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Heavy Metals & Mineralogy in Sediment Cores from a Tropical Coastal Lagoon, Mexico

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Concentrations of Fe, Co, Ni and Cd in this lagoon are comparable to similar but affected systems. Cu, Zn, Cr and Pb are, however, lower than those found in contamined estuaries. One core (CP-3) shows an exponential increase of all metals toward the surface. This distribution may lead to erroneous interpretations, attributing it to pollutant input. Clay minerals of the cores consist of kaolinite (41-69%), illite (21-52%), montmorillonite (1-12%) and traces of gibbsite. Variable proportions of illite and kaolinite in the Copala river core can be explained by a depositional environment with varying influence from non-marine to marine conditions. Quartz, feldspar and amphiboles found in the silt fraction of all cores indicate that the sediments in all parts of the lagoon are composed mainly of detrital material.

The importance of coastal lagoons has been well established[1-9]. Though elemental composition and mineralogy in estuarine sediments have been studied intensively with a view to assessing the impact of man's activities and understanding the geochemical processes in this transition area, comparatively tropical coastal lagoons have received little attention.

The present work has been undertaken to collect data on Fe, Co, Ni, Cu, Cd, Cr, Pb, Mn, Zn concentrations and clay mineralogy of Chautengo lagoon, a tropical coastal lagoon situated on the West coast of Mexico and to elucidate the processes responsible for the observed variations in the lagoon.

Chautengo lagoon has an area of 36 km^2 and a depth range of 1-1.8 m, the climate of the area is subhumid tropical (type AW[10]), with a marked seasonal distribution of rainfall. There is no human activity in the drainage basin.

Materials and Methods

Sediment cores (5 cm diam.) were collected in May 1981 from 5 locations (Fig. 1) using a polyvinyl chloride pipe in a modified Phleger corer. General characteristics of the cores are shown in Table 1. The cores were immediately frozen with dry-ice and, once in the laboratory, were X-rayed to ascertain the presence of sediment structure. Organic matter was analysed as CO_2 using a Strölein tube (550°C)[11]. Carbonates were determined by a modification of the technique of Dean[12], also using the Strölein tube and measuring CO_2 after ignition at 1000°C.

Metals—The dry sediment (1-3 g) was treated[13] with concentrated HCl, HF, HNO_3 and $HClO_4$. The metals were extracted with dilute acid solution and appropriate dilutions were made for determination of heavy metals on a Varian Techtron 1200 atomic absorption spectrophotometer. The precision of the analysis was within limits[13]. The residues, after acid digestion, were further analised to investigate the possible occurrence of Fe, Co, Ni, Cd, Cr, Cu, Mn, Zn and Pb. Repeated analysis with X-ray fluorescence (Cr-radiation 50KV, 20mA) revealed that the residues are consistently composed of Al, Zr, Sr, Rb, Ti, Ca and Ba.

Size distribution and mineralogy—Each sample was dispersed in deionized-distilled water and additionally treated, in an ultrasonic bath, with Na-phyrosphosphate ($Na_4P_2O_7$) as dispersing agent[14]. Three size fractions (>62, 2-62 and <2μm) of each section were

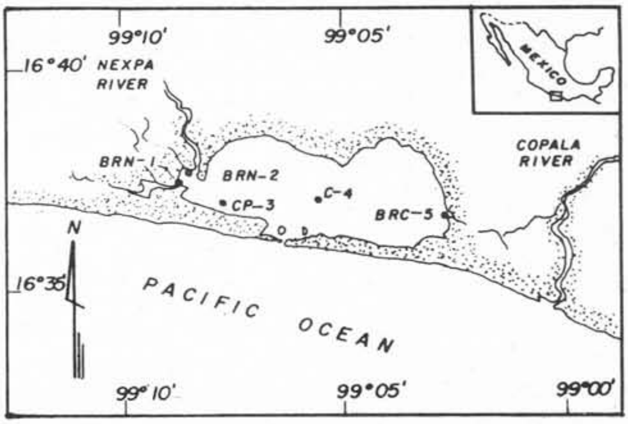

Fig. 1—Locations of Chautengo lagoon cores, Mexico

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*For correspondence.

Table 1—General Characteristics of Sediment Cores (adapted from Páez-Osuna *et al.*[11])

Core	Texture	Depth (m)	Environment (Berner[23] criteria)	Collection site
BRN-1	clayey silt	0	Post-oxic	Inundation zone at the mouth of Nexpa River
BRN-2	sandy silt	0	Post-oxic	
CP-3	sand-silt-clay	1.2	Oxic	Main channel
C-4	silty clay	1.6	Sulfidic	Basin in the center of the lagoon
BRC-5	clayey silt	1.0	Post-oxic	Mouth of Copala River

separated by wet sieving and decantation. The last 2 fractions were analyzed for mineralogy by X-ray diffraction.

For clay mineralogy 2 slides were prepared for each sample (≥ 4.4 mg.cm^{-2}); one was glycolated[15] and the other was untreated. The specimens were analysed on a Philips PW1410 X-ray diffractometer using Copper Kα radiation. Relative abundance of the minerals present was determined by a modification of Biscaye's method[16].

Results

Organic carbon and carbonates—Concentration of organic carbon varied between 0.74 and 6.74% in all cores (Table 2). The sediment core CP-3 showed lowest values while cores C-4 and BRN-2 showed higher values. An increase of organic carbon towards the surface in cores BRN-1 and CP-3 was evident.

Concentrations of carbonates did not vary significantly (0-2.20%). Most carbonates in the sediments seem to be of organic origin, chiefly composed of molluscan broken shells. The whole shells separated in cores C-4 and BRC-5 were identified as ***Polymesoda inflata***[17] although other reports[18-20] ***Mytella strigata*** as the most abundant species in Chautengo lagoon.

Mineralogy and size distribution—Table 3 gives weight percent of the sample in each of 3 size fractions, as well as relative proportion of clay minerals. C-4 core has the greater part of the solid phase in $<2\mu$m size class. CP-3 core shows a dominance of $>62\mu$m size fraction, while the silt fraction (2-62μm) is dominant in the river sediment cores.

CP-3 and BRC-5 cores show increase or decrease in exponential size distribution of sediment particles with depth depending the size class considered, and the remaining 3 cores do not show a consistent pattern.

Clay mineralogy was markedly uniform from surface to bottom in all cores, with the exception of core BRC-5 which showed variations in the relative concentrations of illite and kaolinite (21-52% and 41-69% respectively). In each core, kaolinite was the predominant clay mineral followed by illite and montmorillonite.

In the finest fraction ($<2\mu$m) the presence of peak 4.85 Å of gibbsite was observed in all samples. Quartz and feldspars were more abundant in the silt fraction, but small proportions of amphibole occurred in this fraction of the 5 cores. Additionally, pyrite was found in the silt fraction of core C-4 and the bottom sections (16-26 cm) of core BRN-2.

Heavy metals—The data (Table 2) reveal the following trends in the distribution pattern of the elements studied: (1) core BRN-1 shows an increase in metal concentrations with depth, being more significant for Mn; (2) core BRN-2 shows uniform concentrations of heavy metals over its entire length; (3) core CP-3 shows an exponential increase of all metals toward the surface; (4) in core C-4 the concentrations of Cd, Co, Cu, Cr and Ni do not vary significantly, while Fe, Mn and Zn variations do not show a systematic pattern with depth; (5) core BRC-5 shows lowest concentrations in its middle sections (4-16 cm); and (6) concentrations of Pb were below 9 ppm in all samples.

Correlation coefficients calculated from the results of each core are given in Table 4. Observations based on the data are as follows: (1) In core BRN-1, significant correlation is found between clay size fraction and Cd, Co, Mn, Ni and Zn concentration; Cr, Fe, and Cu show greatest correlation with the silt size fraction; for Zn and Cu the correlation is slightly better with the $<62\mu$m size class. (2) In core BRN-2, a positive correlation is observed for Cr with Fe but it is negative for Mn; Fe shows a positive correlation with Zn and the silt size class. (3) In core CP-3 there is a strong correlation between each parameter, and only for the $>62\mu$m fraction correlation is negative. (4) A negative correlation between organic carbon and clays is found in the cores BRN-1 and C-4 and, while lesser level of significance exists in core BRN-2. (5) For core BRC-5 a correlation coefficient of 0.96 is obtained for Cr versus silt fraction and Fe versus Mn; Zn with Fe and Mn also gives an $R > 0.93$.

Table 2—Chemical Analysis of Sediments

[Results expressed in ppm (except for Fe in %) are on dry weight basis]

Core	Depth (cm)	C-organic (%)	$CaCO_3$ (%)	Residue[a] (%)	Cd	Co	Cr	Cu	Fe	Mn	Ni	Zn
BRN-1	0- 2	6.74	-	14.2	1.2	16	50	23	2.5	326	23	42
	2- 5	2.94	1.36	17.6	2.1	31	53	30	4.1	414	47	90
	5- 8	1.89	0.51	10.7	2.1	31	54	33	3.9	469	48	94
	8-11	1.50	0.35	4.3	1.8	29	54	32	3.6	401	46	87
	11-15	1.41	0.41	17.2	1.9	30	67	33	6.4	461	50	99
	15-19	0.93	0.54	17.7	2.1	31	81	40	4.5	467	56	101
	19-23	1.66	0.49	12.8	1.9	34	55	35	5.0	554	51	111
	23-27	0.92	1.26	16.0	2.3	29	51	30	3.7	576	47	86
BRN-2	0- 2	3.11	-	-	2.5	31	56	34	4.7	515	44	92
	2-4	4.03	0.98	-	2.7	29	49	22	3.5	521	40	75
	4- 6	5.25	0.61	-	2.5	33	43	29	3.6	580	45	65
	6- 8	6.00	1.33	-	2.3	32	55	29	4.5	488	48	98
	8-10	5.16	-	-	2.0	30	44	30	4.0	610	49	89
	10-11	3.01	0.60	1.6	2.1	30	42	32	4.1	618	48	95
	11-13	2.92	1.04	18.2	2.1	31	58	33	4.4	424	51	95
	13-16	2.34	0.57	-	1.8	28	60	31	4.3	423	49	88
	16-19	5.12	0.74	-	1.8	29	51	31	4.4	523	48	92
	19-22	2.91	0.21	-	1.7	28	48	27	3.9	469	43	91
	22-26	5.47	1.12	-	1.8	28	53	34	3.7	469	42	81
CP-3	0- 2	1.90	0.59	5.4	2.5	31	48	40	3.9	630	48	135
	2- 4	1.43	1.27	7.8	1.7	24	44	22	3.2	463	35	69
	4- 7	1.09	0.60	13.8	1.5	22	37	23	2.8	401	37	63
	7-10	0.74	0.40	10.3	1.1	21	26	15	2.0	401	25	41
	10-30	0.87	0.40	9.6	1.4	26	20	14	2.0	351	27	43
C-4	0-10	1.90	-	-	3.1	36	60	42	5.0	998	61	109
	10-14	2.69	0.69	13.3	2.2	33	64	41	6.2	1063	70	119
	14-18	3.21	0.97	5.1	2.4	34	58	41	5.2	332	48	106
	18-22	3.25	-	16.5	2.5	33	62	46	7.7	911	56	96
	22-26	4.02	1.94	1.3	2.8	30	50	35	6.9	938	52	97
	26-30	3.31	1.09	20.7	2.1	26	55	37	4.7	669	47	88
	30-34	3.07	2.63	9.9	2.1	33	58	43	5.0	315	56	89
	34-38	2.76	0.47	0.5	2.9	29	55	37	5.0	875	50	101
	38-43	3.04	0.53	11.3	2.3	26	55	34	5.8	866	53	109
BRC-5	0- 2	3.62	-	-	2.9	34	68	34	4.4	430	58	79
	2- 4	3.26	-	28.4	2.2	34	64	31	4.8	356	53	71
	4- 8	2.58	0.90	-	2.2	23	58	26	3.1	345	50	74
	8-12	2.91	1.28	14.9	1.7	29	58	29	3.1	272	55	67
	12-16	6.59	1.46	3.9	1.9	29	50	38	2.6	321	46	71
	16-20	5.27	1.36	0.2	2.4	28	53	31	6.9	878	47	100
	20-25	2.65	2.25	10.3	2.5	38	55	45	8.3	1048	58	104

a= residue after acid digestion

Table 3—Size Distribution and Clay Mineralogy of Sediments

Core	Depth	Size fraction, %			Montmorillonite	Illite	Kaolinite
	(cm)	>62μm	2-62μm	<2μm	(%)	(%)	(%)
BRN-1	0- 2	46.5	49.0	4.5	1	41	58
	2- 5	18.1	61.8	20.1	6	37	57
	5- 8	18.0	63.2	18.8	3	40	57
	8-11	16.5	56.9	16.6	4	40	56
	11-15	13.2	64.9	21.9	5	39	56
	15-19	2.7	74.2	23.2	5	39	56
	19-23	1.9	69.0	29.2	5	42	53
	23-27	20.0	51.5	28.5	6	35	59
BRN-2	0- 2	30.5	52.4	17.1	3	36	61
	2- 4	63.5	28.0	8.5	2	41	59
	4- 6	58.3	31.2	10.5	2	40	58
	6- 8	39.3	48.8	11.9	3	32	65
	8-10	34.2	47.4	18.3	5	32	63
	10-11	8.5	67.8	23.7	3	36	61
	11-13	26.6	47.3	26.1	4	38	59
	13-16	42.0	47.7	10.3	3	39	58
	16-19	38.6	56.0	5.4	5	41	54
	19-22	43.3	50.5	6.2	4	37	59
	22-26	73.2	20.5	6.3	3	38	59
CP-3	0- 2	36.9	31.3	31.8	8	39	53
	2- 4	41.2	33.8	25.0	7	37	56
	4- 7	55.3	25.3	19.4	6	39	55
	7-10	73.3	15.0	11.7	6	38	56
	10-30	71.9	16.5	11.6	9	40	51
C-4	0-10	1.1	36.3	62.6	7	43	50
	10-14	0.6	39.6	59.8	9	42	49
	14-18	1.8	39.1	59.1	7	46	47
	18-22	6.6	39.4	54.0	9	44	47
	22-26	18.8	43.4	37.8	9	42	49
	26-30	7.9	36.6	55.5	12	40	48
	30-34	17.9	34.9	47.2	12	39	49
	34-38	12.7	36.3	51.0	10	43	47
	38-43	8.4	36.7	54.9	12	43	45
BRC-5	0- 2	10.6	78.9	10.5	7	52	41
	2- 4	17.7	68.2	14.1	5	44	51
	4- 8	24.3	53.1	22.6	5	44	51
	8-12	26.7	43.6	29.7	5	46	49
	12-16	31.5	39.1	29.4	4	42	54
	16-20	19.2	39.9	40.9	3	37	60
	20-25	25.3	44.3	30.4	10	21	69

Discussion

The dynamic nature of Chautengo lagoon may be illustrated by the hydrologic cycle which shows 4 phases[21], viz. (1) closing of the barrier and reduction of water volume with predominance of evaporation (annual av. 1900-2200 mm); (2) increase of water volume and decrease of salinity (annual precipitation av. 1200 mm); (3) aperture of the barrier, drainage of the lagoon body and discharge of rivers through the lagoon, with considerable variation in this discharge (Nexpa River- 1970: 119 × 10^6 m^3 and 1974: 1045 × 10^6 m^3); and (4) water exchange between the lagoon and the littoral zone, and gradual increase of salinity (typical annual sal. range[20], is 5-30 × 10^{-3}). The continental weathering products of the lagoon are the result of the action on ultrabasic and basic rocks from the Acatlan and Cholapa complexes[22].

In Table 1 each core is classified according to Berner's[23] criteria based on the presence of dissolved oxygen and dissolved sulfide in the sediments. This table reflects obviously different types of sedimentary environments depending on lagoon site.

In all the lagoon sediments kaolinite is the predominant clay mineral, illite occurs in significant proportions and montmorillonite is the least abundant. The relative concentration of clay minerals can be explained by weathering processes that act in the coastal plain. Tardy[24] suggests that rain water falling on high ground leaches the rock extensively, and a kaolin mineral is formed. When the same water reemerges at lower levels, it is more concentrated. Reaction between this water and primary rock minerals (or previously formed kaolinite) will characteristically produce montmorillonite.

Regardless of the intensity of the weathering processes in the Chautengo lagoon region, as the narrow coastal plain provides a very small surface, the erosion is not significant and therefore the concentrations of montmorillonite are relatively low (2-12%). A similar value is found in the sediments from the Mitla lagoon[25] in the same region. Montmorillonite in all samples is uniformly low particularly in the cores from Nexpa River inlet (Table 3).

The influence of non-marine and marine conditions during deposition has been considered in order to explain the variation in the proportion of kaolinite and illite in the Tansley mudrocks[26]. Likewise, the tendency of illite to be more abundant in marine sediments than in fresh-water sediments has been reported[27]. This might suggest that the sediments of core BRC-5 are earlier deposited under influence of non-marine or less marine conditions. The hydrologic cycle in Chautengo lagoon is very dynamic and variable in time and it would not be improbable for the duration and intensity of each phase to be changing over the years. Unfortunately this is not observed in the other cores.

The lineal correlation found for the sediment core CP-3 between organic carbon and particle size has been commonly observed in aquatic sediments[28-30]. But the negative correlation for core C-4 is anomalous and difficult to explain. Core C-4 shows bivalves and broken shells and high emanations of H_2S indicating that the sediment column underwent an evolution from oxidizing to reducing conditions.

The sediment cores of Chautengo lagoon offer the possibility to examine certain features of the metal distributions in an area which has no apparent metal contamination. Regional comparisons with texturally equivalent sediments show that the concentrations of Fe, Co, Ni and Cd for Chautengo lagoon are of the same order of magnitude or even higher than most of the data reported for environments believed to be subject to anthropogenic metal inputs[31,32]. The lagoon sediments contain lower concentrations of

Table 4—Correlation Coefficients Between Various Components of Each Core
[BRN-1 (n = 8); BRN-2 (n = 11); CP-3 (n = 5); C-4 (n = 9); BRC-5 (n = 7)]

	Core	Corg	Cd	Co	Cr	Cu	Fe	Mn	Ni	Zn
<2µm	BRN-1	-0.85	0.83	0.86	0.25	0.67	0.59	0.94	0.84	0.86
	BRN-2	-0.37	0.20	0.43	-0.03	0.40	0.38	0.22	0.58	0.41
	CP-3	0.98	0.93	0.67	0.96	0.93	1.00	0.91	0.95	0.93
	C-4	-0.75	-0.06	0.31	0.71	0.36	-0.32	0.09	0.34	0.55
	BRC-5	0.38	-0.37	-0.27	-0.87	0.15	0.33	0.52	-0.50	0.50
2-62µm	BRN-1	-0.56	0.41	0.72	0.76	0.90	0.67	0.33	0.78	0.80
	BRN-2	-0.42	-0.24	0.06	-0.06	0.27	0.67	0.22	0.60	0.76
	CP-3	0.97	0.75	0.44	0.94	0.72	0.92	0.70	0.80	0.71
	C-4	0.60	0.18	0.08	-0.20	-0.14	0.72	0.34	0.07	0.17
	BRC-5	-0.37	0.60	0.32	0.96	-0.19	-0.11	-0.32	0.53	-0.28
>62µm	BRN-1	0.86	-0.68	-0.93	-0.57	-0.93	-0.60	-0.66	-0.96	-0.97
	BRN-2	0.46	0.10	-0.22	0.06	-0.36	-0.65	-0.25	-0.68	-0.73
	CP-3	-0.95	-0.85	-0.57	-0.97	-0.84	-0.98	-0.82	-0.89	-0.71
	C-4	0.60	0.00	-0.37	-0.70	-0.34	0.08	-0.02	-0.39	-0.66
	BRC-5	-0.11	-0.79	-0.30	-0.82	0.21	-0.25	-0.08	-0.43	-0.14
<62µm	BRN-1	-0.85	0.83	0.86	0.25	0.91	0.59	0.94	0.84	0.89
	BRN-2	-0.37	0.20	0.43	-0.20	0.40	0.37	0.22	0.58	0.41
	CP-3	0.99	0.93	0.67	0.96	0.93	1.00	0.91	0.95	0.93
	C-4	-0.60	-0.06	0.31	0.71	-0.21	-0.32	0.09	0.34	0.55
	BRC-5	-0.16	-0.37	-0.27	-0.87	0.15	0.33	0.52	-0.50	0.50
Corg	BRN-1	1	-0.85	-0.88	-0.43	-0.81	-0.60	-0.70	-0.94	-0.88
	BRN-2		0.13	0.33	0.33	-0.09	-0.23	-0.12	-0.11	-0.26
	CP-3		0.97	0.78	0.91	0.94	0.98	0.93	0.94	0.95
	C-4		-0.32	-0.44	-0.59	-0.33	0.44	-0.25	-0.33	-0.50
	BRC-5		-0.16	-0.19	-0.55	0.17	-0.17	-0.04	-0.73	0.00
	Cd	BRN-1	1	0.82	0.24	0.61	0.39	0.74	0.83	0.74
		BRN-2		0.64	-0.14	-0.40	-0.13	0.32	-0.32	-0.41
		CP-3		0.89	0.80	0.96	0.93	0.93	0.94	0.98
		C-4		0.21	-0.20	-0.06	0.19	0.48	0.00	0.21
		BRC-5		0.45	0.51	0.28	0.54	0.48	0.44	0.55
		Co	BRN-1	1	0.05	0.80	0.65	0.70	0.95	0.98
			BRN-2		-0.17	0.09	0.19	0.35	0.27	-0.13
			CP-3		0.45	0.76	0.67	0.76	0.71	0.83
			C-4		0.62	0.79	0.11	-0.07	0.52	0.30
			BRC-5		0.31	0.75	0.60	0.45	0.69	0.39
			Cr	BRN-1	1	0.77	0.27	0.10	0.57	0.44
				BRN-2		0.32	0.70	-0.88	0.20	0.37
				CP-3		0.85	0.96	0.83	0.88	0.82
				C-4		0.79	0.14	0.12	0.71	0.44
				BRC-5		0.34	-0.09	-0.32	0.66	-0.29
				Cu	BRN-1	1	0.60	0.52	0.91	0.87
					BRN-2		0.56	-0.12	0.46	0.39
					CP-3		0.94	0.96	0.98	0.99
					C-4		0.22	-0.18	0.41	-0.04
					BRC-5		0.56	0.60	0.30	0.55
					Fe	BRN-1	1	0.44	0.68	0.75
						BRN-2		-0.27	0.60	0.79
						CP-3		0.91	0.96	0.93
						C-4		0.46	0.27	0.10
						BRC-5		0.96	0.31	0.93
						Mn	BRN-1	1	0.67	0.70
							BRN-2		-0.02	-0.22
							CP-3		0.89	0.97
							C-4		0.51	0.49
							BRC-5		0.16	0.99
							Ni	BRN-1	1	0.96
								BRN-2		0.56
								CP-3		0.96
								C-4		0.63
								BRC-5		0.12

total Zn, Pb, Cr and Cu than the sediments from the German Bight[33] and Los Angeles Harbour[31].

Positive correlation between clays and organic carbon found in core CP-3 indicates that the trace metal accumulation is directly related to the deposition of fine grained inorganic and organic matter at this point of the lagoon. According to Loring[34], these correlations imply either a primary association or a secondary relationship, since organic matter also increases with decreasing grain size. Covariance between Zn, Cd and Fe with Mn in this core suggests scavenging of metals onto freshly precipitated manganese and iron oxides[35].

This may partly contribute to the surface enrichment of metals observed. Different studies have established that the oxides and hydroxides of Fe and Mn constitute significant sinks of heavy metals in aquatic systems[36]. The physical and chemical factors in the main channel (core CP-3) of Chautengo lagoon present favourable conditions (Table 1) for the formation of hydrous Fe and Mn oxides.

Significant correlations between silt size fraction with Cu, and Cr in core BRN-1 and with Cr alone in core BRC-5 may be explained by the existence of minerals (probably amphiboles) associated with these metals. The correlation of those elements with Fe appears, therefore, to be secondary.

Except for the negative association between organic carbon and clay size fraction in core C-4, no significant relationship is found between the remaining components. The uniform concentrations of Cd, Co, Cr, Cu and Ni over the entire core, may be explained by the presence of molluscs in this core.

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