

**Final Report to the Synthetic Based Muds (SBM) Research Group**

**Concentrations of Total Mercury and Methylmercury in  
Sediment Adjacent to Offshore Drilling Sites  
in the Gulf of Mexico**

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# **Concentrations of Total Mercury and Methylmercury in Sediment Adjacent to Offshore Drilling Sites in the Gulf of Mexico**

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## **EXECUTIVE SUMMARY**

This report presents the results from a study of concentrations of total mercury (Hg) and methylmercury (MeHg) in seabed sediments near six offshore drilling sites in the Gulf of Mexico. The purpose of this study is to help determine whether drilling discharges lead to enhanced concentrations of MeHg in sediments near drilling sites. Surface (0-2 cm) and subsurface (2-20 cm) sediments for this study were collected during May 8-20, 2002, within the following three zones at each of six drilling sites: <100 m (nearfield), 100-250 m (midfield) and >3 km (farfield).

Total Hg levels in sediment (n = 196) from this study range from 11-92 ng/g (parts per billion, dry weight) for all farfield samples and 25-558 ng/g for all nearfield samples. Concentrations of total Hg are significantly higher at nearfield stations than at farfield stations for five of the six drilling sites due to inputs from drilling discharges. In nearfield sediments where total Hg levels exceed background levels, concentrations of barium (Ba) range from 2-28% (dry weight), relative to ambient Ba concentrations of about 0.05-0.15%. A strong linear relationship is observed between concentrations of Ba and total Hg in sediment from nearfield stations. The strong linear relationship between Ba and total Hg, coupled with the high levels of Ba as barite (BaSO<sub>4</sub>) in these sediments, support the contention that barite, a common additive to drilling mud, is the primary source for anthropogenic Hg in these sediments. Furthermore, the relationship between concentrations of total Hg and Ba at a given site can be used to estimate total Hg levels in the industrial barite used during drilling. Estimated average concentrations of total Hg in industrial barite at different sites, based on the Ba versus Hg relationships, range from about 400-1000 ng/g. These estimated concentrations of total Hg in barite are consistent with regulations by the U.S. Environmental Protection Agency that set allowable total Hg levels in industrial barite at 1000 ng/g.

Concentrations of MeHg range from 0.11-1.05 ng/g for all farfield sediments and <0.03-2.7 ng/g for all nearfield sediments. In contrast with results for total Hg, this study shows that concentrations of MeHg in surficial (0-2 cm) sediment from all six drilling sites do not vary significantly between nearfield and farfield stations. When subsurface samples (at depths of 2-20 cm) are included, no significant differences between MeHg concentrations at nearfield and farfield stations are observed at five of the six sites. At a sixth site, significantly higher concentrations of MeHg are found at nearfield versus farfield stations due to the presence of anomalous, sandy sediment with low levels of total Hg and MeHg at three of the farfield stations from this one drilling site.

Concentrations of MeHg average  $0.44 \pm 0.27$  ng/g for all farfield sediments (0-20 cm) and  $0.45 \pm 0.41$  ng/g for all nearfield sediments (0-20 cm). However, considerable variability is observed in concentrations of MeHg at several sites. For example, MeHg concentrations range from <0.03-0.40 ng/g within one nearfield zone; whereas, they range from 0.35-2.7 ng/g within another nearfield zone. Observed variability in concentrations of MeHg is partly related to local variability in redox state in the top 10 cm of sediment. Low to non-detectable levels of MeHg are observed in nearfield stations where the redox potential (Eh) is <-100 mV (anoxic and highly reducing) in the presence of abundant total H<sub>2</sub>S (>1 millimolar, mM). Higher values of MeHg are found in a few nearfield stations where levels of TOC are higher and where Eh values are about 0 mV (anoxic, moderately reducing). These observations are consistent with previous studies that suggest that optimum conditions for formation of methylmercury are in anoxic sediment with sulfide-poor interstitial water and sufficient levels of biodegradable organic matter and nutrients.

Overall, the results from this study show that excess total Hg in sediments at the drilling sites studied is associated with barite. Furthermore, statistical comparisons of MeHg levels in nearfield versus farfield sediments at six drilling sites, along with data from two of those sites that show lower levels of MeHg in some nearfield sediments than farfield sediments, suggest that elevated levels of MeHg in sediments around drilling platforms are not a wide-spread phenomenon in the Gulf of Mexico. The data presented in this report also make a reasonable initial argument for the conclusion that Hg introduced with barite during offshore drilling cannot be directly linked to enhanced levels of MeHg in nearfield sediments. At most drilling sites, nearfield samples with high levels of total Hg (i.e., 200-500 ng/g) have similar or lower levels of MeHg than found at background (farfield) stations. Results for a few samples from one site are somewhat ambiguous in that concentrations of MeHg are enhanced; however, the MeHg values are equivalent to ~3% or less of natural concentrations of total Hg. Therefore, these anomalously high levels of MeHg could have either a natural or an anthropogenic source of Hg.

## INTRODUCTION

The purpose of this study is to provide data that can be used to help determine whether drilling discharges lead to enhanced concentrations of MeHg in sediments near offshore drilling sites. The impetus for this study developed because concentrations of total mercury (Hg) in sediment adjacent to offshore drilling sites in the Gulf of Mexico are often two to ten times higher than in nearby natural sediment (see summary by Neff, 2002). Most of the excess Hg in sediment at offshore drilling sites is believed to be associated with barite ( $\text{BaSO}_4$ ) as a component of spent drilling mud that is discharged during drilling. Present regulations set the upper limit for total Hg in barite at  $1 \mu\text{g/g}$  ( $1000 \text{ ng/g}$ ; EPA, 1993). Questions have been raised about the degree to which excess total Hg in sediment around offshore drilling sites becomes methylmercury (MeHg) and whether conditions in sediments near drilling sites are more conducive to the formation of MeHg than those in nearby ambient sediment.

No data are presently available for concentrations and reactions involving MeHg in sediment near exploration and production sites in the Gulf of Mexico. The work described here was carried out to help fill the data gap for concentrations of total Hg and MeHg in sediment from the Gulf of Mexico. Sampling for this study was completed during May 8-20, 2002, as a supplemental part of ongoing research on the environmental effects associated with the discharge of cuttings drilled with synthetic-based mud (SBM) in the Gulf of Mexico. The SBM study was not designed specifically to investigate the fate and effects of Hg in the Gulf of Mexico. Thus, the results presented here cannot be used to estimate the rates of methylation or demethylation of Hg, the rates of diffusion of any MeHg within the sediment and to the overlying water, or to address uptake of MeHg by organisms. However, the data presented in this report do provide the first comparisons of MeHg levels in sediment at drilling sites relative to nearby reference sites in the Gulf of Mexico as well as present some information for developing a preliminary interpretation of observed concentrations.

The information acquired during this study helps to advance the process of determining whether drilling discharges lead to enhanced levels of MeHg in sediments near offshore-drilling sites. Preliminary answers to the four questions raised below will be given in the conclusions to support discussion and decisions regarding the need for additional investigations.

- Are the excess amounts of total Hg found in sediment near drilling sites associated with barite?
- Are concentrations of MeHg elevated in sediment adjacent to offshore drilling sites?
- Can any increases in sediment levels of MeHg be directly attributed to Hg introduced by oil and gas activities?
- Do drilling discharges create an environment that is more favorable to the conversion of Hg to MeHg?

## METHODS

### *Sampling*

Sediment samples were collected from areas surrounding six offshore-drilling sites during May 8-20, 2002 (Figure 1). Three of the sites were situated at water depths of 60-119 m on the continental shelf and three were at depths of 534-556 m on the upper slope (Figure 1 and Table 1). Platforms were present at three of the sites (MP299, MP288 and EI346) during sampling and seafloor templates or wellheads were in place at the remaining three sites. Sediments in the nearfield (NF) were collected at six random stations within 100 m of each drilling site and two fixed (discretionary) stations within 100 m of each drilling site. The discretionary stations were chosen based on previous data that showed elevated levels of Ba and synthetic-based mud (SBM) at specific locations near each drilling site. Surface samples (0-2 cm) were collected at each NF site. Subsurface (2-20 cm) samples were collected from five successively deeper layers below the sediment-water interface from two NF discretionary (D) stations at all six sites. Subsurface samples also were collected at one random NF station for three drilling sites (MP299, MP288 and MC496). Farfield (FF) samples were collected from six random stations around each drilling site at a distance >3 km from the structure. Surface samples were collected from each FF location and subsurface samples were collected at one FF location from each site. In addition, samples also were collected for each drilling site at two to six midfield (MF) locations that were at distances of 100-250 m from the drill site.



Figure 1. Map showing locations of offshore drilling sites in the Gulf of Mexico where sediment samples for this study were collected. Exact locations and water depths for each site are given in Table 1.

**Table 1. Summary location data for offshore drilling sites.**

Site	Name	Water Depth (m)	Latitude (Degrees, Min., N)	Longitude (Degrees, Min., W)	SBM Type	Surface Structure Present *	# of SBM Wells**	Total Wells Drilled at Site
Main Pass 299	MP299	60	29°15.43'	88°46.38'	Linear Alpha Olefin	yes	3	20
Main Pass 288	MP288	119	29°14.39'	88°24.57'	Internal Olefin	yes	4	31
Eugene Island 346	EI346	92	28°09.83'	91°22.14'	Internal Olefin	yes	3	6
Ewing Bank 963	EW963	540	28°00.65'	90°07.47'	Internal Olefin	no	3	3
Green Canyon 112	GC112	534	27°51.32'	90°44.09'	Internal Olefin	no	4	4
Mississippi Canyon 496	MC496	556	28°27.03'	89°22.44'	Internal Olefin	no	1	3

\* Surface structure "yes" indicates that a platform rising above the sea surface is present at the site. Sites without surface structures have subsea wellheads or other seabed structures at the drill site.

\*\* The number of wells drilled with synthetic-based drilling fluids.

Sediments were collected using a stainless steel box corer (50 cm x 50 cm x 50 cm). Once on deck, the surface 2 cm of sediment were removed using a Teflon® spatula and ~30 mL of sediment were placed in 50-mL, polystyrene vials (for Ba, TOC and total Hg) and ~30 mL of sediment were placed in 60-mL Series 300 I-CHEM, cleaned glass containers (for methylmercury). The polystyrene vials were sealed with a layer of Parafilm® and stored frozen. Samples in glass containers were frozen immediately after collection and shipped using dry ice. At a total of fifteen stations, the box core was carefully subsampled by pushing a Teflon® tube into the sediment. The sediment was extruded from the bottom in 2-cm increments. The outer few millimeters of sediment from each increment were removed and the remaining portion was placed in polystyrene and glass containers. All sampling equipment was cleaned with acid and rinsed with distilled-deionized water (DDW). The Teflon® tubes were decontaminated between each use with soap, water, nitric acid, water, acetone and DDW. All sampling of the box core was carried out away from the stainless steel walls.

One subsample from every box core was collected for probe measurements of dissolved oxygen and Eh. The pH was measured in sediment cores from stations where interstitial water also was collected. The core was immediately analyzed for oxygen using a 5-cm long microprobe (Microelectrodes, Inc. MI-730 O<sub>2</sub> probe) lowered from the top of the core. The probe was mounted on a microscope stage that was fixed vertically above the core. By lowering the microscope stage in millimeter increments, according to the attached scale, oxygen measurements were taken to the depth of oxygen depletion. Next, Eh and pH were measured through holes pre-drilled at 2-cm intervals in the wall of the core tube. The holes were covered with tape during sampling of the box core, and the tape was removed immediately before inserting a probe. The Eh was measured first, using an Orion Model 96-78-00 Platinum Redox Electrode, and pH and temperature measurements were then carried out using a Sentron Red Line pH probe.

All probes were calibrated prior to use for each core. The oxygen probe was calibrated using two beakers of water, one that was equilibrated with the atmosphere via an air stone and one that was de-oxygenated by purging with nitrogen. The meter was adjusted to 20.9% while the probe was immersed in the first solution and was zeroed with the probe submerged in deoxygenated water. A one point calibration with an Orion standard was performed for the Eh probe. The pH probe was calibrated with pH 7 and pH 10 buffers.

In addition to the data collected with oxygen, redox and pH probes, samples of interstitial water also were collected at selected sites, some of which matched cores collected for MeHg. Some of the results obtained for the interstitial water will be presented in this report to support inferences from the oxygen and redox probes. The detailed methods for sampling and at sea analyses for ammonia and total H<sub>2</sub>S are described in McElvaine (2001). The interstitial water data will be compiled in the final report of the SBM study. Interstitial water was obtained by taking one 7-cm diameter subcore and transferring it to a whole core squeezer, similar to that described by Bender et al. (1987), for pore water extraction. Samples (~10 mL) were collected directly into acid-washed glass syringes at 1-cm intervals in the uppermost 5 cm, 2-cm intervals from 5 to 13 cm, and 3-cm intervals below 13 cm.

### *Analytical Methods*

Measurements of total Hg and supporting parameters were made at Florida Institute of Technology. Methylmercury concentrations were determined at Frontier Geosciences, Inc., under the direction of Lucas Hawkins.

#### *Total Mercury and Supporting Parameters*

Sediment samples were thawed and brought to room temperature. Each wet sediment sample was homogenized in the original 50-mL polystyrene vial using a Teflon® mixing rod. Then, a portion (~ 20 g) of each sample was transferred into a pre-weighed plastic vial to determine water content. Once transferred, the wet sediment and the vial were re-weighed. In addition, about 2-4 g of sample were transferred to polypropylene-copolymer centrifuge tubes to determine the Hg content of the sediments. Samples



intended for water content measurement were frozen, freeze-dried, and re-weighed to determine the water content. The dried sediment samples were again homogenized using a Teflon® mixing rod.

Sediment samples to be analyzed for Hg were digested by heating 2-4 g of wet sediment in acid-washed, polypropylene-copolymer centrifuge tubes with 4 mL nitric acid (HNO<sub>3</sub>) and 2 mL sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) as described by Adeloju et al. (1994). Sample tubes were heated for 1 hour in a 90°C water bath and allowed to cool. Each tube was centrifuged at 2,000 rpm and the supernatant decanted into a 25-mL graduated cylinder. The sediment pellet was rinsed twice with 5 mL distilled-deionized water (DDW), centrifuged, and decanted into the graduated cylinder before diluting to a final volume of 20 mL with DDW. The final solutions and procedural blanks were analyzed by cold-vapor atomic absorption spectrometry (CVAAS) using a Laboratory Data Control Mercury Monitor with manual injection 0.5 mL of solution.

Labware used in the digestion process was acid-washed with hot, 8N HNO<sub>3</sub> and rinsed three times with DDW. Two procedural blanks, two duplicate samples, and two certified reference materials (CRMs) were prepared with each set of 40 samples. The sediment CRM MESS-2, obtained from the National Research Council of Canada, was used to help establish data quality for total Hg, Al, and Ba.

For Al and Ba analysis, 20 mg of sediment were digested with HClO<sub>4</sub>-HNO<sub>3</sub>-HF and diluted to 20 mL. For samples found to have very high concentrations of Ba, based on residual white solid after digestion, a smaller mass of sample (<10 mg of sediment) was digested and analyzed for Ba. The digested samples were analyzed for Al by flame atomic absorption spectrometry (FAAS) using a Perkin-Elmer Model 4000 instrument. Concentrations of Ba were determined by inductively-coupled plasma-mass spectrometry (ICP-MS) using a Perkin-Elmer ELAN 5000 instrument.

In preparation for analysis of sediment for total organic carbon (TOC), inorganic carbon was removed by adding 10% phosphoric acid to the samples. The samples were weighed before the addition of acid and after drying of the acid to account for mass changes during the decomposition of carbonates. The TOC content of dried sediment samples was determined by combustion with a Shimadzu TOC-5050A using an attached solid sample module (SSM-5000A). For TOC analysis, sucrose was analyzed to generate a calibration curve and MESS-2 was analyzed as a CRM.

For the interstitial water results mentioned in this report, concentrations of nitrate and sulfate were determined using a Dionex DX-600 ion chromatograph (IC). Concentrations of total H<sub>2</sub>S were determined at sea using standard colorimetric methods as described along with additional details in McElvaine (2001).

For this project, Quality Control measures included balance calibration, instrument calibration (FAAS, CVAAS, ICP-MS, TOC analyzer), matrix spike analysis for each metal, duplicate sample analysis, CRM analysis, procedural blank analysis and standard checks. With each batch of up to 40 samples, two procedural blanks, two CRMs, two

duplicate samples and two matrix-spiked samples were analyzed. The Quality Assurance/Quality Control (QA/QC) results are summarized in Appendix I.

### *Methylmercury*

Frozen sediment samples were sent directly from Louisiana to Frontier Geosciences, Inc., Seattle, in coolers packed with dry ice. Chain of custody sheets are included in Appendix I.

Methyl mercury in sediments was isolated by acid bromide/methylene chloride extraction and the aqueous phase was analyzed by ethylation, isothermal GC separation, and CVAFS detection (Frontier SOPs FGS-045, FGS-070). The methods used by Frontier Geosciences have evolved from a long history of analyzing samples for MeHg (e.g., Bloom and Crecelius, 1983; Bloom, 1989). All results are reported on both a wet and dry weight basis. More detailed information on methodology and QA/QC is presented in Appendix I.

## RESULTS AND DISCUSSION

### *Total Mercury in Sediment*

The results for total Hg in sediment from this study are used as a framework for introducing and discussing the MeHg data. The data for total Hg from this study also provide a link to previous results for total Hg in sediment from the Gulf of Mexico. This link helps establish the degree to which concentrations of total Hg from this study are representative of drilling sites in the Gulf of Mexico. Concentrations of total Hg also can be correlated with Ba levels in sediment to help show whether barite is the primary source of excess Hg in sediments near drilling sites.

Concentrations of total Hg range from 11-92 ng/g for all FF samples (parts per billion, dry weight) and 25-558 ng/g for all NF samples. Data for concentrations of total Hg for surficial sediment (0-2 cm) are summarized in Table 2 and Figure 3. The complete data set is tabulated in Appendix II. Data for surficial sediment, as opposed to surface plus subsurface sediment, are introduced first because they incorporate all stations evenly and avoid the bias of including values for deeper, background sediment in averages for NF cores. Furthermore, the top 2 cm of sediment are important as a possible source of MeHg to benthic food webs and the overlying water column. In Figure 2, and elsewhere throughout the text, data for surface sediment and all data (surface plus subsurface) are compared and discussed individually and together as appropriate.

Overall, concentrations of total Hg are significantly higher at NF stations relative to FF stations for all drilling sites except MP299 (t-test at  $\alpha = 0.05$ , double-tailed for surface or collective data set for surface + subsurface samples, detailed results in Appendix III). For drilling sites EI346, EW963 and GC112, average concentrations of total Hg at NF stations are 3.9, 2.5 and 3.1 times greater than at FF sites. The NF stations at each of these sites contain higher levels of total Hg and barium than at FF stations, as discussed below. The distinctly higher levels of total Hg at the NF sites are observed whether using just the surface 2 cm of sediment or surface plus subsurface sediment (Figure 2).

The small standard deviations for concentrations of total Hg in FF samples from each drilling site show the overall uniformity in background levels of total Hg on a site-by-site basis. For example, at site MC496, the mean concentration of total Hg is only about one-third higher in the NF than FF; however, due to the low standard deviation for the FF samples, the difference in means is significant.

For site MP299, concentrations of total Hg are not significantly different among NF, MF and FF sites for comparisons based on surficial data or all data. Based on measured Ba concentrations for sediment at site MP299 discussed below, sediments at this site contain small amounts of drilling mud. At station MP288, sediment from stations FF1, FF2 and FF3 were sandy, naturally low in Al, Ba and total Hg, and not similar in texture (grain size) to any NF, MF or other FF stations from the area around site MP288 that contained

**Table 2. Concentrations of total Hg (ng/g, dry wt.) in surficial sediment (0-2 cm) from nearfield (NF), midfield (MF) and farfield (FF) stations at each of the six drilling sites studied.**

Site	Parameter	NF Total Hg (ng/g)	MF Total Hg (ng/g)	FF Total Hg (ng/g)
<b>MP299</b>	<b>Mean</b>	<b>58</b>	<b>59</b>	<b>61</b>
(Water Depth 60 m)	Std. Dev.	7	7	6
	Maximum	72	66	66
	Minimum	48	47	51
	(n)	8	6	6
<b>MP288</b>	<b>Mean</b>	<b>52</b>	<b>54</b>	<b>29*</b>
(Water Depth 119 m)	Std. Dev.	11	5	20*
	Maximum	73	62	54
	Minimum	41	48	11*
	(n)	8	6	6*
<b>EI346</b>	<b>Mean</b>	<b>185</b>	<b>72</b>	<b>47</b>
(Water Depth 92 m)	Std. Dev.	84	23	3
	Maximum	291	88	49
	Minimum	64	55	42
	(n)	8	2	6
<b>MC496</b>	<b>Mean</b>	<b>96</b>	<b>78</b>	<b>71</b>
(Water Depth 556 m)	Std. Dev.	27	9	5
	Maximum	154	94	78
	Minimum	66	67	65
	(n)	8	6	6
<b>EW963</b>	<b>Mean</b>	<b>180</b>	<b>106</b>	<b>71</b>
(Water Depth 540 m)	Std. Dev.	109	30	3
	Maximum	422	130	76
	Minimum	74	72	68
	(n)	9	3	7
<b>GC112</b>	<b>Mean</b>	<b>248</b>	<b>101</b>	<b>79</b>
(Water Depth 534 m)	Std. Dev.	64	26	8
	Maximum	323	119	92
	Minimum	117	82	68
	(n)	8	2	7

\* Includes sandy samples from stations FF1, FF2 and FF3.

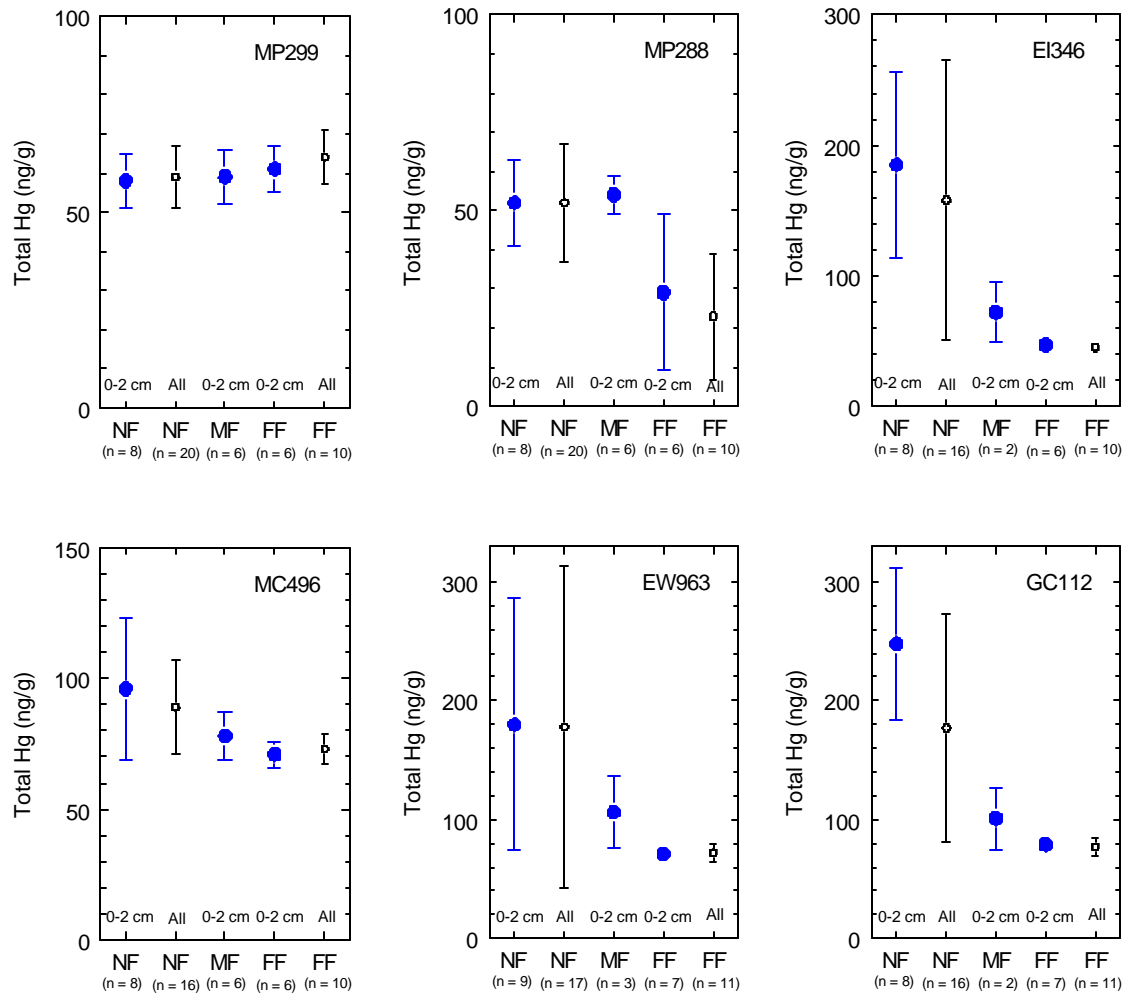


Figure 2. Concentrations of total Hg at nearfield (NF), midfield (MF) and farfield (FF) stations at each of six drilling sites. Solid circles show mean concentrations and lines show standard deviations for surficial sediment (0-2 cm). Open circles show mean concentrations and lines show standard deviations for all sediment samples. The number of data points (n) is shown for each mean and standard deviation. When the standard deviation line is not visible, it is smaller than the circle.

more clay and Al. Additional detail regarding Al and Ba follow below. The low concentrations of total Hg in the sandy samples at site MP288 yield a standard deviation for total Hg in the FF samples that is large relative to the other sites.

Most of the discussion in this report will focus on NF and FF samples because they make up the most pertinent and complete data sets. The data for the midfield (MF) samples are included in the summary tables and figures (e.g., Table 2 and Figure 2). In general, mean concentrations of total Hg at the MF stations are closer to those from FF stations (Figure 2). Concentrations of total Hg at MF and FF stations are not significantly different except at site MP288 where values for the sandy FF sediments distort the mean value for total Hg as described previously.

Overall, total Hg levels in sediments from the six drilling sites studied for this report are representative of concentrations of total Hg in sediments at most sites where offshore activities have been carried out in the Gulf of Mexico (Figure 3). Total Hg levels >1000 ng/g are uncommon and have been reported only for the area immediately adjacent to HIA389 (Neff, 2002).

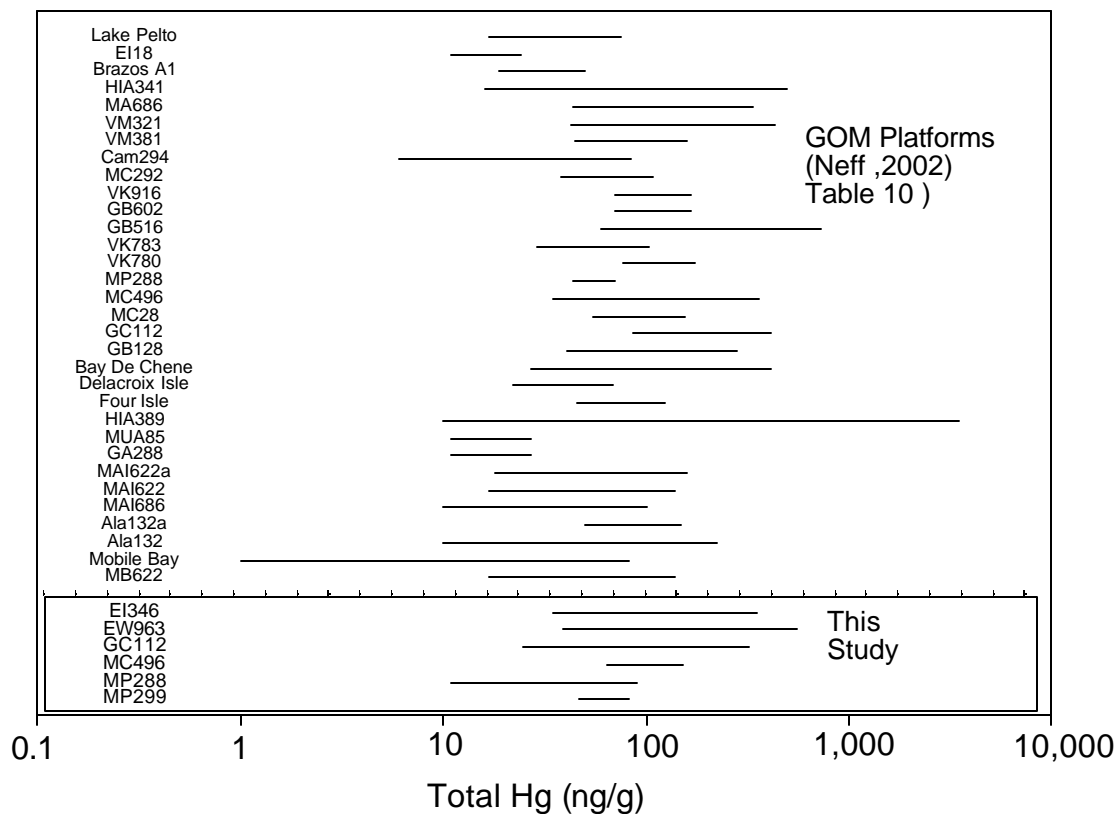


Figure 3. Ranges in concentrations of total Hg in sediments from areas adjacent to offshore drilling sites in the Gulf of Mexico from Neff, 2002). Box at bottom of figure highlights results from this study.

### ***Total Mercury and Barium in Shelf Sediment (Sites MP299, MP288 and EI346)***

Natural levels of total Hg are lower in shelf sediments (40-60 ng/g) than in upper slope sediments (70-90 ng/g). The background ratio of total Hg/Al also is lower for shelf sediment ( $7.3 \pm 1.7 \times 10^{-6}$ ) than for sediments from the upper slope ( $9.1 \pm 1.0 \times 10^{-6}$ ). This difference is mostly due to the slower sedimentation rate on the upper slope and increased scavenging time for particles to adsorb Hg from the water column. For this reason, continued discussion of the total Hg data in sediment from the shelf and upper slope will be carried out separately.

Concentrations of total Hg in natural sediment from the Gulf of Mexico are positively correlated with concentrations of Al. Fine-grained, clay-rich sediment contains higher concentrations of Al and most trace metals, including Hg due to the greater abundance of metal-rich aluminosilicates and greater surface area for adsorption of metals. The coarser fraction contains more quartz sand and/or calcium carbonate, both of which contain very low levels of Al and total Hg. In previous studies, including one that we carried out in Florida Bay, the relationship between TOC and Hg has been strong and the natural relationship for total Hg in sediment has been developed with concentrations of Hg versus TOC or Hg versus TOC + Al (e.g., Lindberg and Harriss, 1974; Kang et al., 2000). However, for sediments in this study from the shelf and upper slope of the Gulf of Mexico, concentrations of TOC were <1% in all FF samples and a weak correlation was observed between TOC and total Hg ( $r = 0.38$ ). Thus, a plot of Al versus Hg with a good correlation coefficient (Figure 4a,  $r = 0.91$ ) was used to normalize concentrations of total Hg for FF shelf sediment from this study. Natural sediment from the area is expected to plot within or close to the 95% prediction intervals shown on Figure 4a. Figure 4a shows data from shelf stations (MP299, MP288 and EI346), and not slope stations, because of differences in the Hg/Al ratio between sediments from the shelf and upper slope.

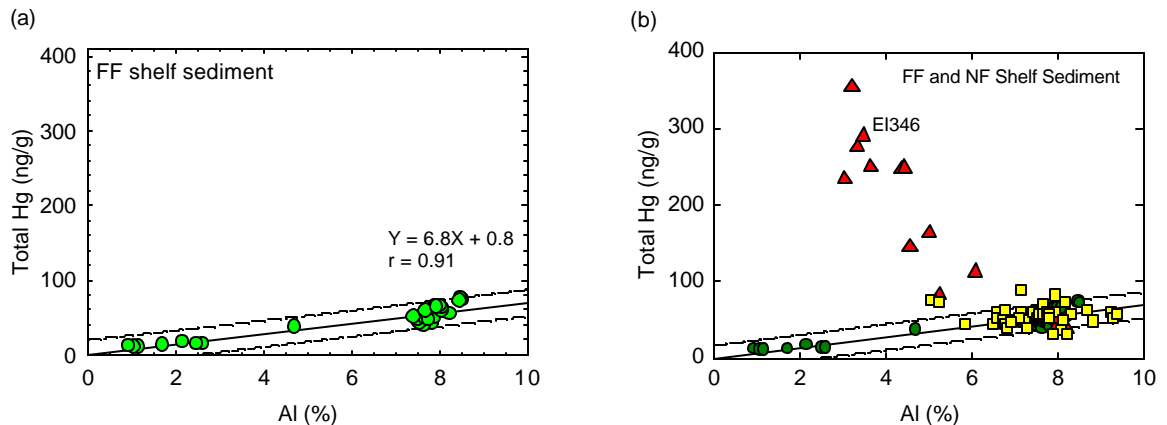


Figure 4. Concentrations of Al versus total Hg in shelf sediment from (a) farfield (FF) sites at MP299, MP288 and EI346. The solid line is from a linear regression (with equation and correlation coefficient) and dashed lines showing 95% prediction interval and (b) FF sites (circles) along with nearfield (NF) shelf sediment from sites MP299 and MP288 (squares) and EI346 (triangles). Linear regression lines are the same as in figure (a).

When concentrations of total Hg from the NF stations are added in Figure 4b, most of the data points from sites MP299 and MP288 fall within the 95% prediction interval as expected based on previous discussion about total Hg levels at these two sites. In contrast, many of the data points from NF stations at site EI346 show considerable enrichment of total Hg relative to background levels.

Correlations between concentrations of Ba and total Hg can be used to assess the likelihood that excess total Hg in sediment is associated with inputs of barite. Such comparisons also can be used to calculate the levels of total Hg in the barite used at a particular site. Mercury is most often present in sulfide impurities as part of the original barite ore (Kramer et al., 1980; Trefry, 1998). Barite has been specifically identified by x-ray diffraction in many NF samples from this study. Figure 5a shows that total Hg concentrations are directly related to Ba levels in FF sediment from shelf locations in much the same way as shown in Figure 4a for concentrations of total Hg and Al. The weaker fit for Ba versus total Hg, relative to Al versus total Hg, results in part from the somewhat elevated levels of Ba, not total Hg, in sediment from the area of Main Pass.

When data for the NF stations are added in Figure 5b, a strong linear relationship is observed for Ba versus total Hg in sediment from site EI346. The strong correlation suggests that Ba (i.e., barite) is the primary variable controlling the excess amount of total Hg (i.e., Hg at levels above ~50-60 ng/g) in the NF sediment from site EI346. If the line in Figure 5b is extrapolated to pure barite at 58.8% Ba, the concentration of total Hg is 653 ng/g (obtained by substituting 58.8% Ba for x in the equation in Figure 5b). Typical “industrial barite” contains 85-95% barite (i.e., 50-56% Ba). Based on the range of Ba levels in industrial barite (50-56% Ba), the average total Hg content of barite used at site EI346 is estimated at 594 ng/g (from the average of 563 ng/g at 50% Ba and 624 ng/g at 56% Ba).

These estimated values are in line with EPA regulations that allow a maximum Hg level of 1000 ng/g in barite (EPA, 1993). Concentrations of Ba in sediment from NF stations at sites MP299 and MP288 are too low to permit a reasonable extrapolation to the total Hg content of any barite that may be present.

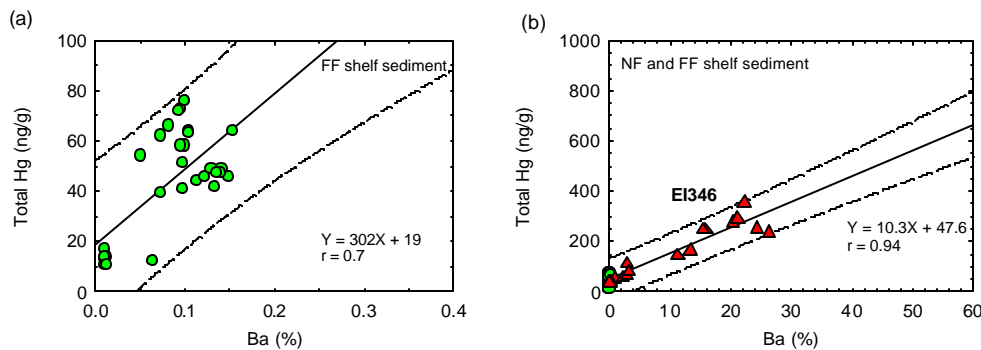


Figure 5. Concentrations of Ba versus total Hg in shelf sediment from (a) farfield (FF) sites at MP299, MP288 and EI346. The solid line is from a linear regression (with equation and correlation coefficient) and dashed lines showing 95% prediction interval and (b) FF sites (circles) along with nearfield (NF) shelf sediment from sites MP299 and MP288 (squares) and EI346 (triangles). The square markers for FF samples from MP299 and MP288 are not clearly visible because of the larger scale used for the axes. The solid line is from a linear regression of Ba versus total Hg for site EI346 and the dashed lines denote the 95% prediction interval.



**Total Mercury and Barium in Upper Slope Sediment (Sites MC496, EW963 and GC112)**

Concentrations of total Hg for all FF sediments from the upper slope in the Gulf of Mexico average  $74 \pm 7$  ng/g with a relatively uniform Hg/Al ratio of  $9.1 \pm 1.0 \times 10^{-6}$ . The Hg/Al ratio is ~25% higher in FF sediments from the upper slope than in FF sediments from the shelf ( $7.3 \pm 1.7 \times 10^{-6}$ ) as previously discussed. No significant relationship was found for concentrations of TOC versus total Hg for FF sediments from the upper slope ( $r = 0.13$ ). The key use of the Hg/Al relationship here is to identify the relative degree of enrichment of total Hg concentrations in NF samples relative to FF samples and to point out the difference in ambient Hg levels between shelf and slope sediment. Figure 6 shows that concentrations of total Hg in many NF samples from sites GC112 and EW963 are significantly greater than levels found in FF samples as represented by the straight line and cluster of points on the lower right side of Figure 6.

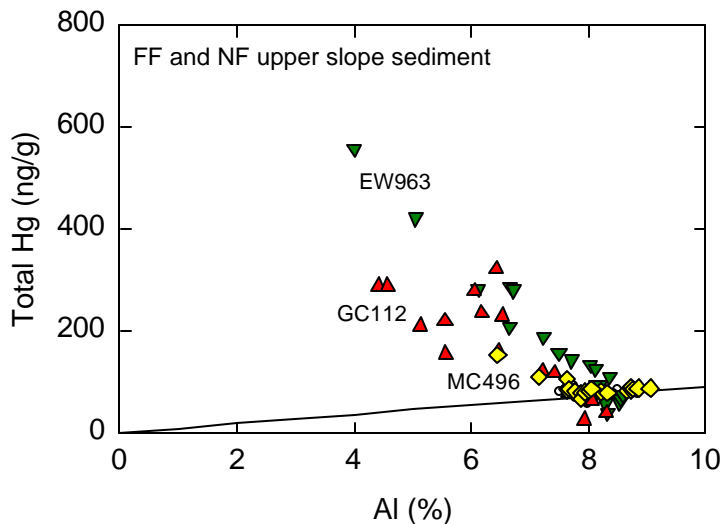


Figure 6. Concentrations of Al versus total Hg for sediment from farfield (FF) stations on the upper slope (hidden circles) along with nearfield (NF) stations from the upper slope for sites MC496 (diamonds), EW963 (inverted triangles) and GC112 (triangles). The solid line shows the slope for the Hg/Al ratio for sediment from FF stations.

In FF sediment from sites on the upper slope, total Hg concentrations are not well correlated with Ba levels (Figure 7a,  $r = 0.28$ ). This weak correlation is due to natural diagenetic effects that sometimes yield Ba-rich layers in sediment (e.g., van Os et al., 1991) and to the widespread distribution of small amounts of anthropogenic and natural barite (Trocine and Trefry, 1983). However, the strong relationship between total Hg and Ba (barite) for NF samples on the expanded x-axis (Figures 7b-d) can be used to estimate the total Hg content of the industrial barite used at each site.

If the lines in Figures 7b-d are extrapolated to pure barite at 58.8% Ba, the concentrations of total Hg are as follows: 449 ng/g for site MC496, 1077 ng/g for site EW963 and 768

ng/g for site GC112. The estimated average concentrations of total Hg in the industrial barite used at each site (with an average of 53% Ba) are as follows: 413 ng/g for site MC496, 978 ng/g for site EW963 and 698 ng/g for site GC112, values that are in line with EPA regulations. Once again, the strong relationships between concentrations of Ba and total Hg support the contention that the excess total Hg in sediment near drilling sites is associated with barite.

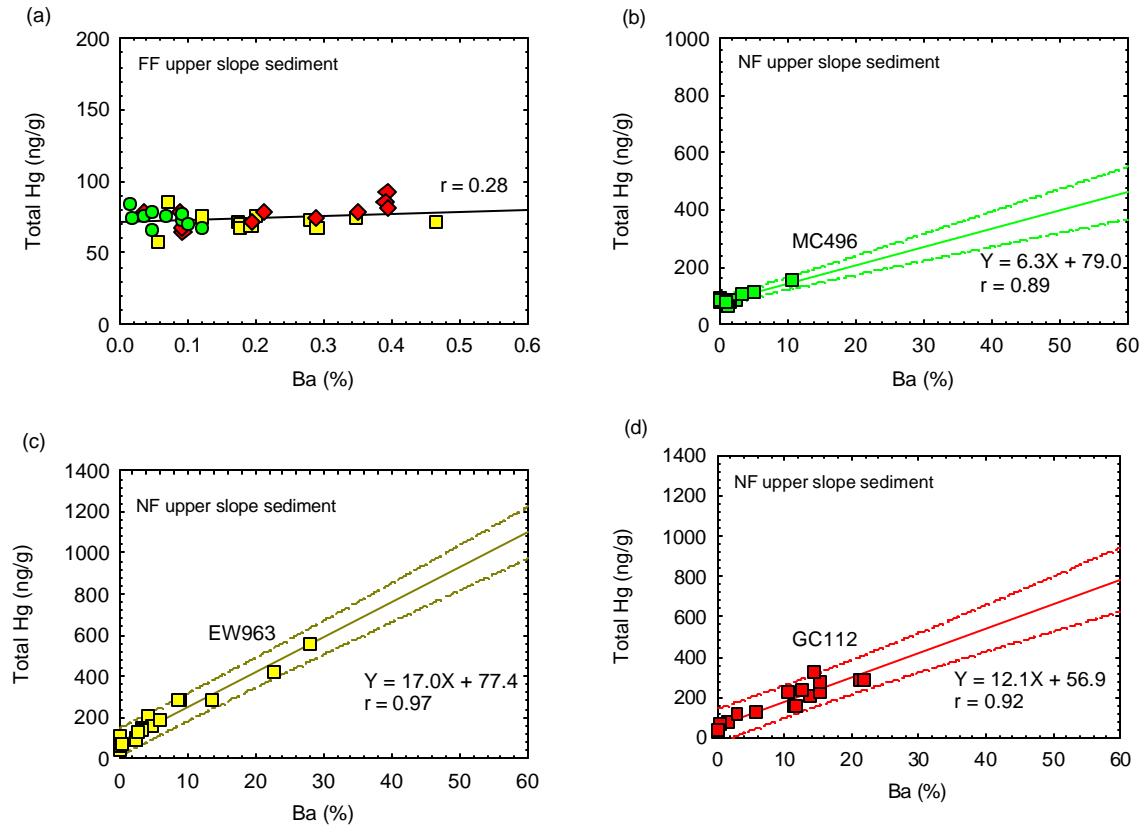


Figure 7. Concentrations of Ba versus total Hg in sediments from the upper slope for (a) farfield (FF) stations at sites MC496 (circles), EW963 (squares) and GC112 (diamonds), (b) NF stations at site MC496, (c) NF stations at site EW963 and (d) NF stations at site GC112. Solid lines show linear regression fits to the data with equation, correlation coefficient ( $r$ ) and 95% prediction interval (dashed lines).

### ***Methylmercury in Sediment***

Concentrations of MeHg in sediments from this study range from 0.11-1.05 ng/g for all FF samples and <0.03-2.7 ng/g for all NF samples. The grand means  $\pm$  standard deviations for MeHg in all samples from this study are as follows: FF =  $0.44 \pm 0.27$  ( $n = 62$ ), MF =  $0.49 \pm 0.17$  ( $n = 25$ ) and NF =  $0.43 \pm 0.41$  ng/g ( $n = 109$ ). Data for surficial sediment (0-2 cm) are summarized in Table 3. The complete data set is tabulated in Appendix II.

**Table 3. Concentrations of MeHg (ng/g, dry wt.) in surficial sediment (0-2 cm) from nearfield (NF), midfield (MF) and farfield (FF) stations from each of the six drilling sites studied.**

Site	Parameter	NF MeHg (ng/g)	MF MeHg (ng/g)	FF MeHg (ng/g)
<b>MP299</b>	<b>Mean</b>	<b>0.34</b>	<b>0.39</b>	<b>0.42</b>
(Water Depth 60 m)	Std. Dev.	0.10	0.12	0.20
	Maximum	0.58	0.46	0.70
	Minimum	0.25	0.22	0.18
	(n)	8	6	6
<b>MP288</b>	<b>Mean</b>	<b>0.34</b>	<b>0.44</b>	<b>0.29*</b>
(Water Depth 119 m)	Std. Dev.	0.07	0.09	0.17*
	Maximum	0.48	0.58	0.58
	Minimum	0.30	0.32	0.14*
	(n)	8	6	6*
<b>EI346</b>	<b>Mean</b>	<b>0.19</b>	<b>0.34</b>	<b>0.30</b>
(Water Depth 92 m)	Std. Dev.	0.15	0.07	0.10
	Maximum	0.40	0.39	0.40
	Minimum	<0.03	0.29	0.11
	(n)	8	2	6
<b>MC496</b>	<b>Mean</b>	<b>0.49</b>	<b>0.50</b>	<b>0.51</b>
(Water Depth 556 m)	Std. Dev.	0.21	0.13	0.18
	Maximum	0.85	0.67	0.79
	Minimum	0.24	0.34	0.35
	(n)	8	6	6
<b>EW963</b>	<b>Mean</b>	<b>0.52</b>	<b>0.77</b>	<b>0.65</b>
(Water Depth 540 m)	Std. Dev.	0.19	0.24	0.24
	Maximum	0.81	1.0	1.0
	Minimum	0.24	0.76	0.29
	(n)	9	3	7
<b>GC112</b>	<b>Mean</b>	<b>1.42</b>	<b>0.61</b>	<b>0.87</b>
(Water Depth 534 m)	Std. Dev.	0.81	0.07	0.20
	Maximum	2.7	0.66	1.0
	Minimum	0.35	0.56	0.49
	(n)	8	2	7

\* Includes sandy samples from stations FF1, FF2 and FF3.

No statistically significant differences in concentrations of MeHg in surficial sediment between NF and FF stations are observed for any of the six sites studied (based on Student's t-test at  $\alpha = 0.05$ , double-tailed, as shown in Figure 8 and Appendix III). When surface and subsurface data are combined, no significant differences in concentrations of MeHg at NF versus FF stations are observed for sites MP299, EI346, MC496, EW963 and GC112; however, MeHg levels are significantly higher at the NF versus FF stations for site MP288 (Figure 8).

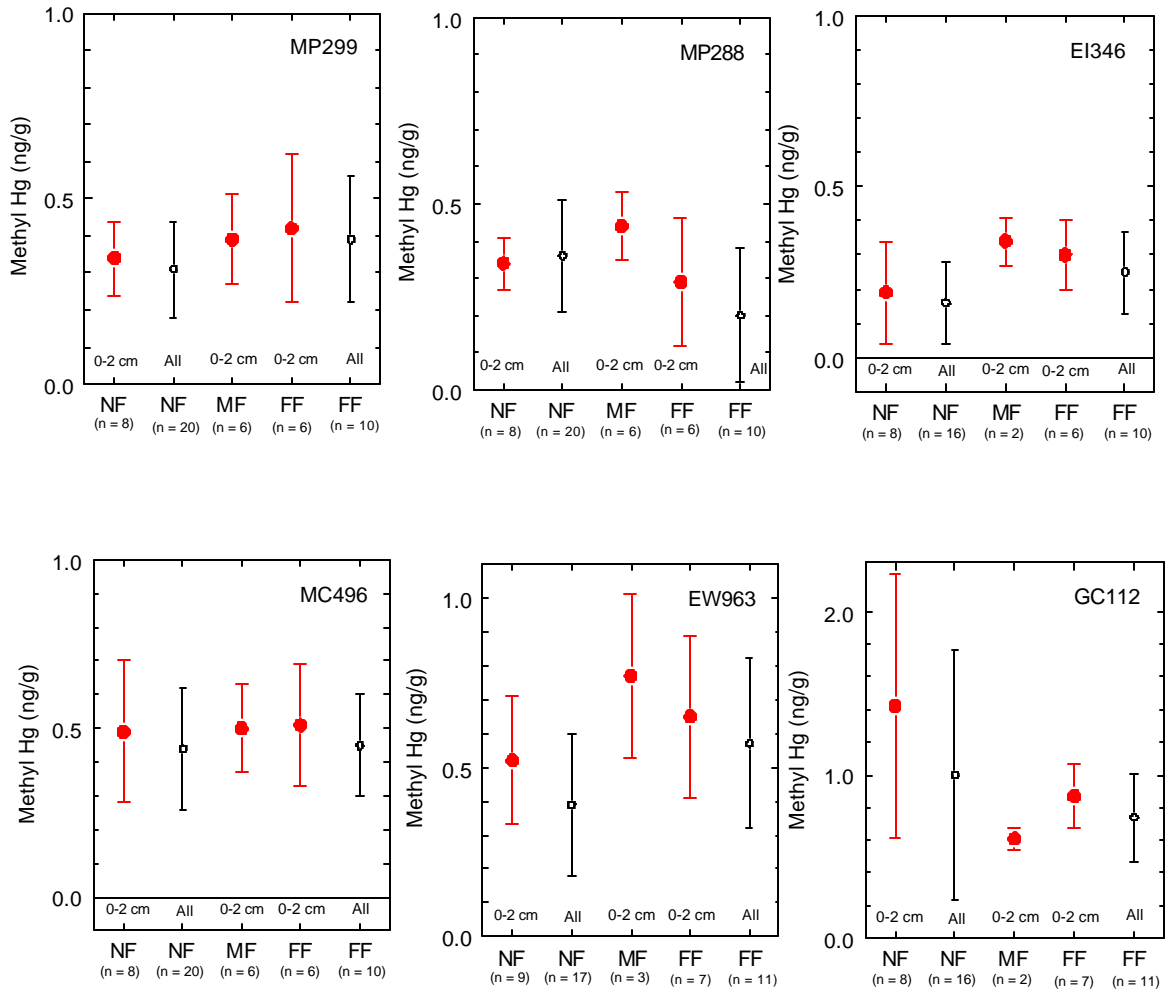


Figure 8. Concentrations of methylmercury at nearfield (NF), midfield (MF) and farfield (FF) stations at each drilling site. Solid circles show mean concentrations and lines show standard deviations for surficial sediment (0-2 cm). Open circles show mean concentrations and lines show standard deviations for all sediment samples. The number of data points (n) is shown for each mean and standard deviation.

A more detailed perspective for concentrations of total Hg and MeHg in surface sediment is given in Figures 9-11. These figures show the uniform distribution of total Hg in the FF stations, except for the sandy samples from site MP288. They also show the variable, but higher levels of total Hg in the NF stations from sites EI346, MC496, EW963 and GC112.

For MeHg, Figures 9-11 show the within-site and site-to-site variability in concentrations and the generally higher levels of MeHg in the upper slope stations. For example, mean values for MeHg in sediment at FF stations on the shelf are ~0.3-0.4 ng/g relative to 0.5-0.8 ng/g in sediment from FF stations on the upper slope (Table 3, Figures 8-11). The observation of generally higher concentrations of MeHg in ambient sediments from the upper slope versus the shelf is related to higher background levels of total Hg and different redox conditions in sediments from the upper slope versus the shelf, as discussed later in the report.

Concentrations of MeHg are least variable in NF stations at sites MP299 and MP288 (CV<30%), most likely due to the lower and relatively uniform levels of total Hg (Figure 9) and more uniform redox conditions in sediment at these two sites. Significantly higher levels of MeHg in NF than FF sediments at site MP288, when all samples are considered, are identified because of sandy sediment in some FF samples. A low level of total Hg and MeHg in surface samples at stations FF1, FF2 and FF3 and throughout the core at station FF1 is due to naturally occurring sand found only at these FF locations. These low levels skew the mean for FF stations relative to NF stations.

Concentrations of MeHg are below detection limits of 0.03 ng/g in surface sediment from three NF stations at site EI346. High concentrations of total H<sub>2</sub>S (>1 mM) and low values for Eh (<-100 mV) help explain this observation for NF sediments from site EI346. Greater variability in concentrations of MeHg (CVs of 30-40%) is common to NF and FF stations from sites MC496 and EW963 where no significant differences are observed between NF and FF stations for levels of MeHg in surface sediment. At GC 112, the largest variability in levels of MeHg (CV = 70%) and higher concentrations of MeHg in surface sediment are found for the NF stations. These observations for GC112 appear to be a complex function of total Hg concentrations and redox conditions as discussed below.

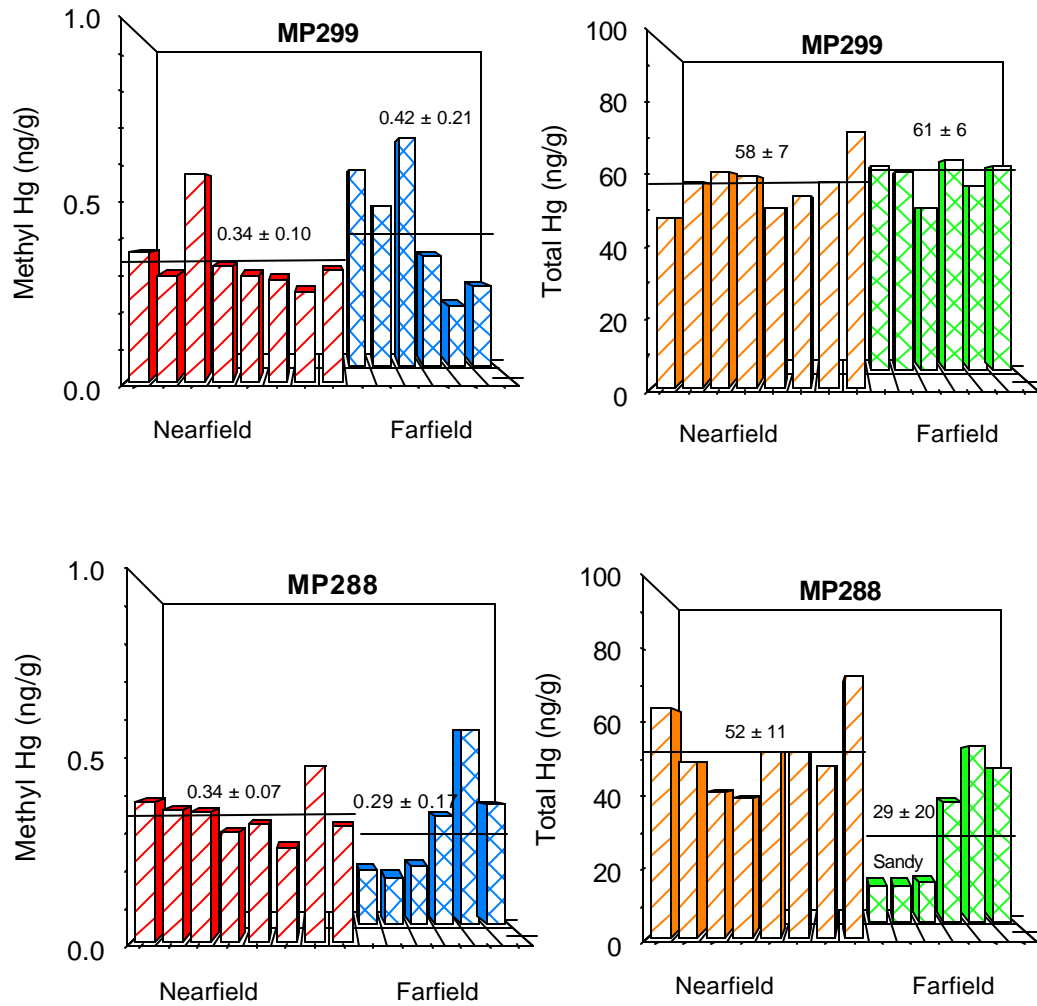


Figure 9. Concentrations of methylmercury and total Hg for surface (0-2 cm) sediment from nearfield and farfield stations at shelf sites MP299 and MP288. Numbers above each data set show mean  $\pm$  standard deviation and solid line is drawn at the mean concentration.

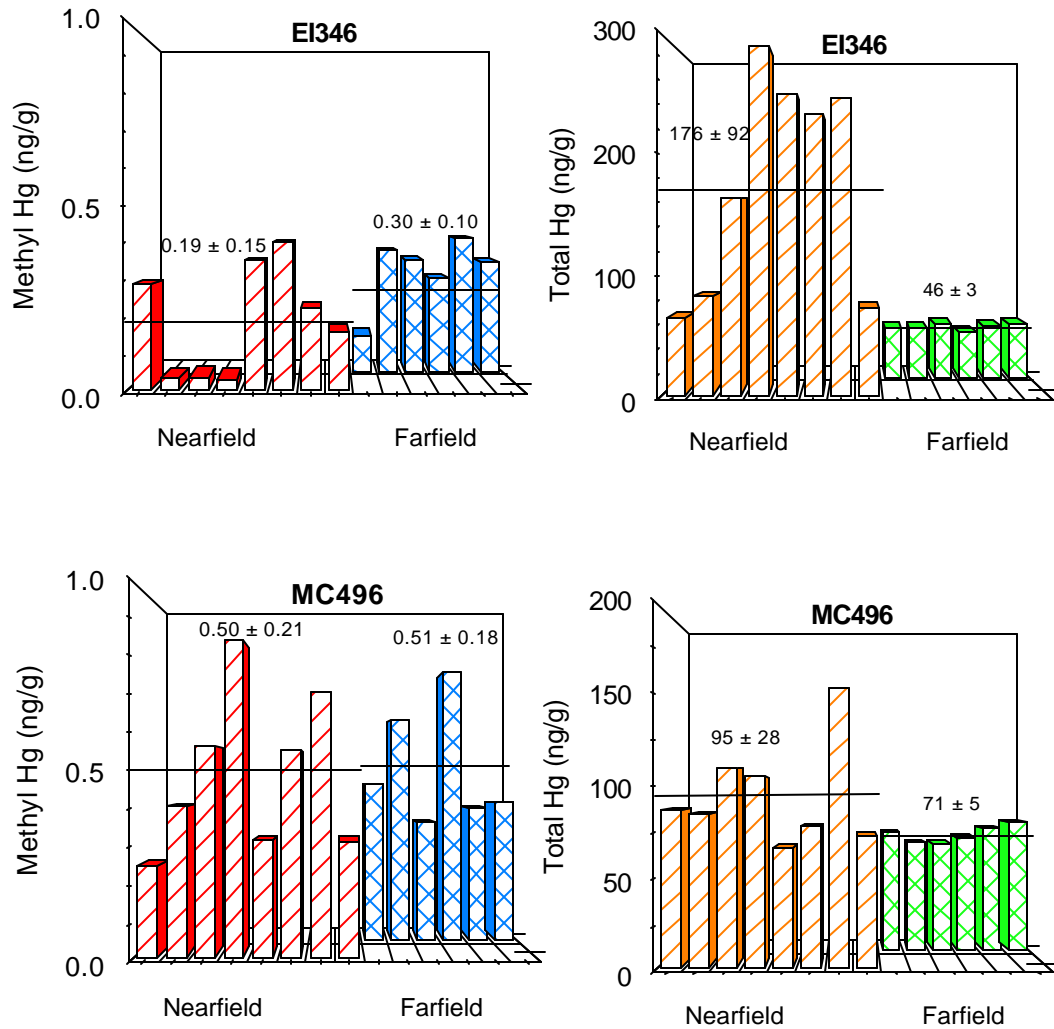


Figure 10. Concentrations of methylmercury and total Hg for surface (0-2 cm) sediment from nearfield and farfield stations at shelf site EI346 and upper slope site MC496. Numbers above each data set show mean  $\pm$  standard deviation and solid line is drawn at the mean concentration.

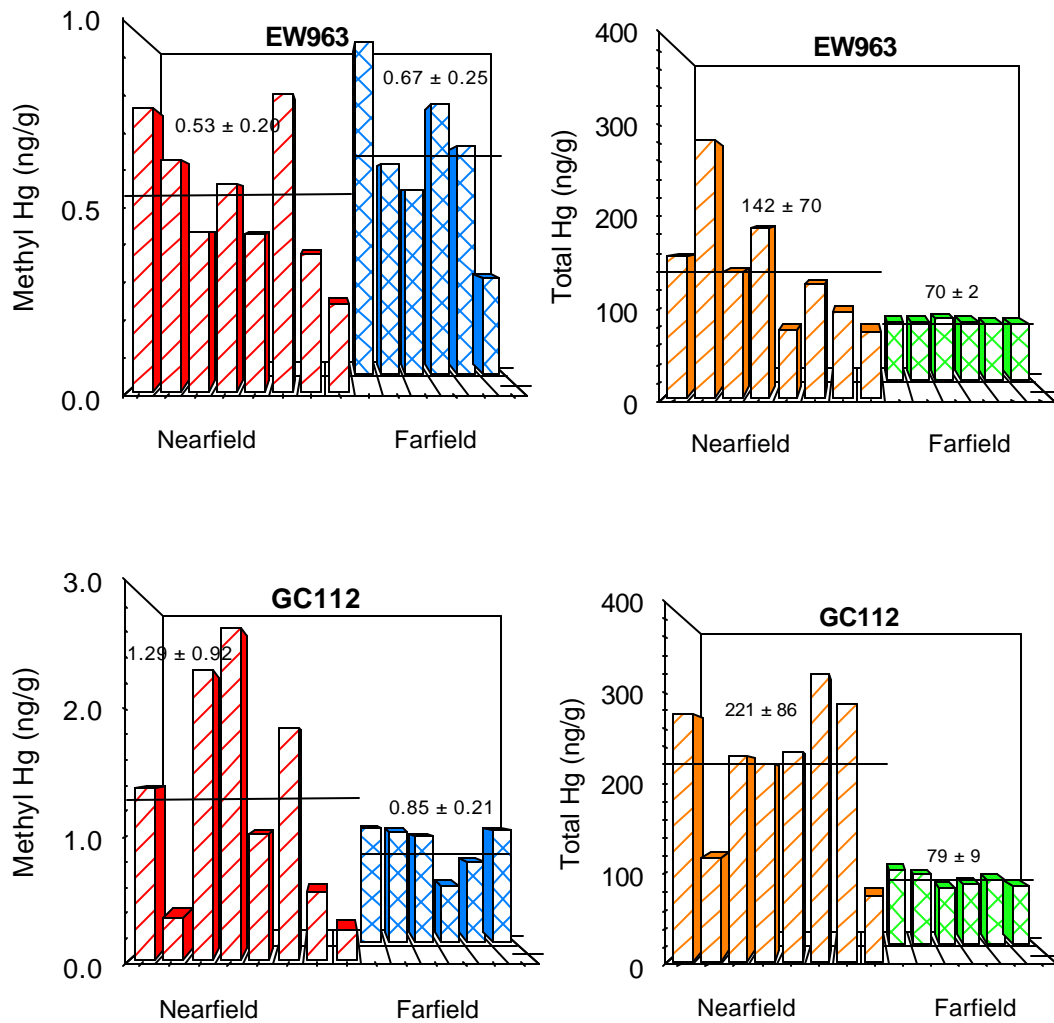


Figure 11. Concentrations of methylmercury and total Hg for surface (0-2 cm) sediment from nearfield and farfield stations at upper slope shelf sites EW963 and GC112. Numbers above each data set show mean  $\pm$  standard deviation and solid line is drawn at the mean concentration.



Previous studies in various sedimentary environments show that optimum conditions for methylation of Hg occur in anoxic, but weakly sulfidic (low total H<sub>2</sub>S) sediments (Gilmour et al., 1992, Gagnon et al., 1996). Neff (2002) summarizes previous results for MeHg in sediments from numerous U.S. and foreign locations. Concentrations of MeHg range from 0.03-10 ng/g and total Hg levels are as high as 783 ng/g in the sediments from Lavaca Bay, Texas, where a chlor-alkali facility was in operation during the late 1960s (Bloom et al., 1999). Kannan et al. (1998) reported a range of <0.001-0.32 ng/g for MeHg in various estuaries along the Gulf of Mexico coast of Florida. In studies of sediment cores from the Saguenay Fjord, Canada, Gagnon et al. (1996) showed that concentrations of MeHg rose from <0.1 ng/g in the oxic surface layers of sediment to ~2 ng/g at 1-2 cm and >10 ng/g at 6-8 cm where total Hg levels were 145, 175 and 700-800 ng/g, respectively. Concentrations of MeHg in sediment from our study in the Gulf of Mexico are below values from Lavaca Bay and are within the lower range of values reported for the Sanguenay Fjord in Canada.

### *Methylmercury in Shelf versus Slope Sediment*

The mean value for MeHg in all FF sediment from the shelf is  $0.28 \pm 0.17$  ng/g relative to a mean of about two times more MeHg (at  $0.59 \pm 0.26$  ng/g) for FF sediments from the upper slope (Figure 12). A similar trend is observed for all NF stations where average levels of MeHg are  $0.28 \pm 0.16$  ng/g and  $0.59 \pm 0.52$  ng/g, for shelf and upper slope sediments, respectively (Figure 12). These trends in concentrations of MeHg are consistent with general trends for concentrations of total Hg (Figure 12) with ~60-70% higher levels of total Hg at both NF and FF stations on the upper slope relative to the shelf. Concentrations of total Hg alone do not explain the variance in the data for MeHg as will be discussed in more detail below. However, a key observation from Figure 12 is that concentrations of both MeHg and total Hg increase from shelf to upper slope sediment for the sites studied.

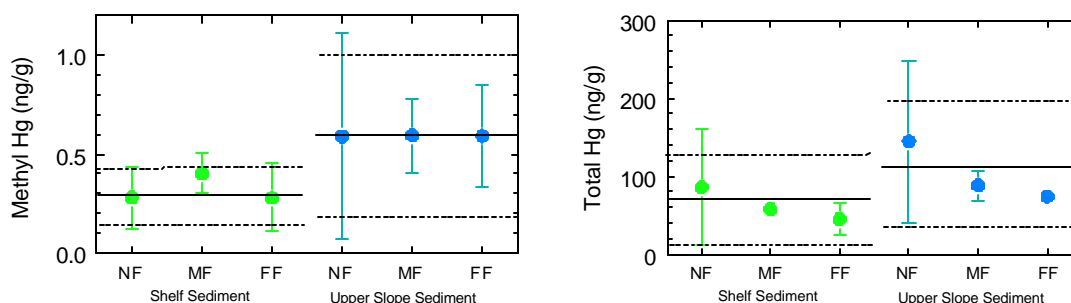


Figure 12. Means (solid circles) and standard deviations (vertical lines) for concentrations of (a) methylmercury and (b) total Hg in sediment from nearfield (NF), midfield (MF) and farfield (FF) stations on the shelf and upper slope. Solid horizontal lines show means and dashed horizontal lines show standard deviations for all shelf or upper slope samples.

Concentrations of MeHg range from 0.16-1.47% of total Hg levels in all FF sediment and <0.01-1.45% of total Hg levels in all NF samples (Figure 13). The grand average for the fraction of total Hg that is present as MeHg is  $0.60 \pm 0.31\%$  for all shelf sediment, the same as the value of  $0.60 \pm 0.32\%$  for all upper slope sediment. Although these average percentages are similar, some variations within the data set are observed.

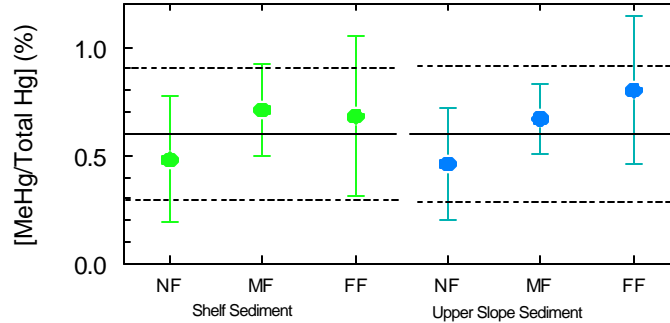


Figure 13. Means (solid circles) and standard deviations (vertical lines) for the percent of total mercury that is methylmercury in sediment from nearfield (NF), midfield (MF) and farfield (FF) stations on the shelf and upper slope. Solid horizontal lines show means and dashed horizontal lines show standard deviations for all shelf or upper slope samples.

Concentrations of MeHg are positively correlated ( $r = 0.60$ ) with concentrations of total Hg for FF samples from the shelf, partly due to the influence of the Hg-poor, sandy samples from site MP288 (Figure 14a). When data for NF sediments from the shelf are added in Figure 14b, most of the data points from sites MP299 and MP288 fit within the prediction interval established for the FF sediments in Figure 14a. In other words, no significant differences in the concentrations of total Hg, MeHg or the percent MeHg are observed between NF versus FF stations at sites MP299 and MP288. At site EI346, many samples with elevated levels of total Hg contain lower levels of MeHg than expected based on the natural distribution for FF samples (Figure 14b). For example, at the extreme, five samples from NF stations at site EI346 contain total Hg levels >200 ng/g; however, concentrations of MeHg are non-detectable (<0.03 ng/g) and account for <0.02% of the total Hg. The observation for site EI346 suggests that the excess Hg in barite at site EI346 is not being converted to MeHg. Nearfield sediment from site EI346 also contains high levels of total  $H_2S$  (>1 mM). The presence of reduced sulfide is thought to inhibit methylation because Hg precipitates as  $HgS$  (Gilmour et al., 1998).

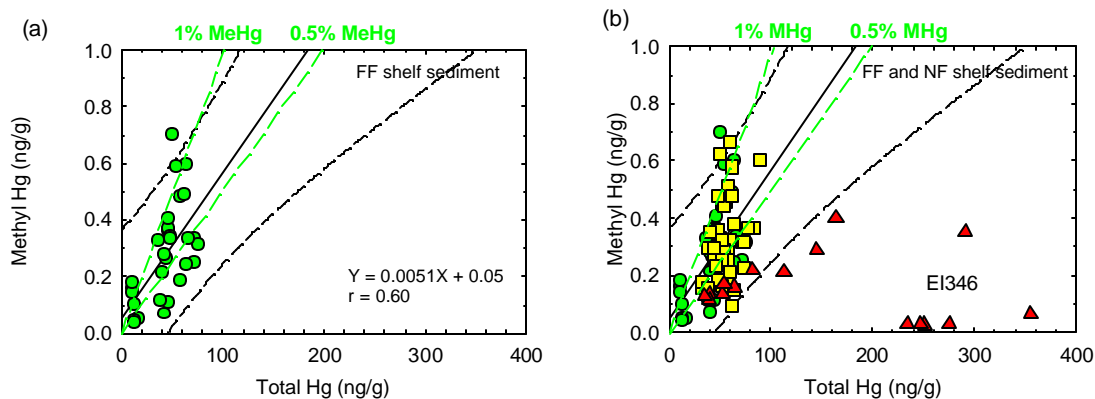


Figure 14. Concentrations of total Hg versus MeHg in shelf sediment from (a) farfield (FF) stations at shelf sites MP299, MP288 and EI346. The solid line is from a linear regression (with equation and correlation coefficient) and dashed lines around solid line show 95% prediction interval, and (b) FF stations (circles) along with nearfield (NF) shelf sediment from sites MP299 and MP288 (squares) and EI346 (triangles). The solid line is from a linear regression for the FF data and dashed lines around solid line show 95% prediction interval (the line, equation and correlation coefficient for the line are the same as in graph a). Dashed lines with labels of 0.5% MeHg and 1% MeHg on both graphs are reference lines that provide a convenient perspective for estimating the percent of total Hg that is present as methylmercury for each data point.

In FF sediment from the upper slope, concentrations of MeHg range from 0.2-1.05 ng/g and show no significant relationship ( $r = 0.12$ ) with concentrations of total Hg (Figure 15a). When data for FF stations from the shelf are added (Figure 15b), the distinctly higher concentrations of both total Hg and MeHg in ambient sediments from the upper slope are clearly shown. The combined data set for FF samples from the shelf and upper slope is used here to establish a better and more significant frame of reference for comparing results for NF samples. Samples from NF stations at site MC496 group close to the FF samples from the upper slope (Figure 15c). However, the NF samples from site EW963, with high levels of total Hg, have levels of MeHg that are consistent with FF sediments (Figure 15c). This observation for site EW963 is similar to that made for site EI346 on the shelf and again supports the argument that excess Hg in barite at site EW963 is not being converted to MeHg. In the case of EW963, this trend also is related to the presence of total  $H_2S$  in the sediment at some stations. In sharp contrast to the observations for NF samples from MC496 and EW963, seven NF samples from site GC112 contain higher levels of both total Hg and MeHg than observed at FF sites from the upper slope (Figure 15d). However, an additional four NF samples from site GC112, with total Hg concentrations  $>100$  ng/g, contain MeHg at levels that are below the average of  $\sim 0.6$  ng/g for ambient sediment from the upper slope. The above trends show that enhanced levels of barite-related total Hg in NF sediments around drilling sites do not generally lead to higher levels of MeHg, with the possible exception of several stations at site GC112. However, even at site GC112, the highest concentration of MeHg (2.7 ng/g) is only  $\sim 3\%$  of the ambient concentration of total Hg and thus the additional MeHg Hg could be from either an anthropogenic or natural source of Hg.

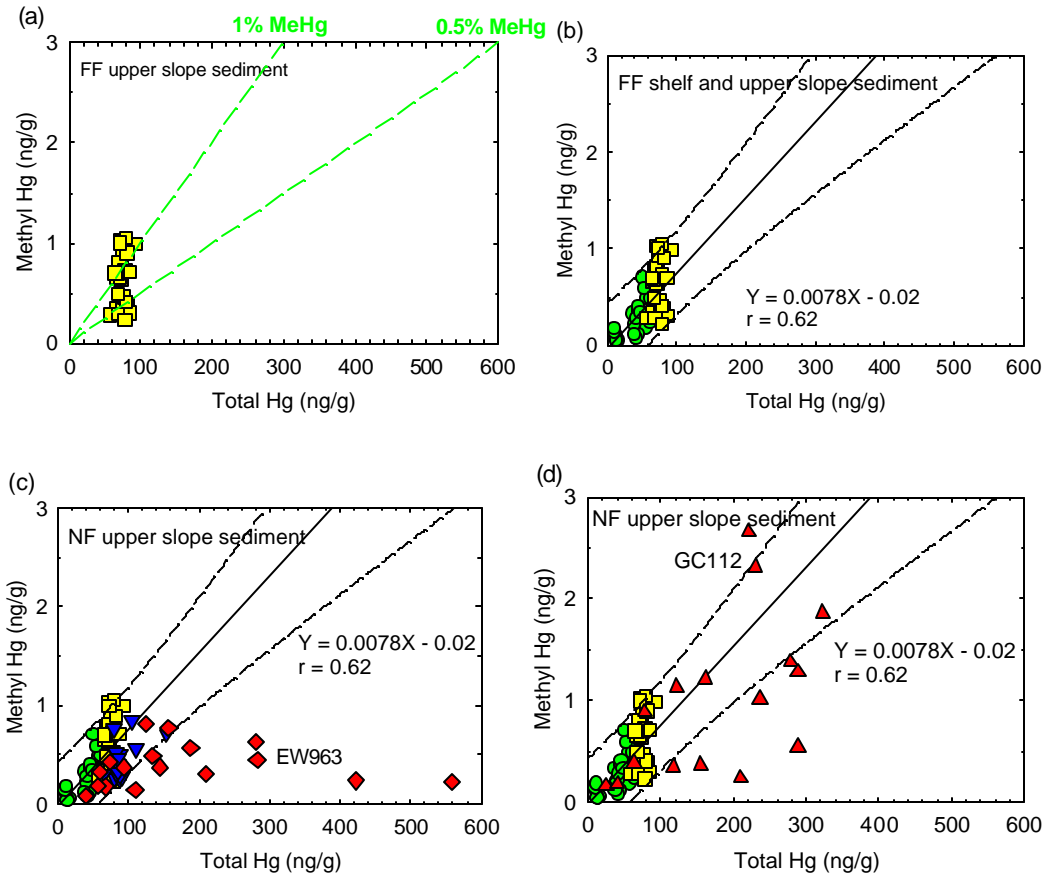


Figure 15. Concentrations of total Hg versus MeHg in sediment from (a) farfield (FF) stations on the upper slope at MC496, EW963 and GC112, (b) FF stations from the upper slope (squares) and the shelf (circles), (c) FF stations from the upper slope (squares) and the shelf (circles) along with nearfield (NF) sediment from upper slope sites MC496 (inverted triangles) and EW963 (diamonds), (d) FF stations from the upper slope (squares) and the shelf (circles) along with NF sediment from upper slope site GC112 (triangles). Dashed lines with labels of 0.5% and 1% MeHg on graph (a) are reference lines that provide a convenient perspective for estimating the percent of total Hg that is present as methylmercury for each data point and can be visually applied to all four graphs.

### ***Total Organic Carbon in Sediment***

The importance of organic matter for microbial methylation of Hg is well documented (e.g., Compeau and Bartha, 1985; Gagnon et al., 1996). As the rate of deposition of organic matter in sediments increases, a more reducing environment is created. The optimum environment for formation of MeHg in marine sediment seems to be one that is enriched with organic carbon and nutrients, anoxic, yet low in concentrations of dissolved sulfide (Gagnon et al., 1996). Discharges of cuttings with SBM (olefin-rich organic substances) or increased deposition of organic matter from organisms inhabiting offshore structures may alter the sediment environment and render it more favorable for methylation of Hg. Thus, TOC also is an important factor to consider in the overall assessment process.

Concentrations of TOC in surficial sediment (0-2 cm) at FF stations from this study range from 0.06% in sandy sediment at site MP288 to 1.39% at MP299. At NF stations, levels of TOC range from 0.73-4.1%, with both the minimum and maximum values at site EI346. The grand mean for TOC at all NF stations of  $1.43 \pm 0.91\%$  is about 50% greater than the grand mean of  $0.96 \pm 0.35\%$  for all FF stations. The maximum concentration of TOC was 5.89% in subsurface sediment from station NFD1 at site EI346. Data for surficial sediment (0-2 cm) are summarized in Table 4. The complete data set is tabulated in Appendix II.

No significant differences in concentrations of TOC in surficial sediment are observed between NF and FF stations for sites MP299, MP288, and MC496 (based on Student's t-test at  $\alpha = 0.05$ , double-tailed, as shown in Figure 16 and Appendix III). However, levels of TOC are significantly higher in surficial sediment at the NF versus FF stations for sites EI346, EW963 and GC112. When surface and subsurface data are combined, no significance differences in concentrations of TOC at NF versus FF stations are observed for sites MP299 and MC496 and significantly higher levels of TOC are found at NF sites for MP288, EI346, EW963 and GC112 (Appendix III). The significant differences observed for NF versus FF stations at site MP288 are related to very low levels of TOC in sandy sediment at three FF stations.

Concentrations of TOC at FF stations on the upper slope ( $1.15 \pm 0.20\%$ ) are about 40% higher than on the shelf ( $0.80 \pm 0.41\%$ ). A similar trend for TOC occurs for NF stations on the upper slope ( $1.67 \pm 0.82\%$ ) versus the shelf ( $1.21 \pm 0.95\%$ ). Variability in TOC levels at FF stations (average CV = 8%, excluding site MP288) is much lower than in the NF stations (average CV = 37%) showing both the relative uniformity in TOC in ambient sediments and the patchiness in TOC levels near drilling sites. Increased variability in the NF zone is most likely related to the irregular distribution patterns of drilling discharges.

**Table 4. Concentrations of total organic carbon (TOC as %) in surficial sediment (0-2 cm) from nearfield (NF), midfield (MF) and farfield (FF) stations from each of the six drilling sites studied.**

Site	Parameter	NF TOC (%)	MF TOC (%)	FF TOC (%)
<b>MP299</b>	<b>Mean</b>	<b>1.20</b>	<b>1.26</b>	<b>1.24</b>
(Water Depth 60 m)	Std. Dev.	0.35	0.11	0.09
	Maximum	1.93	1.43	1.39
	Minimum	0.75	1.16	1.14
	(n)	8	6	6
<b>MP288</b>	<b>Mean</b>	<b>0.96</b>	<b>1.01</b>	<b>0.51*</b>
(Water Depth 119 m)	Std. Dev.	0.19	0.23	0.49*
	Maximum	1.21	1.30	1.24
	Minimum	0.67	0.73	0.08*
	(n)	8	6	6*
<b>EI346</b>	<b>Mean</b>	<b>1.81</b>	<b>1.01</b>	<b>0.86</b>
(Water Depth 92 m)	Std. Dev.	1.12	0.01	0.03
	Maximum	4.10	1.01	0.92
	Minimum	0.73	1.00	0.82
	(n)	8	2	6
<b>MC496</b>	<b>Mean</b>	<b>1.80</b>	<b>1.30</b>	<b>1.29</b>
(Water Depth 556 m)	Std. Dev.	0.78	0.20	0.13
	Maximum	3.28	1.55	1.42
	Minimum	1.08	0.95	1.06
	(n)	8	6	6
<b>EW963</b>	<b>Mean</b>	<b>1.68</b>	<b>1.30</b>	<b>1.13</b>
(Water Depth 540 m)	Std. Dev.	0.67	0.30	0.06
	Maximum	2.87	1.93	1.20
	Minimum	1.15	1.10	1.03
	(n)	9	3	7
<b>GC112</b>	<b>Mean</b>	<b>2.06</b>	<b>1.31</b>	<b>0.89</b>
(Water Depth 534 m)	Std. Dev.	0.60	0.48	0.14
	Maximum	2.76	1.65	1.05
	Minimum	1.02	0.97	0.64
	(n)	8	2	6

\* Includes sandy samples from stations FF1, FF2 and FF3.

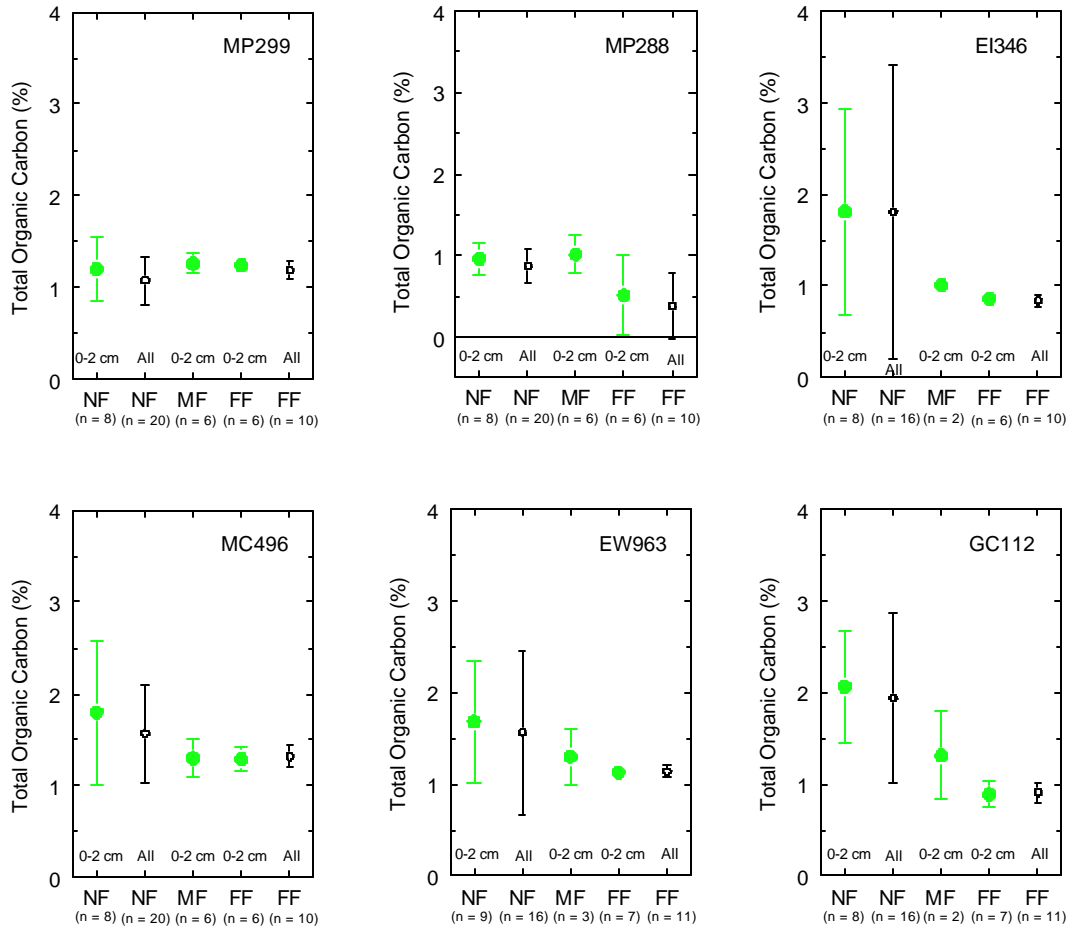


Figure 16. Concentrations of total organic carbon (TOC) for nearfield (NF), midfield (MF) and farfield (FF) stations at each drilling site. Solid circles show mean concentrations and lines show standard deviations for surficial sediment (0-2 cm). Open circles show mean concentrations and lines show standard deviations for all sediment samples. The number of data points (n) is shown for each mean and standard deviation.

Concentrations of TOC correlate positively with concentrations of total Hg for sediments from the shelf ( $r = 0.72$ ) and the shelf plus upper slope ( $r = 0.81$ , Figure 17a), but not for the upper slope data alone ( $r = 0.11$ ). This trend is analogous to the positive relationship between Al and total Hg shown previously (Figure 4), where higher levels of TOC corresponded to increased amounts of aluminosilicate clays. When data for NF stations from the shelf are added (Figure 17c), results for NF stations at sites MP299 and MP288 plot with the FF data. In NF sediment from site EI346, elevated concentrations of total Hg coincide with elevated levels of TOC (Figure 17c). This trend is related to the presence of both total Hg and TOC (as SBM) in the drilling discharges. Greater scatter in the relationship between TOC and total Hg (Figure 17c) than for total Ba versus total Hg (Figure 5b) occurs because the Hg is directly associated with the barite and not the TOC (as SBM). A similar trend for the co-occurrence of elevated levels of TOC and total Hg is observed in NF sediment from sites EW963 and GC112 (Figure 17e).

Concentrations of MeHg correlate positively with TOC in sediment from FF stations on the shelf ( $r = 0.63$ , including sandy samples from site MP288); however, no significant correlation was observed in FF sediments from the upper slope ( $r = 0.13$ ) or the combined data set for FF sediments from the shelf and upper slope ( $r = 0.38$ , Figure 17b). These trends for TOC versus MeHg in FF sediment show that TOC alone is not a key variable in determining how much MeHg is in sediment. However, low levels of MeHg in the sandy, TOC-poor sediment from three FF stations at site MP288 show that sediments with very low levels of TOC (i.e.,  $<0.2\%$ ) are likely to have low levels of MeHg.

When data for NF stations at sites MP299 and MP288 are added to the data for FF stations, the points overlap almost completely (Figure 17d). At site EI346, sediment containing higher levels of TOC contains lower concentrations of MeHg (Figure 17d). The lower levels of MeHg at higher concentrations of TOC in these sediments may be the result of higher levels of total  $H_2S$  ( $>1$  mM) that inhibit methylation of Hg.

Some NF sediments at upper slope sites MC496, EW963 and GC112 contain 2-4 times more TOC than the other NF stations; however, levels of MeHg are within the same range as the other NF and FF stations from these sites (Figure 17c). In contrast, sediment from several stations at site GC112 with elevated levels of TOC (about double ambient TOC concentrations), are marked by the highest concentrations of MeHg (as much as 2-3 times higher than ambient concentrations). These varied trends will be discussed in more detail below. However, the TOC relationships are complicated because olefins in synthetic-based mud may account for 50-100% of the TOC-rich sediment from NF stations.



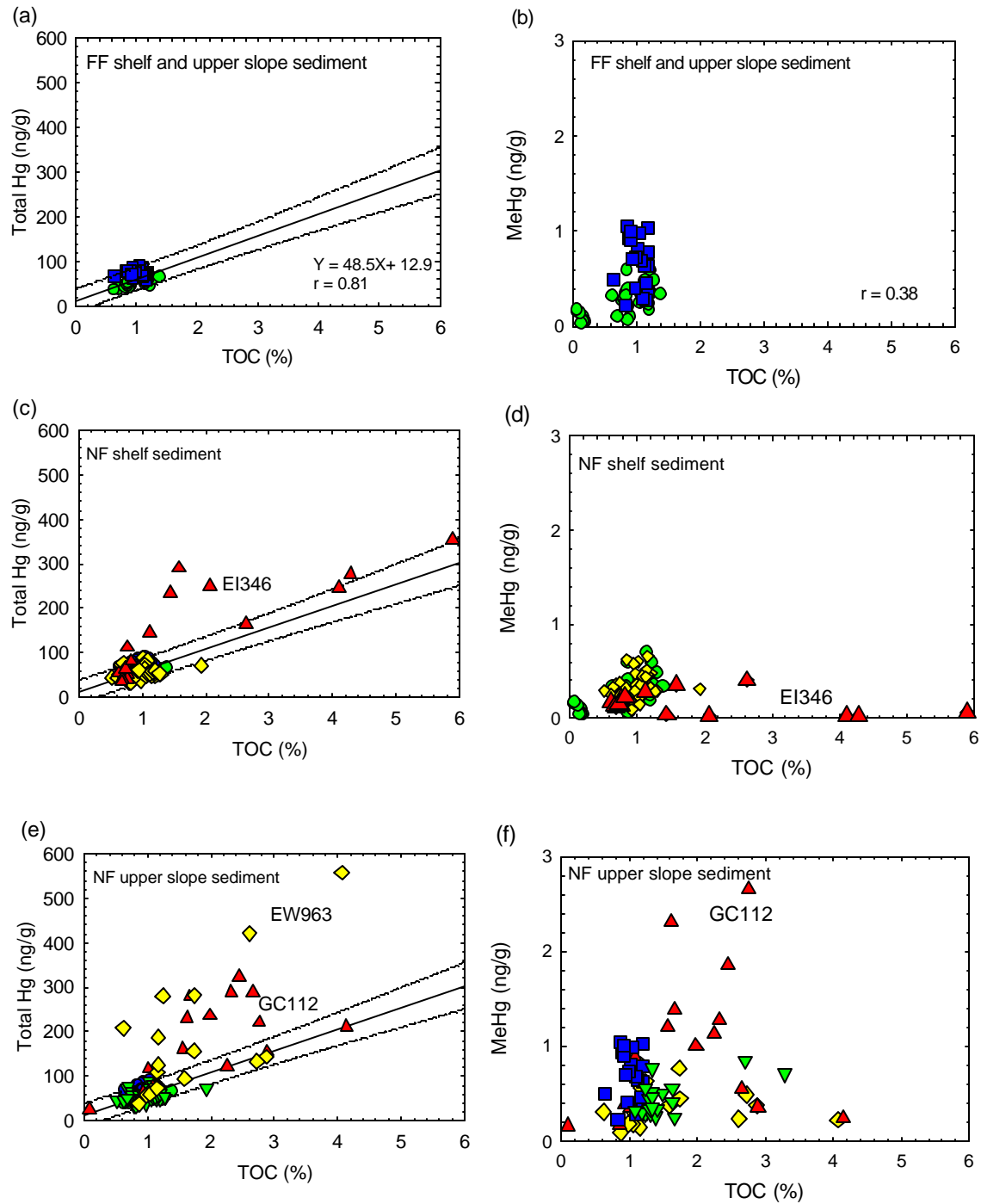


Figure 17. Concentrations in sediment of total organic carbon (TOC) versus (a) total Hg from farfield (FF) stations on the shelf (circles) and upper slope (squares), (b) MeHg in FF stations on the shelf (circles) and upper slope (squares), (c) total Hg from farfield (FF) stations on the shelf (circles) and upper slope (squares), and nearfield (NF) stations MP299 and MP288 (diamonds) and EI346 (triangles), (d) MeHg in FF stations on the shelf (circles) and nearfield (NF) stations MP299 and MP288 (diamonds) and EI346 (triangles), (e) total Hg from farfield (FF) stations on the shelf (circles) and upper slope (squares) and nearfield (NF) stations from upper slope stations MC496 (inverted triangles), EW963 (diamonds) and GC112 (triangles) and (f) MeHg from farfield (FF) stations on the upper slope (squares) and nearfield (NF) stations from upper slope stations MC496 (inverted triangles), EW963 (diamonds) and GC112 (triangles).

### ***Vertical Distributions of Total Mercury and Methylmercury and Relationships to Redox Conditions***

Vertical profiles for concentrations of MeHg and total Hg were obtained for 11 cores from the shelf (sites MP299, MP288 and EI346) and 10 cores from the upper slope (sites MC496, EW963 and GC112). Eighteen of these profiles are presented in Figures 19-24 with the results for dissolved oxygen and Eh.

The measured Eh values represent the sum of all oxidation and reduction reactions that are occurring in the sediment. An approximate Eh value can be given for the occurrence of various redox reactions (Figure 18). For example, the onset of bacterial reduction of nitrate (a replacement oxidizing agent for oxygen) to ammonia occurs at an Eh ~200 mV. The onset of sulfate reduction to H<sub>2</sub>S occurs as Eh values fall below 0 to -100 mV (Figure 18). The redox environment defined in this report will be mainly based on the Eh; however, in some cases, supporting concentrations for interstitial water are available from the SBM study. All probe and interstitial water data will eventually be compiled in the final report of the SBM study.

At shelf site MP299, concentrations of MeHg in the sediment column at the FF stations ( $0.39 \pm 0.14$  ng/g) are not significantly different than at NF stations ( $0.29 \pm 0.13$  ng/g) (Figure 19). Concentrations of total Hg in FF ( $68 \pm 7$ ) and NF ( $60 \pm 10$  ng/g) cores are relatively uniform (CV<20%) and not statistically different. Levels of dissolved oxygen decrease to below detection limits (<1  $\mu$ M) within the top 0.2-1.0 cm and Eh values are uniformly distributed at 80-100 mV in both NF and FF cores (Figure 19). The highest concentrations of MeHg (0.4-0.6 ng/g) in any of the cores from site MP299 were

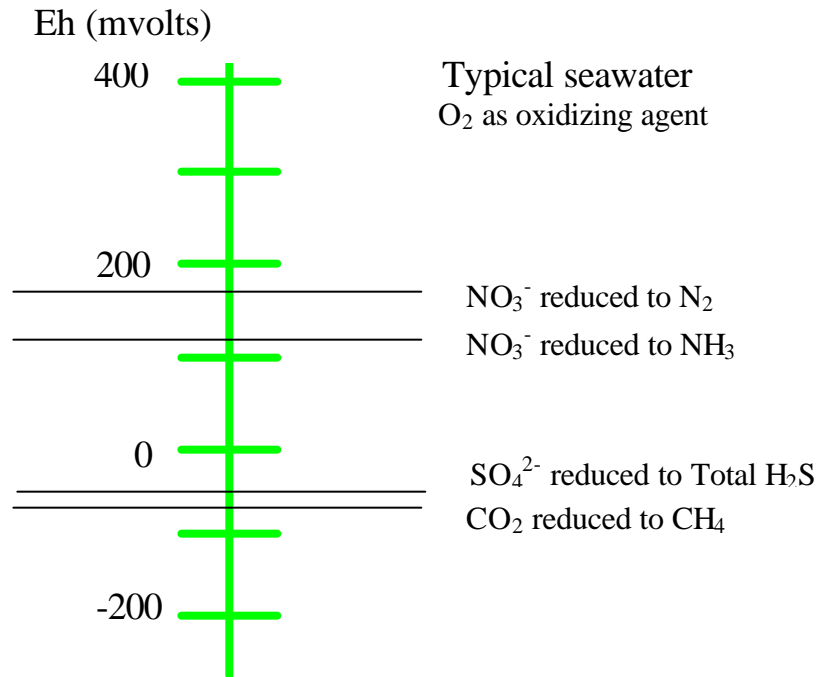


Figure 18. Approximate Eh values for various redox reactions in water (after Drever, 1997)

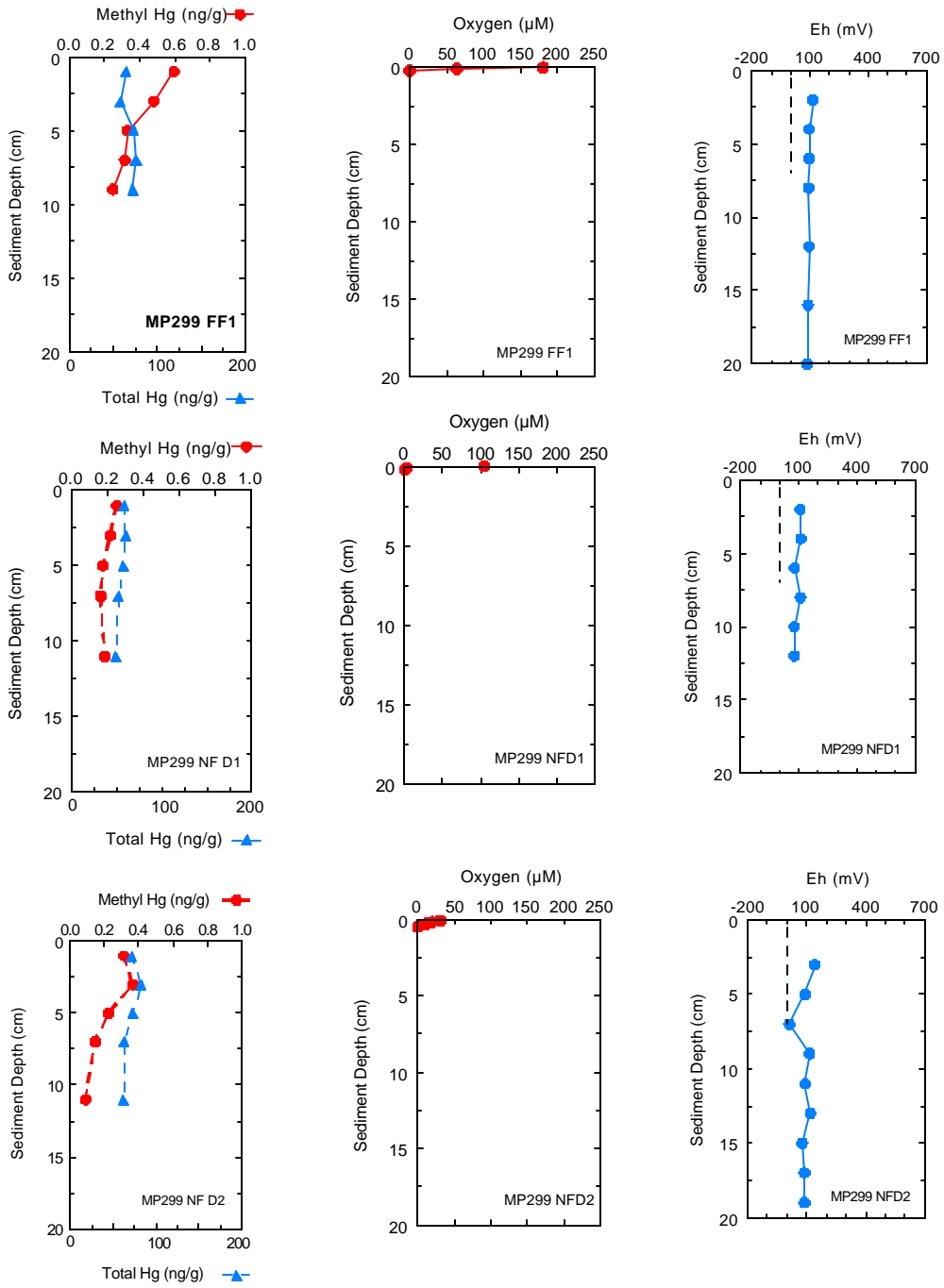


Figure 19. Vertical profiles for concentrations of total mercury, methylmercury, dissolved oxygen and Eh in sediment cores from site MP299 on the shelf.

observed in the surface layer from station FF1 (Figure 19) and the subsurface layers from station NF1 (Appendix II). Such similar distributions of MeHg in NF and FF sediment at site MP299 are consistent with relatively uniform levels of total Hg and redox conditions in NF and FF sediment. Once again, sediments from this site contain small amounts of drilling mud and cuttings.

At site MP288, low levels of MeHg (<0.2 ng/g) in the sediment core from station FF1 are consistent with low levels of total Hg in the sandy-textured deposit. Unfortunately, the probes did not easily penetrate the sand and thus oxygen and Eh data are unavailable. In contrast with the sandy FF core, concentrations of MeHg were at 0.4 ng/g or higher in the top few centimeters of the NF cores (Figure 20). Concentrations of dissolved oxygen are depleted by depths of <0.5 cm in all NF cores. A sharp redoxcline (sharp change in Eh) also is observed from available data for stations NFD1 and NFD2 (Figure 20). The decreases in Eh are commensurate with ongoing nitrate reduction. No sulfate reduction is observed in the top 30 cm of sediment at site MP288 based on interstitial water data for stations NFD2 and FF6.

The most striking observation in the vertical profiles for site EI346 is that concentrations of MeHg are below detection limits (<0.03 ng/g) in the top 5 cm of sediment from station NFD1, even though concentrations of total Hg are almost eight times greater than ambient levels (Figure 21). Oxygen is depleted in the top mm of the core from NFD1 and the Eh is about -150 mV (Figure 21). As predicted from the Eh data, sulfate reduction is occurring in the top few centimeters of the core from station NFD1 where levels of dissolved total H<sub>2</sub>S are >1mM. Such conditions are consistent with observations by other investigators that methylation of Hg is inhibited under such conditions (Gagnon et al., 1997).

In contrast with the MeHg profile for station NFD1 at site EI346, oxygen penetrates to a depth of ~2.5 cm in the sediment at station FF1, a point below which the Eh approaches 0 mV and there is an increase in sediment levels of MeHg (Figure 21). At station NFD2, the Eh ranges between 50 and -60 mV, and concentrations of MeHg are greater than at the FF1 station. No interstitial water data are available for these sites. However, the three vertical profiles for MeHg at site EI346 suggest that some MeHg is formed and retained in these sediments at Eh levels of +100 to about -50 mV. When Eh values are lower at levels of about -150mV, the methylation process appears to be inhibited.

In sediment from upper slope site MC496, the strongest redoxcline is observed in the top 5 cm at station NFD1 where concentrations of MeHg peak at 0.76 ng/g relative to levels of 0.45 ng/g at station F1 and 0.4-0.79 ng/g in the top 2 cm at the FF stations (Figure 22). The Eh in the sediment at the base of the redoxcline at station NFD1 also is about 0 mV, and lower than observed at the other stations (Figure 22). Furthermore, the decrease in Eh is greatest over the top few centimeters at station NFD1. Comparison of the Eh profiles for stations FF1, NFD2 and NF1 (Figure 22) show that the peak levels in MeHg roughly parallel the trend in Eh.

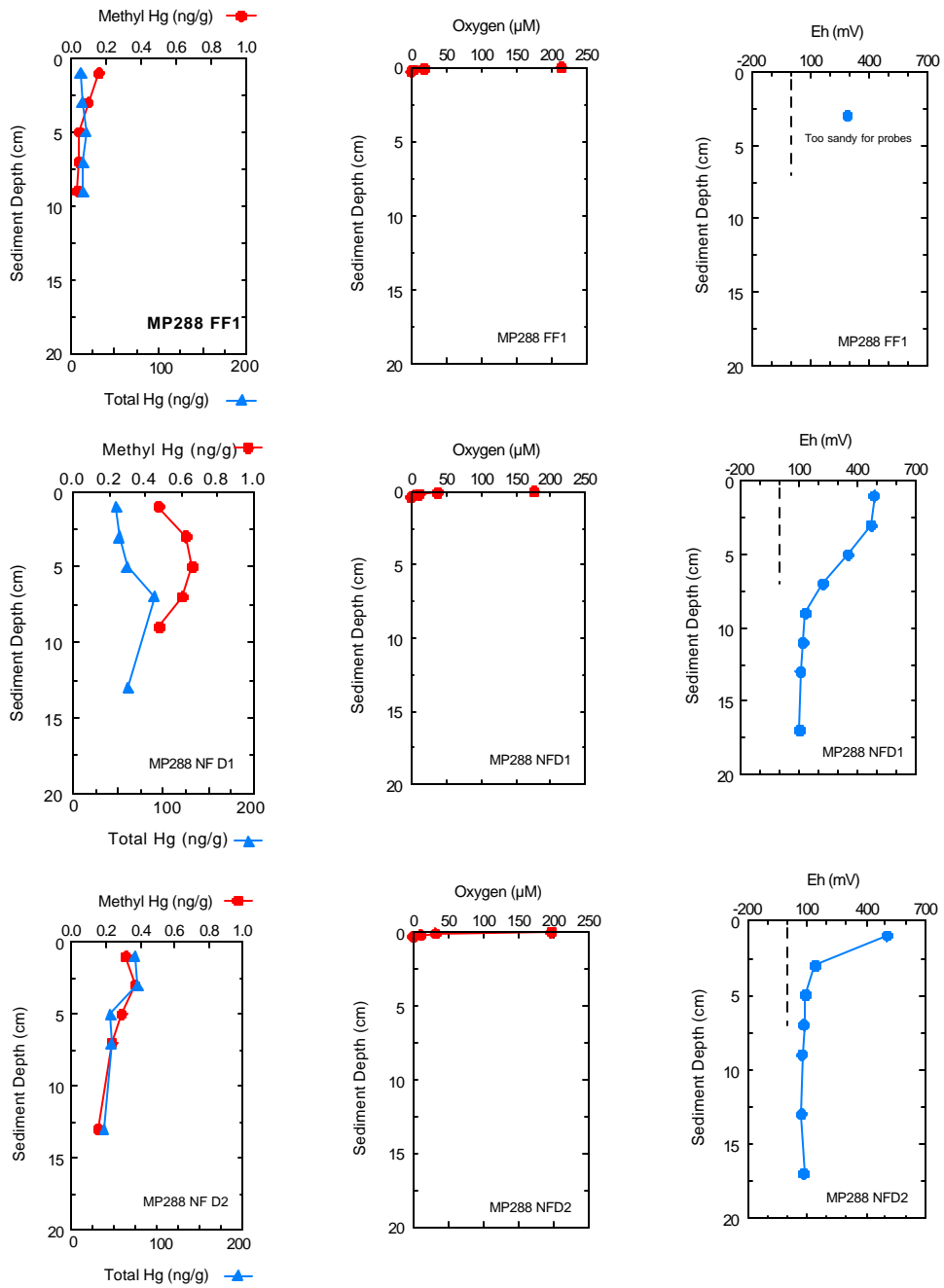


Figure 20. Vertical profiles for concentrations of total mercury, methylmercury, dissolved oxygen and Eh in sediment cores from site MP288 on the shelf.

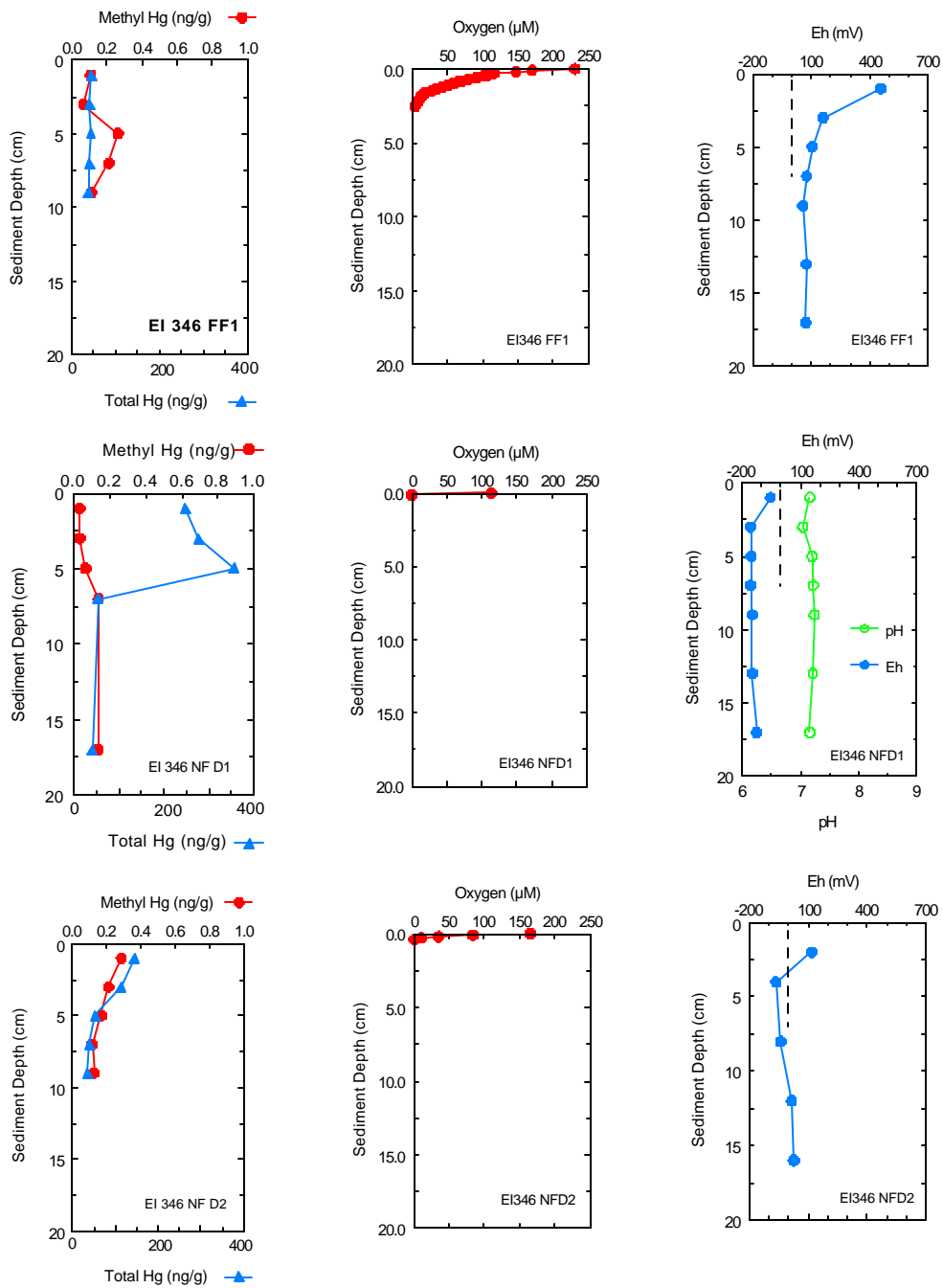


Figure 21. Vertical profiles for concentrations of total mercury, methylmercury, dissolved oxygen, Eh and pH in sediment cores from site EI346 on the shelf.

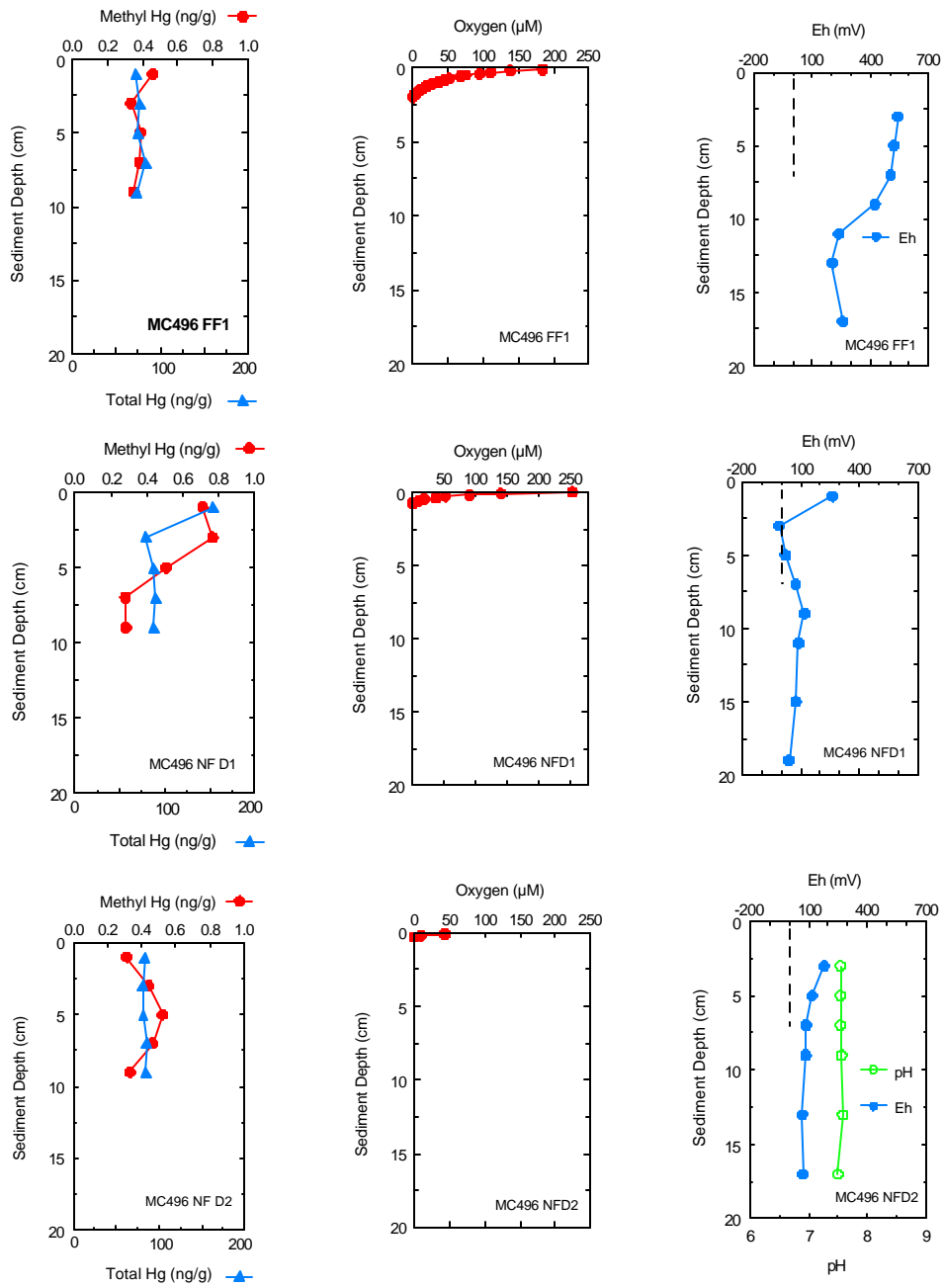


Figure 22. Vertical profiles for concentrations of total mercury, methylmercury, dissolved oxygen and Eh in sediment cores from site MC496 on the upper slope.

At site EW963, very low Eh values (about -100 mV) and oxygen depletion in the top 1 mm of sediment are found in sediment at station NFD2 in concert with low levels of MeHg (Figure 23). No interstitial water was collected from these sediments; however, it is reasonable to expect a significant amount of total H<sub>2</sub>S. A somewhat similar scenario is also observed at station NFD1 (Figure 22). In contrast, at station FF1, oxygen persists to a depth of 3 cm, a modest redoxcline is observed with nitrate reduction and concentrations of MeHg are the highest observed at this site. Thus, at site EW963, the drilling mud may have led to a slight weakening of the methylation process and thus the FF sediment contains significantly more MeHg than the NF sediment.

Finally, at GC112, the redoxcline for most FF and NF stations is quite strong (Eh of 300 to 400 mV in the top 10 cm) with Eh values in the top 10 cm at NF stations are close to or slightly less than 0 mV (Figure 24). For the sediments studied for MeHg, at station NFD1, no redoxcline is observed and the Eh is rather uniform at -100 mV. Under this condition, the amount of MeHg in the surface 5 cm is lower than in sediment from station FF1. However, higher levels of MeHg are observed in sediment from station NFD2. These trends are more complicated than observed at the other sites and are beyond the scope of this report.



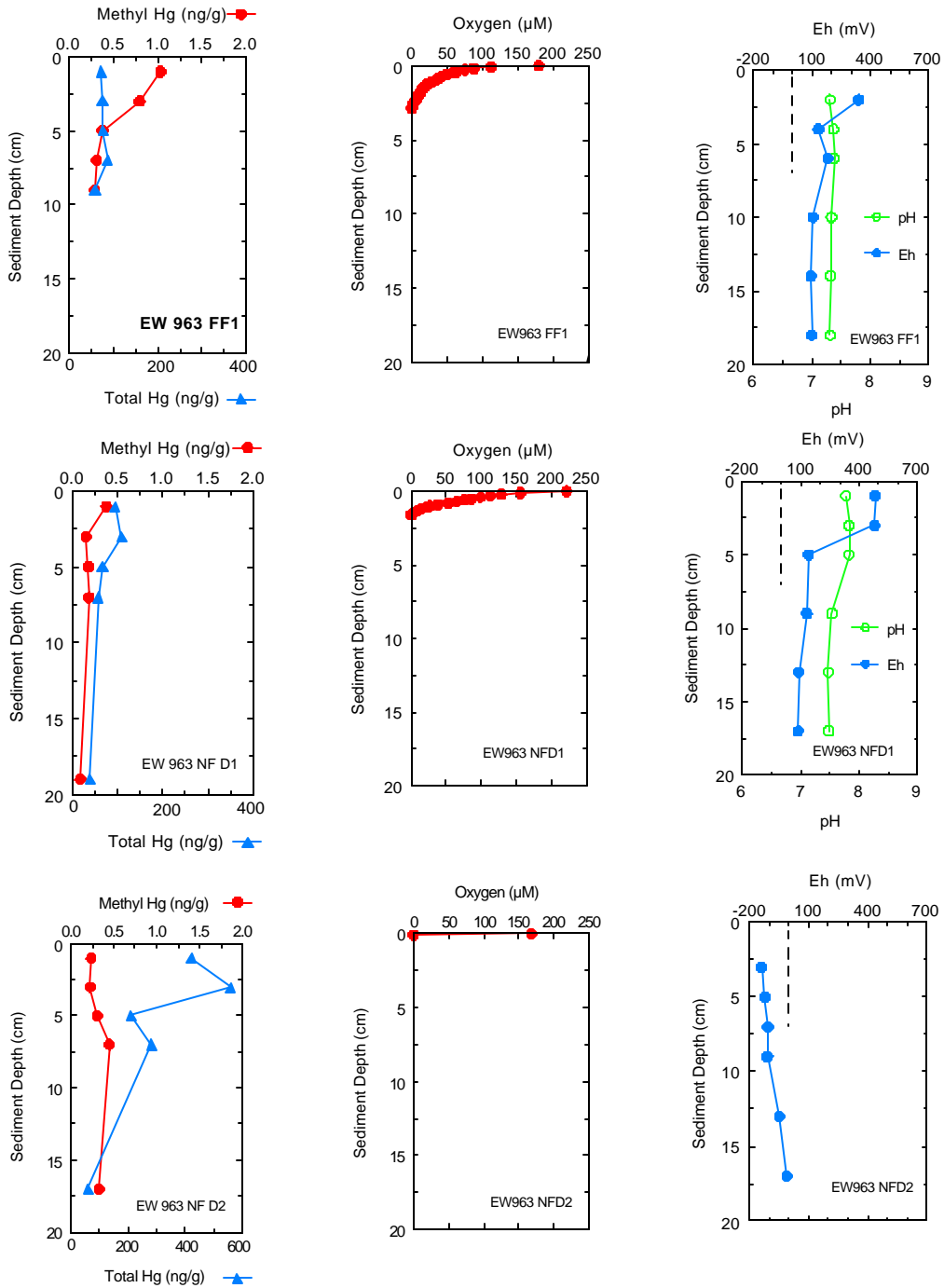


Figure 23. Vertical profiles for concentrations of total mercury, methylmercury, dissolved oxygen, Eh and pH in sediment cores from site EW963 on the upper slope.

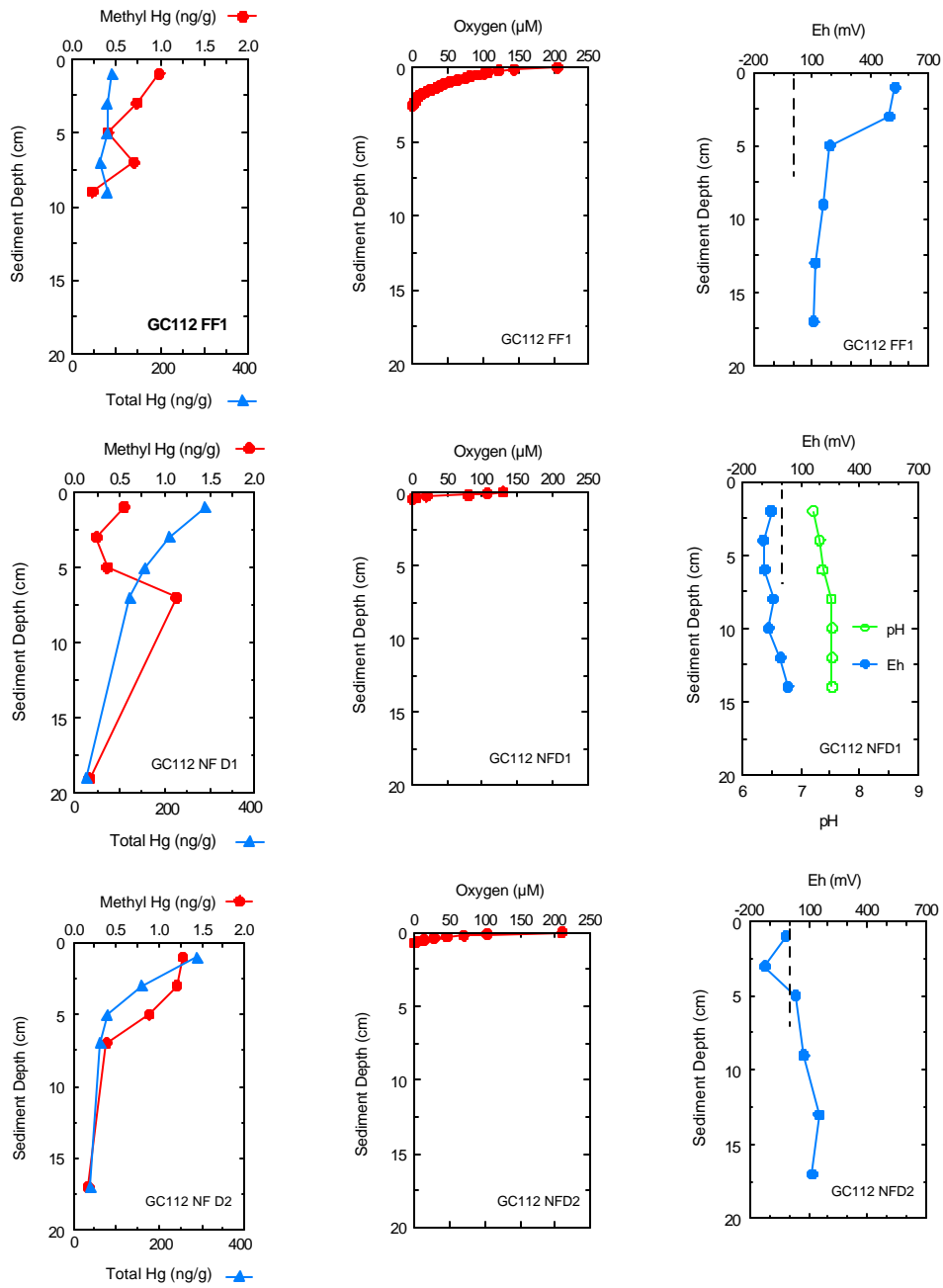


Figure 24. Vertical profiles for concentrations of total mercury, methylmercury, dissolved oxygen, Eh and pH in sediment cores from site GC112 on the upper slope.

## CONCLUSIONS

The results from this study provide the first data showing the distribution of MeHg in sediments near offshore-drilling sites in the Gulf of Mexico. The new information acquired during this study advances the process of determining whether drilling discharges lead to enhanced levels of MeHg in sediments near offshore-drilling sites. Preliminary answers to the four questions raised in the Introduction can be used to support discussion and decisions regarding the need for additional investigations.

- Are the excess amounts of total Hg found in sediment near drilling sites associated with barite?

The data presented here support the argument that excess total Hg in sediments at the drilling sites studied is associated with barite. Concentrations of total Hg in sediments from reference sites for this study range from 11-92 ng/g relative to values of 48-558 ng/g for sediment collected within 100 m of drilling sites. Strong linear relationships (r values of 0.89-0.97) are observed between concentrations of Ba and total Hg in sediment from NF stations where total Hg levels exceeded background levels by a factor of 3-10. Barium levels in these NF sediments range from 20-28%, relative to ambient Ba concentrations of ~0.05-0.15%. The presence of barite was definitively identified in the sediment as part of the SBM Program. The strong linear relationships between total Hg and Ba, coupled with the high levels of Ba (as barite) in these sediments, support barite as a common source for both metals and facilitate estimation of the total Hg content of the industrial barite used during drilling. Average concentrations of total Hg in the industrial barite used at each site, as calculated from the Hg/Ba ratio, are below the limit of 1000 ng/g set by EPA for Hg in barite.

- Are concentrations of MeHg elevated in sediment adjacent to offshore drilling sites?

The results from this investigation show that concentrations of MeHg in surficial (0-2 cm) sediment do not vary significantly between nearfield and farfield stations at any of the six sites studied. When subsurface samples (2-20 cm) are included, no significant difference between MeHg concentrations at nearfield and farfield stations is observed at five of six sites. At a sixth site, significantly higher concentrations of MeHg are found at nearfield than at farfield stations due to the presence of sandy sediment with low levels of total Hg and MeHg at three farfield stations from this one site.

The average concentration of MeHg for all FF sediments ( $0.44 \pm 0.27$  ng/g) is nearly identical to the average for all NF sediments ( $0.45 \pm 0.41$  ng/g), although greater variability in values is found at NF stations due to the patchiness of drilling discharges. The range in concentrations of MeHg is 0.11-1.05 ng/g for all FF sediments and <0.03-2.7 ng/g for all NF sediments. Levels of total Hg are 60-70% higher in ambient (FF) sediments from the upper slope versus the shelf and MeHg concentrations in ambient sediments from the upper slope ( $0.59 \pm 0.26$  ng/g) are double values of  $0.28 \pm 0.17$  ng/g

in shelf sediments. These trends in concentrations of total Hg and MeHg from the shelf to the upper slope identify an interesting natural variability in the Gulf of Mexico that may be one of the more important contributions of this study to global Hg issues.

Results from several stations at one shelf site (EI346) and one site from the upper slope (EW963) show that redox conditions in sediment at NF stations (especially production of total  $H_2S$ ) can lead to levels of MeHg at NF stations that are 3-10 times lower than in ambient (FF) sediment. In contrast, at site GC112 on the upper slope, concentrations of MeHg are higher by a factor of 1.2 to about 2.5 in a few NF samples relative to FF samples. The combination of factors that led to higher values in the sediments from site GC112 seems to be higher levels of TOC and total Hg, along with what may be optimal redox conditions. In contrast, however, four NF samples from the GC112 site have lower than ambient levels of MeHg.

Overall, the statistical results from this study of six offshore drilling sites, coupled with data from sites EI346 and EW963 that show lower levels of MeHg in some NF sediments than FF sediments, suggest that elevated levels of MeHg in sediments around drilling platforms are not a wide-spread phenomenon.

- Can increases in sediment levels of MeHg be directly attributed to Hg introduced by oil and gas activities?

The data presented here make a reasonable initial argument for the conclusion that Hg introduced with barite during offshore drilling cannot be directly linked to enhanced levels of MeHg in NF sediments. The opposing argument that sediment levels of MeHg are attributable to Hg introduced during offshore drilling is certainly weak based on results from this study.

Graphs showing concentrations of total Hg versus MeHg are most useful in addressing this question. At sites EI346 and EW963, for example, samples with high levels of total Hg (i.e., 200-500 ng/g) have similar or lower levels of MeHg than found at background (FF) stations. Such observations show that despite 4-10 times higher levels of total Hg, concentrations of MeHg are not elevated and are often depleted relative to ambient sediments. As an example, the sample with the highest concentration of total Hg (558 ng/g), contained only 0.23 ng/g of MeHg, less than half the mean for MeHg at FF stations from that site. These observations support the argument that excess Hg held in barite is not being converted to MeHg. Results for site GC112 are somewhat ambiguous in that concentrations of MeHg are enhanced at a few stations; however, the higher MeHg values are equivalent to ~3% or less of natural concentrations of total Hg. Therefore, these anomalously high levels of MeHg could have either a natural or an anthropogenic source of Hg.

- Do drilling discharges create an environment that is more favorable to the conversion of Hg to MeHg?

The results from this study suggest that, in most instances, changes in redox environment associated with the presence of drilling mud and cuttings do not lead to higher concentrations of MeHg in sediments. Relative to ambient sediments, much lower levels of MeHg are found in NF sediment adjacent to drilling sites where the sediments are anoxic, highly reducing and enriched with dissolved  $\text{H}_2\text{S}$ . In a few cases, more MeHg was found in NF sediment than FF sediment when the sediments were less sulfidic.

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