Sampling

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Factors that NOAA considers when determining spill complexity (Michel et al., 2011)

- Spill volume
- Product released (especially if unusual or dangerous)
- Spatial extent of oiling (e.g., number of miles or acres affected)
- **Number and complexity of shoreline types potentially affected**
- **Sensitivity of oiled shoreline types**
- Uniformity/complexity of oiling
- Multiple zones of oiling within segments prevalent vs. one continuous band
- “3-dimensional” oiling (e.g., oiling on stems or branches of marsh/mangrove)
- Spill conditions (e.g., buried or sunken, oil (evaporation, transport) or ocean conditions changing rapidly?)
- Sources changing (fuel oil versus plastics?)
- **Logistical constraints to shoreline access**
- Resource concerns that need to be specifically confirmed in the field
- **Recreational or industrial use of the oiled shorelines, seasonal use factors**
- **Commercial, recreational, and/or subsistence consumption of resources**
- Aesthetic requirements (which might require use of chemical agents or other means to reach endpoints)
- Degree of cooperation among the Responsible Party (RP) and Natural Resource Trustee agencies (Trustees)

Conceptual Site Models

A conceptual site model is a useful tool for selecting sampling locations. It helps ensure that sources, migration pathways, and receptors throughout the site are considered before sampling locations are chosen.

- *Potential Sources*: Site (waste pile, lagoon); drum dump; sewage plant outfall; agricultural activities.
- *Potential Migration Pathway (Surface Water)*: Runoff from the waste pile, lagoon, drum dump, or agricultural activities; outfall from the lagoon or sewage plant.
- *Potential Migration Routes*: Ingestion or direct contact with water in the river, lake, or aquifer (e.g., ingestion of drinking water, direct contact with water at the public beach)
- *Potential Receptors of Concern*:
- Human Population (Residents/Workers/Trespassers): Ingestion or direct contact with contaminated water in the river, lake, or aquifer (e.g., swimming, drinking).
- Biota: Endangered/threatened species or human food chain organisms suspected of ingesting or being in direct contact with contaminated water.

Sample Collection

- When sampling, several things must be considered to ensure that your sample is representative.
  - points of sampling
  - Frequency of sampling
  - Maintenance of integrity with respect to samples prior to analysis

- Things to consider
  - Prior actions at the site
  - Properties and characteristics of the suspected contaminants
  - Topographic, geologic, hydrologic and meteorological conditions
  - Habitats and human vulnerability

Essentials components of the sampling plan

- What are the data use and quality assurance objectives
- Sampling objectives
- Sampling equipment and methodology
- Sampling design
- SOP
- Analytical methods
- Decontamination goals
- Sample handling and shipment
- data validation

Sampling types ("average" concentration within area, flow etc)

- Grab- discrete aliquot from one specific sampling location at a specific point in time, and may be considered representative of homogenous conditions over a period of time and/or geographical area (consider depth stratification)
  - Generally preferred – minimizes time and expense, reduces risk exposure for personnel, preserves sample integrity because you avoid storage of samples in less than ideal conditions while you collect a composition sample.

- Composite – non discrete containing two or more aliquots, collected at various locations and times. Combines grab samples collected at defined intervals – areal (equal aliquot grab samples collected in identical manner, over a defined area), vertical, flow proportional (proportional to a flow rate using time varying/constant volume or time constant/varying volume), and time (varying number of discrete aliquots collected at equal time intervals during g the period of time over which you are collecting the composite samples).

Sampling considerations:

- Hydrology
- Topography
- Water quality data and measurements (chemical, physical)
- stratification
- Measurements at 1m for CTD parameters

QA/QC

- Precision (variability in the data collection process)
- Accuracy (bias)- bias in the analytical process
- Completeness -how many of the sampling points passed the tests
- Representativeness – to which degree are the sample data accurately and precisely represent the characteristics and concentrations of the site contaminants.
- Comparability – evaluation of the similarity of conditions (depth etc) under which separate sets of data are produced

Data quality objectives

- Decisions to be made or questions to be answered by data
- Why analytical data are needed and how will it be used
- Time and resource constraints on data collection
- Descriptions of the analytical data to be collected
- Applicable model or data interpretation used to arrived at a conclusion
- Detection limits of analytes of concern
- Sampling and analytical error.

How to decide what to sample

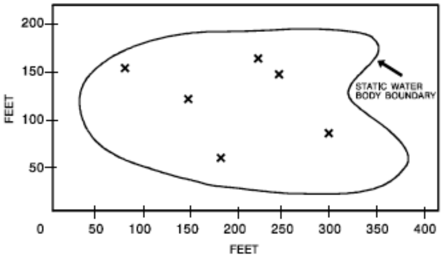
- Rely on historical data or previous monitoring efforts

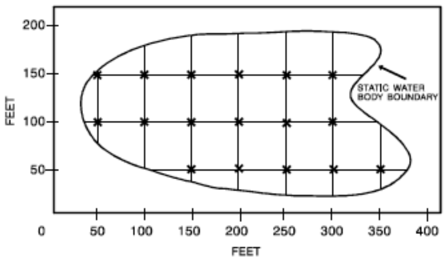
- If historical data are not helping determining which pollutants/sources are important then go to the field screening approach.
- Field screening assists with selection of sampling locations and depths or samples to be sent for laboratory analyses by narrowing the groups or classes of chemicals. Effective and economical for gathering lots of data.

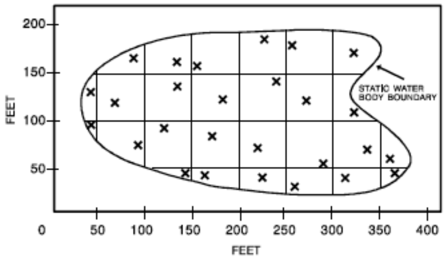
- If screening results of inconclusive then send a subset of samples from the areas of concern for a full chemical characterization by off site. (GC/MS, ICP and IR)

Sampling approaches

- Judgmental sampling (biased, not good for statistics)
- Random sampling – samples having similar contaminants within define boundaries of the area. Best used when there is no easy way to decide where to sample.
- Grid sampling – square or triangular grid
- Systematic random sampling- random sampling within grid squares.

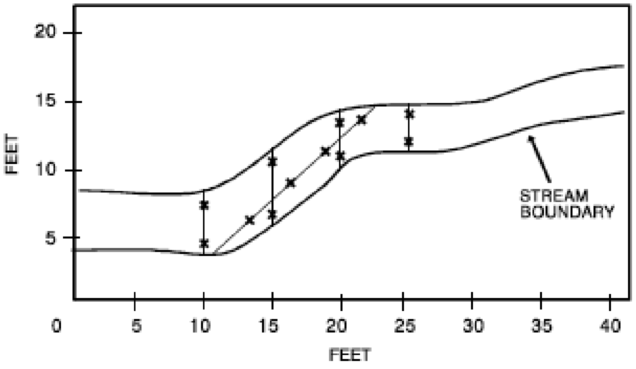






Sampling approaches

- Transect sampling
- Stratified sampling to enable different strategies to be used in different strata- chosen based on areas where separate clean-up decisions need to be made or varying contaminants or concentrations are expected (better for sediments)
- 3D sampling (systematic but with depth included)



Surface water and sediment field analytical screening

Instrument	Use(s)	Advantage(s)	Disadvantage(s)
Direct - Reading/ Real - Time Instruments	Portable monitoring instruments used to measure or identify specific parameters under field conditions including: pH, specific conductivity, temperature, salinity, and dissolved oxygen	• Portable and easy to operate and maintain in the field • Qualitative identification • May be used with probes placed directly into the sample medium	• May return a reading with a high degree of error
Field Test Kits and Colorimetric Indicator Tubes	Used for detecting specific compounds, elements, or compound classes in surface water and sediment	• Rapid results • Easy to use • Kits may be customized to user needs	• Limited number of kit types available • Interference by other analytes is common • Subjective interpretation is needed • Can be prone to error • May have limited shelf life • Colorimetric tubes may be used for ambient air only
Photoionization Detector (PID)	Detects and measures total concentration of volatile organic compounds (VOCs) and some non-volatile organic and inorganic contaminants in ambient air or container headspace; used to evaluate existing conditions, identify potential sample locations, or identify extent of contamination	• Immediate results • Easy to operate and maintain • Detects to parts per million (ppm) level for headspace analysis	• Limited use to quantify specific substances • Does not detect methane • Readings can be affected by high winds, humidity, condensation, dust, power lines, and portable radios • Probe should not be placed directly into sample medium
Flame Ionization Detector (FID)	Detects and measures the level of total organic compounds (including methane) in ambient air or container headspace; used to evaluate existing conditions, identify potential sample locations, or identify extent of contamination	• Immediate results • Detects to ppm level for headspace analysis • Rugged • Available with a GC mode to detect specific VOCs	• Does not respond to inorganic substances • Does not recognize and may be damaged by acids • Requires training and experience • Requires a hydrogen fuel source • Probe should not be placed directly into sample medium

EPA

Surface water and sediment field analytical screening

Instrument	Use(s)	Advantage(s)	Disadvantage(s)
Hazard Categorization (hazcat)	Performed as an initial screen for hazardous substances to provide identification of the classes/types of substances in the individual surface water or sediment sample	• Rapid categorization of unknown liquids • Good for screening and determining contaminant compatibility	• Not analyte-specific, yields only basic information (e.g., base vs. acid, chlorinated vs. non-chlorinated substance) • Requires numerous chemical reagents • Requires interpretation of results
Portable Gas Chromatograph (GC)	Used to measure occurrence and concentration of VOCs and some semi-VOCs	• Can screen "hot spots" • Determines potential interferences • Conducts headspace analysis • Semi-quantitation of VOCs and semi-VOCs	• Highly temperature sensitive • Requires set-up time, many standards, and extensive training
Radiation Detector	Detects the presence of selected forms of radionucliides in sediments	• Easy to use • Probes for one or combination of alpha, beta, or gamma emitters	• Units and detection limits vary greatly • Time intensive for detailed surveys • Experienced personnel required to interpret results
Portable X-ray Fluorescence (XRF)	Used to detect heavy metals in sediments	• Rapid sample analysis • Detects to ppm level (detection limit should be calculated on a site-specific basis)	• Requires trained operator • Sediment must be dried • Potential matrix interferences • Detection limit may exceed action level • Radioactive source • Cannot be used for surface water samples

Surface Water

Sampler	Uses	Advantages	Disadvantages
Laboratory-cleaned Sample Container (Direct Method)	Used to collect samples from surface and shallow depths of surface water bodies	• Quick and easy to use • No decontamination required • Disposable • Reduces risk of cross-contamination from sampling equipment • Reduces the loss of volatile fraction during transfer to a sample container • Preferred if there is an oily layer on the sample surface; the layer will not stick to a sampling device and thus miss being transferred to the sample container	• Cannot be used for other water bodies, such as waste impoundments, where contact with concentrated contaminants is a concern • Labelling can be difficult • May not be possible when containers are pre-preserved
Scoop, Ladle, Beaker (Transfer Devices)	Stainless steel, Teflon®, or other inert composition material devices to transfer the sample directly into a sample container at a near shore location	• Easy to use and decontaminate • Allows collection without a loss of preservative in the sample container	• Difficult to maneuver sample especially if placing into VOA vials • Avoid equipment with painted or chrome-plated surfaces • May aerate sample releasing VOCs, or some contaminants may adhere to the surface of the transfer device
Weighted Bottle Sampler	Used to collect samples in a water body or impoundment at predetermined depth	• Easy to decontaminate • Simple to operate • Sampler remains unopened until at desired sampling depth	• Cannot be used to collect liquids that are incompatible with the weight sinker, line or actual collection bottle • Sample container may not fit into sampler, thus requiring additional equipment • Sample container exposed to matrix
Pond Sampler	Used for near shore sampling where cross-sectional sampling is not appropriate and for sampling from outfall pipe or along a disposal pond, lagoon, or pit bank where direct access is limited	• Easy to fabricate using a telescoping tube; not usually commercially available • Can sample at depths or distances up to 3.5 meters (can sample areas difficult to reach with extension)	• Difficult to obtain representative samples in stratified water bodies • Sample container may not fit into sampler, thus requiring additional equipment
Peristaltic Pump	Used to extend the reach of sampling effort by allowing the operator to reach into the water body, sample at depth, or sweep the width of narrow streams through the use of Teflon® or other tubing	• Very versatile • Easy to carry and operate; fast • With medical-grade silicone, it is suitable to sample almost any parameter including most organic contaminants • Sample large bodies of water • Capable of lifting water from depths in excess of 6 meters	• Depth limited to 7.5 meters/25 feet • Cannot be used if volatile compounds are to be analyzed • Lift ability decreases with higher density fluids, increased wear on silicone pump tubing, and increases with altitude • Oil and grease contaminants may adhere to tubing and thus decrease concentration in sample • Must often change tubing between locations to decrease cross-contamination; must always have extra tubing on hand • At high flow, must weight tubing in stream

Surface water

Sampler	Uses	Advantages	Disadvantages
Bailer	Used for collecting samples in deep bodies of water where cross-sectional sampling is not appropriate	• Easy to use • No power source needed • Bailers can be dedicated to sample locations • Disposable equipment available • Can be constructed of a variety of materials	• Transfer of sample may cause aeration, thus not appropriate for VOCs • Inappropriate for strong currents or where a discrete sample at a specific depth is required
Kemmerer Bottle/Van Dorn Sampler	Used when access is from a boat or structure such as a bridge or pier, and where discrete samples at specific depths are required	• Can take discrete samples at specific depths • Can sample at great depths • Kemmerer Bottle lowers vertically; Van Dorn Sampler lowers horizontally, which is more appropriate for estuary sampling	• Sampling tube is exposed to material while traveling down to sampling depth • Transfer of sample into sample container may be difficult • May need extra weight • Often constructed of materials incompatible with sample
Bacon Bomb Sampler	Used to collect samples from discrete depths within a water body; generally used when access is from a boat or structure	• Remains unopened until the sampling depth • Can collect a discrete sample at desired depth/stratum • Widely used and available	• Difficult to decontaminate • Difficult to transfer sample to sample container • Tends to aerate sample thereby losing volatile organic constituents
Wheaton Dip Sampler	Useful for sampling liquids in shallow areas or from areas where direct access is limited; also useful when sampling from an outfall pipe	• Long handle allows access from a discrete location • Sample container is not opened until specified sampling depth • Sampler can be closed after sample is collected ensuring integrity • Easy to operate	• Depth of sampling is limited by length of extension poles • Exterior of sample container may come in contact with sample • Sample container may not fit into sampler
Depth-Integrating Samplers	Used to collect water and suspended sediment samples; used with the EWI and EDI composite sampling techniques	• Allows for collection of representative samples of suspended materials • Samples proportionate to the velocity of the water body	• Requires experienced operator
PACS Grab Sampler	Used to collect water samples from impoundments, or ponds with restricted work areas	• Allows discrete samples to be collected at depth	• Depth of sampling is limited by length of extension pole • Difficult to decontaminate

Sediments

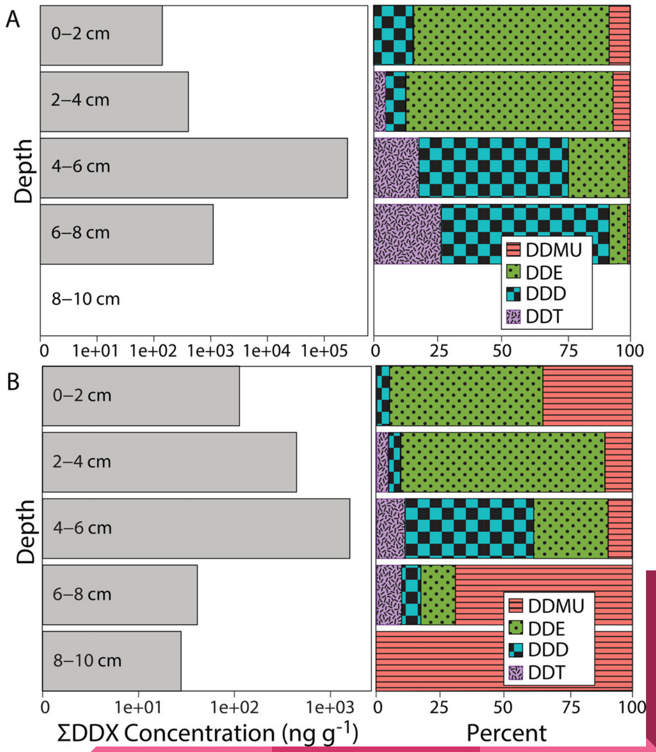
Sampler	Uses	Advantages	Disadvantages
Scoops, Trowels, Dippers, Shovels (Direct Method)	Used for surface sediments where water depth is shallow (limited to near surface)	• Quick and easy to use • Easy to decontaminate • Available in a variety of materials • Appropriate for consolidated sediments • Disposability reduces the risk for cross-contamination • Laboratory scoop is less subject to corrosion or chemical reactions than commercially available garden or household tools (less risk for sample contamination)	• Disturbs the water/sediment interface and may alter sample integrity; fine fraction is lost • Not efficient in mud or other soft substrates • Difficult to release secured undisturbed samples to readily permit subsurface sampling • Difficult to maneuver sample especially if placing into VOA vials • Limited by depth of aqueous layer • Avoid equipment with painted or chrome-plated surfaces (common with garden trowels)
Vertical-pipe, Core Sampler	Used to collect samples of most sediments to depths of 75 cm (30 in.)	• Easy to use • Can collect undisturbed sample (minimum loss of fine fraction) that can profile any stratification as a result of changes in deposition • Provides historical record of deposition	• When used in impoundments, penetration depths could exceed that of substrate and damage the liner material • A relatively small surface area and sample size result in the need for repetitive sampling to obtain an adequate amount for analysis
Ponar/Ekman/ Peterson Dredges	Ponar dredge is used to sample most types of sediments -- Ekman dredge is used where bottom material is unusually soft, such as thick organic sludges -- Peterson dredge is used when bottom is rocky, in deep water or in a stream with high velocity	• Ponar is easily operated by one person; light weight • Available in a "petite" size which can be operated without a winch or crane • Appropriate for most sediment types from silts to granular materials -- • Ekman can obtain samples of bottom fauna -- • Peterson can be used in rocky substrates and high velocity water bodies • Easily operated by one person	• Dredges are normally used from a boat, bridge or pier due to the weight of the equipment which may require a boom for lowering or raising • Penetration depths for Ponar and Ekman dredges do not exceed more than 4-6 inches • Not capable of collecting undisturbed sample and may cause agitation currents that may temporarily resuspend some settled solids -- • Ekman is not suitable for sandy, rocky, and hard bottoms, vegetation-covered bottoms, and streams with high velocities • Should not be used from a bridge more than a few feet high because spring mechanism could be damaged • Not capable of collecting an undisturbed sample and may cause agitation currents that may temporarily resuspend some settled solids -- • Peterson can displace and miss light materials if allowed to drop freely
Thin-Wall Tube Auger	Used to collect consolidated sediments at surface and at depth	• Easy to use • Preserves core sample	• Limited by the depth of the aqueous layer • May be difficult to remove core sample from auger • Possible washout during retrieval
Veihmeyer Sampler	Used for sampling most types of soil and sediments, except very wet or stony sediments	• Can achieve substantial depths with appropriate length of tubing • Various driveheads available for different sediment types	• Very difficult to clean • Parts needed for sampler are not appropriate for certain analyses • Not appropriate in rocky substrate

Sediments

Sampler	Uses	Advantages	Disadvantages
PACS Grab Sampler/Sludge Getter	Used for collecting grab samples from ponds and impoundments at depth	• Allows discrete samples to be collected at depth • Can be used in heavy sediments or sludges, or moderately viscous materials	• Not useful in very viscous materials • Depth of sampling is limited by length of extension pole • Heavy, possibly requiring more than one person to operate
Sampling Trier	Used to collect sediments up to 40 inches depth from water surface	• Preferred for moist or sticky samples	• Difficult to use in stony or sandy substrates • May be difficult to remove sample from sampling device
Soil Coring Device/ Silver Bullet Sampler	Used when a core sample is required	• Contains a collection tube which holds core relatively intact • Bit of silver bullet sampler is replaceable	• Difficult to use in rocky or tightly packed substrates • Depth restrictions
Sludge Judge	Used to collect a core of sediments or water and sediments	• Easy to use • Core allows delineation of settled state of sediments or physical state of water body	• Use is limited due to possible reactivity of construction material • Difficult to decontaminate • Not useful in thick sediments
Hand Corer	Used for sediments in water that is very shallow (a few inches)	• Easy to use • Preserves sequential layer of deposit (useful for historical information) • Appropriate for trace organic compounds or metals analyses • May have a check valve on top to prevent wash-out during retrieval	• Can be disruptive to water/sediment interface • May cause disruption to sample integrity • Delivers small sample size requiring repetitive sampling
Gravity Corer	Collects core samples from most sediments; can be used in water deeper than 5 feet	• Collects undisturbed samples • Can collect to a depth of 75 cm (30 in.) within the sediment substrate • Preserves sequential layer of deposit (useful for historical information) • Has a check valve to prevent washout during retrieval	• May damage liners in impoundments if penetration is too deep • Not suitable for obtaining coarse-grained samples
Bucket and Posthole Augers	Used for direct method samples	• Direct sample recovery • Fast and easy to use • Provides a large volume sample	• Disturbs sediment horizons • May cause disruption to sample integrity • Posthole augers that are designed to cut through fibrous, rooted swampy areas have limited sample collection utility

Regarding questions about length of monitoring

- Palos Verdes shelf dumpsite, large coastal spill sites.
  - Comprehensive survey undertaken at some point to delineate area of contamination and resources contaminated (so bottom feeding fish and locally caught fish were studied as well), marine top predators were also studied. Then follow up with studying sediments (i.e., source) periodically (e.g. every year after the first year and fading to every 3 years, for example) to see how the contaminant load is decreasing or changing at the source. Periodically monitor subsets of the food web (to predators, fish).



Monitoring for baselines – Palos Verdes example

- this site couldn't be cleaned up and is assumed to be contaminated for a very long time (may be forever)- indefinite monitoring

To evaluate the potential losses in natural resources associated with the presence of contaminated sediments at the PV Shelf. The NRDA included the following components:

• Collection and analysis of sediment core samples on the shelf, slope, and adjacent basins to describe the vertical and horizontal extent of contamination.

• Evaluation of potential biological effects levels for sediment concentrations of DDTs and PCBs

• Evaluation of potential effects on different receptors including fish, birds, and mammals.

• Predictive models of changes in concentrations of DDTs (the majority of DDT has been converted to dichlorodiphenyldichloroethene [DDE]) at two shelf locations (through the year 2100) as a result of natural physical and biological processes.

--- Comprehensive study, at some point, undertaken to characterize the nature of the disaster site; monitor (every 3 years or so) using a basic set of parameters to see if their models of transport/degradation are right and to see whether/how thing have changed.

But not all disasters need to be monitored indefinitely

- Objectives matter: if your goal is to say that the spill is no long important then you have to show that some references point has been reached in your samples of interest. For example, PAHs in fish after a spill. Sample long enough until you can figure out the depuration rate. Community composition of primary producers and primary production measurements may be a useful way to demonstrate that a system is back to normal

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ITOPF guidance on monitoring duration

- Duration of the monitoring program and frequency of repeat sampling depends on the program objectives and the inherent characteristics of the specific parameters that are being measured. Example
    - If oil concentration in a particular environment is what you care about then you are likely to need weeks to months of monitoring before background concentrations are re-established
    - If the objective is to determine whether a particular response was effective – i.e. dispersant addition – then immediate implementation of monitoring and rapid processing of results would be crucial to enable a timely decision to be made

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.*

Regarding questions about length of monitoring

- What you spill matters – nitric acid, likely dissociates and becomes "undetectable" fairly quickly (soluble spills), oil could stick around for a while especially along the shoreline, marine debris may sit in sediments for a while or collect on shorelines (but this can be handled by visual surveys fairy easily and you can employ local stakeholders to help with those "sightings."

Sri Lanka ”reference methods (Size, Shape, Color)

Bryan James, Lihini Aluwihare, and Chris Reddy

May 12, 2023

Develop/assist “standard methods Xpress Pearl

- Provide a common currency of analytical results for researchers and interested folks to study in the aftermath of Xpress Pearl

- All valuable measurements from “low-cost” and up.

Methods (Easiest and valuable) and publishable

- **Mass:** Pellets are 25 mg (possible weathering already) and burnt remants.
  - Need an analytical balance at ideally 0.1 mg ($150) and one reference mass; 10 or 30 mg ($40 but varies on tolerance)
- **Size/shape/color:** Use Bryan's program (some details published and more in preparation.) (Alternative would be ruler, calipers and reference color sheets).
  - Need microscope ($125) from Amazon

Methods (more challenging)

- **Solvent-extractable mass:** Need solvent, hood, balance, and syringe. (Need to ensure balance for mass is suitable; see below too)
- **Density (PE vs etc):** Need methanol/ethanol, syringe, and balance.
- **Loss-on-ignition:** Need muffle oven and balance.

Methods (Challenging)

- **FTIR:** Instrument access and reference (determine polymer composition: reference library comparison (https://openanalysis.org/openspecy/) ; upload spectrum and post process within the database (statistical comparison)
    - Weathering: there is some evidence with FTIR. Forensic value.
- **TGA?:** Thermogravimetric analysis

Make a case to use these previous, simpler results for more complex analyses

- Elemental analysis
- GC-based techniques
- LC-based techniques
- High-resolution MS
- ??