Oil Dispersants

New Ecological Approaches

L. Michael Flaherty, editor

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Foreword

ASTM Committee F-20 on Hazardous Substances and Oil Spill Response sponsored a state-of-the-art review of "Dispersants: New Ecological Approach through the 90's" at its symposium held in Williamsburg, VA, 12–14 Oct. 1987. Over 145 people from 7 countries attended to learn of the latest technological advances in spill countermeasures. L. Michael Flaherty, formerly with the Environmental Protection Agency and now an independent consultant, was chairman of the symposium and served as editor of this book. William B. Katz, Illinois Chemical Corp., and Stephan Kaufmann, Sunshine Technology Corp., served as cochairmen of the symposium.

A Note of Appreciation to Reviewers

Many new and exciting things have been happening in the field of environmental response activities, and these formed the cornerstone of our Williamsburg symposium. The successful transfer of information, however, is dependent not only on those who contributed documentation but also on those who reviewed this documentation for clarity, comprehensiveness, and completeness. Without them, we could not adequately get our message to the public and, without them, we could not be assured that our publication would meet the highest professional standards. Our appreciation is heartfelt.

Contents

Overview

The Symposium on Dispersants: New Ecological Approach Through the 90's held in Williamsburg, Virginia, in October 1987, summarized research and development on dispersants and other chemical countermeasures and their use during the past 5 years. It was one of the best attended symposia of Committee F-20 on Hazardous Substances and Oil Spill Response in many years with over 145 total participants representing 7 countries.

In the January 1987 call for papers, the chairman requested that papers be submitted stressing the positive developments and uses of innovative countermeasures. There was sound reasoning behind this request. Since the Torrey Canyon grounding in 1967, little "good" or "positive" has been said or written about dispersants. In the United States, the two major agencies controlling the use of dispersants have had what many refer to as an *unwritten* prohibition on their use. This may have been somewhat warranted because of the toxicity of the early first generation dispersants produced from the late 1960s through the early 1970s. However, in the case of the Torrey Canyon spill, the oil itself was highly toxic, the dispersants were almost totally improperly applied, and explosives and napalm were also heavily used. Just the latter two on their own were responsible for tremendous fish kills.

The time has come to add to the technical literature positive papers that address many new and advanced areas, such as guidelines for dispersant use in freshwater and the effects of elastomers on the efficiency of oil dispersants. Several papers in this book discussed modern computer usages to assist response application while another paper described using a computer for both training and contingency planning. Other papers also related the crisis in response training, while another makes an indepth analysis of the behavior of dispersed and nondispersed fuels in sewer systems. The papers assembled in this book break new ground in many innovative areas of chemical countermeasures.

Let it be said from the beginning that the preferred countermeasure will always be to recover the oil as completely as possible and recycle it. Up until recently, recovery of oil was confined to small-scale operations in calm waters and, because it was a labor intensive endeavor, it was generally not very cost-effective. Now, new products and techniques discussed in this book make recovery both a broader and more economical reality.

In the past five years, noted marine biologists, oceanographers, and environmental scientists have spoken out on the positive aspects and overall usefulness of dispersants. Again, it is important to qualify the application of dispersants by repeating what must always be understood . . . When a properly selected dispersant is applied with correct techniques at an approved rate and in a timely manner to an oil that is fresh and known to be dispersible, in water of 10 m or more with some current or flushing action, then one should expect to obtain good results. While this may connote an idealistic scenario, emergency response personnel can today use dispersant chemicals correctly with only minimal training and good contingency planning.

We are definitely in the third generation of dispersants (many will say the fourth). While these newer dispersants are slightly more specialized in their applicability, they are considerably more effective and less toxic than the earlier generations of products. Generally, when we spoke of dispersants in the past, we simply meant a chemical formulation of surfactants, solvents, and additives which, when applied and agitated, formed an oil-in-water emulsion. Today, there are products listed as dispersants that are designed and formulated for land use only while others may be formulated primarily to emulsify oil or gasoline on street or highway spills. Some products are designed for use in holding ponds and small streams; yet others are designated to be used to clean offshore rigs or bilge tanks. Furthermore, there are probably another half dozen cleaners or emulsifiers for specialized applications that are also called "dispersants." It is, therefore, a case of caveat emptor. One must scrutinize carefully what one buys in order to stock for the appropriate application.

For those of you who may read this book with the intention of formulating or designing a new dispersant or other type of chemical countermeasure, let us in a few words address what might be considered an ideal product. It should be reasonably priced, effective on all types of oil (both fresh and weathered), and easy to apply from shipboard, aircraft, or fire hose. It should be nontoxic to fish and other aquatic life, good for both fresh and saltwater, be self-mixing or require minimal agitation, should help break down the "mousse," and perhaps even be effective on land as well as on the sea. It is obvious that no product could possibly satisfy all these criteria, but low toxicity and high effectiveness are the key elements, and the ability to work on a wide variety of oils (weathered and otherwise) is also crucial.

One can see from the above list of effectiveness standards that there are many qualifications involved in formulating and marketing a new product. A true dispersant should principally be designed for water application rather than as a cleaning agent. Furthermore, a really *good* dispersant will serve naturally as a deterrent to fires and subsequent explosions.

It is also important that we consider the cost-effectiveness of dispersant used in cleaning up spills to navigable waters. When an effective dispersant is used on an oil known to be dispersible, in water which has adequate current or wave action and is of sufficient depth, there is now little doubt that dispersants are probably the most cost-effective method of cleanup short of total removal by vacuum truck or skimmers followed by recycling. Use of dispersants at sea is certainly 10 to 30 times safer and more economical and effective than any attempts to remove an oil slick on shore.

There is a soon-to-be-released (if not already published) National Academy of Sciences, National Research Council, Marine Board two-and-one-half year study on dispersants which, in essence, states that third and fourth generation dispersants are both effective and of minimum toxicity. It was hoped that this book would contain an executive summary of these findings; however, the printing deadline did not allow the release of the data in time.

Over the past five or six years (and perhaps longer), a new breed of oil spill countermeasure products has come to the attention of the Environmental Protection Agency. The first of these were called gelling agents. They originated in Japan and have been in use there for quite some time. These products work well in still waters but are labor intensive and require disposal after utilization. Another group of products is known as emulsifiers. Emulsifiers differ from dispersants in the manner in which they suspend the oil. On the other hand, dispersants disperse it in very small droplets in the upper 3 or 4 m of water. Finally, there is a relatively new line of products known as elasticizers or viscoelastic enhancing agents. One of these is a two-step chemical procedure that forms the oil into a carpet, which can be rolled up and retrieved from the aqueous environment; another process, accomplished in one step, temporarily congeals oil into an elastic bond which can be vacuumed or collected by a skimmer with little or no water separation required. Initially, it was believed that this latter product could only be used in the relatively calm waters of bays or tributaries; however, recent trials 25 miles (40 km) off the coast of Saint Johns, Newfoundland, indicate that it can achieve outstanding results in open, heavy seas and particularly in holding oil within boomed areas. Films of the test spill of 18 000 gal (68 000 L) of oil indicated great increases in oil recovery using this new agent.

In addition to dispersants, other innovative countermeasure products were demonstrated during the "show-and-tell" session and indicated great increases in oil recovery using this new agent. Products that show tremendous potential are the new sorbents, which for the first time can truly be called ABsorbents in that they collect and retain oil. These absorbents and this viscoelastic enhancing agent indicate great hope for future oil spill cleanups. Some were demonstrated at a special show-and-tell period during the last days of the Williamsburg symposium. The session included about ten booths and was greeted enthusiastically by participants. It is hoped that organizers of future symposia will consider this as an educational and profitable element of the overall program.

Appreciation of help in the review and critique of papers should be recognized. A special expression of gratitude is extended to Bill Katz and Stephen Kaufmann, who, as assistant chairmen gave greatly of their time and valuable knowledge that contributed to the success of the symposium and the completion of this book.

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Effects of Chemical Dispersant Agents on the Behavior and Retention of Spilled Crude Oil in a Simulated Streambed Channel

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ABSTRACT: Field experiments were performed to obtain first-step estimates of the effects of selected chemical dispersant agents (OFC D-609 and Corexit 9550) on the behavior and retention of spilled crude oil in a shallow freshwater streambed environment in southcentral Alaska. Comparisons between experiments with and without prespill additions of dispersants to the oil included measurements of oil in sediment and water samples. Sediment and water contamination by oil was quantified by flame ionization detector capillary gas chromatography (FID-GC) as well as visual observations in the simulated streambed channel following the spill events. Inclusion of dispersants in the oil produced the intended result of enhancing dispersion of oil into the aqueous phase. However, distributions of oil in aqueous and sediment samples were controlled by interactions between a variety of factors including rheological properties of the oil (for example, oil/water interfacial surface tension values), particle size distributions of sediment matrices, exposure of sediment surfaces to oil, and in situ water flow characteristics at specific streambed channel sites. The results imply that use of chemical dispersants to mitigate effects of oil spills in freshwater streambed environments must include an understanding of the interplay between variables related to both the type of oil released and the specific streambed environment.

KEY WORDS: chemical dispersants, crude oil, freshwater streambed, sediments, water, oil dispersion, surface oil slick, rheological properties, interfacial surface tension, sediment particle size distribution, water flow properties

Oil exploration, development, production, and transportation operations in nearshore and inland areas of Alaska and Canada may result in the release of oil into cold, low salinity waters. In addition to habitats for indigenous biological communities, the coastal freshwater rivers and streams in this region serve as sites of (or routes to) spawning areas for migratory species such as pink, coho, chinook, chum, and sockeye salmon. The estuarine zones at the mouths of rivers and streams also serve as crucial nursery regions for juvenile forms of other vertebrate and invertebrate species. Consequently, methods need to be

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developed and evaluated for the mitigation and removal of potential oil spills in the cold, freshwater streambed environments in these arctic and subarctic regions.

One approach for minimizing problems associated with potential oil spills would involve the application of chemical dispersant agents to an impacted area. Application of a dispersant to an oil slick on water is intended to lower oil/water interfacial surface tension values and facilitate dispersion of small oil droplets into the water phase. This in turn can lead to the transport and dilution of the oil droplets by subsurface water currents.

In laboratory tests of several commercially available chemical dispersant formulations [*1*], Corexit 9550 (Exxon Chemical Co.) and OFC D-609 (ChemLink Petroleum, Inc.) were found to be effective dispersants under conditions of varying salinity (0 to 33 parts per thousand) and temperature (1 to 10°C). However, it has been noted in other studies [*2,3*] that the effectiveness of a dispersant agent will depend on numerous factors including: (1) the composition of the dispersant formulation, (2) characteristics of the oil (that is, its viscosity, density, and chemical composition), (3) the dispersant to oil ratio (D:O), (4) methods of application of the dispersant to the oil, (5) methods of mixing of the dispersant with the oil, (6) ambient water and air temperature, and (7) the salinity of the water. Therefore, extrapolating results from laboratory tests to "real world" situations must be done with a considerable degree of caution. Furthermore, existing information on the behavior of dispersed oil in shallow freshwater streambed environments is still incomplete for supporting predictions of relative environmental impacts of chemically dispersed versus nondispersed oil. This paper presents results from a series of experiments that were conducted to determine effects of dispersant additions on the behavior and fate of oil released into a confined bench scale test model of a streambed. Effects of dispersants on retention of oil by the streambed (for example, in sediment matrices) were of particular interest. The model contained flow regimes and sediment mediums and topography that were patterned after those observed in natural streambed environments in southcentral Alaska.

Materials and Methods

Experimental Streambed Construction and Maintenance

The bench scale test model for the streambed channel was constructed at the National Oceanic and Atmospheric Administration (NOAA) field laboratory at Kasitsna Bay, Alaska. For maximum use of available space and to increase access to sampling sites, the channel bed (Fig. 1) consisted of three sets of adjacent, parallel "runs" connected in series by two short runs. Each long run was 0.42 m wide and 4.66 m long. A false bottom was installed in the channel bed to create an even slope with a 0.91-m drop over the total 29.3-m length of the empty channel bed.

Freshwater from a natural stream adjacent to the lab was introduced at the start of Run 1 at a flow rate of 30 L/min. Water left the streambed at the end of Run 6. The water exiting the channel was either diverted into a 360-L reservoir or discharged onto the beach adjacent to the lab. For the streambed experiment, the reservoir was used to collect the freshwater and major portion of an oil slick immediately after a spill event. Oil sorbent pads were placed at the discharge point on the beach to aid in the cleanup and collection of oil that was not captured in the 360-L collection reservoir.

Before experiments were undertaken, careful observations were made of the natural flow path of water through the empty channel bed. This flow regime served to direct the placement of fill materials in the bed to simulate more closely natural stream conditions. Typical characteristics of natural streams and creeks in the southcentral Alaska area were also surveyed and duplicated in the test channel as closely as possible. Fill for the empty channel was collected from natural stream and beach environments adjacent to the lab. This

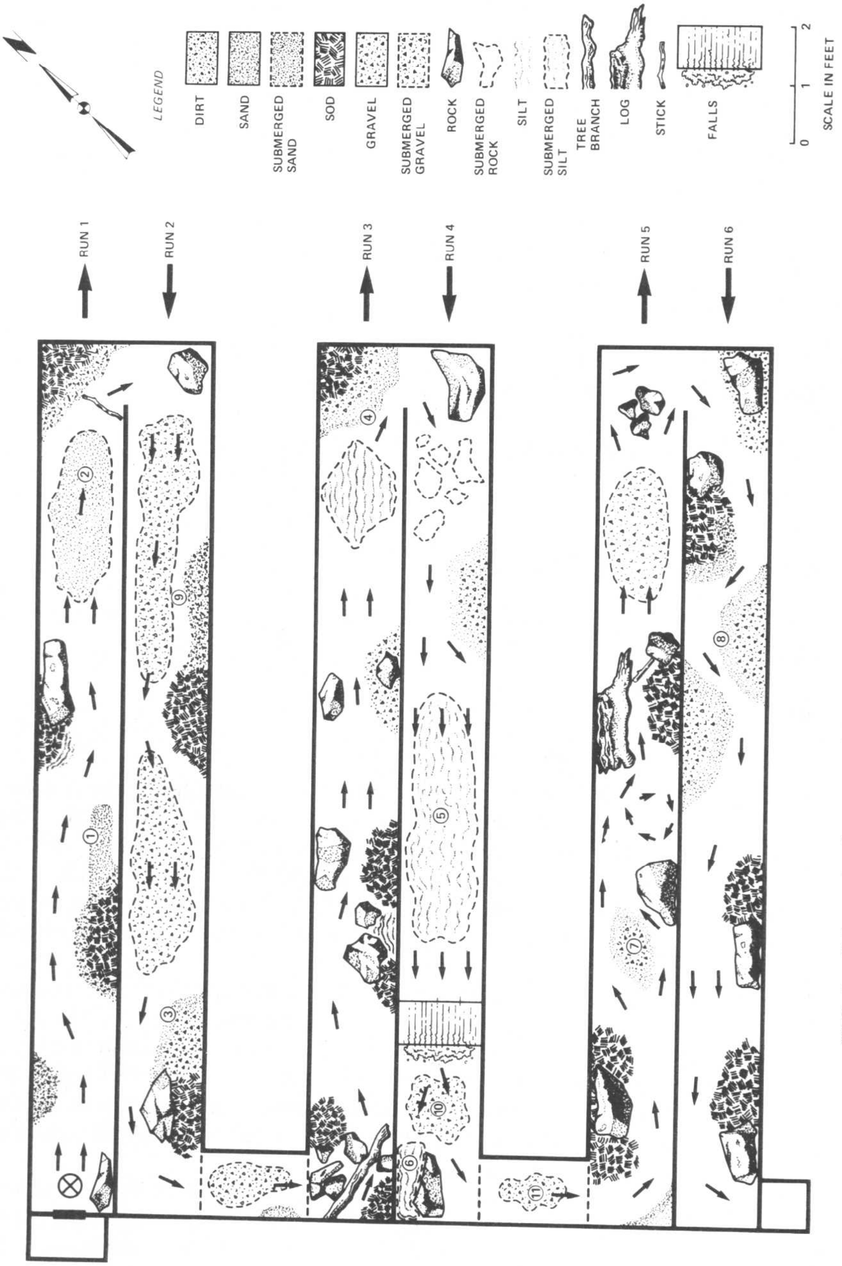

FIG. 1—*Schematic plan view of the experimental channel used for oil and oil/dispersant studies. Blank areas indicate submerged substrate, not an absence of sedimentary materials. Sediment sampling sites are designated by numbers. The location for the oil spills is indicated by the* X *at the start of Run 1. Arrows indicate the direction of water flow. (Note: for length scale 1 ft = 0.305 m.)*

fill consisted primarily of mud, sand, gravel, rocks, sod, dirt, sticks, logs, and tree branches. These materials were placed in the channel in configurations to augment not only predisposed flow patterns in the empty channel, but also approximate characteristics observed in the natural streambed environments. Following the addition of fill to the channel and before any experiment was started, the channel was maintained with running water for 24 to 72 h. This "acclimation" period was adopted to allow for natural flow mediated redistribution and sorting of sedimentary materials throughout the channel. The 24- to 72-h period proved sufficient to yield reasonably stable sedimentary profiles in the channel. During experiments water temperatures in the channel ranged from 8 to 11°C depending on ambient sun and weather conditions.

Prominent features of the bench scale test model are shown schematically in Fig. 1. It should be emphasized that empty portions of channel bed shown in the figure indicate only submerged substrate surfaces rather than an absence of sedimentary material. The entire channel was filled with sedimentary material. The general appearance and composition of the completed channel bed can be better observed in the photographs of selected runs in Figs. 2 and 3. Because three experiments were performed with this test configuration (that is, one experiment with oil only and two with oil plus a chemical dispersant agent), portions of the channel fill had to be replaced between experiments. Particular care was taken to insure that channel configurations were the same in the three experiments. A much more detailed schematic drawing of Fig. 1 as well as photographs of previous channel configurations were used for direction in each subsequent channel reconstruction effort. Furthermore, only those portions of a previously used channel bed that retained oil were replaced with new fill material.

FIG. 2—*Experimental channel:* (left) *Runs 1 and 2 and* (right) *Runs 3 and 4.*

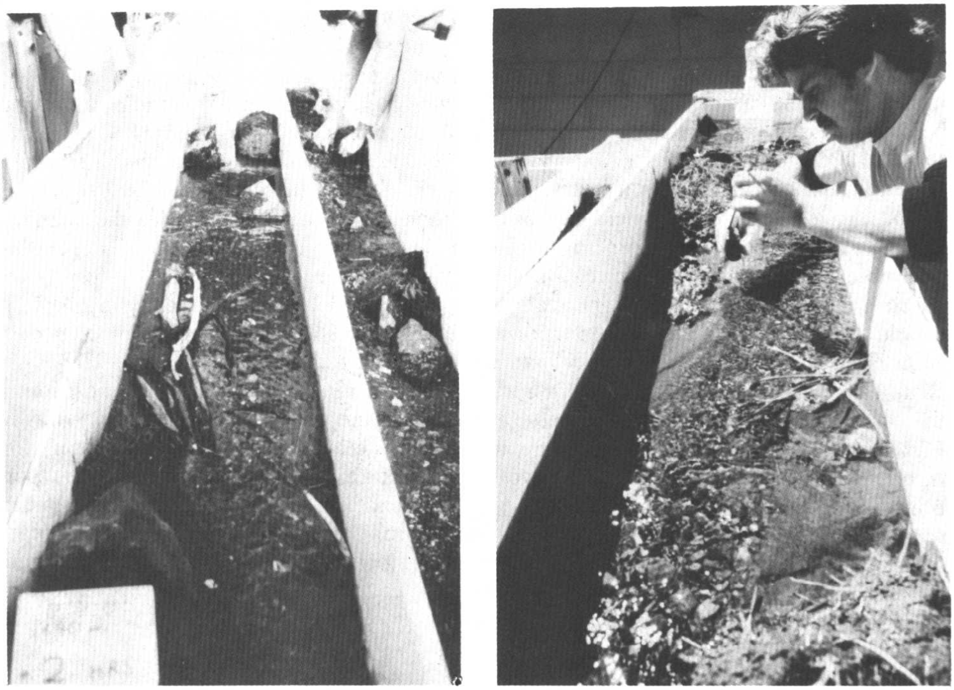

FIG. 3—*Experimental channel and sediment sampling procedure:* (left) *Runs 5 and 6 (sampling at Site 8, Run 6) and* (right) *sampling at Site 2, Run 1.*

Eleven sites were selected for sediment sampling to monitor oil levels in the channel bed following a spill event. Site selections were made with the intention of providing information on oil loadings in a variety of sediment types (that is, varying particle size distributions) under a variety of water flow regimes. The sites are shown in Fig. 1. Samples were collected from Sites 1 through 9 at the following times relative to a spill event: time zero or background (0.5 to 1 h before the spill event), 0.5, 2, 4, 8, 24, 48, 72, 120, 168, and 190 to 220 h. Because of the multiple sampling events over time at each of these nine sites, careful efforts were made to sample randomly each site and leave representative site material for subsequent sampling events. Samples at Sites 10 and 11 were only collected at the final sampling time in each experiment. More frequent sampling at these latter two sites was not feasible because of the nature of their substrates (that is, large gravel and sand) that necessitated large volume collections to obtain representative samples.

Detailed descriptions follow for the sediment sampling sites and the general composition and sediment types in the channel runs in Fig. 1.

Run 1—Inflowing water to the test channel entered through an initial catch basin. The submerged portion of the upper half of Run 1 was composed mostly of gravel. Two major beach areas occurred approximately mid-run. The first of these was protected by an upstream sod embankment, and included a point bar comprised of sand and a protected backwater area on the downstream side. This point bar formed sampling Site 1. The second half of Run 1 was primarily an expanse of submerged sand overlying pebbles. The flow of water over this area resulted in a slow migration and sorting of sand grains in the downstream direction to expose periodically underlying pebble substrate. This submerged sandy area formed sampling Site 2.

Run 2—The entire submerged portion of Run 2 was composed of gravel, small rocks, and sand. Side bars occurred in the middle and lower half of the run. The first of these bars (comprised of gravel, intermittent sand, and some fine silt and clay) occurred on the upstream side of a sod embankment and formed sampling Site 9. Further downstream, the second side bar (also composed of gravel, sand, and some fine silt and clay) occurred on the upstream side of a rock/sod embankment and formed sampling Site 3.

Run 3—Water flowed through a complex arrangement of rocks, sod, and tree branches at the start of Run 3 before passing over a more open gravel bottom. Large rocks and clumps of sod combined to support moderate sized beaches in the middle part of the run. The lower half of the run contained the upper portion of a deeper pool created by the cinder block dam in Run 4. Correspondingly, the depth of the water column increased and the longitudinal flow rate of water decreased in the second half of Run 3. A layer of fine silt, clay, and detrital organic material covered a gravel substrate in the bottom of this pool. A large sod embankment with an accompanying side bar of sand and gravel occurred at the end of Run 3. This bar around the sod embankment formed sampling Site 4.

Run 4—The upper three quarters of this run was dominated by a relatively deep pool of water (12 to 15 cm in depth) forming upstream of a waterfall (10- to 12-cm drop) constructed by a cinder block dam. An embankment with an accompanying sand and gravel side bar occurred midway through the pool. Sampling Site 5 occurred in the pool downstream of the sand/gravel embankment. Sediment in the bottom of the pool at Site 5 consisted of a nonuniform thin layer of fine organic detritus, silt, and clay overlying a sandy substrate. Sediment immediately below the waterfall formed sampling Site 10 and was comprised almost exclusively of large gravel as a result of the force of the falling water. A backwater area comprised of fine silt and mud overlying sand and gravel was formed in an eddy behind a large rock at the end of Run 4. This area served as sampling Site 6. The subsequent short runway between Runs 4 and 5 was composed of sand and large gravel and formed sampling Site 11.

Run 5—The majority of the submerged streambed in Run 5 was comprised of gravel. A small longitudinal bar consisting of sand and gravel occurred in the middle of the channel approximately one third of the way down the run. This mid-channel bar formed sampling Site 7. A subsequent configuration of rocks, sod, logs, and sticks combined to produce an area of restricted water flow with an accompanying upstream clockwise eddy pattern.

Run 6—The upper half of Run 6 consisted of a narrow, sinuous channel with a greater elevation drop than that occurring in other parts of the test channel. Steep gravel and sod embankments with accompanying point bars of sand formed the sides of this channel. Water flow through this portion of the channel bed was relatively faster and more turbulent than that in other areas. The sandy point bar at the midpoint through this sinuous channel served as sampling Site 8. The second half of Run 6 consisted of a submerged gravel substrate with accompanying sod and rock embankments.

Spill Scenario

Three experiments were performed in the test channel with the following spill solutions (dates are shown in parentheses): (1) fresh Prudhoe Bay crude oil with no dispersant addition (6–14 June 1985), (2) fresh Prudhoe Bay crude oil and OFC D-609 (30 June–8 July 1985), and (3) fresh Prudhoe Bay crude oil and Corexit 9550 (15–24 July 1985). The choice of dispersant agents was based on results from previous laboratory studies that indicated that OFC D-609 and Corexit 9550 were effective chemical dispersant agents in freshwater systems [*1*]. A total of 5.0 L of crude oil was used for each experiment. In experiments with OFC D-609 or Corexit 9550, 500 mL of the dispersant agent were mechanically mixed into the oil (that is, a D:O ratio of 1:10 v:v) immediately before the spill. The spill solution was then gently poured over a 3-min period onto the surface of the water at the head of Run 1. When the leading edge of the oil slick reached the end of Run 6 (approximately 5 min after the spill), the channel effluent was diverted into the 360-L collection reservoir. After the reservoir was filled, the effluent water was diverted onto the oil sorbent pads on the adjacent beach.

Sediment Sampling—Hydrocarbon Methodology and Extraction Procedures

As described previously, sediment samples were collected over time from the sites shown in Fig. 1. The samples were collected with stainless steel or Teflon® coated spatulas or scoops, placed in glass containers with aluminum foil or Teflon cap liners, and kept at 2 to 4°C until the times of analyses. Figure 3 illustrates the sediment sampling procedure (as well as photographic detail of certain locations in the channel bed). Although sediment samples were collected up to 190 to 220 h following a spill event, hydrocarbon analyses were performed on samples from Sites 1 through 9 only up to the point when the analytical measurements of hydrocarbon concentrations returned to time zero background levels. Triplicate samples for hydrocarbon analysis were periodically collected from randomly selected sites during each experiment to allow for estimates of sample variability through the complete collection and analytical procedures (see below).

For hydrocarbon analyses, a known wet weight of sediment (usually 30 to 60 g) was transferred to a 200-mL glass container and mixed with methanol. The methanol was then decanted into a 1000-mL separatory funnel. The methanol dried sediment was then sonicated three times with (1) 100 mL of methylene chloride:methanol (65:35 v:v), (2) 100 mL of methylene chloride, and (3) 100 mL of methylene chloride. Each sonication lasted 3 min and was performed with a Heat Systems-Ultrasonics, Inc. sonicator (Model W-375; pulsed mode; output control setting 7; 50% duty cycle). The solvent extracted sediment was dried in an oven (100°C) to determine the dry weight of sample extracted. The combined methanol-methylene chloride extracts were backextracted with a 3% sodium chloride (NaCl) solution (precleaned with methylene chloride) to remove the methanol, and the NaCl-methanol solution was then backextracted two more times with 25-mL volumes of methylene chloride. The combined methylene chloride fractions were dried with anhydrous sodium sulfate (Na_2SO_4) and reduced to appropriate volumes for analysis. Gas chromatography with flame ionization detection (FID-GC) was used to quantify hydrocarbons in the final sample extracts. A Hewlett-Packard Model 5840A gas chromatograph (splitless injection mode, 1.0-μL automatic injection volume) containing a fused silica capillary column (DB5 stationary phase, J & W Scientific, Inc.) was used for all GC analyses. Hydrocarbon quantities were determined by comparing sample chromatograms with those from a combined *n*-alkane standard (*n*-C_{12} through *n*-C_{32}, plus pristane and phytane).

Representative hydrocarbon chromatograms of not only the fresh Prudhoe Bay crude oil but also prespill and postspill sediment samples are shown in Fig. 4. Because prespill sediments (Fig. 4 [middle]) contained naturally occurring (biogenic) hydrocarbons such as plant wax *n*-alkanes with odd carbon numbers (for example, *n*-C_{25}, *n*-C_{27}, *n*-C_{29}, and *n*-C_{31}) and mono- and poly-olefinic compounds in the range of C_{19} to C_{21} [*4*], the sum of *n*-alkanes with an even number of carbon atoms between *n*-C_8 and *n*-C_{32} was selected as the *indicator* for the occurrence of oil in samples. In replicate sediment samples from the channel bed, mean coefficients of variation (CVs) for "oil" (that is, the sum of even *n*-alkane) concentrations were 13% when concentrations were >1.00-μg/g dry weight. CVs increased to approximately 64% when "oil" concentrations were less than 1.00-μg/g dry weight.

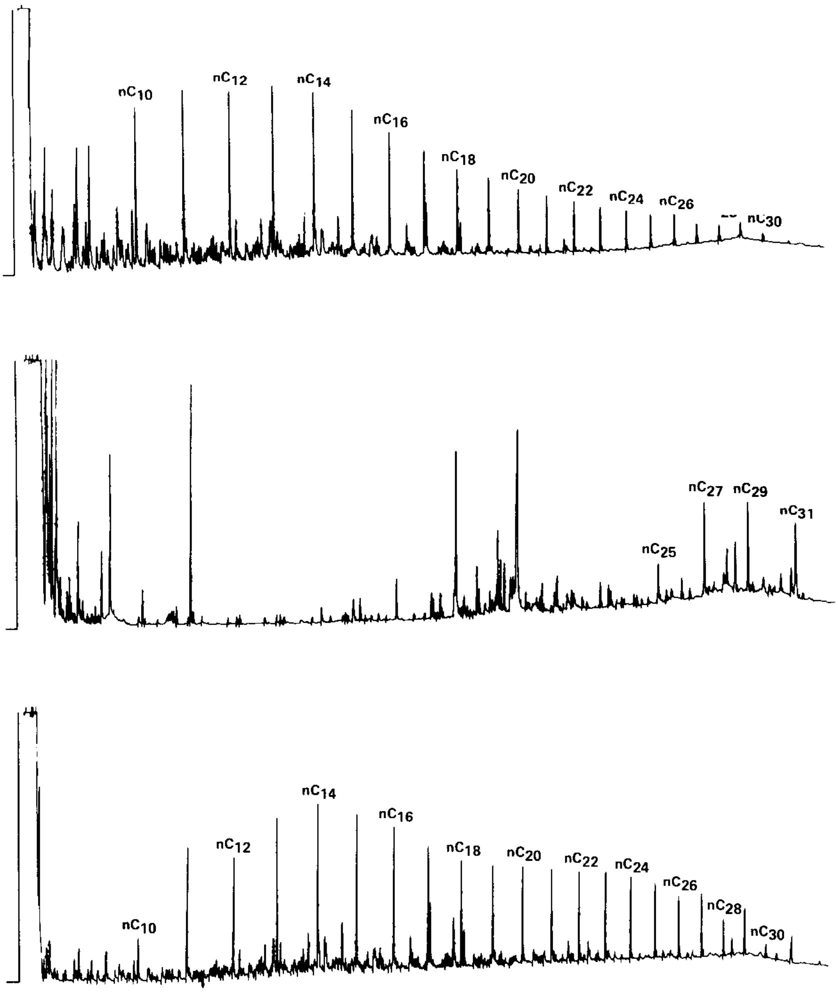

FIG. 4—*FID-gas chromatograms of* (top) *fresh Prudhoe Bay crude oil,* (middle) *prespill sediment hydrocarbons (Site 4, Experiment 2), and* (bottom) *sediment hydrocarbons after a spill event (Site 4, Experiment 2, 2 h postspill). Positions of selected* n-*alkanes are noted in chromatograms. The spill mixture for Experiment 2 was fresh Prudhoe Bay crude oil plus OFC D-609.*

Method blanks without sediment were periodically processed through the entire analysis procedure to correct for any background contamination. Methanol and methylene chloride used for extractions were distilled-in-glass, pesticide quality (Burdick and Jackson). Na_2SO_4 was placed in an oven at 500°C for at least 12 h before use.

Water Sampling—Hydrocarbon Methodology and Extraction Procedures

Known volumes of effluent water (approximately 1600 mL) were collected from the channel bed. These samples were partitioned against three sequential 100-mL volumes of methylene chloride. The combined methylene chloride fractions were concentrated and