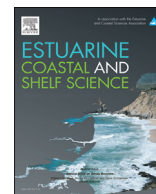




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Baseline for PAHs and metals in NW Gulf of Mexico related to the Deepwater Horizon oil spill

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ABSTRACT

As a rapid response to the massive oil spill caused by the sinking of the Deepwater Horizon (DWH) Platform in the northern Gulf of Mexico in April 2010, a baseline study was initiated. The study focused on determining the concentration of crude oil petroleum hydrocarbons and trace metals (Cr, Ni and V) in water and surface sediments from Mexico's EEZ, in the NW Gulf of Mexico. A total of 60 samples obtained from the shelf-slope regions were analyzed by GC/FID for 16 EPA priority polycyclic aromatic hydrocarbons (PAHs) and ICP/MS for Cr, Ni and V. The concentrations of PAHs in the surface water were below detection limits (<0.003 – $0.03 \mu\text{g L}^{-1}$) while in sediments, ranged from 0.01 to $0.070 \mu\text{g g}^{-1}$. International sedimentary quality guidelines (ERL-ERM) indicated a low probability of harmful effects to benthic organisms. Similarly, metal concentrations in sediments exhibited low concentrations (Cr 25.2 – 117 , Ni 9.6 – 50.8 , V 42.9 – $150.8 \mu\text{g g}^{-1}$). These metals were traced to a lithogenic source related to the heavy sediment load contributed by local rivers; no traces of anthropogenic inputs from oil related operations were identified. Significant enrichment of Ni and V was recorded in deep sediments whose ERL limits did not represent adverse conditions to benthic communities except for few sites on the upper continental slope. During the first two years of environmental monitoring of Mexico's EEZ in the NW Gulf of Mexico, no evidence of the DWH oil spill have been detected.

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1. Introduction

The environmental equilibrium of the Gulf of Mexico (GoM) was severely threatened by the massive oil spill caused by the accidental Deepwater Horizon (DWH) blowout in the deep waters off Louisiana, USA, in April 2010. For nearly four months, approximately 4.3 million barrels of crude oil and an equivalent of methane gas were spilled on the surface and deep waters of the northern GoM. Based on surface circulation models of the GoM (Zavala-Hidalgo et al., 2003, 2013), there was a probability that crude and weathered oil derivatives from the Macondo well could disperse to the northeastern coast of Mexico and the waters of Mexico's Exclusive Economic Zone (EEZ) in the central gulf. As a consequence of this critical environmental emergency, in the summer of 2010 Mexico deployed a task force to monitor systematically 42 physicochemical and biological variables in water and sediments from the continental shelf and upper slope of the NW GoM (Soto and Vázquez-Botello, 2013).

Even after the Macondo well was finally capped in mid-July 2010, many research uncertainties remain as to the trajectory of surface and subsurface oil slicks, and the persistence of oil and its derivatives in shallow and deep sea habitats. The current knowledge on the concentration of oil hydrocarbons and metals in the NW Gulf are restricted to the continental shelf off Tamaulipas, Mexico (Ponce-Vélez et al., 2006). These authors reported for Σ PAHs (16 priority PAHs USEPA, 2009) average concentration of $4.5 \pm 7.4 \mu\text{g g}^{-1}$ in sediments from this area that were attributed to both petrogenic and pyrolytic sources associated with the expanding activity of the local oil industry. They also recorded the presence of petrogenic metals such as Ni in negligible concentrations in comparison with those of Cr that reached higher concentrations and were presumably contributed by different industrial sources in the area. Unfortunately, there is a dearth of information on many hydrographic and geochemical processes (transportation and degradation of contaminants) occurring in deeper regions of the GoM, which hinders our attempts to predict the fate of the oil by-products dispersed by subsurface hydrocarbon plumes originated in the DWH's accident.

Our own research efforts in the first two years (2010–2011) of monitoring the proposed area of study (Fig. 1) specifically targeted

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the concentration of PAHs, Cr, Ni and V contained in water and surface sediments. The sampling design considered the two contrasting hydrographical conditions that prevail during the summer (MARZEE-I) and winter (MARZEE-II) season in the GoM. The surface circulation in the NW Gulf is predominantly to the north in the summer; whereas in winter, there is a marked intrusion of colder and more diluted water from the Louisiana–Texas shelf that flows towards the SW. Presumably, the latter hydrographical conditions would facilitate the transportation of oil contaminants into the NW Gulf. On the other hand, the deep sea circulation of the Gulf would eventually promote the slow deposition of oil derivatives on the sea floor.

The identification of Macondo oil crude in this research poses a significant scientific challenge due to its possible overdispersion by surface and bottom currents, and to weathering and biodegradation processes. However, mid- and long-term effects of oil contaminants in the marine environment cannot be overruled. Therefore, the present study focused on first building baseline information on the concentration of PAHs and Cr, Ni and V in the water and surface sediments of the shelf and slope systems of the NW GoM. Secondly, this study also focused on the detection of concentrations of oil contaminants possibly derived from the Macondo oil spill.

1.1. Study area

The area of study extends in the NW GoM between 26–22°N and 95–97°W including the shelf and upper slope from 50 to

>2200 m (Table 1). This sector of the Gulf is strongly influenced by the cyclone and/or anticyclone gyres derived from the Loop Current. When these processes are absent in the NW Gulf, the surface oceanic circulation predominantly is towards the north. The salinity and density vertical profiles obtained during the winter season indicated the intrusion of cold and diluted water originated from the Louisiana–Texas continental shelf (Zavala-Hidalgo et al., 2012). The sedimentary conditions on the shelf are profoundly influenced by the river runoff of three main rivers namely, Bravo, Soto La Marina, and Pánuco, and by the exporting capacity of two major coastal lagoons: Madre and Tamiahua. Deep-water sediments are essentially biogenic with predominance of silt–clay and are impoverished in organic material. Table 1 shows the main sedimentary properties recorded at 35 localities.

2. Materials and methods

To assess the content of hydrocarbons and trace metals in surface water and near-surface sediments, sixty samples were collected during two oceanographic campaigns conducted on board the R/V “Justo Sierra” in July 2010 (summer) and January 2011 (winter). The sampling took place along the continental shelf and upper slope of NW GoM (Fig. 1). For PAHs, water samples were taken with one gal glass container; the pre-extraction was performed immediately after collecting the sample with high purity hexane, and the extract was kept frozen until analysis in the laboratory (UNESCO, 1976; Keith, 1991). The sediments, to both metals and to PAHs, were obtained using a Reineck box-corer at depths

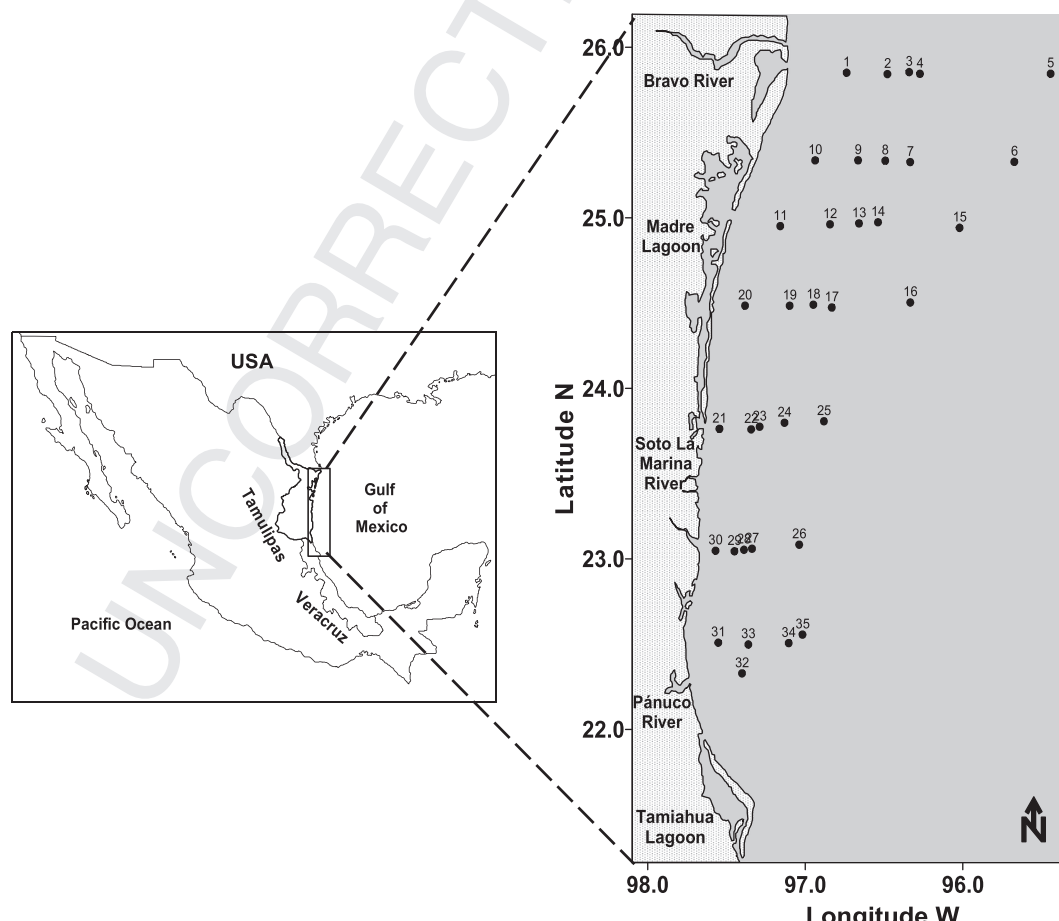


Fig. 1. Location of study area and sampling sites in the NW Gulf of Mexico during July 2010 (MARZEE-I) and January 2011 (MARZEE-II).

Table 1

Sampling data and main parameters of surface sediments from the continental shelf and upper slope of the NW Gulf of Mexico.

Site	Latitude N	Longitude W	Depth (m)	Sand (%)	Silt (%)	Clay (%)	Sediment types	Organic carbon (%)
1	25.851467	–96.737350	48.11	1.01	72.12	26.88	Silty	1.05
2	25.843417	–96.478483	83.40	0.60	74.45	23.95	Silty	1.49
3	25.855050	–96.340783	180.00	0.17	64.49	35.33	Silty	1.52
4	25.844750	–96.272150	454.00	0.68	72.45	26.88	Silty	1.74
5	25.845467	–95.443383	2329.00	0.75	67.26	31.99	Silty	1.03
6	25.328367	–95.673550	1443.00	1.90	71.35	26.75	Silty	0.33
7	25.327433	–96.333967	502.00	0.43	74.72	24.85	Silty	1.59
8	25.335317	–96.492500	170.00	0.90	72.44	26.66	Silty	1.56
9	25.338067	–96.664850	102.52	0.75	75.40	23.85	Silty	1.76
10	25.337183	–96.937000	52.00	1.31	74.73	23.96	Silty	1.83
11	24.951700	–97.158600	52.00	1.52	75.73	22.75	Silty	1.74
12	24.962133	–96.842483	107.00	1.35	77.32	21.33	Silty	1.83
13	24.967483	–96.658917	200.00	0.24	63.53	36.23	Silty	1.40
14	24.974183	–96.538217	502.28	0.01	63.86	36.13	Silty	1.76
15	24.941700	–96.021183	1596.00	0.06	63.91	37.02	Silty	1.07
16	24.503683	–96.333650	1504.37	0.01	60.25	39.73	Silty	1.53
17	24.474333	–96.831817	474.00	0.12	68.68	31.20	Silty	1.80
18	24.490650	–96.948567	194.00	0.39	69.20	30.41	Silty	1.93
19	24.484567	–97.098917	107.00	0.01	62.06	37.93	Silty	1.72
20	24.485033	–97.381700	53.00	1.11	74.43	24.46	Silty	2.04
21	23.762600	–97.544650	50.50	2.22	75.64	22.14	Silty	1.83
22	23.759483	–97.342917	112.00	0.33	70.58	29.09	Silty	2.16
23	23.774867	–97.289217	184.00	0.31	72.61	27.09	Silty	2.30
24	23.798333	–97.131667	492.00	0.01	58.22	41.77	Silt–clay	1.86
25	23.806950	–96.881500	1403.00	0.37	62.01	37.62	Silty	1.44
26	23.082983	–97.038417	1487.00	0.35	66.05	33.60	Silty	2.00
27	23.059367	–97.337517	554.00	0.33	68.96	30.71	Silty	1.60
28	23.053083	–97.388750	220.00	0.67	74.57	24.76	Silty	1.88
29	23.044283	–97.449350	98.00	0.53	68.68	39.79	Silty	1.81
30	23.047333	–97.569417	49.93	1.39	70.75	27.86	Silty	1.71
31	22.508267	–97.552200	50.00	2.47	73.00	24.54	Silty	1.71
32	22.328183	–97.401317	92.50	0.62	65.38	34.00	Silty	1.57
33	22.497783	–97.361367	442.00	0.12	57.62	42.26	Silt–clay	1.81
34	22.505867	–97.105200	751.00	0.55	71.37	28.08	Silty	1.74
35	22.555450	–97.017283	1604.00	0.21	63.57	36.22	Silty	1.24

from 50 to >2200 m and stored frozen in clean containers until analysis in the laboratory.

Trace metals. The technique used for metals was that described by Suwandana et al. (2011) consisting of a digestion in a microwave oven (CEM Mars5x) with 3 mL of HF, 10 mL of reagent water and 5 mL of super-pure HNO₃. The samples were read in an ICP-MS (ICP 7500c). Analytical quality was controlled using approved standards, reference material certified for marine sediments (IAE-433).

Recuperation percentages were 89% for Cr; 102% for Ni and 97% for V. A reference blank was analyzed every 10 samples. Detection limits were: Cr 0.0226, Ni 0.021 and V 0.0213 µg g^{–1}.

PAHs. The samples were analyzed for the 16 EPA priority PAHs (USEPA, 2009) following the methods recommended for surface waters (UNESCO, 1976; Keith, 1991) and sediments (UNEP/IOC/IAEA, 1992) used worldwide in marine pollution studies (Readman et al., 1987; Tolosa et al., 2004, 2009; Kapsimalis et al., 2010).

The PAHs included naphthalene (Naph), acenaphthylene (Aceph), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (An), fluoranthene (Flu), pyrene (Py), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IP), dibenzo[a,h]anthracene (DBA) and benzo[g,h,i]perylene (BPE). ΣPAHs refers to the sum of the 16 PAHs. For surface waters, the hexane extract was concentrated in a rotary evaporator (35 °C/40 psi) to 5–7 mL; the clean-up extract step is the same as that used for sediments. The method for sediments involved the organic extraction with n-hexane:methylene chloride 50:50 v/v; the extract was concentrated in the same manner as samples of surface water; clean-up for surface water and sediments extracts was done

using a silica pack, aluminium oxide and anhydrous sodium sulphate, eluted with n-hexane to obtain the paraffinic fraction, and later with n-hexane:methylene chloride 80:20 and 50:50 to obtain the aromatic fraction. The aromatic fractions were concentrated under a soft N₂ current to the point of dryness. All analytes were quantified using a Hewlett–Packard 5890 series II gas chromatograph (GC) equipped with an HP-5 silica fused capillary column (30 m × 0.25 mm i.d. with a 0.25 µm film thickness). A flame ionization detector (FID) was used. Quantification was carried out following an internal calibration method based on a five-point calibration curve for individual components. Four perdeuterated PAHs (naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀ and chrysene-d₁₂) were added to duplicate samples prior to extraction in order to quantify procedural recoveries. The recovery percentages ranged from 85% to 105%. For each batch of ten samples, a procedural blank, a spiked blank and for sediments reference standard material was processed (IAEA-417). The analytical blank contained no detectable amount of the target analytes. Detection limits (DLs) for surface water were <0.003–0.03 µg L^{–1} and for sediments were 0.01 µg g^{–1}, calculated considering the average +3σ for each analyte after obtaining the chromatographic data of 15 injections of the lowest standard. All sediment data are reported as dry weight. Organic carbon determination in sediments was based on the method of Gaudette et al. (1974) in which exothermic heating and oxidation with K₂CrO₇ and concentrated H₂SO₄ are followed by titration of the excess dichromate with 0.5 N Fe(NH₄)₂(SO₄)·6H₂O. Granulometric analysis of sediments was conducted with the aid of a Beckman Coulter LS230 laser diffraction particle size analyzer adjusted for samples with a range size of 0.04 y 2000 µm.

Table 2

International marine surface waters and sediment quality guidelines used for classifying sites by probability of adverse effects (Buchman, 2008).

Analyte	*Marine surface waters ($\mu\text{g L}^{-1}$)		*Marine sediment ($\mu\text{g g}^{-1}$)	
	Acute	Chronic	ERL	ERM
Naphthalene	2350.0	†	0.16	2.10
Acenaphthylene	300.0	†	0.04	0.60
Acenaphthene	970.0	40.0	0.02	0.50
Fluorene	300.0	†	0.02	0.50
Phenanthrene	7.7	4.6	0.24	1.50
Anthracene	300.0	†	0.09	1.10
Fluoranthene	40.0	†	0.60	5.10
Pyrene	300.0	†	0.70	2.60
Benzo[a]anthracene	300.0	†	0.30	1.60
Chrysene	300.0	†	0.40	2.80
Benzo[b]fluoranthene	300.0	†	†	†
Benzo[k]fluoranthene	300.0	†	†	†
Benzo[a]pyrene	300.0	†	0.40	1.60
Indeno[1,2,3-cd]pyrene	300.0	†	†	†
Dibenzo[a,h]anthracene	300.0	†	0.06	0.30
Benzo[g,h,i]perylene	300.0	†	†	†
Σ PAHs	300.0	†	4.00	44.80
Cr	†	†	81.00	370.00
Ni	74.0	8.2	20.90	51.60
V	†	50.0	†	†

* Buchman (2008).

† Not reported.

3. Results and discussion

3.1. Polycyclic aromatic hydrocarbons (PAHs)

Water. In most of the July 2010 sampling sites, the PAHs concentrations in the surface waters were below the analytical detection limit (<0.003 – $0.03 \mu\text{g L}^{-1}$); the Σ PAHs concentrations were of 0.01 – $0.02 \mu\text{g L}^{-1}$. Benzo[a]anthracene, chrysene, benzo[b]

fluoranthene and indeno[1,2,3-cd]pyrene were recorded in 14.3% of the sites. Similarly, in January 2011, only benzo[b]fluoranthene was recorded in 28% of the samples, with a value of $0.01 \mu\text{g L}^{-1}$. The low concentrations registered for individual hydrocarbon compounds precluded the estimation of the indexes normally recommended for the identification of possible PAH sources (Yunker et al., 2002; Arias et al., 2010; Wagener et al., 2010; He et al., 2014). However, the compounds recorded in surface waters in the studied area are part of these rates. They are included in the proportions $\text{BaA}/\Sigma 228$ and $\text{IP}/\Sigma 276$, and it has been documented that high molecular weight (HMW) PAHs (≥ 202) with four and five rings do not contribute significantly to the composition of refined petroleum products (Yunker et al., 2002). According to NOAA's quality criteria for seawater (Buchman, 2008), there are acute and chronic thresholds well established for the 16 PAHs whose presence in the marine environment is considered critical. In our study, the quantifiable concentrations of these compounds ($<0.01 \mu\text{g L}^{-1}$ vs $300 \mu\text{g L}^{-1}$) indicated no adverse effects in surface waters (Table 2).

Sediments. The Σ PAHs recorded in surface sediments in the two seasons had concentrations $< 1 \mu\text{g g}^{-1}$, with the highest concentrations of 0.70 and $0.51 \mu\text{g g}^{-1}$ corresponding to the summer season in July 2010 and the winter in January 2011. These concentrations were recorded at the Mexico–USA border at depths of 454 and >2000 m, respectively. The spatial distribution of the Σ PAHs clearly shows the influence of rivers discharge in the northwestern GoM (Fig. 2).

Individually, the PAHs with the highest concentrations were acenaphthene, fluorene, anthracene, chrysene, phenanthrene, benzo[fluoranthenes (*b* and *k*), indeno[1,2,3-cd]pyrene, benzo[*g,h,i*]perylene, benzo[*a*]anthracene, benzo[*a*]pyrene and dibenzo[*a,h*]anthracene, with averages of 0.06 ± 0.013 to $0.02 \pm 0.002 \mu\text{g g}^{-1}$.

Considering the criteria for sediment quality established by Long et al. in 1995 and used internationally as a reference of possible biological damages to the benthos (Buchman, 2008), the

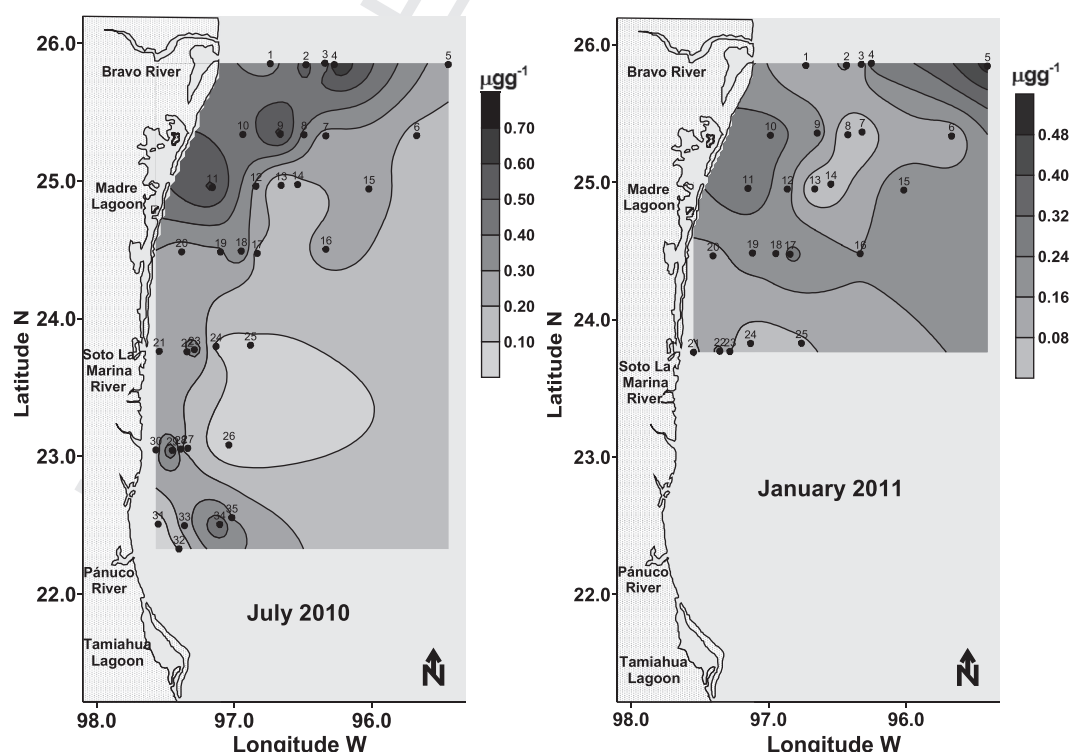


Fig. 2. Distribution of PAHs ($\mu\text{g g}^{-1}$) in surface sediments of the NW Gulf of Mexico, July 2010 and January 2011.

individual concentrations of acenaphthene, fluorene, chrysene and dibenzo[a,h]anthracene were >ERL (*Effects Range Low*) <ERM (*Effects Range Median*) in July 2010. In January 2011 acenaphthene had only two values above this ERL guideline and fluorene had values greater than the ERL (>0.02 µg g⁻¹) in 64% of the samples but <ERM (<0.50 µg g⁻¹). The total concentration of PAHs in sediments in the area of study (ΣPAHs 0.01–0.70 µg g⁻¹) indicated low probability of causing adverse biological effects (<ERL 4.0 µg g⁻¹, Table 2). However, the persistence of these heavier organic compounds can pose an environmental risk since they may retain some toxic properties for years (Sammarco et al., 2013).

Molecular PAHs rates that provide information on the main sources of their origin were estimated. In Table 3, the An/Σ178, Flu/

Σ202, BaA/Σ228, IP/Σ276 and $R \leq 3/\geq 4$ aromatic rings are shown for marine sediments of this study (Yunker et al., 2002; Arias et al., 2010). The main source of PAHs in the studied area was pyrolytic, originated by the ignition of plant material. However, small fractions of petrogenic hydrocarbons like acenaphthylene and acenaphthene were also detected in certain sites, as a result of fossil fuels combustion (Table 3).

The identification of PAHs sources requires an integral analysis. This may be complex as these types of organic compounds are subject to processes of atmospheric and fluvial dispersion where environmental parameters such as particle diameter, currents, temperature, fuel raw matter characteristics and physicochemical conditions, among others, determine their accumulation in a

Table 3

Selected polycyclic hydrocarbon ratios for identification of main sources determined and contamination level from surface sediments of the NW Gulf of Mexico.

Site	^a An/Σ178		^a Flu/Σ202		^a BaA/Σ228		^a IP/Σ276		^{b,c} R _{Σ3/Σ4}		^{a,b,c} MAIN SOURCE		^d Contamination level for ΣPAHs (µg g ⁻¹)	
	July 2010 (MARZEE-I)	January 2011 (MARZEE-II)	July 2010 (MARZEE-I)	January 2011 (MARZEE-II)	July 2010 (MARZEE-I)	January 2011 (MARZEE-II)	July 2010 (MARZEE-I)	January 2011 (MARZEE-II)	July 2010 (MARZEE-I)	January 2011 (MARZEE-II)	July 2010 (MARZEE-I)	January 2011 (MARZEE-II)	July 2010 (MARZEE-I)	January 2011 (MARZEE-II)
1	0.33	ND	0.50	ND	0.12	ND	0.60	ND	0.27	1.00	MS	ND	0.35	0.08
2	0.25	ND	0.50	0.33	0.83	0.43	0.50	ND	0.23	0.29	PDC	MS	0.54	0.18
3	0.20	ND	1.00	ND	0.04	ND	ND	ND	0.28	ND	MS	ND	0.37	0.08
4	ND	ND	N.d.	ND	0.02	1.00	1.00	ND	0.06	3.83	MS	C	0.7	0.29
5	0.50	0.33	0.50	0.67	0.50	0.33	1.00	ND	0.26	4.67	MSC	BC	0.24	0.51
6	0.50	ND	0.50	ND	0.50	1.00	1.00	ND	0.45	2.33	MSC	C	0.16	0.1
7	0.50	ND	0.50	ND	0.66	ND	0.33	ND	0.73	ND	PDC	ND	0.26	0.04
8	0.20	ND	0.50	1.00	0.71	ND	0.66	ND	0.32	ND	MSC	BC	0.37	0.01
9	0.33	ND	0.60	ND	0.18	0.75	0.61	0.29	0.34	0.17	BC	PDC	0.63	0.21
10	0.20	0.25	1.00	0.50	0.06	1.00	0.43	0.25	0.22	1.15	PDC	PDC	0.44	0.28
11	0.13	ND	0.50	0.50	0.57	ND	0.33	0.25	0.72	1.23	PDC	PDC	0.62	0.29
12	ND	ND	1.00	ND	0.07	1.00	ND	0.40	0.22	0.90	MS	PDC	0.28	0.19
13	ND	ND	ND	ND	ND	ND	1.00	ND	0.13	ND	BC	ND	0.09	ND
14	0.17	ND	1.00	ND	0.50	1.00	ND	1.00	1.00	ND	BC	BC	0.18	0.05
15	0.25	ND	0.50	ND	0.33	1.00	0.33	0.63	0.44	0.20	PDC	BC	0.23	0.24
16	0.11	ND	0.50	ND	0.50	0.67	0.50	0.60	1.18	0.14	PDC	BC	0.24	0.16
17	0.50	ND	0.50	ND	0.50	ND	0.75	0.50	1.00	0.69	MSC	PDC	0.14	0.27
18	0.17	ND	0.50	ND	0.20	0.50	0.40	ND	0.41	1.29	PDC	C	0.41	0.16
19	0.20	ND	0.50	0.50	0.60	1.00	0.43	ND	0.40	1.63	PDC	PDC	0.28	0.21
20	0.50	ND	0.50	ND	0.33	1.00	0.66	ND	0.25	1.17	MSC	C	0.25	0.13
21	0.33	ND	0.50	ND	0.50	1.00	0.50	ND	0.33	0.67	PDC	C	0.24	0.05
22	0.25	ND	0.50	ND	0.33	0.20	0.38	0.40	0.33	0.36	PDC	MSP	0.28	0.19
23	0.17	ND	0.50	ND	ND	0.50	0.67	ND	0.31	0.60	MSC	C	0.38	0.08
24	ND	ND	ND	ND	ND	ND	ND	ND	0.75	0.50	ND	ND	0.07	0.03
25	ND	ND	1.00	ND	ND	ND	ND	ND	1.25	1.33	BC	ND	0.09	0.07
26	ND	NC	ND	NC	ND	NC	ND	NC	ND	NC	ND	NC	0.01	NC
27	ND	NC	1.00	NC	ND	NC	0.44	NC	0.13	NC	MSC	NC	0.17	NC
28	0.25	NC	0.50	NC	1.00	NC	0.20	NC	0.80	NC	PDC	NC	0.18	NC
29	0.33	NC	0.40	NC	0.66	NC	0.42	NC	0.23	NC	PDC	NC	0.54	NC
30	ND	NC	0.50	NC	0.50	NC	0.75	NC	0.53	NC	MSC	NC	0.23	NC
31	ND	NC	N.d.	NC	ND	NC	ND	NC	ND	NC	ND	NC	0.04	NC
32	ND	NC	1.00	NC	ND	NC	ND	NC	3.50	NC	BC	NC	0.09	NC
33	0.20	NC	0.66	NC	0.50	NC	0.60	NC	0.66	NC	BC	NC	0.25	NC
34	0.20	NC	0.66	NC	0.16	NC	ND	NC	0.28	NC	MS	NC	0.5	NC
35	0.13	NC	0.66	NC	0.09	NC	ND	NC	0.93	NC	MS	NC	0.29	NC

An anthracene; Flu fluoranthene; BaA benzo(a)anthracene; IP indeno(1,2,3-cd)pyrene; ^aYunker et al. (2002); Arias et al. (2010); ^bCai et al. (2007); ^cPing et al. (2007); ^dMaliszewska-Kordybach (1996); ND not determined due to insufficient data; NC not collected; MS Mixed Sources; PDC Petroleum Derivatives Combustion; MSC Mixed Sources Combustion; BC Biomass Combustion; MSP Mixed Sources Petroleum; C Combustion.

Contaminated	Weakly contaminated	Not contaminated
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particular place. Furthermore, environmental processes generate an additive effect, *i.e.*, synergy, which may result in two opposite scenarios: they either favour a greater dispersion of organic pollutants to distant places, or may contribute to their accumulation in sites adjacent to the spill (Commins, 1969; Baumard et al., 1998; Soclo et al., 2000; Guinan et al., 2001; Yunker et al., 2002; Hartmann et al., 2004; Luo et al., 2006; Arias et al., 2010). What is most important is to try to identify the sources as precisely as possible in order to use that information in the decision-making process to either avoid harmful ecological impacts or reverse them.

It is our contention that the PAHs concentrations reported here in sediments from the northwestern GoM are not sufficient proof to exclude potential long-term adverse environmental effects from the DWH oil spill in Mexico territorial waters. The persistence of subsurface hydrocarbon plumes (Spier et al., 2013) and its eventual deposition on the sea floor of the GoM depends on many converging processes such as weathering, dissolution, dispersion and biological degradation. Even though, there is clear evidence of the lingering biological effects of residual petroleum in coastal habitats for several decades (Burns et al., 1994; Reddy et al., 2002), in the GoM the long-term environmental consequences caused by the DWH oil spill remain unanswered.

Recently, Sammarco et al. (2013) examined the geographic extent of petroleum hydrocarbons associated with DWH oil spill in the GoM and drew attention to the high concentration of total petroleum hydrocarbons (THP) and PAHs found in sediments of the

western GoM, particularly off Galveston, TX. These authors presume that hydrocarbons compounds derived from the DWH oil spill may have reached this region of the Gulf ~500 km from the spill source, due to the near-shore currents west of the Mississippi River. Another fact that somewhat makes the Mexican EEZ in the GoM vulnerable to the slow transport of oil spill derivatives is the Loop Current (LC) system and its eddy shedding process. Liu et al. (2011) were able to detect small volume of the surface oil entrained in the northern part of the LC system a month after the DWH blowout. However, these authors recognized the difficulties of following the evolution of the surface oil slicks due to weathering and biological degradation factors. In addition, Sammarco et al. (2013) have pointed out that the LC system is known for producing eddies that when they break free, they potentially may carry petroleum hydrocarbons to the west along the edge of the continental shelf.

Considering the criteria discussed by Maliszewska-Kordybach (1996) to classify the degree of Σ PAH pollution, in this study the analyzed sediments was also evaluated. For July 2010, 60% of the sampling sites were classified with a low pollution ($0.2\text{--}0.6\text{ }\mu\text{g g}^{-1}$), 31.4% were not polluted ($<0.2\text{ }\mu\text{g g}^{-1}$) and only 8.6% were polluted levels ($0.6\text{--}1.0\text{ }\mu\text{g g}^{-1}$). For January 2011, 68% of the sampling sites were non-polluted ($<0.2\text{ }\mu\text{g g}^{-1}$), and the other 32% had low pollution levels ($0.2\text{--}0.6\text{ }\mu\text{g g}^{-1}$) providing a different pattern for the two samplings (Table 3). Thus, it follows that the sedimentary record of PAHs found in this region of the GoM on most sites

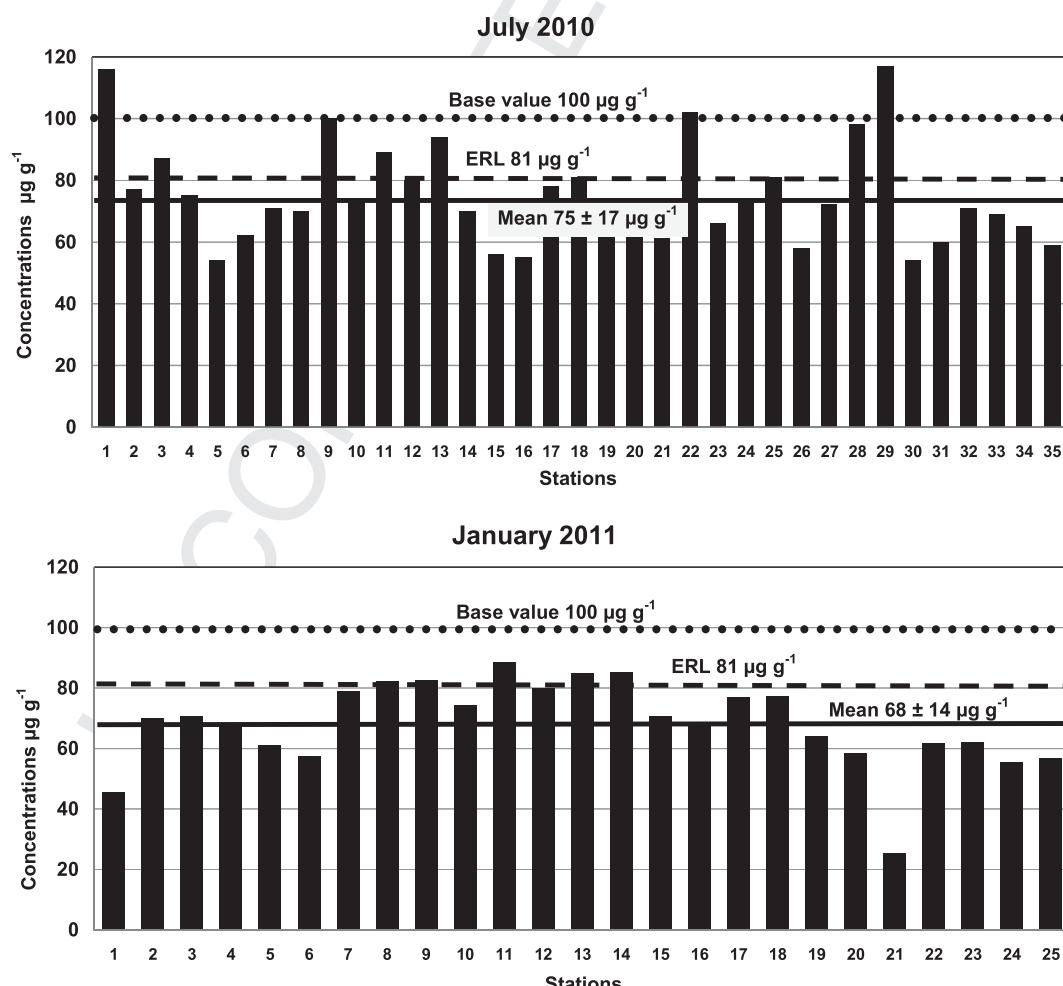


Fig. 3. Distribution of chromium in surface sediments of the NW Gulf of Mexico. July 2010 and January 2011.

evaluated is not a hotspot of contamination by this type of persistent compounds. However, among the PAHs considered as potentially carcinogenic we identified: chrysene, benzo[fluoranthene] [bk], indeno[1,2,3-cd]pyrene, and also benzo[a]pyrene and dibenzo[a,h]anthracene; these findings constitute signs of potential environmental and public health risks (IARC, 2011), which supports the need of a monitoring programme.

The PAHs content determined in July 2010 showed a significant correlation ($r > 0.5$, $p < 0.05$) with geochemical variables such as sediment type, organic carbon, V and Cr. In contrast, the correlations were not significant ($p > 0.5$) for January 2011, probably due to the lower hydrocarbons concentrations. A spatial variability was noted in the PAHs values between the shelf (<500 m) and the upper slope (>500 m). Such variability was attributed to the influence of shallow water circulation and the rivers runoff along the coast, whereas the deep currents have a greater impact on the sediment transport and deposition processes in the open ocean.

3.2. Trace metals in sediments

In January of 2011, the Cr spatial distribution was fairly homogeneous in sites just off Madre Lagoon (7, 9, 11–14, 17 and 18). Around this area, the concentrations gradually decreased. The minimum concentrations (45.9 and $25.24 \mu\text{g g}^{-1}$) were recorded at sites 1 and 21, located off the Bravo and Soto La Marina river mouths, respectively (Fig. 3). The registered concentrations ranged

from 25.24 to $88.51 \mu\text{g g}^{-1}$ with a mean \pm SD of $68.14 \pm 14.25 \mu\text{g g}^{-1}$. This concentration was inferior to the variation interval of the July 2010 sampling campaign which fluctuated between 54 and $117 \mu\text{g g}^{-1}$ with a mean \pm SD of $74.14 \pm 16.57 \mu\text{g g}^{-1}$. The Cr highest concentrations distribution was displaced in the direction of the Loop Current during the winter storm season. Interestingly, the average concentration of Cr recorded in this research exceeded that previously reported by Ponce-Vélez et al. (2006) on the Tamaulipas continental shelf (mean \pm SD) ($37.0 \pm 21.7 \mu\text{g g}^{-1}$). This significant increment might be attributed to chronic continental input. Rosales et al. (2005) reported that the sediments supplied by Pánuco river (Tamaulipas) move toward to the northeast and are deposited on the northeastern end of this coastal region.

Nonetheless, the above mean value comparatively remained considerably below concentrations reported by Reddy et al. (2004) in the Alang-Sosiya coast and Mahuva in the Cambay Gulf, India (mean \pm SD) ($290.18 \pm 63.18 \mu\text{g g}^{-1}$) and even from those known for sediments (10.3 and $161.8 \mu\text{g g}^{-1}$ with a mean of $21.6 \mu\text{g g}^{-1}$) in Naples, Italy estimated by Adamo et al. (2005). The concentrations of the deep-water marine sediments obtained by Chester (2000) were of $100 \mu\text{g g}^{-1}$. In this study, none of the sampled sites exceeded such threshold (Fig. 3). Recently, the geochemical composition of sediments presumably affected by the DWH blowout off the Mississippi delta was assessed by Liu et al. (2012). These authors reported Cr concentrations that fluctuated from 7.4 to $9.4 \mu\text{g g}^{-1}$ depending on the distant gradient from the

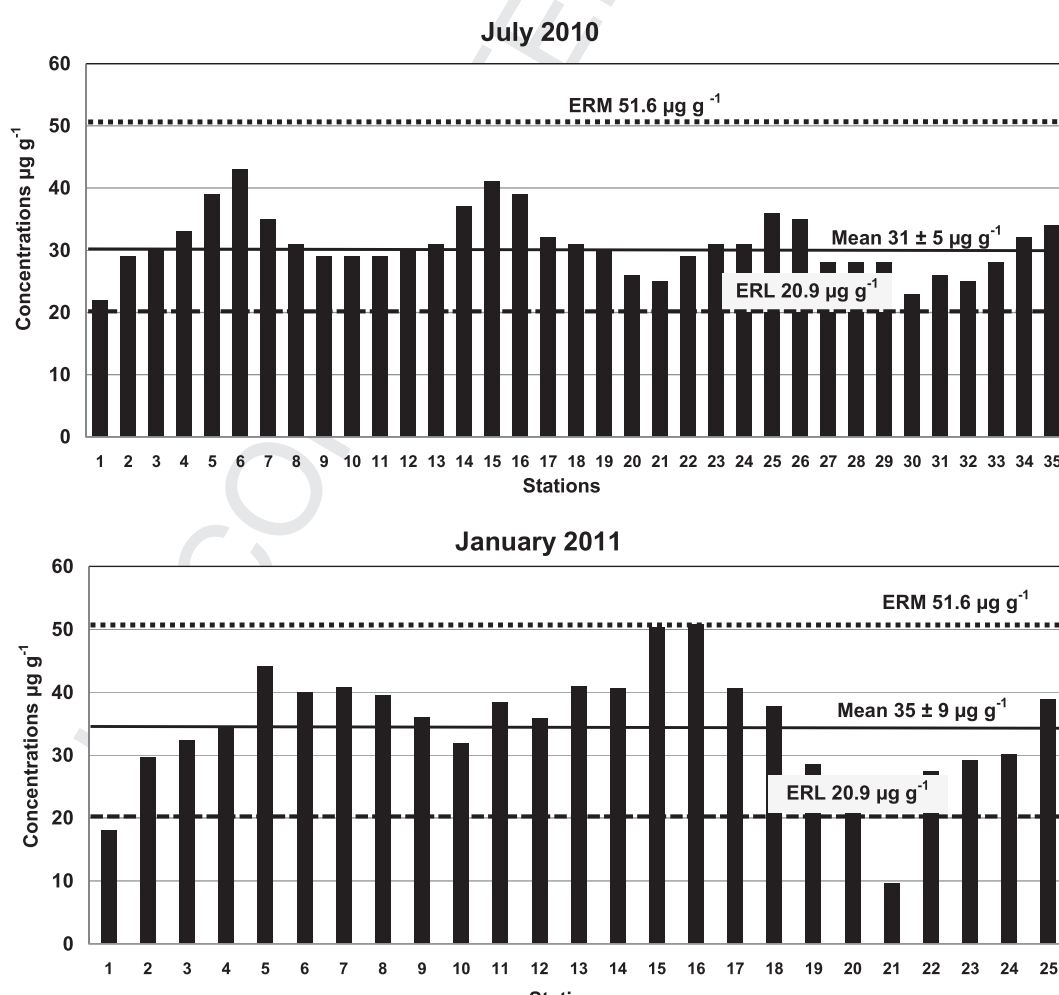


Fig. 4. Distribution of nickel in surface sediments of the NW Gulf of Mexico. July 2010 and January 2011.

Macondo's wellhead. They argued that after the accidental oil spill, weathering factors exerted a significant change on the concentrations of the examined trace metal. Nonetheless, their reported range for Cr in the Mississippi area fall below the one reported herein.

We estimated that between 20 and 23% of the recorded metal concentrations were $> \text{ERL}$ ($> 81.0 \mu\text{g g}^{-1}$) and $< \text{ERM}$ ($< 370.0 \mu\text{g g}^{-1}$) and, therefore, did not represent a severe adverse effect for the benthic communities in the area of study (Fig. 3).

The Ni showed a similar distribution pattern during the two sampling campaigns. The highest concentrations were obtained in deeper water, decreasing towards sites on the inner shelf. The lowest concentrations were recorded on the shelf and, as in the case of the Cr, sites 1 and 21 showed the minimum concentrations: 17.98 and $9.64 \mu\text{g g}^{-1}$, respectively (Fig. 4). The Ni variation interval in the winter storm season fluctuated between 9.63 and $50.79 \mu\text{g g}^{-1}$ with a mean \pm SD of $35.35 \pm 9.16 \mu\text{g g}^{-1}$, slightly higher than the concentrations of the onset of the summer season (July 2010); 22 and $42 \mu\text{g g}^{-1}$ with a mean \pm SD of $31 \pm 4.87 \mu\text{g g}^{-1}$. Rosales-Hoz et al. (2007) reported concentrations of 21 – $54.9 \mu\text{g g}^{-1}$ in sediments adjacent to the Sacrificios Island off the Port of Veracruz, which were similar to those reported in the present study. Ponce-Vélez et al. (2006) in their study of trace metals in sediments from the Tamaulipas' shelf in the NW GoM, reported Ni concentrations ranging from 1.9 to $76.1 \mu\text{g g}^{-1}$ and an average \pm SD of $26.8 \pm 16.7 \mu\text{g g}^{-1}$. These values are similar to those determined

in this research (Fig. 4). In contrast, in the Mississippi area, Ni concentration in sediments only reaches 4.2 – $7.7 \mu\text{g g}^{-1}$ (Liu et al., 2012). The value reported by Chester (2000) that indicates the deep-water marine sediment elemental composition was of $200 \mu\text{g g}^{-1}$. The Ni concentrations of this study were significantly lower ($p < 0.05$) than this value (Fig. 4). More than 92% of the Ni determinations made in our study were $> \text{ERL}$ ($> 20.90 \mu\text{g g}^{-1}$) and $< \text{ERM}$ ($< 51.60 \mu\text{g g}^{-1}$), indicating a low probability of causing biological damage (Fig. 4).

The spatial distribution of V closely followed the homogeneous pattern previously described for the Cr, just off Madre Lagoon, with concentrations of $126.73 \mu\text{g g}^{-1}$ and decreased towards both ends of the area studied. The lowest concentrations were found on two sites (1 and 21) along the inner shelf, 78.43 and $42.92 \mu\text{g g}^{-1}$, respectively (Fig. 5). The variation interval values were 42.93 and $159.8 \mu\text{g g}^{-1}$ with a mean \pm SD of $126.37 \pm 27.4 \mu\text{g g}^{-1}$, slightly higher and showed more variation than the concentrations of the campaign of July 2010 (92 – $145 \mu\text{g g}^{-1}$ with a mean \pm SD of $121.74 \pm 14.44 \mu\text{g g}^{-1}$).

The low concentrations of V (1.0 – $1.7 \mu\text{g g}^{-1}$), recently reported by Liu et al. (2012) in sediments sampled in the Mississippi delta were attributed to the crude oil degradation processes. Such concentrations are significantly lower than those included in the present study.

Interestingly, in contrast with another metal here analyzed, V does not have a sedimentary quality threshold to assess its

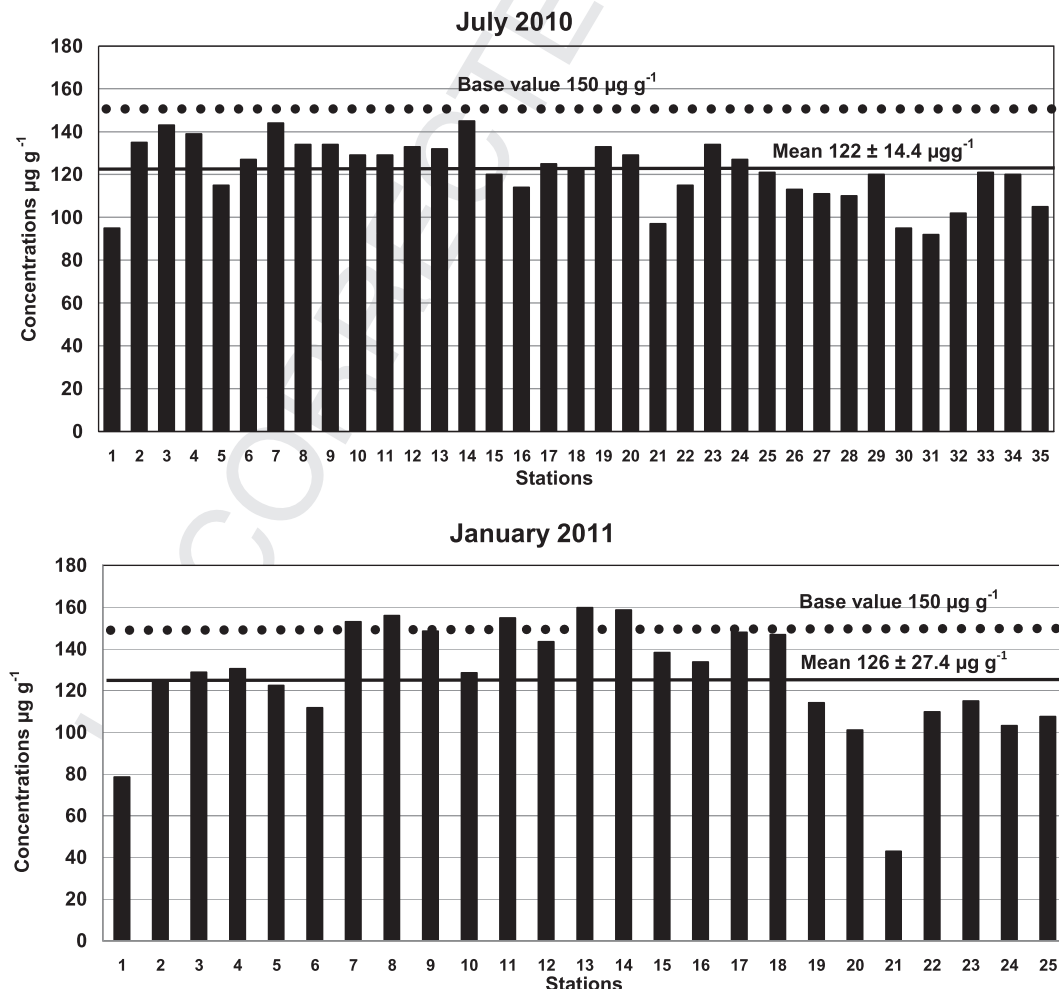


Fig. 5. Distribution of vanadium in surface sediments of the NW Gulf of Mexico, July 2010 and January 2011.

potential environmental damage effect upon benthic communities. Nonetheless, the recorded concentrations of V in the present study fell below the base level of $150 \mu\text{g g}^{-1}$ provided by Chester (2000) for marine sediments.

The V distribution pattern in both seasons was very similar. Therefore, the variation interval in this study was lower than the one reported by Rosales-Hoz et al. (2007) in the sediments adjacent to Sacrificios Island, Veracruz ($99.9\text{--}257 \mu\text{g g}^{-1}$). According to the mean values of the Enrichment Factor (EF) estimated in the present study, it was confirmed that they originated from natural rather than anthropogenic sources. The V concentrations showed values slightly below those established by Chester (2000) where the value was of $150 \mu\text{g g}^{-1}$ except in sites 7, 8, 11, 13 and 14 (Fig. 5).

4. Conclusions

PAHs in surface waters presented low concentrations, with less than 30% of the samples having values near $0.01 \mu\text{g L}^{-1}$. The higher concentrations of the aromatics in surface sediments were recorded in the northern region of the study area, from the inlet of Madre Lagoon, Tamaulipas to the Bravo River. The most abundant compounds were fluorene and chrysene, apart from phenanthrene, benzo[fluoranthene] [bk], indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene. The PAHs > ERL < ERM were acenaphthylene, acenaphthene, fluorene, benzo[a]anthracene, chrysene and dibenzo [a,h]anthracene, and indicated a low probability of benthic damage. The level of benzo[a]pyrene was <ERL, which means there was no risk of this carcinogenic compound altering the benthos. The dominant origin of the PAHs was pyrolytic, mainly from the incomplete burning of plant carbon, grass, wood and other plant components and to a lower degree from the burning of fossil fuels (oil, diesel). A smaller petrogenic component was recorded in specific areas off the Bravo River, the Madre Lagoon and the Pánuco River. In this research it was observed that river inputs, silty sediments and organic carbon were important environmental factors for the accumulation of PAHs on the sea floor of the studied area.

The concentrations of the trace metals revealed a lithological origin, mainly due to the load of suspended terrigenous sediments transported by the rivers, especially off Madre Coastal Lagoon and the Bravo and the Soto La Marina rivers, without anthropogenic inputs from oil industry activities. The greatest enrichments of Ni and V were recorded in the deep-water sediments. However, no significant differences were detected in sediments from the continental shelf and upper-slope regions given their similar sedimentary texture (silt and clay), except for one in-shore sandy site off a river inlet. The concentrations of Ni surpassed the ERL guideline, where adverse conditions for benthic organisms are rarely observed. There were only two sites on the upper-continental slope in which Ni concentrations dropped slightly below the ERM sediment quality criteria, indicating potential harmful effects to benthic inhabitants. Concentrations of the three trace metals here reported did not show significantly seasonal differences between the period of observations (summer–winter). The detected variations observed in the concentrations of trace metals here analyzed were attributed to local terrigenous input.

Uncited reference

Q4 Cai et al., 2007; Ping et al., 2007.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.ecss.2014.11.010>.

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