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Heavy Metals in Sediments from Coatzacoalcos River, Mexico

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Discharges of waste waters into estuarine systems and their effects in the natural cycles of trace elements have been studied recently by many authors (De Luca Rebello et al., 1986; Ravichandran M. et al., 1995). The distribution of metals in non-contaminated surface sediments of different areas has been used as a reference for any amounts of anthropogenic inputs of heavy metals to these areas compared to areas where inputs are evident (Mat, 1994); in order to evaluate the degree of metal pollution in sediments, we measured the non-residual (non-lattice held) trace metals and total metal concentrations in two such areas. Coatzacoalcos River mouth is located in Veracruz State. The river originates at more than 2,000 m elevation in Oaxaca state and several smaller streams (Corte, Chichihua, Almoloya, Malatango Sarabia, Jaltepec, Uxpanapa and Calzada) discharge waters into its main branch, draining an area of 14,207 Km^2 (Paez-Osuna et al., 1986).

The lower reaches of Coatzacoalcos River, from Coatzacoalcos Port to Minatitlan City, 17 Km of the port, is an area where many industrial developments have taken place. Surface sediment samples were collected along Coatzacoalcos River. Sediments from three different effluents in the higher river reaches were sampled too (Fig. 1). The physical and chemical characteristics of the sediments were studied to assess the type of sediments that are naturally in the system; total metals, non-residual trace metals, and enrichment factors were evaluated.

The weather in the area is warm, with average temperatures of 24 °C. The higher river reaches are very rainy, diminishing in intensity in the low-lands. The rainy season is June to October in the low-lands; hurricanes that occur in the Gulf of Mexico, June to November, produce maximum rain in September with high variability in flows and values to 7,061 m^3/sec in the rainy season.

MATERIALS AND METHODS

Eleven sites were sampled across the upper, middle, and lower reaches of

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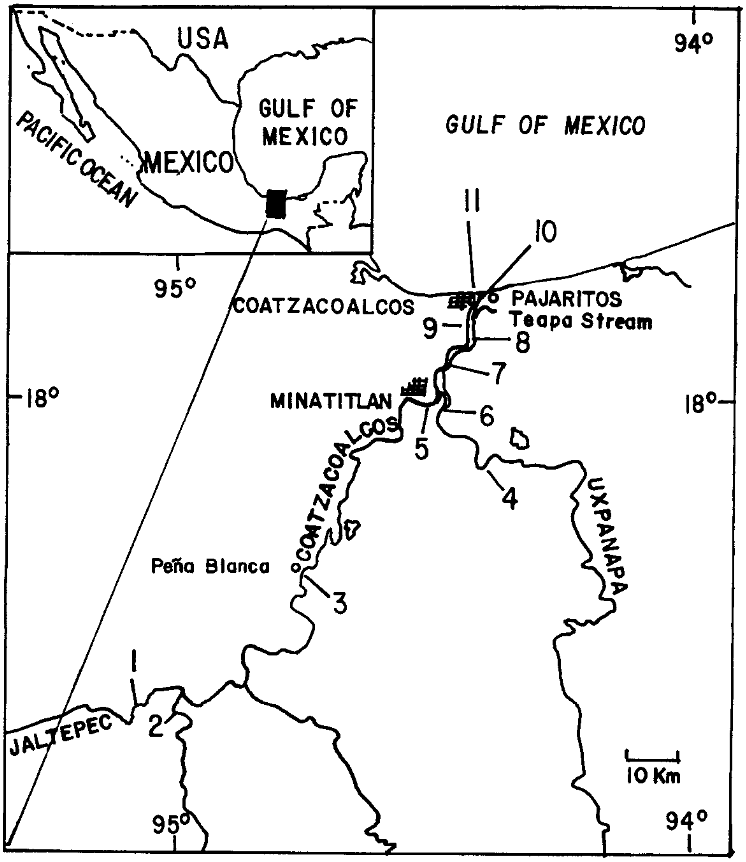

Figure 1. Coatzacoalcos River area.

Coatzacoalcos River at the end of April, 1994. Sampling sites are shown in Fig. 1. Mean water depth was 5 m or less at the first six stations; 9 m at stations 7, 8, 9 and 10, and 14 m at station 11. In the higher river reaches, two samples were collected using a plastic hand shovel at each sampling point, one from 0.5 m depth which was usually muddy (sample B), and one in the river margin, which was sandy (sample A). In the lower river reaches samples were collected by boat using a Van Veen grab; care was taken to ensure that sediments collected were not in contact with the dredge. Sediment samples were put into plastic bags and kept refrigerated until chemical analysis.

Granulometric analysis of sediments was made following Folk (1974). Percentages of traction (rolling or sliding), saltation and suspension populations (Table 1) were determined according to the methodology of Visher (1969).

Total metal concentrations in the bulk sediments, were made by microwave

Table 1. Physical characteristics of sediment samples.

Sample No.	Size (ϕ)	Traction %	Traction Int. (ϕ)	Saltation %	Salt. Int. (ϕ)	Suspension %	Susp. Int. (ϕ)
1A	3.050	10.50	-2.80-(-0.10)	86.45	-0.10-2.25	3.05	2.25-5.00
1B	3.840	18.00	-2.78-3.78	10.00	3.78.5.40	72.00	5.40-8.08
2A	-0.926	43.80	-3.25-0.80	55.20	0.80-3.95	1.00	3.95-5.00
2B	3.034	16.30	-3.00-1.55	63.60	1.55-4.22	20.10	4.22-5.00
3A	2.750	0.13	-0.26-1.29	99.87	1.29-5.05	0.00	0.00
3B	3.034	1.42	-2.25-1.40	85.08	1.40-7.00	13.50	7.00-8.08
4A	2.214	1.40	-2.75-0.54	97.92	0.54-3.5	0.68	3.50-4.00
4B	2.189	1.79	-2.50-(-0.57)	75.21	-0.57-2.70	23.00	2.70-10.2
5	5.585	1.15	0.00-4.00	61.85	4.00-7.00	37.00	7.00-8.00
6	5.565	1.95	0.00-4.03	2.35	4.03-6.95	95.70	6.95-7.95
7A	2.685	1.90	0.50-1.99	96.55	1.99-3.40	1.55	3.40-5.92
7B	2.631	0.14	-0.24-1.80	99.07	1.80-3.26	0.79	3.26-5.40
8	2.172	0.00	-0.10-0.50	99.92	0.50-3.20	0.08	3.20-4.55
9	5.879	3.80	1.00-4.03	47.40	4.03-7.00	48.50	7.00-8.00
10	4.571	1.07	0.00-0.92	25.73	0.92-3.75	73.20	3.75-8.00
11	4.280	0.34	1.00-2.25	85.66	2.25-5.70	14.00	5.70-8.00

extraction of sediments in acidic conditions and analysis by AA spectrophotometry.

Non-residual trace metals (Cu, Ni, Cr, Cd, Zn, and Pb) were extracted by the method used by Mat et al. (1994). The coefficient of variation (%) and the detection limit (ppm), (in parentheses) for the trace metals studied in the samples were: Cu: 2.69, (0.012); Cd: 2.71, (0.034); Cr: 3.44, (0.033); Ni: 2.69, 0.154); Zn: 2.69, (0.0043); Pb: 2.77, (0.021). The accuracy and precision of the method employed was estimated by means of control sample SDN1/2 (IAEA, 1985); all metals reported in the present work were within IAEA (1985) accepted confidence interval, at a level of significance of 0.05. Organic carbon content in sediment samples was determined using the method of Gaudette et al., (1974). The coefficient of variation of the method was 2.64 %.

RESULTS AND DISCUSSION

Water column data collected are shown in Table 2. Water temperatures were 30-31 °C. Salinity values increased gradually from sampling station 5 to the river mouth. Oxygen was 5.55 to 8.46 ml/l except at sampling station 10. This site is located at the entry of Teapa stream, where discharges from an hydrocarbon processing industry take place; low oxygen (0.58 ml/l) and pH values (3.4) were observed at this point. The pH values at other points were 7.0 to 8.2, as expected. Calcium and magnesium increase with

Table 2. Background data from Coatzacoalcos River area.

Sampling Site	Temp. °C	Salinity	Oxygen ml/l	pH	Mg ppm	Ca ppm	Susp. Mat. mg/l
1	31	0.06	7.67	7.50	2.80	9.00	17.00
2	31	0.05	7.53	7.20	2.20	8.00	10.50
3	31	0.07	6.42	7.30	2.40	9.00	9.40
4	30	0.20	6.15	8.10	7.20	50.00	18.80
5	30	1.62	6.34	7.00	24.00	17.00	4.90
6	30	2.82	5.55	7.40	80.00	60.00	8.80
7	31	6.30	8.46	8.00	140.00	90.00	28.20
8	30	7.62	7.29	8.10	250.00	150.00	23.30
9	31	7.37	6.29	7.90	220.00	140.00	58.60
10	30	8.87	0.58	3.40	230.00	130.00	22.90
11	30	12.56	8.24	8.20	450.00	230.00	14.00

distance from higher river reaches, where values of 8 to 9 ppm Ca and 2.2 to 2.8 ppm Mg were observed, to 230 and 450 ppm respectively in the river discharge area.

To account for the type of fluvial sediments that are present in Coatzacoalcos River, and due to the fact that natural trace metal concentrations in estuarine sediments can vary by a factor of 2 to 3 (depending on the sediment grain size and concentration of Al, Fe, Mn and organic carbon), (Ravichandran et al., 1995), analyses of physical characteristics (Table 1) and chemical composition of the sediment samples (Table 3) were undertaken. In the higher river reaches, the sediment grain size varies greatly, sometimes within a distance of a few meters. Sandy samples show greater size and grain saltation population content (Table 1), as reported by Visher (1969). Finer samples are located at stations 5, 6, 9 and 10 . Station 10, where anomalous pH and oxygen values in water were observed, has fine sediments with large amounts of suspended grains, suggesting that fine muds are anthropogenically incorporated as a result of discharges from Teapa gulch.

The correlation analysis of the evaluated parameters, shows high correlation of Al with Ca(0.74), Mg(0.56), K(0.59) and Na(0.71) (values above 0.553, represent a significant correlation in the 95 % confidence interval), suggesting these elements are present as Ca and Na feldspars and K plagioclases.

The organic matter concentration shows average values of 0.23 % in the higher river reaches where there is no industrial activity; from station 6 to station 9 organic matter values average 2.15 %, with values up to 4.16 % at station 8, located in a river retreat with reduced river flow. Even through a high correlation has been reported for organic matter and trace metal content of sediments (Wangerski, 1986), no statistically significant

Table 3. Chemical composition of sediment samples from Coatzacoalcos River (%).

Samp.	Km to sea	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	MnO	CaO	MgO	K_2O	Na_2O	LOI	OM
1A	130	12.57	78.96	3.07	0.86	0.45	0.21	0.16	2.59	0.58	0.55	0.38
1B	130	18.72	59.80	5.15	2.97	0.06	1.03	1.04	3.17	6.69	1.35	0.85
2A	123	11.07	72.38	2.55	1.80	0.04	0.25	0.32	2.14	8.48	0.96	0.15
2B	123	12.89	63.19	4.57	2.98	0.07	1.02	0.61	3.43	9.34	1.91	0.27
3A	73	16.28	62.81	4.58	3.50	0.07	1.37	0.85	3.70	4.27	2.56	0.28
3B	73	3.65	84.97	4.25	3.84	0.10	0.25	0.14	1.07	0.51	1.22	0.02
4A	42	11.78	74.98	2.50	2.00	0.04	0.70	0.81	1.72	2.80	2.67	0.11
4B	42	5.26	76.21	5.17	3.13	0.05	0.47	1.23	3.32	0.96	4.20	0.04
5	28	12.08	67.10	6.63	1.66	0.09	0.39	0.16	2.17	1.11	8.61	0.04
6	24	6.74	67.77	7.40	2.50	0.11	0.48	0.29	1.89	0.52	12.31	2.28
7A	15	11.78	72.80	6.17	3.89	0.10	0.37	0.23	2.53	0.64	1.48	1.17
7B	15	3.65	81.85	3.64	1.84	0.05	0.19	0.18	2.00	1.01	5.58	1.92
8	9	8.40	80.91	4.10	1.40	0.40	0.28	0.16	1.55	1.71	1.09	4.16
9	8	17.26	53.10	7.35	2.67	0.07	0.68	1.75	2.82	3.66	10.64	1.21
10	2	13.78	54.84	5.25	2.67	0.03	0.57	1.66	2.80	4.88	13.52	0.50
11	0.2	11.35	66.80	5.79	1.47	0.02	0.28	0.15	2.35	4.87	6.93	0.38

correlation was observed between organic matter and trace metals in this study.

The trace metal concentration in the area is given in Table 4. The use of mild extraction conditions gives information on the non-residual trace metal concentration, which is the fraction potentially bioavailable for aquatic organisms.

Coarser samples 1A and 2A, show lower trace values; coarser grained material often acts as dilutant of trace metal concentration in bulk sediments as reported by Ravichandran (1995).

Sample 10, located where the Teapa Stream joins Coatzacoalcos River, shows higher values of Cu, Cr, Zn and Pb, as well as higher non-residual Cd, Cu, Ni, Cr, Zn and Pb; industrial discharges at this site, produce additionally to higher loading at this area. Excluding station 10, the greatest Cu and Zn concentrations were found in samples 6 and 8, where higher values of organic matter were observed. Copper is mainly complexed by organic materials which are slowly mineralized on their way to the sea; particulate Cu is desorbed when there is an increase in pH. Concentrations of Cu in non-contaminated soils is in the range 20-30 mg/Kg (Merian, 1991). Values found in the Coatzacoalcos River area (4.66-34.26 mg/Kg), without taking into consideration station 10, are within expected values for “normal soils”. The highest percentage of non-residual Cu is found at station 10. Bryan (1992), reports the highest levels of Cu in estuarine organisms specimens from anoxic sediments, and points out the need to consider the influence of low redox potentials and pH on the bioavailability of sediment cu.

Table 4. Trace metal concentration (ppm) in Coatzacoalcos River sediments.

No	Cd NR	Cd Tot	Cu NR	Cu Tot.	Ni NR	Ni Tot.	Cr NR	Cr Tot	Zn NR	Zn Tot	Pb NR	Pb Tot
1A	ND	2.33	0.99	4.66	0.99	12.84	0.99	25.70	2.98	16.34	1.00	26.84
1B	ND	2.31	8.93	25.46	2.98	32.40	2.98	39.35	21.83	101.84	4.96	32.40
2A	ND	2.36	1.99	7.07	1.00	14.14	0.55	25.93	4.98	25.93	1.00	21.21
2B	ND	2.74	1.98	9.96	0.99	18.55	0.99	30.18	5.95	49.19	1.98	24.59
3A	ND	2.54	4.95	15.27	1.98	24.08	2.97	25.80	10.89	60.43	3.96	32.89
3B	ND	2.33	2.98	11.66	0.99	13.99	1.00	27.98	7.94	76.95	1.98	38.59
4A	ND	2.06	4.94	20.59	4.94	15.98	10.87	53.53	32.61	90.59	3.95	32.45
4B	ND	2.31	6.00	16.19	21.98	76.78	11.00	152.69	12.99	50.90	5.00	32.39
5	0.99	2.16	13.86	28.08	6.93	36.73	2.99	43.86	43.57	118.82	7.92	34.56
6	0.99	2.10	17.84	33.63	21.81	46.25	6.93	92.49	54.52	138.74	9.91	33.63
7A	ND	2.27	4.98	9.11	16.95	19.43	0.99	21.58	21.93	49.85	1.99	32.95
7B	ND	2.26	6.80	9.62	7.70	18.13	1.98	19.25	42.34	49.88	5.77	30.59
8	1.00	2.14	14.01	34.26	14.96	23.55	5.77	70.66	44.04	141.32	12.87	34.42
9	ND	2.20	5.99	11.00	11.97	24.21	0.99	48.41	10.97	48.41	6.98	26.41
10	1.98	2.14	95.81	141.19	43.56	47.06	99.00	94.12	65.84	164.72	37.21	53.48
11	ND	2.22	9.91	22.16	6.81	33.25	3.99	39.90	21.94	97.52	1.99	26.59

*NR = Non-residual.

Cadmium values were very homogeneous throughout the studied area (2.06-2.74 mg/Kg). Sediments of non-polluted waters show Cd concentrations from 0.04 to 0.8 mg/Kg, and in polluted rivers levels range from 30 to 400 mg/Kg (Merian, 1991). The uniformity of the observed Cd values in this area suggests a natural source for this metal; mobilization of Cd occurs when river waters mixes with sea water, and the formation of Cd-Cl complexes lead to the release of Cd from particles.

The average reported concentration for Ni in non-contaminated soils (Merian, 1991) is in the 7-50 mg/Kg range; levels observed in the studied area (4-77 mg/Kg), with the highest value at station 4B located in higher Uxpanapa River, suggest a natural source for Ni. A significant correlation (0.48) of Ni with Fe was observed; apparently, both metals are associated with the same mineral facies.

Zn values from 10 to 300 mg/Kg have been reported in soils (Merian, 1991). In the Coatzacoalcos River area, values below 165 mg/Kg (with 40 % in the non-residual form) were found. Bryan (1992), reports that bioavailability of Zn is diminished by high levels of iron oxides; station 78 has 85 % of Zn content in the non-residual fraction and very low Fe_20_3 (3.64 %) concentration, however this correlation was not observed at the other studied stations.

Table 5. Enrichment factors of the studied metals against average soil.

Sample	Cr	Cu	Ni	Pb	Zn
1A	0.39	0.17	0.27	1.51	0.19
1B	0.40	0.61	0.46	1.22	0.81
2A	0.45	0.29	0.34	1.35	0.35
2B	0.45	0.35	0.38	1.34	0.57
3A	0.30	0.42	0.40	1.42	0.55
4A	0.87	0.78	0.36	1.93	1.14
5	0.69	1.04	0.82	2.01	1.46
7A	0.35	0.35	0.44	1.97	0.63
9	0.54	0.28	0.38	1.08	0.42
10	1.31	4.57	0.92	2.73	1.78
11	0.67	0.87	0.79	1.65	1.28

Chromium values observed (19-94 mg/Kg) are within expected values (10-40 mg/Kg) in natural soils. Lead values expected in natural sediments (10-40 mg/Kg) are exceded in station 19 (53.48 mg/Kg). It is important to note that the higher metal contents observed at stations 6 and 10 can be associated with the higher values in suspension grain population found at these sites, due to the fact that significant correlation values (95 % significant values above 0.468) were observed between metal concentration against grain suspension percentage for Cu (Coef. Corr Cu Tot = 0.527; Coef Corr. Cu NR = 0.514), Ni (Coef. Corr. Ni Tot. = 0.52, Coef. Corr. Ni NR = 0.522) and Pb (Coef. Corr. Pb NR = 0.523).

Salomons and Forstner (1984), suggested standarizing the metal content in sediments to that of a standard material such as average soil, to calculate the enrichment factor (EF), which is the ratio between metal/Al in the sample and metal/Al, in average soils. Using the average soil values of Bowen (1979) as a normalizer (Cr/Al=5.22, Cu/Al=2.24, Ni/Al=3.73, Pb/Al=1.42, Zn/Al=6.72), the EF, for samples studied was calculated (Table 5). Due to the fact that average soil values used by Bowen (1979) have Al concentration of 13.4 %, samples with Al values below 8 % (3B, 4B, 6, 7B, 8) were not considered in the EF analysis.

The EF for Cr and Cu are below 1 in all samples except station 10, where Cu enrichment is 4.57. The EF for Ni are below 1 throughout the area. Pb is above 1 in all samples with the highest value at station 10. At this station the EF is 2.73 times the standard soils. Zn shows enrichments at sites 4A, 5, 10, and 11, with greatest enrichment at station 10.

Published data for metal concentrations in sediments of the Mexican coastal zone of the Gulf of Mexico (Villanueva and Botello, 1992), indicate that Coatzacoalcos River has the greatest trace metal concentrations. Comparison of Coatzacoalcos River mean metal concentrations in sediments located in the stream affected by industrial activities (Cu:36.13, Ni:31.1, Cr:53.78, Zn:101.16, Pb:34.1) with data (Cu:11.3, Ni:13.9, Cr:40.8, Zn:76.7,Pb:52.7) from Sabine-Neches Estuary, Texas (Ravichandran et al., 1995), also influenced by anthropogenic inputs, show greater metal concentrations in the Coatzacoalcos River area. According to Ravichandran (1995), only Zn and Pb exceed the natural values found in the area, while in Coatzacoalcos all metals investigated except Cd are above natural values found in the area.

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