Why Sample? - Understanding Common Sampling Objectives for Oil Spill Response

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ABSTRACT #2017-204: There is a growing recognition of the role science plays in supporting oil spill response coupled with increasing reliance on data-driven management and decision-making approaches. Collecting samples for analysis of hydrocarbons and other chemicals potentially used during oil spill response (e.g., dispersants) has become common place on many spills. While the rationale and approaches for oil spill sampling may be well known to experienced chemists and environmental scientists, the response community is still gaining experience in integrating sampling programs into dynamic oil spill response and decision-making. This paper reviews common sampling objectives for three key aspects of spill response: operational decision-support, environmental impact assessment (including natural resource damage assessment), and source identification. These broad categories span a range of interrelated sub-topics including, among others, public/worker health and safety; understanding how physical and chemical properties of oil influence selection of response options; monitoring cleanup effectiveness, especially for alternative response technologies such as dispersants; identifying and differentiating between spill and non-spill pollution sources; and evaluating potential impacts to resources at risk. Methods for achieving sampling objectives, including development of Sampling and Analysis Plans, are discussed with the goal of increasing awareness among response managers and improving response capability among staff who may be tasked with sampling support during training exercises or actual incidents. Relevant considerations for study design, collection methods, and analytical parameters are also reviewed.

INTRODUCTION

One purpose of environmental sampling is to characterize (as presence/absence and/or concentration) chemical constituents derived from the spilled oil (or chemical countermeasures) in various environmental media. Immediately following a hydrocarbon release, certain data should be collected to assess environmental conditions and implement safe and effective response strategies. These data are used by response organizations to make decisions regarding operational activities, ensure safety and health of response workers and the public, evaluate cleanup progress, and assess environmental impacts.

Sampling during an emergency response is a complex undertaking, often made more challenging due to the fast-paced and multi-dimensional nature of the spill response, paucity of information, limited resources, and potentially conflicting priorities. Identifying and reaching agreement on the key sampling objectives for an incident is an important first step before undertaking any work. This focuses the effort and ensures that valuable sampling and associated logistical resources are not wasted on collection and analysis of extraneous data that do not support decision making, or make a valuable contribution to understanding impacts.

SAMPLING OBJECTIVES

Prior to collecting samples, it is important to understand and articulate why samples will be collected and how the results will be used. The answers to these questions represent the initial formulation of sampling objectives. Sampling objectives are the foundation upon which an incident-specific Sampling and Analysis Plan (SAP) should be developed and play a key role in determining the number, type, location, and priority of initial samples as well as the frequency and duration of follow-up sampling.

Incident-specific objectives are typically defined by the response managers working as part of the Incident Command, and usually fall into three primary categories: Response Operations; Environmental Impact Assessment; and Source Identification. These key categories and their related sampling objectives are described below. Furthermore, this paper focuses on sampling of environmental media for chemical analysis.

Response operations

Oil released in the environment poses risks to people and natural resources. Samples assist with characterizing those risks, which helps inform how best to mitigate them. Samples of source oil, spilled oil, air, water, sediment, and/or biota provide information on how to protect responders, the public, and ecological resources. Sampling objectives in support of response operations often include, but are not limited to the following: Assessing and monitoring potential health and safety risks to responders and the general public; Characterizing the chemical and physical properties of the spilled material, including how they may change over time as a result of weathering; Monitoring the progress and effectiveness of cleanup activities; and Characterizing recovered material for waste disposal purposes.

Public and responder health and safety

Contaminants in the environment can present threats to the health and safety of the general public as well as response workers during containment and cleanup activities. Potential exposure routes can include inhalation, dermal contact, and ingestion (i.e., drinking contaminated water or eating contaminated food). Therefore, identifying and quantifying these contaminants through sampling of air, potable water supplies, and food sources is essential. Monitoring air quality aids in the selection of personal protective equipment for respiratory protection, delineation of areas where protection and/or evacuations are needed, assessment of potential health effects of exposure, and determination of the need for hazard communication (e.g., risk of inhalation or fire/explosion hazards) and medical monitoring. Results are usually compared to the lowest known Occupational Exposure Limits for the contaminants of concern in order to make Personal Protective Equipment (PPE) recommendations for responders. Sampling potable water sources (e.g., groundwater wells, drinking water intakes, and reservoirs) provides critical information for public health officials, utility owners, and residents so they can make informed decisions regarding the need for treatment or use of alternative drinking water sources. Spills may also threaten to foul industrial facilities that use surface water for cooling or processing. Sampling may be requested to support decision-making similar to potable water intakes.

The Environmental Unit may also be tasked with supporting regulators or public health officials with the decision to close and eventually re-open fisheries. Fisheries and harvest areas (e.g., shellfish beds) are often closed automatically based on the threat of impact. Re-opening fisheries once they have been closed is typically more challenging and often requires sampling to support risk assessment. Chemical testing of seafood is often conducted after an oil spill to determine whether seafood tissues are contaminated with petroleum compounds. These results can be used to evaluate risk to human health through consumption. Contamination of seafood can affect subsistence, commercial, and recreational fishing. Tissue analysis and monitoring for oil in harvest areas provides necessary information for decisions about advisories, closures, gear restrictions, etc. Sampling should be conducted in both impacted and un-impacted areas to monitor depuration rates and understand background levels of contaminants. In some cases, qualitative sensory testing (i.e., assessing odor and/or flavor) may be warranted to determine whether seafood is contaminated. See Yender, et al (2002) for further discussion of monitoring and testing seafood.

Chemical and physical properties

Chemical and physical properties (e.g., specific gravity, viscosity, pour point, flashpoint, and water content) of the released material(s) provide information that can be used to understand how the spilled material will behave in the environment. For example, these properties can be used to predict if the spilled material will float or sink in freshwater or seawater. Understanding how these properties change over time in the environment (e.g., weathering) helps predict the behavior of the material under different environmental conditions. Therefore, collection of spilled oil at various times during the response (e.g., fresh versus weathered oil) and under differing conditions is important for understanding how the material will behave as it weathers. This information is critical for planning and implementing effective recovery operations since there may be time-critical windows of opportunity for certain response alternatives such as dispersant application and in-situ burning.

Cleanup effectiveness

In addition to visual observations, samples of water, spilled or recovered oil, and sediment, provide valuable information for assessing and monitoring the effectiveness of cleanup efforts. Following on-water mechanical containment and recovery, samples of the recovered oil are often collected in order to determine its water content and calculate volume of pure oil that was recovered.

Dispersants are sometimes used to break up large slicks of floating oil into smaller droplets to facilitate their dispersion and natural biodegradation processes in the water column. Special Monitoring of Applied Response Technologies (SMART) protocol involves monitoring activities (e.g., aerial observations, water quality measurements, fluorescence monitoring, and chemical sampling) used to assess effectiveness and efficiency of dispersant application and characterize horizontal and vertical movement of the dispersed oil (USCG, et al 2006).

When controlled burning of oil on water is used as a response tactic, SMART protocols are often followed to assess the effectiveness of burning and ensure worker and resident safety during operations. Pre-burn oil/emulsion and post-burn residue samples can also be collected to evaluate burn effectiveness as well as potential changes in oil properties and toxicity of residues.

Waste characterization

Recovery operations result in several waste streams that include recovered oil, water, oily liquids and solids generated by cleanup activities, decanting, and decontamination. Sampling is needed to characterize wastes to determine if they meet applicable regulatory criteria for disposal facilities. For example, not all disposal facilities are permitted to accept materials classified as hazardous. Waste classification may also be needed for transportation purposes. Waste sampling data may also be used for fingerprinting or to estimate the volume of oil removed from the environment for mass balance calculations.

Environmental impact assessment

In addition to guiding response operations, samples may be collected to evaluate potential impacts to natural resources (e.g., natural resource damage assessment in the U.S.). Considering the dynamic nature of spills and the limited window of opportunity for some types of sampling, environmental sampling could be included in the initial sampling plan if feasible and appropriate.

Often, the data collected for response purposes can be utilized for impact assessment as well. Sampling objectives supporting environmental impact assessment often include, but are not limited to the following: Defining the spatial and temporal extent of the spill and assessing the potential for natural resource impacts; Documenting pre-impact conditions (i.e., baseline); Documenting affected resources (e.g., natural, cultural, and recreational resources) and monitoring ecological recovery; and Assessing weathering, toxicity, and biodegradation of the spilled material.

Spatial and temporal delineation of the spill

Sampling water, sediment, and biota can help define the spatial and temporal extent of the spill and assess the pathways through which natural resources may be impacted. These data are used to document the presence/absence and relative amount (e.g., concentration) of the spilled material and its components in different media. The concentrations of petroleum hydrocarbons in some media (e.g., water column) are highest in the first few hours to days following a release and then may decrease rapidly as the result of various environmental fate and weathering processes. Given the ephemeral nature of these types of data, it is critical that sampling begin as soon as possible, ideally within the first hours after the release occurs.

Background conditions

Sampling water, sediment, and biota in areas that have not been impacted by the released material, as well as areas that are outside the potentially affected area is important for documenting background or reference conditions (sometimes also called “baseline”), including toxic compounds such as hydrocarbons that may be present in the environment from other sources before the release. Data collected from impacted areas can be compared to reference data to determine what portion of the petroleum hydrocarbon mixture present in the various media is a result of the spill and to help understand potential impacts to natural resources. Baseline data become very important during efforts to quantify spatial and temporal impacts to natural resources, which can be an important basis for determining the amount of monetary or restoration-based compensation (i.e., damages) required to offset injuries.

Affected resources

Sampling is essential for determining the potential injuries to natural resources. Visual assessments are helpful for some types of resources; however they have limitations because spill impacts cannot always be seen. Physical oil can be observed, but dissolved constituents that may be toxic to natural resources cannot be detected visually. Therefore, it is necessary to conduct chemical analysis to determine the presence or absence as well as the concentration. This can include chemical sampling of plant and animal tissues directly, but occurs most frequently through sampling of abiotic media such as water, sediment, and soil, which serve as the pathways through which most biotic exposures occur. Ongoing monitoring and sampling may also be conducted to document recovery of affected ecological resources and provide data necessary to understand when affected resources will return to pre-spill conditions.

Weathering, toxicity, and degradation

Oils are complex mixtures that change after a short time in the environment. Samples of the spilled oil should be collected periodically to document the degree and rate of weathering and provide an understanding of changes in the oil properties and toxicity through time. These data are used to help understand long-term impacts to natural resources and can also be relevant for short- and medium-term response decisions.

Source identification

Sampling objectives in support of identifying the source of the spilled material include identifying the specific type of hydrocarbon/source material released to the environment, and linking environmental samples to the spill source or differentiating them from unrelated sources. Chemical analysis is needed to establish the chemical fingerprint (i.e., unique ID) of the spilled material and potentially other sources of hydrocarbon pollution within the spill area. Environmental samples are analyzed to determine the degree to which they match one or more identified sources. Fingerprinting analysis also provides information on changes in oil composition in various media due to weathering. Additional forensic analyses may be conducted to provide more details about the source. The PIANO analysis is used to determine the amount of paraffins (P), isoparaffins (I), aromatics (A), naphthenes (N), and olefins (O) that are present in the mixture. These individual hydrocarbon groups are important to oil spill forensic evaluations and are of particular importance to light-end refined product fingerprinting. Petroleum biomarkers, a class of larger aromatic compounds that are highly resistant to weathering, are useful in the identification of petroleum and refined products regardless of the state of weathering.

ACHIEVING OBJECTIVES

Once sampling objectives are defined and agreed upon, a study plan that outlines how those objectives will be achieved can be developed and implemented. A Sampling and Analysis Plan (SAP) can be developed that provides guidance to response managers and others (particularly members of the Environmental Unit) who may be involved in various types of environmental sampling performed when responding to spills of oil and oil-products. A spill response SAP should focus on the key sampling activities that should be conducted immediately following a release, including collection of oil samples, ephemeral environmental samples (e.g., transient data that can only be obtained in the first few hours or days after a spill), and background/reference samples. A SAP is a tool used to efficiently organize and convey an otherwise unwieldy amount of information critical to achieving sampling objectives. Due to the incident-specific nature of sampling, it is impossible to develop a complete oil spill SAP before an incident occurs. However, developing a template beforehand can help reduce the burden after a spill occurs and minimize time spent planning and tracking down information that can be prepared before a spill occurs.

Development of a Sampling and Analysis Plan

An initial SAP should provide relevant information to guide the collection and analysis of environmental samples to meet specified objectives. The following key information should be included: Sampling Objectives; Target media (e.g., oil, water, sediment, etc.)/sample types; Number and Location of Samples; Sampling Frequency and Duration; Sample Collection Methods and Equipment; Sample Handling and Preservation; Analytical Parameters and Test Methods; and Quality Assurance and Quality Control Parameters. Incident-specific objectives, such as those discussed above, form the basis for successfully developing a SAP. Developing a SAP also requires careful evaluation of spill and site conditions, potential impacts, as well as logistical constraints such as personnel and equipment availability and accessibility to desired sampling locations.

Consideration of sample media, oil type, possible government agency requirements, and laboratory capabilities are all factors that can influence the selection of analytical test methods for samples. It is important to consider turn-around time (i.e., how long until results are received) and sample hold time (i.e., how long before the sample must be extracted and analyzed for the results to be valid) when developing the SAP. Some laboratory analyses may take several days or longer to conduct, in which case, results may not be received in the necessary timeframe for making decisions, especially those related to time-sensitive operations (e.g., dispersant application or in-situ burn). Additionally, it is important to identify what data are needed (e.g., type, number, and location) and how the data will be utilized in order to make decisions regarding appropriate sampling methods, analytical parameters, and data quality requirements.

Study design considerations

The number and types of samples, priority, frequency and duration of sampling, target sampling media, and locations are typically based on spill and site conditions as well as logistical constraints such as personnel, equipment availability, site accessibility, and laboratory capabilities. It is usually not possible to collect all the necessary samples simultaneously. Therefore, it is necessary to set priorities among sampling objectives. Personnel protection must always be the highest priority and safety hazards should be assessed and taken into consideration.

In general, sample efforts during the immediate response should focus on distribution, rather than replication. Ideally, numerous samples (replicates) would be collected from a variety of locations (distribution) during the immediate response efforts. However, if logistical constraints (e.g., personnel, equipment, time) are significant, it is generally advisable to collect fewer samples at a given location (reduced replication), and sample more locations (greater distribution).

Sample locations should ideally be distributed along expected concentration gradients in order to determine the spatial extent of potential impacts based on the range of petroleum concentrations present. A time-series sampling program (e.g., repeat sampling at fixed locations) will enable the location and duration of maximum oil concentrations to be determined. This aspect of sampling is important for determining whether toxic thresholds were exceeded, and if so, for how long and over what areal extent.

Background samples should be collected in order to characterize the areas that are unaffected by the released oil (e.g., reference areas upstream of the release or areas "ahead of the spill", for instance downstream of the point of product entry along a river, prior to exposure to oil). This is important to distinguish between spill-related effects and those attributed to pre-existing contamination, if any.

Sample collection

Sampling requires a variety of procedures and equipment, depending on the media being collected. Samples of the unweathered spilled material should be collected directly from the source (e.g., holding tank, pipeline, etc.) when possible (i.e., should not have contact with the environment) and should be collected as soon as safe and practical. Additional samples of the oil should also be collected after it has been released into the environment (i.e., fresh oil). Fresh oil is typically found in the slick near the source. Collecting weathered oil samples will help to identify the degree and rate of weathering and provide an understanding of changes in the oil properties through time. Weathered oil samples may consist of the floating oil slick, tar balls, mousse, or oil deposits on the shoreline or in bottom sediment. Oil samples should consist of mostly oil with only minimal amounts of other media (e.g., water, soil). Source oil and weathered oil samples should be kept separate from all other environmental samples to avoid potential cross-contamination.

Water samples may be collected from various depths below the surface depending on the objectives. If the objective is to measure the water accommodated fraction/dissolved concentrations in order to assess aquatic toxicity, it is important that samples do not contain any floating oil or sheen as these would bias the results relative to this objective. However, if the purpose is to document the presence of oil in the water, inclusion of the surface layer of oil may be useful.

Like water samples, sediment and soil are collected from the surface or subsurface depending on the sampling objectives. For biota, the selection of specific species is incident-specific, but commonly includes fish, crustaceans, and/or mollusks. The choice of procedure should be determined by site-specific conditions, such as the type of surface water body, the water depth, species targeted for tissue sampling, and the holding times and conditions of the samples.

Air quality is monitored using direct-read instruments or by laboratory analysis of collected samples. Real-time measurements provide immediate information for worker and community exposure scenarios and, with the use of appropriate site safety measures, help prevent overexposures. However, real-time samples do not necessarily represent conditions experienced throughout the workday and can substantially underestimate or overestimate exposures potentially experienced by workers and residents. Therefore, analytical air sampling may be conducted for the purpose of collecting data that represents concentrations of contaminants over a specified period of time. For additional details about air quality monitoring, refer to the U.S. Department of Human Health Services' Air Monitoring Standard Operating Procedures (1985).

Analytical parameters

The most common chemical analyses conducted after a release of oil, fuel, or related materials are for the chemical parameters that are used to provide a broad characterization of the spilled material and those constituents for which toxicity thresholds have been developed. In some instances, forensic analysis (e.g., fingerprinting) provides information used to help identify the spilled material and the potential source(s). Table 1 lists the analyses for various petroleum products that are recommended to characterize the spilled material and its potential effects in various environmental media. The selection of any additional or more specific analytical parameters should consider the potential needs for fingerprinting. For further discussion of recommended chemical analyses, see Sauer and Boehm (1995).

Table 1. Recommended Analyses for Petroleum Product Categories

Petroleum Category	**Analytical Parameters**						
	PAH[1]	**TPH**[2]	**PIANO**[3]	**BTEX**	**MTBE**[5]	**Lead**[6]	**Sulfur**
Gasoline	●	●	●	●	●	●	●
Jet Fuels and Kerosene (No. 1 Fuel Oil)	●	●	●	●			●
Diesel/Heating Fuel	●	●		●			●
No. 2 Fuel Oil	●	●					●
Light Crude	●	●	●	●			●
Most Crudes	●	●	●	●			●
Heavy Crudes	●	●					●
No. 6 Fuel Oil	●	●		●[4]			●
Bunker C	●	●		●[4]			●

[1] Polycyclic aromatic hydrocarbons, including parent and alkylated compounds

[2] Total petroleum hydrocarbons (plus saturate hydrocarbons and total extractable hydrocarbons [TEH], *n*-C8 to *n*-C44)

[3] Paraffins, Isoparaffins, Aromatics, Naphthenes and Olefins

[4] Benzene, toluene, ethylbenzene and xylenes

[5] Methyl tert-butyl ether

[6] Organic lead by gas chromatography using an electron capture detector (ECD)

Additional analyses should be considered that can provide information on the chemical and physical characteristics of the released material. This information may be useful for informing response operations as well as understanding potential impacts to natural resources. Depending on the nature of the spilled material, certain metals may be of interest to the identification of the source of contamination in impacted samples. Total organic carbon (TOC) and sediment grain size provide information used to estimate the bioavailability (e.g., the fraction available to the biological resources) of petroleum hydrocarbons in sediment. This information is valuable when looking into potential impacts to resources. Water chemistry characterization may be of interest to assessing the impacts on an aquatic system, and would typically include analysis of total nutrients (e.g., total nitrogen, nitrite, nitrate, ammonia, total phosphorous), dissolved organic carbon (DOC), and total suspended solids (TSS).

There are standard requirements for the analysis of various chemical parameters. Therefore, it is important that the appropriate sample containers are used, including preservatives when necessary, and adequate sample volume is collected. Table 2 summarizes potential laboratory analyses, required sample volumes for each laboratory analysis, appropriate sample containers, preservation methods, and holding times for oil samples. Recommendations for other media (e.g., water, soil/sediment, and tissue) are not included in this table. This information is intended for guidance only and specific requirements should be confirmed directly with the laboratory.

Table 2. Potential Analyses, Sample Volume, and Preservation Considerations for Oil Samples

Analyte	Test Method [1]	Sample Volume and Containers [2]	Preservation	Sample Holding Time [3]
VOCs	EPA Method 8260B/C	3 x 40-ml glass vials, with Teflon lid[4]	Cool, 4°C or Freeze at -20°C	14 days when shipped to laboratory within 48 hours at <6°C and frozen (-12°C) upon receipt.
TPH[5]	Modified EPA Method 8015 (GC/FID)	2 x 40-ml glass vials, with Teflon lid [4]	Cool 4°C or Freeze at – 20°C	14 days at 4°C
PAH	Modified EPA Method 8270 (GC/MS-SIM)	2 x 40-ml glass vials, with Teflon lid [4]	Cool 4°C or Freeze at – 20°C	14 days at 4°C
PIANO	Modified EPA Method 8260B	2 x 40-ml glass vials, with Teflon lid [4]	Cool 4°C or Freeze at - 20°C	14 days

Petroleum Biomarkers [6]	Modified EPA Method 8270D (GC/MS-SIM)	2 x 40-ml glass vials, with Teflon lid [4]	Cool 4°C or Freeze at -20°C	NE – but use PAH criteria
Fingerprinting	NORDTEST	Total of 100 ml: (3) 40 ml glass vials or (1) 4oz wide mouth glass jar, Teflon-lined	Cool 4°C	14 days
Density	ASTM D5002, ASTM D4052	Consult lab	Consult lab	Consult lab
Specific Gravity	ASTM D1298	Consult lab	Consult lab	Consult lab
Viscosity	ASTM D7042	Consult lab	Consult lab	Consult lab
Flash Point	ASTM D93	Consult lab	Consult lab	Consult lab
Pour Point	ASTM D97	Consult lab	Consult lab	Consult lab
Water Content	Karl Fisher Titration	Consult lab	Consult lab	Consult lab
Sulfur content	ASTM D2622	Consult lab	Consult lab	Consult lab

Metals	EPA Method 6020A	2 x 40-ml glass vials, with Teflon lid[4]	Cool 4°C	14 days

[1] Additional test methods may be used that are specific for the analytical laboratory, media/oil type, or as required by various states.

[2] Sample size excluding volumes for QA/QC analyses (i.e., replicate sample analyses). It is recommended that all samples be collected in duplicate containers in case of breakage during storage, transport or shipping.

[3] Sample holding time before extraction.

[4] Volumes reported for "oil" are for source oil samples. For fresh and weathered oil samples, a total of 2 x 1.0 liter samples should be collected in amber glass bottles.

[5] TPH (plus saturate hydrocarbons and/or TEH, *n*-C8 to *n*-C44).

[6] Biomarkers: steranes, hopanes, terpanes.

Additional considerations

Sampling methods are often dictated by the site-specific conditions and safety considerations. Standard operating procedures (SOPs) should be developed or referenced for appropriate sampling methods. For further information on sample collection methods, the American Petroleum Institute has developed numerous guidelines and standard operating procedures for oil spill sampling (1999). Data quality requirements are typically addressed in a project-specific Quality Assurance Project Plan (QAPP), which describes appropriate field measurement and sampling procedures, sample handling and custody, critical quality control samples, laboratory analytical methods, acceptable detection limits, and data handling and reporting requirements. The purpose of the QAPP is to ensure that the data are of suitable quality and quantity for decision making. The SOPs and the QAPP are important references that should be followed to ensure the quality and consistency of the data being collected, reduce errors, and improve efficiency in the field. These materials may be included in the SAP if separate documents cannot be prepared readily.

CONCLUSIONS

Sampling and environmental monitoring is an important activity to consider in the context of spill response. Sample results can provide valuable information to responders and decision makers, and serve as the basis for assessing any potential environmental impacts. Although sampling objectives and details of sampling programs will vary in each individual situation, planning for these activities and developing strategies for integrating sampling into response efforts will allow for a more efficient program development and deployment in the field should the need arise. This integration can be practiced in the planning and preparedness phase during oil spill response training and exercises.

FURTHER READING

This paper is intended to provide a high-level overview of key topics related to environmental sampling for oil spill emergency response and considerations for planning purposes. More detailed discussion of the topics introduced in the preceding sections is beyond the scope of this overview. Readers wishing additional detail should consider further review of available guidance on specific topics, including the references listed below

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