

## Cluster and Principal Components Analyses on the Contents of (Total and Sorbed) Trace Metals in Fresh Marine Sediments from the Southwest of the Gulf of Mexico

### *Análisis de componentes principales y clusters de metales trazas (totales y sorbidos) en sedimentos marinos recientes del Suroeste del Golfo de México*

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#### Abstract

The amounts of total and sorbed Al, Ba, Cr, Fe, Mn, Ni, and V present in three sediment cores from the South of the Gulf of Mexico (N1, N2, and N3) were determined. Of the three samples studied herein (N1, N2, and N3), one of them (N2) is associated to a natural "chapopotera". ICP/MS analyses show that total concentrations of Al, Fe, Mn, Ba, Cr, Ni, Pb, and V for N1 and N3 were found to be *ca.* 4.2, 2.3, 206.5, 165, 91, 72, 14 and 97 mg kg<sup>-1</sup>, and *ca.* 5.2 (Al<sub>2</sub>O<sub>3</sub>), 4, 401.50, 269, 89, 62, 18, and 118 mg kg<sup>-1</sup> for N2. As evidenced by the correlation matrices, there is a positive association among metals distribution, except for the case of Mn, regardless of the sediment core. Nevertheless, Cluster and Principal Components Analyses denote variability in metal-spatial distribution, signature variability in the composition of the water column. Magnitude values for the enrichment factor (EF) relative to background values found in the Southern Gulf of Mexico (bulk seawater) for Al, Fe, Mn, Ba, Cr, Ni, Pb, and V were estimated. The outcome of this work show distinctive EF values, ranging from moderate to high EF values, regardless of the core source.

#### Keywords:

- trace metals partitioning
- enrichment factor
- "chapopotera"









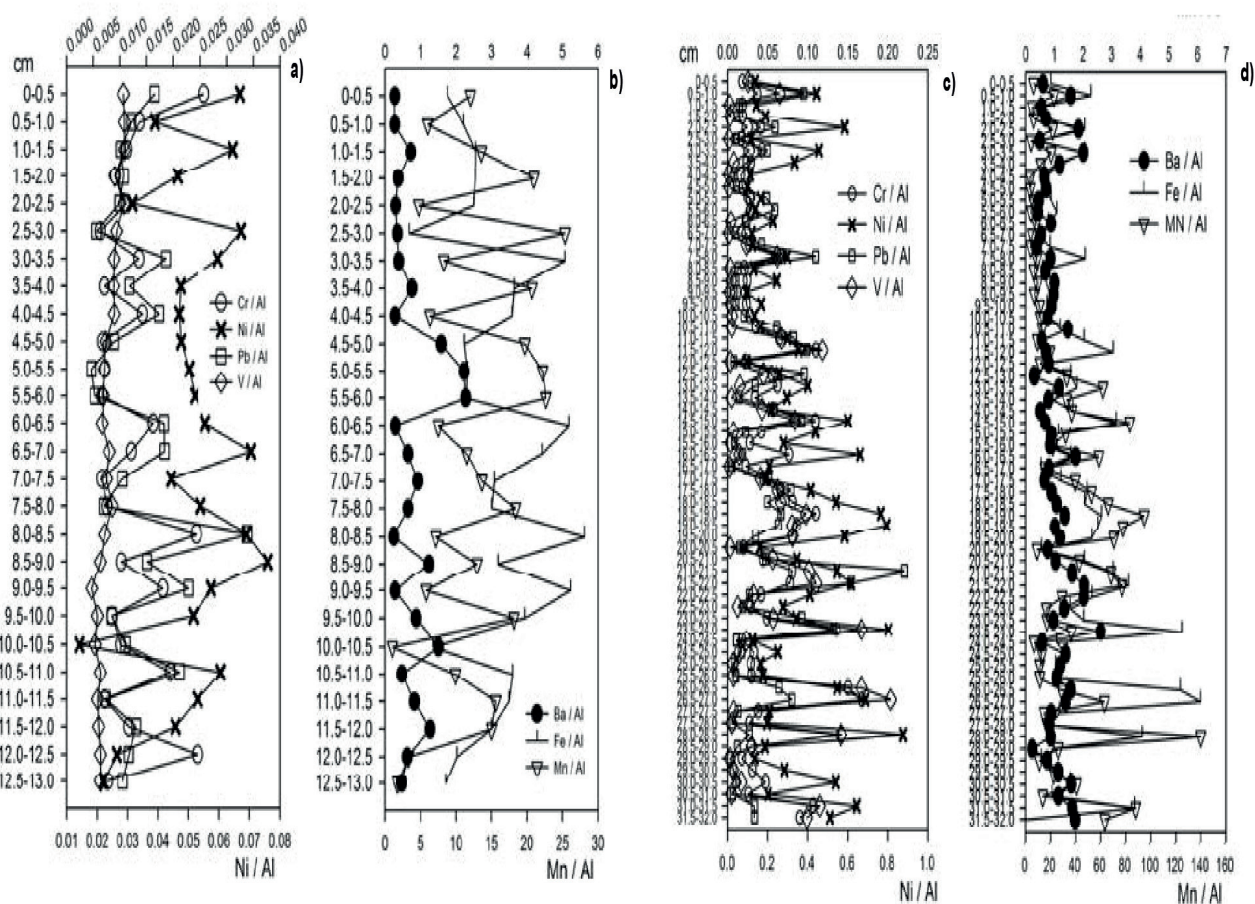


Figure 3. Normalized absorbed metals to Al

Core N2. Cluster and principal components analyses of normalized data for total metals in N2 are explained because prevailing similarities between geochemical processes with depth. Data conglomerates become evident (S4, Supplementary Information Section). Normalization on the accumulation of total metals show similar changes for all metals with depth (Figure 3) A high correlation of normalized-total metals, except for  $Ba_T$  and  $Mn_T$  ( $p < 0.05$ ,  $N = 64$ ) (Table 1) (PEP-UNAM, 2008) was observed.

Normalization of data trends for sorbed metals show significant changes along the core. Data variability becomes more notorious compared to N1. This is particularly true for the cases of  $Ba_a$  and  $Fe_a$ . The close proximity of natural "chapoteras" and high concentrations of oil derivatives is thought to influence the compartmentalization of metals.

Magnitude values for  $Fe_a$  serves as an indication of metal mobility with depth. By contrast, obtained values for  $Cr_a$  and  $Ni_a$  suggest variations to a lesser degree and, thereby, a lower mobility. Particularly so, for the case of  $Ni_a$ . Hence, natural "chapoteras" have an effect on the environmental mobility and compartmentalization of  $Cr_a$  and  $Ni_a$ . Variations in  $V_a$  magnitude values determined along the core is in agreement with vanadium input originated from natural "chapoteras", arguably in the form of either vanadium-porphyrin or vanadium-non-porphyrines complexes (Fish and Komelenic, 1984). The behavior of  $Pb_a$  denotes little changes along the core, with accumulation in the deep zones only (Balsam *et al.*, 2007).

Our results show a lack of correlation between normalized absorbed metals data trends ( $p < 0.05$ ;  $n = 64$ ). However, data trends for  $V_a$  show a significant correla-

tion with data trends for  $Cr_a$  and  $Fe_a$ , in consistency with the idea of supplies in the deep zone originated from the Grijalva River (Table 1; PEP-UNAM, 2008; Vázquez *et al.*, 2000).

Core N3. Normalization of data trends for total metals show variations for the Fe/Al and Mn/Al ratios, in consistency with normalized data trends for N1. These findings can be explained in part because both zones receive water supply from the Grijalva River (Figure 1). Perhaps the decreases in magnitude values observed can be attributed to reactions between Fe and Mn with  $HS^-$ ,  $S^{2-}$ , and/or other metals (Stumm and Morgan, 1996).

The Ba/Al ratio shows variations probably because the formation of Ba-carbonates (e.g.,  $BaCO_3$ ) or sulfates ( $BaSO_4$ ; Hurtgen *et al.*, 1999). The Cr/Al ratio presents similar variations, with no indication of the presence of Cr in the beaches of Tabasco (Vázquez *et al.*, 2006;

Fuschsman *et al.*, 2007). The Ni/Al and V/Al ratios present similar variations along the core and in agreement with those observed for N1. The Pb/Al ratio in the top (5 to 6 cm) show high values that may be a result of an unusual Pb supply originated from either the Grijalva River, the atmospheric supplies, or the oil-industry related activities (Varela, 2007). Furthermore, a correlation analyses of normalized data for total metals, namely Fe/Al with Mn/Al, Ni/Al with V/Al, and Ni/Al with V/Al were found to be statistically significant ( $p < 0.05$ ;  $n = 24$ ; Table 1). These results further confirm an influence of sediments originated from oil wells. Additional cluster and principal components analyses for normalized data of total metals reveal four conglomerates formed by the Fe/Al, Mn/Al, Ni/Al and V/Al ratios, while those presenting no statistical significance were found to be the Pb/Al and Ba/Al ratios (Balsam *et al.*, 2007), (S4, Supplementary Information Section).

Table 1. Multiple correlation for total and sorbed metals

	N1						
	BA/AL <sub>1</sub>	CR/AL <sub>1</sub>	FE/AL <sub>1</sub>	MN/AL <sub>1</sub>	NI/AL <sub>1</sub>	PB/AL <sub>1</sub>	V/AL <sub>1</sub>
BA/AL <sub>1</sub>	1.000						
CR/AL <sub>1</sub>	0.543	1.000					
FE/AL <sub>1</sub>	0.525	0.992	1.000				
MN/AL <sub>1</sub>	0.484	0.963	0.982	1.000			
NI/AL <sub>1</sub>	0.54	1.000	0.992	0.963	1.000		
PB/AL <sub>1</sub>	0.589	0.957	0.940	0.907	0.957	1.000	
V/AL <sub>1</sub>	0.534	0.991	0.999	0.978	0.991	0.948	1.000
	N2						
	BA/AL <sub>2</sub>	CR/AL <sub>2</sub>	FE/AL <sub>2</sub>	MN/AL <sub>2</sub>	NI/AL <sub>2</sub>	PB/AL <sub>2</sub>	V/AL <sub>2</sub>
BA/AL <sub>2</sub>	1.000						
CR/AL <sub>2</sub>	0.873	1.000					
FE/AL <sub>2</sub>	0.911	0.982	1.000				
MN/AL <sub>2</sub>	0.166	0.237	0.229	1.000			
NI/AL <sub>2</sub>	0.856	0.968	0.961	0.380	1.000		
PB/AL <sub>2</sub>	0.888	0.942	0.935	0.172	0.892	1.000	
V/AL <sub>2</sub>	0.872	0.984	0.987	0.273	0.972	0.914	1.000
	N3						
	BA/AL <sub>3</sub>	CR/AL <sub>3</sub>	FE/AL <sub>3</sub>	MN/AL <sub>3</sub>	NI/AL <sub>3</sub>	PB/AL <sub>3</sub>	V/AL <sub>3</sub>
BA/AL <sub>3</sub>	1.000						
CR/AL <sub>3</sub>	0.807	1.000					
FE/AL <sub>3</sub>	0.878	0.982	1.000				
MN/AL <sub>3</sub>	0.177	0.262	0.299	1.000			
NI/AL <sub>3</sub>	0.769	0.971	0.972	0.419	1.000		
PB/AL <sub>3</sub>	0.800	0.958	0.928	0.119	0.875	1.000	
V/AL <sub>3</sub>	0.813	0.992	0.989	0.321	0.990	0.924	1.000

Cores N1, N2, and N3. Principal components analyses of total metals data sets for the three cores show three different groupings (S5, Supplementary Information Section). The core N3 shows a metal grouping, with the exception of Pb/Al and Ba/Al. A second group of conglomerates in N2 is observed, with the exception of Ba/Al. A third metal conglomerate becomes evident for N1, with the exception of Mn/Al. The later results are explained in part by a higher input of Mn to N1 relative to N2 or N3 originated from heterogeneous-industrial activities at the Coatzacoalcos River vicinity (Vázquez *et al.*, 2000; PEP-UNAM, 2008; Geissen *et al.*, 2009).

Finally, normalized data trends obtained for N1 were found to be similar to those reported for the time series of stations near the influence of the Coatzacoalcos River (PEP-UNAM, 2008). Likewise, normalized data trends obtained for N2 were found to be similar to those reported for the time series for stations near the “chapopoteras” (PEP-UNAM, 2008). Normalized data

trends obtained for N3 were found to be similar to those reported for the time series of stations near the Grijalva River (Vázquez and Virender, 2004; Vázquez *et al.*, 2006).

### Metal enrichment factors in marine sediments

Diverse methods have been proposed for evaluating the degree and enrichment of metals in marine sediments (Salomons and Förstner, 1984; Abraham and Parker, 2008). The simplest method for estimating the level of pollution factor involves the normalization of concentration values to grain size (Rubio *et al.*, 2000). The Enrichment Factor (EF) is calculated on the basis of the AIT (where AIT is total aluminum and AIL is lixivate aluminum) values according to supplementary information (S6 Supplementary Information Section).

Calculated EF values are classified according to Table 2 (Kumar and Edward, 2009).

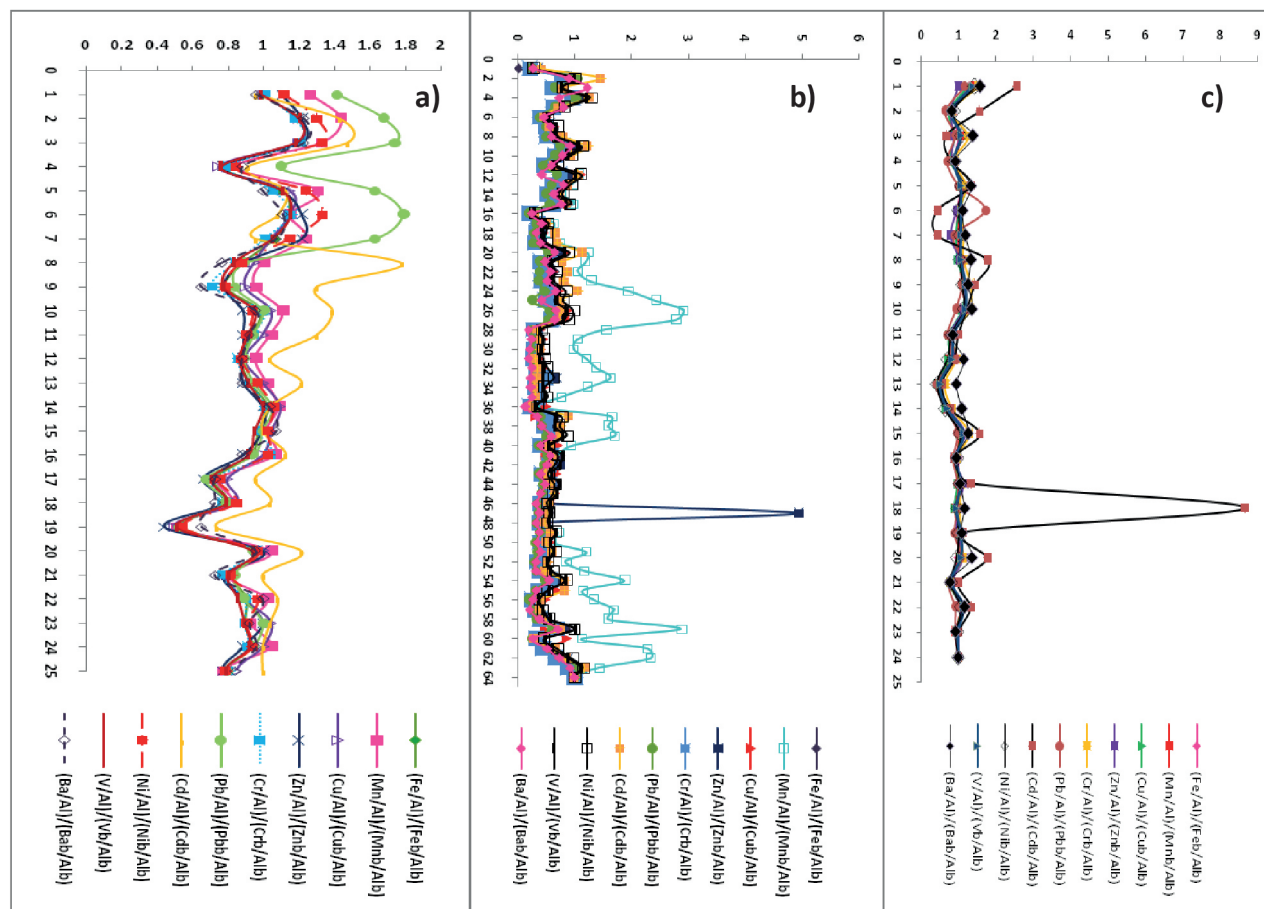


Figure 4. Enrichment factor values relative to the horizon of the cores

Table 2. Classification of EF values according to Kumar and Edward (2009)

EF < 2	Deficient to minimum enrichment
2 ≤ FE ≤ 5	Moderate enrichment
5 < FE ≤ 20	Significant enrichment
20 < FE ≤ 40	High enrichment
EF > 40	Extremely high enrichment

Our results for N1 (Figure 4) show that Cr and Ni present a minimum enrichment, Fe and V a moderate enrichment, and Ba, Mn and Pb a significant enrichment. The significant enrichment of Ba, Mn and Pb can be explained by industrial supplies and natural drainage received from the Coatzacoalcos River. Except for the case of Ba, data trends for all metals show decreases in EF values with core depth (Figure 4).

Results for N2 at *ca.* 0.5 to 7.5, 18.0-27.0, and 30.0-32.0 cm depth indicate high EF values, except for the case of Mn (Figure 9). These results can be explained by the manganese oxides in organic matter mineralization or secondary environmental reactions (Luther *et al.*, 1997; Hulth *et al.*, 1999; Anschutz and Blanc, 1995; Anschutz *et al.*, 2005).

Results for N3 show EF values corresponding to significant-to-high enrichment (Table 2; Figure 4). These results are all based on the proximity of the coast to the sampling site; therefore, EF values provide an indication of the influence from the Grijalva River on metal accumulation in sediments. Barium, Fe, Pb, Ni, and V showed EF values that correspond to the category of significant enrichment, and manganese to the category of high enrichment.

These results may not be attributed to anthropogenic activities, but to the diagenetic processes instead. In contrast, chromium showed an EF value that corresponds to the category of high enrichment. We explain these latter values due to the presence of chromite in the coasts of Tabasco (PEP-UNAM, 2008). The EF values determined in N3 for Cr were found to be high relative to those determined in N1 or N2 (Figure 4).

## Conclusions

The metals were normalized with respect to Al, which maintains a natural change in the south of the Gulf of Mexico. The analysis of conglomerate and principal components allowed us to compare metal the three sediment cores obtained from in close proximity to the Coatzacoalcos River, a natural “*chapopoteras*” and the Grijalva River. Analyses of EF values showed that me-

tals present with the same core can present diverse enrichment behavior. Value for EF of Mn in N2 is consistent with a significant enrichment not attributed to anthropogenic activities (PEP-UNAM, 2008). Values EF for Mn accounts only import to Mn distribution. Either is necessary to distribute between Mn in geochemical processes and those introduced by the anthropogenic activity. In N3, EF values for Cr<sub>T</sub> were found to be high perhaps due to the precipitation-dissolution processes of chromite in the coast of Tabasco.

## Contents of the supplementary information section

- S1 Box plots of changes of total metals (T) and absorbed (L).
- S2(a) Change of the horizon of the depth of the total metals (Ba and Al).
- S2(b) Change of the horizon of the depth of the total metals (Fe and Cr).
- S2(c) Change of the horizon of the depth of the total metals (Ni and Mn).
- S2(d) Change of the horizon of the depth of the total metals (V and Pb).
- S3(a) (b) (c) (d) Change of the horizon of the depth of the metal absorbed.
- S4(a) (b) (c) Cluster diagram and major components of the total metals in the sediment cores (N1, N2 and N3)
- S5 Principal component analysis for the three cores.
- S6 Formulae 1
- S7 Location of sampling points in the southern Gulf of Mexico.

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