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Geospatial Synthesis of Biogeochemical Attributions of Porphyrins to Oil Pollution in Marine Sediments of the Gulf of México

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Abstract: Porphyrins are highly persistent in the environment and represent a helpful biogeochemical attribute to assess the spatial distribution of the effects of oil spills on ecosystems and their resilience. In areas prone to natural and human-originated oil spills, the measurement of VO– and nickel–porphyrins in marine–sediment samples can identify the effects of oil pollution across spatiotemporal scales. The goal is to explore whether or not these compounds can be useful indicators of the geospatial attributions of oil contamination in the surficial sediments. We hypothesize that the geospatial gradients of porphyrins in marine sediments from petroleum spills and seepage activities—related to traditional indices of oil pollution, such as heavy metals and polycyclic aromatic hydrocarbons—can be identified in small sediment samples and concentrations. The objectives are two-fold: (1) extract and measure VO– and nickel–porphyrins from small marine sediment samples using high-pressure liquid chromatography, and (2) use cluster analysis and the canonical correlation analysis to identify the biogeochemical and geospatial attributions between VO–porphyrins and another index of oil pollution extracted and analyzed from sediments of the Campeche Shelf, in the Gulf of Mexico. High-pressure liquid chromatography with diode array detectors, two inverse phase columns and an isocratic separation method, was used to analyze the marine sediments. We identified 5.1 ng/g to 240.3 ng/g to VO–porphyrins concentrations with gradients toward areas identified as potential sources of oil pollution. Similar patterns were present for nickel–porphyrins, with values two orders of magnitude below those for the VO–porphyrins. The results represent a valuable opportunity to measure the biomarkers associated with oil pollution in small sediment samples. Furthermore, the results can find the potential drawbacks of benthic ecosystem resilience.

Keywords: oil pollution; metalloporphyrins; marine pollution; canonical correlation analysis; attribution

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1. Introduction

Porphyrins are the diagenetic product of chlorophyll and are considered part of a complex mixture of organic compounds in oil [1–3]. Porphyrins are highly persistent in the environment, a biogeochemical attribute useful to assess the spatial distribution of the effects of oil spills on ecosystems and their resilience. The goal is to explore the reliability of vanadyl (VO) and nickel–porphyrins in marine–sediment samples distributed in areas prone to natural and human-originated oil spills. Metalloporphyrin compounds demonstrate different tetrapyrrolic structures (DPEP and Etio) bounded to metallic elements, including V, Ni, Cu, Ga, and Fe [2,4]. In some cases, oil activities such as exploration, exploitation, and transport may result in contamination affecting the vicinity of the working areas after the occurrence of recorded and non-recorded oil spill events [5]. Both direct and indirect methods can study these effects. Among these, some that are frequently used

are the benzene–toluene–ethyl–xylenes (BTEX) measurements, total hydrocarbons, and polyaromatic hydrocarbons (PAHs), as well as biological indexes [6–9]. Direct methods are characterized by the analyses of short-life time molecules in the environment, resulting from physical (weathering, dissolution, evaporation) and biological (biodegradation) effects [10,11]. For example, [6,12] studied the hydrocarbon content in sediments and organisms to illustrate the effect of oil activity on the biological distribution at the species level. Authors [13] reported that the contaminant gradients could be registered through the abundance and diversity of the benthic population at the family level; and [14] identified the bioaccumulation of hydrocarbons in benthonic organisms after the Deepwater Horizon oil spill in the Gulf of Mexico. High levels of thermally mature organic matter usually imply the presence of petroleum in surficial sediments. However, the presence of mature oil on surface sediments can be explained by at least three mechanisms. It can be caused by hydrothermal activity (in situ formation); it can also be due to the presence of surficial seeps and pollution [6,15]. For instance, [16] evaluated the presence of Ni– and VO–porphyrins in soils associated with oil pollution, and [9,17] have studied the effect of such pollutants on organisms in the ocean and rivers.

Frequently, the surficial sediments closer to oil activity areas are sampled to measure the petroleum-products content. In coastal zones, most of these pollution-indicator molecules may undergo alterations produced by physical, chemical, and biological processes. These processes result in the lowering of concentrations of contaminants. However, according to [18–20], metalloporphyrins show a high resistance to thermal decomposition over time. At the same time, the modifications experimented via the porphyrin molecule are often indicative of the thermal maturity of organic matter. They can yield information on the diagenetic steps of the tetrapyrrolic ring degradation. Among these molecules, it has been proposed that etioporphyrin is the most stable form. Previous studies [20,21] describe the prevalent environmental conditions for the V and Ni enrichment of porphyrins in the organic matter matrix.

In the southern Gulf of Mexico, particularly in the Campeche Shelf, the distribution and concentration of the total n-hydrocarbon in previous studies unclearly have an effect on the abundance and diversity index gradients displayed by the benthonic organisms [22,23]. This effect may be explained by the action of physical, microbiological, and ecological processes that diminish the effect of hydrocarbon concentrations on the aquatic systems [12,24]. Yet, it is unclear whether or not the distribution of hydrocarbon concentrations and benthic communities are emerging properties of the complex socioenvironmental and biogeochemical processes in the area.

Metalloporphyrins are stable compounds in the petroleum matrix. The VO–porphyrins and nickel–porphyrins are two of the most abundant families of the tetrapyrrolic compounds in the oil. The hypothesis is that porphyrins can indicate the petroleum spills and seepage activities in aquatic sediments as they relate to traditional indices of oil pollution, such as heavy metals and polycyclic aromatic hydrocarbons. The objectives are two-fold: (1) extract and quantify VO– and nickel–porphyrins from a small marine sediment sample using high-pressure liquid chromatography; and (2) use cluster analysis (CA) and the canonical correlation analysis (CCA) to identify the biogeochemical and geospatial attributions between VO–porphyrins, and another index of oil pollution extracted and analyzed from sediments of the Campeche Shelf, in the Gulf of Mexico.

2. Materials and Methods

2.1. Sampling

Sediment samples were taken from the Campeche Shelf during the oceanographic cruise Xaman Ek I in 1993; 27 box-core samples were collected at five transects located in the southern part of the Gulf of Mexico (Figure 1). This area is known as the central oil production region in the south of the Gulf of Mexico. The Campeche Shelf oil fields are located over three different sedimentary provinces. Those provinces are characterized by a high presence of carbonates in the eastern side of the Gulf to high levels of clays near

the vicinity of the Terminos Lagoon. In the middle, a mixture of these two environments can be found. The data used in this study were extracted from sediment sampled using a box corer Kessler–Sandia-type MK-II. The first 10 cm were sub-sampled at three different sedimentary levels (0–2, 2–6, and 6–10 cm). These sub-samples were used to analyze the content of metalloporphyrins, as well as other geochemical variables. Other variables such as carbonates, organic matter content, heavy metals [25], aliphatic, aromatic, and total hydrocarbons [22] were also measured and called geochemical variables to integrate the assessment of the effects of oil activities.

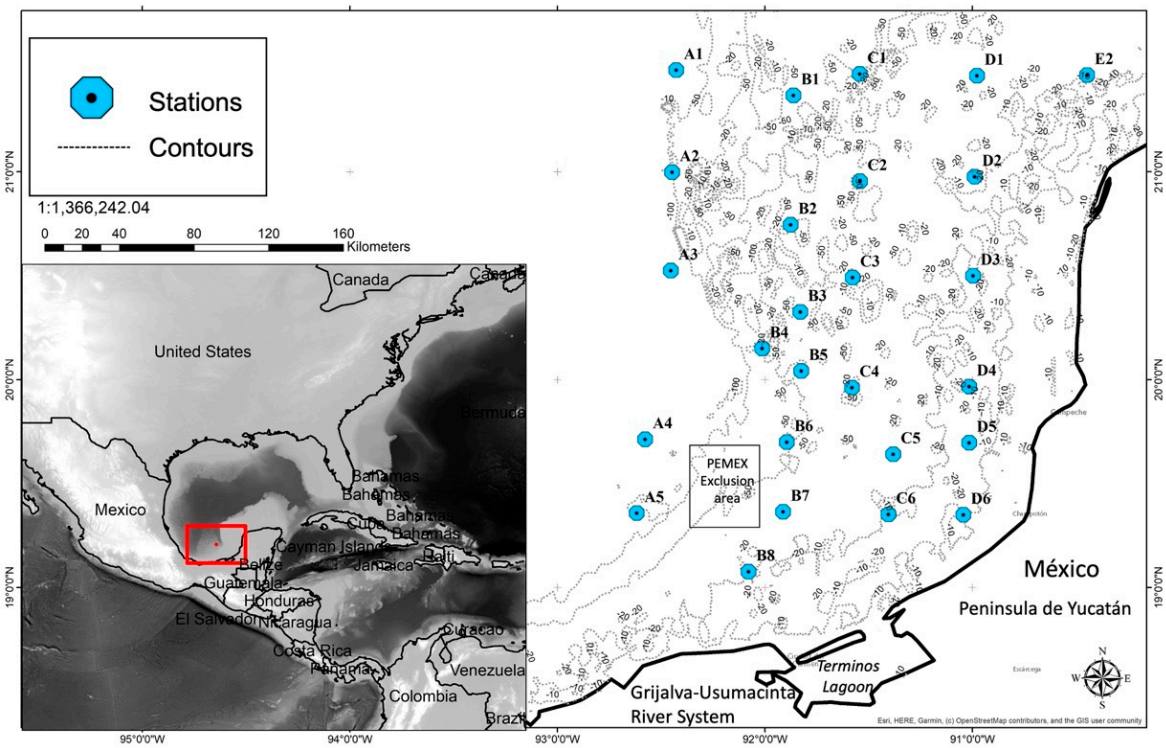

Figure 1. Area of study where the samples were collected. Sediment samples of the Campeche Sound were monitored through five transects (A, B, C, D, and E) and 26 stations.

2.2. Porphyrin Analysis

2.2.1. Extraction

All sediment samples were kept frozen until analysis. The samples were lyophilized and stored until the extraction sequence. The extraction procedure consists of a modification of the method proposed by [26]. Briefly, it consists of the extraction of about 4 g samples. In this paper, the reflux system was substituted by an ultrasonic extraction method. First, we used an extractant mixture of toluene:methanol (34:66 V:V) followed by chloroform:methanol (87:13 V:V). The combined volumes of extractant are concentrated. After the concentration, the concentrate is transferred to a 15 cm chromatographic column prepared with alumina 5% deactivated. Toluene is first used to eliminate the polyaromatic hydrocarbons and saturated compounds. Then, chloroform is used to obtain a first porphyrins mix. This mixture is again concentrated and eluted through a second chromatographic column. This column is filled with a 1% deactivated silica gel. A solvent mixture of 2% and 8% of ethyl acetate in hexane is used to obtain the VO– and nickel–porphyrins, respectively. Smaller columns were used to reduce the elution times, solvent usage, and time of the analysis. The extract was concentrated to dryness, and first, the porphyrin mixture was eluted, and later, the VO– and nickel–porphyrins were isolated by the method described above.

As an alternative for a sediment reference material was used, the method suggested by [27] for the elaboration of the eluted oil sample to be analyzed by liquid chromatography. It consists of the addition of an etioporphyrin standard solution, to a sediment matrix, followed by the thorough homogenization and evaporation of the solvent.

2.2.2. Instrumental

The porphyrin samples were analyzed using a high-pressure liquid chromatography (HPLC) system Hewlett Packard, model 1090 Series II equipped with a diode array detector. It was followed by the method of [28] with some modifications, using two inverse phase columns (C18). One from phenomenex (150 × 2 mm), and a second one from Hewlett Packard (100 × 2.1 mm). At the same time, it was used as an isocratic separation method. The liquid phase was 2% pyridine in methanol, and 47.5% of methanol, 47.5% acetonitrile and 5% water for the nickel– and VO–porphyrins, respectively. The wavelengths used were 390 nm for the nickel–porphyrins and 406 nm for the VO–porphyrins; and 8 nm bandwidths in both cases. The identification and quantification of porphyrin used an external standard analysis based on the standards of VO– and nickel–porphyrins (Porphyrin Products Inc., Logan, Utah).

2.3. Statistical Analysis

To define the spatial patterns established by the distribution of the porphyrin variables, CA and the CCA were implemented. The CA was applied to the data set composed by the porphyrin and environmental variables. With the number of objects, defined spatially by the sampling sites, the clustering technique used the chordal distance as a dissimilarity measure. This distance type of the measurement is applied to variables with different units. The proximity measure among groups and objects was the unweighted pair group method average (UPGWMA).

For the CCA, the groups of variables to be compared were standardized with the logarithmic function. In addition, the analyzed variables were classified into two groups; the first contains the porphyrins, and the second the environmental variables across the Campeche Shelf, respectively. The variables of each classification were grouped before the primary analysis to eliminate the collinearity. Once the groups were conformed, variables representative of the same variation groups were used on the CCA.

3. Results

The distribution of porphyrins over the Campeche Shelf at three different levels is used to evidence patterns of the spatial distribution of metalloporphyrins that indicate the occurrence or persistence of oil pollution in marine sediments. The evidence that the extraction and instrumentation approaches is found below, followed by the multivariate statistical analyses of geospatially distributed samples.

Traditionally, the sample sizes of source materials, such as oil, source rock, or highly mature organic matter, were not limiting factors for VO– and nickel–porphyrins [29]. These studies used techniques that efficiently extract metalloporphyrins with ketone alcohols. The source materials are typically heavy oil residues such as asphaltenes. However, when the extraction processes are applied to sediment matrices, the sample size becomes critical for extraction, identification, and their use as environmental indices of oil pollution. Authors such as [16] studied oil-polluted soils to define the use of porphyrins as tracers of this contaminant. The amount of soil used varied between 20 and 40 g, ww. The present study used marine–sediment samples from the Campeche Shelf area, and the available amounts varied from 3.5 g to 6 g dry weight. This study required a meticulous extraction process based on the use of syringes as chromatographic columns that allowed a reduction of the elution and analysis times by 25%, and a reduction of solvent usage by 40%. The approach was validated against a mixture of porphyrin standards. The decrease in the recovery time enabled the concentration of the tetrapyrrolic molecules needed for small sediment samples. The estimated recovery efficiencies from synthetic standard reference materials

were 97.2 ± 3.8% and 56.4 ± 4.3% for the VO– and Ni–porphyrins, respectively, which validates these quantifications.

The VO–porphyrins and Ni–porphyrins were used as tracers of the environmental quality in marine sediments, rather than the proxies of the geochemical diagenesis of organic matter. This thesis allows us to prime the concentration of porphyrin aggregates over the structural representation of these compounds. For this purpose, we modified the instrumentation techniques reported by [28,30,31], which typically eluted these tetrapyrrolic molecules at retention times between 30 and 80 min [16,20,31]. In the present study, the estimated retention times obtained for the surficial sediments were less than 20 and 25 min for the C-32 VO–porphyrins and Ni–porphyrins, respectively (Figure 2).

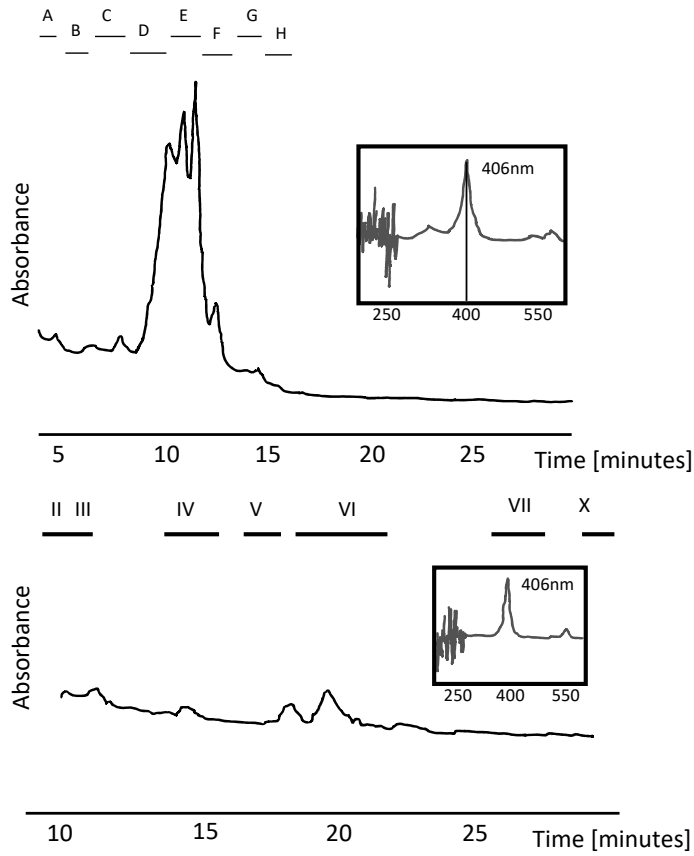

Figure 2. Chromatograms for VO– and nickel–porphyrins as well as the length wave used for detection in HPLC.

The distribution of porphyrins over the study area at 0–2 cm, 2–6 cm, and 6–10 cm depth showed different patterns of variability, which evidence the persistent oil pollution based on the illustrated gradients porphyrin concentration. At the surficial layer, the concentration of VO–porphyrins fluctuated between 0.7 ng/g and 240.3 ng/g. The horizontal variability had a content gradient toward the southwest (station A5). Transects A and B presented the highest average concentrations (71 ng/g and 20 ng/g, respectively), representing two orders of magnitude above the other transects (Figure 3a). Ni–porphyrins showed a similar spatial pattern of variability with detectable concentrations ranging from 0.6 ng/g in most transect B stations (Except B7) to 3.7 ng/g in station A5 (Figure 3b). The eastern transects (C, D, and E) presented Ni–porphyrin contents below the detection limits. Stations A5, A3, and B7 revealed the highest concentration levels for both porphyrins.

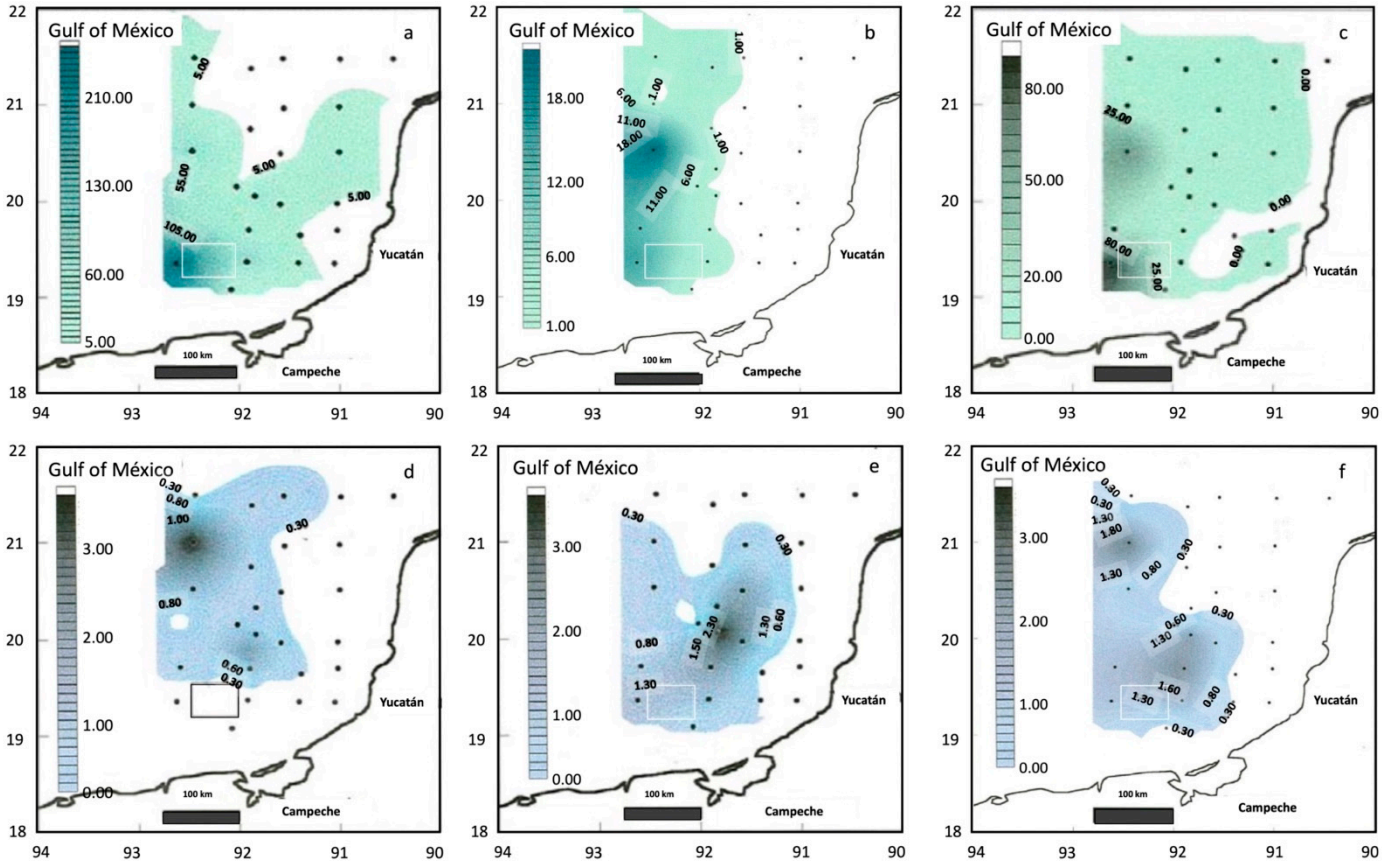

Figure 3. Panels (**a**–**c**) show the concentrations of VO–porphyrins for 0–2, 2–6, and 6–10 cm depths, respectively; panels (**d**–**f**) illustrate the gradients of nickel–porphyrins for the same depths described above.

On the other hand, the mid-layer sediments (2–6 cm) had some differences when it comes to the upper layer. While in the surficial sediments, the VO–porphyrin content gradient was directed toward station A5, in the next sedimentary layer, the gradient was directed to station A3 with 252 ng/g. In this layer, the gradient of Ni–porphyrins changes toward station B5 (3.8 ng/g). Similarly, the average concentration of VO–porphyrins in this layer was about 30% higher than in the first layer.

In the third layer (6–10 cm), the variability of VO–porphyrins reproduced the same pattern of variability observed at the sediments in the top sedimentary layer, except for station B7. The gradient is directed toward station A5 (90 ng/g), and contrasts with the previous layers; the difference between this station and B7 is less than 30 ng/g. Additionally, the relatively homogeneous distribution of these tetrapyrrolic molecules contrasts with the more pronounced gradients in the first layers. Authors [32] reported VO–porphyrins and Ni–porphyrins content in surficial sediments (26.62 to 66.1 ug/g and 3.3 to 11.1 ug/g, respectively), which are two and three orders of magnitude above the concentrations obtained in this study. However, these measured concentrations at the Campeche Shelf surficial sediments were located no closer than 35 km from the potential source. For the Ni–porphyrins, two main gradients are directed toward stations A2 (2.7 ng/g) and B5 (2.3 ng/g). A key feature in the distribution of Ni–porphyrins in all layers is that the concentrations are within the same order of magnitude. These patterns of variability can be observed as emerging properties of a system that responds to dynamic changes in marine sediment transport, inputs of river sediments, and the intrinsic biogeochemical responses of the compounds to the changing environment.

Figure 4 shows the clusters formed by evaluating all geochemical variables, including porphyrins. A single variable was included when variables were associated, avoiding

the effect of collinearity [33]. The CA contributes to revealing the clustering of spatial patterns of variation registered of different variables, indicating a common response to multiple processes, such as the source of the contaminant and physical dynamics of the coastal environment. Contrasting with the studies developed by [22,25,34], the stations clustered integrate the variability given by the petroleum variables assessed in the three sedimentary depths. In the first layer, the mentioned areas (or mineralogical provinces) showed differences mainly in response to the porphyrin increments in the fine-grained regions (stations A3 and A5) and the location of the mixed zone (station B6). At the same time, stations A1, A2, and A4 were clustered into area II. The formation of this group might be due to the low concentrations in Ni–porphyrins and the low detection limits. Furthermore, because of the carbonate content characteristic of the mixed zone (76–86%). The third cluster or area III is also an area with high carbonate content and high values of some oil-related variables, based on similar spatial distributions.

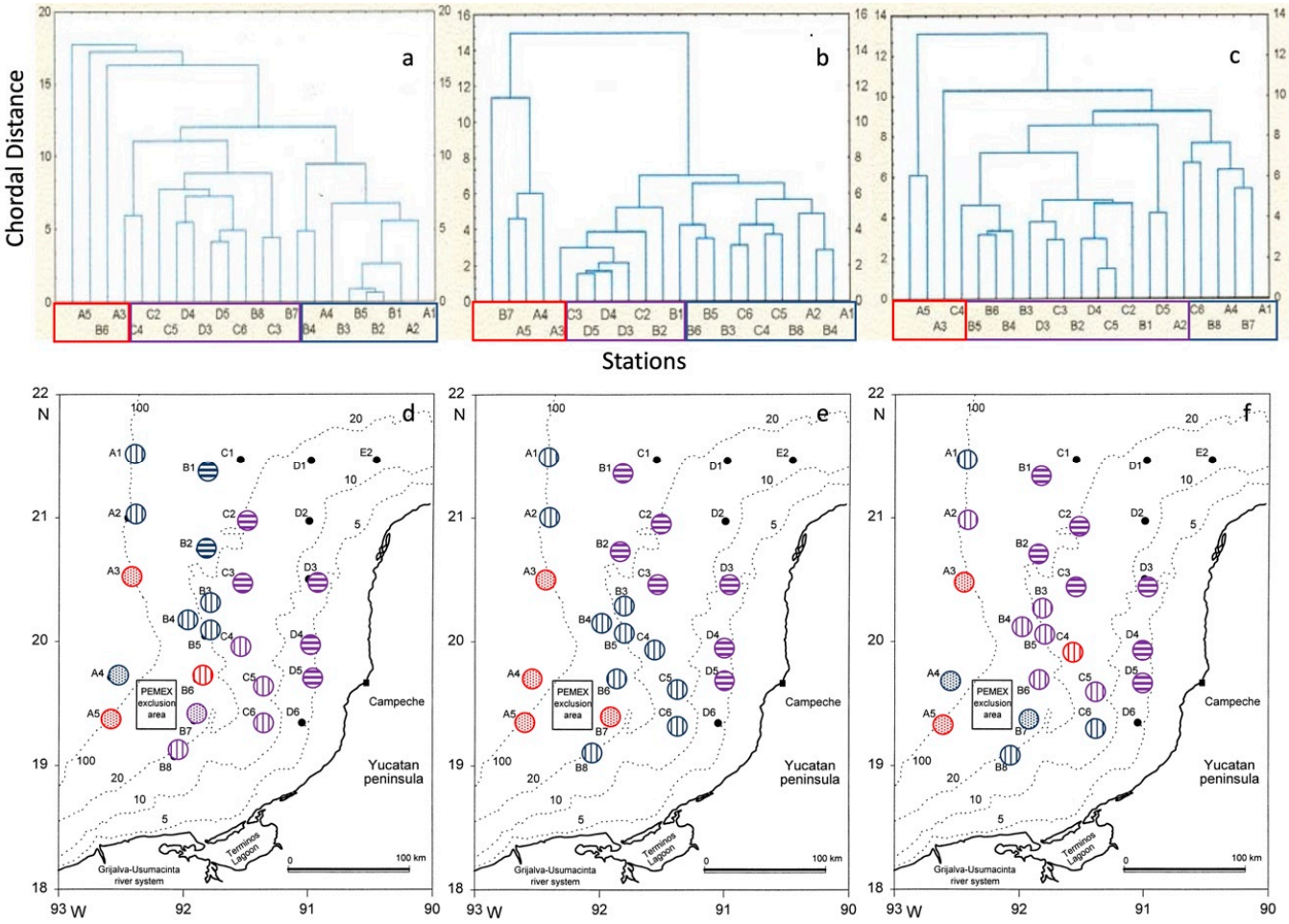

Figure 4. Panels (**a**–**c**) show the results of the CAs for three depths, 0–2 cm (**a**,**d**); 2–6 cm (**b**,**e**); and 6–10 cm (**c**,**f**). Porphyrins (VO– and nickel–porphyrins as in Figure 2) and geochemical variables (Ni, V, Cu, Zn, Cr, Cd, Pb, as % of FeCO3, organic carbon, carbonates, aliphatic compounds, aromatic compounds, UCM, total [25]) for the stations listed in the *x*-axis were used to form the clusters. The *y*-axis shows the chordal distance, according to the used unweighted pair group method with arithmetic mean hierarchical clustering analysis. The maps show the clusters formed according to the magnitude of the chordal distance. The filling for each circle corresponds to the terraneous (dots), transition (vertical lines), and carbonate (horizontal line) zones as reported by [25,34] for the top layer.

The areas were well defined and associated with the mineralogical patterns in the mid-depth layer, and the bottom layer is probably a mix between the first and second layers. The high concentrations characterize the presence of stations A3 and A5 as a group in porphyrins and low carbonate contents; furthermore, the A1, A2, and A4 stations are part of zone II. This pattern denotes the similarities in variables' spatial distribution, particularly for the porphyrins. Additionally, station C4 is found to be an independent group due to its high hydrocarbons content.

The CCA determines the association between two groups of variables [35]. The relationship between the spatial distribution of the geochemical and the porphyrinic variables can indicate the contaminant source and its persistence in the aquatic environment. The differences between the spatial distribution of the multiple geochemical conditions integrated by the CCA responds to the influence of short- to long-term external factors, such as aromatic hydrocarbons or heavy metals. Figure 5 shows the significant canonical variables for 0–2, 2–6, and 6–10 cm sedimentary layers. According to the first pair of canonical variables in the surficial sediments, the associations between the distribution of the Ni–porphyrins and VO–porphyrins to the distribution of carbonate content and vanadium were negative and positive, respectively (Figure S1). These relations support the idea of a common origin between porphyrins and geochemical variables, which was previously suggested by [20,21,36]. These authors showed the presence of V and Ni in different organic matter diagenetic steps. With less contribution to the system variability, the second pair of significant canonical variables relates the porphyrins negatively with the aliphatic and aromatic hydrocarbons. Moreover, [22] also referred to this association with the same spatial distribution pattern between them.

One pair of canonical variables was statistically significant for the next sedimentary depth (2–6 cm). In this case, the association of the porphyrins with the total hydrocarbons was positive and contrasting for the previous layer. In this layer, the distribution of the carbonates content presented a low and negative relationship with the porphyrins. This relation was confirmed by the spatial distribution that showed a less marked gradient of porphyrins.

The deepest layer (6–10 cm) presented one significant pair of canonical variables, indicating a wider distribution of the porphyrins (mainly VO–porphyrins). The positive porphyrin–carbonate content association confirmed this assessment. Considering that the carbonate content was practically constant through the different depths, the high presence of detected porphyrin concentrations in the study area, near to 85% coverage of the area, indicates a different scenario at this depth. Furthermore, the relationship between Ni and V was inverted, and the negative correlation between carbonate content and V implied the participation of different processes in the distribution and control of the porphyrins and heavy metals, both associated positively in the surficial layers. The high concentrations of spatially distributed porphyrins evidenced that a possible above-normal input of contaminants preceded controls observed in layers 1 and 2.

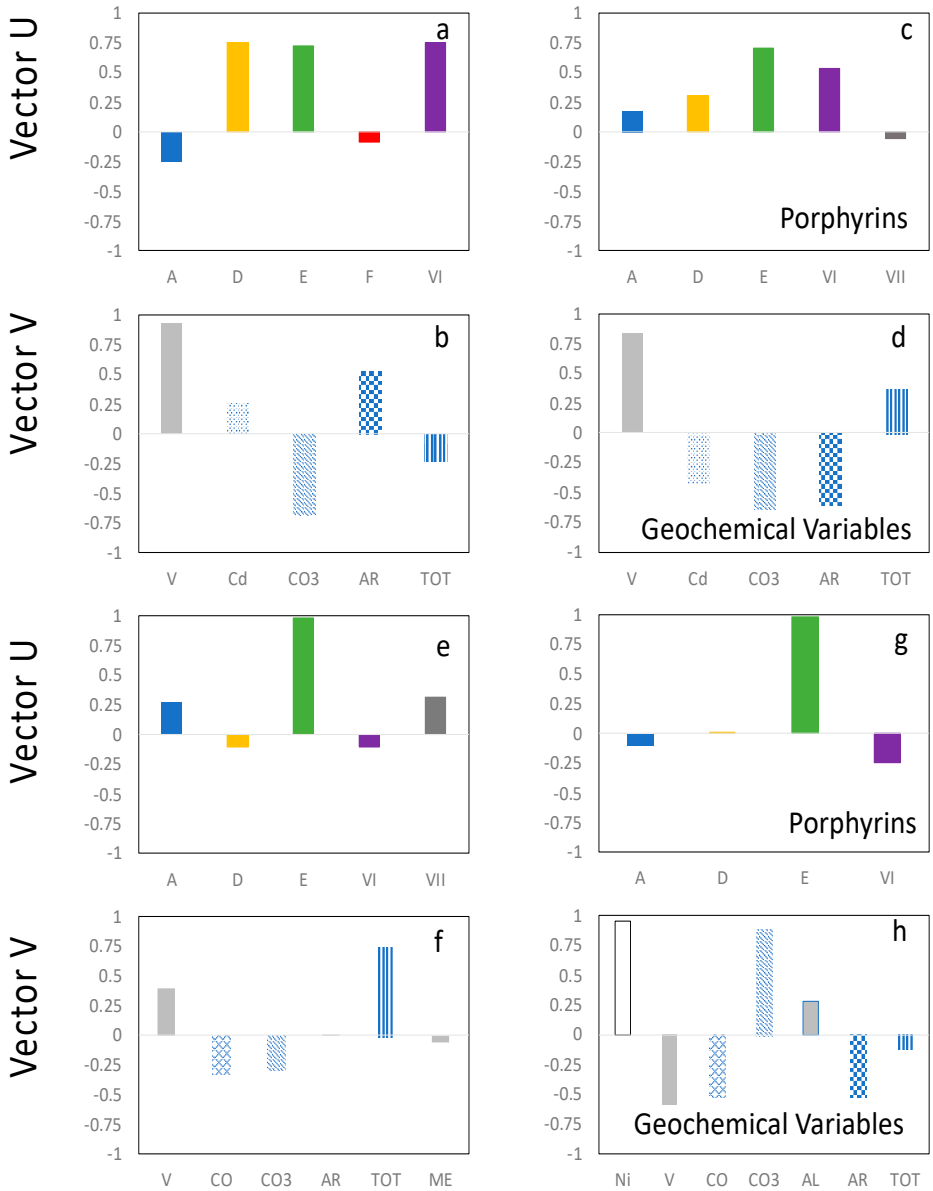

Figure 5. Panels (**a**–**d**) show two significant canonical pairs for the 0–2 cm depth; panes (**e**,**f**) for a single pair of significant canonical vectors for the 2–6 cm depth; and a single significant pair of canonical variables for the 6–10 cm depth (**g**,**h**). The variables in each panel characterized all the possible families of VO– and nickel–porphyrins, heavy metals, hydrocarbons, and carbonates. The values in the plots are canonic correlation coefficients.

4. Discussion

Multiple and multi-term efforts have explored the temporal, geospatial, process- and operational-based attributions between oil spills and the biogeochemical, physical, geological, and ecological conditions in the marine environment [23,25,37–40]. Some of these studies suggest that oil derivates and metabolites in sediments and water experience microbial degradation, leading to low levels of contaminants in the environment. Other studies indicate that an accelerated metabolic activity, typical of tropical ecosystems, may result in communities resilient to oil spills of natural or human origin in the Gulf of Mexico [39]. Yet, these efforts unclearly justify why some communities experience stress even when concentrations of traditional oil pollution indices are low [22,23,41]. The thesis of this paper state that the integration of extraction and instrumentation improvements and multivariate statistics can foster the use of metalloporphyrins as geospatial surrogates

to the traditional oil pollution indices in sediments of the Campeche Sound. We support this thesis based on three premises: (1) efficient extraction and the use of high-pressure liquid chromatography separate, identify, and quantify VO– and nickel–porphyrins from marine sediments of twenty-one stations at three depths across the Campeche Sound; (2) spatial distribution and temporal variability of VO– and nickel–porphyrins contribute to elucidating alternative patterns of variability to traditional oil pollution indices, indicative of the persistence of pollution in the region; and (3) statistically connected porphyrins and other biogeochemical variables contribute to identifying the spatial patterns of common variability, denoting emerging variability patterns using CA and CCA in the study area.

Large-scale and multi-objective oceanographic campaigns remain challenging sampling endeavors to explore the alterations of coastal sediment biogeochemical processes and biosystems in marine sediments, in response to chronic or accidental oil spills [23,37,41]. Sediment samples, benthic organisms, data collection, curation, and syntheses reflect the intricacies of ecological and sedimentary processes across spatial and temporal scales in complex coastal systems. In this study, the efficiency in the extraction of VO– and nickel–porphyrins (90% and 60%, respectively) in small sediment samples (6 to 8 g) enables the inference of structural differences of these tetrapyrrolic compounds and the possible effects on their distribution across surface sediments of the Campeche Sound. We use modified approaches to extract porphyrins from source materials like oil, oil rock, or bitumen, which use similar sample sizes, but contain higher porphyrin concentrations [28,29,42]. The extraction of these tetrapyrrolic compounds from sediments near the source of, or affected by, oil pollutants is more difficult due to the low concentrations or the random geolocation of the sampling sites [16]. Thus, the efficient extraction and quantification of porphyrins enhanced the data available, elucidating emergent patterns that otherwise will be hidden by the microbial and natural degradation of traditional indices of oil pollution. Furthermore, the distribution of stations in our study incorporates the randomness of sampling, mapping patterns of variability, and including the interactions between the porphyrins and other biogeochemical variables across the Campeche Sound.

Discrepancies in the spatial distribution of porphyrins and the biogeochemical variables evidence the effects of oil pollution and the underlying influence of multiple Earth System processes. First, the regions of carbonate content defined by Carranza Edwards and those reported by [25]—who integrate heavy metals into a CA—presented similar patterns to those observed in the second layer of Figure 4e and Figure S1a. The inclusion of porphyrin variables in the CA led to the emergence of two other patterns of variability for the top and bottom layers (Figure 3a,b). CA is complemented with CCA to reveal that the porphyrins' patterns of spatial variability are likely attributed to short-term disturbances and long-term fluctuations in sediment transport driven by oceanographic, hydrologic, biological, and atmospheric processes in the Campeche Sound. The distribution of suspended sediments and sedimentary rates in shallow depths reported by [25,34] is key to identifying the intricacies of the physical and biological processes that distribute the porphyrins and other biogeochemical variables in the south of the Gulf of Mexico. The three layers of sediments in this study represent 80–140 years based on the estimated sedimentary rates of 0.8–1.4 mm/year from the isotope 210Pb [25]. The suspended sediments, the sedimentary rates, the spatiotemporal variation in the porphyrins, and biogeochemical variables evidence the region's influence on oceanic and fluvial processes [25,34,43]. At the same time, the coastal circulation and the generation of streamflows and sediment loads from the Grijalva–Usumacinta River system are modulated by atmospheric and land surface conditions in these latitudes [44–46].

The Ixtoc-I blowout in June of 1979 caused an oil spill equivalent to more than 3.4 million barrels of crude oil in 9 months [39]. This event occurred within the top layer's 16-to-28-year time span (0–2 cm depth). The content of porphyrins in A1 in the top and the bottom layers is the highest. Station A1 is near the area of exclusion, and the sediments are primarily formed of terrigenous materials attributed to the influence of the Grijalva–Usumacinta River system. The first canonic variable U for porphyrins (D, E, and

VI) and canonic variable V for carbonates (negative relation) and aromatic hydrocarbons (positive connection) in the top layer suggests that the high concentrations of porphyrins can be attributed to the Ixtok-I blowout. The second pair of canonic variables in the top layer captures the antagonistic relation between porphyrins and carbonates in the central and eastern regions (Figure 4). In the bottom layer, the spatial distribution of porphyrins shows a gradient of VO–porphyrins toward station A1 and one significant pair of canonic variables. However, the porphyrins and carbonates contrast with vanadium, aromatic hydrocarbons, and organic carbon. In this layer, sediments date before the 1930s, indicating the effect of chronic pollution or natural seepages, since porphyrins and carbonates increase while vanadium, aromatic hydrocarbons, and organic matter decrease, possibly due to degradation [39]. The second layer represents 40 years starting in the 1970s. The variations of carbonates and organic matter were similar and negatively related to the VO–porphyrins, suggesting changes in the deposit of terrigenous materials, likely attributed to a decrease in sediment loads from the Grijalva–Usumacinta River system. Thus, the Angostura and Malpaso dams' construction before 1975 [44], the largest reservoirs in the basin, might be responsible for interrupting sediment loads to the Campeche Sound.

5. Conclusions

We present the geospatial attributions of distributed VO– and nickel–porphyrins in the marine sediment of the Campeche Sound. In twenty-one stations, the porphyrins were extracted from 6 to 8 g of marine sediment samples. We identified three sedimentary provinces using CA on porphyrin and other biogeochemical variables. Terrigenous materials dominate one, the second by carbonates, and the third represents a transition zone between both. At the same time, such provinces, and the use of CCA, contribute to characterizing three patterns of spatial variability in three layers (0–2 cm, 2–6 cm, and 5–10 cm). We suggest that each pattern of variability encompasses the Ixtoc-I blowout in June 1979, the diversion of streamflows due to the construction of massive water storage in the 1960s and the 1970s, and chronic and natural oil spills before the mid-1930s, respectively. The patterns of variability of porphyrins emerge from the balance between terrigenous materials and carbonates, regulated by the coastal transport of sediments and the fluvial contributions of the Grijalva–Usumacinta system. Thus, the highest concentrations of porphyrins occur near the exclusion zone in the top and bottom layers, at the top layer attributed to the intensification of the oil activity, and at the bottom, unclearly attributed to natural oil spills. Extreme hydrometeorological and climate events like "Nortes" and cyclones can alter the spatial patterns of variability. While this study evidences the reliability of porphyrins as oil pollution indices, we still need to test whether stressed benthic communities in the Campeche Sound are associated with chronic or natural oil spills, blowouts, or other phenomena.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/geosciences12020077/s1, Figure S1. Spatial distribution of (a) Carbonates [%], (b) Vanadium [μg/g], and (c) Total Hydrocarbons [μg/g]. The lines represent the gradients of VO–porphyrins [ng/g] in the top layer (0–2 cm).

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