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Nickel and Vanadium Concentrations and Its Relation with Sediment Acute Toxicity

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Abstract Sediments from Pánuco River historically have contained elevated levels of numerous contaminants that may pose risks to ecological receptors and humans. Sediments were sampled and characterized to determine the acute sediment toxicity and its relationship with contaminants. Results demonstrated that toxicity was significantly correlated with fitness index ($r = 0.82$, $p < 0.001$), TOC ($r = 0.55$, $p < 0.5$), Ni ($r = 0.95$, $p < 0.001$), and V ($r = 0.93$, $p < 0.001$), but not with PAHs ($r = 0.20$, $p < 0.5$) during rainy and dry seasons. Although a great heterogeneity exists, the river outlet presents the biggest problems, due to dredging allow the metal desorption from solid to water phase, increasing the metal bioavailability.

Keywords Estuary · Ni · V · EC_{50}

Heavy metals are a concern in the Pánuco estuarine environment, which is located in Tamaulipas State, Mexico. The study area continues to receive wastewater from industrial sources, mainly petroleum industry, which may settle on the bottom and become incorporated into sediment. Nickel and vanadium have been considered as a serious problem at the study area due to its accumulation in sediment (IMP 1998). Both metals have been re-suspended into the environment by dredging and boating activities, and potentially threaten the integrity of the ecosystem. The most serious human health effects occur when nickel is inhaled: carcinogenic forms like nickel oxide are known. The major human health effects from breathing high levels of vanadium are on the lungs and throat. There is no evidence that any vanadium compound is carcinogenic (Thomassen et al. 2004).

Numerical sediment quality guidelines (SQGs), an integrated framework for assessing sediment quality conditions, have been developed using matching sediments chemistry and laboratory toxicity data (Ingersoll et al. 2001). The toxicological evaluation integrates the effect of many environmental variables. Because the sediment is a storage compartment for many pollutants and provides a habitat for the biota, bottom-dwelling organisms are exposed to diverse chemicals and may pose a risk to human health if consumed (NOAA 1998). A critical component in the application of SQGs, is to predict the absence or presence of toxicity in field-collected sediments (MacDonald et al. 2000). The objective of this study was to determine the acute toxicity of the superficial sediments, and to analyze the relationship between toxicity, and Ni and V concentrations.

Materials and Methods

A Van Veen grab of 20 kg capacity was used to collect sediment samples in duplicate. The sampling was carried out during both the rainy (December 1998) and dry (May 1999) seasons. Along the river (from 22° 12′ 18.4″and 97° 53′ 33.8″ to 22° 15′ 47.7″ and 97° 47′ 42.9″) there were five transects (Fig. 1), and in each one, sediment samples on both banks (right bank denoted as A, left bank denoted as C) and center of the river (denoted as B) were taken.

Table 1 shows the characteristics and methods for sediment characterization. Ni and V concentrations were analyzed (due to the accumulation tendency at the study

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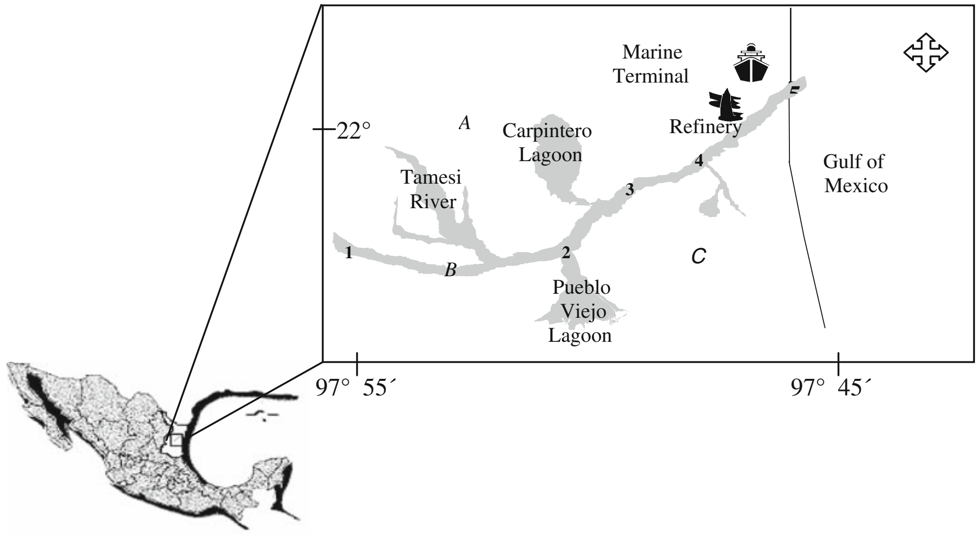

Fig. 1 Sampling sites along River Pánuco, Tamaulipas, Mexico, including five transects (1–5) and A, B and C riverbanks. Polyaromatic hydrocarbons (PAHs) were analyzed by gas chromatography/mass spectrometry (GC/MS), using a Top Fisons with an AS800 autosampler

Table 1 Sediment parameters and analytical methods

Parameters	Methods
Size grain	Folk (1969)
Fitness index	Satsmadjis and Voutsinou-Taliadouri (1983)
Mineralogy	Rothwell (1989)
Organic matter	Walkley–Black (Nelson and Sommers 1982)
Total organic carbon	TOC Shimadzu S-5000A (Shimadzu 1998)
Nitrogen	EPA 351.3 (US EPA 1998)
Phosphorus	EPA 365.2 (US EPA 1998)
pH	EPA 9045 (US EPA 1998)
CEC	EPA 9081 and EPA 7770 (US EPA 1998)
Fecal coliforms	SM9221 B (APHA 1995)
Ni and V	Digestion EPA 3050A
	GFAAS analysis[a] EPA 7000 (US EPA 1998)
PAHs	Extraction clean up (EPA 3611)
	GC/MS analysis (EPA 8270C) (US EPA 1998)[b]
Toxicity	Microtox® (Anzuren 1998)

[a] The detection limit for Ni and V was 0.02 and 0.2 mg kg^{-1}, respectively

[b] Detection limit, 0.002 mg Kg^{-1}

area) by atomic absorption spectrophotometry, using a Perkin Elmer 403 spectrophotometer.

The method of acute toxicity evaluation was Microtox®. The bioluminescence reduction was measured with a photomultiplier coupled to a light sensor and the results about the toxicity are expressed as EC50 at certain time (Anzuren 1998). Sediment toxicity was determined analyzing the elutriate, which was obtained with 1 g sediment in 5 mL of NaCl 35% solution, and making an extraction (at 25°C) by ultrasonic (Cole-Parmer mod 8845-40) for 15 min.

The sample was filtered (using filter columns of 45 μm pore), and the acute toxicity was analyzed during 5 and 15 min, by means of the light measurement emitted by the bacteria, in comparison with a witness from the saline solution to 35%. The toxicity, expressed as toxicity units (where TU = 100/EC50) were calculated in order to provide a direct measurement of the toxicity. The samples were classified from non toxic to very toxic according to the classification of Kwan and Dutka (1996) (Table 2).

Correlation matrix between toxicity, metals and sediment parameters were performed using SAS statistical analysis package (SAS 1988).

Results and Discussion

The minimum and maximum levels of analytical data along with the Ni and V concentration are shown in Table 3. Sediment toxicity was significantly correlated with fitness index (r=0.82, $p < 0.001$), TOC ($r = 0.55$, $p < 0.5$), Ni ($r = 0.95$, $p < 0.001$), and V ($r = 0.93$, $p < 0.001$), but not with PAHs ($r = 0.20$, $p < 0.5$) during dry season (Table 4) and similarly on the rainy season (data not shown).

Table 2 Toxicity units and EC_{50} classification (Kwan and Dutka 1996)

TU	Classification	EC_{50} (%)
<50	No toxic	>2
50–100	Doubtful toxic	1–2
101–134	Less toxic	0.75–0.99
135–200	Under toxic	0.5–0.74
201–400	Toxic	0.25–0.49
>400	Very toxic	0.0–0.24

Table 3 Main analytical data along with the Ni and V concentration

	Texture (%)									N (mg Kg^{-1})			O matter (%)		
	S A-R L	A-R Cl	A-R S	B-R L	B-R Cl	B-R S	C-R L	C-R Cl	C-R	A-R	B-R	C-R	A-R	B-R	C-R
Min	13	42	5	0	0	0	0	0	0	321	89	463	0.6	2.6	0.2
Max	50	79	9	94	61	7	36	71	14	941	692	760	4.1	33.9	2.8
	S A-D	L A-D Cl	A-D S	B-D L	B-D Cl	B-D S	C-D L	C-D Cl	C-D	A-D	B-D	C-D	A-D	B-D	C-D
Min	9	5	1	15	22	2	8	4	0	524	566	450	3.5	3.4	2.8
Max	82	73	18	66	75	16	94	72	14	760	905	844	8.3	9.4	7.5
	P (mg Kg^{-1})			CEC (meq 100 g^{-1})			pH			Ni (mg Kg^{-1})			V (mg Kg^{-1})		
	A-R	B-R	C-R	A-R	B-R	C-R	A-R	B-R	C-R	A-R	B-R	C-R	A-R	B-R	C-R
Min	3	2	2	11	12	13	8	7	8	30	27	25	19	20	17
Max	67	1	9	46	24	22	8	9	9	37	37	36	25	25	25
	A-D	BD	CD	AD	B-D	C-D	A-D	B-D	C-D	A-D	B-D	C-D	A-D	B-D	C-D
Min	0	0	0	13	15	10	8	8	8	11	13	17	35	37	67
Max	158	54	51	20	18	18	9	9	9	25	28	25	91	65	108

A, Right bank; B, Center; C, Left bank; R, Rainy season; D, Dry season; T, Transect; L, Loam; S, Sand; Cl, Clay

Table 4 Correlation matrix between toxicity, metals and sediment parameters

	1	2	3	4	5	6	7	8	9	10	11	12	13
1	1												
2	0.75**	1											
3	0.45	0.47	1										
4	−0.11	0.43	0.32	1									
5	−0.37	−0.14	0.44	0.39	1								
6	0.21	−0.27	0.47	0.55*	0.49	1							
7	0.14	0.27	0.38	−0.22	0.14	0.25	1						
8	0.35	0.38	0.51*	0.48	0.31	0.48	0.47	1					
9	0.37	0.21	0.14	0.58*	0.14	0.4	0.44	0.39	1				
10	0.52*	0.89**	0.31	0.55**	0.47	0.44	0.41	0.42	−0.12	1			
11	0.49	0.81**	0.49	0.51	0.39	0.31	0.49	0.47	0.47	0.55**	1		
12	0.13	0.41	0.51	0.85**	0.49	0.39	0.25	0.24	0.09	0.51*	0.39	1	
13	0.48	0.82**	0.31	0.55*	0.12	0.27	0.43	0.32	0.11	0.95**	0.93**	0.2	1

1, size grain; 2, fitness index; 3, mineralogy; 4, total organic carbon; 5, N; 6, P; 7, pH; 8, CEC; 9, fecal coliforms; 10, Ni; 11, V; 12, PAHs; 13, toxicity. Values marked with ** or * are significant at 0.001 and 0.05 probability levels, respectively

Figure 2 shows the toxicity during both seasons. During rainy season, sediment had an average value of 1434 ± 613 TU on the right bank, 507 ± 348 TU in the center and 21933 ± 246 TU on the left bank. This indicates the furthest bank from the Refinery and Marine Terminal was the most toxic, which could be determined by the hydrodynamic of the system (transporting of fine particles), as it shows by the positive correlation between metals and fitness index.

Following the toxicity approach reported by Kwan and Dutka (1996), 100% of the stations of the right bank were very toxic, while 80% of the sites in the center and on the left bank were very toxic and 20% were toxic. That means that the river sediment is highly toxic (except in the station 2B, located on transect 2, at the river center), although a seasonal variation was registered.

The maximum toxicity was found in the transect 3 on the left bank (106657 ± 987 TU). This toxicity is most likely related to the contributions of the Pueblo Viejo Lagoon, which produces the fine sediment particles re-suspension and drives. Another factor that could have influenced in the high toxicity levels was the combination

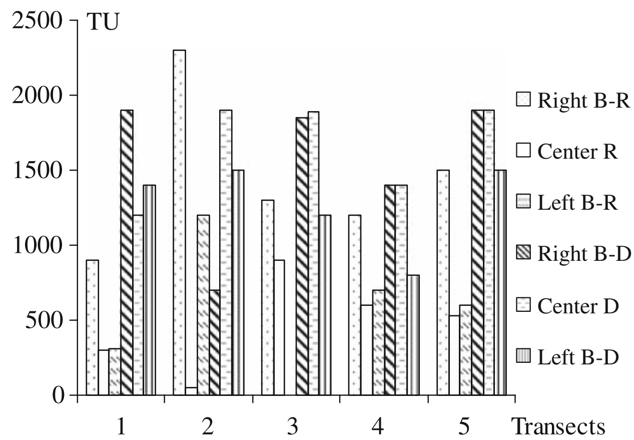

Fig. 2 Toxicity units (TU) during both rainy (R) and dry season (D), and three zones of the River Pánuco

of grain size, high quantity of clays and high concentrations of TOC, which function as metal adsorption surface. The combination of those factors forms an appropriate substrate for not only metal adsorption, but also organic pollutants (PAHs), which are presented at the study area at concentrations of 9–684 μg kg^{-1}. However, there was not a significant ($p < 0.005$) correlation between toxicity and PAHs. About space variation for transects (Fig. 2), the highest toxicity were detected in transect 3A and 3B.

On dry season, the TU average value was 1253 ± 385, with the highest and lowest value of 1557 ± 203 and 607 ± 37 TU, respectively. The river center was the most toxic area, followed by the right and left bank, although it can be evidenced toxicity differences along each bank. Regarding the variation for transects, sediment of transects 3 and 5 were very toxic to *Vibrio fischeri*, because of the contribution of the Pueblo Viejo Lagoon and due to the combination of physical (fitness) and organic matter in the river outlet that provides a wide area of adsorption. A relatively heterogeneous pattern of toxic sediment distribution is observed in the area, that which can be been the result of an incomplete mixture due to the season hydrodynamic, finding high concentrations of pollutants in certain places of the aquatic systems or near the bottom (Chapman 1991).

Although a great heterogeneity exists, the river outlet presents the biggest problems, due to higher concentrations of metals. In addition, the dredging allows the metal desorption from solid to water phase, increasing the bioavailability of the Ni and V (see Amezcua-Allieri and González 2007). This situation is reflected in a greater toxicity.

In the near sediment to a marine oil platform in the Gulf of Mexico (Chapman et al. 1991), the average value of the toxicity units was 13.72 (10 times less to those found in this study). However, the toxicity was associated with aromatic hydrocarbons instead of metals. Since the sediment from a marine platform only receives effluents coming from the oil industry, the dynamic of the Pánuco estuary system differs from a marine type. As it was previously shown, a significant positive correlation (r^2=0.9773, $p < 0.001$) was found between the toxicity and concentration of Ni and V. During the rainy season, the highest V concentrations and toxicity were found. On dry season, the highest Ni concentrations were found, and after dredging activities, the toxicity diminished. Fine sediments tend to accumulate greater concentrations of metals. When these sediments are removed during dredging activities, the inferior sediment layers have a better quality.

Diverse toxic effects have been related with Ni. These can be acute or chronic, depending on the type of nickel compounds, the class of exposed organisms and time of exposition. The toxic potential of vanadium, although smaller than the Ni, is equally important for the aquatic organisms. The solubility of Ni compounds is variable, chlorides, sulfates and nitrates of nickel are soluble in water, while the carbonates and oxides are not. Nickel is one of the compounds that quicker and easily absorbed by the biological membranes, while the dissolved nickel can form complex and to bind to the organic matter (IPChS 1991).

Ni concentrations during rainy season were from 18.4 to 27.7 mg kg^{-1}, while during dry season, concentrations were higher (25.35–37.32 mg kg^{-1}), under which physiological effects associated to the V are linked with the enzymatic activity and reproductive capacity decrease. Ringelband and Karbe (1996) reported an inhibition of the ATPasa Na-K in the eel and Ringelband (2000) reported the ceasing in the reproduction at 8–10 mg kg^{-1} V concentrations in *Cordylophora caspia* and kinetics of vanadium accumulation.

The approaches of sediment quality criteria to protect aquatic life is a valuable tool that helps to interpret sediment chemistry data and to evaluate the potential toxic effect of pollutants present, as well as the effect on the aquatic organisms. Canada and United States have developed toxicological approaches for fresh water and marine water based on two levels: threshold effect level (TEL), which is represented by the smallest concentration of adverse effects in a low frequency and the probable effect level (PEL) that defines the level on which the adverse effects can happen more frequently (Munawar and Dave 1996). In accordance with these approaches, the average concentration of the nickel in the River Pánuco during the two seasons, stayed among the two thresholds (18 mg kg^{-1} TEL and 35.9 mg kg^{-1} PEL) (Fig. 3), which marks a percentage incidence of adverse biological effects (IABE) of 18% in all the sampling sites.

Another method to identify metal toxicity is based on declaring samples as not toxic when the quantity of sulfuric

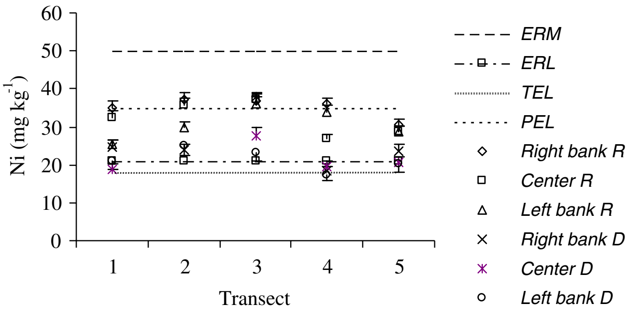

Fig. 3 Toxicological approaches for Ni (ERL, effects range low; ERM, effects range medium; TEL, threshold effect level; PEL, probable effect Level) during rainy (R) and dry season (D)

acid moles is greater than the sum of the masses of the metals. This method defines critical concentrations, which are obtained from the tenth to the fifth percentile of the concentrations associated with the effects (Solomon and Tacks 2002). Those percentiles are designated as ERL (Effects Range Low) that refers to the pollutant concentration that will have some ecological effect, with 10% probability in the population and ERM (Effects Range Medium), which is the concentration that will have ecological effects approximately in 50% of the measurements, based on published studies. The values for nickel are 21 mg kg^{-1} for the ERL and 52 mg kg^{-1} for the ERM (Fig. 3) (NOAA 1998). For the ERL and ERM approaches, the average values registered exceed, at last twice, the ERL values, but not the ERM approach. This observation is in agreement with the results in Louisiana (NOAA 1998), where the probability that some adverse effect exists in the aquatic system was located between 10 and 50%, similar percent obtained by TEL and PEL approaches. Transect 5 (the closest to the refinery and marine terminal) had the worst quality, which agrees with the physical and chemical parameters of the sediment, suggesting the river outlet as the most vulnerable area, due to high concentrations of both metals, pH, cationic exchange capacity and organic matter.

The identification of the river outlet as vulnerable area needs to take into account: (1) the outlet is a nutritious trap that partly is physical and, partly biological; (2) the estuaries benefit the diversity of producers; (3) water transports nutritious elements, so that the organisms can conserve an immobile posture that does not require a lot of metabolic energy for the excretion and food capture; and (4) a great number of fishing species of great commercial value is developed, so the environmental protection of this area because of the fishing must be in agreement with refinement processes. Due to both activities, it is required a deep conciliation between the technological development and the protection of aquatic ecosystems.

The best sediment quality is found during the dry season mainly because of dredging activities, since superficial layers were removed before sampling. Another important factor is a massive transport of polluting substances during rainy season, producing the re-suspension of the finest material. Toxicological analysis appears to be a viable approach in quality sediment assessment.

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