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**WORKSHOP
ORGANIZED AND
PROCEEDINGS EDITED
BY**

SCIENTIFIC AND
ENVIRONMENTAL
ASSOCIATES, INC.
ALEXANDRIA, VA

WORKSHOP PROCEEDINGS

**THE USE OF
CHEMICAL
COUNTERMEASURES
PRODUCT DATA FOR
OIL SPILL PLANNING
AND RESPONSE**

VOLUME I

APRIL 4-6, 1995

**XEROX DOCUMENT UNIVERSITY AND
CONFERENCE CENTER**

LEESBURG, VA

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FOREWORD

Interest in the potential uses of chemical countermeasure products in mitigating the environmental impacts of spilled oil has grown tremendously in the last several years. These Proceedings, published in two volumes, endeavor to address many of the issues related to reasoned application of such products in circumstances satisfactory to the entire response community. Volume I contains synopses of the Workshop deliberations and the summary statements from each of the concurrent sessions (environmental effects, effectiveness, and **decision-making**). Volume I also includes background information which describes the classes of CCPs, their chemical behavior, **and** their response niches.

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LIST OF ABBREVIATIONS, ACRONYMS, AND SYMBOLS

Term	Abbreviation, Acronym, or Symbol
Area Committee	AC
Area Contingency Plan	ACP
American Petroleum Institute	API
Chemical Countermeasure Product	CCP
United States Department of Commerce	DOC
United States Department of the Interior	DOI
Joint Group of Experts on the Scientific Aspects of Marine Pollution.....	GESAMP
Median lethal concentration	LC ₅₀
Marine Spill Response Corporation	MSRC
National Oil and Hazardous Substances Pollution Contingency Plan	NCP
National Oceanic and Atmospheric Administration	NOAA
Oil Pollution Act	OPA
Occupational Safety and Health Administration	OSHA
On-Scene Coordinator	OSC
Part per million	ppm
Part per million-hour	ppm-hr
Regional Contingency Man	RCP
Regional Response Team	RRT
Responsible Party	RP
United Kingdom	U.K.
United States	U.S.
United States Environmental Protection Agency	EPA
United States Coast Guard	USCG
United States Fish and Wildlife Service	USFWS

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Gail Thomas	U.S. Environmental Protection Agency

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Environmental Effects	James Clark, Exxon Biomedical Sciences Jeffrey Underwood, U.S. Fish and Wildlife Service
Effectiveness	Ron Goodman, Imperial Oil Resources Ken Keane, U.S. Coast Guard
Decision Making	Michael J. Donohoe, U.S. Coast Guard David Lopez, U.S. Environmental Protection Agency

Finally, the energetic and enthusiastic efforts of the Workshop participants, who, along with the session moderators and Steering Committee members, reviewed these Proceedings, are gratefully acknowledged.

Workshop Proceedings: The Use of Chemical Countermeasure Product Data for Oil Spill Planning and Response

Abstract

On April 4-6, 1995, a Workshop was held in Leesburg, Virginia on how to appropriately interpret and apply chemical countermeasure product aquatic toxicity and effectiveness data. Workshop participants included professionals in environmental effects, effectiveness, response operations, and decision making. Specific questions addressed during the Workshop included: 1) what useful information can be gleaned from existing effectiveness and effects data? 2) with existing data, can responsible judgements be made? 3) what necessary information is absent? 4) what actions can be accomplished now? and 5) what is the best way we can accomplish these actions?

The original intent of the Workshop was to address all chemical countermeasure product classes; however, it was apparent that most information and experience pertained to dispersants and their use. Consequently, most of the recommendations and conclusions were specific to dispersants. Where the characteristics or use of other chemical countermeasure products may be similar to dispersants, then conclusions about dispersants have been broadened to apply to these other countermeasures.

Specific conclusions reached by participants at the Workshop included: 1) the encouragement of multiple applications of dispersants; 2) the acknowledgement of the difficulties of monitoring and the low likelihood that meaningful information from such activities will be available within the short, fast-paced period during spill response; and 3) the identification of a dispersed oil concentration threshold where no adverse ecological effects are expected in open water areas. In addition, participants proposed an outline for a reference document on the implementation of pre-spill planning which focused on dispersants.

1.0 Introduction

The recognized limits of commonly used mechanical countermeasures in recovering spilled oil or combating the effects of oil spilled into the environment have long frustrated the oil spill response community. The question on how to make response more effective is not answered by simply acquiring more of the same (booms, skimmers, and associated support equipment) but in supplementing current tools with additional technologies, including chemical countermeasure products (CCPs) which can be used separately or in tandem with mechanical countermeasures. While dispersants and emulsion breakers have been successfully used for treating oil spills in other parts of the world, use in the United States (U.S.) has been extremely limited.

CCPs offer the potential to reduce the net adverse impacts from oil spilled into the environment when conditions are appropriate. Yet, in some circumstances, U.S. policy and decision makers have been reluctant to request use of CCPs during spills. **This** reluctance has been due to a number of factors, including:

- Fear that the addition of CCPs to spilled oil may increase the potential for environmental stress;
- Uncertainty surrounding the performance of CCPs;
- Lack of understanding and/or familiarity with existing data on either effectiveness or aquatic toxicity for those CCPs on the U.S. Environmental Protection Agency (EPA) National Oil and Hazardous Substances Pollution Contingency Plan (NCP) Product Schedule;
- Over-confidence in the adequacy of mechanical measures;
- Failure to examine and balance the toxicity and effectiveness of CCPs against toxicity and effectiveness of alternative response techniques (mechanical measures, no action, etc.); and
- Fear of making a poor decision. The feeling is widespread that if only more information were available about the effectiveness and ecological impacts of CCPs added to spilled oil versus that of the spilled oil alone, a more defensible decision could be made.

Consequently, opportunities for employing technologies which might improve

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spill response probably have been missed. During the last few years limited use of two CCPs, dispersants and elastomers, has been approved by some Regional Response Teams (RRTs) and Area Committees (ACs), although their actual use during response remains limited.

In an effort to encourage and support planning efforts at RRTs and ACs, representatives from five organizations joined together to organize a Workshop: American Petroleum Institute (API), the U.S. Coast Guard (USCG), Marine Spill Response Corporation (MSRC), EPA, and National Oceanic and Atmospheric Administration (NOAA). The Workshop was held in Leesburg, Virginia on 4-6 April 1995 and included experienced professionals in environmental effects, product effectiveness, response operations and environmental decision making. The underlying theme of the Workshop was that oil spill response in the U.S. must promote the opportunity to use "all the tools in the toolbox." The Workshop Steering Committee and participants agreed that: 1) substantive progress can be made in understanding the use of known toxicity and effectiveness data; and 2) this greater understanding would promote decision making relative to all CCPs in advance of a spill event.

Pre-spill decision making is critical for at least one type of CCP, dispersants, because they are usually most effective in the early phases of a spill. Such use is only possible when sufficient quantities of, and delivery systems for, dispersants are stockpiled in advance.

There are very few stockpiles of CCPs of any kind around the U.S. and it is generally agreed that this situation will not change until pre-spill decisions are made, which authorize their use, based on the judgement of the spiller and/or the On-Scene Coordinator (OSC) at the time of the incident. Immediate, i.e., within a few hours, availability is critical for dispersants and necessitates local stockpiles. The utility of other CCPs is less time critical, hence regional or national stockpiles are appropriate. One significant issue affecting willingness to stockpile such necessary materials and equipment may be the potential for planholders to offset (reduce) mechanical stockpiles as they scale up CCP equipment and expertise.

1.1 Workshop Objective

The purpose of the Workshop was to generate consensus recommendations on how best to interpret and use CCP toxicity and effectiveness data. The goal was to develop a process to foster informed decisions

on the use of CCPs in the U.S. In pursuing this goal, the Effectiveness and Environmental Effects Workgroups laid the groundwork by addressing the following questions in sequence:

- What useful information can be gleaned from the *existing* data?
- With existing data, can responsible judgements be made?
- What necessary information is absent?

Chapters 3 and 4 of this volume reflect their considered answers to each of these questions. Their conclusions provided the framework for the follow-on Decision-Making Workgroup to determine (as summarized in Chapter 5):

- What actions can be accomplished *now*?
- What is the best way we can accomplish these actions?

1.2 Workshop Format and Approach

The Workshop used plenary and concurrent Workgroup sessions. Appendix B provides the agenda for the meeting.

Discussions focused on the pre-spill planning process. During the opening plenary session, participants concluded that on-scene evaluation of existing CCP data to determine use during actual spill response operations was inappropriate, as it would be for any response technique. Response operations do not lend themselves to the slower, deliberative pace of pre-spill planning. Without prior planning for the contingency of using CCPs, it is almost guaranteed that CCP stockpiles and necessary application equipment will not be available.

The conceptual format used to foster discussions during the Workshop was to pose three hypotheses, discussed below, regarding CCP data and their use. Further, the **tradeoff** concept of evaluating anticipated net effects associated with CCP use or non-use decisions during spill response was highlighted to remind participants of the balance in reasoning to be made. Many people, both inside and outside the spill response community, have posed these hypotheses and a determined effort was made to provide reasoned answers to their questions. Those "answers" and discussions of issues and questions beyond the initial hypotheses are summarized in these Proceedings.

1.2.1 Chemical Countermeasure Product Environmental Effects

Existing dispersant toxicity data, consisting of test results from constant exposure conditions and various species and life stages of test organisms, are most useful when relative comparisons are made during pre-spill planning. The most appropriate and common use is to screen dispersants for their relative toxicity to identify the least or most toxic compounds. Little data are currently available for CCPs other than dispersants. A more in-depth discussion of current efforts related to toxicity issues is contained in the papers in Volume II.

Hypothesis: Existing toxicity data are sufficient to support pre-spill planning decisions regarding dispersant use.

Note: The NCP dispersant acute toxicity test uses a conservative, continuous exposure of 96 hours which significantly overestimates short-duration events that are followed by rapid dilution. Such rapid dilution appears to be typical even in the largest spills.

Conceptual tradeoffs: The oil has already been spilled; now what is the most effective response. Can the potential environmental stresses from a spill be reduced by the application of a CCP? Is some level of short-term toxicity acceptable if net long-term effects of the spilled oil are reduced? Does the use of a CCP reduce the environmental impact as compared to other response techniques?

1.2.2 Successful Performance of Chemical Countermeasure Products

The most common use of effectiveness testing is to screen chemicals for their relative effectiveness. Several tests have been developed to determine the effectiveness of dispersants on unweathered oil and EPA recently adopted a new standard effectiveness test for dispersants. However, EPA has not yet adopted standard effectiveness tests for other CCPs. Environment Canada **and** EPA have both done some effectiveness testing on shoreline cleaners. Laboratory test results of CCP effectiveness would be useful to compare relative performances among CCPs for pre-spill planning. A more in-depth discussion of current efforts related to effectiveness issues is contained in the papers in Volume II.

Hypothesis: Existing effectiveness data are sufficient to support pre-spill planning decisions.

Note: Laboratory methods have distinct energy regimes and equipment effects which do not mimic specific field conditions. Dispersant and demulsifier performance can also be influenced (positively or negatively) by differences in salinity and temperature. Further, EPA currently requires a minimum performance of 45 percent “**effective**” using its test protocols for a dispersant to be included on the NCP Product Schedule.

Conceptual tradeoffs: In each oil spill response, is the **tradeoff** between the effects of the response and the effects of the spill (no response) evaluated?

1.2.3 Benefits of Pre-spill Planning

It has long been recognized that it is virtually impossible to recover or mitigate satisfactorily all oil spilled in an incident using mechanical countermeasures alone. Yet, government and industry, in preparing the response and contingency plans mandated by the Oil Pollution Act (OPA) of 1990, relied solely on mechanical countermeasures in calculating how to respond to spill scenarios they might encounter. By relying solely on mechanical countermeasures in pre-spill planning calculations, the response community is accepting a commensurately limited response capability.

Pre-spill planning that includes the potential use of CCPs avoids time-consuming decision making “by committee” during the response. This is especially true when a very limited window of opportunity exists for some CCPs such as dispersants. Pre-spill planning would allow and encourage government, response contractors and the petroleum industry to stockpile appropriate CCPs so that, where approved, they are available for use in a timely manner. A broader discussion of CCP decision-making issues is contained in the papers in Volume II.

Hypothesis: CCPs have a role in spill response.

Note: Any use would be according to Area Contingency Plans (ACPs) and Regional Contingency Plans (RCPs).

Conceptual tradeoffs: Under what circumstances can CCPs be used (alone or in combination with other response measures) to help reduce environmental stresses from spilled

oil (recognizing any inherent toxicity or effectiveness issues)? If CCPs are not used, are we accepting increased risk of environmental stress?

1.3 Use of the Proceedings

These Proceedings present the conclusions reached during the Workshop regarding the appropriate use of toxicity and effectiveness data by decision makers, and other stakeholders, in pre-spill planning. Discussions in the three concurrent Workgroups went beyond the initial hypotheses into a much wider range of CCP effects and application strategies.

These Proceedings provide background and technical review information (including the history and use of CCPs) which should be useful to scientists and managers associated with spill response issues. Hopefully, the document will provide a common starting point for future work.

1.4 Organization of the Proceedings

The Proceedings is divided into two volumes. Volume I contains synopses of the Workshop deliberations and the summary statements from each of the concurrent sessions (environmental effects, effectiveness, and decision making). Volume I also includes background information which describes the classes of CCPs, their chemical behavior, and their response niches. Volume II contains specific issue papers prepared prior to the Workshop as background information for Workshop participants to identify questions for resolution or to act as a catalyst for consensus.

2.0 Background

The Workshop was intended to consider all CCP classes and surface water types. A synopsis of CCP classes is presented below. The surface water types considered included: marine, estuarine, and freshwater. Further, some distinctions were drawn according to the diluting or flushing potential of a waterbody and the nearness to shore (e.g., medium size lake versus large river versus estuary versus open marine waters). It is recognized that the greatest amount of information is available concerning the use of dispersants in open marine waters. However, all CCP classes were examined at least to a limited extent.

2.1 Identification and Characterization of Chemical Countermeasure Products

In 1992-1993, MSRC sponsored a study to examine the potential use of chemical oil spill treating agents during oil spill response (Walker et al. 1993). As part of the study, a list of CCPs and their definitions was developed. The following is excerpted from Walker et al. (1993)¹ and modified to incorporate information on dispersants, which had been excluded from that study. The scheme for categorizing CCPs was based on two factors: 1) the effect the product was designed to achieve; and 2) the mechanism employed for achieving the effect (mechanism for action).

Dispersants are defined as products which cause oil on the water surface to break into small droplets; i.e., to form an oil-in-water dispersion (API 1986). They enhance natural dispersion, presumably making the oil more available for, and accelerating, natural biodegradation. There are no sub-classes of dispersants, they all work by the same mechanism of action. Dispersed oil droplets of <70 µm are not recoverable, nor do they generally re-surface or coalesce (see Background Paper #6 in Volume II of these Proceedings). Chemical dispersants enhance the natural dispersion process and remove the oil from the water surface. This reduces or eliminates the possibility of birds and aquatic mammals contacting surface oil. The dispersed oil enters the water column as small particles (<70 µm), which have a larger surface area than that of the surface slick. This **enlarged** surface area accelerates the rate of dissolution and increases the amount of subsurface exposure to the toxic components of the oil. Since the oil is subsurface, it does not evaporate and thus reduces the amount of vapor in the atmosphere. This reduces the fire hazard and the exposure of responders and the

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public to volatile organic hydrocarbons (VOCs). Dispersed oil will not form emulsions and reduces the amount of oil on the surface that needs to be recovered.

Dispersants alter the adhering property of oil droplets. This helps prevent oil from adhesion to bird feathers, beach **sand/rock** and vegetation (Exxon 1994).

The effectiveness of dispersants is strongly affected by changes in salinity and their performance degrades in brackish and freshwaters. Some dispersants have been designed to be used in freshwater, but they are less effective than those designed for marine waters. Dispersed oil droplets have less buoyancy in freshwater and particle surface changes tend to make droplets more likely to coalesce than in salt water.

Herding agents are defined as products which push or compress oil slicks on the water surface by exerting a higher spreading pressure than the oil. To be an effective herding agent, a product must be insoluble in water and have a high spreading pressure. There are no sub-classes of herding agents; they all have the same mechanism of action. Herding agents can be used to direct the movement of oil on the water surface to produce a thicker oil film and enhance recovery. There is no physical change in the oil; it's simply a thicker film. Water jets used to push oil on the water surface are the mechanical equivalent of herding agents. Unlike herders, water jets can increase emulsification.

Emulsion-treating agents are defined as products which prevent formation of or break water-in-oil emulsions. Emulsion inhibitors prevent the formation of emulsions. Emulsion breakers or de-emulsifying agents break emulsions into discrete phases. The resultant separated oil resembles and exhibits the physical properties of the original spilled oil with some degree of weathering.

Solidifiers are defined as products which mix with and immobilize the oil. One solidifier type mechanically encapsulates the oil forming a rubber-like solid. Another type chemically bonds with the oil as part of a rubber or plastic like polymer solid. A third type is a gelling agent which acts on the oil to form a highly viscous liquid with little mechanical strength. Some of these agents require the application of two or more separate compounds which react with each other and solidify the oil.

Elasticity modifiers are defined as products which impart elasticity to the oil. These products modify the mechanical properties of the oil, causing an effect similar to tiny interlocking springs, which makes the oil more elastic. The treated oil remains a liquid which facilitates recovery by skimmers.

Shoreline-cleaning agents are defined as products which, when applied to oil stranded on the shoreline, increase the ease or efficiency of oil removal by flushing with water. For oil spills affecting the intertidal zone, they **are** applied

during low tide so they have time to work prior to immersion by the rising tide. They are also known as surface washing agents. There are two sub-classes of shoreline-cleaning agents: hydrocarbon solvents and surface-active agents. Hydrocarbon solvents lower the viscosity of the oil by dilution. Surface-active agents contain surfactants and may be tailored so that the released oil floats and is recoverable rather than dispersed.

Two CCPs (shoreline **pre-treatment** agents and oxidizing agents) are not commercially available and are included here for record purposes only. Neither of these is included in the more detailed discussions of specific products appearing later in the Proceedings.

Shoreline pre-treatment agents could be applied to the shoreline prior to the landfall of oil to prevent oil from adhering to the shoreline. There are two sub-classes: film-forming agents and wetting agents. Film-forming agents reduce or prevent oil adherence and penetration by forming a physical barrier or coating on the substrate. Wetting agents affect the oil/water interface and thus help displace the oil from the substrate.

Oxidation agents are defined as products which enhance the photo-oxidative degradation of oil. No sub-classes were identified in this class.

2.2 Response Niches for Chemical Countermeasure Products

A response niche, or the situation for which a countermeasure is best suited, can be characterized in a number of ways, such as by matching the countermeasure with the problem to be remedied; the type of oil with the countermeasure that is most appropriate; and the timing between when the countermeasure needs to be implemented and the logistical requirements for use.

Mechanical countermeasures fill a limited number of response niches and some of those only poorly. This Workshop focused on use of CCPs to fill those niches either not filled or poorly filled by mechanical countermeasures. In addition to categorizing and defining the CCP classes, the MSRC study (Walker *et al.* 1993) recommended preliminary response niches for the various CCP classes. The following is excerpted from Walker *et al.* (1993)¹ and modified to incorporate information on dispersants.

Information regarding the potential benefits associated with using CCPs is tentative **due** to the paucity of laboratory data and information on field use for some agents. This section summarizes only the situations where CCPs offer

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potential benefits, not their practicality; *i.e.*, the logistical problems that could impede their application. It is important to decide in advance whether potential response benefits warrant expending the effort to overcome anticipated logistics and application shortfalls.

Table 2.1 summarizes the potential uses of CCPs during oil spill response. This table identifies specific niches that mechanical countermeasures have been unable to fill and that CCPs may alleviate. This table also indicates the spill conditions under which applying products in that class are likely to be most effective along with anticipated limitations affecting their use.

Table 2.2 illustrates the types of oil that are expected to respond well to treatment by the different classes of CCPs. Rather than identify specific grades of oil and refined products, this table uses a relative scale; *i.e.*, light to heavy, to indicate oil type. In this way, the information presented takes into account the weathering of various types of oil, given that most oils become heavier as they weather.

Table 2.3 depicts the potential niches for CCPs, in relation both to other countermeasures and the stages of response operation, during a major marine oil spill. Although generalized, this table provides a perspective on timing, and gives an example of the relative windows of opportunity for using CCPs, by product class. This table also provides a graphic overview of the interrelationships of all types of countermeasures during the stages of response in which they would probably be employed.

2.2.1 Dispersants

Dispersant use should be considered along with mechanical recovery as part of a first response strategy for an oil spill in order to minimize environmental impacts (National Research Council 1989). The typical scenario is on a spill in the open ocean which is moving towards sensitive shorelines and/or bird, aquatic mammal, and amphibian habitats. Since dispersed oil is not subject to wind action, it remains away from the shoreline as waves naturally disperse, currents dilute and allow biodegradation of the oil at sea. The trade-off is an increased short-term exposure of water column organisms to dispersed oil.

Past spill experience in the U.S. has demonstrated that mechanical techniques have distinct limitations associated with recovery rates (especially for large spills spreading quickly over large areas) and with weather conditions (such as currents above 1 knot and/or wave heights above 1-2 meters). Dispersants are not as limited, and may work very well under a much wider range of weather conditions. Also, aerial application makes it possible to mitigate large, quickly spreading spills, and/or portions of large spills, much more rapidly and entirely

Table 2.1 Summary of Potential Uses of CCPs (modified from Walker et al. 1993)

Situation	Applicable Treating Agent	Anticipated Conditions for Use	Possible Disadvantages
Rapid oil spreading with no control options	Dispersants	Some energy needed to disperse oil	Puts oil into water column where it may negatively impact organisms
	Herding agents	Thin oil; calm water only	Multiple applications may be needed; need to recover oil
	Solidifiers	Requires thorough mixing	Solidified oil may not be recoverable
Oil heading to shoreline	Dispersants	Some energy needed to disperse oil	Puts oil into water column where it may negatively impact organisms
	Herding agents	Thin oil; calm water only	Multiple applications needed; need to recover oil
Oil will form an emulsion	Emulsion inhibitors	Agent must contact unemulsified oil	Agent may not stay with the oil
Oil has formed an emulsion	Emulsion breakers	Agent must contact emulsified oil	May impact other countermeasures; discharge of separated water may be restricted
Light oil difficult to recover/skim	Elasticity modifiers	Most effective on light oils	Critical dose requirements; will leave sticky residue
Oiled shoreline needs cleaning; oil remaining on shoreline difficult to remove	Shoreline cleaning agents	Oil to be recovered; requires flushing	Oil not always recoverable

Table 22 Potential Uses of CCPs by Oil Type (modified from Walker et al. 1993)

Agent	Oil Type/Degree of Weathering		Remarks
	Light	Heavy	
Dispersants			early application; some ocean energy enhances dispersion
Herding			calm water, no wind, no currents thin oil
Emulsion Inhibitor	? 	? 	early application
Emulsion Breaker	? 	? 	open water or in containers
Solidifier			use if easier to handle a solid; tidal equipment an issue; do not overdose
Elasticity Modifier			do not overdose
Shoreline Cleaning			must act within tidal cycle

Most effective
Moderately effective
Least effective/appropriate
Ineffective
Lack of data



Table 2.3 Potential roles of CCPs During Response to a Major Oil Spill (modified from Walker *et al.* 1993)

Stage and Type of Strategy	1 Secure Source	2 Contain/ Protect	3 On-water Response	4 Shoreline Cleanup	5 Disposal*
Incident Start ▶ ...hours... ▶ ..hours/days.. ▶ ...weeks... ▶ ...months...					
Conventional Response Countermeasures (Examples)	Close Valves Patch Pump/Offload	Boom Dike	Skimmers Sorbents Vacuum Trucks	Sorbents Manual Mechanical Equipment	On-site Storage Recycle Landfill
Chemical Treating Agents Countermeasures	Emulsion Treating Agents Solidifiers	Dispersants Emulsion Treating Agents Solidifiers Herding Agents	Dispersants Herding Agents Solidifiers Emulsion Treating Agents Elasticity Modifiers	Shoreline Cleaning Agents Solidifiers	Emulsion Treating Agents Solidifiers
Other Countermeasures		In-situ Burning	In-situ Burning	Bioremediation In-situ Burning	Bioremediation Incineration

* This phase includes both temporary storage of recovered oil/waste and permanent disposal. Temporary storage would begin during stage 3.

than mechanical methods. Because they are applied while the oil is still waterborne, prior to landfall, they are a strategy to be implemented during the early stages of response, specifically stages 2 (**contain/protect**) and 3 (on-water response) (Table 2.3).

Dispersants are applied to the surface of an oil slick and reduce the interfacial tension by about an order of magnitude. This means that wave action can more readily cause the slick to break up into small particles which are readily dispersed into the water column. Dispersants enhance the rate of the natural dispersion process, and thus reduce the time that the slick remains as a coherent slick on the water surface. Dispersants remove oil from the surface in a matter of minutes to hours, where natural dispersion can take days to weeks. The time required for either chemical or natural dispersion is strongly dependent on surface-wave energy.

Dispersants remove oil from the surface and transfer the oil in fine hydrocarbon particles into the near surface volume of the water column. The depth to which the oil penetrates is dependent on the wave energy available locally. The oil in the near-surface water is rapidly dispersed horizontally due to natural processes and thus the concentration of oil in the water decreases rapidly with time.

Dispersants can be used nearshore to minimize oil deposition on the shoreline, thereby avoiding longer term environmental damage due to the oil itself and/or the clean up efforts. Dispersant use would not be recommended, however, in shallow waters with poor circulation, such as in protected bays and inlets. Dispersants may be used on a spill in conjunction with mechanical recovery; they need not be considered an **either/or** option since treated oil which does not disperse would still be recoverable.

Weathering and emulsification of spilled oil at sea can reduce the effectiveness of a dispersant application, even to the extent that it is ineffective. However, recent laboratory and field studies have shown that the window of opportunity for use of dispersants is not necessarily limited by the higher viscosity of emulsions (Lewis and Daling 1995; Lewis *et al.* 1995). Sometimes dispersants have the ability to function as demulsifiers to break viscous emulsions and subsequently disperse the oil. The need to demulsify oil could delay and slow the dispersion process and may require an additional dispersant treatment on the thicker areas of emulsion.

2.2.2 Herding Agents

Herding agents have limited application and have not been well studied. They offer potential benefits in situations where oil is spreading rapidly in

enclosed waters or toward sensitive shoreline environments. They appear to work best on slicks where the oil has spread very thin and the waters are calm with little or no wind. Generally, they appear to work best on light oils, because these oils readily spread to thin layers. However, herding agents may also be effective on heavier oils if incident-specific conditions cause heavier oils to spread in thin slicks. Because they are applied while the oil is still waterborne, prior to landfall, they are a strategy to be implemented during the early stages of response, specifically stages 2 (**contain/protect**) and 3 (on-water response) (Table 2.3).

Herding agents are considered to be useful primarily on nearshore open waters, along seawalls and piers, and near sensitive habitats. Under very limited sea and wind conditions, currently available products could be recommended for use to improve skimmer recovery rates of spreading oil at sea. One of the most likely uses of this product class would be in harbors, for moving slicks trapped under piers and docks (enabling increased recovery of small spills). Herders could also be considered for use to collect oil and prevent slicks from passing over sensitive nearshore habitats, such as **seagrass** beds and coral reef habitats, and to keep slicks away from marshes. Herding agents are not a substitute for booms, but may be used for short-term protection and enhanced recovery where deploying booms could cause damage or be of limited effectiveness. Given their low application rates, acute toxicity of these products may be of concern only under special conditions, such as in very shallow waters with limited flushing rates and high concentrations of early life-stage organisms. Their effectiveness does not appear to be hampered by use in cold water.

2.2.3 Emulsion-Treating Agents

Emulsion-treating agents offer potential for use as a conventional response tool with net environmental benefit. Water-in-oil emulsions may greatly increase the volume of the surface slick and severely hamper the efficiency and effectiveness of skimmers, dispersants, and **in-situ** burning. Emulsion-treating agents may be applied to fresh oil to prevent emulsification or to emulsified oil to separate the oil and water. In either application, these agents serve to reduce surface slick volume and to enhance mechanical, dispersant, and **in-situ** burning applications. The net result is reduced risk of shoreline and wildlife impacts.

Because of the environmental benefit that would be gained by applying them prior to landfall of the oil, the optimal strategy for use is during the early stages of response, specifically stages 1 (secure source), 2 (**contain/protect**), and 3 (on-water response) (Table 2.3) where it would be used to treat recovered

oil/water in skimmers to reduce the volume of temporary storage necessary at sea. A more conventional and less time-critical use would be to inject these agents into storage tanks containing recovered emulsified oil to break the emulsion. This could enable decanting of the water, increased storage capacity, and possibly recycling of the recovered product. This use would occur during stage 5 (disposal).

There are concerns about how oil treated with emulsion-treating agents behaves, particularly as to whether the treated oil is more likely to disperse and how it behaves once oil has stranded or is in contact with birds. The use of emulsion-treating agents where water depths are shallow or mixing somewhat restricted is of concern since little is known about the effects. It should be noted that no emulsion-treating agents are currently on the NCP Product Schedule.

2.2.4 Solidifiers

Solidifiers may offer benefits where oil is rapidly spreading and responders have no other feasible control options. Once applied on the oil, they work as a self-creating barrier to stop the spread of oil, either on water or on land; e.g., in front of storm drains. They also may be useful in preventing penetration of oil into gravel beaches, when used in a shoreline protection mode. They appear to be most effective on light to medium oils. For some products, treated oil may be returned to a liquid state, which would allow for oil to be recovered. Whether on water or on land, solidifiers may enhance the ability to remove spilled oil from the environment. This is a benefit which needs to be further evaluated. These products appear to have potential roles during all the stages of response, although the greatest benefit may be gained by using them during stages 2 (contain/protect) and 3 (on-water response) (Table 2.3), if effective application rates and techniques can be developed.

Recommendations for use of solidifiers during spills of light to heavy oils vary by product sub-class. Solidifiers may be useful for open-water application, although the desirability of having solid, semi-solid, and liquid mixtures on the water surface has yet to be fully evaluated. There may be conditions where solidification could reduce the impacts to marine birds, water-column resources, or benthic habitats, although semi-solid mixtures can stick to fur and feathers. Solidification may be beneficial to treat heavy oil accumulations on the shoreline, particularly where stranded oil could penetrate deeply into the sediments, such as gravel beaches. Solidifier products are not thought to be beneficial for use on tidal flats and wetlands because untreated oil usually does not penetrate these sediments and because of the increased likelihood of trampling of vegetation and mixing of oil deeper into the substrate during

application and retrieval. Site- and spill-specific concerns about the amount of product needed to solidify the oil would have to be considered for each spill situation.

2.2.5 Elasticity Modifiers

Currently, there is only one product identified in this class, Elastol. The principal application is to make light oils more recoverable. It produces visco-elastic properties in oil and is designed to enhance recovery of floating slicks and sheens from the water surface. If over-application occurs, the treated oil can become very sticky, which raises concerns about unrecovered treated oil that subsequently comes ashore or in contact with birds. Because the elasticity modifier is applied to waterborne oil, it would most often be employed during stages 2 (contain/protect) and 3 (on-water response) (Table 2.3).

2.2.6 Shoreline-Cleaning Agents

Shoreline-cleaning agents are likely to be of benefit in enhancing mechanical countermeasures, such as water washing, when oiled shorelines need cleaning and the remaining oil is difficult to remove. Available information indicates that these agents will work well on heavy oils and, depending on the degree of weathering, on lighter grades of oil. They are used during shoreline clean up, stage 4 in Table 2.3.

Shoreline-cleaning agents may be beneficial for use on gravel-dominated beaches and rocky shores. The use of some shoreline-cleaning agents in wetlands may be of limited benefit. The use of shoreline cleaners in heavily oiled wetlands should be considered, particularly where natural removal rates are expected to be very slow.

3.0 Workshop Results: Environmental Effects

The Environmental Effects Workgroup agreed that the use of chemical countermeasures for the purpose of treating a spill of oil is viable and should be addressed in the ACPs. Workgroup participants developed a technical framework to be used by ACs and other pre-spill planners when considering pre-approval of chemical countermeasures. Environmental effects of concern include toxicity (including lethal and sublethal damage to organisms), bioaccumulation and food chain transfer, and tainting of seafood. Most of our current knowledge of effects deals with toxicity of dispersants and dispersed oil.

In general, the most effective available response countermeasures should be used to clean up or remove spilled oil from the sea surface. To make timely decisions regarding the use of any spill response countermeasure, we need to: 1) know how spilled oil will affect the resources at risk; and 2) establish priorities regarding what resources are to be protected and why. The priorities among various resources are based on ecological, human-use, or economic values. The tradeoffs in setting these priorities can lead to response decisions that result in adverse effects to certain resources while protecting higher priority resources. Such decisions are influenced by the rates of recovery for resources at risk or the presence of rare and endangered species. Water column organisms are assigned lower priority due to their relatively rapid rates of recovery. Such decisions also often exclude the reality that the pristine environment is already degraded by the spilled oil. The appropriate comparison to make is the trade-off comparison between dispersed oil and non-dispersed oil; i.e., water column organisms versus surface and shoreline resources at risk.

The technical framework for assessing environmental effects associated with the possible use of CCPs includes the following steps, which are addressed in each of this chapter's subsections:

1. Identify the resources of concern to be protected from oil spills (resource protection).
2. Use existing toxicity data in the planning process by:

Using product application data to calculate an expected environmental concentration for given scenarios; and

- Comparing these exposure concentrations to existing toxicity information, taking into account the mixing and dilution potential

associated with CCPs in given scenarios. This is most applicable for dispersants and emulsion breakers.

3. Establishing a threshold level of concern for CCPs in given scenarios.

Comparison of the results of steps 2 and 3 above would provide ACs with guidelines to decide on the environmental acceptability of using a CCP within their area. The intensity and extent to which these activities are carried out depends to some degree on the size of the spill under consideration. The relative risks of exposure for various resources on the water surface, in the water column, or along shoreline habitats is a function of the spatial and temporal extent of the spill incident. Small spills may not persist long enough or contaminate sufficient quantity of habitat to warrant **tradeoff** decisions. The larger the spill, the more serious the consequences of exposure for any resource, and the more serious the basis of any response decision to use or not use CCPs will become. The discussions during this Workshop tended to focus on large spill scenarios, but recommendations do apply to spills of all sizes.

A considerable amount of environmental fate and toxicity data are available for a wide variety of marine species and sensitive life stages in the published literature and are relevant to assessing potential environmental effects of dispersed oil. Fate and toxicity data must be taken together to characterize relevant exposure-response relationships for estimating ecological effects. However, the Workgroup agreed that knowledge of specific laboratory toxicity data are not normally necessary to make determinations on chemical countermeasures use. Field data are essentially never available; decisions can be based on the interpretation of general fate and distribution information. Several schemes for relating laboratory and field data have been considered. The Workgroup agreed that the part per million-hour (**ppm-hr**) measure of exposure is a reasonable basis to estimate acutely toxic effects for aquatic organisms. Not all data are of sufficient technical quality and reported test methods do not always contain sufficient detail to assess consequences of response decisions.

The Environmental Effects Workgroup participants developed criteria for evaluating these data and their usefulness. The participants felt that historical data are sufficient to support some conservative statements which could set bounds for expected environmental effects, based on worst case scenarios. Without considerations for rare and endangered species or other economic effects such as tainting of consumable resources, the consensus from this Workgroup provides a basis for planning response options or ranking anticipated consequences from the use of chemical countermeasures.

3.1 Resource Protection—Legislation, Regulations, and Concepts

The Ecological Effects Workgroup considered the potential effects from CCP use beyond just aquatic toxicity. In 1990, the 101st Congress passed OPA which established limitations on liability for injuries resulting from oil pollution, mandated specific activities for spill response, established requirements for pre-spill planning, and put a new emphasis on natural resources. Section 1011 of OPA specifies that affected trustees are to be consulted on the appropriate actions to be taken during any discharge of oil. Section 4201(b), also called for the amendment of the NCP, [Section 311(d) of the Federal Water Pollution Control Act], to reflect the emphasis on pre-spill planning and natural resource concerns, among others. The amendments to the NCP require that ACs be established to plan for potential spills and their effects on natural resources. The ACs are to develop ACPs. One component of the ACPs is the establishment of a protocol to "expedite decisions for the use of dispersants and other mitigation substances and devices." The expediency of the decision process to use dispersants involves "pre-planning" for use within a given set of criteria established by each AC.

For the ACs to make decisions in advance of a spill, specific information should be available concerning weathering characteristics of the spilled oil and the resources that are potentially at risk for oil-induced injuries. Consideration should be given to the types of resources in the area and to the appropriate treatment that would result in the most benefit to the response and the natural resources. Each AC will have its own issues of greatest concern which will probably drive many of the decisions made regarding the use of a CCP. The USCG and NOAA developed "The Mechanical Protection Guidelines" (Michel *et al.* 1994) as a template for making decisions on the type of mechanical protection for different habitats. Although this manual is for mechanical protection only, the framework used in the suggested decision-making process can be utilized for pre-spill planning and pre-approval of CCPs.

The main objectives for AC consideration in protecting natural resources may include (Michel *et al.* 1994):

- Identification and prioritization of sensitive natural resources,
- Identification of the potential types of CCPs to be used in these areas,
- Guidance on CCP use strategies in identified areas, and

Establishment of monitoring guidelines in the event of CCP use in identified areas.

Sensitive resources are designated as such because they are of environmental, economic, or cultural importance. They may be contaminated by a discharge, and that contamination may have a detrimental effect. There are three main categories that deserve consideration for planning and identifying sensitive resources. They include:

- Habitats,

Fish and wildlife resources, and
- Human-use resources.

Prioritizing sensitive resources is crucial to executing successful early response actions to protect the resources. The **ACs** will have their own set of factors used to evaluate and determine the relative priority for the resources of concern.

Additional guidance for protecting sensitive resources is specified in the NCP, Section 300.210(c)(4), the Fish and Wildlife and Sensitive Environments Plan. This Plan delineates a framework which should be incorporated into pre-spill planning processes in order to achieve "...the immediate and effective protection, rescue, and rehabilitation of, and minimization of risk of damage to, fish and wildlife resources and their habitat that are harmed or that may be jeopardized by a discharge." To attain consistent and compatible approaches for the identification process, the Fish and Wildlife and Sensitive Environments Plan is intended for use by the **ACs** in the development of the **ACPs**. The nine points identified for consideration during the pre-spill planning process are:

- Identify and establish priorities for protection of fish and wildlife resources and habitats, and other sensitive areas requiring protection from any direct or indirect effects from discharges that may occur;
- Provide a mechanism for use during a spill response for timely identification of protection priorities of those fish and wildlife resources and habitats and sensitive environmental areas that may be threatened or injured by a discharge;
- Identify potential environmental effects on fish and wildlife, their

habitat, and other sensitive environments resulting from removal actions or countermeasures, including the option of no removal;

- Provide for pre-approval for application of specific countermeasures or removal actions that, if expeditiously applied, will minimize adverse spill-induced impacts to fish and wildlife resources, their habitat, **and** other sensitive environments;
- Provide monitoring **plan(s)** to evaluate the effectiveness of response activities in protecting fish and wildlife, their habitats, and sensitive environments;
- Identify and plan for the acquisition and utilization of necessary response capabilities for protection, rescue, and rehabilitation of fish **and** wildlife resources **and** habitat;
- Identify appropriate federal and state agency contacts and alternates responsible for coordination of fish and wildlife rescue and rehabilitation and protection of sensitive environments;
- Identify and secure the means for providing, if needed, the minimum required Occupational Safety and Health Administration (OSHA) and EPA training for volunteers, including those who assist with injured wildlife; and
- Define the requirements for evaluating the compatibility between this annex and non-federal response plans (including those of vessels, facilities, and pipelines) on issues affecting fish and wildlife, their habitats, and sensitive environments.

Additional guidance clarifying the types of information necessary to identify and establish priorities for the sensitive resources can be found in the NOAA document entitled "Guidance for Facility and Vessel Response Plans Fish and Wildlife and Sensitive Environments", Federal Register Notice of March 29, 1994 (vol. 59, no. 60). This guidance provides basic environmental materials for use in the development of response plans for vessels and facilities. The overall concept is consistent with that for ACP development and can be followed when developing pre-approval plans for use of CCPs. Subpart J of the NCP, Use of Dispersants and other Chemicals, stipulates that "...ACPs shall, as appropriate, include applicable pre-authorization plans and address the specific contexts in

which such products should and should not be used." It also emphasizes that if the RRT representatives and the Department of Commerce (DOC) and Department of the Interior (DOI) natural resource trustees approve in advance the use of certain products delineated in the pre-authorized plan, the OSC can authorize the use of the specific products without obtaining additional concurrences.

The process of approval for emergency use and pre-approval includes consultation with natural resource trustees. It is vital that this consultation be appropriately utilized. The trustees are required to evaluate the impacts that may result from both the use and non-use of CCPs. Whatever the decision, supporting data and information should be available to maintain records for future evaluations, potential questions, and defense of the actions taken (or not taken). It is highly recommended that monitoring guidelines be established as part of the ACPs, so that in the event of the use of CCPs, the proper actions can be "immediately" taken. If the natural resource trustees desire to have effects monitoring as part of the CCP pre-approval, then a set protocol should be developed. These should be realistic in terms of time and equipment required. Nevertheless, while monitoring is important and should be an elemental part of CCP use, the lack of such a protocol or the inability to follow through with an established protocol should not impede the OSC's ability to take appropriate removal actions during an oil discharge.

The health and marketability of fish and shellfish stocks are always a concern during discharges of oil, especially when the use of dispersants in a particular area are considered. Dispersants may increase the potential for tainting of fish and shellfish resources by increasing the concentration of oil in the water column. Very little information is available on this effect. Walker and Field (1991) observed that during a large spill the fishing and seafood industry can be adversely affected, both by perceived and real effects. They concluded that more information is needed to appropriately dispense with some concerns, including some laboratory testing to determine if dispersed oil taints the flesh of commercial aquatic species any differently than undispersed oil. More research is also needed in areas that have commercial stocks or recreational fisheries, regarding potential injuries to those fisheries resulting from not using a CCP.

In 1993, the Joint Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP) in its report "Impact of oil and related chemicals on the marine environment" stated they found no published evidence of the effect of dispersants on tainting in fish. However, they did conclude that because dispersants do not alter uptake or toxicity, dispersant use is not likely to affect tainting. They also reported finding no studies on dispersed oil contacting fishing gear. However, they suggested that it is reasonable to presume that because

dispersed oil is less adherent to surfaces, then fouling of fishing gear, and nets and floats at aquaculture facilities, would be mitigated by application of dispersants to an oil slick (GESAMP 1993).

According to Moller *et al.* (1989), numerous laboratory studies have examined the effects of dispersants and dispersed oil on fisheries and mariculture and not found any conclusive evidence that shows any toxicity in field investigations. However, the report did find that organisms in confined areas are at risk from tainting. While biological processes may not show an effect from the dispersed oil, the fact is that low concentrations can cause an oily **taste/odor** in the flesh of the organism. Filter-feeding organisms, such as shellfish, and zooplankton (Conover 1970) can readily ingest the minute droplets of dispersed oil. Also, organisms that have a high fat content may have a greater tendency to accumulate lipophilic compounds in their systems. Therefore, Moller *et al.* recommends not using dispersants close to aquaculture facilities and that any instance of a discharge of oil in the vicinity of an aquaculture facility should be taken seriously, since even the smallest amounts might cause a decrease in the "market confidence" for an extended period of time.

3.2 Application of Available Toxicity Data

The Ecological Effects Workgroup focused most of their efforts on dispersant toxicity data since the most information exists for this class of CCP.

3.2.1 Evaluation and Utilization of Toxicity Data

Toxicity data have two major uses for the oil spill response community. The first is to screen candidate CCPs. The second is to estimate the potential for ecological effects from using a CCP in the field. In the first instance, standard toxicity data can be used to rank chemicals in order of their desirability, provided that the test conditions and the species used are appropriate and equivalent. With respect to the second issue, decision makers (and resource managers) prefer to have data on local organisms and communities under circumstances similar to that expected during a spill response. However, that information is essentially never available, and will never be available for all possible conditions, so decisions must be based on interpreting other kinds of information for application to the situation at the spill. Types of relevant data include studies or observations at other spills, controlled ecological studies on oil spills or oil spill countermeasures effects (either in the environment or in the laboratory), and laboratory toxicity data. Laboratory toxicity data are most common and are routinely introduced for consideration when questions are raised about potential

environmental effects of oil, or chemical oil spill countermeasures.

There are several considerations associated with the use of laboratory toxicity data, which relate to the quality of the data as well as extrapolation into real-world situations. These are:

- The appropriate application of laboratory data in the field;
- Determination of effects thresholds from existing data;
- Quality and reliability of available data;
- The use of acute versus chronic test data; and
- Species to species comparisons.

The following discussion summarizes the conclusions of the Workshop participants on these issues relative to CCPs that cause oil to move into the water column; i.e., dispersants. A background paper (Paper #2) offering a more in-depth discussion of these issues, along with the references, is included in Volume II.

Most available toxicity data are not appropriate for direct application to circumstances in the field. The standard acute toxicity test, which uses a continuous exposure for 96 hours (sometimes less) is a very poor estimator of episodic, short duration events which are followed by rapid dilution. Such episodic events are typical for even relatively large spills in open waters and are especially true for chemically dispersed oils. Based on the rapid dilution observed in the few field studies available, which show undetectable or background levels within several hours after application of a dispersant, static 96-hour tests would over-estimate oceanic exposures by more than 100-fold. In the case of the wreck of the MV *Braer*, total hydrocarbon levels in the water column near the wreck were less than 10 ppm within several days. The *Braer* had grounded on the coast of the Shetland Islands in January 1993. The entire cargo of 85,000 tonnes (approximately 25,000,000 gallons) of Gulfaks crude naturally dispersed in nearshore waters. The use of data from acute 96-hour tests is rationalized by the fact that it is a conservative (overprotective) estimate of real-world exposure. In most cases, proponents of this approach do not realize how large this over-estimation of exposure time may be. They often fail to appreciate the consequences of concluding that there is an acute toxicity problem in using CCPs when none, or an insignificant problem, exists.

The Ecological Effects Workgroup discussed the findings from toxicity tests

and field data. They concluded that: in field situations, available data suggest that exposures to concentrations of more than 10 ppm of dispersed oil are unlikely, except within ten meters (depth) of the slick, and that concentrations, even within one meter depth of the slick rarely exceed 100 ppm. Total hydrocarbon concentrations under naturally (physically) dispersed oil slicks are even less of a concern.

There are a number of toxicological end points reported in the literature, but by far the most common is the LC₅₀. Other endpoints, such as the No Observed Effect Concentration or the Lowest Observed Effect Concentration are conceptually attractive to ecologists, but rarely reported. The Environmental Effects Workgroup concluded that the use of LC₅₀ data, expressed as part per million-hour (ppm-hr), is the best currently available approach. The effects of concentration and duration are considered to be direct multipliers in the concept of the ppm-hour. Intuitively, there are limits beyond which the concept does not apply, but it appears valid for time periods of 1 hour to 4 days based on some experimental evidence. Several toxicity testing programs are currently investigating the use of spiked or pulse exposures of dispersed oil with sensitive aquatic species. Results are expected to provide a stronger scientific basis for establishing toxic threshold exposures for aquatic life affected by oil spills.

Much of the available experimental data on the toxicity of oil and/or dispersed oil have been generated in experiments with notable analytical and/or design flaws. Experimental data based on realistic exposure duration and exposure concentrations which bracket those expected in the field are preferred. Decisions should not be based on data from toxicity tests using nominal concentrations of hydrocarbon exposure because of wide variations in experimental procedures and the inherent difficulties in mixing oil and water. This data problem is discussed in detail by the National Research Council (1989). Care must be used even when analytical hydrocarbon data are available because of the variety of methods for calculating total hydrocarbon concentrations. Other factors, e.g., whether the containers were open or closed, agitation, and whether the tests were static or not, can significantly affect the results. These factors can be adjusted for if sufficient analytical hydrocarbon data are available at intervals during the experiment.

Toxicity tests, and the resulting data, are often referred to as being acute or chronic. Both terms reflect exposure times and refer to lethal or sub-lethal effects. Most acute lethal responses occur within a short time period, so 96 hours is used as a standard exposure time. Typically, the concentration calculated to be lethal to 50% of the test population is reported, as these conventions provide for the greatest test accuracy and repeatability (Rand and Petrocelli 1985). Chronic tests can be used to assess effects of a toxicant over multiple life stages of an animal.

These tests often evaluate growth rates and reproductive capacity for test populations. Chronic effects do not appear to be associated with infrequent, short, low-level exposures to spilled oil or dispersed oil, although they are well documented for cases of long-term hydrocarbon pollution, such as in contaminated harbors or near wastewater outfalls. While the Workgroup participants support the collection of additional chronic toxicity data based on realistic exposure scenarios, chronic effects are not considered to be a major concern for open water, marine events.

There are standard test species commonly used for toxicity testing. These include both freshwater and saltwater animals that live either in the water column, on the bottom surface, or within the sediment layer. Some of these species are distributed widely within geographic regions of the U.S., while others tend to be localized. Common marine species used in the U.S. to address toxicity issues for oil spills and response chemical use in marine habitats include:

Acartia tonsa (copepod)
Artemia salina (brine shrimp)
Crassostrea virginica and *C. gigas* (oyster) (embryos or larvae)
Mysidopsis bahia (mysid)
Fundulus heteroclitus (salt marsh killifish)
Cyprinodon variegatus (sheepshead minnow)
Menidia beryllina and *M. menidia* (inland and Atlantic silversides)
Atherinops affinis (topsmelt)

There is an even larger number of freshwater test species commonly used in toxicity testing, although effects of petroleum products and CCPs on freshwater biota have been less studied relative to marine species. Among the most common freshwater species used in toxicity tests are:

Daphnia magna (Water flea)
Ceriodaphnia dubia (Daphnid)
Pimephales promelas (Fathead minnow)
Onchorhynchus mykiss (Rainbow trout)

It is not intuitively obvious how to apply data collected on one species to a situation involving another. There is a tendency on the part of regulators to want to develop their own, unique set of test organisms for use in their geographic region. While this has some obvious attractions, it is neither practical nor necessary to collect laboratory data on all species which might be of concern. A common practice is to use sensitive species (or sensitive life stages) toxicity

data as a basis for decision making, on the assumption that it provides protection for less sensitive organisms. The difficulty is in determining that the test species is in fact "sensitive" enough to fulfill its assigned function. Another option is the use of statistical formulas to estimate confidence intervals around available data sets containing toxicity information for a number of species. The formulas can be used to define conservative criteria to protect the majority of exposed species. This approach has been used in developing water quality regulations and could be used to set exposure criteria for marine organisms.

It should be remembered that toxicity tests are not intended to be conducted during response to a spill. Toxicity data can be a useful tool for pre-spill planning for CCP use or for improving our understanding of the relative effects from oil alone in surface waters. The choice of species for assessing a particular toxicant's impact in a specific area must be considered carefully. In general, the term "sensitive species" can refer to biological, ecological, or commercial sensitivity. A biologically sensitive animal is one that displays harmful effects from low concentrations of a toxicant relative to other species. In general, early stages of development are considered more sensitive than later stages. Extrapolation of laboratory test data to make decisions that will be protective of site-specific resources can be made with more confidence if the species fulfills one or more of these "sensitive" roles. Acute toxicity tests, because of their short duration, generally only expose the animal during one lifestage. It is important to know what lifestage was used when interpreting toxicity data.

The Workgroup participants concluded that the use of appropriate sensitive species data; e.g., abalone larval and juvenile crustacea, provides sufficient protection. For example, the data for *F. heteroclitus* and *A. salina* are usually inappropriate for interpretation of field effects because of their known hardiness, but can be used to estimate relative toxicity of CCPs. The other commonly used test species are appropriate. The collection of additional data for other species in a variety of taxonomic groups is desirable, but not critical for dispersant use decisions in open water situations. Additional data on a variety of near-shore or estuarine species, or adequate surrogates, would be useful in determining whether to extend the areas where dispersants can be considered.

3.2.2 Treated Oil Fate and Disposition–Source of Uncertainty

Many of the conservative assumptions used for estimating potential water column concentrations are compounded during the calculation process. Unrealistically high estimates of exposure result. Dispersants do not act instantaneously to move oil into the water column. Rather, portions of the oil

are dispersed continuously over time so that water column concentrations never approach the theoretical extremes.

Other factors affect the rate and extent of oil concentrations attained under a dispersed slick. The effectiveness of the dispersant and the solubility of the oil can vary dramatically depending on the physiochemical properties of the spilled petroleum product, its rate of weathering, the time lapsed between release and dispersant application. In addition, the mixing action and dilution by waves and currents do not act with uniform force throughout the upper water column, leading to variable dispersed oil concentrations in vertical and lateral dimensions. Depending on the predominance of the various physical components that lead to mixing and dilution, exposure concentrations in the field may vary significantly, even in the immediate area of the spill.

There is a considerable difference between the expected concentrations of dispersed oil in the water column beneath an oil slick and the reported exposure concentrations for water column organisms residing in the immediate area of an oil slick (National Research Council 1989, Lunel 1994). Field monitoring data suggest that worst case exposures rarely materialize, despite the masses of oil which are quickly moved from the water surface into the water column following dispersant applications. This discrepancy leads to a high degree of uncertainty in: 1) estimating field exposures of marine biota during oil spills; and 2) expectations as to potential toxicity to water column organisms as a consequence of that response.

In the absence of accurate and reliable field data, considerations for approval and use of CCPs tend to default to conservative protection guidelines for broad and general decision making. During actual incidents, this degree of conservatism may prohibit the use of effective and safe response options. Better linkages between laboratory test data, fate and exposure modeling, and empirical data from experimental field trials are being developed in an effort to reduce the uncertainty, and thus conservatism that supports decisions outlining appropriate uses of CCPs.

3.3 Establishment of Threshold Level of Concern

Here again, the Ecological Effects Workgroup focused on dispersants, the class of **CCP** for which most data exist. Due to the uncertainty of environmental concentrations of dispersed oil that might be encountered following dispersant application to an oil slick, the Environmental Effects Workgroup developed a conservative, worst-case estimate of water column concentrations using simple dilution estimates. This approach was used to set the bounds for expected environmental effects, based on acute toxicity data from laboratory and field

testing. The Workgroup recognized that water column organisms may experience adverse effects as part of the tradeoffs in establishing response priorities, but the extent of these effects can be minimized by the rates of dilution and mixing common to open waters.

Reasonable judgements regarding threshold levels of concern for dispersants are expressed in the seven points below:

- ***The available acute toxicological data support the conclusions that, at water column concentrations at or below 10 ppm dispersed oil for 2-4 hour exposure duration, adverse ecological effects are not expected.***

The published literature (see references cited in Paper #2 of Volume II of these Proceedings) contains several approaches which have been used to synthesize data from numerous laboratory toxicity tests and relate them to what is known from field observations of environmental exposures and effects. Data from standard, acute toxicity tests typically generate LC₅₀ estimates for 24 to 96 hour exposure durations. Field exposures in open water habitats often are dynamic, transient, and have little relevance to standard toxicity test conditions. Few laboratory toxicity tests have been conducted using short-term, dynamic exposure regimes, although this is an area of increasing research focus. By using data extrapolations and integrative concepts such as ppm-hr exposures, several synthesis documents and reviews have attempted to define exposure conditions which define a threshold where ecological effects begin to occur. Our recommendation that 10 ppm concentrations for 2 to 4 hour durations be used as a no-effect benchmark is a consensus assessment from conservative interpretation of these data. For many environments, exposure at higher concentrations or longer durations may yield no effect as well. The Workgroup recommendation is based on extrapolations to a broad range of environmental settings, and therefore is somewhat conservative in nature.

- ***For planning purposes, it is unlikely that exposure concentrations of 10 ppm dispersed oil, and 2-4 hour duration, will be exceeded in open marine waters at depths below the top 10 meters of the water column.***

This calculation assumes that, for a 0.1 mm slick at an application rate of <1:15, 100% of the surface oil is driven into the water column and is

uniformly distributed (see Paper #2 of Volume II of the Proceedings). The continuous mixing and dilution capabilities of open water can lead to this uniformity and are sufficient to reduce exposure concentrations to less than 10 ppm within 2-4 hours. The 0.1 mm slick thickness assumption may not be too conservative, but other factors that counter this estimate are discussed below. The 0.1 mm was chosen as an average thickness for spill response based on the expected delays in response staging and logistics.

- ***For the scenario given above, dispersant use decisions can be made independent of site-specific species data where threatened or endangered species are not present.***

Because the historical data set on toxicity of oil to aquatic organisms incorporates a wide diversity of species, the statement of no effects at exposures of 10 ppm dispersed oil for 2 to 4 hours can be applied to all areas where threatened and endangered species are not present. The range of sensitivities among species present at any particular site will be similar to the range of species sensitivities represented in the historical database. Therefore, it is not necessary to generate new, site-specific information before dispersant approval decisions can be made. As discussed in more detail below, when local conditions result in exposure conditions which might exceed 10 ppm dispersed oil or cause the duration to exist beyond 2 to 4 hours, it may be necessary to review the historical toxicity information to determine if sufficient information exists to make an assessment as to the potential effects on local species.

- ***In general, evaporation, lateral mixing, and other physical factors should cause concentrations to be less than the 10 ppm threshold limit of concern and exposure durations to be shorter than 2-4 hours. Also, the toxicity of spilled products decreases rapidly as the more toxic aromatic light ends evaporate early in a spill. Dispersants tend to work over a period of time, so 100% dispersion is not instantaneous.***

The 10 ppm water column concentration, delineating a threshold between ecological effects and no observed ecological effects, is made more conservative by the dilution factors associated with these physical influences. The evaporation of oil from the slick reduces the slick thickness, to less than the 0.1 mm example, thereby reducing the

volume that enters the water column following dispersant application. The amount of evaporation is related to the content of the volatile hydrocarbons in the oil (the greater the composition of volatile hydrocarbons the greater the evaporation). The evaporation rate is influenced by ambient water and air temperature and wind speed. The volatilization of the aromatic hydrocarbons also increases with temperature. Higher temperatures lower oil viscosity and increase the ability of the dispersant to penetrate to the **oil/water** interface and work more efficiently in dispersing the oil into the water column.

Both treated and untreated oil are naturally dispersed by lateral movement and agitation created by wind and wave action. Wave action, a result of wind, adds high energy agitation to the **oil/water/dispersant** interface and has the potential to thoroughly break-up and **dilute/disperse** the surface oil at an increased rate. In addition to generating waves, wind also creates a surface current which moves horizontally and tends to keep maximum oil concentrations lower.

- ***For dispersant use in waters other than those described above, site-specific resources should be considered within the context of existing data.***

For spills into open marine waters less than 10 meters in depth, **site-specific resources/habitats** and **environmental/physical** conditions should be considered. For shallow water marine habitats (e.g., seagrass beds, corals) decision **makers/resource** trustees should examine the tradeoffs between the effects of untreated oil slicks and chemically dispersed oil. Although untreated oil may undergo natural dispersion, concentrations in the water column will not approach the likely levels of most chemically dispersed oil. This comparison of tradeoffs is necessary because the fate and transport of chemically dispersed oil can be dramatically different in affecting different habitats. Environmental and physical conditions may have a greater role in the fate and transport of chemically dispersed oil in shallow waters because less volume is available for dilution, relative to deep water, and the physical mixing process may increase exposure concentrations. Therefore, it must be determined which habitat (submerged or shoreline) has the priority for protection to determine if dispersants are appropriate. In **marine/estuarine** areas of limited devth or in

freshwater systems, the same assessment of ecological tradeoffs must be implemented. Priority protection assigned to shoreline or wetland habitats may justify use of dispersants in shallow marine or freshwater habitats. These site-specific assessments can be best implemented following pre-approval deliberations for various sites or scenarios.

- ***It is not likely, nor has it been demonstrated, that short-term exposures to petroleum hydrocarbons will lead to chronic toxicity effects, based on current data. Only long-term, continuous exposures have been shown to result in chronic effects.***

Toxicity is a function of contaminant concentration and duration of exposure. During an oil spill dispersant application operation, exposures to dispersed oil are expected to be of short duration (i.e., a few hours) at sublethal levels. While such conditions could result in a temporary depression of physiological functions in some organisms, the existing data indicate that these levels are unlikely to result in chronic effects. Likewise, aquatic organisms have the ability to metabolize and/or depurate petroleum hydrocarbons. The existing data have shown that complete depuration occurs when the source of the contamination is removed. It is unlikely that significant amounts of petroleum hydrocarbons will be accumulated by aquatic organisms during a dispersant application because of the short duration and low concentration expected in the water column. Under such conditions, any accumulated petroleum hydrocarbons should be rapidly depurated. As a result, no long-term effects on the exposed animals are expected.

- ***Within the normal range of operating dosages, ecological effects are due to the dispersed oil. The dispersant alone is unlikely to contribute significantly to adverse effects, even in multiple applications.***

The concern for ecological effects lies with the dispersed oil, not with the dispersant. Even when multiple dispersant applications are made to the same oil slick, it is unlikely that the water column concentrations would exceed adverse effects levels of the dispersant and dispersed oil. Given that adverse ecological effect stems from the dispersed oil, and the 10 ppm water column concentration is based on 100% dispersion of the surface slick, the additive effect of multiple dispersant application is not likely to significantly exceed the 10 ppm threshold. The reason for this is that once a dispersant is applied to a

surface slick, the chemical is bound within the dispersed oil plume, and is therefore no more bioavailable than the dispersed oil itself. The need for multiple applications assumes that previous applications were not 100% effective (i.e., that at the decision point to make a second application, 100% dispersion has not been accomplished) and therefore the 10 ppm concentration has not been reached. According to the NCP, the usual planning ratio for dispersant effectiveness is 1:10. Therefore, if application dosages approach a 1:5 ratio, serious consideration should be given to the effectiveness of the operation. Dosages in excess of a 1:5 ratio should not be considered unless potential ecological effects have been weighed.

4.0 Workshop Results: Effectiveness

Historically, during emergency response to oil spills in the coastal zone of the U.S., RRTs tasked with deciding whether or not to approve the use of dispersants, in response to a request from an OSC, have been unable to complete the decision-making process within the time frame considered necessary for such products to be useful. Exceptions to this general statement are acknowledged, but experience overwhelmingly supports this notion. One of the major stumbling blocks to a rapid decision has been the uncertainty concerning the performance (effectiveness) of CCPs in general and for incident-specific conditions.

Pre-authorization documents developed by ACs, and approved by RRTs, should expedite the process of considering CCPs during an environmental emergency. Such documents would: 1) eliminate the need to deliberate aspects of CCPs in those areas identified as unacceptable for chemically enhanced response operations; and 2) permit responders to expeditiously employ the agents in areas approved for CCP use.

In an attempt to facilitate pre-authorization development, the Effectiveness Workgroup participants identified the issues of pre-spill approval for all eight classes of the CCPs. The participants analyzed what useful effectiveness information exists for these classes of products and considered whether or not that information was sufficient to support a decision regarding use of a CCP. As part of this analysis, Workgroup participants discussed existing CCP test protocols, procedures, and data in relation to effectiveness.

4.1 Definitions of Effectiveness

As defined by the Workgroup participants, the CCP effectiveness is the measure of how well the CCPs perform what they were intended to do, under real-world conditions. Effectiveness, in this context, is not an absolute standard (quantitative), but a relative measurement. It is an observable change in the conditions on-scene resulting from a CCP application. Laboratory effectiveness tests are designed to allow a **comparison/relative** ranking of CCPs intended for the same purpose; e.g., comparison of one dispersant to another. Therefore, the "effectiveness" values measured in laboratory tests are not indicative of field performance; that same result should not be expected in the natural environment. The EPA has indicated that, at least in the case of dispersants, the testing protocols were not developed with the intent of replicating possible real-world situations (Federal Register Vol. 59 No. 178, Sept. 15, 1994). Guidance on effectiveness determination needs to clearly signal that numbers and percentages are of no real value in estimating performance in the field. They allow

discrimination on the general acceptability of the product, but do not define the specific expectation in an operational situation. Consequently, the decision on whether to approve or deny a responder's request to use a CCP should not be encumbered by the issues of comparative laboratory test data as measures of field effectiveness. If a dispersant is on the NCP Product List, then it should be deemed "effective" for purposes of deciding whether or not to use. The decision to employ a CCP should be made primarily on the basis of tradeoffs; that is, comparing the anticipated merits of using CCPs to lessen the impact of a spill versus the impacts associated with not using them.

For a dispersant product to be listed in the NCP, it must undergo effectiveness testing prescribed by the EPA (as stated in Federal Register Vol. 59 No. 178, Sept. 15, 1994). Although various dispersant products which have been listed on the NCP Product Schedule may perform better or worse in laboratory tests in relation to other similar products on the Schedule, all tested dispersant products listed must be considered "effective" in their own right; that is, they function effectively as intended. EPA does not require effectiveness testing for CCPs other than dispersants. The issue papers in Volume II describe current effectiveness testing issues in detail. Walker et al. (1993) also discusses effectiveness criteria and available effectiveness data for CCPs other than dispersants.

4.2 Application and Effectiveness Testing of Six Classes of Chemical Countermeasure Products

CCPs have been divided into 8 classes: dispersants, herding agents, emulsion-treating agents, solidifiers, elasticity modifiers, shoreline-cleaning agents, shoreline pre-treatment agents, and oxidation agents. The first six of these (those that are commercially available) were considered to determine whether or not sufficient data and information exists to support a decision for use. Where data and information was considered inadequate, participants attempted to identify the data requirements. Additionally, methods of measuring successful application of a CCP were summarized. A compilation of these issues and participants' conclusions are presented in Table 4.1. Please note that these agents were analyzed for marine, estuary and freshwater applications.

4.2.1 Dispersants

When a dispersant passes the effectiveness test, described in the 1994 revision to the NCP (Federal Register Vol. 59 No. 178, **Sept. 15, 1994**), it will be listed on the NCP Product Schedule. Once listed, a dispersant should be

Table 4.1 Summary of the Effectiveness Issues Concerning 6 Classes of CCPs

Agent	Sufficient Data Available for Use Decision?	What's Missing?	What Method Exists to Determine Success?
Dispersants	Yes	Field data	Visual and analytical tests (water samples)
Herding Agents ¹	1. Have been used in marshes and under piers 2. Limited sales in last year 3. No known data except surface tension - not enough to make a decision	1. Clear need for product not defined (can use fire hose instead)	Visual
Emulsion Treating Agents ¹	1. Open environment a) Not sufficient data for decision b) U.K. has conducted field tests 2. Closed environment a) Yes, sufficient for use but not for toxicity b) Is used widely (oil platforms, etc.)	1. Open environment a) Lab and field data b) No accepted standard effectiveness test	Analytical tests (water samples)
Solidifiers ¹	1. Not sufficient data to decide to use in an open environment	1. No effectiveness test 2. Very limited need for product identified in open environments	Visual
Elasticity Modifiers ¹	1. Sufficient for limited application in specific environment	1. Lab and field data	Visual Small scale test
Shoreline Cleaners ¹	1. Sufficient data to decide 2. Published data	1. Standard test (in development)	Visual Small scale test

No effectiveness testing required listing.

considered effective and the OSCs and RRTs should use the NCP Product Schedule as a baseline for comparing suitability of those products for treatment of oil types found in their region. After deliberation, the Effectiveness Workgroup participants agreed that after passing the NCP effectiveness criterion, trial applications to check performance were redundant. Consequently, trial applications during a spill are neither necessary nor desirable. This conclusion is intended to reduce the incident-specific decision making and improve the chances of using a dispersant during its window of opportunity.

Based on recent United Kingdom (U.K.) and Norway field tests, it may be difficult, in some situations, to measure or observe effectiveness of dispersants (Lunel 1995; Brandvik *et al.* 1995; Lunel *et al.* 1995). Changes to the slick may not be noticeable or measurable when dispersants are first applied to an oil spill, particularly if it has formed an emulsion. Field tests in Norway (Lewis and Daling 1995; Lewis *et al.* 1995) showed that dispersants can be effective on emulsions, since the dispersant can act initially to lower the risk of emulsion formation and later as a demulsifier to break the emulsion. It is important to note that the absence of a visual confirmation does not mean the dispersant is not working; *i.e.*, ineffective. In some cases, a dispersed oil plume will be observed soon after application of dispersants; in other cases, the visual evidence may not be apparent for 24 hours or more.

The question of how large of an area to treat at one time or multiple times; *e.g.*, single dispersant passes, full treatment of an oil slick, and multiple passes was deliberated by the Effectiveness Workgroup. It was agreed that since dispersants on the NCP list would have passed the effectiveness criterion, applying only single passes of dispersants, while awaiting confirmation of "effectiveness", would be a poor use of resources. Once a decision has been made to apply dispersants, all appropriate areas of an oil slick should be sprayed. The participants agreed that, since the response goal is to disperse the slick, multiple applications are acceptable and may be necessary. Specific strategies for dispersant application may be dictated by the circumstances of the actual response. Once started, however, dispersant application should continue until the surface oil is dispersed to the maximum extent practicable into the water column. Multiple applications of dispersants may be desirable in some cases, particularly if the available information suggests dispersant effectiveness may be increased by applying dispersants to the "**thick**" areas of the slick, not to exceed an application ratio of 1:5 (dispersant to oil ratio). One multiple application option may be to apply a light dose of dispersant initially to help differentiate thicker parts of the slick, followed by application of a heavier dispersant dose to the thickest concentrations. Another may be to apply a heavy dose initially followed by lighter doses applied to the remaining slick.

Improved and more universal education processes are necessary to inform the public regarding dispersant effectiveness and net environmental benefit of dispersant use during spills. The **U.S.** needs pre-authorization documents to enable the most efficient use of dispersants during the window of opportunity and provide the best effort to mitigate the effects of an oil spill.

4.2.2 Herding Agents

There are two herding agents listed on the NCP Product list and both have been used successfully to move oil away from marshes and piers. Product effectiveness is readily determined by visual observation. With the exception of surface tension data, there is insufficient information to make a decision regarding use on a spill. Although field tests indicate that this class of CCPs does herd oil, there is no evidence of demand for either of these products.

4.2.3 Emulsion-Treating Agents

Emulsion-treating agents, specifically emulsion breakers employed in a closed system (e.g., a storage container) have been shown to be very effective in reducing water content and viscosity of recovered emulsified oil. This capability helps increase the recovered oil capacity of oil recovery vessels by enhancing oil/water separation and discharging the water. However, the potential toxicity of the effluent water, that could be discharged back into open water, is an unresolved issue. Laboratory tests (Fiocco *et al.* 1995; Fingas *et al.* 1994) in Canada, U.S., Norway, and the U.K. have also shown other emulsion-treating agents to be effective. Field testing in the U.K. has demonstrated the effectiveness of one particular agent (Walker and Lunel 1995). Emulsion inhibitors and breakers offer the potential to be effective as an adjunct and complement to *in-situ* burning and dispersant applications on the open water. Existing data are sufficient to support a decision to use these agents in closed environments: i.e., within a tank, but toxicity data are lacking to support decisions to employ these agents in open environments: e.g., open water, and for permitting effluent discharge from closed systems. No standardized effectiveness test method is known to exist for emulsion-treating agents.

4.2.4 Solidifiers

There are insufficient data and information to render decisions regarding use of solidifiers in open environments. In addition, there are no known standardized effectiveness tests for these products. Visual observation; i.e., "did