

The Georges Bank Monitoring Program 1985: Analysis of Trace Metals in Bottom Sediments During the Third Year of Monitoring

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Marine geologists preparing for sediment sampling near a semisubmersible drilling platform on Georges Bank. Art work for cover by K. King and *P.* Forrestel. Drafting included in the body of the report by *P.* Forrestel and J. Zwinakis, U.S. Geological Survey, Woods Hole, Mass.

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The Georges Bank Monitoring Program 1985: Analysis of Trace Metals in Bottom Sediments During the Third Year of Monitoring

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ABSTRACT

Of the 12 elements analyzed in bulk (undifferentiated) sediments collected adjacent to drilling rigs on Georges Bank, only barium was found to increase in concentration during the period when eight exploratory wells were drilled (July 1981 until September 1982). The maximum postdrilling concentration of barium (a major element in drilling mud) reached 172 ppm in bulk sediments near the drill site in block 410. This concentration is higher than the predrilling concentration at this location by a factor of 5.9. This maximum barium concentration is within the range of predrilling concentrations (28-300 ppm) measured in various sediment types from the regional stations of this program. No drilling-related changes in the concentrations of the 11 other metals have been observed in bulk sediments at any of the locations sampled in this program.

We estimate that about 25 percent of the barite discharged at block 312 was present in the sediments within 6 km of the rig, 4 weeks after drilling was completed at this location (drilling period was December 8, 1981-June 27, 1982). For almost a year following completion of this well, the inventory of barite decreased rapidly, with a half-life of 0.34 year. During the next year, the inventory decreased at a slower rate (half-life of 3.4 years). The faster rate probably reflects resuspension and sediment transport of barite-rich material residing at the sediment surface. Elevated barium concentrations in postdrilling sediment-trap samples from block 312 indicate that such resuspension can occur up to at least 25m above the sea floor. As the remaining barite particles are reworked deeper into the sediments by currents and bioturbation, removal by sedimenttransport processes is slower.

The barite discharged during the exploratory phase of drilling is associated with the fine fraction of sediment and is widely distributed around the bank. We found evidence for barium transport to Great South Channel, 115 km west of the drilling, and to stations 2 and 3, 35 km east of the easternmost drilling site. Small increases in barium concentrations, present in the fine fraction of sediment only, were measured also at the heads of both Lydonia and Oceanographer Canyons, located 8 and 39 km, respectively, seaward of the nearest exploratory well.

INTRODUCTION

This study was designed to establish the concentrations of trace metals in sediments prior to drilling on Georges Bank and to monitor the changes in concentrations that could be attributed to petroleum-exploration activities. Some of the specific questions addressed were (1) Where do discharged drilling muds accumulate on Georges Bank? (2) How much do trace metals increase as a result of accumulating drilling mud? and (3) In areas where drilling-mud components increase, how long do these components remain at an elevated concentration after the drilling is completed?

This U.S. Geological Survey (USGS) study supports the main thrust of the Georges Bank Monitoring Program; that is, to evaluate potential adverse effects of drilling effluents on bottomdwelling organisms. The other studies (and contractors) within the Georges Bank Monitoring Program include (1) the analysis of benthic infauna (Battelle New England Laboratories and the Woods Hole Oceanographic Institution), (2) the analysis of hydrocarbons in bottom sediments and the analysis of hydrocarbons and trace metals in benthic fauna (Scientific Applications, Inc.), and (3) the analysis of previous benthic infauna samples from Georges Bank (Taxon, Inc.) (Michael and others, 1983). The concentrations of trace metals and hydrocarbons in commercially important species of fish and shellfish on Georges Bank have been determined in ongoing programs conducted by the National Oceanic and Atmospheric Administration (Cooper and others, 1981; Cooper and others, 1983). This report is based on data generated by the USGS during all 3 years of the program. Only the data generated in the third year is tabulated in this report. Thbulation and interpretation of data obtained during year 1 and year 2 are contained in the final reports for each year (Bothner and others, 1984a, b).

The first cruise of the monitoring program **FIELD SAMPLING AND SAMPLE PREPARATION** occurred just before exploratory drilling commenced in July 1981, and subsequent cruises have Positioning of the ship on each monitoring cruise been conducted on a seasonal basis (November, was based on the Loran-C navigation network. A February, May, and July) over a 3-year period. On Northstar 6000 (Digital Marine Equipment Corp., February, May, and July) over a 3-year period. On Northstar 6000 (Digital Marine Equipment Corp., each cruise, samples were collected at regional sta-
Bedford, Mass.) receiver was used to read time each cruise, samples were collected at regional sta-
tions 1-8 (fig. 1A) and at 29 site-specific stations delays and to calculate latitude and longitude. The tions 1-8 (fig. 1A) and at 29 site-specific stations delays and to calculate latitude and longitude. The (fig. 1B). Regional stations 19, 20, and 21 were latitude and longitude values reported in this paper (fig. $1B$). Regional stations 19, 20, and 21 were latitude and longitude values reported in this paper added to the program during the July 1983 cruise, are not as accurate as those calculated by using added to the program during the July 1983 cruise. are not as accurate as those calculated by using
Locations indicated by a triangle on figure $1A$ are a more modern algorithm, and workers who wish Locations indicated by a triangle on figure $1A$ are sites of sediment cores that were taken on other cruises during the postdrilling period. The 18 should rely on the time-delay values rather than regional stations were positioned to evaluate changes with time over different environments within the entire region. For example, stations 13 time delays for each station. At station 5, for exam-
and 13A are thought to be areas of deposition for ple, $\pm 0.3 \mu$ s converts to an error in positioning of and 13A are thought to be areas of deposition for material winnowed by currents from Georges Bank ± 140 m drms (distance root mean square; see (Bothner and others, 1981; Twichell and others, Bowditch, 1977, p. 1231). Navigation data for each (Bothner and others, 1981; Twichell and others, 1981), as are stations 14 and 14A in the Gulf of sample analyzed for chemistry are compiled in Maine and stations 7A and 9 in the heads of appendix tables lA-IC. Lydonia and Oceanographer Canyons. Station 15 Special steps were taken to minimize contaminais in an area of eroding coarse sediment. Given the tion of sediment samples at sea. The samples for mean current flow to the west on the southern chemical analyses were collected with a 0.1m^2 flank of Georges Bank (Butman and others, 1982a), stainless steel Van Veen grab sampler with teflon the stations in transect I (stations 1, 2, and 3) are coating on all surfaces in contact with sediment. considered to be upstream controls for stations A polyethylene-coated cable was used to lower the among the major lease blocks (transect II) and for grab to the sea floor. Upon recovery of a sample, stations downstream of the lease blocks (transect the overlying water was siphoned off with a glass Ill). (Station 13A was added on cruise 4. Because tube, and the upper 2 em of material was (1) colthe sediment texture varied considerably over lected with a noncontaminating utensil, (2) placed short distances at stations 7 and 14, the positions in an acid-washed polyethylene container, and (3) were changed in the second year of the program frozen until analyzed. Because individual grab to locations labeled 7A and 14A; see fig. 1A. Sta- samples were subsampled for both trace-metal and tions 15 and 14A were discontinued after the hydrocarbon analyses, the grab sampler was rinsed eighth and ninth cruises, respectively.) with distilled methanol and hexane before each use.

The site-specific survey, designed to monitor Sediment cores were collected on other USGS changes close to a rig, was centered around the cruises in the study area with a hydraulically platform operated by Mobil in block 312 (regional damped gravity corer similar to the one described station 5), where drilling took place between by Pamatmat (1971). This apparatus has a slow December 1981 and June 1982. A less detailed rate of penetration controlled by a water-filled local survey was conducted with three stations piston, and it collects cores as long as 70 cm (in

(regional stations 16, 17, and 18) near the Shell Oil Company platform that operated in block 410 between July 1981 and March 1982.

Eight exploratory wells have been drilled to date on Georges Bank. The first was started on July 22, 1981, and the last well was completed on September 27, 1982. Each of the exploratory wells was classified as a dry hole with no commercial quantities of hydrocarbons. There has been no additional drilling on Georges Bank in the period between September 27, 1982, and February 15, 1985.

to plot or to reoccupy the stations of this program
should rely on the time-delay values rather than when the ship was within ± 0.3 μ s of the target time delays for each station. At station 5, for exam-

chemical analyses were collected with a $0.1-m^2$ the overlying water was siphoned off with a glass

FIGURE 1A.-Regional sampling station array. Site-specific array in block 312 is centered at station 5. Triangles indicate locations of cores analyzed during the third year of monitoring. Station 7 is within the area covered by the dot labeled 7 A.

Cores containing the undisturbed water-sediment particles larger than 2 mm were removed. Drill interface were collected in thin-walled fiberglass cuttings, identified by their angular edges and core barrels and were frozen after collection. The unusual color, were not removed. These samples samples were later extruded, thawed, and cut into are referred to as bulk sediments (undifferen-1-cm sections for analysis. tiated with respect to size) throughout this

Core 8309-B was collected from the Continen- report. tal Slope (fig. lA) by using a conventional box To maximize the analytical resolution in identicorer. A subcore was sectioned into 1-cm depth fying drilling mud components, sand and coarser intervals. The depth distribution of metals also material were removed from selected samples. was determined on samples removed in 2-cm depth Filtered distilled water was used to wash the silts intervals from grab samples. and clays through a $60-\mu m$ nylon sieve. (A $63-\mu m$

homogenized, and subsampled under a laminar in the standard textural analysis procedures, was flow hood. Aliquots from individual grabs and unavailable in a nonmetal material.) The resultant sample blends, made up of equal weights from slurry was dried in a teflon-coated oven and then the individual grabs, were separated for chemi- ground and analyzed by the same methods used cal and textural analyses. Samples for chemical for bulk sediments. Corrections were made for the analyses were dried to a constant weight at 70 $^{\circ}$ C weight of salt contributed by the interstitial water in an oven having teflon-coated surfaces and a by using the following relation between chlorinity filtered nitrogen atmosphere. Dried samples were (Cl) and salinity (S):

mud) with minimal disturbance of the sediment. ground in an agate grinder after shell or sediment

In the laboratory, the samples were thawed, sieve, used to separate sand from finer material

FIGURE $1B$.-Site-specific sampling station array around regional station 5 (block 312). Stations 5-7, 5-13, 5-15, 5- 17,5-19, 5-21, 5-23, 5-24, 5-26, and 5-27 are secondary stations (of lower priority) and have not been analyzed routinely.

$S=0.03 + 1.805$ (Cl)

(Sverdrup and others, 1942). Chloride was measured in samples of the separated fine fraction by using the method of Aruscavage and Campbell (1982). This technique utilizes a specific ion electrode that measures most of the bromide as chloride and thus estimates the total chlorinity of the sample. The ratio of measured chloride to the total precipitated sea salts used to make salt corrections was 0.5535. The algorithm for making corrections for each metal concentration is

$$
C=U/(1-(Cl/0.5535))
$$

where C is the corrected metal concentration, U is the uncorrected concentration, and Cl is the measured chloride concentration in percent multiplied by 10^{-2} .

The field numbers (for example, M09-13-00-G and M10-05-28-BL) that identify samples in each data table have the following code. The first three characters indicate the cruise number; M09 stands for monitoring cruise 9. The station number appears after the first dash. In the examples given, 13-00 is a station in the regional sample array; station 05-28 is one of the site-specific stations around Exactly 0.5 g of ground bulk sediment or 0.2 g of regional station 5 (see fig. 1B). A single alpha the fine fraction was added to a covered teflon beaker

character at the end of the field number identifies one of three replicates taken at each station for trace-metal analysis. Alternatively, the notation BL at the end of the field number indicates a blended composite sample made up of equal weights from each of the three replicates. Field numbers ending in X indicate that analyses were performed on the fraction of sediment finer than 60 μ m.

GRAIN-SIZE ANALYSIS TECHNIQUES

Textural analyses were performed on wet sediments to avoid the formation of clay aggregates. Homogenized samples were wet sieved by using a dispersant (5-percent Calgon) through a $63-\mu m$ sieve to remove silt and clay. The coarse fraction (containing shells, if present) was dried, weighed, and then sieved through a 2-mm screen to remove the gravel, which was not further sized. The sand fraction was analyzed with a Rapid Sediment Analyzer (Schlee, 1966). A gravimetric determination of the silts and clays was made by filtering. The size distribution of the silts and clays was determined with a Coulter Counter. Statistical parameters (mean, median, standard deviation, and so forth) were determined by the method of moments (Krumbein and Pettijohn, 1938). All textural data are expressed in phi (ϕ) units, which are defined as $-Log₂D$ where D is the grain diameter in millimeters.

Samples from sediment traps, sediment cores, and depth profiles from grab samples were often too small for a complete textural analysis. In such cases, the samples were passed through a $60-\mu m$ nylon sieve, and the percentage of dry sediment coarser and finer than 60 μ m was determined gravimetrically.

TRACE-METAL ANALYSIS PROCEDURES

The analyses of trace metals in marine sediments were carried out by the U.S. Geological Survey Branch of Analytical Laboratories, Reston, Va Concentrations of the following elements were determined: aluminum (AI), barium (Ba), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Ph), manganese (Mn), mercury (Hg), nickel (Ni), vanadium (V), and zinc (Zn). The various procedures employed in each of the analyses are detailed below and summarized in table 1.

PREPARATION OF STOCK SOWTION A

TABLE *l.-Summary of analytical conditions*

2800°C atom temperature

TABLE 1. *-Summary of analytical conditions-Continued*

Element	Instrument	Instrument conditions	Extraction procedure	Procedure determination limit in sample, µg/g	Average blanks, as measured in μ g/g in solution
		Pyrolytic curtin tube Normal gas flow (high) $W.1.-318.4 \text{ nm}$ $Slit=0.7$ nm.			
	$Zn------$ Flame AA.-------	Oxidizing; air-acetylene flame $W.1 = 213.9$ $Slit=0.7$ nm.	Butyl acetate---		.01

and digested overnight with 5 mL of $HClO₄$, 5 mL of $HNO₃$, and 13 mL of HF at approximately 140 ^oC. The covers were removed, and the temperature was increased to between 180° and 190° C, first producing fumes of $HClO₄$ and then evaporating the solution to dryness. The residue was dissolved and diluted to exactly 25 mL with 8 N HCI. This solution is referred to as stock solution A.

'1\vo blanks containing all reagents were analyzed along with samples. All reagents were analyzed for contaminants before use, as is always necessary. The Canadian reference sediment standard MESS-I was analyzed in each set of samples. A series of solutions was prepared that approximated the concentration levels expected in the samples; this series was used as the standard in calibrating the inductively coupled plasma (ICP) spectrometer and atomic absorption (AA) spectrophotometer.

PREPARATION OF STOCK SOLUTION B

Stock solution B was made by adding 10 mL of butyl acetate (distilled to remove impurities such as copper) to 15 mL of stock solution A in a 60 mL separatory funnel. This solution was then vigorously agitated by an automatic shaker for 6 minutes to extract iron. The layers were separated, and the extraction step was repeated with an additional 10 mL of butyl acetate. The aqueous layer was evaporated to dryness at 150 \degree C in a 50-mL beaker. The residue was dissolved and diluted to 25 mL with 1 *N* HCl.

BARIUM

The measurements for Ba were made by ICP spectrometry by using 2 mL of stock solution A diluted to 4 mL with distilled $H₂0$.

ALUMINUM, IRON, CHROMIUM, NICKEL, AND VANADIUM

Concentrations of AI and Fe were determined by ICP spectrometry by using 1 mL of stock solution A diluted to 10 mL with $H₂O$. The measurements for Cr, Ni, and V were made by injecting 20 μ L of diluted (1:10) stock solution A into a graphitefurnace AA spectrophotometer.

LEAD, COPPER, AND CADMIUM

Fifteen mL of 0.5-percent (weight : volume) diethyldithiocarbamic acid diethylammonium salt $(DDTC)$ in chloroform were added to 10 mL of solution B in a 60-mL separatory funnel and mixed for 10 minutes by an automatic shaker. The chloroform layer was drained into a 30-mL beaker, and the aqueous layer washed with 10 mL of chloroform. The second chloroform layer was combined with the first, and the total volume of chloroform was evaporated to dryness at 90 °C. The organic matter was destroyed by adding 0.1 mL of concentrated $HNO₃$ and was evaporated to dryness. This residue then was dissolved in 2 mL of warm 1 N HCI. The beaker was rinsed four times with 2 mL portions of distilled $H₂O$, and the solution was transferred to a small polyethylene container. The measurements for Ph, Cu, and Cd were made by injecting 20 μ L of the final solution into a graphitefurnace AA spectrophotometer.

MANGANESE AND ZINC

The measurements for Mn were made by ICP spectrometry with a solution made by diluting 2 mL of stock solution B to 4 mL with H_2O . Zinc was measured by flame AA directly from stock solution B.

MERCURY

Mercury concentration was determined on a separate portion of the sample. Two hundred milligrams of sediment (100 mg, if sample concentrations were expected to be >50 parts per billion) were decomposed in a 1-oz teflon screw-top vial with 2 mL of concentrated $HNO₃$ (J. T. Baker Chemical Co.) and 2 mL of $HClO₄$ (G. Frederick Smith Chemical Co. (GFS)) double distilled from Vycor, a pure silica glass. The mixture was heated in a capped vial until the solution reached 200 °C. The solution was then heated with the cap off for about 45 minutes, after which the samples were removed from the heat source. Immediately, 1 mL of concentrated $HNO₃$ was added; the vial was filled with $H₂O$ and capped tightly until used. The sample solution then was added to a flask containing 125 mL of $H₂O$ and 4 mL of 10-percent (weight: volume) SnC12 in 20-percent HCL Nitrogen was passed through the solution to remove elemental Hg, which was collected on gold foil located in the center of the coils of an induction furnace. Activation of the furnace released the Hg, which was measured by a cold-vapor AA technique. Blanks, standard rocks, and internal sediment standards were analyzed for each set of samples. A series of solutions was prepared that had the same Hg-concentration range expected in the samples.

The concentrations of Hg in bottom sediments determined during the first year of the monitoring program were typically less than the detection limit of 0.01 ppm. During the second and third year of monitoring, we tested new procedures designed to lower the detection limit.

The contribution of Hg from various brands of nitric acid was determined. Baker "analyzed reagent grade" contained less than 0.5 ppb Hg, the lowest concentration of the acids tested. Baker "ultrex" contained 2 ppb Hg, and Mallinckrodt nitric acid contained 1.3 ppb Hg. During the checks of $HClO₄$, we found that some bottles of GFS double-distilled $HClO₄$ contained 5 ppb Hg. We ultimately selected GFS $HClO₄$ double distilled from Vycor, which was found to contain less than 0.5 ppb Hg. The Hg concentration of each new bottle of acid and of every other reagent was determined before the reagent was used for analysis. The Hg contribution from the combined reagents was reduced to 0.5 ng \pm 0.1 ng.

We tried to lower the detection limit by increasing the sample size. Subsamples weighing 1 g were analyzed with various combinations of nitric and perchloric acids. The results were not encouraging because digestion was incomplete when small acid volumes were used or because blanks were too high when large acid volumes were used. The high sediment concentration in suspension during the gasstripping procedure may have adsorbed some of the Hg and accounted for the lower concentration measured for large samples.

Another method of increasing sample size was successive plating of Hg vapor from three 200-mg aliquots onto the gold foil of the induction furnace. This technique yielded poor reproducibility among replicates and decreased the number of samples that could be analyzed in a day by a factor of 3.

The selection of reagents having the lower Hg concentration, the addition of a digital readout voltmeter, and the optimization of the optical system in the cold-vapor AA detection system (manufactured by Laboratory Data Control, Inc.) reduced the detection limit of our procedure from 0.01 ppm to 0.005 ppm.

The magnitude of Hg lost while oven drying sediment samples also was evaluated. Aliquots of bulk sediments from station M06-13A and aliquots of the fine fraction from station M05-16 were analyzed wet, and the results were compared to samples that were oven dried at different temperatures. We found no evidence of Hg loss as a result of drying bulk sediments at temperatures between 40 and 100 °C, but we observed some loss (about 42 percent) when drying fine-fraction samples at 100 °C.

ADDITIONAL METHODS

Results of Ba and Cr analyses on selected Georges Bank samples were cross-checked by an energy-dispersive X-ray fluorescence technique (Johnson, 1984). The determination of Ba concentration was made with a Kevex 0700 energydispersive X-ray fluorescence spectrometer. Powdered samples of about 1 g were analyzed with a gadolinium secondary target for excitation of the K-alpha line. The ratio of Ba intensity to the gadolinium Compton scatter intensity was used to correct for absorption effects. This ratio then was compared to a standard calibration curve to determine the concentration of Ba.

The X-ray fluorescence technique was used on all samples found to have more than 500 ppm Ba during the first analysis by acid decomposition and ICP spectrometry. The X-ray fluorescence technique is highly accurate in samples enriched with $BaSO₄$, which is a difficult mineral to dissolve completely if present in high concentration.

Justification of the alternative methods is presented in Bothner and others (1982).

ANALYTICAL ACCURACY AND PRECISION

Analytical accuracy was determined by analyzing rock standard MESS-1. All of the metals are within one or, at most, two standard deviations of the "best values" established for this standard (table 2). Excellent agreement also exists among aliquots of samples submitted as blind replicates (appendix table 2).

Analytical precision was determined by periodically analyzing replicate aliquots taken from a single sample. Coefficients of variation shown in table 2 indicate that the standard deviation is typically less than 10 percent of the mean value, except for concentrations at or near the detection limit of the method.

'lb maintain our internal quality control and to provide typical sample material for interlaboratory comparisons, four sediment standards representing different textural types were prepared from large samples of Georges Bank sediment. The levels of trace metals are being established by several analytical methods. Splits of these materials are available to those interested in cross-calibration studies.

RESULTS AND DISCUSSION

SEDIMENT TEXTURE

The texture of the surface sediments sampled in the third year of monitoring (appendix table 3A, textural data of other samples in appendix tables *3B* and 3C) is very similar to the texture measured in the first two years (fig. 2) as defined by the average mean ϕ values at each station for a given year. Low yearly variability of the mean ϕ grain sizes occurs, as demonstrated by the close match of the data patterns. Mean ϕ values range from about 1 ϕ (coarse sand) at station 5-1 (fig. 1B) to about 6.3 ϕ (medium silt) at station 13A, located south of Martha's Vineyard. The error bars (standard deviation about the mean of samples from each of four seasons) indicate tha_t the within-station variability is much smaller than the between-station variability.

The sediments on Georges Bank are typically greater than 95 percent sand and contain minor amounts of gravel, silts, and clays. The sand is primarily medium to coarse grained, ranges in coloration from a clear or translucent yellow to a tan iron-oxide stain, and has an angular to subrounded grain shape. The minerals making up the sand fraction are primarily quartz with minor amounts of feldspar and trace amounts of heavy minerals. Authigenic minerals such as framboidal pyrite and ferromanganese micronodules have been found at various locations on the bank in very low concentrations (Poppe and others, 1984).

The concentrations of silts and clays in the regional samples are generally less than 4 percent (fig. 3), and the mean station values for year 3 are similar to those of years 1 and 2. The relative paucity of silts and clays reflects the strong winnowing processes associated with tidal and storm-generated currents on Georges Bank (Butman and Folger, 1979; Butman and Moody, 1983; Butman and others, 1982a; Parmenter and others, 1984). We sampled transects I, II, and III (fig. lA), and found that the content of sediment finer than 63 μ m (silt plus clay) increases slightly toward the shelf edge, perhaps in response to increasing water depth.

Areas that showed a significant concentration of fine sediments (finer than 63 μ m) during each sampling cruise were located at regional station 14A (80-90 percent fines) in the Gulf of Maine, regional station 7A (22-30 percent fines) at the head of Lydonia Canyon, and regional stations 13 and 13A (34-50 and 92-97 percent fines, respectively) located south of Nantucket Island. This last area, known as the Mud Patch, is thought to be one of the depositional sites for sediments from upstream areas on Georges Bank (Bothner and others, 1981; Twichell and others, 1981). The close correlation between the concentrations of fine sediment, organic carbon, and trace metals was discussed in the report for year 1 (Bothner and others, 1984a).

Determination of the major minerals in the clay fraction of the sediments by X-ray diffraction indicates that illite is predominant, with moderate amounts of chlorite and small concentrations of kaolinite present (Bothner and others, 1979). Montmorillonite is present only in trace amounts, or it is absent. The origin of the illite and chlorite in the clay fraction is thought to be unweathered material eroded from Paleozoic and older rocks in the northem Appalachian region and transported to the Continental Shelf during glacial periods (Hathaway, 1972).

The concentration of gravel is variable and ranges from 0 to almost 16 percent (appendix table 3A). The gravel is composed of rock fragments or shell hash or a mixture of both. Drill cuttings were

Sediment Al Ba Cd Cr Cu Fe Mn Ni Pb V Zn standard (%) (ppm) (ppm) (ppm) (ppm) (%) (ppm) (ppm) (ppm) (ppm) (ppm)

TABLE *2.-Analysis of sediment standard and replicate sediment samples*

1Coefficient of variation.

 2 Values reported by the Marine Analytical Chemistry Standards Program, National Research Council, Canada.

observed in the gravel fraction at the drill sites in blocks 312 and 410. A few cuttings were found during both year 2 and year 3 at station 17, 2 km to the east of the drill site in block 410. On cruise 9, cuttings were observed at all stations within 500 m of the drill site in block 312. The cuttings are angular, range in size from 2 to 8 mm, and are primarily gray in color. By using Xray diffraction analysis on a few cuttings, L. J. Poppe (USGS, written commun., 1984) identified calcite as the predominant mineral with lesser amounts of dolomite and layered silicates. These minerals are common throughout the subsurface Jurassic and Cretaceous sediments (Arthur, 1982). The highest concentrations of cuttings, which were localized at the drill sites, represent less than 1.5 percent of the total sample weight. The cuttings did not occur in a recognizable pile in the vicinity of the drill site in block 312, according to R. A. Cooper, National Marine Fisheries Service (written commun., Oct. 14, 1983), who conducted visual and photographic surveys of the drill site from a submersible.

TRACE METALS IN BULK SEDIMENTS

During the first year of this program, we established that the concentrations of trace metals in sediments collected before drilling began were low compared to their average concentrations in crustal rocks and that they were characteristic of uncontaminated coarse-grained sediments. We found the variability in trace-metal concentrations from station to station to be closely correlated with the content of fine-grained material and organic carbon in the sediments, as commonly occurs (Crecelius and others, 1975). Pb values higher than average crustal abundances were measured only at the location south of Martha's Vineyard where fine-grained sediments are

accumulating and where previous studies (Bothner and others, 1981) have suggested tetraethyl lead from gasoline as a source of the elevated Ph found in this area

Throughout the 3 years of monitoring, the concentrations of Ba in bulk sediments from the upstream control stations (transect I, stations 1- 3) were fairly consistent with time (fig. 4, appendix table 4A). On the basis of these data, we judge that no increase in Ba had occurred at these stations. We found no increases in the concentration of other metals as a result of drilling at these upstream locations during the 3 years of monitoring.

. In contrast, there were measurable changes in the concentrations of Ba in block 410 (stations 16, 17, and 18, fig. 5). Drilling began in this block immediately after the first sampling cruise in July 1981 and continued (with some interruptions) until March 31, 1982. The mean current flow on this part of the Continental Shelf is to the west, although tidal and storm currents can reverse the mean flow (Butman and others, 1982a). Relative to the mean current flow, stations 17 and 18 are upstream and downstream of the rig position, respectively (fig. 5).

At station 16, located within 200 m of the drill rig in block 410, average Ba concentrations apparently increased steadily from a predrilling concentration of 32 ppm to the maximum concentration of 172 ppm measured on cruise 6, an increase by a factor of 5.9. Drilling was completed before cruise 4, and we expected that the maximum concentration of Ba would be found on the fourth cruise. However, no statistical difference exists in the Ba concentration between cruises 4 and 6 at the 95-percent level of confidence $(\alpha=0.05)$ because of the large within-station variability in the Ba distribution (fig. 5).

The concentration decreases at the time of cruise 7 remain at a fairly constant level of about 80 ppm from cruises 8 through 12, except for cruise 11. The

FIGURE 2.-Mean grain size of samples collected during years 1 (circle), 2 (square), and 3 (triangle). Error bars represent the standard deviation among samples collected in a given year. Stations are listed in order of increasing water depth.

anomalously high value of 430 ppm (fig. 5) was excluded from calculation of the mean. The scatter in the data probably indicates that Ba is not distributed homogeneously over the sampling area This heterogeneity is probably caused by the intermittent discharge of drilling fluids into a current field that continuously changes direction of flow throughout the tidal cycle.

In agreement with the expected transport of drilling fluids to the west by the mean current flow, Ba concentrations were higher to the west than to the east. At station 18 (2 km to the west of the drill rig), maximum increase in Ba concentrations was about a factor of 2 as a result of drilling. The concentrations of Ba decreased to predrilling levels, at the time of cruises 8 and 9 and then increased again. At the time of cruise 12, Ba concentrations were 36 percent higher than predrilling levels and the difference between mean values of cruises 1 and 12 is statistically significant at the 99-percent level of confidence (α =0.01). In contrast, at station 17 (2 km to the east of the drill rig), the maximum increase was only about 1.3 times the background Ba concentration. A decrease in concentration was also seen at station 17 for cruises 8 and 9, then followed by an apparent increase. However, the concentration measured on cruise-12 samples is not significantly different from the cruise-1 concentration at the 95-percent level of confidence.

The concentration of Cr in these same samples (fig. 5) did not increase as a result of drilling even at the drill site. Similarly, we observed no changes in the concentrations of other metals in the bulk sediments during this period of monitoring.

In block 312 at station 5, the location of the sitespecific survey, increases in Ba were observable following the initiation of drilling on December 8, 1981 (fig. 6). The greatest increase (factor of 4.7 above background) was observed at the drill site (station 5-1). At this location, there is a large standard deviation among three individual replicates, and a considerable amount of scatter exists in the data following cruise 5. These trends are similar to those observed at station 16, also adjacent to a drill rig, and may reflect the heterogeneity of drilling mud distribution in the sediments near the rig. At stations more than 0.5 km from the drill site, slightly higher increases were observed to the west than to the east, which is consistent with the preferential direction of transport. At all but station 5-10, the maximum concentration was observed during cruise 5, which was conducted immediately after drilling was completed. At most stations, the concentrations decreased rapidly by cruises 6 and 7 and remained essentially constant through cruise 12.

The concentration of Cr (fig. 6) or of other metals in bulk sediments at block 312 did not increase as a result of drilling.

TRACE METALS IN THE FINE FRACTION OF SEDIMENT

Within the sediment fraction finer than 60 μ m (appendix table $4B$), the Ba concentrations increased dramatically at stations near the drill rig at block 410 (fig. 7). At station 16, adjacent to the rig, the average Ba concentrations reached 8,000 to 10,000 ppm between the third and seventh cruises. Lower concentrations were measured in

FIGURE 3.—Percent silt plus clay in samples collected at each regional station during years 1 (x), 2 (triangle), and 3 (circle). Stations are listed in order of increasing water depth.

four out of the last five cruises, but by cruise 12, the concentration of Ba in the fine fraction was still more than 10 times higher than in the predrilling sample. At station 17, 2 km upstream of the drill rig, the Ba concentrations increased less than at station 18, 2 km downstream of the drill rig. The effect of the mean westerly current flow, which would indicate preferential transport to the west, seems to be illustrated by these data

The concentration of Cr (fig. 7) increased slightly at station 16 in an apparent response to drilling, reached a maximum concentration of approximately 2 times background levels by the third cruise, and then decreased to background concentrations again. No increases in Cr concentration were observed at

FIGURE 4.-Concentrations of barium in bulk sediment at upstream control stations on different sampling occasions. Drilling began after the first cruise and ended at all locations before the sixth cruise. Station locations are shown in figure lA.

stations 17 or 18. The concentration of AI, Cu, and Hg in the fine fraction at station 16 also increased and decreased with similar magnitude and timing, as did that of Cr. We did not identify systematic increases of these metals at any other station.

At block 312, the drilling began just after the second cruise and was completed just before the fifth cruise. The Ba concentrations in the fine fraction of sediment clearly increased after drilling began and, at most stations, apparently decreased after the drilling ended (fig. 8). Concentrations of Cr did not increase during the drilling period. The other metals showed no changes attributable to drilling.

The temporal change of Ba in the fine fraction at the site-specific survey suggests a westward transport of Ba-rich fine sediment during this monitoring period. At station 5-28, the easternmost station of this detailed survey, Ba concentrations reach a lower maximum than at most other stations and, with the exception of cruise 10, are at or near background levels for cruises 7-12. At station 5-2, located 0.5 km east of the drill rig, Ba concentrations reach a maximum after the completion of drilling (cruises 4 and 5) and decrease at the time of cruises 6 through 10. Ba concentrations at station 5-29, 6 km to the west, continue to increase between the completion of drilling and the time of cruise 8. This continued postdrilling increase and maintenance of high concentrations through cruise 12 may be caused by the transport and deposition of Ba-rich fine sediment originally deposited closer to the rig. These results suggest that Ba was being dispersed from the immediate vicinity of the drilling rigs.

1b see how far the Ba from drilling mud could be traced, we analyzed the fine fraction of sediment at stations 10 and 12, approximately 65 km west of the block 312 drill site, and stations 2 and 3, approximately 35 km to the east of the easternmost drill site. At stations 12 and 10 we measured maximums

FIGURE 5.-Concentrations of barium (circle) and chromium (x) in bulk sediment on different sampling occasions near the drill site at block 410. Drilling began after the first cruise and ended prior to the fourth cruise. Error bars are one standard deviation among three individual replicates. Anomalous value of 430 ppm in one of the three replicates at station 16 was omitted from calculation of the mean. $ND = no$ data.

in the Ba concentrations at the time of cruises 8 and 10, respectively (fig. 9A). We were surprised to find that maximums in the Ba concentrations, although of lower magnitude, were also recorded at similar times at stations 2 and 3. The maximum value at station 3 on cruise 7 is statistically higher than the mean of the first 6 cruises at the 99.5 percent level of confidence (t test).

The Ba/Al ratio (fig. 9B) that was plotted for each sampling period is also used to show relative changes in the Ba levels. Typically Al is highly correlated with the percent of clay minerals in marine As a special study initiated during this program, sediments. As a result, AI is used in the ratio to we used nylon sieves to separate bulk sediment from remove the variability introduced by different Georges Bank into various grain-size classes and anamounts of clay in the fine fraction on different alyzed the material in each size class for trace sampling dates. The Ba/Al ratio also eliminates the metals. We used this approach to determine how small error introduced in making the chloride cor-
those trace metals (notably Ba) whose concentrarection necessary to determine metal concentrations tions are elevated by drilling are distributed within of the fine fraction in mass units. The BaJAI ratio the sediment-size fractions. This information may is at a maximum value at stations 2, 3, and 12 on be useful in predicting the transport and dispersion cruises 7 or 8. The value for the relatively small of metals carried by various sediment-size classes. maximum at station 3 is statistically higher (t test) Judging on the basis of the textural analyses of at the 99.5-percent level of confidence than the mean standard barite by the American Petroleum Instiof cruises 1-6. No Al data are available for samples tute, only about 4 percent of the barite used in well from station 10. The figure of the drilling is in the 60-150 μ m fraction, and the

gest that Ba in the finest fraction of drilling mud mud is known to adhere to drill cuttings, however, may be transported over very wide areas of the which are often greater than 1,000 μ m in size. bank, to the east as well as to the west. Butman Samples were collected on cruises 4 and 10 from and others (1982a) have stated that the mean the 0- to 2-cm interval at stations 16 and 5-2 adjawesterly flow can reverse on the southern flank of cent to drilling sites. To determine the natural dis-Georges Bank in response to strong winds from the tribution of metals in different size classes, sedisouthwest. Transport of sediment to stations on ment was collected on the same cruises from transect I from the easternmost drilling locations control station 2. (blocks 410 and 145), approximately 35 km, could Figures lOA and lOB show the distribution of have taken place during these eastward current sediment in weight percent among various size

flows. We plan to examine meteorological data and any available current records to determine if a strong easterly current flow occurred sometime before cruise 8. It is also possible that the Ba particles carried in the Georges Bank gyre could have been transported from drilling locations in a clockwise circular motion to stations 2 and 3.

TRACE METALS IN DIFFERENT SIZE FRACTIONS OF SEDIMENT

These findings are significant because they sug- remaining 96 percent is finer than 60 μ m. Drilling

FIGURE 6.-Concentrations of barium (circle) and chromium (x) in bulk sediment on different sampling occasions near the drill site at block 312. Stations are located on east-west and north-south transects through the drill site (see figure lB). Drilling began after the second cruise and ended just before the fifth cruise. Error bars are one standard deviation among three individual replicates. ND=no data.

FIGURE 7.-Concentrations of barium (circle) and chromium (x) in the fine fraction (less than 60 μ m) on different sampling occasions near the drill site at block 410. Drilling began after the first cruise and ended prior to the fourth cruise. Error bars are one standard deviation among three individual replicates. ND=no data.

at these three locations. For cruise 4, all three sta- removed the fine material. In the time between tions have similar modes and less than 1 percent cruises 4 and 10, the Ba contained in the $30-60 \mu m$ silt plus clay. The size distributions are similar on fraction decreases from about 50 percent to 10 perboth sampling dates, except that the sample at sta- cent (fig. 12A). The distribution of Ba is bimodal tion 5-2 has a modal size in the 500-1,000 μ m range for each cruise, but the distribution changes from for cruise 10 and a modal size in the 210-510 μ m one in which the fines are carrying a large Ba invenrange for cruise 4. tory as a result of drilling mud accumulation (cruise

different size classes (fig. 11A) is distributed in the of Ba in the uncontaminated sediment (cruise 10). same pattern as the sediments are distributed (fig. The interpretation of data collected at station 16 However, the Ba concentrations of the fine fractions 4 was lower than that collected on cruise 10. This and only minor differences exist between samples in sediment adjacent to the drilling rigs as dis-

among the different size classes at station 5-2 are size (fig. 13A), similar to the distribution at control considerably different on cruises 4 and 10 (figs. $12A$ station 2 (fig. 11A) and a small enrichment of Ba B). The concentration of Ba in the finer sediments in the finer size fractions compared to the unconis much lower on cruise 10 than on cruise 4. The taminated control station. At station 16 on cruise differences indicate that while the rig was operating 10, we measured a higher total concentration of Ba, (cruise 4), fine-grained sediments containing high with higher concentrations distributed in the finer levels of Ba were being deposited (accumulating) in fraction of cruise 10 than of cruise 4 (fig. 13B). The the sediments and that since drilling has ended, the distribution of the Ba inventory for station 16 on

classes for sediments collected on different cruises processes of sediment transport have preferentially At control station 2, the Ba inventory among the 4) to one which begins to resemble the distribution

 $10A, B$). Most of the Ba (more than 80 percent) is is somewhat complicated because the net concencontained in the modal size class of 210-500 μ m. tration of Ba in the sample collected during cruise are higher than in the coarser fractions (fig. 11B), may be related to the high spatial variability of Ba from cruises 4 and 10 at this location. cussed on page 12. The inventory at station 16 for The inventory of Ba and the concentration of Ba cruise 4 has a strong peak in the 210-500 μ m-modal

FIGURE 8.-Concentrations of barium (circle) and chromium (x) in the fine fraction (less than 60 μ m) on different sampling occasions near the drill site at block 312. Drilling began after the second cruise and ended just prior to the fifth cruise. ND=no data.

cruise 10 (fig. 13A) is similar to the distribution at station 5-2 on cruise 10 (fig. 12A). We are planning to analyze a third sample from each station collected on cruise 12 and to resample a blend from cruise 4 at station 16 if sufficient archived material remains.

Among the other metals analyzed in the sizeseparated samples (AI, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn), only AI and Pb concentrations (and V for cruise 10) in the fractions finer than 30 μ m at the drill sites are higher than those at the control station (Bothner and others, 1984b; and appendix table 4C). Concentrations of the remaining metals are distributed similarly at the three stations.

TRACE·METAL CONCENTRATIONS OF SEDIMENT-TRAP SAMPLES

The objective of the sediment-trap experiment was to measure the concentration of drilling mud components in suspended matter and to determine if drilling mud was transported to the head of Lydonia Canyon. Sediment traps were deployed at various heights above the sea floor in the vicinity of block 312 and in Lydonia Canyon (appendix table $1C$). This experiment was part of a joint USGS and Minerals Management Service (MMS) program designed to measure currents and sediment transport on the Continental Shelf and in the major submarine canyons that cut into the southern flank of Georges Bank (Butman and others, 1982b; Butman, 1984). Because the sediment traps used here were no fur. ther than 50 m above the bottom and because of the high current velocities at all the mooring locations, the traps primarily collected sediments that were resuspended from the bottom. However, particles falling from surface waters (such as discharged drilling mud), biological material produced in the water column, and particles introduced from the atmosphere also were collected by the traps.

Among the trap samples from locations in the vicinity of block 312, the concentration of Ba is clearly higher in postdrilling samples than in predrilling samples (table 3). The highest concentration of Ba (1,900 ppm) was measured in sediment trap ST424, which was positioned 1 km west of the drill rig in block 312 while drilling was underway. The sediment in this trap was collected in a long tube that was later sectioned into length intervals that represent different time intervals of the deployment. The last material to enter the trap was deposited at the top of the tube. The variation in Ba concentration from interval to interval suggests that the flux of Ba to these traps was not constant. A variable flux was expected because the rate of Ba discharge and the current field around the drilling rig were not constant.

The trap-sample material that was collected at the drill site in block 312 and 1 km to the west of the drill site after drilling was completed contained Ba concentrations five times higher than the predrilling concentrations. The increase in concentration suggests that the barium sulfate deposited in the sediments was periodically resuspended to at least 25 m above the sea floor (the depth of our shallowest trap near the drilling sites) and transported with the prevailing currents.

FIGURE 9A. AND 9B-Concentrations of barium (9A) and the barium-to-aluminum ratio (9B) in the fine fraction of sediment blends on different sampling occasions at station $2(X)$, $3(*)$, 10 (\square), and 12 (\circ).

Sediment traps also were deployed 6 km east of the drilling rig in block 312 while drilling was in progress (ST426) and after drilling was completed in this block (ST513 and ST515). The Ba concentrations of these sediments are also higher than those of predrilling samples. Some of the material contributing to the elevated Ba concentrations measured in these samples may have originated from the four drilling rigs operating between 5 and 45 km to the south or to the east of these trap locations. Alternatively, storm and tidal currents could have transported material eastward.

There is a weak but positive indication that drilling mud was transported in measurable concentrations to the expected depositional site at the head of Lydonia Canyon (fig. 14, table 3). Drilling began during the second period in which sediment traps were used to collect suspended sediment (fig. 14). The concentration of Ba in the fine fraction of trap sediments from the head of Lydonia Canyon increases slightly from the first deployment until the fourth deployment and then appears to increase more dramatically at the time of the fifth deployment, which includes the period when four wells were finishing drilling activity on the bank (fig. 14). On the basis of these increases in Ba concentration, which were measured in traps at two levels in the water column (10 m and 20 m above bottom), we suggest that a small drilling mud signal was present in the suspended matter in Lydonia Canyon. No such indication is apparent from the analysis of the bulk sediment-trap material-for which the Ba concentrations during the period of drilling are generally within one standard deviation of the concentrations determined in predrilling trap samples (table 3).

TRACE-METAL VARIATIONS WITH DEPTH IN SEDIMENT

During the second and third year of monitoring, sediment cores and grab samples (appendix table *4D;* Bothner and others, 1984b) were subsampled as a function of sediment depth to determine the depth profiles of metal concentrations. A gradient in the depth profile of a metal concentration can indicate the introduction or removal of the metal. Our first objective was to extend our search for drilling-related Ba to locations on the bank where data from seasonal cruises may not be available. Second, we hoped to make some inferences about the extent and rate of downward mixing of newly introduced Ba by benthic organisms and (or) currents by examining profiles at stations adjacent to drilling operations.

We examined the profiles of Ba and Ba/Al in four areas where the introduction of drilling mud was not expected (fig. 15A-D; location of samples shown in fig. 1). Although there is some scatter in the Ba values, particularly in sample $M11-$ 03- 00-AX, the Ba/Al ratio is constant with depth at all four locations. This observation is particularly important because it argues against the possibility that the naturally occurring Ba dissolves in response to reducing conditions in

TABLE *3.-Chemical analyses of sediment-trap samples collected before and after drilling began*

19

1Bothner and others, 1984b.
2Depth interval (cm) in sediment-trap sample. 3W=whole sediment trap homogenized before analysis.

subsurface sediments and migrates upward into oxidizing sediments, where it precipitates. Sufficient reducing conditions in the sediments for the characteristic migration and precipitation of Mn have been observed in the interstitial water of core 83G9-B (K. 0. Buesseler and E. R. Sholkovitz, Woods Hole Oceanographic Institution, written commun., July 1984) as well as in the total sediment phase (appendix table 4D). The absence of a gradient in Ba or Ba/Al at all four locations, which represent different sediment types, suggests that the gradients measured closer to drilling sites are not due to diagenetic reactions.

An additional point regarding core 83G9-B, from 1,250-m water depth on the slope, is that concentrations of Ph are higher in the surficial sediment than in the subsurface sediment (appendix table $4D$). The source of this Pb is probably the burning of lead alkyls in gasoline in coastal metropolitan areas, which began in 1924 and which has dramatically increased each year since 1940 until the recent switch to unleaded gasoline. Atmospheric transport of Ph with the prevailing westerly winds would introduce Ph to surface waters offshore. Similar profiles of lead were observed in sediments near Station 13A collected before drilling began (Bothner and others, 1981).

We also analyzed sediment profiles from locations west of the drilling activity where deposition of transported drilling mud was expected (fig. 16). Both Ba and Ba/AI at station M10-12-00-GX are slightly enriched in the surface 8 em compared to the deeper section of the core (fig. 16C). This enrichment supports the conclusion that Ba has been transported to this station (see p. 13 and fig. 9). At locations OC140-39 and OC140-41 to the east of transect III (fig. 1), the Ba concentrations of fine-fraction samples in the upper 5 em are about the same as those in deeper sections in the sediments, but there is a slight enhancement in the Ba/Al ratio in the surface sediment (fig. $16A$, B). This enhancement is statistically significant at the 99.9-percent level of confidence (t test). At stations M12-19 and M12- 21, small increases in the Ba/Al ratio occur in the surficial sediment, but no increase occurs in the Ba concentration (fig. 16D, F). Profile M12-20 shows no increase in either Ba or Ba/Al (fig. 16E). At stations 19, 20, and 21, an increase in both Ba and Ba/Al in the surface sediments was measured at the time of cruise 9 (reported in Bothner and others, 1984b).

The Ba and Ba/Al profiles at stations M12-05 and M12-16, adjacent to drilling locations in blocks 312 and 410, respectively, show much higher concentrations than at any of the other more distant stations (fig. 17A, B). These profiles illustrate two points. First, fine-grained Ba-rich particles have penetrated to a depth of at least 15 em since the drilling began at these locations. Second, the subsurface maximum in concentration suggests either that new sediments, having a lower Ba concentration, have accumulated on top of the drilling mud components or that new sediments have been exchanged (no net accumulation)

FIGURE *lOA.-*Weight percent of sediment in different size fractions of bottom sediment collected on cruise 4 at control station 2, regional station 16, and site-specific station 5-2 on Georges Bank.

for the drilling mud components by a combination of sedimentation, sediment mixing, and erosion.

A future followup of this study should be undertaken to determine the Ba concentration and the Ba/Al ratio in profiles by using the bulk sample. Comparison of profiles of the bulk sample and the fine fraction is necessary to determine the amount of Ba that is missed by the standard field sampling technique of collecting the upper 2 em of sediment. In addition, longer core samples (30-40 em) should be taken at the drill sites to determine whether the decrease in Ba concentration in the surface sediment is due to actual removal or to downward mixing.

BARIUM INVENTORY AND DECREASE AT BLOCK 312

The high density of stations and the frequent sampling at the drill site in block 312 allowed us to estimate the inventory of barium in the sediments before, during, and after drilling. One objective of this exercise is to determine how much of the Ba actually discharged by the drilling rig was deposited within 6 km of the drill site at the time of well completion. We were particularly interested in an estimate of the rate at which Ba concentrations decreased in the surface sediments after drilling was completed. The barium added by the drilling can be considered to be a tracer for sediment transport processes. Although barium sulfate has

FIGURE lOB.-Weight percent of sediment in different size fractions of bottom sediment collected on cruise 10 at control sta· tion 2, regional station 16, and site-specific station 5-2 on Georges Bank.

may provide some insight into the fate of future is calculated from the field data with the follow· contaminants that reach the sediments on Georges ing relation: Bank.

To determine the inventories of Ba within the 6-km-radius circle (fig. $1B$), the Ba concentrations on each ring of the sample pattern were aver- where A =area of each annulus, $d=$ bulk density aged and then used to estimate a representative of dry sediment (1.6 g/cc), $Z=$ depth interval (0-2 site. We assume that the Ba added by the intro- $BaSO_4/Ba$ =the ratio of molecular weights.
duction of drilling mud is contained within the We estimate that the inventory of BaSO₄. of $BaSO₄$ used in the drilling operation, we have

a greater density than the average sediment on the converted both predrilling and postdrilling Ba bank, the rates of removal determined for barium concentrations to BaSO₄. The inventory of barite

$$
Total = \sum A \cdot d \cdot Z \cdot C \cdot (BaSO_4/Ba)
$$

concentration for each annulus around the drill cm), $C=$ concentration of Ba (μ g/g), and

duction of drilling mud is contained within the We estimate that the inventory of $BaSO₄$ in the sampling depth interval of 0-2 cm. This assump-upper 2 cm of sediment in the 6-km circle totals upper 2 cm of sediment in the 6-km circle totals tion is valid until at least cruise 5, based on core 0.59×10^6 to 0.62×10^6 lb before drilling began profiles from station 5-1 reported in the second (cruises 1 and 2). The inventory increases to year final report. For comparison to the amount 0.86×10^6 lb on cruise 5 just after drilling stops of BaSO₄ used in the drilling operation, we have (net increase of 0.27×10^6 lb) and decreases to

FIGURE 11A.-Relative amount percent of total barium in different size fractions of bottom sediment collected on cruises 4 and 10 at control station 2 on Georges Bank.

last four cruises (fig. 18). range, 1,250,000 lb, for the total barite discharged

The total barium sulfate used in drilling the to the ocean while drilling this well. exploratory well at block 312 was 2,387,800 lb The net mass of barite added by drilling within (Danenberger, 1983). An estimated 630,000 lb was the 6-km circle at the time of cruise 5 represents left in the hole when the rig was moved off the loca- 25 percent of the total amount discharged tion. If mud was not lost to porous subsurface rock $(270,000/(1,250,000*(0.85))(100)$. The factor 0.85 formations while drilling, which is highly unlikely, represents the fraction of pure $BaSO_4$ contained then the total barite discharged to the ocean was in mined barite. then the total barite discharged to the ocean was 1,757,800 lb. This estimate is considered an upper In our evaluation of the rate at which barite limit because some loss to porous formations is decreases within the site-specific survey, we have expected. E. P. Danenberger (Minerals Manage- considered only the area between the 0.5- and 2 ment Service, oral commun., Sept. 21, 1983) km circles. This choice includes 20 of the 29 staestimated that, on the basis of drilling records, the tions and excludes the area of the outer two rings maximum losses to porous formations would where half of the total area is controlled by as few reduce the barite discharge to 800,000 lb. as four stations. We have also excluded the actual Danenberger suggested that the most likely range drill site, where large within-station variability was

values between 0.68×10^6 and 0.60×10^6 lb for the million lb. We will assume the middle value of this

of barite discharge is between 1 million and 1.5 measured. Another advantage in considering this

FIGURE !lB.-Concentrations of barium in different size fractions of bottom sediments collected on cruises 4 and 10 at control station 2 on Georges Bank.

smaller area is that data on Ba in the fine fraction are available from most of these 20 stations and so permit an additional rate calculation. The changes in inventory of Ba as $BaSO₄$ in the 0.5-2 -km area are shown in figure 19.

For cruise 5, we assigned a value of 1 to the net barite inventory (total barite minus background barite)for the 0.5-2 -km area and calculated the net barite for each successive cruise relative to cruise 5. A semilog plot of the data appears to have two relatively straight line segments (fig. 20) and approximates the mathematical model for radioactive decay for two isotopes having different halflives. If we use this model and least squares regression to describe the removal of barite from the surface sediments, the initial half-life or half-time of barite within this area of the site-specific survey is 0.34 year. For cruises 5, 6, and 8, $r=-0.99$.

A second slower rate is more arbitrarily defined by the data at the end of the monitoring program. The linear regression of cruises 8-12 gives a half life of 3.4 years $(r=-0.40)$ as shown in figure 20, but cruises 9-12 did not predict a decrease with time. The average inventory of barite between 0.5-2 km from the drill site during cruises 9-12 is 5.5 ± 0.1 ($\times 10^4$) lb. This value is 12 percent higher than the average predrilling inventory of 4.9 ± 0.1 ($\times10⁴$) lb calculated for cruises 1 and 2 (fig. 19). The total inventory (fig. 19) should be monitored again at annual intervals to determine the slower rate of removal.

A similar calculation of the change in net barite inventory of the fine fraction (fig. 21) yields a rapid initial half-time of 0.25 year. The secondary rate after cruise 8 appears. much slower, or zero; however, there are insufficient data for an estimate.

This model is certainly oversimplified but retains some merit. One basic assumption of this exponential decay model is that each particle has the same probability of escaping. In this case, the mechanism of escape is thought to be suspended or bed-load transport away from the drill rig or downward mixing and exchange with uncontaminated sediments below. Although larger barite particles generally would have a lower probability of eroding than finer particles, there are relatively few barite particles large enough to resist sediment transport by resuspension. Bottom stresses on Georges Bank are frequently greater than 1.7 dynes/cm^2 , the stress required to resuspend barite particles 63 μ m in diameter (Butman and Moody, 1983). Since about 96 percent of the barite used in drilling is finer than 63 μ m, we assume that most of the whole size range of barite particles will be moved frequently by resuspension. Therefore, we attribute the initial rapid rate of Ba removal to the effects of resuspension and transport within the water column.

The slower rate of barite disappearance from the upper 2 em measured after cruise 8 is probably related to the effect of downward mixing into the sediment. This process decreases the concentration in the surface 0- to 2-cm layer by dilution rather than by actual removal. Consequently, the removal process is actually slowed by mixing processes, since larger storms (which are less frequent) are necessary to erode sediments to the increasing depths of Ba penetration.

The slower rate of barite disappearance after cruise 8 also could be caused by sediments having lower Ba concentration accumulating on top of sediments having higher Ba concentrations.

FIGURE 12A.-Relative amount percent of total barium in different size fractions of bottom sediment collected on cruises 4 and 10 at site-specific station 5-2 on Georges Bank.

Although Georges Bank as a whole is considered to be eroding, processes of sediment redistribution and local accumulation have been identified (Twichell, 1983).

What is the fate of the barite that is discharged by drilling operations and subsequently eroded from the sediments near the drill rigs? Some of the barite may dissolve into seawater that is undersaturated with respect to $BaSO₄$ (Chow, 1976; Dehairs and others, 1980). However, the rate of dissolution is likely to be slow, and the Ba released by dissolution may be reprecipitated by certain planktonic organisms or reprecipitated during the decomposition of suspended-organic matter (Dehairs and others, 1980).

The fate of Ba added to Georges Bank seems, at present, to be linked to sediment transport processes. We have found small Ba increases in the fine fraction of sediment at distant stations both to the west and to the east of the drilling area. To the west at station 12, we have found Ba concentrations in

the surface sediment that are higher than those at greater sediment depth. At both stations 10 and 12, we observed peaks in the Ba concentration of postdrilling samples. At coring stations 50 km west of transect III (OC140-39, 41), we observed an enrichment of the Ba/Al ratio in surface sediments and interpret this as evidence for a small recent addition of Ba. Also to the east, along transect I, we measured Ba increases in some of the postdrilling samples, although these are of smaller magnitude than those at stations 10 and 12. There is no evidence of an increase in Ba at stations 13 or 13A from the analysis of surface samples or from sediment cores, although a small signal is more difficult to identify here because of a higher predrilling Ba concentration.

A rough calculation made in an earlier report (Bothner and others, 1984b) suggested that 69 percent of the barite discharged by all eight exploratory wells could be accounted for in the sediments within the western half of a circle 130 km in

FIGURE 128.-Concentrations of barium in different size fractions of bottom sediments collected on cruises 4 and 10 at sitespecific station 5-2 on Georges Bank.

diameter and centered on station 5. Inclusion of areas to the east of station 5, particularly in light of the small increases in Ba measured during the third year at stations 2 and 3, would increase the percentage of drilling-related Ba accounted for in the sediments.

We conclude that the barite from drilling mud is associated with the fine-sediment fraction in low concentration and is widely distributed.

The overall results of this study have important implications in predicting the fate and effects of any contaminants discharged on Georges Bank, which have an affinity for sediments or suspended particulates. For those contaminants that are rendered harmless by dilution, the tidal and storm currents are sufficient to disperse material over wide areas. Benthic organisms can assist in dispersing a contaminant that is added to the sea floor to deeper horizons in the sediments. These processes act quickly; half of the barite inventory at the station 5 drill site was removed from the 0- to 2-cm sediment layer in 0.34 year. For those contaminants known to be dangerous or potentially dangerous at any concentration, or for those contaminants that are added in excess of the system's capacity to dilute, the same energetic processes of dispersion will endanger a wide area of the bank.

SUMMARY OF IMPORTANT FINDINGS

1. Barium (present in barite, a major constituent of drilling mud) has increased by a factor of 5.9 in bulk (unfractionated) sediments 200m from the drill site in block 410 as a result of drilling. The maximum barium concentration (172 ppm) was within the range of predrilling concentrations (28-300 ppm) measured at other sampling stations of this program. Because of the low toxicity of barium in the form of barite $(BaSO_4)$,

FIGURE 13A.-Relative amount percent of total barium in different size fractions of bottom sediment collected on cruises 4 and 10 at regional station 16 on Georges Bank.

no adverse chemical stress to bottom-dwelling organisms is expected from. these measured increases in barium concentrations. This prediction is being tested by the biological studies conducted within the monitoring program (Battelle-WHO!, 1984). No drillingrelated changes in the concentrations of chromium or of other metals have been observed in bulk sediments from any of the locations sampled in this program.

- 2. Of the barite discharged to the ocean waters while drilling in block 312, we estimate that 25 percent was present in the sediments within 6 km of the well at the time of the fifth monitoring cruise, which was conducted 4 weeks after drilling was completed.
- 3. The inventory of barite, which accumulated as a result of drilling in block 312, has decreased steadily for almost a year during the period following drilling with a half-life of 0.34 year. A much slower rate (half-life 3.4 years) is estimated for the period between cruises 8 and 12. At the time of cruise 12, the Ba inventory between 0.5 and 2 km from the well site was
- 4. The barite from drilling mud is associated with exploratory phase of drilling is distributed over

the fine-sediment fraction in low concentration and is widely distributed. The fate of this barite is closely linked to the energetic sedimenttransport processes characteristic of this region. We found evidence for Ba transport and deposition to the west of the drilling activity. The Ba accumulated at stations 10 and 12 along transect Ill, at new coring stations 50 km west of transect III, in sediment-trap material and sediments from the head of Lydonia Canyon, and in sediments near the head of Oceanographer Canyon. In addition, we found peaks in the concentration of Ba with time at upstream control stations 2 and 3, located 35 km northeast of the nearest drilling activity. The data from sediment·trap analyses suggest that barite that is originally deposited near a drill site in this area can be resuspended to at least 25m above the sea floor.

RECOMMENDATIONS FOR FUTURE WORK

approximately 12 percent higher than the pre- In this 3-year study we have shown that Ba drilling value. introduced to Georges Bank during the

FIGURE 13B.-Concentrations of barium in different size fractions of bottom sediments collected on cruises 4 and 10 at regional station 16 on Georges Bank.

FIGURE 14.-Concentrations of barium in the fine fraction of material collected in sediment traps deployed at the head of Lydonia Canyon on different deployment dates. Traps were recovered just prior to the next deployment.

wide areas of the bank. The rates at which the concentrations of Ba decrease in the surface sediments near a well have been estimated. The processes responsible for the decrease in concentration and for the redistribution of Ba are (1) resuspension and transport in response to strong currents, (2) physical and biological mixing of the surficial sediments, and (3) possible dilution by the local accumulation of less contaminated sediments. Because these findings have application in predicting the fate of future pollutants on Georges Bank, we recommend that the following specific studies be continued beyond the third year of this monitoring program:

1. Three replicate grab samples should be collected for chemical analysis at each of the 29 sitespecific stations during the fourth and fifth years after the initiation of this program. These data are needed to more accurately determine

FIGURE 15.-Distribution of barium and the barium-to-aluminum ratio in four areas where the introduction of drilling mud was not expected. Analyses were performed on the fine fraction of sediment. Stations 2 (Ml0-02-00-JX) and 3 (Mll-03-00- AX) were sampled with a grab sampler. Samples OC140-8B and 8309-B were collected with a hydraulically damped gravity corer and a box corer, respectively.

FIGURE 16.-Distribution of barium and the barium-to-aluminum ratio in locations west of drilling sites. Analyses were performed on the fine fraction of sediment. Samples were collected with a grab sampler.

sediments over a longer time interval.

the slower rate of Ba removal from surface 2. Undisturbed sediment cores 30-40 em long should be collected near the drill sites at

FIGURE 17.-Distribution of barium and the barium-to-aluminum ratio at locations adjacent to drilling sites in,(A) block 312 and (B) block 410. Samples were collected with a grab sampler.

FIGURE 18.-Total inventory of barite (calculated from barium concentrations) within a 6-km radius around station 5 on different sampling occasions. ND=no data.

FIGURE 19.-Total inventory of barite (calculated from barium concentrations) within the annulus between 0.5 and 2 km from station 5 on different sampling occasions. ND=no data.

stations 5 and 16 at least once per year for at least 2 years. Ba depth profiles of the fine and bulk sediment will determine the rates of sediment mixing processes and will determine the relative importance of erosion and mixing in explaining the decrease in the Ba concentration in surface sediment.

3. Stations that will be sampled for benthic infaunal studies beyond the third year of this program also should be sampled for metals. Particular emphasis should be given to stations to the west of the drilling area (stations 7 A, 8, 9, 12, 13, 13A, and control station 2) to evaluate any long-term accumulation of Ba in expected areas of deposition.

4. Further analysis and publication of these results should be accomplished in order to maximize the scientific value of this program.

FIGURE 20.-Computed decrease of the net barite inventory in bulk sediments within the annulus between 0.5 and 2 km from station 5 with time. Fraction remaining is relative to the amount present at the time of cruise 5, 4 weeks after drilling was completed.

FIGURE 21.-Computed decrease of the net barite inventory in the fine fraction within the annulus between 0.5 and 2 km from station 5 with time. Fraction remaining is relative to the amount present at the time of cruise 5, 4 weeks after drilling was completed.

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Appendix table *lB.-Navigation data for sizefractionization samples and for core and grab samples subsectioned into sequential depth intervals*

Appendix table *lC.-Sediment-trap locations and deployment dates*

Trap		Water Meters					
number	depth	above	Latitude	Longitude	Deployed	Recovered	General location
	(m)	bottom	(degrees)	(degress)	(Yr Mo Dy)	(Yr Mo Dy)	
ST001	64	3	41.038333	-67.55817	791215	800525	Georges Bank Shelf-Georges Bank Tripod 183: Predrilling
ST103	290	20	40.52583	-67.71367	801128	810428	Lydonia Canyon axis-Station LCB: Predrilling
ST222	288	50	40.526001	-67.71400	810429	810926	Lydonia Canyon axis: Drilling starts 810724
ST301	290	20	40.526001	-67.71300	810927	820128	Lydonia Canyon axis-Station LCB: Drilling in progress
ST301	290	20	40.526001	$-67,71300$	810927	820128	Lydonia Canyon axis-Station LCB: Drilling in progress
ST403	300	20	40.525333	-67.71383	820131	820707	Lydonia Canyon axis-Station LCB: Drilling in progress
ST424	81	5	40.652702	-67.77071	820201	820611	1 km west of rig: Drilling in progress
ST426	300	5	40.662704	-67.69229	820201	820611	6 km east of rig: Drilling in progress
ST501	79	25	40.656502	-67.77451	820710	821111	Rig site-Block 312: Post drilling
ST502	79	20	40.656500	67.76783	820710	821111	Rig site-Block 312: Post drilling
ST505	79	3	40.656502	-67.76779	820710	821111	Rig site-Block 312: Post drilling
ST506	79	25	40.657997	-67.77499	820710	821111	1 km west of rig: Post drilling
ST508	79	10	40.657997	-67.77499	820710	821111	1 km west of rig: Post drilling
ST510	79	3	40.657997	-67.77499	820710	821111	Post drilling l km west of rig:
ST513	77	10	40.662292	-67.69099	820711	821111	6 km east of rig: Post drilling
ST515	77	3	40.662292	-67.69099	820111	821111	6 km east of rig: Post drilling
ST536	295	20	40.52480	-67.71321	820708	821111	Lydonia Canyon axis-Station LCB: Drilling in progress
ST537	295	10	40.52483	-67.71317	820708	821111	Drilling in progress Lydonia Canyon axis-Station LCB:

Appendix table *2.-Chemical analyses of blind replicates* [Values are accurate to two significant figures]

Field	Lab	Ä1	Ba	Cd	cr	Cu	Fe	Hg	Mn	N1	Pb	v	2n	Blind no.
number	number	(2)	(ppm)	(pp ₀)	(ppm)	(pp _n)	(2)	(ppn)	(pp _m)	(pp _n)	(ppn)	(pp _m)	(pp ₀)	
M11-01-00-BL	$W - 225548$	0.810	130	0.020	6	1.0	0.38	0.00	72.0	$\langle 2$	4	6	4.2	
M11-01-00-BL	$W - 225598$.820	130	$\langle .020$	6	1.7	.39	0.00	68.0	$\langle 2$	3	4	5.0	Blind $#49$
M11-03-00-AX6	$W - 226062$	4.807	252	.229	92	30.	3.43	0.00	331.9	45	45	160	92.7	
M11-03-00-AX6	W-226067	4.630	227	.226	86	21.	3.39	0.00	327.5	50	35	158	96.0	Blind $#56$
M11-04-00-BL	W-225554	1.200	180	ζ .020	10	1.0	.51	0.00	87.0	$\langle 2$	6	8	6.1	
M11-04-00-BL	$W - 225599$	1.100	180	$\langle .020$	9	1.2	.52	0.00	86.0	$\langle 2$	5	8	6.6	Blind $#50$
M11-05-01-IX	$W - 225862$	4.080	5712	.299	49	24.	2.99	0.00	2584.	35	38	84	81.6	
$M11 - 05 - 01 - TX$	$W - 225891$	3.563	5700	.168	53	23.	2.80	0.00	2316.	31	43	64	84.0	Blind $#53$
M11-05-06-BL	W-225584	$\hspace{0.05cm}$ $\hspace{0.05cm}$	35	--	--	--	--	0.00	--	--	--	--	--	
M11-05-06-BL	W-225600	.220	34	.020	4	1.0	.41	0.00	330.0	$\langle 2$	4	13	4.2	Blind #51
M11-13-00-BLX	$W - 225868$	5.551	316	.109	69	13.	2.83	0.00	446.3	33	27	120	71.8	
M11-13-00-BLX	W-225890	4.952	291	.076	67	13.	2.69	0.00	430.6	33	31	99	71.0	Blind $#52$
M12-16-00-BL	$W - 226820$.380	73	.020	3	1.0	.21	0.00	160.0	$\langle 2 \rangle$	3	$\langle 2$	5.8	
M12-16-00-BL	$W - 226832$.360	73	.020	$\langle 2$	<1.0	.20	0.00	160.0	$\langle 2$	4	$\langle 2$	5.8	Blind $#57$
M12-16-00-BL	W-226833	.360	73	.020	$\langle 2$	1.0	.20	0.00	170.0	$\langle 2$	3	$\langle 2$	5.8	Blind $#58$
OC140-41X8-10	W-226056	4.863	238	.283	83	25.	3.39	0.00	328.0	45	44	147	96.1	
oc140-41X8-10	W-226065	4.709	247	.200	86	21.	3.30	0.00	341.4	42	46	165	95.3	Blind $#54$
OC140-41X1214	$W - 226058$	5.081	236	.236	95	26.	3.66	0.00	366.3	47	35	165	102.	
OC140-41X1214	W-226066	4.415	226	.269	81	20.	3.23	0.00	312.3	42	38	151	92.6	Blind $#55$

Appendix table *3A.-Textural analysis of station blends and individual samples* [Values accurate to two significant figures)

Appendix table *3A.-Textural analysis of station blends and individual samples-Continued* [Values accurate to two significant figures)

Appendix table 3A.-*Textural analysis of station blends and individual samples-Continued* [Values accurate to two significant figures]

Appendix table *3A.-Textural analysis of station blends and individual samples-Continued* [Values accurate to two significant figures]

Appendix table *3B.-Textural analyses of samples from depth intervals oj cores and grabs*

Appendix table *3C.-Textural analyses of samples from sediment traps*

Appendix table *4A.-Chemical analyses of station blends and individual samples* [Values accurate to two significant figures]

Appendix table *4A.-Chemical analyses of station blends and individual samples-Continued*

Appendix table *4A.-Chemical analyses of station blends and individual samples-Continued*

Appendix table *4A.-Chemical analyses of station blends and individual samples-Continued*

Field	Lab	$\overline{A1}$	Ba	$\overline{\mathrm{c}\mathrm{d}}$	$\overline{\text{Cr}}$	Cu	Fe	Hg	Mn	$\overline{\mathtt{N1}}$	Pb	\overline{v}	\overline{z} n	C ₁
number	number	(%)	(ppm)	(ppm)	(ppm)	(ppm)	(%)	(ppm)	(ppn)	(ppn)	(ppm)	(ppm)	(ppm)	(2)
M12-05-03-BL	W-226834	$\qquad \qquad -$	38	--	---	--	--	--	--	--	--	--	--	$-$
M12-05-04-BL	$W - 226835$	$-$	37	--	$-$	--	--	--	--	--	--	--	--	--
M12-05-05-BL	W-226836	--	42	--	--	--	-1	--	--	--	--	--	--	--
M12-05-06-BL	$W - 226837$	--	33	--	--	--	--	--	--	--	--	--	--	--
M12-05-07-BL	W-226838	--	32	--	--	--	--	--	--	--	--	--	--	--
M12-05-08-BL	$W - 226839$	--	43	--	--	--	--	--	--	--	--	--	--	--
M12-05-09-BL	$W - 226840$	--	43	--	--	--	$-$	--	--	--	--	--	--	-1
M12-05-10-BL	W-226841	--	47	--	--	--	--	--	--	--	--	--	--	--
M12-05-11-BL	W-226842	--	40	--	--		--	--	--	--	--		--	--
M12-05-12-BL	W-226843	--	40	--	$-$	-1	--	--	--	--	--	--	--	--
M12-05-13-BL	W-226844	$\qquad \qquad -$	43	--	--	--	--	--	--	--	--	--	--	--
M12-05-14-BL	W-226845	--	31	--	--	--	--	--	--	--	--	--	--	--
M12-05-15-BL	W-226846	--	33	-1	--	-1	--	--	--	--	$=$	--	$-$	\overline{a}
M12-05-16-BL	$W - 226827$.26	36	$\langle .020$	4.0	1.0	.29	--	190	2.0	3.1	5.5	5.0	--
M12-05-17-BL	$W - 226847$	--	40		--		--	--	--	--			--	\overline{a}
M12-05-18-BL	W-226828	.24	40	$\langle .020$	6.5	1.2	.42	--	300	<2.0	4.0	12.0	5.0	--
$M12 - 05 - 18 - G$	W-226848	--	39	--	--	--	--	--	---	--	--	--	--	--
M12-05-18-H	W-226849	$\overline{}$	43	--	--	--	--	--	--	--	--	--	--	--
M12-05-18-I	$W - 226850$	$-$	40	--	--	--	-1	--	-1	--	--	--	$-$	$-$
M12-05-19-BL	W-226851	$- -$	41	--	--	$-$	--	--	-1		--	--	--	$-$
M12-05-20-BL	W-226829	.21	35	$\langle .020$	3.5	\triangleleft 1.0	.30	--	230	$\langle 2.0$	3.1	8.5	3.3	--
M12-05-21-BL	W-226852	--	30	--	--	--	--	--	--	--	--	--	--	--
M12-05-22-BL	W-226853	$\qquad \qquad -$	32	--	-1	--	--	$-$	--	--	--	--	--	-1
		--		--	--	--	-−	--	--		--	--	--	--
M12-05-23-BL	W-226854		38	--	--	--	--	--	--	--	-1	--	--	$\overline{}$
M12-05-24-BL	$W - 226855$	--	53							--	-1		--	--
M12-05-25-BL	W-226856	---	48	--	--	--	--	--	--			--		
M12-05-26-BL	$W - 226857$	$\qquad \qquad -$	49	-1	--	--	--	--	--	--	--	--	--	--
M12-05-27-BL	W-226858	--	40	--	--	--	--	--	$-$	--	--	--	$-$	\overline{a}
M12-05-28-BL	W-226830	.21	28	$\texttt{<.020}$	2.5	<1.0	.24	--	130	2.0	2.3	3.0	2.5	$-$
M12-05-28-G	W-226859	$-$	33	--	$\overline{}$	--	--	--	--		--		\rightarrow	--
M12-05-28-H	$W - 226860$	$-\,$ $\,$	31	--	--	--	--	--	$-$	--	--	--	--	\overline{a}
M12-05-28-I	W-226861	$\qquad \qquad -$	34	--	--	--	--		--	<u></u>	--	---	--	--
M12-05-29-BL	$W - 226831$.84	120	$\langle .020$	9.5	1.0	.77	$-$	150	< 2.0	4.6	20.0	9.1	--
M12-05-29-G	$W - 226862$	--	120	—…	--	--			--	--	--	--	--	--
M12-05-29-H	$W - 226863$	$\hspace{0.05cm}$ – $\hspace{0.05cm}$	130	$--$	--	$-$	--	--	--	$-$	--	--	$-$	$- -$
M12-05-29-I	W-226864	$\overline{}$	120	$-$	$-$	$-$	$-$	$- -$	$-$	--	$-$	--	$-$	--
M12-06-00-BL	$W - 226808$.90	110	< .020	14.0	$\langle 1.0$.47	--	140	< 2.0	3.7	12.0	9.1	--
M12-07-A0-BL	W-226809	2.70	250	.073	32.0	4.2	1.40	--	220	8.4	11.0	30.0	27.0	--
M12-08-00-BL	$W - 226810$.45	45	$\langle .020$	5.0	1.0	.56	--	110	< 2.0	2.9	4.0	9.1	\overline{a}
M12-09-00-BL	$W - 226811$	1.10	110	ζ .020	14.0	1.0	.63	\overline{a}	190	2.0	4.6	14.0	12.0	--
M12-10-00-BL	$W - 226812$	1.00	87	.025	8.5	1.0	.40	$-$	200	< 2.0	3.7	6.0	7.1	--
M12-11-00-BL	$W - 226813$	1.60	210	.025	16.0	1.7	.86	--	130	2.0	7.5	18.0	12.0	--
M12-12-00-BL	$W - 226814$.71	57	$\langle .020$	8.5	2.1	.62	--	130	< 2.0	7.9	6.0	11.0	--
M12-13-00-BL	W-226815	3.50	240	.063	35.0	4.3	1.60	$\qquad \qquad -$	280	10.0	15.0	52.0	38.0	$- -$
M12-13-A0-BL	W-226816	4.00	300	080ء	55.0	9.3	2.40	$-$	300	24.0	17.0	73.0	60.0	--
$M12 - 13 - AO - G$	$W - 226817$	3.80	300	.098	55.0	9.6	2.40	.01	300	24.0	16.0	73.0	60.0	--
M12-13-A0-H	$W - 226818$	4.90	300	.091	67.0	10.0	2.50	--	310	26.0	19.0	86.0	60.0	--
$M12 - 13 - A0 - I$	$W - 226819$	5,10	300	.071	55.0	11.0	2.50	--	320	27.0	20.0	75.0	61.0	--
M12-16-00-BL	$W - 226820$.38	73	$\langle .020$	2.5	< 1.0	-21	--	160	< 2.0	3.3	< 2.0	5.8	--
$M12 - 16 - 00 - G$	W-226821	.41	81	$\langle .020$	2.0	1.4	.23	--	300	< 2.0	17.0	4.0	7.5	--
M12-16-00-H	$W - 226822$.34	84	ζ .020	2.0	$\triangleleft 1.0$.17	--	110	< 2.0	3.7	<2.0	4.2	$-$
$M12-16-00-I$	W-226823	.34	56	$\langle .020$	<2.0	1.2	.19	$\qquad \qquad -$	86	< 2.0	22.0	<2.0	24.0	--
M12-17-00-BL	W-226824	.25	29	$\mathsf{<}.020$	< 2.0	\triangle 1.0	.11	--	67	< 2.0	1.5	<2.0	2.5	--
$M12 - 17 - 00 - G$	W-226865	$\qquad \qquad \textbf{---}$	29	--	--	--	--	$-$	--	--	--	--	--	$-$
M12-17-00-H	W-226866	$- -$	39	--	$- -$	--	--	--	--	--	--	--	--	--
M12-17-00-I	W-226867	$-$	34	--	--	\rightarrow	-1	--	--	--	--	--	\overline{a}	--
M12-18-00-BL	W-226825	.33	45	ζ .020	2.5	< 1.0	.17		95	<2.0	2.7	<2.0	5.0	--
$M12 - 18 - 00 - G$	W-226868	$\overline{}$	48	--	$-$	--	--	$-$	--		--		--	--
M12-18-00-H	W-226869	$-$	47	--	--	--	--	--	$-$	--	--	--	-1	$\overline{}$
												--	--	-1
$M12-18-00-I$	W-226870	--	51	$-\!$ $\!-$	--	--	$- -$	--	--	--	--			

Appendix table 4B.-Chemical analyses of fine fraction (less than 60 μ m) from station blends and individual samples [Values are accurate to two significant figures]

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Appendix table 4B.-Chemical analyses of fine fraction (less than 60 µm) from station blends and individual samples-Continued

 $\begin{array}{c} \end{array}$

*Estimated value, based on average Al value for this station.

Appendix table *4C.-Chemica/ analyses of the following size fractions of bottom sediment*

[SO, undifferentiated; Sl, >1,000 μ m; S2, 1,000-5,000 μ m; S3, 500-210 μ m; S4, 210-105 μ m; S5, 105-60 μ m; S6, 60-30 μ m; S7, 30-10 μ m; S8, 10-1 μ m; S9, <1 μ m.]

Table *4D.-Chemical analysis of core samples and grab samples subsectioned in sequential depth intervals* (Depth interval, in em, is given at end of field number)

Field	Lab	$\overline{A1}$	Ba	ळ	Сr	cu	Fe	$\overline{\text{Hg}}$	Mn	N ₁	Pb	$\overline{\mathtt{v}}$	\overline{z} n	C1
number	number	(2)	(ppn)	(ppn)	(ppm)	(ppm)	(2)	(ppn)	(ppn)	(ppm)	(ppm)	(ppm)	(ррш)	(2)
M10-02-00-JX 00-02	$W - 225158$	0.88	77	0.096	4.2	13.2	0.77	--	1046	10.5	14.9	16.7	19.0	28.9
M10-02-00-JX 02-04	$W - 225159$	1.27	95	.127	6.0	16.1	1.03	--	1270	13.1	15.1	20.2	30.2	27.9
M10-02-00-JX 06-08	$W-225161$.87	93	.349	5.8	27.0	.90	--	872	5.8	17.7	11.6	26.4	36.3
M10-02-00-JX 08-10	$W - 225162$.99	90	.134	5.8	18.3	1.05	--	1191	8.7	18.3	23.2	32.0	36.3
M10-02-00-JX 10-12	$W - 225163$.84	81	.336	< 5.6	12.6	.98	--	1009	8.4	17.7	16.8	25.5	35.6
M10-02-00-JX 12-14	W-225164	97.	77	.072	5.0	13.6	.94	--	867	7.4	16.3	17.3	27.2	33.0
M10-12-00-GX 00-02	$W - 225165$	4.08	250	.109	52.7	23.7	3.29	--	461	40.8	63.2	92.1	76.3	13.3
M10-12-00-GX 02-04	$W - 225166$	4.41	252	.164	56.7	27.7	3.40	--	441	45.3	81.9	108.3	83.1	11.4
M10-12-00-GX 04-06	$W - 225167$	4.47	241	.181	60.4	27.8	3.38	--	386	47.1	84.5	111.1	83.3	9.5
M10-12-00-GX 06-08	$W - 225168$	4.55	246	.197	62.7	28.3	3.44	--	356	47.9	89.7	117.9	88.5	10.3
M10-12-00-GX 08-10	$W - 225169$	4.60	230	.266	61.7	30.2	3.39	--	315	48.4	82.3	118.6	90.7	9.6
M10-12-00-GX 10-12	$W - 225170$	4.89	232	.245	67.3	30.6	3.55	--	306	48.9	80.7	134.6	91.7	10.1
M10-12-00-GX 12-14	$W - 225171$	4.54	233	.356	63.7	28.2	3.43	--	294	49.0	74.8	134.9	85.8	10.2
M11-03-00-AX 00-02	W-226059	3.70	179	.281	57.5	28.1	2.30	--	281	40.9	66.4	127.7	93.2	12.0
M11-03-00-AX 02-04	W-226060	4.94	256	.366	76.8	42.1	3.48	--	878	58.6	91.5	162.8	118.9	25.1
M11-03-00-AX 04-06	$W - 226061$	4.28	222	.443	64.9	30.1	2.69	--	428	50.7	82.4	158.4	96.6	20.4
M11-03-00-AX 06-08	$W - 226062$	4.81	252	.229	91.6	29.8	3.43	--	332	44.6	44.6	160.2	92.7	7.0
M11-03-00-AX 08-10	$W - 226063$	3.73	201	.316	58.9	38.8	2.30	--	273	43.1	79.0	132.1	93.3	16.8
M11-03-00-AX 10-12	$W - 226064$	3.09	161	.334	50.7	22.3	1.98	--	346	34.6	64.3	110.1	77.9	10.6
M12-05-01-HX 00-02	$W - 226527$	3.96	951	.238	53.5	19.4	3.37	--	3367	51.5	49.5	103.0	105.0	27.4
M12-05-01-HX 02-04	$W - 226507$	3.49	894	.220	49.6	20.2	2.94	--	3488	40.4	45.9	88.1	84.4	25.2
M12-05-01-HX 04-06	$W - 226508$	4.04	1542	.289	59.7	23.1	3.47	--	5968	57.8	77.0	121.3	105.9	26.6
M12-05-01-HX 06-08	$W - 226509$	4.25	1226	.196	65.4	19.6	3.43	--	2943	54.0	44.1	114.5	98.1	21.5
M12-05-01-HX 08-10	$W - 226510$	4.45	918	.191	65.1	22.2	3.34	--	1906	52.4	41.3	120.7	88.9	20.5
M12-05-01-HX 10-12	$W - 226511$	4.77	844	.184	67.9	22.0	3.67	--	2019	56.9	47.7	119.3	97.3	25.2
M12-05-01-HX 12-14	$W - 226512$	3.96	594	.234	57.6	23.4	3.06	--	1512	43.2	57.6	100.8	86.4	24.6
M12-05-01-HX 14-16	$W - 226513$	4.11	596	.246	57.5	22.6	3.08	--	1992	45.2	49.3	98.6	94.5	28.4
M12-16-00-IX 00-02	W-226540	4.00	4264	.220	54.0	24.0	3.00	--	941	42.0	68.1	82.1	220.2	27.7
M12-16-00-IX 02-04	$W - 226514$	4.28	7502	.196	61.2	30.6	2.85	--	754	42.8	108.0	89.7	326.2	28.2
M12-16-00-IX 04-06	$W - 226515$	4.24	4948	.212	57.8	25.0	2.70	--	443	42.4	65.5	84.7	231.0	26.6
M12-16-00-IX 06-08	$W - 226516$	4.60	5105	.300	64.1	32.0	2.80		380	52.0	70.1	112.1	200.2	27.7
M12-16-00-IX 08-10	$W - 226517$	4.97	4253					-- --	338	55.6	89.4	117.3	190.8	27.5
M12-16-00-IX 10-12	$W - 226518$	4.76	2115	.556	65.6 64.8	33.8	2.98		343	53.3	104.8	133.4	162.0	26.3
M12-16-00-IX 12-14	$W - 226519$	4.99	957	.343		28.6	2.67	-- --	359	55.8		125.7	131.6	27.6
M12-19-00-HX 00-02				.339	63.8	33.9	2.79				67.8			
M12-19-00-HX 02-04	$W - 226489$ $W - 226490$	4.66 5.44	311	.092	77.7	12.9	3.11	.05	634	37.5	25.9	117.8	66.0 93.5	12.6
			321	.168	99.1	20.9	3.63	.06	628	44.7	37.7	153.6		15.7
M12-19-00-HX 04-06	$W - 226491$	5.36	301	.196	88.9	19.6	3.53	06ء	588	45.7	34.0	156.8	95.4	13.0
M12-19-00-HX 06-08	$W - 226492$	5.43	310	.233	86.5	23.3	3.62	06،	620	49.1	36.2	155.0	94.3	12.5
M12-19-00-HX 08-10	$W - 226493$	5.51	303	.234	102.0	23.4	3.72	06،	607	48.3	46.9	151.6	96.5	15.2
M12-19-00-HX 10-12	W-226494	6.01	323	.293	108.5	24.9	4.11	--	601	51.3	45.5	161.3	99.7	17.6
M12-19-00-HX 12-14	$W - 226495$	5.42	304	.198	100.5	23.8	3.84	--	569	50.3	31.7	132.3	87.3	13.5
M12-20-00-GX 00-02	$W - 226496$	4.29	395	.206	84.1	20.6	3.26	.08	566	39.5	41.2	108.1	87.5	23.1
M12-20-00-GX 02-04	W-226497	4.51	434	.234	80.1	20.0	3.51	08.	551	43.4	48.4	111.9	88.5	22.2
M12-20-00-GX 04-06	$W - 226498$	4.24	396	.594	76.3	21.2	3.11	07.	410	42.4	65.0	118.8	84.8	16.2
M12-20-00-GX 06-08	W-226499	3.60	335	199ء	67.1	17.4	2.61	.05	348	34.8	31.1	96.9	65.8	10.8
M12-20-00-GX 08-10	$W - 226500$	4.55	396	.249	85.0	22.0	3.37	06.	513	44.0	49.9	114.4	89.4	17.6
M12-21-00-IX 00-02	$W - 226501$	4.01	448	.148	74.1	18.5	3.24	.05	757	41.7	47.9	97.3	84.9	19.5

Table *4D.-Chemical analysis of core samples and grab samples subsectioned in sequential depth intervals-Continued*

Field		Lab	$\overline{\mathtt{AI}}$	Ba	$_{\text{Cd}}$	$\overline{\text{cr}}$	\overline{cu}	Fe	Hg	Mn	N1	P _b	$\overline{\mathbf{v}}$	$\overline{z_n}$	$\overline{c}\overline{1}$
number		number	(%)	(ppm)	(ppm)	(ppm)	(ppm)	(2)	(ppm)	(ppm)	(ppn)	(ppn)	(ppn)	(ppm)	(\mathbf{X})
M12-21-00-IX 02-04		$W - 226502$	4.32	479	.232	78.7	24.7	3.24	.06	463	41.7	49.4	120.4	86.5	19.5
M12-21-00-IX 04-06		$W - 226503$	4.85	469	.291	95.3	27.5	3.56	.07	452	48.5	67.9	139.0	98.6	21.1
M12-21-00-IX 06-08		W-226504	4.75	428	.238	99.8	23.8	3.48	07.	443	47.5	47.5	136.2	88.7	20.4
M12-21-00-IX 08-10		$W - 226505$	5.07	428	.253	87.1	23.8	3.64	.08	491	49.1	42.8	126.7	95.0	20.4
M12-21-00-IX 10-12		W-226506	5.24	456	.355	89.6	28.7	3.72	.07	541	50.7	57.5	148.7	106.5	22.6
OC140-39X	00-02	$W - 226045$	4.20	234	.112	74.0	18.5	3.09	--	457	37.0	35.8	80.2	80.2	10.5
OC140-39X	$02 - 04$	$W - 226046$	3.94	220	.139	73.0	18.5	2.89	$\hspace{0.05cm}$ – $\hspace{0.05cm}$	394	37.1	30.1	89.2	78.7	7.6
OC140-39X	$04 - 06$	$W - 226047$	4.10	211	.133	85.3	19.9	2.88	$-$	377	39.9	33.2	121.9	77.6	5.4
OC140-39X	$06 - 08$	$W - 226048$	4.33	228	.182	80.9	20.5	3.08	$- -$	433	39.9	28.5	148.1	83.1	6.8
OC140-39X	$08 - 10$	$W - 226049$	4.75	244	.171	90.1	23.1	3.53	--	463	45.1	31.7	158.4	93.8	9.9
OC140-39X	$10 - 12$	$W - 226050$	5.07	254	.254	105.2	22.8	3.93	--	469	50.7	20.3	177.5	95.1	11.7
OC140-39X	$12 - 14$	$W - 226051$	4.68	234	.222	93.5	21.0	3.39	--	409	44.4	25.7	128.6	88.9	8.0
OC140-41X	$00 - 02$	$W - 226052$	4.28	245	.196	79.5	23.2	3.06	--	367	36.7	31.8	134.6	80.7	10.1
OC140-41X	$02 - 04$	$W - 226053$	4.41	255	.106	79.0	18.6	3.13	--	372	39.5	34.8	139.3	81.3	7.7
OC140-41X	$04 - 06$	W-226054	4.28	236	.191	75.4	19.1	2.93	$\overline{}$	326	36.0	33.8	123.8	76.5	6.2
OC140-41X	$06 - 08$	$W - 226055$	4.81	259	.210	85.2	18.5	3.33	--	370	43.2	33.3	148.1	90.1	10.5
OC140-41X	$08 - 10$	$W - 226056$	4.86	238	.283	82.6	24.9	3.39	--	328	45.2	44.1	147.0	96.1	6.4
OC140-41X	$10 - 12$	$W - 226057$	5.79	362	.362	188.1	41.0	4.82	--	2267	60.3	132.6	164.0	135.1	32.4
OC140-41X	$12 - 14$	$W - 226058$	5.08	236	.236	94.5	26.0	3.66	--	366	47.3	35.5	165.4	101.6	8.5
$0C140-8BX$	$00 - 01$	$W - 225172$	5.35	299	.065	60.8	14.4	2.99	05.	360	31.9	33.0	88.6	70.0	1.6
OC140-8BX	$01 - 02$	$W - 225173$	5.05	299	-134	56.6	15.4	2.99	.06	340	31.9	33.0	91.6	70.0	1.6
OC140-8BX	$02 - 03$	$W - 225174$	4.92	287	.082	56.4	14.4	2.77	07.	339	33.9	32.8	89.3	69.8	1.4
OC140-8BX	$03 - 04$	$W - 225175$	5.03	304	.209	62.8	16.8	2.72	05.	346	34.6	33.5	90.1	72.3	2.5
OC140-8BX	$05 - 06$	$W - 225176$	4.64	299	.083	61.9	15.5	2.89	06.	330	35.1	27.9	88.7	71.2	1.7
OC140-8BX	$07 - 08$	$W - 225177$	4.64	310	.073	56.7	15.5	2.79	06ء	330	34.0	23.7	94.9	71.2	1.7
OC140-8BX	$09 - 10$	$W - 225178$	4.54	299	073.	59.8	15.5	2.89	06ء	330	37.1	25.8	88.7	71.2	1.7
OC140-8BX	$11 - 12$	$W - 225179$	4.23	299	.060	61.9	16.5	2.79	.05	320	35.1	23.7	94.9	71.2	1.7
BULK SAMPLE PROFILE		83G-9 (BOX CORE)													
$83G - 9 - B$	$00 - 01$	$W - 225180$	4.93	360	.063	51.4	21.6	2.98	.05	483	39.1	23.6	94.6	83.3	1.5
$83G-9-B$	$01 - 02$	$W - 225181$	5.03	369	.065	51.3	21.5	3.08	.05	472	41.0	20.5	88.2	72.8	1.4
$83G - 9 - B$	$02 - 03$	$W - 225182$	5.12	369	073.	52.2	21.5	3.17	.05	604	39.9	20.5	85.0	67.6	1.3
$83G - 9 - B$	$03 - 04$	$W - 225183$	5.13	380	.043	55.4	18.5	3.18	.04	441	39.0	17.4	88.2	67.7	1.4
$83C - 9 - B$	$04 - 05$	$W - 225184$	5.02	358	.088	54.3	19.5	3.07	04.	297	41.0	17.4	91.1	67.6	1.3
$83G-9-B$	$05 - 07$	$W - 225185$	5.11	378	.143	58.3	24.5	3.07	.03	307	40.9	17.4	94.0	69.5	1.2
$83C - 9 - B$	$07 - 09$	$W - 225186$	4.92	369	.113	56.3	17.4	2.87	.03	297	39.9	17.4	88.1	67.6	1.3
$83G-9-B$	$09 - 11$	$W - 225187$	4.90	378	.173	52.0	18.4	2.86	.04	306	36.7	15.3	93.9	65.3	1.1
$23G-9-B$	$11 - 13$	$W - 225188$	4.96	372	.103	52.7	18.6	2.89	.03	300	37.2	15.5	92.0	63.1	1.8
$83G - 9 - B$	$15 - 17$	$W - 225189$	4.91	378	.098	54.2	19.4	2.86	.03	296	40.9	15.3	87.9	64.4	1.2
$83G - 9 - B$	$17 - 19$	$W - 225190$	4.82	380	.088	52.3	14.4	2.87	.02	298	39.0	15.4	91.3	67.7	1.4
$83G-9-B$	$23 - 25$	$W - 225191$	4.80	368	.102	52.1	19.4	2.86	-03	286	39.9	14.3	91.0	65.4	1.2
$83G - 9 - B$	$25 - 31$	W-225192	5.12	369	.088	56.3	11.3	3.17	.03	307	41.0	10.2	89.1	67.6	1.3

 $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{0}^{\infty}\frac{1}{\sqrt{2\pi}}\left(\frac{1}{\sqrt{2\pi}}\right)^{2\alpha} \frac{1}{\sqrt{2\pi}}\int_{0}^{\infty}\frac{1}{\sqrt{2\pi}}\left(\frac{1}{\sqrt{2\pi}}\right)^{\alpha} \frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\int_{0}^{\infty}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}$ $\frac{1}{2}$ $\frac{1}{2}$

