Dispersed Oil Monitoring Plan (DOMP)

Monitoring Dispersed Oil and its Effects in the Sea

Analysis Prepared for the
California Department of Fish and Game
Office of Spill Prevention and Response
(OSPR)

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Table of Contents

Introduction 1
Background 1
Dispersant Application and Efficacy 2
Environmental Effects of Dispersed Oil 3
Physical Dispersion 4
Chemical Dispersion 4
The Net Environmental Benefit Analysis (NEBA) Process 5
California Dispersant Plan (CDP) 6
Dispersants and Dispersed Oil Behavior 7
Special Monitoring of Applied Response Technologies (SMART) 7
Sampling Design Considerations from Past Field Studies 8
Spill of Opportunity Trials 14
Objectives 21
Environmental Impact Assessment 21
Natural Resource Damage Assessment (NRDA) 22
NEBA verification 22
Methods 23
Problem Definition 23
Model Description 25
Oil Fates and Effects Model 25
Oil Toxicity 25
Scenarios and Model Inputs for Scaling Concentration Plumes and Potential Impacts 28
Model Results: The Scale of Concentration Plumes and Impacts 28
Modeling Procedure for Evaluation of Oil Spill Impacts on Water Column Biota 29
Sampling Protocol: Physical-Chemical 30
Dispersed oil tracking 31
Sampling location and depth 31
Dispersed Oil 32
Reference water (control) 32
Chemical sampling: Collection methodology 32
Sample filtration 32
Sample preservation 34
Chemical Analysis: Standards and reporting units 34
Source oil 37
Dispersant product 37
Control 37
Sampling Protocol: Biological component 38
Holoplankton 38
Meroplankton and Ichthyoplankton 39
Bioassays 40

Logistical Requirements for Environmental Data Collection 41
Boats 41
Aircraft 41
Communications 42
Sampling Equipment 42
Discussion 42
References 44

Appendix A. Model Runs and Analysis of Results

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INTRODUCTION

Background

The 1989 grounding of the *T/V Exxon Valdez* in Prince William Sound, Alaska lead to the implementation of the Oil Pollution Act, 1990 (OPA 90) by the US federal government. The *Exxon Valdez* event combined with the spillage from the T/V *American Trader* off Huntington Beach, California in 1990 resulted in the Lempert-Keene-Seastrand Oil Spill Prevention and Response Act (SB2040). These combined legislative acts significantly altered the business of oil spill prevention, planning, and response in California. A substantial amount of effort has since been expended to prepare for the release of oil into the marine environment by developing regionally based Area Contingency Plans (ACP) that identify available response resources, environmentally and economically sensitive sites, and devise response strategies to protect those environmentally sensitive locations. Beginning with the Methods section of this document, the reader will find the rationale and protocols developed to verify the impacts associated with dispersed oil in the event that dispersants should ever be used along the coast of California. The field protocols are also set out under a separate cover as "A Field Guide for Implementing the California Dispersed Oil Monitoring Plan (DOMP)" (Payne et al. 2008a).

The National Oil and Hazardous Substances Pollution Contingency Plan (National Contingency Plan - NCP) directs Regional Response Teams (RRT) and Area Committees to address, as part of their planning activities, the desirability of using appropriate dispersants, surface washing agents, surface collecting agents, bioremediation agents, or miscellaneous oil spill control agents listed on the NCP Product Schedule, and the desirability of using appropriate burning agents. Regional Contingency Plans (RCP) and Area Contingency Plans shall, as appropriate, include applicable authorization plans and address the specific contexts in which such products should and should not be used (40 CFR ¤ 300.910). Within California statute, the Administrator of the Office of Spill Prevention and Response (OSPR) has the State's authority over the use of all response options, including dispersants [Government Code Section 8670.7(f)]

The use of dispersants in marine waters off California requires detailed foresight and planning. In an effort to expedite a decision to use dispersants and reduce first strike response time, in August of 2000, the RRT IX adopted formal changes to the planning and operations RCP. These sections detail a dispersant use planning process to be undertaken by each of the six California marine area committees. The first task, designation of approval zones, has been completed by all area committees. In February 2003, the last area committee zone recommendation was approved by the RRT and now, all the marine waters between 3 and 200 nautical miles (nmi) off the State of California coast have been designated as "Dispersant Pre-Approval Zones" or "RRT approval required zones" for the use of dispersants. As a part of the RCP and ACP processes, a California Dispersant Plan (CDP 2008) has been developed to address the appropriate use

of dispersants in all marine waters off the coast of California, including areas designated as Dispersant Pre-Approval Zones as well as those zones still requiring an incident-specific RRT approval.

The application of dispersants on floating oil off the coast of California has proven to be a very challenging strategy, both politically and environmentally. The use of aromatic degreasing solvents (petroleum distillates) as a dispersant following the grounding of the *T/V Torrey Canyon* near the coast of Great Britain in 1967 was an ecological catastrophe. Since then, far less injurious dispersant chemical formulations have been developed to reduce the toxicity of the dispersant compounds while increasing the effectiveness of the dispersant. Corexit 9527 is one of several products developed commercially specifically for the purpose of enhancing the dispersion of floating oil (ExxonMobil Research and Development Co. 2000). It has been demonstrated to be reasonably effective on heavy oils that may be candidates of treatment off California. A subsequent refinement of the product resulted in the even more effective Corexit 9500 formulation (NRC 2005). Corexit 9527 is glycol ether based while Corexit 9500 contains a mixture of food-grade aliphatic hydrocarbons (n-C9 to n-C16) as the solvent to enhance penetration into heavier and more viscous oils (NRC 2005). Both dispersant concentrates have been approved for use in California.

The use of dispersants as an oil spill response strategy now has a higher probability of occurrence than prior to 2004. However, it is recognized that the use of dispersant is not a panacea. It is a trade-off between impacts to water surface-related environmental and economic resources, and sub-surface resources. It is the recognized potential for impacts to water column environmental resources that drives the development of this plan. It should also be emphasized that the use of dispersant off California is primarily intended for crude oil products. In some instances it may be approved for heavy fuel (bunker) oils, but it is not intended for use on light fuel oils such a kerosene, diesel, jet fuel, or gasoline.

Dispersant Application and Efficacy

The effectiveness of dispersants has been an ongoing study since the earliest attempt to chemically alter the tendency of oil to float on water during the *T/V Torrey Canyon* spill event in 1967. Considerable research effort has been expended to develop better dispersion agents along with improved delivery methods. Most monitoring effort has been directed toward proving that dispersants can work when properly applied and to establish the relative toxicity values of the dispersion agents. To ensure maximum dispersion effectiveness, monitoring of the application process should be routinely conducted utilizing aerial spotters and water column monitoring as covered under SMART (Special Monitoring of Applied Response Technologies) (U.S. Coast Guard, et al. 2001). Methodologies have been developed during the past ten years that demonstrate the type of efficacy monitoring protocols to consider in future dispersant use events (Hillman et al. 1997; NRC 2005).

Presently a SMART plan exists to monitor the application of dispersant for the purpose of establishing the effectiveness, or ratio of oil to dispersant (Gugg et al. 1999). That monitoring effort is unrelated to the purpose of this plan. SMART monitoring addresses

only the presence of dispersed oil in the surface water layer in order address the need for adjustments of the dispersant application rate or to document the dispersant efficacy. SMART protocols are not designed to address natural resource damages and they cannot be used to validate fate and transport models.

Environmental Effects of Dispersed Oil

Dispersed oil is known to have the potential to adversely affect aquatic resources that reside in the affected volume of water as dilution and degradation processes progress over a period of hours to days. For some period of time after dispersant application, toxic levels of dispersed oil are possible within a volume of water. Determining the dimensions of that volume, rate of dilution, and characteristics of the affected aquatic community are important to understanding the trade-off value of dispersant use compared to mechanical recovery with respect to environmental resources at risk on the water surface and shorelines threatened by floating oil. It is important to recognize that dispersant use is an alternative with identifiable benefits as well as adverse effects. Defining those actual effects with any dispersant application is the purview of regulatory trustee agencies. With sufficient database development such monitoring may someday be supplemented with, or even replaced by, computerized injury assessment modeling.

Information is available to theorize the nature of environmental damage within a marine water mass following the application of dispersant to oil. Theoretical models have been described and some physical measurements of dispersed oil concentrations have been reported. However, more complex issues such as rates and distances of dispersion through the affected water mass, and the biological characterization of that same water mass are important to the understanding of the adverse effects of dispersed oil. Collection of data describing the motion of dispersed oil is a rigorous undertaking. It requires the use of oceanographic vessels, trained personnel, and specialized equipment working in offshore waters tracking an expanding area of contaminant with potentially inclement weather. The greatest likelihood of collecting the appropriate type and quantity of data to adequately describe the fate and effect of dispersed oil will rest with a well conceived monitoring plan in advance of dispersant application.

A number of publications have been prepared describing various aspects of dispersant characteristics, fate and effects, and monitoring efforts (NRC 1989, 2005; Scholtz et al. 1999a,b). The majority of the SMART Protocol monitoring research effort has been directed toward application and efficacy of dispersants. The need for monitoring of dispersed oil is emphasized with respect to the processes of fate and effects of the dispersed oil as it moves through the water column and interacts with associated biological resources. The physics and biology of oceanic environments are often poorly defined except in the most general terms. Extant conditions define the true fate and effects of dispersed oil during a specific application event. The need for monitoring environmental effects is pointed out by ExxonMobil Research and Engineering (2000) as different from dispersant application monitoring, and substantially more complex. It is in

the interest of understanding the full range of environmental resource impacts that case specific dispersed oil water column biotic resource monitoring is appropriate and necessary.

Physical Dispersion

The physical dispersion of oil is driven by several discrete processes, each relying on differing properties of oil to affect the outcome, which represents the process of natural weathering. Some petroleum components (monocyclic aromatic hydrocarbons, MAHs) will both dissolve and readily evaporate into the atmosphere (from both the oil and water phases), while others (polycyclic aromatic hydrocarbons, PAHs) are more persistent in the oil phase leading to dissolution into the water column over a longer time period. Water surface turbulence can mechanically force oil droplets into the water column, but such droplet sizes are quite variable, and resurfacing in the absence of turbulence can occur if the droplets are greater than 80-100 µm (NRC 2005). Water can also be forced into the oil creating a stable and highly viscous water-in-oil emulsion or "mousse" (Payne and Phillips 1985a; Fingas 1996; Fingas et al. 1998; 1999; 2000a,b; 2002a,b, 2003a; Fingas and Fieldhouse 2003; 2004a,b). The natural weathering process begins quickly and can be well advanced within 24 hours (NRC 1985, 1989, 2005; Scholz et al. 1999a) thereby inhibiting natural dispersion (Payne et al. 1983, 1984, 1991a; Payne and McNabb 1984; Delvigne and Sweeney 1988; Lewis et al. 1994) and substantially affecting the effectiveness of chemical dispersants. The natural weathering process removes the lighter molecular weight components and leaves the heavy, higher molecular weight components of oil (asphaltenes); thus, heavy crude oils, heavy fuel oils, and previously weathered oils are more likely to be found floating or stranded on the shore months to years after release.

Chemical Dispersion

The chemical dispersion of oil differs only slightly from the physical dispersion process. The chemical substance used to disperse oil functions as a surfactant to lower the oil-water interfacial surface tension and thereby enhance the breakup of an oil slick into very small droplets of oil that will remain suspended in the water column. The intent of the dispersant application is to increase the surface area of oil through the formation of dispersed oil droplets (approximately 5 to 70 µm) allowing natural biodegradation through aerobic bacteria to metabolize the oil at an accelerated rate (Swannel and Daniel 1999), and to aid in the distribution of oil droplets through an increasingly large volume of water. This process also helps the oil droplets remain in the water column where the oil can be dispersed by local currents; impacts to the environment are then better limited in both time and space. Chemical dispersion, like physical dispersion, is dependent upon wave energy turbulence to assist in the process. The dispersant has little influence on the most volatile components, and marginal effect on the heavy, large molecular weight components.

Dispersants are most effective on oils of intermediate viscosity (generally less than 4,000-6,000 cP) before they have undergone extensive evaporative weathering and water-in-oil emulsification (mousse formation). As oil weathers, and the lighter fractions are removed by evaporation, the heavier molecular weight components become more concentrated and can begin to precipitate out of solution within the continuous oil phase. When this happens, these components can coat finite water droplets that become mixed into the oil phase. This inhibits water-droplet coalescence within the oil phase and leads to stable water-in-oil emulsions with much higher viscosities than the starting oil. During most of the 1980s, oils or emulsions with viscosities greater than 2,000 cP were considered to be difficult or impossible to chemically disperse (NRC 1989). More recent studies (e.g., Guyomarch et al. 1999; Fiocco et al. 1999) have shown that a number of intermediate fuel oils and weathered water-in-oil emulsions with viscosities ranging from 10,000 to 20,000 cP can at least be partially dispersed in laboratory and field trials with multiple applications of newer hydrocarbon-solvent-based dispersants (e.g., Corexit 9500, Inipol IP 90, and Slickgone NS). As a result, these researchers have concluded that there is no hard and fast rule for the upper viscosity limit for dispersability of heavier fuels (and possibly water-in-oil emulsions). Consequently, the most effective window of opportunity to use surfactants occurs within the first several hours to days following a release, before significant natural weathering can begin. In wave-tanks experiments with Prudhoe Bay crude oil in subarctic conditions, the ambient temperature (12-14^{o} C) *in situ* viscosity increased from around 68 to 2,300 cP after only three days (Payne et al. 1984, 1991a). For fall/winter ice-free experiments at 2-4^{o} C, the *in situ* viscosity increases were more significant, with initial values increasing from 270 to 5,600 cP after only 24 hours (Payne et al. 1984). In the presence of slush ice and a 4-6 cm wave field, Prudhoe Bay crude oil formed a stable water-in-oil emulsion with an *in situ* viscosity of 25,000 cP (measured at -2^{o} C) in as little as 4 hours (Payne et al. 1987, 1991b).

The Net Environmental Benefit Analysis (NEBA) Process

Once oil is spilled to the ocean there will be inevitable impacts to the environment within the geographical area of the spill, no matter how much effort is put into spill response. The primary goal of any oil spill response is to minimize the area of impact and remove the spilled oil from the water's surface as fast as possible, thus minimizing the impact to the organisms inhabiting or passing through the air-sea interface and intertidal/terrestrial or estuarine regimes.

The assessment and comparison of the impacts of an oil spill and associated cleanup activities on the biological resources were conducted in all six of California's Area Committees using a Net Environmental Benefit Analysis (NEBA). NEBA examined and compared the risk to the environment associated with available oil spill response options. Spill response options evaluated were: no on-water response, mechanical cleanup, *in situ* burning, and dispersant use. The risks of these cleanup options were examined using a NEBA risk matrix, which qualitatively combined the risk to the biological resource resulting from both the magnitude (percentage) of the population impacted with the expected time for the population to recover from the impact.

General findings:

- In offshore response settings, and/or where spill distance from shore significantly increases the response time, mechanical cleanup techniques and *in situ* burning may, by themselves, provide very little improvement over the no response option.
- When used in an appropriate and timely manner, dispersants can remove a significant amount of oil from the water surface.
- While dispersants may measurably reduce the risk of oil to surface and coastal biological resources, there may be an increase in risk to the water column community.
- Shoreline cleanup methods may not be available or appropriate for use in some sensitive coastal habitats (e.g., marshes and wetlands); their inappropriate use may pose a greater risk to these sensitive habitats and dependent species than the oil itself. The goal in this case shifts to keeping the oil from ever reaching sensitive coastal and inland areas.

NEBA results suggested that the appropriate and timely use of dispersants (on oil spills characterized as "dispersible") could greatly enhance the ability to remove significant quantities of oil from the offshore water surface. This may greatly reduce the risk of spilled oil reaching the more abundant and sensitive habitats and species found in the more inshore, coastal areas. While dispersing oil into the water column can pose a risk to the plankton community inhabiting the upper few meters of the water column, the impacts will be to a geographically limited area, and the temporal duration will be relatively short.

California Dispersant Plan (CDP)

The CDP is designed to be a stand-alone document which provides the policies and procedures for the appropriate use of dispersants to address a marine oil spill in the waters off the California coast. The CDP includes an updated Federal On-Scene Coordinator (FOSC) checklist, a series of discussion and decision boxes to facilitate the FOSC decision as well a number of appended materials that put oil, dispersant, natural resource and response resource information close at hand in one document. The CDP also includes a number of blank forms that can be removed, duplicated as needed, and used in the field during a spill response to provide orderly and timely information to the FOSC as the spill unfolds and a decision whether or not to use dispersants becomes imminent. Other report forms document bird and mammal presence, dispersant application methods, and dispersant effectiveness.

The primary focus of the CDP is on the federal offshore waters that have been designated as "Pre-Approval Zones" for dispersant use. To date, this includes the waters 3 – 200 nmi from shore and not within a National Marine Sanctuary. This CDP also addresses waters closer than 3 nmi from shore or within a National Marine Sanctuary, which fall, until further notice, under the RRT Approval Process. The CDP was adopted by the RRT in the autumn of 2008.

Dispersants and Dispersed Oil Behavior

Historically, the primary mode of surface oil removal in open water has relied on mechanical boom and skimming equipment. This has generally resulted in oil recovery levels of 10-15% or less in the open ocean (NRC 1989). Applied response technologies, specifically oil spill dispersants, offer a second approach to removing significant quantities of spilled oil from the ocean's surface.

Oil spill dispersants are a group of chemical compounds, primarily surfactants and a water or non-aromatic hydrocarbon-based solvent, used to aid natural processes in the dispersion of spilled oil by reducing the oil-water interfacial tension, stabilizing oil droplets in the water column, and preventing the coalescence of the oil droplets (NRC 1989, 2005). This process helps the oil droplets remain in the water column where the oil can be dispersed by local currents; impacts to the environment are then better limited in both time and space. The size of the dispersed oil droplets (approximately 5 to 80 microns) also increases the surface area of the oil available for natural biodegradation (Swannel and Daniel 1999).

Dispersed oil can pose a short-term threat (measured in minutes to hours) to biological communities in the upper few meters of the water column, where patchy distributions of total dispersed oil concentrations can reach 20-40 parts per million (ppm) or more (McAuliffe et al. 1981). The actual hydrocarbon concentrations and magnitude of the threat to biological resources is dependent on many parameters, including the mixing energy, the type of oil dispersed, the amount of weathering that has occurred prior to dispersant application, dispersant effectiveness, and the length of organism exposure to dispersed oil.

Once dispersed in the water column, oil concentrations decrease fairly rapidly due to mixing and other natural dispersion properties of the open ocean, and should reach undetectable levels within several hours after application (McAuliffe et al. 1980; Mackay and Wells 1983; NRC 1989, 2005; French-McCay and Payne 2001; French-McCay et al 2006). Due to the three dimensional mixing of the dispersed oil and the associated reduction in concentration, impacts on the pelagic community are expected to be short-lived. In comparison, oil remaining on the surface of the ocean can pose a long-term threat to birds and fur-bearing mammals for weeks to months (French-McCay et al 2005a,b).

Special Monitoring of Applied Response Technologies (SMART)

The need for protocols to monitor response technologies during oil spills has been recognized since the early 1980s. Technological advances including much reduced toxicity of dispersants and their application have resulted in increased acceptance and the designation of "Dispersant Pre-Approval Zones." California designated dispersant use pre-approval zones for large areas of its coastline beyond 3 nmi in 2004 (CDP 2008).

SMART establishes a monitoring system for rapid collection and reporting of near-real-time scientifically based information of dispersant application effectiveness in order to assist the Unified Command with decision-making (U.S. Coast Guard, et al. 2001).

When dispersants are used during oil spills, the Unified Command needs to know whether the operation is effective in dispersing oil. The SMART dispersant monitoring module is designed to provide this information in near-real-time. Because dispersant operations vary greatly, SMART recommends a three tiered approach: (I) visual monitoring; (II) Combination of visual monitoring and on-site single depth water column fluorometry and water sampling; and finally (III) the expansion of sampling to several water depths (U.S. Coast Guard, et al. 2001).

It is important to note that SMART does not monitor the fate, effects, or impacts of dispersed oil. The California DOMP is designed to fill this void.

Sampling Design Considerations from Past Field Studies

The National Research Council publication *Using Oil Spill Dispersants on the Sea* (NRC 1989) reviewed the results of several field trials conducted off southern California and New Jersey in the late 1970s and early 1980s. No controlled field experiments on dispersant effectiveness and potential biological effects have been conducted in United States waters since those studies, but a number of controlled field trials of dispersant effectiveness have been conducted in Canada and Europe (Bradvik et al. 1995, 1996; Lunel and Lewis 1993a,b; Walker and Lunel 1995; Lewis et al. 1995a,b; Lunel 1993, 1994a,b, 1995; Lunel and Lewis 1993a,b; Lunel et al. 1995a,b,c; Lunel and Davies 1996; McDonagh and Colcomb-Heiliger 1992; Strom-Kristiansen et al. 1995). Many of these studies have been summarized recently by SL Ross (1997), and the proceedings of a two-day symposium on oil-spill dispersant applications in Alaska (held in Anchorage, AK in March 1998) are also available (Trudel 1998a). No attempt will be made to duplicate or even briefly cover the findings presented in these documents. Instead, several of the most significant lessons learned -- specifically with regard to applications and dispersant-treated oil behavior -- will be briefly highlighted in the following paragraphs.

It is known that oil spills are composed of thick slicks (usually thicker than 1 mm) that contain most of the oil volume (the rule-of-thumb is that 90 percent of the oil volume is contained in 10 percent of the area), and that these patches are surrounded by thinner sheens (about 1 to 10 µm or 0.001 to 0.01 mm) (SL Ross 1997). This combined thick and thin slick spreading is of great importance with regard to dispersant effectiveness. From field trials and actual dispersant use to treat accidental oil spills, it is now generally accepted that the one pass concept for dispersant application is not appropriate for dealing with the thicker part of spills, and that the multi-pass approach (as has always been used in United Kingdom) is the only way to completely dose the thicker portions of marine spills (Lunel et al. 1997). For example, the application rate required to treat 1 mm of oil at a dispersant to oil ratio of 1:20 is approximately 50 gallons per acre, and this can

only be achieved by multiple passes by a Hercules C-130 aircraft equipped with an Aerial Dispersant Delivery System (ADDS) pack that typically doses at only about 5 gallons per acre (SL Ross 1997).

The phenomenon of slick "herding" has been recognized for many years, and yet, it is not addressed as a problem to be avoided in most dispersant use-plans that exist in the U.S. today (S.L. Ross 1997). Anyone who has ever added a drop of dish soap to the oily film over greasy dishwater has witnessed the phenomenon of herding as the oil film is quickly dispatched to the edges of the sink. Dispersants have higher spreading forces than oil, and as a result, a thin film of oil surrounded by a layer of dispersant on the water surface will be forced or "herded" into a narrow ribbon of oil. This will happen if the dispersant misses its target and lands on the water adjacent to the oil, or if the dispersant droplets are too large compared to the surface slick thickness and they break through the slick into the underlying water. When herding occurs, it often looks from observation aircraft as if the dispersant was very effective in clearing oil off the water surface. Specifically when viewed from the air, the thin ribbons of oil are barely visible, and the water surface will look clear until the dispersant on the water has naturally mixed into the water phase. After about 15 minutes the oil will then re-spread on the surface (Fingas 1985).

Daling and Lichtenthaler (1986) compared the results of laboratory effectiveness tests with the results from several small field trials. They showed that the correlation between effectiveness measured using three different laboratory test systems and between field and laboratory tests was poor. There was, however, fairly good correlation between the mean results for the different dispersants from the three laboratory tests and field tests. That is, dispersants that performed poorly in the laboratory also performed poorly in the field, but the lab tests were not able to predict the dispersability of a specific oil by a specific dispersant under defined conditions at sea with any satisfactory level of accuracy. The most significant results from the field trails were the measured oil concentrations under the dispersant-treated slicks, which ranged from 1-3 ppm compared to the untreated control slicks, which were generally around 0.1 ppm.

Dispersant concentrate-to-oil ratios in these field tests were equal to 1:10, and oils with kinematic viscosities ranging from 10 to 635 were tested (Daling and Lichtenthaler 1987). Treated slick thicknesses ranged from 0.06 to 0.1 mm. Water samples were collected 10 to 20 minutes after treatment at depths of 0.6 and 1.2 m. In addition, oil concentrations were continuously monitored *in situ* by a beam-transmittance meter. The beam-transmittance meter data showed extreme variability and patchiness in the oil concentrations beneath the treated slicks, and the dispersed plume was mostly observed towards the rear of the slick and not under the leading edge, which contained the biggest patches of remaining surface oil. Also, the dispersed oil plume did not show the same spreading development as the surface oil making it difficult to sample.

Numerous recent field trials completed in Europe have confirmed these earlier observations, and from these studies it can be concluded that it is difficult to estimate average concentrations under treated slicks because of the significant heterogeneity both horizontally and with depth into the water column (Brandvik et al. 1995; Lewis et al.

1998). Figure 1 (from Lewis et al. 1998 and NRC 2005) shows the horizontal and vertical distribution of total petroleum hydrocarbons from test spills as determined by UV/Fluorescence before and after dispersant treatment. Before treatment, the maximum concentration in the surface waters (< 0.5 m) was less that 1 ppm, but during treatment, this increased to nearly 6 ppm with lesser concentrations at depth. After approximately 45 minutes, concentrations at depth also increased, but generally to only 1-2 ppm.

A large number of at sea trials were conducted between 1993-1994, and Table 1 (from Lunel et al. 1995b, and SL Ross 1997) presents a summary of the dispersant efficiency data for different oils tested and the different energy regimes encountered. There is a clear ranking in percentage of oil that the different formulations successfully dispersed into the water column in the field as the encountered energy regime increased; however, it should be noted that the overall percent dispersed values were generally pretty low. Although this ranking had been well documented for laboratory tests, these data were the first set from field trials were the ranking could be quantified. The tested dispersants increased the rate of dispersion by 6 to 10-fold compared with natural dispersion in the case of MFO and 3-fold in the case of Forties crude oil. Comparison of the dispersion data for the low-energy regimes (0-5 m/s wind speed; 0-10 knots) with the higher-energy regimes (6-10 m/s wind speed; 12-20 knots) shows that natural entrainment is enhanced through the use of dispersants by about the same factor in low-energy regimes (10-fold) and in higher-energy regimes (6 to 10-fold). Table 2 (from SL Ross 1997) summarizes the measured peak oil concentrations detected as a function of depth after several at-sea trials. In general, the observed dispersed oil distributions were very heterogeneous, and maximum concentrations of 20-40 mg/L were limited to the upper 1 m of the water column. Concentrations at 3 m ranged from 0.02-9 mg/L, and concentrations at 9 m ranged from non-detected to 0.9 mg/L.

From the early API tests in 1975 and 1979 to the most recent field trials and measurements completed in 1997, only one well-documented spill in which modern dispersants have been used has been studied in an efficient and controlled manner (Lunel et al. 1997; Lunel 1998). That was the *Sea Empress* oil spill in Milford Haven, UK in 1996. The spill involved over 72,000 tons (250,000 barrels) of Forties Blend crude oil released over the period from February 15-21, 1996. The oil spill was treated with over 445 tons of dispersant (150,000 gallons) applied by aircraft between February 17-22, 1996 targeting the fresher and thicker slicks as they were released over time from the stricken vessel (SEEEC 1996).

In situ monitoring of oil concentrations in the water column was conducted to verify effectiveness. Before dispersant applications, oil droplet concentrations were on the order of 1-3 ppm in the upper one meter, declining to less than 0.5 ppm at a depth of approximately five meters. During the dispersant application, oil concentrations on the order of 3 ppm were measured from the surface to approximately five meters. According to Lunel et al. (1997), the elevated oil concentrations and lack of a concentration gradient between the surface and the five-meter depth were indicative of effective dispersant application. The very turbulent sea conditions allowed small oil droplets to be dispersed

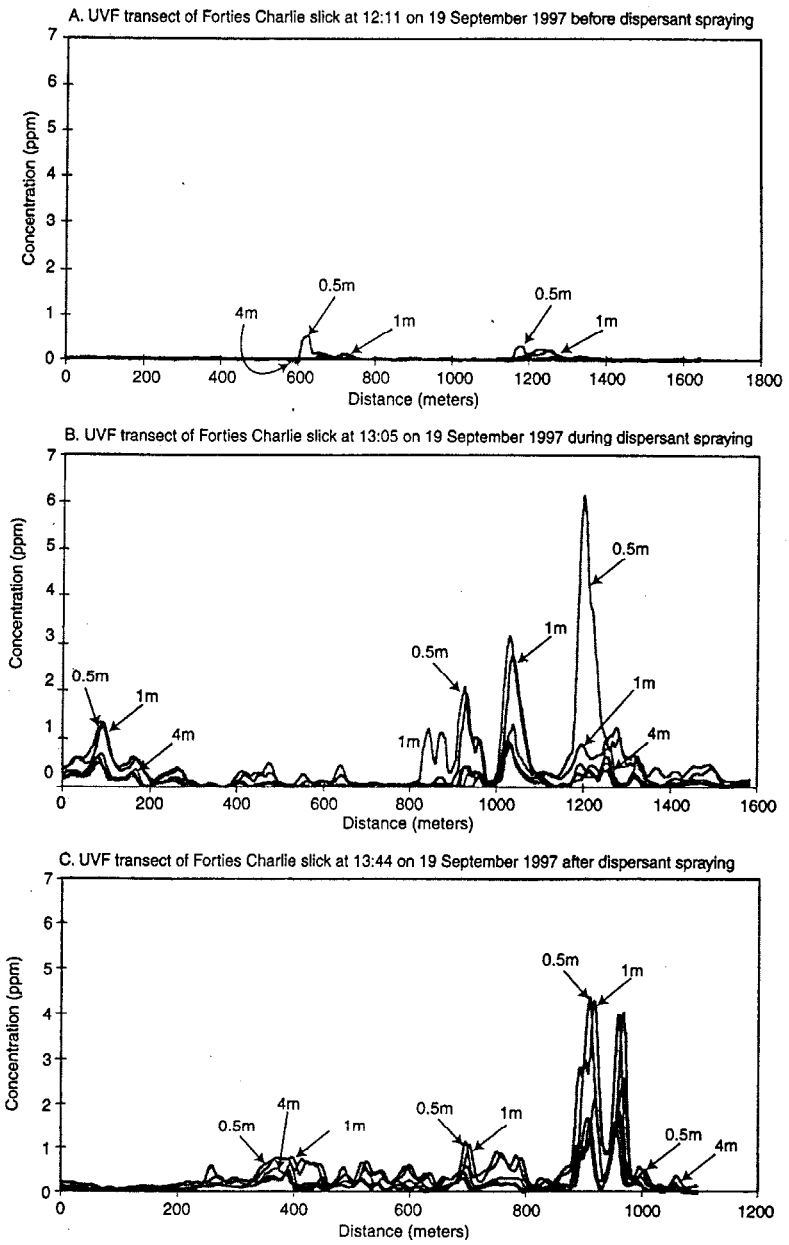

Figure 1 Dispersed oil concentrations under an approximately 27 m^3 surface slick of Forties crude oil (a) before, (b) during, and (c) after spraying with 2,250 liters of Corexit 9500 during the 1997 North Sea field trials. Sampling depths for the major peaks in dispersed oil concentrations are labeled, and in many, for not all cases, the 0.5 and 1.0 m depths were very similar (from Lewis et al. 1998b and NRC 2005, with permission).

Table 1. Summary of the dispersant efficiency data for the 1993/1994 sea trials. From S. L Ross 1997, with permission.

Energy regime	Wind speed (m/s)	Date	Oil-Dispersant	% Dispersed (mean)	Standard deviation
Low	3	7/9/93	MFO	0.8	0.7
Low	5	19/8/94	MFO-Slickgone NS	8	4
High	10	7/9/93	MFO	2	0.7
High	7	22/8/94	MFO	4	2
High	7	25/8/94	Forties	5	3
High	6	23/8/94	MFO-LA1834	4	3
High	10	7/9/93	MFO-1100X	10	4
High	10	7/9/93	MFO-Slickgone NS	17	6
High	6	23/8/94	MFO-Slickgone NS	16	7
High	6	25/8/94	Forties-Slickgone NS	16	6
High	7	22/8/94	MFO-Corexit 9527	26	10
High	10	7/9/93	MFO-OSR5	30	7

Energy Regime	**Percent Dispersed**		**Ratio of Chemical Dispersion to Natural Dispersion**
	MFO	**MFO-Slickgone NS**	
Low	0.8	8	10
High	3	17	6

Table 2. Peak dispersed oil concentrations (ppm) measured at various depths under treated slicks during sea trials. From S L Ross 1997, with permission.

Oil Type Volume	Treatment	Application Ratio Single Pass, gallons per acre	D:O Ratio	Estimated Effectiveness, percent	Time After Spraying, minutes	Depth Beneath Slick		
						1m	3m	9m
Prudhoe Bay, 20 bbl (1)	Sprayed	14.8	1:19	78	15 min	40	9	0.9
Prudhoe Bay, 20 bbl (1)	Sprayed	10.4	1:27	60	4-27 min	6	2.7	0.2
Prudhoe Bay, 10 bbl (1)	Sprayed after 2	7.4	1:19	45	7-26 min	5	4	0.5
Prudhoe Bay, 10 bbl (1)	Boat	10	?	62	?	21	9	0.4
Prudhoe Bay, 10 bbl (1)	Boat	5-10	?	11	?	2	1	0.2
Prudhoe Bay, 20 bbl (1)	Control	--	--	0.5	--			
Reconstituted fuel oil, 63 bbl (2)	Sprayed	? (3)	1:75	?	1 hr	18	0.8	-
Reconstituted fuel oil, 63 bbl (2)	Sprayed	?	1:5	?	30 min	32	4	-
Reconstituted fuel oil, 63 bbl (2)	Control	?	0	?	--	0.5	0.2	-

1. McAuliffe et al. 1981.
2. Lichtenthaler and Daling 1983, Reconstituted fuel oil prepared from Stratfjord crude oil fractions to yield a product with density 0.852 g/ml, viscosity 12 cSt @ 11 C, pour point -15 C
3. ? = not known

into the surface waters and throughly mixed throughout the water column to that depth. Lunel et al. (1997) estimated that approximately 50 percent (or 36,000 tonnes) of the oil from the *Sea Empress* was dispersed into the water column by natural and/or chemical means. By February 27th, several days after dispersant applications had ceased, concentrations in surface waters throughout Carmarthen Bay had dropped from 3 ppm to approximately 0.2-1 ppm. By 5 March, concentrations had declined to less than 0.2 ppm. By June, they declined to background concentrations of 5-20 ppb.

These data provide substantial evidence that exposure concentrations in the upper water column beneath dispersant treated oil slicks will be modest and very patchy/heterogeneous, on the order of a few ppm to as much as a few tens of ppm dispersed oil, even during a very efficient dispersant operation on a massive spill.

The mass balance estimates put forward by Lunel et al. (1997) indicate that the targeted use of dispersants probably prevented 57,000-110,000 tons of emulsion from drifting and being driven by the wind to impact the shoreline and potentially result in greatly increased impact on sea birds, coastal waders, intertidal vertebrates and invertebrates, and amenity beaches. These benefits were believed to significantly outweigh any potential impacts associated with the elevated, but temporary oil concentrations in water column. The provisional mass balance for the spilled oil is as follows: evaporated 28,000 tons (39 percent); dispersed (naturally and chemically) 35,000 tons (49 percent); recovered at sea 4,000 tons (5 percent); recovered onshore 5,000 tons (7 percent); total spilled 72,000 tons (100 percent). Oil pumped out from the vessel 58,600 tons, oil recovered in dry dock 400 tons; total cargo 131,000 tons.

The concentrations discussed in the previous paragraphs are in the same range with dispersant-treated and untreated slicks examined in the 1975 and 1979 sea trials conducted off the United States (McAuliffe et al. 1981). Generally, under the worst case measurements completed in those trials, concentrations of a few tens of ppm total petroleum hydrocarbons were observed in the upper mixed layer. Those data were considered worst case, because they were peak concentrations, not average values, and the tests were conducted under conditions that would produce high levels of effectiveness.

Based on the early at-sea trials in the United States and earlier trials in Europe, the NRC (1989) concluded that hydrocarbon concentrations under naturally dispersed slicks would range from 0.5-1 ppm, with elevated concentrations limited to only the upper one meter. For chemically dispersed slicks, concentrations up to 40 ppm might be observed in the upper one meter, with elevated concentrations (usually less than 10 ppm) observed at greater depths (3-6 meters). In actual fact, elevated concentrations at these levels have seldom been observed in any of the at-sea trials completed in the 1980s and 1990s making the 1989 NRC estimates an upper bound.

More recent field trials (Lunel 1994a, b; Brandvik et al. 1996) and the observations at the *Sea Empress* oil spill have confirmed the conclusion that it is unlikely that dangerously high concentrations of hydrocarbons would develop below the top ten meters of the water

column (CCP workshop, 1995). Most importantly, Lunel and Davies (1996) have shown that dispersion takes place over an extended time period during dispersant application, and continues for approximately one-half hour after the spraying stops. In general, oil concentrations increase in the water column under the treated slicks for a few moments until an equilibrium is established at which point the smaller dispersed oil droplets are carried away from the underside of the slick by turbulent diffusion as quickly as they enter the water column. As a result, high concentrations of dispersed oil have not been observed to accumulate under the slick (even under a few meters of water column) in any of the field trials completed to date.

Spill of Opportunity Trials

While large spills in offshore U.S. waters have been, thankfully, quite rare, there are several ports around the country where the volume of crude oil traffic is so large that small 'nuisance' spills are somewhat common. In these ports, it might be possible to develop plans for using dispersants as a first strike tool to respond to a small spill that would ordinarily be cleaned up mechanically. Information gained from extensive water-sampling efforts at such trials would be extremely valuable in assessing dispersant effectiveness and potential environmental impacts. In anticipation of such an event, draft Spill of Opportunity Contingency Study Plans have been or are being prepared for several Regional Response Teams (RRTs) in different parts of the country. Before the preparation of the CA DOMP, the most formalized of these documents was the *Texas General Land Office "Spill of Opportunity" Dispersant Demonstration Project Description* (Aurand et al. 2004).

The plan that was submitted to the Region 6 RRT proposes to use oil spills of between 250 and 500 bbls in either Galveston Bay or Corpus Christi Bay to demonstrate the effectiveness of treatment with chemical dispersants. The primary objectives are to evaluate the operational efficiency of dispersant application and monitoring under realistic spill-response conditions, assess the fate of the dispersed oil plume, and evaluate the interaction of the dispersed oil plume with sediments in shallow estuarine waters. If possible, a study team will be supplied with an aircraft for dispersant application and spotting, and a surface boat crew will be deployed to monitor the dispersed oil plume in the water column after dispersant application. Alternatively, boats may be used to apply dispersants if suitable aircraft are not available. The monitoring teams will use *in situ* fluorometry to collect data on hydrocarbon concentrations in the water column along transects through the dispersed oil plume at frequent intervals after application of the dispersant. These *in situ* measurements will be supplemented by collection of water samples for more detailed laboratory analyses of the oil concentration and composition in the water column. Sediment and shellfish-tissue samples will also be collected as needed.

There were two instances in U.S. waters over the last 17 years where spill-of-opportunity studies were conducted *ad hoc* during real spill events (Payne et al. 1991c, 1993). During the September 1987 *PAC Baroness* oil spill off Point Conception, California (a sub-surface release of fuel oil from the sunken vessel), the effectiveness of treatment of a 100 m by 700 m portion of the slick with forty-one gallons of Corexit 9527 by helicopter was

documented (Payne et al. 1991c). A U.S. Coast Guard H-3 helicopter compiled a photographic record of the slick's behavior, and the U.S. Coast Guard AirEye Falcon Jet monitored the slick using side-looking airborne radar (SLAR) from an altitude of 5,000 ft and IR/UV scans from 400 ft. Continuous subsurface UV fluorescence measurements and grab samples of water from beneath the slick were also obtained from a support vessel before and after dispersant application. Unfortunately, the results of the tests were equivocal because the slick was very thin in the treated area (Figure 2) and only a small portion of the slick was treated. The thicker portion of the slick immediately above the submerged *PAC Baroness* could not be tested because it would have been impossible to differentiate dispersed oil from surfacing oil released from the vessel itself. In addition, 15-to-20 knot crosswinds caused significant breakup and dispersion of the current-controlled surface slick in both the treated and untreated control areas. The SLAR data were of limited value because of the resolution of the technique from 5,000 ft was not sufficient to observe changes in the small treated area. The aerial UV scans suggested that changes occurred in the treated slick, but the *in situ* UV fluorescence measurements and subsequent chemical analyses did not indicate that significant dispersant-enhanced entrainment occurred.

With lessons learned from the initial attempts, additional plans were developed to repeat the *PAC Baroness* studies under two different idealized wind conditions (Figures 2 through 5), but the tests could never be completed due to limited visibility (100 ft ceilings) and diminishing oil volumes released from the vessel over the next two days. The lessons learned from this study led to development of detailed plans for investigating dispersant effectiveness and potential water-column impacts at future spills of opportunity (Payne et al. 1991c), and the recommendations included:

- The need for preparing detailed plans for different coastal regions in advance. Planning should include identification of personnel and logistical support services, procurement of all required permits, and identification of potential sources of emergency funding. In addition, communication links should be developed and tested before the day of the spill to ensure reliable communication between all platforms.
- During execution of the plan, target areas for dispersant application should be identified with smoke bombs for dispersant application and tracking, and sufficient smoke bombs should be available to continuously mark the treated area by replacing old ones before they become extinguished. In addition, under conditions of a cross-wind, the smoke bombs should be deployed on the downwind side of the target area to allow for drift over the course of the experiment (Figures 4 and 5).
- The dispersant should be applied into the wind to minimize drift away from the target area, and two surface vessels should be used in addition to a helicopter observation platform for documentation of dispersant effectiveness. As shown in Figures 2 and 4, the surface vessels and/or observation helicopter should be configured perpendicular-to and in-line (up wind) with the dispersant application flight line to document dispersant drift off of the target area.

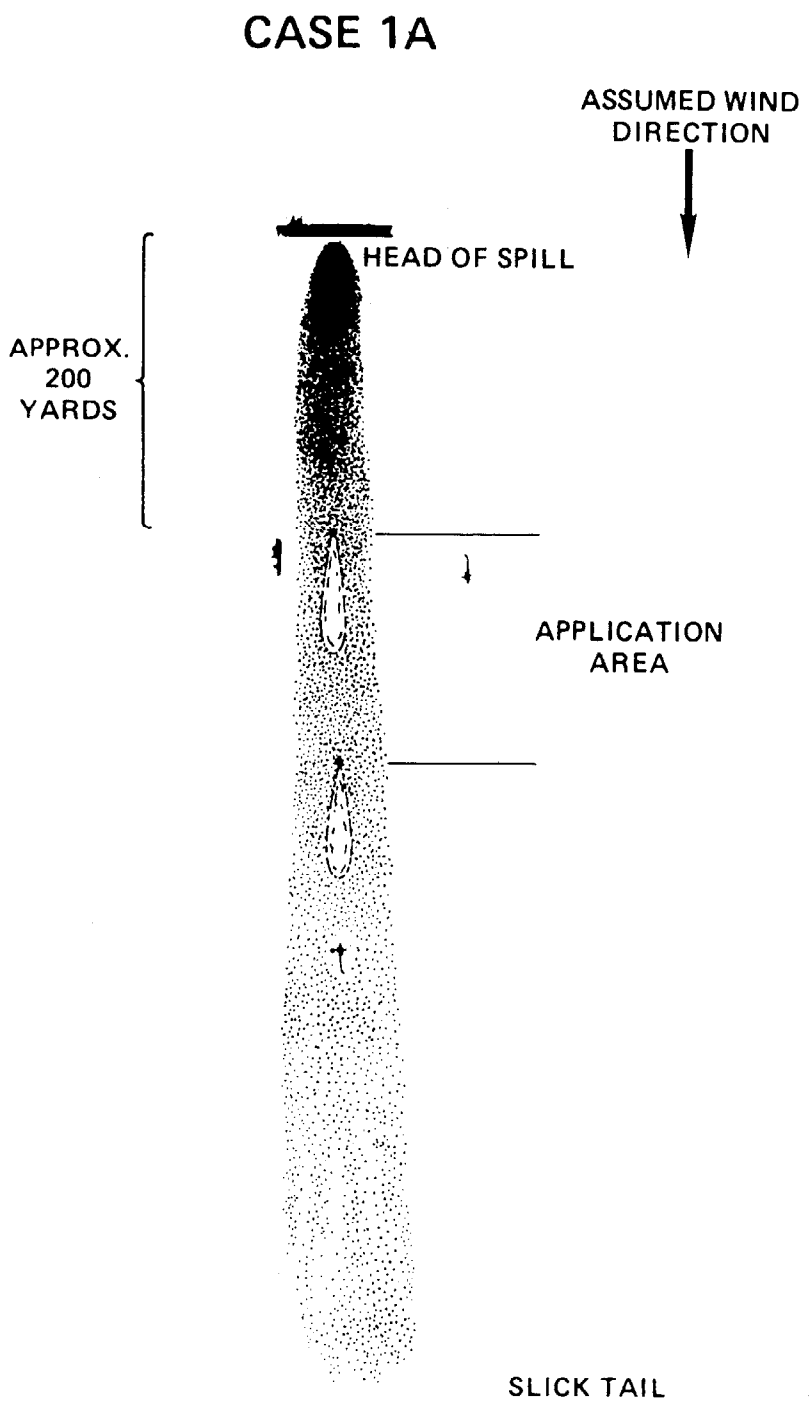

Figure 2. Idealized configuration of surface response vessels (*Mr. Clean III* and *Dash),* the smoke bombs marking the dispersant target area, and helicopters with wind parallel to current-controlled slick drift (from Payne et al. 1991c). In this study, fuel oil was being released at depth from the sunken vessel, the *PAC Baroness,* and the dispersant application area had to be selected approximately 200 yards from the subsurface source to avoid confusing dispersed oil with oil coming up from the vessel itself.

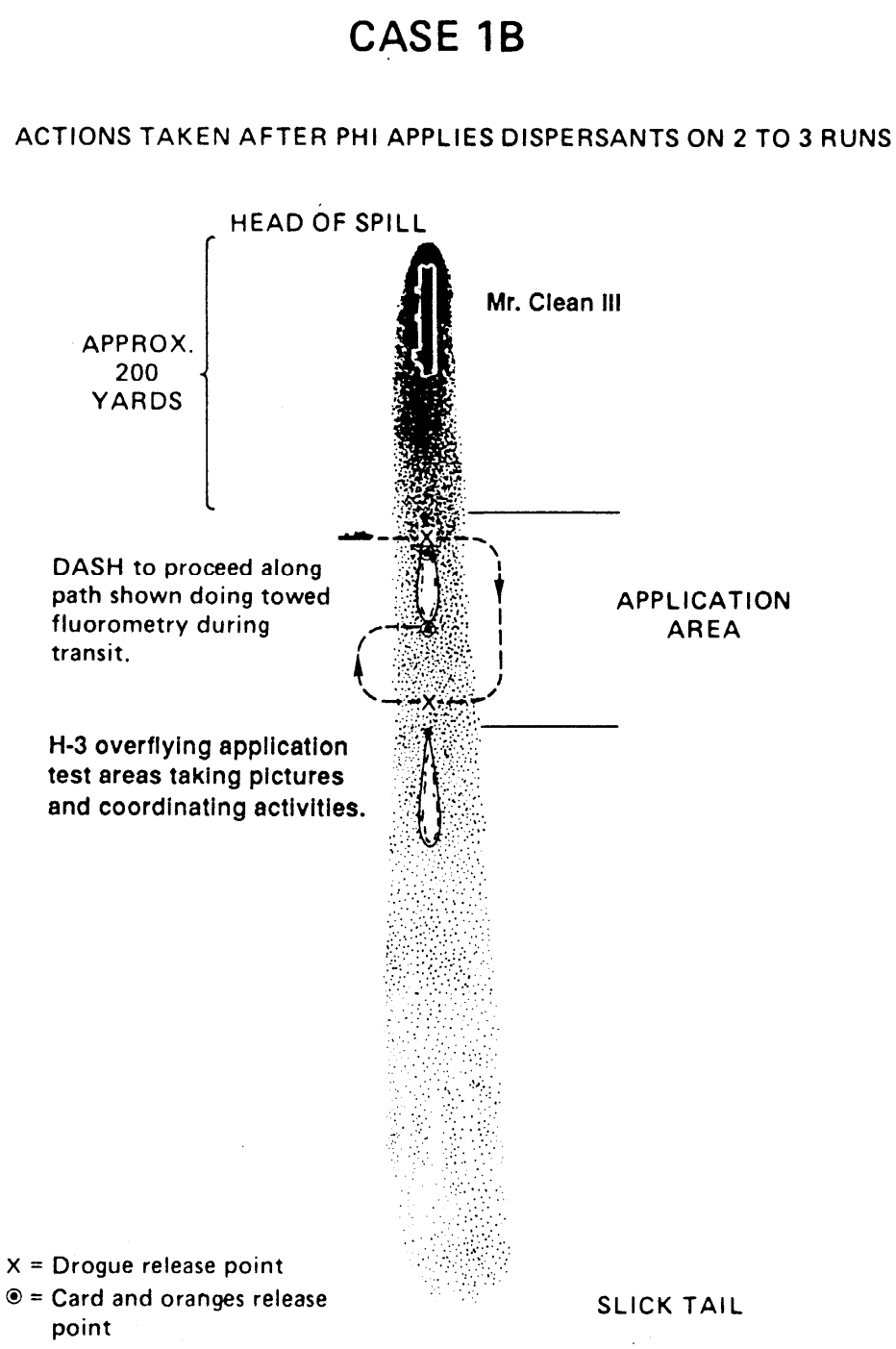

Figure 3. Idealized representation of vessel movements for the *Dash* and *Mr. Clean III* (response vessels) after dispersant application to the surfacing *PAC Baroness* oil assuming a wind direction parallel with the current-controlled slick drift (see Figure 2) (from Payne et al. 1991c).

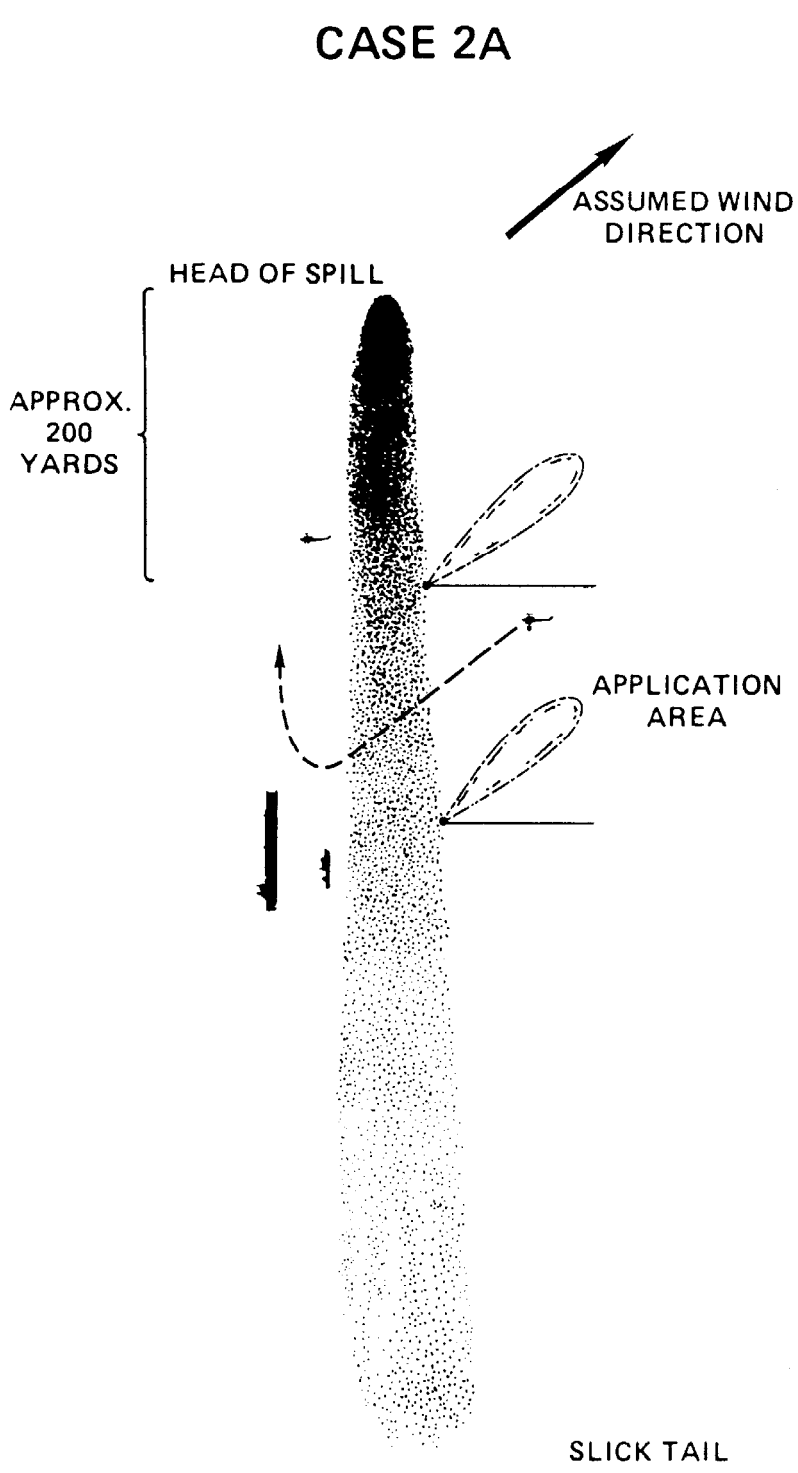

Figure 4. Idealized configuration of surface response vessels and helicopters in the event of a wind blowing across the current-controlled *PAC Baroness* surface slick before dispersant application (from Payne et al. 1991c). The smoke bombs are positioned to still be in the slick as it drifts to the right with the wind.

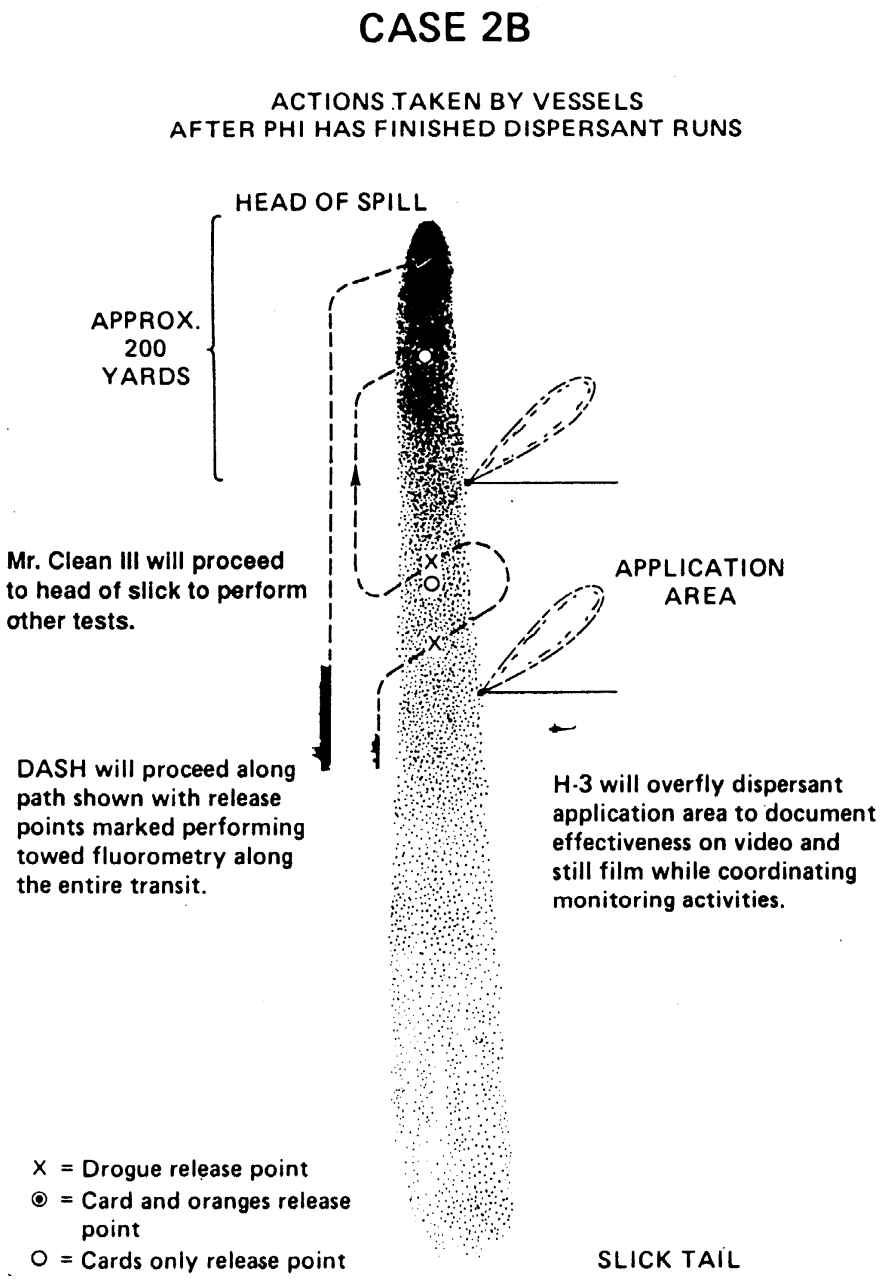

Figure 5. Idealized representation of surface vessel movement into the *PAC Baroness* slick for subsurface sampling and drogue and drift card deployment after the dispersant application under the case in which a cross wind is blowing across the main axis of the current-controlled surface slick (see Figure 4) (from Payne et al. 1991c).

- Both videotape and 35 mm (or digital) photography should be used to document the experiment, and whenever possible, a surface vessel or smoke bomb should be in the field of view as a point of reference and for scale. Chronological activities and other verbal communication should be recorded on the video tape if possible.
- Water-column oil concentrations should be measured using *in situ* UV fluorescence and chemical analysis of grab samples of effluent from the UV fluorescence system as well as more conventional water column samples obtained by water-bottle and hydrowire from one or both vessels within the slick before and after dispersant application. In addition, water column samples and UV fluorescence measurements should be completed in a control (non-treated) portion of the slick. At least one (and preferably several) subsurface drogues should be used to track the subsurface plume from the treated area.
- If a large area (several square miles) can be treated with dispersant, remotely monitor the slick using SLAR at 5,000 to 7,000 ft (which is useful under all weather conditions) and IR/UV at 400 ft (effective only in clear weather). If IR/UV runs are attempted, begin at the head or thicker part of the slick to allow time for aircraft roll adjustments before flying over the treated area. (More recent reviews of additional remote sensing approaches are contained in Brown and Fingas (2005)).

Utilizing the lessons learned from the *PAC Baroness* study, additional spill-of opportunity dispersant trials were undertaken at the *M/V Mega Borg* fire and oil spill off Galveston, Texas in 1990 (Kennicutt et al. 1991; Payne et al. 1993). The ship's cargo was a light Angola Planca crude oil (API gravity = 38.9; viscosity = 4.58 cSt at 30^{o} C) Smoke bombs and coded 3-m drogues marked the target and control areas, and water samples were collected to determine whether enhanced PAH dissolution due to dispersant-treatment could be observed. Dispersant effectiveness was monitored by concurrent observations from the command/control aircraft and the Texas A&M research vessel *HOS Citation*, which monitored UV fluorescence continuously at a depth of 4 meters along transects through the slick and completed a discrete water sampling program. Surface vessel transects and the locations of the discrete 30-liter water sampling stations (at 1-9 m) were aided by the smoke bombs, the positions of the free-drifting drogues, and directions from the command/control aircraft.

As in the planned oil-spill dispersant experiments discussed above, the distribution of dispersed oil droplets in the *M/V Mega Borg* studies was very heterogeneous and reflected the patchy distribution of oil on the water surface before dispersant application. Maximum concentrations of dispersed hydrocarbons in the center of the treated zone were 22 mg/L for total aliphatics (primarily dispersed droplets) and 5.4 µg/L for total aromatics 60 to 90 minutes after dispersant application. Elevated levels were generally limited to the upper 1-3 meters of the water column. Concentrations in the upper 1-3 meters of the untreated control zones were significantly lower (1.2-3.9 mg/L and 0.8-1.7 µg/L for total aliphatic and aromatic hydrocarbons, respectively). The dispersed aliphatic hydrocarbon concentrations at a depth of 9 m in the treated and control areas were similar (2.5-2.7 mg/L), suggesting that they represented a background, steady-state concentration

of very fine, physically dispersed oil droplets that were formed by natural dispersion of the slick during the six days before the dispersant tests began. The ratio of the concentrations of aliphatic to aromatic hydrocarbons (2133:1 and 2875:1 in the control and treated zones, respectively) showed no evidence of significantly enhanced dissolution of lower- and intermediate-molecular-weight aromatics as a result of chemical dispersion. If such dissolution had occurred, however, it is possible that the dissolved-phase PAH were lost to evaporation directly from the 84^{o} F seawater in the upper mixed layer before the water samples were collected.

One of the major disadvantages identified in both of these spill-of-opportunity studies was that many of the resources (boats, aircraft, USCG and other response personnel, etc.) necessary to assist with the execution of the programs were tied up with response activities. Also, radio communications between all the operating platforms (observation aircraft, directional aircraft, dispersant application aircraft, sampling and observation boats, and USCG (Unified Command) personnel) were difficult at best, and often non-existent during the field operations. Finally, both spill of opportunity studies were relatively far from land (15-25 miles) and refueling of the observation/command control aircraft coordinating the dispersant trials was problematic. In the case of the *PAC Baroness*, the USCG helicopter had to return to Santa Barbara for refueling, and over 2 hours of spill behavior/documentation immediately after dispersant application could not be obtained. During the *M/V Mega Borg* study, it was possible to refuel the command/control helicopter from an operating oil platform several miles from the spill, but even then, over 30 minutes were lost, and upon returning to the test area, great difficulty was encountered in relocating the coded 3-m drogues. They could not be tracked successfully from the water surface, so relocating them from the air was critical to directing the *HOS Citation* back into the subsurface plume; by the time they were located, it was time to refuel again and return to shore because of darkness.

Although documentation of dispersed oil was possible during the *M/V Mega Borg* study, the measured subsurface oil concentrations were extremely patchy, and there was no way to integrate or average the concentrations over time and space to even begin to approach a percent dispersed oil calculation. Finally, during spill of opportunity studies, the oils may not be amenable to chemical dispersion, or as in the case of the *M/V Mega Borg*, the oil may be so light, that it disperses naturally, making comparisons of treated vs. non-treated areas tenuous at best.

OBJECTIVES

Environmental Impact Assessment

The California Department of Fish and Game has functioned as the State's lead trustee agency for oil spill response since its inception in the late 19th century. But only with the implementation of OPA 90 and SB-2040 did such a significant degree of focused attention and effort become manifest. Protection of environmental resources and response to environmental injuries has long been the Department's mission, but following the events of the early 1990's a whole new level of emphasis was recognized as necessary. Given the magnitude and hazard levels associated with modern commerce and California

coastal development, SB-2040 mandated that the Department enter into a newly defined level of preparation for protection of environmental resources with an associated recognition for the need to restore damaged resources.

The OSPR mission is to "provide the best achievable protection for California's natural resources by preventing, preparing for, and responding to spills of oil and other deleterious materials, and through restoring and enhancing affected resources."

Assessing environmental impacts is but a portion of the activity associated with oil spill response. But within that capacity, the evaluation of trade-offs between differing response strategies becomes an important element of the oil spill response effort.

Natural Resource Damage Assessment (NRDA)

Natural Resource Damage Assessment (NRDA) is the process of establishing a suitable monetary value for fish, invertebrate, wildlife and habitat injuries resulting from a defined environmental insult. The California Department of Fish and Game is designated as the Trustee Agency for wildlife resources for the State of California. In addition, it is designated as the Lead Agency for marine oil spill response. Assessing injury is an arduous task under the best of circumstances. A satisfactory outcome is one that has reasonably defined the full range of impacts, has arrived at a monetary compensation value that fairly reimburses the citizens of California for the loss of resource value, and identifies a mechanism for restoring the injury to a suitable state or condition.

With the application of dispersant to an oil spill, some portion of that floating oil mass will be transferred to the water column. The purpose of this Monitoring Plan is to determine the distribution of dispersed oil, the concentration of oil in the water column, and the adverse impact on the aquatic resources of the affected water body. In its capacity as trustee agency, the Department of Fish and Game will endeavor to establish the extent of environmental injury, determine the monetary value of that injury, and propose strategies for restoring the injury.

NEBA verification

Utilization of the NEBA process was instrumental in the development of dispersant use zones and more specifically the "Dispersant Pre-Approval Zones". Although this process is well established, it is, by its very nature, a qualitative exercise that requires that resource experts utilize their "best professional judgment" when specific toxicity as well as fate and effects data are not available. This makes the process quite sensitive to both "species and ecosystems of special concern," often the very areas where specific data are lacking. Fate and effects monitoring could provide a critical mechanism for independent verification of the appropriateness of the assumptions made during the dispersant zone development process. Subsequent revisions to both the "Dispersant Pre-Approval Zones" as well as the CDP would be made, as appropriate and necessary to minimize the net environmental damage caused by an oil spill and the subsequent response options.

METHODS

Problem Definition

The successful application of dispersants may reduce the impacts to certain types of wildlife (e.g. seabirds, sea otters) and shoreline habitats. Model predictions and laboratory toxicity studies indicate a rapid dilution of dissolved and dispersed oil after a spill. However, little or no data are available from oil spills in the field to evaluate potential aquatic impacts. This is in part because toxic concentrations and the evidence of impacts disappear after hours to a few days. Pre-planning of sampling to document water column effects is needed in order to perform the needed sampling in the time window where effects might be measured.

Aquatic organisms may be adversely impacted either directly or via the food web by the toxic effects of oil components that enter the water column, particularly the soluble compounds (i.e., monoaromatic hydrocarbons, MAHs, and Polynuclear (or Polycyclic) Aromatic Hydrocarbons, PAHs) and microscopic oil droplets mixed by waves into the water. Evaluations of bioassays and modeling have shown that while the MAHs are initially dissolved in higher concentrations into water, the PAHs are more toxic and persistent, and they may affect biota via dissolved concentrations or by uptake from dispersed oil droplets (French-McCay 2002, 2003). Other soluble and semi-soluble hydrocarbons in oil may also contribute to aquatic toxicity (NRC 2005). Non-aromatic hydrocarbons are much less soluble, so are less bioavailable.

Overall, adverse impacts increase the larger the spill size. However, there is great variability related to the environmental conditions after the spill: aquatic organisms suffer much more adverse impact under windy conditions where high waves mix unweathered oil (which still contains the volatile and soluble components) into the water than in calm weather (French-McCay and Payne 2001; French-McCay et al. 2002; French-McCay 2003; French-McCay 2006; see also Appendix A). Dispersants lower the oil-water interfacial tension, which promotes increased entrainment and dissolution of oil components into the water column. Use of dispersants on fresh oil could potentially increase the water column impact analogous to those under windy conditions where natural dispersion occurs, while prolonged weathering before dispersants are applied reduces the concentrations of MAHs and PAHs in the surface oil and consequently in the water column (French-McCay and Payne 2001).

Concentrations of oil hydrocarbons in water are a complex function of environmental conditions (e.g., wind, turbulence, temperature) and dilution volume (volume of water into which the oil is dispersed). An oil fates model (French et al. 1996; French-McCay 2003, 2004) that estimates the distribution of oil (as mass and concentrations) on the water surface, in the water column, on shorelines, and in the sediments was used to evaluate potential water concentrations that might result from natural dispersion and dispersant use under different environmental conditions (Appendix A). The results indicate the magnitudes and spatial/temporal scales of dispersed oil plumes in the water which may be used to inform field monitoring and sampling plans. In addition, the model

results quantify the volume of water where impacts to aquatic biota (fish and invertebrates) of varying sensitivity to hydrocarbon toxicity would be expected under differing environmental conditions.

In the event of a spill, it is often not cost-effective or even possible to quantify spill impacts to water column biota using field data collections. Comprehensive sampling of each of the species affected would be needed in the exposed and unaffected areas. Because marine organisms are so patchy in their distribution, large numbers of stations and samples within stations are needed to accurately map abundance. Such extensive sampling of all (or even selected) species affected is often not feasible, given the rapidity at which the evidence disappears (by scavenging of killed organisms and by migration of animals into the impacted area).

What is feasible and cost-effective, is to estimate impacts using existing knowledge of the fates of oils and their toxicity in the form of an oil fates and biological effects model. The oil fates model provides a continuous and complete description of the surface area swept by oil and of the subsurface concentrations in three dimensions over time. The biological effects model evaluates exposure concentrations and the duration of that exposure, which are the determinants of acute toxic effects.

Modeling allows quantification of spill impacts using as much site-specific data as available, as input or as validation of model results. For example, the *North Cape* oil spill in Rhode Island (USA) in January 1996 caused significant injury to shallow water invertebrates and fish, as evidenced by millions of dead animals stranded on the shoreline after the spill. Modeling was used for injury quantification in this spill for all but the most commercially important species, the American lobster (*Homarus americanus*). Lobster injury based on field data collections was used to validate the model, such that the model-predicted injuries to other aquatic biota were convincing and allowed for a rapid settlement of the case (French-McCay 2003).

The injury to water column biota in the *North Cape* case was the largest of any spill natural resource damage assessment to date. In other spills, quantification of water column injury based on field sampling would be more difficult than in that case, and has not been attempted. Thus, oil fates and effects modeling would be used to estimate injuries to water column biota in the event of a spill. Water column sampling of hydrocarbon concentrations in the dispersed plume would allow the oil transport and fate model to be calibrated and verified. Sampling of biota to identify exposed species and life stages, as well as to estimate pre-spill densities, would allow quantification of injuries to those species using biological effects modeling. Bioassays on the exposed species of most concern would reduce the uncertainties of these injury estimates. Procedures for this modeling are described below, following the description of the model used for analysis herein and the results of the scoping model runs used for planning of sampling.

Model Description

Oil Fates and Effects Model

The oil spill modeling was performed using the Spill Impact Model Application Package (SIMAP, described in French-McCay 2003, 2004 and summarized in Appendix A), which uses wind data, current data, and transport and weathering algorithms to calculate the mass of oil components in various environmental compartments (water surface, shoreline, water column, atmosphere, sediments, etc.), oil pathway over time (trajectory), surface oil distribution, and concentrations of the oil components in water and sediments. Processes simulated include slick spreading, evaporation of volatiles from surface oil, transport on the water surface and in the water column, randomized (eddy) diffusion, emulsification, entrainment of oil as droplets into the water column, resurfacing of larger droplets, dissolution of soluble components, volatilization from the water column, partitioning, sedimentation, stranding on shorelines, and degradation. Oil mass is tracked separately for lower-molecular-weight aromatics (MAHs and PAHs), other volatiles, and non-volatiles. The lower molecular weight aromatics dissolve from both from the surface oil slick and whole oil droplets in the water column, and they are partitioned in the water column and sediments according to equilibrium partitioning theory.

The biological effects model (French et al. 1996; French-McCay 2003, 2004) estimates short term (acute) exposure of biota of various behavior types to floating oil and subsurface contamination (in water and subtidal sediments), resulting percent mortality, and sublethal effects on production (growth). For each wildlife behavior group, a portion of the animals in the area swept by surface oil over a threshold thickness is assumed to die, based on probability of encounter with the oil on the water surface multiplied by the probability of mortality once oiled. Toxicity to aquatic biota in the water and subtidal sediments is estimated from dissolved aromatic concentrations and exposure duration, using laboratory-based bioassay data for oil hydrocarbon mixtures (French-McCay 2002). Losses are estimated by species or species group for fish, invertebrates and wildlife as percent of exposed biota killed and equivalent area or volume of 100% loss (see Appendix A).

Oil Toxicity

The following is a summary of scientific understanding of oil toxicity to water column organisms, based on the evaluation and oil toxicity model development in French-McCay (2002). Appropriate toxicity values based on this analysis were used in the modeling. A more complete description of the oil toxicity analysis is in Appendix A.

Studies have shown that dissolved concentrations of the lower molecular weight aromatic hydrocarbons, i.e., MAHs and especially PAHs, cause most of the acute toxicity to aquatic organisms (Anderson et al., 1974, 1987; Neff and Anderson, 1981; Malins and Hodgins, 1981; McAuliffe, 1987). Lower molecular weight aliphatic hydrocarbons may also contribute to toxicity, particularly in gasoline and other products where they form a major portion of the fuel. These toxic components are volatile, making it difficult to expose organisms to constant concentrations in bioassay tests, particularly with oils.

Thus, exposure concentrations of each compound in the mixture, as well as their toxicities, must be known to estimate the toxicity of oil to water column organisms (French-McCay 2002; Appendix A).

For mixtures of chemicals that cause toxicity by the same mechanism, the acute toxic effects of each chemical are additive (Swartz et al. 1995; French et al. 1996; DiToro et al. 2000; DiToro and McGrath 2000; French-McCay 2002). MAHs and PAHs (as well as lower molecular weight aliphatic hydrocarbons) in oil are a mixture of chemicals that cause the acute toxic effect narcosis (Veith et al., 1983; Abernethy et al. 1986, 1988; Verhaar et al., 1992). Thus, their toxic effects are additive (McCarty et al. 1992a,b). As water concentrations decrease rapidly after an oil spill, the primary effect on water column organisms is acute toxicity by narcosis. Other toxic modes of action have been observed for PAH contamination in sediments over long exposure times, but the primary concern for dispersant use offshore is acute (short-term) exposure of water column biota to potentially toxic hydrocarbon concentrations (French- McCay 2002).

An additive toxicity model and available LC50 data for individual compounds may be used to estimate the LC50 (lethal concentration to 50% of exposed organisms) of the mixture of MAHs and PAHs in oil to which aquatic organisms are exposed. Oil toxicity is a function of MAH and PAH content and composition in the oil. The toxicity of oils and refined products has been estimated and verified with available bioassay data. The verified oil toxicity model may be used to estimate toxicity of untested oils under varying environmental conditions (French-McCay 2002; Appendix A).

Narcotic chemicals impact organisms by accumulating in lipids (such as in the cell membranes) and disrupting cellular and tissue function. The more hydrophobic the compound, the more accumulation in the tissues and the more severe the impact. However, the more hydrophobic the compound, the less soluble it is in water, and so the less available it is to aquatic organisms. Thus, impact is the result of a balance between bioavailability (dissolved-component exposure) and toxicity once exposed (see review in DiToro et al. 2000).

PAHs are more hydrophobic than MAHs, and so are more toxic. There is a continuum from the most soluble and least toxic benzene (simplest MAH) through the naphthalenes (2-ring PAHs) to the 3- and 4-ring PAHs. The more complex 4-ring PAHs are so insoluble that they are not dissolved or bioavailable to a significant extent. This functional relationship can be described by a regression model using available data on a variety of compounds and species (French-McCay 2002). A similar approach has been used to develop US Environmental Protection Agency (USEPA) water and sediment quality criteria for PAHs (DiToro et al. 2000; DiToro and McGrath 2000).

Because of the relative solubility and volatility of various MAHs and PAHs, and the relative concentrations of the various compounds in oil, most of the acute toxicity is caused by substituted naphthalenes (C2- and C3-naphthalenes). However, all the compounds in the mixture contribute to toxicity (French-McCay 2002).

Toxicity varies with time of exposure, the LC50 decreasing as exposure time increases (Sprague, 1969; Abel, 1980; Mancini, 1983; Bailey et al., 1985; McAuliffe 1987; Heming et al., 1989; McCarty et al. 1992a,b; French et al. 1996; French-McCay 2002). This is due to the accumulation of toxicant over time up to a critical tissue concentration that causes mortality. The accumulation is slower for more hydrophobic compounds. The accumulation is also slower at colder temperature. Thus, for brief exposures at low temperature, toxic effects require a higher concentration than would be necessary at higher temperature or for instances where exposure times are longer (see Figure 6). Because the aromatic mixture in fuel and crude oils has a toxicity equivalent to C2- or C3-naphthalenes, and oil exposures are hours to days, duration and temperature of exposure need to be considered to determine an appropriate LC50 and toxic effects to water column organisms (French-McCay 2002).

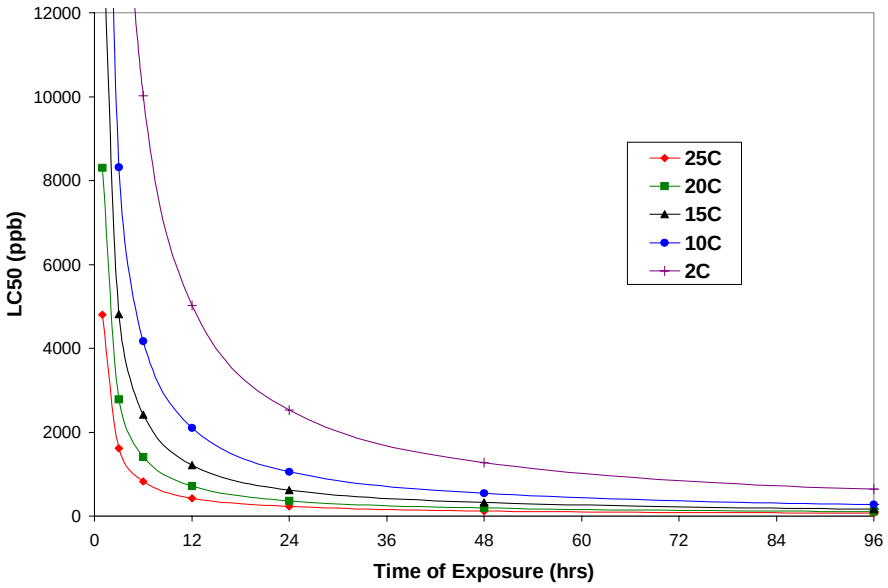

Figure 6. Variation in LC50 with exposure duration and temperature.

The volatilization rates of hydrocarbons from surface slicks are faster than the dissolution rates into the water. Thus, dissolution from oil droplets in the water column is the main source of concentrations dissolved in the water. Entrainment of oil into the water column is insignificant in less than 12 knots of wind, the wind speed where breaking waves begin to form. As the wind becomes stronger, the oil entrainment rate increases, as do concentrations in the water. Dilution by transport and volatilization causes the concentrations to decrease rapidly after the spill. Thus, water samples must be taken in the first few days after a spill if exposure to acutely toxic concentrations is to be documented. The toxic effects of the concentrations depend on the duration of exposure (French-McCay 2002).

Typically, for surface releases of fuel and crude oils, only the PAHs are dissolved in sufficient quantity and remain in the water long enough for their toxic effects to be significant. The more turbulent the release (i.e., if it is during a storm or from a blowout or pipeline under pressure), the higher the relative concentrations of the more toxic PAHs in the water, and the higher the impacts to water column organisms. However, for a subsurface release deep in the water column or for a gasoline or other product spill where the MAHs and lower molecular weight aliphatics are significant fractions of the oil, all of these compounds may cause significant acute toxic effects (see Appendix A). The relative composition of hydrocarbons in the dissolved and particulate phases determines the toxicity of the mixture. Thus, concentrations of both phases should be measured within the plume to estimate toxicity values (French-McCay 2002).

Species vary in their sensitivity to the narcotic chemicals in oil. For a turbulent release or after natural or dispersant-induced entrainment, the LC50 for PAH exposure of >4 days is about 50 μg/L total PAH for the species of average sensitivity. Species sensitivity varies from 6 to 400 μg/L (ppb) of PAH, covering 95% of species (French-McCay 2002). Similar estimates result from using regressions for bioassays reviewed in DiToro et al. (2000). The LC50 values from French-McCay (2002) were used in the modeling. For additional details on the development of the toxicity model and parameters, see Appendix A.

Scenarios and Model Inputs for Scaling Concentration Plumes and Potential Impacts

Model estimates were made of concentrations (dissolved hydrocarbons and dispersed oil droplets) that would be expected in the water column for the largest potential volume of oil that could be dispersed at any one location and time: that amount that could be dispersed by a single sortie of a C-130 (100,000 gal of light crude oil, 100 μm thick and 3.78 km^2 in area, dispersed at 80%, 45% or 20% efficiency). Runs assuming no-dispersant use were compared to those where dispersant was applied after 8 or 16 hours of weathering, for two wind conditions: 2.5 m/s (5 kts) and 7.5 m/s (15 kts).

The dispersed oil was assumed to remain in the surface mixed layer. Two mixed layer conditions were examined: 10m and 20m deep. Background currents were assumed to be negligible, 0.25 kts opposing the wind and 0.25 kts toward the down-wind directions. This speed is a typical current speed based on drifter studies during periods when the California Current prevails.

Model Results: The Scale of Concentration Plumes and Impacts

For a spill of short duration, as opposed to a continuous release, dispersant would not be applied until some hours after the release and the oil would be partially weathered. Based on the model results (Appendix A), by 8 hours after release, two thirds of the MAHs would evaporate, and by 16 hours after release only 5% of the MAHs would remain in

the floating oil. Thus, if the oil were dispersed, most of the resulting dissolved hydrocarbon concentrations would be PAHs. These would be the components to monitor with field sampling. However, for a continuous release where fresh oil would be dispersed, MAHs should also be measured.

With 5 kt winds and no dispersant, the concentration plume (dissolved aromatic concentrations >1 ppb) would be relatively small and short-lived (hours). In 15 kt winds, natural dispersion would be considerable and dispersant at 80% efficiency would increase the volume affected by >1ppb by a factor of 2-3. Dispersant application at lower efficiencies would result in a proportionately smaller plume volume. Variation of other model inputs resulted in smaller changes in affected volume. Additional details are in Appendix A.

Potential impacts assuming a range of toxicity values characterizing 95% of species were summarized as equivalent water volumes of 100% loss. The impacted volume for a sensitive (2.5th percentile) species was negligible in 5 kts of wind with no dispersant, on the order of 1-2 million m^3 (e.g., a surface mixed layer 10-20 m deep with an area of 0.1 km^2) in 15 kts of wind for 100,000 gal (326.3 MT) of naturally-dispersed oil, 20-40 million m^3 (2 km^2 by 10-20 m deep) in 15 kts of wind for 80,000 gal (261.0 MT) of chemically-dispersed oil, and 70-200 million m^3 (7-10 km^2 by 10-20 m deep) in 5 kts of wind for 80,000 gal (261.0 MT) of chemically-dispersed oil. Thus, the highest impacts were when chemical dispersant was applied under light wind conditions where dilution was relatively slow. Volumes and areas impacted would be much less if the oil were patchy or more spread out (because each patch would be a smaller volume and there would be more edge where mixing and dilution would occur), or in the cases where the efficiency of the dispersant application is less than 80%.

Modeling Procedure for Evaluation of Oil Spill Impacts on Water Column Biota

The modeling approach for estimating injury to water column biota is as follows:

- Oil fate and concentrations of oil components are estimated in space and over time.
- The fates model predictions are verified by comparison with observed oil distributions and hydrocarbon concentrations (particulate and dissolved).
- Organism mortality is estimated based on exposure to water column dissolved and (potentially) particulate (droplet) concentrations.
- The biological model's estimated kills are compared to those estimated by field methods to verify the model, as data are feasible to collect and available.
- The verified model is used to estimate injuries for resources where field estimates are unavailable.

For the oil trajectory and fates model, the following model inputs are needed. In some cases these data are available from automated meteorological and oceanographic measurement stations, and data may be collected later. However, for spills in remote

areas and where these stations and temporarily non-operational, such data will need to be measured. In addition, local conditions may be quite different from the automated station locations.

- Wind speed and direction, at least hourly;
- Air temperatures;
- Water temperature and salinity in the surface mixed layer;
- Currents in the surface mixed layer (current meters, drogues, Coastal Ocean Dynamic Applications Radar (CODAR), and/or other instrumentation);
- Horizontal and vertical diffusion rates (e.g., by tracking dye concentrations over time, see Payne et al. 2007a,b, French-McCay et al. 2007, 2008);
- Spill volume and duration of release (time course of the spill);
- Oil characteristics (density, viscosity, water content, chemical composition, etc.);
- Time history of all cleanup activities with details of mass/volume removed; and
- Time history of dispersant application and effectiveness estimates.

Observed oil distributions and hydrocarbon concentrations should be collected to provide data to calibrate the model. Thus, they need not be synoptic in time and space, but should provide enough information to calibrate the physical model at key times after the spill. Typically, given how quickly oil disperses, the data collections should be in the first few days after a large spill, and immediately following application of dispersants.

As it will not be possible to synoptically sample both in and out of the plume in a design where statistical differences could be shown, the biological sampling should be designed to establish pre-spill baseline (by number and weight for each species and life stage and by size classes, as appropriate) and what types of organisms were exposed. Biological effects modeling may then be used to quantify injury. If it is feasible, field data collections could be focused on exposed species of particular concern, such that enough data might be collected to indicate and possibly quantify injury. If this is possible, such data may be used to verify the modeling results.

Modeling may be used to estimate the range of potential injuries, given the range in species sensitivity that has been observed in laboratory-based bioassays performed and reported previously (French-McCay 2002; Appendix A). Given the large variation in sensitivity of various species and life stages, and that many important species have not been tested, acute toxicity bioassays should be performed on exposed organisms of concern to provide more accurate estimates of injury.

Sampling Protocol: Physical-Chemical

Do not delay response operations for the DOMP. In implementing the CA OSPR Dispersed Oil Monitoring Plan, it is critically important to emphasize that planned or on-going dispersant operations as part of the response effort should not be delayed while assembling the sampling team and equipment necessary to implement the DOMP. Ideally, standby contracts for individuals and the necessary equipment and sampling/ observation platforms should be in place before the spill event, and efforts should be undertaken to begin staging equipment and personnel at locations convenient to the spill

site (with direct communication links to the Incident Command Center) as soon as the decision to utilize dispersants is made.

Dispersed oil tracking

The only practical way to track dispersed oil in the water column is through the use of drifters drogued at specific depths within the mixed layer. Deployment of drifters should be at the center of the dispersant-treated area. The location of this zone is best achieved through the use of smoke bombs as described in Payne et al. (1991c). Smoke bombs should be deployed before dispersant application to mark the target area, and replaced before they are extinguished to guide drifter placement and initial sample collection. Ideally, multiple sets of depth-specific drifters (1-, 3-, and 10-meter) should be deployed from two or more sampling/observation vessels. The drifters should be coded with colored flags and flashing beacons (or preferably frequency specific radio transponders) to allow tracking of water masses at specific depths from all sampling vessels and/or shoreline stations.

During previous spill of opportunity studies, Payne et al. (1991c, 1993) noted that tracking drogues from the sea-surface became difficult with increasing sea states, and helicopter support was required to find the drogues and direct the sampling vessels back into the center of the dispersed oil plumes. For this reason alone, it will be important to equip the drogues with flashing beacons, and possibly to equip the observation aircraft with a receiver to assist in locating the drogues in less than optimal operational conditions. During recent dye studies off Point Loma (San Diego), CA, GPS tracking was used to monitor drifter distributions over time, and that information was transmitted back to the sampling vessels (Payne et al. 2007a,b; 2008).

Sampling location and depth

Utilizing depth dependent drifters to track the center of the dispersed oil plume will facilitate continuous subsurface water sampling at 1-, 3-, and 10-meters with UV fluorescence equipment similar to that used for the SMART protocols. Ideally, three separate UV-fluorescence monitors should be utilized to continuously monitor the different depths. Subsurface tubing feeding each UV-fluorescence unit can be held in place with a subsurface mast securely mounted to the side of the sampling vessel. If separate fluorometers are not available, a three-way valve/manifold system may be placed in line to direct the subsurface water flow from the different depths to the fluorometer as a function of time. This switching system should be automated and integrated into the continuous recording signal so that the sampling depth will be noted on all measurements. During recent dye studies off Point Loma (San Diego), CA, samples from two discrete depths were pumped through dual Turner Design 10-AU continuous-flow fluorometers, and a towed Wet Labs *in situ* fluorometer (sampling at 3 Hz) was coupled to a programmed downrigger allowing continuous profiles over a 1-10 m range to be obtained during across- and along-plume transects (Payne et al. 2007a,b; 2008). All fluorometer data and GPS position and time were automatically transferred to a data logger on board the vessel.

Transects through the dispersed oil plume should be repeated for a minimum of two hours, and they should extend into non-contaminated water to better define the structure

of the subsurface plume. The direction of the sampling vessels into and out of the treated zones should be provided by the observation aircraft.

Dispersed Oil

Finite measurements of dispersed oil concentrations will be possible if seawater samples are filtered at the time of collection and the filtrate (containing the dissolved-phase) and the filter (which retains the dispersed oil droplets) are analyzed separately (Payne et al. 1999). This is discussed further below in the section on chemical sampling.

Reference water (control)

Transects should run through the dispersed oil plume and extend from the edges into non-contaminated water. It is important to obtain finite water samples beneath the non-dispersant-treated slick to evaluate background physical entrainment of oil in the water column before dispersant applications are conducted. These water samples must be collected at the same depth intervals as the samples collected in the dispersed oil plume. Chemical sampling methods are described below, however, it will be important to obtain samples for continuous UV/fluorescence measurements as well as grab samples of whole (and filtered) water as described in the following section.

Chemical sampling: Collection methodology

Samples of effluent from the UV/fluorometers should be periodically collected at fixed time intervals, and immediately after real-time UV/fluorescence signals indicating the presence of dispersed oil droplets. Volumes of 1 L can be readily contained in commercially-available pre-cleaned narrow-mouth amber glass bottles with Teflon®-lined lids. The samples can be preserved by addition of 3-4 mL 6 N HCl from an auto pipette dispenser onboard the sample collection vessel. The samples will contain both dissolved constituents and dispersed oil droplets, and it will not be possible to differentiate the relative proportions of each; however, the data will be useful for correlating UV/fluorescence measurements to whole-oil concentrations in the water column. Every fifth sample from the UV/fluorometer effluent should be filtered as described below to provide differentiation of dissolved and particulate/oil-phase fractions.

Where the results from the continuous flowing UV/fluorescence measurements indicate elevated levels of dispersed oil droplets, finite grab samples at 1, 3, and 10 m should be collected with conventional water column sampling equipment (Go-Flo® bottles or equivalent). With these samples, it is recommended that both dissolved-phase and particulate oil droplets be collected (Payne et al. 1999; Payne and Driskell 2003) so that measured concentration data can be used to validate computer-model predictions of the separate phases. These data can then be compared to values typically used in water accommodated fractions (WAF) generated for dispersed oil toxicity evaluations.

Sample filtration

Payne et al. (1999) designed and fabricated a portable large volume water sampling system (PLVWSS) for collecting 3-4 L volumes of seawater to meet the quantitation requirements to support Natural Resource Damage Assessment (NRDA) toxicity determinations and modeling efforts following an oil spill. This system (Figure 7)

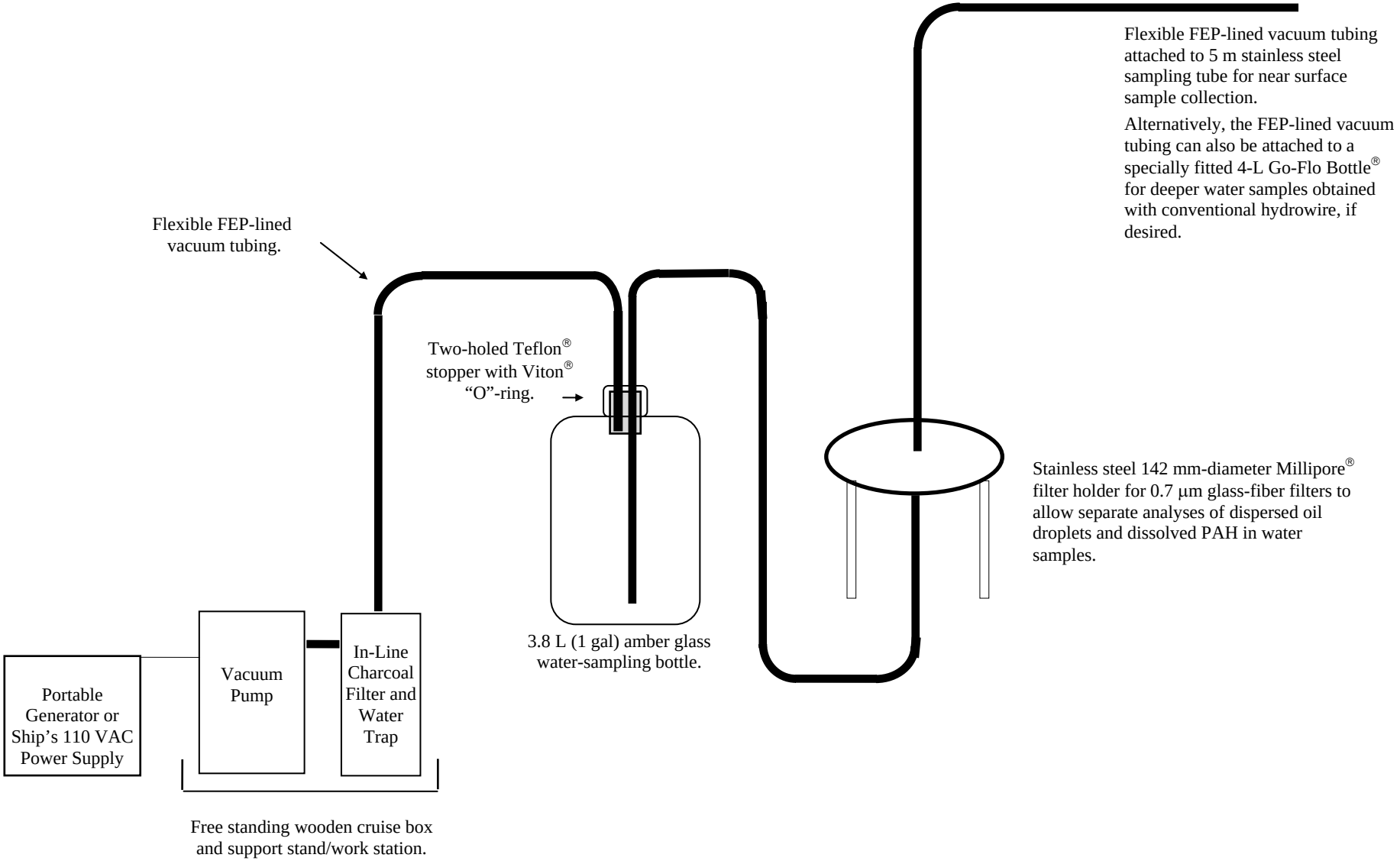

Figure 7. Schematic diagram of the Portable Large Volume Water Sampling System (PLVWSS) used for collecting dissolved and particulate/oil phase samples (from Payne et al. 1999).

is a significant improvement to conventional water sampling equipment and includes the ability to filter water samples at the time of collection, thereby providing critical differentiation between truly dissolved constituents and dispersed oil droplets. The system can be quickly and easily deployed from vessels of opportunity to provide essential data during the early stages of a spill. In combination with conventional water sampling equipment (e.g., Go-Flo® Bottles) the PLVWSS can be used to collect finite water samples for subsurface water-column profiling and measurement of dispersed oil droplet and dissolved component concentrations at depth.

Because of the time required for PLVWSS filtration (approximately 3-5 minutes per sample), unfiltered whole-water grab samples should also be collected for increased resolution of water-column hydrocarbon burdens. Although these whole-water samples will not allow differentiation of dissolved and dispersed oil-droplet phases, they can provide additional information on the overall hydrocarbon distributions throughout the water column.

Sample preservation

Whole water column samples can be preserved by the addition of six normal HCl to lower the PAH to < 2. For 1 L samples addition of 3 mL of 6 N HCl from an auto pipette dispenser should be sufficient to drop the pH of seawater to < 2.0. For the nominal 3.5 L samples collected with the PLVWSS, 12 mL of 6 N HCl will be required. In addition to acid preservation, holding collected water samples on ice is recommended. Alternatively, water samples can be preserved by the addition of methylene chloride, although this will start the extraction process and introduces the finite possibility of sample contamination by handling organic solvents on a rolling boat where diesel or gasoline exhaust fumes may be present. Discrete glass fiber filters from the PLVWSS containing dispersed oil droplets can be preserved by addition of 3 mL of 6 N HCl and/or by freezing.

Preserved samples should be shipped in Igloo coolers containing Blue Ice to the analytical laboratory by overnight courier. Complete chain-of-custody forms should be included with each cooler indicating the cooler's contents and desired analyses. A sample chain-of-custody form is shown in Figure 8.

Chemical Analysis: Standards and reporting units

All collected samples should be extracted by the analytical laboratory and analyzed for the SHC and alkylated PAH components identified in Table 3. The n-alkanes should be quantified by flame ionization detector gas chromatography (FID GC), and the data used to quantify concentrations of whole oil droplets. Alkylated PAH should be analyzed by selected-ion-monitoring (SIM) gas chromatography/mass spectrometry (GC/MS).

These analyses will allow quantification of both dispersed oil droplet and dissolved-phase components in the water column. The alkylated PAH measurements will be particularly important for correlation to dispersed oil toxicity studies and model-predicted dispersed oil behavior.

CHAIN OF CUSTODY — ***PECI Chain of Custody/Analytical Request Form***

PWS RCAC Tom Kuckertz, PWS RCAC, 339 Hazelet Avenue, Valdez, AK 99686 (907) 834-5050

PROJECT NAME	BWTF_BTT	SAMPLER	JR Payne
PROJECT/ACCT NUMBER		FIRM	PECI
RECEIVING LAB	**WHG**		1991 Village Park Way, # 206B
ADDRESS	**375 Paramount Drive, Suite 2**		Encinitas, CA 92024
	Raynham, MA 02767-5154	PHONE	(760) 942-1015
PHONE	**(508) 822-9300**	SIGNATURE	
CARRIER	Fed Ex		
AIRBILL	833079566943		
DATE SHIPPED	1/12/2005		

COLLECTION DATE	COLLECTION TIME	SAMPLE SOURCE & DESCRIPTION	SAMPLE ID	COMP or GRAB	MATRIX	PRESERVATIVE	NUMBER OF CONTAINERS: GLASS	PLASTIC	VOA VIALS		Container Size	Total Samp Size	ANALYSIS REQUESTED (Complete the analysis (TPH, PCB's etc.) in boxes below)						REMARKS
1/11/2005	14:31	Jan_05_Biorate time 0.5	01/05 BTEX Biorate 2 - 0.5	Lab Study	H2O	HCl	***	***	***	2	40 mL	40 mL	BTEX +	***	***	***	***	***	***
1/11/2005	15:01	Jan_05_Biorate time 1	01/05 BTEX Biorate 2 - 1	Lab Study	H2O	HCl	***	***	***	2	40 mL	40 mL	BTEX +	***	***	***	***	***	***
1/11/2005	16:01	Jan_05_Biorate time 2	01/05 BTEX Biorate 2 - 2	Lab Study	H2O	HCl	***	***	***	2	40 mL	40 mL	BTEX +	***	***	***	***	***	***
1/11/2005	18:01	Jan_05_Biorate time 4	01/05 BTEX Biorate 2 - 4	Lab Study	H2O	HCl	***	***	***	2	40 mL	40 mL	BTEX +	***	***	***	***	***	***
1/11/2005	22:01	Jan_05_Biorate time 8	01/05 BTEX Biorate 2 - 8	Lab Study	H2O	HCl	***	***	***	2	40 mL	40 mL	BTEX +	***	***	***	***	***	***
1/11/2005	14:01	Jan_05_Biorate time 0	01/05 Biorate 2 - 0	Lab Study	H2O	HCl	***	***	***	1	60 mL	60 mL	Alk PAH	SHC	***	***	***	***	***
1/11/2005	14:31	Jan_05_Biorate time 0.5	01/05 Biorate 2 - 0.5	Lab Study	H2O	HCl	***	***	***	1	60 mL	60 mL	Alk PAH	SHC	***	***	***	***	***
1/11/2005	15:01	Jan_05_Biorate time 1	01/05 Biorate 2 - 1	Lab Study	H2O	HCl	***	***	***	1	60 mL	60 mL	Alk PAH	SHC	***	***	***	***	***
1/11/2005	16:01	Jan_05_Biorate time 2	01/05 Biorate 2 - 2	Lab Study	H2O	HCl	***	***	***	1	60 mL	60 mL	Alk PAH	SHC	***	***	***	***	***
1/11/2005	18:01	Jan_05_Biorate time 4	01/05 Biorate 2 - 4	Lab Study	H2O	HCl	***	***	***	1	60 mL	60 mL	Alk PAH	SHC	***	***	***	***	***
1/11/2005	22:01	Jan_05_Biorate time 8	01/05 Biorate 2 - 8	Lab Study	H2O	HCl	***	***	***	1	60 mL	60 mL	Alk PAH	SHC	***	***	***	***	***
***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***
***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***
***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***

RELINQUISHED BY (PRINT/SIGN):	DATE/ TIME	RECEIVED BY:	RELINQUISHED BY (PRINT/SIGN):	DATE/ TIME	RECEIVED BY:	RECEIVED FOR LABORATORY (PRINT/SIGN):
RELINQUISHED BY (PRINT/SIGN):	DATE/ TIME	RECEIVED BY:	RELINQUISHED BY (PRINT/SIGN):	DATE/ TIME	RECEIVED BY:	SAMPLE RECEIPT (Temp, Condition,COC Seals)
						/ /

COMMENTS TO LAB:

Figure 8. Example Chain-of-Custody and Analytical Request Form.

Table 3. Target analytes that should be requested for analysis in support of NRDA studies on the impacts of dispersant use to combat oil spills.

Analytes	Abbreviation	Analytes	Abbreviation
PAH[1]			
Naphthalene	N	Benzo(e)pyrene	BEP
C1-Naphthalene	N1	Benzo(a)pyrene	BAP
C2-Naphthalene	N2	Perylene	PER
C3-Naphthalene	N3	Indeno(1,2,3-cd)pyrene	IP
C4-Naphthalene	N4	Dibenzo(a,h)anthracene	DA
Biphenyl	BI	Benzo(g,h,i)perylene	BP
Acenaphthylene	AC	Total PAH	TPAH
Acenaphthene	AE		
Fluorene	F	**SHC[2]**	
C1-Fluorenes	F1	n-Decane	C10
C2-Fluorenes	F2	n-Undecane	C11
C3-Fluorenes	F3	n-Dodecane	C12
Dibenzothiophene	D	n-Tridecane	C13
C1-Dibenzothiophene	D1	n-Tetradecane	C14
C2-Dibenzothiophene	D2	n-Pentadecane	C15
C3-Dibenzothiophene	D3	n-Hexadecane	C16
C4-Dibenzothiophene	D4	n-Heptadecane	C17
Anthracene	A	Pristane	Pristane
Phenanthrene	P	n-Octadecane	C18
C1-Phenanthrene/Anthracene	P/A1	Phytane	Phytane
C2-Phenanthrene/Anthracene	P/A2	n-Nonadecane	C19
C3-Phenanthrene/Anthracene	P/A3	n-Eicosane	C20
C4-Phenanthrene/Anthracene	P/A4	n-Heneicosane	C21
Fluoranthene	FL	n-Docosane	C22
Pyrene	PYR	n-Tricosane	C23
C1-Fluoranthene/Pyrene	F/P1	n-Tetracosane	C24
C2-Fluoranthene/Pyrene	F/P2	n-Pentacosane	C25
C3-Fluoranthene/Pyrene	F/P3	n-Hexacosane	C26
C4-Fluoranthene/Pyrene	F/P4	n-Heptacosane	C27
Benzo(a)Anthracene	BA	n-Octacosane	C28
Chrysene	C	n-Nonacosane	C29
C1-Chrysenes	C1	n-Triacontane	C30
C2-Chrysenes	C2	n-Hentriacontane	C31
C3-Chrysenes	C3	n-Dotriacontane	C32
C4-Chrysenes	C4	n-Tritriacontane	C33
Benzo(b)fluoranthene	BB	n-Tetratriacontane	C34
Benzo(k)fluoranthene	BK	Total SHC	TSHC

1. Analyzed by SIM GC/MS
2. Analyzed by FID GC

Concentrations of alkylated PAH identified by the SIM GC/MS technique should be adequately quantified down to approximately 40 ng/liter for the 1 L samples. Concentrations as low as 5-10 ng/liter may be obtained from the nominal 3.5 L water samples collected with the PLVWSS.

Source oil

Samples of the source oil should be collected from the stricken vessel or through coordination with the US Coast Guard and the Unified Command center. Source oil samples should be shipped under full chain of custody to the analytical laboratory in a separate cooler (away from any water and SPM samples) and characterized for the same suite of analytes identified in Table 3. In addition, aliquots of the source oil should be provided to the field sampling crew for possible preparation of calibration standards for use with the UV/fluorescence units.

Usually, UV-fluorescence instrumentation is calibrated with fluorescein dye, and these solutions should be used for reporting UV-fluorescence concentrations from the water column. Calibration of UV fluorescence units with oil from the spill incident is important, but extremely difficult to complete because of separation of oil and water phases over time. It is recommended that mixtures of the dispersant and oil be volumetrically measured and diluted into known volumes of clean seawater. Calibration standards solutions should be throughly mixed/agitated in sealed volumetric containers and used immediately as oil and dispersant phases may separate from the water on standing. The use of dispersed oil droplets in addition to fluorescein dye for calibrating the fluorometers is recommended to provide a secondary standard.

Dispersant product

Samples of the dispersant must be collected directly from the aircraft or boat used for dispersant applications. Dispersant samples should be shipped under full chain-of-custody to the analytical laboratory and characterized for the same suite of analytes identified in Table 3. In addition, aliquots of the dispersant should be collected for evaluation of UV/fluorescence properties using the analytical equipment on board each sampling vessel. Data on dispersant volumes applied (times, pump rates, nozzle calibration, etc.) should also be obtained from the flight/dispersant application crew after each sortie.

Control

Because most of the anticipated concentrations that will be measured from the field samples are expected to be very low (10-40 mg/liter for whole-oil droplets and 0.5-10 µg/L for dissolved PAH in the center of the dispersed oil plume, and possibly one to two orders-of-magnitude lower in control areas), it will be important to ensure that background contamination from the sampling vessels and other sources is kept to an absolute minimum. For this reason it will be important to minimize or curtail any bilge water or on board wastewater discharges from the vessel at the time of all water sample collections. In addition, all sample manipulations (removal of filters from PLVWSS-collected samples, acid preservation, etc.) should be completed upwind of sampling vessel exhaust discharges. To minimize sample cross-contamination, samples from clean/control areas should be collected before samples from the center of the dispersed oil plume whenever possible. It may also be prudent to maintain additional supplies of

sampling hose, which should be replaced from subsurface sampling systems after particularly high concentrations of dispersed oil droplets are encountered.

Finally distilled water should be obtained from the analytical laboratory supplying the sample bottles and used for collection of field/method and trip blanks. If possible, the analytical laboratory should analyze and certify the background SHC and PAH levels in their distilled water used for preparation of these blanks. If the laboratory cannot provide certified distilled water, commercially purchased distilled water may be used; however, it has been found that most commercial distilled water sources contain traces of parent and alkyl-substituted naphthalenes. Because of these limitations, it is sometimes appropriate to simply use seawater collected from stations remote from the spill and all dispersant applications for background controls and evaluation of sampler contamination.

Sampling Protocol: Biological component

The justification for utilization of dispersant is to remove floating oil from the water surface where it can adversely affect resources such as birds, mammals, and shorelines. By transferring the oil to the water column the surface resource exposure potential is reduced (or ideally eliminated). The dispersed oil is then permitted to mix with the water column thereby providing the opportunity to accelerate the process of bacterial degradation while allowing the product to dilute into an ever increasing volume of water. These two process working in unison will (ideally) render the dispersed oil non-toxic in a short period of time. The affected water mass is occupied by an assemblage of vertebrates, invertebrates, and plants that can be adversely impacted by components of the dispersed oil as the process develops. It is that assemblage for which this plan is interested in understanding the manifestation of impacts.

Holoplankton

The component of the plankton community which spends its entire life as a planktonic organism is thereby vulnerable to the potential adverse effect of dispersed oil at any point in its life history. These holoplanktors comprise a long list of plants and animals that form the all-important food-web base. The process of documenting injury to that assemblage in the affected water mass is comprised of determining the assemblage components and measuring the degree of injury to representatives of the assemblage. As it will not be possible to synoptically sample both in and out of the plume in a design where statistical differences could be shown, the sampling should be designed to establish pre-spill baseline (by number and weight for each species and life stage) and what types of organisms were exposed. Oil fates and effects modeling may then be used to quantify injury.

Because the holoplankton include numerous small algal and invertebrate species, it would not be practical to evaluate injury to each species individually. In most cases, the most efficient approach would be to estimate baseline biomass or production rates and the percentage loss due to toxicity of oil hydrocarbons in the water (using modeling, as described above). Thus, water and net tow sampling for measurement of phytoplankton and zooplankton biomass (g dry weight by size classes of biota) should be sufficient to

characterize the smaller plankton groups. Zooplankton collections should be examined under a microscope at a shore-based facility to identify dominant groups.

The presence of certain larger micronekton species of importance to the food web, such as krill (euphausids), may warrant specific counts of individuals per unit volume to estimate baseline biomass to use in injury quantification. Micronekton are typically sampled with towed nets. Volume flow through the net should be measured, allowing estimation of volume sampled. Counts should be made, by species, and a representative subsample measured to provide a size-frequency distribution of animals present and exposed during the spill.

As many micronekton vertically migrate on a daily basis, sampling during all parts of the day and night should be performed to evaluate pre-spill density in each time period of the diel cycle. Horizontal patchiness should also be considered. Typically, if the tows are sampled over a long horizontal distance, the patchiness is integrated. For a surface spill, and where dispersants are applied, the tows should be made only in the surface mixed layer, as that is where hydrocarbon exposure would be expected. Sampling should be performed before exposure to the spilled hydrocarbons or in a reference area.

Meroplankton and Ichthyoplankton

The component of the plankton community that begins its existence in the classical "plankton" assemblage (but later develops into a free swimming, mobile benthic, or sessile benthic organism) may be vulnerable only during the planktonic phase of its life history. Some meroplankton and ichthyoplankton may have only limited geographic distributions, which if impacted during certain critical periods could substantially impact that species at a population level. A number of commercially important species begin their maturation from eggs and larval stages as planktonic organisms. The processes of documenting the presence of these organisms and measuring the degree of injury to the assemblage (or represented species) are the underlying issues. Examples of meroplankton and ichthyoplankton groups that could be injured by exposure to dispersed oil or dissolved hydrocarbons in the surface layer include abalone larvae, crab larvae, urchin larvae, and fish eggs and larvae. Losses of eggs and larvae would be reflected in lowered recruitment to older age classes, either locally or over a larger area, depending on the movement patterns of the species during its life cycle.

Again, as it will not be possible to synoptically sample both in and out of the plume in a design where statistical differences could be shown, the sampling should be designed to establish pre-spill baseline (by number and weight for each species and life stage) and what types of organisms were exposed. Oil fates and effects modeling may then be used to quantify injury. Sampling should be designed to provide quantitative estimates of pre-spill density of each species group and size/age class/stage within that species. As with micronekton, meroplankton and ichthyoplankton are typically sampled with towed nets (such as paired "bongo nets" with two mesh sizes). Volume flow through each net should be measured during each tow, allowing estimation of volume sampled. Counts should be made, by species, and a representative subsample measured to provide a size-frequency distribution of animals present and exposed during the spill.

Some meroplankton and ichthyoplankton vertically migrate on a daily basis. Thus, sampling during all parts of the day and night should be performed to evaluate pre-spill density in each time period of the diel cycle. As for the micronekton after a surface spill, and where dispersants are applied, the tows should be made only in the surface mixed layer, as that is where hydrocarbon exposure would be expected. Sampling should be performed before exposure to the spilled hydrocarbons or in a reference area.

Bioassays

Modeling may be used to estimate the range of potential injuries, given the range in species sensitivity that has been observed in laboratory-based bioassays performed and reported previously (see summary above and Appendix A). Given the large variation in sensitivity of various species and life stages, and that many important species have not been tested, acute toxicity bioassays should be performed on exposed organisms of concern to provide more accurate estimates of injury. This bioassay work would need to be in real time using sampled organisms from the area of the release. The micronekton, meroplankton and ichthyoplankton sampling, along with considerations of population status and ecological and commercial importance, would indicate the species of concern in a given situation.

Bioassays with whole oil are difficult to quantify and interpret for a number of reasons: (1) Oils contain a large number of hydrocarbons, with variable toxicity and environmental fate, and spill conditions are not necessarily replicated in the laboratory test. (2) Experimental designs, which maintain a constant exposure regime to experimental organisms, are difficult to construct, and variable conditions make interpretation difficult. (3) Measurement of the components requires several specialized and expensive methods. (4) It is likely that only certain components are available to the organisms and causing the toxicity, complicating the interpretation of the results.

To simplify the task such that it would be feasible, bioassays with individual aromatic compounds of a range of solubility (e.g., toluene, naphthalene and phenanthrene) should be done to determine the sensitivity of the species/stage to narcotic effects of soluble aromatics (the primary mode of action for acute effects). Species that are sensitive to one aromatic are equally sensitive to other PAHs and to MAHs. Thus, bioassays on individual compounds may be used to determine how sensitive the tested species is to mixtures from oil (French-McCay 2002). Bioassays should be performed on several individual aromatics across the range of K_{ow} for soluble and semisoluble aromatics. This approach would introduce less uncertainty than the interpretation of oil bioassay tests. The basis for this approach is described in Appendix A.

These measurements would be recommended for larger spills under conditions where significant water column impacts would be expected. This would be for surface releases under storm conditions (high turbulence), spills where dispersants are applied, and subsurface releases (pipelines and blowouts). The higher the volume of PAH released (i.e., the combination of oil volume and PAH content) and the more turbulent the conditions, the greater the dissolution of the more toxic compounds into the water. Thus, these conditions would lead to the highest exposure to the most toxic compounds. Use of chemical dispersants on a large volume of oil concentrated in a relatively small area

could lead to toxic concentrations in the surface mixed layer of the area where oil is entrained.

In many cases where water toxicity occurs, the source oil composition may be used to evaluate the fraction of each aromatic in the soluble fraction of the oil, and thus the toxicity of the oil. Because of the uncertainty of how environmental conditions will influence relative amounts of soluble aromatics in the water, however, water sample measurements will provide a more accurate direct measurement of dissolved hydrocarbon composition.

For heavier crude oils and fuels (e.g., heavier refined products such as bunker C, No. 6 fuel oil and Intermediate fuel oil), only the PAHs are significant for evaluation of toxicity. However, in light-medium crude oil and light products, BTEX, other MAHs and C4-C20 aliphatics can form significant fractions of the oil. At a minimum, the source oil should be analyzed for these constituents to establish the amounts in the oil and determine which fractions need to be considered in toxicity assessments. If the MAHs and C4-C20 aliphatics form a significant fraction, and especially if the release is deep in the water column, water samples should be measured for all fractions. For surface spills of heavier oils, PAH measurements should be sufficient.

Logistical Requirements for Environmental Data Collection

Below is brief description of the minimum logistical support that will be required for monitoring a dispersed oil spill. These recommendations are based on seven die studies off Point Loma (San Diego), CA in 2005 and 2006 to evaluate the proposed methods in the DOMP for data and information gathering (Payne et al. 2007a,b; 2008).

Boats

A minimum of two boats should be available to implement the DOMP. They should be of sufficient size to support a combined scientific party and crew of 6-8 personnel, safely navigate in near-shore open-water conditions, and be equipped with USCG approved navigation and communication equipment. Ideally, they should have 120 V AC power available, although this can also be supplied by portable generator. At least one of the vessels should be equipped with a conventional hydrowire and winch for subsurface water-column sampling and towing plankton nets or other biological sampling systems. A programmable down rigger useful for high resolution *in situ* fluorescence profiling can be mounted to the gunnel/rail on almost any vessel of opportunity. Satellite communications would now allow for the system to be expanded providing real-time information to shore-based decision makers.

Aircraft

One observation aircraft (either fixed wing or helicopter) should be dedicated to supporting and photo-documenting the plume behavior and on-water sampling activities. The aircraft should have sufficient fuel capacity to sustain flight operations for 4-5 hours, if possible. A fixed-wing aircraft with a mounted digital camera with GPS recording

capabilities (recording latitude, longitude, and altitude for multiple points in each transect/overflight) for georeferenced images is the ideal platform.

Communications

At-sea and boat-to-aircraft communications are critical, and they are always problematic. Available options include: handheld California Department of Fish and Game radios, marine band radios, air band radios, and cell phones. The ability to use multiple modes of communication can be critical in all the field experiments, as at times one or more forms of communication are often unavailable. Satellite phones should be used if at all possible.

Sampling Equipment

At a minimum, CTD and *in situ* as well as continuous-flow fluorometers should be available. GPS and radio-telemetry equipped drifters drogued at several depths will be required to track the subsurface plume over time after (or if) it is not readily visible from the surface vessels or observation aircraft. For the sake of simplicity in this discussion, we typically refer to drifters drogued at 2- and 4- meters; however, in practice we recommend completing a 30-meter CTD cast in the test area before dispersant operations commence to determine the vertical extent of the near surface mixed layer. Then, drogue depths of the drifters should be set at a range of depths across the surface mixed layer to account for any shear present within the near-surface layer (Payne et al. 2007a,b, 2008). In addition, finite water-column sampling equipment, such as 4L Go-Flo® Bottles, should be provided for water column sampling at depth. Grab samples should include bulk (unfiltered) seawater for total petroleum hydrocarbon (TPH) measurements and samples processed through on-station filtration at the time of collection (such as that provided by the Portable Large Volume Water Sampling System (PLVWSS) described above (Payne et al. 1999)). This will allow differentiation of dissolved-phase PAH components and whole-oil droplets to support modeling and toxicity estimates (French-McCay 2002, 2003, 2004; Payne and Driskell 2003). Biological samples (zooplankton) should be collected with "Bongo" net tows for organisms in the water column and "Manta" nets for organisms at the water surface. Care should be taken during biological sampling to avoid surface oil and the dispersant-treated plume to minimize equipment and sample contamination. Aircraft observations/support may be particularly useful in this regard to ensure that biological sampling nets are not towed through a surface slick or subsurface oil plume not immediately visible from the sampling vessel.

DISCUSSION

If dispersants are to be applied, such applications should not be delayed while assembling the sampling team, boats, and equipment necessary to implement the DOMP. However, individuals involved in the sampling effort should be notified as soon as the decision to use dispersants is made, and efforts should immediately be undertaken to begin staging equipment, boats, observation aircraft, and sampling personnel at locations convenient to the spill site with direct communication links to the Incident Command Center. Ideally, standby contracts for these individuals and the necessary equipment and sampling/observation platforms should be in place long before the spill event.

Background CTD casts and water column and biological sampling should be completed in at least 2-3 areas well away from the surface floating oil and the dispersed oil plume(s). If possible, this should be done both inshore and offshore of the slick to assess water-column structure as well as biological and (background hydrocarbon) chemistry variability, and it should occur before the dispersant application and treated-slick sampling. If time doesn't allow for this, background sampling can be completed after those activities if proper precautions are taken to decontaminate sampling equipment. It is also important to obtain water samples beneath the non-dispersant-treated slick to evaluate background physical entrainment of oil into the water column before dispersant applications are conducted. These water samples should be collected at the same depth intervals as the samples collected in the dispersed oil plume. Biological sampling gear (Otter trawls, plankton nets, etc.) should not be used in an area with surface oil or to sample within the dispersed oil plume because of extensive decontamination issues.

Sampling and analyses of water-column impacts should be done on an identified part of the oil slick as part of normal dispersant operations. That is, if dispersant operations are planned or on going, a spotter aircraft should be used to identify a portion of the surface oil that can be marked with smoke bombs and subsurface-drogued drifters, and then tracked/sampled over time as described above without interfering with other ongoing response operations. If possible, infrared (IR) video should be utilized by the dispersant applications contractor or spotter aircraft to identify the thicker portions of the slick to be treated.

During transit to the spill location, telephone and radio communications should be established and double checked. This includes communications with the Incident Command Center and between all surface vessels and the spotter/observation aircraft. In addition, telecommunications should be completed with personnel responsible for satellite-tracking of the drogued drifters to ensure that they are transmitting properly before being deployed. This communication link will also be critical later to provide correct latitude and longitude coordinates for GPS tracking and recovery of the drifters over time.

In addition to the biological and chemistry samples, aerial photography from the spotter aircraft (with time and GPS data integrated into the digital image) should be collected throughout all operations. Additional oceanographic data should include:

- CTD casts before dispersant applications (to assist in selecting optimal drogue depths), and as the evolution of the dispersed oil plume occurs to document potentially changing water-column stratification over time.
- Wind and wave data from nearby oceanographic buoys.
- High frequency radar measured surface currents.
- Fluorometer calibrations.

Usually, UV-fluorescence instrumentation is calibrated with fluorescein dye, and these solutions should be used for reporting UV-fluorescence concentrations from the water column. If possible, these calibrations should be completed before moving equipment into the field (Payne et al. 2007a,b; 2008). Calibration of UV fluorescence units with oil

from the spill incident is important, but extremely difficult to complete because of separation of oil and water phases over time. It is recommended that after the field sampling activities are completed, mixtures of the dispersant and oil from the spill event (collected from the Responsible Party) be volumetrically measured and diluted into known volumes of clean seawater. Calibration standards solutions should be throughly mixed/agitated in sealed volumetric containers and used immediately as oil and dispersant phases may separate from the water on standing. The use of dispersed oil droplets in addition to fluorescein dye for calibrating the fluorometers is recommended to provide a secondary standard.

Proper implementation of the DOMP will require a multidisciplinary effort involving numerous personnel from different state and federal agencies along with the private sector. The approach outlined in this document also may be useful in providing additional information to incident responders regarding dispersant effectiveness and potential impacts from dispersed oil plumes entering sensitive biological areas, if modifications to the data collection and storage systems can allow transmission of pertinent information to the Incident Command Center in a near real-time manner.

Obviously, these types of coordinated measurements are extremely difficult to execute (particularly during the emergency-response phase of a spill), so it is critically important to have a detailed plan in place before a spill event and to utilize a team with familiarity in the strengths and inherent weaknesses of the sampling and observation methods as well as past experience in working together as a coordinated unit to successfully execute such a plan.

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