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Heavy Metals and Acid-Volatile Sulfides in Sediments of the Tijuana Estuary

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The Tijuana Estuary in San Diego County, CA is a wetland-dominated estuary, which has been designated a National Estuarine Sanctuary for protection of a number of endangered species and their habitat. For decades, raw sewage from the city of Tijuana, Mexico has flowed into the Tijuana River and across the international border into the Tijuana Estuary. This problem has worsened in recent years with the substantial growth of Tijuana's population along with intensive industrial development. Unfortunately, due to many factors, an industrial pretreatment program similar to one implemented in the United States, has not been initiated in Mexico, and the threat of chemical contamination of the Tijuana Estuary exists. To date, however, the degree and spatial nature of such contamination has not been well assessed. We report here on the levels of selected toxic metals in the sediments of the estuary. Additionally, we measured both acid-volatile sulfides (AVS) and simultaneously extracted metals (SEM) in order to estimate the potential toxicity of these estuarine sediments.

MATERIALS AND METHODS

Core sediment samples were collected in late January and early February 1996 from eight sites throughout Tijuana Estuary (Fig. 1). Cores were then extruded from their container and subsampled at three depth intervals: Top sediment surface to 2.5 cm below sediment surface (BSS)(top), 14.0 cm BSS to 16.5 cm BSS (middle), and 27.5 cm BSS to 30.0 cm BSS (bottom). These sub-samples were digested in Teflon-lined stainless steel digestion bombs at 180°C with deionized water and concentrated nitric acid. After the digested bombs were cooled, 30 % hydrogen peroxide was added to the mixture to complete the digestion. The sediment digests were filtered and diluted prior to flame atomic absorption spectrometry (AAS) analysis to determine the concentration of cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn). On two occasions, triplicate samples were analyzed for metal concentrations from the top (site 1) and bottom (site 7) section of sediment cores. The standard deviations for these triplicate analyses were within 20% of the mean values for all metals except Cd, which showed a standard deviation of +/- 100% at near the method level of detection. Sediment samples for AVS analysis were collected on three days throughout February, 1996 from three of the eight sediment-core sampling sites. These were sites 1, 3, and 7. The AVS protocol used in this research was a modified method

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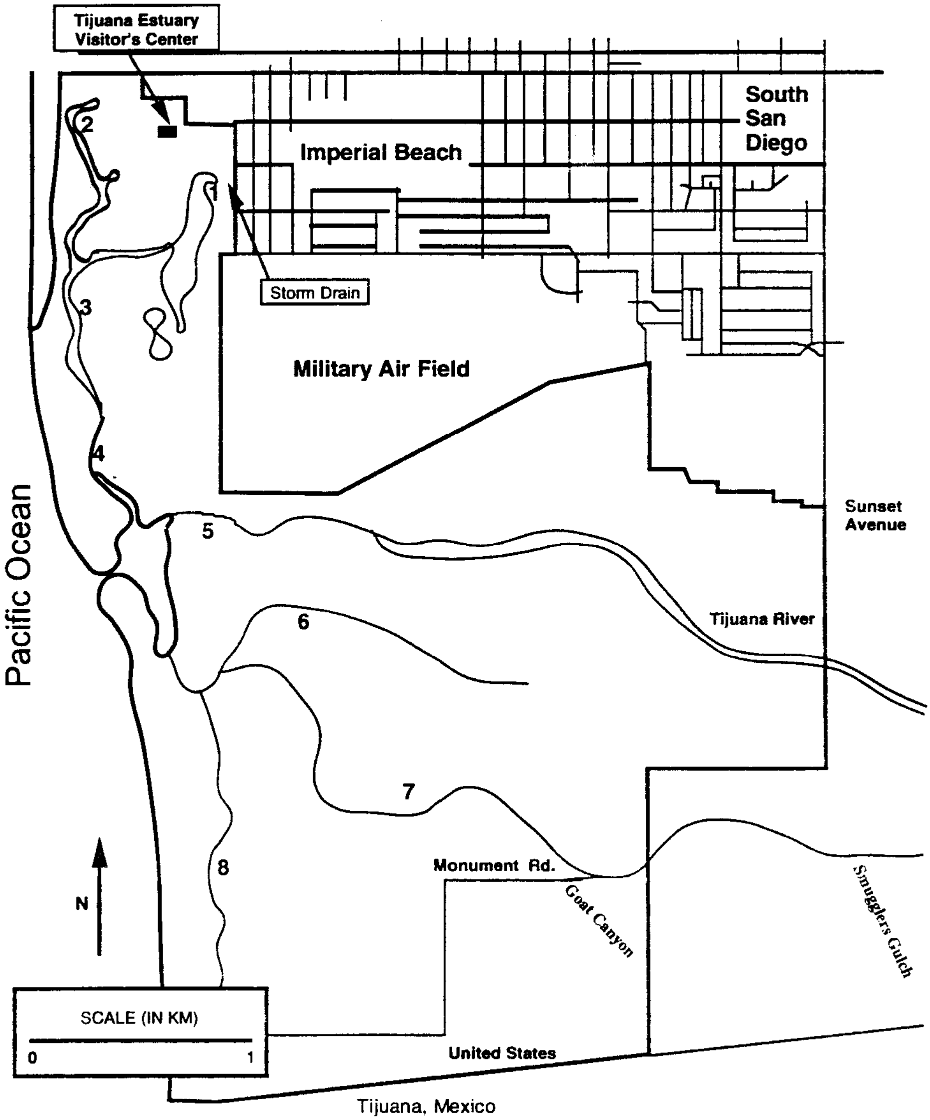

Figure 1. Diagram of Tijuana Estuary, including eight (numbered) sediment-core sampling sites. AVS sampling occurred at sites 1, 3, and 7. Predominant freshwater flows into the estuary are from the Tijuana River (denoted in figure). However, during wet weather, stormwater flows via Goat Canyon, Smuggler's Gulch, the military air field, and the City of Imperial Beach (denoted in figure) also enter the estuary.

based on the cold-acid purge-and-trap technique described in detail by DiToro et al. (1990) and Ankley et al. (1991). A sodium sulfide standard was analyzed for quality assurance and calibration of the AVS apparatus. The AVS method used in this study quantifies the solid phase sulfide in wet bottom sediments that is soluble in cold acid by releasing it in the form of hydrogen sulfide gas and capturing it as a silver sulfide precipitate (DiToro et al. 1990).

A Perkin-Elmer 2380 flame AAS was used to determine the concentrations of the metals Cd, Cu, Ni, Pb, and Zn for both sediment core digestions (total metals) and cold acid digestions for SEM. The Cd, Cu, and Pb standards were from EM Science (Gibbstown, NJ), Lot #‘s CX0011-1, 3000901, and 3000801, respectively. The Ni standard was from Mallinckrodt (Paris, KY), Lot # H552 KCCC. The Zn standard was from Bance Laboratory Chemicals (Fort Worth, TX), Lot # GI-28. A calibration blank and an intermediate concentration calibration standard were run every ten samples. Techniques used for determining the accuracy and precision of the analytical procedures were digestion blanks, triplicates, spikes, and standards. Standardization of the AVS apparatus was conducted using digestion blanks, triplicate runs on the same sample, and analysis of a sodium sulfide standard solution of known concentration. Percent recoveries of the sodium sulfide standard for each of three separate trials were 91%, 93%, and 93%. A standard reference sediment was not available for comparison to our analyses. The detection limit of this method is approximately 0.5 μMg^{-1} (DiToro et al. 1990).

Comparison of mean metal concentrations between sites were determined by the proper use of a one-tailed analysis of variance (ANOVA) test where $p < 0.05$ indicated a significant difference in analyte concentrations between sites.

RESULTS AND DISCUSSION

Figure 1 shows the sampling sites in the Tijuana Estuary. The major freshwater input to the estuary is from the Tijuana River, although during wet weather, runoff from Mexico may flow directly into the southern part of the estuary (via Goat Canyon and Smuggler’s Gulch), while runoff from the city of Imperial Beach may directly enter the northern arm of the estuary via stormdrains. Previous studies have found moderate to high levels of metals in the Tijuana River. A study conducted from 3 April, 1990 through 2 May, 1990 found mean levels of 0.041 mg L^{-1} (0.215 maximum) for Cr, 0.116 mg L^{-1} (0.707 max.) for Cu, 0.030 mg L^{-1} (0.768 max.) for Pb, 0.067 mg L^{-1} (0.301 max.) for Ni, 0.099 mg L^{-1} (1.68 max.) for Zn, and < 0.009 mg L^{-1} (0.01 max.) for Cd (US Army Corps of Engineers 1990). Studies by the Southern California Coastal Water Research Project (SCCWRP 1990) found that metal levels in the Tijuana River were highest (as high as 3.8 mg L^{-1} Pb, 1.9 mg L^{-1} Zn, 0.4 mg L^{-1} Cu, and 0.28 mg L^{-1} Cr) at the time of peak flows in the river (the first flush), and then decreased markedly in a pattern similar to the hydrograph. Although discharges from the Tijuana River only accounted for 2% of total gauged runoff to the Southern California coastal ocean in 1987, and 6% in 1988, it contained the highest concentrations of suspended solids, Cd, Cu, Ni, Pb, Zn, and PCB's among the eight largest creeks and rivers in Southern California (SCCWRP 1992). SCCRWP (1992), using flow-weighted mean concentrations, estimated that the mass emission of metals from the Tijuana River for the year 1987-1988 was 7,385 kg for Cr, 16,706 kg for Cu, 39,684 kg for Pb, 46,22 1 kg for Zn, and 205 kg for Cd. Obviously, significant loading of these toxic heavy metals to the Tijuana Estuary is occurring.

Heavy metal concentrations in the surlicial sediments (top 2.5 cm) for each of the sites are shown in Table 1. Levels were generally lowest at sites 4 and 7, and highest at site 1. At the latter site, the levels were 78, 205, 112, 346, and 13 mg kg^{-1} for Pb, Cu, Ni, Zn, and Cd, respectively, and were significantly ($p>0.05$) higher than any of the other estuary sites. Only at site 1 were any of the metal concentrations above the Effects Range-Median (ERM) values of 50 mg kg^{-1} Ni , 270 mg kg^{-1} Zn, and 9 mg kg^{-1} Cd, which are the concentrations approximately midway in the range of reported values associated with biological effects (National Oceanic and Atmospheric Administration 1991). Site 1 is located approximately 20 meters from a major storm drain that receives urban runoff from a large part of the City of Imperial beach, northeast of the estuary. This could explain the high degree of metal contamination, but also would indicate that urban runoff from developed areas in the U.S. may be a more significant source of metal contamination than the riverine flows in the sewage-contaminated Tijuana River flowing across the border and into the estuary.

The values of Cd found in this study ranged from a high of 12.8 mg kg^{-1} (at site 1) to a low of 1.2 mg kg^{-1} (at site 5) in the top 2.5 cm of sediment. Langston (1986) found that Cd levels varied from about 0.7 mg kg^{-1} to 4 mg kg^{-1} in the Mersey Estuary, which is considered relatively polluted. Salomons and Mook (1980) in a study of metal levels in the Rhine River, which is regarded as highly polluted, found Cd levels as high as 4.4 mg kg^{-1}. By comparison, surficial sediment at sites 1, 2 and 6 in the Tijuana Estuary showed Cd levels exceeding 4 mg kg^{-1}.

In a previous study of the metal levels in the sediments of Tijuana Estuary, Gersberg et al. (1989), found mean values (in the top 3 cm of sediments at 40 estuary sites) to be 0.89 mg kg^{-1} Cd, 9.87 mg kg^{-1} Cu, 11.33 mg kg^{-1} Ni, 15.34 mg kg^{-1} Pb, and 44.94 mg kg^{-1} Zn. A comparison of these values to the present study indicates that metal concentrations appear to have increased considerably in the eight intervening years between studies, with values for Cd, Cu, and Ni in surficial sediments approximately four-fold higher, and those for Pb and Zn nearly three-fold higher than values reported in 1989. The apparent increase may simply be the result of spatial heterogeneity; however, it is also possible that metal loading to the estuary has increased substantially over the past decade as a direct result of the industrial maquiladora (in-bond manufacturing and assembly plants) program in Mexico, as well as the North American Free Trade Agreement (NAFTA). This explanation is also supported by the vertical profile of metal concentrations as a function of sediment depth (Table 1). Mean metal concentrations in the top

Table 1. Mean metal concentrations (mg kg^{-1}) (± sample standard deviation, SD) from three sampling dates, arranged by site.

Site No.	Lead (SD)	Copper (SD)	Nickel (SD)	Zinc (SD)	Cadmium (SD)
Top	2.5 cm				
1	77.9 (31.4)	204.9 (124.2)	112.4 (63.8)	346.2 (96.7)	12.8 (2.6)
2	32.3 (17.6)	31.0 (1.7)	35.7 (2.3)	123.8 (5.9)	4.9 (3.1)
3	38.3 (10.2)	27.4 (5.1)	35.3 (4.7)	117.0 (6.3)	2.4 (1.9)
4	20.0 (9.4)	3.7 (4.0)	20.8 (11.5)	35.5 (14.5)	1.7 (0.9)
5	39.6 (20.0)	20.2 (15.0)	28.9 (8.1)	103.0 (45.3)	1.2 (0.7)
6	24.2 (1.9)	20.3 (5.1)	28.6 (1.4)	87.4 (23.5)	4.1 (2.6)
7	22.3 (1.0)	7.9 (2.5)	25.2 (7.8)	33.1 (4.6)	2.9 (2.0)
8	30.0 (12.3)	27.6 (9.7)	34.7 (3.6)	105.6 (2.4)	3.2 (2.4)
Middle	2.5 cm				
1	28.8 (13.2)	45.8 (9.4)	30.8 (2.5)	105.8 (37.9)	5.8 (3.3)
2	22.3 (6.2)	32.8 (12.9)	20.2 (13.7)	111.2 (14.4)	3.7 (2.6)
3	31.7 (3.2)	30.3 (1.4)	24.1 (8.1)	102.4 (1.9)	1.6 (1.4)
4	19.4 (4.8)	4.7 (3.4)	24.1 (5.0)	57.8 (40.1)	2.3 (1.8)
5	24.6 (4.4)	18.1 (13.3)	21.2 (1.5)	58.3 (16.4)	1.5 (0.7)
6	34.3 (2.7)	21.2 (3.1)	27.1 (6.0)	92.8 (19.1)	3.7 (1.9)
7	52.7 (64.4)	9.3 (2.5)	26.3 (11.4)	38.7 (13.1)	3.9 (4.4)
8	17.4 (11.4)	20.5 (6.8)	23.8 (2.7)	91.2 (4.4)	5.2 (4.4)
Bottom	2.5 cm				
1	24.6 (20.2)	17.8 (18.8)	12.8 (3.2)	42.0 (17.4)	2.0 (2.2)
2	17.5 (11.9)	26.2 (1.4)	12.8 (5.1)	96.2 (2.6)	2.0 (1.3)
3	27.1 (11.2)	28.8 (2.5)	9.1 (3.3)	127.6 (6.7)	2.4 (1.8)
4	4.2 (5.1)	7.0 (6.6)	8.3 (2.2)	30.3 (25.3)	2.0 (2.2)
5	18.1 (17.5)	11.3 (5.3)	12.2 (7.1)	54.1 (13.6)	2.0 (2.0)
6	21.6 (14.8)	16.1 (10.5)	11.2 (2.1)	77.3 (35.1)	3.2 (0.1)
7	11.9 (2.7)	4.9 (1.9)	8.5 (0.9)	40.6 (5.7)	2.0 (1.3)
8	17.5 (6.2)	24.9 (1.9)	13.9 (6.9)	105.5 (7.4)	4.6 (1.3)

sediment sub-samples were significantly ($p<0.05$) higher than the middle sub-samples, which were significantly higher than the bottom sub-samples. However, without much more information on the sedimentology of the Tijuana Estuary, a definitive temporal analyses based on the vertical profiles cannot be made.

In order to estimate the potential toxicity in the Tijuana Estuary sediments, we analyzed AVS and SEM at three sites (sites 1, 3, and 7) on three different dates. Simultaneous toxicity bioassays performed by DiToro et al. (1990) demonstrated a clear threshold of toxicity at the SEM:AVS molar ratios above 1.0. The range of AVS concentrations for Tijuana Estuary was 4.3 1 to 49.55 $\mu M g^{-1}$ of dry sediment (Table 2) and was similar to that for San Elijo Lagoon, CA (Urbach 1994) and Long Island Sound (Aller 1980) with AVS values ranging from 5.53 to 39.84 $\mu M g^{-1}$ and 14.6 to 43.2 $\mu M g^{-1}$, respectively. The mean SEM:AVS ratios for sites 1, 3 and 7 were 0.004 (n=6), 0.002 (n=6), and 0.002 (n=4), respectively. Even at the most contaminated site in the estuary (sitel), the SEM:AVS ratio was several orders of magnitude lower than the potential toxicity threshold of 1.0

Table 2. Concentrations of SEM and AVS, and SEM:AVS ratios in sediments of the Tijuana Estuary on the three sampling dates.

Sampling Date	Site	Concentration of SEM/AVS ($\mu M g^{-1}$)	SEM:AVS Ratio
3 February, 1996	1	0.10/41.5	0.002
	3	0.07/41.0	0.002
	7	0.02/15.3	0.001
11 February, 1996	1	0.10/22.6	0.004
	3	0.08/31.2	0.003
	7	0.02/4.3	0.005
19 February, 1996	1	0.11/24.8	0.004
	3	0.08/38.7	0.002
	7	0.02/8.1	0.002

Despite significant metal loading to the Tijuana Estuary in recent years, the sediment SEM:AVS ratios indicate that the sulfides in the sediments should be more than sufficient to bind to the metals and prevent toxicity. This does not mean that increased efforts to reduce further input of metals into the estuary should not be made. The construction of a treatment plant on the Tijuana River to intercept and treat raw sewage flows (94,697 $m^3 d^{-1}$) from Mexico before it enters the Tijuana Estuary, may help reduce contaminant input. However, the results from this study indicate that the Tijuana River is not the only source of metal contamination, and attention should also be focused on non-point source contamination by urban runoff from the City of Imperial Beach, CA.

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REFERENCES

Aller R (1980) Diagenetic processes near the sediment-water interface of Long Island Sound. I. Decomposition and nutrient element geochemistry (S, N,P).

In: Saltzman B (ed) Estuarine Physics and Chemistry: Studies in Long Island Sound. Academic Press, New York. p 238

Ankley G, Phipps G, Leonard E, Benoit D, Mattson V, Kosian P, Cotter A, Dierkes J, Hansen D, Mahoney J (1991) Acid-volatile sulfide as a factor mediating cadmium and nickel bioavailability in contaminated sediments. Environ Toxicol Chem 10: 1299-1307.

DiToro D, Mahony J, Hansen D, Scott K, Hicks M, Mayr S, Redmond M (1990) Toxicity of cadmium in sediments: The role of acid-volatile sulfide. Environ Toxicol Chem 9: 1487-1502

Gersberg RM, Trindade F, Nordby C (1989) Heavy metals in sediments and fish of the Tijuana Estuary. Border Health 5: 5-15

Langston WJ (1986) Metals in sediments and benthic organisms in the Mersey Estuary. Est Coastal Shelf Sci 15: 255-266

National Oceanic and Atmospheric Administration (1991) The potential for biological effects of sediment-sorbed contaminants tested in the National Status and Trends Program. NOAA Technical Memorandum NOS OMA 52.

Salomons W, Mook WG (1980) Biogeochemical processes affecting metal concentrations in lake sediments (Ijsselmeer, the Netherlands). Sci Total Environ 16: 217-229.

Southern California Coastal Water Research Project (1992) Surface runoff to the Southern California Bight. Annual Report 1990-91 and 1991-92. SCCWRP, Westminster, CA.

Southern California Coastal Water Research Project (1990) Data report on stormwater runoff. SCCWRP, Westminster, CA.

Urbach P (1994) Acid-volatile sulfide and metal levels in sediments of San Elijo Lagoon, Masters Thesis, San Diego State University.

U.S. Army Corps of Engineers (1990) Tijuana River monitoring data by Boyle Engineering Corporation for the U.S. EPA Standby Interceptor Project Alternatives Study-Bi-national Wastewater Treatment Project. Contract DACW-09-87-C-0035.