2 Spill Site Investigation in Environmental Forensic Investigations

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2.1 Introduction

The first step in all forensic investigations surrounding surface oil spills is to characterize the spill site and the affected area to determine the nature and scale of the problem and to identify acute safety issues. Scaling the problem is critical to a forensic investigation and involves essentially defining the source, type, amount, and location of the spilled oil. These elements provide the necessary framework for an assessment of the environmental variables that control the transport and weathering of the oil, and for identification of amplifying evidence on the nature of the spill itself. The identification of safety issues, typically as part of a site safety plan, provides the backbone of all spill-related activities and sets limits on what actions operations personnel and site investigators can and cannot take at the spill site and in the affected area.

There is a fundamental difference between the behavior of oil spilled on land and on water that determines the speed at which spilled oil moves or spreads and the resulting size of the affected area. This difference has a significant influence on the scale and character of the site investigation. Oil spilled on land, except in rare circumstances, flows down slope and typically collects in depressions or against topographic or manmade barriers (Table 2-1). The rate of down-slope movement is a function of the oil viscosity, air/ground temperatures, slope steepness, and the surface condition (roughness, vegetation type, soil type, permeability, etc.). Land surfaces are rarely flat, so that the thickness of layers of oil varies considerably. Oil that reaches creeks, streams, or rivers and oil spilled directly on water is transported and spread by winds and/or surface currents, so that the extent of the affected area, weathering rates, and therefore the scale of the problem, typically increase dramatically.

In this chapter we describe appropriate methods to characterize the spill site in terms of environmental and safety issues, the survey tools that have been developed to define and describe the spill site and the affected area, sampling considerations for spills where the source is known and for "mystery spills," and data management techniques to capture, organize, and present the results of the investigation.

2.2 Environmental Site Characterization and Reconnaissance Survey

An early challenge for spill site investigation is the competing demand and need for emergency response. Initial response activities usually include spill and safety assessment studies, sampling programs, oil containment and treatment, and recovery activities. For any forensics investigation, it is essential to have a clear understanding of the natural site

Table 2-1 Characteristics of Spills on Land and Water (Adapted from Owens, 2002)

Oil on Land	*Oil on Water*
• spilled oil is generally slow-moving or static • the oil collects in depressions or against natural and man-made barriers • usually the size of the affected area is small and it is easy to define the location and amount of surface oil • only light oils spread to form a thin layer; often considerable pooling of oil • weathering slows considerably after approximately 24 hours	• spilled oil is moved by winds and/or currents and often remains in motion for days and sometimes weeks • the size of the affected area increases with time and it can be difficult to locate some or all of the oil; may submerge or sink • oil on the water surface typically spreads to form a very thin layer • weathering and emulsification are dynamic processes that continually alter the physical and chemical properties of the oil

conditions, potential spill sources, factors that influence the area as well as the fate of spilled oil, and safety risks associated with activities and the environment itself. Objectives for site characterization and reconnaissance surveys are to:

- define site features that influence oil fate and persistence,
- delineate areas affected by the spill,
- identify background and incident-specific contributions of oil at the field site,
- describe variations in oil's physical character, concentration, and mode of occurrence in space and time,
- evaluate the variability of oil concentrations and oil penetration depth,
- provide data to help forecast residence time of surface and subsurface oil from knowledge of *in situ* weathering processes,
- provide data of potential use to understand the short- and long-term effects of oiling on resource use.

A first step in site investigation is to establish a scope or scale of the problem: starting with a broad picture and working toward detail. The exact design, size, duration, and scope of the survey program will vary with each spill situation, the environmental conditions, and the operational response. ASTM (American Society for Testing Materials) standards for site investigations of oil and hazardous chemical sites list a number of variables to be considered in a site investigation (ATSM 1995, 1998a, 1998b). Additionally, protocols for study of oiled shorelines are described in detail in PERF (Petroleum Environmental Research Forum) Guidelines (e.g., Owens, 1999).

A site investigation and delineation must take into account steps typical of an ecological risk assessment: identify potential contaminant sources, identify potential receptors that may be affected by exposure to oil, and identify the transport processes that can place oil in contact with receptors (Table 2-2). ASTM Standard D 5745–95 (1999) indicates that site investigation entails assembling existing available information and developing a conceptual site model, including:

- identification of contaminants (oils),
- characterization of background/conditions,
- contaminant (oil) source characterization,
- migration pathway characterization,
- contaminant (oil) mass estimate.

The source(s) of spilled oil may be known, but a site investigation must also clearly identify other potential sources of petroleum hydrocarbons that may pre-exist or naturally occur (e.g., oil seeps, abandoned or active industrial sites, runoff, wrecks, etc.) in the area. Receptors include ecological, human, and economic resources that could be affected by the spill. Transport pathways include surface and subsurface routes. Hence, site investigation and reconnaissance typically must conceive a three-dimensional and temporal model of source and fate of the spilled oil. The type of information to be assessed for site characterization should lead to a clear

Table 2-2 Examples of Factors to be Assessed as Part of a Site Investigation

Attribute	*Example — Terrestrial*	*Examples — Marine*
Physical Characteristics	Buildings, structures, landmarks, topography, soils (homogeneity, distribution), debris	Landmarks (points, islands, inlets), topography (nearshore and subtidal), sediments (homogeneity, distribution)
Ecological Use	Vegetation, avifauna, burrows, wildlife, freshwater habitats (lentic, lotic)	Nearshore and intertidal biota (algae, vegetation), epi- and infauna, sessile and mobile organisms, wildlife
Human Use	Industrial, residential, commercial use, public use (parks), transportation (rail, roads, etc.)	Industrial, coastal residential, commercial use, public use (parks), transportation (ports)
Spill Sources	Tanks and pipelines (surface or buried), hoses, tankers (truck, rail), industrial histories, seeps	Vessel traffic, effluent discharges, submerged wrecks, industrial histories, seeps
Surface Pathways	Drainages, surface water (runoff, streams, rivers — direction, speed)	Surface currents, wind, waves and tidal action
Subsurface Pathways	Infiltration (stratigraphy and permeability), groundwater (depth), hydraulic gradient (groundwater speed, direction)	Burial processes, heavier than water oils (initially or after weathering), currents, upwelling, infiltration (stratigraphy and permeability)

understanding of the spilled oil's source and fate. Examples of factors to be assessed are provided in Table 2-2 and in ASTM E-1943 (see Table X2-1, in ASTM, 1998b).

2.3 Site Entry and Safety Issues during the Emergency Response Phase

Scientific and technical support personnel may have an immediate need to rapidly collect ephemeral data and samples during the first response phase as part of a forensic investigation. However, this initial phase of the response is the most uncertain in terms of assessment and characterization of risks to personnel. Scientific and technical staff must be cognizant of any potential safety hazards and of the prescribed safe operating procedures that apply in the area affected by the spilled oil.

One of the paramount concerns of every response operation is for the health and safety of the public and oil spill personnel (MCA, 1998). There are numerous industry standards and governmental guidelines, regulations, and policies regarding human health and safety in the emergency response to spill incidents. The concept of safety guidelines and practices varies from country to country and can fall anywhere along a spectrum of rigid laws and regulations governing safety risks and practices to a case-by-case risk assessment process (IPIECA, 2002). In general, concerns regarding the safety of the work site and working conditions are easier to address and to understand than concerns about exposure to the spilled products themselves (Holliday and Park, 1993).

Key themes in safe site entry following an oil release include site security and management, risk assessment and characterization, chemical toxicity of the spilled material(s), work environment safety, and personal protective equipment (PPE). Personnel entering a spill zone must be trained to appropriate levels in safety protection procedures. Example safety training guidelines are provided in ASTM procedures for hazardous materials and oil spill responders (ASTM, 1986, 2001a, 2001b).

2.3.1 Management of Safety

One of the first appointed roles in emergency spill response management is the safety

Table 2-3 Priorities of the Safety Officer during an Oil Spill (Adapted from IPIECA, 2002)

Safety Management Priorities

1. Site Assessment:
   - Analyze the hazards and document this hazard analysis process
   - Hazard identification
   - Identify appropriate PPE
   - Identify control zones
   - Identify decontamination areas
2. KEY: must use trained, experienced personnel in management of safety issues.
3. Must train all personnel in safety awareness and practices.
4. Develop and implement a site-specific safety plan.
5. Attend daily planning and safety meetings in command center.
6. Correct unsafe acts or conditions as soon as possible.
7. Establish first aid and emergency medical stations and procedures.
8. Conduct safety briefings and communication daily and as needed.

officer(s). Responsibilities assigned to the safety officer are to characterize the nature of existing and dynamic safety hazards, establish and implement safety guidelines, develop a site-specific safety plan, and implement the necessary precautions. This individual, or team of safety personnel, is responsible for monitoring hazardous and unsafe situations and maintaining awareness both of active and developing situations (Table 2-3).

2.3.2 Risk Assessment and Characterization

The safety officer's first step in implementing a safety program is a thorough site assessment and characterization to obtain adequate information on the spill location and the particular character of the spill site, including environmental conditions, to develop specific safe operating procedures (MSRC, 1993). It is best to use standardized procedures or protocols for site assessment, site characterization, and site safety plan development (MSRC, 1993), which can be modified as appropriate to meet the specific conditions of each incident. This comprehensive risk assessment and hazard analysis is conducted immediately after the incident to determine if responders or the general public are in danger. Some of the principal questions that must be answered by this site assessment include (from IPIECA, 2002):

- Is there a risk of explosion or fire?
- Is there a need to monitor for flammable or toxic fumes?
- Is there a need to evacuate people?
- Is the environment safe for people to enter or work in?
- Will oil enter systems that may affect people?
- Is there a need to establish safety or exclusion zones?

Once these key questions have been answered satisfactorily, the safety officer must then determine any risks posed by particular operations or at specific locations within the spill site. These need to be assessed on a case-by-case basis. It is also imperative to document the site risk assessment; many standard forms exist, or one can be created or modified to fit the situation.

The purpose of conducting the initial site risk assessment then is to identify all the potential hazards presented by the incident itself, the work site(s) (including risks inherent to the ambient environmental conditions), and of the response operations. This allows some ability to predict the probability and severity of any potential safety hazard or incident. The response managers, through the safety officer, can then prioritize potential hazards and appropriate guidance and precautions. A common practice is to identify three levels of safety response zones:

HOT — with higher safety risks; stricter PPE requirements; activities include source control, sampling, and cleanup

WARM — general lower personnel exposure; decontamination activities; and

COLD — nonoiled zones; PPE not required for contact with spilled oil, support activities.

Once the safety hazards and their likelihood have been characterized, and appropriate precautions have been determined, safety personnel continue to evaluate their appropriateness and effectiveness as many of the safety risks and potential hazards associated with an oil spill are not static and change with time and/or the response operations. For a continued hazard, there is a common hierarchy of priorities in establishing safety priorities (from IPIECA, 2002):

1. prevent access to the hazard (site control and security),
2. organize the work site(s) so as to reduce exposure to the hazard (safety zones),
3. select and employ appropriate PPE for all personnel in the area.

2.3.3 Chemical Toxicity of the Spilled Oil

Each type of spilled product will have its own inherent chemical properties and associated risks to the safety of the general public and on-site personnel. It is important to remember that these properties or characteristics will change with time as most petroleum products weather (i.e., change their chemical and physical properties when exposed to weather and the natural environment) when spilled, particularly in an open area with exposure to wind, waves, sunlight, etc. Information on the spilled products' properties, such as found in the Material Safety Data Sheets (MSDS), can be used to assess the basic chemical properties and physical characteristics of the spilled product and its hazards to personnel.

The principal health hazards from petroleum products themselves include flammability, the presence of explosive vapors, hydrogen sulfide gas (heavier than air) in sour crudes, exclusion of oxygen, toxicity, and the slippery nature of the oil. The first four of these hazards are generally very short-lived threats, especially for spills in open environments. Except in cases of confined spaces (e.g., trenches, tanks, under docks), the vapor cloud diminishes rapidly, typically within hours after a release.

All of these hazards are a priority when assessing and characterizing the site following a spill and before allowing access to the spill site. Characterization of any of the above explosive or vapor hazards can be accomplished with a comprehensive air monitoring protocol. Air monitoring data are then matched with appropriate safe working exposure limits. For example, guidelines for conducting operations in the presence of potentially explosive vapors are (ExxonMobil, 2002):

- **<10% LEL** — continue response operation. An LEL reading of 10% is equivalent to an airborne concentration of 100,000 ppm, which will require appropriate respiratory protection.
- **≥10% LEL and <25% LEL** — explosion hazard present. Withdraw from area immediately. Proceed with care, especially where there is poor air movement or circulation.
- **>25% LEL** — leave the area quickly and carefully.

Air monitoring must be conducted to define required breathing protection as part of personnel PPE and ensure safe operating conditions. Air and exposure monitoring are conducted using a variety of instruments, including various electronic monitors, Draeger tubes, personal monitors, or passive diffusion monitors.

Although some components of oil are toxic, the actual risk of toxic exposure by responders or the general public to spilled oil is in most cases very low. Spilled petroleum toxic components have a number of pathways of exposure to humans — inhalation of vapors, direct dermal contact, absorption through the skin or eyes, ingestion, or injection (IPIECA, 2002). As with other hazards from spilled products, the risk of a toxic exposure is greatest immediately following a spill, particularly of products containing volatile aromatic compounds such as benzene. Benzene and similar oil compounds are carcinogenic. Safe exposure standards and limits have been defined (see, for example, the NIOSH Pocket Guide to Chemical Hazards, 2005). Air monitoring must be conducted, even though these aromatic components are volatile and generally dissipate rapidly to below prescribed exposure limits, and proper PPE for responders must be prescribed until air monitoring ensures that the risk of exposure to these carcinogens has diminished.

2.3.4 Working Environment Safety

There are numerous characteristics of a spill site that pose hazards to technical personnel. Environmental factors such as spill location, weather conditions, tidal fluctuations, access to cleanup sites, terrain, etc., cannot be controlled. Access points, PPE, and personal security can be controlled, thereby minimizing safety hazards, and site-specific procedures can be used to effectively minimize potential hazards.

Weather is a significant consideration in the safety of response personnel. Response personnel may be exposed to the elements for many hours. Safety hazards can include a range of health issues from hypothermia or frostbite to heat stroke/exhaustion, sunburn, and dehydration. Preventative measures include selecting appropriate clothing, shelter, survival training, selecting appropriate work/rest schedules, and proper communications equipment and weather forecasts (IPIECA, 2002).

Oil spills can occur in a broad range of environments, often within the same spill — e.g., exposed, rocky coasts, ice- and snow-covered tundra or remote mountainous terrain. Safe access and egress must be established for personnel and equipment that accounts for shoreline substrate (cliffs, mangroves, sand, mud, etc.), tidal ranges, riverbank gradients, watercourse flow rate, and depth, and water table characteristics. Indigenous flora and fauna, such as slippery algae, poisonous plants, snakes, alligators, and other dangerous plants and animals must be identified and proper safety precaution briefings given to personnel.

The most common injuries to personnel at spill sites are from slips, trips, and falls. Any surface that encounters spilled oil likely will be slippery. In addition, the work site for the collection of samples may by nature be difficult terrain — rocky coastlines, intertidal zones, cliffs, remote areas, rough sea states, etc. Appropriate PPE and site assessment and sampling equipment can be cumbersome and can make movement or specific actions difficult for scientists or technicians, particularly once clothing or equipment has become oiled.

2.3.5 Personal Protective Equipment (PPE)

Concerns over exposure to spilled contaminants can be addressed by applying broad, conservative standards of PPE and exposure time limits, which could significantly hamper an individual's ability to perform physical activities for prolonged periods, creating a need to balance the risk of exposure to the spilled product with an appropriate, adequate level of PPE (Holliday and Park, 1993). Nonetheless, PPE is essential for each responder to ensure he is able to work safely around chemicals and other materials that may be hazardous to his health.

Decontamination procedures must be established and implemented safely for all personnel and equipment. Technical personnel must be briefed on these procedures, which take place in predesignated locations within the WARM zone. The primary goal of decontamination is to allow personnel and equipment to exit the HOT zone while avoiding cross or secondary contamination. Typically, decontamination procedures are established for both personnel and equipment.

The primary objective of every oil spill response must always be to ensure the safety of the response personnel and the general public. The response management makes a commitment to safety by establishing a safety program led by a safety officer to assess and characterize the potential hazards from the spilled contaminants and the response operations. All personnel in an oil spill site, including scientific and data collection staff, must understand their obligations to work in a safe and responsible manner within the established operating guidelines. Forensic investigation personnel must be adequately trained to a level commensurate with the tasks they will be assigned (ASTM, 2001b; OSHA, 2001).

2.4 Determination of Geographic Boundary and Definition of Different Zones within the Affected Area: 1. Terrestrial Oil Spills

Determination of the geographic boundaries and zones for spills are important to establish safety zones (hot, warm, and cold) for operational concerns, priorities for initial cleanup, and to provide a spatial reference for decision making relative to cleanup, monitoring, and remediation. In terms of a forensics investigation, the boundaries of a terrestrial oil spill site are typically more restricted relative to a waterborne spill primarily because of the limited transport factors in the former: infiltration into soils, retention on vegetation, and possible transport though surface and/or subsurface hydrologic regimes. Delineation of safety zones within terrestrial spills will entail an initial broad reconnaissance followed by detailed site investigation once safety requirements for site entry have been identified and are in place.

An initial assessment of a spill site must consider potential spill sources, which may range from obvious visual surface expression to more difficult subsurface diffusion zones and plumes. Initial delineation of a spill area typically is based on identifying spill source, runoff, and infiltration directions, and delineation of surface and subsurface oil concentrations. Tools for defining the extent of the site under investigation and more in-depth inspection and sampling are

- site aerial photos,
- detailed topographic maps,
- geographic positioning satellite (GPS) receivers (standard or differential),
- survey tie-in to fixed and known reference points (stakes, benchmarks, landmarks, structural features),
- cameras (digital, video, 35 mm).

After establishing safe-site entry requirements and procedures, a site investigation team will

- identify physical aspects and habitats that characterize the site,
- identify potential receptors (sensitive resources),
- identify known or potential spill sources (lines, tanks, tubing),
- delineate surface expressions of spill (visible oil),
- characterize surface and subsurface oil concentrations, distribution, and continuity through pits, trenches, or borings.

A clear record of the above information is best captured through sketches on a field map, accompanied by cross-referenced photographs, samples, and video with narrative. All observations, samples, and photographic evidence should be geographically defined through GPS linkages or surveyed in to fixed features that will allow subsequent assessments to return to the same location. The above information can later be transferred to a geographic information system (GIS) mapping program and associated database for easy reference and subsequent reporting and analysis (see Section 2.9).

A delineated study site should reveal safety zones (hot, warm, cold), oiled areas (concentrations, distribution, surface, and subsurface), nonoiled areas (confirmed), and areas at potential risk of oiling due to identified transport pathways. Because spilled oil is rarely static, site investigation and definition of oiled zones requires additional assessments. The frequency of these assessments depends on how quickly conditions may be expected to change at the site. The use of adopted and standard site-study protocols will help in comparing and interpreting study results for multiple surveys.

2.5 Determination of Geographic Boundary and Definition of Different Zones within the Affected Area: 2. Marine/Coastal Waterborne Oil Spills

Determination of the geographic boundaries and zones for marine and coastal waterborne spills is similar to the process described above for terrestrial spills. A key difference, however, is that waterborne spills typically undergo faster change such that the temporal aspect of site investigation may be more important. For oil spills, an adopted best international practice for characterizing coastal sites and oiling is the Shoreline Cleanup Assessment Technique (SCAT) (Owens, 1999; Owens and Sergy, 2002; ASTM, 1997a, 1997b). Sites along shorelines are identified as specific segments or subsegments, as these are defined by their relative continuity and homogeneity. If shoreline segment maps have not been prepared, the segmentation and site boundaries should consider

- prominent geological features (headlands, streams, etc.),
- changes in shore/sediment types
- changes in oil conditions, or
- habitats.

Once a site has been selected or a shoreline delineated through segmentation, a detailed site study is undertaken. As with terrestrial spills, site investigation will entail delineation of surface oil, subsurface oil (through pits or trenches), and recognition of processes that transported oil to where it was found. Because landmarks may not be as readily available for coastal areas and offshore, GPS (standard and/or differential) and/or field survey techniques (transit, tape and bearing, theodolite, etc.) tied into fixed reference points (particularly underwater) are highly recommended. These benchmarks should serve not only as horizontal controls but also as vertical reference points, particularly where coastal dynamics may change the beach morphology. Tide level can be used as a proxy for a fixed datum; however, apparent tidal level can be affected by winds and groundwater levels. PERF Method 3.2, Monitoring Program Procedures, provides guidelines on tools and methodologies for shoreline surveys and monitoring (Taylor, 1999).

For a recurring or long-term site investigation and monitoring program, transects should be set up across a site, at representative or randomly selected locations, depending on statistical needs of the study program. Periodic surveys are conducted to monitor changes in oil cover, site geomorphology, sediment distribution, types and densities of biota, oil penetration, and other parameters. Study site lengths (measured alongshore) are small enough to obtain adequate resolution and detail on the distribution of oil. PERF Method 3.1, Site Selection and Setup (Taylor, 1999), suggests most study sites would allow for at least 10 across-shore transects spaced no closer than 3 m and no greater than 20 m. Generally, study sites should be in the range of 40 m to 120 m long, and encompass the supratidal to subtidal zones, as appropriate to study requirements.

For offshore areas, definition of geographic locations will vary depending on the spill, and its potential for impact to offshore habitats. Two general categories of offshore study sites are considered: (1) subtidal extension of onshore study sites and (2) offshore areas of potential interest. Taylor (1999) highlighted criteria considered for identifying offshore areas of interest:

- areas underlying oceanographic convergence zones where oil on water is concentrated;
- areas where sediment influx is substantial and represents an important flocculation mechanism;
- areas underlying burned oil or sinking oil; and
- areas in the vicinity of other potential oil sources to the environment (i.e., seeps and wellheads).

The delineated study sites should denote safety zones (hot, warm, cold), oiled areas (concentrations, distribution, surface and subsurface), nonoiled areas (confirmed), and areas at potential risk of oiling due to identified transport pathways. Because spilled oil in the marine environment can be expected to be dynamic, site investigation and definition of oiled zones require frequent assessments. In the initial phases of spill response, these assessments may need to be repeated on the scale of days to weeks.

2.6 Collection of Physical, Ecological, and Environmental Data

The collection of adequate data following an oil spill is integral to characterizing the nature and extent of the release and its potential impacts. Data collected during this time should also consider any forensic questions that might need to be addressed — e.g., the potential source(s) of a "mystery" spill or the establishment of "background" conditions (i.e., pre-existing hydrocarbons in the environment). This section describes an approach to selecting candidate data types that ensure sufficient information is collected, at appropriate temporal and spatial scales, to determine the character, extent, and source(s) of the spill and its potential impact on the environment.

The first set of information to collect is generally related to physical data, such as samples of the spilled material from the release site and, in the case of a known source of oil, from the source. In the case of a "mystery" spill in a marine, lake, or river environment, this would include obtaining samples of slop tank oils, bunkered fuels, and petroleum cargoes from any vessels that recently transited the area. Sample collection may not be a straightforward activity in terms of initially identifying candidate sources and then being able to actually collect a sample. A common situation exists where several or many vessels may have transited the area in which a mystery spill is observed. This was the case for the Dalco Passage oil spill in Puget Sound (2004: Washington, USA), a very busy port area, in which there were "around twenty potential suspect boats" (http://www.epa.gov/oilspill/pdfs/0105update.pdf). In this type of incident, investigators attempt to collect samples from each vessel to try to obtain a match, as well as from potential shore-side sources such as terminals, sewers, rivers and streams, or from sub-sea pipelines. This type of investigation requires the cooperation of suspect parties and may involve the collection of samples from onshore facilities if a vessel has bunkered before leaving a port. Additional challenges to the collection of these vital data are the natural environment itself. Wind, waves, currents, and tides all can have a significant impact on the practicality and feasibility of plans to collect samples of oil, water, or sediments. The nature of the spilled product, whether it floats, submerges, or sinks, also is a factor in sample collection. The spill location, access to the site, and safety considerations play a key role in the ability to collect data to support a forensic investigation. Spills can occur on snow and ice, on frozen or soft, peat-covered tundra, in turbulent rivers, in mangrove forests, on flat, sandy beaches or on steep, rocky cliffs pounded by waves. Spills can be difficult to characterize when they occur on land as pipelines may traverse remote, mountainous regions with rough terrain.

Many types of physical environmental data are ephemeral in nature so that a sampling plan for these data must be designed very early into the spill to capture essential information. The key to the design of an appropriate data collection program to support sampling for a forensic study, particularly in the case of a "mystery spill," is to quickly determine the questions that need to be answered. Example questions are: Where did the oil come from? When did the spill occur? What was the transport pathway? What parameters have affected the weathering of the oil?

Quick identification and collection of the data or observations are required to understand the environmental factors that controlled transport and weathering of the spilled oil and to support the interpretation of the results of sample analyses. Wind speed and direction and weather observations or measurements (temperature and precipitation) may be collected on site or obtained from public service organizations. Current and wave data may be more difficult to obtain and nonsystematic observations may be the only practical option in the early stages of a response. If the study is concerned with transport pathways to determine the origin of a "mystery spill" at sea, in a lake, or on a river, then the collection of meteorological and hydrographic or oceanographic data may be the first priority.

2.7 Sampling Plan and Design: 1. Spills with Known Source

As part of the site characterization of a forensic oil spill investigation, an appropriate sampling plan must be designed and implemented. For spills with a known source, sampling is still integral to determination of the spill pathway and to scaling the nature of the problem in terms of the type, amount, and extent of the spilled material(s). Also integral to this type of spill investigation is the characterization of the pre-existing "background" conditions in the area of the spill. This section describes elements of designing an adequate sampling plan for spills of a known source, with primary focus on the options of discrete water sampling, continuous water sampling, and oil source sampling. Sampling on land is less of a concern as source identification is, in most cases, straightforward. The exceptions occur with spills of light oils, which can penetrate surface soils or sediments and travel through the subsurface, or with underground spills from tanks or pipelines.

Sampling plans are not necessarily lengthy documents. Approved plans are necessary, however, to ensure that the sampling team knows the procedures they are required to follow in order to collect samples that can be analyzed for meaningful and defensible information. Sampling plans should define, at a minimum:

- the type of collection procedure (grab, core, surface, subsurface, etc.),
- the number and location of samples,
- the required procedures for transferring material(s) and the types of container(s) to be used,
- the required procedures for handling, storing, and tracking the sample(s),
- the required procedures for numbering and labeling the sample containers,
- on-site data to be recorded at the time of sampling (GPS coordinates, depth, wind speed and direction, sample team members, etc.),
- site hazards and safety procedures.

2.7.1 Water Column Sampling

Priorities for water column sampling are chosen based on what data or information is required to answer specific questions (Brown, 1999). One method to prioritize water sampling methods or elements is to first evaluate those questions that are time-sensitive. Petroleum products, when spilled into the open environment, undergo rapid physical and chemical alterations when exposed to wind, sunlight, waves, and other natural forces. The greatest rate of change during this weathering process in most cases occurs within the first few hours to the first day after a spill. This ephemeral nature of the oil's physical and chemical properties underscores the importance of initiating sampling as early as possible, adjusting the frequency of sampling to be greatest during the initial hours after a release, and the need to prioritize sampling based upon a rapidly changing time scale. For example, a time-sensitive priority for sampling of an offshore oil slick is to first collect discrete water samples beneath the slick to determine the degree of natural dispersion and/or dissolution of oil components. This can be achieved by continuous water sampling beneath the slick, with attention given to planning for the slick's movement and transport downwind.

Discrete water sample collection and subsequent laboratory analysis provide detailed information on the concentrations of those components of the spilled oil that are of greatest concern, at distinct times after the release. These analyses also provide data for fingerprinting of the oil type and an evaluation of the toxic nature of its components. The potential does exist for contamination by surface oil when collecting subslick samples, so proper sampling procedures and contamination avoidance must be outlined clearly in any sampling plan. Discrete water sample analysis provides integral data to many aspects of the oil spill response and impact assessment and is an essential aspect of all oil spill investigations (Brown, 1999). Samples also should be collected from areas unaffected by the spill in order to provide "background" levels of contamination, which may be a significant factor in an industrialized environment or if there have been prior spills in the region.

2.7.2 Oil Source Sampling

Oil source samples, even in spills in which the source is obvious and known, should always be taken immediately following a release. Laboratory analysis of these samples can provide important information in the detection and investigation of the source. The chemical fingerprint of the source oil obtained from this analysis provides data that are then used to evaluate the potential fate and effects of the oil, both in the short and in the long terms. These detailed, and usually quite accurate, analyses can also shed light onto other background pollutants in the area, potential sources of the oil, and the potential risk to organisms and habitats the oil might encounter.

The approach to setting priorities for oil source sampling is similar to that taken with water column sampling — with a temporal hierarchy based on the ephemeral nature of oil once spilled into the open environment. Below is an example of priorities for several types of oil source samples (adapted from Brown, 1999):

- First priority: collect oil samples from the known or suspected source(s) itself, from the ship's oil tanks, or from the pipeline, well, tank car, or other source. If the source is a ship, take samples from as many segregated tanks as are on the ship, including possible lube oil tanks, oil–water separators, bilges, slops tank(s), fuel oil tanks, and cargo oil tanks, as well as any other petroleum product storage areas.
- Second priority: collect "source" samples of the spilled oil from the spill site itself, from the oil slick, or from a pool of oil on the riverbank or shoreline. Continue to collect samples of the spilled oil at an adequate frequency to characterize its physical and chemical changes as it weathers into such states as mousse or tar balls, if applicable. This sampling can be done concurrently with discrete water column sampling efforts.
- Third priority: sample oil that becomes stranded on shorelines or riverbanks. Continue to collect samples of shoreline oil at intervals adequate to characterize the weathering effects and changes to the oil's physical and chemical properties with time and exposure to the elements.

2.7.3 Sampling on Land

The sampling of oiled sediments, soils, or groundwater on land can be accomplished by surface grab samples, coring, or the installation of groundwater wells, all of which are standard procedures. If multiple potential sources exist, as may be the case in an urban area with a number of active, inactive, or removed underground storage tanks, the sampling design takes into consideration the three-dimensional analysis of potential transport pathways between the location of the oil and the possible sources.

2.7.4 Sampling Plan Design

Discrete water column samples are important for every oil spill, whether the source is known or not and analyses of these samples provide key information on the chemical and physical properties of the oil, its potential toxicity to organisms, its projected persistence in the environment, and other details to aid in spill response decision making. Several elements must be considered when designing a sampling plan, whatever the purpose of the samples

(Brown, 1999). First, there must always be collection of clean, reference samples for comparison. When possible, samples should be collected in triplicate and stored frozen in solvent-washed glass jars.

When choosing the location for sample collection, consideration must be given to the locations directly underneath and in the immediate vicinity of the slick, particularly if sensitive resources are in the area. Within the water column, it is usually the upper 1 meter, or "near surface," that contains the greatest concentration of spilled oil and is usually of most interest for sampling purposes. Selection of specific depth intervals should account for overall water depth and water column mixing conditions (Brown, 1999). In water of 50-m depth or less, under relatively calm conditions, such as in a lake or sheltered coastal bay, mixing is likely confined to the upper few meters and sampling depth intervals at 1 m, 2 m, and possibly 5 m should suffice. Alternatively, for deeper water with greater mixing forces, such as rough weather or seas, discrete water samples may need to be collected from depths deeper than 10 m (Brown, 1999).

Sampling during the early part of a spill must include collection of water from representative background reference sites (i.e., not in the affected or oiled zone). The location of these reference sites can be based upon oil spill trajectories or projected transport pathways of the slick. These projections can identify areas that likely will remain unoiled throughout the spill as well as those areas that are initially unoiled but could later be affected. At each reference site, a minimum of three replicate water collection stations should be established. This replication will facilitate analysis of statistical variability; however, time, equipment, weather, or other constraints may impede this practice (Brown, 1999). Reference samples should be collected at each replication station at each reference site, at the preselected depths and times. Once samples from oiled sites are collected, samples must then be taken as soon as possible at the reference sites. A final important element in the design of a sampling plan is to ensure that sample contamination is avoided during the collection of the water sample, particularly when operating near the slick itself. Specific equipment types and procedures have been developed to assist in the prevention of sample contamination, and due attention should be given this issue in the sampling plan design.

Designing a comprehensive oil source sampling plan is integral in the investigative efforts of an oil spill, and collection of oil from the source is crucial to any forensic program. Oil must be collected from the source tanks, pipeline, well, etc. and from the spill location itself (Brown, 1999). This allows accurate fingerprinting of the spilled oil and helps determine the presence of other oil pollutant sources (i.e., background oil or other sources of hydrocarbons). One set of initial samples must be collected immediately following the event, as close as possible to the source (ship, pipeline, tank, etc.), and then at a given frequency following the release. Samples of floating oil, mousse, tar balls, and beached oil need also to be collected (Brown, 1999).

2.8 Sampling Plan and Design: 2. "Mystery" Spills

The primary goal of sample collection following a "mystery spill," or spill of unknown source, is source identification. The sampling plan is designed to identify potential transport pathways and also to rule out potential spill sources. Most mystery spills occur in marine, lake, or river environments, as it is relatively straightforward to backtrack spills on land. Water column samples must be collected to provide information on likely as well as unlikely sources and on the physical and chemical properties of the spilled material.

An example sampling plan design for a marine mystery spill could include the following elements:

- Investigators first identify and then systematically rule out specific potential sources, including passing vessel traffic in the vicinity; submerged sources such as natural seeps, subsurface pipelines and wells, and shipwrecks; potential source samples are collected. Oils and wastes contained in a suspected vessel's tanks are sampled with the same thoroughness as are those of a known source (described above). It is important to obtain samples from each of a suspected vessel's tanks since it is possible that no single one of the oils will provide a match to the spilled oil, but a mixture of several oils may (see Chapter 8 herein).

- Samples are collected from oil on water and/or stranded oil in the affected areas and even from affected wildlife.
- Samples are analyzed to determine the type of product and its degree of weathering and to compare oil fingerprinting results with potential source sample analyses.

This information is vital to determine whether the source was a bunker fuel or a cargo from a ship, or whether it could be from a subsurface source such as a pipeline, wreck, or seep. Analyzing the degree of weathering provides information on the relative age or time the oil spent floating on water before it became stranded. This information can then be used, along with historical weather and current information, to calculate a "hindcast," or reverse trajectory, to indicate potential areas of source location (e.g., see Chapter 13 herein). On land, dye tests can be used at a suspected source to determine if the dye follows the same transport pathway and reaches the site of a "mystery" spill. As these clues begin to rule out likely suspect sources, additional information such as from databases of local shipwrecks and vessel transit information from local vessel traffic services can also identify potential source vessels. Further investigation into where and when vessels were in the area can shorten the list of potential suspects to a few, which can then be boarded at their most recent port and samples of their bunkers, bilges, and/or cargoes can be collected and compared to the oil samples taken from the shoreline or affected areas. Should this not provide a match, a closer look must be taken at the submerged sources.

In a case of repeated mystery slicks off San Francisco Bay in 2001, a shipwreck that had been submerged for over 50 years, the M/V *Jacob Luckenbach*, was considered a suspect source early in the investigation. Searches of records for the vessel characteristics revealed that this was a cargo ship operated by the U.S. Navy to transport materials across the Pacific Ocean during the Korean War in 1951 (McGrath et al., 2003). Investigators learned that the Navy fueled such vessels with a particular blend of Navy Fuel Oil (NFO) during that time. A nearby "mothball" fleet of old Navy vessels in San Francisco Bay housed similar vessels of the same era, and an industrious investigator thought to take samples from one of the NFO bunkers to compare with the stranded shoreline oil samples (McGrath et al., 2003). Significant weathering of both samples prevented any conclusive comparisons in this case, but the approach used illustrates how a creative and thorough investigator can uncover the potential source of a "mystery" spill.

Sample designs for mystery spills on land follow similar considerations to those noted in the above. A series of samples may be required to establish a spatial or three-dimensional model of the oiled area and to track the transport pathway to the source. As noted earlier, for coastal or river spills it may be necessary to sample on-land sources, such as sewers or stormwater runoff channels, to investigate potential sources. In the offshore environment where there are multiple operations, such as exploration, production, and gathering or transportation (pipelines), a further sampling challenge occurs when a number of locations or operations have oils derived from similar sources.

2.9 Data Management

Effective and efficient data management begins with the project design so that data are collected, transferred, validated, catalogued, processed, archived, copied, and distributed in a systematic and consistent manner. The most critical elements of data management are to define prior to or at the beginning of the study

1. the parameters that are to be measured or documented,
2. the data collection procedure(s) and method(s) (tools),
3. the format and type of media that are to be used to capture the data,
4. the pathway the data will follow from the field to the final depository, and
5. the quality assurance (QA) and quality-control (QC) procedures.

This discussion summarizes the guidelines developed for the management of scientific data developed by Gundlach and Coogan (1999) and for the application of data management concepts to the documentation of oiling conditions generated by the SCAT method by Lamarche et al. (2005). The QA/QC process is summarized from Chamberlin (1999). These three documents provide a level of detail that can be used to establish the data generation and management protocols in the study design phase.

The use of standardized procedures to collect or measure the raw field data provides a consistent dataset. This approach is best exemplified by the SCAT method to document oiling conditions. This method is based on systematic procedures, standardized terms and definitions for the parameters that are measured or described, and the use of standard paper or electronic forms (Owens and Sergy, 2000). With this approach, multiple field teams generate data that are consistent in space and through time.

The objective of data management is to ensure that the information generated in the field is accurate, reliable, available, and in a suitable and usable format. The types of data that are generated by site investigations typically include both paper documents and digital files that can include field log books, data and chain-of-custody forms, cassette and video tapes, and photographic and digital still or video images. Data management is facilitated if paper documents can be scanned so that the electronic files can be easily stored, copied, and distributed.

The intent of data reduction or processing is to make the raw data available in a suitable format to describe the site or the environmental parameters that have been described or measured. The output can be in the form of tables, diagrams, charts, or maps. As an example, Figure 2-1 summarizes the results of a sampling project related to the grounding of the *New Carissa* and illustrates that a large proportion of the samples did not match any of the source oils on the vessel even near the site of the accident. GIS tools provide a rapid and efficient method to undertake spatial analysis of single or multiple parameters and generate maps that document the geographic variability of selected features. Geographic accuracy is often a critical factor in determining the location of a sample or a specific feature and in the analysis of spatial distributions so that the use of a GPS is now a standard tool that should be included in the study design in order to achieve the necessary level of accuracy for which the data are intended.

The proliferation of digital cameras has benefits and disadvantages for field studies. The ease with which pictures can be taken, and the number of images that can be stored in a camera's internal memory, have led to a very large increase in the number of images that are captured. The documentation and cataloguing of these images can be a very time-consuming process and may not be adequate unless some form of electronic tagging is used that links the images to GPS coordinates. Commercial software is available that enables such links to be applied so than the date, time, latitude, longitude, and other information can be attached to each image. This linkage is a valuable data management tool as it enables images to be stored, catalogued, and retrieved based on location, date, time, photographer's name, etc. A potential problem with digital images is that they can be modified easily and so be made invalid for legal documentation unless strict protocols are followed, for example, as described by Lamarche and Roberts (2004).

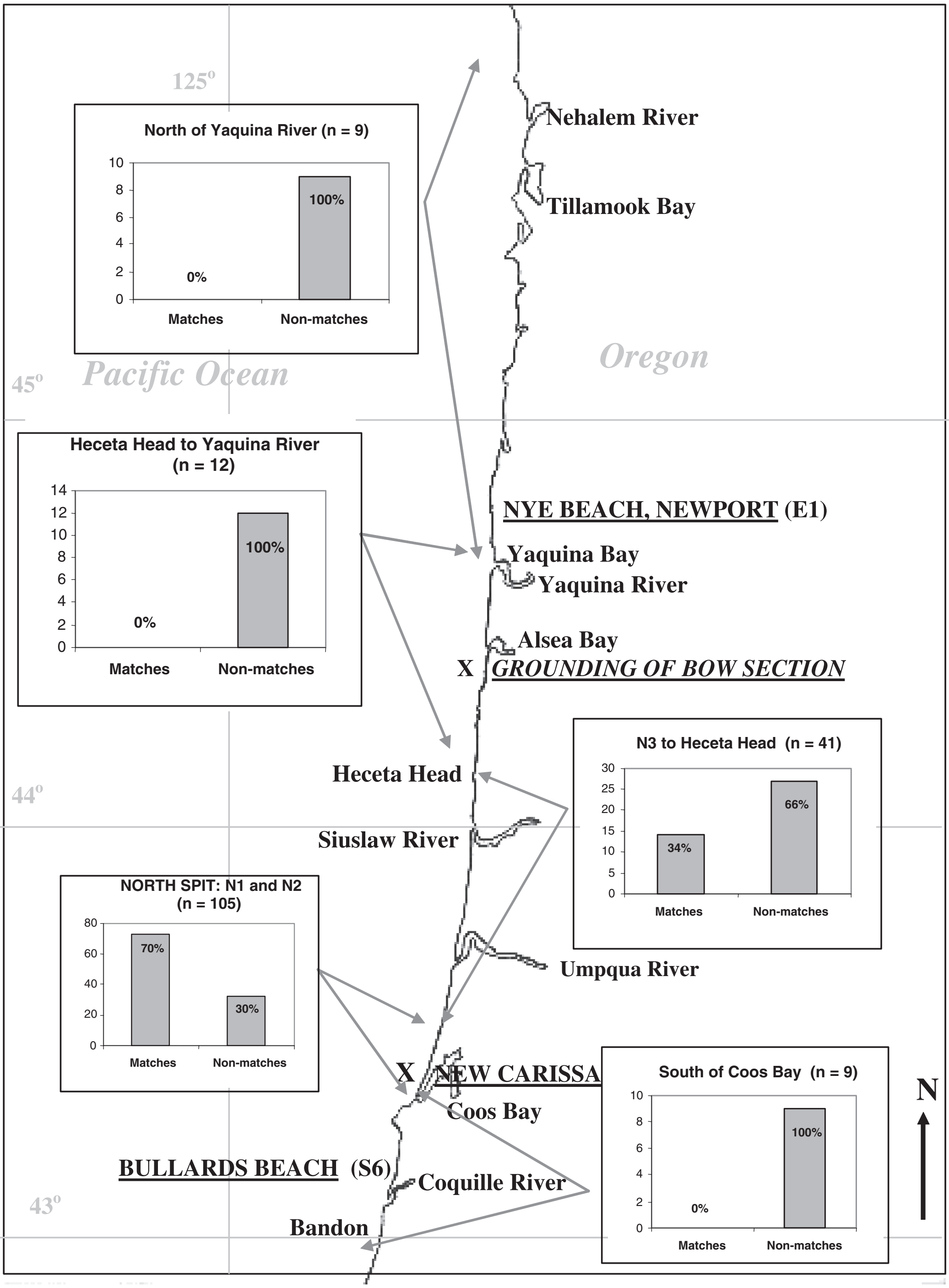

Figure 2-1 Map of tar ball distribution indicating those that matched the source oils on the vessel and those that did not match (adapted from Owens et al., 2002).

Company Name

CHAIN OF CUSTODY RECORD

PROJECT #	PROJECT NAME:
CLIENT	LOCATION:
SAMPLER (SIGNATURE)	

LABORATORY I.D. NUMBER	CLIENT SAMPLE I.D.	DATE	TIME	ANALYSIS REQUESTED	LOCATION / REMARKS

RELINQUISHED BY: (signature)	DATE / TIME	RECEIVED BY: (signature)	DATE / TIME
RELINQUISHED BY: (signature)	DATE / TIME	RECEIVED BY: (signature)	DATE / TIME
RELINQUISHED BY: (signature)	DATE / TIME	RECEIVED BY: (signature)	DATE / TIME

Figure 2-2 Example of chain-of-custody form.

One important element of data management is chain-of-custody (COC) documentation to track the location of samples (Gundlach and Coogan, 1999). Tracking information for every sample that is collected is entered and stored on a standard form (Figure 2-2) that should include, at a minimum,

- the sample ID number,
- the name of the individual who collects the sample,
- the location, date, and time of collection, and boxes for
- the signatures of the individuals that relinquish and receive the sample,
- the date and time that a sample is relinquished and received, and
- the transfer or transportation form (mail, courier, by hand, etc.).

Additional information can be included on the matrix (e.g., oil, water, sediment), preservative used (if any), the type of analysis that is requested, the address to which the sample will be sent, and any appropriate contact information (e.g., names, addresses, and telephone numbers of the client, project manager/chief scientist/team leader, or laboratory).

Quality assurance (QA) and quality-control (QC) procedures ensure that the type, amount, and quality of data are adequate to meet the objectives of the study and are particularly critical if any of the data are to be admissible in court. If data are collected with legal proceedings in mind, a Quality Assurance Project Plan (QAPP) contributes to ensuring that the data will bear critical scrutiny and be scientifically and legally defensible. QA/QC and documentation procedures should be applied from the beginning of the study to ensure that all appropriate data required to meet the study objectives are collected or generated. QA is a management function based on a systematic approach to data collection and documentation linked to the policies or regulations that determine and define the study objectives. QC is the procedure applied to check the quality of the data generated by the field program and covers measurement, documentation, sampling, and analytical techniques. Although these are integral tasks within any oil spill investigation, it is important to remember that they are support services that ensure the quality of the data and, themselves, are not an end product (Robilliard et al., 1991).

2.10 Conclusions

A systematic and well-designed study approach is key to successful forensic oil spill investigations. In the first phase following a spill, or detection of a spill, time is always of the essence, as the situation is dynamic and many data elements and observations integral to the investigation are ephemeral. Key parameters need to be evaluated, measured, and documented as soon as possible. Immediate priorities should be defined so that appropriate samples are collected at necessary locations, times, and frequency to capture critical forensic elements. We can learn from past cases, such as the techniques used to source the “mystery” slicks from the *Luckenbach*, but since every oil spill is different, in a unique environment, a successful study typically involves a degree of creativity that extends beyond simply employing standard investigative and scientific procedures. Creativity and thoroughness are critical in order to adapt to specific spatial and temporal conditions. In this respect, for spills in marine, lake, or river environments, the scientist is not that different from the spill responder in attempting to act quickly and safely in a dynamic and ever-changing situation. The study design should include a QA/QC and a data management plan to ensure a comprehensive, systematic investigation. Although the need to quickly initiate an investigation and comprehensive sampling plan is an inherent and required aspect to all oil spills, an important caveat to note is that rapid actions are not a substitute for quality and carefulness, particularly if study results are not defensible and cannot be used to precisely identify the source.

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