United States
Environmental Protection
Agency

Environmental Research
Laboratory
Gulf Breeze FL 32561

Research and Development

EPA-600/S3-84-071 July 1984

EPA

Project Summary

A Survey of the Toxicity and Chemical Composition of Used Drilling Muds

Chemical characterization and toxicity of oil drilling fluids were investigated by the Edgerton Research Laboratory from 1 October 1979 to August 1983 as part of a comprehensive research program sponsored by the U.S. Environmental Protection Agency (EPA) to determine fate and effects of such fluids in the marine environment. Drilling muds used in the research were supplied by the EPA, the Petroleum Equipment Suppliers Association (PESA), and the American Petroleum Institute (API). The drilling muds were designated "May 15," "May 29," "Sept. 4," "Exxon," "Gilson," "Mobile Bay," "Jay Field," and "PESA." Investigations during the first year centered on the chemical composition and the acute toxicity of drilling muds and the effects of drilling muds on the recruitment of benthic organisms. In the second year, studies focused on toxicity testing with planktonic copepods, chemical characterization of the toxicity test phases, bioaccumulation studies, and the effects of muds on larval and adult benthic organisms. Investigations during the third and fourth years examined sublethal effects of drilling fluids on clam larvae, trace metal and organic constituents in both drilling fluids and toxicity test-phases, and the preliminary development of a drilling fluid solid phase toxicity test. Toxic components of the used drilling muds tested were present as dissolved components or associated with very slowly settling particles. Some used drilling muds contained lipophilic fractions that were similar to hydrocarbons found in #2 fuel oil in the liquid fraction and suspended particulates fraction and contained #2 fuel oil in whole muds. Muds that contained those components were more toxic than those that did not. Juvenile copepods (*Acartia tonsa*) were not more sensitive to toxic drilling mud solutions than adults of this species. In general, *Cancer irroratus* larvae appeared to exhibit toxicity responses to drilling muds that were similar to the copepods tested. Arrested shell development induced by exposure to drilling muds appeared to be a sensitive indicator of stress in bivalve larvae. Total chromium concentration showed no correlation to toxicity in the drilling muds that were tested; however, the highest concentrations of CR(VI), the most biologically toxic form of chromium, occurred in the test phases that exhibited the greatest toxicity to *Mercenaria mercenaria* larvae. The muds designated "May 15" and "Sept. 4" appeared to be relatively non-toxic to *Pseudopleuronectes americanus* and to *Menidia menidia*, although the "May 15" mud was toxic to *Neomysis americana* and to *Acartia tonsa*. A study of the effects of drilling mud on invertebrate recolonization of defaunated sediment showed that recolonization decreased in drilling mud layered on top of sediment when the muds were mixed with sediments. *Capitella capitata* was much more numerous in recolonization sediments that contained drilling mud. Test results showed that the methods used to prepare drilling mud test media affect the apparent toxicity of the muds.

This Project Summary was developed by EPA's Environmental Research Lab-

oratory, Gulf Breeze, Fl, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The possible environmental effects of offshore oil-well drilling operations have come under increasing scrutiny since the mid 1970's. The discharge of spent drilling muds, which are used in large quantities during drilling operations for drill-bit lubrication, borehole stabilization, blow-out prevention, cooling, and removal of drill cuttings, represent a potential source of damage to the marine environment. Drilling muds are composed of barite, clays (e.g. bentonite, attapulgite), deflocculants (e.g. lignosulfonate), chelators and organic lubricants in varying amounts. The concentration of some drilling mud components is changed intentionally to match the varied geological formations, temperature, and pressure changes encountered in a drilling operation. In addition, the composition of a particular mud is affected by the characteristics of the geological substrate and the drilling conditions. Because there is no truly standard drilling mud, the task of determining the potential toxicological effects of this heterogeneous assemblage of mixtures is complex. The most appropriate approach for toxicity testing has been to test the effects of spent drilling muds on a variety of marine animals using standard aquatic bioassay techniques.

The toxicity of both the liquid phase and suspended solid phase of twelve spent drilling muds was evaluated with a new bioassay procedure using larvae of the marine bivalve mollusc, *Mercenaria mercenaria* The settled solids phase of one of these drilling fluids was assessed for toxicity using both a laboratory and field recolonization study. These results are presented below in summary form under three headings: (1) Effects of used drilling fluids on the embryonic development of the hard clam *Mercenaria mercenaria;* (2) Trace metals in drilling fluid/sea water toxicity-test phases; (3) Solid phase recolonization studies.

Effects of Used Drilling Fluids on the Embryonic Development of the Hard Clam, *Mercenaria mercenaria*

Recent investigations have shown that invertebrate larvae are much more susceptible than adults to many pollutants This phenomenon has been confirmed in our laboratory studies on larval and adult bivalve molluscs. An understanding of the effects of drilling mud components on bivalve larvae is particularly important in view of the commercial value of such species as *Arctica islandica, Placopecten magellanicus* and *Spisula solidissima* These species are abundant in offshore waters where drilling operations may be initiated. Although the hard clam, *Mercenaria mercenaria*, is not found in these offshore areas, the convenience of utilizing this species for laboratory conditioning, rearing, and toxicity testing makes it a suitable organism for larval bioassay research. In addition, studies in our laboratory showed that the response of *M. mercenaria* larvae to spent drilling muds is similar to that of larvae of the sea scallop, *Placopecten magellanicus*, a bivalve that is much more difficult to maintain and culture in the laboratory. A new 48-h bioassay procedure was developed using 1-h old, fertilized eggs of *M. mercenaria* for assessing the toxicity of both liquid and suspended solid phases of spent drilling muds

Materials and Methods

Adult *M. mercenaria* were conditioned in the laboratory to allow spawning throughout the year. Spawning was initiated by slow temperature increase. Following a 1-h fertilization period, developing eggs were washed, counted, apportioned to toxicity test vessels (Pyrex test tubes; 50 ml of test phase; 10-15 embryos mL-1) and maintained at constant temperature (27° C) for 48 h. Several concentrations of both the liquid phase (supernatant from mud suspension settled 72 h) and the suspended solid phase (supernatant from mud suspension settled 1 h. [This test phase includes the liquid phase components.]) of twelve spent drilling muds were tested. At the completion of the 48-h bioassay period, animals were fixed with Lugol's solution and examined under a dissecting microscope. The criteria for toxicity were death (i.e. empty shells) or obvious abnormal shell development that would eventually lead to death. A 48-h EC50 value was generated for each drilling mud test phase using Probit analysis.

Results

The suspended solids phase of spent drilling muds was generally more toxic to *M. mercenaria* developing larvae than the liquid phase fractions alone (Fig. 1, 2). However, these results were statistically significant only for the spent muds designated P1, P2 and P3. The remaining eight muds did not show an appreciable difference in toxicity between the two test phases.

The 48-h EC50 values for the liquid phase of 8 of the 12 muds ranged from 85-712 ppm (vol/vol mixture of a 72 h-settled drilling mud suspension and 0.45 μm-filtered natural sea water to yield the indicated concentration of drilling mud liquid phase in sea water), whereas the range for the suspended solids phases of these muds was 64-382 ppm (vol/vol mixture of 1 h-settled drilling mud and 0.45 μm-filtered sea water). The EC50 values for the remaining 4 muds exceeded 2000 ppm, indicating that marked differences exist in the composition of spent drilling muds.

Discussion

The results of our tests showed that fertilized eggs of *M. mercenaria* are very sensitive to both the liquid and suspended solids phases of a diverse assortment of used drilling muds. This larval quahog toxicity test should serve as a useful tool for identifying the potential impact of drilling muds and other environmental pollutants on the survival of commercially important bivalve mollusc species in the offshore environment. The data generated in this study should be useful in determining maximum permissible mud discharge rates in coastal zones that serve as important seasonal nurseries for commercially valuable bivalve species.

Developing quahog embryos have been shown to be sensitive to a variety of used drilling muds. However, it has been impossible to correlate toxicity conclusively with specific mud components. Further toxicological studies are needed to delineate the effects of turbidity and particle loading, the adsorption of toxicants to particulates, and the role of microorganisms in the biodegradation of various drilling mud components.

Trace Metals in Drilling Fluid/Sea Water Toxicity Test Phases

Trace metal analysis of the drilling mud/sea water toxicity test phases was conducted in order to identify inorganic components of muds that may be toxic. The metals of interest included barium, cadmium, chromium, copper, manganese, nickel, lead, and zinc. These metals can occur in several different forms, or species, in the marine environment. The forms that metals assume in solution affect their bioavailability and, thus, their toxicity. For this reason, a scheme was

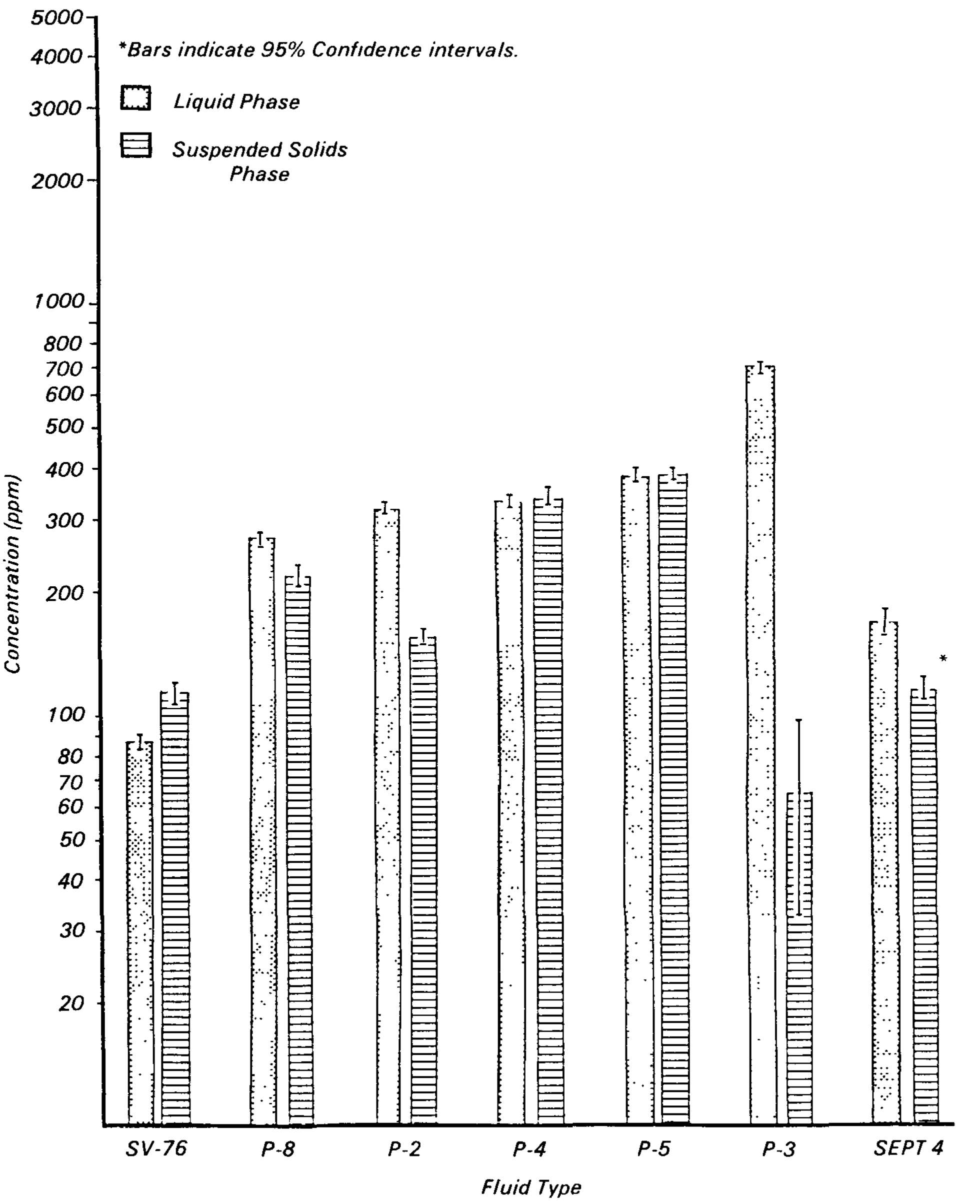

Figure 1. *EC_{50} values for* M mercenaria *larvae after a 48-hour exposure to drilling fluid.*

developed to determine the various forms, or species, of the trace elements listed above, as well as their total concentrations in drilling mud/sea water mixtures.

Three general types of metal species were targeted in the speciation scheme; these were: free ionic forms including inorganic complexes (i.e. chloro-, hydroxy-, etc.), organically bound metals, and metals associated with particulates. These classes of trace elements are typically considered to be the major types present.

In addition to the metal species discussed above, chromium can exist in two oxidation states in sea water. Chromium(VI) is present as CrO_4^{2-} and is considered highly toxic, whereas Cr(III) as $Cr(OH)_2^+ \cdot 4H_2O$ is much less toxic Determination of the oxidation state and species of Cr was also included as part of the speciation scheme.

Methods

The concentrations of several metals in sea water mixtures of drilling fluids were measured simultaneously using dc plasma emission spectrometry. Total metal concentrations were measured by directly aspirating dilute sea water suspensions of drilling fluids into the plasma after settling times of 1 h (suspended solids phase) or 72 h (liquid phase). Solution phase metals were determined after centrifugation of the same mixtures.

Free metal concentrations were determined by performing equilibrium dialysis separations of the drilling mud/sea water mixtures before spectrometric analysis. A 1000 molecular weight cut-off dialysis bag containing filtered sea water was placed in the mixture Metal species small enough to pass through the pores of the membrane migrated into the bag and were measured and assumed to be primarily free, hydrated metal ion.

Chromium was further speciated by separating free Cr(III) using Donnan dialysis with cation exchange membranes The difference between total free Cr and free Cr(III) gives the Cr(VI) concentration. The Cr(VI) concentration was also measured where possible, using differential pulse polarography

Results

Results from the measurement of trace metals in drilling fluid-sea water mixtures showed that the average concentrations of the detectable elements decreased in the order Ba>Cr>Mn>Zn>Cu. The concentrations of Cd, Ni and Pb were below the detection limits of the measurement system (0.02, 0.01 and 0.2 mg/L respectively). All metals exhibited some particle association in 1 h settled phases (suspended solids) with Ba being present principally in the particulate form. Chromium and Cu were bound, probably as lignosulfonate complexes, but Mn and Zn were primarily in free forms. A significant portion of the Cr was present as highly toxic Cr(VI) in two of six muds analyzed for this form of Cr.

Table 1 gives a breakdown of some Cr species for some of the muds that were tested and is an example of the metal speciation results obtained For each drilling fluid, the liquid and the suspended solids test phases were analyzed at specific concentrations of drilling fluid in filtered sea water. The liquid phases showed only a small difference between solution Cr and total Cr concentrations. As expected, only a small amount of presumably colloidal Cr remains suspended after the 72 h settling time. Conversely, the suspended solids phases have substantially more Cr associated

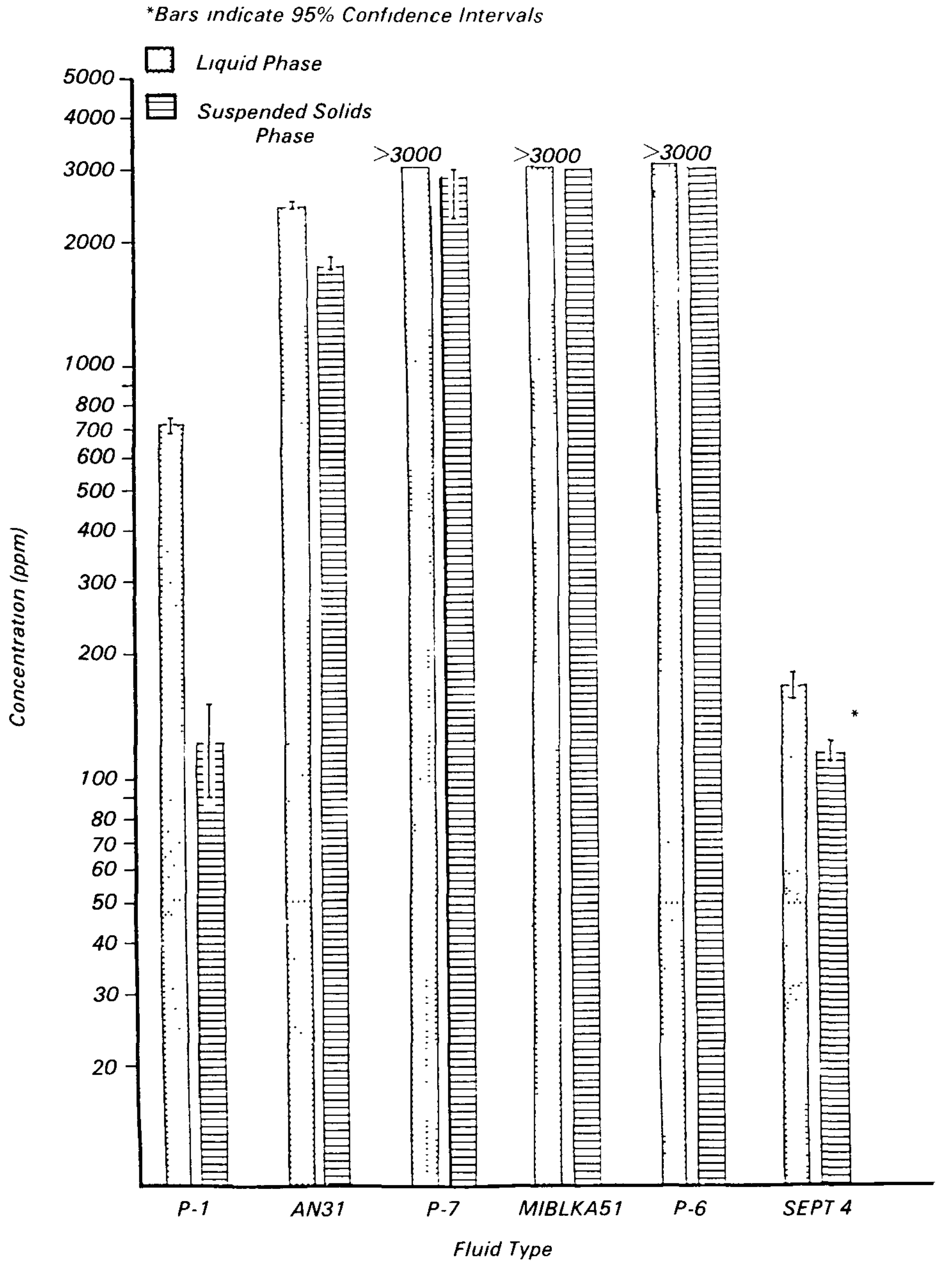

Figure 2. *EC_{50} values for* M. mercenaria *larvae after a 48-hour exposure to drilling fluids*

with particles than is present as dissolved species.

The free Cr concentrations found for the liquid phases accounted for approximately half of the dissolved Cr present for all but the P8 drilling fluid. This result was somewhat surprising, based on the relatively high concentration of lignosulfonate and lignite present in these muds with which Cr could react.

Further speciation of free Cr into free Cr(III) and free Cr(VI) for some of the muds tested is presented in Table 2. An interesting point is that the free Cr(III) values listed (Table 2) are all very close to 0.020 mg/L, while the total free Cr (Table 2, column 1) values vary by almost an order of magnitude. This strongly suggests that the Cr(III) concentrations were solubility limited.

The difference between free Cr(III) and total free Cr gives the free Cr(VI) concentration (Table 2, column 3) The Cr(VI) *concentration found for SV76 was the* highest by far, with P1 being the only other drilling fluid with a significant concentration The determination of Cr(VI) directly by an alternate method, differential pulse polarography, resulted in values that were somewhat lower by approximately a factor of two. These results indicate that previous assumptions asserting the absence of potentially toxic Cr(VI) in drilling fluids were incorrect. Chromium (VI) is present in some used drilling fluids and in dilute sea water mixtures of these fluids at levels that could result in toxic effects on marine organisms

The potential threat of metal toxicity, bioaccumulation, and food chain biomagnification is greater from Cr than from other elements tested. Although most of the Cr is probably present as Cr(III) complexes of lignosulfonate, its concentration is relatively high The lack of toxicity usually observed for Cr(III) has been attributed to its low solubility Lignosulfonate forms complexes of Cr(III) and increases its solubility, thus increasing the potential threat of this form of Cr in drilling muds. In addition, Cr(VI) is often the form of Cr added to lignosulfonate to prepare chrome or ferrochrome lignosulfonate Chromium(VI) salts are sometimes added to drilling muds as well, and large quantities are used during preparation, making it very likely that some Cr(VI) will remain unreacted in muds with pH *conditions that are unfavorable for Cr(VI)* reduction. In oxygenated sea water, the stable form of dissolved Cr is Cr(VI). It has been demonstrated that Cr(III) is present, but slow oxidation occurs in the presence of O_2 and is catalyzed by manganese oxide. This suggests that any Cr added to the ocean, regardless of the form, is potentially harmful.

Solid Phase Recolonization Studies

The assessment of toxicity in solid phase pollutants has traditionally been much more difficult than in water soluble or suspended solid pollutants. One approach has been to measure either survival or physiological and biochemical effects of solid phase pollutants on infaunal invertebrates A second approach, reported here, has involved monitoring the recolonization of natural, defaunated sediments containing potentially toxic solid phase pollutants to determine toxicity. Laboratory-based and field-based experiments were used to evaluate the toxicity of a spent drilling fluid based on its effects on the recolonization of natural sediments by benthic organisms

Table 1. *Concentration and Speciation of Chromium in Drilling Fluid/Seawater Test Phases*

Drilling Fluid	Type of Phase[a]	Phase Conc. (mL/L)[b]	Concentration of Chromium (mg/L)		
			Total	Solution	Free[c]
SV76	Liquid	3.0	0 59±0.02	0.543±0 004	0.214±0 007
	Suspended	0.15	0.135±0.008	0 051±0 003	
P1	Avg. Liq. (2)	3 0	0 155±0 004	0.15 ±0.02	0.067±0.002
	Suspended	1.0	0 110±0.003	0.037±0.003	
P2	Avg. Liq. (2)	3 0	0 044±0.005	0.041±0.003	0.025±0 002
	Suspended	0 5	0 083±0.003	0 016±0.003	
P8	Avg. Liq (2)	3 0	0 27 ±0 02	0.264±0.008	0 031±0.006
	Avg Sus. (2)	3.0	0 6 ±0 2	0.275±0.003	

[a]Replicate phases are expressed as an average with number of replicates in parentheses
[b]Concentrations are mL of whole mud per L of 0.45 μm filtered sea water.
[c]Used 1,000 molecular weight cut-off membranes for one test phase in duplicate (see text).

Table 2. *Free Chromium (III) and Chromium (VI) from Donnan Dialysis of Drilling Fluid/Seawater Liquid Phases[a]*

Drilling Fluid	Concentrations of Chromium (mg/L)		
	Free Cr[b]	Free Cr(III)	Cr(VI) by difference[c]
SV76	0.214±0.007	0.025±0.007	0.19 ±0.01
P1	0.067±0.002	0.020±0.004	0 047±0.004
P2	0 025±0 002	0 014±0.007	0.011±0.007
P8	0 031±0 006	0 022±0.009	0.009±0.009

[a]All phases were 3.0 mL of drilling fluid per L of 0.45 μm filtered sea water
[b]From Table 1.
[c]Cr(VI) concentrations are the difference between free Cr and Cr(III) values.

Materials and Methods

The matrices of the laboratory- and field-based experiments were identical The tests included three treatments of sediment: a natural, fine-grained, defaunated reference sediment (control); a drilling mud mixed with the reference sediment (homogeneous test); and drilling mud deposited on the surface of the reference sediment (surface test). Five replicate samples of each treatment were removed after two weeks, four weeks, and six weeks of recolonization exposure.

Upon collection, samples from both the laboratory and field studies were sieved through a 0.25 mm screen and preserved in 10% formalin. All animals were subsequently identified to the lowest possible taxon and counted.

Three parameters were used for statistical analysis of samples from each recruitment period of each experiment. (1) number of individuals; (2) number of species; and (3) ratio of numbers of species and individuals. The number of individuals indicates the overall abundance in a unit area. The number of species is a measure of variety of species richness Both of these determine the third parameter, number of species/number of individuals (S/N), which is a simple estimator of diversity, uncorrected for sample size or evenness of species distribution. Analysis of variance and the Student-Newman-Keuls multiple range test were performed to compare the treatments for the above parameters Student's t-test was used for groups of data in which only two treatments were being compared. In all statistical tests, a 95% confidence level was used ($P < 0.05$). Recolonizing populations were also characterized qualitatively by distribution of individuals within a phylum and by species predominance. Species were considered predominant on the following basis each predominant species occurred in at least 60% of the replicates and contributed at least 4% of the total animals in a treatment. Less abundant species were also included until 75% of the total animals in a sample were accounted for.

Results

Mean numbers (± standard deviation) of animals recovered for all samples analyzed in both experiments are displayed in Figure 3. Numbers of animals increased over time in both laboratory- and field-based experiments. The latter experiments had a higher number of animals than the former after both two- and four-week recruitment periods. In general, the homogeneous test and control sediments displayed higher mean and total numbers of individuals, number of species, and number of phyla than the surface test samples.

Discussion

In general, the data show that a used drilling fluid affected recolonization when layered on top of defaunated sediment but not when mixed with it. In both experiments, deposition of a new layer of detrital material on top of the drilling fluid seemed to reduce or reverse the effects; following six weeks of exposure, the effects of the drilling fluid were no longer obvious.

The reduced numbers of individuals found in surface-test samples could have been caused by physical or chemical aspects of the drilling fluid. The evidence suggests a physical mechanism for the observed reduction in recolonization in surface tests. First, if the effect was chemical, adverse effects would be expected to occur to a lesser extent in the homogeneous test samples. This was not the case. In fact, when homogeneous samples differed from the other two treatments, they contained slightly higher numbers of animals. Second, the effect ceased when animals were no longer in direct contact with the layer of drilling fluid, yet chemical effects would probably have persisted, since toxicants could continue to leach upward from the drilling fluid through a thin detrital layer. Finally, additional analyses of organic and trace metal components of the drilling mud used in the benthic recolonization toxicity test showed this mud to have a relatively low toxicity.

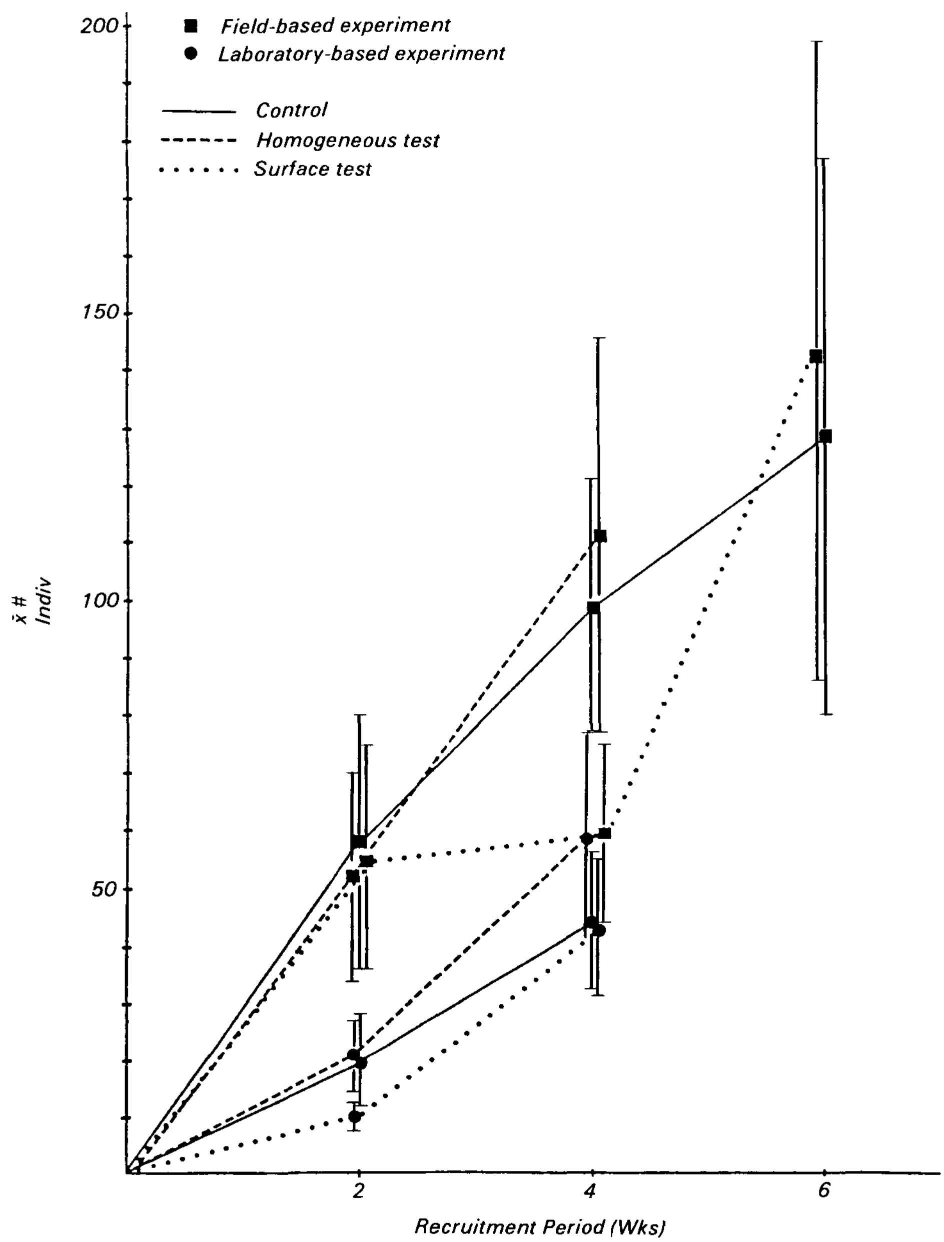

Figure 3. *Mean number of individuals collected after two-, four-, and six-week recruitment periods for control, homogeneous and surface test treatments in laboratory- and field-based experiments. Data are mean of individuals for n = 5 replicates (except for lab-based two-week homogeneous test, where n = 4). Vertical bars indicate standard deviations.*

☆U. S. GOVERNMENT PRINTING OFFICE: 1984/759-102/10627

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__T. W. Duke__ is the EPA Project Officer (see below).

The complete report, entitled "A Survey of the Toxicity and Chemical Composition of Used Drilling Muds," (Order No. PB 84-207 661; Cost: $13.00, subject to change) will be available only from:

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