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EVALUATION OF POTENTIALLY TOXIC METAL CONCENTRATIONS IN THE TERMINOS LAGOON, CAMPECHE, GULF OF MEXICO

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Abstract: The Terminos Lagoon is a region of great environmental and economic importance, due to its biodiversity, abundance of natural resources and proximity to the Campeche Sound. These characteristics encourage the development of numerous human activities in its surroundings, including oil, agricultural, industrial, urban and sanitary activities. We evaluated the concentration of Cr, Ni, Pb and V in surface sediment samples from Laguna de Terminos, Campeche, Mexico. The results obtained show that the concentrations of Cr and Pb remained below the ecological criteria of the minimum and maximum adverse ERL and ERM conditions for the biota, as well as within the ranges reported for other coastal lagoons in the Gulf of Mexico, with the exception of Pb, which decreased by almost 100%. Ni recorded values above the ERL and ERM, which have shown fluctuations in concentrations depending on the rainy and dry seasons. V maintained its concentrations below 27.73 mg/kg. High correlations were found between metals Cr – V, Cr – Ni and Ni – V, suggesting that these elements share the same source of origin. The statistics show that there are significant differences between the sampling sites PLZ and C, and PLZ and CDL. The reduction may be due to a decrease in urban, tourist, fishing and agricultural activities.

Keywords: heavy metals, sediments, contamination, Pollution indices

1. INTRODUCTION

Mexico has approximately 125 coastal lagoons that cover 33% of its coastline and it is estimated that more than 60% of commercially important species depend at some point on their habits on lagoon ecosystems. Lagoons also function as pollution filters and as protection barriers against floods and extreme hydrometeorological events (de La Lanza & Hernández, 2011). In addition to the benefits of wetlands, they represent a great variety of goods, services, uses and functions of value for the society, flora and fauna as well as in the maintenance of natural systems and processes.

On the other hand, the sediments of these ecosystems constitute the final deposit of many substances present in the water column. Due to the strong affinity that exists between sedimentary particles and metals, their accumulation allows the chemical and biological compositions of the water column to be recorded in the sediments, from which it is possible to obtain valuable information on supply trends of these components to aquatic systems.

The Terminos lagoon located in the southern Gulf of Mexico, is a fluvial-lagoon ecosystem considered the largest in Mexico (Ramos-Miranda & Villalobos, 2015) and recognized as a Wetland of International importance (RAMSAR Site No. 1356), since February 2, 2004. It acts as a refuge for biological diversity and cultural heritage (Amador-del Ángel et al., 2013; Valencia, 2020), likewise, since 1994 it was decreed as a protected natural area, under the category of "Area for the Protection of Flora and Fauna (APFFLT) (CONAP 2014).

However, the Terminos lagoon is under high environmental pressure mainly because of land use change, urban expansion and the development of the oil industry, which is the most important activity in the region, and contributes 80% of crude oil and 30% of natural gas of national production (RAMSAR 2003; Garcia et al., 2004). It directly receives the effluents of the Grijalva and Usumacinta river systems, which discharge nutrients, particulate organic matter and sediments, in addition to the urban discharges of Ciudad del Carmen (Tapia-Fernandez et al., 2017). These effluents notably modify the water quality of the Terminos lagoon (Yáñez-Arancibia et al., 2014; Armstrong-Altrin & Machain-Castillo, 2016).

The objective of this study is to determine the behavior of potentially toxic metals such as Ni, Pb, V and Cr in surface sediments in the lagoon area.

2. STUDY AREA

Terminos lagoon belonging to the state of Campeche, is located on the Gulf of Mexico coast at coordinates 18°36'28" N and 91°33'2" W; it has approximately 2500 km^2 of surface and an average depth of 3.5m. The climate is humid tropical with an annual rainfall between 1100 to 2000mm; the diurnal tide has amplitude of 0.5 to 0.7m. There are three climatic seasons in a year, rainy (June to September, northern (October to January), and dry (February to May). Salinity, turbidity and nutrients are influenced by the climate, the winds and the prevailing currents that cause the entry of seawater into the lagoon through the mouth of Paso Real and the exit of estuarine water through the mouth of Ciudad del Carmen (Fuentes-Yaco et al., 2001; Carvalho et al., 2009; Armstrong-Altrin et al., 2017, 2022) (Figure 1).

Its importance lies in having large extensions of mangroves, wetlands, fish and shrimp production and high biodiversity; therefore, it has the designation of Flora and Fauna Protection Area granted on 06/06/1994 (CONANP, 2014), as well as RAMSAR site 1356 designation on 02-02-2004 (RAMSAR, 2004).

3. METHODOLOGY

Surface sediment samples were collected in a network of 12 fixed stations (Figure 1) during three samplings corresponding to the months of October 2020, February 2021 and May 2021. The sediments were recovered with the help of a Van-type dredge, and they were stored in plastic bags, frozen for later analysis. The concentrations of potentially toxic metals such as Ni, Pb, V for the samples collected in three seasons were analyzed. In addition, the analysis of Cr for the last two samples was included, because this metal is closely related to the urban, industrial and oil activities that take place in the area of influence of the Terminos lagoon. Likewise, for the third sampling, Al was added as a conservative element to calculate the Enrichment Factor (EF), which compares the current concentrations of metals in the analyzed ecosystem with the average values of the earth's crust. In this method, the measured metal content is normalized with respect to a reference sample such as Al, whose fluxes from the upper continental crust are considered to be uniform.

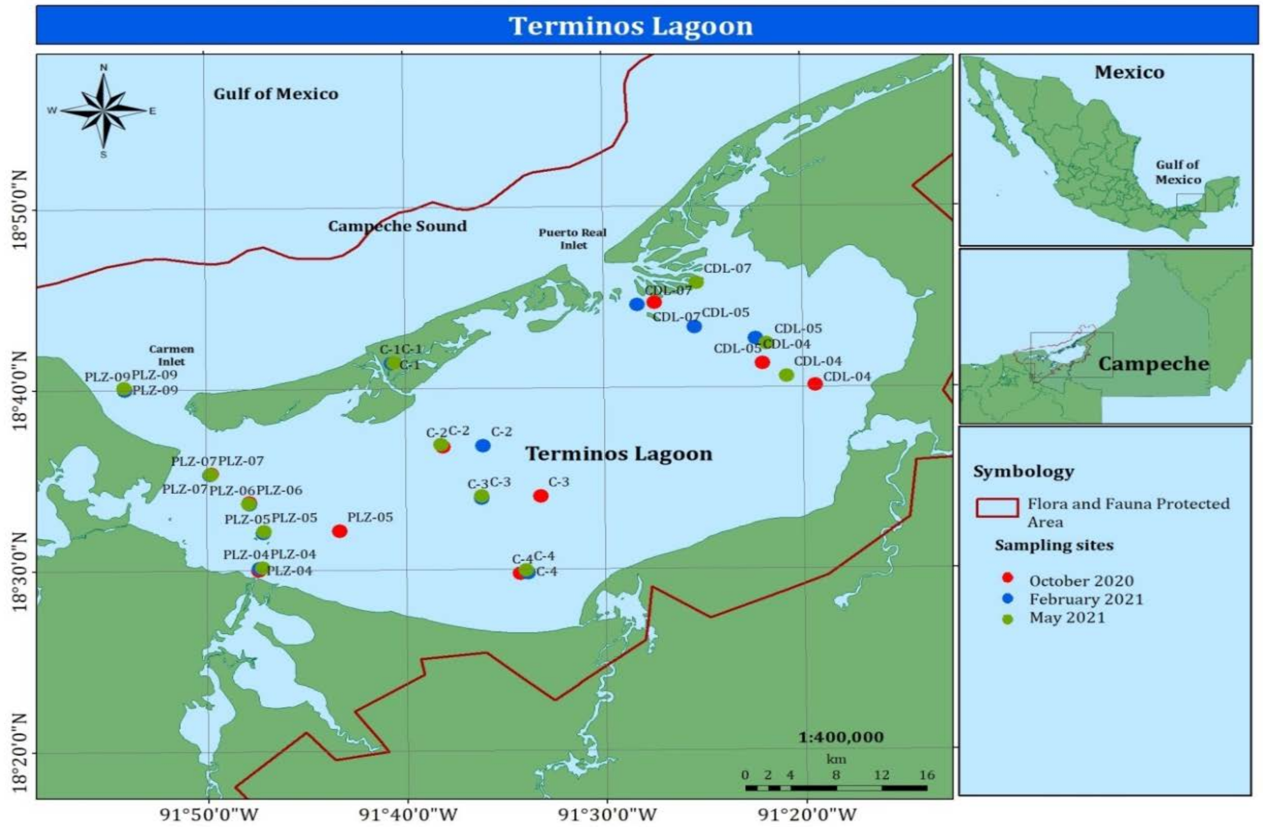

Figure 1. Study area and sampling points during the three collections in Terminos lagoon, Campeche, Mexico

The analytical method used for the analysis of Al, Cr, Ni Pb and V is that of the US EPA 6010D-2018 (INTERTEK+ABCAnalitic). This is a performance-based method that specifies quality control (QC) for the validity of the calibration and the method detection limit (LDM), which was 1.0 mg/kg, as well as the practical limit of quantification (LPC) which is 10.0 mg/kg. The sample preparation procedure used is similar that described in EPA 3051A, which is a total digestion method, which extracts the metals that are available and consists of digestion by means of microwaves, using conventional heating with nitric acid (HNO_3), or alternatively, nitric acid and hydrochloric acid (HCl), for the reading of the metals, an induction plasma equipment (ICP) model Thermo Scientific, brand ICAP 7400 was used.

This laboratory is accredited by the EMA Assay laboratory, has legal recognition from COFEPRIS, CONAGUA, and PROFEPA, among others. It also has the ABS Quality Evaluations Certificate of Conformance ISO 14001:2004 certification and has evolved to ISO 14001:2015.

4. RESULTS AND DISCUSSION

The sample locations, depth and time of collections are listed in Table 1. In addition, the total concentrations of Cr, Ni, Pb, V and Al of the three seasons are also reported in Table 1.

Chromium: The results of Cr for the February and May 2021 seasons are discussed below:

As shown in Figure 2, the stations that recorded the highest values are PLZ-04, PLZ-05, PLZ-06, PLZ-07 and PLZ-09 collected in October 2020 (50.8 mg/kg - 69.55 mg/kg). The low concentrations were in the center and mouth of the lagoon and increased towards the interior for the samples collected in February 2021. The values fluctuated between 9.28 mg/kg and 69.55 mg/kg for the month of February 2021, which corresponds to the north season, and from 11.13 mg/kg to 55.78 mg/kg for May 2021, which corresponds to the dry season.

The factors that could influence this increase during the north season would be the wind and rain that could cause a drag of continental material, together with the organic matter originating from the surrounding mangrove swamp, as well as the discharges from the Palizada River. The stations with the lowest concentrations were C-1, C-5 and C-7 with 9.28 mg/kg to 15.07 mg/kg. In the twelve stations, values below the ERL are presented, which is 81.00 mg/kg (Figure 2).

The average values of Cr in both seasons indicate a very homogeneous distribution, with a range from 32.94 mg/kg (dry season) to 39.8 mg/kg (north season). This indicates the fact that Cr has a low affinity for organic matter, it can remain associated with particulate or sedimentary material, which favors low or null bioavailability. This promotes a minimal risk or low potential to exert an adverse effect in the biota.

The mobility of Cr in an aquatic environment depends mainly on the content of iron oxide and the amount of organic matter present in sediments, as well as influenced by the urban discharges that arrive from the Palizada River to the lagoon. In this way, it can be inferred that during the time that human and industrial activities remained limited in the study area, Cr levels remained similar to those reported for other coastal lagoons in the Gulf of Mexico, such as lagoon Verde (37.89 mg/kg) located in the state of Veracruz (Olivares, 2021) and below those reported by Ponce-Vélez & Botello (1991) (47.2 mg/kg) for this same lagoon.

Nickel: Figure 3, shows the distribution of Ni concentrations in sediments collected during the northern and dry-early rainy seasons. The spatio-temporal behavior of Ni showed significant changes over time. During the three sampling seasons, the spatial distribution was very heterogeneous, the stations with the PLZ nomenclature presented high values between 90.53 mg/kg to 41.86 mg/kg, which recorded concentrations up to an order of magnitude higher with respect to the stations located in the center and southern part of the lagoon (Figure 3).

Ni concentrations are above the lower ERL limit of the ecological criteria (20.90 mg/kg) and those that can produce minimal adverse conditions for the organisms that inhabit the biota, except for stations C-1 and CDL -07. At stations PlZ-04, PLZ-05 and PLZ-09 Ni content increases above the ERM (51.6 mg/kg), which can cause adverse conditions for some organisms (Long et al., 1995).

Comparing the average values of Ni (34.13 mg/kg) of this study with those reported by Botello (1980) (45.5 mg/kg), as well as those of Olivares (2021) for the Farallón lagoon (50.79 mg/kg), the Tamiahua lagoon (59.18 mg/kg) both in the state of Veracruz, and for the Yucateco lagoon (58.38 mg/kg) located in the Tabasco State (Guzmán-Amaya et al., 2005, Villanueva & Botello 2005, Botello et al., 2015), it is observed that these concentrations are higher compared with this study. This indicates that in the northern epoch the influence of, wind, rain and discharges from rivers from the continent influenced the accumulation and distribution of Ni.

On the other hand, sediments associated with mangroves can simultaneously act as reservoirs and sources of metals in coastal areas due to their biogeochemical interactions.

Table 1. Trace element concentrations (mg/kg) in surface sediments of the Terminos lagoon, Campeche

October 2020									
Station	Latitude	Longitude	Date	Time (hrs)	Depth (m)	Sechii (m)	Ni	Pb	V
C-1	18 41. 411	91 40.673	12/10/2020	08:54	1.4	3	6.75	2.73	3.40
C-2	18 36.817	91 38.142	12/10/2020	16:13	1	4	18.26	4.32	7.84
C-3	18 34. 052	91 33. 225	12/10/2020	15:45	1.5	5	30.20	3.73	12.84
C-4	18 29.794	91 34.293	12/10/2020	15:13	1	4.3	33.21	43.88	12.86
CDL-04	18 40.134	91 19.386	12/10/2020	12:12	1	3.2	28.20	3.07	10.69
CDL-05	18 41.347	91 22.050	12/10/2020	11:56	1	4	40.67	4.90	15.53
CDL-07	18 44.700	91 27.454	12/10/2020	11:02	1	3.5	8.96	3.95	4.44
PLZ-04	18 30.009	91 47.403	13/10/2020	10:12	0.55	2.6	90.53	5.67	27.73
PLZ-05	18 32.190	91.43.346	13/10/2020	10:28	0.5	4.2	55.42	7.64	23.39
PLZ-06	18 33.770	91 47.864	13/10/2020	10:44	0.6	4.6	48.79	5.23	17.97
PLZ-07	18 35.354	91 49.763	13/10/2020	11:02	0.9	4.45	41.86	6.83	16.73
PLZ-09	18 40.047	91 54. 105	13/10/2020	11:32	0.75	4.8	60.18	45.23	21.04
*** method detection limit**							**1.00**	**1.00**	**1.00**

February 2022										
Station	Latitude	Longitude	Date	Time	Depth (m)	Sechii (m)	Cr	Ni	Pb	V
C-1	18 41 25.4	91 40 40.0	23/02/2020	09:00	1.2	2.1	9.28	7.38	2.22	4.14
C-2	18 36 50.1	91 36 06.4	23/02/2020	17:50	1	3	28.69	21.98	37.98	10.05
C-3	18 33 58.0	91 36 11.9	23/02/2020	17:16	0.6	5	25.05	22.55	57.51	7.87
C-4	18 29 48.9	91 33 53. 2	23/02/2020	16:40	0.9	3.5	42.16	34.57	31.54	13.26
CDL-05	18 42 43.0	91 22 22.7	23/02/2020	16:48	1	3.5	46.23	34.52	3.04	15.58
CDL06	18 43 20.0	91 25 27.1	23/02/2020	14:58	0.25	2	16.2	9.44	33.32	5.09
CDL-07	18 44 35.8	91 28 18.3	23/02/2020	14:37	0.3	4	15.07	7.83	1.81	4.41
PLZ-04	18 30 07.1	91 47 22.5	24/02/2020	12:21	0.4	1	69.55	70.48	5.24	21.22
PLZ-05	18 32 05.1	91 47 11.3	24/02/2020	12:45	0.5	2.5	55.42	51.46	4.24	18.33
PLZ-06	18 33 39.3	91 47 51.6	24/02/2020	13:13	0.6	3.5	50.8	46.24	4.33	16.28
PLZ-07	18 35 18.1	91 49 49.5	24/02/2020	13:40	0.2	2	55.12	50.91	6.23	18.81
PLZ-09	18 39 58.6	91 54 06.3	24/02/2020	14:34	0.5	4	63.99	57.13	6.53	23.13

June 2021										
Station	Latitude	Longitude	Date	Depth (m)	Sechii (m)	Cr	Ni	Pb	V	Al
C-1	18 41.466'	91 40.5495'	18/05/2021	2.4	1.7	12.05	8.25	2.87	4.97	2186.1
C-2	18 36.910'	91 38.2325'	18/05/2021	4.5	50	26.06	19.99	7.4	9.41	6679.6
C-3	18 34.061'	91 36.1850'	18/05/2021	4.6	40	31.55	24.43	3.1	10.91	8134.5
C-4	18 29.959'	91 33.9883'	18/05/2021	4.2	60	48.86	38.44	3.88	16.11	13348.4
CDL-04	18 40.656'	91 20.8044'	19/05/2021	3.5	70	31.34	23.8	3.5	10.44	8868.7
CDL-05	18 42.427'	91 21.8281'	19/05/2021	3.6	40	30.15	24.86	3.43	9.38	7402.8
CDL-07	18 45.791'	91 25.3313'	19/05/2021	1.2	30	11.13	7.22	2.17	4.06	1631.8
PLZ-04	18 30.066'	91 47.3636'	17/05/2021	1.7	50	55.78	56.63	5.09	16.64	11909.8
PLZ-05	18 32.163'	91 47.1494'	17/05/2021	3.8	50	27	24.52	4.51	8.88	5971.9
PLZ-06	18 33.726'	91 47.9135'	17/05/2021	3.9	50	27.3	32.61	4.44	9.1	4417.2
PLZ-07	18 35.315'	91 49.813'	17/05/2021	3.5	40	51.88	44.85	4.66	19.29	13543.5
PLZ-09	18 40.108'	91 54.1330'	17/05/2021	4.2	50	42.04	45.67	5.3	14.67	7070.3

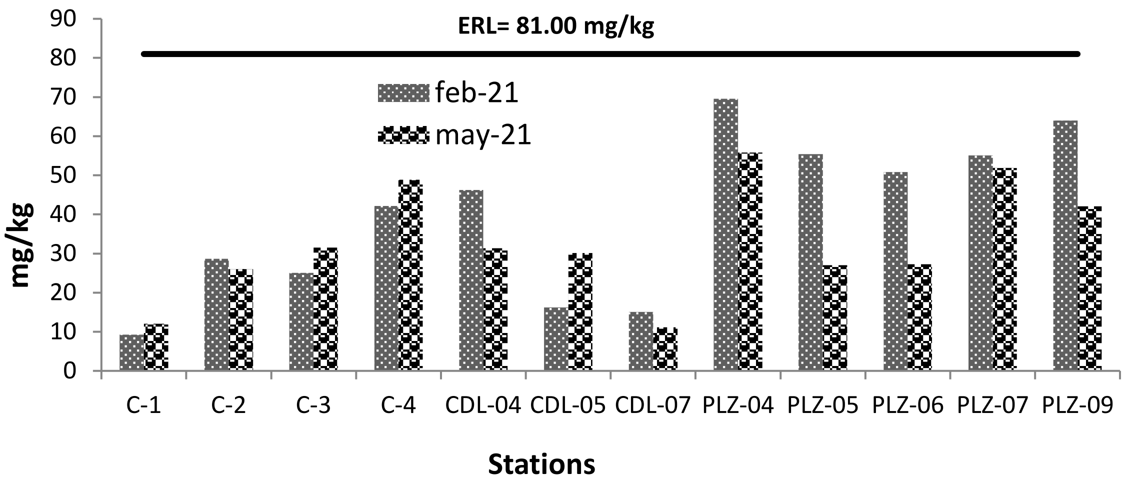

Figure 2. Cr concentrations (mg/kg) in surface sediments of the Terminos lagoon

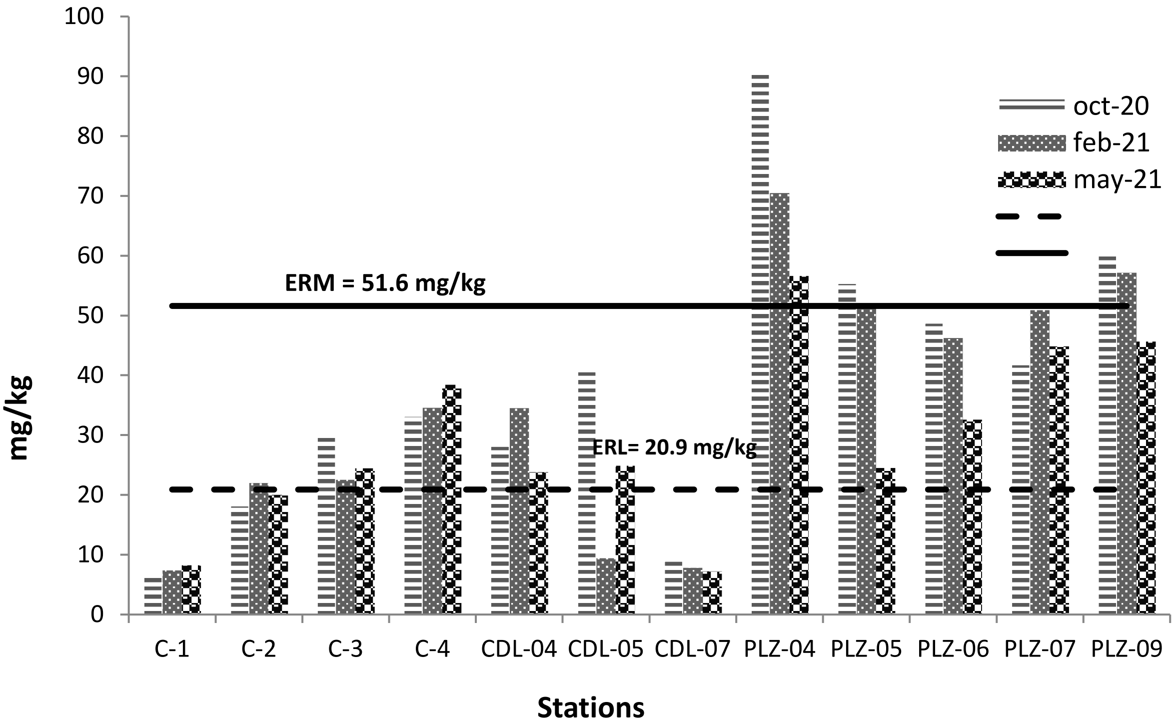

Figure 3. Ni concentrations in sediments of the Términos lagoon

Lead: Major industrial sources of Pb pollution include metal smelting and processing, secondary metal production, Pb battery manufacturing, pigment and chemical manufacturing, and Pb-contaminated waste. Widespread contamination from previous use as a primer in gasoline is also of concern. Pb released to groundwater, surface and terrestrial water is generally in the form of elemental Pb, lead oxides and hydroxides, and lead-metal oxyanion complexes (Smith et al., 1995).

Likewise, there are numerous studies on the importance of atmospheric transport as a source of this metal, highlighting the contribution of Pb, which has managed to demonstrate its presence both in the North Pole and in Greenland, where concentrations of the order of 0.200 mg/kg in ice (Murozumi et al., 1969; Mapel-Hernández et al., 2021). This shows the fact that the atmospheric contribution, far from being insignificant, even becomes the main source of Pb supply to terrestrial and marine ecosystems. Total Pb presented a relatively homogeneous spatio-temporal distribution in the lagoon throughout the study, with values between 2.17 mg/kg for the CDL-07 station and 7.64 mg/kg for the PLZ-05 station. The time where the high values quantified are in February 2021, varying from 31.54 mg/kg (C-4) to 57.51 mg/kg (C-3), as well as the two C-4 stations (43.88 mg/ kg) and PLZ-09 (45.23 mg/kg) collected during October 2020. As shown in Figure 4, only station C-3 exceeded the ecological criterion ERL (46.7 mg/kg). Among twelve stations, samples collected during February 2021 registered the highest value (16.16 mg/kg), followed by October 2020 (11.43 mg/kg). The samples collected during May 2021 registered the lowest value (4.2 mg/kg).

The average value of Pb in this study is lower than (10.60 mg/kg) reported by Ponce-Vélez & Botello (1991) (50.9 mg/kg), by Olivares (2021) for the Verde lagoons (53.19 mg/kg) and la Mancha (50.9 mg/kg), both in the state of Veracruz, however, in the Tampamachoco lagoon north of Veracruz, presented the highest concentration (84.3 mg/kg). The decrease in the concentration of Pb in this study, contrary to Cr and Ni, could be due to the fact that Pb is a volatile metal that is largely distributed by atmospheric routes (Ekoa Bessa et al., 2021a, b).

Vanadium: Weathering of rocks and minerals releases V into the water and air (Armstrong-Altrin et al., 2018, 2021a, b). The average concentration of this metal in the soil is considered to be around 100 mg/kg of dry weight, but in soils near metallurgical plants the values exceed 400 mg/kg (Lagerkvist et al., 1986; IPCS 1988, 2001). It is more soluble in oxidizing waters than in reducing waters, which makes it enrich OM-rich sediments (generally anoxic environment). Under exogenous conditions, V is transported in marine and river waters mainly in the form of VCl_3, VCl_4, VOCl, $VOCl_3$ salts, also adsorbed by Fe and Al hydroxides (Vasallo, 2008; Chougong et al., 2001a).

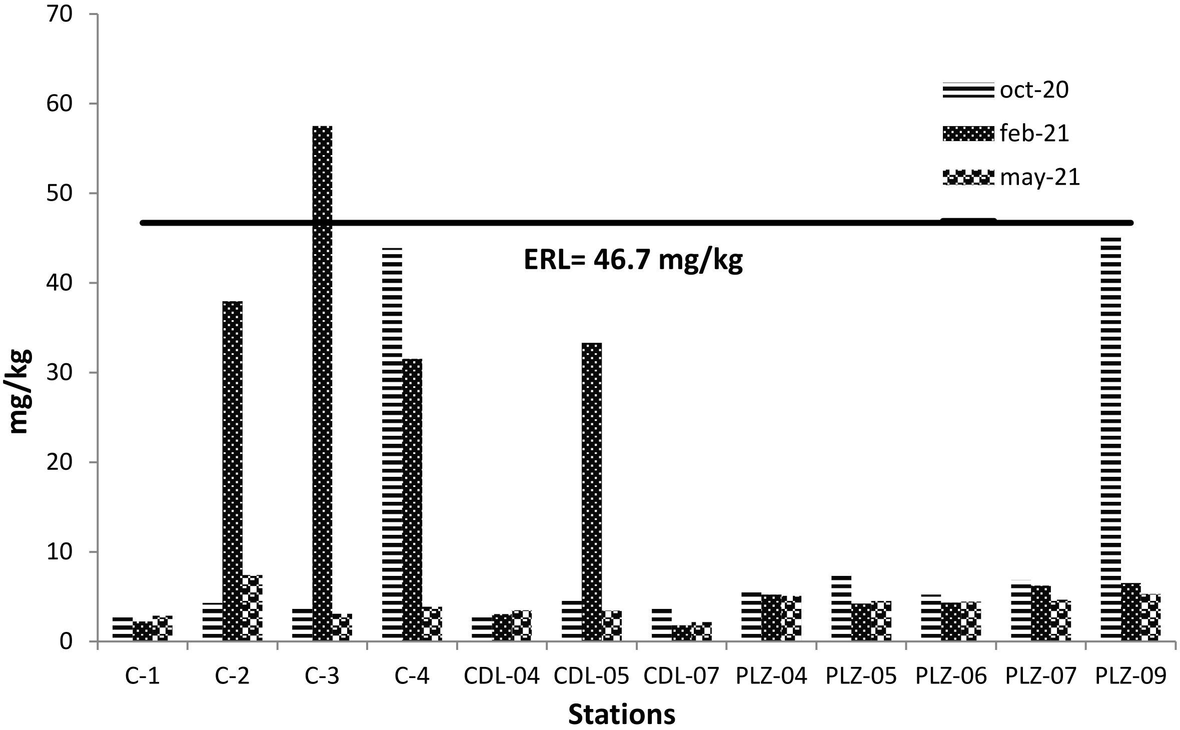

Figure 4. Pb concentrations (mg/kg) in sediments of the Téminos lagoon

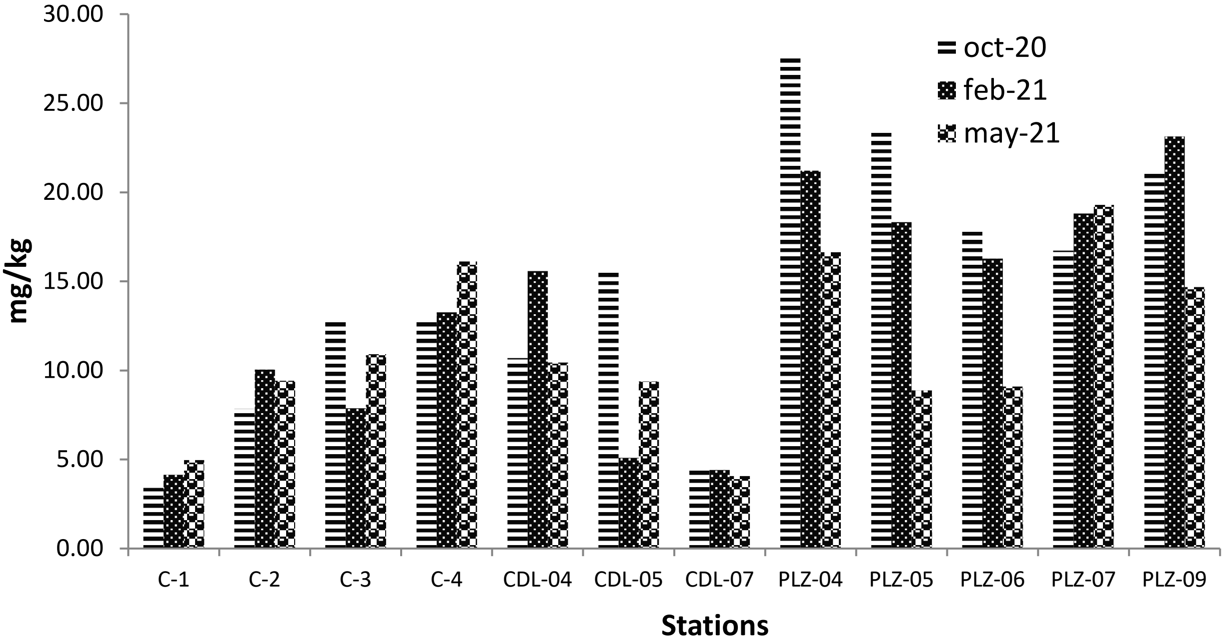

Figure 5. V concentrations in sediments (mg/kg) of the Términos lagoon

The stations with the lowest concentration of V are C-1 (3.40 mg/kg to 4.97 mg/kg) and CDL-07 (4.06 mg/kg to 4.44 mg/kg), the stations with intermediate values are 10.05 mg/kg and 16.11 mg/kg for stations C-2 and C-4, respectively. However, stations that are located in the vicinity of the Palizada River discharge recorded concentrations above 20 mg/kg for the October 2020 sampling and February 2021 (Figure 5).

As background, there are high Ni and V contents in crude oil around the world, with values reaching up to 340 and 1580 mg/kg, respectively (Barwise, 1990). Martínez et al., (2015) reported maximum Ni and V values for crude extracted in Venezuela of 105 and 1321 mg/kg. Likewise, López & Mónaco (2017) reported Ni and V values in Venezuelan crudes of up to 156 and 1417 mg/kg, respectively, and in rocks of 135 and 1932 mg/kg, for each of them. In the Iraqi region, Barbooti (2015) reported Ni and V values in crude oils of 45 and 256 μg/mL, even though the abundance of other trace elements in crude oils is generally less than 100 mg/kg (Filby, 1994; Chougong et al., 2001b).

The studies carried out in coastal lagoons of the Gulf of Mexico are scarce. The concentrations obtained in this study (12.96 mg/kg) are similar to those reported by Villanueva et al., (2016) for the Tampamachoco lagoon with 13.91 mg/kg. Cr, Ni, Pb and V, as well as other metallic elements, are related to the oil industry, particularly with effluents from crude oil refining processes, as well as from the fertilizer production industry, from the transportation industry and foundries (Wittman, 1979); therefore, their sources of contribution to coastal systems are varied (Armstrong-Altrin, 2015, 2020).

5. STATISTICAL TESTS

Table 2 presents the descriptive statistics of Cr, Ni, Pb, V and Al. The coefficient of variation allows comparing the dispersions of the distribution of metals Cr (48.31%), Ni (58.47%), V (48.99%), Pb (137.5%) and Al (51.40%). Pb is with the highest CV, therefore, greater dispersion of the mean value (mean 10.6, standard deviation 14.57), which indicates a greater heterogeneity in concentrations of this metal. The rest of the metals show similar coefficients of variation (48.31% - 58.47%). Table 3 presents the correlation matrix of the Pearson test where it is shown that there is a high positive correlation ($p < 0.05$) between the metals Cr–V (0.99), Cr – Ni (0.97), Ni – V (0.97), Cr – Al (0.93) and between V – Al (0.93). Such high correlations may indicate a common provenance source or process.

Table 2. Descriptive statistics

	N	Mean	Min	Max	Std	C.V. (%)
Cr	24	36.36	9.28	69.55	17.57	48.31
Ni	36	34.13	6.75	90.53	19.96	58.47
Pb	36	10.60	1.81	57.51	14.57	137.5
V	36	12.96	3.40	27.73	6.35	48.99
Al	12	7597	1632	13544	3905	51.40

In the Cluster test, the amalgamation results show that the level of similarity decreases slightly from step 1 (98.98) to step 2 (96.41) and then the similarity decreases sharply in step 3 (88.64). These results indicate that 3 clusters are appropriate for the final partition. The dendrogram was "cut" at a level of similarity of approximately 88.64, leaving three final conglomerates that associate the metals Cr – V, Al and finally Ni, as shown in the graph (Figure 6).

Table 3. Correlation matrix

	Cr	Ni	Pb	V	Al
Cr	1.00				
Ni	0.97	1.00			
Pb	-0.17	-0.01	1		
V	0.99	0.97	-0.019	1.00	
Al	0.93	0.77	0.303	0.93	1.00

Table 4 shows the cumulative proportion to determine the total amount of variance explained by the Principal Components and that meets the Kayser criterion. From the sedimentation graph, the number of components that explain most of the variation in the data (99.3%) was identified and they were 3 (3.945, 0.8115 and 0.2121) (Fig. 6).

Table 4. Principal Components and that meets the Kayser criterion

Own value	3.946	0.812	0.212	0.029	0.002
Proportion	0.789	0.162	0.042	0.006	0
Accumulate	0.789	0.951	0.994	1	1

Table 5 shows the results where the first Principal Component has large positive associations with Cr, Ni, V and Al, so this component is measuring a source of common origin and could be related to the presence of hydrocarbons in the sediments of the studied area. Porphyrin complexes have been identified to be associated with metals such as V and Ni that contribute to the emulsification of crude oil, especially fresh oil (Bojórquez-Sánchez et al., 2018). Most crude oils form water-in-oil emulsions in contact with water. The stability of these emulsions varies. When spilled crude oil emulsifies, it becomes viscous and expands in volume, making recovery, chemical dispersion, or ignition more difficult. The ability to predict the emulsion formation behavior of a specific crude oil could help decision making in the event of a spill (Cannevari & Fiocco, 1997). The problem is complex due to the various stabilization mechanisms.

Likewise, the presence of these metals has been found in sediments of the Lagoon Complex of the Isthmus of Tehuantepec, Oaxaca, related to accidental hydrocarbon spills in the area (Velandia-Aquino, 2010).

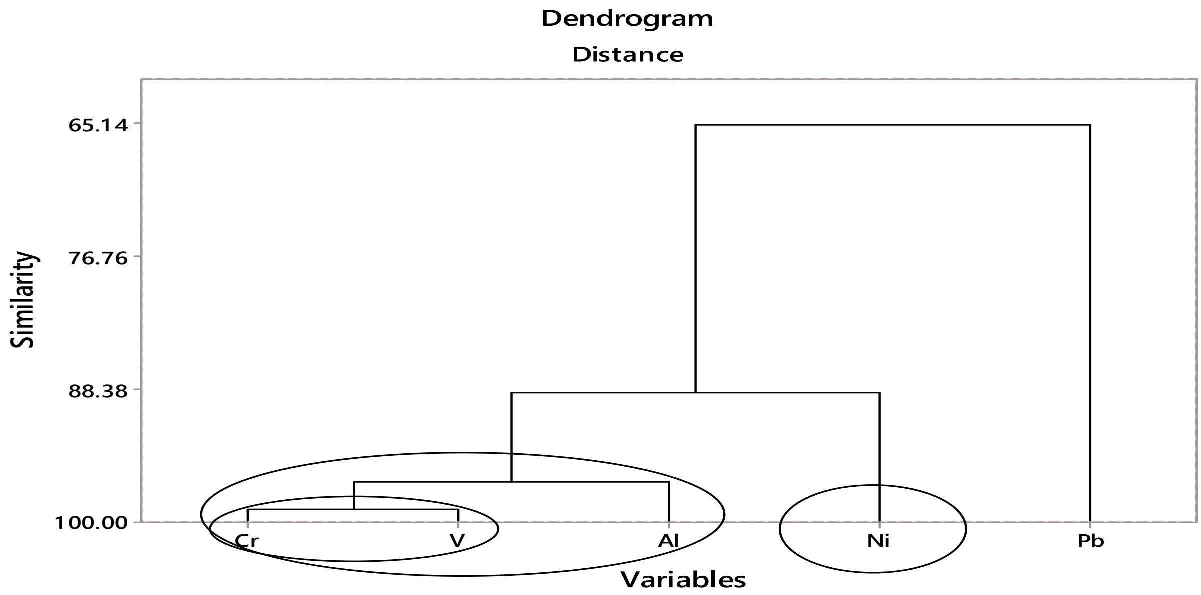

Figure 6. Cluster Test- Dendrogram of similarity for the Metals analyzed

Table 5. Principal Component (F) analysis for trace element concentrations

Variable	F1	F2	F3
Cr	0.499	-0.136	0.082
Ni	0.475	-0.009	0.715
Pb	0.255	0.953	-0.16
V	0.495	-0.117	-0.055
Al	0.465	-0.244	-0.673

The Principal Components graph visually shows the results of the first two components, where Cr, Ni, V and Al have large positive influences on Component 1 (Factor 1) where 78.91% of the total variance is explained and in terms of Component 2 Pb has a large positive influence (12.23% of the total variance), which may be associated with a different source of origin of this metal (Figures 7 & 8).

Table 6. Levene's test which measures the homogeneity of the variances

	MS	MS	F	p
Cr	*	*	*	*
Ni	120.762	132.864	0.909	0.4128
Pb	692.928	61.566	11.255	0.0002
V	17.870	11.302	1.581	0.2209

Levene's test (Table 6), which measures the homogeneity of the variances (for $p > 0.05$) for Ni concentrations, determines that $p = 0.412$, therefore the variances are homogeneous. For Pb concentration $p>0.05$, it determines that $p = 0.000188$, therefore, the variances are not homogeneous and the ANOVA test cannot be applied.

For the concentrations of V $p>0.05$, determine that $p = 0.220936$, therefore the variances are homogeneous. For the univariate results (Table 7) where $p < 0.05$ indicates that there is a significant difference, $p = 0.5318$ obtained for Ni and $p = 0.434$ obtained for V, show that there are no statistically significant differences in the concentrations of Ni and in the concentrations of V in the three samplings. In order to determine the significant differences in the concentrations of Cr, Ni, Pb and V for the three sampling zones (C, CDL and PLZ), the ANOVA statistical test was applied for each metal. The results are described below:

Table 7. Univariate results

Metal	p
Cr	*
Ni	0.5319
Pb	*
V	0.4340

Levene's test (Table 8) that measures the homogeneity of the variances (for a $p > 0.05$), in Cr determines that $p = 0.96481$, therefore the variances are homogeneous; for Ni it determines that $p = 0.7357$, therefore the variances are homogeneous; for Pb it determines that $p = 0.0017$, therefore, the variances are not homogeneous and for V it determines that $p = 0.8474$, therefore, the variances are homogeneous. For the univariate results (Table 9) where $p < 0.05$ indicates that there is a significant

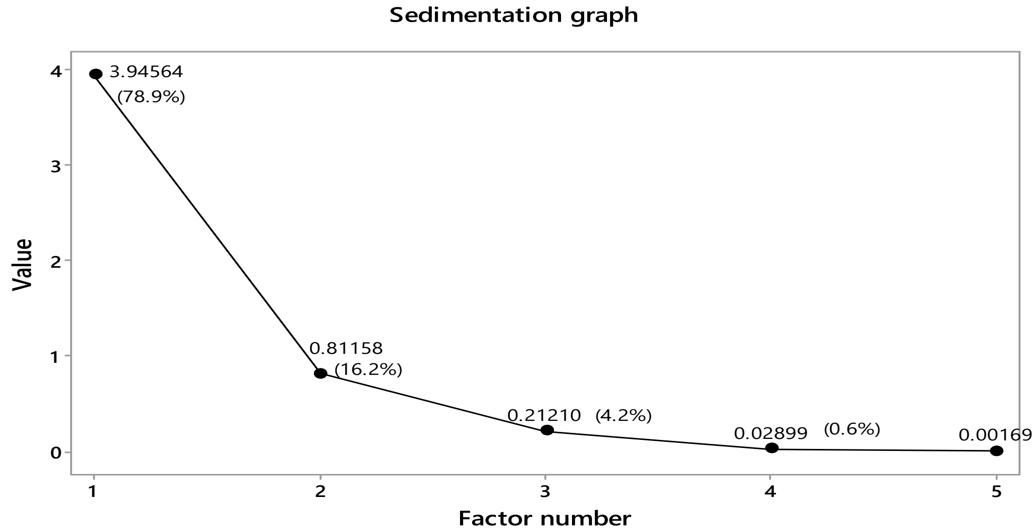

Figure 7. Principal Component analysis, that meets the Kayser criterion

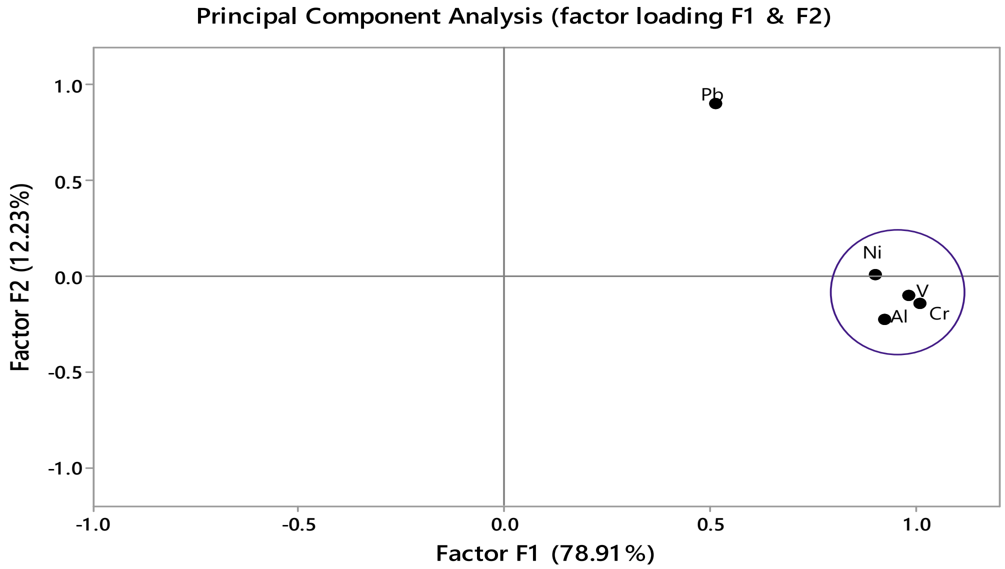

Figure 8. The Principal Component analysis.

Table 8. Levene's test that measures the homogeneity of the variances

	MS	MS	F	p
Cr	2.2308	62.1629	0.0359	0.9648
Ni	21.4977	69.4029	0.3098	0.7357
Pb	577.2979	74.3444	7.7652	0.0017
V	1.2259	7.3681	0.1664	0.8474

difference, p = 0.00202 obtained for Cr, p = 0.000001 obtained for Ni and p = 0.000009 for V show that if there are significant differences in the concentrations of Cr, Ni and V, respectively, among three sampling cites, while p = 0.196953 for Pb shows that there are no statistically significant differences for the concentrations of Pb between the three zones analyzed.

Applying the Scheffe test (Table 10), the statistically significant differences in metal concentrations among three zones (C, CDL and PLZ) are shown.

Table 9. Univariate results

Metal	p
Cr	0.00202
Ni	0.000001
Pb	0.196953
V	0.000009

Table 10. Scheffe test

Metal	Site	Zone	{1}	{2}	{3}
Cr	1	C		0.92403	0.01048
	2	CDL	0.92403		0.00768
	3	PLZ	0.01048	0.00768	
Ni	1	C		0.96572	0.00001
	2	CDL	0.96572		0.00002
	3	PLZ	0.00001	0.00002	
V	1	C		0.95369	0.00012
	2	CDL	0.95369		0.00015
	3	PLZ	0.00012	0.00015	

The concentrations of Cr, Ni and V show significant differences between the C zone and the PLZ zone, as well as between CDL and PLZ zones, while between C and CDL zones there are no statistically significant differences in any of the three metals, as illustrated in Figure 9.

To evaluate the EF in sediments of the Terminos lagoon, the normalizing element of Al and the concentration values of the upper continental crust reported by Rudnick & Gao (2003) are used.

The FE values for Cr, Ni and Pb are above 1.5, therefore, it is suggested that a significant part of the metal has originated in non-crustal or anthropogenic processes and within class 3 (moderate enrichment) to 5 (severe enrichment) (Winchester, 1979, Samhan et al., 2011). In contrast, the EF for V was found in most of the stations and samples between 0.5 and 1.5, so said metal must be entirely from crustal materials or natural weathering processes (Ayala-Pérez et al., 2021; Ramos-Vázquez & Armstrong-Altrin, 2019, 2020, 2021).

The I_{geo} values of the metals Cr, Ni and V are less than zero ($0 < I_{geo} \leq 1$) classified as class 0, which indicates that they are non-contaminated sediments. With respect to the metal Pb, it presented a classification of zero in most of the stations except in stations C1, C2 and CDL of the second sampling, which according to the calculation of the I_{geo} are classified as class 1 (not contaminated to moderately contaminated) and the station C4 from the same sample classified as class 2 (moderately contaminated). Relatively high values of Pb located in the central part of the Terminos lagoon. Pb is

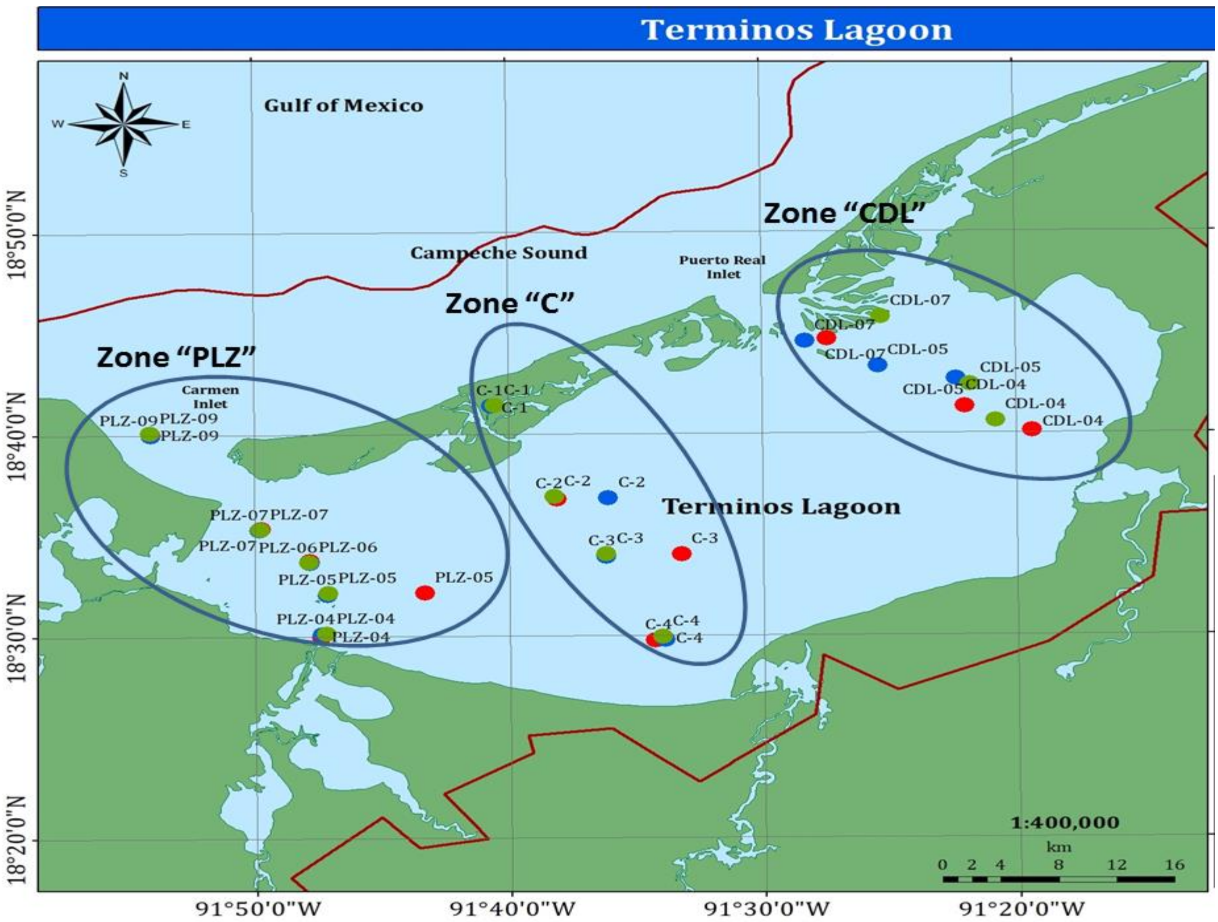

Figure 9. Map showing sites with statistically significant differences in metal concentrations

usually associated with the metal extraction, processing and smelting industries and can be found in industrial oil refineries, petrochemical and steel plants in the state of Campeche (Abdallah, 2008).

6. CONCLUSIONS

The concentrations of Cr and Pb remained below the ecological criteria of the minimum and maximum adverse conditions ERL and ERM for the organisms that inhabit the biota. None had values above the ERL and ERM, except for stations C-01, C-02 and C-07, and V maintained its concentrations below 27.73 mg/kg. Cr, Ni and V recorded the highest concentrations at the mouth of the Palizada and Carmen Rivers. Although it is considered that the sediments are not impacted by these activities, this area represents the most contaminated area on a temporary basis. Another point that presented higher concentration values, particularly Pb, is at the mouth of the Chumpan River. It can be deduced that the contribution of Ni to this lagoon have remained without considerable changes.

There have also been no fluctuations in sediment concentrations depending on the rainy and dry seasons, increasing during the rainy season. This pattern globally generates an increase in total concentrations.

The lagoon system maintains the concentrations within stable levels, product of the non-alteration of the biogeochemical cycles of the metal during the seasons studied. It is important to note that the concentrations observed in the lagoon are similar or lower than those reported for other coastal systems in the Gulf of Mexico. V showed a decrease in concentrations for the last stage of the analysis, which seems to be due to the neutral-alkaline pH characteristics currently present in the system. No significant differences were observed among different seasons, the Metallic Contamination Index was higher in February 2021, which could be related to the use of agrochemicals in the river-lagoon systems. Enrichment Factor values reveal that there is a greater heterogeneity in the quality of the sediments in February 2021. It is concluded that the decrease and restriction of human activities, including oil wells, agricultural, industrial, urban and sanitary in the coastal area are favorable to control the sediment contamination.

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