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Iron, Cadmium, Chromium, Copper, Cobalt, Lead, and Zinc Distribution in the Suspended Particulate Matter of the Tropical Marabasco River and its Estuary, Colima, Mexico

E. Shumilin,[1] A. Meyer-Willerer,[2] A. J. Marmolejo-Rodríguez,[1] O. Morton-Bermea,[3] M. A. Galicia-Perez,[2] E. Hernández,[3] G. González-Hernández[3]

[1] Interdisciplinary Center of Marine Sciences, Av. IPN s/n, Col. Playa Palo de Sta. Rita, Apdo Postal 592, La Paz, Baja California Sur, 23096, Mexico

[2] CEUNIVO, University of Colima, Manzanillo, Colima, 28860, Mexico

[3] Institute of Geophysics, National Autonomous University of Mexico, Cd. Universitaria, Coyoacan, 04510, Mexico, D.F., Mexico

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Tropical rivers are important sources of heavy metals to the coastal marine environment (Martin and Meybeck 1979). This also applies to the west coast of central Mexico, where heavy rainfall originating in mountains during the summer-autumn rainy seasons brings a huge amount of suspended load into coastal lagoons of the Eastern Pacific Ocean. One such dynamic sedimentary systems is Marabasco River separating the states of Colima and Jalisco in tropical Mexico. The river discharges fresh water and suspended sediments into the Barra de Navidad Lagoon and the Barra de Navidad Bay on the Pacific Ocean. Principal features of the hydrography of this river and bathymetry of the lagoon are briefly described by Meyer et al. (2003). A peculiarity of local ecological importance of this drainage system is the occurrence of iron ore deposits (mainly magnetite, limonite, and hematite) and the "Peña Colorada" iron ore mines in the Sierra El Mamey near Minantitlán in the upper watershed of this river (Anonimous 1994). The "Benito Juarez" consortium, the leading producer of iron ore in Mexico, extracts iron as a magnetite by means of electromagnets and uses the water from the upper Marabasco River for its technological operations. Huge deposits of tailing wastes, only several hundred meters from the upper river's course, are subjected to a massive flushing during heavy rains. In its lower course, the Marabasco River supplies fresh water for irrigating a large lowland agricultural area, the Cihuatlán banana plantations, and finally flows into the Barra de Navidad Lagoon, which is a part of the famous international resort zone.

Suspended particles are well known as a principal carrier of some elements in the riverine and estuarine waters (Chester 2003; Salomons and Förstner 1984). Therefore, both scientific interest and the environmental concerns dictate a need to investigate distribution, movement, and deposition of iron and heavy metals mobilized and transported with the suspended particulate matter (SPM) in the Marabasco River and its estuary during high flow conditions and to compare them with a composition of river bed and lagoon sediments.

MATERIALS AND METHODS

Water samples were collected 9-13 November 2002 from the surface layer of

Correspondence to: E. Shumilin

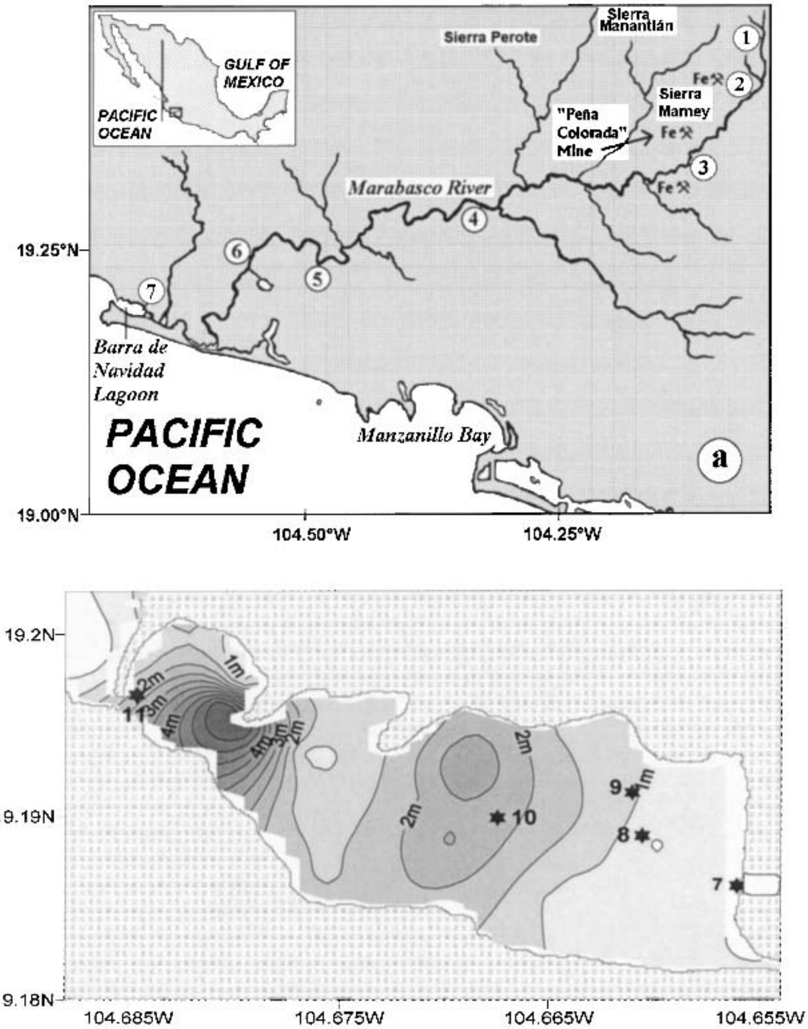

Figure 1. Study area and sampling sites: (a) the Marabasco River and its delta; (b) the Barra de Navidad Lagoon.

the river and estuary after several days of strong rains (59.2 mm cumulative rainfall from 1-13 November 2002). Marabasco River discharge at the Cihuatlán station at that time varied from 35.4 to 137.6 m^3s^{-1}. Locations of sampling stations are shown in Figure 1.

Polyethylene bottles cleaned with acid were used to store samples in a cold place. Water samples were rapidly delivered to a laboratory, and filtered with a vacuum pump, trough precleaned and pre-weighed 0.4-μm pore size Nuclepore filters, fixed in clean plastic Millipore funnels. The filters with the collected SPM were rinsed twice with a small volume of MilliQ deionized water, dried in a desiccators to constant mass and stored in plastic Petri dishes. Fe, Co, Cr, Sc, and Zn in SPM samples were measured using instrumental neutron activation analysis (Shumilin et al. 2001). For determinations of Cu and Cd contents, SPM samples were digested in a mixture of concentrated strong acids (Shumilin et al. 2002) and resulting solutions were analyzed by ICP-MS (Model PQ,VG Elemental). Standard reference materials SRM 1646a (Estuarine sediment), IAEA-356 (Polluted marine sediment) and SD-N-1/2 (IAEA) have provided reliable calibration and reproducibility.

RESULTS AND DISCUSSION

Table 1 displays iron and trace metal concentrations in the SPM collected at the section along the Marabasco River and in the Barra de Navidad Lagoon.

Concentrations of iron in the SPM of the Marabasco River-the Barra de Navidad Lagoon system ranged from 24.0 g kg^{-1} to 89.5 g kg^{-1}. The higher levels of iron are characteristic for the SPM of the river, with a maximum value in a sample from Station 3, located in the upper course of the river only 2.1 km downstream from the mine. Gradual declines in concentration of iron in the SPM further downstream at La Chacala, El Charco, and the river mouth are probably due to a natural self-purification. Sc-normalized iron concentrations in the SPM of the Marabasco River also reflect enrichment of SPM in iron. The Fe/Sc ratio value was 2589–3862 for SPM samples at Stations 1 and 2 (before the Peña Colorada mine), increasing to 5988 at Station 3 (after the mine), and then decreasing to 2898 at the mouth (Station 7).

Fe in the SPM from the upper part of the river is generally higher, than Fe concentrations in the sediments at the corresponding river stations (15.4-58.3 g kg^{-1}).In contrast, Fe concentrations in SPM from lower plain course of the river are much lower than those of related river bed sediments (155-168 g kg^{-1}) and especially in the bed sediment deposit at the El Charco station, which is enriched in a magnetite (380 g kg^{-1} Fe; Meyer-Willerer, personal communication). Slow water current on the plain below the Cihuatlán, near a river mouth, favors to a settling of Fe-enriched coarse particles, such as a magnetite and other ore minerals.

Samples of SPM from the estuarine mixing zone contained somewhat lower Fe contents (24-59 g kg^{-1}), compared with a SPM of the upper and middle sections of the river. Some enrichment of particles in Fe was found in the low and moderate salinity region, followed by a decrease in Fe contents in the middle estuary with salinities greater than 15 $^{o}/_{oo}$, and the lowest concentration was recorded in the sample from Station 11 at the outlet of the Barra de Navidad Lagoon. This low and moderate salinities′ Fe enrichment in SPM, clearly seen also by Fe/Sc concentration ratios (3774-3337 in the eastern and central part of the lagoon versus 2711-2530 in SPM collected near its outlet) is probably controlled by a flocculation of dissolved iron, possibly colloidal Fe oxyhydroxides and iron incorporated into fine aluminosilicate particles at the

Table 1. Sampling site locations, Fe (g kg^{-1}) and trace metal concentrations (mg kg^{-1}) in the SPM collected along the course of the Marabasco River and in its estuary.

Sample number	Sampling site	Fe	Cd	Co	Cr	Cu	Pb	Zn
1	San Antonio	52.5	3.5	15.1	22.7	703	8.8	11.3
2	Minatitlán Alto	45.1	0.4	14.1	11.0	393	2.3	230
3	Minatitlán Bajo	86.5	2.7	71.2	15.7	1655	9.9	190
4	La Chacala	73.6	5.8	24.0	32.0	394	7.1	131
5	El Charco	60.3	1.2	26.1	25.5	1072	29.3	46.8
6	Cihuatlán	61.8	3.7	25.2	19.1	555	8.1	62.5
7	River mouth (S=0.7°/oo)	47.7	28.4	14.4	19.4	31	2.7	73.9
8	Low salinity Zone (S=14.7°/oo)	59.4	1.0	13.5	20.1	154	22.9	107.7
9	Moderate salinity zone (S=17.1°/oo)	56.6	59.4	15.5	8.8	656	18.7	17.0
10	Middle estuary (S=21.9°/oo)	38.4	5.1	18.1	29.9	763	117.9	52.7
11	Near the outlet of the lagoon (S=31.1°/oo)	24.0	1.4	14.2	18.8	1182	76.8	82.6

low and intermediate salinities. This leads to fast removal of Fe from the water column and accumulation on the bed of the estuary, a process reported in other estuaries (Chester 2003; Salomons and Förstner 1984). This mechanism is supported by the existence of a broad band of high Fe/Al concentration ratios (exceeding 0.45) in sediments in the middle of the estuary, where fine-grained clay particles prevail. The coarse sandy sediments in the western portion of the lagoon probably do not retain particles enriched in Fe, displaying generally very low concentrations of this element, usually less than 10 g kg^{-1} because of the dilution of a terrigenous constituents by biogenic carbonates, which are highly abundant there (Meyer-Willerer, personal communication).

Cobalt in the SPM is also variable, generally slightly higher in the river than in the lagoon. In SPM, it ranged from a low 14-15 mg kg^{-1} above the zone of mining operations to 71.2 mg kg^{-1} at Station 3, 2.1 km below the mine. In the middle and lower course of the river, the concentrations were 24-26 mg kg^{-1} SPM and 13.5-18.1 mg kg^{-1} in the lagoon. Typical amounts of Co in the sediments of the river (6.4-25 mg kg^{-1}) and the lagoon (1.5-20 mg kg^{-1}) are low, except for the sediments collected near the mine (290 mg kg^{-1}) or a sample of deposit from El Charco (66 mg kg^{-1}) that is anomalously enriched in magnetite (Meyer-Willerer, personal communication). The Co/Sc ratios were close to unity (0.81-1.57) for SPM in the river and lagoon with the exception of particles of the area immediately affected by mining operations, where Co/Sc ratio reached 4.77.

Chromium concentrations in the SPM of the river (11.0-32.0 mg kg^{-1}) and lagoon (8.8-29.9 mg kg^{-1}) are relatively low being almost in the same range as in sediments of the river (5.8–38.5 mg kg^{-1}) and of the lagoon (3.6– 36.4 mg kg^{-1}) (Meyer-Willerer, personal communication) and never exceed the average concentration in the earth's crust (100 mg kg^{-1}).

Cadmium contents in SPM ranged from 0.4 mg kg^{-1} to 5.8 mg kg^{-1} in the river and from 1.0 to 59.4 mg kg^{-1} in the lagoon. Extremely high enrichment of Cd of SPM (59.4 mg kg^{-1}) was observed at Station 9, the inland part of the lagoon, with salinity of 17.1 $^{0}/_{00}$, and turbidity of 36 mg kg^{-1} exceeding the levels usually reported for the estuarine SPM (1-5 mg kg^{-1}, Seine estuary, Chiffoleau et al. 2001; 6-14 mg kg^{-1}, Gironde estuary, Jouanneau et al. 1990; 8.8 mg kg^{-1} , Scheldt estuary, Bayens, 1998). One possible cause of this phenomenon could be intensive remobilization of Cd from the sediments because of tidal resuspension of mud bank or direct diffusion of Cd from the interstitial waters through a sediment-water interface into the overlaying water column, followed by a selective re-adsorption of Cd or biological uptake of this trace metal by the constituents of the estuarine SPM (Chester 2003; Salomons and Förstner 1984). A coprecipitation of Cd with Fe and Mn oxyhydroxides, formed in estuaries because of the removal of dissolved iron of riverine origin (Chester 2003; Fox and Wofsy 1993; Salomons and Förstner 1984), especially in a barrier zone of the salinity gradient or as a consequence of the recycling of Fe and Mn from a interstitial water intrusion into the suboxic upper estuary (Zwolsman and van Eck 1999) could lead to such enrichment in SPM in Cd.

Copper concentrations were high in almost all SPM samples, reaching 1655 mg kg^{-1} below the mine at Station 3. Other high Cu values were detected at Station 1 (703 mg kg^{-1}), Station 5 (1072 mg kg^{-1}), and Station 6 (555 mg kg^{-1}). Related sediments of the riverbed have much lower concentrations of Cu, with the exception of several samples from the lower river course between Station 6 and Station 7 (235 and 461 mg kg^{-1})(Meyer-Willerer, personal communication). Hydrological and physico-chemical conditions in this part of the river favor removal of Cu from the water to the sediments. Showing a low content in the SPM from the Station 7 at the mouth (31 mg kg^{-1}), Cu displays enrichment in particles at the more saline portions of the lagoon (154 mg kg^{-1} at Station 8 near the mouth, 656 mg kg^{-1} at Station 9, 763 mg kg^{-1} at Station 10, in the middle estuary and 1182 mg kg^{-1} at Station 11 near the outlet of the lagoon). Cu concentrations in the underlying surface sediments of the lagoon range from 5.1 to 87.5 mg kg^{-1} with an area of higher levels in the middle of the lagoon, where fine-grained Al, Fe, and organic carbon-rich sediments are accumulated (Meyer-Willerer, personal communication). Cu enrichment is related to its high affinity for clay particles, usually rich in iron hydroxides and organic matter (mainly humic and fulvic acids).

Lead in the SPM of the river was low, ranging from 2.3 to 29.3 mg kg^{-1} (Table 1). These concentrations could be considered a natural baseline level of lead in this catchment basin, which is a sparcely populated, mountainous area, covered by almost pristine rainforest vegetation, with only a few roads cutting through it. Pb concentrations in the SPM of the lagoon are almost the same (2.7-22.9 mg kg^{-1}) with the exception of 117.9 mg kg^{-1} at Station 10, an area of the lagoon with high traffic of tourist boats. These concentrations are generally much lower than the contents of Pb in SPM and sediments of urbanized water bodies, e.g. of the southern German Bight of the North Sea and inflowing rivers (Hinrichs *et* al. 2002), of similar range as Pb concentrations in the surface sediments of the La Paz Lagoon, southwestern Baja California Peninsula, Mexico (Shumilin et al. 2001) and slightly lower than Pb contents (approx. 50 mg kg^{-1}) in the sediments of the lower course of the Culiacán River and coastal lagoons of the state of Sinaloa on the northwestern coast of mainland Mexico (Green-Ruiz and Páez-Osuna 2001; Ruiz-Fernández et al. 2003).

Zinc in the SPM of the river ranged from 11.3 to 230 mg kg^{-1}. At Station 1, Zn level in SPM was only 11.3 kg^{-1}. Higher concentrations along the river course were found at Station 2 (230 mg $kg^{-1)}$, Station 4 (130.5 mg kg^{-1}), Station 6 (62.5 mg kg^{-1}), Station 8 (107.7 mg kg^{-1}). Zn concentration in the SPM of the lagoon ranged from 52.7 to 82.6 mg kg^{-1} at stations of the middle and marine parts of the estuary. They are in the same range as Zn concentrations in the riverbed sediments (25-133 mg kg^{-1}) and lagoon sediments (15-142 mg kg^{-1}). Zn in the SPM of the river and its estuary does not display any significant anthropogenic influence and generally corresponds to the levels of this element in the sediments of the Culiacán River estuary in the state of Sinaloa in northwestern mainland Mexico (90-230 mg kg^{-1})(Ruiz-Fernández et al. 2003).

The Zn/Sc ratio was lowest in SPM at Station 1 (0.83), highest in SPM at Station 2 (13.25) and ranged from 2.81 to 8.70 along the river and the lagoon.

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