Prince William Sound Dispersants Monitoring Protocol: Implementation and Enhancement of SMART (Special Monitoring of Applied Response Technologies)

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Developed by:

Prince William Sound RCAC
Regional Citizens' Advisory Council

Citizens promoting the environmentally safe operation of the Alyeska Terminal and associated tankers

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Introduction

*This protocol provides a stepwise approach to **implement enhancements** to the SMART dispersant monitoring protocol in Prince William Sound, Alaska by:*

**Adding to pre- and post-application data collection parameters*
**Identifying thresholds for evaluating dispersant efficacy and effects in Alaska*
**Incorporating long-term monitoring*

Background

Monitoring protocols are used to make decisions about whether to start or sustain the application of chemical dispersants in response to an oil spill, and to document effectiveness, fate, and effects.

In the U.S., the Special Monitoring of Applied Response Technologies (SMART) protocol is widely used for collecting information to inform decision-making during dispersant applications. SMART was developed through a joint effort including the U.S. Coast Guard, NOAA, the U.S. Environmental Protection Agency, the Centers for Disease Control and Prevention, and the Bureau of Safety and Environmental Enforcement.

The widespread and sustained use of chemical dispersants during the 2010 response to the Deepwater Horizon well blowout in the Gulf of Mexico yielded a number of observations and recommendations for improving dispersant monitoring by building on SMART. The protocols presented in this document synthesize many of these lessons learned into an enhanced monitoring protocol for Prince William Sound, Alaska with the following components:

- Background surveys to characterize application environment
- Pre-application biological monitoring
- Additional methods for field efficacy testing
- Visual effectiveness monitoring process based on standard characterizations
- Instrument monitoring of dispersed plume composition and movement with criteria for assessing effectiveness
- Monitoring of dispersed oil plume toxicity based on water sample analyses

This enhanced monitoring protocol was developed for use in Prince William Sound, but could be applied in other regions of Alaska or the U.S.

Purpose

The primary purpose of dispersant monitoring is to provide feedback about effectiveness and potential adverse impacts to inform the decision to apply, or continue applying, dispersants. A secondary purpose is to evaluate the potential biological toxicity from the application.

This document outlines a dispersants monitoring protocol that builds on the SMART protocol, providing two levels of effectiveness monitoring as well as a detailed biological monitoring component. It also specifies additional pre- and post-spill monitoring activities to complement field testing during a dispersant application, and identifies existing sources of long-term monitoring and environmental data for Prince William Sound that may inform dispersant use and monitoring. This protocol can be applied by the Unified Command to inform decisions about whether to initiation or continue dispersant application.

This document was developed with the intent to enhance the available information to support decision-making by working within the existing response framework.

Scope

This protocol is organized into sections that correspond to steps in the monitoring process. Enhanced field monitoring is carried out immediately prior to and during dispersant applications. Long-term monitoring should be carried out both before and after the emergency response to an oil spill.

- **Enhanced Field Monitoring** uses the same terminology and approach as the SMART protocol, but enhances the types of data collected, includes pre-application data collection, and provides thresholds for evaluating results. The field monitoring is conducted in situ or using oil and water samples from the intended application location to evaluate efficacy and effects of the dispersant application.

  Activities that take place immediately prior to dispersant applications:

  - **Pre-Application Surveys** collect real-time data about environmental conditions and biological receptors in an area where dispersants may be applied at the time of the oil spill.

  - **Pre-Application Field Efficacy Tests** evaluate and monitor the potential efficacy and effects of a full-scale dispersant application.

  Activities that take place during dispersant application operations:

  - **Tier 1** is visual monitoring from an aircraft to evaluate the effectiveness of dispersant application.

  - **Tier 2** involves towing instruments under the un-dispersed and dispersed oil slicks at various depths and using the collected data to assess the effectiveness of dispersant application.

  - **Tier 3** involves collection of water samples for onboard and laboratory analysis of chemistry and biological toxicity.

- **Long-term Monitoring** collects background data that can be used to characterize areas where dispersants may be applied. These ongoing studies may be designed specifically to collect data to inform dispersant use decisions or as part of a broader long-term environmental monitoring program or effort. Pre-spill monitoring occurs in areas that have not experienced dispersant application. Post-spill long-term monitoring is conducted after the dispersant application is complete to evaluate long-term effects to key species. Similar data collection and analytic methods are applied for each.

The key elements associated with each phase of the monitoring process are summarized in Table 1. The specific elements of this enhanced SMART protocol are identified in Table 2.

Table 1. Elements of the Dispersant Monitoring Process

ELEMENT	ENHANCED FIELD MONITORING					LONG-TERM MONITORING
	Pre-Application		During Application			
	Surveys	Field Efficacy Tests	Tier 1	Tier 2	Tier 3	
Timing	At the time of a spill, prior to dispersant application		At the time of a spill, during dispersant application			Weeks, months, or years before a spill occurs and/or beginning immediately after dispersant applications are completed
Location	Vicinity of oil slicks where dispersant application is being considered		Areas where dispersants are being applied			Areas where dispersants were applied and adjacent areas as well as areas identified in Alaska Subarea Plans as appropriate for dispersant application
Documentation	Documentation collected by field personnel at the time of an oil spill and potential dispersant application		Documentation of real-time data collected by field personnel at the time dispersant application			May be documented in existing Subarea Contingency Plans, agency maps and atlases, academic publications, geospatial databases, or other resources available through trustee agencies
Environmental Conditions that Influence Dispersant Effectiveness	Collect real-time measurements of temperature, salinity, water depth, mixing energy, weather, and other factors that may influence effectiveness		Data collected during pre-application surveys may inform the evaluation of results during Tier 1, 2, and 3 monitoring			Compile information about salinity, temperature, water depth, mixing energy, and other factors that could influence dispersant effectiveness
Dispersant Effectiveness Monitoring	Conduct field effectiveness test using actual oil and surface waters from application location	Collect real-time data on conditions that may impact dispersant effectiveness (temperature, sea state, salinity, etc.)	Conduct visual observation	Conduct in situ instrument measurements	Collect samples for chemical analysis and toxicity testing	Not applicable

ELEMENT	ENHANCED FIELD MONITORING					LONG-TERM MONITORING
	Pre-Application		During Application			
	Surveys	Field Efficacy Tests	Tier 1	Tier 2	Tier 3	
Biological and Ecological Resources	Conduct aerial or vessel-based surveys of potential dispersant application areas and adjacent areas to inventory resources-at-risk	Not applicable	Information about the presence of resources at risk may be recorded by observers on overflights or vessels			Compile data on biological resource location, abundance, and sensitivity. Compile habitat and environmental sensitivity atlases. Compile endangered and threatened species data.
Plankton Sampling	Conduct plankton sampling in potential dispersant application area and adjacent areas	Not applicable	Not applicable			Compile data about distribution and abundance of plankton species and planktonic life stages, including seasonality or other trends
Biological and Ecological Effects	Collect real-time information about resources at risk in the oil spill and dispersant application area to inform environmental trade-off analyses.	Not applicable	Not applicable		Collect samples of water and local species for chemical analysis and toxicity testing	Collect samples of environmental media and local species for laboratory analysis and comparison against pre-spill baseline data, pre-application survey data, and Tier 3 monitoring results
Background Hydrocarbons	Not applicable	Collect data on background hydrocarbon levels for comparison with Tier 2 and 3 monitoring results	Not applicable			Compile data on background hydrocarbon levels in water, sediment, and local species for comparison with pre-spill baseline and post-dispersant application data

Enhanced Monitoring Components

Table 2 summarizes the enhancements to SMART contained in this document.

TABLE 2. PRINCE WILLIAM SOUND ENHANCEMENTS FOR DISPERSANT MONITORING

MONITORING	SMART PROTOCOL	PWS ENHANCEMENT
Pre-application surveys	Not included	Survey and data collection on background conditions and ecological sensitivities at the time of application, to inform dispersant use decisions and design of enhanced monitoring process
Field efficacy tests	No method specified	Recommend use of bottle test to improve accuracy and simplify/expedite process of assessing potential effectiveness of dispersant application. Quantitative thresholds for effectiveness (>50% dispersed after 20 minutes settling time).
Tier 1	Visual assessment of efficacy by trained observer based on qualitative evaluation	Establishes thresholds for timing of visual assessment (within 30-60 minutes of application) to ensure standard approach. Establishes quantitative threshold for minimum effectiveness determination at 50% of undispersed slick area showing appearance of effective dispersion (e.g. coffee color plume).
Tier 2	Real-time instrument monitoring using fluorometry, supplemented by sample collection and analysis. No quantitative thresholds.	Use of integrated fluorometer/particle size analyzer to evaluate effectiveness against quantitative thresholds for concentrations (30-minute LISST data at 2m shows integrated particle count at least 10 times higher than background) and particle size (30-minute LISST data at 2m shows typical VMD of less than 50 μm over most of tow zone).
Tier 3	Recommends additional data collection to expand evaluation of dispersant effectiveness and explore fate and behavior of oil. Biological/toxicological monitoring is contemplated but no specific methods identified.	Specifies additional monitoring and analytic techniques to evaluate dissolved hydrocarbons. Specifies toxicological assessment techniques and equipment, and identifies target components for toxicological analysis.

Relationship between this Document and Oil Spill Response Framework in Prince William Sound

There are a number of existing plans and protocols that govern oil spill response operations and authorization/decision-making for dispersant use in Prince William Sound and Alaska. There are also many different agencies and organizations with roles in oil spill response generally and dispersant application specifically. Figure 1 shows how the Prince William Sound Dispersant Monitoring Protocol can be accommodated into this broader framework when an oil spill occurs.

Oil Spill Response Plans

In Alaska, the Unified Plan and Subarea Contingency Plans establish guidelines for oil spill response decision-making, and the Dispersant Authorization Guidelines (Appendix I to Annex F) establish criteria for dispersant authorization and use decisions. The Prince William Sound Subarea Contingency Plan supplements the Unified Plan with information about resources-at-risk in the region, and establishes additional parameters for dispersant use in the region.

Under Alaska and federal laws, oil industry operators are also required to develop oil spill contingency plans that identify dispersant use policies and specify operational resources and logistical support for their deployment. Oil spill removal organizations (OSROs) develop tactics guides and maintain equipment stockpiles to support these industry plans.

Consultation Authorities

As specified in the Unified Plan, both state and federal natural resource trustee agencies and the Alaska Regional Response Team have consultative roles in making decisions about dispersant use, including both the authorization process and monitoring.

Monitoring Procedures and Protocols

The SMART Protocol establishes Tier 1 and Tier 2 monitoring procedures, and recommends approaches to Tier 3 monitoring. This document enhances the SMART Protocol with specific considerations for Prince William Sound and Alaska. Nothing in this document is meant to replace or supersede SMART; this document should be used as a companion to the SMART Protocol.

Integration with Incident Command System and Field Monitoring Operations

The enhanced protocol described in this document will likely be carried out by a number of different organizations, coordinated within the Planning Section. The USCG National Strike Force (NSF) and Strike Teams have the operational capability to implement SMART, but they do not necessarily have the training and equipment needed to implement this enhanced protocol. The Prince William Sound Science Center (PWSSC), along with trustee agencies, plays an important role as stewards of multiple data sets that establish baseline conditions for the region. The PWSSC and Prince William Sound Regional Citizens Advisory Council (PWSRCAC) may supply resources, including trained personnel, specialized instrumentation, and deployment platforms, to support enhanced monitoring. Enhanced monitoring personnel would operate under the direction of the SMART Group Supervisor and within the established safety and field operation protocols established for the incident.

The NOAA Scientific Support Coordinator (SSC) will play an important role in interpreting enhanced monitoring data to inform Unified Command decision-making. The USCG, trustee agencies, OSROs, and the Oil Spill Recovery Institute/Prince William Sound Science Center have access to equipment and technologies to equipment and technologies that may be of use in collecting and analyzing dispersant monitoring data.

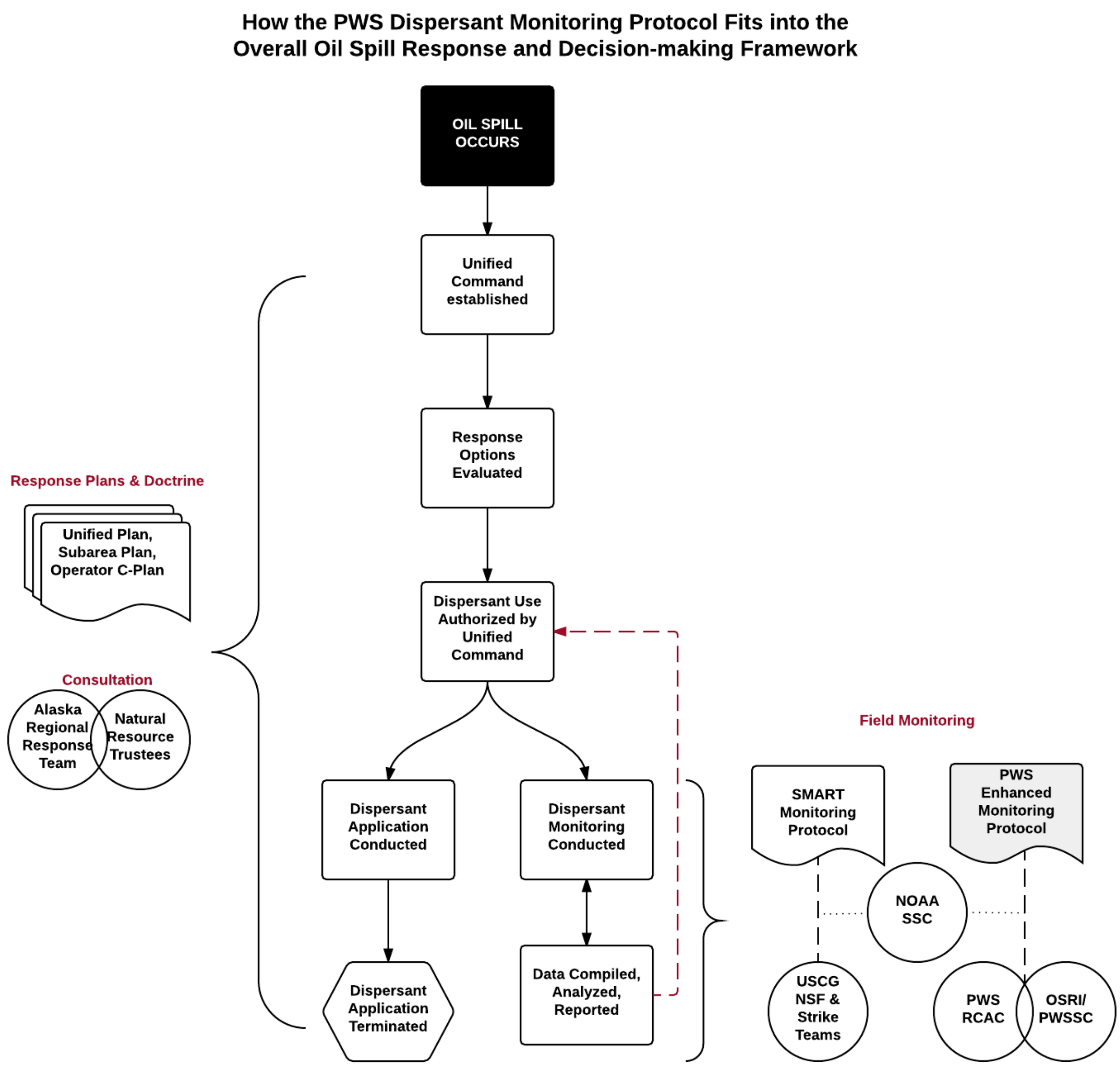


FIGURE 1. HOW THIS PROTOCOL FITS INTO THE PRINCE WILLIAM SOUND OIL SPILL RESPONSE FRAMEWORK

Decision-making Process

The decision to use dispersants as an oil spill response tool is dictated by federal and state guidelines and regulations, which establish parameters for evaluating environmental benefits and trade-offs. This monitoring protocol focuses on the compilation of information that will inform decisions about site-specific dispersant applications **after the decision to use dispersants has been made.**

Data collected at each level is used to inform decisions about whether to initiate or continue dispersant applications at a specific site based on effectiveness and biological impacts. Figure 2 summarizes this process and shows how each component of this monitoring protocol fits into the monitoring of dispersant efficacy and effects.

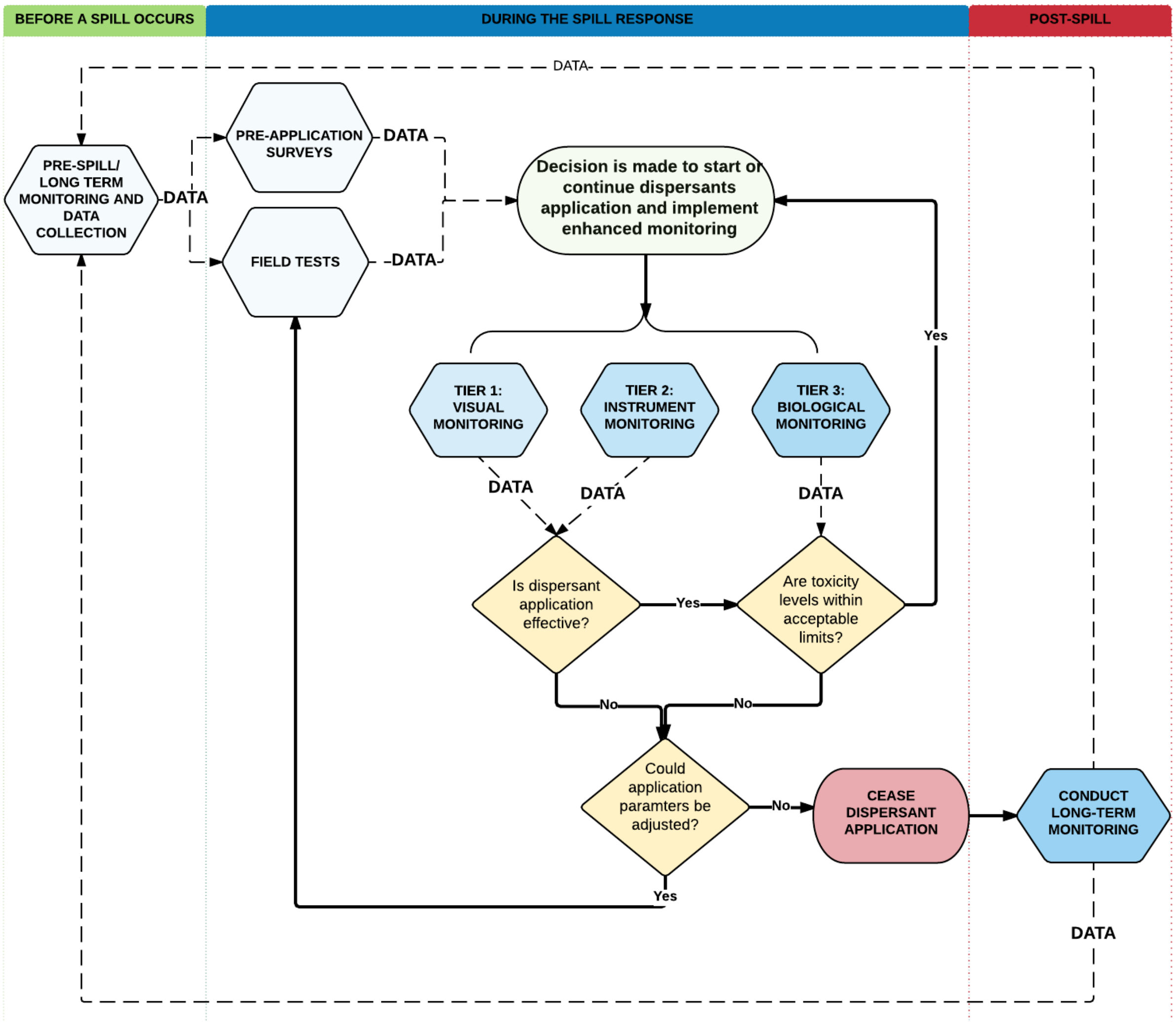


FIGURE 2. DISPERSANT MONITORING PROCESS BEFORE, DURING, AND AFTER AN OIL SPILL

Organization of this Document

This document is organized into the following sections:

- **Section 1** describes pre-application surveys that may be used to collect real-time data regarding environmental conditions and resources-at-risk in the dispersant application area.
- **Section 2** describes procedures for enhanced in-situ field efficacy tests to evaluate potential effectiveness of a dispersant application in Prince William Sound.

- **Section 3** describes enhanced visual (Tier 1) monitoring, which provides visual indications of the effectiveness or lack of it for a specific dispersant application.

- **Section 4** describes enhanced instrument (Tier 2) monitoring, which evaluates the effectiveness of a specific dispersant application by towing instruments to measure dispersion under the target slick then comparing the results to measurements taken under an undispersed slick.

- **Section 5** describes enhanced biological (Tier 3) monitoring, which expands on SMART Tier 3 data collection, and suggests thresholds for evaluating dispersant efficacy and effects.

- **Section 6** describes both pre-spill and post-spill long-term monitoring, which serve different purposes but may be conducted using similar or identical types of studies. Pre-spill monitoring may provide a baseline for evaluating enhanced dispersant sampling results or to direct the type of enhanced monitoring that is put in place. Post-spill monitoring begins after a spill response is complete to evaluate long-term effects to key species. This information may also inform dispersant use decision-making, but that is beyond the scope of this document.

*This document presents procedures and protocols for **monitoring, sampling, and field assessments** to support the evaluation of dispersant application effectiveness and biological impacts. The primary purpose of this protocol is to support monitoring of dispersant applications in Prince William Sound, Alaska – **not** to guide decision-making about selecting dispersants as a response option.*

1. Pre-application Surveys

Objectives

The objectives of pre-application surveys are to:

- Verify that there are no sensitive ecological species in or near areas where dispersant use may be authorized.
- Conduct surveys and collect samples, as feasible, to establish a baseline for determination of short- and long-term effects from dispersant application.
- Document actual environmental conditions (salinity, temperature, mixing energy) in areas where dispersant application is imminent.

Pre- application surveys are conducted at the time of the spill, prior to full-scale dispersant applications, to collect real-time environmental data that informs the decision to apply or continue applying dispersants based on predicted efficacy and effects.

Methods

Characterize Biological and Ecological Resources

Trained observers should evaluate the presence, location, and abundance of biological resources, including sensitive and endangered species, in the potential dispersant area. These surveys can be used to document the distribution and abundance of other types of wildlife, including birds, fish, and marine mammals. Standard methods for wildlife or environmental surveys may be applied. Biological sampling should also consider historical data for the area. Data compiled through written logs, photo or video surveys, or mapping should be transcribed onto an ICS-232 form (Resources at Risk Summary).

When an oil spill occurs anywhere in the U.S., there is an established process whereby state, federal, and local resource trustees collate information on resources-at-risk for review by the Unified Command. This data will be important to characterizing the biological and ecological resources potentially impacted by dispersant application.

Natural resource trustee agencies may have historical or real-time information available (as discussed in Section 6). This information should be consulted prior to surveying resources and included in an ICS-232 form. Data about biological and ecological resources can be used to identify areas that may not be appropriate for dispersant application. This data can also be compiled and considered during post-application monitoring of any long-term impacts.

Sample Plankton Populations

Time and resources permitting, plankton sampling may be carried out in the area immediately before dispersant application to provide information about resources at risk in the water column. Sampling of plankton populations is nontrivial – plankton span several orders of magnitude in size and abundance. In general, smaller plankton are the more abundant; larger plankton are less abundant, and more prone to net avoidance from both hydrodynamic (the pressure wave preceding a sampler) and visual signals. Many larger plankton including some copepod species (notably *Metridia* spp., one of the more common copepods in the Gulf of Alaska) and most krill species also undergo daily vertical migrations of hundreds of meters. Migrating species usually spend the day at depth (away from the lit surface layer, where their predators can see them), and migrate to the surface at night.

Special consideration should be given to sampling sensitive species and sensitive early life stages of ecologically and economically important species. Many fish and shellfish have pelagic eggs and larvae. Pre-application plankton sampling could also provide a background of the planktonic diversity and loading for characterizing the effects of dispersant application. This should be carried out using standard procedures consistent with pre-spill plankton surveys and other background studies, as described in Section 6 (Pre-Spill Surveys and Long Term Monitoring).

Plankton nets have a given "mesh size", the nominal size of the space between the meshes of the net. Smaller meshes are better able to sample smaller taxa, but are more prone to clogging, and produce a larger pressure signal ahead of the net that will alert larger plankton and elicit a larger degree of net avoidance. Plankton nets also come as a single net with a bridle ahead of it, or a double "bongo" net with two nets on either side of the lowing line/wire. Lacking a bridle, bongo nets results in a smaller hydrodynamic signal, and less net avoidance.

In the event of an oil spill in the PWS region, it will be advantageous that any plankton samples collected can be compared with those taken by prior studies. A list of previous studies is included in Section 6.

For small zooplankton, a 150 or 202 μm mesh net will be best, in a bongo configuration with a 60 cm mouth diameter. This net may be towed vertically, day or night, from depth to the surface. While previous studies typically tow from a depth of 50m or greater, plankton sampling that is conducted as part of enhanced SMART monitoring may be limited to the upper 10m of the water column. While it would be informative to do a tow from the bottom to the surface, sampling depths may be adjusted based on time or logistical constraints.

For larger zooplankton and larval fish, a 500/505 μm net is recommended. A larger net is better than a small one, but a 60 cm bongo net should be adequate. This net should be towed obliquely (i.e. raised and lowered while the vessel is steaming), to increase the amount of water filtered: larval fish can be quite dilute, and large amount of water (>100 m^3) must be sampled to collect and appropriately sized sample. Oblique tows can be done near surface as well (0-50 m or 0-100 m).

All plankton nets should be fitted with a flow meter, which will permit estimating the amount of water filtered by the net (so that plankton abundance may be expressed as a concentration). Plankton nets should be dyed black prior to use to reduce visual net avoidance. Samples should be preserved in 2-5% borax buffered formaldehyde for later enumeration. In the case of bongo nets, the side without the flowmeter is usually enumerated because the flowmeter may cause some net avoidance. The flowmeter sample may be retained as a backup, or may be made available for other studies where a quantitative sample is less important (e.g. it can be preserved in ethanol for genetic studies, or frozen for biochemical studies). Vertical tow speeds should be 0.75 to 1 m s^{-1}, and oblique tows should be done at slow speed: 1.5 to 2 knots if possible, or the minimum vessel speed if not.

Sample Hydrocarbon Levels

Hydrocarbon sampling within the water column may be conducted to quantify the levels of hydrocarbons in the dispersant application area prior to commencing operations. Sampling methods should be the same as specified for Tier 2 and 3 monitoring. Background hydrocarbon data can be compared to Tier 2 and 3 monitoring data to assess dispersant efficacy. Background hydrocarbon levels may be used to establish incident-specific thresholds for fluorometry.

Characterize Conditions that Influence Dispersant Effectiveness

Pre-application surveys inform decision-makers about the suitability of certain areas for dispersant application based on effectiveness criteria. These may include temperature, salinity, water depth, and mixing energy. They should also collect information about on-scene weather conditions (visibility, wind speed and direction, wave height, etc.) that may influence effectiveness. Recommended minimum thresholds for Prince William Sound are 10° C temperature and 30 parts per thousand salinity in the upper 10m of the water column. Below these levels, dispersant application may not be effective. (Fingas, 2004)

Pre-application survey data on physical conditions that may influence dispersant effectiveness may be considered in selecting locations for field efficacy tests, based on suitability for dispersant application.

Implementation

Responsibilities

In Prince William Sound, pre-application surveys may be carried out by a number of different agencies and organizations, under the direction of Unified Command. For the purpose of compiling and accessing this data to inform the enhanced monitoring of dispersant applications, the following organizations have responsibility:

- **NOAA Scientific Support Coordinator (SSC)** will coordinate with natural resource trustees (state and federal agencies) and local scientists (PWSSC/OSRI) to identify the type and extent of pre-application survey data that may inform the response.
- **Prince William Sound Science Center/Oil Spill Recovery Institute (PWSSC/OSRI)** is a primary repository for environmental data sets relating to Prince William Sound, and has a staff of trained scientists with the equipment and expertise needed to collect pre-application data. PWSSC/OSRI can inform or direct pre-application surveys based on seasonal, temporal, and geographic factors that may influence dispersant effectiveness or toxicity.
- **Prince William Sound Regional Citizens' Advisory Council (RCAC)** will work in close coordination with the PWSSC/OSRI to assist with the compilation of data and prioritization of pre-application surveying to inform the enhanced monitoring process. Enhanced monitoring data will be supplied to the NOAA SSC and/or through the Environmental Unit/Planning Section to inform decision-making.

Resources

Resources for a pre-application survey include:

- One or more vessels for sampling and survey activities
- Trained scientists and biological monitoring personnel
- Sampling supplies

These may be contracted directly or provided by natural resource trustee agencies, the PWSSC/OSRI, or the Responsible Party.

Considerations

- The top 10m of the water column is of greatest interest because this is the area where dispersed oil plumes would be most concentrated. Pre-application surveys should focus on the top 10m of the water column.
- Data collected immediately after an oil spill and prior to a dispersant application may inform decisions associated with the response in general, and specifically decisions about chemical dispersant use and the design and conduct of enhanced dispersant monitoring.
- Consideration of pre-application survey data must be balanced against the need for rapid decision-making in the event of an oil spill.

2. Pre-application Dispersant Efficacy Testing

Pre-application dispersant efficacy tests are simple screening tests that apply one of several valid methods to evaluate the potential effectiveness of the dispersant on the oil spilled based upon the actual field conditions at the time of the spill. These efficacy tests, conducted in the field, inform the final decision about whether to apply dispersants by providing an indicator as to the potential effectiveness. They can also provide information to inform environmental trade-off analyses.

Pre- application field efficacy tests are conducted at the time of the spill, prior to full-scale dispersant applications, to collect information about potential dispersant effectiveness using a simple screening test.

These pre-application efficacy tests are different from the test applications that may be conducted as part of dispersant operations. Pre-application efficacy tests inform the decision about whether or not to proceed to test applications.

Objectives

The objective of pre-application efficacy tests is to inform the decision about whether to proceed with dispersant application by evaluating the potential effectiveness of the dispersant based on the characteristics of the spilled oil, conditions of the receiving water, and chosen dispersant product.

Methods

Collect Samples of Water and Oil

Water and oil for the test are collected separately.

Water is collected away from the slick, but close enough to the spill to represent water from that area. Clean water without oil on the surface is taken. Sufficient water for all tests is collected and placed into a clean bucket that can hold enough water for one round of tests (8 L is recommended). Water can be collected from a boat using a clean ladle.

Oil is sampled once the boat has moved into the vicinity of a slick. Four different areas are sampled for one round of tests. Collected oil should be representative of the age and condition of the oil that is to be dispersed. At each location, the following steps should be taken:

- Collect enough oil to run two tests: one with dispersant and a control without dispersant
- Take photographs of each sampling
- Note the geographic coordinates of the sampling site
- Number each sample and bucket (e.g. 1, 2, 3, 4) to track the different samples
- Note the appearance and approximate location of the sample (in case test results are questioned later).

Oil can also be collected with a ladle (different than the ladle used for water collection). The ladle should be cleaned with only a paper laboratory towel between samples. Dirty towels are placed in a garbage bag. Water in oil samples is removed by gravity and poured into the liquid waste can.

Conduct Effectiveness Tests

A number of standard methods exist to test dispersant effectiveness in the field. Most involve combining dispersant, oil, and water samples in a flask or container, applying mixing energy, and then evaluating the resulting degree of dispersion using qualitative or quantitative measurements.

When ready to conduct the field test, the boat is stopped or brought to a safe location. Six test bottles are set up on a shelf or similar location. Buckets, test bottles and oil measuring cylinders are marked with test numbers and information as necessary. Each test bottle is marked under the water line with the sample number or name of the oil it will receive (e.g. 1, 2, 3, 4, control, test) so that the oil samples are distinct. Water is measured from the water bucket using a graduated cylinder. Each test bottle of water is then marked at the top line or the water using a crayon or a piece of masking tape. The numbers should correspond to the oil sample bucket numbers.

Oil that was collected from the slick is measured and added to the test bottles. Dispersants are added to the test bottles at the prescribed application ratio, but the control bottles will contain only water and oil. Each test bottle is shaken or agitated for 1 minute or 10 shakes (varies depending on method; see Table 3), then allowed to settle before being evaluated against effectiveness criteria.

Evaluate Results

After the sample bottles are settled for 20 minutes, close-up photographs are taken of each and a crayon line marked at the top of the re-settled oil line. The results are then evaluated as follows:

- If all 4 test bottles clearly show dispersion below the effectiveness threshold (see Table 3) - the oil is ***not dispersible***
- If all 4 test bottles clearly show dispersion above the effectiveness threshold (see Table 3) and the control flasks do not show dispersion - the oil is ***dispersible***
- If there is a discrepancy between test bottles, the tests should be repeated
- If the control(s) show significant dispersion, the oil is naturally dispersible or already has some dispersant in it; this information should be communicated to Unified Command for evaluation

Table 3 summarizes three methods for field testing that include effectiveness criteria. The test identified as "PWS Field Test" is the preferred option , because of its relatively simple method and clear criteria for determining effectiveness.

TABLE 3. FIELD TESTING METHODS AND EFFECTIVENESS CRITERIA

TEST	EQUIPMENT (for single replicate)	SPECIFICATIONS		PROCEDURE	EFFECTIVENESS CRITERIA
Recommended field testing method:					
PWS Field Test[1]	2 each 1000 mL clear glass bottle	Bottle #1 (test): 750 mL water 80 mL oil 4 mL dispersant (1:20 ratio)	Bottle #2 (control): 750 mL water 80 mL oil	Bottles #1 and #2: Shake 1 min Settle 20 min Mark top of water and top of oil in each bottle before and after shaking to compare	Bottle #1 (test with dispersant) should have at least 50% of the oil dispersed
Other methods with effectiveness criteria:					
Fingas 2003	2 each wine bottle or similar	Bottle #1 (test): 1000 mL water 10 mL oil 1 mL dispersant (1:10 ratio)	Bottle #2 (control): 1000 mL water 10 mL oil	Bottles #1 and #2: Shake 1 min Settle 10 min Mark top of water and top of oil in each bottle before and after shaking to compare	Bottle #1 (test with dispersant) should have at least 40% of the oil dispersed
OSRL[2]	2 each glass jars (size not specified)	Jar #1 (test) Fill jar to ¾ volume with water 20 mL oil 1 mL dispersant (1:20 ratio)	Jar #2 (control) Fill jar to ¾ volume with water 20 mL oil	Jars #1 and #2: Shake 10 times Settle 60 min Visually compare jars	"Significant" difference in appearance between two jars

Implementation

Responsibilities

In Prince William Sound, field tests for dispersant effectiveness are typically carried out by trained responders from oil spill removal organizations or USCG Strike Teams.

Resources

Pre-application field tests will require trained personnel to implement the tests and analyze results, testing equipment, and vessel transportation to the testing site(s). This may be provided by the Unified Command as part of the dispersant application mission if it was thought that in-situ conditions were especially atypical. Alternately, a local, specialty team (i.e. provided by PWSSC or PWSRCAC) may implement this prior to arrival of out-of-state or agency personnel. The findings of such pre-application field tests could be communicated back to the IMT to facilitate timely decision-making.

Considerations

- Oil and water used in effectiveness tests should be collected separately. Oil should come directly from the area of slick that would be targeted for dispersant application; water should be clean but come from the surface near the slick location to mimic the temperature, salinity, etc.

[1] Fingas, 2014.

[2] OSRL, 2011a

- Standard methods for sample collection and tracking should be utilized.
- When analysis is completed, the water, oil, and dispersant mixture must be properly disposed of as oily waste.
- In PWS, local, trained technicians may be deployed to support enhanced monitoring.

3. Enhanced Visual (Tier 1) Monitoring

Purpose

Enhanced visual (Tier 1) monitoring expands the SMART monitoring process by providing specific guidance for the real-time visual evaluation of the efficacy of dispersant applications.

Enhanced visual monitoring expands on the Tier 1 monitoring process in the SMART protocol. Tier 1 monitoring provides visual indications of the effectiveness or lack of it for a specific dispersant application. Visual monitoring is carried about by a trained observer during and immediately after a dispersant application.

The SMART protocol describes monitoring approaches, identifies roles and responsibilities for conducting dispersant monitoring, and provides forms and job aids to support dispersant monitoring applications. This document recommends standard methods that enhance the SMART protocol for use in Prince William Sound, Alaska.

Objectives

The objectives of visual (Tier 1) monitoring are:

- To collect real-time information that can be used to assess the effectiveness of the dispersant application, and
- To inform decisions regarding whether to continue or halt application.

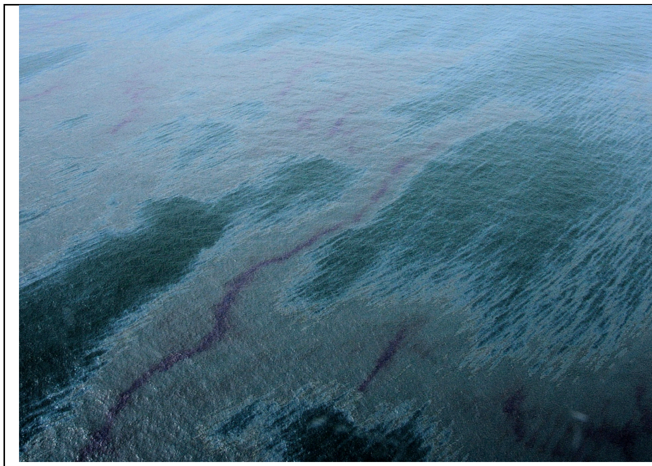
NOAA's Dispersant Observer Job Aid and the SMART Protocols provide a framework for Tier 1 monitoring. Tier 1 monitoring is necessarily qualitative and subjective, and it is strongly recommended that Tier 2 and Tier 3 monitoring are conducted to validate Tier 1 results. However, Tier 1 monitoring is sometimes the only or best option. This protocol enhances the Tier 1 monitoring in SMART by creating clear thresholds to inform decision-making.

Method

Tier 1 monitoring should be implemented as specified in the SMART protocol. The Prince William Sound enhanced Tier 1 monitoring recommends a standard timeframe for conducting visual monitoring, and establishes semi-quantitative criteria for determining effectiveness.

Visual Observation

At least two trained visual observers overfly the slick before and after dispersant application. Photographs and video should be used to capture images of the slick pre- and post-dispersant application. The size (area) and thickness of the slick should be estimated using standard methods. During the pre-application overflight, observers must determine whether the slick appears dispersible. Figure 3 shows examples of oil that is and is not dispersible.

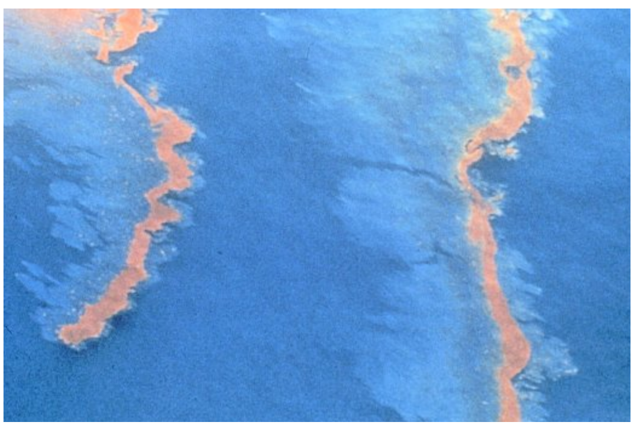


This slick contains oil that is emulsified in the center to sheen at the outer edges. The portion of oil between the emulsion and the heavier oil beside the sheen may be dispersible.

This slick contains heavy oil and little sheen or emulsion. It may be a good target for dispersant application.

Swaths of heavy oil which may be dispersible, but this slick could be difficult to target because of its widespread distribution.

An area of ocean with streaks of sheen, but no dispersible oil slick.



Emulsified oil surrounded by sheen. There is no dispersible oil slick.

This highly emulsified oil slick is not dispersible.

FIGURE 3. EXAMPLES OF OIL SLICKS AND THEIR DISPERSIBILITY

Since dispersions decline with time, visual assessment should include a standard time factor. SMART protocols specify visual observation and evaluation at 60 minutes post application; the PWS Enhanced protocol recommends additional observation intervals to more accurately characterize the effectiveness. The dispersed oil plume usually forms within half an hour of application, so it is recommended that visual observation of the slick be conducted between 30 and 60 minutes after the dispersant application. To evaluate the long-term effectiveness of the application, visual observations should be repeated at regular intervals (30 or 60 minutes) for up to 24 hours after the application.

The same intervals should be used throughout the dispersant operations to provide a consistent framework for assessing effectiveness.

Assessing Effectiveness

The NOAA Dispersant Application Observer Job Aid provides a standard reference for Tier 1 monitoring, showing examples of dispersed and un-dispersed oil plumes. The appearance of a dispersant plume changes with time. After formation, which for an aerial application typically takes about 30 minutes, an effective dispersion results in a coffee-coloured plume. A whitish dispersant plume typically means the application was not effective. Occasionally, the dispersant will leach some oil off a heavier slick and form a light brown patchy area. This is not an effective dispersion either. Sometimes the dispersant will herd the oil (move the oil around on the surface) resulting in an open path, typically with no plume in the area. This is also classed as ineffective.

Effectiveness is assessed by evaluating two criteria: (1) is there visual evidence of effective dispersion; and (2) what percentage of the slick has been dispersed. Tier 1 observers should estimate the area of dispersed oil and compare it against the size of the undispersed slick. For the application to be considered effective, at least 40% of the treated area of the targeted slick should be effectively dispersed (coffee color).

Figure 4 contains examples of effective and ineffective dispersant application.

Implementation

Responsibilities

Trained observers conduct Tier 1 monitoring from aircraft. Typically, agency personnel or contractors serve as visual observers. Prince William Sound RCAC has trained visual observers on staff that are available to support Tier 1 monitoring.

Resources

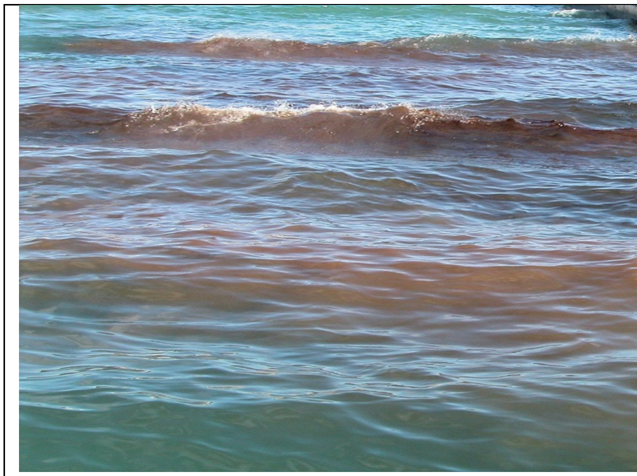
The resources for Tier 1 monitoring are typically provided as part of the dispersant application operations.

Considerations

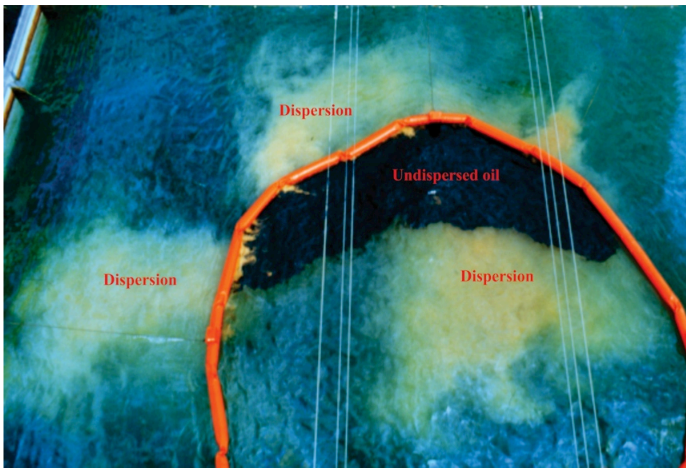
- If multiple observers are conducting Tier 1 monitoring, it is important to ensure that they are calibrated to use the same standards for evaluating slicks.

Applicable Standards

- ASTM F1779-08 Standard Practice for Reporting Visual Observations of Oil on Water
- ASTM F2534-12 Standard Guide for Visually Estimating Oil Spill Thickness on Water

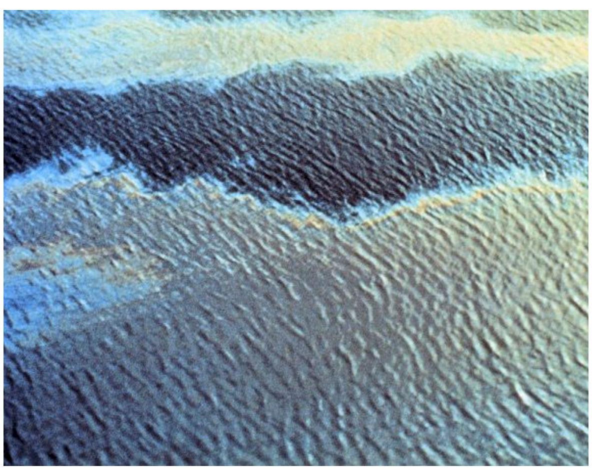


Examples of effective dispersion.



A mix of effective and ineffective dispersion in a test tank.

A missed application. The whitish slick to the right is dispersant.



Dispersant herds oil but does not effectively disperse the slick.

Dispersant was applied to this heavy oil slick but the dispersant ran off the slick without effective dispersion.

FIGURE 4. EXAMPLES OF EFFECTIVE AND INEFFECTIVE DISPERSANT APPLICATION

4. Enhanced Instrument (Tier 2) Monitoring

Purpose

Enhanced instrument (Tier 2) monitoring expands the SMART monitoring process by providing quantitative thresholds for evaluating dispersant efficacy as measured using instruments.

Enhanced instrument monitoring expands on the Tier 2 monitoring process in the SMART protocol. Tier 2 monitoring evaluates the effectiveness of a specific dispersant application using towed instruments that measure dispersion under the target slick and compare the results to measurements from an undispersed slick. While SMART relies primarily on fluorometry readings, the enhanced Tier 2 monitoring also incorporates a particle analyzer for a more accurate indication of dispersant effectiveness. During the Deepwater Horizon oil spill response, dispersants monitoring demonstrated that particle size is an important parameter for evaluating dispersant effectiveness, potential for resurfacing, and distinguishing between physical and chemical dispersion.

Objectives

The objectives of enhanced instrument monitoring are:

- To collect real-time information that can be used to assess the effectiveness of the dispersant application against established thresholds, and
- To inform decisions regarding whether to continue or halt application.

Methods

Deploy Particle Analyzer/fluorometry unit

Tier 2 monitoring is conducted by towing instruments and sampling units at different depths under dispersed and untreated oil slicks. For the Prince William Sound enhanced monitoring, an integrated particle analyzer/fluorometry unit provides more accurate information about the degree of dispersion achieved. The general process for conducting particle size analysis during Tier 2 monitoring is:

- Test all equipment and rig particle analyzer system for towing at desired depth (typically, 2m and 5m below surface)
- Calibrate particle analyzer with deionized water
- Load sufficient sample bags for the intended tow(s)
- Program analyzer to take samples at desired intervals, or trigger manually
- Gently deploy analyzer in an area where there is no surface oil to avoid contamination
- Prior to the dispersant application, tow unit at desired depth under area where Tier 2 monitoring is to be conducted

  - Limit tow speed to 3 knots or less
  - First tows establish **background concentrations** and should be conducted in the vicinity of the targeted slick **prior to** dispersant application (avoiding areas where heavy oiling may foul the unit)
  - Tow first at 5m depth, then at 2m depth to avoid contamination of equipment (note that subsequent tows are conducted at 2m first, then at 5m)
- After dispersant application, repeat the tow, targeting the darkest area of the plume (as identified by trained aerial observer) under the approximate center of the dispersant application area
  - Conduct 2m tow no less than 30 minutes after dispersant application
  - Conduct 5m tow no less than 1 hour after dispersant application (preferably immediately after the 2m tow)
  - Repeat tows at regular intervals for up to 3 hours after the dispersant application to yield a time-concentration data set
  - Repeat tows again at intervals of 6, 12, and 24 hours
- If unit is fouled, or if fouling is suspected, withdraw the equipment, clean it, and redeploy it

Table 4 lists the key equipment and data collection parameters for enhanced Tier 2 effectiveness monitoring.

TABLE 4. ENHANCED TIER 2 EFFECTIVENESS MONITORING EQUIPMENT AND PARAMETERS

UNIT	SAMPLING DEPTH	TYPE OF DATA COLLECTED	DATA USE	EFFECTIVENESS THRESHOLD
Particle size analyzer (e.g. LISST-100X)	2m and 5m	Volume mean diameter (VMD) Relative total petroleum hydrocarbons (TPH)	Indicator of dispersant effectiveness used to inform decisions about continuing or ceasing application. Also provides information about plume dynamics.	30-minute particle analyzer data shows: ◆An integrated particle count at least 100 times higher than background. ◆A typical VMD of <50 µm over most of tow zone.
Flourometer (e.g. Cyclops-7)	2m and 5m	Relative total polyaromatic hydrocarbons (TPAH)	Confirms that particle analyzer is measuring oil.	Confirmation that hydrocarbons are being measured by particle size analyzer.
Water sampler (e.g. Alpha Sampler)	2m and 5m	Water samples for lab analysis	Confirmation of TPH and TPAH concentrations as measured by particle size analyzer and fluorometer.	

Analyze Results

As shown in Table 4, the dispersant application is considered **effective** if:

(1) the 30-minute particle analyzer data at 2m shows an **integrated particle count at least 10 times higher** than the background readings;

(2) the 30-minute particle analyzer data at 2m shows a **typical VMD of less than 50** over most of the tow zone; and
(3) the fluorometer confirms that the particles being measured are hydrocarbons. If relying solely on fluorometer readings, fluorescence should be at least 100 times higher under the dispersed slick than under an undispersed slick.

The 1-hr particle analyzer data at 5m cannot be used to evaluate effectiveness right away, but can be used to evaluate long-term effectiveness based on trends.

Collect Water Samples

Water samples are taken to confirm the in-situ instrument readings. Collect water samples at pre-established times or upon triggering from the surface. If triggered from the surface, samples should be taken during times of both peak and minimum particle concentrations and at least 3 times along a particular tow.

Samples should be handled according to laboratory parameters, and sent off for analysis of TPH and TAH to validate in-situ monitoring.

Implementation

Responsibilities

Enhanced Tier 2 monitoring should be integrated with SMART monitoring. Personnel trained in enhanced monitoring techniques and equipped with appropriate instrumentation may be provided by PWSSC and PWSRCAC to support enhanced Tier 2 monitoring. Data generated by enhanced Tier 2 teams would be provided to the NOAA SSC and Environmental Unit/Planning Section for consideration along with other SMART monitoring data.

Resources

The equipment needed for enhanced Tier 2 monitoring include:

- Particle analyzer and fluorometer (integrated system recommended, such as Sequoia LISST Particle Size Analyzer and Turner Cyclops-7 fluorometer – see Appendix A)
- Subsurface water sampler (such as Niskin bottles or Alpha sampler)
- Tow and transmit cables for particle analyzer and water sampler
- Vessel with towing bridle
- Depth measurement device

Considerations

- Implementation of enhanced Tier 2 monitoring requires access to particle size analyzers along with trained personnel to deploy the equipment and interpret results.
- Deployment of an integrated particle analyzer/fluorometer requires similar equipment (vessels and towing configuration) as a fluorometer alone, and should not introduce significant additional logistical burdens.

Applicable Standards

- EPA 8270 Analysis of Semivolatile Organic Compounds by Combined Gas Chromatography/Mass Spectometry
- EPA 8015
- ASTM D3328 Standard Test Methods for Comparison of Waterborne Petroleum Oils by Gas Chromatography
- ASTM D5739 Standard Practice for Oil Spill Source Identification by Gas Chromatography and Positive Ion Electron Impact Low Resolution Mass Spectrometry
- ISO 28540:2011 Water Quality – Determination of 16 PAH in water – method using gas chromatography with mass spectrometric detection

5. Enhanced Biological (Tier 3) Monitoring

Purpose

Enhanced biological (Tier 3) monitoring expands the SMART monitoring process by providing quantitative thresholds for evaluating dispersant efficacy and effects.

Enhanced biological monitoring expands on the Tier 3 monitoring process in the SMART protocol. Tier 3 monitoring collects water samples from sites around the dispersant application and analyzes samples in the field and in the laboratory to evaluate effectiveness and toxicity.

The SMART protocol describes monitoring approaches, identifies roles and responsibilities for conducting the three tiers of monitoring, and provides forms and job aids to support dispersant monitoring applications. This document recommends specific techniques and procedures that enhance the SMART protocol for use in Prince William Sound, Alaska.

Objectives

The objectives of enhanced monitoring are to compile information about the toxicity of dispersed oil and environmental impacts of dispersant applications.

Methods

Enhanced Tier 3 monitoring should include sample collection for analysis of data to evaluate effectiveness and toxicity, using the following methods:

- Chemical analysis of water samples
- On-board toxicity testing
- Toxicological analysis of water samples in off-site laboratories
- Analysis of water for dispersant alone

Given the timeframe for conducting enhanced Tier 3 monitoring, this data may not be integrated into the dispersant decision making process for short-term dispersant applications. It may be feasible to collect, analyze, interpret and apply Tier 3 data in scenarios that involve extended dispersant operations. Table 5 summarizes the enhanced monitoring equipment, data collection, and analysis.

TABLE 5. ENHANCED TIER 3 CHEMICAL MONITORING EQUIPMENT AND ANALYSIS

UNIT	SAMPLING DEPTH	DATA COLLECTED	TYPE OF ANALYSIS
PLVWSS/Payne sampler	2m and 5m	Separates dissolved and particulate oil in water sample and measures total petroleum hydrocarbons (TPH), total polyaromatic hydrocarbons (TPAH), and specific compounds	Quantitative measurements of hydrocarbons and their components in water sample can be used to assess effectiveness based on chemistry. Results from chemical analysis can be used to validate Tier 2 analysis.
Alpha sampler	2m and 5m	Collects water samples for chemical (TPH, TPAH, and compounds) and toxicological analysis	Utilize samples for chemical analysis, onboard toxicity testing and laboratory toxicity testing. Results from chemical analysis can be used to validate Tier 2 analysis. Results from toxicological testing may inform decisions on continued application of dispersants and may inform long-term monitoring.

Collecting Water Samples

Water samples from the dispersed slick may be collected for chemical analysis using appropriate sample collection systems and analytic techniques. Two options for collecting water samples in Prince William Sound include the Portable Large Volume Water Sampling System (PLVWSS), also called the Payne sampler, or the Alpha sampler. Both devices are described in Appendix A. Standard procedures for water sampling should be followed.

Chemical Analysis of Water Samples

Table 6 summarizes the chemical components that may be analyzed using the enhanced Tier 3 methods. These measures can be used to correlate data collected in Tier 2 monitoring using flourometry and particle size analysis. While the Tier 2 monitoring results provide a relative indicator of effectiveness, the analysis of the chemical composition of dispersed oil in Tier 3 provides a quantitative measurement.

TABLE 6. TARGET COMPOUNDS FOR ENHANCED TIER 3 CHEMICAL ANALYSIS

COMPOUNDS	POTENTIAL TARGETS						
N-Alkanes	n-C8 n-C9 n-C10 n-C11	n-C12 n-C13 n-C14 n-C15	n-C16 n-C17 n-C18 n-C19	n-C20 n-C21 n-C22 n-C23	n-C24 n-C25 n-C26 n-C27	n-C28 n-C29 n-C30 n-C31	n-C32 n-C33 n-C34 n-C35	n-C36 n-C37 Pristane Phytane Total n-alkanes

COMPOUNDS	POTENTIAL TARGETS		
Polyaromatic Hydrocarbons (PAH)	Naphthalene C1-Naphthalenes C2-Naphthalenes C3-Naphthalenes C4-Naphthalenes Biphenyl Acenaphthylene Acenaphthene Dibenzofuran Fluorene C1-Fluorenes C2-Fluorenes C3-Fluorenes Anthracene Phenanthrene	C1-Phenanthrenes/Anthracenes C2-Phenanthrenes/Anthracenes C3-Phenanthrenes/Anthracenes C4-Phenanthrenes/Anthracenes Dibenzothiophene C1-Dibenzothiophenes C2-Dibenzothiophenes C3-Dibenzothiophenes C4-Dibenzothiophenes Benzo(b)fluorene Fluoranthene Pyrene C1-Fluoranthenes/Pyrenes C2-Fluoranthenes/Pyrenes C3-Fluoranthenes/Pyrenes C4-Fluoranthenes/Pyrenes	Benz(a)anthracene Chrysene C1-Chrysenes C2-Chrysenes C3-Chrysenes Naphthobenzothiophene C1-Naphthobenzothiophenes C2-Naphthobenzothiophenes C3-Naphthobenzothiophenes C4-Naphthobenzothiophenes C4-Chrysenes Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(a)fluoranthene Benzo(e)pyrene Benzo(a)pyrene Indeno(1,2,3-cd)pyrene Dibenz(a,h)anthracene Benzo(g,h,i)perylene

Onboard Toxicity Testing

Onboard toxicity testing uses field methods to conduct a preliminary assessment of the toxicity of dispersed oil to marine organisms. One of the available technologies – the Microtox system – uses photoluminescent bacteria to evaluate toxicity. (See Appendix A.)

Laboratory Toxicity Analysis

There are many options for conducting toxicity tests off site. Tests on standard and site-relevant species should be considered. If necessary, extra samples could be taken specifically for toxicity tests.

Limitations include the amount of sample water taken and also the declining concentration of hydrocarbons once the samples are exposed to air. It is also important to consider that once oil is treated with dispersant, it will continue to spread and dilute, changing over time. Therefore, laboratory toxicity analysis may not capture this continuum, instead providing data based on oil characteristics at a single point in time.

Table 7 summarizes some options for offsite laboratory toxicity tests, based on the published literature.

TABLE 7. DISPERSED OIL TOXICITY TESTS

TOXICITY TESTS	DESCRIPTION
Microtox Assay	Off-site duplication of field assay using a microtox system under controlled (laboratory) conditions. This system uses photoluminescent bacteria (*Vibrio fisheri*). A light reading is taken of the bacteria before and after exposure to the solution. The difference in light emission is the toxicity of the solution administered. (Dussauze, 2011; Paul et al., 2013).
Deepwater Horizon Bioassays	Paul et al. (2013) applied three rapid bioassays during several cruises in the Gulf of Mexico, during and after the Deepwater Horizon Spill theses could be applied in the laboratory as well. The QwikLite assay uses light emission from the dinoflaggellate *Pyrocystis lunula*, to provide a rapid proxy of phytoplankton toxicity. The Microscreen Mutagenicity test uses a λ-containing lysogenic strain of *Escherichia coli*, to act as a rapid test for mutagenicity. This test is an overnight test. Similarly McDaniel and Kovach (2013) studied the toxicity after the Deepwater Horizon Spill.
Pacific Oyster tests	Luna-Acosta et al. (2011) evaluated the effects of chemically dispersed oil on juvenilles of the Pacific oyster, *Crassostrea gigas.*
Toxicity to Plants	Wilson and Ralph (2012) developed a protocol for the testing of the effect of oils on plants. This is an ex-situ method in which portions of seagrass are cut and taken to a laboratory and exposed to the oils in small jars. The photosynthetic yield and chlorophyll concentrations are measured and used to measure stress.
Undiluted toxicity on fish, shrimp, and diatoms	Benkinney et al. (2011) carried out toxicity studies on undiluted samples using the estuarine inland silversides fish (*Menidia beryllina*), planktonic mysid shrimp (*Mysidopsis bahia*, also known as *Neomysis americana*), and the marine diatom (*Skeletonema costatum*) following standard test procedures.

Monitoring for Dispersant Components in Water

Certain components of dispersants were sampled in the water following the Deepwater Horizon spill. These may be sampled, however the partitioning of these components between water and oil has largely not been established. Table 8 summarizes methods that may be used to monitor for dispersant components.

TABLE 8. MONITORING FOR DISPERSANT COMPONENTS

ANALYSIS	DESCRIPTION	MONITORING METHODS
Dioctyl sulfosuccinate (DOSS) Monitoring	Dioctyl sulfosuccinate (DOSS) is a major component of Corexit dispersants and has an aquatic toxicity of approximately double that of the dispersant itself. DOSS is difficult to sample and analyze in seawater as it partitions to surfaces such as tubes and glassware.	Mathew et al. (2012) developed a method to quantify DOSS concentrations in sea water to a reporting limit of 20 g/L (20 ppb), which was below the U.S. Environmental Protection Agency's 40 µg/L DOSS Aquatic Life Benchmark. Mathew et al. analyzed DOSS in Gulf of Mexico water samples by direct-injection reversed-phase liquid chromatography –tandem mass spectrometry (LC–MS/MS). Sample preparation with 50% acetonitrile enabled quantitative transfer of DOSS and increased DOSS response 20-fold by reducing aggregation. This increased sensitivity enabled the detection over the calibration range of 10-200 g/L.
		Ramirez et al. (2013) developed a LC-tandem mass spectrometry (MS/MS) method and a direct-injection LC-MS/MS method for the analysis of dioctyl sulfosuccinate in seawater at trace levels, with method detection limits of 7.0 and 440 ng/L and run times of 7 and 17 min, respectively. Stability and preservation studies demonstrated that samples at 4.7 µg/L could be preserved for up to 150 days without loss of analyte when stored with 33 % acetonitrile in glass containers. A modification of the direct-injection method also allowed quantitation of 2-butoxyethanol, a dispersant component specific to the Corexit EC9527A formulation. This method was used to simultaneously quantify DOSS and 2-butoxyethanol in two Corexit formulations and extracts from a Deepwater Horizon source oil standard. The method detection limits in crude oil were 0.723 and 4.46 mg/kg, respectively.
		Gray et al. (2013) studied DOSS concentrations in the Gulf of Mexico waters after the Deepwater Horizon blowout. Samples of water taken during the blowout at various depths were frozen for 6 months and then analyzed by LC-MS. The detection level was established as 0.05 µg/L (The EPA reporting level is 40 µg/L). Detections in several water samples were made, always corresponding to those samples that contained hydrocarbons as evidenced by fluorescence. Only water samples that showed oil fluorescence showed DOSS content. Only one sample showed a high DOSS content and that was of 200 µg/L.
Use of Dipropylene glycol n-butyl ether (DPnB) as a Marker	Several groups studied the use of dipropylene glycol n-butyl ether (DPnB), a solvent component of Corexit dispersants, as a possible marker for the fate and effectiveness of oil dispersion.	Mudge et al. (2011) studied DPnB as it related to the Deepwater Horizon dispersant application. The DPnB present in Corexit EC9500A was found to be a good indicator of the dispersant in the Gulf of Mexico. There was a statistically significant relationship (R^2=0.50, n=27) between the DPnB concentration measured in water samples collected beneath dispersing slicks and the crude oil-derived hydrocarbons. This may provide a measure of the efficacy of the dispersant. The group carried out experiments in open jars which indicated an initial half-life of ~30 days, which is long enough to enable samples to be collected after application. There are questions about the partitioning of the marker between oil and water and the fate of the marker.

Implementation

Responsibilities

Enhanced Tier 3 monitoring should be integrated with SMART monitoring. Personnel trained in enhanced monitoring techniques and equipped with appropriate instrumentation may be provided by PWSSC and PWSRCAC to support enhanced Tier 3 monitoring. Data generated by enhanced Tier 3 teams would be provided to the NOAA SSC and Environmental Unit/Planning Section for consideration along with other SMART monitoring data.

Resources

The equipment needed for enhanced Tier 3 monitoring include:

- Water sample collection devices, such as Payne or Alpha samplers (see Appendix A)
- Tow and transmit cables for water samplers
- Sampling bottles with appropriate storage, labels, and cleaning supplies
- Documentation forms
- Vessel with towing bridle
- Depth measurement device
- Microtox unit (e.g. Delta Tox, See Appendix A)

Considerations

- Implementation of enhanced Tier 3 monitoring requires access to specialized equipment along with trained personnel (likely to be different from/in addition to agency personnel) to deploy the equipment and interpret results.
- Take precautions to ensure proper handling of samplers and water samples to avoid cross-contamination.
- Follow standard chain-of-custody procedures for water samples that are sent out for laboratory analysis.

Applicable Standards

- EPA 8270 Analysis of Semivolatile Organic Compounds by Combined Gas Chromatography/Mass Spectometry
- EPA 8015
- ASTM D3328 Standard Test Methods for Comparison of Waterborne Petroleum Oils by Gas Chromatography
- ASTM D5739 Standard Practice for Oil Spill Source Identification by Gas Chromatography and Positive Ion Electron Impact Low Resolution Mass Spectrometry
- ISO 28540:2011 Water Quality – Determination of 16 PAH in water – method using gas chromatography with mass spectrometric detection

6. Long-Term Monitoring

Purpose

Long-term monitoring activities include background surveys and other studies that are conducted apart from an oil spill that may provide useful data to inform decisions about potential efficacy and effects of dispersant use.

Long-term monitoring activities compile data over months or years characterizing the conditions at a site where dispersants may be or have been applied. Data may be collected to assess ecological sensitivities and other factors related to dispersant efficacy or effects. Background data on hydrocarbon levels can be used as a baseline for evaluating post-spill impacts and documenting the presence and abundance of certain species.

Long-term monitoring is conducted apart from an oil spill incident, either before or after an oil spill occurs. Both types of studies should consider other related studies that may be ongoing in a region. For example, in Prince William Sound there are several biological studies that may provide data relevant to dispersant application (e.g., Payne et al., 2013; Gulfwatch, 2014; PWSSC, 2014). Long-term monitoring data may be used as a baseline against which to compare enhanced monitoring results, and may also inform the design of enhanced dispersant monitoring programs.

Objectives

The objectives of long-term monitoring are to:

- Develop baseline information about environmental conditions (salinity, temperature, water depth, mixing energy) in areas where dispersant use may be authorized.
- Develop baseline information about sensitive ecological species and life stages in and near areas where dispersant use may be authorized.
- Survey background hydrocarbon levels in areas where dispersants may be authorized.
- Develop baseline information about distribution and abundance of biological stocks (birds, fish, mammals, phytoplankton, zooplankton) in and near areas where dispersant use may be authorized.

Process

Pre-spill background studies and long-term monitoring may provide valuable historic data sets to inform decisions about dispersant monitoring.

Characterize Conditions that Influence Dispersant Effectiveness

Pre-and post-spill long term data collection may be used to inform decision-makers about the suitability of certain areas for dispersant application based on effectiveness criteria. These may include:

- **Temperature.** Dispersant application may be less effective at sea surface temperatures below 10°C, and is typically not effective at temperatures below 4°C (Belore et al., 2009). Pre-spill mapping may identify seasonal and geographic parameters for surface water temperatures to inform dispersant use decisions during times when surface water temperatures are below these thresholds.

- **Salinity.** Dispersant application may be less effective in low salinity waters. When salinities at the sea surface and down to 10m-depth fall below 30 parts per thousand (ppt), dispersants may be less effective. At salinities below 20 ppt, dispersants may not be effective at all. Pre-spill surveys may identify areas, seasons, or other conditions (such as recent major rainfall events) that impact surface water salinities to inform dispersant use decisions. (Fingas, 2004)

Long-term monitoring data about temperature, salinity, and other environmental factors (e.g. mixing energy, water depth) should be verified by actual observational data at the time of a potential dispersant application (see Section 1).

Characterize Biological and Ecological Resources

Long-term monitoring of biological and ecological resources is used to inform sampling and monitoring activities prior to, during, and after a dispersant application.

Data about the location, abundance, and sensitivity of biological resources may be compiled ahead of an oil spill. In most regions, there are a number of references and ongoing studies that provide historical data on the location, seasonality, and abundance of resources ranging from plankton to marine mammals. Habitat atlases and sensitivity index maps identify sensitive coastal and marine areas. Federal and state agencies identify particularly vulnerable populations through listings such as endangered or threatened species. Oil spill contingency plans may compile this information for a specific region.

Marshes, shorelines and sea grass beds may be impacted by oil spills and drift from treated oil slicks and are considered highly vulnerable ecosystems. In general, these near-shore habitats are too shallow for dispersant use, but their sensitivity could be a consideration in dispersants application offshore. Baseline data on coastal ecosystems near a dispersant application should be obtained.

Sample Plankton Populations

Baseline studies can be used to characterize plankton populations within a potential dispersant application area (or more generally across the region), and may inform initial decision-making about dispersant use by providing context for the general distribution and abundance of certain organisms and life phases that may be particularly sensitive to dispersed oil.

Planktonic organisms include marine algae and animals (including adults and larvae of invertebrates and larval stages of vertebrates) that have limited powers of locomotion and spend their life cycle or part of it in the water column. Phytoplankton is an important food source in marine ecosystems. Oil spill impacts to plankton are typically short-term and can be difficult to measure; however, in unusual circumstances oil spills may have significant impacts to certain localized populations (Premiam, 2011). Embryonic and larval fish are particularly sensitive to oil; exposure can cause immediate or delayed mortality that can have population-level impacts on fish species (Incardona et al., 2015). Tiers of polycyclic aromatic hydrocarbons (PAH) in zooplankton may be used as an indicator of oil pollution, particularly in isolated or semi-isolated waters (Carls et al., 2006; Hansen et al., 2012; Huang et al., 2010; Rico-Martinez et al., 2013).

In the event of an oil spill in the PWS region, it will be advantageous that any plankton samples collected can be compared with those taken by prior studies. The following table summarizes some of the studies and time series observations that have been done recently. The list is not exhaustive, and focuses for the most part on studies that were conducted for several years with zooplankton monitoring in mind, and ichthyoplankton work (primarily focused on larval herring) done after the Exxon Valdez Oil Spill.

Investigator	Affiliation	Target group	Time span	Net type	Mesh size
Cooney, R.T.	UAF	zooplankton	1989-1996	Single, 60 cm mouth	303 µm
Norcross, B.	UAF	larval herring	1989, 1995	1 m^2 Tucker Trawl	505 µm
Brown, E.D.	ADF&G	larval herring	1989	Bongo, 60 cm mouth	303 & 505 µm
Hopcroft, R.	UAF	small zooplankton	1998-present	Quad, 25 cm mouth, day tows	150 µM
Hopcroft, R.	UAF	large zooplankton	1998-present	0.25 m^2 Multinet, night tows	500 µm
Campbell, R.	PWSSC	zooplankton	2009-present	Bongo, 60 cm mouth	202 µm

Methods

Conditions that Influence Effectiveness

Pre-spill monitoring can be used to identify areas where dispersant use may be effective while ruling out other areas that do not meet minimum effectiveness criteria. Data collection methods may include field surveys along with compilation of published references. This information may be synthesized into maps that are included in Subarea plans or other guidance documents that would be consulted at the time of a spill.

Biological and Ecological Resources

Data about biological and ecological resources can be used to identify areas or seasons that may not be appropriate for dispersant application. This data also provides an important baseline that can be compared with monitoring results generated during and after the dispersant application.

Methods for surveying biological and ecological resources pre-spill may include field sampling using the same methods as pre-application surveys or post-spill monitoring. Biological and ecological data compiled and maintained by resource trustee agencies or established monitoring programs, like the Prince William Sound Long Term Environmental Monitoring Program (LTEMP), also provide baseline information about pre-spill resources.

Plankton Sampling

General sampling should be conducted using usual net methods and published procedures to collect phytoplankton and zooplankton, as described in Section 1 of this protocol. Other standard methods exist, and depending upon the scope and purpose of plankton sampling these may also be used to provide long-term data sets. The EPA method uses sampling bottles to collect plankton from a range of depths, which vary according to the water body type and level of stratification (EPA, 2002). The ASTM method specifies the use of a conical net deployed at a specific depth towed over a specified distance (ASTM, 2012). PWSSC uses standard methods to collect plankton samples to monitor ongoing conditions in the region (PWSSC, 2014). Other references for plankton sampling in association with oil spills and/or dispersant application include:

- California Dispersant Oil Monitoring Plan (DOMP) https://nrm.dfg.ca.gov/FileHandler.ashx?DocumentID=19879
- UK Post-Incident Monitoring Guidelines http://cefas.defra.gov.uk/premiam/publications/post-incident-monitoring-guidelines/premiam-post-incident-monitoring-guidelines-(pdf,-6-mb).aspx

Phytoplankton concentrations can also be estimated using aircraft lidar (laser sensing) systems or through satellite imagery that indicates chlorophyll levels as a proxy for phytoplankton. There are also instruments available that continually measure phytoplankton (Churnside and Thorne, 2005; Xiu et al., 2014).

Implementation

Responsibilities

In Prince William Sound, pre-spill monitoring is carried out by a number of different agencies and organizations. For the purpose of compiling and accessing this data to inform the enhanced monitoring of dispersant applications, the following organizations have responsibility:

- **Prince William Sound Science Center/Oil Spill Recovery Institute (PWSSC/OSRI)** is a primary repository for environmental data sets relating to Prince William Sound. PWSSC/OSRI will work in coordination with the Prince William Sound RCAC to designate all relevant data sets so that they may be easily accessed and reviewed during a potential or actual dispersant application.
- **Prince William Sound RCAC** will work in close coordination with PWSSC/OSRI to designate existing datasets as relevant to the enhanced dispersant monitoring protocol and will develop a system to track these data, including information such as recency, reliability, etc. In the event of a potential or actual dispersant application where the monitoring protocol might be implemented, Prince William Sound RCAC and PWSSC/OSRI will assist the NOAA SSC with the quick compilation of these data sets to inform the enhanced monitoring process.
- **NOAA Scientific Support Coordinator (SSC)** will maintain some familiarity with the relevant data sets available to support enhanced dispersant monitoring in Prince William Sound. In the event of a potential dispersant application, the NOAA SSC will alert the PWSSC/OSRI and PWS RCAC of the need for data synthesis based on the specific incident. The NOAA SSC will consult this data and may utilize it to inform the implementation of some or all aspects of the enhanced monitoring protocol.
- **Natural resource trustee agencies** are typically involved in a range of long-term studies that may contribute to the baseline data available to support dispersant monitoring during an oil spill. Apart from their role in dispersant use decision-making, the trustee agencies also provide important subject matter expertise and knowledge regarding local environmental conditions, wildlife, and habitat.

Resources

Pre-spill survey and long-term monitoring data may be available as databases, printed reports, geospatial data sets, maps, atlases, or some combination of these. Some of this data may be informative to other aspects of spill response decision-making. To the extent possible, this data should be provided in a format that is readily transferable to an ICS-232 form (Resources at Risk summary). It may be possible to periodically populate ICS-232 forms with the results of pre-spill monitoring.

Appendix B contains a list of long-term monitoring and other data sets currently available for the Prince William Sound region.

Considerations

- Data collected immediately prior to an oil spill/dispersant application may inform decisions associated with the response in general, and specifically the design and conduct of enhanced dispersant monitoring.
- Compiled data and reports should not substitute for local knowledge and real-time data or observations. Whenever possible, data verification should be conducted.
- Consideration of historical data from pre-spill surveys or long-term monitoring must be balanced against the need for rapid decision-making in the event of an oil spill. In some cases, it may be preferable to conduct real-time surveys to evaluate certain factors, rather than relying on historical data.
- Data from long-term monitoring may help to focus enhanced dispersant monitoring based on environmental conditions, resource or habitat sensitivities, human use, or other factors.

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Appendix A. Equipment to Support Enhanced Dispersant Monitoring

The enhanced Tier 2 and Tier 3 dispersant monitoring may require additional equipment or technologies not currently stockpiled in Prince William Sound. The basic parameters from some of this equipment is summarized here. While specific models are described, this does not represent and endorsement of any specific technology and other models that meets the sampling needs may be available.

LISST Particle Analyzer

Enhanced Tier 2 monitoring suggests an additional method – particle size analysis – for use in Alaska. Figure A1 shows the Sequoia LISST-100X, a particle size measuring that can be used for Tier 2 monitoring. The unit outputs particle size information including volume mean diameter (VMD) and an integrated value, which can be used to approximate total petroleum hydrocarbons (TPH). As the unit counts any particle as oil, a fluorometer is needed to discriminate oil from other particles. The Sequoia accommodates Turner Cyclops-7 fluorometer (also shown in Figure A1) and also transmits the signal from this unit. Other models of particle analyzer could be used in place of the LISST model.

Water sampling can be conducted simultaneous with the particle analysis and fluorometry (and at the same locations) to validate the results. All equipment should be deployed as indicated in manufacturer instructions and user manuals.

FIGURE A1. SEQUOIA LISST PARTICLE SIZE ANALYZER (LEFT) AND TURNER CYCLOPS-7 FLUOROMETER, WHICH CAN BE INTEGRATED WITH THE SEQUOIA TO MEASURE OIL CONCENTRATIONS BELOW A DISPERSED OIL SLICK TO ESTIMATE EFFECTIVENESS AS PART OF TIER 2 MONITORING

Payne Sampler

The Payne sampler, otherwise known as the Portable Large Volume Water Sampling System (PLVWSS), is a device that separates the dissolved and particulate oil in the water sample (Payne et al., 1999; Payne and Diskell, 2003). The PLVWSS filters a 3.5 L water sample through a 0.7 µm glass fiber filter, allowing separate analysis of the particle or dispersed-oil droplets (trapped on the filter) and the dissolved-phase components collected in a 3.8 L (1-gallon) glass bottle.

NOAA has published detailed procedures to operate the Payne sampler (NOAA, 2010). The unit is illustrated in Figure A2, below.

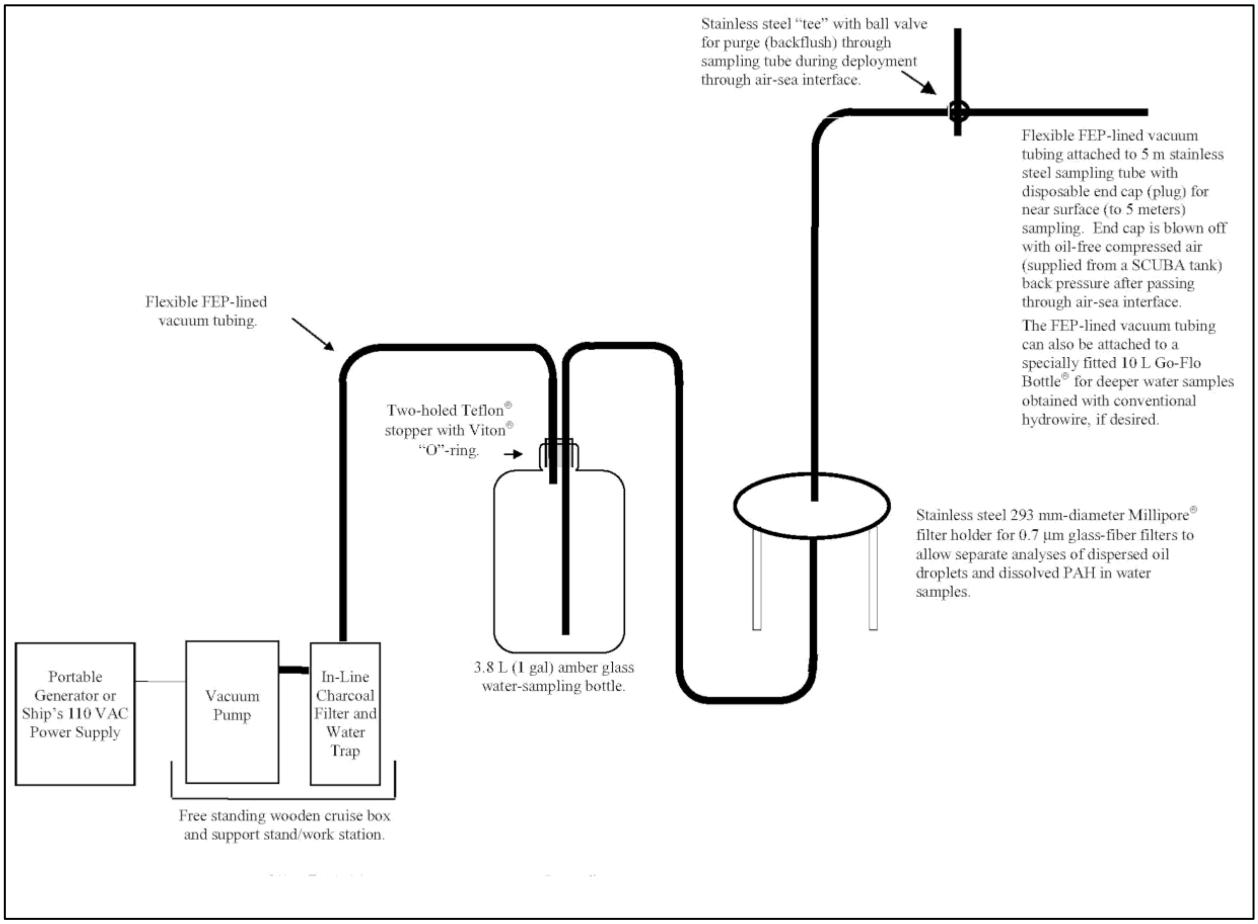

FIGURE A2. PAYNE SAMPLER (FROM PAYNE ET AL., 1999)

Alpha Sampler

The Alpha sampler, shown in Figure A3, holds 2.2 L of water, which can then be used for chemical or toxicological analysis.

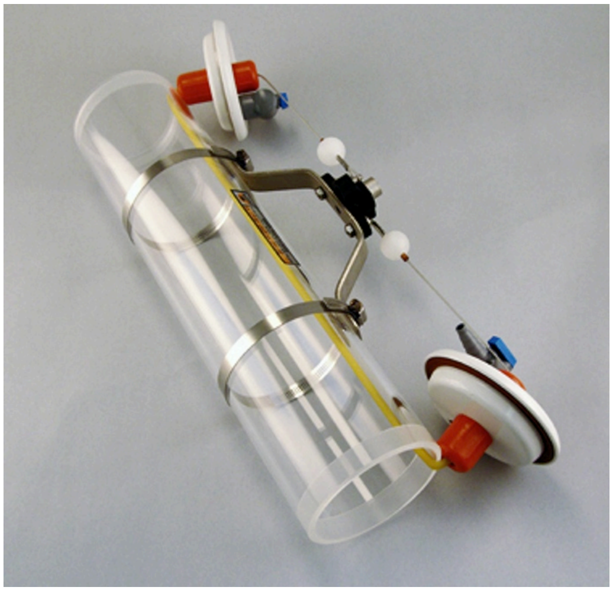

FIGURE A3. ALPHA SAMPLER

Delta Tox Unit

The Microtox system can be used in the field for testing toxicity directly on site. This system uses photoluminescent bacteria (*Vibrio fisheri*). A light reading is taken of the bacteria before and after exposure to the solution. The difference in light emission is the toxicity of the solution administered. A field portable version of this test is available and is called DeltaTox, shown in Figure A4 (Dussauze, 2011). Testing on this device shows that it produces realistic numbers consistent with other testing.

The Delta Tox unit requires training and practice to operate.

FIGURE A4. DELTA TOX UNIT

Appendix B. Prince William Sound Long-Term Monitoring Data Sets

Table B1 identifies long-term monitoring and other pre-spill baseline data sets that may be consulted in designing and implementing enhanced dispersant monitoring.

TABLE B1. PRINCE WILLIAM SOUND LONG-TERM MONITORING DATASETS

Data Type	Link/Citation
Historic Sea Surface Temperature	http://ourocean.jpl.nasa.gov/PWS/ http://www.pwsrcac.org/wp-content/uploads/filebase/programs/environmental_monitoring/saline_layering_in_pws.pdf
Historic Salinity Data	
Real-time Observational Data on Water Temperature and Salinity	
Background Hydrocarbon Levels	
Plankton **William Sound Science Center has an ongoing plankton monitoring program that has collected phytoplankton and zooplankton data during spring and fall at 12 locations across Prince William Sound since 2007**	http://www.gulfwatchalaska.org/ http://pwssc.org/research/marine/plankton/
Commercial Fish Stocks	http://www.adfg.alaska.gov/index.cfm?adfg=commercialbyareapws.main http://alaskafisheries.noaa.gov/sustainablefisheries/catchstats.htm

Data Type	Link/Citation
Forage Fish	
Bird Population Trends	http://www.gulfwatchalaska.org/monitoring/pelagic-ecosystem/pws-marine-bird-population-trends/
Endangered and Threatened Species	http://www.endangeredspecie.com/
Sea Otter Populations	http://www.evostc.state.ak.us/index.cfm?FA=status.seaotter
Environmental Sensitivity Maps	http://alaskarrt.org/files/PWS_D- Sensitive AreasWorkingDraftFINALDRAFT.pdf
Marine Mammals	Observer Manual, Alaska Marine Mammal Observer Program Manual, 2007 Observer Manual, General Marine Mammal Observation Protocol and Sentinel Procedures Manual, 2008