



SAMPLING AND MONITORING OF MARINE OIL SPILLS

TECHNICAL INFORMATION PAPER

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Introduction

Following a spill of oil, governments and other organisations often wish to know the extent of contamination of key resources or the impact of the incident on the marine environment. This information is important to determine if prompt action may be required to protect human health or sensitive resources. To facilitate decision-making, monitoring programmes may be undertaken, which will often involve surveys and the collection of samples of oil, water, sediment or biota for chemical analysis.

This paper provides a broad overview of the monitoring and sampling procedures that can be used for qualitative and quantitative monitoring of oil contamination. While qualitative analyses can confirm the source of oil contamination, monitoring programmes are often concerned with the quantitative changes in hydrocarbon levels over time. Guidance on analytical best practice is given and common terminology is explained. However, the techniques and observations required to monitor specific ecological or biological effects and to monitor contaminants in the air are beyond the scope of this paper.

Overview

Following a spill, monitoring can be undertaken in a number of different ways depending upon the objectives of the monitoring programme. Documenting the extent of oil contamination through the use of aerial reconnaissance, boat- or shore-based surveys is usually undertaken as a first step in any monitoring programme. This enables the distribution and extent of the pollution to be identified and, for resources at risk, it may be possible to formulate response strategies for their protection. Delineating the extent of the contamination visually (*Figure 1*) will assist with the design of any monitoring programme and allow sampling stations within and outside the area affected to be identified according to the specific objectives of the monitoring. The rationale for undertaking monitoring after an oil spill varies from incident to incident. Monitoring may not always be necessary, especially if the spill is small and resources are not at risk, or if the effects of the oil on a particular resource are well known. Where monitoring has taken place, it has often been carried out with the following objectives, to:

- authenticate the origin of the oil pollution;
- establish the risk of transfer of contaminants to the human food chain;
- ascertain the effects of the pollution on commercial fish and shellfish to support decision-making regarding the need, or otherwise, to impose fishing restrictions;
- verify the cause and effect; that is, to establish whether or not any environmental effects observed are directly attributable to elevated oil concentrations arising from a particular pollution event;
- measure hydrocarbon concentrations in sediment or water to aid decision-making over the continuation or termination of the response;
- determine the decline of hydrocarbon concentrations in the marine environment and to monitor recovery;
- identify conditions appropriate for initiating and sustaining restoration measures;



◀ *Figure 1: Following an oil spill, a monitoring programme may be required to determine the changes in the level of contaminants in the environment.*

- demonstrate that damage caused by a spill has been evaluated, that recovery is underway and that concentrations of oil in the marine environment are returning to background levels;
- address monitoring requirements set out under applicable national regulations, such as standards for bathing waters.

The aim of any monitoring programme must be to provide reliable, objective and useful information to answer specific, rational concerns about the presence of oil spilt in the environment. Determining the extent and level of contaminants in the environment over time forms the cornerstone of most monitoring programmes and, for the vast majority of incidents, these are the only parameters that are necessary to measure. Further studies to investigate the potential for environmental impact as a result of oil contamination can be conducted alongside contaminant monitoring, but the methodologies employed to study individual resources or habitats are varied and numerous. As such, this paper focuses on the rationale and methodology for conducting contaminant monitoring to support decision-making during the response.

While it is important that the objectives of any monitoring programme are defined as precisely as possible before work starts, a phased approach may be appropriate to allow for additional objectives to be included, or the initial objectives to be adjusted, depending on the results from an earlier phase of the study.

Three complementary approaches to conducting monitoring programmes are possible:

- comparison of post-spill and pre-spill data;
- comparison of data from contaminated areas and uncontaminated reference sites, and
- monitoring changes over a period of time.

Monitoring forms an important interface between the scientific, legal, operational, and financial aspects of an incident. Results produced systematically may be used to confirm the source of the spill and thus the legal liabilities, to validate the decisions made during the clean-up operation (for example, appropriate methods and optimal termination end points) and to follow environmental recovery. As the outcome of monitoring studies can have a significant bearing on compensation and other financial issues, the most constructive approach to monitoring is one in which all parties work co-operatively. This can be achieved through joint sampling and analysis, through the use of an independent third party, or by one party undertaking the sampling and analysis and sharing the results. Although differences of opinion may arise in the interpretation of the results, each of these approaches reduces the duplication of effort and costs and maximises the opportunity for agreement on the basic facts.

Designing a monitoring programme

An understanding of the fate, behaviour and effects of spilled oil and the potential pathways by which resources may be exposed to hydrocarbons will facilitate consideration of

whether or not a monitoring programme is needed and, if so, will assist with its design¹. The geographical extent of the pollution enables the area of study to be delineated, although these boundaries may need to be redefined in cases of a continual oil release, where remobilisation of stranded oil is a factor, or where the results of the initial sampling and analysis indicate that the area affected is different than first thought. The type of oil spill and the extent to which natural resources are likely to be exposed are also key parameters to consider when designing a monitoring programme. Taking into account these factors, as well as potential exposure pathways, enables appropriate spatial and temporal parameters to be applied.

When designing a monitoring programme, the first stage is to define the objectives of the study clearly and to determine the information and data necessary to achieve these objectives. The objectives will define the scope and content of the programme and are normally set by a government authority or in response to potential claims against the polluter. In either case, the scope of the study and the plan for its implementation need to be agreed at an early stage and, ideally, cooperatively as explained earlier.

Having agreed the objectives, a detailed monitoring plan can be created that establishes the type of data or information to be acquired and whether samples need to be taken, the distribution of sampling stations and the type, number and volume of samples to be taken at each station. The frequency of sampling, the type of analysis and the overall timeframe of the study will depend on the objectives of the monitoring. For example, if the objective is to establish that oil concentrations in the environment are decreasing to background levels, the study can be considered complete once background levels have been reached or the results show a satisfactory rate of decline. In many ship-source oil

¹ See the separate ITOPF papers on *Fate of Marine Oil Spills*, *Effects of Oil Pollution on Fisheries and Mariculture*, *Effects of Oil Pollution on Social and Economic Activities* and *Effects of Oil Pollution on the Environment*.

Location	Monitoring objective	Monitoring activity
South America	To determine the extent of oil contamination and the need for continued clean-up measures.	Extensive boat and shoreline surveys were conducted to document visually the presence and absence of oil on the water and the extent of shoreline oiling. Oiled sites requiring clean-up were identified and appropriate clean-up techniques recommended. Continual observations made during the clean-up operations and a final inspection once the work had been completed allowed for recommendations to be made regarding appropriate termination of clean-up work.
Europe	To establish the level of oil contamination in sediments at key sites oiled as a result of the incident.	Sediment samples were collected from beaches and shallow waters from key sites known to have been oiled during the incident over a period of 3 months. Samples were analysed for THC and PAHs. The results of the monitoring showed that most of the sediment was relatively unaffected by the oil spill.
Indian Ocean	To ascertain whether drinking water in water wells located on the shoreline had been contaminated as a result of the loss of the cargo of phosphate and bunker fuel.	Samples of water were taken from wells along the contaminated shore and from wells outside of the area and analysed for phosphate, PAHs and heavy metals. Comparison of the average values for water taken from the reference wells and wells in the contaminated area showed no significant difference, allowing the conclusion that the incident had not caused contamination of the local drinking water supply.
Atlantic Ocean	To establish the spatial extent and duration of potential contamination to a fishery.	A sampling programme was instigated to collect species samples from the affected area and from reference sites and over a number of months. Samples were analysed to monitor depuration rates of PAHs and compared with background levels reached.

▲ Table 1: Examples of monitoring objectives and activities in past oil pollution incidents. The various parameters analysed are discussed later in Box 1.

spills, little in the way of appropriate pre-spill data exists and there will be few opportunities to obtain true control samples. For this reason, monitoring programmes often rely upon control data collected during an incident from unaffected, reference sites nearby. It is important to ensure that the reference sites selected are representative of the habitat types being studied within the area affected and that they are comparable in terms of biota, topography and physical nature, for example, exposure to currents or wave action. Furthermore, surveys intended to provide quantitative data must take into account the natural variability that typically occurs in any ecosystem. Comparison of a time series of measurements from reference sites and from within the area affected allows naturally occurring variability and seasonal changes to be taken into account.

Table 1 provides examples of monitoring objectives from past oil pollution incidents and provides a summary of the monitoring activities undertaken.

Location and number of monitoring sites

Field surveys can be useful for rapidly collecting geographically-referenced information on the location and extent of the oil. Surveys can also be useful for monitoring qualitatively the effectiveness of shoreline clean-up operations or the progress of natural recovery, especially when carried out at regular intervals. The location and number of sites that should be included in field surveys or sampling stations will depend largely on the variability of impact and the variability and extent of the shoreline affected. Care should always be taken to ensure that the sites chosen are representative of the area being cleaned, the contamination observed or habitat being monitored. However, most oil spill scenarios do not require the use of sophisticated statistical procedures to determine the number of sites to be surveyed or the number of samples to be collected. In reality, compromises and a certain degree of pragmatism are often called for in order to satisfy both the demands of statistical reliability and the practicality of accounting for the full spatial and temporal variation of complex ecosystems within the available timeframe and financial constraints. Furthermore, there are few universal rules regarding the optimum location and number of sampling stations for post-spill monitoring studies. Instead, this will depend on the objectives of the monitoring programme and on a number of case-specific variables such as the:

- quantity and type of oil spill;
- weathering behaviour of the oil (e.g. spreading, dissolution, etc);
- physical characteristics of the area affected (e.g. sandy, exposed, etc);
- nature and location of sensitive resources;
- means available for sampling and analysis; and
- physical conditions that might constrain sampling (e.g. access or weather).

In the simplest situations, for example where the objective is to establish the source of contamination, probability-based sampling designs are not required. Instead, a very small number of samples taken from the oil slick or contaminated

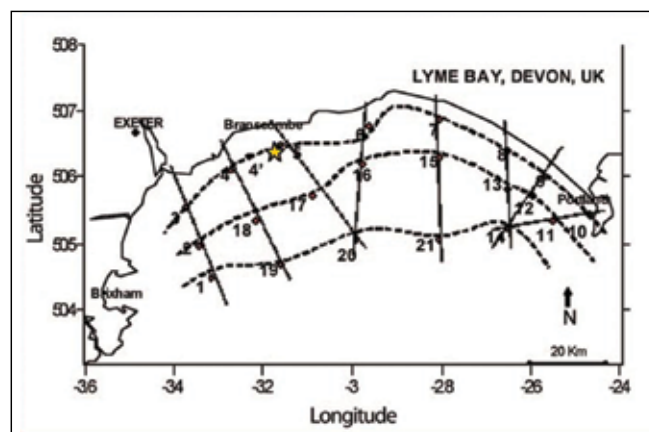
shoreline would usually be accepted by all parties as representative of that contamination.

In some cases, the optimum locations and number of sampling stations can be deduced by overlaying a map of the study area with a grid showing the oil contamination, annotated with GPS co-ordinates. A transect or a series of transects can be useful for defining trends in relation to distance from the pollution source (*Figure 2*) or to other environmental variables, such as tidal height. This systematic approach may be particularly useful for areas of relatively homogenous shoreline, such as wide areas of marsh or sand. In nearshore areas with some complexity in physical characteristics (for example, separate bays), or in spills affecting extensive areas of coastline, the area may be sub-divided into smaller, stratified zones to be monitored individually. In practice, sampling stations should be selected to reflect the distribution of oil and natural environmental gradients, and in this respect it is helpful to draw upon local knowledge when planning the monitoring programme.

Entirely random approaches to sampling are possible, but they are rare when sampling solely for contaminants in a monitoring programme. Although a random approach would enable greater use of statistical inference in the reporting of results, a significantly large number of samples would need to be analysed at much greater cost for little improvement in the data obtained. Instead, in complex cases, a useful compromise can be achieved by making certain elements of the study random, for example, using stratified random sampling, or implementing more sophisticated phased (i.e. cluster) or composite sampling. Setting up an appropriate probability-based sampling design in such cases may call for the services of an environmental statistician. Various approaches to designing the statistical approach for sampling plans are summarised in Table 2.

Timing of the monitoring programme

While there are no definitive deadlines for contaminant monitoring and sampling activities following a spill, the sooner monitoring is started, the sooner short-lived



▲ *Figure 2: Location of water sampling stations in proximity to a vessel's beached position (yellow star). (Source — Environmental monitoring conducted in Lyme Bay following the grounding of MSC NAPOLI in January 2007, with an assessment of impact. CEFAS Aquatic Environmental Monitoring Report no. 61 — <http://cefas.defra.gov.uk>).*

Sampling design	Main characteristics in relation to post-spill monitoring
Judgemental sampling	Easy to implement, 'common sense' approach, especially good for fingerprinting and consensual, low effort monitoring programmes. An example of non-probability sampling, based on the judgement of the person sampling.
Simple random sampling	Samples are chosen entirely by random from a larger group. Statistically sound, easy to implement in homogenous areas (open waters, long and constant coastlines, fisheries); difficult in areas of varied coastline and varied contaminant levels.
Stratified random sampling	A 'judgemental' variation of simple random sampling where areas are broken up into case-relevant sub groups (or stratum) for random sampling. Good in heterogeneous areas (diverse in character) when sub-groups within an overall group vary.
Systematic (grid) sampling	Appropriate for large areas with little known variation, especially for vessel-based sampling where transects can be made. Statistically troublesome where other variables may be systematically involved (e.g. other contaminant sources).
Cluster sampling	Efficient, multiple-phase approach that allows a second, more detailed study of hot-spot areas identified in first phase (often a grid design).
Composite sampling	Extremely efficient phased approach where large areas can be screened by combining samples for analysis. Not appropriate in areas of highly varied contamination.

▲ *Table 2: Typical statistical approaches to sample station distribution in post-spill monitoring.*

(ephemeral) effects can be detected and the changing extent of contamination recorded. Where sampling is necessary, samples of oil from potential sources should be secured and preserved at the same time as gathering samples from the areas affected to verify the source and collecting samples for ephemeral data (in particular water samples). As many impact assessments are based on model predictions, ephemeral data may be important in order to document the actual concentration to which biota have been exposed to verify the predictions.

The duration of the monitoring programme and frequency of repeat sampling depends on the programme objectives and the inherent characteristics of the specific parameters that are being measured. For example, measurement of total oil concentration in a contaminated environment is a parameter that may require weeks or months of monitoring before background concentrations are re-established. On the other hand, if the objective is to determine the efficacy of a particular response technique, such as the use of dispersants, the immediate implementation of monitoring and rapid processing of results would be crucial to enable a timely decision to be made.

The availability of resources, such as trained staff and suitable sampling vessels, also needs to be taken into account, as well as the logistics and costs involved. The rate at which samples can be safely and correctly taken will depend on the weather, sea state, and the accessibility of sampling sites. Additionally, where ephemeral effects are to be measured, the area of concern may need to be adjusted or the desired intensity of sampling may have to be adapted in order to

take samples within the time available. In all cases, the timing and the overall programme design should take into consideration the likely time required for the processing of samples at analytical laboratories and the speed with which the results are required. For example, when investigating whether fisheries could be affected by a spill, the timing of sampling and analysis is likely to be influenced by the need for data to inform decisions on the closure or re-opening of the fishery.

Budgeting for the cost

Responsibility for paying for the monitoring programme depends on the legal regime applicable within the country in which the incident or damage occurs. Regardless of who is to pay, it is good practice to produce a proposal containing an itemised budget early in the process (*Table 3*). Where relevant, this may be discussed with the bodies paying compensation prior to the commencement of the work.

Generally, the overall cost of monitoring should reflect the level of effort involved, the frequency of surveys undertaken, the number of samples or sampling stations, the types of analysis required, and be in proportion to the scale of the issues being addressed. However, because some costs are fixed, for example vessel hire, the final cost per sample is not necessarily affected by the total number of samples taken and there may be opportunities to take more than the minimum number of samples at little additional cost. Nevertheless, because analysis costs tend to be directly related to sample numbers, it is often recommended to analyse only the minimum number of samples and keep the remaining samples in appropriate storage in case they are needed later.

Background	Sampling	Analysis	Logistics
<ul style="list-style-type: none"> Case name, dates, location Names and affiliations of scientific team Objectives, methods, and procedures 	<ul style="list-style-type: none"> Period and frequency Geographic scope Sample types 	<ul style="list-style-type: none"> Laboratories undertaking analyses Analytical plans and related costs Date commitment for publishing report 	<ul style="list-style-type: none"> Description and costs of equipment and materials Costing of any special logistical support Costing of travel and accommodation needs

▲ *Table 3: Typical components of a budget proposal.*

Use of a phased approach is another strategy to keep monitoring costs in proportion. Compared with an initial phase of sampling that might take place shortly after a spill, later phases are often narrower in scope. Criteria for termination of the monitoring programme need to be considered early on, but contaminant monitoring would usually conclude once a return to background levels has been detected.

Selection of the laboratory

The laboratories tasked with undertaking sample analysis should be selected and agreed by all parties at the programme design stage. The laboratory must have the capacity to deal with the anticipated sample numbers and offer the techniques required to meet the programme objectives. Some of the preliminary enquiries that might be made to establish the suitability of a particular laboratory include:

- Are the laboratory technicians experienced and qualified in the analysis of hydrocarbons?
- Does the laboratory have the requisite equipment, primarily UVF, GC-FID and GC-MS (as described later in this paper)?
- Is the laboratory nationally accredited or internationally recognised?
- What quality assurance and quality control procedures are in place?
- Can oil spill work be given priority over routine activities?
- What are the costs associated with screening the samples and undertaking the analysis?
- How will the results be reported?
- Is the laboratory willing to explain and defend its results in court if required?

Quality control

To maintain a high quality of sampling and analysis, every monitoring plan should incorporate two key elements:

- quality assurance (QA) to ensure that processes and procedures are in place to check that the aspects of the monitoring plan, such as sampling and analysis, are being carried out in the correct manner (an audit of the process); and
- quality control (QC) to ensure that the monitoring plan delivers the planned objectives (a check of the product).

Samples may be divided in a number of ways for quality control purposes and this is decided prior to sample collection:

- split samples: each fully-homogenised sample is divided after being drawn or taken, giving two or more parties the opportunity to undertake independent analyses;
- field duplicate/replicate samples: the same device and procedures are used at the same location to take two or more samples which should be identical. Such samples are used to test sample variance and their identity may not always be made known to the laboratory; or
- laboratory duplicate/replicate samples: split samples given to the same laboratory for analysis, yet described as being two different samples. These can be used to check the precision of laboratory analysis.

Implementing the sampling and monitoring programme

The type and extent of field data and information collected depends on the objectives of the monitoring being carried out. For example, to monitor the effectiveness of dispersant application, in addition to visual observations by trained observers, ultra-violet fluorometry (UVF) can be used to collect data on oil concentrations in the water column². Clearly, to be useful for decision making, the results from field surveys need to be forwarded to the command centre in a timely manner.

Although aerial surveillance is useful for gathering information on the overall geographical extent of oil at sea and on the shoreline, more detailed shoreline surveys aimed at rapidly documenting shoreline oiling provide crucial information to help determine appropriate clean-up techniques. In addition to written notes and sketches, it is common practice for shoreline surveys to document findings using photographs and videos. For both aerial surveillance and shoreline surveys, it is useful to record images using GPS data, thereby allowing straightforward referencing of data and information³.

Where the properties of the oil and the environmental conditions at the time of the spill indicate that significant quantities of oil may have sunk, underwater surveys may be required to establish whether or not this has occurred and to determine the extent of any areas affected. Such surveys could be achieved through a variety of methods, such as visual assessment, either by divers or a remotely operated vehicle (ROV), acoustic sensors and sonar, or mechanical methods. Mechanical methods in the form of sorbent materials anchored in fixed positions or towed across the seabed (*Figure 3*) have been used to detect the presence of sunken oil in past cases.

² See the separate ITOPF paper on *Use of Dispersants to Treat Oil Spills*.

³ See the separate ITOPF papers on *Aerial Observation of Marine Oil Spills and Recognition of Oil on Shorelines*.



▲ *Figure 3: Using sorbents for sub-tidal sampling. The frame, with sorbent attached, is towed along the seabed. The presence of oil on the sorbent when raised allows the geographical extent of sunken oil to be determined.*

Description	Indication of minimum required quantity (per sample)
Pure oil source sample	30–50 ml
Contaminated oil (e.g. emulsified oil, oil from the sea or shore, sandy tarball, etc.)	10–20 g
Debris with oil, oil stained sand	Sufficient quantity that oil content is approx. 10 g
Oiled feather	5–10 feathers depending on oil quantity present
Fish, shellfish (flesh and organs)	Multiple individuals of same species totalling 30 g
Water sample with visible oil	1 litre
Water sample with no visible oil	3–5 litres

▲ Table 4: Guidelines for the amount of sample typically required for hydrocarbon analysis.

Regardless of the type of field data and information being collected, protocols, such as SCAT (Shoreline Clean-up Assessment Technique or Team), should be developed to ensure accuracy and consistency in how the data and information are collected. Furthermore, the personnel undertaking the surveys should be appropriately trained. Any field data or information collected should be suitably categorised, stored and archived, enabling it to be linked to the results of any other monitoring studies that may be undertaken.

Sample collection

Sample collection procedures should conform to international best practice and should be described in detail in the monitoring plan. This approach ensures that the sampling teams follow the same protocols in the field and that sufficient information is available to enable the results to be interpreted correctly. If internationally accepted best practice has been followed, it is also more likely that the results can be defended in court, if this becomes necessary. Guidelines for the amount of sample of various types are provided in Table 4.

Source samples

Among the most important samples to obtain early on in a monitoring programme are clean and verified samples of oil

from all potential sources (Figure 4). When the source is known, such as a ruptured pipe or ship's tank, and accessible, samples can be taken directly by qualified personnel (Figure 5). Where the source is not known, samples may need to be taken from several candidate sources. While oil in cargo tanks can generally be sampled from one location, the contents of bunker tanks or bilges are rarely sufficiently homogenous to be sampled from a single point and samples are often taken from multiple depths through the tank, usually top, middle and bottom.

Samples of oil are normally taken when cargo or bunker oil is being loaded onto the ship and these are kept as a matter of standard operating practice in case of commercial dispute. While they may be useful as source samples, it is important to note that there may be quality and chain of custody issues involved in using them, in particular if they have been stored in plastic containers. When the source of the oil is a sunken wreck and access for sampling is not feasible, it may be possible to collect an oil sample as the oil rises to the sea surface, directly above the wreck. If oil removal operations from the wreck are undertaken later, a small amount of recovered oil may be obtained from the salvage team. In cases where it is not possible to obtain a sample from the source, multiple samples of oil from contaminated shorelines can be used as proxy source samples.



▲ Figure 4: Decanting a bunker fuel source oil sample on board a casualty.



▲ Figure 5: Ship-source sampling is a highly technical and potentially dangerous activity that should be carried out by vessel crew, marine surveyors or salvors.



▲ *Figure 6: Capturing floating oil with a clean sorbent pad.*

Sampling spilled oil

Samples of floating or stranded oil are taken generally for qualitative purposes to confirm the source of the oil, rather than quantitatively to map concentrations. Only small quantities of oil (i.e. 10–20 g) are usually required for analysis. Samples from the water surface can be collected directly with sampling jars or sorbent pads (*Figure 6*). If access is restricted, samples may be collected using a bucket on a rope or by using extension poles. Samples should be taken from the bow of the sampling boat, avoiding any sheens from the sampling vessel's hull and engine exhaust or cooling water.

Occasionally samples of thin oil sheen are required, for which specialist sampling equipment exists, such as fine-mesh sampling nets. Only very small amounts of oil are obtained from sheens and, the thinner the films that are to be sampled, the greater the risk of sample contamination (for example, from the sampling vessel or equipment). For quality control, unused sampling nets or sorbent pads should be provided to the laboratory as references for analysis alongside the sample.

The procedure for sampling oil stranded on shorelines or within an intertidal zone generally involves scraping or gathering the oil into a sample jar (*Figure 7*), taking care to minimise the sand and debris content.

Environmental samples

Sampling and monitoring that is intended to quantify hydrocarbon contamination involves a shift from targeting the spilled oil to sampling the medium that has potentially been contaminated. The initial approach is often to take samples from the water column, as this is the pathway through which the oil migrates to reach shorelines, sediments and biota. Depending on the objectives decided at the outset of the monitoring, evidence of elevated oil concentrations in the water column may provide the trigger for extending the sampling regime to other targets, such as biota. In other cases, an intensive environmental monitoring programme (i.e. contaminant monitoring and biological impact assessment) may be initiated, requiring a suite of water, biota and sediment samples, but this is usually necessary only if the pollution has been extensive and the impacts are potentially significant.



▲ *Figure 7: Sampling stranded oil on the shoreline.*

It is important to ensure consistency throughout the sampling effort and, where possible, to ensure that comparable specimens are targeted. For example, when monitoring shellfish contamination at a number of locations, the same species of shellfish, and ideally at the same stage in their life cycle, should be targeted at all locations in order to allow meaningful, quantitative comparisons.

The volume or mass required for each sample depends on the number and types of analyses planned, the concentration of oil in the sample, the number of participant organisations requiring their own split sample and the number of duplicates or replicates required for quality control purposes. Modern testing procedures require only very small samples for relatively pure oil (*Table 4*).

Water sampling

Water column monitoring may be undertaken by field measurements *in situ* or by manual collection of samples that are preserved and transported to a laboratory for analysis. Field measurements include basic water quality and oil-specific detection, both of which involve portable field sensors that provide real-time output:

- Electronic water quality sensors measure such chemical and physical variables as pH, salinity, conductivity, chemical oxygen demand (COD) or biological oxygen demand (BOD). These do not have direct relevance for oil contaminant monitoring, but they may be useful in related ecological monitoring studies.
- Field sensors, specific to oil spills, such as towed multi-wavelength fluorometers find greater application in response operations than environmental monitoring, for example, to indicate dispersed oil concentrations.

Manual collection of water samples can be undertaken with specialist sampling devices that are lowered to the desired water depth in the closed position (*Figure 8*). Once there, the device is opened to take the sample, then closed for



▲ *Figure 8: Decanting water samples from the sample collection device into glass bottles, for split samples.*

retrieval to avoid contamination by oil films that may be present on the sea surface. Manual collection for subsequent laboratory analysis remains the mainstream practice for contaminant monitoring.

Sediment sampling

The quantitative measurement of total oil, or the changing composition of oil in sediments as it degrades, often forms part of contaminant monitoring programmes (*Figure 9*). Sub-tidal sediments are generally sampled from vessels and, because of the low migration rate of oil into these sediment types, shallow grabs are frequently used. Well designed grabs avoid the contents being washed out during retrieval and it is good practice to rinse the grab with an appropriate solvent between collecting samples. Diver-operated corers are sometimes used, particularly if the presence of pre-existing contamination from other sources is suspected.

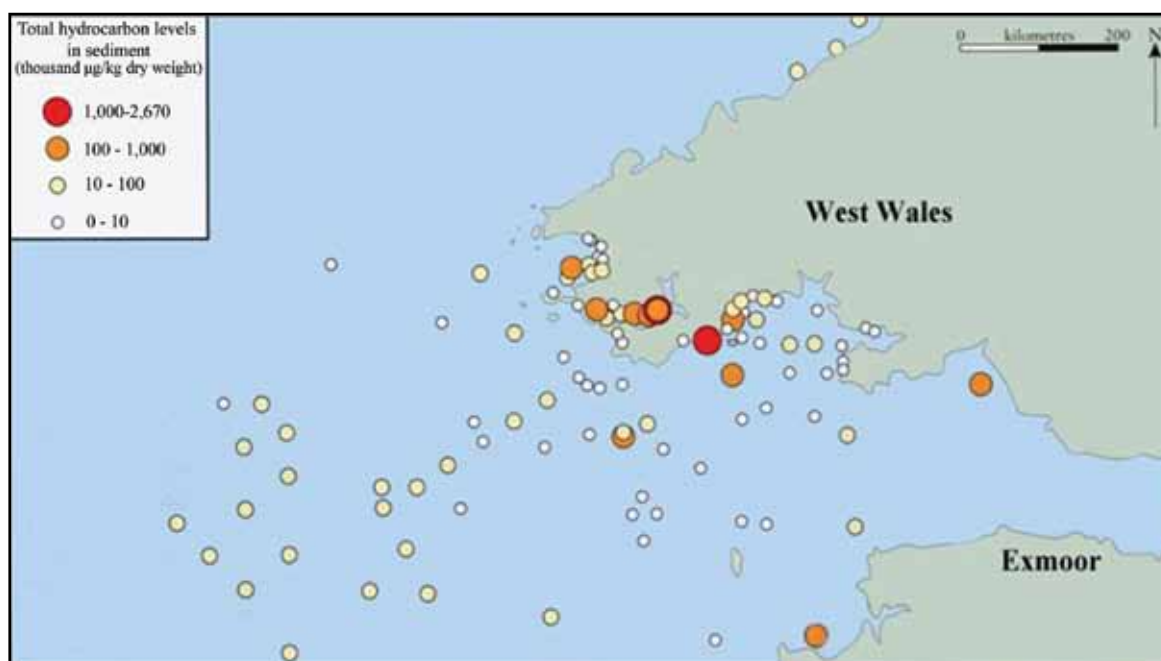
Sampling intertidal sediments is usually carried out either using surface scrapers or with corers. The results might be used, for example, to aid decisions on when to terminate clean-up operations.

Biota sampling

Sampling procedures for biota are varied and will depend on the organisms and habitats to be included, for example demersal and pelagic species (i.e. those near the seabed or in the water column), benthic species (living on the seabed or in sediments), as well as birds and mammals. Studies should focus on trends within the ecosystem, rather than attempt to document every fluctuation from the norm, and the use of key indicator species has been shown to be the best approach. These species are often either commercially important or by their nature and exposure offer good opportunities to document contamination (for example mussels and other filter feeders). Samples can be either organ-specific (i.e. the same organ from a number of individuals) or whole-organism, with all soft parts homogenised (*Figure 10*).

Biota samples may involve both wild species and farmed species, such as those found in mariculture facilities. Mariculture should be sampled jointly with the facility operator and ideally at representative locations selected by the sampling team. For wild stocks of commercially exploited species, samples may be purchased from fishermen, although this approach has many quality control issues regarding where and when the fish were caught and the risk of cross-contamination. Collecting samples together with fishermen avoids these issues and is perhaps most appropriate in an artisanal fishery where the catch is local and brought ashore on a daily basis.

Birds, mammals or other higher organisms are not typical test subjects in oil contaminant monitoring because the



▲ *Figure 9: Sample station locations selected for the assessment of seabed sediment contamination by oil after the SEA EMPRESS oil spill in Wales, UK. Following this large spill, it can be seen that sediment contamination some six months after the spill persisted mainly in shallow waters close to the coast. (Source: The Environmental Impact of the SEA EMPRESS Oil Spill; SEA EMPRESS Environmental Evaluation Committee (SEEEC) 1998).*

contamination can usually be noted visually and the variability is greater than with lower indicator species, such as mussels. Samples from oiled animals tend to be taken from carcasses or in a non-intrusive manner from live animals, for example oiled feathers or oiled fur.

Handling samples

In many instances, the eventual use of a sample and analysis results are not known at the time the sample is taken. In order to maintain the integrity of the sample so that it can be used later, proper handling and storage protocols should be followed. The handling of samples in the field involves storage, labelling, pre-laboratory stabilisation, packaging, shipping and management of the process. The associated chronological documentation is referred to as the chain of custody.

Storage

Storage is an intrinsic part of sampling, because the material is placed immediately and directly into the storage container in order to minimise cross contamination and degradation. In some cases, the container itself is used as the collection device, such as when floating oil is skimmed or oiled sand is transferred into a glass jar. Ensuring a supply of appropriate containers for storage should be pre-planned. The use of non-specialist containers, such as plastic water bottles, should be avoided unless no other suitable container is available. If there is a risk of contamination from dissolved plastic, the container itself may be analysed and used as reference against the result of the analysis. Many characteristics of appropriate storage containers are provided in Table 4 and Figures 11 and 12.

Labelling

Storage and labelling should be considered in tandem, because the chain of custody effectively begins as soon as the sample is put into a container. A programme of spatial or temporal sampling will require multiple containers and the scope for confusion and inadvertent mixing of containers is great. To avoid this, standard sample labels should be prepared, allowing the user to allocate a unique identifying reference for the sample, together with detailed information

on where, when and by whom the sample was taken. If the sample is part of a joint sampling exercise, the name and contact details of a witness to the sampling should be included.

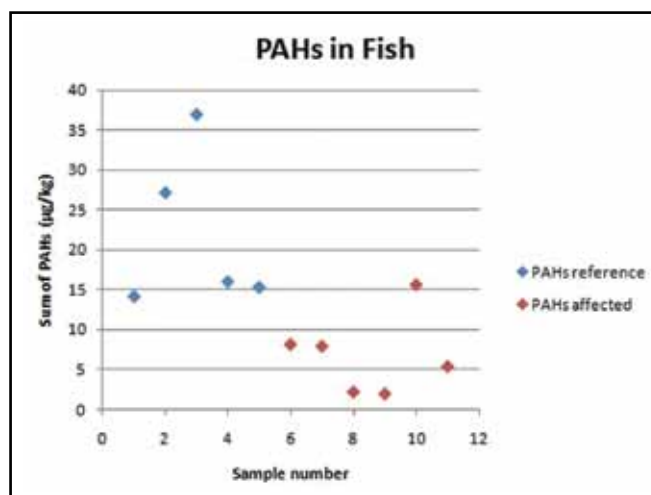
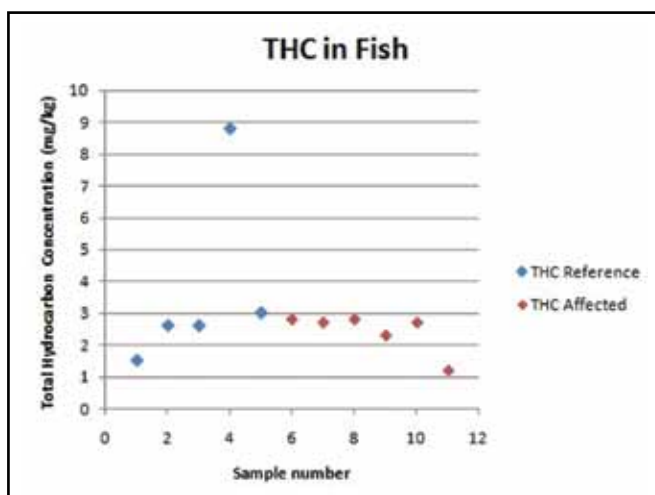
A parallel sample inventory should be maintained, for example, as an electronic spreadsheet, in which the same information is recorded and copies of which can be made available to interested parties and to the analytical laboratory. In addition to recording purely scientific variables, sampling teams should document the names, dates, places and other details surrounding the custody of the samples as they are transferred from one party to another. Protecting the chain of custody ensures that the samples are not exposed to any risk of physical tampering, cross-contamination or any other alteration, whether intentional or not.

Stabilisation

Many samples will remain stable for some time and can be kept in their original sample containers because they are not particularly susceptible to degradation, for example weathered tar balls or pure oil, or because they are cooled or frozen, for example fish tissue samples. Depending on the monitoring protocol, water and sediment samples may need to be stabilised in the field if there is to be a delay in delivery to the laboratory in order to ensure their continued integrity. While samples may be acidified or biocides added, the general practice is to carry out solvent extraction on the same day that the samples are collected. Even when frozen, a risk exists that samples may deteriorate and material may become absorbed onto the walls of containers. Consequently, the permitted storage time for samples may be strictly prescribed under some analytical protocols. Care must also be taken to procure only the purest solvents for extraction. Contaminants in solvents can confuse or mask the detection of compounds of interest, particularly when these compounds are at very low concentrations.

Packing & shipping

Samples are stored primarily in glassware and need to be packed carefully prior to transport to avoid breakage, loss



▲ Figure 10: The results of testing carried out to measure total hydrocarbon (THC) and polycyclic aromatic hydrocarbon (PAH) concentrations in fish.

or degradation of samples. Padded boxes with dividers are useful as are hard-shelled cooler boxes if these can be delivered securely to the analytical laboratory. In all cases, good practice includes minimising free water in oil samples, respecting the appropriate temperature for biological material, labelling any outer container with the name of the incident and enclosing an inventory of the samples within the package. As domestic shipping requirements differ from one country to the next, advice should be sought locally. International shipping of samples is generally more complicated and may involve adhering to stringent packaging and labelling rules where the characteristics of the oil, for example the flashpoint, will affect the required packaging and mode of transport.

Analytical techniques for oil contamination

Once a suitable laboratory has been selected and the samples have been collected in the field, work can commence to analyse the samples to determine the source of the oil or the level of contamination. While non-specialists are not expected to undertake analysis, an appreciation of the different analytical techniques and their purpose is useful for those involved with planning and conducting monitoring programmes.



▲ Figure 11: Well labelled bunker samples in wide mouth glass jars (in this case split samples from a single tank).

In order to appreciate the rationale for using a particular analytical technique to determine the level of oil contamination in samples, and to confirm the source of particular oil, knowledge of the chemical composition of oil can be helpful, as summarised in Box 1, overleaf.

No single international standard or set of guidelines covers the analysis of oil pollution samples worldwide. However, a number of relevant protocols at international and national levels can be followed during sample analysis, including those published by the:

- American Society for Testing and Materials (ASTM);
- American Petroleum Institute (API);
- US Environmental Protection Agency (EPA);
- Canadian Council of Ministers of the Environment (CCME);
- European Committee for Standardisation (CEN); or
- Euro-Asian Council for Standardisation in Russia (EASC).

On arrival at the laboratory and before the analysis work can commence, the samples should be cleaned to remove extraneous material and to concentrate the hydrocarbon compounds. The most common techniques are solvent-extraction and chromatography. The nature of this preparation step is dependent on the final analytical techniques to be used and the condition of the sample. For example, debris will need to be removed from sediment samples, emulsions will have



▲ Figure 12: Clear, narrow-mouth bottles (left) or plastic bottles (right) are not ideal containers for monitoring purposes.

General guidelines	Remarks
Samples should be contained in clean glass jars with Teflon lids or lids lined with clean aluminium foil. Fluid source oils may be collected in stainless steel containers. Solid or semi-solid samples can be transferred with an unused lollipop stick or wooden tongue depressor. Nitrile gloves should be worn (Figure 7).	Plastic containers can contaminate the sample. Sample jars should be rinsed first with an appropriate solvent. New sampling sticks must be used for each sample. Gloves avoid the risk of contamination by trace oils from skin during handling.
Use amber bottles or keep samples in the dark during transfer and storage.	Protection against photo-oxidation and degradation for water column samples, in particular.
Use 30 ml or larger sample jars for pure oil and oiled sediments. Wide necks and screw caps are recommended.	Narrow mouth and thin glass are harder to fill and may break during transport.
Do not fill the sample jars with liquid or oily debris completely.	Allow some space for thermal expansion, especially if there is a risk of freezing.
Sample jars should be correctly labelled with a unique reference number, location, time and date, type of sample and other relevant information (e.g. depths).	Prepare standard labels with as much information as possible just before taking the sample. Use permanent pen and cover the label with clear tape to maintain its legibility.
Secure lid to avoid spillage and to prove that no tampering took place along the chain of custody.	Use tape to ensure the lid is secure.
Avoid contamination.	Clean sampling devices between samples with solvent. No smoking! Keep away from boat exhaust or similar.

▲ Table 4: General guidelines for the storage of samples.

to be broken (i.e. the water released and decanted), and oil samples extracted, even if apparently pure in appearance (Figure 13).

Chromatography is one of the many techniques where a mobile phase (containing the sample to be purified) passes through a stationary phase. Two of the most commonly used techniques to fractionate and separate groups of hydrocarbon molecules are silica column gas chromatography (GC) and high-performance liquid chromatography (HPLC). While GC is available relatively widely, HPLC requires highly sophisticated equipment and very pure solvents and so is less prevalent. However, HPLC provides increased sensitivity and the ability to identify PAHs reliably.

To promote cost effectiveness and to expedite the process overall, samples are usually screened to select those that merit more detailed investigation and so reduce the number of samples for which full analysis is required. The combined technique of gas chromatography and flame ionization detection (GC-FID) is typically employed for screening but UVF spectroscopy and sensory testing may also be used. Sensory testing involves the use of a trained panel of sensory assessors working in a controlled environment to evaluate suspect and control samples for flavour, odour and appearance⁴.

⁴ See the separate ITOFF paper on Effects of Oil Pollution on Fisheries and Mariculture.

Box 1: Oil composition

Oil is a highly complex mixture of compounds ranging from simple low molecular weight hydrocarbon molecules to resins and other dense macromolecules that incorporate metals and other elements. In many oil spill incidents, the focus for the monitoring programme will be to establish the **total hydrocarbon content (THC)**, or synonymously **total petroleum hydrocarbons (TPH)**, which represents the sum of aliphatic and aromatic compounds. THC usually describes the measurable amount of hydrocarbons present in an environmental sample, but it does not provide information on the individual constituents. As the amount of THC measured depends on the extraction methods used and the absorption of infrared light by the extract, the results are dependent upon the method used. When more detail is required as to the nature of the oil contamination within a sample, for example within seafood or for identification of the source of the oil spill, specific hydrocarbon compounds can be analysed individually.

Normal **alkanes** (n-alkanes) are compounds composed of straight chains of carbon atoms and typically comprise a large proportion of fresh crude oil or distillate products. Low molecular weight n-alkanes are sensitive to evaporation and biodegradation. Consequently, weathered oils tend to have a lower proportion of n-alkanes than their fresh counterparts. Iso-alkanes, so called branched-chain compounds, are equally abundant in fresh oils and are also sensitive to biodegradation. Some iso-alkane compounds can be useful as indicators of biodegradation.

Alicyclic compounds are cyclic, saturated hydrocarbons that are relatively resistant to biodegradation. The term saturated refers to molecules that are fully hydrogenated and have only single carbon-carbon bonds. Their relative stability makes some of the higher molecular weight alicyclic compounds particularly useful as distinctive features by which to identify individual oils. These compounds are referred to as biomarkers* because they were transformed from biological material during the geological process of oil formation.

Aliphatic hydrocarbons comprise straight, branched or (non-aromatic) cyclic chains of carbon atoms and include both n-alkanes and alicyclic compounds.

Aromatic compounds are unsaturated cyclic hydrocarbons, typically with alternating double and single carbon-carbon bonds and one or more rings of six carbon atoms (benzene rings) and include Volatile Organic Compounds (VOCs) and Polycyclic Aromatic Hydrocarbons (PAHs). VOCs include the low molecular weight compounds, for example benzene and toluene, that evaporate quickly and therefore sample collection and analysis of VOCs is a challenge requiring specialised techniques.

Polycyclic aromatic hydrocarbons (PAH) are toxic and carcinogenic compounds and are therefore a focal point of many environmental monitoring programmes. In particular, 16 PAHs identified by the US EPA (Environment Protection Agency) as 'priority pollutants', are commonly measured and are discussed in further detail in the separate ITOFF paper on Effects of Oil Pollution on Fisheries and Mariculture. The variation in PAH mixtures that arise when oil is formed, mean that each oil has its own unique signature or PAH profile. This, combined with a high resistance to weathering, makes PAH an important method for identifying different oils. The study of PAH can also be used to help determine the possible sources of water contamination because the analysis is able to distinguish between pyrogenic (combustion products), petrogenic (originating from crude oil) and biogenic (originating from biological processes) sources of oil.

* In environmental monitoring, the term biomarker can refer, as here, to compounds used in fingerprinting oils or to compounds indicating levels of enzyme activity in animals. For the latter, please see the separate ITOFF paper Effects of Oil Pollution on the Marine Environment.

Ultra violet fluorescence (UVF)

Ultra violet fluorescence spectroscopy is a qualitative and quantitative analytical method that can be used for detecting the presence of oil either in the water column *in situ* with portable devices, or in samples prepared in the laboratory. The material to be tested is exposed to specific frequencies of UV radiation, which excite aromatic molecules to fluoresce (i.e. emit lower energy light) and are then detected by the spectrometer. The oil-specific composition of PAHs makes UVF a good technique for identifying different oil types (Figure 14) and also for determining the THC in a sample. It is also capable of detecting very low concentrations of oil in water, typically down to 1.0 µg/l (i.e. ppb) in the field, 0.1 µg/l in the laboratory and 1.0 mg/kg (i.e. ppm) in sediments provided that calibration with a known source sample is performed. UVF is considered a quick and valuable screening technique but it is not routinely used to confirm a source sample, as this would necessitate the analysis of individual oil compounds such as those highlighted in Box 1. UVF is not appropriate for fingerprint analysis, because non-hydrocarbon molecules present can emit at the same excitation wavelengths and can interfere with PAH signals.

Gas chromatography–flame ionization detection (GC-FID)

GC is an analytical technique involving the separation of the complex mixture of hydrocarbons in oil into component molecular groups. A small liquid sample is injected into a long and narrow metal column which is heated at a controlled rate through a pre-determined temperature range. The column is flushed continuously with a carrier gas, usually helium. Special coatings within the column interact with the vaporized compounds as they pass through, separating the molecules by their chemical properties, such as volatility, resulting in each compound being eluted from the column at different time intervals, or retention times.

A flame ionization detector (FID) is a sensor that responds to ions released from the combustion of molecules eluting from a GC column as they are burned in a hydrogen flame. Lighter molecules pass through the column more quickly than heavier ones, so retention time in the column can



▲ Figure 13: Extraction of oil samples using a separation funnel (image courtesy CEFAS).

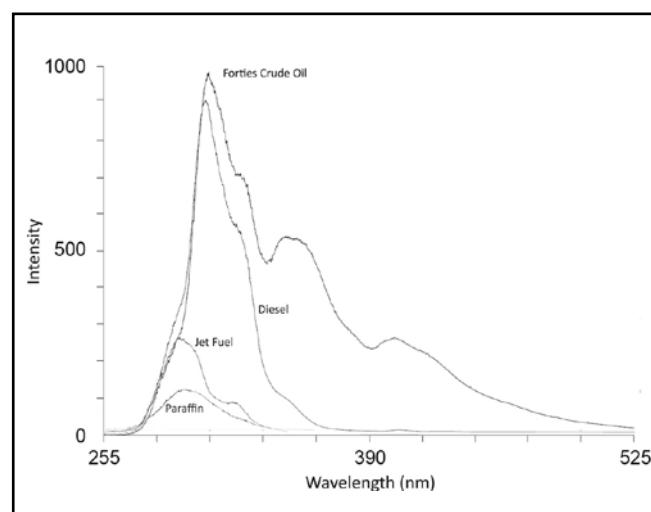
be related to molecular weight and, by the introduction of standards, individual hydrocarbons can be identified. The higher the concentration of a particular compound, the stronger the FID signal, which, after computer processing, is displayed as a peak in the resulting chromatogram. GC-FID can be used as a relatively fast combined screening and fingerprinting technique and it is also an appropriate technique for quantitative measurement of hydrocarbons.

Because each type of oil has its own distribution pattern or fingerprint, many oil samples can be identified by a comparative study of GC-FID chromatograms for spill and source samples. In some cases, GC-FID alone may be sufficient to confirm that two samples do not match (e.g. a spill sample does not match the source sample), especially for relatively fresh oils. When results are inconclusive and there is only a possible match or when there is a need to quantify particular compounds, further study may require the higher resolution of GC-MS.

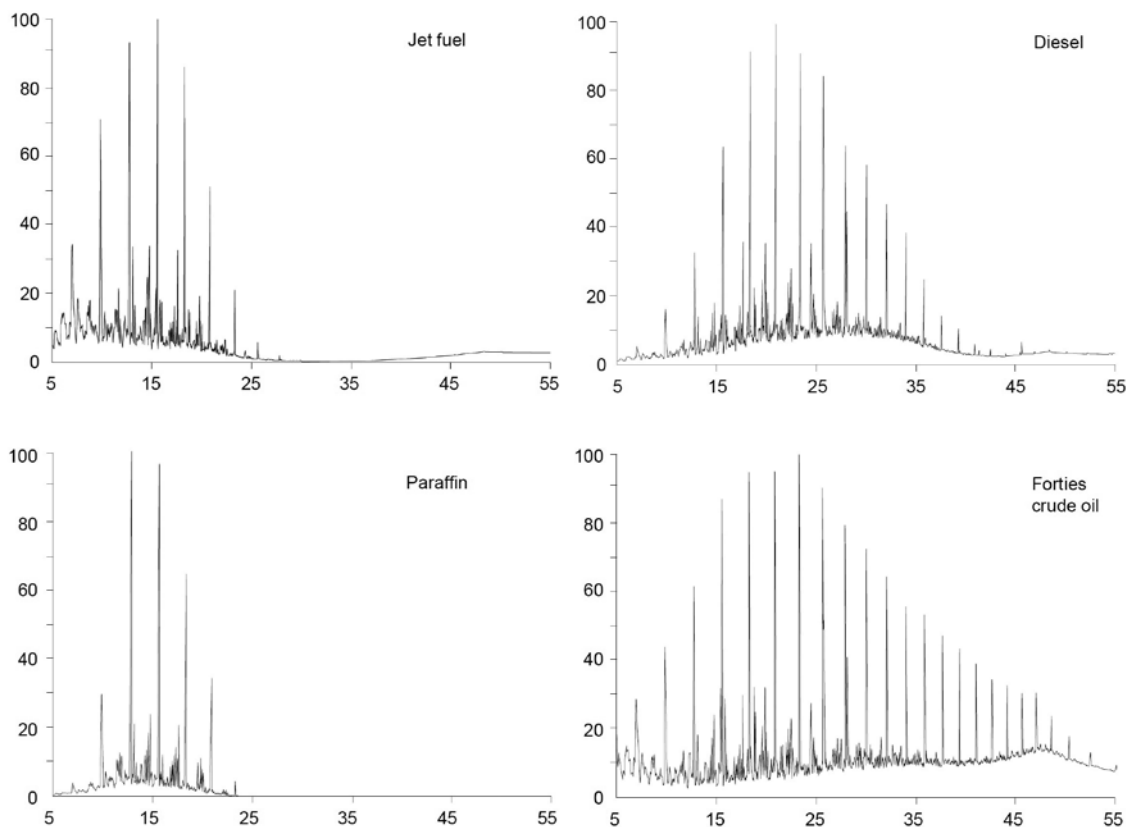
Gas Chromatography–Mass Spectrometry (GC-MS)

The coupled GC-MS process consists of a gas chromatograph linked to a mass spectrometer (MS), which detects and analyses each molecule separately, enabling the accurate, high resolution detection and identification of molecules. Mass spectroscopy involves a four-step process of ionisation, fragmentation, magnetic deflection and detection of positive ions. By counting and representing graphically the different ion fragments, the overall structure of the molecule is revealed (Figure 15).

Because of its high resolution, GC-MS is a prime technique for the identification of biomarkers, VOCs and specific PAHs. The limits of detection for GC-MS are typically in 0.1 µg/kg but techniques are available that can detect levels down to parts per trillion (i.e. ng/kg), although the relevance of this level of detection in the context of monitoring ship-source marine pollution is open to debate.



▲ Figure 14: UVF emission spectra for four different types of oils combined. This can be contrasted with the GC-MS chromatograms for the same oils overleaf. (Adapted from CEFAS Aquatic Environmental Report No. 12 – Methods for Analysis for Hydrocarbons and PAH in Marine Samples, 2000).



▲ Figure 15: Four typical total ion chromatograms (GC-MS) for a jet fuel, a diesel, paraffin and Forties crude oil. The diesel shows a predominance of light ends. The Forties crude oil shows a dual pattern of both light oil and heavier oil. (Adapted from CEFAS Aquatic Environmental Report No. 12 - Methods for Analysis for Hydrocarbons and PAH in Marine Samples, 2000.)

Selection of analysis technique

Selection of the appropriate technique is determined by the objectives of the monitoring programme (Table 5). If the objective is to prove that spill samples were derived from a suspected source, then qualitative analysis using GC-FID screening and GC-MS analysis of biomarkers is the approach most frequently followed. UVF or GC-FID techniques may be used if the monitoring programme is simply concerned with following total hydrocarbon concentrations in environmental samples and recording the return to background levels. GC-MS would usually be used for analysis of biota and particularly the analysis of species intended for human consumption, when measurement of the concentrations of PAH might be required.

Interpretation and reporting of the analysis results

The interpretation of results from the analytical techniques described above requires a thorough knowledge of the methodology used and experience in reviewing the analysis outputs and is, therefore, beyond the scope of non-specialists. Challenges to interpreting the results include the weathering processes to which the oil was subjected prior to being sampled, as well as the presence of other petrogenic and biogenic sources of hydrocarbon compounds commonly found in oil.

The results and conclusions of oil analyses should be interpreted in the context of the observations made on site

following the incident. In order to fully understand the extent and pathways of the contamination caused by the oil spill, results of samples from sediments, biota and the water column at different locations need to be interpreted in relation to the background hydrocarbon levels for each location.

In reporting the results of a monitoring programme, it is important to present the details of the sampling and analytical protocols applied. Interpretation of the results should be accompanied by the raw data collected, including, for example, the chromatograms developed.

For reporting visual observations and quantitative data where there are relatively few samples analysed, numerical tables, graphs and text descriptions may be adequate (Figure 16). However, where oil contamination is distributed across complex geography, numerical tables can be supplemented with maps indicating the degree of contamination observed or results from individual sample stations.

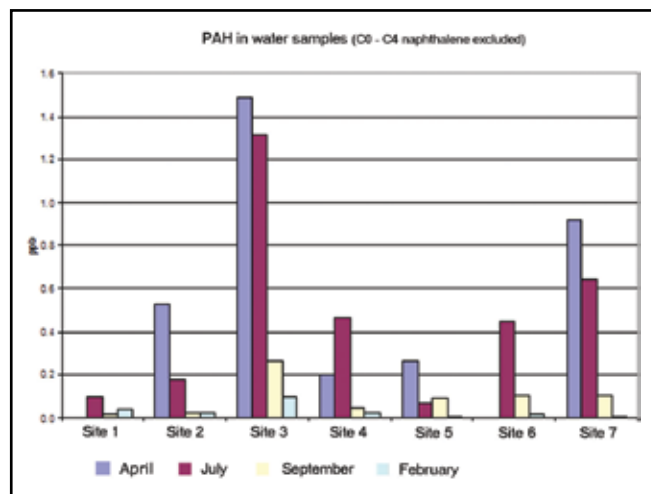
Compounds	UVF	GC-FID	GC-MS
n-alkane		X	X
iso-alkane		X	X
biomarkers		X	X
VOCs		X	X
PAHs	X	X	X
THC	X	X	

▲ Table 5: Analytical techniques used to analyse molecular groups.

Concluding monitoring activities

During the design phase of a monitoring programme, consideration should be given to the expected duration of any field sampling and the criteria used for the termination of the programme. Given the many factors, both occurring naturally and deriving from the response, that will influence the continued presence of oil contamination within the marine environment, it can be difficult to predict a suitable duration for monitoring. As a result, monitoring programmes are often iterative, whereby the results of previous sampling events are used as a basis for determining the requirement and scale of the next sampling event and to aid decision making on when to conclude the monitoring programme.

Monitoring programmes for oil within the environment will not be necessary after all spills and would normally be most appropriate in the case of major incidents, where oil has spread over a wide geographic area and where the oil has either the potential to cause significant environmental damage, presents a risk to seafood safety or where monitoring can assist directly with response activities. It is important that the monitoring is carried out with scientific rigour, objectivity and balance, with the aim of providing reliable information that can be used to assess the scale and extent of the oil contamination. The results of a well executed contaminant sampling and monitoring programme can, in



▲ Figure 16: Results of a study to monitor the return of PAHs to background levels off coastal waters during shoreline clean-up. Sites 1 and 6 are reference sites.

some circumstances, be used in conjunction with, or to justify, a longer term more complex study of environmental impacts.

While there may be political and public pressure to undertake extensive monitoring programmes following an incident, it is rarely necessary or practical to monitor all resources and ecosystems that may or may not have been affected. In ITOPF's experience, well planned and focused monitoring programmes with clear objectives linked directly to the incident are those most likely to be effective.

Key points

- Monitoring may not always be necessary if the spill is small and resources are not at risk, or if the effects of the oil on a particular resource are well known.
- Joint sampling and analysis provides a constructive co-operative approach to monitoring.
- A monitoring programme should clearly define the objectives of the study and the information and data necessary to achieve these objectives.
- The objectives and the specific factors of the incident define the optimum location and number of sampling stations.
- The costs of the programme should be clearly budgeted and, where relevant, discussed with the body paying compensation prior to the start of the work.
- Reference sites selected should be representative of the habitat types affected and being studied.
- Collection of source samples should be a high priority, but may require the involvement of personnel qualified to enter enclosed spaces.
- Proper protocols for handling and storing samples should be followed to ensure their integrity for analysis.
- Results from the analysis of samples taken earlier in the monitoring programme can define the extent and duration of further monitoring.
- The techniques used to analyse samples will depend on the objectives of the monitoring, but screening techniques can be useful to limit the number of samples requiring more sophisticated analysis.

TECHNICAL INFORMATION PAPERS

- 1 Aerial Observation of Marine Oil Spills
- 2 Fate of Marine Oil Spills
- 3 Use of Booms in Oil Pollution Response
- 4 Use of Dispersants to Treat Oil Spills
- 5 Use of Skimmers in Oil Pollution Response
- 6 Recognition of Oil on Shorelines
- 7 Clean-up of Oil from Shorelines
- 8 Use of Sorbent Materials in Oil Spill Response
- 9 Disposal of Oil and Debris
- 10 Leadership, Command & Management of Oil Spills
- 11 Effects of Oil Pollution on Fisheries and Mariculture
- 12 Effects of Oil Pollution on Social and Economic Activities
- 13 Effects of Oil Pollution on the Environment
- 14 Sampling and Monitoring of Marine Oil Spills
- 15 Preparation and Submission of Claims from Oil Pollution
- 16 Contingency Planning for Marine Oil Spills
- 17 Response to Marine Chemical Incidents

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