CALIFORNIA DEPARTMENT OF FISH AND WILDLIFE OFFICE OF SPILL PREVENTION AND RESPONSE (CDFW-OSPR)

REPORT ON BEST ACHIEVABLE TECHNOLOGY Applied Response Technologies (ART)

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EXECUTIVE SUMMARY

There have been considerable advances in the last two decades in the fields of oil spill response research and oil spill response planning that address the use of Applied Response Technologies (ART).

There are two basic categories of ARTs: The use of an oil spill cleanup agent (OSCA), or the use of in-situ burning of oil (ISB). The OSCA category is fairly broad, and can include dispersants, surface washing agents, sorbents, solidifiers, herders, de-emulsifiers, and bioremediants.

Provided in this report are:

- ART and OSCA product overviews;
- Descriptions of the federal (EPA) and State (OSPR) authorities in reviewing OSCA products, and federal and state roles in authorizing the use of various types of ART specific to actual incidents;
- Case history examples describing ART approaches been used in past oil spill responses;
- Scientific research results from both testing and actual use of OSCAs or ISB on spills;
- Scientific research that explores the environmental or human health issues related to each product's use;
- The benefits or constraints presented by use of each ART;
- Federal and State policies regarding ART use;
- The update status of each ART use plan and the OSPR licensing program.

This report concludes with a set of OSPR Findings and Recommendations related to each OSCA product category, in-situ burning, and OSCA licensing. We address how our efforts have met previous BAT goals related to the potential use of any ART, and offer recommendations for further development and refinement of ART research, response planning, and response policies.

SECTION I. APPLIED RESPONSE TECHNOLOGY (ART) OVERVIEW

A. Expectations of Mechanical and ART Contributions to an Oil Spill Response

The forces of the natural environment influence spilled oil in ways that are impossible to fully control and difficult to accurately predict. The use of any oil spill response countermeasure, whether conventional or applied, assumes that use of one or several response approaches can offer a better environmental outcome than using one tool alone, or none at all. As all response options have inherent limitations, our responsibility is to consider the best role of various ARTs in supporting mechanical response, balance the benefits and consequences of each response action, and ultimately choose the combination of tools that provide the greatest resource protection.

1. Offshore Response

The most common and preferred approach in oil spill response, and the one considered in first response efforts, is to use mechanical tools such as containment boom and skimming equipment for recovering and removing spilled oil. These approaches typically remove less than 20 percent of oil spilled onto ocean waters (NRC, 2005). This seems like an unacceptably low recovery rate that can be improved by adding more mechanical recovery resources to the problem. However, the low oil recovery and removal rates using mechanical technologies are largely due to the low "encounter" rate of vessels as they slowly tow containment boom through an on-water oil slick, or by high sea states. Even the most efficient skimming systems can only process the amount of oil that is delivered to them via the containment effort, and as they skim the collected oil they generally recover an oil and water mix that is predominately water. Under the best of operating conditions, winds and currents can spread the slick faster than vessels can work. As sea state or weather conditions worsen, offshore water conditions become too rough to work in safely. The ability to contain the oil is significantly reduced once waves exceed 4-6 feet, common conditions for California offshore waters. In-situ burning (ISB) of oil is also an offshore spill response option, but it too requires that oil be gathered into a thicker layer before successful burning can occur.

A more controversial approach to move significant amounts of oil off the water surface is to use dispersants to deliberately and quickly move oil from the surface and into the large body of underlying water. A decision to use dispersants will bring its own set of environmental benefits and consequences that must be understood and weighed carefully well in advance of a spill response.

2. Shoreline Cleanup

There are also limits to how much oil stranded on and within various types of shoreline habitats can be feasibly and safely recovered. On-shore mechanical recovery becomes limited as stranded oil becomes stuck on vegetation, beach bluffs, constructed shoreline surfaces, or buried in sand and soil or among rocks, making it more difficult to find and

remove without creating additional adverse effects to organisms and their habitats.

On-shore cleanup of spilled oil can take advantage of various ARTs. Like on-water spill response, mechanical cleanup is still the traditional and preferred response tool. Sorbents, surface washing agents, self-contained solidifiers, bioremediation, and in-situ burning are specific ARTs that can play a strategic support role when added to the suite of on-shore cleanup techniques.

3. The No-Response Option

Another approach to on-water or on-shore cleanup is to simply allow the natural forces of nature to proceed. No oil is removed from the environment, but parts of it will compartmentalize into different environmental realms -- volatile oil compounds evaporate, parts of the surface oil slick naturally disperse or dissolve into underlying water or mix into shoreline sands, and the surface slick gradually breaks into smaller patches that drift away. If a slick is near or on a high energy beach, wave action can remove stranded oil from the surface areas in a relatively short period of time. This approach is less practical in low energy areas (marsh, wetlands, tidal flats, lagoons, inland ponds and lakes) where the removal of oil is the result of degradation processes (e.g., photo-oxidation, biodegradation) and not wave energy.

B. Categories of ART and Oil Spill Cleanup Agents (OSCAs)

There are two basic categories of ARTs:

- 1) The use of an oil spill cleanup agent (OSCA), such as dispersants, surface washing agents, sorbents, solidifiers, herders, de-emulsifiers, and bioremediants. Each of these is discussed in more detail in Section II.
- 2) The use of in-situ burning of oil (ISB). This topic is covered in Section III.

SECTION II OIL SPILL CLEANUP AGENTS (OSCAs)

A. OSCA Overview

An Oil Spill Cleanup Agent (OSCA) is defined by the state of California as any chemical, or any other substance, used for removing, dispersing, or otherwise cleaning up oil or any residual products of petroleum in, or on, any of the waters of the state. California reviews OSCAs when their use, even if not directly on or in state waters, would have a potential to affect those waters. California also reviews OSCAs under the California Fish and Game Code §5650 regarding otherwise non-toxic agents that might pose deleterious risks to the state's trustee resources.

- B. Government Regulation of OSCAs
 - 1. Federal: The National Contingency Plan (NCP) Product Schedule and Subpart J

The federal Environmental Protection Agency (EPA) has primary responsibility for the listing of products on the National Contingency Plan (NCP) Product Schedule, regulated under Subpart J of the NCP. An OSCA must be on the NCP Product Schedule before it can be considered for use on a spill to federal waters. To be included on the NCP Product Schedule, OSCA information addressing toxicity, efficacy, chemical composition, safety considerations, and application procedures must first be submitted to the EPA. If the product information is checked and considered by the EPA to be complete, the OSCA is added to the Product Schedule.

Federal regulations for OSCAs only address chemical and biological agents. Federal regulations do not address sorbent products, as the EPA considers all sorbents as inert and thus do not require that they be reviewed or listed on the NCP Product Schedule.

2. State: OSPR Review and Licensing Process

As of January 1, 1996, the primary authority for OSCA licensing was transferred from the State Water Resources Control Board to OSPR pursuant to Government Code Section 8670.13.1. The licensing process gives OSPR the opportunity to review product information, including toxicity, efficacy and degradation characteristics, in a non-emergency situation. The environmental benefits (and potential consequences) of product use are considered. During an actual incident, the Incident Command/Unified Command (IC/UC) then benefits from having this information already available. Although it is possible to use an unlicensed product during a spill incident, this can only be done on an experimental use basis. The use of an unlicensed product should only be considered if such use provides a result that cannot be obtained through use of an already licensed product.

The information required for the OSPR review and licensing of an OSCA, regardless of whether the request to use it comes before or during an actual spill event, includes:

- Name and address of manufacturer;
- Name and contact information of technical representatives;
- Material classification and analytical data (chemical name and percentage of each component is treated as confidential by the OSPR and its agents);
- Physical properties of the OSCA (solubility in water of specified salinities, color, viscosity, conductivity, flash point, pH, freezing point, specific gravity);
- Hazards to operators: inhalation hazard (acute LC₅₀), skin irritation or sensitivity concentration, eye irritation, sensory threshold properties, hazardous gases

produced on combustion, chronic hazards, inclusion of Safety Data Sheet;

- Aquatic toxicity: complete laboratory analysis detailing the methods, materials, test species, reference toxicant and results, including No Observable Effects Concentration (NOEC) and Lowest Observation Effects Concentration (LOEC), at LC₅₀ or LD₅₀, heavy metals, and total chlorinated hydrocarbons. Includes additional toxicity testing on red abalone larvae, a sensitive life stage of a California endemic species;
- Performance efficacy (with complete laboratory report of materials and methods used to test efficacy);
- Treatment concentrations.

The state licensing guidance document and forms are under revision, but are awaiting finalization of federal updates to Subpart J of the NCP Product Schedule. Once revised and finalized, the new state OSCA guidance and forms will be posted to the OSPR web site: <u>https://www.wildlife.ca.gov/OSPR/Preparedness/Oil-Spill-Cleanup-Agents</u>. In the interim, the state OSCA licensing application, along with all other guidance and policy information, can be procured from the OSPR ART Lead Technical Specialist/OSPR Licensing Representative¹.

Sorbents are not automatically exempted by OSPR from licensing for use in state waters. Pursuant to Title 23, Chapter 10, of the California Code of Regulations, sorbent adsorption, absorption, and sinking tests, in addition to the toxicity and analytical data required for the review and licensing of any OSCA for use in state waters, may need to be provided to OSPR to determine whether or not, upon review, 1) an exemption from licensing will be granted, or 2) the product must undergo the full licensing procedure. Government Code Section 8670.13.1(b) states that sorbents and other cleanup devices that do not employ the use of active chemical cleanup agents, or otherwise determined not to cause aquatic toxicity for purposes of oil spill response, are not subject to the licensing provisions.

In addition, the Fish and Game Code (Division 6, Part 1, Chapter 2, §5650(6)) states that it is unlawful to "deposit in, permit to pass into, or place where it can pass into the waters of the state any …" "… substance or material deleterious to fish, plant life, mammals, or bird life." To meet the requirements of §5650, OSPR licensing and/or exemption review may also include evaluations of physical and chemical properties of a product (such as pH, coatings that enhance product floatation, presence of particulates that could be perceived by fish and wildlife as food, formation of particles that can sink or not be recovered), as these may pose risks to wildlife even if a product is otherwise non-toxic. It may be possible to mitigate some of these possible risks, such as limiting the use of loose or particulate sorbent and solidifier products to "self-contained" boom/sock/pillow forms. An exemption letter is issued if a product is determined to be

¹ OSCA licensing and lists are currently maintained by: Ellen Faurot-Daniels, <u>ellen.faurot-daniels@wildlife.ca.gov</u>

non-toxic and/or is packaged and used in a manner that does not pose unacceptable risks to fish and wildlife. Unless it is apparent on its face that a product is inert, it must be reviewed by OSPR prior to its use, and much of the same information for licensing review will also be required for exemption review.

The purpose of state licensing and exemption is not to limit the state's use of products to just those that are risk-free. The purpose is to understand the properties, risks and advantages of each product well enough that it can be evaluated and matched to the unique aspects of each spill situation, without creating additional and unnecessary hazards for the fish and wildlife in the spill area.

Although a product may receive a state license for use, that does not guarantee it can or will be used to address all circumstances. At the federal level, use of any ART or OSCA is at the discretion of the Federal On-Scene Coordinator (FOSC). The use of any chemical cleanup countermeasure must also be approved by the Regional Response Team IX (RRT IX), as outlined below. Use of an ART or OSCA that is in, on, or could threaten state waters will also require separate approval from the OSPR Administrator.

OSCA licenses issued by the OSPR are valid for five years, with renewals necessary to maintain current product listing. A list of products currently licensed by the state, or reviewed and subsequently determined to be license-exempt, can be found on the OSPR web site: <u>https://www.wildlife.ca.gov/OSPR/OSRO/Oil-Spill-Cleanup-Agents</u>

C. Government Authorizations for Use of ARTs

Policies directing the use of all applied response technologies are in the RRT Region IX Regional Contingency Plan (RCP): <u>https://www.wildlife.ca.gov/OSPR/Preparedness/Fed-Region-Contingency-Plan</u>

The current RCP has separate ART plans for: 1) dispersants, 2) ISB, 3) bioremediation, and 4) other OSCAs. All ART plans are in the process of review and revision, and the updates to each plan will be reflected in future updates to this report.

1. Federal: Regional Response Team IX (RRT IX) Authorization for Use

During an oil spill, the Federal On-Scene Coordinator (FOSC) can request the use of an OSCA. This is done through a formal request by the FOSC to the RRT IX. The FOSC may consult with the Unified Command (UC) overseeing the spill response to make sure they are also in support of the request. <u>All ARTs must be authorized by the RRT IX in advance of their use</u>. Authorizations are only given to a FOSC; they are not given to any other member of the UC, or directly to the Responsible Party (RP).

RRT IX pre-authorization policies exist for some OSCAs, including the marine offshore use of chemical dispersants. Pre-authorization policies indicate that sufficient preplanning and risk/consequence analyses have taken place in advance of a spill. In the case of dispersant use in some offshore areas and under certain conditions, advanced planning using a thorough Net Environmental Benefit Analysis (NEBA) process has allowed the RRT IX and federal Trustee agencies (National Marine Fisheries Service (NMFS), US Fish and Wildlife Service (USFWS)) to review those limited uses ahead of time. Pre-authorization policies allow the FOSC to skip the incident-specific RRT IX consultation if all pre-authorization conditions have been met, and apply dispersants to the spill at their own discretion.

The Regional Contingency Plan (RCP) for RRT IX applies statewide, and addresses oil spill threats to federal and state marine and inland waters. Each ART plan within the RCP provides guidelines and helpful forms the FOSC can use to facilitate and document the review and approval of OSCAs or ISB. These forms cover the following subject areas:

- Issue statement (e.g., requesting a specific OSCA(s) to address incident-specific response areas);
- Problem statement (i.e., why the OSCA or ISB is expected to improve response beyond what can be achieved by traditional mechanical means, and the natural resources at risk in the area to which some probable impacts can be mitigated in part by use of an OSCA or ISB);
- Background information (e.g., site-specific, spill-specific or resource-specific information, and any pertinent spilled product information that indicates which ART approach would be most effective);
- Possible response alternatives (this could include the "do nothing" response);
- Recommendation of the FOSC;
- Procedures and methodologies for implementation.

Regardless of whether oil spill cleanup agent use is considered for state or federal waters offshore California, and regardless of zone or use type (RRT IX Pre-Authorization or RRT IX Incident-Specific Authorization) the NOAA Scientific Support Coordinator (NOAA SSC) and the OSPR ART Lead Technical Specialist will be available to assist the FOSC in consulting with the various trustee agencies, gathering incident-specific information on environmental resources at risk, and determining which (if any) ART use can be expected to result in a "net environmental benefit" when considered and balanced against all other available oil spill response options.

2. State: OSPR Administrator Approval for Use

OSPR is a member of the RRT IX, and will be one of the incident-specific members of the RRT authorizing use of ARTs (including use of OSCAs) when considered for use in, on, or threatening state waters.

Per Government Code Section 8670.7(f), and separate from his/her role on the RRT,

the OSPR Administrator has an <u>additional</u> responsibility to review and approve the use of any applied response technology in, on, or threatening state waters.

D. Dispersants

1. Dispersant Overview

Dispersants cannot remove spilled oil from the environment, but they can move oil away from critical, long-lived, and sensitive resources that can be killed by a surface oil slick (e.g., birds, mammals); they do this by creating a diffuse plume of oil droplets that shifts into the larger space of the deep water below. The effectiveness of this method has been reported to range from near zero to 100 percent depending on the type of petroleum spilled, the chemical agent used, and the tests used to estimate the effectiveness (NRC, 2005).

Part of every oil slick spreading along the water surface will naturally begin to mix into the water column as a function of wind, currents, waves, and chop. The primary purpose of an oil spill dispersant is to "jump start" normal oil degradation through physical mixing, and oil slick breakup processes by moving spilled oil from the surface of the water into the water column. The dispersant accomplishes this by reducing the surface tension at the oil-water interface, which allows the treated oil to enter the water column as small droplets. Once treated oil enters the water column, it can be acted upon in a third dimension, and undergo quicker dispersion by the water currents, as subsurface water currents are typically stronger and more consistent than the winds that act on oil at the water's surface. Dispersants break oil into smaller droplet sizes than can be accomplished through natural dispersion, and these smaller droplets stay in suspension rather than coalescing and re-surfacing. There is also compelling evidence that development of smaller oil droplets may increase the natural degradation rate of the spilled oil by microbes in the water that use oil as their food source (Venosa and Holder, 2007; Campo et al., 2013).

2. Dispersant Properties

Initial dispersant formulations, developed in the 1950s, were primarily highly aromatic solvents, such as kerosene, and non-biodegradable emulsifiers (NRC, 2005). As was apparent during the *Torrey Canyon* spill, these first generation dispersants, although effective in dispersing oil, were highly toxic and caused great ecological damage to the intertidal and shallow water biological communities.

In the late 1960s, a second generation of oil spill dispersant was developed. These products had lower amounts of aromatic hydrocarbons, and biodegradable emulsifiers with relatively lower toxicity. However, these dispersants were less reliable than their predecessors in dispersing oil and thus of questionable use to the response community (NRC, 1989).

During the 1970s, the third generation of dispersants was developed. These are the commercial products available to the oil spill response community today. Although dispersant formulations are proprietary, it is known that they are composed primarily of nonionic (15-75 percent) and anionic surfactants (5-15 percent) and a solvent. The solvent is present primarily to dissolve solid surfactant compounds and reduce the viscosity of the surfactant to expedite the application and penetration of the dispersant into the spilled oil (NRC, 1989).

The current NCP Product Schedule lists the oil spill dispersants registered for use in U.S. waters. The State of California, under the requirements of Title 23, Chapter 10, of the California Code of Regulations, currently has reviewed and licensed four of these products for use in state waters.

It is the policy of the RRT IX that any dispersant use in California offshore waters, even outside of state waters, will use a dispersant product that is both on the NCP Product Schedule and licensed by OSPR.

- 3. Dispersant Efficacy
 - a. Efficacy Testing in Advance of a Spill

The effectiveness (or efficacy) of an oil dispersant is primarily related to the physical properties of the spilled oil within the context of current environmental conditions. Most data on dispersant efficacy are derived from laboratory or wave tank tests. A limited number of past field tests were conducted on controlled spills and "spills of opportunity." Lab tests can be used to compare one dispersant to another, or one oil to another, but cannot fully predict actual effectiveness in the field. Each spill response will be faced with drastically different turbulence regimes that will affect initial droplet formation and subsequent dispersion.

Although the dispersants licensed for use in California are formulated to work with the average ocean water temperature and salinity found in our estuarine and marine waters, their efficacy on spilled petroleum will also be strongly related to other environmental conditions and the length of time spilled petroleum has been exposed to the environment and subject to weathering. Some of these considerations include:

- Operational effectiveness (encounter rate and the ability of dispersant to incorporate into the floating oil);
- Hydrodynamic effectiveness (the spill-dependent mixing conditions that further the three-dimensional mixing and spreading of the in-water dispersed oil plume), and;
- Chemical effectiveness (the portion of the oil that will transfer into a stable inwater plume of small droplets, rather than resurface).

Operational effectiveness can be difficult to simulate in lab-scale settings, and

hydrodynamic effectiveness cannot be tested in lab-scale systems or wave tanks. In principle, full-scale field studies can test hydrodynamic effectiveness, but this is difficult and not always done. Chemical effectiveness has been investigated in the laboratory, wave tanks and at sea, but various definitions of effectiveness and different measurement protocols results in some confusion when attempting to compare results (NRC, 2005).

An interesting set of studies conducted in 2005, comparing results from Ohmsett wave tank testing with at-sea trials (S.L. Ross, 2005), and including some lab-based results, were designed to:

- Compare the results of dispersant effectiveness tests completed at the BSEE Ohmsett wave tank in New Jersey with those completed under actual at-sea conditions during sea trials in the UK in June 2003;
- Assess the reliability of visual and in-situ fluorescence methods for determining the effectiveness of dispersant applications; and
- Compare test results from (four) existing laboratory and (two) wave-tank effectiveness tests with dispersant performance at sea using the same oils (IFO 180 and IFO 380) and dispersants (Corexit 9500, Superdispersant 25, Agma 379) (Note: Superdispersant 25 and Agma 379 are not currently on the NCP Product Schedule or licensed for use in California).

This Ohmsett study was one of five in which the oils, dispersants, and dispersant-to-oil ratios (DORs) tested in the UK sea trials were retested in laboratory effectiveness tests and wave tank tests. The following tests were completed using bench-scale laboratory apparatus: a) Swirling Flask Test (SFT) (EPA standard, Environment Canada standard), b) Baffled Flask Test (BFT) (developed by EPA to replace the SFT), c) Exxon Dispersant Effectiveness Test (EXDET), and d) Warren Spring Laboratory Test (WSL Test) (UK standard), as well as in the S.L. Ross intermediate scale wave tank and the large scale Ohmsett wave tank. In short, most laboratory and wave tank tests produced high levels of effectiveness at sea. The exception was the SFT, which produced very low estimates of effectiveness under conditions of relatively low mixing energy.

The S.L. Ross study concluded:

- The UK at-sea tests showed that the limiting factor of oil viscosity might vary with mixing energy (wind speed, wave energy). In winds of 7-10 knots the limiting viscosity for Corexit 9500 was between 2075-7100 cP at 15°C, but at higher wind speeds the limiting oil viscosity exceeds 7100 cP at 15°C;
- Superdispersant 25 and Agma 379 produced some dispersant effectiveness at sea, but neither produced the high levels of effectiveness shown by Corexit 9500;

- All other bench-scale and wave tank test methods used in the study produced moderate to high levels of Corexit 9500 effectiveness for IFO 180 and IFO 380;
- None of the bench-scale or wave tank tests predicted the oil viscosity limitation on Corexit 9500 dispersion observed in the at-sea tests at low wind speeds; and
- All methods showed IFO 180 to be more dispersible with Corexit 9500 than IFO 380.

Not all oils are dispersible or should be considered for chemical dispersion. For example, spills of refined petroleum products (e.g., gasoline, jet fuel, kerosene, diesel) generally result in thin sheens that evaporate quickly; dispersants are not recommended for use on these types of spills. Based on lab tests with crude oils, the average effectiveness of dispersants, based on oil viscosity, is generally as follows:

Heavy crude:	1 percent	Light crude:	30 percent
Medium crude:	10 percent	Very light crude:	90 percent

As spilled crude oil changes through various natural "weathering" processes, its viscosity increases and with many types of oils (those with significant levels of asphaltenes, aromatic and polar compounds), water-in-oil emulsions are formed. Both weathering and water-in-oil emulsions are impediments to dispersant efficacy. The weathering process removes compounds with which current dispersant formulations are designed to react, while water-in-oil emulsions form a semi-solid mixture which negates the dispersant action.

Crude oil shipped through California marine waters is primarily of medium to heavy viscosity. This suggests that it would be impractical to rely on currently available commercial dispersants alone to clean up a significant petroleum spill in California marine waters.

Due to the weathering process and emulsion formation, the use of dispersants is typically limited to the initial spill response (12-72 hours), although some crude oils (e.g., Alaska North Slope) may remain dispersible for 6 days or more. In general practice, dispersants should be used as soon as possible after most of the volatiles have evaporated (about 12 hours post-spill), but before the oil has weathered too much (~ 24-48 hours, depending on oil type), and until the viscosity of the spilled oil reaches a level of 10,000 centistokes (cSt).

b. Efficacy Testing as a Result of a Spill

Additional efficacy testing of several dispersants listed on the EPA Product Schedule, in addition to Corexit 9500 and Corexit 9527, occurred following the 2010 Deepwater Horizon spill (the additional dispersant <u>toxicity</u> testing following DWH is discussed below in section 4.b.i). The additional efficacy testing included the two Corexit products, Dispersit SPC 1000, Finasol OSR 52 and JD 2000 (Aurand et al., 2010). In these tests, Corexit 9500, Corexit 9527 and Finasol OSR52 consistently performed well in all of the

effectiveness tests, accomplishing complete dispersion of the oil in the high-energy wave-tank tests in 6-10 minutes, while Dispersit SPC 1000 and JD 2000 required the full 20-minute trial period to disperse the test oil. In a low-energy wave-tank test setting, the performance of Dispersit SPC 1000 and JD 2000 further declined, while the Corexit and Finasol products achieved dispersion that approached 100%. The four other dispersants tested previously – Nokomis 3-AA, Nokomis 3F4, SAF-RON Gold and Sea Brat #4 – performed no better than did the water-oil control. Initial toxicity screening conducted as part of this research was unsuccessful, and it was not possible to differentiate among the six products on the basis of toxicity.

- 4. Dispersant Toxicity
 - a. Toxicity Testing in Advance of a Spill

Testing dispersant and dispersed oil toxicity in an open ocean environment is not generally possible. Research has instead primarily focused on testing selected species through exposure to selected test solutions of known concentrations or dilutions, in a laboratory or wave tank setting where exposure conditions can be controlled and monitored. The art of the science is to be able to use the benefits of toxicity testing within a lab setting and generate results that can be extrapolated to the real – and uniquely variable – world of an actual oil spill, where the setting in which organisms will be exposed to chemically dispersed oils is largely uncontrolled.

The predominant concern with a dispersant addition to spilled oil is that the application will result in the release of additional petroleum to the water column, in the form of both small oil droplets and a dissolved fraction, elevating both oil-related acute and chronic toxicity to living natural resources. Field studies in the United Kingdom demonstrated that the addition of dispersants increased the water column concentration of oil within the upper five meters by 16-27 times over that found under an untreated slick (Lunel, 1994). Studies by Mackay et al. (1982) reported average dispersed oil concentrations of 41 parts per million (ppm) at one meter under a treated slick, thirty minutes after dispersant application, with concentrations falling to 1-2 ppm after three hours. Similar values have been reported in studies conducted in Europe (NRC, 1989). Results from these studies indicate that dispersed oil concentrations typically did not exceed 1 ppm at a depth of ten meters (Mackay et al., 1982; Lunel, 1994; Aurand et al., 2000; NRC, 2005).

As the early life stages of fish and invertebrates are particularly vulnerable to oil spills, particularly the PAHs in oils (NRC, 2005; Logan, 2007), any spill-related research or models that help further assess the environmental impacts of oil or chemically-dispersed oil to fish and invertebrate eggs and larvae have particular value. Vikebø et al. (2015) conducted simulations of the overlap of fish eggs and larvae with oil from different oil-spill scenarios, both without and with the dispersant Corexit 9500. The model simulated a release of 4500 m³ of crude oil per day for 30 days at three locations along the Norwegian coast. Overlaid with the release of oil was a modelled release of

fish eggs were from nine different known Norwegian spawning grounds, which the model tracked for 90 days following the spill "start." The overlap between spawning products and oil concentrations gave a total polycyclic hydrocarbon (TPAH) concentration of more than 1.0 or 0.1 ppb (μ g/l). Acute mortality or sublethal effects were expected at those respective concentrations. In general, adding dispersants resulted in higher concentrations of TPAHs in a reduced volume of water when compared to not adding dispersants. In addition, the TPAHs were displaced deeper into the water column. Model simulations of the spill scenarios showed that addition of chemical dispersant in general moderately decreased the fraction of eggs and larvae that were exposed above the selected threshold values.

The effect of the reported concentrations of dispersed oil on the water column community is difficult to determine. The literature contains several studies that have attempted to address the dispersed oil toxicity question, but because of different testing and experimental exposure protocols, the results of these studies are difficult to correlate to "in-situ" conditions. Results of the studies do clearly indicate that dispersed oil concentrations reported from the upper few meters of the water (Mackay et al., 1982) are sufficient to result in acute toxicity to many water column organisms for the first few hours following the addition of dispersant. The hydrocarbon concentrations below undispersed oil are also likely sufficient to cause acute toxicity in the upper meter or more of the water column. What was unclear was the effect of dispersed oil deeper than the upper one to two meters of the water column, where dispersed hydrocarbon levels can decrease within a few hours to concentrations of 1 ppm or less.

The general factors that influence toxicity tests in the laboratory include test organism and life stage, the condition of the oil as tested (i.e., whether fresh or weathered), the method of test solution preparation, exposure conditions of the selected organisms to the test solutions, and the choice of an organism's response reactions to evaluate as part of the tests (NRC, 2005). Commonly used test organisms include fish (such as trout, smelt, sculpin, silverside, minnow, bass, salmon), mollusks (such as red abalone, scallops, clams, oysters, marine snails), crustaceans (such as copepods, shrimp, crabs), annelids (worms), and algae. The choice of organism used will depend on a combination of factors including the potential risk an organism has of being exposed to chemically dispersed oil, sensitivity of the organism (compared to other organisms) to dispersed oil, how well that species handles test conditions, and the relative ecological and economical significance of exposing that organism to dispersed oil during a real oil spill.

The choice of response parameters that are being evaluated for each organism undergoing the tests will depend on whether dispersant is being tested by itself (which can cause disruptions to membranes and general narcosis) or whether the solution being tested is dispersant mixed with oil (which can cause toxic effects through multiple pathways).

Mixing and "loading" energies affect the relative concentrations of oil and dispersant to

which test organisms are exposed, so the method of preparing test solutions is very important. <u>How</u> the chosen test organisms are exposed can vary by the test apparatus chosen (e.g., closed versus open), the exposure pattern (e.g., static or flow-through conditions, spiked or continuous additions of toxicants), the exposure pathway (e.g., via water or food), the test duration, temperature, salinity and buffering capacity. The test duration must be chosen carefully, as it can overestimate or underestimate the toxicity being simulated. Much of the literature on toxicity of dispersant alone and dispersant mixed with oil is based on typical static exposures of 48-96 hour duration, and while results from these tests provided data on the relative product toxicity, the results were also criticized as potentially overestimating the toxicity of untreated oil alone versus chemically dispersed oil in actual spill scenarios (NRC, 1989; George-Ares and Clark, 2000).

In response to these concerns, the Chemical Response to Oil Spills Environmental Research Forum (CROSERF) was organized and, in the 1990s, developed a declining-flow-through toxicity test protocol that used shorter exposure times and standardized water preparations (Singer et al., 1990). The purpose of CROSERF was to mimic real world exposure regimes typically found in nature and thereby better characterize oil and dispersed oil aquatic toxicity (Aurand and Coelho, 2005). The forum consisted of academic institutions from five universities within the US, as well as team members from industry; federal agencies including NOAA, MMS and EPA; and many international groups. Significant toxicological information generated using the new CROSERF protocols addressed the relative toxicity of different dispersants (both alone and when mixed with oil), and the relative sensitivity of test organisms (Singer et al., 1998; Singer et al., 2001a; Singer et al., 2001b; NRC, 2005).

Results of testing programs of the past three decades indicate that third generation dispersants (including the Corexit and Nokomis products licensed for use in California waters) are significantly less toxic than previous generations of dispersants. Further, the test results indicate that these dispersants, by themselves, are significantly less toxic than the crude oils commonly transported through state waters (NRC, 2005).

What must also be kept in balance is the recognition, during both planning and response, that:

- 1) An untreated surface slick will continue to drift and spread over a larger area and for a longer time, exposing more animals to its effects;
- The normal fate of some of the surface oil is to physical disperse into the water column, regardless of other response actions;
- 3) Use of dispersants in a smaller area of the ocean will limit the exposure that would otherwise occur, fewer long-lived species will suffer acute affects and death, and the acute affects will primarily be to organisms that have short life spans and/or a large population, and whose lost portion of the population will more readily recover;

- 4) Actual use of dispersant will follow practices that avoid direct spraying over or near wildlife aggregations, and even animals already trapped in the oil will be avoided to the greatest extent possible.
 - b. Toxicity Testing as a Result of a Spill
 - i. Additional Dispersant Product Toxicity Testing Following the Deepwater Horizon (DWH) Spill

Following the DWH spill, the federal EPA did additional comparative efficacy, toxicity, and endocrine disruption testing on eight of the dispersants listed on the NCP Product Schedule (Dispersit SPC 1000, Nokomis 3-F4, Nokomis 3-AA, ZI-400, SAF-RON Gold, Sea Brat #4, Corexit 9500, and JD-2000), both alone and when combined with Louisiana Sweet Crude oil (LSC) (EPA(a), 2010; EPA(b), 2010; EPA(c), 2010). The exposure concentration range for each dispersant was chosen to bracket the estimated median lethal concentration (LC₅₀) values reported in the NCP Product Schedule. The LC₅₀ is defined as the concentration of a substance causing mortality in 50% of test organisms for a specified time interval, in this case, 48-hours for the mysid shrimp test and 96-hours for the silverside fish test. To evaluate the cytotoxicity and potential for interaction with the androgen and estrogen receptors (AR, ER) ORD staff and outside collaborators carried out a number of separate studies that were run using in vitro (cellbased) assays. A total of 8 cytotoxicity assays, 3 AR agonist assays, 1 AR antagonist assay and 4 ER agonist assays were run on the 8 dispersants and reference compounds. Tests were run across a wide range of dispersant concentrations (0.001 to 10,000 parts per million, or ppm).

Following are the main conclusions of those three studies:

- While the dispersant products alone (not mixed with oil) had roughly the same impact on aquatic life, JD-2000 and Corexit 9500 were generally less toxic (measured as LC₅₀) to small fish, and JD-2000 and SAF-FON Gold were least toxic to mysid shrimp. Corexit 9500 was generally not more or less toxic than the other available alternatives.
- None of the eight dispersants tested, including Corexit 9500, displayed biologically significant endocrine disruption activity. Two dispersants showed a weak signal in one of the four ER assays, but integrating over all of the ER and AR results these data do not indicate that any of the eight dispersants display biologically significant endocrine activity via the androgen or estrogen signaling pathways. All of the dispersants showed cytotoxicity in at least one cell type at concentrations between 10 and 1000 ppm. Both JD 2000 and SAF-RON GOLD tend to be less cytotoxic than the other dispersants. Likewise, DISPERSIT SPC 1000 tends to be more cytotoxic than the other dispersants in the cell-based assays.
- All dispersants alone were less toxic than the dispersant-oil mixture. Oil alone was found to be more toxic to mysid shrimp than the eight dispersants when

tested alone. Oil alone posed similar toxicity to mysid shrimp as the dispersantoil mixtures, with the exception of the mixture of Nokomis 3-AA and oil, which was found to be more toxic.

- Initial oil-only tests for small fish were inconclusive, so retesting occurred. The
 additional data showed LSC oil alone to be more toxic to the silverside fish than
 the eight dispersants alone. Additionally, the oil alone had similar toxicity to the
 silverside fish as the dispersant-oil mixtures, with the exception of the mixture of
 Dispersit SPC 1000 and Nokomis 3-AA, which were found to be more toxic than
 oil alone.
 - ii. Components Analysis of Corexit Dispersants

While the environmental and toxicological effects of Corexit 9500 have been extensively researched in laboratory and wave tank settings, real-world knowledge of its use on actual spills was fairly rare until the DWH spill, when both Corexit 9527 and Corexit 9500 were used. Corexit 9500 is the more recently developed and less toxic formulation and was used more extensively once stockpiles of Corexit 9527 were substantially depleted.

With the exception of one proprietary component, the chemical compositions of Corexit 9527 and Corexit 9500 were identified in Safety Data Sheets submitted to EPA as required by Subpart J of the NCP, Sec. 300.915 (U.S. Environmental Protection Agency, 2010a). As it became apparent that large volumes of dispersants were being used to combat the subsurface and surface oil spill, EPA requested and received a disclosure from the manufacturer of the proprietary component (i.e., dioctyl sodium sulfosuccinate, or DOSS). This allowed additional evaluations by NOAA and the Food and Drug Administration (FDA) of the components of these two most commonly used dispersants (Dickey and Dickhoff, 2011). Corexit constituents and FDA assessment of the risks they post to human health are listed in Table 1.

Relative to their evaluation of Corexit dispersants used in the DWH spill response for the Gulf of Mexico (GOM), the authors provided the following statement:

"In considering the potential for chemical dispersants to compromise the safety of GOM seafood, initial questions concerned the potential toxicity of dispersant constituents, their concentrations and persistence in the environment, their potential for bioconcentration in seafood species, and their disposition and persistence in seafood species. With the exception of dipropylene glycol monobutyl ether, the constituents of Corexit® dispersants are recognized direct or indirect food additives under prescribed conditions of use. Corexit® dispersants used to treat the DWH oil spill were rapidly and extensively diluted in GOM waters, and environmental concentrations estimated and measured, were commensurately low (i.e., ppb) when detected. The physicochemical characteristics and scientific literature indicate that the dispersant constituents are susceptible to chemical and biological degradation, and that the potential for

modeling, experimental and field assessments performed during the response to the DWH oil spill, as well as ancillary literature, indicated that Corexit® dispersants did not pose a threat to the safety of GOM seafood during or after their use. Oil spills in different parts of the world are known to differ in the nature and extent of public and environmental health hazards entailed, and consequently response strategies are rarely the same. There are numerous dispersant formulations available or in development for mitigation of oil spills under different physical conditions. Future responders would benefit from a systematic assessment of less known dispersant constituents, and their fate in aquatic species."

Name of dispersant component	In Corexit 9527	In Corexit 9500	FDA assessment in terms of human health	
2-Butoxyethanol (ethylene glycol mono-n-butyl ether)	Х		Common uses as a solvent and degreaser in industrial, residential and personal care products including lacquers and paints, agricultural chemicals, household cleaners, and liquid soaps and cosmetics at concentrations of up to 10%. FDA-approved as an indirect and direct food additive in antimicrobial agents, defoamers, stabilizers and adhesive components. FDA approval means that the compound is safe for its approved intended uses and the human exposures associated with those uses.	
Propylene glycol	х	х	Common uses include commercial foods, drugs, cosmetics, and personal care products (e.g. toothpaste, shampoo, mouthwash). Approved by FDA as a Generally Recognized As Safe (GRAS) ingredient; direct and indirect food additive.	
Dipropylene glycol monobutyl ether	х	х	Common uses include as a solvent for industrial and residential cleaners/degreasers, paints and plasticizers. Propylene glycol ethers as a class are rapidly absorbed and exhibit low acute toxicity by oral exposure.	
Dioctyl sodium sulfosuccinate (DOSS)	х	х	Common uses include wetting and flavoring agent in food, industrial, and cosmetic applications, and a medicinal stool softener in over-the-counter use (e.g., docusate). FDA has approved this compound as a GRAS ingredient, and as indirect and direct food additives under prescribed conditions of use.	
Petroleum distillates, hydrotreated light fraction		х	Common uses include as a solvent for paints, varnishes, polishes, and lubricants, and general purpose cleaners and degreasers. FDA has approved similar odorless light petroleum hydrocarbons as indirect and direct food additives.	
Sorbitan, mono-(9Z)- 9-octadecenoate	х	х		
Polyoxy-1,2- ethanediyl derivatives of sorbitan, mono- (9Z)-9-octadecenoate	х	х	Numerous chemical synonyms and trade names are used for these materials (such as Span 80, Tween 80). Common uses are as wetting agents, solubilizing agents, or emulsifying agents in cosmetic and personal care products. Widely used in food	
Polyoxy-1,2- ethanediyl derivatives of sorbitan, tri-(9Z)-9- octadecenoate	х	х	products, oral pharmaceuticals, and parenteral products. They include GRAS ingredients and direct and indirect food additives commonly known as polysorbates.	

A database (Chemical Aquatic Fate and Effects or "CAFÉ"), created by Adriana Bejarano of Research Planning, Inc. and released to key response agencies in early 2014, compares all currently available research literature for dispersant toxicity, and offers a searchable tool for use during oil spill response and response planning. <u>http://response.restoration.noaa.gov/oil-and-chemical-spills/chemical-spills/responsetools/cafe.html</u>

> iii. Other Research and Concerns Regarding Dispersant and Dispersed Oil Environmental Toxicity Following DWH

Following the DWH spill, substantial research funding was allocated to further examine the fate, effects, and toxicity of oil and dispersed oil in the aquatic environment (Coelho et al., 2013). A number of publications attempted to address these issues using laboratory testing and extrapolation procedures that were not fully reliable measures for those environmental assessments (Bejarano et al., 2014). One example (Rico-Martinez et al., 2013) serves to show how the use of incorrect laboratory testing approaches can severely limit the ability to reliably extrapolate the test results to meaningful real world assessments. Below are some of the most salient points addressing dispersed oil toxicity studies following the DWH spill.

Coelho et al. (2013) reported that the problem with much of the post-DWH dispersant research, and its ability to support future dispersant use decision-making, is twofold:

- Performing toxicity testing with complex hydrocarbon mixtures in seawater presents challenges due to the inherent difficulties in interpreting and quantifying exposure concentrations when the toxicant consists of compounds with varying degrees of volatility and water solubility. As a result, a reliable characterization of exposure during toxicity tests is critical to ensure correct interpretation of the results.
 - A standardized methodology must be used for preparing test solutions of oil and dispersed oil to ensure that test results are comparable between different research laboratories;
 - Toxicity tests must emphasize the quantification of actual oil exposure concentrations in terms of specific analytical measurements, namely the concentrations of Total Petroleum Hydrocarbons (TPH) and Total Polycyclic Aromatic Hydrocarbons (TPAH) in water;
 - A minimum list of target analytes must be identified and included in the chemical analysis of all test solutions so that the TPH and TPAH values can be compared among different test conditions (e.g., different species, different oils) and different research laboratories.

This is necessary to ensure that differences in oil exposures that result from dispersant treatments are not confused with higher toxicity. The toxicity of oil

does not change when dispersants are added. Rather, the dispersant has effectively changed both the rate and location of organism exposure to the oil (i.e., making the oil more bioavailable to the organisms in question) by moving it from the water's surface to the water column. The real world utility of laboratory toxicity tests lies in the ability to compare concentrations of oil that cause impacts on laboratory test species with measured concentrations of oil and dispersants in the water column following dispersant use during actual oil spills, thus providing a sense of the likely impacts. This requires reporting water-column concentrations of total hydrocarbons, PAHs and detailed chemical characterization of laboratory exposure solutions for those comparisons.

- 2) The second fundamental problem with much of the post-DWH dispersant toxicity research was that many studies failed to put the research into the context of NEBA, or any other environmental risk versus consequence analysis. Dispersants are used to combat oil spilled on open water to purposefully and strategically change the fate of the spilled oil. There is a clear understanding by response and trustee agencies that when a decision is made to apply dispersants, even in a well-mixed open-water environment, there will be resultant short-term increases in water column exposure concentrations. However, these short-term increases (which persist for minutes to hours) are rapidly diluted to concentrations well below acute thresholds (McAuliffe et al., 1981; NRC, 1989; Wright et al., 1994; Coelho et al., 1998, Coelho et al., 2013). The decision to use dispersants should involve the assessment of environmental resource trade-offs such as through a thorough NEBA.
 - 5. Dispersed Oil Monitoring

Two types of dispersed oil monitoring are generally considered. One has to do with how <u>effective</u> the dispersant application has been on targeting, contacting, mixing, and dispersing a surface oil slick into the underlying water column; the other has to do with the expected acute and chronic <u>effects</u> of dispersed oil on sensitive species and life stages within and downstream of the operational area.

a. Special Monitoring of Applied Response Technologies (SMART)

The simplest and probably most readily deployable measures of effectiveness range from subjective visual observations to fluorometry measurements and are described in the SMART (Special Monitoring of Applied Response Technologies) protocols. The SMART protocols were developed by NOAA and are most commonly implemented using trained personnel from USCG Strike Teams. However, of the three Tiers of monitoring described by SMART, Tier I (visual observation of effectiveness) can be conducted by trained observers other than those on the Strike Team. While these protocols are also in the process of being updated, including the addition of Quality Assurance/Quality Control (QA/QC) data review recommendations, the current protocols are available from the NOAA web site:

http://response.restoration.noaa.gov/oil-and-chemical-spills/oilspills/resources/smart.html

SMART monitoring currently is more qualitative in nature rather than quantitative. Tier I involves determining, based on visual observation only, whether dispersant has "successfully" mixed with the oil. Even this lowest tier of observation requires some experience and judgment on the part of the SMART observer. Tier I observations can be extremely helpful to the FOSC and RRT in determining whether dispersant approvals should be initially considered, or if already approved, how and whether they should continue or be modified to address changes in the on-going response. Tiers II and III of SMART monitoring use towed fluorometry arrays, which provide data on whether more material has moved into the upper water column after a spray operation. However, the data do not distinguish whether the material in the water is from oil or other sources. Fluorometry readings from one or several depths (up to 10m deep) can be taken outside the slick area before spraying and then under the slick before and after spraying. The fluorometer readings do not provide certainty that the additional material that might be detected in the water is from dispersed oil. However, coupled with Tier I observations, they can provide some good evidence of probable dispersion. Tiers II and III do not provide data on oil concentration, although if water samples are collected from various depths (e.g., 1m, 5m, 10m) below the treated slick, they can be later analyzed for oil concentrations. Although the resulting data will arrive too late to allow their use in tactical decision-making (and are not intended for that purpose), these samples, once analyzed, may 1) help validate the assumptions made during planning about how quickly the dispersed oil plume spreads, and 2) be helpful in determining the toxicities to organisms in the affected area based on concentration of dispersed oil at various depths and distances from the surface slick.

b. DWH: Laser In-Situ Scattering and Transmissometer (LISST)

During the 2010 DWH spill and at the request of the U.S. government and BP PLC, research scientists and technicians from the Centre for Offshore Oil Gas and Energy Research (COOGER) and Fisheries and Oceans Canada (DFO) conducted at-sea monitoring operations with other scientific experts on board vessels R/V Brooks McCall and R/V Ocean Veritas to assist in a comprehensive environmental monitoring program in response to the spill. (This was in addition to SMART monitoring). Throughout the period from May 8 to August 24, the DFO COOGER team maintained a continuous monitoring program that recovered a total of 3,197 unique water samples from 404 stations at depths down to 2,000m for analysis of dispersant effectiveness by characterizing oil droplet size and UV-fluorescence. In direct support of U.S. EPA directives to monitor the efficacy of subsurface oil dispersant injection and the fate and transport of dispersed oil as part of the larger coordinated spill response operations, COOGER's primary operational objectives were as follows: 1) Find and characterize dispersed oil by LISST particle size analysis and fluorescence analysis; 2) Perform ongoing sampling and analysis to track the subsurface oil plume emanating from the blown-out wellhead; and 3) Verify plume modelling outputs provided by NOAA, SINTEF, and others. DFO and COOGER compiled a detailed report that provides descriptions of monitoring methods used, LISST standard operating procedures, and analysis methods. This report, entitled "Deepwater Horizon Oil Spill Response Dataset," is archived with this dataset in NODC Accession Number 0086284. The LISST-100X Particle Size Analyzer: User's Manual, Version 4.65 is available from Sequoia Scientific, Inc. 2700 Richards Road, Suite 107, Bellevue, WA 98005 and through the Sequoia online library: <u>http://www.sequoiasci.com/wp-content/uploads/2016/02/LISST-200X Users Manual v1 1.pdf</u>

The Deepwater Horizon Oil Spill dataset, including more than two million chemical analyses of sediment, tissue, water, and oil, as well as toxicity testing results and related documentation, is also available to the public online: http://www.nodc.noaa.gov/deepwaterhorizon/specialcollections.html

c. California Dispersed Oil Monitoring Plan (DOMP)

When dispersants are used during oil spills, the UC needs to know whether the operation is effective in dispersing oil. The SMART and LISST dispersant monitoring described above is designed to provide this information in near-real-time. It is important to note that SMART and LISST dispersant effectiveness monitoring do not monitor the fate, effects, or impacts of dispersed oil. The California Dispersed Oil Monitoring Plan (DOMP) (French McCay et al., 2008) was designed in 2008 to fill this void. However, development of the DOMP followed the finalization of the 2008 California Dispersant Plan.

The 2008 DOMP acknowledges that the evaluation of trade-offs between differing response strategies becomes an important element of the oil spill response effort. Using a NEBA as part of oil spill response planning, as California did, is instrumental in the development of dispersant use zones. Although this process is well established, it is, by its very nature, a qualitative exercise that requires that resource experts use their "best professional judgment" when specific toxicity as well as fate and effects data are not available. This makes the process quite sensitive to both "species and ecosystems of special concern," often the very areas where specific data are lacking. Fate and effects monitoring could provide a critical mechanism for independent verification of the appropriateness of the assumptions made during the dispersant zone development process.

The 2008 DOMP provides background to the models used to more effectively quantify relative risks to wildlife at the surface versus plankton, small fish and eggs/larvae that may be present in the upper water column during an oil spill and dispersant use. It also provides suggestions for field sampling before, during and after a use of chemical dispersants to validate dispersed oil concentrations and movement behavior of the dispersed oil plume.

The 2008 DOMP is due for an update to incorporate lessons-learned from the DWH spill response and any benefits or improvements that can be gained from the extensive use of SMART and LISST during that spill. The revision will incorporate new model runs and analysis (French McCay, D. and E. Graham, 2014). Absent this additional work, elements of the DOMP may still be included as a Job Aid to the updated RRT IX DUP.

d. Fate of Oil and Dispersed Oil from DWH Spill

It is estimated that a total of 4.9 million barrels (about 206 million gallons) of oil was released during the DWH spill. Of that, it is estimated that burning, skimming and direct recovery of oil from the wellhead removed 25% of it. Another 25% naturally evaporated or dissolved, and 24% was naturally (16%) or chemically (8%) dispersed. The residual amount of 26% remained either on or just below the surface as light sheen and weathered tar balls, washed ashore or was collected after it stranded on shore, or was buried in sand and sediments. Oil in the residual and dispersed categories is in the process of being degraded (Lubchenco et al., 2010).

A total of approximately 2.1 million gallons of dispersant were applied during the DWH spill. Of this total, 1.4 million gallons were applied at the surface and 0.77 million gallons were applied directly at the wellhead (Kujawinski et al., 2011. Two dispersants were used extensively: Corexit 9527 (surface applications only) and Corexit 9500 (use in both surface application and directly at the subsea wellhead). Almost all of the components of the two dispersants dispersed to non-detectable levels too quickly to be used as tracers. However, one component of both formulations, dioctyl sodium sulfosuccinate (DOSS), was detectable for up to a few weeks after application and was therefore the tracer used to chart the fate of the dispersant once it was in the water.

The bulk of elevated DOSS concentrations occurred in waters between 1,000 and 1,200m depth and was attributed to dispersant injections at the wellhead. Data suggest that the surface and deep water dispersant applications did not substantially intermingle throughout the water column. The deep water dispersed oil plume appeared to be restricted to deeper depth horizons but was not transported toward the surface (Kujawinski.et al., 2011); some decreases in deep water DOSS concentrations may possibly be attributable to biodegradation or sedimentation. The dispersed oil plume created after surface application of dispersants was separate from this deep water plume formed from dispersant injected at the wellhead. All of the naturally dispersed oil and some of the oil that was chemically dispersed remained well below the surface in diffuse clouds where it was able to further dissipate and biodegrade. Analyses during the DWH response indicated evidence of diffuse clouds of dispersed oil between 3,300 and 4,300 feet in very low concentrations (parts per million or less). Oil that was chemically dispersed at the surface moved into the top 20 feet of the water column where it mixed with surrounding waters and began, as expected, to disperse and biodegrade (Lubchenco et al., 2010).

i. Implications for California

There is a very low potential for a large or sustained release of oil from California offshore platforms or their associated transfer pipelines. The wells for the most part have no or little positive pressure that could lead to a blow-out. All underwater transfer pipelines have shutoff valves. Because a subsea application of dispersants for spills in California is improbable the fate of a dispersed oil plume that results from surface use of dispersants is of greater interest to oil spill responders and planners, which makes the lessons-learned from the use of surface-applied dispersants during DWH the most relevant to California use.

The fate of the surface-applied dispersant during the DWH response, in terms of its three-dimensional spreading and rapidly lowering concentrations from near the surface to about the 30 feet water depth, closely matched the planning assumptions used in California's NEBA planning. The effects on environmental resources from the large volume and sustained use of dispersants during DWH does <u>not</u> match the California planning assumptions; California planning assumes a much more limited (5-7 day) window of use, therefore targeting much smaller spills with correspondingly smaller dispersant volumes. Data from the spill and further research underway or planned for the near future will provide for additional discussion and dialogue about the environmental costs and benefits when long-term and large-volume dispersant applications are used. These data could support and/or refine the assumptions and conclusions about "safe" volumes and time periods that might apply to a California dispersant use decision.

6. Dispersant Application Technology

The three primary modes of dispersant application are boats, helicopters, and airplanes (NRC, 1989). Specific response vessels/boats as well as vessels-of-opportunity can be fitted with dispersant application equipment. Typical application equipment includes conventional boom applicators, used with diluted dispersant and "neat" boom application equipment used with undiluted dispersant (NRC, 1989). In addition, fire monitors (water application systems on fire boats) have also been used as a tool for dispersant application. The principal disadvantages of using boats as a platform for dispersant application are the small volume of dispersants carried, their relatively slow speed, susceptibility to sea state, and the limited sea surface area covered with each pass of the boat. For these reasons, dispersant application from boats is typically limited to small spills of fewer than 1,000 barrels (NRC, 1989).

Helicopters provide the advantage of speed, quick deployment, maneuverability, accuracy, and cost effectiveness in responding to small oil spills (NRC, 1989). Further, the helicopter may be used as a first response tool in large spills until larger aircraft become available. The major disadvantage of this delivery system is the limited volume (250-790 gallons) of dispersant they can carry.

Fixed wing aircraft come in a variety of sizes and payload capabilities and may be the

only or best option for long distance or long duration dispersant operations. They are the primary dispersant application platform for large on-water oil spills. Planes like the C-130 provide the advantages of extended range, large dispersant carrying capacity, speed, and extended aerial coverage. Small aircraft, such as crop dusting planes, may be fitted with dispersant application equipment and used on small spills. Their relatively small load capacities make them impractical for use on large spills.

There are many general factors important in the effective aerial application of dispersants, including the altitude of release, wind speed and direction, major droplet characteristics, boom configuration, and swath width. Proper application targets the thickest and freshest areas of oil, avoids areas of clear water, and operates at a low altitude to minimize the drift of dispersant by the wind.

Table 2 on the following page lists the OSRO dispersant platforms, personnel, products and general response timeframes for a California dispersant response.

Table 2. General California Dispersant Application Platform Information

Application method	Weather limitations	Advantages	Disadvantages	
C-130	Winds: 30 – 35 kts Waves: 17 – 23 ft	 Suitable for very large spills with longer (several day) time windows, greater distance from shore, or remote areas. Greatest delivery capacity; might be capable of fully treating all of the oil spilled as a large batch spill (≥ 10,000 bbl). Able to meet 7 hr response time following a spill notification and/or FOSC approval. 	 At present the nearest units are outside the state; Requires suitable runway. 	
DC-4	Similar to above	 Suitable for very large spills with longer (several day) time windows. (1) NRC plane can complete Tier 1 spraying (2100 gal) within 12 hrs (7 hrs for approval and flight time, 5 hrs on-scene spray time) 	 Delivery capacity is less than that of C-130; Need to allow for more frequent returns to airport for dispersant reloading. 	
Single-engine planes (e.g.,Winds: $17 - 21$ ktsCessna AT-802 "Agtruck")Waves: $6 - 9$ ftCessna AT-802 "Agtruck"Ceiling: ≥ 1000 ft		 Suitable for small- to mid-sized spills that occur at considerable distance from the response centers; Purpose-built for aerial spraying; capable of relatively short start-up time; A number of Agtrucks available for use in a large spill. 	 Smaller payload; more limited range; Time window needs to be long enough to allow for more frequent dispersant re-loading. 	
Medium-size helicopter	Winds: 17 – 27 kts Waves: 6 – 17 feet	 Available; highly maneuverable; capable of being re-supplied near spill site; good operational efficiency; lands almost anywhere; Above sea blowouts from oil platforms (of oils with a <u>medium</u> emulsification rate) are good candidates for treatment helicopter platforms because they can remain on-scene and deliver dispersants constantly when needed. May be adequate to deal with small tanker spills close to their re-supply bases; Could also respond to mid-sized spills provided the time window is long enough. 	 Limited by small payload and range; two are available in southern CA; use neat dispersant only; Blowouts of high emulsification rate oils will <u>not</u> be good candidates for dispersion from any platform type. Ship-based delivery may be limited by slow transit speed and small payload; These platforms are limited for spills at a distance from their base of operations, either because of slow transit speed or limited operating range; limitations can be overcome in some circumstances by re- supplying them at or near the spill. 	
Work boat	Winds: 7 – 21 kts Waves: 1 – 9 feet	 Good control; mixes water; Above-sea blowouts from oil platforms (of oils with a <u>medium</u> emulsification rate) are good candidates for treatment by ship and helicopter platforms because they can remain on-scene and deliver dispersants constantly when needed; May be adequate to deal with small tanker spills close to their re-supply bases; could also respond to mid-sized spills provided the time window is long enough. 	 Moderate transit speed; limited to small spills; limited swath width; Blowouts of high emulsification rate oils will <u>not</u> be good candidates for dispersion from any platform type. Ship-based delivery may be limited by slow transit speed and small payload; These platforms are limited for spills at a distance from their base of operations, either because of slow transit speed or limited operating range. These limitations can be overcome in some circumstances by re-supplying them at or near the spill. 	

7. RRT IX Dispersant Use Plan for California -- Structure and Use

Nearly two decades ago, California recognized the value of the NEBA approach to support the dispersant use planning process. NEBAs (also sometimes called a Consensus Ecological Risk Assessment (Consensus ERA) were used by California coastal Area Committees (ACs) and their multi-stakeholder Dispersant Subcommittees. This was the means by which dispersant authorization zone recommendations were developed by each AC for their coastal area of responsibility. There was strong reliance on the dispersant efficacy and toxicity studies conducted by well-qualified and experienced dispersant researchers, using established standardized test protocols. The zone recommendations developed through this NEBA and research-review process were accepted and implemented by the RRT IX in their Dispersant Use Plan for California, and the summary results of the NEBA evaluations are included as a Job Aid to the RRT IX Dispersant Plan for California.

Three additional Consensus ERAs were sponsored by USCG for the San Francisco, Santa Barbara and California-Mexico border areas. While a separate effort and using different workgroups from the AC NEBA evaluations, the Consensus ERAs followed the same approach, resulted on conclusions consistent with those of the ACs, and the efforts were well-documented in follow-up reports. Reviewing these reports provides critical insight into the depth and breadth of stakeholder-involved NEBAs and Consensus ERAs. The California Consensus ERAs are available at:

http://www.rrt9.org/go/doctype/2763/131663 http://www.hdrinc.com/sites/all/files/assets/knowledge-center/santa-barbara-final.pdf http://www.rrt9.org/go/doctype/2763/131659

As a result of RRT IX acceptance of AC recommendations, the RRT IX Dispersant Use Plan for California (DUP) includes two dispersant zone types: 1) Pre-Authorization Zone; and 2) RRT Incident-Specific Authorization Zone). It specifies spill-specific conditions of dispersant use, FOSC decision-making flowcharts and checklists for working through the decision-making process in both types of zones, and provides all the forms, informational Job Aids, and Record of Decision templates. The DUP also provides information on dispersant use monitoring, wildlife monitoring, public outreach, and seafood safety. It articulates and provides records of communications to the RRT IX. The DUP is part of the Region IX Regional Contingency Plan (RCP). The RCP (including all of the ART plans within it) are currently being updated, and will be reposted to the OSPR web site when the updates are complete and finalized.

Any time dispersants are considered, special attention will be paid to their potential effects on wildlife, the method of application, and monitoring during application. The application of dispersants over concentrations of marine mammals, sea turtles, birds and other recognizable aggregations of sensitive species would be avoided. Areas where concentrations of wildlife have been observed during reconnaissance flights and

other wildlife operations should be eliminated from operational plans when dispersant use is considered.

In areas where the dispersant use has not been pre-authorized by the RRT, the NOAA SSC and the California ART Lead Technical Specialist (ART Lead TS) will help the FOSC and RRT decide whether there will be a reasonable expectation of achieving a net environmental benefit for a dispersant application in California offshore waters. Sensitive resource identification and mapping resources may come from NOAA's Environmental Response Management Application (ERMA) information platform, Area Contingency Plans (ACPs), NOAA's ESI charts, surface current information from Central Coast Ocean Imaging System and Southern California Ocean Imaging System (CenCOOS, SCOOS), other near real-time aerial imaging, real-time resources at risk information from natural resource trustee agency experts, previous biological assessments and ESA Section 7 consultations, and databases. The presence of an especially sensitive wildlife resource in the path of a spill trajectory might prompt or preclude the use of dispersants, even in a pre-authorization zone. The integration of pre-spill (baseline) data and reconnaissance information provide the FOSC, NOAA SSC, Planning Section Chief, EUL, and ART Lead TS with the ability to develop a common understanding and strategy to protect resources at risk during a response involving dispersants.

Following any RRT IX authorization to use dispersants, the ART Lead TS and/or NOAA SSC will work with the Dispersant Operations Section to make sure all RRT IX conditions of authorization and NMFS/USFWS Best Management Practices are included in operational practice. As operations commence and continue, results from dispersant use monitoring (e.g., SMART program, wildlife spotters) will be acquired and reviewed to ensure the dispersant operation is effective and operating within the conditions of approval. Dispersant operations will only continue while safe for operators and while providing a net environmental benefit.

- a. Conditions and Expectations of Dispersant Use
- Zones currently being considered as RRT IX Pre-Authorized for dispersant use (the pre-authorization is granted by the RRT only to the FOSC) are <u>only</u> in waters no closer than 3 nautical miles from the nearest (mainland or island) shoreline, not within 3 miles of the CA/Mexico border, and not within the boundaries of a National Marine Sanctuary;
- During the breeding season period for marbled murrelet (between March 24 and September 15), the pre-authorization zone for application of dispersants is to be 5 to 200 nm (rather than 3 to 200m) from shore off the northern and central California coasts (CA/Oregon border to Monterey/San Luis Obispo county border);
- Dispersant application aircraft will not fly directly over offshore islands or rocks with significant numbers of roosting birds or hauled-out marine mammals. Caution will be taken to avoid spraying within NMFS-determined buffer areas near congregations of

marine mammals, sea turtles, surface aggregations of bait fish and brown sea nettles, or rafting flocks of birds;

- Subsea applications of dispersants, or use of dispersants at the water surface for more than 4 days, are not pre-authorized uses (RRT IX incident-specific authorization is instead required);
- Dispersants cannot be applied to any spill of diesel or other similar light-weight and quickly-volatilizing Group 1 fuels or products (e.g., gasoline, kerosene, jet fuel, diesel), as doing so does not provide a net environmental benefit;
- Surface application of dispersant is not recommended in or over waters shallower than 60 feet;
- Care should be taken when considering dispersant use over waters >60' deep but subject to strong tidal flow (e.g., over deep/dredged channels in bays) or near river mouths, as dispersed oil droplets may bind to sediment and sink, rather than dispersing and spreading through the water column as intended;
- The SMART controller/observer should be over the spray site before the start of the operation. If possible, a DOI/DOC-approved marine wildlife observation specialist will accompany the SMART observer, scan the area for wildlife in advance of application, help direct the operation to the spray zone with no sighted wildlife, and follow along behind the application to observe wildlife that appear in the spray zone after spraying has begun;
- The marine wildlife observer is strongly encouraged to use the Wildlife Spotting Protocols (or comparable forms, protocols and job aids within the DUP). However, the operation will not be delayed for this function;
- Personal protective equipment for personnel on-site will conform to the appropriate dispersant Safety Data Sheet (SDS);
- Additional considerations apply if the dispersant spray platform is a vessel, including vessel speed limits, stand-off distances from various whale species, and a requirement to have wildlife monitors on board each spray vessel.
 - 8. Other Dispersant Issues
 - a. Government Requirements for Dispersants and Response Times
 - i. Federal

Under the implementing authority of the Oil Pollution Act of 1990 (OPA 90), the U.S. Coast Guard passed rules for vessel and facility response plans that specified the minimum required equipment capabilities for oil containment and recovery for the most likely maximum spill volumes. As mechanical recovery is not always effective, OPA 90 included a mandate directing national and regional response teams to develop guidelines for other on-water response strategies, specifically the use of chemical

dispersants and ISB (the RRT IX and California effort to address the OPA 90 mandate is summarized in section II.D.7 above). The RRT IX Dispersant Use Plan for California is kept within the Regional Contingency Plan, although general policy outlines and web links are provided in each regional ACP. All ART use plans are statewide in nature and are included as appendices or enclosures of the RRT IX RCP.

In 2002, the U.S. Coast Guard changed its regulations for oil spill response capabilities to include minimum capabilities for dispersant application in all zones where dispersant use has been pre-authorized. This allows evaluation of factors such as dispersant effectiveness and effects, which are the major drivers in any response and trustee agency decision about whether or not dispersants should be used on a particular incident. This is an evaluation emphasis that is in addition to documenting the availability of dispersant application assets (dispersant, application aircraft and vessels, trained staff).

The U.S. Code of Federal Regulations (CFR; Title 33, Part 154) describes response plan development and requirements for facilities that handle, store, or transport Group I through Group IV petroleum oils; this includes vessels that transport oil to facilities within the inland, nearshore or offshore areas where pre-authorization for dispersant use exists. Contingency plans must identify and ensure that sufficient volumes of dispersants on the NCP Product Schedule, application platforms and systems that meet stipulated performance criteria, and trained personnel are capable of commencing dispersant application operations at the site of a discharge within 7 hours and within 50 miles of shore following a decision by the Federal On-Scene Coordinator to use dispersants. (Please refer to CFR Title 33 Part 154.1045 for additional detail on federal dispersant regulatory requirements).

The RRT IX Dispersant Use Plan for California lists the location of all dispersant stockpiles, application platforms, and trained personnel that can respond for dispersant operations within the California offshore pre-authorization zones and/or be "cascaded" in for on-going or more distant operations. The dispersant resources available for the offshore pre-authorization zone are also available for dispersant responses in any of the RRT IX Incident-Specific Authorization Required zones.

ii. State

The California Lempert-Keene-Seastrand Oil Spill Response Act of 1990 describes, in several sections, both broad and specific responsibilities of the OSPR Administrator for dispersant research in particular, licensing of oil spill cleanup agents (including dispersants) in general, and any subsequent approval for oil spill cleanup agent use for oil spills on, in, near, or threatening state waters. California Government Code §8574.7(c)(6) calls for an expedited decision making process for dispersant use in coastal waters and Administrator assurance that a comprehensive testing program is carried out for any dispersant proposed for use in California marine waters. The statutory authority for the OSPR licensing program is in Government Code §§8670.13.1

and 8670.13.2, and regulations for oil spill cleanup agent licensing are part of Title 14, Subdivision 4, Sections 884-886.5.

California law and regulations do not currently require oil spill response contingency plan holders (or their rated Oil Spill Response Organizations) to acquire or maintain dispersant resources, application platforms, or trained personnel for a possible operation within state waters. The dispersant resources for the offshore preauthorization zone could nevertheless be available for an RRT IX Incident-Specific Authorization in state marine waters.

For ART (including dispersant) use in state waters, the OSPR Administrator has approval authority (in addition to the OSPR Administrator "vote" as a member of the RRT IX) as described in California state regulations (Title 14, Subdivision 4, §886.1(a)).

b. Dispersant Planning for California State and Inland Waters

There are currently no plans of the state or RRT IX to seek dispersant pre-authorization for state or inland waters. Use of dispersants in state or inland waters continues to be subject to a spill-specific request for use by a FOSC and subsequent review and authorization by the incident-specific RRT IX.

c. New Dispersant Formulations or Approaches

ExxonMobil is currently working on a gel-based matrix for Corexit, which would give it a longer retention time on the oil slick and allow for greater efficacy. However, greater toxicity may be an outcome as well, so additional trade-off decision-making regarding efficacy versus toxicity will need to be conducted if and when this product formulation comes to market. All California NEBAs to date have revolved around the efficacy v. toxicity of liquid Corexit dispersants (and by extension, to the other CA licensed liquid dispersant produced by Nokomis). The Section 7 consultations conducted under the Endangered Species Act (ESA) have been limited to current formulations and application systems for liquid Corexit and Nokomis products.

d. Current Limits to Expanded Use of Dispersants

There are currently no plans of the state or RRT IX to expand the use of dispersants, beyond continuing to seek all permits and permissions for the offshore (federal waters, 3-200 nm from shore) pre-authorizations as discussed above. This specifically includes the types of dispersants licensed by the State of California and on the NCP Product Schedule, and previously subject to NEBA analyses and ESA Section 7 consultations.

Use of dispersants products not previously subject to NEBA or ESA Section 7 analyses may require further evaluation before they can be considered for pre-authorization or incident-specific use.

e. Continuing Challenges to the Use of Dispersants

Considerable scientific research has been conducted on both the efficacy and the environmental toxicity of the most commonly used and stockpiled dispersants. As part of advance planning, extensive NEBAs/ Consensus ERAs, consultations with federal Trustee agencies under the Endangered Species Act, and federal consistency discussions with the California Coastal Commission have also occurred. There are stringent policies of the RRT IX that direct, limit, and condition any authorized use, and the trustee agencies have identified ways to minimize risk and mitigate the worst and less-reversible effects of an oil spill (and spill response) in favor of the lesser and more reversible consequences. The DWH spill generated a great deal of additional research on the environmental and human health effects that may result from large oil spills (with and without chemical treatment), and this research will be providing data and evaluation material for years to come.

Even with renewed research interest and funding, the "science" of dispersants and their use can never be complete. Nevertheless, the large body of research of the past several decades offers a considerable body of trusted information about the fate and effects of the most commonly available and stockpiled dispersants. This in turn allows informed and rigorous environmental analyses and construction of RRT IX policies for dispersant use that are the most highly protective of the habitats and species at greatest risk in any particular oil spill response.

The prospect of dispersant use has always been publicly and politically contentious, and the DWH response did not make these planning discussions any easier. No amount of science, pre-planning, establishment of limited policies for use, or biological assessments of effects will result in greater general acceptance or belief that the spill response and trustee agencies have diligently and impartially planned for this possible response option or adequately considered all risks.

The most critical challenge therefore lies with the need to conduct continued, thoughtful, and respectful outreach to response and trustee agency staff and management, industry, environmental organizations, elected representatives, and the general public. Risk communication on an issue as complex as dispersant use is difficult to package for these different audiences, especially when the memories of the last spill response begin to fade and personnel changes occur within previously-involved agencies and organizations. Risk communication will be the most critical and persistent element of describing how OSPR, as the state's lead trustee agency during oil spill response, implements its mandate to study and plan for possible use of dispersants while protecting living natural resources and their supporting habitats and ecosystems.

E. Non-Dispersant Oil Spill Cleanup Agents

The types of oil spill cleanup agents considered here include sorbents, surface washing agents, solidifiers (and related oil modifying agents), herding agents, de-emulsifiers, and

bioremediants. Each of these may have a discrete response utility, or niche, in which it may best match an incident-specific need that mechanical recovery, natural recovery, dispersant, or ISB cannot adequately address. Some are better known and used than others, and some currently have limited use or utility. Future research and subsequent response policy changes may elevate some of these to being more relevant response tools. Bioremediants, discussed at the end of this section, are included in this category but are not considered a "first response" tool because of their need for a long action time.

- 1. Sorbents
 - a. Sorbent Overview

Sorbents are materials that soak up liquids. Those used for oil spills should be oil attractive (oleophilic) and water repellent (hydrophobic). Although the use of sorbent products is probably the second most commonly used oil recovery technique, they are not intended for recovering the main volume of a spill. Some sorbent products (especially expanded foam synthetics) can sorb a broad range of oil viscosities, but most sorbent types are used for recovery of oil sheens or in the final polishing process of the cleanup. As such, sorbents are usually considered auxiliary spill control materials used for the pickup of small volumes or sheens of oil that are not easily recovered by other mechanical means. They can be very valuable tools for shallow water habitats, such as marshes, and for spills of guickly sheening fuel oils, such as diesel (which is commonly more toxic than crude oil). Sorbents are also useful in harbor areas where large oil spill response organizations are not responding to smaller but more frequent fuel spills (but local harbor masters are). The widespread use of sorbents is generally limited by the intensive labor required and the amount of solid and hazardous waste generated. Since oil is often defined as a hazardous waste, any sorbent coated with oil (even one considered biodegradable) would also be considered a hazardous waste.

Sorbents work in two distinct ways: They can either a<u>d</u>sorb oil (the oil sticks to the surface of the sorbent) or they a<u>b</u>sorb oil (the oil penetrates into the sorbent). Absorption only includes those cases in which the oil combines with the sorbent material in such a way that it neither leaks out nor can be squeezed out (Schulze, 1993). For purposes of this report, the term sorption will be used to include both processes and sorbent will be used to describe the material itself.

b. Types and Testing of Sorbents

Sorbent materials may be organic, inorganic, or synthetic and can come in many forms including sheets, pillows, socks, sweeps, clusters (pom-poms), booms, and loose particulates. Several specific properties are considered advantageous for sorbent materials. A sorbent should be oleophilic and hydrophobic, it should pick-up oil quickly, retain it without significant "re-sheening", and should sorb a large amount per unit weight of sorbent. It should be easy to apply and recover as well as strong enough to

be handled without coming apart. Sorbents used on water should be able to take on large amounts of oil without sinking. Since no product exists which can boast all of these advantages, sorbents will be reviewed for specific advantages and disadvantages based on product type and how sorbents may be improved in the future.

Sorption capacity or efficiency is almost always measured in terms of weight of oil sorbed per weight of sorbent (since this is a ratio, units are not important). Although sorbency ratio is the most frequently used measure of sorbent effectiveness, other sorbent characteristics are also important. Sorbency according to viscosity of oil tested is important as well as the amount of water picked up. Sometimes it may appear that a sorbent is highly effective until the user discovers that the recovered mixture may be predominately water (Potter, 2013).

There are two ASTM (American Society for Testing of Materials) standards for the testing of sorbents: F269-81 - Sorbent Performance of Absorbents and F716-82 - Sorbent Performance of Adsorbents.

i. Organic

These products are plant or animal based and include straw, peat, saw dust, wood chips, cellulose, chicken feathers, and other readily available "natural" substances. They are often used because they are abundant in nature or are waste products from some other industry. Most organic sorbents can pick up from 1 - 10 times their weight in oil and some can have even higher ratios (Schulze, 1993). Generally, organic products must be treated to be oleophilic or they would also sorb water and may eventually sink. One example of such a product is wood chips, which can become waterlogged and sink if they are not coated in a way that allows them to instead remain afloat and absorb oil (coating materials may be evaluated as part of the OSPR licensing/exemption process). Since most organic sorbents are granular or loose materials, collection can become a problem, especially when spread on water. It is the policy of both the RRT IX and OSPR that, to the greatest extent possible, materials deployed to recover spilled oil are to be collected after use. As a result, organics used on water are generally enclosed in mesh or netting. In California, the majority of licensed sorbents are organic products.

The test results and considerations for use described in the sections below come from the World Catalog of Oil Spill Response Products (Potter, 2013).

<u>Saw dust</u>: Sorbency ratio of about 4:1 for diesel to just under 10:1 for Bunker C. Water content was about 16% for diesel decreasing sharply to 1-2% for weathered crude and Bunker C.

<u>Ground corn cobs</u>: Sorbency ratio of about 4:1 for diesel increasing to about 7:1 for Bunker C. Water content about 4% for diesel increasing to about 30% for weathered crude and Bunker C.

<u>Processed cellulose</u>: Sorbency ratio of about 3:1 for diesel increasing to about 6:1 for Bunker C. Water content is less than 2% for diesel and close to zero for Bunker C.

<u>Straw</u>: Sorbency ratio of about 2:1 for diesel, fresh and weathered crude and about 5:1 for Bunker C. Water content is about 12% in diesel, goes to about 25% in weathered crude, and drops to near zero in Bunker C.

<u>Wood chips</u>: Sorbency ratio of about 1:1 in diesel going up to about 3:1 in Bunker C. Water content is about 1% in diesel, 3% in fresh crude, then nearly zero for weathered crude and Bunker C.

<u>Wool</u>: Sorbency ratio of about 9:1 in diesel, up to 18:1 in weathered crude, and about 12:1 in Bunker C. Water content is about 6% in diesel and near zero in more viscous oils.

<u>Peat</u>: Sorbency ratio of about 8:1 in diesel decreasing to about 6:1 in Bunker C. Water content is about 1% in diesel, 9% in fresh crude, and very low in weathered crude and Bunker C.

<u>Cork</u>: Sorbency ratio of about 4:1 in diesel decreasing to about 3:1 in Bunker C. Water content is very low (less than 2%) for all test oils.

None of the above products sank during the 48-hr tank test. Some products (e.g., wool, peat, cork and processed cellulose) can be re-used. Clay products were not tested with the other organic sorbents as their sorbency rate was very low, and they quickly sink. Organic sorbents may be selected because they are made from waste materials and therefore are less expensive than synthetic products. Use of organics may be justified under the following conditions:

- Sorbent efficiency (as measured by sorbency ratio) is adequate;
- Materials do not take on so much water that they sink;
- Materials are packaged (e.g., as pads, self-contained boom, pom-poms) so that they can be used on water;
- Materials (including packaging) are strong enough to be deployed and recovered easily (e.g., boom available in linked sections), without rupturing;
- Materials have a reasonable shelf life and storage volume is not excessive;
- There is an easy means of appropriate disposal; and
- Inadvertently released loose materials are not too labor intensive to recover or destructive of skimming and pumping equipment

There have been proponents for the use of other types of inexpensive "organic" sorbent boom and mat material (e.g., pet or human hair, other cellulose products such as hay, kenaf, bagasse), but these generally sorb more water than oil and soon sink below the surface. Hay can introduce seed that could be considered invasive depending on the environment of use, and hair may potentially and unnecessarily introduce additional skin

oils and residual chemicals into the spill environment. Conventional sorbent materials are more effective, do not pose leaching concerns, are readily available, and are strongly preferred. All products should be pH neutral, seed free, and self-contained for use on water. The State of California and the RRT IX may approve other products or forms of use depending on the exigencies of any particular oil spill response.

ii. Inorganic

These products are generally mined substances, such as perlite, vermiculite, or volcanic rock, but also include glass wool. Inorganic sorbents may sorb about 4 - 8 times their weight and occasionally up to 14 times their weight in oil (Schulze, 1993). Some of these materials can be difficult to apply because they are light and, when broadcast, blow in the wind. Others are hazardous to apply and require operators to wear breathing masks. Some inorganic sorbents sink and therefore would not be appropriate for on-water use. The advantages of inorganic sorbents are that they are abundant and inexpensive.

There are not enough independent test data on inorganic sorbents to describe or compare their performance in general terms, but past studies on some specific mineral-based products can offer a sense of what to expect (Potter, 2013).

- Sorbency ratio is fair to good for some of the products when tested in a 2.5 or 5mm slick; however, when used in a thin slick, they all recover a large amount of water. Since cleaning up thin slicks is an important application for sorbents, this characteristic is adverse.
- Most of the mineral-based sorbents are intended to be broadcast with blowers, creating unintended drift during application and problems in recovery. Potential application hazards to personnel should be considered. Some of the mineralbased sorbents sink when applied on water, which limits them to use on land. Current California and RRT IX policies restrict the use of loose or broadcast sorbents for some of the reasons stated here.
- Mineral-based sorbents may present disposal problems.
 - iii. Synthetic

These products include man-made polymer materials, such as polyurethane, polyethylene, polypropylene, nylon fibers, and urea formaldehyde foam. Highly oleophilic and hydrophobic, synthetics are excellent for recovering small quantities of oil floating on the water. Synthetic sorbents typically sorb from 5 - 20 times their weight in oil and some foam sorbents have a sorbency ratio of as much as 40 to1 (Schulze, 1993). Synthetics can be strong enough to be used several times. The pore size of plastic foams can be controlled over a wide range, allowing their use on oils of most viscosities. The disadvantages of synthetics are that they are generally more expensive than organics, and they are not biodegradable. <u>Polypropylene sorbents.</u> These represent the majority of sorbents used for oil spills. Of these, the melt-blown polypropylene pads and rolls are used most often, although pompom constructions are also commonly seen. Pads and rolls can come in different thicknesses, generally 1/16" or 1/8".

Tested sorbency of these products are generally similar (ranging from about 8:1 sorbency on light oils up to about 15:1 for heavier oils), regardless of manufacturer. Expected water content can be very low for fresh crude and almost zero for all other products. Pom-pom constructions are most effective on highly viscous products (sorbency ratios vary from 2:1 for diesel up to 18:1 for Bunker C), and water retention is relatively low. This is a very positive result and one of the reasons that melt-blown polypropylene is so often used in oil spills. Newer products with the polypropylene prepared in different forms may result in a higher level of performance than those tested more than 30 years ago.

Polypropylene products as continuous sheets do not require additional packaging in order to be in the "self-contained" form that California and the RRT IX prefer or require.

<u>Flash spun polyethylene, ground polyurethane and scrap polyolefin.</u> These synthetics are particulate or fiber clump materials that require additional packaging before they can be used for spills on water. Some of these products have excellent sorbency ratios:

- Flash spun polyethylene is about 6:1, with water retention of about 12%;
- Ground polyurethane is 5:1 for diesel and up to 14:1 for Bunker C, with water retention of about 5%;
- Scrap polyolefin is 13:1 for diesel and up to 23:1 for weathered crude oil, with water retention of about 5%.

<u>Polyethylene and polyurethane foam.</u> These are treated synthetic sponge materials. There are several products of this type on the market that have properties different from other synthetic sorbents. Following are some key comparisons:

- Synthetic foams may have a high sorbency ratio for low viscosity oils (about 22:1 for diesel, up to 38:1 in weathered crude, and around 33:1 in Bunker C, with water retention generally less than 5%).
- Once the products have been used, or "primed" with oil, their sorbency improves, particularly with the high viscosity oils. This sets them apart in that most other synthetic sorbents have very similar performances on their second use.

Synthetic sorbents can be specially fabricated for use on oil spills and are generally the most effective materials available. They store well (relatively small volume) and do not deteriorate, as long as they are not exposed to sunlight. The more common types are continuous materials that make them easier to deploy, recover, and use as a sweep. Foam products have very high sorbency ratios, particularly in viscous products, and can be re-used many times. Synthetic sorbents also have the advantage of being available

almost anywhere and manufactured in many locations, so re-supply is not an issue.

Environment Canada and the Marine Spill Response Corporation (MSRC) completed a series of studies to evaluate oil sorbent materials (Cooper et al., 1994). The main objective was to study the relationship between oil sorbent material type and oil viscosity, as they pertain to oil pick-up ratios. Sorbents were placed into three categories: organic (plant or animal based), inorganic (mineral based), and synthetic. Approximately 60 different sorbents underwent preliminary testing. Based on these tests, one representative sorbent from each category was selected for further testing. The results of these final tests are summarized on the following page in Table 3.

Oil Viscosity Range (cP)	Organic (g oil/g sorbent)		Inorganic (g oil/g sorbent)	Synthetic (g oil/g sorbent)	
10 - 100	Feathers	30.0	3.6	Flexible collagen sponge	72:1
	Cellulose mat	15:1		Polyamine flakes	38:1
	Peat	6:1		Polyurethane foam	22:1
	Millet	4:1		Polyethylene pulp	12:1
	Coconut	2:1		Polypropylene mat	11:1
	Average	10:1		Average	22.8:1
100 - 300	Feathers	60:1	4.8	Polyamine flakes	66:1
	Cellulose mat	9:1		Polyurethane foam	32:1
	Cellulose	7:1		Flexible collagen sponge	20:1
	Millet	5:1		Polypropylene mat	20:1
	Peat	10:1		Polyethylene pulp	18:1
	Coconut	3:1		A	23.2:1
	Average	15.4:1		Average	23.2.1
	Feathers	39:1	4.9	Polyamine flakes	47:1
300 - 1000	Peat	8:1		Polyurethane foam	25:1
	Cellulose mat	6:1		Flexible collagen sponge	22:1
	Cellulose	6:1		Polyethylene pulp	18:1
	Coconut	5:1		Polypropylene mat	15:1
	Millet	3:1			
	Average	11.1:1		Average	18.5:1
1000 - 3000	Feathers	35:1	3.6	Flexible collagen sponge	45:1
	Cellulose mat	12:1		Polyamine flakes	40:1
	Peat	7:1		Polyurethane foam	16:1
	Cellulose	6:1		Polyethylene pulp	15:1
	Millet	4:1		Polypropylene mat	9:1
	Coconut Average	2:1 11:1		Average	18.4:1

Table 3. Sorbent Capacity

Oil Viscosity Range (cP)	Organic (g oil/g sorbent)		Inorganic (g oil/g sorbent)	Synthetic (g oil/g sorbent)	
3000-8000	Coconut	18:1	5.5	Flexible collagen sponge	40:1
	Feathers	16:1		Polyamine flakes	15:1
	Cellulose mat	11:1		Polyurethane foam	14:1
	Peat	9:1		Polyethylene pulp	12:1
	Cellulose	9:1		Polypropylene mat	8:1
	Millet	7:1			-
	Average	11.8:1		Average	12.5:1
8000 - 15000	Coconut	18:1	4.5	Flexible collagen sponge	40:1
	Feathers	12:1		Polyurethane foam	16:1
	Cellulose mat	8:1		Polyethylene pulp	14:1
	Cellulose	8:1		Polyamine flakes	12:1
	Peat	7:1		Polypropylene mat	8:1
	Millet	7:1		<i></i>	
	Average	10.3:1		Average	13.8:1
15000 - 25000	Feathers	20:1	*	Polyurethane foam	14:1
	Coconut	10:1		Polyethylene pulp	13:1
	Cellulose	9:1		Polypropylene mat	11:1
	Cellulose mat	5:1		_	
	Average	7.3:1		Average	12.8
25000 - 50000	Feathers	19:1	*	Polyurethane foam	15:1
	Coconut	11:1		Polypropylene mat	13:1
	Cellulose	6:1		Polyethylene pulp	9:1
	Cellulose mat	4:1			
	Average	6.8		Average	12.6:1

Table 3. Sorbent Capacity, cont.

* Could not be tested

In both 1978 and 1985, Environment Canada performed 48-hour immersion tests in which sorbents that showed loss of structural strength were reported to be "weakened." In these tests, the natural fiber sorbent enclosed in polypropylene mesh was found to be weakened in all test fluids; the standard melt-blown polypropylene pad was weakened in crude and Bunker C; and the foam sorbents were weakened in all test fluids. Most open mesh sorbents can be expected to be weakened after a prolonged exposure to spilled oil. Further, when they have become saturated with highly viscous oil, they will tend to sag, tear, or even come apart when they are lifted from the water. Conversely, some sorbent materials, such as pom-poms and snare booms, show no weakening after prolonged exposure to highly viscous oil. As a result, these are popular products for recovering highly weathered crude oils and mousse (Schulze, 1993).

Synthetics have a much higher sorbency ratio than organics, but several issues should be noted. Synthetics are generally much more expensive than organics, and it may not be practical to use them in quantity. Some of the materials tested may not be available

for use in the field (i.e., not available as self-contained for use on water) or not available in commercial quantities. Some of the highest performing synthetic materials, such as polyurethane foam, may not be practical for wide use in the field. Finally, some of the highest performing synthetic materials may present disposal issues.

c. OSPR-Sponsored Scientific Studies

A report released in 2009 as part of the OSPR Scientific Study Evaluation Program (SSEP) evaluated several particulate sorbents as oil spill response tools (Whiting et al., 2009). This study compared ten oil sorbent products made of peat moss, agricultural cellulose, recycled material cellulose, mineral dust, and polymer plastic. They were evaluated for their ability to adsorb and/or absorb Alaska North Slope oil and thereby reduce the immediate and longer term potential of oiling birds and fur bearing animals as well as minimize contamination of shore vegetation. The study resulted in the following conclusions:

- Applying a particulate sorbent material to petroleum-contaminated marsh vegetation and water will immediately render it less sticky to fur and feathers.
- The adherence of crude oil to feathers and fur can be evaluated by "wiping" with feathers and wool pads on oil-treated vegetation and water surfaces.
- Different particulate sorbents likely vary in their effectiveness to absorb spilled oil on marsh vegetation and water and in the ability to reduce the adherence of oil to feathers and fur.
 - d. Spill of Opportunity Sorbent Testing
- There was an effort during the DWH oil spill to field test several types of sorbent and solidifier self-contained products on the spilled oil. The boom brands that were acquired for trial were: Nochar, Imbiber, Rubberizer, CIAgent, bagasse, and kenaf. Pillow forms of sorbent or solidifier products gathered for trial were Rubberizer, SmartSponge, and SheenGuard. These types of products have their greatest efficacy on sheen or thin oils, and some have the advantage of being adaptable for capturing both surface and suspended oil (e.g., in shallow water habitats such as wetlands, or when towed behind a vessel to capture subsurface plume oil), being especially able to absorb (not just adsorb) and retain captured oil without resheening. An additional possible advantage is that some types are reusable.

Several lengths of trial boom were prepared for testing per protocols developed by the Alternative Response Technology Evaluation System (ARTES) team based in the Houma, LA Command Post. Field tests were overseen by ARTES team members or completed by the O'Briens response group. Several attempts were made to find sheen oil offshore or in Barataria Bay, LA, but appropriate sheen or thin oils were not seen or found on any of the several trips made. Eventually, boom samples were deployed in patches of thick oil, but as expected, none of the

experimental boom types worked any better in the thick oil than did conventional sorbent boom. Because conventional pom-pom boom worked best to pick up the thick oil, and it was readily available and relatively inexpensive, its continued use on thick oil was operationally preferable to any further experimental testing of self-contained sorbent and solidifier products.

- During DWH, sorbents were also used to partially line nets being towed through the subsurface plume of oil, in part to sample the oil in the upper water column and in part to determine if this would prove to be an additional use of sorbent pads and pillows to capture some of the dispersed oil that was still entrained in the upper water column. While it provided a useful oil sampling tool, towing sorbent-lined nets through the upper water column to collect oil was not considered by the UC or conducted any further as part of this response.
- The Shoreline Cleanup Assessment Technique (SCAT) leaders during Deepwater Horizon received permission from the RRT VI to conduct a limited test of several types of loose natural sorbent materials (e.g., peat, bagasse, kenaf), blown onto oiled marsh vegetation, to determine what might work best to reduce the contact stickiness of oil to nesting birds. While there were some conclusions reached about the most effective product, chop size, and application methods, there was no subsequent large-scale application of loose sorbents to oiled marsh vegetation.
- There were several requests of the RRT VI and the UC to allow aerial application of large amounts of bagasse (a plant product) to oiled and unoiled shorelines in Louisiana. However, permission to do so was refused by both the RRT VI and the UC due to potential environmental concerns (e.g., hazing of wildlife, smothering of unoiled vegetation, and inability to retrieved oiled bagasse) that outweighed the response benefits.
 - e. Sorbent Product Forms and Configurations

Sorbent products are available in a great many forms, including 1) roll, sheet, pad, blanket or web, 2) loose, or 3) particulates or foam enclosed in boom, sock, pillow or other similar fabric or web-bound constructions, or strips bound into sorbent pom-poms to act as "sweeps." Although all sorbents use the same mode of action (sorption), the delivery method becomes an important factor in sorbent effectiveness when the sorbent is used in a self-contained form.

Some of the previous tank tests of sorbent boom (Schrader, 1991) on diesel, light crude and heavy crude oils showed that the booms sank somewhat as they sorbed oil. Booms containing folded or rolled sheets had a lower surface area than the particulate or shredded material and produced less wicking. Additionally, the denser outer surface of the rolled sheets inhibited penetration of more viscous oils. The packing of shredded materials was found to be important to the performance of the booms. Loose packing causes segmentation in the booms, allowing free oil to flow through open channels. After extended use, sorbent boom that is towed may sorb four to eight times its original weight in water. As water sorption increases, the ability of the boom to sorb oil decreases. The particulate boom may pick up oil more quickly at first, but it may become ineffective after a short time because of water saturation. Further, tears in the casing of particulate boom may release sorbent particles, requiring additional cleanup. Rolled foam boom takes up less water and is more durable, but does not sorb oil as well. Sorbent boom may not be effective in mousse or with oil-soaked debris (Potter, 2013).

Criteria for selecting sorbents for a particular use may include consideration of 1) how oleophilic and hydrophobic the product is, 2) rate of sorption, 3) surface area, 4) buoyancy, 5) oil retention, 6) reusability, 7) ease of retrieval, 8) disposal options, 9) storage, and 10) cost.

f. Recycling and Waste Disposal

One of the major disadvantages of using almost any sorbent material is the large amount of both solid and hazardous waste that is generated. In the *Exxon Valdez* spill, where only four percent of the spilled oil was recovered, approximately 33,000 tons of oily solid waste was generated (Carpenter et al., 1991). As stated previously, since oil is often defined as hazardous waste, any sorbent coated with oil (even a sorbent considered biodegradable) may also be considered hazardous waste.

One way to reduce hazardous and solid waste generation would be the continued development of reusable sorbents. Although many synthetic sorbent pads can currently be reused, the process of removing the oil from the sorbent can be cumbersome, making reusability more frequently a perceived rather than a real benefit. If wringers and storage containers for released oil are not widespread and immediately available, the reuse benefit is forfeited. Repeated handling of oiled sorbents may pose hazards to workers that need further evaluation. Certainly, improvements in the process could greatly increase the efficiency and potential utility of reusable sorbents as part of cleanup operations.

- 2. Surface Washing Agents
 - a. Surface Washing Agent Overview

The principal use of surface washing agents (also sometimes referred to as beach cleaners or shoreline cleaning agents) is to lift stranded oil from surfaces (primarily oil stranded in intertidal areas or on constructed surfaces) and transfer it back <u>onto</u> the water surface where it can be recovered by on-water recovery methods. These agents should not act to further disperse the oil <u>into</u> the water (Clayton et al., 1993; Clayton, 1993). The following three types of chemical treating agents can potentially be used for cleanup of shorelines and other hard surfaces (e.g., rocky rip rap, pier pilings, ship hulls) (Clayton, 1993; Walker et al., 1999):

- Non-surfactant-based solvents;
- Surface-active agents (products containing surfactants, additives, and solvents, and formulated specifically to remove oil from substrates and prevent oil redeposition), and;
- Chemical dispersants specifically formulated for shoreline cleanup rather than offshore use. (However, California does not license any type of chemical dispersant for use as a surface washing agent).

The non-surfactant-based solvents used historically were primarily petroleum-based distillates, similar to kerosene or vegetable oils, which had enough aromatic compounds to be toxic to biota. They are not used today.

The products with surface-active agents can be further divided into two categories: those that <u>lift and disperse</u> oil into the water column, and those that <u>lift and float</u> the oil onto the water surface where it can be recovered. Only products that provide lift and float action are licensed for use in California.

Presently, there are two surface washing agents licensed for use in California (CytoSol, Accell Clean SWA).

b. Efficacy

The effectiveness of a surface washing agent may depend on many factors (Walker et al., 1999):

- Properties and chemistry of the spilled oil;
- Composition of the cleaning agent;
- Type of substrate that is oiled;
- How the agent is applied;
- Ratio of the amount of agent used to the amount of oil to be cleaned;
- Air temperature;
- Water salinity;
- Time required for "soaking" before wiping down oiled surfaces or flushing with water; and
- Field treatment parameters including flush water volume, pressure, and temperature.
 - i. Efficacy Testing in Advance of a Spill

Laboratory testing of surface washing agents demonstrates that several have good effectiveness. Environment Canada (Fingas et al., 1991) and the U.S. EPA (Walker et

al., 1999) conducted tests of several products on the NCP Product Schedule (Corexit 9580, PES-51, CytoSol), using slightly weathered crude oil on a stainless steel substrate, and found effectiveness ranging from 33-53% removal when compared to water alone.

It can be difficult to conduct lab-based efficacy testing of surface washing agents (Clayton, 1993) and as a result neither the EPA Product Schedule nor OSPR OSCA licensing requirements currently require (or offer a protocol) for lab-scale efficacy testing of surface washing agents. This may change when the EPA finalizes its updates to the federal Subpart J Product Schedule listing regulations, and OSPR is likely to follow with updates to its state licensing requirements that will mirror the federal requirement. The surface washing agent efficacy protocol may be based on earlier protocol update work conducted by EPA staff (Koran et al., 2005; Koran et al., 2009).

ii. Efficacy Testing as a Result of a Spill

Field trials and spill-of-opportunity testing and use have provided additional information to supplement the laboratory tests. A few are listed here:

- PES-51 was tested and compared to hot-water flushing to treat a fuel-oil spill on a cement walkway during the 1991 *Bouchard 155* spill in Tampa Bay (Walker et al., 1999). Hot-water washing was determined to be as effective, so product was not further used.
- Corexit 9580 was tested on riprap coated with crude oil from the 1994 San Joaquin River spill in Texas. Cleanup was considered effective (Michel et al., 2001).
- Corexit 9580 field tests in 1989 and 1990 showed effective oil removal from oiled mangrove roots and *Spartina* plants, preventing mortality (Walker et al., 1999).
- Corexit 9580 was tested on *Spartina* plants oiled with IFO 180 following the *Julie N* spill Portland, Maine. Product was tested on vegetation that had been oiled 9 days before and combined with a 15 minute soak time, followed by low-pressure flushing with ambient water. Visual observation showed evidence of 40-50% oil removal from the top sides of plants, but oil remained on the bottom sides of the plants and it appeared that the released oil was not immediately recoverable from the surrounding water (Walker et al., 1999).
- PES-51 and Corexit 9580 were tested on natural beach rock and man-made structures following the 1994 *Morris J. Berman* spill of No. 6 fuel oil. Both proved more effective than water alone in removing the oil, with Corexit 5980 slightly more effective than PES-51 (Walker et al., 1999).
- PES-51 was tested in 1993 on a cobble/gravel shoreline in Prince William Sound, Alaska, on residual oil from the *Exxon Valdez* spill. Treatment was considered effective and subsequently used to remove residual oil from important subsistence areas around a native village (Walker et al., 1999).

- Surface washing agents were used during the DWH spill, both in cleaning oiled boom, boats and other mechanical equipment, and in shore-based sand washing systems.
- CytoSol has been used in California in several spills: to clean oiled river rock (Kyberz River spill), in pilot testing with other surface washing agents during the 2007 *Cosco Busan* oil spill (Payne et al., 2008), and for cleaning rock within a dry creek bed (2016 Grove Incident).
 - c. Environmental Considerations

PES-51, tested as a beach cleaner in Florida, Alaska, and during the DWH spill, cannot presently be licensed in the state due to having a product flash point below the required temperature of 170° Fahrenheit.

Corexit 9580 was demonstrated in earlier tests in Prince William Sound, Alaska, to be an effective beach cleaner when used with high pressure wash water. This product was reported to produce minimal dispersion of oil in the Alaskan tests and exhibited low toxicity to marine animals (Fiocco et al., 1991). The product was again used in the 1994 *Morris J. Berman* Spill, in Puerto Rico, with mixed results. In the Puerto Rico application, Corexit 9580 was relatively effective in removing stranded oil when used with heated high pressure wash water, but the product readily dispersed the removed oil into the receiving water. Corexit 9580 is listed as a surface washing agent on the U.S. EPA's National Contingency Plan Product Schedule but has not been licensed for use in California.

Recommended uses of a surface washing agent will depend on the oil spill environment (e.g., land, moving water, still water, surface oil, buried oil) and whether or not the surface being cleaned has living organisms attached to it. Some general considerations should include:

- Protect the area surrounding the treatment zone with hard and/or sorbent boom, to allow capture and recovery of re-surfaced floating oil.
- Use spray-on/wipe-off application approaches whenever possible to minimize runoff (may not require RRT IX or OSPR Administrator approval if no runoff).
- Mix product with ambient water, at recommended dilution (application at stronger than recommended concentrations may change product behavior).
- Use with low-pressure flooding and/or cold or warm water may be safe in most cases, even on surfaces with attached living organisms (e.g., intertidal cobble, pier pilings). Using with high-pressure or hot water should be limited to areas where there are no attached living resources (e.g., ship hulls and equipment cleaning, seawalls and rip rap above high tide line). Depending on spill location, this use will require RRT IX and OSPR Administrator approval.
- Using for in-situ beach sand cleaning can be considered if catchment trenches

or pools are established and floating oil is recovered. Depending on spill location, this use will require RRT IX and OSPR Administrator approval.

- Surface washing agents can be used ex-situ (e.g., in pools, roll-off bins, truckbased systems, constructed sand-washing structures) without additional RRT IX or OSPR Administrator approval for the <u>product</u>, although additional permissions from other agencies may be necessary (e.g., for heavy equipment access to beach, creation of temporary facility pad sites). State Water Board rinse water quality and other discharge thresholds and conditions will apply.
 - d. Operational Considerations

The first beach cleaners were primarily non-surfactant petroleum-based solvents, typically highly toxic. For this reason, they are no longer accepted as beach cleaning agents.

Chemical dispersing agents, designed to disperse on-water oil spills, are also not considered good beach cleaning agents as they disperse oil into water, which leads to additional contamination in the intertidal region (i.e., allowing oil to penetrate below the intertidal surface). Further, Title 23 of the California Code of Regulations prohibits the use of dispersants on shorelines.

Surfactant-based products have been specifically designed for beach cleaning. This type of product is designed to lift spilled oil off intertidal substrate and allow the oil to coalesce at the water's surface where it can be collected. The actual rate of mobilization of oil from intertidal substrate will depend on the type of oil spilled, the state of oil weathering, and the air and water temperatures. Chemical beach cleaning agents can be used alone (oil removal results from wave energy), applied with mechanical beach washing equipment, or used with high pressure washing equipment.

e. Other Issues

When truck- or facility-based systems are used for cleaning, oily sand is removed from the beach by earth moving equipment and deposited into the sand cleaning machine. The machine (which may just use warm water, or warm water plus a cleaning agent), strips the sand of oil, takes it through a series of rinses, and then the cleaned sand is removed and stockpiled in the high intertidal until time to replace it on the original beach. The process, though it cleans the contaminated sand, also destroys the biological community present in the excavated beach material (although it can be argued that those resources would also be lost if the sand was excavated for disposal, or left in place but not cleaned). Once clean sand is placed back on the beach, and nearshore waters recovered, sandy beach intertidal infauna should be able to "re-inoculate" using the eggs and larvae from nearby un-oiled beaches and waters. The disadvantage of this process is that heavy equipment and/or facilities will be on or near the impacted beach, and if not used and staged properly, risk tracking oil over clean beaches or driving oil deeper into already oiled beaches. This risk can be minimized

through proper planning. The advantage of onsite truck or facility based sand cleaning is that the sand is more thoroughly cleaned, and as opposed to excavation of sand for disposal, this process returns clean sand of identical grain size, color and type to the beach of origin.

Ex-situ cleaning of oiled sands might not be necessary if the beach is lightly oiled, or there is sufficient normal wave action to agitate the sand and allow the oil in it to naturally degrade. However, heavily oiled beaches, or beaches were the oiled sand has become buried in layers not subject to re-mixing and aeration by waves, might be good candidates for a more focused sand cleaning operation.

The greatest limit to further use of surface washing agents is the general perception that they are "chemicals" being used on or near sensitive shoreline resources. They can be mistaken for or perceived as dispersants. However, the two products currently licensed by California as surface washing agents are bio-based, are considerably milder than the detergents we commonly use (even for washing oiled wildlife), are safely used in the agriculture and dairy industries to wash edible produce and animals, are safe to use (as instructed) on oiled surfaces, and would allow for release and recovery of oil that might otherwise become buried or stranded. They can work on weathered oil but work best on fresh oil on warm days. Used ex-situ, they can provide better cleaning of sand and cobble that cannot be cleaned as well in-situ and may also allow for quantification of the removed and recovered oil.

- 3. Solidifiers/Elasticity Modifiers/Gelling Agents
 - a. Solidifier/Elasticity Modifier/Gelling Agent Overview

Solidifiers turn oil into a more cohesive or solid mass. They are usually available in dry granular form (Walker et al., 1994) for use either in a loose and broadcast form, or as a more easily recoverable self-contained product (e.g., boom, sock, pillow, pad). Unlike sorbents that physically soak-up liquid, the solidifiers bond the liquid into a mass with minimal volume increase. When the product is used in a self-contained form, the oiled mass is easily recovered. The bonded material also eliminates dripping (common with sorbents) and thereby minimizes re-sheening, residue, or cross-contamination of otherwise unoiled areas. Some types of solidifiers can convert the oil to a rubber-like substance, although the reaction of these types of solidifiers is not reversible. There is minimal volume increase and little change in the specific gravity of the treated oil (Walker et al., 1994).

Gelling agents, a sub-class of solidifiers, are usually two or more compounds applied as separate products that react with each other and the oil to form a gel-like structure (Walker et al., 1994). Products are composed of polymerization catalysts and cross-linking agents (Fingas et al., 1991) and must be mixed uniformly for gelling to occur. The mechanical strength of gels is weak, thus they can be broken down and the oil returned to its original liquid state.

In the early 1970s, the U.S. EPA and Exxon conducted research on the potential use of solidifiers for vessels in eminent danger of sinking or breaking up but which still contained most of their oils (Walker et al., 1994). The strategy was to solidify the oil in the holds of the vessel to prevent release to the water. Esso Research also studied the use of gelling agents for immobilizing oil in tankers (Corino, 1970; Fuller 1971). Several limitations (Walker et al., 1994) were identified with the use of solidifiers in this manner:

- Difficulty associated with uniform mixing of the product and oil in large tanks;
- Vessel accessibility;
- Access to all necessary injection and pumping equipment;
- Amount of product needed (ranging between 10 40 percent of cargo).

The state currently has one licensed liquid gelling agent (Elastol) and two particulate solidifiers (ClAgent, ClearTec Rubberizer). Elastol and ClAgent are also on the NCP Product Schedule. ClearTec Rubberizer was reviewed by EPA and given a sorbent exemption. Only the ClearTec Rubberizer does not need any further RRT IX approval before use in a self-contained form, although as with any sorbent or particulate solidifier product, use in a loose and broadcast form is limited and would require RRT IX review and authorization before use.

The OSPR Administrator issued a Pre-Approval for solidifiers used in a self-contained form. CIAgent and ClearTec Rubberizer are the only two solidifying products that come in a self-contained form for use on spills to, on, or near open waters. Those are the two products that can currently be used without an incident-specific OSPR Administrator approval. CIAgent, although pre-approved by the state for use in self-contained form, still requires incident-specific RRT IX approval before use.

Both CIAgent and ClearTec Rubberizer are impressive in their ability to capture and retain oil. Both products come in a variety of boom diameters and pillow forms and would have greatest utility on spills of light-medium oils, sheens, upper water column capture of suspended oil, in sensitive habitats (marshes, wetlands, mudflats) for collection of re-sheening oil, and for secondary containment and capture of oil in created sandy beach trenches or dry creek beds.

A liquid agent can be used in an otherwise contained structure (e.g., leaking storage or vessel tanks), but additional approvals may be needed if it cannot be assured that any product + oil leaking from the tank breach can be subsequently contained and recovered (since a gelled oil is structurally weak, it may be difficult to recover mechanically once it gets onto water). Use of liquid gelling agents may therefore be very limited for on-water oil spills.

Both the RRT IX and the state have restrictions on the use of any particulate solidifier when used in a loose and broadcast form, as subsequent recovery of the loose solidifier

can be problematic. Use in this manner would therefore need incident-specific approval from both the RRT IX and the OSPR Administrator (if use is on, in, or threatening state waters). Use of loose particulate forms of solidifiers, even within an area confined by containment boom, is currently seen as an unlikely use on open-ocean oil spills, although it may find greater future acceptance for use in smaller, calmer and more controllable spill settings (e.g., shallow waters of marshes and harbors).

b. Efficacy

The effectiveness of a solidifier is based on the amount of product and time it takes to "fix" a given volume of oil. The less effective products require larger amounts to solidify oil. Between 13 and 44 percent by weight of the product was required to solidify Alberta Sweet Crude over a 30 minute period (Fingas et al. 1993). Fingas also found that the laboratory-measured rates are much higher than the manufacturer recommended application rate. In one large scale field test, double the laboratory-measured rate was required to solidify the oil. Effectiveness is likely to decrease for emulsified, weathered, thick, or heavy oils due to difficulties in mixing (Walker et al., 1994).

c. Environmental Considerations

Walker et al. (1994) reported that solidifiers have relatively low toxicity or no toxicity. The primary environmental concern is the fate and secondary effects of (1) treated but unrecovered oil and (2) unreacted product. Though it appears that solidifiers biodegrade slowly, they were unable to evaluate the ultimate fate of product residue in the environment with the data available at the time. Some products may even be considered a micro-plastic; unrecovered product could pose a persistent presence and long break-down period in the receiving environment. There is also an untested concern that some products, used loose, could be perceived by birds or fish as food. Ingestion of particulate solidifiers, even if non-toxic or not covered in oil, could give the fish or bird a sense of fullness that could lead to starvation. Because many species of fish and seabirds normally reject indigestible materials, ingested flakes of solidifier would not be expected to cause adverse health effects unless consumed in large amounts.

Secondary environmental concerns of using a solidifier in a loose and broadcast form are related to (1) physical disturbance of habitats during application onto stranded oil and (2) smothering. Workers would have to enter the treatment area twice - once to apply the product and again to recover the solidified oil. Repeated foot traffic likely disturbs soft substrates, which are characteristic of important mudflat and marsh habitats. Extreme care would be needed to prevent trampling of vegetation and epifauna. At the recommended application rates, large amounts of the product would have to be applied to shorelines. The product alone could smother intertidal fauna and flora (Walker et al., 1994).

d. Operational Considerations

In general, the two most important limitations to the wide-scale use of solidifiers are the potentially large amount needed of a liquid or loose/particulate form and the inconsistent application rates or mixing that can result in solid, semi-solid, and liquid oil (Walker et al., 1994). Some liquid products on the NCP Product Schedule and available for FOSC consideration for spills in federal waters require the mixing of two or more components. This could prove to be almost impossible for large, uncontrolled, on-water spills. Fingas (1992) raises several issues on the open-water utility of liquid/loose solidifiers and gelling agents:

..."how does the solidification actually help the situation? Solid oil is more difficult to recover than liquid oil. Skimmers and pumps can only handle liquids. Furthermore, oil on the sea surface rapidly becomes increasingly solid - and this is considered to be a problem and not a solution. Research on open-water solidifiers does not appear to offer benefits."

Some product manufacturers contend that gelled or moderately solidified oils can be recovered by mechanical skimmers and may even impart a cleaning action to a brush skimmer, but this claim needs to be better tested and supported. There also needs to be further demonstration of whether gelled oil can be effectively pumped out of the skimmer recovery tank. It is expected that fully solidified oil left on the water surface as mats may have to be recovered by hand-raking rather than mechanical skimmers, and for smaller spills or within otherwise boomed areas, this may be possible if water conditions are safe and manageable.

Use of the solidifier in self-contained form does not pose the same collection concerns, which is why they are preferred. Oiled solidifier boom or pillows attached to a line can be easily retrieved using conventional equipment and strategies. Some manufacturers say their products can be wrung out and re-used, or oiled boom can be burned as fuel.

- e. Pilot Projects and Pre-Approvals
 - i. Navy Pilot Project

On June 1, 2007, the RRT IX issued "Policies and Procedures for the Pre-Approved Use of Loose Particulate Form of Licensed Solidifying Agents for use by the Navy in San Diego Bay." This pre-approval was instituted for a one-year period, with the possibility for extension. Conditions of the pre-approval were that the solidifying agent was to be licensed by the state and either not require listing on the NCP Product Schedule or be listed on the Product Schedule as a solidifier. Loose products could only be used within the confines of a boom, in accordance with approved application methodologies and as monitored by CDFG personnel. The Navy was to report back on the amount of oil estimated spilled, how much solidifier product was used to treat the spill, the effectiveness of treatment, ease of deployment, ease of removal, and any

additional concerns or factors. There is no record of any subsequent use of this preapproval on any Navy spills in San Diego Bay.

ii. Lake Tahoe Marina Operators

Starting May 23, 2007 and ending September 23, 2007, the OSPR Administrator issued "Policies and Procedures for the Pre-Approved Use of Sock and Boom Form of Licensed Collecting Agents for use in Lake Tahoe." Pre-approval guidelines stipulated that a collecting agent could be used if 1) it was licensed by the state and did not require listing on the NCP, 2) the IC/UC would ensure that all products were used

consistent with the guidelines, and 3) CDFG personnel would monitor cleanup operations. There is no record of if or how this pre-approval was implemented.

Spill responses in harbors and marinas are not always under the direction of the IC/UC or monitored by CDFW. Rather, the harbor or marina operator provides the response resources and oversight and may not have the same response reporting requirements. Actual use of this pre-approval may have gone un-noted.

iii. State Pre-Approval for Solidifiers in "Self-Contained" Form

On September 2, 2001, the OSPR Administrator issued "Policies and Procedures for the Pre-Approved Use of Sock and Boom Form of Collecting Agents for use in Waters of the State." For the purposes of this pre-approval, a collecting agent was defined to include both sorbents and elasticity modifiers (e.g., solidifiers). The Pre-Approval was initially instituted for a period of one year, ending September 1, 2007, with re-evaluation by the Administrator after that date to consider extension. There has been no subsequent OSPR Administrator action to suspend or revoke this pre-approval.

Similar to the Lake Tahoe pre-approval, the OSPR Pre-Approval guidelines stipulated that a collecting agent could be used if it was licensed by the state and did not require listing on the NCP, could only be used in a self-contained form such as boom, socks or pillows, the IC/UC would ensure that all products were used consistent with the guidelines, and CDFG personnel would monitor cleanup operations.

Spill responses that use exempted or pre-approved products cannot be expected to have the same response reporting requirements as other responses with other product uses. Actual use of this pre-approval may be largely unreported. However, if the other Pre-Approval conditions are met (i.e., use of a licensed product in self-contained form, removal after use), a lapse in reporting of use may result in a lack of observational data but not an adverse environmental outcome. This argues for keeping the OSPR Pre-Approval in place.

- f. Other Issues
 - i. Liquid

The operational considerations discussed above suggest little foreseeable on-water use of liquid oil gelling agents. Recovery of gelled oil may pose problems for mechanical skimmers, and the gelled mass may not have enough rigidity or integrity to be raked and removed by hand. Wave-tank testing of the ability by mechanical skimmers to recover gelled oil, without harm to the skimmers, could lead to greater future consideration of liquid gelling agents for on-water spills.

The possibility of using of liquid gelling or loose solidifying agents in a ruptured vessel or tank is also unlikely for several reasons. If the rupture is at or below the water line or allows escape of gelled product to open water, it might elude subsequent capture. A lack of capacity in the ruptured tank may prohibit the addition of the required large volume of gelling or solidifying agent. The agent needs to be thoroughly mixed with the oil, which could be problematic within deep and confined spaces. If the agent + oil were able to successfully bind, then the resulting solid or semi-solid mass may not be extractable, leading to loss of the vessel.

On-land use of a gelling or solidifying agent within a tank or other confined space that is <u>not</u> leaking to water does not require use of a product on the NCP Product Schedule or licensed by the state, nor does it require any RRT IX or OSPR Administrator approvals.

ii. Loose Particulate

Although several limitations to use of loose particulate solidifiers have been identified, there may be certain instances where they could fill specific on-water response functions. Because they react with the first oil they contact, they could potentially be used as a self-creating barrier, although the integrity and recoverability of this solidifier-based barrier has not yet been demonstrated. Future wave tank testing could test the integrity of solidified oil edges under various swell heights and time periods, to help determine whether this use of solidifiers provides any improvement over mechanical containment boom.

iii. Self-Contained Particulate

Use of solidifiers in self-contained form may provide advantages over the use of conventional sorbent products and, if so, should be more broadly considered and used in marine and inland spill response environments. They are claimed to be more effective than many conventional sorbents, do not allow dripping or re-sheening of oil, can be reused, work in a variety of otherwise sensitive or hard-to-reach environments, and help minimize the considerable amount of sorbents that become part of the oil spill response waste stream.

Self-contained solidifier products are more expensive than conventional sorbent boom and pads, and there is no regulatory incentive for Oil Spill Response Organizations (OSROs) to make them part of their inventory if they cannot demonstrate greater efficiencies or other benefits. However, response agencies (especially USCG, EPA and OSPR) should become more familiar with the various potential utilities of self-contained solidifier products. If it is decided that use of a self-contained solidifier product provides additional benefits to a response than conventional sorbents (i.e., providing a Best Achievable Technology for a given response), then the agencies can specifically ask for their use in specific marine or inland spill responses. Spill response equipment trailers, especially those placed at harbors, marinas, and lakes, should consider stocking some self-contained solidifier for a more effective response to the more common light-end spills (e.g., gasoline, diesel) and sheens.

- 4. Herding Agents
 - a. Herding Agent Overview

Spilled oil spreads out very quickly to form thin films or slicks several microns to tenths of a millimeter thick. This thinning makes it difficult to contain and collect the oil by either mechanical means or to support ISB.

Chemical herding agents work by exerting a spreading pressure on the water surface greater than the oil slick. The spreading pressure that a specific product can exert is based on the degree to which it can reduce the interfacial tension of the water (Walker et. al, 1994). This action is created through the interaction of the oleophilic (oil-soluble) and hydrophilic (water-soluble) portions of the chemical with the environment. When a herding agent is applied to the water surface, it arranges itself similarly to the configuration of a cell membrane. The water-soluble component of the molecule aligns itself with the water and the oil-soluble group aligns itself with the air.

When used in conjunction with conventional containment and recovery devices, herding agents help prevent oil from spreading (Dewling and McCarthy, 1980). Optimal uses of herding agents include controlling slicks under docks or piers where conventional equipment cannot reach and in harbors where the equipment can be pre-staged and ready to use early in the spill (Walker et al., 1994). Also, herders may be effective in keeping shallow water slicks pushed away from contacting sensitive marshes. Herding agents are not a substitute for booms but may be used for <u>short-term</u> protection and enhanced recovery where deploying booms could cause more damage or be of limited effectiveness (Walker et al., 1994).

The use of surface-active agents to control oil slicks on water was first reported by Zisman (1942) who studied their use during World War II to push burning oil away from tankers (Walker et al., 1994). Herding agents were used in Hawaii in the 1970s on diesel spills in harbors. They have been tested by researchers at Warren Springs Laboratory (Nightingale and Nichols, 1973) and used at various spills. An oil herder was used to prevent oil from contacting a marsh where the water was too shallow to

deploy conventional boom (Walker et al., 1994). More recent studies (Buist et al, 2010; Buist and Meyer, 2012; Buist et al., 2013; Lane et al., 2012; S.L. Ross, 2015) have evaluated the use of next-generation chemical herders to thicken oil slicks (as an alternative to containment with fire boom) for ISB operations in icy Arctic waters. Lessons learned related to open-water use of herders, or for use on spills in icy lakes, will have research value for California response.

The herding agent developed and used by the Navy in the 1970s had a hydrocarbonbased surfactant as the active ingredient. The next-generation herding agents were developed with fluorosurfactants and silicon-based surfactants (Buist et al., 2010). Labscale tests in 2007 and 2008 on the suitability of these new herding agents for thickening oil slicks in or near drift ice for ISB demonstrated that the fluorosurfactantbased herder did not perform significantly better than the hydrocarbon-based herder developed by the Navy. The silicone-based surfactant herder initially produced higher herded slick thicknesses, but these thicker accumulations declined after one hour to about the same level as the Navy herding agent.

Additional experiments in 2009 (Buist et al., 2010) continued to explore the use of oilherding agents as an alternative to booms for thickening slicks in drift or broken ice. These tests used three new silicone-based surfactant herder formulations in small-scale test pans and in larger-scale lab settings. One of the newer silicone surfactant formulations (Silsurf A004-UP) significantly outperformed the Navy herder. The presence of frazil ice restricted the oil from spreading, and the effectiveness of the herder and short, choppy waves in the test tank caused a herded slick to break into small patches. Longer, non-breaking waves did not appear to cause the herded slick to break up, and may have instead helped by promoting the spread of the herder.

The exigencies of oil spill response in the Arctic, where the delivery and use of conventional containment and fire boom to cause thickening of oil for an ISB operation, make the continued development of oil spill herders (which can be more immediately applied to an oil slick via helicopter) an interesting research avenue. There may be limited use for chemical herders in a California oil spill response except in those situations discussed above.

There are currently no chemical herders licensed by the state.

b. Environmental Considerations

Herding agents are applied directly to the water surface and not to the oil. They do not disperse the oil or increase its solubility. Thus, the greatest environmental risk is the aquatic toxicity of the product to neustonic organisms (those in the top 2 centimeters of water) and contact toxicity to intertidal vegetation. Acute toxicity of these products (e.g., 2.0 - 2.5 ppm) is of concern only under special conditions, such as in very shallow waters with limited flushing rates and abundant organisms in early life stages. Currently, there are no data on the contact toxicity of these products to vegetation.

c. Efficacy and Operational Considerations

Herding agents are applied in small quantities (2.5-35 liters per linear kilometer) to the perimeter of a slick. Application is by spray systems which are hand-held, vessel-mounted, or mounted in fixed-wing aircraft or helicopters. Walker et al. (1994) identified the following important operational considerations for use of herding agents:

- They are most effective on low viscosity oils. Thus, for crude oils, they should be used soon after release, prior to any weathering or emulsification that increases the oil's viscosity;
- The practical limit of application is for small, confined areas, up to a maximum of several kilometers in length;
- Herders are more effective on thin films;
- The very small application rates are difficult to achieve;
- The neat agent should not come into contact with operational parts of oilrecovery devices because it will repel oil away from them; and,
- Weather and sea conditions are limiting factors.

Heavy rains can break the surface film and reapplication may be necessary. Winds greater than 3 meters/second and breaking waves significantly reduce operational effectiveness (Nagy, 1973). Temperature does not seem to affect agent performance, although solidification in the application device may occur if temperatures are below the pour point (Pope et al., 1985).

Even under favorable conditions, achieving proper application can be problematic (Walker et al., 1994), although recent tests in the Arctic with aerial application seem positive. More herding agent is not always better, and over-application can result in decreased effectiveness or negative effects. In fact, improper application can push oil away from recovery devices, and if the product contacts sorbent materials, the oil will be pushed away from the sorbents as well.

d. Other Issues

Use of chemical herders for a California offshore oil spill response may be limited until herders are developed that can herd and sustain a slick under open-ocean conditions of large waves and swells or heavy chop. These are the conditions under which the use of conventional containment and fire boom also become problematic. If seas are sufficiently calm to support use of herders, they will also be able to support the use of conventional fire boom. A distinct advantage to the use of herders to contain oil is that they can be aerially applied to an offshore oil slick, used early while the slick is still relatively small, periodically reapplied to maintain the slick boundaries, used instead of fire boom or until fire boom arrives, and does require an on-water ISB burn team that would be subject to any ISB particulate exposures. On-water personnel would still need

to be on hand ready to collect any recoverable burn residue, and the need for wildlife, SMART and air monitoring teams prior to and during a burn operation would need to be addressed, as they would for any ISB operation.

As mentioned above, the other potential for use of chemical herders in California spill response settings is to assist with oil and sheen recovery from areas with difficult access (e.g., under docks and around pier pilings) or adjacent to sensitive habitats (e.g., marsh, wetland, mudflats) where use of other mechanical and hand removal methods would be too damaging.

- 5. De-Emulsifiers
 - a. De-Emulsifier Overview

One potential approach to extending the window of opportunity for the use of dispersants or ISB is through the application of de-emulsifying agents. The employment of these agents would at least theoretically depress the formation of water-in-oil emulsion, or break an existing emulsion, allowing for the extended application of dispersants.

De-emulsifying agents have been developed by the oil industry to prevent the formation of emulsions or to break water-in-oil emulsions developed during the initial extraction of crude oil from the ground. Though de-emulsifying agents have been used in oil production for many years, there is little information on their use during on-water oil spill response.

b. Efficacy and Operational Considerations

Walker et al. (1994), after reviewing the available literature of that time, identified three emulsion treating agents (Vytec, Gamlen EB 439, and Breaxit OEB-9) from throughout the world whose performance and environmental effects had been examined primarily through laboratory testing. It is difficult to compare the performance and environmental effects of the three agents because standardized efficacy and toxicity tests were not employed during the product testing. Moreover, laboratory tests may not accurately reflect actual conditions in waters affected by a spill.

Two agents, Alcopol and LA 1834, were reported by their manufacturers as effective deemulsifiers (Walker et al., 1994). Several countries (e.g., Norway, France, United Kingdom, and Canada) conducted some research into the development of less watersoluble de-emulsifying agents (Walker et. al., 1994).

Also in the 1990s, a research emphasis focused on burning of water-in-oil emulsions, as burning of oil from the *Exxon Valdez* spill was limited (Allen, 1991). Research in North America, Canada, and Norway (Cooper et al., 2013) investigated burning of emulsified oil slicks on open water and within ice in various environmental conditions, including waves. The principal conclusions were as follows:

- Emulsified water content in excess of 25%, for most crude oils, will preclude ignition, although very light crude oils that do not form a stable emulsion may be burned as long as water content is less than 60%;
- Burn rates and efficiencies decrease as water content increases;
- Wave action makes ignition more difficult, slows the burn rate, and increases the thickness of burn residue.

Research was also conducted to investigate the use of de-emulsifiers, prior to ignition, to enhance burning (Buist et al., 1997). New formulations were also developed for use in a Heli-torch to improve ignition. Enhancements included the following:

- Use of fresh crude oil instead of gasoline to provide a hotter ignition flame;
- Adding de-emulsifier to the igniter fuel to ignite emulsions with water content greater than 25%;
- Adding anti-foaming agents to suppress foaming of burning emulsions.

There was a successful offshore field test in the UK using an emulsion-breaking igniter, with evaporated crude containing 25% emulsified water (Guénette and Thornborough, 1997).

More recent research on the possible use of de-emulsifiers to extend the window-ofopportunity for ISB (Cooper et al., 2013) was conducted in response to research objectives identified as part of the DWH spill. In that spill, ISB was used extensively and successfully to eliminate a considerable amount of oil. Those burning operations were successful because the continuing subsea release created a continuous supply of relatively fresh and un-emulsified oil for burning. However, oil burning in other types of spill scenarios could be faced oil becoming less combustible as it becomes more weathered and emulsified. In that response setting, de-emulsifiers might be recommended as a means to extend a burning operation on a contained oil slick. Lab and wave-tank tests (Cooper et al., 2013) looked at three oils (6.5% evaporated Endicott crude, 11.6% evaporated Endicott crude, Hibernia crude) and one deemulsifier (Alcopol). Emulsions in each type of oil were created up to 25%, 50%, and 60% water content. Small amounts of each emulsion were placed within floating containment systems on the surface of a wind/wave tank, and de-emulsifier was added dropwise onto the surface of each slick. Samples were taken from each slick over a period of an hour (runs were extended up to 24 hours in some cases), analyzed for water content, and subjected to various ignition and burn tests under various wave regimens. Following are the wave tank results:

- Waves had minimal impact on emulsion breaking;
- There were some promising indicators in some of the test runs using 60% water

content emulsions and low dose de-emulsifiers, as well as two higher wave energy runs. However, emulsions exposed to higher mixing energies also readily broke;

- There were good outcomes for the 50% water content emulsion tests that used lower doses of de-emulsifier, with some differences seen dependent upon the parent oil used;
- The emulsions with the 25% water content gave the best results;
- Burn tests with the Endicott crude 6.5% evaporated, subjected to wave tests (deemulsifier) did not show much improvement over baseline;
- Better results were achieved with Endicott crude 11.6% evaporated and the Hibernia crude; results indicated that the de-emulsifier was starting to have a positive impact in breaking the emulsion, but the right mixing energy may not have been imparted during the wave tank tests;
- Additional testing to evaluate if higher wave energy would be sufficient to increase the positive impact of the de-emulsifier, and to determine the impact of additional parameters (such as wind), was recommended.
 - c. Other Issues

A significant obstacle in the use of the de-emulsifying agents is product availability. None of the agents tested more than two decades ago were off-the-shelf products (Walker et. al., 1994). Problems with the commercial availability of tested and suitable de-emulsifier products continue today. There are no de-emulsifiers listed on the current (2016) NCP Product Schedule, and none have been reviewed or licensed by the state.

Most of the oils produced in California, and several of those transported through it, tend to emulsify relatively quickly, so additional research into the efficacy (and possible hazards) of using de-emulsifiers to support or prolong ISB is very relevant to the California oil spill planning community, as are further tank studies of the general ignitibility of California-produced oils.

On-water use of de-emulsifying agents, whether to support expansion of dispersant or ISB windows of opportunity, will require additional research before de-emulsifiers can be considered or used as a standard oil spill response tool. While recent research has helped provide greater understanding of what constitutes a stable emulsion and led to the development of some methods for measuring the physical properties of an emulsion and developing emulsions in the laboratory, work needs to continue on developing standardized methods for measuring these emulsion properties, and in standardizing methods for testing the efficacy and toxicity of de-emulsifying agents.

6. Bioremediants

a. Bioremediant Overview

Once oil enters the environment, oleophilic bacteria and other microorganisms begin to naturally alter and break down the contaminant into materials that include fatty acids, carbon dioxide, and water. Biodegradation is one of the primary natural processes in the weathering of spilled oil. The rate of the process is controlled by several factors including temperature, oxygen levels, and available nutrients (especially nitrogen and phosphorus) (Bragg et al., 1992). The primary pathway for microbial degradation of oil is aerobic (requiring oxygen), though some degradation occurs under anaerobic (without oxygen) conditions. Bioremediation does not increase the ultimate extent of hydrocarbon degradation, but only the rate of biodegradation while easily degradable hydrocarbons are present. Some oil compounds are resistant to microbes, especially the higher molecular weight PAHs and the polar molecules containing nitrogen, sulfur and oxygen (Atlas and Bragg, 2009). Once the more easily degraded alkanes and lower-molecular-weight aromatics are removed from the oil through weathering or other degradation processes, the continuing biodegradation of the remaining weathered oil residues is no longer limited only by nutrient availability, and the biodegradation rate naturally slows.

Bioremediation is the process by which nutrients (fertilizers) are added to a substrate to increase the rate of hydrocarbon biodegradation. The addition of fertilizers is generally only considered for land-based bioremediation. The microorganisms responsible for the biodegradation may be either endemic to the treated area or, if native microorganisms are unavailable in suitable numbers, added to the site along with nutrients (Hoff, 1991).

There are three principal areas where the use of bioremediation has been considered. These areas include on-water, rocky and sandy intertidal regions, and marshes and mudflats.

i. Use in On-Water Applications

Some bioremediant manufacturers have proposed their product for on-water application. The current reluctance to use a bioremediant in this manner is primarily due to the emergency nature of an on-water oil spill response where the intent is to expedite the removal of spilled oil. In contrast, bioremediation typically works in a time frame of weeks to months and thus is not generally considered or used as a first response tool, but rather considered for later stages in an oil spill response. Further, volatile components of crude oil, those components typically lost during the initial stages of a spill, are toxic to most oleophilic bacteria and must evaporate before the biodegradation process can begin (Hoff, 1991).

The use of bioremediation in open water has also received little consideration from agencies and other oil spill responders due to the lack of underlying data from qualified

researchers to discern exactly how some of the products proposed for this use (e.g., those with enzymes and surfactant components) will actually behave once on and in the water, and what the resulting effects might be. The bioremediation products presently on the market that profess to effectively remove on-water oil were originally designed for terrestrial application. Some of these products include a surfactant, which may move the treated oil into unintended areas (such as into the water column), not play a productive role (e.g., enzymes that do not support the breakdown of oil), or include a component that poses its own environmental consequences (e.g., sugar, preservatives). The presence of surfactant in the product, if it serves to disperse oil into the water, would preclude use of that bioremediant product on California shorelines.

Other bioremediation products that have been specifically designed for on-water application contain ingredients such as clay or other material that attach to or encapsulate the oil. This process ensures oleophilic microbes and nutrients maintain contact with the spilled oil, but may also sink the oil particles and potentially reduce microbe effectiveness depending on how deep the particle sinks.

Generally speaking, use of bioremediants in on-water applications is still not considered a first-response tool, although future research may enhance our understanding of how some enzyme- or surfactant-based products truly work and lead to new opportunities for use of bioremediants beyond their current utilities for shoreline and other land-based uses. At this point, they are valued as products that can enhance the biodegradation of oil by breaking the slick into smaller particles, which is the same benefit provided when using a dispersant as a biodegradation enhancer.

The use of bioremediation along marine shorelines and in freshwater wetlands is much more recognized as an oil spill response tool. Guidelines for the use of bioremediation in these response contexts are available (Zhu et al., 2001) and some examples of their use in previous oil spill responses are further discussed below.

ii. Use in Rocky and Sandy Intertidal Applications

The primary use of bioremediation in the rocky and sandy intertidal habitat is generally focused on light to medium oiled areas or as a polishing or finishing step in areas previously cleaned by mechanical means. Bioremediation is not very effective in removing pooled oil, tar balls, mousse, or other heavy concentrations of beached oil. Bioremediation is also not very effective in removing oil from low physical energy environments, such as below the surface of the intertidal sediments. This is due primarily to the anaerobic character of these areas. The presence of a reliable and continuous supply of oxygen is the primary requirement for successful bioremediation.

The addition of fertilizers to the intertidal substrate may present a threat to the existing environment by introducing additional contaminants (e.g., heavy metals) and producing toxic materials such as ammonia (U.S. Congress, Office of Technology Assessment, 1991). Further, the physical application and monitoring process may excessively

disturb or damage the existing biological community. The benefit of the bioremediation process must be weighed against the potential for associated damage before a decision is made to use it.

In addition to nutrients, bioremediation products can contain strains of microorganisms known to degrade petroleum. These are added to increase oil biodegradation in the treated area, although there is little evidence that "seeded" bacteria have a significant effect on the rate of biodegradation. Conversely, there is evidence that native microorganisms in marine intertidal habitats will quickly out-compete introduced organisms and be the responsible agent for any significant petroleum biodegradation.

iii. Use in Marsh and Mudflat Applications

Marshes and mudflats are sensitive environments which are easily impacted by the types of physical and mechanical oil spill cleanup techniques otherwise used on spills in the rocky intertidal region. For this reason, the less intrusive bioremediation process is a potentially important cleanup tool for oil spilled in soft substrate habitats.

Bioremediation may not be necessary in marshes, wetlands, or mudflats if high concentrations of nutrients are normally present and therefore not a limit to native bacterial growth and oil biodegradation processes. In these cases and habitats, the addition of bioremediation agents (e.g., fertilizers) will have little or no effect on oil biodegradation. Other controlling factors, such as the availability of oxygen, may be more significant in the marsh/mudflat environment than is the addition of nutrients or additional microbes (Hoff, 1991).

- b. Efficacy
 - i. Efficacy Testing in Advance of a Spill

Lab-based efficacy testing of bioremediants is required for listing on the federal EPA Product Schedule. Currently, no bioremediant toxicity tests are required (although this may change when the EPA completes its changes and updates to Subpart J). In licensing a bioremediant for use in California, OSPR generally just requires that a copy of the application sent to EPA also be sent to OSPR for use in its licensing review. There are currently no scientifically reviewed and supported testing protocols that can be used for field-based bioremediant efficacy testing in advance of a spill.

ii. Efficacy Testing as a Result of a Spill

Estimating bioremediation efficacy in the field is very difficult to determine due to the variability of the process over a study area and the difficulty in quantifying changes in petroleum concentrations. Summarized below are some key points from use of bioremediation approaches in past spills. Each case represents a different type of use. Some cases highlight when bioremediation was evaluated as part of a particular incident response, but then not actually implemented if natural processes or remediation

actions were considered sufficient for the response

Rocky Intertidal Use - 1989 Exxon Valdez Oil Spill

For two years after the 1989 *Exxon Valdez* oil spill (EVOS) in Prince William Sound (PWS), considerable effort was directed toward studying the efficacy of bioremediation on the oiled rocky intertidal areas (Bragg et al., 1992; Atlas and Bragg, 2009). **B**ioremediation efforts began following the physical removal of as much surface EVOS oil as possible, and in the following two years a total of 107,000 pounds of nitrogen (as 2237 applications) were added to shoreline sites in Prince William Sound. The findings of some follow up studies are summarized below:

- In 2001 and 2003, the NOAA conducted random sampling of 4982 pits dug at 114 sites in PWS, and found that 97.8% of the pits had no oil or light oil residues, even though these sites had been heavily oiled during the spill and previously had significant levels of subsurface oil (Short et al., 2002, 2004, 2006);
- ExxonMobil conducted a separate set of gridded surveys in 2002 and 2007. The 2007 survey (Boehm et al., 2008) sampled 744 pits at 22 sites that had been found during NOAA's 2001-2003 surveys to have been the most heavily oiled. Of those pits, 71% had no subsurface oil, 21.8% had light levels or only trace oil, 4.6% had moderate subsurface oil, and 2.6% had heavy levels of remaining subsurface oil. Pits with heavy oil were in widely scattered small patches, with the oil mostly sequestered under rock;
- Even where subsurface oil remained, it was highly weathered, and almost no resolvable alkanes remained in the samples collected from 2002 through 2007 (Atlas and Bragg, 2009). The belief was that 70% depletion of total PAH is the approximate threshold above which bioremediation is unlikely to be effective;
- The concentration of nitrogen naturally available within sediment pore water was also analyzed, as the ratio of nitrogen/non-polar subsurface oil, and indicated the presence of relatively high levels of natural nutrients. The conclusion was that natural biodegradation was no longer nutrient limited because the lower rate of biodegradation (18 years after the spill) had decreased the demand for nitrogen. The researchers further concluded that further addition of nitrogen into the system, to work on remaining pockets of weathered subsurface area, would be ineffective.

Bioremediation may increase the rate of petroleum degradation by as much as threefold (Bragg et al., 1992). Results reported by other authors (Hoff, 1991) suggest the actual rate of bioremediation in the rocky intertidal habitat may be highly variable and differ significantly from area to area. It has also been suggested that if the biodegradation rate cannot be accelerated by at least a factor of 2, it may not be worth considering (citations within Atlas and Bragg, 2009).

Marsh and Wetland Use - 2004 Suisun Marsh Pipeline Spill

In April 2004, an estimated 100,000 gallons of diesel spilled from a pipeline and into Suisun Marsh, a salt marsh habitat east of San Francisco Bay. About 200 acres of marsh and slough habitat were contaminated, with 20 acres of that considered the more heavily contaminated area and subsequently selected for an active bioremediation project. In addition to the pipelines, a rail line runs through the Suisun Marsh, and a busy highway borders it on one side.

Conducting an ISB of the marsh vegetation or excavating impacted soils and using many truck trips to haul it off site were considered as response options, but they were discounted as not safe or viable. As the marsh is home to the protected salt marsh harvest mouse and other migratory and endemic species, a primary environmental goal was to remove as much oil as possible with as little disturbance as possible. The spill occurred at a time of year when there would be sufficient time (several months) during which a longer-term bioremediation project could be implemented and completed before fall rains began.

- Before bioremediation could begin, affected parts of the broken pipeline were replaced, oiled soil under the pipeline was excavated and removed, and free oil was recovered from trenches dug through parts of the marsh. A conservation plan included trapping and relocation of the salt marsh harvest mouse prior to any soil scraping and tilling. Prior to the soil scraping, a stockpile of the native seed base in clean top soils was moved to a safe place at an upland site.
- Active bioremediation activities began two months after the spill, after free oil was recovered and other preparatory actions had occurred. The soil was tilled to allow greater oxygenation of oiled soils, and an irrigation system was installed through which nitrogen fertilizers would be delivered with the irrigation water over the next two months. The addition of microbes was not considered necessary. Soils were monitored for moisture and nutrient levels and were sampled weekly to confirm that bioremediation parameters were being met. The ratio of the hydrocarbon biomarkers, heptadecane and pristane, in the analyzed soil samples was used as a measure of how well the oil was degrading.
- Typical of bioremediation, there were large initial decreases of oil within the first several weeks, then a leveling off. Nitrogen fertilizer additions stopped after two months, and while bioremediation continued, it proceeded at a slower rate. An additional measure of petroleum reduction used sheen testing of soils (equal volumes of soil were mixed with water in a bucket, agitated, and observed for release of oil sheen). This observational approach was also used as a "soft" cleanup endpoint. Two months following the start of the Suisun Marsh bioremediation project, the biomarker and sheen test results were used by the cleanup sign-off agencies to determine that the bioremediation endpoints had been successfully met.

 As discussed above with the EVOS experience, there is a point at which the microbes have effectively degraded all the digestible oil compounds they can. The more recalcitrant compounds are not very amenable for microbial consumption, and providing additional nutrients is no longer helpful or necessary. Even after the most successful bioremediation effort, there is very likely to be residual and persistent oil that will remain for an extended period, very slowly breaking down over time.

2010 Deepwater Horizon (DWH) Oil Spill

Biodegradation of Oil Droplets in the Water Column

Native microbial communities in the open ocean played major roles in natural remediation of oil spilled during the DWH spill. Although no additional open-ocean bioremediation projects were conducted, various studies (Hazen et al., 2016; citations within Mearns and Rutherford, 2013, especially Lu et al., 2012; Redmond and Valentine, 2012; Du and Kessler, 2012, Ziervogel et al., 2012) did extensively investigate how natural biodegradation worked to help break down the spilled oil.

- Lu et al. (2012) analyzed changes in the functional composition and structure of the microbial community of the deep water oil plume and discovered microbial enrichment in those samples, compared to non-oil plume samples. There were also a variety of other metabolic genes important to carbon, nitrogen, phosphorous, sulfur and iron cycling, metal resistance, and bacteriophage replications.
- Redmond and Valentine (2012) used samples of oil to test the effects of temperature (4° C and 20° C) on the oil-degrading communities; they found that the microbial community of the deep water plume was distinct from surface waters and dominated by three groups of gammaproteobacteria. Temperature appeared to have a strong influence on which of those three species was in greater abundance. Cold-adapted species continued to successfully biodegrade hydrocarbons even in deep water.
- Valentine et al. (2012) examined how currents and mixing processes during and after the DWH blowout influenced the microbial ecology and hydrocarbon degradation in the deep waters of the Gulf. They found that currents and mixing oscillations functioned to reintroduce water parcels to the source area, resulting in autoinoculation and enhanced hydrocarbon biodegradation.
- Three possible mechanisms were suggested as responsible for formation of unusually large and mucus-rich marine snow particles. Hydrocarbon-degrading bacteria associated with oil slicks were responsible for producing these webs and, through further incorporation into phytoplankton aggregates, promoted more rapid biodegradation (Passow et al., 2012).
- Samples of DWH oil in bottles formed aggregates containing dense bacterial colonies that exhibited high enzymatic activity associated with oil degradation.

The water around the oil aggregate showed enhanced activity, likely from the increase in dissolved organic carbon (Ziervogel et al., 2012).

Microbial Response on Oiled Shorelines and Marshes

Beach and marsh microbial communities also had natural (unassisted) responses to stranded oil from the DWH spill:

- Heavily oiled beaches on Dauphine Island, in Mobile Bay, Alabama, and on Grand Isle, Louisiana, were studied using marker genes and morphological studies (Bik et al., 2012). Pre-spill sediments were dominated by nematode species, while post-spill sediments were dominated by fungal and oil tolerant species. Additional temporal sampling was recommended to determine whether these shifts in community structure would be maintained or if the community would, after recovery, return to pre-spill assemblages.
- A positive relationship was found between hydrocarbon degrading gene abundance and TPH levels and a significant increase in the indigenous microbial populations containing known hydrocarbon degrading bacteria, in a coastal salt marsh at Point Aux Pins peninsula (near Bayou L Batre, Alabama) during and after oiling (Beazley et al., 2012). Rhizosphere microbial populations were also considered to have possibly contributed to hydrocarbon degradation.
- In sediment cores collected from transects that encompassed unvegetated areas, seagrass, and marsh vegetation in an oiled Alabama marsh ecosystem, all samples contained alkane and total hydrocarbon degraders, but PAHdegraders were below detection limits at all sites (Horel et al, 2012). Seasonal differences in nutrient concentrations in pore waters were observed, but there was no seasonal change to the alkane and total hydrocarbon degrading microbial communities.

Evaluation of Bioremediation for DWH-Oiled Marshes

The potential use of bioremediation products and processes were also evaluated for direct use in oil impacted marshes of Bay Jimmy, Louisiana. A BioChem Strike Team (BCST) was established consisting of experts from USCG, BP, LSU, LDEQ, OSPR (California), EPA, NOAA, and highly experienced oil spill response consultants. The evaluation began with a laboratory screening of commercial bioremediation products with respect to their efficacy for degrading crude oil, compared to the process of natural attenuation, in the Gulf of Mexico waters and coastline. Products were evaluated by a specialized team set up by the ARTES program in response to the spill. The BCST determined that 10 bioremediation products already on the NCP Product Schedule (S-200, BioWorld, System E.T. 20, Oppenheimer Formula, Pristine Sea II, Oil Spill Eater (OSEII), Micro-Blaze, Munox, Soil RX, and WMI-2000) warranted further testing to determine their effectiveness in degrading oil under the specific environmental, climatic, and ecological conditions generated by the spill. The selected products were analyzed

in a controlled flask-study in the aquatic toxicology laboratory at Louisiana State University (LSU) to determine their remediation potential on weathered crude oil recovered from south Louisiana marshes (Portier and Basirico, 2011).

The ten tested products demonstrated the ability to biodegrade and/or reduce total concentrations of Bay Jimmy weathered oil (including alkanes and PAHs). The flask study additionally verified that the remaining dispersed and weathered oil in coastal environments along the Louisiana and northern Gulf of Mexico would continue to biodegrade. This was not a new finding, and it had been the opinion of many scientists that natural biodegradation would be a reasonable outcome for any oil spill affecting the coastlines of Gulf States. However, the study did demonstrate a capability to accelerate biodegradation strategies over time.

Parallel to the laboratory evaluation and over the course of the following year, members of the BCST also identified sites within Bay Jimmy that could be used for more active bioremediation projects, and the Regional Response Team VI was engaged to seek their permission to use lab-tested products and approaches. Ultimately, the decision of the RRT VI was to allow natural biodegradation to proceed without further intervention or disturbance.

2015 Refugio Beach

In May 2015 an estimated 120,000 gallons of a heavy crude oil leaked from a pipeline onto soils just east of Refugio State Beach. Approximately 20,000 gallons of that oil traveled through an under-highway culvert, down a shoreline cliff, and onto the beach. An extensive area of mixed sand and cobble beach and nearshore water was impacted, as were sedimentary beach bluffs and marine terraces that included sites of cultural and environmental sensitivity. The beaches themselves receive high recreational use.

Use of an active bioremediation approach was considered for the Refugio Beach oil spill but not used due to the lack of an appropriate setting. Use of one suggested product (OSEII) directly on affected shorelines was heavily promoted by representatives of the product's manufacturer, but it was not considered for use on the shoreline due to a lack of certainty regarding how the surfactant component in the product would behave in and near water (as discussed above, California regulations do not allow use on shorelines of products that could potentially behave as a dispersant). Use of any bioremediation product at the inland spill site was also removed from further consideration as those soils were not considered particularly sensitive and the UC had already authorized full excavation and removal of the affected soils. Retaining some of the soils on-site for bioremediation was not considered environmentally necessary or beneficial.

2016 Grove Incident

In June 2016 an estimated 45,000 gallons of crude oil from a pipeline owned by the Crimson Company spilled into a dry creek bed in the Hall Canyon area near Ventura,

CA. The dry creek bed is surrounded by steep canyon walls, and many areas were largely inaccessible to heavy equipment and, in some areas, to response personnel using hand tools. About 24,000 gallons of oil were estimated to have been recovered from the site using some limited excavation and cobble washing for gross oil removal.

However, oil remained buried in the creek bed, to a depth of 24" in some areas. Due to limited access, the area could not be tilled or land-farmed in a manner consistent with other bioremediation efforts. An adapted plan for bioremediation of the buried oil (using the Micro-Blaze bioremediation product, delivered through an irrigation system) was generated, and approved activities began at the end of August. The area to be treated was about 2,400 feet long, 10 feet wide, and an average depth of 24", resulting in an estimated amount of 1,800 cubic yards of area to be treated in place via bioremediation.

A sprinkler system was constructed to deliver water plus the bioremediant into the sand and cobble creek bed. The Micro-Blaze product is on the NCP Product Schedule and licensed by OSPR. It contains a surfactant and a blend of microbes that will work both with oxygen and without oxygen. The addition of microbes was considered necessary in this case as native oil-eating microbes were not likely to be abundant. The facultative anaerobes in the product (which do not require oxygen) would allow some limited bioremediation to still occur after the excavated area was back-filled. The surfactant allows for greater "wetting" of the sand and delivery of the microbes to buried oil. There was no expected runoff to state waters, and the underlying water table would not be affected. Consequently, there were no RRT IX or OSPR Administrator approvals required for this use. The UC and RP were not required to use a bioremediant on the NCP Product Schedule and/or licensed by OSPR, but they nevertheless recommended Micro-Blaze, as more is known about the product's components and possible effects of use. OSPR staff consulted on the bioremediation plan.

Bioremediation activities needed to occur within a relatively short period of time (4-5 weeks) before the excavated areas would need to be backfilled in advance of seasonal rains. While the project was not expected to achieve the highest degradation rates within the limited time, it was expected to provide at least some additional benefit, and no additional harm would be created. It was the last response tool used before leaving remaining oil in place to degrade over time. Bioremediation effectiveness results are not yet available.

c. Operational and Environmental Considerations

Assessing the operational feasibility of bioremediation is basically a two-stage process. The first stage determines whether a particular spill is a candidate for bioremediation treatment. The second stage determines whether bioremediation can be implemented effectively, given the logistics of application and monitoring.

The extent to which the chemical constituents of spilled oil remain after initial volatilization and weathering must be assessed before bioremediation treatment is

considered further. Biodegradation is typically useful on moderately to heavily oiled substrates, after other techniques have been used to remove as much oil as possible, and on lightly oiled shorelines where other techniques are destructive or not effective. When used on diesel-type and medium oils that do not have large amounts of high molecular weight, slowly degrading components, bioremediation is most effective. On thick oil residues, it is least effective. However, bioremediation should not be considered for gasoline spills, which will be completely removed by evaporation at faster time frames than by microbial degradation (Walker et al., 2000). See Table 4 on the following page for additional detail on environmental habitats and conditions under which bioremediation presents a best advisable option (Walker et al., 2000).

Table 4. Habitat Types Supporting the Best Use of Bioremediation Products and Approaches

Habitat type	Optional vs. Not Advisable	Explanation
Fine-Grained Sand Beaches; Sandy Banks	Optional	On outer beaches with low recreational use, bioremediation may be an option, particularly for light oiling or residual oil left after other countermeasures have been completed. Beaches in more sheltered areas (bays, river banks) may not be amendable to mechanical oil removal. Manual removal of heavy accumulations of oil or oiled wrack may be conducted, followed by bioremediation for sites with light oiling or residual oil.
Mixed Sand & Shell Beaches; Shell Beaches or Banks	Optional	For lightly or moderately oiled beaches and banks, particularly where mechanical cleanup may result in removal of large amounts of sediment or be logistically difficult. This option is best considered for sites without significant recreational use. A "no action" approach may also be justifiable.
Salt to Brackish Marshes; Freshwater Marshes	Optional	Most cleanup options pose significant impacts to these sensitive habitats. A "no action" response may be the preferred option. However, there may be conditions under which bioremediation may be considered, particularly for lighter oils. In wetlands with shallow, poorly mixed water bodies, the potential increase in eutrophication and ammonia caused by aggressive bioremediation needs to be considered.
Exposed Scarps in Clay and Wave-Cut Clay Platforms	Optional	Because of their erosional nature, removal of lightly oiled sediments may not be recommended on these habitats. Bioremediation may be an option to allow the oil to be treated in place.
Riprap, Exposed and Sheltered	Optional	Oil on riprap can occur as a coating on the boulders or as persistent accumulations of oil in the void spaces between the boulders. Neither type of oil is amendable to effective removal by bioremediation techniques under most conditions. Thus, bioremediation treatment would be optional, depending on spill- specific conditions.
Open Water; Offshore; Tidal Inlets; Water Intakes	Not Advisable	Bioremediation is not effective for the time frames of concern, relative to the potential of transport of the oil to areas where it could affect more sensitive resources.
Small Ponds; Lakes; Rivers & Streams	Not Advisable	Bioremediation is not applicable for gasoline and light oils due to their rapid evaporation. There is insufficient information on impacts and effectiveness for other oil types, however there are special concerns about nutrient overloading in small, restricted water bodies.
Solid Man-Made Structures (Exposed and Sheltered)	Not Advisable	Oiling of exposed sea walls usually occurs as a band at the high-tide line. This type of oiling is not amenable to bioremediation because of difficulty of application and low effectiveness.
Exposed Tidal Flats; Sheltered Tidal Flats	Not Advisable	Both of these habitats are inundated daily by high tides which results in rapid dilution and flushing of applied nutrients. Bioremediation is not likely to be effective under these conditions. There are significant toxicity concerns for use of bioremediation agents in shallow, poorly flushed areas, such as sheltered tidal flats, or subtidal habitats where there are concentrations of sensitive life stages of fish and shellfish, such as sea grass beds and oyster reefs.

Walker et al. (2000) have additional guidance related to the development of any bioremediation work plan, biomonitoring plan, and suggested field-monitoring parameters. These are also addressed in the RRT IX Regional Contingency Plan:

<u>https://www.wildlife.ca.gov/OSPR/Contingency/Fed-Region-Contingency-Plan</u> and in other references (Zhu et al., 2001). The RCP's plan for Bioremediation, along with the other RCP ART plans, is undergoing an update. Revised plans will be posted on the above web site once they are completed, finalized, and approved by the RRT IX.

- d. Other Issues
 - i. Open Water Use

In spite of the significant push over the last few years from some bioremediant product manufactures to have their products used as on-water first response tools, until these are scientifically tested in open/off-shore waters it cannot be determined how they will react in the environment and what role they will play in a major spill. Some lab-scale research currently underway, funded through the Oil Spill Research Institute and conducted by experienced scientists, should be informative for future discussions. Lab-scale test results may lead to further work, including tests in wave tanks under a variety of wave conditions and with different oil types. It would still need to be determined if any unbounded, open-water setting with real waves and chop will be a suitable setting for bioremediants. However, all previous experience and knowledge of the role of bioremediants makes this use unlikely.

ii. Shoreline Use of Bioremediants Containing a Surfactant

Several bioremediant products contain some form of surfactant, because (as with surface washing agents and dispersants), this provides a means for oil to be broken into small particles that are then more amenable to microbial biodegradation. However, use of surfactant-containing products on shorelines, if that product can run to water, would need additional incident-specific review before use to assure that the product does not have dispersant qualities; if it does, the environmental fate and effects of those product components must be understood and determined by the trustee and response agencies to be acceptable.

iii. Establishing Bioremediation Product Pilot-Test Areas During An Active Oil Spill Response

The ART Committee of the RRT IX has informally discussed the possibility of establishing set-aside areas on land for testing various OSCA products (e.g., surface washing agents, loose solidifiers, and bioremediants). No such areas have yet been established for this type of field testing, in part because of foreseen difficulties in testing these products in the context of a deliberate spill of oil.

The current policy is that establishment and use of pilot test areas during an active oil spill response, regardless of the type of product being considered, will be decisions made by the OSPR Administrator and the RRT IX on an incident-specific basis.

iv. Expected Changes to the NCP Product Schedule and State OSCA Licensing Regarding Bioremediants

The EPA is currently significantly revising Subpart J of the NCP, which directs the required efficacy and toxicity testing for oil spill cleanup agents before they are listed on the NCP Product Schedule and made available to the FOSC and the RRTs for consideration in oil spill response. It is anticipated, based on the EPA's draft revisions to Subpart J, that there will be additional tests and toxicity thresholds that will need to be met by all categories of OSCAs, including bioremediants, to gain future Product Schedule listing. In the case of bioremediants, the draft revision also anticipated new toxicity test requirements.

Depending on what changes are promulgated for the final revised Subpart J, the state may also change its licensing regulations and guidance to mirror the federal approach. If the federal approach falls short of what the state must require in the way of product licensing requirements, then there may be additional testing and threshold requirements established at the state level for all OSCAs, including bioremediants. These topics will be re-addressed in future updates to the BAT report for ART.

SECTION III. IN-SITU BURN

A. In-Situ Burn Overview

In-situ burning (ISB) is the combustion of spilled oil on water or land. Past on-shore or inland ISB has included salt marshes (Gonzalez and Lugo, 1994). Shoreline burning will present a different set of concerns than on-water oil burning in the marine environment. Both marine (on-water) and on-land (e.g., marsh, dry land, snow) ISB applications will be discussed in this section.

Marine on-water ISB has been an appealing response option since the late 1960s, when it was first tried during the 1967 *Torrey Canyon* oil spill. Burning has distinct advantages over other oil spill countermeasures. It offers the potential to rapidly convert large quantities of oil into its primary combustion products while leaving a small percentage of unburned residue byproducts (Evans et al, 1992). The combustion products are then generally readily dispersed to inconsequential levels (when at least 500 meters from the burn site) by atmospheric forces. This technique could be the most effective of all in dealing with a large spill at sea and in removing large quantities of oil from the water before it comes ashore (S.L. Ross Environmental, 1990). This response technology typically raises concerns regarding worker and public safety related to the nature of the combustibility of oil on water (Evans, et al., 1992). The first large scale and successful use of ISB on water was during the 2010 Deepwater Horizon oil spill.

Since the 1980s, the U.S. Department of the Interior-MMS has funded studies researching the use of ISB as an oil spill response technique to determine both the

utilities and the limitations of this response strategy (Tennyson, 1991). The first phase of research identified specific physical variables and their effect on spill removal efficiency, including slick thickness, degree of weathering, sea state, wind velocity, air and water temperatures, and degree of emulsification. The next phase of research supported a quantitative analysis of the pollutants created by ISB (including the chemical composition of the parent oil, burn residue, and airborne constituents). The third phase involved evaluation of the effects of scaling up the research conducted in the laboratory, while the fourth phase involved full-scale field verification on the open ocean. The Newfoundland Off-shore Burn Experiment (NOBE) was conducted by the U.S. MMS and Environment Canada (as well as 48 other agencies) on August 12, 1993, in which two lots of oil of about 50 tons (15,750 gallons) each were released into confining fire-proof boom and burned. The primary purpose of the 1993 NOBE was to gather detailed scientific data on the effects of ISB under "real-world" conditions.

B. Operational Considerations

Although ISB is a relatively simple technique, its safe and effective use can be limited by spill circumstances. The degree to which oil burns is dependent on the interplay between a number of physical factors related to the oil itself and the extent to which the oil has been exposed to the environment. These include oil thickness, degree of emulsification, and degree of weathering. These factors generally change over time, and such changes make burning more difficult. As a consequence, ISB is most easily and effectively implemented during the early stages of a spill.

1. Ignition

If ISB is to be used as a response method, the spilled oil must be ignited safely and effectively. Several methods have been used to ignite oil slicks, both experimentally and operationally. These include pyrotechnic igniters, laser ignition systems, and aerial ignition systems. Pyrotechnic devices have been successfully used to ignite floating oil slicks under a range of environmental conditions. Disadvantages to their use are associated with safety, shelf life, availability, speed of deployment, and cost (Spiltec, 1987). Laser ignition, while a promising technique, remains experimental because of drawbacks associated with difficulties in beam-focusing from the air, wind effects during oil preheating, energy requirements, and cost. Aerial ignition systems using gelled gasoline dropped from helicopters appear to be a more viable technique applicable in a range of environmental conditions. A helitorch system was used during the NOBE open-water test burns. Simple hand-held igniters were used for all of the burns conducted during the 2010 DWH spill.

2. Physical Factors

Physical factors affecting the ability of spilled oil to burn include oil thickness, degree of weathering, and emulsification. These can reduce the <u>ignitability</u> or <u>combustibility</u> of the oil.

Studies of the physical processes driving the combustion of oil on water have indicated that it is not the liquid oil that burns but rather the heated vapors. As such, a fire will burn only if the heat feedback to the oil surface is equal to the heat required to maintain vapor flow back to the fire (Shigenaka, 1993). According to Buist (1987), an oil slick will continue to burn until its thickness reaches some threshold, below which the heat loss to the water is great enough to quench the fire. This threshold thickness has been reported to range between 0.8 mm (Buist, 1987) and 3 mm (Tennyson, 1991; Tebeau, 1994). Additionally, controlling the thickness of an oil slick provides a simple means of controlling a burn (thickening it for optimal burning, or quickly quenching it for emergency suppression).

Oil weathering decreases ignitability and combustibility of oil. Experiments studying the effects of weathering were performed by Hossain and Mackay (1981). They found that weathering resulted in loss of volatile compounds, more difficult ignition, slower combustion, and surprisingly in some cases, a higher proportion of oil burned. Percent weathering, up to about 20 percent, appeared to not affect the burn efficiency of crude oil. Weathering of between 20 and 35 percent of the oil increased the burn efficiency, beyond which efficiency declined. Twardus (1980) found that despite the loss of most volatiles in crude oil during the first two days of aging, in-situ combustion of weathered oils was still possible through the use of a priming material.

Emulsification can significantly influence the effectiveness of an ISB. Burning of wateroil emulsions was found to be possible with mixtures of up to 20-30 percent water. As water-in-oil emulsions approach 50%, the spill becomes difficult to ignite and may be impossible to ignite at 50-70% (Tebeau, 1994). During the DWH ISB, it was found that emulsified oil would burn if it was "fed into" an already active burn (Allen, 2011).

The use of de-emulsifiers has been considered as a means to extend the ISB "window of opportunity," but this research has not matured to the point at which de-emulsifiers can be used on an open-water spill to support continuing ISB operations.

Before a portion of an oil slick can be burned, it must be physically contained within a boom (this also allows the slick to be drawn into a thicker layer). Generally, some type of specialized fire boom is used for containment; it is the type of boom that resists burning while the bounded oil is getting burned off. Fire boom has evolved significantly over the last few years, and particularly since the 2010 DWH spill. Five types of fire-resistant boom were used for the DWH ISB: Elastec Hydro-Fire boom, Elastec American Marine 3M boom, AFT Pyro Boom, Oil Stop, and Kepner (Allen, 2011). Each system is constructed differently, but each successfully supported multiple burning operations. See Potter (2013) for additional construction and utility details for the first three types of fire boom listed above. Allen (2011) notes how many systems of each boom type were used, the longest continuous burns, and average number of barrels burned per system.

As discussed in the previous section on herders, considerable work is currently underway in the Arctic that explores the use of herders as a way to limit oil spreading and thicken the oil to support ISB. This would reduce the reliance for delivery of specialized fire boom to the spill site before ISB can occur. This research may eventually mature to the point where it offers more timely and effective ISB response for California as well, particularly for more spills in distant offshore waters.

C. Efficacy

Although the efficiency of ISB is highly dependent on a number of physical factors, test burns and applications in actual spill situations in years past suggest that it could be very effective in removing large quantities of crude oil from the water. Earlier laboratory studies demonstrated burn efficiencies of 54-90 percent (Benner et al., 1990; Brown and Goodman 1986).

1. Efficacy Testing in Advance of a Spill

Laboratory tests of 17 different crude oils with varying API gravities were conducted to determine the likelihood of successful burning of each oil type (McCourt et al., 2001). When the results of the separate tests were grouped together, trends in suitability were noted. In particular, API gravity was shown to be a reasonably good predictor of success for ISB of light oils. Oils with API <21 were more burnable, heavy oils with API < 38 were essentially not burnable. Burning success with oils of intermediate API gravities was varied. One of the California crude oils tested, Carpinteria (API 24), fell into this intermediate category, and further burn testing of that oil might be recommended. Three other California crude oils (Point Arguello, API 21; Santa Clara, API 20; Santa Ynez, API 17) were the heaviest tested. All three formed stable emulsions, even when fresh, and were not ignitable when emulsified. Emulsion breakers worked poorly on these oils. All were concluded to be poor candidates for burning.

One type of oil produced from California offshore oil fields (Dos Cuadras) falls within the same API range as the tested Carpinteria oil, and further burn testing on this oil type might also be warranted. The other oils in California offshore oil fields (Beta, Hondo, Hueneme, Pescado, Pitas Point, Point Pedernales, Sacate, and Sockeye) all have APIs < 22 and, like the three tested crude oils within this API range, may prove impossible to burn.

Test burns conducted in the first days of the 1989 *Exxon Valdez* spill in Prince William Sound, Alaska resulted in the burning of approximately 15,000 to 30,000 gallons of Prudhoe Bay crude oil, at an estimated efficiency of 98 percent or better (Allen, 1990). Findings from the NOBE burns indicate greater than 99 percent efficiency (Fingas, et al., 1995).

2. Efficacy Testing as a Result of a Spill

On-water oil spills that occurred before the 2010 DWH spill, where ISB was used, include (Mabile, 2013):

<u>U.S.</u>	SS Sansinema (1976), Argo Merchant (1976), Buzzard's Bay (1969, 1977), Exxon Valdez (1989), New Carissa (1999), DWH (2010)	
<u>Canada</u>	McKenzie River (1958), Arrow (1970), Nipisi (1976, 1982), Imperial St. Clair (1979)	
<u>S. America</u> :	Aegean Captain (1979)	
Overseas:	Torrey Canyon (1967), Othello (1979), Castillo de Bellver (1983: unintentional), Haven (1991), Kolva River (1994)	

The 2010 DWH oil spill was the largest use of on-water ISB. Estimates of the total amount of oil burned, in 419 burning events, range from ~220,000 – 310,000 bbls (9,240,000 million – 13,020,000 gallons) (Allen, 2011). Even though this represents only 5% of the oil spilled during the DWH event (Federal Interagency Solutions Group, 2010), it is equivalent to the entire amount of oil spilled during the 1989 *Exxon Valdez* oil spill. The 2010 DWH ISB operation provided a safe and successful removal of a significant amount of on-water oil.

Although ISB has been tested most often with crude oil spills, the feasibility with other kinds of products (including marine diesel and Bunker C fuels) has also been demonstrated (Twardus, 1980). The physical and chemical characteristics of non-crude oils make them less amenable to burning. This results primarily from the difficulties in establishing and maintaining necessary slick thicknesses (in the case of lighter, lower viscosity oils) and difficulties with ignition (for heavier, less volatile oils).

- D. Environmental Effects
 - 1. Air Monitoring/Testing in Advance of a Spill

The production of copious amounts of heavy smoke over the course of an oil burn is both unsightly and a potential health threat to oil spill responders or the general public. Since many of the concerns associated with burning result from the generation of a large smoke plume, the airborne components of burn by-products were the subject of previous intense study in both small-scale and large-scale burn experiments. Despite the highly visible character of smoke generated by the burning of oil, Evans et al. (1988a, 1988b) determined that only about ten percent of the original amount of a crude oil was converted into smoke during combustion. The smoke was largely comprised of elemental carbon (90 percent), while the primary gaseous product was carbon dioxide ($C0_2$). Results from a mesoscale test burn in Mobile Bay, Alabama, indicated that oxygenated compounds of concern, such as dioxins or dibenzofurans, were not produced in measurable quantities during the burning of crude oil on seawater (Evans,

1994).

Burning crude oil also results in combustion products that are irritating or toxic, including carbon monoxide (CO), carbon dioxide (CO₂), sulfur oxides, nitrogen dioxide (NO₂), various polycyclic aromatic hydrocarbons, acid aerosols such as sulfuric acid, aldehydes, and acrolein (ATSDR, 1991). Quantitative analytical data from the NOBE burn showed that these emissions from in-situ oil fires were less than expected. All compounds and parameters measured were below health concern levels beyond about 150 meters from the fire, and very little was detected beyond 500 meters. Pollutants were found to be at lower values in this burn than they were in previous mesoscale pan tests. The reasons for this are not fully understood, however the off-shore test appears to have resulted in more efficient combustion.

Many human health experts feel that the most significant human health risk resulting from ISB would be inhalation of the fine particulate material that is a major constituent of the smoke. An early assessment of health concerns attributable to the Kuwaiti oil fires identified the less than 10-micron particulate matter (PM_{10}) as representing the greatest health hazard in that situation (ATSDR, 1991). It has been well-documented from long-term studies in exposed human populations that PM_{10} presents a significant health problem. The extent to which these particles would present a health risk during a burn would depend on the concentration and duration of exposure (ATSDR, 1991). Both the EPA and California Air Resources Board (CARB) have established particulate thresholds for PM_{10} and $PM_{2.5}$; the CARB threshold is the more stringent.

The risk from particulates emitted during ISB may be smaller than previously estimated (Shigenaka, 1993). Analysis of oil pool fires in Kuwait determined that combustion was more efficient than expected. Approximately 95 percent of the fuel was converted to CO_2 , 2 to 3 percent to soot (10-12 percent had been predicted), and the rest was composed of hydrocarbons and gases (Ferek et al., 1992). The highest concentrations of total particulates found in Kuwait were 5.4 mg/m³ at ground level in the plume (Campagna et al., 1992) and 1.1 mg/m³ of respirable particulates in the upper plume (Ferek et al., 1992). These values nevertheless exceed the EPA and California CARB thresholds for particulates; air plume monitoring becomes critical during ISB on actual spills to make sure particulate dispersion occurs in a manner that assures minimal inhalation risks to workers and the public.

2. Air Monitoring/Testing as a Result of a Spill

The air monitoring that occurred during the DWH oil spill assessed (1) air impacts from volatile gases related to the spilled oil itself versus those from in-situ oil burning and (2) potential human health impacts from volatile gases or particulate matter (soot) to either the response personnel or to the general public (Schrader, 2010; EPA, 2011; Middlebrook et al., 2012). Air monitoring early in the DWH response had shown that particulate levels near the ISB were not an issue (Schrader, 2010), but air was periodically monitored by the USCG Atlantic Strike Team (using Special Monitoring of

Applied Response Technology ([SMART)) to document that the plume did not exceed the established air quality standard of 150 μ g of PM₁₀ per m³, averaged over a 12-hr period. The U.S. EPA also set up a high resolution monitor to gather real-time measurements of hydrogen sulfide (H₂S) in the outdoor air near Venice, Louisiana. The Airborne Spectral Photometric Environmental Collection Technology (ASPECT) was deployed, as were several NOAA aircraft and vessels (Middlebrook et al., 2012). Monitoring detected four sources of primary air pollutants attributable to the DWH spill: (1) hydrocarbons (HCs) evaporating from the oil, (2) smoke from ISB, (3) combustion products from the flaring of recovered natural gas, and (4) ship emissions from the recovery and cleanup operations. Also examined in addition to these primary emissions was the subsequent production of ozone and secondary organic aerosols (Middlebrook, 2012).

Air monitoring data indicated that leaking oil and natural gas at the DWH spill site and the associated recovery and cleanup operations led to emissions of pollutants into the atmosphere. The HCs evaporating from the oil slick were the largest source of primary air emissions. Once in the air, these HCs produced the secondary organic aerosols (SOAs) and other gaseous pollutants such as ozone, nitric acid (formed from nitrogen oxides emitted from natural gas flaring and ship operations close to the spill site), and other oxidation products. Large concentrations of polycyclic aromatic hydrocarbons (PAHs) were not found in the SOAs. The emission factors for nitrous oxides (NO_x), CO, and soot from ISB, flaring, and ship emissions were similar to those reported from previous studies. The soot particles from the burns were confined to narrow plumes, so the absolute concentrations of particles from the burns were much higher in the plume area. Heat associated with the burning, however, lofted some of the soot particles above the marine boundary layer, where they could be transported farther away (Middlebrook, 2010).

There are recent reports (Jariyasopit et al., 2014) that raise potential future concerns regarding novel types of compounds produced by certain types of chemical reactions, such as those found in vehicle exhaust. These are hundreds of times more mutagenic than their PAH parent compounds. Although the concern over these compounds (which result when PAHs interact with nitrogen to become "nitrated," or NPAHs) primarily relates to air impacts in heavily industrialized or urban areas, there could also be concerns raised over whether NPAHs are created, or created in an amount or concentration that rises to a level of concern, during an ISB of an oil spill that produces high levels of particulates. When conducting ISB adjacent to highly industrialized or urban areas in California (e.g., Los Angeles), monitoring for NPAHs should be taken into consideration.

While ISB presents a series of health concerns, it should be noted that not burning an oil spill also introduces its own air quality concerns. Analysis of the physical behavior of spilled oil (using, for example, the NOAA-U.S. Coast Guard's ADIOS oil weathering software) has shown that 50 percent of a light crude oil spill can evaporate fairly readily and that it is the acutely toxic lighter fractions of a crude oil mix that quickly move into

the atmosphere (Shigenaka, 1993). Such light-end fractions include benzene, toluene, ethylbenzene and xylene (BTEX). All of these chemicals are known to cause liver toxicity in humans, and benzene is a human carcinogen and teratogen (Berliner, 1994). The high temperatures associated with ISB destroy the ring-structure of these chemicals and significantly reduce their air emissions (Fingas et al., 1994).

3. Air Emissions

Though the effects of smoke on many marine animals are not fully known, it is unlikely to be worse than the oil remaining as a slick on the water surface (Ames, 1994). Pelicans, for example, are notorious for diving into oil slicks (veterinarians believe the spill is mistaken for a school of fish). Sea otters and fur seals are especially vulnerable to oil, both through physical contact, which causes loss of the air/water barrier of their fur (resulting in hypothermia), or mucus membrane irritation from the oil volatiles. Results from the NOBE test showed negligible impact of smoke on selected wildlife species (Fingas et al., 1994). Overall indications from these burn trials were that emissions from ISB are low relative to other sources of emissions and result in acceptable concentrations of air contaminants (Fingas et al., 1994).

During the DWH spill, wildlife monitors were on-board vessels involved in ISB and assured no sea turtles, marine mammals, or birds were visible within the area to be burned. There were no observed impacts of the DWH ISB on seabirds or other marine wildlife.

For any ISB on California offshore waters or on land, the appropriate trustee agencies would be consulted regarding fish, birds and other wildlife likely to be in the burn area at the time of the intended burning operations. Wildlife observers would be provided on platforms (aerial or vessel) involved in the ISB operation to assist in implementing wildlife avoidance measures and to document any wildlife seen near or entering the area during burning operations.

4. Surface Microlayer: Temperature and Toxicology

The surface of the water and the area immediately below it (the surface microlayer) is habitat for many sensitive life stages of marine organisms, including eggs and larval stages of fish and crustaceans and reproductive stages of other plants and animals.

The surface area on the water affected by ISB is likely to be small relative to the total surface area and the depth of the underlying water. However, this does not necessarily preclude adverse ecological impacts that might occur with the technique, particularly for rare or sensitive species that use the waters in question. The organisms that may be impacted by ISB include those that use the uppermost layers of the water column, those that may come into contact with residual material, and possibly some benthic plants and animals. These considerations must be weighed against the impacts that would result from natural dispersion of the oil into the water column or allowing the slick to remain on the water surface.

Burning oil on the surface of the water could adversely affect those organisms at or near the interface between oil and water through elevated temperature impacts, although the size of the area affected would presumably be relatively small (Shigenaka, 1993). Evans et al. (1988) observed that during the peak of the burn period for an experimental combustion of crude oils on water within a shallow enclosure, the water immediately below the oil was brought to a vigorous boil. However, observations during the large-scale burns using towed containment boom (Evans et al., 1990) did not give any indication of such an impact on the waters. Water temperature tests were conducted underneath the burn site during the NOBE study and no detectable increase in water temperature was noted (Fingas et al., 1994). It has been suggested that because ambient temperature seawater is continually supplied below the oil layer during ISB, the residence time of the burning layer over the water surface may be too brief to induce boiling (Fingas, et al., 1994). Finally, it is important to keep in mind that oil floating on the water surface is itself highly toxic to surface microlayer organisms.

5. Burn Residues

Beyond the direct impacts of high temperature, the by-products of ISB may be of toxicological significance (Shigenaka, 1993). Hydrocarbons will be present in the environment regardless of whether or not the oil is burned. Although analysis of water samples collected from the upper 20 cm of the water column immediately following a burn of crude oil yielded relatively low concentrations of total petroleum hydrocarbons (1.5 parts per million), compounds that have low water solubility or that associate with floatable particulate material tend to concentrate at the air-water interface (U.S. EPA, 1986). Strand and Andren (1980) noted that the aromatic hydrocarbons in aerosols that originate from combustion sources of human origin (a <u>pyrogenic source</u>) will accumulate in the surface microlayer until absorption and sedimentation remove them. Higher molecular weight aromatic hydrocarbons, such as those produced by the combustion of petroleum (a <u>petrogenic source</u>), have been associated with the histopathological abnormalities in populations of marine fish and possibly with reproductive disorders (Shigenaka, 1993). Some of these heavier aromatic hydrocarbons are known carcinogens in humans and other mammals.

However, serious pathologies like tumors have generally been associated with longerterm (chronic) exposures to hydrocarbons. Exposures attributable to ISB would likely be much shorter term and may not result in toxicologically significant exposures (Shigenaka, 1993), nor would they be worse than exposure to the crude oil alone. When water samples under the NOBE burns were analyzed, no compounds of concern could be found at the detection level of the methods employed. Toxicity tests performed on this water did not show any adverse effect (Fingas et al., 1994).

From an ecological perspective, there may be cause for concern that burn residue could sink due to increased oil density. As Moller (1992) observed at the Haven spill, residues sank following the intense burn. Moller discussed this as a problem from a

fishing gear and seafood contamination perspective, but large amounts of sunken burn residues could also affect benthic resources of an area that would not otherwise be significantly impacted by a spill at the water surface. Moller cited the example of a spill of Arabian heavy crude from the *Honam Jade* off South Korea in 1983. Here, cleanup contractors ignited the main slick, which measured about three kilometers in diameter. The fire burned intensely for about two hours. The resultant burn residue sank and adversely affected crab being reared in nearby submerged pens.

While the potential for burn residues sinking cannot be ignored, it is also important to point out that the Haven incident involved burning the heavy crude oil while it was within the cargo holds of the vessel. This burn resulted in very high temperatures that produced results similar to a crude oil refining and distillation process, where "cracking" the oil produces lighter components that are driven off while denser materials remain. Moller suggested that the circumstances specific to the Haven situation should not be used as the basis for generalization to all burning scenarios (Shigenaka, 1993).

Burn residues could also be ingested by fish, birds, mammals, and other organisms, and may be a potential source of fouling of fish gills, feathers, fur, or baleen. Floating or sinking burn residue could impact organisms that use surface and upper layers of the water column or benthic habitats. As impacts can also result from mechanical response actions, all potential response options should be included in an overall assessment of potential effects, and subsequent response strategies chosen that present the best response option(s) for the spill situation.

- E. Other Aspects of Human Health and Worker Safety
 - 1. Personnel Safety During Ignition and Burn Phases

The burning of large amounts of combustible liquids on the surface of the water presents some unique safety concerns for workers (Shigenaka, 1993). Allen (1990) used his experience from the *Exxon Valdez* to further address the heat generated by ISB and its potential effects on response personnel. In the *Exxon Valdez* spill, the size of the area with burning oil was easily controlled by adjusting the speed of the towing vessels. At the peak of the burning, when flames extended 45 to 60 meters into the air, and the distance from the stern of each towing vessel was about 200 meters, heat from the fire was noticeable but not uncomfortable or dangerous. The practices used during the extensive ISB during DWH (Allen, 2011) were shaped on previous experience, and led to well-controlled burning that did not pose safety risks to personnel.

2. Soot Reduction

Evans (1991) noted that the addition of water to oil resulted in less smoke produced during a burn and decreased the production of polynuclear aromatic hydrocarbons by up to one half. The addition of a compound called ferrocene may also markedly reduce the amount of smoke produced in the combustion of crude oil (Mitchell, 1990). Although

the mechanism is not entirely understood, it is thought that the presence of iron in the combustion products causes the carbon which would otherwise form the basis for soot and smoke to be converted back into a gas phase in the form of carbon monoxide. Researchers found that the addition of relatively small amounts of ferrocene (2 - 4 percent by weight) to crude oil resulted in a 71 to 94 percent reduction in soot (Moir et al., 1993).

Ferrocene and its alkyl derivatives are considered to be relatively nontoxic, and though preliminary studies have been conducted in mice and dogs, additional studies need to be conducted. Finally, another combustion product potentially found in the soot is particulate iron oxide (rust). Long-term exposure to air contaminated with iron oxide is considered to present a respirable dust hazard with no long-term health effects. For ISB, neither the concentration nor time of exposure is considered sufficient to justify a health concern (Moir et al., 1993).

- F. Other In-Situ Burn Issues
 - 1. In-Situ Burning in Inland and Upland Habitats
 - a. Environmental Effects

There are environmental conditions under which burning should be considered as a response option for oil spilled in inland and upland habitats (Zengel et al., 2003). Past inland burns (these occurred outside California) have been conducted mostly in marshes and open fields. Nearly half of past burns of a known volume of spilled oil were for quantities of less than 1500 liters (396 gallons). The most common type of oil burned was crude oil; there was only one case where a heavy crude oil was burned. Post-burn monitoring was seldom conducted for any period of time on these past spills. Burning, especially of small spills, is routinely conducted in some states, but there is often little documentation available other than the fact that the oil was burned (Zengel et al., 2003; Dahlin et al., 1998).

2015 East Wax Lake Spill

An exception to this is the marsh burning conducted as part of the East Wax Lake Spill response in July, 2015. Approximately 1,050 gallons of mixed crude oil condensate and produced water were released into the marsh following a break in a fluid line associated with a Belle Isle well, St. Mary Parish, Louisiana. The proposed 1.61 acre burn site (within the 5.5 acre spill site) was located within a freshwater marsh, predominantly comprised of the marsh plants *Sagittaria*, spike rush, and *Polygonum*. Crude oil was trapped within floating marsh mats and dense vegetation, effectively preventing the oil from migrating. Initial cleanup efforts focused on cutting and raking dead vegetation and using sorbent materials. While some oil and oiled vegetation was recovered, the methods did not prove effective. As a result, ISB was discussed by the UC and was determined to be the most effective method of oil removal (Coast Guard News, 2015).

Primary proposed methods of ignition included road or marine flares; a secondary method was a marine flare affixed to plastic jugs containing diesel (which were not considered an accelerant). Air monitoring was conducted by the Gulf Strike Team, from monitoring vessels adjacent to the burn. SMART monitoring was used, optimized for measuring fine particle fractions of airborne dust, smoke, fumes and mists. The level of concern for particulate matter was established at 150 μ g/m³ of PM₁₀ within a 15-minuite STEL (Short Term Exposure Limit) (Texas Petroleum Investment Company, 2015)). Baseline and post-burn soil/sediment, water surface, and water bottom samples were also collected. Photo surveys were conducted to document vegetation regrowth. The water and sediment samples were evaluated for Constituents of Concern (COC), a term used by the USEPA to describe those constituents which potentially pose the greatest risks to human health and the environment. COCs for the East Wax Lake Spill were selected according to relevant agency guidelines (USEPA 1989a, LDEQ 2003) and evaluated for crude oil, chlorides, and trace metals.

A Site Conceptual Exposure Model (SCEM) was used to depict the site and its environment(s) and delineate potential chemical sources, chemical release and transport mechanisms, affected media, migration routes, and potential human and ecological receptors. The SCEM provided a framework for problem definition, aided in the identification of data gaps, and helped identify key exposure pathways and associated media in order to focus assessment activities. Exposure was understood to occur only when there was potential for a receptor to directly contact released constituents or when there was a mechanism for the released constituents to be transported to a receptor. Without exposure, there is no risk.

For this spill and ISB site, all potential exposure pathways were combined in a single SCEM. The SCEM identifies the 5 ½" fluid line leak as the primary release mechanism of constituents to soil/sediment at the site (crude oil and produced fluids). From soils, the COCs leached into surface water. Resulting transport media included surface soil/sediment, potential surface soil/sediment, and surface water. Exposure routes included ingestion, dermal contact, and inhalation. Due to the unoccupied and industrial/commercial nature of the area of concern, it was expected that future use would be very similar to existing conditions at the site and in surrounding areas. Exposure to groundwater was minimal, because there were no water supply wells within 1 mile of the site. No exposure was considered applicable to this site for groundwater media (Forefront Emergency Management, 2015).

Based on the way the burn progressed and the photos from the day of and the day following the burn, the NOAA SSC believed the stated objective of removing a substantial portion of the oil from the environment was met (Doelling, 2015). There also appeared to be substantial integrity left to the vegetation mat, as the amount of open water created within the original burn area of floating vegetated mats was minimized. Some of the vegetation rhizomes in the area that burned most intensely died, but sufficient vegetation mat remained to provide nutrients and accelerate regrowth in those

areas.

2. Operational Considerations

The above inland burning case histories (Zengel et al., 2003) provide information on the state of the practice in terms of inland burning. In the past, spilled oil has been burned for the following reasons:

- To quickly remove oil and prevent its spread to sensitive sites or larger areas;
- To reduce the generation of oily wastes, especially where transportation or disposal options are limited;
- Access to the site is limited by shallow water, soft substrates, or the remoteness of the location; and,
- As a final removal technique, when other methods begin to lose effectiveness or become too intrusive.

Favorable conditions for burning are also identified from case histories (Zengel et al., 2003):

- Remote or sparsely populated sites;
- Mostly herbaceous vegetation (e.g., fields, crop land, marshes);
- Dormant vegetation (not in active growing season);
- Unvegetated areas (e.g., dirt roads, ditches, dry stream beds);
- In wetlands, the presence of a water layer covering the substrate and protecting roots and rhizomes;
- In cold areas, presence of snow and ice which provide natural containment and substrate protection;
- Calm winds; and,
- Spills of fresh crudes or light refined products which burn more efficiently.

Operational and post-burn considerations developed from the case histories include (Zengel, 2003):

- Avoid physical disturbance of the vegetation and substrate;
- When oil does not ignite readily, an accelerant may be needed;
- A crust or residue (which may hinder revegetation) is often left behind after burning and may need to be broken up or removed;
- Erosion may be a problem in burned areas if plant cover is reduced;

- Vegetation in and adjacent to burn sites can be affected by burning, including long-term changes in the plant community; and,
- Burning can severely impact organic soils, such as peat found in certain wetlands.
- G. Agency Authorizations

The FOSC currently has the authority (via RRT IX Pre-Authorization or RRT IX Incident-Specific Authorization), to use ISB as an oil spill response tool. The process is broadly similar to that for authorization to use a dispersant or other OSCA.

Necessary authorizations for ISB will vary for marine versus inland spills. Marine authorizations will vary by distance offshore and may be influenced by whether or not an accelerant is used. Authorizations for on-shore burning (inland or upland) will vary depending on which agency is providing the FOSC for the response (USCG versus USEPA), whether the burn could affect state waters, whether the burn uses an accelerant (versus simple igniter), and which local Air District might be affected and involved in how the ISB decision is implemented.

1. Marine On-Water ISB

The most recent finalized RRT IX ISB Plan (2005) includes a Letter of Agreement (LOA) signed in 1997 among the USCG, EPA, DOC, and DOI providing concurrence of those agencies for the use of ISB for oil discharges on waters within the jurisdiction of the RRT-IX California Mainland and for 35-200 nautical miles off the coast. This concurrence was given to the federally pre-designated USCG FOSC and provided guidelines to the FOSC for timely use of ISB. Waters inshore of 35 nautical miles would require the FOSC to seek and receive Incident-Specific RRT IX authorization before burning could commence.

Discussions led by CDFW-OSPR with local Air Districts more than 15 years ago led to development of Air District "Quick Approval" Zones for marine offshore areas. It was agreed that ISB can occur at the following minimum distances from shore, without additional Local Air District approval to the UC or RRT IX, if <u>winds are blowing offshore</u> <u>or parallel to shore</u> during the burn operation. The negotiated offshore distances for each California Air District are as follows:

North Coast Air Quality Management District: Mendocino Air Quality Management District: Bay Area Air Quality Management District: North Sonoma Air Quality Management District: Monterey Bay Air Resources District: San Luis Obispo County Air Pollution Control District: Santa Barbara County Air Pollution Control District: Ventura County Air Pollution Control District:

- \geq .5 miles from shore
- ≥ .5 miles from shore
- ≥ .5 miles from shore
- ≥ .5 miles from shore
- No QA zones (winds too variable)
 - \geq 3 miles from shore
 - \geq 3 miles from shore
 - \geq .5 miles from shore

South Coast Air Quality Management District: San Diego Air Quality Management District: \geq 8 miles from shore \geq .5 miles from shore

The 2005 RRT IX ISB Plan was to also include a letter from the EPA to coastal Air Districts, assuring them that in the event of a RRT IX or EPA authorized ISB as an emergency response to spilled oil, Air Districts would not be faced with a violation for exceeding their mandated air quality attainment thresholds. That letter is missing from the RRT IX ISB Plan. As a copy cannot be found, it needs to be re-created and placed back in the RCP.

The 2005 RRT IX ISB Plan and the included Letter of Agreement describe the authority of the RRT IX to grant ISB authorizations, regardless of whether or not an accelerant is used, to initiate or support an on-water burning operation. If an accelerant is to be used, it must be one listed on the NCP Product Schedule.

2. Inland (Marsh, Upland) ISB

ISB proposed for oil spilled into a water-inundated or water-proximate vegetated area in the marine zone (e.g., marsh, wetland, dunes, river mouths), where the USCG is the FOSC, would require Incident-Specific Authorization from the RRT IX to the FOSC and separate approval from the OSPR Administrator. Clear communications with the local affected Air District would also be required to address their concerns over air quality attainment thresholds (and whether or not an EPA emergency exemption or an Air District emergency variance is required to serve in lieu of a standing EPA exemption letter). At the state level, Health and Safety Code 41801(g) allows the OSPR Administrator to authorize in-situ burning for remediation of an oil spill, without needing an Air District permit.

RRT IX ISB policy is not clear as to what federal or RRT IX authorizations are required if the ISB is on oil spilled in a vegetated area on, into, or near state and/or navigable waters. Outside of the marine zone, the EPA rather than the USCG would typically provide the FOSC for the response. The NCP is clear that the agency providing the FOSC and making a request of the RRT for use of an ART cannot <u>also</u> be voting as a member of the RRT to authorize that action. The EPA member of the RRT IX could not, under the NCP, authorize an ART use requested by an EPA FOSC.

These issues could perhaps be further articulated and resolved with an updated Letter of Agreement (LOA) among the federal agencies and OSPR, addressing inland use and authorization processes for all ARTs, including ISB. Until this is fully resolved, inland ISB may yet require the EPA, as an agency and outside of their role on the RRT IX, to issue override approvals or waivers to an affected Air District before the burn can proceed.

Regardless of how RRT IX or separate EPA authorizations manifest themselves, the OSPR Administrator approval is still required.

ISB proposed for oil spilled into a dry creek bed, if that bed is defined by the state as a "blue line" waterway, raises somewhat similar questions about the role of the RRT IX in authorizing a burn. It is likely that the RRT IX would have no authorizing role in this case, but the EPA (as an agency) and the OSPR Administrator need to issue their respective agency approvals.

ISB proposed for dry land that will not affect state waters may not require OSPR Administrator approval, but the CDFW may want assurances from OSPR that the ISB will not pose "other deleterious effects" to state trustee resources per California Fish and Game Code §5650. The EPA would need to issue override approvals or waivers to the affected Air District before a burn could proceed.

- H. ISB Policy Update
 - 1. Possible Effects of Proposed Subpart J Revisions on ISB Decision-Making

The EPA's finalized revisions to Subpart J of the NCP Product Schedule may also significantly affect how future ISB use decisions are handled. As the NCP and the Product Schedule stand now, the RRT (this applies to <u>any</u> RRT) is only involved in an ISB authorizing role if an accelerant is used to initiate or support a burning operation. The accelerant would need to be selected from those on the NCP Product Schedule. However, the 1997 LOA within the RRT IX RCP describes, and provides concurrence for, a more involved RRT IX authorization role for ISB decisions, regardless of how the burn is ignited.

Revised Subpart J requirements may stipulate that a RRT authorization is not needed even if an accelerant is used, providing all of the accelerant is consumed as part of burning. Accelerants would not then be listed on the NCP Product Schedule. This would remove RRTs from the authorization process and/or make unnecessary any offshore RRT pre-authorization zone, unless an ISB LOA in the RCP is updated to state otherwise. Subpart J changes might also result in ISB being re-categorized as a mechanical technology rather than an ART. It is presumed that the EPA would still review ISB operations proposed by the UC and provide any necessary override or waiver letters to affected Air Districts.

For the state, ISB is likely to remain categorized as an ART, but future discussions would be needed to resolve respective federal (RRT IX or EPA), state (OSPR or CDFW), and local (Air District) issues as they relate to a variety of potential ISB response settings, particularly for inland and upland ISB scenarios.

2. Use of New ISB Resources and Guidance

Updates to the RRT IX ISB Plan will occur after the EPA NCP Subpart J revisions are finalized. The updated plan will incorporate, at minimum:

- Materials from NOAA, other RRTs, and science- and industry-developed ISB protocols developed since the RRT IX's last ISB update in 2005;
- Any changes in types and scope of authorization zones;
- An inland ISB element, including clarity on EPA role when/if the RRT IX is not involved and/or the EPA is not the FOSC;
- Job aids and templates for ISB monitoring;
- New EPA waiver letter (likely issued to the California Air Resources Board, for use by individual Air Districts) that will clarify the EPA role in authorizing an ISB for emergency oil spill response, in a manner that does not result in local Air Districts violating their ambient air quality attainment thresholds;
- A re-visiting of the Air District Quick Approval Zones for offshore marine waters.
 - 3. The Need for an EPA Waiver Letter

At oil spill drills where ISB is discussed and an Air District is involved, there is persistent confusion over the authority of the FOSC, under the NCP, to order an emergency oil spill burn. At the state level, the OSPR Administrator has clear authority to authorize an ISB. Generally, Air Districts are unaware of the federal and state emergency authorities that prevail during an oil spill response or of the Quick Approval Zones negotiated so many years ago. Air Districts continue to view ISB as needing to meet regular Open Burn rules, and if a particular air basin is already near, at, or exceeding the ambient air quality standards set by the EPA, there is a strong reluctance to concur with other authorizations that would allow the burn. An EPA waiver letter is needed to assure local Air Districts that an ISB ordered as part of an emergency oil spill response does not fall under typical Air District rules and that the EPA will not at a later date serve Air Districts with a notice of violation.

- I. Other Issues
 - 1. Availability of Fire Boom

A past lack of fire boom available in or to California within 24 hours of a spill is no longer an issue (at least with nearshore areas), as the Marine Spill Response Corporation (MSRC) has added 1000' of fire boom (two 500' sections) to their inventory in Long Beach, CA. There is still additional fire boom located in Everett, Washington, 24 hours away, as well as at various other staging areas around the country. MSRC would be the Oil Spill Response Organization (OSRO) typically responding to an offshore oil spill in California for which burning was being considered.

The Clean Seas OSRO, based in Carpinteria, CA, responds to spills from offshore platforms. They do not currently have fire boom within their response inventory. Based on previous crude oil testing (McCourt, 2001), most of the platform oils may be

unburnable. The Bureau of Safety and Environmental Enforcement (BSEE) is in the process of evaluating whether Clean Seas has a regulatory responsibility to maintain fire boom. Additional burn tests of platform crude oils may be conducted to resolve this question.

SECTION IV. ART FINDINGS AND RECOMMENDATIONS

The findings and recommendations below are those of OSPR and address whether past and future ART planning supports the OSPR BAT goals. These findings and recommendations have been reviewed by outside parties, and all comments of those parties have been considered. However, not all outside party comments may have resulted in a substantive change to the OSPR findings and recommendations, nor is it presumed that outside reviewers agree with all recommendations presented here.

- A. Oil Spill Cleanup Agents
 - 1. Dispersants
 - a. OSPR has met previous BAT Goals Regarding Dispersant Use.
 - OSPR has been very proactive in dispersant research since the mid-1990s and was instrumental in funding and supporting development of the CROSERF dispersed oil toxicity protocols;
 - OSPR led the NEBA dispersant risk analyses of the early 2000s. These NEBAs supported the Area Committee recommendations to the RRT IX regarding offshore marine dispersant use zones;
 - OSPR steadily and actively partners with the RRT IX in policy development and co-authored the 2008 California Dispersant Plan (CDP);
 - OSPR provided 2005 and 2012 drafts of biological assessment materials used for ESA Section 7 consultations by USCG with the NMFS and the USFWS;
 - OSPR works with the federal trustee agencies (NMFS, USFWS) in discussing and integrating suggested Best Management Practices (BMPs) for inclusion in the RRT IX dispersant plan;
 - OSPR provides the ART Lead Technical Specialist in frequent drills of the CDP;
 - OSPR participates in all Area Committees and serves as the lead state agency in California spill response planning, drills, and response;
 - OSPR is an active member of the RRT IX and co-chairs the RRT's ART Committee;
 - OSPR continues as the primary agency responsible for drafting update

materials for the RRT IX Dispersant Use Plan for California and associated dispersant decision support checklists and job aids (e.g., interagency contacts, dispersant resources, properties of CA oils, efficacy, wildlife and water monitoring protocols, risk communication, seafood safety, dispersant use documentation forms);

- OSPR coordinates with the California Coastal Commission to assure the RRT IX dispersant plan is reviewed under the Coastal Zone Management Act;
- OSPR is part of on-going dispersant workshops and other response technology work groups (e.g., NOAA-CRRC, BC-States, NRT Science and Technology Committee, Gulf of the Farallones Vessel Spills Workgroup);
- OSPR uses the biennial Response Technology Workshop as an opportunity to present background information on dispersant use, and new developments in the field;
- OSPR tracks the dispersant research being conducted by other agencies and institutions, nationally and internationally (e.g., Ohmsett, SL Ross, Environment Canada, OSRI, SINTEF, CEDRE, Research Planning, Inc., SEA Consultants);
- OSPR provides outreach and training on the RRT IX dispersant plan (e.g., RRT IX meetings, CG briefings and trainings, EROS classes, National Marine Sanctuary events, OSRO trainings).
- b. Continuing BAT Improvements for Dispersants
 - i. Research

OSPR no longer has funds dedicated for further dispersant research. We continue to actively follow the exciting research and future findings of other well-respected and experienced research and research evaluation partners (e.g., USCG, NOAA, NOAA-CRRC, EPA, USCG and USCG Strike Teams, BSEE/Ohmsett, SL Ross, Environment Canada, Research Planning, Inc., SEA Consults, Oil Spill Recovery Institute (OSRI) UC Davis, SINTEF, CEDRE, and other rigorous academic environmental toxicology programs).

Some additional dispersant research of particular interest:

 Continued research (begun by Kemp, 2013; Lochhead, 2015) into a lecithinbased dispersant that turns a thick oil slick into in a thin, floating, dispersing oil mass. Purportedly, this thin slick would not stick to wildlife. Effectively an oil spreader rather than an oil dispersant, research would need to evaluate whether a thin slick that spreads (and evaporates) using two dimensions, rather than a plume of dispersed oil that spreads in three-dimensions, results in lower durations and concentrations of exposures to fish and wildlife to TPAH, PAH, and PAH degradation products. It would have to be assumed, for planning purposes, that the thinner slick would not then be expected to be mechanically recoverable.

- Continued research and wave tank testing of the use of high-pressure water to disperse oil. If this technology is successful, the fate and effects of micro-droplet dispersion of oil into the water column, and resultant TPAH and PAH exposures to environmental resources, should be evaluated using NEBA and ESA Section 7 consultations, just as chemical dispersants currently are.
- Research into chemical dispersant formulations that do not have solvents, or solvent actions, that interfere with the enzymatic ability of microbes to biodegrade the oil micro-droplets formed after an effective use of dispersants.
- OSPR is tracking the current ExxonMobil work on development of a gel-based matrix for Corexit dispersant, which would give it a longer retention time on the oil slick and allow for greater efficacy. However, greater toxicity is likely to be an outcome as well, so additional trade-off decision-making regarding efficacy versus toxicity will need to be conducted if and when this product formulation comes to market. A separate state OSCA license for this product would also be required.
- Research comparing the relative toxicity to wildlife of chemical dispersants versus common detergents, including those used for cleaning oiled wildlife. Earlier studies by Environment Canada indicated that some household detergents could be orders of magnitude more toxic to wildlife than chemical dispersants, yet we also know that these detergents are commonly used to safely clean wildlife. Additional research in this area could better inform discussions with wildlife professionals regarding acceptable risks to wildlife of any response or rehabilitation approach.
 - ii. Planning and Policy

Using OSPR's well-embedded role in response planning, including dispersant planning, we conclude that many of the science-based assumptions used leading up to the 2008 plan are still valid, even following the DWH experience. However, clarifications and updates will be suggested for the updated RRT IX Dispersant Use Plan for California to reflect the applicable lessons-learned from the DWH response. Changes and updates will include the following:

- The two types of dispersant authorization zones (RRT IX Pre-Authorization, RRT IX Incident-Specific Authorization) will occur on one chart;
- The Appendices of the 2008 California Dispersant Plan will instead become Job Aids covering the same topics (e.g., monitoring for dispersant effectiveness, wildlife monitoring, water column monitoring, seafood safety, dispersant resources, pre-planning NEBA results, public and RRT communications, ESA Section 7 and CZMA consultation results);

- New Job Aids will include more operational templates and an ART Task Book;
- Subsea use, or surface use of dispersants for more than 4 days, will become "RRT IX Incident-Specific Authorization" required, regardless of the zone in which dispersant actions are being considered;
- Boxes are added to the Decision Flowchart to address baseline criteria for dispersant use, incorporate BMPs for wildlife avoidance into the FOSC and RRT IX decision processes, suggest early outreach to various parties (RRT IX, other trustee agencies, the public) about dispersant decision steps being taken, and provide additional coordination between the Planning and Operations Sections to assure all recommended or required BMPs are implemented and monitoring teams are appropriately deployed.

Other dispersant application platforms that deserve further attention (while acknowledging that in some incidents, less area can be treated):

- Use of the Neat-Sweep for more targeted application of dispersants;
- OSRO acquisition of dispersant spray arms that can be mounted to vessels for more targeted application of dispersants from small boats.

OSPR's past decades of dispersant research, NEBA risk analyses, dispersant and technology workshops, dispersant use planning and job aid development, the unique state licensing program for oil spill cleanup agents, and continued knowledge of dispersant research and policy development occurring nationwide sets CDFW-OSPR apart from any other state in providing ART Best Achievable Protection using Best Available Technology.

- 2. Sorbents
 - a. OSPR Has Met Previous BAT Goals for Sorbents
 - OSPR is the only state that has an OSCA licensing program, and does not offer a categorical exemption to sorbents. As with all other OSCAs, sorbents are evaluated for toxicity (sorbent leachates are used in the red abalone larvae test), for their ability to meet State Ocean Plan thresholds for pH, flash point, and trace metals, and whether their use would provide any "other deleterious effects" per California Fish and Game Code §5650.

There are, very simply, practical limits to how much can be expected in the way of surface oil recovery from the use of sorbents, whether used loose or in a self-contained form (boom, sock, pillow, pad, sheet). Most sorbents work best on thinner oil slicks and sheens and, with the possible exception of sweep and pom-pom configurations, have limited efficiencies on thick oil. Sorbents have great utility in smaller response settings where spills of lighter products or sheens of thicker oils in low energy habitats (such marinas, harbors, and along marsh and wetland shorelines) are a good match for

sorbent use. Finding products that repel water while absorbing oil, while avoiding the tendency to sink once they become saturated, is a challenge. Several of the sorbent products (especially the synthetics) are configured to work very well in these capacities, sorbing high ratios of oil for the amount of sorbent deployed.

The current policies of the RRT IX and OSPR are to limit sorbent configurations to "selfcontained" boom, socks, or pillows. This decreases the amount of sorbent surface area that can contact the oil. Use of any of these products in loose (but otherwise containment-boomed areas) would increase sorption rates for the greater area that can be covered but may pose consequent problems with recovery of oiled sorbent.

- b. Continuing BAT Improvements for Sorbents
 - i. Research

There are enough types of sorbent products with current state licenses or exemptions from OSPR, and exempted from listing on the NCP Product Schedule, to address current allowed uses.

- ii. Planning and Policy
- The OSPR should support further use of OSPR <u>licensed or exempted</u> sorbent technologies, even those products not currently held in OSRO inventories. Rather than relying solely on the conventional sorbent products the OSROs are willing to purchase and stock, OSPR State On-Scene Coordinators and Environmental Unit Leaders can request a RP, during a actual incident, to procure and use the types and configurations of sorbent products that could better support BAT. These products or product uses could include the following:
 - Configurations using sorbent pillows, along the water surface or suspended in the upper water column, to capture oil slicks, sheens and physically dispersed oil. These can be particularly helpful on slow water spill environments (marsh, wetland, mudflats) where capture of resheening oil can be maximized.
 - Using extruded foam or other sorbent materials within the oil production and fracking industries for treatment of produced water before re-injection, or to treat spills of production water (these sorbents are often good at capturing the trace metals and other contaminants, besides oil, found in production waters);
 - Use of sorbent products as buried secondary capture systems (boom, curtain, or vaults) within stream beds (including dry creek beds) for subsurface oil capture and filtering;
 - Use of sorbent pads or pillows to line towed nets and for capture of subsurface (physically or chemically) dispersed oil;

- Use of loose cellulose-based sorbents (e.g., peat, coconut husk) to sorb oil on intertidal rocks before other hand cleaning;
- Use of loose cellulose-based pH neutral and seed-free sorbents (e.g., coconut husk, kenaf, bagasse), blown onto the stems of oiled vegetation in marsh/wetland habitats, to reduce the "contact stickiness" of oil to birds and marsh wildlife;
- Use of loose cellulose-based pH neutral and seed-free sorbents (e.g., coconut husk, kenaf, bagasse) as a binder and bulking agent for liquid bioremediants used in land-based/land-farming bioremediation projects.
- Efforts should also focus on use of sorbent products that can reduce the amounts of generated waste. This would include focused attention on use of reusable sorbents and of sorbent products that can be converted to other uses when soiled (fuel, road base materials), rather than landfill disposal;
- Continued work is necessary with the RRT IX to increase their understanding and acceptance of the limited and strategic application of loose sorbents, whether on oiled marsh and wetland vegetation to reduce contact stickiness of oil already stranded on plants or in nearshore open-water response contexts within an area protected by containment boom. Even though sorbents are categorically exempted from listing on the NCP Product Schedule, and so technically do not need additional RRT IX approval before use, current RRT IX policy continues to allow only for the limited and experimental use of loose sorbents on the basis of demonstrated need. Clarification is needed of the authorization role of the RRT IX when sorbent products are used in loose form. At the state level, OSPR Administrator incident-specific approval will be necessary regardless of whether RRT IX authorization applies.
 - 3. Surface Washing Agents
 - a. OSPR Has Met Previous BAT Goals for Surface Washing Agents
 - OSPR has only issued OSCA licenses for surface washing agents categorized as "lift-and-float" so that there is an opportunity for additional oil washed from hard surfaces or sediments to be contained and recovered.
 - OSPR fully appreciates the value that surface washing agents can bring to an oil spill response, supporting and seeking appropriate authorizations for use in past spill responses (e.g., Kyberz River, Grove Incident) or actively supported additional pilot testing during responses (e.g., Cosco Busan, Refugio Beach).
 - b. Continuing BAT Improvements for Surface Washing Agents
 - i. Research

- OSPR supports the additional investigations the EPA is conducting into lab-based effectiveness tests for surface washing agents.
- Additional research is needed into the possible uses of surface washing agents in inland spill response settings (e.g., for flooding of oiled dry creek bed sediments and capture of re-floated oil).
 - ii. Planning and Policy
- OSPR encourages additional investigations into the possible use of truckbased systems, use of roll-off bins, or construction of temporary sandcleaning facilities as a means to promote future site-based sand cleaning. This approach was effectively used during the DWH spill and has value in California spill response as it would allow cleaning and replacement of native sand, rather than excavation and off-site disposal of oiled sand. This is of particular value for California beaches where retention of clean native sands is a high priority.
- OSPR will work with the RRT IX and the OSPR Administrator to identify their respective authorization responsibilities when surface washing agents are used in an ex-situ manner (no runoff to water) versus in-situ (when there is likely or potential runoff to water).
- OSPR and the RRT IX can investigate whether there are any likely circumstances in California marine or inland uses of a surface washing agent where pre-authorization could provide additional and timelier response value.
- 4. Solidifying Agents
 - a. OSPR Has Met Previous BAT Goals for Solidifying Agents
- OSPR has only issued OSCA licenses for solidifiers or other elasticity modifiers that can be used in a proper form. For example, liquid gelling agents can only be used in a spill response context where the oil + gel matrix cannot escape to water or be unrecoverable if it escapes (these restrictions lead to a low likelihood of use). The particulate solidifiers licensed for use have met the OSCA licensing requirements for toxicity and State Ocean Plan thresholds for trace metals, pH, flash point, etc. In self-contained form, they also meet the requirements of California Fish and Game Code §5650.
- OSPR fully appreciates the value that self-contained solidifiers can bring to an oil spill response, supporting and seeking appropriate authorizations for use in past spill responses (e.g., DWH, Grove Incident), and supporting pilot testing of loose particulate or self-contained particulate solidifiers (e.g., Navy Pilot Project, Lake Tahoe Marine Operators).

- In 2001, OSPR issued "Policies and Procedures for the Pre-Approved Use of Sock and Boom Form of Collecting Agents for use in Waters of the State." This pre-approval for use of self-contained solidifiers has not since been rescinded.
 - b. Continuing BAT Improvements for Solidifying Agents
 - i. Research

Although OSPR does not currently have any research monies to invest, the following are some suggested projects, exploring novel uses of solidifiers. Results from these studies could help the response community better meet our collective Best Achievable Technology goals:

- Further research into whether liquid gelling agents, or loose particulate forms of solidifiers, could be used as a self-creating barrier to bound surface oil slicks.
- Further research into the use of loose/broadcast particulate solidifiers on gravel beaches where deep oil penetration is of great concern. In this scenario, solidifiers could be applied to the shoreline just prior to oil stranding, to keep the oil on the surface. The ability to recover the solidified oil mat would pose a challenge that would need to be addressed.
- Further investigations of whether oil + loose particulate can be recovered by mechanical skimmers or whether recovery of a mat of solidified oiled can only be done by hand (e.g., raking).
 - ii. Planning and Policy
- There are specific spill situations when solidifiers may be not only be appropriate but help us further meet our BAT goals. However, there remain operational disadvantages associated with solidifiers that make them impractical for large, on-water spills if recovery of the sorbed solidifier cannot be assured. If such disadvantages can be overcome, solidifiers may become a useful response tool. Solidifiers also may have promise with respect to stopping vessel or pipeline leaks. Therefore, the evolution of this technology should be followed and evaluated to determine how or if it can be applied to oil spill cleanup operations.
- The RRT IX and OSPR Administrator should further consider use of loose particulate solidifiers, within a containment-boomed area, for treatment of spills near wetlands and on ponds and lakes.
- The RRT IX should complete and finalize its Pre-Authorization for the use of solidifiers in self-contained form, to mirror the one issued by OSPR.
- OSPR should support further use of OSPR licensed or exempted self-

contained solidifier technologies, as these are products not currently held in OSRO inventories. Rather than relying solely on the conventional sorbent products the OSROs are willing to purchase and stock, OSPR State On-Scene Coordinators and Environmental Unit Leaders can request a RP, during a actual event, to procure and use the types and configurations of self-contained solidifier products that could better support BAT. As with many of the sorbent products, broader use of the more effective self-contained solidifiers could include the following:

- Configurations using particulate solidifier pillows, along the water surface or suspended in the upper water column, to capture oil slicks, sheens, and physically dispersed oil. These can be particularly helpful on slow water spill environments (e.g., marsh, wetland, mudflats) where capture of re-sheening oil can be maximized;
 - Using solidifying materials within the oil production and fracking industries for treatment of production water before re-injection or to treat spills of produced water (these solidifiers are often good at capturing the trace metals and other contaminants, besides oil, found in production waters);
 - Use of self-contained solidifier products as buried secondary capture systems (boom, curtain, or vaults) within stream beds (including dry creek beds) for subsurface oil capture and filtering;
 - Use of solidifier pads or pillows to line towed nets and for capture of subsurface (physically or chemically) dispersed oil.
- Efforts should also focus on use of self-contained solidifier products that can reduce the amounts of generated waste. This would include focused attention on use of reusable self-contained solidifier products that can be converted to other uses when soiled (fuel, road base materials), rather than landfill disposal.
- 5. Herding Agents
 - a. OSPR Has Met Previous BAT Goals for Herding Agents
- While OSPR does not have any licensed herding agents, it has actively followed the research being conducted by other agencies and institutions on herding agents used to support ISB.
 - b. Continuing BAT Improvements for Herding Agents
 - i. Research
- Chemical herding agents may, in the future, prove useful for controlling the spread of oil in a specific spill situation and improve mechanical oil recovery efficiency. OSPR will follow any advancement in this use of herding

technology and, when data are available, further evaluate the use and applicability of chemical herders to California oil spill response.

- OSPR will continue to track the research underway by ExxonMobil, evaluating the use of herding agents to contain and support ISB. Research results to date indicate that positive effects of herding agents are short-lived and subject to disruption by advanced sea states.
- BSEE (at the Ohmsett facility) also has several wave tank studies planned that will further investigate the properties and efficiencies of herders under a variety of test conditions. The OSPR will be tracking the results of these studies.
 - ii. Planning and Policy

Neither the RRT IX nor the OSPR Administrator has specific plans for the use of herding agents. There are processes within both the RRT IX Regional Contingency Plan and OSPR licensing regulations that allow consideration of an OSCA, such as a herding agent on an emergency, incident-specific basis. This is the current approach related to potential use of herders in an oil spill response.

- 6. De-Emulsifiers
 - a. OSPR Has Met Previous BAT Goals for De-Emulsifiers
- Although OSPR does not have any licensed de-emulsifying agents, it has been involved in many past discussions about the potential benefits of deemulsifiers to support use of either dispersants or ISB.
 - b. Continuing BAT Improvements for De-Emulsifiers
 - i. Research
- OSPR does not have any research monies to dedicate to further research of de-emulsifiers but continues to follow national and international research being conducted by other agencies and institutions.
 - ii. Planning and Policy
- Neither the RRT IX nor the OSPR Administrator has specific plans for the use of de-emulsifying agents. There are processes within both the RRT IX Regional Contingency Plan and OSPR licensing regulations that allow consideration of an OSCA such as a de-emulsifying agent on an emergency, incident-specific basis. This is the current approach related to potential use of de-emulsifiers in an oil spill response.

- 7. Bioremediants
 - a. OSPR Has Met Previous BAT Goals for Bioremediants
- OSPR has reviewed and licensed a variety of bioremediants. Most contain primarily nutrients (fertilizers) to support native microbes. Others may also contain additional microbes. Individual bioremediant formulas may also contain several enzymes, surfactants, or preservatives.
- OSPR has used bioremediation processes in past spill responses (e.g., 2004 Suisun Marsh pipeline spill, 2016 Grove Incident) and evaluated them in other spill responses (e.g., 2015 Refugio Beach) for potential use, although in many cases, bioremediation is determined to not be necessary (e.g., 2010 DWH spill) or not advised because it does not meet the objectives of the UC (e.g., 2015 Refugio Beach).
 - b. Continuing BAT Improvements for Bioremediants
 - i. Research OSPR supports the research recently funded by the Oil Spill Research Initiative (OSRI) to do a components analysis of one bioremediant product (OSEII) that the manufacturer claims can be used in on-water and shoreline applications. While on-water bioremediation technology does not currently present a feasible option to conventional cleanup technology, the OSRI-funded research will help determine whether this technology will evolve into a significant response tool.
 - ii. Planning and Policy OSPR supports the EPA's proposed revisions to the NCP Product Schedule Subpart J, requiring both efficacy and toxicity tests (with established thresholds) for bioremediants. This will be useful information for the state, as it will directly apply to the state's revised OSCA licensing regulations and guidance.
- 8. In-Situ Burn
 - a. OSPR Has Met Previous BAT Goals for ISB
- OSPR has actively engaged with the RRT IX in development and updates to the RRT IX ISB Plan;
- OSPR assisted the RRT IX in determining the boundaries of the In-Situ Burning Pre-Authorization Zone;
- OSPR actively engaged with coastal Air Districts in the development of offshore Quick Approval Zones;
- OSPR is the state lead on all oil spill drills that exercise ISB, often negotiating

with local Air Districts and the U.S. EPA on what is required for Air District concurrence with the emergency burning of oil;

- OSPR is leading the revisions to the RRT IX ISB Plan, with an emphasis on adding elements related to inland burning.
 b. Continuing BAT Improvements for ISB
 - i. Research
- OSPR does not have any research monies to dedicate to further research of ISB but continues to follow national and international research being conducted by other agencies and institutions, including research related to use of herders to support ISB;
- OSPR will track research that further explores the formation of nitrated PAHs and whether they would be a human health or environmental concern during ISB in California;
- OSPR supports the BSEE in any future tests regarding the burnability of California crude oils;
- OSPR is tracking research into the use of de-emulsifiers to prolong an ISB window of opportunity.

ii. Planning and Policy

- As part of updates to the RRT IX ISB Plan:
 - Based on finalized revisions to the EPA's Subpart J, determine the respective authorities of the RRT IX and the OSPR Administrator to approve offshore and inland/upland burns;
 - Based on finalized revisions to the EPA's Subpart J, determine whether ISB will be considered a mechanical approach, rather than an ART;
 - Based on finalized revisions to the EPA's Subpart J, determine if there is still a need or basis for an offshore Pre-Authorization Zone for ISB;
 - If an offshore Pre-Authorization Zone is retained, the RRT IX should reconsider the boundaries to accommodate a better understanding of what offshore species might be present and potentially affected (e.g., consider a Pre-Authorization Zone boundary just seaward of the Continental Shelf, as numbers and diversity of species diminish seaward of the Shelf);
 - Re-visit the Air District offshore marine Quick Approval Zones, and determine if there should be additional offshore "buffers";
 - Memorialize and include (perhaps as an MOU with the California Air Resources Board) clarifications of federal and state override provisions

already in regulation regarding emergency ISB;

- Include in the updated RRT IX In-Situ Burn Plan an EPA waiver letter for Air District reference. This letter should clarify that EPA will waive an affected Air District's ambient air quality attainment thresholds in cases where there is a federal and state authorized burn. The waiver should clearly acknowledge that Air District Open Burn rules do not apply during federal- or state-ordered emergency ISB operations. If ISB is requested by the FOSC and approved by the EPA, exceedance of ambient air thresholds will not result in an Air District violation.
- Include Job Aids in the updated RRT IX ISB Plan that provide relevant contacts as well as operational templates for air monitoring, wildlife monitoring, operational practices to minimize environmental impacts, and public outreach, media messaging, and risk communication tools.
- 9. OSPR Licensing of Oil Spill Cleanup Agents
 - a. OSPR Has Met BAT Goals for OSCA Licensing
- OSPR is the only state that maintains an OSCA review and licensing program that is separate from the EPA's review and listing of OSCAs on the NCP Product Schedule. The OSPR licensing program currently has more stringent requirements of an OSCA than does the EPA. OSPR's licensing requirements include:
 - Toxicity testing on red abalone larvae (in addition to the fish and invertebrate testing required by EPA);
 - Toxicity tests measuring for Effects Concentration (EC), in addition to the Lethal Concentration (LC) test required by EPA;
 - OSPR OSCA licensing establishes a toxicity <u>threshold</u>. Products with an EC₅₀ less than 10 ppm (i.e., any effect, such as larval deformation, in more than 50% of the tested sample at a concentration or 10ppm or lower) will not be licensed. (Lower concentration = greater toxicity).;
 - To be licensed (or upon review, granted an exemption from licensing) an OSCA must also meet State Ocean Plan thresholds for pH, flash point, trace metals, chlorinated hydrocarbons, etc.
 - In addition to toxicity tests, OSCAs are also reviewed against Fish and Game Code §5650 for whether the product, even if non-toxic, poses a potential for "other deleterious effects" if used improperly. Examples of this application are particulate solidifiers that could pose an ingestion hazard for fish and birds and low pH sorbents (such as peat moss) that can only be used in well-flushed environments.

- b. Continuing BAT Improvements for OSCA Licensing
- Depending on what changes are promulgated for the final revised Subpart J, the state may also change its licensing regulations and guidance to mirror the federal approach. If the federal approach falls short of what the state must require in the way of product licensing requirements, then there may be additional testing and thresholds requirements established at the state level for all OSCAs.
- Updates to the state's OSCA licensing regulations and guidance will not occur until Subpart J revisions are finalized, and it is not clear when EPA will be ready to release the final revisions to the Subpart J.
- After OSPR revises its licensing regulations and procedures, all OSCA manufacturers currently holding an OSPR license or exemption will be asked to re-apply, incorporating the new EPA and OSPR testing requirements and data in their applications. OSPR will not charge a fee for review of the resubmitted license and exemption applications, although the applicant will still be required to pay for any required efficacy or toxicity testing needed to support the application.

SECTION V. LIST OF ACRONYMS

LC LD	Lethal Concentration Lethal Dose
LISST	Laser In-Situ Scattering and Transmissometer
LOA	Letter of Agreement
LOEC	Lowest Observed Effects Concentration
MMS	Minerals Management Service
NCP	National Contingency Plan
NEBA	Net Environmental Benefit Analysis
NMFS	National Marine Fisheries Service
NMS	National Marine Sanctuary(ies)
NO	Nitrous Oxide
NOAA	National Oceanic and Atmospheric Administration
NOBE	Newfoundland Off-shore Burn Experiment
NOEC	No Observed Effects Concentration
NPAH	Nitrated Polycyclic Aromatic Hydrocarbon
NRC	National Research Council
OPA/OPA90	Oil Pollution Act of 1990
OSCA	Oil Spill Cleanup Agent
OSPR	Office of Spill Prevention and Response
PAH	Polycyclic Aromatic Hydrocarbon(s)
QA/QC	Quality Assurance/Quality Control
RP	Responsible Party
RPI	Research Planning, Inc.
SCAT	Shoreline Cleanup Assessment Team
SCOOS	Southern California Ocean Observing System
SDS	Safety Data Sheet
SFT	Swirling Flask Test
SMART	Special Monitoring of Applied Response Technologies
SOA	Secondary organic aerosols
SOSC	State On-Scene Coordinator
SSC	Scientific Support Coordinator
SSEP	Scientific Study and Evaluation Program
RCP	Regional Contingency Plan
RRT	Regional Response Team
TPH	Total Petroleum Hydrocarbon
TPAH	Total Polycyclic Aromatic Hydrocarbon Unified Command
UC USCG	United States Coast Guard
USEG	US Fish and Wildlife Service
WAF	Water Accommodated Fraction
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