Geochemical patterns in sediments near offshore production platforms

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Abstract: Patterns of the geochemical characteristics of sediments adjacent to three production platforms (22–150 m water depths) in the northwestern Gulf of Mexico were determined by the presence of the structure, the amount and type of materials discharged from the structure, and the local hydrographic setting. Sediments close to platforms (<500 m) were enhanced in coarse-grain materials primarily derived from discharged muds and cuttings. Hydrocarbon and trace metal (Ag, Ba, Cd, Hg, Pb, and Zn) contaminants were associated with these coarse-grain sediments. Contaminants were asymmetricallly distributed around each platform in response to the prevailing currents. Contaminant concentrations at most locations were below levels thought to induce biological responses. At a few locations close to one platform, trace metal (i.e., Cd, Hg) concentrations exceeded levels thought to induce biological effects. In deep water (>80 m), sediment trace metal contaminant patterns were stable over time frames of years. A few metals (Pb, Cd) exhibited evidence of continued accumulation in sediments over the history of the platform.

Résumé : Les caractéristiques géochimiques des sédiments adjacents à trois plates-formes de production (par 22 à 150 , d'eau) dans le nord-ouest du golfe du Mexique ont été déterminées à partir de la présence de l'ouvrage, de la quantité et du type de matériaux libérés par l'ouvrage, et du contexte hydrographique local. Les sédiments proches des plates-formes (< 500 m) étaient chargés de matériaux grossiers provenant surtout des boues et des débris de forage. Ces sédiments grossiers étaient contaminés par des hydrocarbures et des métaux à l'état de traces (Ag, Ba, Cd, Hg, Pb, et Zn). Les contaminants étaient répartis asymétriquement autour de chaque plate-forme à cause des courants dominants. Leurs concentrations étaient presque partout inférieures aux seuils prévus d'induction d'effets biologiques. À quelques endroits près d'une plate-forme, les concentrations de métaux à l'état de traces (Pb, Cd) dépassaient les seuils d'induction prévus. En eau profonde (> 80 m), les concentrations des métaux à l'état de traces dans les sédiments n'ont pas varié pendant des années. Il s'est avéré que quelques métaux (Pb, Cd) se sont constamment accumulés dans les sédiments depuis la mise à l'eau de la plate-forme.
[Traduit par la Rédaction]

Introduction

Offshore petroleum platforms discharge a variety of materials over the lifetime of a field. These discharges are associated with a number of activities including drilling, ship operations, accidental spills, runoff from the platform, discharge of produced waters and sewage, and other platform practices (sand blasting, painting, welding, etc.; Neff et al. 1987; Aurand 1988; Ahfeld 1990; Kendall 1990). The platform structure also acts as a reef and can generate a flux of materials to the seabed resulting from enhanced biological activity in the sur-rounding waters. Over a number of years, these various processes lead to alterations in the benthic environment (Southwest Research Institute 1978; Middleditch 1981; Lake Buena Vista Symposium 1981). These benthic alterations would be predicted to produce changes in the associated biology (Neff et al. 1987; Boesch and Rabalais 1987). The Gulf of Mexico Offshore Operations Monitoring Experiment (GOOMEX) Phase I program was designed to test for responses in the resident biota with particular reference to the chronic introduction of toxic contaminants (Kennicutt et al. 1996). Grain size alteration, substrate changes, and organic enrichment are also suspected to exert significant control over changes in biological patterns. Abiotic and biotic patterns near platforms reflect the cumulative, long-term interaction of the structure, materials emanating from the structure, and local oceanographic conditions.

The two most common contaminants associated with platforms are hydrocarbons and metals (Boothe and Presley 1987; Middleditch 1981; Boesch and Rabalais 1987; Continental Shelf Associates, Inc. 1983, 1985). The release of petroleum from a platform to the surrounding environment can occur during drilling as well as in the production phase of a platform's lifetime. Petroleum hydrocarbons are potentially present in a variety of discharges including drilling fluids,

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cuttings, produced water, spills, deck drainage, and other releases (Kendall 1990). Petroleum-derived hydrocarbons released to the environment can be differentiated from naturally occurring background biogenic hydrocarbons (Brassell et al. 1978; Philp 1985; Boehm and Requejo 1986; Kennicutt and Comet 1992). Petroleum contains (1) a homologous series of *n*-alkanes with one to more than 30 carbons with odd and even carbon number *n*-alkanes present in nearly equal amounts, (2) a complex mixture of branched and cycloalkanes, and (3) an extensive suite of polycyclic aromatic hydrocarbons (PAH). Aliphatic hydrocarbons synthesized by organisms (both planktonic and terrestrial) include a suite of normal alkanes with odd numbers of carbons from 15 to 33. Complex branched and cycloalkanes are rare in organisms. Petroleum PAH mixtures are easily differentiated from PAH synthesized by organisms by the structural complexity of the mixture and the presence of substantial amounts of alkyl-substituted PAH. PAH are some of the more toxic components of oil and as such indicate the potential for biological effects. Based on considerations of petroleum chemistry, biological occurrences, and toxicological effects, aliphatic and aromatic hydrocarbons were chosen as tracers of petroleum contamination (Kennicutt 1995).

Trace metals are also released in discharges from offshore drilling activities (Boothe and Presley 1987; Boesch and Rabalais 1987; Lake Buena Vista Symposium 1981). Metal contamination can potentially affect both infauna and epifauna in the vicinity of platforms (Southwest Research Institute 1978). Many trace metals are priority pollutants (Ag, As, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, and Zn) and are known to be toxic to organisms. These metals are often a constituent of drill muds (Tornberg et al. 1981; Houghton et al. 1981 Rubinstein et al. 1981). Tin is known to be toxic and is present in antifouling paints used on platform structures. Barium is an ideal tracer of the settlable particulate fraction of discharged drilling fluids and cuttings because it occurs in high concentrations in drilling muds and has a low, natural background in ambient sediments (200–500 ppm dry weight; Chow and Snyder 1981; Boothe and Presley 1985, 1987). Barium (as barite, barium sulfate) is the dominant component of drill mud (up to 90% on a dry weight basis). Aluminum and Fe are major constituents of alumino-silicate minerals and can be used to detect changes in sediment type. Vanadium is another metal of interest because it can occur in significant concentrations in crude oil. Sixteen elements were measured in sediments and seven in pore waters (Ba, Cd, Cu, Hg, Pb, V, and Zn).

Other properties measured in sediments included grain size, mineralogy, organic and inorganic C content, and redox potential. Sediment texture (i.e., grain size) is an important variable in the evaluation of biological assemblage data and contaminant distributions in benthic systems. Numerous studies have shown a strong correlation between biology, chemistry, and sediment texture and quality. In benthic ecosystem studies, cross-correlations between study sites are often dependent on substrate characteristics. Correlation of biological response variables with contaminant exposure can be confounded by the effects of variations in substrate. The organic and inorganic C content of sediments is another important measure of sediment quality. The C content of sediments near platforms may be influenced by organic enrichment (i.e., reef

effect), disposal of drill mud and cuttings, and discharges from the platform. The O_2 content of sediment pore water as measured by redox potential is an important factor in determining the quality of the benthic substrate. Redox conditions also play an important role in the mobility and bioavailability of metals.

Methods

The laboratory methods for determining geochemical variables are summarized by Kennicutt et al. (1996). The methods used in this study are those of the NOAA National Status and Trends Program (NOAA 1993). Details of the methods are available in the references cited and the GOOMEX Final Report and will not be repeated here (Kennicutt 1995).

Results

The most dramatic feature of grain size distributions in sediments was the relationship between sand content (percent) and distance from the platform. Sediments out to a distance of 100 m were clearly enhanced in sand content (Fig. 1A). Stations between 200 and 500 m were impacted to varying degrees, depending on water depth, discharge location (i.e., near-bottom shunting), and the amount of materials discharged. The sand content of sediments at the near-field stations was increased above background sediment by 35–60% depending on the site. Indications were that most of this increase in sand-size materials resulted from disposal of cuttings during drilling operations at the platform. Sand content may also be enhanced by winnowing of fine particles by bottom currents, sand disposal during sandblasting activities, and deposition of carbonate skeletal fragments from platform-associated biota. Sediments at the shallowest, highest energy site (MAI-686) exhibited the greatest enhancements in sand content (Fig. 1A). However, the location of the discharges and the magnitude of the volume of the discharged materials were important controls on the sand content of sediments adjacent to the platforms.

An examination of sand fractions using a stereoscopic microscope and reflected light indicated that drill cuttings were present in sediments from the innermost stations at all three sites. The cuttings were characterized as very large rounded quartz-sand grains (two to three times as large as grains in background sediments from the area) and lithoclasts (fossiliferous limestones, chert, and/or fine-grained limestone). In addition, there were some angular, very fine quartz-sand grains presumably derived from sandblasting of the platform during rust-control programs. Small, sand-size metallic spheres were believed to be droplets of molten metal from welders or cutting torches that were quenched by seawater. Also visible was fragmented carbonate skeletal material derived from organisms encrusting the underwater parts of the platform. The most abundant skeletal remains were polychaete worm tubes and barnacles. The enhancement in sand-size particles was clear at all three sites. At HI-A389, an enhanced silt fraction was also evident in a cluster of samples closest to the platform. This indicated the possible addition of silt-sized materials as a result of drilling mud disposal. Sediments at HI-A389 within 50 m of the platform were more than 40% barite in some instances.

Carbon content distributions indicated that multiple pro-

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Fig. 1. Areal distribution of (A) sand content and (B) mean total PAH concentrations in sediments as a composite of all four cruises.
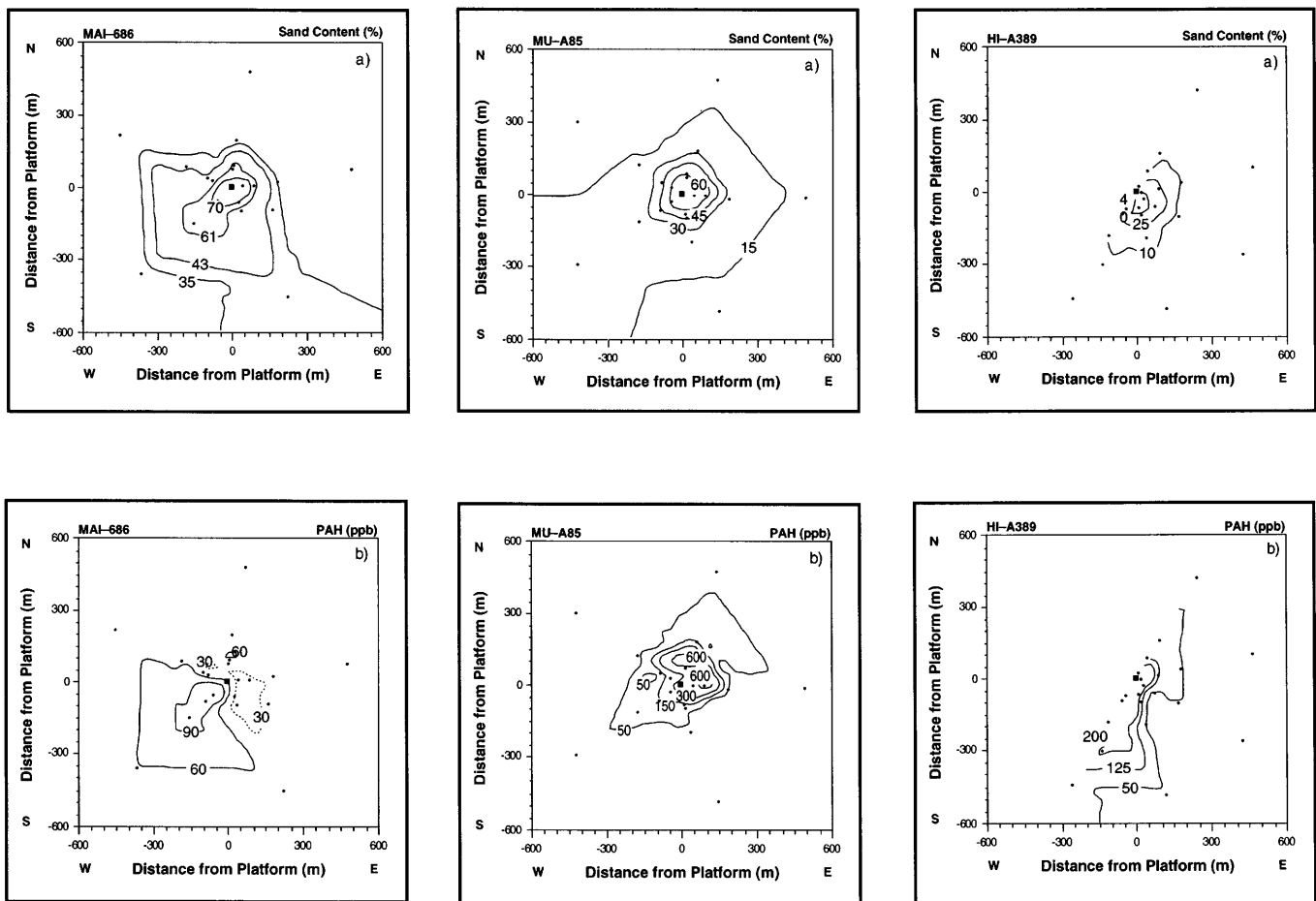
cesses were active. In the most general case, organic C decreased and inorganic C increased near the platform (Table 1). Total organic carbon (TOC) was in part decreased due to the addition of sand. However, TOC decreased by only 30% whereas sand and metals were increased by factors of 5–10 or more, suggesting that there was an additional source of TOC near the platforms. Sediment organic C content can increase due to deposition of organic matter derived from enhanced biological productivity associated with platforms. Enhanced sedimentary microbial populations in response to platform discharges, in particular hydrocarbon-oxidizing bacteria, may also contribute to TOC. Additions of TOC from cuttings is also possible but the significance of this source is unknown. Total inorganic carbon (TIC) content was subject to the sand dilution events as well. Inorganic C is a constituent of debris deposited from platform-associated calcareous biota such as barnacles and serpulids. Cuttings often contain inorganic C and can also be a source of TIC to the sediments. A positive correlation between sediment sand and TIC concentrations was observed.

Sediments from most stations contained little or no evidence of petroleum contamination. Concentrations of the unresolved complex mixture (UCM), total PAH, and total alkanes at most stations were less than 10 ppm, 150 ppb, and 500 ppb, respectively (Table 2). The method detection limit for total PAH in sediment was approximately 100–50

ppb. The areal distribution of the hydrocarbon contaminants was not symmetrical around the platforms, with concentration gradients varying in steepness among radii (Fig. 1B). Concentrations generally reached constant concentrations at distances of 100–200 m from the platform. At MAI-686, extracts from a few stations exhibited gas chromatograms typical of fresh condensate contamination (predominance of lower molecular weight n-alkanes and no UCM during all four cruises, suggesting a recent and continuing discharge of hydrocarbons (i.e., pipeline leak or an active seep)). In contrast, the contaminants at most stations at MU-A85 and HI-A389 lacked n-alkanes and exhibited a large UCM. Sediment extracts at HI-A389 exhibited a range of compositions probably resulting from differential input from multiple sources of hydrocarbon contamination. One station appeared to be contaminated with a low molecular weight fluid. Other stations exhibited a bimodal UCM suggesting two or more sources of petroleum in the area. Hydrocarbon concentrations were similar between cruises, suggesting that the low-level contamination observed was relatively stable. The greatest variations between cruises were detected at stations nearest to the platform, indicating steep, near-platform gradients and a heterogeneous distribution of hydrocarbons in sediments.

Variations in metal concentrations (on a dry weight basis) among cruises are illustrated for selected metals in Fig. 2.

Table 1. Tukey's multiple comparison test results by distance based on sedimentologic variables.

Variable[a]		Distance			
Overall design					
Sand	50 m	100 m	200 m	500 m	≥3000 m
(%)	(60.5)	(49.2)	(21.9)	(13.8)	(12.6)
TOC	≥3000 m	500 m	200 m	100 m	50 m
(%)	(1.02)	(0.98)	(0.89)	(0.69)	(0.61)
TIC	100 m	50 m	200 m	500 m	≥3000 m
(%)	(1.07)	(1.00)	(0.83)	(0.79)	(0.75)
MAI-686					
Sand	50 m	100 m	200 m	500 m	≥3000 m
(%)	(72.8)	(59.8)	(40.8)	(30.6)	(27.4)
TOC	3000 m	500 m	200 m	100 m	50 m
(%)	(0.79)	(0.78)	(0.65)	(0.42)	(0.35)
TIC	50 m	100 m	200 m	500 m	3000 m
(%)	(0.36)	(0.31)	(0.30)	(0.23)	(0.19)
MU-A85					
Sand	50 m	100 m	200 m	500 m	3000 m
(%)	(67.0)	(54.8)	(20.80)	(12.2)	(11.6)
TOC	3000 m	500 m	200 m	100 m	50 m
(%)	(0.93)	(0.92)	(0.90)	(0.62)	(0.55)
TIC	50 m	100 m	500 m	200 m	3000 m
(%)	(1.02)	(0.86)	(0.79)	(0.78)	(0.77)
HI-A389					
Sand	50 m	100 m	200 m	500 m	5000 m
(%)	(40.3)	(33.4)	(8.5)	(3.9)	(3.5)
TOC	5000 m	500 m	200 m	100 m	50 m
(%)	(1.40)	(1.27)	(1.19)	(1.13)	(1.02)
TIC	100 m	50 m	200 m	500 m	5000 m
(%)	(2.66)	(1.96)	(1.71)	(1.66)	(1.62)

[a]% sand–sand content, % silt–silt content, % clay–clay content.

[b]Detransformed means are presented (x) and means that are underlined are not different at the 0.05 level.

Contour plots are presented for Al concentrations, a major elemental constituent of the alumino-silicate minerals. Cadmium and Ba contour plots are presented to illustrate the typical distribution of metal contaminants. The level of contamination by metals was lowest at MAI-686, intermediate at MU-A85, and highest at HI-A389, the same order observed for hydrocarbon contamination (Table 2). Metals exhibited one of three distributions: (1) metal concentrations increased near the platform (Figs. 2A and 2C), (2) metal concentrations decreased near the platform (Fig. 2B), or (3) metal concentrations showed no detectable change. The metals with near-uniform distributions include Ag, As, Cu, Hg, Sb, Se, and Sn. These metals showed little change relative to distance from the platform. An exception to this relatively uniform pattern was an increase for a few of these metals (Ag, As, and Hg) near the platform at HI-A389 where the very highest metal levels were observed. Since a dilution of the sediments with 35–60% added sand had occurred, uniform concentrations suggest that a platform-related source must have been present to counteract the dilution. Several metals showed a decrease in sediments near the platform including Al, Cr (occasionally), Fe, Ni, and V. The remaining metals (Ba, Cd, Pb, and Zn) increased in concentration in sediments near the platforms. The magnitude of the increase was determined, in part, by the metal content of the materials discharged at each site.

Contamination at a site exhibits significant variability in three dimensions. Subsurface pockets of contaminants may influence biotic patterns in sediments. To assess the three-dimensional distribution of contaminants at each of the study sites, subsurface samples were taken at three depths to a depth of 20 cm along radius "C" during Cruise 3. Discharged drilling muds and cuttings (enriched in Ba) formed a thin veneer of materials that was 10–15 cm thick near the platform and thinned with increased distance from the platform. This pattern was also true for the hydrocarbons, with most of the hydrocarbons residing in the top 2 cm of the sediment column. Two sites (MAI-686 and MU-A85) exhibited subsurface Ba maxima illustrating the heterogeneous distribution of contaminants with depth in the sediment.

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Table 2. Ranges in contaminant concentrations in surficial sediments (0–2 cm) from GOOMEX study sites.

|	MAI-686	MU-A85	HI-A389
Hydrocarbons			
PAH (ppb)	7.8–588	17.7–6358.5	11.4–1238.1
Aliphatics (ppb)	72–9568	68–13.960	63–15.927
UCM (ppm)	0.0–119.4	0.0–381.8	0.0–406.1
Metals (ppm)			
Ag	0.1–1.7	0.0–1.0	0.0–3.8
Al	17 700–71 000	29 100–121 626	11 359–75 037
As	4.2–21.6	3.6–39.1	3.4–32.2
Ba	653–4680	720–26 250	785–280 220
Cd	0.0–1.6	0.0–2.3	0.1–63.7
Cr	25.5–82.0	37.8–131.0	35.0–171.0
Cu	3.8–48.9	5.5–36.2	9.0–106.1
Fe	11 940–30 280	13 680–69 940	15 400–36 590
Hg	0.0–0.1	0.0–0.3	0.0–3.5
Ni	0.5–28.5	7.5–28.5	9.2–35.4
Pb	0.2–555	15.2–436	0.2–694.8
Sb	0.3–2.4	0.3–5.5	0.4–7.5
Se	0.0–0.3	0.1–0.8	0.2–0.8
Sn	0.2–3.0	0.7–79.5	0.5–3.2
V	43.3–119.5	27.8–208.5	3.41–145.5
Zn	43.1–3850	54.6–1440	65.7–11 444

Discussion

One important observation was that sand content positively correlated with contaminant concentrations. This contrasts with most environmental studies where contaminants are associated with fine-grain particles (Boehm and Requejo 1986). This is a consequence of the origins of the contaminants, the composition of the materials discharged, the rapidity of the initial discharge, and the energetics of sediment transport at the site of deposition. A gradient in sand content is present at all three sites studied; however, the contaminant gradient is quite different among sites. Little or no hydrocarbon contaminant gradient was apparent at MAI-686. This results from differential redistribution of discharged materials based on grain size association, discharge history, and discharge technique. At MAI-686 the Ba anomaly is weak, suggesting loss of silt-sized materials due to winnowing at this shallow site. Timing of discharges, mode of discharge, and the amount of materials discharged are also important influences on sediment characteristics and cannot be fully resolved by the present study.

Principal components analysis (PCA) was performed on sedimentologic and contaminant variables to define interrelationships between sediment texture and contaminant content and to provide an effective representation of the variance in the data. Sediment texture and contaminant content were closely coupled at the platform sites. The contaminant and sedimentologic variables used for final PCA and score calculations were generated by a two-step data reduction procedure. As previously discussed, many contaminant variables (individual PAH and metals) strongly covary. The sediment metal data set is characterized by a strong covariance (both positive and negative) with Ba. At both HI-A389 and MU-A85, several metals (Cd, Hg, Pb, and Zn) showed highly significant, positive correlations with sediment Ba. For metals such as Cd and Hg, the correlation with Ba suggests a common source in the barite ore. In contrast, the lesser correlation of Pb and Zn with Ba suggests that a source other than drilling discharges is important (e.g., produced-water discharges, lubricants, welding operations, etc.). Lead and Zn have been detected in produced waters and are thought to be derived from the corrosion of galvanized structures on the platform or the oil–water separator system (Neff et al. 1987). Other metals (i.e., Al, Fe, Cr, Ni, Se, and V) associated with indigenous sediments show a weak, if any, correlation with Ba. Finally, As, Cu, and Sn are of mixed origins based on correlations with both Ba and sediment metals (e.g., Fe). For Cu, the correlation with Ba was weak except at high Ba concentrations suggesting that the concentration of Cu in the original barite ore was low.

Initial statistical analysis including all of the sedimentologic parameters produced principal components that reflected the high degree of covariation amongst variables. To more succinctly represent the consortium of materials present, significantly covarying parameters were reduced in number by either summing (TOTPAH) or selecting representatives of classes of contaminants as defined by statistical correlations (i.e., Ba as a marker of drill muds). The reduced set of parameters was then analyzed by PCA to produce a set of covariates that could be used to analyze the results from other study work elements (Table 3). PCA conducted at all levels of complexity (all variables, reduced variables, extended sets of variable) produced similar classifications of the data and thus led to equivalent interpretations. The consistency in the conclusions drawn from a variety of statistical treatments illustrates the robustness of

Fig. 2. Areal distribution of mean (A) Ba, (B) Al, and (C) Cd concentrations in sediments of all four cruises.
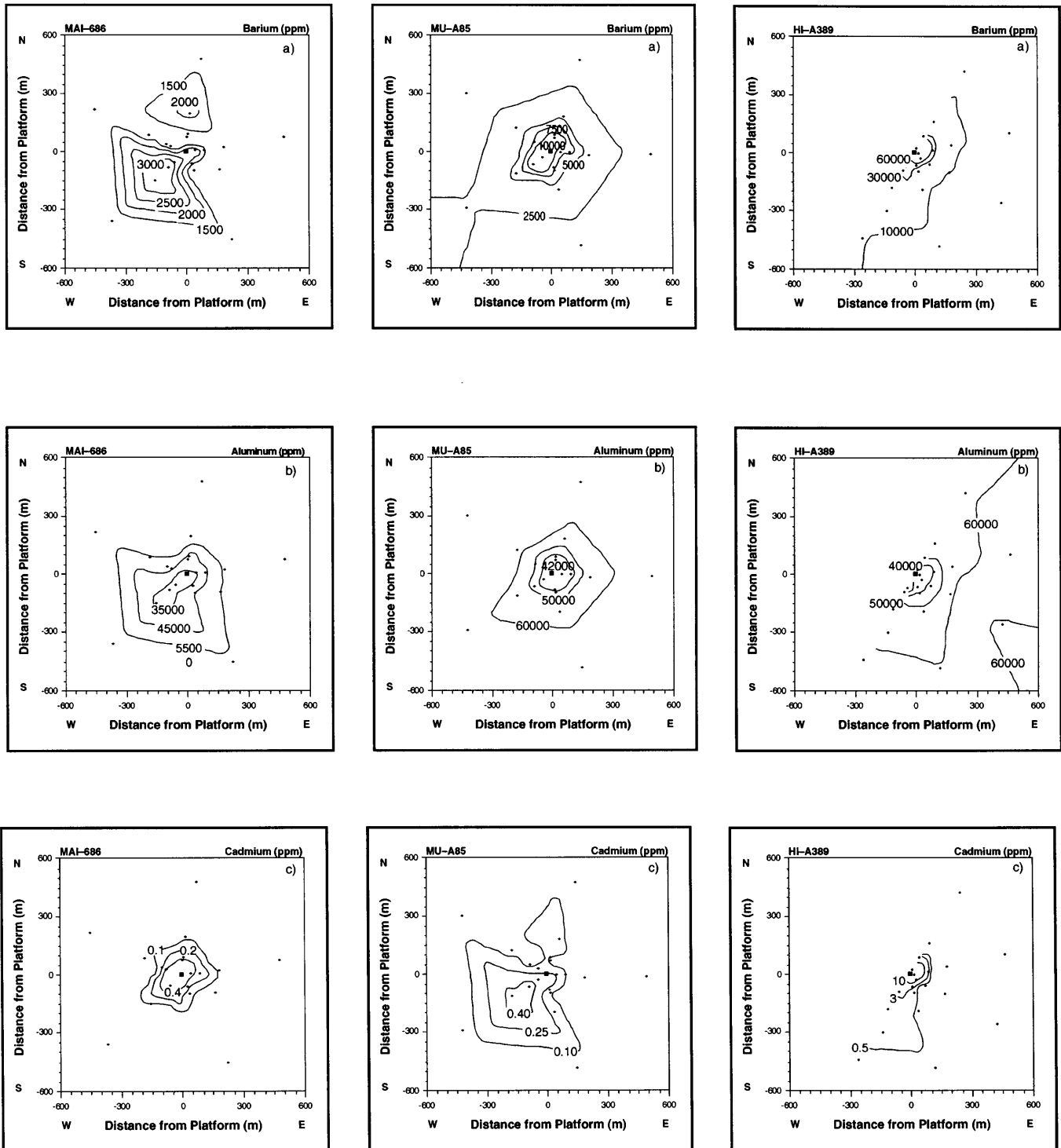
the conclusions to differing approaches to statistical analysis. A crossplot of the first component of the chemical analyses (ChemPC1) versus the second component (ChemPC2) clearly differentiates the stations by distance from platform and by site (Fig. 3). Translated into the variables measured, contamination increased as ChemPC1 increased (i.e., Near stations were more contaminated with hydrocarbons, met-

als, and sand than Far stations). Grain size decreased with distance from the platform. As ChemPC2 increased, fines increased and the sites were classified based on variables affected primarily by water depth and depositional setting.

As mentioned, many sediment contaminant variables covaried; therefore, a subset of representative contaminant and sedimentologic variables is presented to test the chemistry

Table 3. PCA factor patterns for reduced and combined sediment and contaminant variables (all variables were transformed as summarized under Discussion).

Variable	ChemPC1	ChemPC2
Total PAH	0.60	0.54
Total UCM	0.79	0.38
Total alkanes	0.79	0.20
%sand	0.85	−0.48
%silt	−0.61	0.58
%clay	−0.88	0.30
TOC	−0.50	0.63
TIC	0.08	0.64
Redox potential	−0.26	0.03
Fe	−0.61	0.58
Cd	0.69	0.64
Al	−0.86	−0.05
Ba	0.54	0.71
% of variance	43.6	24.7

Fig. 3. Relationship between ChemPC1 and ChemPC2 for sediment contaminant data coded by distance and grouped by site.
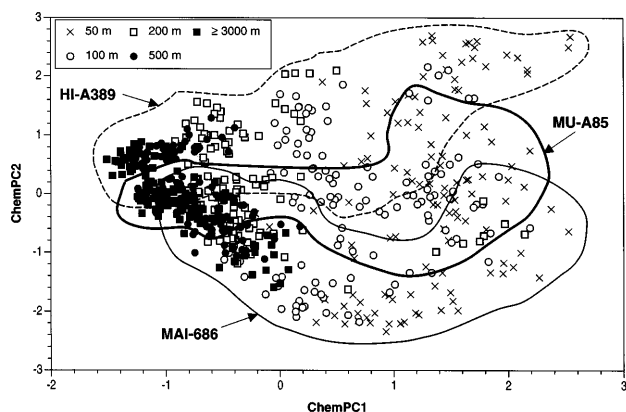
component of the programmatic hypotheses. The overall study design was devised to detect interactions among cruises, platforms, and distances from platforms (Kennicutt et al. 1996). Higher order interactions prohibited a direct interpretation of the main study design elements such as distance. The analysis of hydrocarbons and metals revealed many two- and three-way interactions. Significant interactions due to platform uniqueness were common. Distance and radius interactions were present for all variables, suggesting that many parameters vary not only in relationship to distance from the platform but also among radii within a site. Due to extensive, higher order interactions, more detailed information is provided if the data are tested on a platform-by-platform basis.

On a platform-by-platform basis, significant distance effects were clearly evident at all sites. Significant variations related to distance were independent of the site in that the analysis of data individually at all three sites gives similar and concordant results. Few interactions between cruise and distance were apparent, but distance interactions with radius

were significant at all sites for almost all contaminant and sedimentologic variables. This signifies that most "platform-perturbed" variables have a strong directional orientation, since distances are not equivalent along different radii. While distance is a significant determinant in variable variances, direct indicators of contaminants must be used to investigate biological associations (i.e., distance is insufficient as a surrogate for contamination or exposure).

Another approach for identifying differences among sample means is a multiple comparison test. Tukey's multiple comparisons were effective in summarizing and highlighting differences among distances and succinctly illustrated the attributes of each study site. Hydrocarbon-based variables differentiated stations out to 500 m (Table 4). Stations at greater than 500 m distance from the platform were indistinguishable from each other (i.e., background). Barium content differentiated all distances, suggesting a much wider dispersion of Ba (Fig. 2A). Aluminum, a background sediment constituent, reflected a near-field dilution caused by the addition of sand. Iron was diluted 30% compared with a 45% decrease in Al concentrations, suggesting a secondary source of Fe near the platform. Cadmium distributions were similar to those of Ba and differentiated sediments at all distances. The distribution of Ba and Cd was similar to that observed for sand content. However, Ba and Cd increased by a factor of 10 or more over controls whereas sand increased by only a factor of 5. The distance of recognizable differences based on various variables suggested different modes of transport related primarily to the hydraulic properties of the materials. Various size fractions were also influenced to varying degrees by contaminant additions, either enhanced or diluted. To more fully understand the origins of the sediments at the sites, the distribution of contaminant variables as a function of grain size is needed.

PAH were low and not significantly associated with distance from the platform at MAI-686 (Table 4). Other hydrocarbon parameters were somewhat correlated with distance but the association was weak and most likely related to a pipeline leak or seep along an individual radius that was not a site-wide contaminant event. Metals associated with drill muds (Ba and Cd) were only weakly correlated with distance from the platform. However, a concordant ordering of stations was not apparent. Sediment-associated metals (Fe and Al) reflected dilution with sand, and the sand content differentiated sediments out to 3000 m from the platform. At this site the increases and decreases in variables were relatively concordant, suggesting a common depositional event (i.e., Fe and Al concentrations decreased by 40%; sand content increased by a factor of 2.6).

MU-A85 clearly had enhanced contaminant concentrations near the platform. Hydrocarbon concentrations were significantly higher near the platform than away. The effect was most significant to 100 m, with the 200-m stations not significantly different from the 500-m stations other than for the UCM which differentiated sediments to a distance of 500 m. Barium and Cd concentrations differentiated sites to 500 m and, in the case of Ba out to 3000 m. This distribution was similar to changes in sand content. Iron and Al were diluted in response to the increase in sand content close to the platform. At this site, sand and Ba concentrations increased by 5- and 10-fold; however, Fe, Al, and TOC decreased by only 25–50%.

Table 4. Tukey's multiple comparison test results by distance based on contaminant variables.

Variable[a]	Distance[b]				
Overall					
TOTPAH	50 m	100 m	200 m	500 m	≥3000 m
(ppb)	(114)	(73)	(48)	(35)	(35)
Ba	50 m	100 m	200 m	500 m	≥3000 m
(ppm)	(10 217)	(6065)	(4359)	(2019)	(1149)
Cd	50 m	100 m	200 m	500 m	≥3000 m
(ppm)	(0.73)	(0.25)	(0.13)	(0.07)	(0.06)
Al	≥3000 m	500 m	200 m	100 m	50 m
(ppm)	(61 248)	(61 175)	(54 776)	(41 680)	(33 982)
MAI-686					
TOTPAH	3000 m	500 m	200 m	50 m	100 m
(ppb)	(49)	(43)	(40)	(32)	(30)
Ba	200 m	50 m	100 m	500 m	3000 m
(ppm)	(1625)	(1459)	(1323)	(1134)	(1072)
Cd	50 m	200 m	100 m	500 m	≥3000 m
(ppm)	(0.13)	(0.11)	(0.09)	(0.06)	(0.05)
Al	500 m	3000 m	200 m	100 m	50 m
(ppm)	(59 742)	(57 457)	(50 599)	(42 078)	(34 922)
MU-A85					
TOTPAH	50 m	100 m	200 m	500 m	3000 m
(ppb)	(180.9)	(126.4)	(42.3)	(31.7)	(27.1)
Ba	50 m	100 m	200 m	500 m	3000 m
(ppm)	(10 064)	(9263)	(3706)	(1817)	(1094)
Cd	50 m	100 m	200 m	500 m	3000 m
(ppm)	(0.46)	(0.25)	(0.07)	(0.05)	(0.05)
Al	500 m	3000 m	200 m	100 m	50 m
(ppm)	(64 119)	(63 386)	(57 971)	(41 956)	(37 339)
HI-A389					
TOTPAH	50 m	100 m	200 m	500 m	5000 m
(ppb)	(256)	(103)	(65)	(33)	(32)
Ba	50 m	100 m	200 m	500 m	5000 m
(ppm)	(72 605)	(18 196)	(13 756)	(3993)	(1293)
Cd	50 m	100 m	200 m	500 m	5000 m
(ppm)	(6.4)	(0.65)	(0.29)	(0.11)	(0.08)
Al	5000 m	500 m	200 m	100 m	50 m
(ppm)	(63 082)	(59 776)	(56 027)	(41 011)	(30 091)

[a]TOTPAH, sum of all measured PAH.
[b]Detransformed means are presented (x) and means that are underlined are not different at the 0.05 level.

HI-A389 sediment characteristics reflected the intensity of the contaminant discharges, near-bottom shunting, and the low-energy environment of deeper water. Total PAH concentrations differentiate sediments to 500 m and UCM concentrations were significantly different to 5000 m. Barium and Cd concentrations differentiated sediments to a distance of at least 5000 m. As at the other sites, Fe and Al contents reflected dilution by sand.

The data are also compared with sediment data from previous Gulf of Mexico platform monitoring studies conducted at sites with similar drilling histories. This approach aids in determining if the perturbations observed at the three study sites are similar to perturbations observed elsewhere. Also, since some of the previous studies were conducted at sites that were also chosen for this study, changes in sediments over time can be evaluated. As previously discussed, metal concentrations strongly correlate with sediment grain size. For example, some metal concentrations are much higher in fine-grained, clay-rich sediments than in coarse, sandy ones. This relationship is the result of both physical (i.e., surface area) and chemical (alumino-silicate versus quartz minerals) differences among the grain size fractions in typical marine sediments. Even in pristine, unperturbed sediments, metal concentrations will vary considerably solely on the basis of differences in sediment texture. Therefore, sediment contaminant levels must be compared after a normalization taking into account differences in sediment texture. One normalization approach is to relate metal concentrations to Al content.

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Fig. 4. Relationship between sediment (A) Fe amd Al concentrations, (B) Fe concentrations and distance from the platform, and (C) Ba concentrations and distance from the platform at MAI-686 at two samplings 14 yr apart.
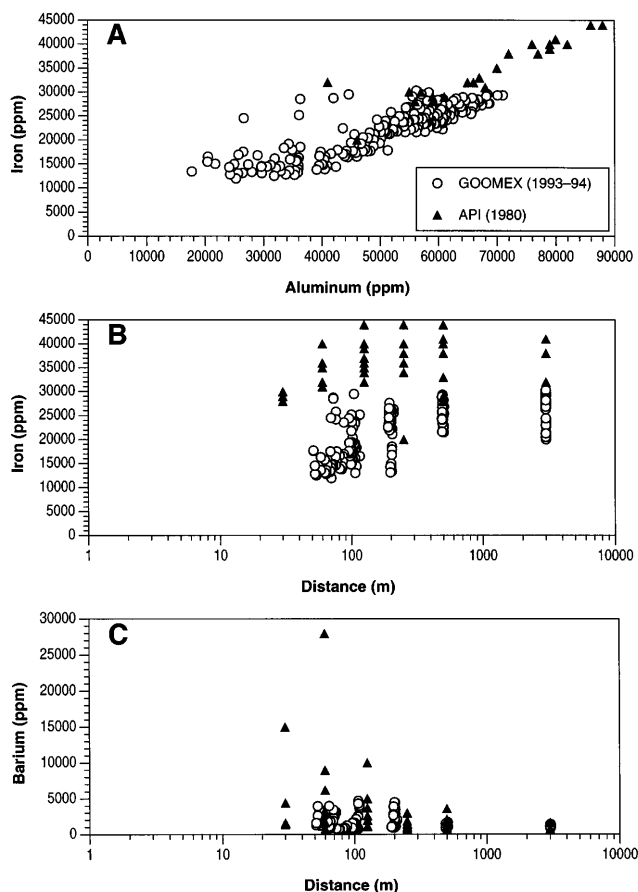
Aluminum is a major component of the minerals comprising most marine sediments (i.e., alumino-silicate clay minerals) and occurs at concentrations at the percent level. It is unlikely that anthropogenic inputs of Al would be sufficient to significantly alter the indigenous concentrations of Al in sediments. Iron is also a percent-level component of sediments and can be used as a normalization factor for trace metal comparisons. However, a suspected source of Fe related to the platform makes these comparisons less useful. The relationships between metal concentrations and Al content are used to evaluate the sediment trace metal perturbations observed in the present study.

Two previous studies were available for comparison. One study sponsored by the American Petroleum Institute (API) sampled sediments (40 stations in a radial pattern) surrounding six drilling sites in 1980 (Boothe and Presley 1985). Barium, Cr, and Fe were determined at all stations and Al, Cd, Cu, Hg, Pb, and Zn at selected stations. A second study, conducted by Continental Shelf Associates, Inc. (CSA), investigated a drilling site at HI-A384 near the West Flower Gardens in 1982 (Continental Shelf Associates, Inc. 1983). Barium and Fe were measured at 44 stations arranged in a similar radial pattern. Chromium was determined at 17 stations. The MAI-686 site was sampled in 1980 as part of the

API study and resampled as part of this study (1993–1994). Eight wells had been drilled prior to the 1980 sampling. The characteristics of the ambient sediments have changed significantly during the 14-yr period between samplings. Much of the finer-grained sediment (Al and Fe rich) has been removed (Fig. 4). Aluminum and Fe contents clearly show a significant change in sediment composition with essentially no overlap in compositions between the two sampling events. The relationship between Fe and distance from the platform for the two studies confirms this conclusion. All of the elevated Ba levels observed in 1980 within ≤125 m of the platform are no longer present. Barium levels beyond 125 m are essentially unchanged over the 14-yr period. The concentration of Hg showed the same decline as Ba. The concentrations of Cd, Cu, and Zn also appear to have decreased between the two sampling events but the decrease was less dramatic. Lead is the only element that increased over the 14-yr period, suggesting a continuing, nondrilling discharge source for Pb (Fig. 5). The change in sediment texture between 1980 and 1993–1984 is the result of a continuing process of sediment resuspension and transport at this shallow-water, high-energy site.

Deeper water development and production sites from the 1980 API study (HI-A341 and V-321) were selected for comparison with the two remaining GOOMEX study sites (MU-A85 and HI-A389). The API sites had similar drilling histories (HI-A341: 8 wells, V-321: 25 wells) and sediment types (based on Al and Fe concentrations). These data sets provide a comparison of metal distributions measured soon after the cessation of drilling (API sites) and again 5–10 yr later (GOOMEX sites). The magnitude of the sediment Ba enrichments within each pair of sites is similar (Fig. 6). The only significant difference in Ba enrichment is the anomalous 18–28% Ba enrichment at the HI-A389 site caused by shunting of the drilling discharges within 10 m of the seafloor. The similarity in Ba concentrations suggests that, for sites with similar drilling histories and in deepwater depositional environments (i.e., ≥50–70 m and lower energy), there has been little change in the ambient sediments with time. The temporal stability of Ba at the deeper water sites is also apparent for other elements. Enrichments in Cr, Cd, Cu, Hg, and Zn at the HI-A341 and MU-A85 sites are similar. Again, as observed for the MAI-686 site, the only exception is Pb which is significantly higher at the MU-A85 site, suggesting a continuing input of this element after the cessation of drilling discharges (Fig. 5). The relationship is similar at the more highly contaminated V-321 and HI-A389 sites. Even excluding the high-Ba samples (Fig. 6), Pb levels are several-fold higher at HI-A389 than at V-321 (Fig. 7). In addition, Cd and Zn levels are significantly higher at the HI-A389 site suggesting a continuing input of these metals after cessation of drilling operations.
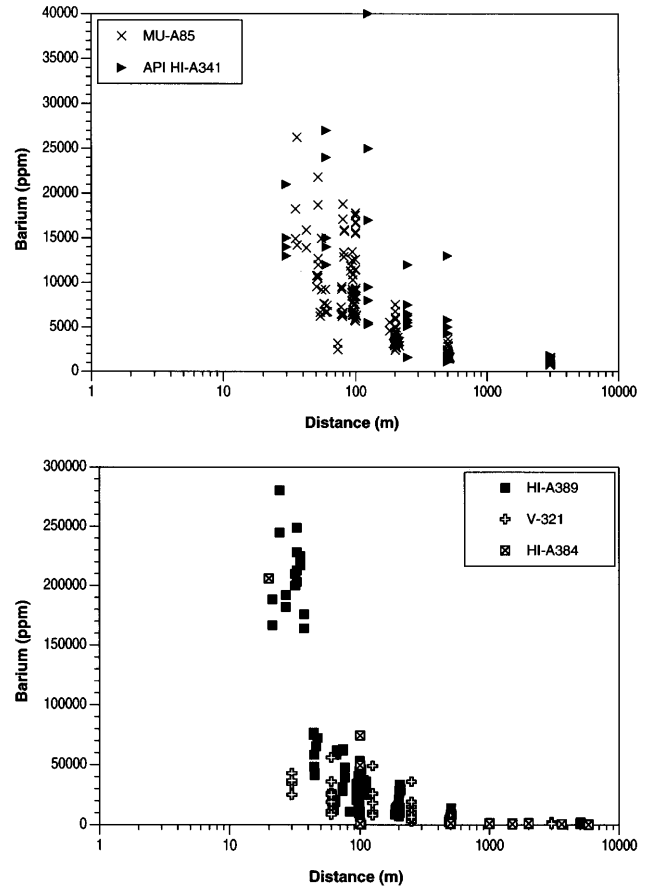
The CSA study in 1982 (Continental Shelf Associates, Inc. 1983) suggested that the magnitude of surface enrichments from drilling discharges among sites within similar depositional environments (i.e., judged by water depth) was similar regardless of the number of wells drilled. Differences in the amount of drilling resulted in a thicker veneer of metal-enriched sediments overlying the native sediment, but no clear difference in the magnitude of surface enrichment was apparent. This may indicate that the contaminant to inert

Fig. 5. Relationship between sediment Pb concentrations and distance from the platform at two samplings (recent: MAI-686, MU-A85, HI-A389; 14 yr ago: API MAI-686, HI-A341, V-321) (ERL = effects range low; ERM = effects range medium; Long and Morgan 1990).

Fig. 6. Relationship between Ba concentrations in sediment collected immediately (HI-A341, V-321, HI-A384) and 5–10 yr after (MU-A85, HI-A389) cessation of drilling activities.
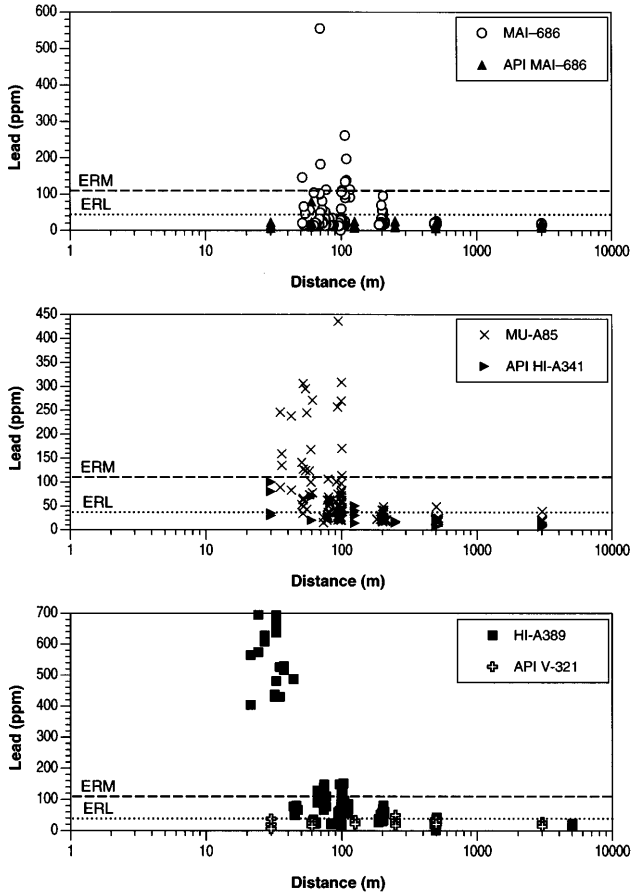
material ratio for the discharges was similar at the sites and this original concentration was the highest value possible at a site. The veneer of materials on top of the indigenous sediments was primarily drilling discharges. The CSA study sampled around a single exploratory well in lease block HI-A384, while six wells were drilled at the GOOMEX HI-A389 site. The two sites are in essentially identical depositional environments and separated by only about 20 km. Both sites are in approximately 120 m of water and both are located in close proximity to a topographic feature (West and East Flower Gardens, respectively). The drilling discharges were also shunted to within 10 m of the seafloor at both sites. The surficial sediment Ba distribution, an indicator of the distribution of the drilling discharge contaminant field, is similar at both sites (Fig. 7). Even the more than 20% Ba enrichment caused by shunting is present at both sites. This comparison is another indication of the stability of the contaminant fields at deeper water sites. The CSA study was conducted immediately after drilling, while the sampling of HI-A389 reported here occurred almost 10 yr after the last drilling event. Although based on only two samples, the levels of Cd and Pb also appeared to be quite similar and elevated above suspected drilling discharge levels at the two sites.

A further evaluation of the contaminant level is provided by a comparison with sediment concentrations known to elicit biological effects. While biological effects were directly measured, comparison with literature values provides an assessment of the potential for effect. The concentration of total PAH at the study sites is presented as a frequency distribution along with sediment PAH concentrations from the National Oceanic and Atmospheric Administration National Status and Trends (NOAA NS&T) Program and the Environmental Protection Agency's Environmental Monitoring and Assessment Program-Near Coastal (EPA-EMAP-NC) Programs (Fig. 7). Sediment total PAH concentrations at the platform sites were generally less than 1000 ppb with only a few exceptions close to the platforms at HI-A389 and MU-A85. The EPA-EMAP-NC data represent 183 sites along the Gulf Coast collected on a probability-based sampling design. As expected the median PAH concentrations in shelf sediments are nearly an order of magnitude lower than in coastal areas of the Gulf. However, at a few locations, PAH concentrations at the platform sites approach the highest values observed in coastal bays. To assess the potential for biological effects from the observed near-field sediment, the contaminant levels observed are compared with the effects threshold data of Long and Morgan

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Fig. 7. Comparison of sediment PAH concentrations at GOOMEX sites with the NOAA National Status and Trends (NS&T) and EPA Environmental Monitoring and Assessment (EMAP) databases for coastal Gulf of Mexico sites (ER-L = effects range low; Long and Morgan 1990).
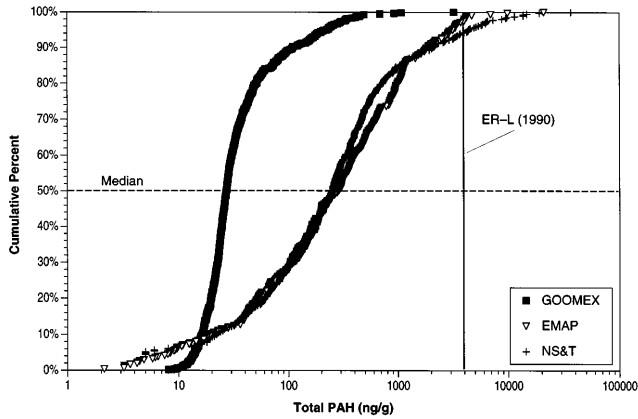
Fig. 8. Percentage of samples from the GOOMEX sites that exceeded the Long and Morgan (1990) (A) 50% and (B) 10% bioeffects criteria.
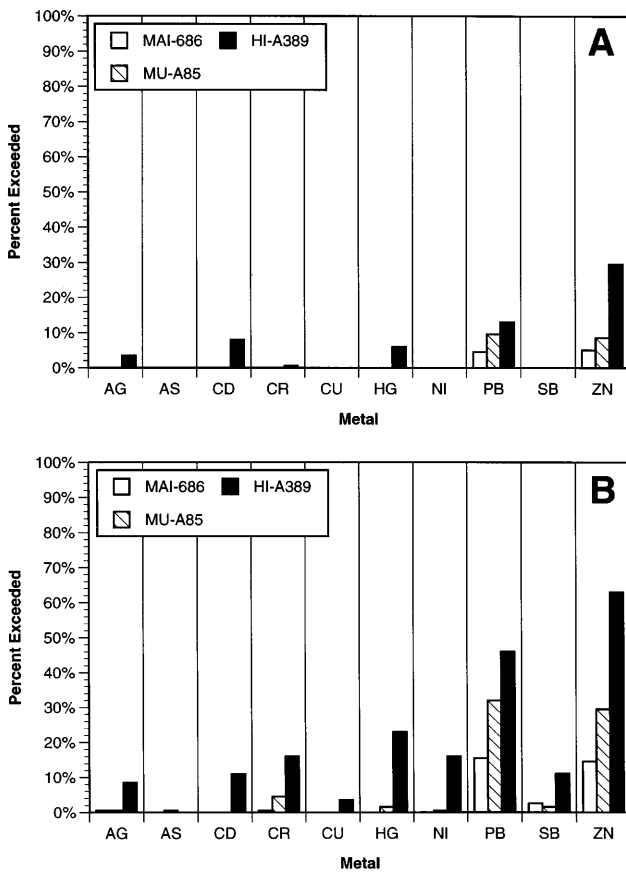
(1990). The PAH values observed at the platform sites are significantly below the Long and Morgan (1990) 10% biological effects criteria of 4000 ppb (Fig. 4). These effects criteria are based on a compilation of the chemical concentrations

observed, or predicted, to be associated with biological effects (broadly defined). Note that the definition of total PAH is highly variable and that these values only serve as a semiquantitative guide. The 10% criterion is defined as the level at which biological effects were observed 10% of the time. Long and Morgan (1990) also noted that compounds such as PAH, which may be mutagenic or teratogenic, may not be toxic in acute tests of mortality. The percentages of sediment samples that exceeded the Long and Morgan low (ER-L, 10%) and median (ER-M, 50%) effects ratios in the present study are compared (Fig. 8). Several metals exceed the effects levels in near-field sediments. These comparisons suggest that a significant percentage of sediments at the study sites might elicit biological responses. While these comparisons are informative, they are not definitive for predicting biological effects. Sediment metals may or may not be bioavailable and a detailed evaluation of redox potential and metal speciation is needed to determine a causal link between sediment metals and observed biological effects.

The three-dimensional nature of the contaminant distributions suggests that assessments of exposure might be more accurately expressed as amount per square metre of surface area or cubic metres of sediment volume integrated over a defined near-field area (i.e., out to a distance of 100 m). The sediment column, especially at the deeper water sites (MU-A85, HI-A389), is not well mixed with respect to Ba despite the long time since cessation of drilling activities. This observation confirms that the sedimentary contaminant field is quite stable over time frames of years. Previous research (Boothe and Presley 1985) has shown fine, undisturbed barite laminations in the sediment column up to a decade after the cessation of drilling discharges.

Conclusions

The following conclusions were derived from the geochemical portions of the GOOMEX Phase I study.

(1) All study sites exhibited an enhancement of sand close to the platform (from 25 to 60% enhancement over a few hundred metres).

(2) A suite of contaminants is associated with platforms: trace metals, hydrocarbons, and sand. PCA analysis groups, aliphatic hydrocarbons, PAH, Ag, Ba, Cd, Hg, Pb, Zn, and percent sand as covariates.

(3) The contaminants are closely associated with large-grain-sized materials at platforms in contrast with many other environmental studies where contaminants are associated with fine-grained materials.

(4) Distance and direction (D·R) were the most important main effects in defining contaminant distributions. The directionality of the contaminant field is in response to the oceanographic setting at each site.

(5) Water depth, discharge history, and ambient physical oceanographic conditions control the intensity, direction, and extent of the contaminant field.

(6) Organic C is decreased near platforms, but not in proportion to the sand dilution event, suggesting possible organic enrichment.

(7) Inorganic C increases close to the platform due to platform-related sources such as biogenic debris (calcareous remains) and disposal of carbonate-containing cuttings.

(8) Compared with marine settings impacted by spills and coastal areas that experience long-term non-point-source chronic contamination, sediment hydrocarbon concentrations were low at the sites studied.

(9) Petroleum contamination is high near a platform and decreases rapidly with distance away from the platform.

(10) Sediment PAH are at levels below documented biological effects thresholds for marine biota. In contrast, sediment trace metal concentrations at several locations exceeded levels known to elicit biological effects.

(11) Some sediment parameters (i.e., Al) decreased near the platform due to dilution with sand.

(12) Several metals appear to have sources other than the cutting/drill mud discharged during drilling (i.e., Pb, Zn, and Cd).

(13) An evaluation of the three-dimensional distribution of contaminants suggests that subsurface pockets of contaminants may influence biotic patterns in the overlying sediment.

(14) A comparison of samplings 14 yr apart at the MAI-686 site confirmed an ongoing loss of fine particulates and contaminants due to dynamic redistribution of sediments at this site.

(15) At all three sites, Pb was shown to continue to accumulate in sediments near the platform over a period of years above that attributable to the initial increase due to drill mud and cutting disposal. Lead concentrations increased to levels known to elicit biological responses.

(16) At deeper water sites (>80 m), a comparison of metal enrichments immediately after cessation of drilling and 5–10 yr after the last discharges showed that similar concentrations were observed confirming the relative stability of the contaminant field over time frames of years, possibly decades (an exception is the observed increase in Pb over time).

(17) At MU-A85 and HI-A389, Cr and Fe concentrations were higher in near-field sediments relative to Al than is typical for background sediments. This enhancement suggests that a platform source of these metals is contributing to sediment concentrations.

These patterns in geochemical characteristics provide a basis for the evaluation of the processes that control biological patterns observed at these sites. An important finding that must be considered when describing the relationship between independent and dependent variables is that many environmental factors including water depth, sediment grain size, organic enrichment, toxic response, and seasonality strongly covary, and thus, cause and effect may be difficult to ascertain from field observations alone.

Acknowledgments

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