Levels of trace metals in water and sediment from the Tecate-Tijuana River

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Abstract

The Tecate-Tijuana River is part of the Tijuana River Basin, which is a binational basin shared by Mexico and the United States of America. The explosive industry growth in the region of Tecate, Mexico has produced several negative environmental impacts in the Tecate-Tijuana River Basin.

At the moment more than 30% of the water is used by industry and commerce in the city of Tecate. Therefore, the efficient use and the reuse of water, as well as the search for alternative water sources have begun to be very important in this region.

The objective of this study is to evaluate the behavior of selected trace metals along the river, which can be retained in the river by adsorption or precipitation.

Four sites were sampled along the Tecate River and seven sites along the Tijuana River during 2005–2006 and samples were analyzed for sixteen trace metals: Al, Cr, Mn, Ni, Fe, Cu, Zn, As, Se, Ag, Cd, Sb, Hg, Ba, Ti and Pb, by ICP-MS techniques.

Concentrations lower than Mexican law limits for trace metals were found for water samples and higher levels than background levels in sediments were found for Cr, Pb, Cu, Zn and Ni along the Tecate-Tijuana River. The results have shown that the local industry discharges high concentrations of trace metals and aquifers can be affected; trace metal sediments are moving down stream in the Tecate-Tijuana River direction.

Keywords: river water quality, trace metals river, river pollution, Tecate Mexico.

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1 Introduction

The free ionic form of a number of trace elements (e.g., Cd, Cu, Pb, Zn) has been found to be considerably more toxic to aquatic biota than complexed, colloidal, or particulate forms (Campbell [5]). In any case, bioavailability and toxicity of a trace metal is dependent on the chemical and physical form of the metal, which is affected by water chemistry (e.g., pH, temperature, salinity) (Renner [16]) in addition to other factors. In freshwater systems, organic matter plays an important role, through complex formation, in controlling the fraction of trace metals that is bioavailable (Burba [4]). This is especially true for Cu, Fe, Ni, Pb, and Al and, to a lesser extent, Cd and Mn.

There have been studies dealing with the enrichment of trace metals in river sediments influenced by industrial wastes (Compest [6]). Some authors have reported Cu, Pb, Zn, Cd, As, Cr, Fe, Ni and Ba concentrations in streams with <0.0625mm fine-grained sediments affected by landfills and water treatment facilities (Mantei and Coonrod [9], Mantei and Foster [9], Rule [17]).

The occurrence of elevated concentrations of trace metals in sediments found at the bottom of the water column can be a good indicator of man induced pollution rather than natural enrichment of the sediment by geological weathering (Davis [7]). The accumulation of trace metals in sediments is controlled by several environmental factors that include, pH, anthropogenic input, type and concentration of organics and inorganic ligands, the hydraulic process within the stream and the available surface area for adsorption caused by the variation in grain size distribution (Axtmann [1], Davis [7], Sondi [21])

Although water is commonly employed as a pollution indicator by trace metals, sediment can also provide a deeper insight into the long-term pollution state of the water-body. Sediment has been described as a ready sink or reservoir of pollutants including trace metals where they concentrate according to the level of pollution (Becker [3], Onyari [13]).

2 Study site

The Tecate River is part of the Tijuana River Basin (4430 Km^2), which is a binational basin shared by Mexico and the USA (Figure 1). The major part of this basin is in Mexico (72%). The Tecate River in natural conditions is an ephemeral stream, which means that water flows only in storm water events and its associated floods. However, discharges from wastewater treatment plants located in Tecate have produced a perennial stream of poor water quality downstream from these discharges (Radilla [15]), flowing from Tecate city in the upper part of the East Tijuana River Basin to 650 m west and confluences with the Tijuana Estuary later meeting the Pacific ocean.

The electroplating industry is the main source of trace metal wastewater discharges in the Tecate River.

The first reported trace metal studies along the Tijuana River Basin (Basil [2]) show trace metal presence impacting in biota, latter studies in the Tecate River found Cr (04 mg/L) Cu (0.5 mg/L), Zn (3.4 mg/L) and Fe (56.8 mg/L). Some others researches (Placchi [14]) evaluated the trace metal concentrations in the runoff in the upper Tijuana River Basin, as well as in the Tecate River. As expected, the highest levels of heavy metals were found in the sites with urban and industrial land use. The storm water runoff in the Tecate River contained Cd (0.4 to 1.6 μg/ L), Cr (33 to 104 μg/L), Pb (3 to 41 μg/L) and Ni (91 to 215 μg/L).

Meyer and Gersberg [12] stated that in the period from 1989 to 1997, the concentration values in the top three cm of sediment from 40 sites in the Tijuana River Estuary increased approximately four times for Cd, Cu and Ni. In the case of Pb and Zn the concentrations were three-fold higher. All are attributed to the increase in the maquiladora industry in the Tijuana River Basin. Recent works (Wakida [22]) reveals the presence of polluted sites in the Tecate River in urban zones where high concentrations of Cd, Ni, Cr and Pb are present.

The Tijuana River basin is noted for small-scale rural agricultural practices both for subsistence and commercial farming, industrial and urban activities.

Obviously, the chemical status of the river would have its influence on the receiving land, which might possibly reflect on superficial and underground water quality.

The need to assess the state and quality of the Tecate-Tijuana River and the sediment in terms of its metallic load becomes imperative since water from the river is being used for domestic, irrigation and livestock activities by people living in the catchment area, in view of the health implications that cut across the food strata.

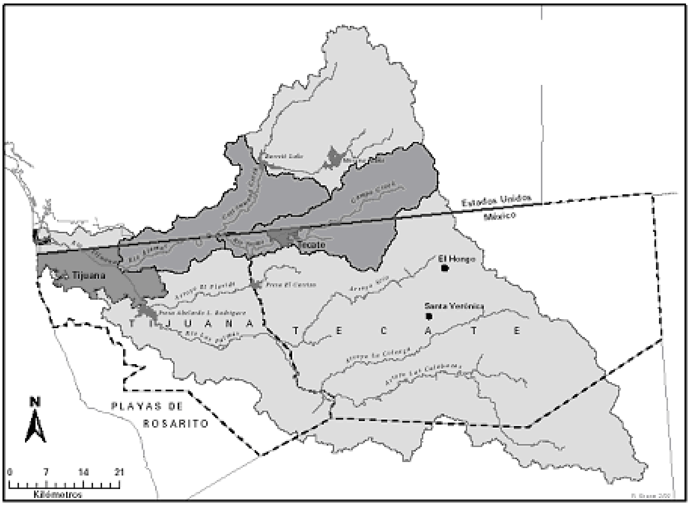

Figure 1: Description of study site.

This study reports data on the Cr, Ni, Zn, Cu and Pb levels in water and sediments of the Tecate-Tijuana River in order to describe how water soluble trace metals are converted to an insoluble form downstream to become discharged and transported by sediments, forming polluted zones.

3 Materials and methods

3.1 Sample treatment and analysis

The treatment and analysis of samples usually took place within 24 h of collection. Sediment samples were allowed to defrost, then air-dried in a circulating oven at 30 °C and thereafter sieved mechanically using a 0.062 mm sieve. All determinations were based on the fine sediment particles obtained since metals are known to adhere to these fine particles.

Table 1: Locations of sampling sites.

Site	Coordinates	Altitude (m)	pH	Use land
S1	32° 32’ 48 N, 116° 40’ 23’’ W	503	8.23	Recreation
S2	32° 33’ 16’ N; 116° 43’ 51’’ W	201	8.23	Agriculture
S3	32° 32’ 58’’ N; 116° 47’ 59’’ W	145	8.23	Agriculture
S4	32° 32’ 47’’ N; 116° 51’ 04’’ W	102	8.23	Agriculture
S5	32° 30’ 55’’ N; 116° 58’ 23’’ W	47	8.11	Urban
S6	32° 27’ 04’’ N; 116° 52’ 35’’ W	137	8.03	Residential
S7	32° 26’ 44’’ N; 116° 53’ 29’’ W	135	8.09	Residential
S8	32° 27’ 12’’ N; 116° 54’ 20’’ W	98	7.88	Urban
S9	32° 29’ 53’’ N; 116° 56’ 45’’ W	50	7.81	Urban
S10	32° 30’ 58’’ N; 116° 59’ 02’’ W	45	7.75	Urban
S11	32° 32’ 22’’ N; 117° 02’ 02’’ W	28	7.78	Urban

Open-beaker digestion (OBD) in block digester protocols was employed for sediment samples treatment. EPA method 200.8 was used for chemical analyses of the water and sediment samples. Three replicate digestions were carried out for each sample. Quality control was provided by parallel analysis of spiked matrix samples with a certified standard from Environmental Research Associates (ERA 508). Four sediment samples were spiked with a known volume of the certified standard. The same sediment samples were analyzed with no spike and the percentage of recovery ranged from 87 to 95% for metals and the variation coefficients ranged from 5 to 14%.

Pretreated samples was introduced in the auto sampler for their determination by the Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) technique, the instrument used was the Ultramass 700, Varian, using Method 3000 (APHA, [11]).

4 Results and discussion

The limits of detection of the analyzed metals were 0.251, 0.146, 0.375, 0.456, 1.833, 1.243 μg/L for Pb, Zn, Cr, Ni, and Cu respectively and the percentage recoveries of quality control standards using the OBD are in the range 100 ± 5% according US EPA, Method 200.

The results of trace metal average concentration in Tecate-Tijuana River water and sediment are shown in Table 2.

The mean concentrations of Cr in the water ranged from 0.005 to 0.026 mg/L in the Tecate River and trace to 0.028 mg/L in the Tijuana River, while that of sediment varied between 1.540 g/Kg to 62.35 g/Kg in the Tecate River. The range obtained from river water was lower than stated in Mexican Environmental Law (SEMARNAT, [19]), which states 1 mg/L and 0.5 mg/L for agriculture and recreation activities respectively.

Table 2: Trace metal average concentration.

Site	Cr		Ni		Cu		Zn		Pb	
	W	S	W	S	W	S	W	S	W	S
S1	0.02	1.54	0.02	1.15	0.04	1.06	0.10	4.358	0.01	0.40
S2	0.01	2.51	0.01	2.05	0.01	1.33	0.04	7.18	0.00	0.60
S3	0.01	43.9	0.02	27.1	<0.013	50.5	0.02	217.21	0.00	9.79
S4	0.005	62.4	0.02	59.4	0.01	81.7	0.02	376.86	0.002	17.478
	W		W		W		W		W	
S5	<LDM		0.097		0.047		0.064		0.005	
S6	0.028		<LDM		0.001		0.078		0.060	
S7	0.013		<LDM		0.100		0.103		0.020	
S8	0.007		0.005		0.075		0.036		0.022	
S9	0.004		0.006		0.016		0.021		0.003	
S10	VNR		0.016		0.018		0.028		0.003	
S11	0.003		0.017		0.045		0.070		0.01	
Soil	0.750		0.000		1.256		4.135		0.090	

W= metal concentration in water in mg/ L, S = metal concentration in sediment in mg/Kg, Soil = background concentration in mg/Kg, Soil background concentration in mg/Kg.

However, the levels of Cr obtained in sediment samples (1.54–62.35 mg/Kg) were higher than background levels in natural soil (0.750 mg/Kg). This means that the river has been affected by external Cr sources and increasing levels when the altitude decreases from S1 to S4 indicates possible transport by storm water runoff from the Tecate River to the lower Tijuana River (Figure 2). This behavior is consistent with pH ranging from 8.02–8.25.

Mean concentrations of Ni in water ranged from 0.005–0.97 mg/L, this was lower than stated by Mexican laws (SEMARNAT, [19]), which is 4 mg/L for agriculture and recreation activities. Sediment samples contained Ni levels ranging from 1.158–59.420 mg/Kg, which is high compared with the background level of 0.00 mg/Kg. Increasing Ni levels in sediments from S1 to S4 with values of pH ranging from 8.02–8.25 suggest possible insoluble nickel species formation and downstream transport of sediments (Figure 3).

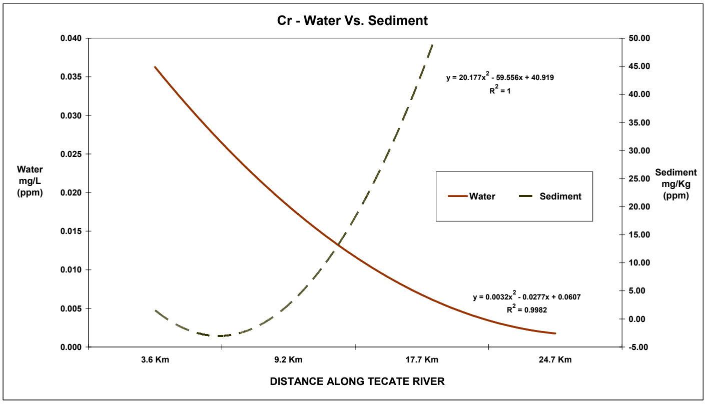

Figure 2: Chromium distribution.

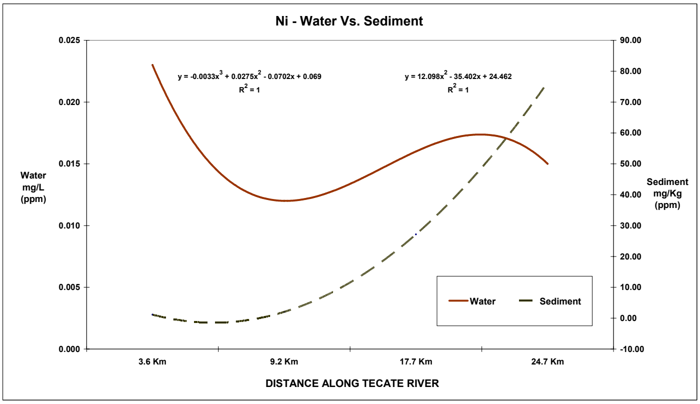

Figure 3: Nickel distribution.

More attention has been focused on the toxicity of Ni in low concentrations, such as the fact that Ni can cause allergic reactions and that certain Ni compounds may be carcinogenic (McKenzie and Smythe, [10]).

Possible sources of Ni in surface water include anthropogenic sources, electroplating industry discharges, old battery wastes, and other Ni alloys.

Levels of Cu in river water ranged from trace to 0.100 mg/L while that in sediment ranged from 1.065 to 81.72 mg/kg (Table 2). The Mexican guidelines for Cu in domestic and agriculture use are 2.0 and 6.0 mg/L respectively (SEMARNAT, [19]). The range obtained was lower than the set value, hence adverse effects from domestic use are not expected as far as this parameter and the results obtained are concerned. However Cu sediment content increases when the altitude of the site decreases, meaning that Cr and Ni in sediments are transported downstream and increased acidity in river water should dissolve Cu from the sediment (Figure 4).

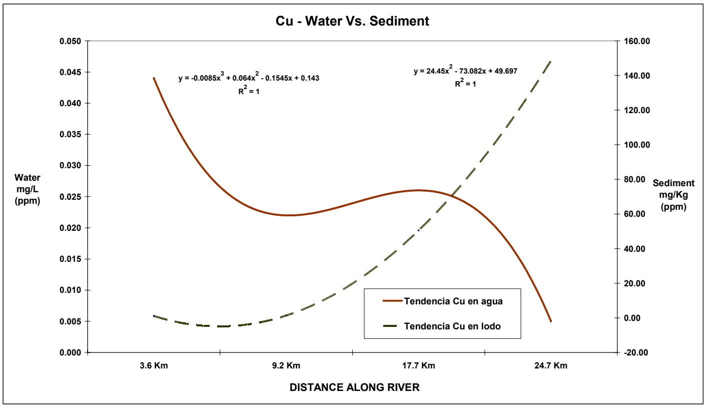

Figure 4: Copper distribution.

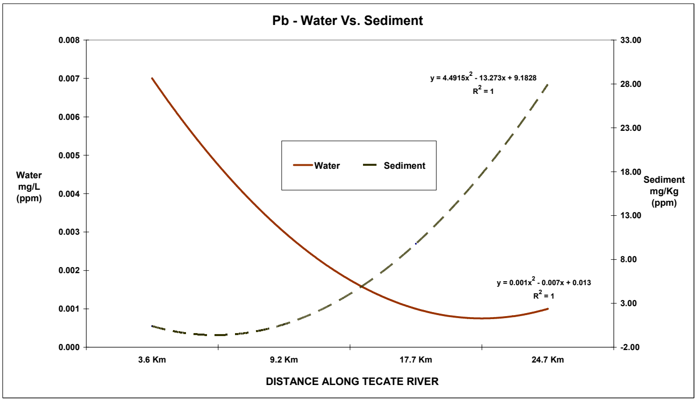

Figure 5: Lead distribution.

Levels of Zn in river water ranged between 0.015 to 1.040 mg/L (Table 2), this was lower than stated by SEMARNAT [19], which is 20 mg/L for agriculture and recreation activities and the Secretary of Health and Assistance (SSA [20]) established 5 mg/L for drinking water.

The water is unfit for the sustenance of the aquatic ecosystem but could still be utilized for irrigation and livestock watering since the range obtained was much lower than the Mexican limits.

Sediment samples contain Zn levels ranged from 4.358 to 376.806 mg/Kg, which is high compared with the background level of 4.135 mg/Kg. As with Cr, Ni and Cu, increasing Zn levels in sediments from S1 to S4 are observed (Table 2).

Levels of Pb in river water varied between 0.001 and 0.060 mg/L and between 0.402 and 17.478 mg/kg in sediment. The limits for Pb in river water state 1 mg/L and 0.4 mg/L for agriculture and recreation activities (SEMARNAT [19]), and most sampling site are accord with this range except S6.

The river water is usable for drinking purposes because it does not exceed limits established by SSA [20] (0.025 mg/L). The levels of Pb obtained in sediment were higher than those in the river water and were also higher than background levels in natural soil (0.090 mg/Kg), this means that river sediment could be transporting Cr and Ni to the lower Tijuana River (Figure 5) and this is an influential factor on the level of Pb in river water along with other enhancing factors such as the current flow and pH, since water acidity is known to influence the solubility and availability of metals.

5 Conclusions

This study revels that the water quality of the Tecate-Tijuana River conforms to quality levels established by Mexican laws, however trace metal levels in sediments are increasing downstream in the Tecate-Tijuana River. It is shown that sediments are a temporal sink of trace metals and acidity changes in the river can increase metal concentration in the water. Trace metal accumulation in sediments increases in the dry season and they are transported downstream to the Tijuana River in the rainy season. It would be interesting to investigate trace metals in the Tijuana Estuary and beach.

Elevated levels of Cr, Ni, Cu, Zn and Pb were detected in the river sediments, which could be directly detrimental to the health of the aquatic ecosystem and indirectly to man since the river water is used to irrigate a nearby farmland. Metals from river water could be a contributing source to the levels in groundwater, hence continual assessment is highly essential.

These results showed that there is an anthropogenic impact in the sediment quality of this stream.

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