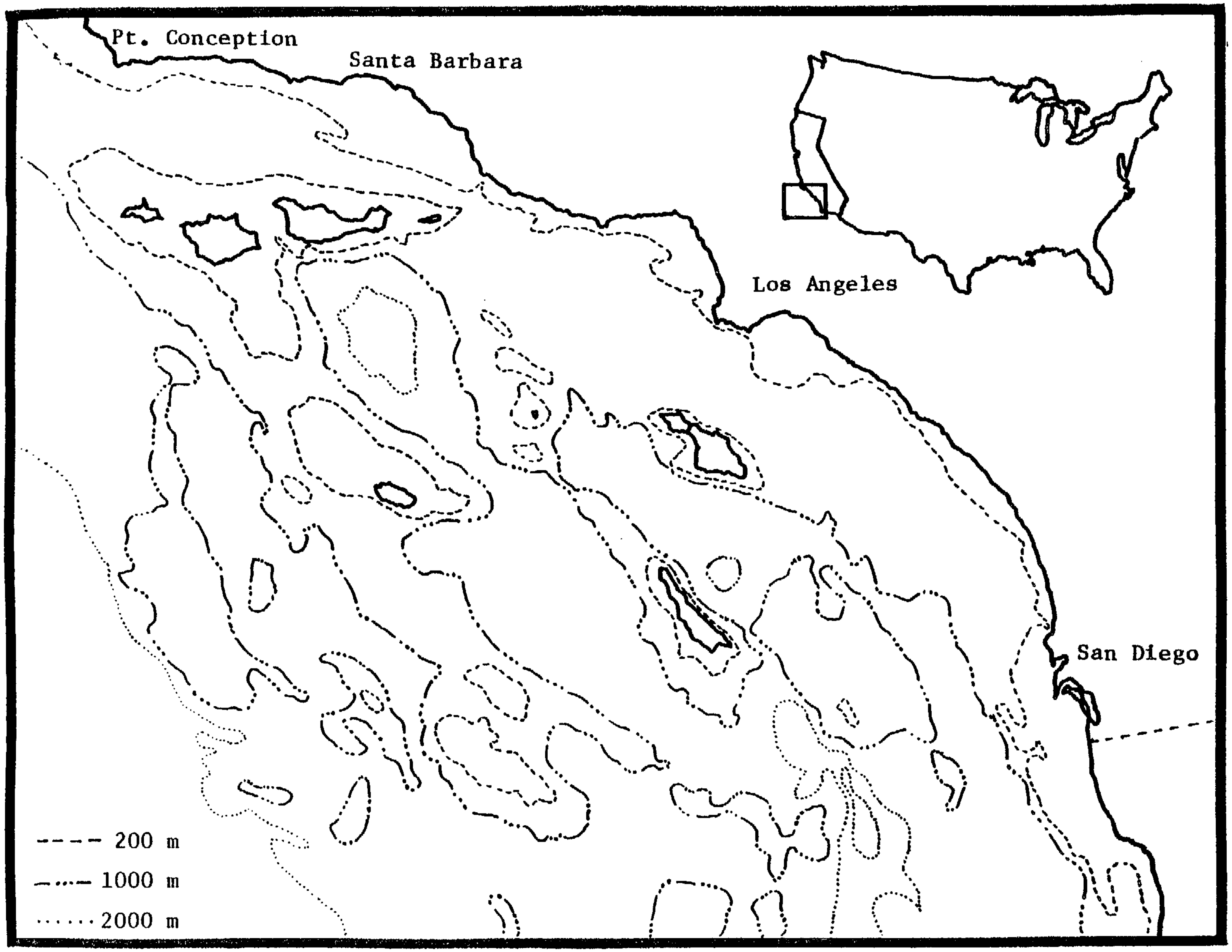

Figure II-9.0-1. Map of the Southern California Outer Con≤inental Shelf.

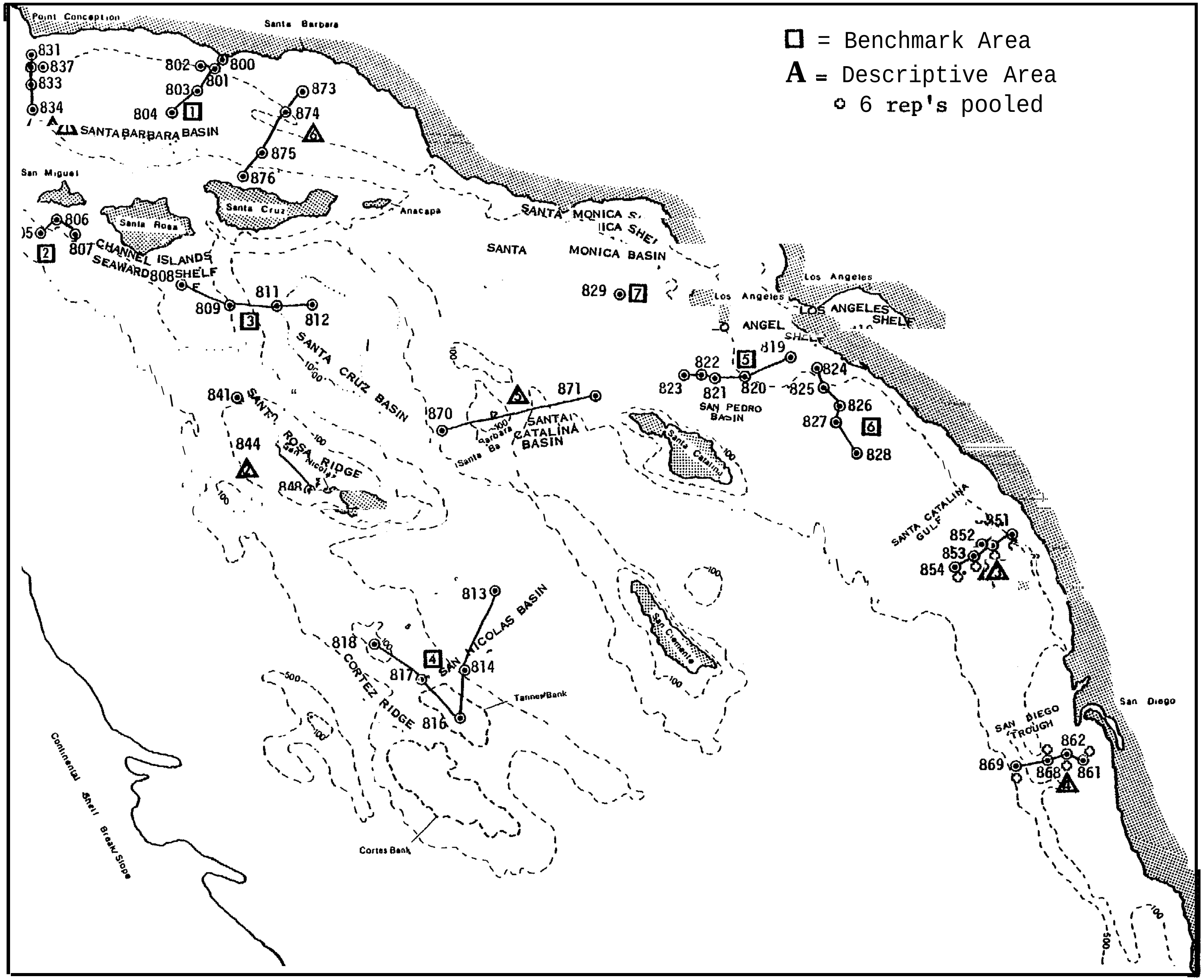

Figure 11-9.0-2. Map showing Benthic geochemical sampling stations.

9.2 METHODS

Instrumental neutron activation analysis (INAA) is a highly sensitive and reliable analytical technique. It involves only irradiation of the sample and gamma-ray spectroscopy of the activated sample. It is inherently free from all yield and blank errors. In this study, for INAA the samples were simply and accurately weighed into acid-cleaned conventional polyethylene vials and sealed, all under clean room conditions. Samples were then taken to the nuclear reactor facility at either the University of California, Irvine (UCI) or the University of Missouri (UM) for irradiations with respective neutron (n) fluxes of 1 x 10^{12} and 1 x 10^{14} neutrons/cm^2-sec. Gamma-ray spectroscopy was then performed either at each reactor facility (for short-lived isotopes) or at SAI's counting laboratory (for long-lived isotopes). The data thus acquired was stored on seven-track magnetic tape, and processed by computer using spectral analysis computer programs designed to enhance accuracy and reproducibility.

INAA could only be used, however, on samples that contained relatively low amounts of elements (such as Na) that can interfere with the gamma-ray spectroscopy. Benthic biota for example, present difficulties in determining the short-lived elements such as V and Al by INAA. INAA was able to be used on the benthic sediment leachates and totals for both short-lived (V and Al) and long-lived (Ba, Cr, Fe and Zn) elements. The long-lived elements in the benthic biota, however, required the enhanced sensitivity afforded by the barium sulfate radiochemical technique (Volume III, Report 9.0).

An acid leach was performed on each sediment sample to approximate the portion of trace metals that might be available to biological systems under naturally occurring conditions. The leaching procedure involved shaking the dry unpulverized sediments with 1 N HNO_3 for two hours at room temperature, and then centrifuging and separating the acid leachate from the solid sediment for subsequent analysis. All sampling procedures are detailed in Volume III, Reports 2.0, 8.0 and 10.0; all sample processing and analysis procedures are detailed in volume 111, Reports 8.0, 9.0 and 10.0.

9.3 RESULTS

9.3.1 Trace Metals in Surficial Sediments

All the benthic sediment and biota, trace metal concentrations determined in this study using neutron activation analysis are listed in Volume IV, Report 9.0 (Tables IV-9.0-15 and IV-9.0-16). The sediment leachable fraction of these metals has proven to be an interesting parameter for the indication of anthropogenic influences, on such elements as V, Ba, and Cr. Table 11-9.0-1 lists all the stations having a leachable V fraction of greater than 20%. This is

Table II-9.0-1. Benthic Geochemical Stations Having <20% Leachable Vanadium

Station	Remarks
803	Santa Barbara Basin off Coal Oil Point
804*	Santa Barbara Basin off Coal Oil Point
812	Santa Crus Basin
813*	San Nicolas Basin
817	San Pedro Basin
823*	San Pedro Basin
829*	Santa Monica Basin
841	Santa Rosa Ridge
848	Santa Rosa Ridge

*Age-date core taken.

a somewhat arbitrary cut-off, but it results in some clear trends. The members of this <20% group are all basinal stations with the exception of the two Santa Rosa Ridge sites. These two samples , however , can be readily differentiated geochemically by their sediment characterization parameters (see Volume IV, Report 9.0, Tables IV-9. O-15 abnd IV-9. O-16. Their high $CaCO_3$ and low clay (percent fines) contents are exactly opposite to the basinal sediment characterization parameters.

Table 11-9. 0-2 compares Ba and V concentrations in sediments characterized by either high $CaCO_3$ or high clay content (greater than 50% fines). Again, the clay-rich sediments show elevated V and Ba concentrations. Table 11-9.0-3 compares these trace metal concentrations to other reported concentrations of Ba and V in marine sediments from the Gulf of Mexico and other locations.

The Southern California OCS can be segregated into four geographic regions to further facilitate comparisons. Table 11-9.0-4 summarizes the mean concentrations of five trace metals analyzed by NAA in the sediments of these regional groups. These groupings can then be compared to means of all benthic stations. The Santa Monica/San Pedro basinal V and Cr leachate concentrations are strikingly high, but the normally unpersistent Fe concentrations are also relatively high in these leachates. Sedimentary Fe, which naturally occurs at percent concentration levels, is normally considered to be impervious to observable alterations by anthropogenic perturbations.

Tables 11-9.0-5 through 11-9.0-8 list the concentrations of the five NAA trace metal according to their station water depth and with respect to these physiographic divisional groupings. For example, Station 876 in the Santa Barbara Basin has unusually low V and Ba, but it can be inferred by the high $CaCO_3$ and coarse texture that the mineral matrix is dominated by metal-poor island shelf materials. Also, the mineralogy of island shelf sediments is characterized by metal contents which are relatively impervious to weak acid leaching. In the case of Stations 802, 875 and 833, a reasonable explanation for the high leachable V could be related to the unusually high organic content and percent fines (particles of diameter less than 62 µm) .

Figures 11-9.0-3 through 11-9.0-14 are maps showing element by element distributions of several trace metals in the benthic sediments. Figures 11-9.0-8 and 11-9.0-13 show areal distributions of Al and Fe, respectively.

In the Southern California OCS, as on most oceanic continental shelves (see Table 11-9.0-3), sedimentary geochemistry is controlled predominantly by the source material. It is often possible to pinpoint anthropogenic influence by examining chemical characteristics associated with particle surfaces and/or by ratioing

Table II-9.0-2. Comparative Barium and Vanadium Concentrations in Major Sediment Characterizations of Southern California OCS Benthic Sediments.

High Carbonate (>50% $CaCO_3$)			Clay Rich (>50% fines)		
Station	Ba (ppm)	V (ppm)	Station	Ba (ppm)	V (ppm)
809	467	30	802	606	163
816	255	41	803	601	119
841	557	53	804	596	126
870	607	72	811	930	112
	±156	±18	812	1150	112
			813	1340	52
			814	1265	61
			821	910	104
			823	996	135
			825	760	75
			827	625	100
			828	1170	75
			829	839	173
			832	830	61
			833	652	84
			834	589	83
			851	591	143
			852	460	79
			853	314	123
			854	640	79
			873	853	91
			874	554	99
			875	517	116
				773	104
				±270	±32

Table II-9.0-3. Comparative Barium and Vanadium Concentrations of Global Marine Sediments

	Total Ba (ppm)	Total V (ppm)
This study		
high carbonate	300-600	30-70
clay rich	500-1000	70-140
Southern California, Year I		
high carbonate	100-200	20-30
clay rich	<8(.)(3	140-160
heavy mineral rich	400-600	20-80
polluted	600-900	80-120
sandy beach	600-900	30-50
Holmes, 1973 (N.W. Gulf of Mexico avg.):	509	54
Holmes, 1973 (N.E. Gulf of Mexico avg.):	140	91
Holmes, 1973 (S. Florida Shelf avg.):	66	25
Horn and Adams, 1966 (worldwide carbonate avg.):	35	13
Horn and Adams, 1966 (Mobile Bay sediment):	133	
Presley, et al., 1976b (E. Gulf of Mexico):		
carbonate rich	<50	5-20
clay rich	400	100
quartz sand	<50	5
Presley, et al., 1976a (N.W. Gulf of Mexico):	700	60-140

Table 11-9.0-4. Mean concentrations of five trace metals in SCOS sediments.

	V	Ba	Al	Cr	Fe	% $CaCO_3$	%< 62 µm	% TOC
ALL BENTHIC STATIONS						16.3±20.0(n=55)	54.9±38.3(n=55)	1.94±1.48(n=55)
Leachable	11±16(n=49)	44± 27(n=49)	1381 ± 683(n=49)	11±16(n=49)	3694±4801(n=49)			
Total	75±40(n=48)	697±342(n=48)	104,700±43,200(n=48)	71±39(n=27)	21,800±9800(n=28)			
Percent Leachable	15%	6%	1%	15%	17%			
SANTA BARBARA BASIN						7.3±12.3(n=13)	63.1±34.2(n=13)	1.94±1.00(n=13)
Leachable	11±12(n=13)	38± 14(n=13)	1338 + 587(n=13)	6+ 4 n=13)	3229~1411 (n=13)			
Total	85±40(n=13)	677±210(n=13)	114,500±39,150(n=13)	89± 8 (n=5)	22,440±9588(n= 5)			
Percent Leachable	13%	6%	34%	7%	14%			
SANTA MONICA & SAN PEORO BASINS						8.1±10.7(n= 9)	65.5±34.7(n= 9)	2.24±1.57(n= 9)
Leachable	20+29(n=12)	50t_ 25(n=12)	1867 + 595(n=12)	23+28(n=12)	6871+8873 (n=12)			
Total	97±36(n=12)	929±464(n=12)	108,230±32,700 (n=12)	77±36(n= 6)	29,017±8237 (n= 6)			
Percent Leachable	21%	5%	2%	30%	24%			
GULF OF SANTA CATALINA & SAN DIEGO TROUGH						6.4± 5.1(n= 8)	54.6±36.4(n= 8)	1.72±1.47(n= 8)
Leachable	5± 3(n= 8)	42± 29(n= 8)	1322 ± 757(n= 8)	6+ 3(n= 8)	2323+1043(n= 8)			
Total	81±43(n= 8)	507±113(n= 8)	138,000±58,000(n= 8)	39+23(n= 6)	23,100±11,800(n=7)			
Percent Leachable	6%	8%	1%	15%	10%			
OUTER REGIONS						35.1±2.05(n=15)	35.7±39.0(n=15)	1.79±1.90(n=15)
Leachable	7+ 7(n=16)	47+ 36(n=16)	1081 + 633(n=16)	8+ 7(n=16)	2374+1672(n=16)			
Total	48±29(n=16)	648±348(n=16)	77,900±29,800(n=16)	77±49(n=10)	16,800±8200(n=10)			
Percent Leachable	15%	7%	1%	10%	-14%			

Table 11-9.0-5. Vanadium, barium, alunium, chromium, and iron concentrations in the sediments of the Santa Barbara Basin.

SITE	DEPTH, METERS	SEDIMENT TRACE METAL MEANS Leach/Total, % Leachable					SEDIMENT CHARACTERIZATION		
		V(μg/g)	Ba(μg/g)	Al(μg/g)	Cr(μg/g)	Fe(μg/g)	% $CaCO_3$	% < 62 μm	% TOC
800*	26	3/ 28 11 %	19/944 2%	394/119,000 0.3%	2/ 87 3%	1113/ 7900 14%	1.3	11.6	1.60
801 *	68	4/ 49 9%	45/977 5%	899/122,000 0.7%	4/104 4%	3015/17,500 17%	0.9	25.8	0.87
873	78	8/ 91 8%	43/853 5%	1516/145,000 1%	9/ND	3740/ND	2.1	81.7	1.09
876	85	2/ 39 6%	10/218 5%	506/ 80,800 0.6%	3/ND	1035/ND	47.6	21.1	0.83
831	102	3/ 47 6%	31/864 4%	590/118,000 0,5%	3/ND	1878/ND	2.3	15.1	0.48
874	190	8/ 99 8%	29/554 5%	1610/147,000 1%	3/ND	3564/ND	3.9	81.0	1.76
832	211	8/ 61 13%	54/830 7%	1422/129,000 1%	6/ND	2847/ND	3.8	63.7	1.76
802*	331	13/163 8%	41/606 7%	2205/199,000 1%	8/ 84 10%	4104/30,800 i 3%	3.9	97.7	2.80
875	335	10/116 9%	44/517 9%	1637/127,000 1%	8/ND	3570/ND	7.3	98.4	3.20
833	355	10/ 84 11%	25/652 4%	1319/ 60,800 2%	6/ND	3109/ND	2.8	99.7	2.10
834	451	7/ 83 8%	55/589 9%	1354/ 53,500 3%	6/ND	3718/ND	4.2	75.1	1.99
803*	501	25/119 21%	57/601 9%	2123/ 83,500 3%	13/84 16%	6517/28,300 23%	5.0	51.5	3.32
804*	574	47/126 37%	42/596 7%	1819/104,000 2%	13/88 15%	3762/27,700 14%	9.2	97,6	3.44
Mean S.D.		11±12/85±40 13%	38±14/677±210 6%	1338± 87/114,500±39,150 34%	6±4/89±8 7%	3229±1411/22,440±9588 14%	7.3±12.3 n=13	63.1±34.2 n=13	1.94±1.00 n=13

*Transect off Coal Oil Point

Table 11-9.0-6. Vanadium, barium, aluminum, chromium, and iron concentrations in the sediments of the Santa Monica and San Pedro Basins.

ITE	DEPTH METERS	SEDIMENT TRACE METAL MEANS Leach/Total, % Leachable					SEDIMENT CHARACTERIZATION		
		V(µg/g)	Ba(µg/g)	Al(µg/g)	Cr(µg/g)	Fe(µg/g)	% CaCO	%62m	% TOC
824*	32	2/ 56 4%	60/1315 5%	923/112,000 0.8%	7/ 40 17%	1164/18,600 6%	0.6	13.4	0.41
819	33	3/ 67 4%	28/ 846 3%	1056/154,000 0.7%	13/ 46 28%	2581/20,100 13%	0.7	15.2	0.57
820	89	3/ND	48/ND	1 539/ND	1 3/ND	3987/ND	ND	ND	ND
825*	255	5/ 75 7%	26/ 760 34%	1968/1 09,000 2%	5/ 64 9%	1748/29,300 6%	2.2	61.7	1.31
871	312	4/ 65 6%	14/ 180 8%	991/ 76,500 1%	7/ND	1739/ND	35.5	40.7	1.14
826*	436	7/ 92 8%	44/ 584 8%	2109/ 66,800 3%	8/ND	2590/ND	ND	ND	ND
827*	502	8/100 8%	47/ 625 8%	2214/144,000 2%	6/ 72 9%	2422/32,200 8%	5,5	94.3	2.51
828*	539	7/ 75 1 0%	45/1170 4%	2051/140,000 1%	4/ND	2160/ND	7.6	77.1	2.17
821	696	12/104 12%	42/ 910 5%	2618/137,500 0.2%	21/106 19%	3916/34,200 11%	4.5	91.1	3.07
822	870	32/125 26%	102/1990 5%	2394/ 59,300 4%	69/ND	19,278/ND	ND	ND	ND
823	880	58/135 43%	91 /996 9%	2469/ 97,400 3%	88/ND	29,467/ND	9.2	98.1	3.98
829	895	94/173 54%	51/839 6%	2073/ 94,000 2%	35/134 26%	11,405/39,700 33%	7.4	98.2	5.00
Mean, S.D.		20±29/97±36 21%	50±25/929±464 5%	1867±595/108,230±32,700 2%	23±28/77±36 30% n=12 n=6	6871±8873/29,017±8237 24% n=12 n=6	8.1±10.7 n=9	65.5±34.7 n=9	2.24±1.5 n=9

*San Pedro Basin

Table 11-9.0-7. Vanadium, barium, aluminum, chromium and iron concentrations in the sediments of the Gulf of Santa Catalina and San Diego Trough.

ITE	DEPTH METERS	SEDIMENT TRACE METAL MEANS Leach/Total, % Leachable					SEDIMENT CHARACTERIZATION		
		V(µg/g)	Ba(µg/g)	Al(µg/g)	Cr(µg/g)	Fe(µg/g)	% $CaCO_3$	%< 62 µm	% TOC
861*	33	2/ 28 5%	2/61 5 <1%	96/ 59,500 0.2%	1/13 1 0%	767/11,900 6%	1.5	9.5	0.09
862*	58	3/ 47 6%	22/557 4%	517/122,000 0.4%	4/ND	1270/18,700 7%	2.7	16.4	0.41
851	139	5/143 4%	20/591 3%	1674/219,000 0.8%	3/64 5%	1970/40,500 5%	2.5	77.9	1.40
868*	158	5/ 79 6%	24/475 5%	1194/141,000 0.8%	5/55 1 0%	2040/26,000 8%	6.9	44.7	1.11
869*	184	3/ 36 1 0%	52/408 13%	959/65,600 1%	7/54 13%	2225/29,100 8%	17.2	18.8	0.76
852	447	8/117 6%	80/460 17%	1994/207,000 1%	7/41 17%	3135/29,700 11%	4.8	83.3	2.42
853	654	8/123 7%	58/314 18%	2013/159,000 1%	8/ND	3550/ND	6.2	88.6	3.30
854	746	9/ 79 11%	76/640 12%	2131/129,000 2%	11/9 113%	3630/ 5600 65%	9.5	97.9	4.25
Mean, S.O.		5+3/81+43 6% n=8	42+29/507+113 8%	1322+757/138,000+58,000 1%	6+3/39+23 15% n=8 n=6	2323+1043/23,100+11,800 10% n=8 n=7	6.4+5.1 n=8	54.6+36.4 n=8	1.72+1 .47 n=8

*San Diego Trough

Table 11-9.0-8. Vanadium, barium, aluminum, chromium, and iron concentrations in the sediments of the Outer Shelves, Banks and Basins.

TE	DEPTH METERS	SEDIMENT TRACE METAL MEANS Leach/Total,% Leachable					SEDIMENT CHARACTERIZATION		
		V(µg/g)	Ba(µg/g)	Al(µg/g)	Cr(µg/g)	Fe(µg/g)	% $CaCO_3$	%< 62 µm	% TOC
848	68	3/ 17 20%	26/ 380 7%	119/ 53,100 0.2%	2/ 8 20%	617/ 5800 11%	ND	ND	ND
816	75	2/ 41 4%	10/ 255 4%	338/ 72,000 0.5%	1/ 30 5%	650/ 9080 7%	69.2	0.1	0.22
806	98	3/ 37 9%	14/ 528 3%	1291/117,000 1%	4/ 73 5%	1740/11,800 15%	19.2	36.6	0.84
807	102	3/ 40 8%	33/ 517 6%	1251/ 89,000 1%	6/ 71 8%	2533/11,500 22%	16.5	22.5	0.81
808	105	4/ 45 9%	24/ 478 5%	782/105,000 0.7%	4/117 3%	1311/18,800 7%	28.7	8.5	0.53
844	111	3/ 26 12%	30/ 741 4%	350/ 93,000 0.4%	5/NO	940/NO	37.8	23.1	0.58
818	174	3/ 14 19%	13/ 167 8%	329/ 20,500 2%	4/ND	505/ND	57.3	0.3	0,23
805	237	3/ 25 13%	43/ 445 10%	792/ 85,000 0.9%	7/ 62 12%	2319/12,600 18%	32.2	17.0	0.94
809	259	5/ 30 18%	50/ 467 11%	886/ 43,000 2%	9/ 64 14%	3335/27,800 12%	64.9	6.8	0.68
841	340	14/ 53 27%	156/ 557 28%	1124/ 28,700 4%	18/ND	3667/ND	51.2	0.4	0.90
870	385	3/ 71 5%	34/ 607 6%	1895/ 77,900 2%	2/ND	507/ND	56.8	26.6	0.63
817	520	8/ 35 23%	63/ 544 12%	1041/ 76,000 1%	27/190 14%	2953/17,400 17%	36.7	10.5	1.31
814	943	8/ 61 13%	70/1265 6%	1352/ 65,000 2%	7/ 68 10%	2658/21,700 12%	22.4	95.5	4.8a
811	1719	17/112 15%	59/ 930 6%	2069/112,000 2%	12/ 87 14%	6030/31,100 9%	7.5	98.4	4.88
813	1740	22/ 52 42%	79/1340 6%	1448/ 91,700 2%	7/ND	2907/ND	19.1	92.1	4.79
812	1866	22/112 20%	47/1150 4%	2222/1 17,000 2%	9/ND	5306/ND	7.7	97.7	4.66
Mean, S.D.		7±7/48±29 15% n=16	47±36/648±348 7%	1081±633/77,900±29,800 1%	8±7/77±49 10% n=10	2374±1672/16,800±8200 14% n=16 n=10	35.1±20.5 n=15	35.7±39.0 n=15	1.79±1.90 n=15

Channel Islands Seaward Shelf - 805, 806, 807, 808, 809

Santa Cruz Basin - 811, 812, 870

Santa Rosa, Cortes Ridge - 816, 818, 841, 844, 848

San Nicolas Basin - 813, 814, 817

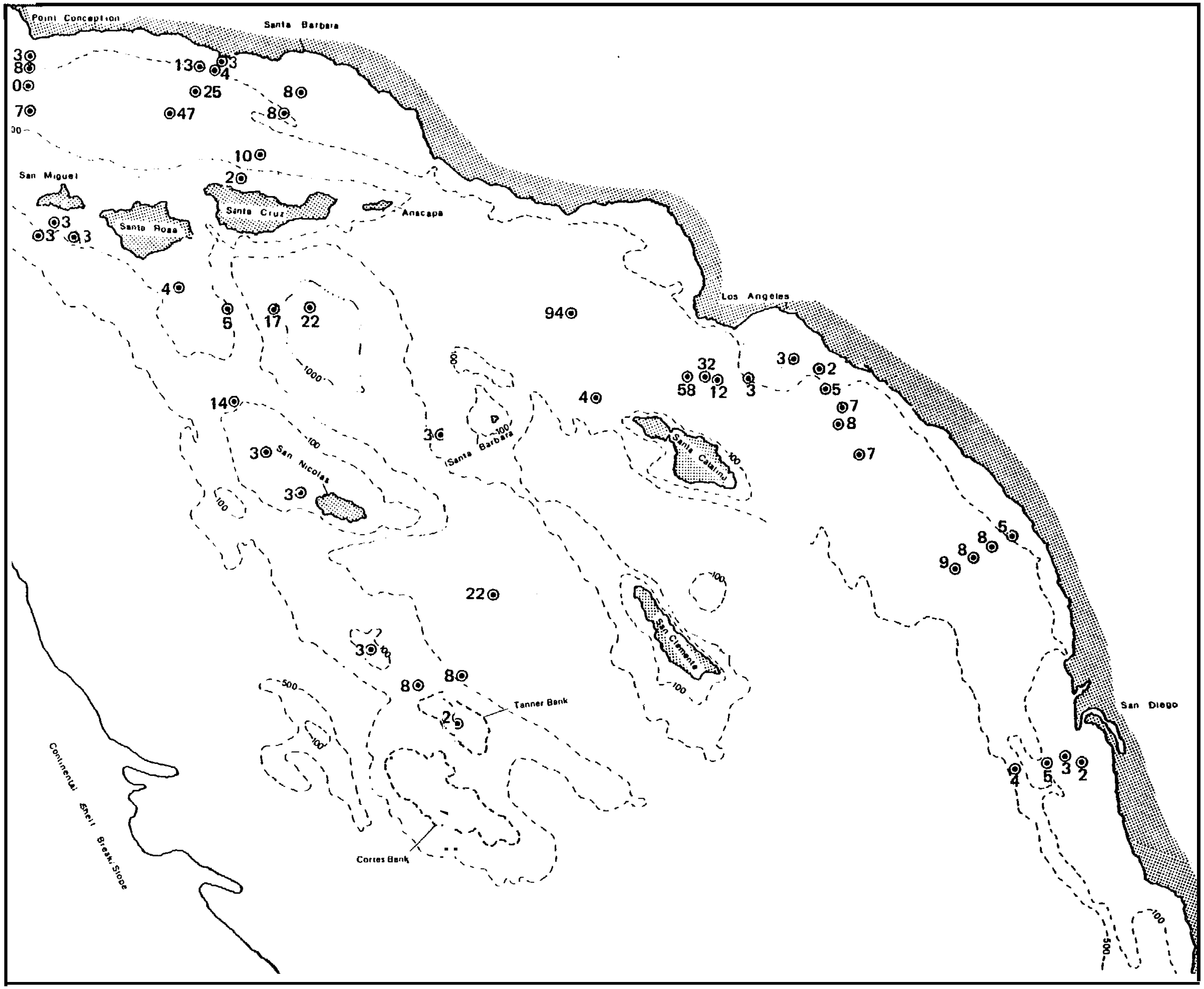

Figure II-9.0-3. Distribution of leachable sedimentary vanadium (μg/g dry weight).

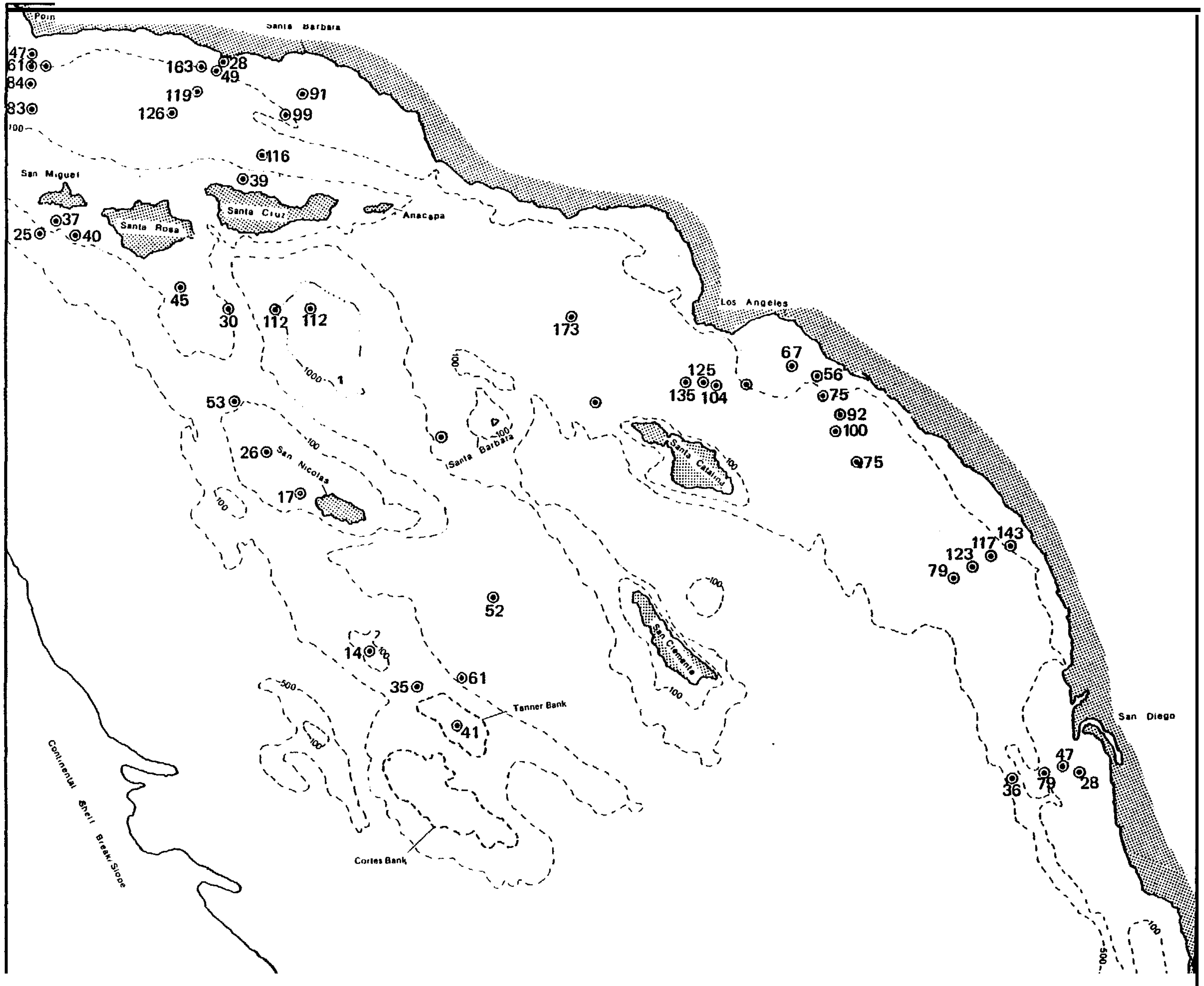

Figure II-9.0-4. Distribution of total sedimentary vanadium (µg/g dry weight).

Figure II-9.0-5. Distribution of leachable sedimentary barium (µg/g dry weight).

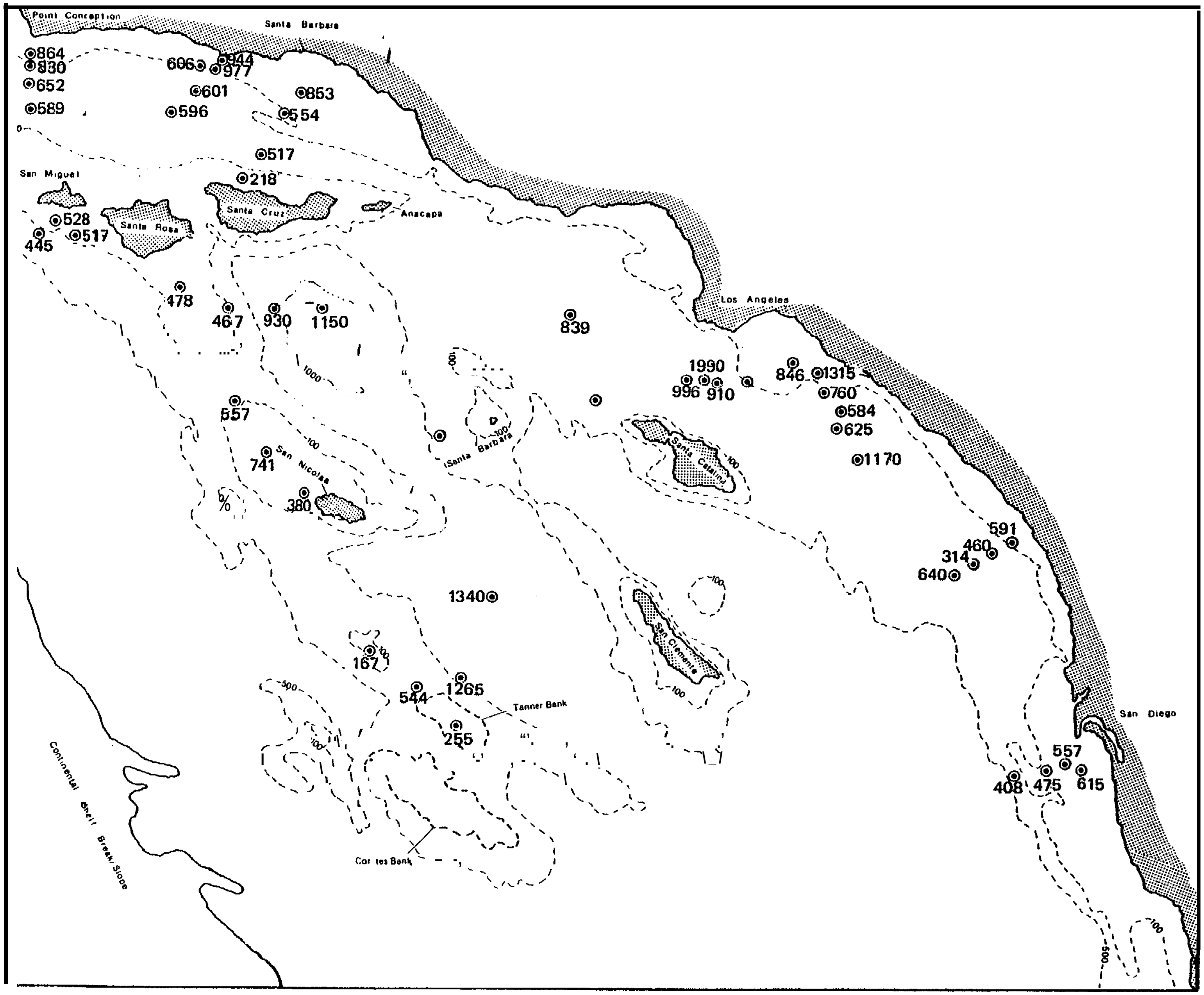

Figure 11-9.0-6. Distribution of total sedimentary barium (μg/g dry weight).

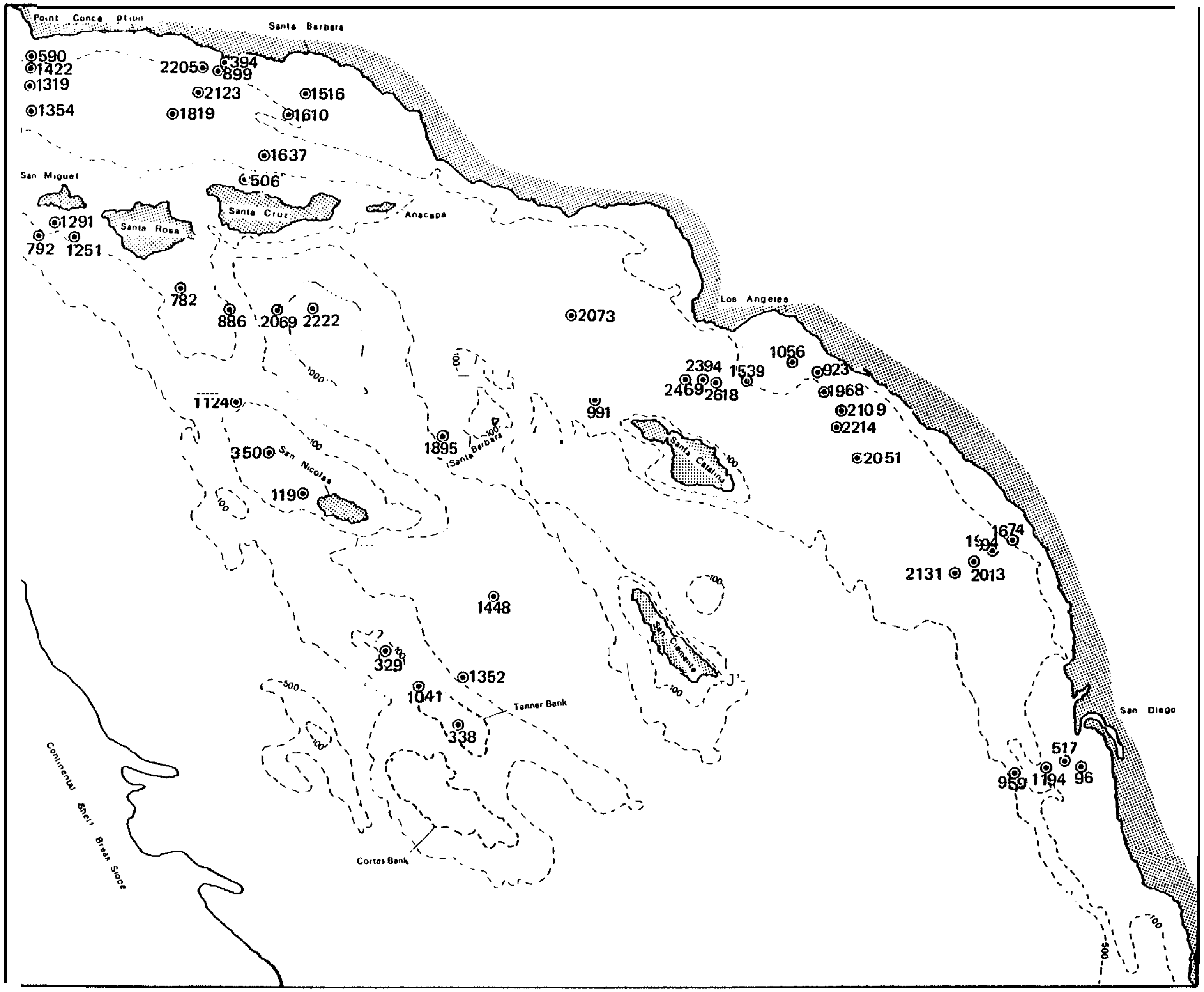

Figure II-9.0-7. Distribution of leachable sedimentary aluminum (µg/g dry weight).

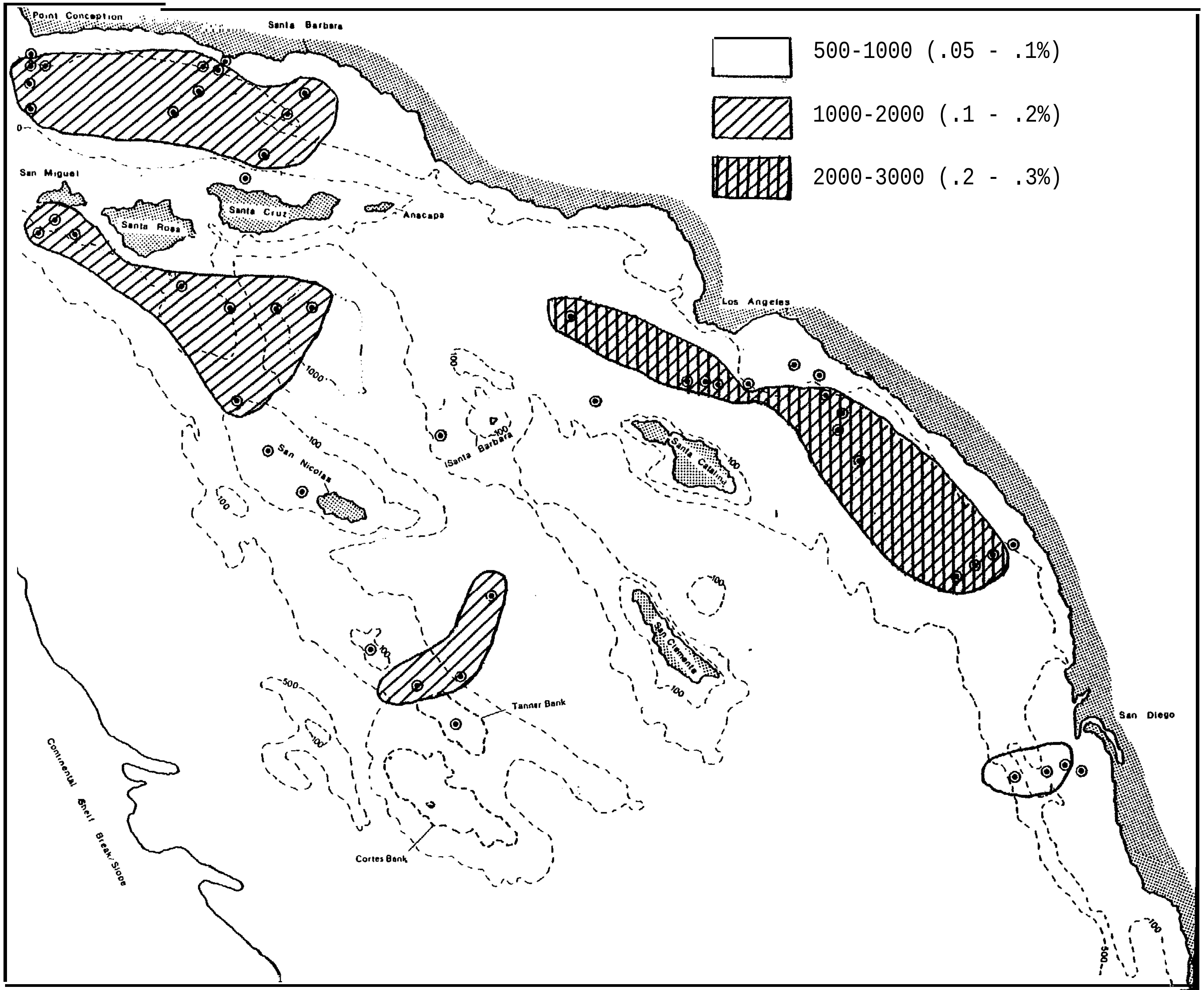

Figure 11-9,0-8. Areal distribution of leachable sedimentary aluminum (μg/g dry weight).

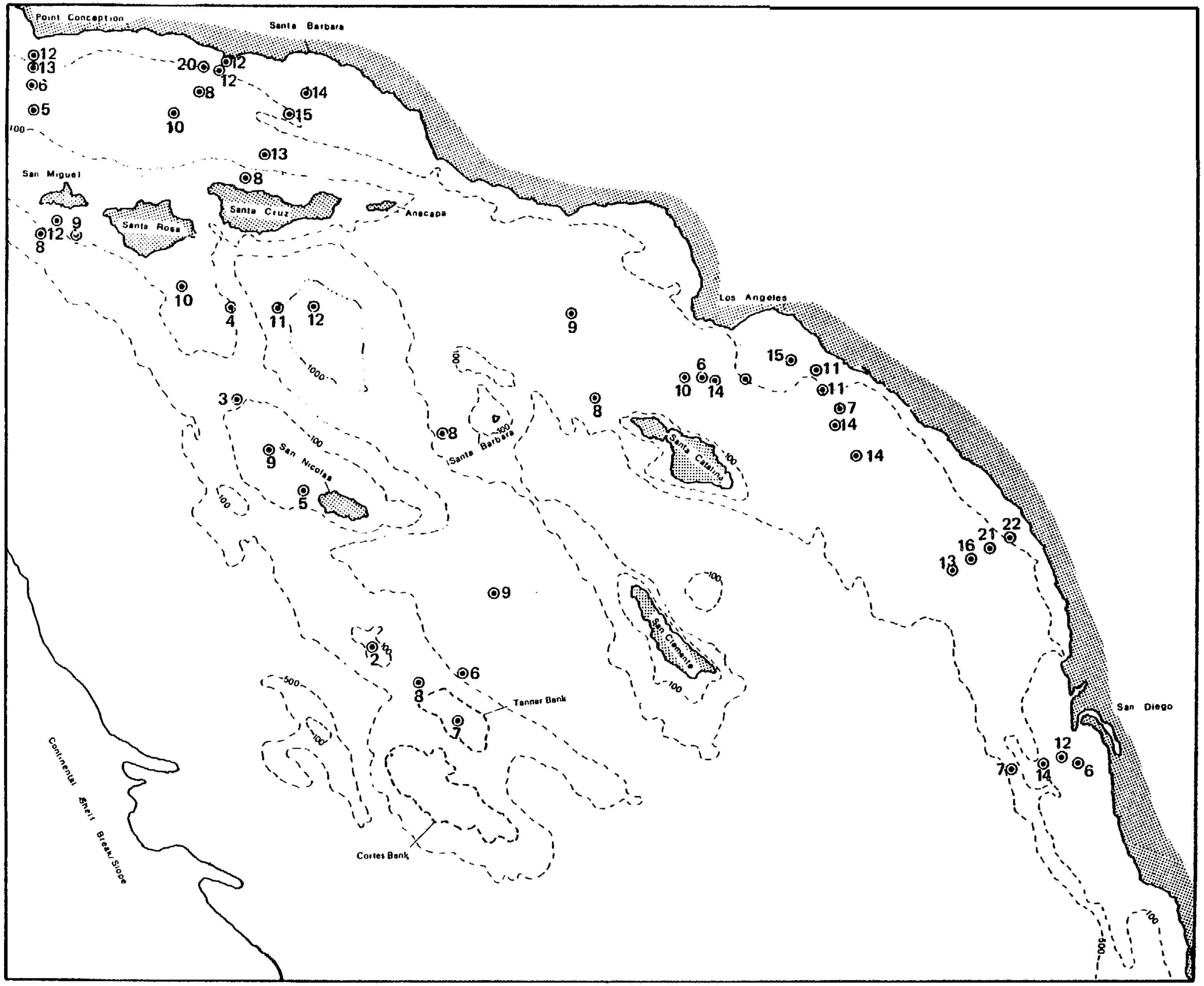

Figure 11-9.0-9. Distribution of total sedimentary aluminum (pph dry weight).

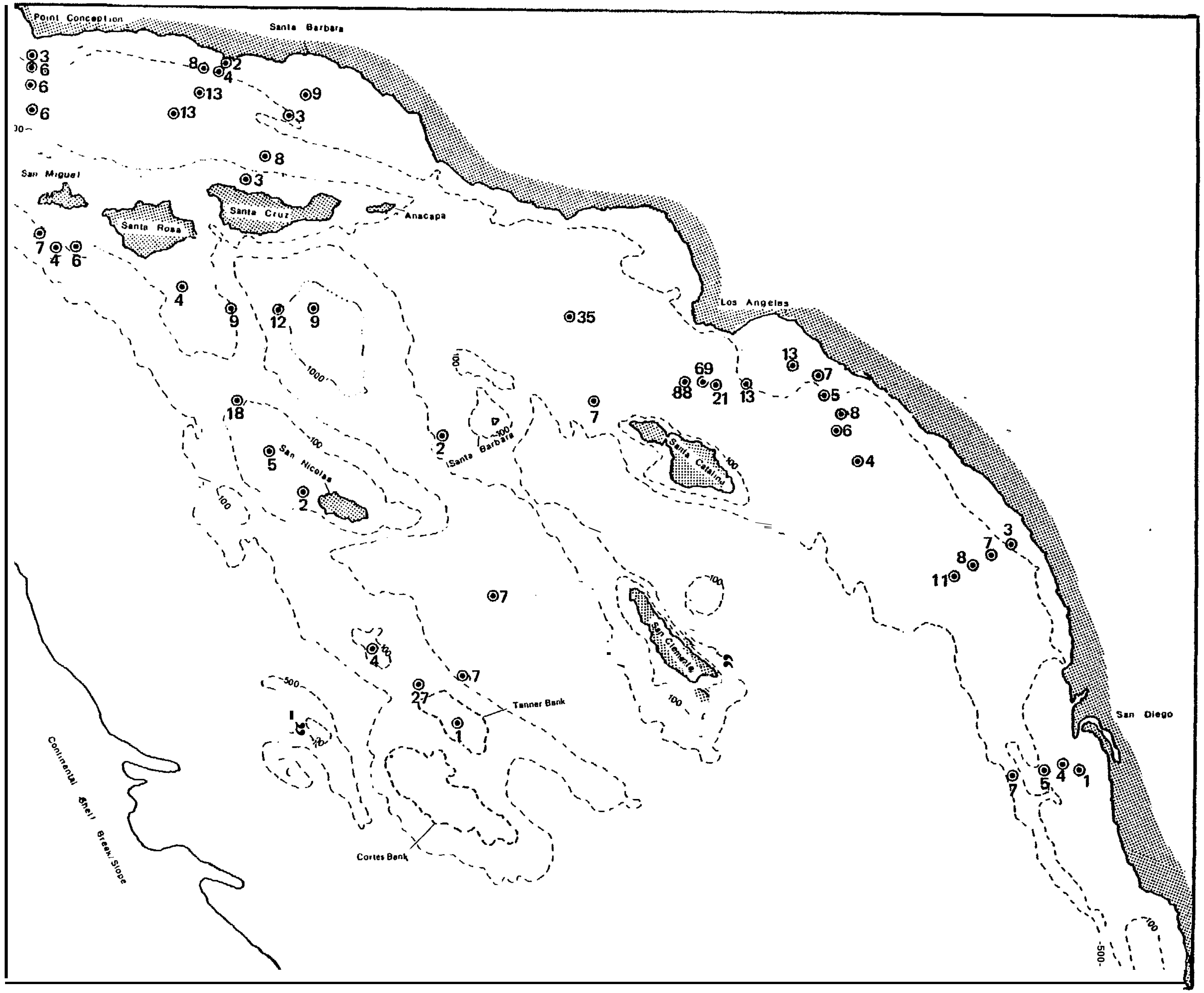

Figure II-9.0-10. Distribution of leachable sedimentary chromium (μg/g dry weight).

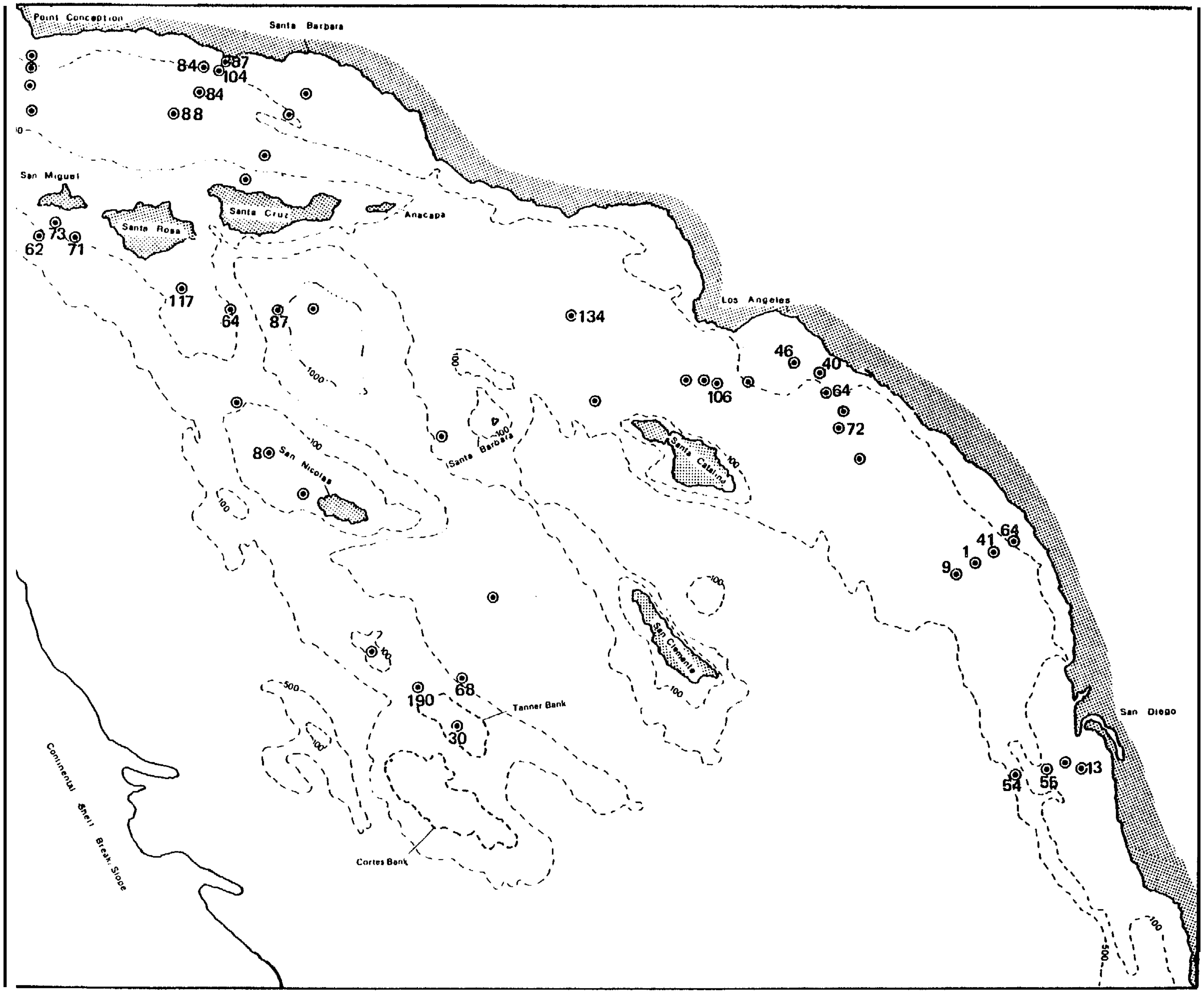

Figure 11-9.0-11. Distribution of total sedimentary chromium (ug/g dry weight).

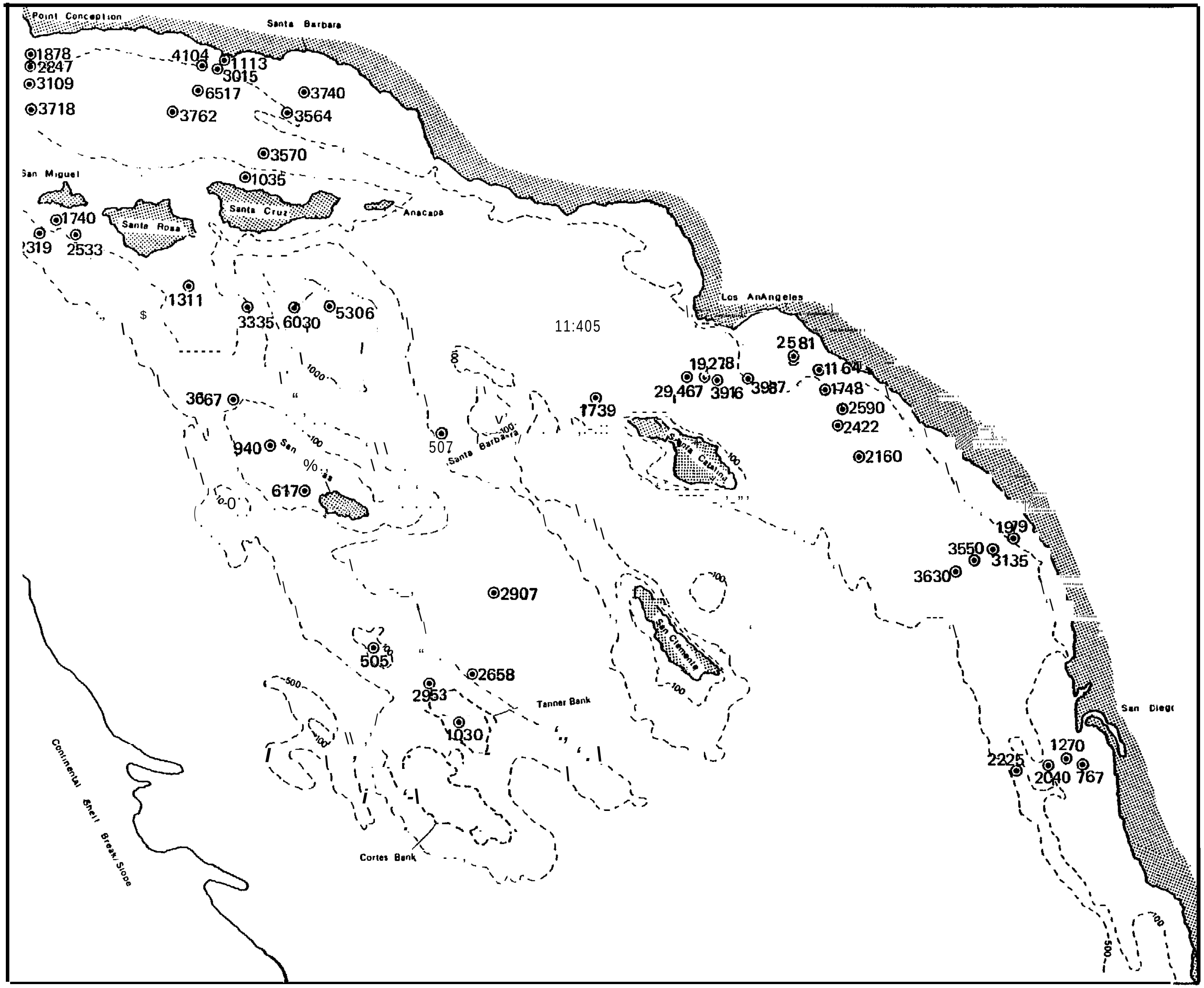

Figure 11-9.0-12. Distribution of leachable sedimentary iron (μg/g dry weight).

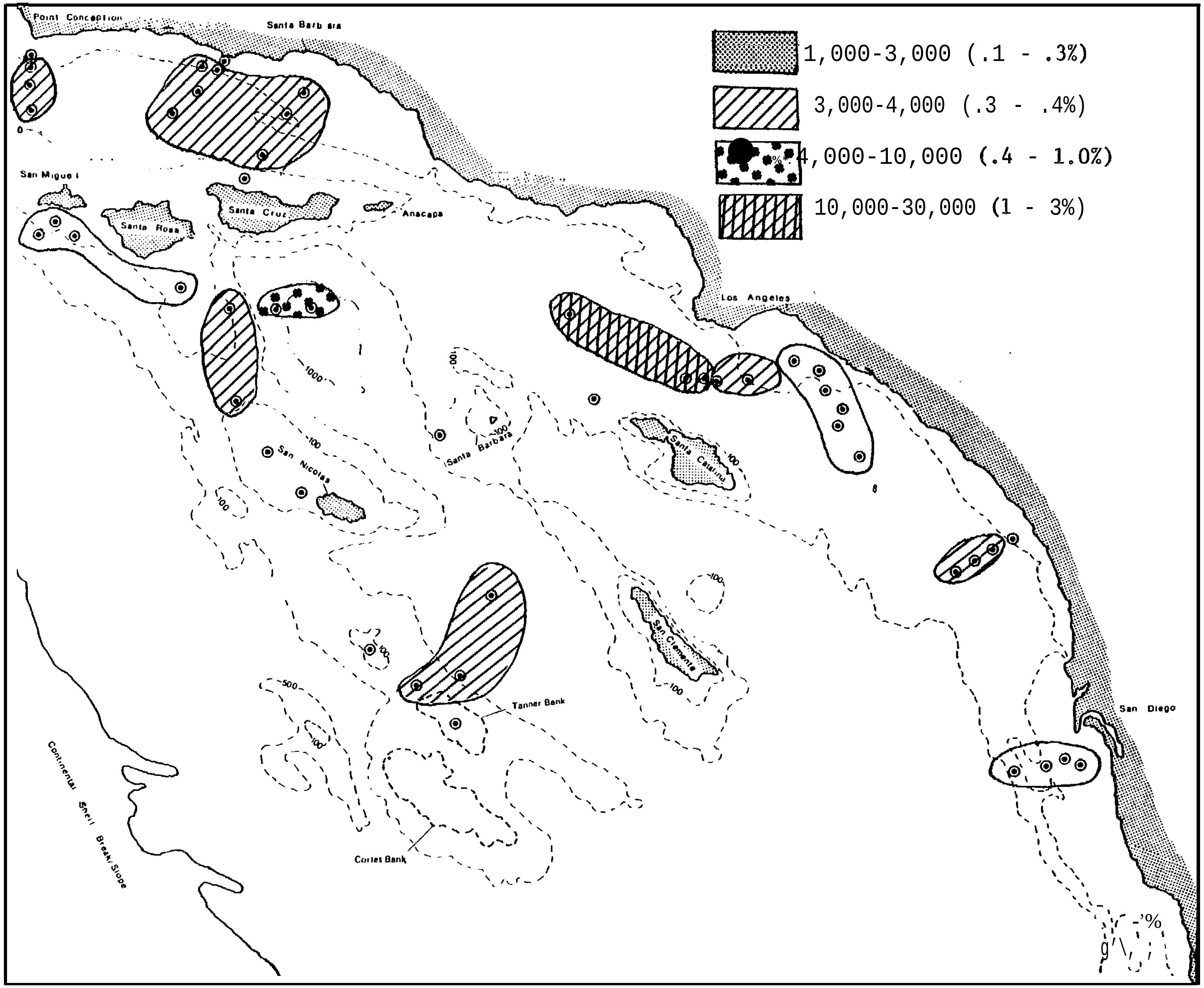

Figure II-9.0-13. Areal distribution of leachable sedimentary iron (μg/g dry weight).

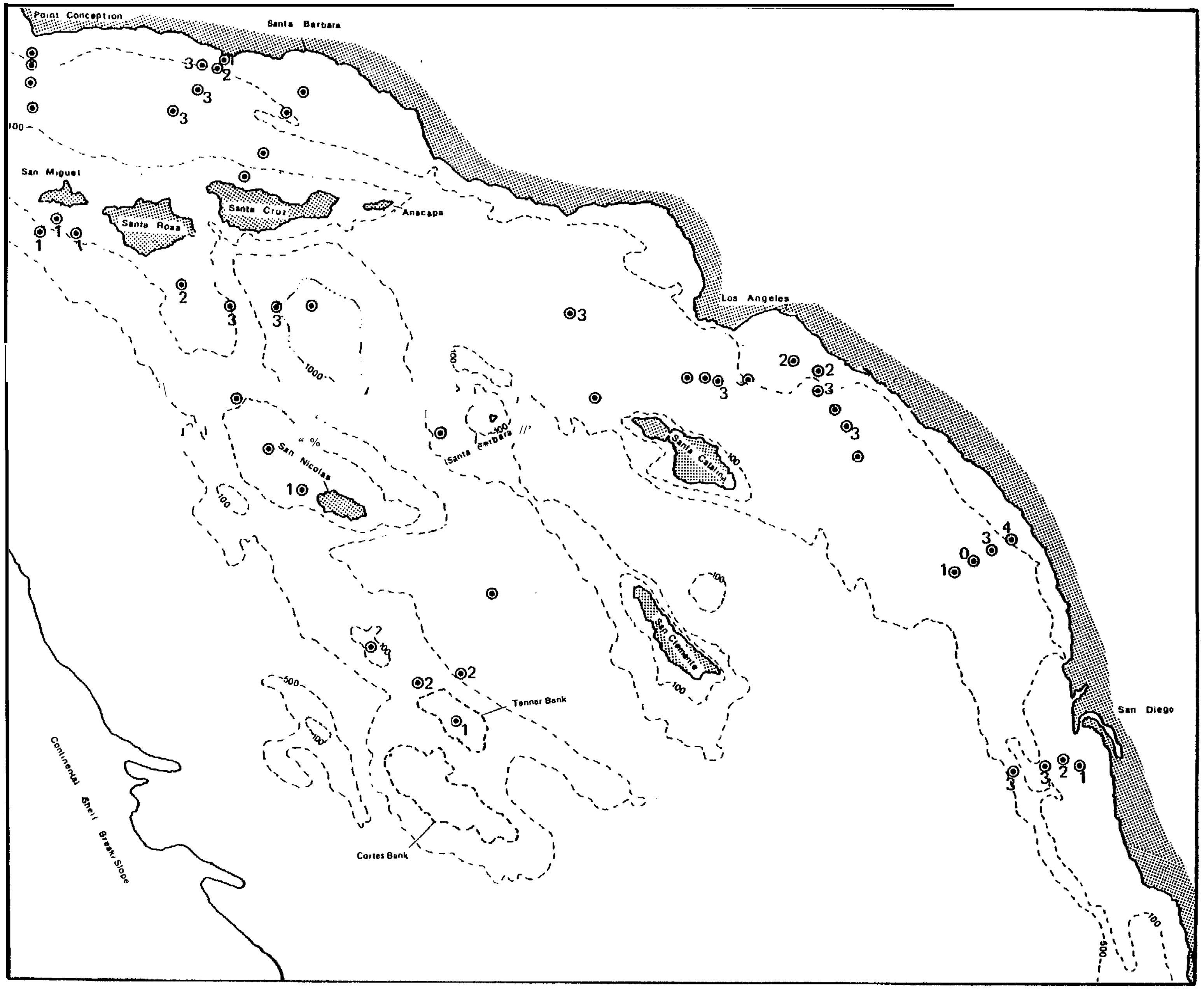

Figure II-9.0-14. Distribution of total sedimentary iron (pph dry weight).

potentially perturbable chemical constituents to others which are usually immune to alteration by virtue of their high natural concentration levels (e.g. , metal/Fe or metal/Al ratios; Shokes et al., 1978).

9.3.2 Trace Metals in Benthic Biota

Volume IV, Report 9.0 contains all the raw tabulated data which includes: Ba and V concentrations in replicate samples of Sebastes saxicola liver tissue (Tables IV-9.0-8 through IV-9.0-10); Ba and V concentrations in replicate samples of Lyopsetta exilis (Tables IV-9.0-11 through IV-9.0-14).

The results of the geographic comparison of the mean Ba and V values for Sabastes saxicola are presented in Table 11-9.0-9. Since only two sites were sampled during the March 1977 (winter) collection (MIG and PC), only this comparison is made and statistically (at $P < 0.05$) there are no significant differences in the mean Ba and V concentrations in the samples collected from these two sites.

In contrast, the mean Ba contents in S. saxicola livers among the three sites sampled during July 1977 (summer) are highest in the samples collected from COP. Also, the samples from PC, while they contain less Ba than those from COP, are greater than the samples from MIG. The mean V concentrations are not significantly different among the samples collected from the three sites.

Table 11-9.0-10 presents the results from the geographical comparison of winter Lyopsetta exilis. There are statistically no differences in the mean Ba values among the samples collected from MIG, NTAN and PC. However, the samples from COP are lower in Ba. Vanadium concentrations follow a somewhat similar trend in that the samples from NTAN, MIG and COP are not statistically different among themselves but are all significantly greater than the samples from PC.

There are no significant geographical differences in either the Ba or V concentrations in the samples collected in July 1977 (summer).

In all instances where the Ba and V mean values are significantly different, the winter samples contain greater values than the summer samples. This is true for both S. saxicola and L. exilis (Tables II-9.0-11 and 11-9.0-12. Similar trends were observed for other metals (Volume II, Report 10.0).

Table 11-9.0-13 presents the results of intraspecies comparison of Ba and V values for S. saxicola and L. exilis. In all but two cases, there is no difference in the mean Ba and V concentrations between the two. L. exilis is significantly higher in V than S. saxicola

Table 11-9.0-9. Seasonal Comparisons of Mean Values for Barium and Vanadium in the Liver of S. Saxicola (concnetrations in µg/g dry weight) March versus July 1977.

	Barium	Vanadium
MIG	0.38-0.04[b]	0.27-0.10
PC	0.49-0.08	ns

[a]ns= not significant at ($P \leq 0.05$) First and second mean values correspond to March and July collections, respectively.

Table 11-9.0-10. Seasonal Comparisons of Mean Values for Barium and Vanadium in the Liver-of L. Exilis (concentrations in µg/g dry weight (March versus July 1977.

	Barium	Vanadium
MIG	ns[a]	ns
PC	0.12-0.05[b]	ns
COP	0.07-0.03	0.96-0.17

[a]ns = not significant at ($P \leq 0.05$) First and second mean values correspond to March and July collections, respectively.

Table 11-9.0-11. Species Comparison of Mean Barium and Vanadium Values in Livers from S. Saxicola and L. Exilis (concentrations in μg/g dry weight).

WINTER (MARCH 1977)

Metal	San Miguel S. Saxicola	San Miguel L. Exilis	Point Conception S. Saxicola	Point Conception L. Exilis	Coal Oil Point S. Saxicola	Coal Oil Point L. Exilis
Barium	0.38±0.31	0.38±0.77	0.49±0.51	0.12±0.07	--[a]	--
Vanadium	0.27±0.12	1.39±1.44[b]	0.23±0.12	0.24±0.22	--	--

SWER (JULY 1977)

Metal	San Miguel S. Saxicola	San Miguel L. Exilis	Point Conception S. Saxicola	Point Conception L. Exilis	Coal Oil Point S. Saxicola	Coal Oil Point L. Exilis
Barium	0.04±0.02	0.06*0.06	0.08±0.05	0.05*0.05	0.31*0.30	0.03±0.02[b]
Vanadium	0.10±0.15	0.76±1.84	0.12±0.15	0.23*0.35	0.15±0.073	0.17±0.27

[a]No samples collected

[b]Significant difference between species at ($P \leq 0.05$).

Table 11-9.0-12. Geographical Comparisons of Mean Values for Barium and Vanadium in the Liver of S. Saxicola (concentrations in µg/g dry weight).

	Barium	Vanadium
March 1977		
MIG VS. PC	ns[a]	ns
July 1977		
MIG vs. PC	0.04-0.08[b]	ns
MIG VS. COP	0.04-0.31	ns
PC vs. COP	0.08-0.31	ns

[a]ns = not significant at ($P \leq 0.05$)

[b]First and second mean values correspond to frst and second location, respectively.

Table 11-9.0-13. Geographical Comparisons of Mean Values for Barium and Vanadium in the Liver of *L. Exilis* (concentrations in µg/g dry weight).

	Barium	Vanadium
March 1977		
NTAN VS. COP	0.17-0.07[b]	ns[a]
NTAN VS. MIS	ns	ns
NTAN VS. PC	ns	1.61-0.24
COP vs. MIG	0.07-0.38	ns
COP vs. Pc	0.07-0.12	0.96-0.24
MIG vs. PC	ns	1.39-0.24
July 1977		
COP vs. MIG	ns	ns
COP vs. Pc	ns	ns
MIG VS. PC	ns	ns

[a]ns = not significant at ($P \leq 0.05$).

[b]First and second mean values correspond to a first and second location, respectively.

from MIG during the winter (March 1977) sampling period and S. saxicola is greater than L. exilis in Ba from COP during the summer (July 1977) sampling period.

9.4 DISCUSSION

9.4.1 The Benthic Surficial Sediments

Some sample areas were designated as benchmark sites and these areas (28 stations) were sampled once in the winter and again in the summer. Six replicate sediment samples were collected during each sampling; the summer benchmark replica tes were pooled (Volume II, Report 8.0) and analyzed as a single sample, whereas the winter replicates were anal yzed individually. Most benchmark stations were locations re-occupied from the initial (just prior) year's sampling.

Samples from 21 descriptive sites were all collected during the winter cruise. Six replicates from nine of these stations were combined (Volume II, Report 8.0) to make a single pooled sample. Single replicates were analyzed from the other 12 stations. Only one descriptive area was a re-occupation of the previous year's sites.

9.4.1.1 Santa Barbara Basin Surficial Sediments

Santa Barbara Basin was sampled in this study by three traverses (13 stations) extending southerly from the mainland. The first traverse is off Point Conception at the basin's western margin. The second is off Coal Oil Point and the third traverse extends out to Santa Cruz Island (Station 876) on the eastern margin of the area (Figure II-9.0-2 shows the station locations). Table 11-9.0-5 presents means of three sediment characterization parameters: percent $CaCO_3$, percent fines (grain diameter less than 62 µm), and percent total organic carbon (TOC). These are arranged in order of increasing station water depth. The Santa Barbara Basin sediments (Table 11-9.0-4) are seen to be relatively low in $CaCO_3$ (except the Santa Cruz Island station), high fines (clay-rich) especially in the deeper samples, and also, tending toward high TOC with increasing water depth.

Following these ambient sediment trends, one can observe similar patterns in the mean concentrations of V, Ba, Al, Cr, and Fe in both the total sediment and the sediment leachate (relative to water depth (Table II-9. 0-5) . The mean leachable fraction of each metal can serve as an indicator of abnormal anthropogenic inputs; however the mean percent leachable fractions presented in Table 11-9.0-4 show no unusual values for this basin, despite the fact that Station 804 in the middle of the basin off Coal Oil Point (Table 11-9.0-5 and Figure 11-9.0-2) has elevated concentrations of leachable V and Cr.

9.4.1.2, Santa Monica and San Pedro Basin Surficial Sediments

The 12 stations that describe Santa Monica and San Pedro Basins are arranged in two traverses extending westerly and southerly from the same point on the mainland (Long Beach); Station 829, however, lies by itself in the deep waters of Santa Monica Basin. Table 11-9.0-6 presents the average sediment characteristics and trace metal concentrations from this area in order of increasing water depth. These two basins contain sediments having some of the highest clay and total organic carbon content in the entire Southern California Ocs. Also, Santa Monica and San Pedro Basins are deepepr than Santa Barbara Basin, and their sediments are lower in $CaCO_3$.

Santa Monica and San Pedro trace metal concentrations are characterized by unusually high mean leachable V and Cr values (Table II-9.0-4). Interestingly, Stations 819 and 824 are located on the mainland shelf rather than within the basins proper. Although the sediments of these two stations are expected to be dominated by terrigenous materials, their metal contents and proximity to the Los Angeles are suggest anthropogenic effects.

9.4.1.3 Gulf of Santa Catalina and San Diego Trough Surficial Sediments

The Gulf of Santa Catalina and the San Diego Trough were each sampled at four stations traversing each region (Figure 11-9.0-2). Table II-9.0-7 presents their sediment characterizations and the NAA trace metal concentrations in order of increasing depth. Table 11-9.0-4 compares the mean concentrations of these data with the other regions described in this study. Examination of these parametric means indicates that this area is characterized by lower trace metal concentrations than are the inner basins previously described and that they compare favorably with the "pristine'" outer regions. The percent fines and organic content are again seen to increase with depth; however, Station 869, the deepest in the San Diego Trough, is seen to have high $CaCO_3$ when compared to the other members of this set.

9.4.1.4 Surficial Sediments of the Outer Regions

The "outer regions" are actually several areas, each with its own characteristic geology. They are reported here as a single grouping so as to differentiate these stations from those located near potential mainland anthropogenic inputs. There are five stations covering the Channel Islands seaward shelf (805, 806, 807, 808, and 809), three stations in the Santa Cruz Basin (811, 812, and 870), and five stations in the San Nicolas Basin (817, 814, 813). Table 11-9.0-4 compares their mean NAA trace metal concentrations with the other regions described above, and Table 11-9.0-8 presents these data station by station, along with the appropriate sediment characterization parameters, in order of increasing water depth.

These sediments are high in $CaCO_3$ with concomitant low fine fractions and TOC. The heavy metal contents are generally low as typical for high carbonate sediments. However, the Ba concentrations are the highest observed in the Southern California OCS, trending positively with the high $CaCO_3$ concentrations.

9.4.2 The Benthic Biota

The results of the Ba and V data obtained during this study are extremely difficult to interpret for several reasons.

The use of teleost fish as indicator species has its advantages and disadvantages. It is true that fish normally contain valid levels of trace elements such as Ba and V when compared to sessile or true benthic invertebrates. Most benthic invertebrates have been documented to contain high levels of metals as a result of sediment entrainment in their digestive tracts, rendering attempts to classify their tissue invalid (Brooks and Rumsby, 1965; Presley et al., 1972; Sims and Presley, 1976). However, when tissues are carefully dissected, cleaned and analyzed one can obtain valid concentrations for benthic invertebrates (Shokes et al., 1978). It is also true that fish are extremely mobile and move from area to area when compared to benthic invertebrates. Thus, one obtains integrated data over a larger area making geographic trends less distinct. Benthic invertebrates in contrast are less mobile.

Gordon et al. (Volume II, Report 10.0) have observed that factors such as age (length), sex, spawning cycle, geographic location, feeding habits, season, and chemical stress (pollution) may all interact to influence trace element levels in organisms.

9.4.2.1 Geographical Comparisons

Only two sites were sampled for S. saxicola during winter 1977 (MIG and PC). From the data presented in Table 11-9.0-9 it can be seen that there are no significant differences (at $P < 0.05$) in the mean Ba and V values between the two sites. Also, during the summer 1977 sampling period there are no differences in the mean V values among MIG, PC and COP. It must be remembered that most of the Ba and V values obtained are extremely low, in most cases being at or near the detection limit, thus adding to the relative error and statistical insignificance of the data. However, geographical differences were seen in the mean Ba values among the sites sampled. Samples from MIG contain the least amount of Ba, while samples from PC contained a higher level and those from COP contained the highest. There were no significant differences in the sizes of the fish collected from these three sites. Therefore the differences in the mean Ba values may indeed be due to geographically-related influences. This is not surprising since MIG is known to be a relatively pristine area. Gordon et al. have noted similar trends for other trace metal values in S. saxicola from these sites (Volume II, Report 10.0).

In the case of L. exilis, there are no significant differences in the mean winter 1977 Ba values among MIG, NTAN and PC. However, there is a significant difference in the levels of Ba between these sites and COP* This is somewhat of a paradox; even though L. exilis is known to be a bottom feeder (Frey, 1971), MIG is a relatively "clean" area and COP is an oil-impacted area. Thus, if L. exilis, because of its feeding habits, can concentrate Ba, it would be expected that samples from MIG and COP would show different results. However, levels for V in L. exilis show similar winter 1977 results, with the mean values among NTAN, MIG and COP being statistically the same, although samples from PC are significantly lower than those from the other sites. In contrast, there are no differences in either the Ba or V levels in the samples collected from among the various sites during the summer 1977 collection. This does not deviate drastically from the observed results during the winter 1977 in which two out of three sites also sampled during the summer 1977 (MIG and PC) are statistically the same in their Ba levels. For V, the COP and MIG sites show no difference in their mean values (as is the case during the winter 1977).

9.4.2.2 Seasonal Comparisons

The mean Be and V levels for both S. saxicola and L. exilis were greater (for all sites) in the livers-from the winter 1977 collection than they were in the summer 1977 (Tables 11-9.0-10 and 11-9.0-11). Several possible explanations exist. Gordon et al. (Volume II, Report 10.0) have shown that in some cases length of fish appeared to show positive correlations with metal levels, whereas in other cases the correlation was minimal. However, correlations among mean liver weight, season and metal level (Ba and V) are, in most cases, quite positive. This is true not only for S. saxicola but also for L. exilis. During collection, it was observed that gonadal maturation in both S. saxicola and L. exilis was quite distinct in winter 1977 when compared to summer 1977. The livers were greatly reduced in size during winter 1977, possibly related to this trend in gonadal maturation. It is not unreasonable to suggest that a decrease in mean liver weight in winter 1977 may be a dominant factor in controlling the mean Ba and V levels. This is especially true if the total amounts of these metals, as measured during the summer, were retained in the smaller "winter livers.

9.5 CONCLUSIONS

9.5.1 The Benthic Sediments

Surficial sedimentary concentrations of V, Ba, Al, Cr, Fe and Zn were seen to relate closely to the geochemical and geographical sediment character zations. The fine grained (clay-rich) and high organic carbon sediments were found to have highest concentrations of V, Al, Cr and Fe. Elevated values were also seen in the pollution zones surrounding Coal Oil Point and the Los Angeles Shelf. Barium was seen to be more directly related to carbonate content than to grain si ze.

The leachable fractions of the benthic sediments provided an interesting parameter for geographical comparisons. When normalized to its total metal concentration, the percent leachable can be used as an indicator of a perturbed environment.

9.5.2 *The* Benthic Biota

Geographical saxicola from MIG contain the lowest levels of Ba. Vanadium levels were not significantly different among the sites. In general there are no geographical trends in Ba and V levels in L. exilis, with many of the mean values being statistically the same.

In all cases, seasonal comparisons in the two fish species show a definite decreases in both Ba and V from the winter to summer 1977. This is probably due to reduction in the liver weight which is in turn related to gonadal maturation.

Species comparisons, for the most part, show no differences in the levels of Ba and V between the two species.

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